Quantum Chaos in the Born-Oppenheimer Approximation

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We show that exponential instabilities and quantum chaos occur in a system with a mixed classical-quantum description. This type of chaos is of general importance and may occur in any quantum system which divides in a natural way into a fast (quantum) and a slow (classical) subsystem.

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Current research in quantum chaos is mainly focused on the classical-quantum correspondence in the semiclassical regime of classically chaotic dynamical systems [1–3]. But yet another main avenue of quantum chaos research may derive from the observation that for some quantum systems of theoretical and practical importance the system divides in a natural way into two interacting subsystems, one of which is treated quantum mechanically, whereas the other is treated in the classical approximation. The mixed quantum-classical description of a dynamical system is justified whenever the quantum effects of one subsystem are negligible compared to the other or when the quantization of the whole system poses a severe challenge and the classical treatment of one part has to serve as a necessary guide in the further investigation. In fact, there are many examples in the physics literature where such a mixed description was already successfully applied. We mention the case of a two-level system interacting with the electromagnetic field of a laser cavity [4,5], the micromaser [6], nuclear collective motion [7], and the exciton transfer in a nonlinear molecular dimer perturbed by an intermolecular vibration [8]. It was demonstrated recently [9] that the number of photons in the electromagnetic maser field can be changed essentially in units of 1 from one photon (quantum limit) to a large number of photons (classical limit). Thus, the importance of quantum corrections in the "classical" subsystem (the cavity field) can be controlled to an astonishing degree. The molecular physics example of the nonlinear dimers is instructive because it provides an example for the justification of the division into a quantum and a classical subsystem. Describing the strong intramolecular interactions in the molecules constituting the dimer in the framework of the nonlinear discrete self-trapping equation (see, e.g., [10,11]) one can use the weakness of the intermolecular forces between the molecules (and correspondingly small frequencies) to use a classical approximation for the intermolecular vibrations perturbing the transfer dynamics. In this case the density matrix dynamics for the exciton transfer of the quantum subsystem is characterized by a homoclinic structure on the Bloch sphere from which by perturbation with the classical oscillator a stochastic layer and chaos develops [8]. A further example is provided by a quantum system with a classical boundary moving in an anharmonic potential [12]. All the models discussed above are characterized by a mixed quantum-classical description. One of the main purposes of this Letter is to show that such systems can display quantum chaos and arise quite naturally within the framework of the Born-Oppenheimer approximation [13,14], which is basic to condensed matter and molecular physics problems [14]. This point is illustrated below by analyzing a simple model which contains all the essential ingredients of the Born-Oppenheimer approximation and exhibits chaotic dynamics.

The Born-Oppenheimer approximation provides a widely accepted procedure for dividing a complex quantum system into a fast and a slow subsystem. In case the first step in the Born-Oppenheimer quantization procedure, the quantization of the fast subsystem ("electrons"), results in well separated energy levels, the second step, consisting in the quantization of the slow subsystem ("nuclei"), can easily be performed resulting in the familiar structure of electronic-vibrational spectra (see, e.g., [14,15]). This procedure is somewhat more complicated, however, if the "electron" levels are not well separated. One of the simplest situations of this kind occurs for two close lying electronic levels coupled by a quasicontinuum of vibrational states for which a classical approximation is justified.

In this Letter we present the results of a systematic study of a model corresponding to such a situation. We study the origin of dynamical chaos in a system with a mixed quantum-classical description which has direct relevance for the adiabatic approximation in the sense of a distinction between fast (quantum) and slow (classical) variables of a given system. In order to be specific and for the sake of clarity we shall use the language of quantum states in a molecular system.

We consider a one-dimensional molecule and separate it into an electron moving in the effective potential

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formed by the nuclei and possible other electrons forming some skeleton. The effective potential is taken in a crude approximation as a one-dimensional box (one-dimensional metal) in which the only spatial coordinate is the width of the box q (the size of the molecule). The system is treated in the adiabatic approximation: the quantum kinetic energy of the electron $K = K(q)$ is considered as a part of the molecular potential energy. Its minima determine the stable configurations of the molecule. The other part of the molecular potential energy is the direct interaction between the constituents of the skeleton. This part is taken as a classical potential energy V which in our case depends on the molecular size only, $V = V(q)$. The molecular coordinate q is considered as a classical dynamic variable. We will consider the complete dynamics of the coupled system consisting of the two quantum states and the classical oscillator.

According to our model assumptions the electronic part of the Hamiltonian $\hat{H}_e$ is of the form

$$\hat{H}_e = \hat{T}_x + V(x,q) \quad , \tag{1}$$

where $\hat{T}_x$ is the operator of the kinetic energy and $V(x,q)$ is the box potential. We take $V(x,q) = 0$ for $0 \leq \mid x \mid \leq q/2$ and $V(x,q) = \infty$ for $\mid x \mid > q/2$. The electronic wave function is expanded in the set of eigenstates of $\hat{H}_e$ for a given q, i.e.,

$$\psi^{\pm}(x,t) = \sum_n A_n^{\pm}(t)\, \phi_n^{\pm}(x,q) \quad , \tag{2}$$

where $\phi_n^+(x,q) = (2/q)^{1/2} \cos[\pi(2n-1)x/q]$ and $\phi_n^-(x,q) = (2/q)^{1/2} \sin[2\pi n x/q]$, $n = 1, 2, \ldots$ are the eigenstates of even and odd parity of (1), respectively. A change of the variable q, i.e., a finite $\dot{q}$, will result in a coupling between different modes of the expansion (2) (only states of the same symmetry will be coupled). In order to obtain the simplest possible model of a mixed quantum-classical system, we will restrict our discussion to the case where the coupling occurs between two modes only. To be specific we consider the coupling between the ground and the first excited state of even parity represented by the coefficients A_1^+ and A_2^+ in (2) (in the following we will suppress the superscripts). Inserting (2) into the time dependent Schrödinger equation and taking account of the finite $\dot{q}$ terms we find

$$i\dot{A}_n = \sum_k D_{nk}\, A_k \quad , \tag{3}$$

where the Hermitian 2×2 matrix D_{nk} is given by

$$D_{nk} = \begin{pmatrix} \epsilon_1/\hbar q^2 & -i\mu_{12}\dot{q}/q \\ i\mu_{12}\dot{q}/q & \epsilon_2/\hbar q^2 \end{pmatrix} \quad . \tag{4}$$

Here, $\epsilon_n = [\hbar\pi(2n-1)]^2/2m$, $n = 1, 2$, $\mu_{12} = 3/4$. Note the q dependence in (4) which is crucial for what follows. Expressing the kinetic energy $K = \langle \psi \mid \hat{H}_e \mid \psi \rangle$ in terms of the coefficients A_1 and A_2 we get

$$K(A_1, A_2, q) = (\epsilon_1 \mid A_1 \mid^2 + \epsilon_2 \mid A_2 \mid^2)/q^2 \quad . \tag{5}$$

The sum of $K(A_1, A_2, q)$ and $V(q)$ (the potential of the skeleton which is independent of the electronic variables A_1 and A_2) is the adiabatic potential for the molecular coordinate q. In the classical approximation the molecular vibrations are described by the Hamiltonian function

$$H_v = P^2/2M + K(A_1, A_2, q) + V(q) \quad , \tag{6}$$

where $P = M\dot{q}$ is the momentum, M is the mass of the vibrating subsystem, and $V(q)$ is the skeleton potential. In the molecular physics language, $V(q)$ describes the motion of a symmetric stretch. It is convenient to represent the quantum evolution by Bloch variables which eliminate the arbitrary global phase in A_1 and A_2. Then, the evolution of the electronic subsystem is represented by a trajectory on the Bloch sphere. The density matrix is defined by $\rho_{mn} = A_m A_n^*$. Introducing the Bloch variables $x = \rho_{12} + \rho_{21}$, $y = i[\rho_{21} - \rho_{12}]$, $z = \rho_{22} - \rho_{11}$ one obtains from (3) and (4)

$$\begin{aligned} &\dot{x} = -\omega_0 y/q^2 - 2\mu_{12} P z/Mq \quad , \\ &\dot{y} = \omega_0 x/q^2 \ , \quad \dot{z} = 2\mu_{12} P x/Mq \quad , \end{aligned} \tag{7}$$

where $\omega_0 = (\epsilon_2 - \epsilon_1)/\hbar$. Equations (7) are complemented by the equations of motion for q. Expressing $K(A_1, A_2, q)$ with the help of the Bloch variable z one finds

$$K(z,q) = (\epsilon_+ + z\epsilon_-)/q^2 \quad , \tag{8}$$

where $\epsilon_{\pm} = (\epsilon_2 \pm \epsilon_1)/2$. Computing the force $-\delta K/\delta q$ exerted by the quantum subsystem on the classical subsystem q of the molecule one has to take account of the q dependence of z in addition to the $1/q^2$ dependence in (8). With $\delta z/\delta q = \dot{z}/\dot{q} = M\dot{z}/P$ and using the third of equations (7) one finds $\delta z/\delta q = 2\mu_{12} x/q$. Hence the equations of motion for the classical subsystem are

$$\begin{aligned} &\dot{q} = P/M \quad , \\ &\dot{P} = -\delta V/\delta q + 2[\epsilon_+ + \epsilon_-(z - \mu_{12} x)]/q^3 \quad . \end{aligned} \tag{9}$$

Equations (7) and (9) constitute the full set of coupled equations for the two interacting subsystems. The integrals of motion for the system are the radius of the Bloch sphere

$$r^2 = x^2 + y^2 + z^2 = 1 \tag{10}$$

and the energy

$$E = P^2/2M + V(q) + K(z,q) \quad . \tag{11}$$

This leaves three independent dynamical variables. The system (7) and (9) has the fixed points $x = 0$, $y = 0$, $z = \pm 1$, $q = q_{\pm}$, where $q_{\pm}$ are the solutions of the last of the equations (9) for $x = 0$, $\dot{P} = 0$, and $z = \pm 1$, respectively. It is easy to verify that these fixed points are stable elliptic if the combined potential $V(q) + K(z,q)$ has a single minimum as a function of q. In these fixed

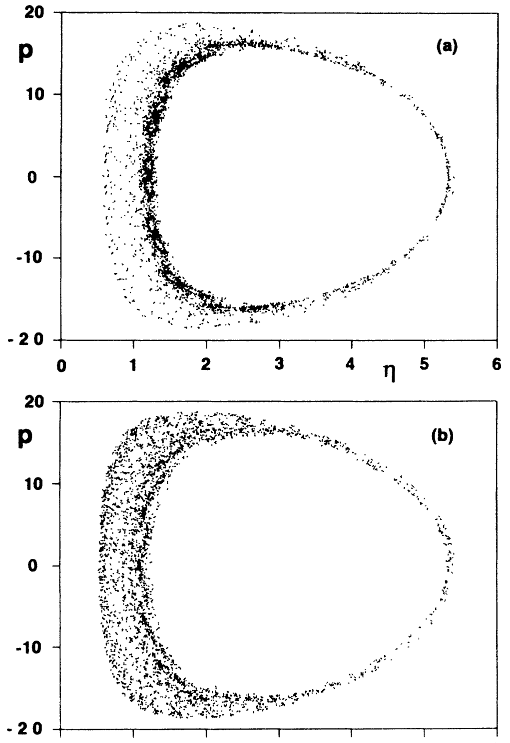

FIG. 1. $x = 0$ Poincaré sections for two different skeleton potentials of the model molecule. (a) The harmonic potential (12); (b) the truncated harmonic potential (13).

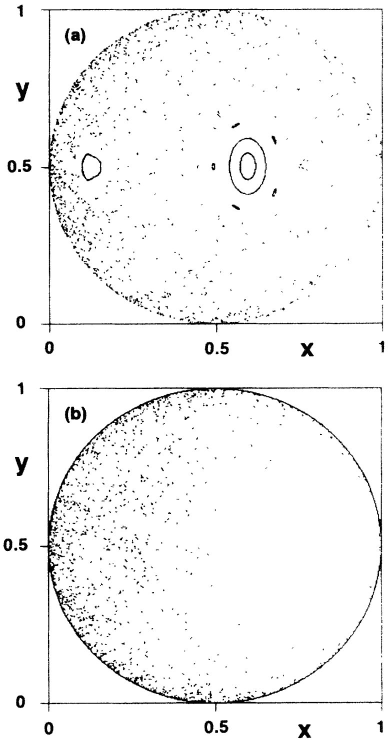

FIG. 2. Quantum chaos on the Bloch sphere of the model molecule. Shown is the phase flow on the northern [(a), $z > 0$] and southern [(b), $z < 0$] hemispheres.

points the electron is in one of its stationary states $n = 1$ or $n = 2$ in equilibrium with the size of the molecule q_- or q_+, respectively.

First we analyze the dynamics for the case of a harmonic skeleton potential

$$V(q) = V_0(q - Q)^2 \quad . \tag{12}$$

In this case the explicit values for q_- and q_+ are given by the solutions of the equation $q - Q = \epsilon_n / V_0 q^3$. One finds $q_+ > q_- > Q$; i.e., the resistance of the quantum particle against localization increases the equilibrium molecular size as compared to the skeleton value Q. Furthermore, $q_+ > q_-$; i.e., the molecular size is larger in the excited state. In Figs. 1 and 2 we present Poincaré sections of the dynamics of the vibronic and electronic subsystems, respectively. Defining the dimensionless quantities $\eta = q/Q$, $p = PQ/\hbar$, $\tau = \pi^2\hbar t/2mQ^2$, $\alpha = m/M$, and $\nu_0 = MV_0Q^4/\hbar^2$ (the total energy E is measured in units of $\epsilon = \pi^2\hbar^2/2mQ^2$), Fig. 1(a) shows the η-p projection of an $x = 0$ surface of section of a trajectory for $\alpha = 0.1$, $\nu_0 = 10$, and $E = 4$ started at $\theta = 0.95\pi$, $x = \sin(\theta)$, $y = 0$, $z = \cos(\theta)$, and $\eta = 1.42$. The resulting η-p Poincaré section clearly shows chaotic features. This impression is corroborated by Fig. 2 which illustrates the quantum flow on the Bloch sphere. Figure 2 shows the successive sections of 40 trajectories in (x, y, z, η, p) space for $\alpha = 0.1$, $\nu_0 = 10$, and $E = 6$ started at the 40 different initial conditions $x_j = \sin(\theta_j)$, $y_j = 0$, $z_j = \cos(\theta_j)$, $\eta_j = 2.4$, $\theta_j = j\pi/40$, $j = 1, 2, \ldots, 40$. This time the Poincaré section is defined by $p = 0$, $dp/dt > 0$ and the projections of the resulting section points in the x-y plane (the equatorial plane of the Bloch sphere) are shown. Because of the topology of the Bloch sphere, every point in the x-y plane actually corresponds to two points on the Bloch sphere. To eliminate this problem, Fig. 2(a) shows the projection of the "northern" hemisphere of the Bloch sphere corresponding to section points with $z > 0$, whereas Fig. 2(b) shows the "southern" hemisphere corresponding to $z < 0$. While the southern hemisphere appears completely chaotic, the northern hemisphere shows elliptic islands. The "spilling of chaos" from the northern to the southern hemisphere of the Bloch sphere indicates stochastic energy exchange between the two quantum modes.

The origin of chaos is the nonlinear resistance of the quantum particle against localization inside the box which apart from the term q^{-3} depends on the Bloch variables according to the last term in (9). It is instructive to isolate the effect of this term. Therefore, we have also analyzed the potential

$$V(q) = \begin{cases} V_0(q - Q)^2, & \text{for } q > Q \\ 0, & \text{for } q < Q \end{cases} \quad . \tag{13}$$

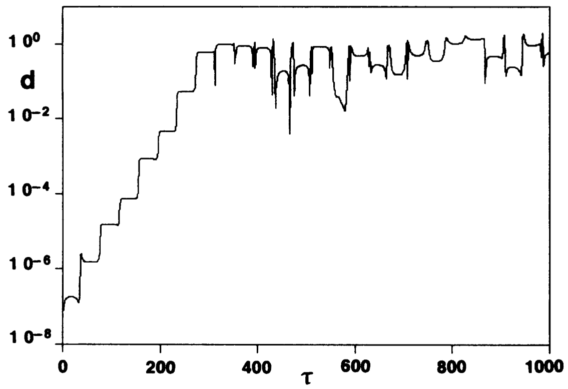

FIG. 3. Euclidean distance $d(\tau)$ of two initially close trajectories on the Bloch sphere.

In this case the skeleton would be unstable against contraction and the finite molecule size is exclusively due to the nonlinear quantum resistance against localization. A Poincaré section for this potential is shown in Fig. 1(b). We chose the same initial conditions as in Fig. 1(a). The resulting chaos in Fig. 1(b) confirms that the main origin of chaos is the "quantum pressure" resulting from the confinement of the quantum system in the dynamic box potential. Therefore, the occurrence of quantum chaos in this system is a direct consequence of Heisenberg's uncertainty principle.

In order to prove that the quantum dynamics on the Bloch sphere is genuinely chaotic, we calculated the Euclidean distance $d(\tau) = \{[x(\tau)-x'(\tau)]^2+[y(\tau)-y'(\tau)]^2+[z(\tau)-z'(\tau)]^2\}^{1/2}$ between two initially close trajectories. For the reference trajectory (x,y,z,η,p) we chose the same initial conditions and energy as in Fig. 1(a). The trajectory (x',y',z',η',p') was started with $x'=x$, $y'=y$, $z'=z$, $\eta'=\eta+10^{-7}$ and p' was computed from energy conservation ($E=4$). The result is shown in Fig. 3. The initial exponential growth of $d(\tau)$ is clearly visible. It corresponds to a positive Liapunov exponent for the quantum subsystem. At $\tau \approx 300$ the exponential growth of $d(\tau)$ breaks. This is natural since d cannot be larger than the diameter of the Bloch sphere which equals 2.

In summary, we showed that the coupling of classical and quantum degrees of freedom can lead to chaos in both the quantum and the classical subsystems even in the simplest model of such systems. Our model system exhibits a mixed phase space with regular and chaotic regions. In the chaotic region we observe *exponential separation of quantum amplitudes* characterized by a positive Liapunov exponent on the Bloch sphere. Our analysis is of general importance since systems with a mixed classical-quantum description are obtained naturally as a result of the Born-Oppenheimer approximation. Whenever a mixed (or chaotic) phase space is obtained in the first Born-Oppenheimer step (quantization of the fast variables), all the methodology of "traditional" quantum chaos theory [1–3] is required to successfully complete the second Born-Oppenheimer step, the quantization of the intricate phase-space structures. Since many systems in solid state and molecular physics are analyzed in the framework of the Born-Oppenheimer approximation, we expect that this novel type of quantum chaos will soon find some important applications.

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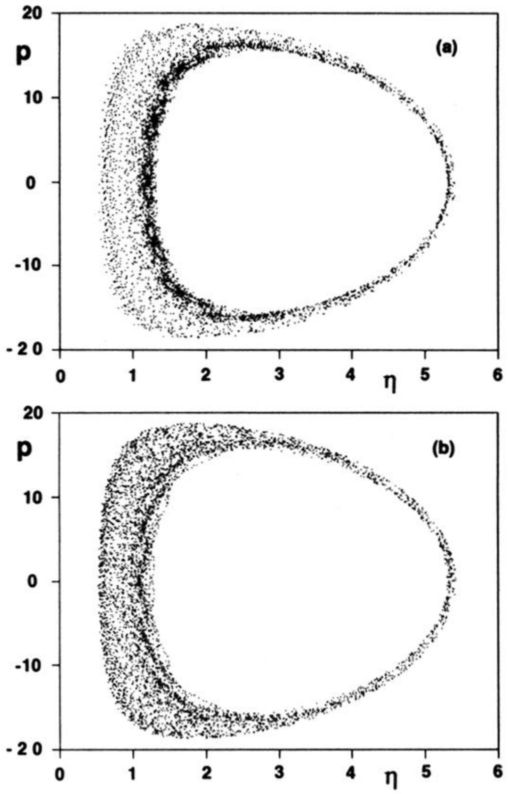

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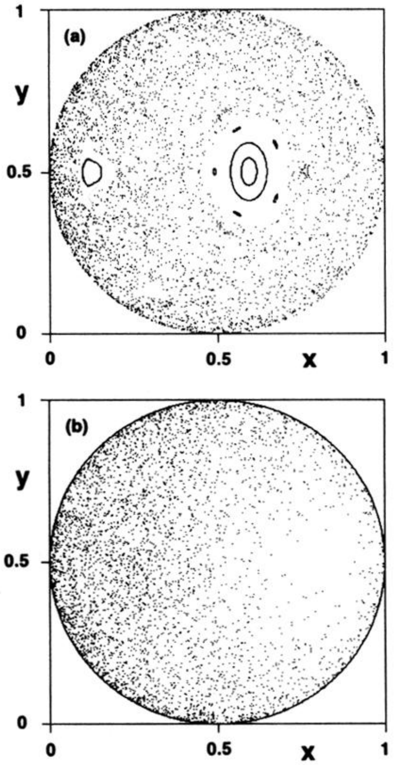

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