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Quantum Map for Molecular Vibrations in High-Frequency Fields

R. Graham and M. Höhnerbach

Fachbereich Physik, Universität Essen Gesamthochschule, D-4300 Essen, Federal Republic of Germany

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Molecular vibrations in a Morse potential driven by a high-frequency electromagnetic field are described by a return map for the energy change within a vibration period and the canonically conjugate phase angle. Quantizing this dynamical system we study the molecular excitation and dissociation for initial states in the classically regular and chaotic regions.

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The quantum dynamics of systems which exhibit chaos in their classical limit has been studied intensively in recent years. The principal example which has been investigated both experimentally[1] and theoretically[2-4] is the ionization of excited hydrogen atoms by microwave fields. As another example, to which the present paper will be devoted, dissociation of diatomic molecules by infrared fields has been considered.[5-7] A convenient way to model this system is to consider the Hamiltonian of a Morse oscillator driven by an external periodic field

$$H_0=\tfrac{1}{2}p^2+\tfrac{1}{2}[1-\exp(-x)]^2-gx\cos(\omega t)\,. \tag{1}$$

[We use units where the dissociation energy equals $\frac{1}{2}$ and the frequency of small oscillations is unity; g is the amplitude of the electric field. For example, for the HF molecule in the field of a CO_2 laser with an electric field strength of 0.45 eV/(Bohr radius), we have in these units $g=0.01$, $\omega=0.25$, $\hbar=0.042$.] Solving Hamilton's equations and the Schrödinger equation corresponding to Eq. (1), Walker and Preston[5] and later, in a refined way, Gioggin and Milonni[7] compared the classical and quantum dynamics of this system, concluding that both descriptions agree well except near multiphoton resonances[5,7] and higher-order classical resonances.[7] While Ref. 5 was restricted to the bound states of the oscillator, Ref. 7 included the continuum but instead used a spatial discretization to solve the Schrödinger equation. In earlier work Leforestier and Wyatt[6] used an optical-potential approach to describe the decay into the continuum.

In the present paper we apply a new approach to the quantum problem posed by (1), which is based on the construction of a suitable return map and its subsequent quantization. The method explicitly takes into account transitions into the continuum in a comparatively simple fashion. In this way we are able to improve the comparison of the classical and quantum dynamics leading to dissociation. Elements of our approach were developed by Casati, Guarneri, and Shepelyansky[8] in their treatment of the hydrogen problem. The general scheme behind the method of quantization was discussed in Ref. 9. While not exact, the approach is numerically very efficient and, where it is comparable to earlier work, it gives an accurate description. In the following we describe our method and present results obtained by its implementation.

In order to derive the return map we introduce the action and angle variables I,θ of the (undriven) Morse oscillator and also describe the external field by a pair of action angle variables N,φ. A total, conserved Hamiltonian $H=H_0(I,\theta,\varphi)+\omega N$ may then be defined. By suitably choosing the origin of N, we may always assume $H=0$. Then $-\omega N$ is the energy of the oscillator in the presence of the external field and has the range $\frac{1}{2}>-\omega N>0$. Solving $H_0+\omega N=0$ for $I\equiv-\tilde{H}(\theta,N,\varphi)$ and using θ as a new effective time variable $\tilde{t}$ measured in units of vibration periods, $\theta=(\tilde{t}+\theta_0)(\mathrm{mod}\,2\pi)$, we can look upon $\tilde{H}$ as the Hamiltonian generating the motion as measured in this redefined time coordinate. Hamilton's equations then read $\varphi_{\tilde{t}}=\tilde{H}_N$, $N_{\tilde{t}}=-\tilde{H}_\varphi$, denoting derivatives by subscripts. These equations are now integrated over one vibration period $\Delta\tilde{t}=2\pi$, assuming that g is sufficiently small $[2\pi g/\omega\ll(1+2\omega N)^{1/2}]$ that a first-order analysis is justified. The analysis proceeds along the lines given in Ref. 9 and will be presented elsewhere. The return map is obtained as[10]

$$\begin{aligned}\varphi_{n+1}&=\varphi_n+\frac{\pi\omega}{(1+2\omega N_n)^{1/2}}+\frac{\pi\omega}{(1+2\omega N_{n+1})^{1/2}}\\&\quad+\frac{g}{2}[f'_-(N_n)+f'_-(N_{n+1})]\cos\tilde{\varphi}_n\,,\\N_{n+1}&=N_n+\frac{g}{2}[f_-(N_{n+1})+f_-(N_n)]\sin\tilde{\varphi}_n\,,\\\tilde{\varphi}_n&=\varphi_n+\frac{\pi\omega}{(1+2\omega N_n)^{1/2}}+\frac{g}{2}f'_-(N_n)\cos\tilde{\varphi}_n\,,\end{aligned}\tag{2}$$

with

$$f_-(N)=-\frac{2\pi}{\omega}\left[\frac{1-(1+2N\omega)^{1/2}}{1+(1+2N\omega)^{1/2}}\right]^{\omega/2(1+2N\omega)^{1/2}} \tag{3}$$

As the molecular energy $(-\omega N)$ over one vibration period is changed most drastically by the infrared field when the nuclear distance passes its minimum, the change effectively occurs via discrete kicks described by the terms proportional to g in Eq. (2). [Physically this description is appropriate as long as the energy change due to a kick, $\omega g f_-$, is large compared to the energy

$(g^2/2\omega^2)$ of the free motion in the external field; cf. the last paper of Ref. 8.] These kicks are superimposed on the integrable dynamics of $-\omega N$ and the canonically conjugate phase φ of the external field, described by the remaining terms in Eq. (2). We took care to maintain the symmetry $\varphi \rightarrow -\varphi$, $n+1 \leftrightarrow n$ of the exact dynamics.

Equations (2) and (3) hold for states below the dissociation threshold, i.e., for $-\omega N < \frac{1}{2}$. However, we find[10] that for a single time step the map can be extended to unbounded states by performing an analytical continuation to the domain $-\omega N > \frac{1}{2}$. The map (2) is extended to this regime by the formal replacements, for $-\omega N > \frac{1}{2}$,

$$f_-(N) \rightarrow f_+(N) = -\frac{2\pi}{\omega}\exp\left[-\frac{\omega \arctan|1+2\omega N|^{1/2}}{|1+2\omega N|^{1/2}}\right], \tag{4}$$

and $(1+2\omega N)^{1/2} \rightarrow |1+2\omega N|^{1/2}$. Dissociation during each step of the map is then taken into account by projecting the state (in general described by an ensemble of points) on the bound states $-\omega N < \frac{1}{2}$ after the application of the map (2)-(4). While Eqs. (2) and (3) are already sufficient for a classical description of the bound states, the extension (4) of the map to unbounded states for a single time step turns out to be indispensable for a proper quantization (cf. below). Close to the dissociation threshold $-\omega N = \frac{1}{2}$ the functions $f_\pm(N)$ simplify to $f_\pm(N) \simeq -(2\pi/\omega \exp\omega)$ and the map (2)-(4) simplifies correspondingly. We shall refer to the simplified version as the "Morse map" in analogy to the corresponding "Kepler map" derived for the Kepler potential in Ref. 8. The full map (2)-(4) we shall refer to as the "refined Morse map." In Fig. 1 the invariant manifolds of the full return map of the Hamiltonian (1), the refined Morse map, and the Morse map are compared. We find good agreement between the numerically constructed full return map and the refined Morse map in the whole range of initial states considered, and with the Morse map in a broad range below the dissociation threshold.

Next we proceed to quantize the map (2)-(4). The quantization is done with a view to the semiclassical limit, which we wish to describe accurately. We quantize in the φ representation by choosing $N = -i\hbar\,\partial/\partial\varphi + \hbar N_0$ with quantum numbers $N_l = \hbar(l+N_0)$, l integer. The parameter N_0 is real, $0 \le N_0 < 1$, and must be fixed by satisfying the condition $H=0$ for the initial state. In our numerical examples below we shall consider free molecular eigenstates with energy E_v $(0 < E_v \le \frac{1}{2})$ as initial states. Then the quantum number l for the initial state and N_0 are given, respectively, by the integer and fractional part of $-E_v/\hbar\omega$. The quantized map, in the Schrödinger picture, takes the form

$$|\psi_{n+1}\rangle = e^{-(i\pi/\hbar)\tilde{H}_0} PUP\, e^{-(i\pi/\hbar)\tilde{H}_0} |\psi_n\rangle . \tag{5}$$

Here

$$U(N,\varphi) = \exp\left(-\frac{ig}{2\hbar}[f_\pm(N)\cos\varphi + \cos\varphi\, f_\pm(N)]\right) \tag{6}$$

is unitary, N and φ are operators, and the subscripts $-,+$ define how U acts on the subspace of bound and unbound states, respectively. For the Morse map U can be written down explicitly in the N representation, in terms of Bessel functions. In order to construct U in the N representation, for the refined Morse map, we differentiate U with respect to g and numerically solve the resulting first-order differential equation in a sufficiently large number of N eigenstates, including those from the unbound subspace, in order to obtain a converged unitary matrix $U_{ll'}$. As $f_\pm$ are pieces of a single analytical function the subscripts $\pm$ can be dropped in Eq. (6).

P in Eq. (5) denotes projection on the bounded subspace; i.e., like in the classical map, the component of the state which has evolved into the unbounded subspace is discarded in each time step. We emphasize, however, that in our numerical construction for the refined Morse map the operator PUP is strongly influenced by the continuum [and therefore our analytical continuation of $f_-(N)$ to $f_+(N)$ is necessary] which appears in intermediate states. Those excitations to the continuum which are deexcited to the bound subspace within one vibration period are fully taken into account in PUP.

Finally, $\tilde{H}_0$ in Eq. (5) need only be specified for the bound subspace. It is diagonal in the N representation with eigenvalues given by

$$\tilde{H}_0 = -1 + [1 + 2\omega\hbar(l+N_0)]^{1/2} .$$

We now describe our results. In order to test the

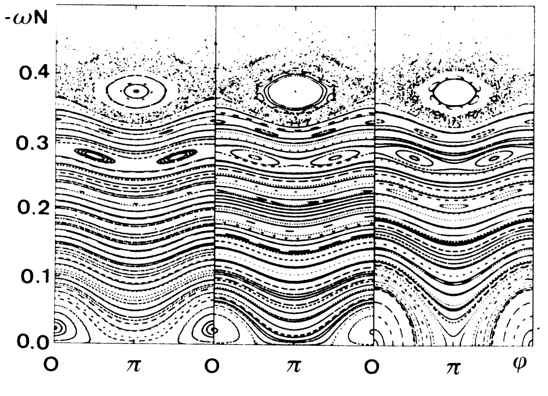

FIG. 1. Poincaré cross section of the full dynamics, the refined Morse map, and the Morse map (from left to right, for $\omega = 1$, $g = 0.01$).

quantum map we first studied the excitation of the molecule from its ground state for the same parameter values as used in Refs. 5 and 7 and found good quantitative agreement. In this case the ground state is in the classically regular regime and the molecule remains bound both in the classical and in the quantum description. Then excited vibrational eigenstates of the molecule were used as initial states and the resulting classical and quantum dynamics determined by numerical iteration of the map for a fixed number of vibration periods. The classical calculations were performed with an ensemble of 1000 initial points of fixed value of N and equidistributed initial phase φ. In Fig. 2 we plot the classical and the quantum probability of dissociation P after 100 vibration periods as a function of the initial molecular energy. On the same scale the phase-space manifolds of the classical map are also given. The classical molecule is seen to dissociate more easily than the quantized one, in general. However, the quantum probability displays pronounced resonances, where states which dissociate relatively easily are bracketed by states, separated by a photon energy, which are comparatively stable. For the parameters chosen in Fig. 2 the two most pronounced quantum resonances appear at the winding numbers (ratio of field and oscillator frequencies) 3 and 4. The classical threshold for the initial value of the oscillator energy where dissociation is first observed coincides with the classical chaos border (as can be seen clearly by comparing with the phase-space plot) and it can be estimated from classical resonance overlap,[11] or, more precisely, by locally approximating the Morse map by the standard map[8,10,12] (B_C in Fig. 2). The quantum dissociation threshold is higher than the classical result; i.e., quantization increases the stability of the molecule. Further computations performed by us[10] show that the pronounced quantum resonances seen in Fig. 2 depend on the infrared field amplitude and generally decrease in strength if the latter is raised.

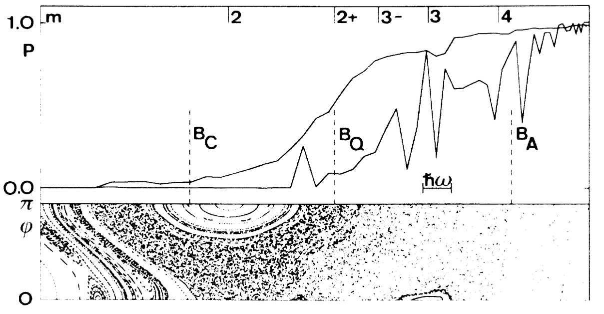

FIG. 2. Dissociation probability P after 100 vibration periods (upper curve is classical, lower curve is quantum) vs initial molecular energy, and corresponding phase-space structure. m is the phase-averaged position of the primary resonances and cantori $2+ = 2+\gamma^{-2}$, $3- = 3-\gamma^{-2}$; B_C is the classical chaos border estimated from a locally equivalent standard map; B_Q is the phase-averaged position of the last impenetrable cantorus; B_A is the delocalization border (for $\omega = 1$, $g = 0.01$, $\hbar = 0.01$; the quantum probability is defined for a discrete set of initial energies, and the continuous curve merely serves as a guide to the eye).

In order to understand the overall stabilizing effect of quantization two hypotheses were explored by us: (i) stabilization by Anderson-type localization[2,8,13] and (ii) stabilization by the presence of cantori in the classical map.[12,14]

In the classically chaotic region the action variable $N = \hbar(l + N_0)$ undergoes a diffusion process $(\Delta l)^2 = \langle (l - \langle l \rangle)^2 \rangle = D_l n$ whose diffusion constant D_l may be estimated by well-known methods. If Anderson-type localization of the action variable in the quantum system occurs, a localization length $L = \Delta l = \alpha D_l$ appears[2,8,13] where α is of order 1. For the Morse map we estimate, with $\alpha = 1$, $D_l = 2\pi^2 g^2 / \hbar^2 \omega^2 e^{2\omega}$. In the presence of localization, dissociation can only take place from initial states l_0 within a localization length from the dissociation border. The predicted threshold is indicated in Fig. 2 as B_A. We see that in the molecular system the predicted dissociation threshold roughly separates the region where complete dissociation occurs within 100 vibration periods from the region where some (but not all) states decay on a considerably longer time scale. However, even in the latter region localization is incomplete at best and, for some initial states, e.g., at $m = 3$, completely destroyed by quantum resonances.

Kolmogorov-Arnol'd-Moser tori in the classical system are broken into cantori which act as obstacles for the classical diffusion and may become impenetrable for the quantum system.[12] The phase-averaged position of the cantori with winding number $2+\gamma^{-2}$ and $3-\gamma^{-2}$ $[\gamma = (1+\sqrt{5})/2]$ are indicated in Fig. 2. Allowing for its deformation towards smaller values of $-\omega N$ in the real map, the cantorus with $2+\gamma^{-2}$ is seen to provide a good quantitative threshold for the first appearance of dissociation in the quantum system. The action ΔW_m per iteration passing the cantorus at winding number $m \pm \gamma^{-2}$ can be estimated by available methods[12] as $\Delta W_m \simeq (0.12\omega/m^3)\ [\ln(39.5 m^3 g/\omega^2 e^{\omega})]^{3.012}$ for the Morse map, if the scaling variable in the brackets is small. For the parameter values of Fig. 2 we find $\Delta W_2 \simeq 5\times 10^{-3}\hbar$, $\Delta W_3 \simeq 1.1\hbar$, but ΔW_3 might be outside the limits of applicability of the scaling formula already; furthermore, the strong dependence of the scaling variable on m renders the simple version of the scaling formula quantitatively unreliable, and the numbers given for ΔW_2 and ΔW_3 should merely be considered as lower and upper bounds, respectively. Thus initial states with winding numbers below the cantorus with $m = 2+\gamma^{-2}$ should be stable against dissociation, in good agreement with our results.

To summarize, we have presented a new method for the efficient investigation of molecular vibrations in infrared fields, and we tested the method against results obtained earlier by different approaches. We then obtained new results for the dissociation probability of initial states in the classically regular and chaotic regimes. On the average a general stabilizing effect of quantization on the molecule was found—however, superimposed by pronounced quantum resonances across which the dissociation probability varies dramatically. Experimentally these resonances should be seen by varying the initial state for fixed field amplitude. However, one has to keep in mind that experimentally time is measured in units of field cycles while the theory uses vibration periods instead. The sharp classical dissociation threshold agrees with the classical chaos border; its quantum-mechanical increase was found to be in reasonable agreement with the mechanism of stabilization by cantori. Again, this result may be tested experimentally. Initial states above this quantum threshold dissociate, but, except near resonances, at a rate smaller than the classical one. The localization length L estimated for this regime provides a reasonable estimate for the distance from the continuum below which the dissociation rate is essentially the classical one.

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