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# Optimal Stimulation of a Conservative Nonlinear Oscillator: Classical and Quantum-Mechanical Calculations

S. Krempl,[a] T. Eisenhammer,[b] A. Hübler, and G. Mayer-Kress[c]
*Center for Complex Systems Research, Physics Department, Beckman Institute, University of Illinois, Urbana, Illinois 61801*

P. W. Milonni
*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

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A new method for nonlinear polychromatic resonant stimulation of conservative nonlinear oscillators is introduced. As an example we consider a Morse potential that serves as a model for the HF molecule. Numerical results show that a large energy transfer to such a conservative oscillator is possible under optimal stimulation with small driving fields. This makes selective excitation of specific modes possible. The classically determined optimal force was also applied to the corresponding quantum system, with similar results in energy transfer and dissociation.

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Recently a very general and elegant method for the resonant stimulation and optimal control of nonlinear systems was introduced. It has been successfully applied to several nonlinear systems such as anharmonic oscillators with dissipation [1]. While in the case of the damped oscillator the resonant polychromatic driving force and the dynamics of the controlled system are given by the time-reversed dynamics of the *uncontrolled* oscillator, this concept fails for conservative systems.

In the present work we introduce a new method for optimal stimulation which can excite conservative systems very efficiently. We apply the classically determined resonant driving force to a classical system and the corresponding quantum-mechanical system and compare the results. Such an approach is suggested by the close correspondence between classical and quantum calculations as has been reported earlier, e.g., for the Morse oscillator with a sinusoidal driving force [2], for Rydberg hydrogen atoms [3], or the dissociation of $H_3^+$ [4]. We consider the Morse oscillator, a well-known model for molecular vibrations [5]. We show that large energy transfer and dissociation are possible for both classical and quantum systems, while for monochromatic driving forces dissociation probabilities are lower by orders of magnitude [2]. The results of quantum and classical calculations are in good agreement.

With a similar goal, optimal control theory—together with full quantum calculations—has been applied to quantum-mechanical systems [6]. Artificial intelligence methods such as genetic algorithms have been used more recently to calculate optimal quantum driving fields [7]. These methods have in common that they use a brute force approach to obtain the optimal solutions. This might be justified for engineering-type applications; it does not provide much physical insight into the problem. In contrast, our methods provide a very general methodology with direct physical interpretations.

Resonant stimulation methods may be of relevance to molecular spectroscopy and laser chemistry. Nearly two decades ago it was found to be possible to dissociate polyatomic molecules with smaller laser powers than had previously been anticipated [8]. Dissociation was found to depend on the total energy in the laser pulse rather than on the intensity. It has been suggested based on purely classical models that such behavior may be due to chaotic dynamics of the driven nonlinear system [9,10]. The early experiments suggested the possibility of selective mode excitation or dissociation. However, it has proven difficult to realize this goal, perhaps because the onset of chaos causes the absorbed energy to spread ergodically over many modes [10]. With the resonant stimulation technique presented here a substantial excitation or dissociation may be possible at field strengths well below those necessary to drive the system into a chaotic regime in which selective state or mode excitation may be difficult [11].

In the following the method for calculating the optimal resonant driving force is presented. As a model we consider a particle with charge $e$ and mass $m$ in a one-dimensional potential $V(x)$. Here, the external driving force is given by the dipole interaction $eE(t)$:

$$H = p^2/2m + V(x) - exE(t) . \tag{1}$$

The optimal driving force is obtained from a variational calculation: A certain amount of energy has to be transferred into the system within a fixed time $T$ at a minimum effort (reaction power). The average squared electric field that is proportional to the energy flux for a plane wave is used as a measure of the effort:

$$\int_0^T dt\, E^2(t) = \text{minimal} , \tag{2}$$

$$\int_0^T dt\, eE(t)p = \text{const} , \tag{3}$$

$$\dot{p} + V'(x) - eE(t) = 0 . \tag{4}$$

The equation of motion (4) is an additional constraint to the variational problem, where the prime denotes the derivative with respect to $x$. The variational problem is given by

$$0=\delta\int_0^T dt\{E^2(t)+\lambda_1 E(t)p+\lambda_2(t)[\dot{p}+V'(x)-eE(t)]\}, \tag{5}$$

where $\lambda_1$ and $\lambda_2(t)$ are Lagrange multipliers. Since our objective is to gain a certain energy transfer, not to reach a distinct point in phase space, a variable end-point variational calculus is used. The variation leads to a differential equation for the electric field:

$$m\ddot{E}(t)+E(t)V''(x)=0. \tag{6}$$

The second Euler equation deduced from the variation corresponds to the equation of motion (4). From the variation at the end point the conditions at the boundaries $(t=0,T)$, $\delta(p^2/2m+V)=0$ and $EV'-\dot{E}p=0$, are obtained. Without loss of generality we shall only regard solutions with initial conditions $x(0)=x_0$, $p(0)=0$, since every trajectory can be thought of as an extension of a trajectory starting at these initial conditions. Considering the end-point condition, $E(0)$ has to vanish. The expression $E(t)=f(t)p$ provides a solution of the variational problem for the specified initial condition:

$$E(t)=2p/e(t+t_0), \tag{7}$$

where $t_0=-2V'(x_0)/e\dot{E}(0)$. For reasonable potential $V(x)$ the solution of the coupled differential equations, Eqs. (4) and (6), is unique for given $x(0)$, $p(0)$, $E(0)$, $\dot{E}(0)$. Therefore Eq. (7) gives the unique solution that provides a specified energy transfer at a minimal flux within a certain time. The constant $t_0$ and $\dot{E}(0)$ are determined by the constraint (3).

Equations (4) and (7) give an ordinary differential equation which can be numerically integrated for given initial conditions. We call this special solution the intrinsic optimal driving field $E^*(t)$. In contrast to the control methods introduced in [12], no feedback from the experimental system is necessary to determine $E^*(t)$. This fact is especially important since in general the initial conditions $(x(0),p(0))$ of an experimental system, e.g., for a molecule, are not known precisely. Therefore, we apply $E^*(t)$ to an ensemble of various initial conditions to gain statistical information about the system's control properties. The stability of the stimulation is obviously of concern. A small initial difference $\epsilon$ between the controlled system $(\tilde{x},\tilde{p})$ with arbitrary initial conditions and the optimally driven oscillation $(x,p)$, $\epsilon(t)\equiv\tilde{x}(t)-x(t)$, develops in first-order approximation according to $\ddot{\epsilon}-(\epsilon/m)\times V''(x)=0$. The difference $\epsilon$ remains small for trajectories of the controlled oscillator that are initially in a neighborhood to the initial conditions of the optimally driven system. The lack of stability allows efficient stimulation only for driving fields of short duration.

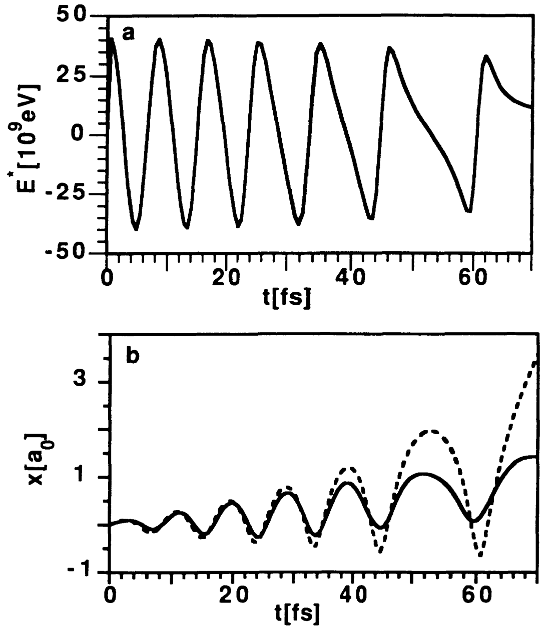

FIG. 1. (a) Example of a resonant driving field $E^*(t)$ computed for the Morse oscillator. Parameters for the calculation of $E^*(t)$ are $t_0=3$ fs, $T=70$ fs, $x(0)=0$, $p^2(0)/2m=16$ meV. (b) Expectation value of position $\langle x\rangle=\langle\psi(t)|x|\psi(t)\rangle$ (solid line) for the quantum system compared to the position $x$ (dashed line) of the optimally driven classical particle. The quantum system was initially in the ground state.

Furthermore, the Hamiltonian of the driven system has to be known to achieve effective stimulation. As discussed later in this paper, parameters of the Hamiltonian can be determined using nonlinear resonance spectroscopy [1].

For the numerical calculations the equation of motion for the Morse oscillator was used:

$$\dot{p}=-2aD[\exp(-ax)-\exp(-2ax)]+d_1E^*(t),$$

where $D$ and $a$ are the dissociation energy and range parameter of the Morse potential, and $d_1$ is the effective charge or dipole gradient. The following parameters were taken for the HF molecule [2]: $D=6.125$ eV, $a=1.1741a_0^{-1}=2.219\times10^{10}$ m$^{-1}$, $d_1=0.7876$ D/$a_0$ $=4.965\times10^{-20}$ C.

Figure 1(a) shows an example of $E^*(t)$. The field oscillates with almost constant amplitude and decreasing frequency, which is consistent with the fact that the quantum level spacings decrease with increasing excitation. A similarly "chirped" driving field was deduced on a phenomenological basis and used successfully earlier [13]. Here the driving field is calculated on a purely analytical basis from a variational principle. As can be seen in Fig. 2, the energy transfer $\Delta H$ to the controlled classical system is selective with respect to the initial phase difference (corresponding to $\epsilon$) to the optimally driven system. The phase was defined as $\Phi=\mathrm{sgn}(p)$

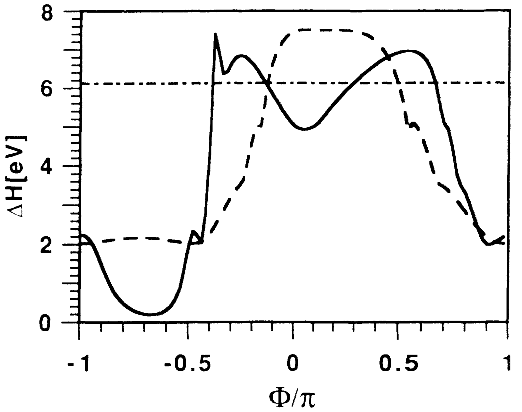

FIG. 2. Energy transfer $\Delta H$ as a function of the intial phase difference between the controlled and the optimally driven system. Parameters for calculation of the driving field as in Fig. 1. Dashed line: initial energy of the controlled system is the same as the optimally driven system. Solid line: initial energy of the controlled system is equal to the quantum-mechanical ground-state energy $H_0 = 0.254$ eV. Dash-dotted line: dissociation energy $D$.

$\times \arctan\sqrt{V(x)/T(p)}$, where $T(p)$ is the kinetic energy. The energy transfer $\Delta H$ was calculated for two different initial energies of the controlled system. In one case the initial energy of the controlled system was equal to the initial energy of the optimally driven system (dashed line). The controlled system is effectively excited and even dissociated by very small forces if the initial phase difference is small. With larger initial energy of the controlled system (solid line) $\epsilon$ is large for any $\Phi$. Nevertheless, a similar number of trajectories exceed the dissociation level. Eventually trajectories of the controlled system come close to the optimally driven system's trajectory and are carried along. Thus, with resonant stimulation a large average energy transfer into the system is possible even without exact information about the initial conditions of the controlled system.

The corresponding quantum system was studied by numerical integration of the time-dependent Schrödinger equation, given by

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + D[1-\exp(-ax)]^2\psi - d_1 E^*(t) x\psi . \qquad (8)$$

Again, $E^*(t)$ is the classically calculated field. The quantum system was prepared to be initially in the ground state. The energy eigenvalues of the Morse oscillator are given very accurately by $H_n = BD(n+\frac{1}{2}) \times [2 - B(n+\frac{1}{2})]$, where $B = (\hbar^2 a^2/2Dm)^{1/2} = 0.0419$. Equation (8) was integrated numerically using a standard algorithm [14]. The dissociation probability $P_d$ was computed using the formula $P_n(t) = |\langle\psi_n|\psi(t)\rangle|^2$, $P_d(t) = 1 - \sum_{n=0}^{23} P_n(t)$, where the $|\psi_n\rangle$ $(n=0,\ldots,23)$ are the analytically given eigenstates of the unperturbed Morse oscillator [15]. The time steps and the number of grid points for the computation were increased until only negligible differences in $P_d$ were found. The size of the box, to which the computation is confined, was increased to about $25a_0$ at a resolution of 4096 grid points. 75000 time steps were used, allowing a relative error $\leq 5\%$ in $P_d$.

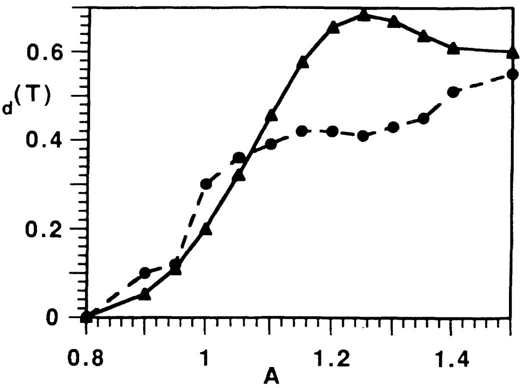

FIG. 3. Dissociation probability $P_d(T)$ as a function of the amplitude factor $A$ for the classical (dashed curve with circles) and quantum (solid curve with triangles) systems. Parameters for calculation of the driving field are the same as in Fig. 1.

In Fig. 1(b) the expectation value of position $\langle x\rangle = \langle\psi(t)|x|\psi(t)\rangle$ is shown in comparison to the position $x$ of the optimally driven classical particle. Especially for short times, the quantum-mechanical system closely follows the oscillations in $x$. For pulses of long duration and low fields the close resemblance between the classical and the quantum system is lost, and the stimulation is less effective.

In order to compare the quantum-mechanical and classical systems a classical $P_d$ was calculated by sampling over a set of 100 initial conditions, equally spaced in phase space with initial energy equal to the quantum ground state. $P_d(T)$ was defined by the fraction of trajectories for which the final energy at time $T$ exceeds the dissociation level $D$.

Figure 3 shows $P_d(T)$ for both the quantum-mechanical and the classical systems as a function of the field scaled by a constant factor: $\tilde{E}(t) = AE^*(t)$. For the quantum-mechanical system $P_d(T)$ can be remarkably increased by minor increases in the field amplitude. Maximum dissociation is obtained by choosing the amplitude factor $A = 1.25$. In the classical case the effect of increased $A$ is smaller.

As suggested for dissipative systems [1], nonlinear resonance spectroscopy is possible by varying the parameter of the potential $\tilde{D} = D + \Delta D$ in the calculation of the optimal driving field. Starting at the same initial conditions the optimal driving field $E^*(\tilde{D};t)$ was calculated with the same parameters until the optimally driven system exceeded the dissociation level $\tilde{D}$ by 10%. The classical and

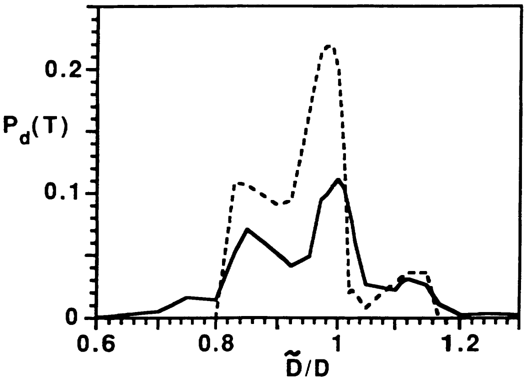

FIG. 4. Resonance curves: dissociation probability $P_d(T)$ as a function of $\tilde{D}/D$ for the classical (dashed line) and the quantum (solid line) system. Parameters for the calculation of $E^*(t)$ are $t_0=3$ fs, $x(0)=0$, $p^2(0)/2m=0.254$ eV, $A=1$.

the quantum-mechanical resonance curves are similar, and in particular the maxima in $P_d(T)$ are at the same positions; see Fig. 4. Both systems show their largest peak in $P_d(T)$ at $\tilde{D}=D$. Neighboring peaks correspond to different numbers of oscillations in $E^*(\tilde{D};t)$. For faster stimulation (smaller $t_0$) and larger $A$ the dissociation becomes more effective, but the resonance curves become broader.

In summary, our numerical calculations indicate that resonant stimulation of a conservative system, as introduced in this paper, may effectively excite and dissociate both classical and quantum systems. The optimal field was found to be parallel to the vibration of the molecule. Its amplitude is a smooth, decreasing function of time, Eq. (7). Numerical simulations show an ac field with decreasing frequency and almost constant amplitude. The appearance of sharp resonance curves suggests the possibility of the kind of nonlinear spectroscopy considered previously for dissipative systems.

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[a] Permanent address: Chaosgruppe an der Technischen Universität München, Arcisstrasse 21, D-8000 München 2, Federal Republic of Germany.

[b] Permanent address: Ludwig-Maximilians Universität, Sektion Physik, Lehrstuhl Professor Dr. R. Sizmann, Amalienstrasse 54, D-8000 München 40, Federal Republic of Germany.

[c] Permanent address: Santa Fe Institute, 1660 Old Pecos Trail, Suite A, Santa Fe, NM 87501.

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