

Resonance Curve and Speed-Gradient Design of Control Algorithms for Dissociation of Diatomic Molecule Ensembles

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Abstract

Two methods for dissociation of diatomic molecules based on nonperiodic excitation generated by feedback control mechanism are described and analyzed by computer simulation for classical and quantum-mechanical ensembles. The first method of control design uses nonlinear resonance curve of the system to fulfill the resonance conditions at any time of excitation. The second method is based on the speed-gradient principle. Implementation of the proposed methods by pulse laser control is described. Efficiency of the proposed methods is demonstrated by the example of hydrogen fluoride (HF) molecule dissociation. Simulations confirmed that new methods are more efficient than the existing algorithms based on harmonic (monochromatic) and linear chirping excitation both for the model case of single molecule and for an ensembles of molecules. It is shown that the dissociation rate for the quantum-mechanical ensemble is just a few percent slower than the one for the classical ensemble. It justifies using classical models for feedback control design in the dissociation problem.

1 Introduction

Since the beginning of the 1990s a growing interest has been observed in the control problems for molecular systems in classical and quantum formulation [1–5]. One of the benchmark problems in the field is the dissociation problem for diatomic molecules [2, 6–10]. In the paper [6] possibilities of dissociation a molecule by monochromatic (single frequency) laser field have been explored for the case of hydrogen fluoride (HF) molecule using Chirikov's resonance overlap criterion. In [7, 8] the case of two-frequency (two-laser) control field was investigated. It was shown that intensity of bichromatic field required for dissociation can be reduced compared to monochromatic case. In [10] the further reduction of the control field intensity has been demonstrated by means of chirping (frequency modulation) the laser frequency with constant chirping rate.

New possibilities for changing of physical and chemical properties are provided by using feedback for control design. In [2] methods based on geometric control theory (inverse control) were proposed for control of molecular systems, including dissociation problems for diatomic and triatomic molecules. In a number of papers possibility of optimal control de-

sign is discussed. Two methods for dissociation of diatomic molecules design by feedback control based on resonance curve and speed-gradient principle were proposed in [11, 12].

In this paper the algorithms of [11, 12] are further developed and analyzed. The first algorithm is based on the dependence of the natural frequency of the nonlinear molecule oscillations on its energy, further referred to as *energy resonance characteristics* or *energy resonance curve* is employed. For control design the knowledge of the energy resonance curve is required. In this paper the case of Morse potential is considered, which allows obtaining this dependence in a simple analytical form. For other potentials, where the analytical solution is too complicated or impossible, the energy resonance curve can be obtained numerically. Efficiency of the proposed algorithm for the case of HF molecule is illustrated by computer simulation. It is shown that the time of dissociation can be reduced significantly.

Second algorithm is based on the speed-gradient method [13, 14]. Design of the algorithm does not rely on the shape of the potential energy of molecule and does not require precalculation of the energy resonance curve. In order to demonstrate applicability of the proposed methods to realistic experimental situations we compare one of the proposed methods with the optimal linear chirping by simulating it for a molecular ensemble. The open-loop pulse control strategy is used that fits modern femtosecond laser pulse experimental technologies [15].

Note that the algorithms of [11, 12] are based on classical models of molecular dynamics. Classical models are often used instead of the quantum ones in dynamics calculations of molecular motion [6, 7, 16–18]. It was shown that classical and quantum dynam-

ics give similar results for model systems with one or two degrees of freedom. Even when the expectation values of the quantum wave packet did not exactly correspond to the averages over classical trajectories, observables such as dissociation probabilities were shown to be quite similar for monochromatic [6, 16] and bichromatic [7] excitation. In this paper we further investigate the possibility of using classical models for control algorithm design. To this end the comparison of the results obtained by simulation of classical and quantum-mechanical ensembles is performed. The problem statement and controlled system equations are given in Sec. II. In Sec. III the case of one molecule is studied. The known dissociation control algorithms (monochromatic excitation and linear chirping) and new control algorithms (resonance curve and speed-gradient methods) based on feedback design are considered. Efficiency of the feedback algorithms for the case of HF molecule is confirmed by computer simulation results. In Sec. IV the application of the feedback technique to the pulse control for a molecular ensembles (classical and quantum) is considered.

2 Model of the Controlled System

Let us consider a diatomic molecular system under the action of the external laser field. Dynamics of such a system can be described by the following controlled Hamiltonian [2, 8]

$$H = \frac{p^2}{2m} + \Pi(r) - \mu(r) u(t), \quad (1)$$

where m is reduced mass, p is momentum, $\Pi(r)$ is potential of interatomic interaction, $\mu(r)$ is dipole moment of the molecule, $u(t)$ is intensity of external field. The value $u(t)$ serves as control variable.

Substitution of (1) into Hamilton equations

$$\frac{\partial r}{\partial t} = \frac{\partial H}{\partial p}, \quad \frac{\partial p}{\partial t} = -\frac{\partial H}{\partial r} \quad (2)$$

yields the following equation of molecular motion

$$m\ddot{r} = -\Pi'(r) + \mu'(r)u(t). \quad (3)$$

Let us use Morse form of the interatomic potential

$$\begin{aligned} \Pi(r) &= D \left(1 - e^{-\alpha(r-r_e)}\right)^2 - D = \\ &= D \left(e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}\right), \end{aligned} \quad (4)$$

where D is the bond energy, r_e is the equilibrium interatomic distance. The corresponding force is

$$f(r) = -\Pi'(r) = 2\alpha D \left(e^{-2\alpha(r-r_e)} - e^{-\alpha(r-r_e)}\right). \quad (5)$$

For the dipole moment the linear approximation is used

$$\mu(r) = Ar \quad \mu'(r) = A, \quad (6)$$

where A is constant. Thus the equation of motion (3) reads

$$\begin{aligned} m\ddot{r} &= 2\alpha D \left(e^{-2\alpha(r-r_e)} - e^{-\alpha(r-r_e)}\right) \\ &+ Au(t). \end{aligned} \quad (7)$$

In the vicinity of equilibrium $r \approx r_e$ equation (7) with harmonic excitation ($u(t) = E \cos(\omega t)$, where E and ω are strength and frequency of the external laser field) can be reduced to the equation of linear forced oscillations

$$m\ddot{r} = Cr + EA \cos(\omega t), \quad C \stackrel{\text{def}}{=} \Pi''(r_e) = 2\alpha^2 D, \quad (8)$$

where C is linear stiffness of the bond. The natural frequency of the linear system is

$$\Omega_0 \stackrel{\text{def}}{=} \sqrt{C/m} = \alpha \sqrt{2D/m}. \quad (9)$$

3 Dissociation Control Design

3.1 Nonfeedback Control Design

The simplest way to control molecular systems is monochromatic excitation with frequency of external laser field $\omega = k\Omega_0$, $k \leq 1$ (Ω_0 - natural frequency of the linearized system). This approach is well known and was investigated in a large number of publications. In this case equation of motion (7) takes the form

$$m\ddot{r} = -\Pi'(r) + AE \cos(\phi_0 + \omega t), \quad (10)$$

where ϕ_0 is the initial phase of control.

In a nonlinear system the resonance frequency is function of the amplitude of oscillations, or, in other words, it depends on the energy of the oscillator. Thus the faster dissociation can be achieved if the excitation frequency is changing (decreasing in our case) while the energy increases. The simplest control algorithm of this kind can be done by linear chirping:

$$\omega = \Omega_0 - \varepsilon t \quad (11)$$

where ε is a constant (chirping rate), which characterizes the speed of the frequency decrease. In this case equation of motion (7) takes the form

$$m\ddot{r} = -\Pi'(r) + AE \cos \varphi, \quad \dot{\varphi} = \omega(t) = \Omega_0 - \varepsilon t. \quad (12)$$

or

$$m\ddot{r} = -\Pi'(r) + EA \cos\left(\phi_0 + \Omega_0 t - \frac{\varepsilon t^2}{2}\right). \quad (13)$$

where ϕ_0 is the initial phase of control.

Simulation results. These nonfeedback dissociation control algorithms was studied by computer simulations for dissociation of the hydrogen fluoride (HF) molecule that has become a benchmark problem for controlled dissociation [2, 8, 19]. This study is necessary for comparing of the efficiency of

old and new methods of dissociation control. The parameters of the model (7), corresponding to HF molecule [2, 8, 19] are as follows: $m = 1732$, $D = 0.2101$, $\alpha = 1.22$, $a = 1.75$, $A = 0.4541$. The intensity of external laser field was chosen $E = 0.005$. All quantities are given in atomic units. The equation was integrated numerically by central differences method with time step $dt = T_0/200$ (integration with smaller time steps yields practically the same results). The initial molecule energy is $W_0 = -0.8689D = -0.1826a.u.$ (corresponds 2-nd energy state in quantum-mechanical model). The dissociation criterion for a molecule is exceeding of the molecule energy the value of dissociation energy $W_* = -0.1185D = -0.0249a.u.$ (corresponds 15-th energy state in quantum-mechanical model). The initial conditions for excitation at the initial energy W_0 is molecule with the minimal interatomic distance, corresponding to this energy value (velocity is equal to 0), i.e. $r = r_{min}(\Pi(r_{min}) = W_0), \dot{r} = 0$.

Note that efficiency of both methods depends on the parameters k_c (in case of monochromatic excitation) and k_l (in case of linear chirping) and on the initial deviations between phases of control (i.e. ϕ_0 in both cases) and phases of molecular motion (for our initial conditions the initial phases of molecular motion are 0). This dependence corresponds to the following condition : for the fastest energy growth control function should be "in phase" with the molecular motion, or, in other words, signs of control and velocity should be the same during the sufficiently long time. The graphs Fig. 1a, Fig. 2a show this dependence for the monochromatic excitation and linear chirping. Graph Fig. 1a shows the dependence of the maximal energy value (for sufficiently long time period) on the value of initial phase deviation for the various constants k_c . Obviously, excitation at constant fre-

quency do not give dissociation with the such small control intensity. Fig. 2a shows the dependence of the dissociation time on the chirping rate for the linear chirping method. We can see that this method is not robust, being insufficiently effective in addition.

3.2 Resonance Curve Control Design

More efficient dissociation can be achieved by taking advantage of the feedback control. In this case the frequency of excitation can be changed according to the oscillator energy so that at any amplitude of oscillations the excitation will act at the resonance frequency. Let $\Omega(W)$ be the natural frequency of the diatomic molecular oscillator at the specified energy W . We call the function $\Omega(W)$ *frequency-energy function*. The graph of this function we call *resonance curve*. It contains important information about dynamics of the molecular motion. The key idea of our approach is that if the function $\Omega(W)$ is known and the energy $W = W(t)$ is observable, then control algorithm $u(t) = E \cos \varphi$ $\dot{\varphi} = \Omega(W)$ $\varphi(0) = \varphi_0$ gives following equation of motion

$$m\ddot{r} = -\Pi'(r) + EA \cos \varphi \quad \dot{\varphi} = \Omega(W) \quad \varphi(0) = \varphi_0 \quad (14)$$

will give the desired excitation at the resonance frequency at any time instant.

The relation $\Omega(W)$ in principle can be calculated for any known potential $\Pi(r)$ using the integral of energy, which is realized when the external force is absent

$$\frac{1}{2} m\dot{r}^2 + \Pi(r) = W \quad \Rightarrow \quad T = \sqrt{2m} \int_{r_1}^{r_2} \frac{dr}{\sqrt{W - \Pi(r)}}, \quad (15)$$

where W is a constant value of energy, T is period of the oscillations, r_1 and r_2 are the minimum and the maximum possible values of radius r for the specified potential energy (the solutions of the equation $\Pi(r) = W$). If period T is known then frequency

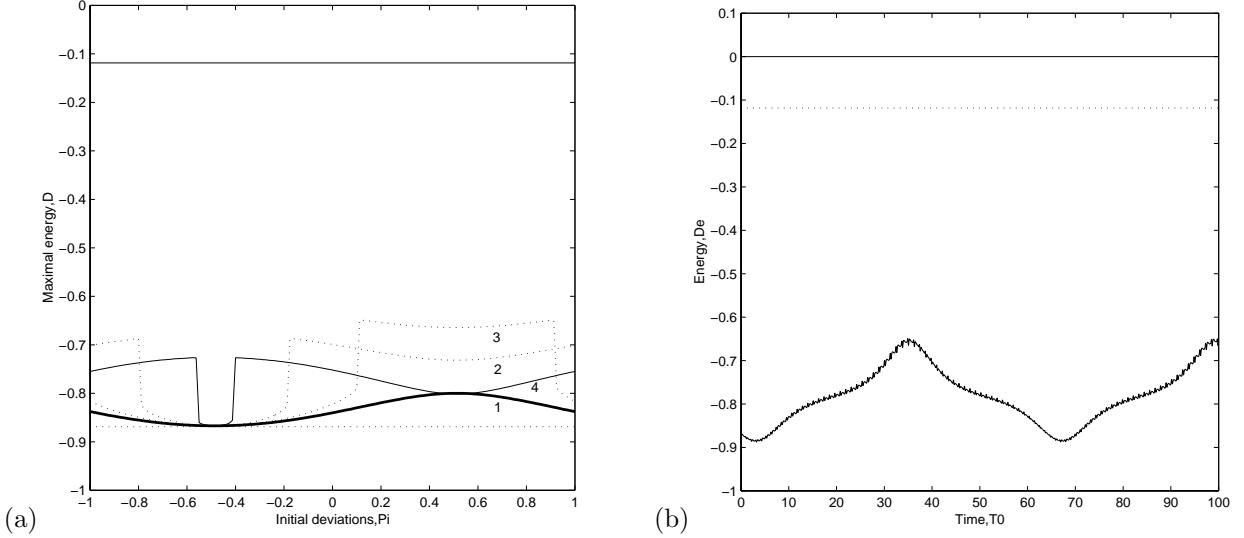


Figure 1: Excitation at constant frequency: (a) dependence of maximal energy value on the initial phase deviation for various frequency multipliers, (b) excitation with best result. Energy is measured in the units of the bond energy D , time is in the units of T_0 (natural period of linear oscillations).

can be obtained as $\Omega = 2\pi/T$. Obviously integral (15) can not be calculated analytically for arbitrary potential and the desired relation $\Omega(W)$ should be evaluated by numeric integration.

Luckily for the Morse potential (4) the integral can be evaluated analytically in the following way. Substitution $\zeta = \zeta(r) = e^{\alpha(r-r_e)}$ transforms the integral (15) in the case of Morse potential to the simple form which can be easily integrated

$$T = \frac{1}{\alpha} \sqrt{\frac{2m}{D}} \int_{\zeta_1}^{\zeta_2} \frac{d\zeta}{\sqrt{\frac{W}{D} \zeta^2 + 2\zeta - 1}} = \frac{\pi}{\alpha} \sqrt{-\frac{2m}{W}}. \quad (16)$$

The above formula is valid if $W < 0$. Otherwise, the motion of the system is not periodic, since the molecule dissociates. Equation (16) provides the following simple relation between energy and natural frequency of Morse oscillator

$$-\frac{W}{D} = \left(\frac{T_0}{T}\right)^2 = \left(\frac{\Omega}{\Omega_0}\right)^2, \quad (17)$$

where Ω_0 is defined by (9), $T_0 = 2\pi/\Omega_0$. The control law (14) therefore takes the form

$$\dot{\varphi} = \Omega(W) = \Omega_0 \sqrt{-\frac{W(t)}{D}}. \quad (18)$$

where $W(t)$ is the current value of the molecule energy.

Simulation results. Efficiency of the proposed control algorithm was confirmed by computer simulations for dissociation of the hydrogen fluoride (HF) molecule with the parameters and initial conditions as described above. Note that, like a previous case, efficiency of the method depends on the initial deviation on a phase (i.e. deviation between initial phase of control and initial phase of molecular motion) and on the multiplier at the frequency. Experiments shows that the best results takes place when multiplier is equal 1 (it is naturally because of this method bases on the strict fulfillment of the resonance conditions). Besides, from the Fig. 3a we can see that minimal dissociation time we have if the initial deviation on phase is approximately zero. Thus, we can see that if we have strict fulfillment of the resonance conditions and start to control "in phase" with the system, we obtain best results. Corresponding graph Fig. 3b shows that the dissociation takes place at $t \approx 52T_0$. This result is better (≈ 1.2 times)

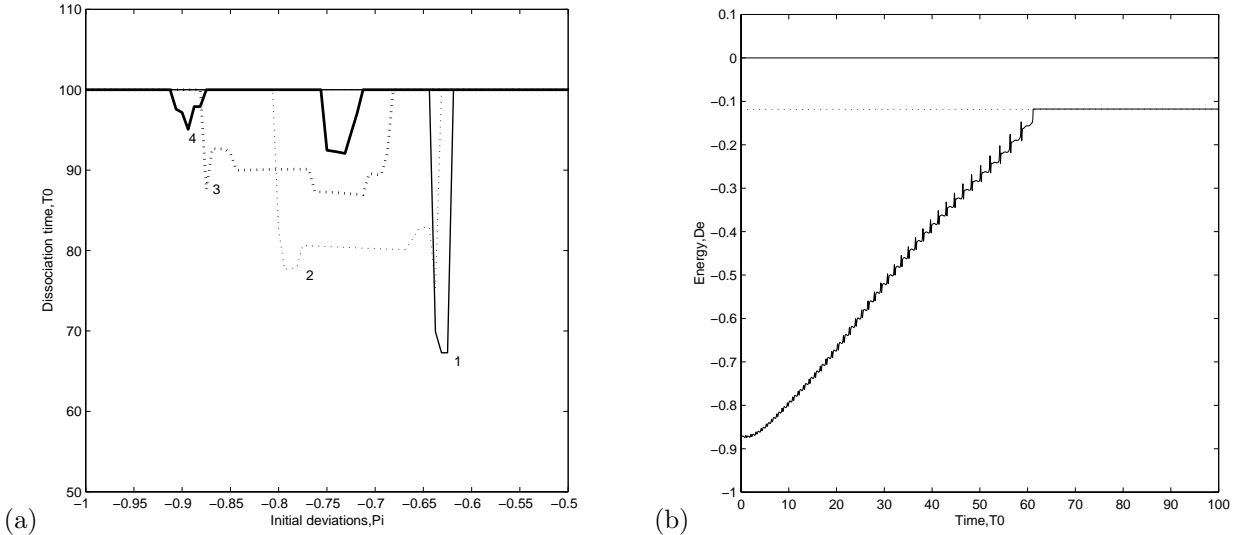


Figure 2: Excitation with linear chirping: (a) dependence of the dissociation time on the initial phase deviation for various chirping rates, (b) excitation with best result. Energy is measured in the units of the bond energy D , time is in the units of T_0 (natural period of linear oscillations).

than the best result, provided by the linear chirping method. Furthermore, from the Fig. 3a we can see that the efficiency of the resonance control depends smoothly and monotonically on the initial phase deviation. Thus we can maintain that the resonance control method is more robust than nonfeedback control methods.

3.3 Speed-Gradient Control Design

Below brief description of the speed-gradient method is given for completeness. More details can be found in [13, 14]. Let the controlled system be modeled as

$$\dot{x} = F(x, u), \quad (19)$$

where $x \in R^n$ is the state and $u \in R^m$ is the input (controlling signal). Let the goal of control be expressed as the limit relation

$$Q(x(t)) \rightarrow 0 \text{ when } t \rightarrow \infty. \quad (20)$$

In order to achieve the goal (20) we may apply the SG-algorithm in the *finite* form

$$u = -\Psi(\nabla_u \dot{Q}(x, u)), \quad (21)$$

where $\dot{Q} = (\partial Q / \partial x) F(x, u)$ is the speed of changing $Q(x(t))$ along the trajectories of (19), vector $\Psi(z)$ forms an acute angle with the vector z , i.e. $\Psi(z)^T z > 0$ when $z \neq 0$ (superscript “T” stands for transpose). The first step of the speed-gradient procedure is to calculate the speed \dot{Q} . The second step is to evaluate the gradient $\nabla_u \dot{Q}(x, u)$ with respect to controlling input u . Finally the vector-function $\Psi(z)$ should be chosen to meet the acute angle condition. E.g. the choice $\Psi(z) = \gamma z$, $\gamma > 0$ yields the *proportional* (with respect to speed-gradient) feedback

$$u = -\gamma \nabla_u \dot{Q}(x, u), \quad (22)$$

while the choice $\Psi(z) = \gamma \text{sign } z$, where “sign” is understood componentwise, yields the *relay* algorithm

$$u = -\gamma \text{sign}(\nabla_u \dot{Q}(x, u)). \quad (23)$$

The *integral* form of SG-algorithm

$$\frac{du}{dt} = -\gamma \nabla_u \dot{Q}(x, u), \quad (24)$$

also can be used as well as combined, e.g. proportional-integral forms.

The underlying idea of the choice (22) is that moving along the antigradient of the speed \dot{Q} provides

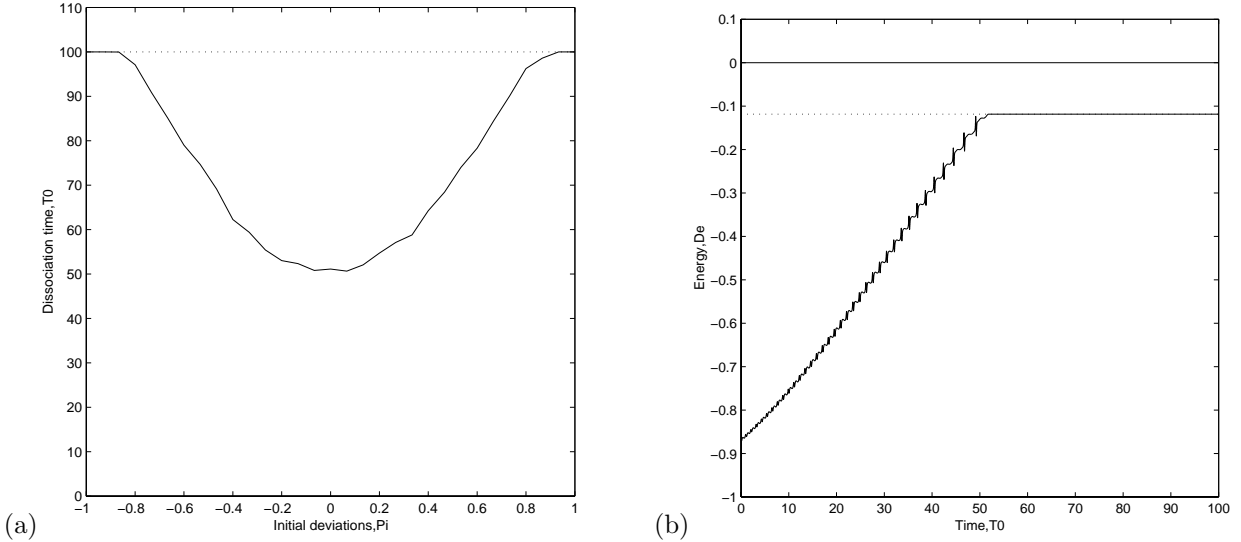


Figure 3: Excitation using frequency-energy relation: (a)dependence of the dissociation time on the initial phase deviation, (b) excitation with zero initial deviation ("in phase"). Energy is measured in the units of the bond energy D , time is in the units of T_0 (natural period of linear oscillations), initial phase deviation - in π .

decrease of \dot{Q} . It may eventually lead to negativity of \dot{Q} which, in turn, yields decrease of Q and, eventually, achievement of the primary goal (20). However, to prove (20) some additional assumptions are needed, see [13, 14].

In the case of dissociation problem the natural goal of control can be expressed in terms of the molecule free energy. In order to control the system to the desired energy level W_* , the energy related goal function $Q = (W - W_*)^2$ can be chosen, where W is the energy of the considered molecule. Performing calculations as above, we arrive at simple feedback laws:

$$u = -E (W - W_*) \dot{r}, \quad (25)$$

$$u = -E \text{sign}(W - W_*) \cdot \text{sign} \dot{r}, \quad (26)$$

where $E > 0$; $\text{sign}(W) = 1$ for $W > 0$, $\text{sign}(W) = -1$ for $W < 0$, and $\text{sign}(0) = 0$. It can be proved (see [13, 14] for general statements) that the goal $W(x(t)) \rightarrow W_*$ in the system (3), (25) (or (3), (26)) will be achieved from almost all initial conditions provided that the potential $\Pi(r)$ is smooth and its

stationary points are isolated. Obviously, Morse potential fits these mild conditions. It is worth noticing that since the motion of the controlled system belongs to the finite energy layer between $W_{\min} = D$ and W_* , the right hand side of (25) is bounded. Therefore, taking sufficiently small field intensity E we can achieve the given energy surface $W = W_*$ by means of *arbitrarily small* control.

The control algorithm (26) can be further simplified if we eliminate energy (e.g., assuming that system energy do not exceed the dissociation threshold):

$$u = \gamma \text{sign} \dot{r}, \quad (27)$$

that looks like introducing negative Coulomb friction into the system.

Below simulation results for the system (3), (27) will be presented.

Simulation results. Simulation was performed for the set of parameters and initial conditions corresponding to HF molecule as described above. Let us note, that control of that type is originally "in phase"

with the system. In Fig. 4a the results of the speed-gradient feedback control (27) are presented. Graph shows the energy as a function of time for the feedback control (27). Obviously, this method provides fastest dissociation at $t \approx 37T_0$. In Fig. 4b we can see results of applying the speed-gradient type impulse with Gaussian envelope to the system. Such situation more acceptable for real systems. Naturally, such adaptation gives a little worse results with dissociation at $t \approx 55T_0$. Graphs Fig. 5a, Fig. 5b shows corresponding control functions.

Thus the feedback control based on the speed-gradient method provides approximately 1.7 times faster dissociation than the best variant of the linear chirping. This method is also faster than the considered before energy-feedback method. However, since the direct implementation of the speed-gradient method is difficult, this method should be modified for experimental use. Such a modification is described below where simulation results for control of an ensemble of molecules are presented.

4 Simulation of Pulse Control for Molecular Ensembles

In the real experiments obtaining the immediate feedback response is problematic. Therefore we precalculate the control function using the feedback technique for a selected representative molecule. Then this precalculated control function is used to control all the molecules in the ensemble (classical or quantum) in the open-loop mode during the specified time interval. The control method is used for shaping the laser pulses while between pulses the system remains uncontrolled. Such a control strategy corresponds to modern femtosecond laser pulse ex-

perimental technologies [15].

4.1 Simulation for Classical Ensemble

Let T_1 be pulse repeating time interval and the pause (time interval between pulses) be T_2 . Then the pulse duration will be $T_3 = T_1 - T_2$. We assume that the pause is sufficiently large in order to allow ergodic properties of the molecular system to become significant enough to forget the influence of the previous pulse. The following additional simplifying assumptions are used.

- Molecules do not interact with each other and with the boundary.
- The molecules are moving in one dimension along the force lines of external laser field, i.e. orientation and rotational effects are neglected.

Therefore the system is modeled as the system of N noninteracting Morse oscillators with parameters corresponding to HF molecule. The measure of efficiency is the fraction of the dissociated molecules (percentage of the total number N). We establish the system parameters and initial conditions in accordance to the previous section (as much as possible). The dissociation criterion for a molecule is exceeding the energy value of $W_* = -0.1185D$. The low intensity control is applied: $E = 0.005$ a.u. The linear expression for the dipole moment $\mu(r) = Ar$ is used. To specify the initial conditions we assume that all the molecules have the same initial energy $W_0 = -0.8689D$ and their initial phases are chosen equidistantly in the interval $[0, T(-0.8689D)]$. Such a choice provides a good approximation for the uniform distribution of initial phases. In our experiments we took the following numerical data: $N = 1000$, $T_3 = 50T_0$, $T_2 = 150T_0$. Graph on Fig. 6a shows the fraction of dissociated molecules for molecular ensemble under linear chirping pulse

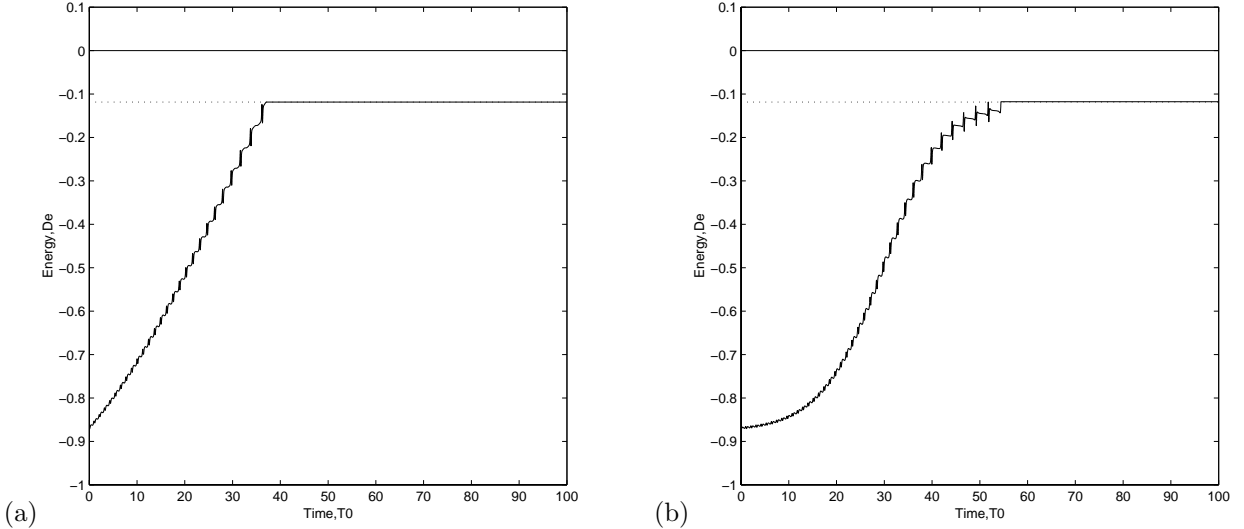


Figure 4: Excitation with speed-gradient feedback control: (a) using the speed-gradient method in form (27); (b) using speed-gradient type impulse with Gaussian envelope. Energy is measured in D , time is measured in T_0 .

control with optimal chirping rate $\varepsilon = 0.01\varepsilon_0$ (this value of chirping rate, providing the best result for control of this type, was obtained experimentally). Graph on Fig. 6b shows the result of applying the speed-gradient pulse control to the ensemble (as representative molecule it was chosen the molecule with median initial velocity).

It can be seen that the control using pulses designed by speed-gradient feedback method ensures a few times better efficiency compared with the linear chirping control with the optimal value of the chirping rate ε .

4.2 Simulation for Quantum Ensemble

For quantum-mechanical simulation the molecular motion was described by the Schrodinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{\hbar^2}{2M} \frac{\partial^2 \Psi}{\partial r^2} + V(r)\Psi + A r u(t)\Psi, \quad (28)$$

$$V(r) = D(e^{-2\alpha x} - 2e^{-\alpha x}), \quad x = \frac{r - r_0}{r_0}, \quad (29)$$

where $\Psi = \Psi(t, r)$ - is the wave function. Dissociation probability was defined as probability of the state with the energy exceeding H_* .

For numerical calculations a finite level approximation was taken, with eigenvalue and eigenfunctions of unperturbed Schrodinger operator evaluated analytically. Same input control function and simulation time as for classical case were used. Initial system state was chosen at the 2-nd energy level, while H_* corresponded to the 15-th energy level of HF molecule, in accordance with the classical simulations. Unlike the classical case, there is no need to make pauses between pulses since the state distribution of the uncontrolled quantum-mechanical system does not change with time.

The simulation results for speed-gradient pulse control are shown in Fig. 7. It is seen that the speed-gradient algorithm provides 14% probability of dissociation after 5 pulses (control pulses were taken identically to studding at the classic model). Thus the quantum-mechanical analysis provides the results qualitatively similar to the classical ones.

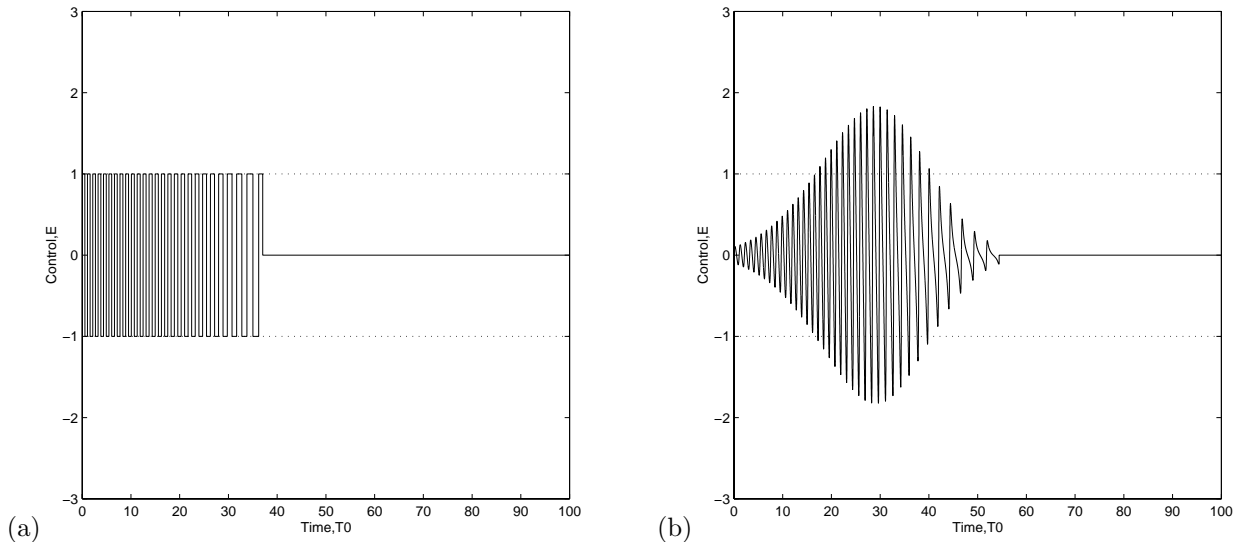


Figure 5: Speed-gradient feedback control functions: (a) speed-gradient method in form (27) ; (b) speed-gradient type impulse with Gaussian envelope. Control is normalized on E , time is measured in T_0 .

Conclusions

The analyzed algorithms have different properties. The design of the first algorithm requires the knowledge of the energy resonance curve of the molecule.

The second (speed-gradient) method provides more than three times faster dissociation than the best variant of the linear chirping for the single molecule case. This method is also faster than the first method, which provides only two times faster dissociation than the linear chirping. In the real experimental situation the control function is precalculated offline for a specified time interval and then applied to the real molecular system in an open-loop mode. Such a control strategy corresponds to femtosecond laser pulse experimental technologies. From our calculations it follows that the control using pulses designed by the speed-gradient algorithm ensures a few times better efficiency compared with the linear chirping control with the optimal value of the chirp rate.

It is shown that the dissociation rate for the

quantum-mechanical ensemble is just a few percent slower than the one for the classical ensemble. This result justifies using classical models for feedback control design in the dissociation problem.

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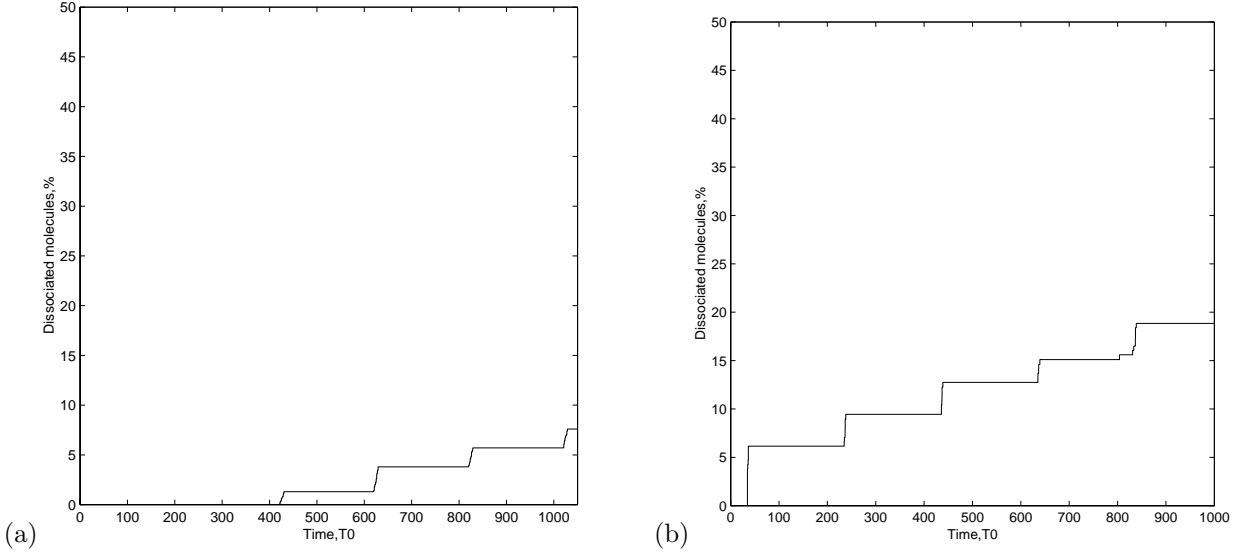


Figure 6: Excitation of the ensemble containing 1000 molecules at the excitation level of $E = 0.005$ a.u.: (a) pulse linear chirping with $\varepsilon = 0.01 \frac{\Omega_0}{T_0}$, (b) pulse speed-gradient control. Fraction of dissociated molecules - in %, time is measured in T_0 .

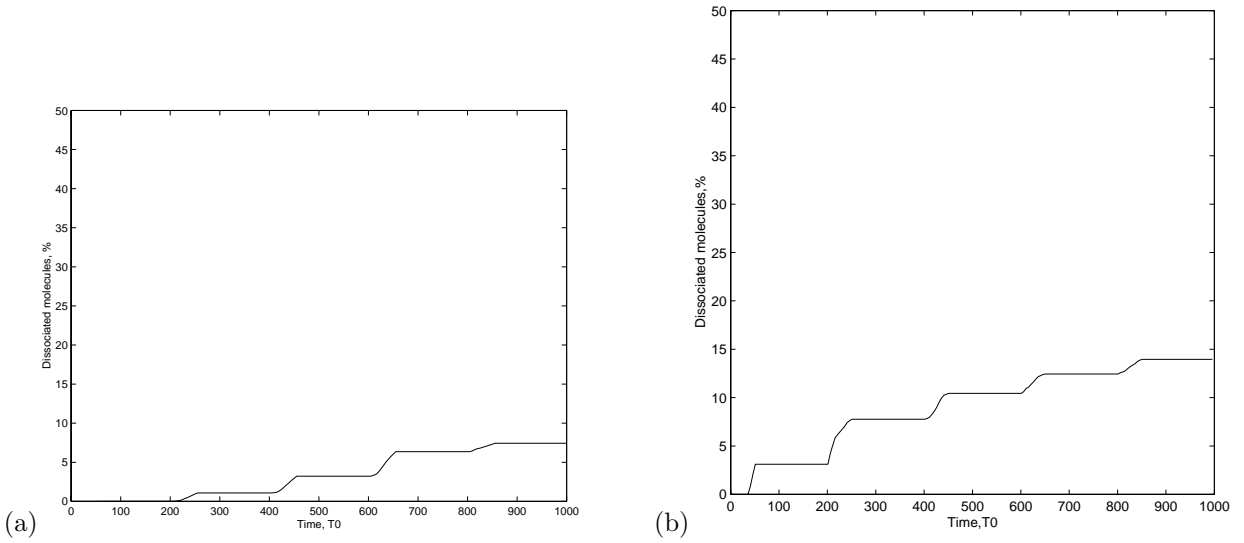


Figure 7: The dissociation probability for quantum-mechanical simulation with $E = 0.005$ a.u.: (a) pulse linear chirping with $\varepsilon = 0.01 \frac{\Omega_0}{T_0}$, (b) pulse speed-gradient control. Dissociation probability - in %, time is measured in T_0 .

References

- [1] M. Dahleh, A. Peirce, H. Rabitz and V. Ramakrishna, "Control of Molecular Motion", *Proceedings of the IEEE*, vol. 84, no. 1, pp. 7-15, 1996.
- [2] C. Yu, P. Gross, V. Ramakrishna, H. Rabitz, K. Mease and H. Singh, "Control of classical regime molecular objectives – applications of tracking and variations of the theme", *Automatica*, vol. 33, no. 9, p. 1617, 1997.
- [3] Special Issue: Laser Control of Quantum Dynamics, *Chemical Physics*, vol. 267, no. 1-3, 2001.
- [4] J. Rice, "Active control of molecular dynamics: Coherence versus chaos", *J. Stat. Phys.*, vol. 101, p. 187, 2000.
- [5] H. Rabitz, R. de Vivie-Riedle, M. Motzkus, and K. Kompa, "Whither the Future of Controlling Quantum Phenomena?", *Science*, vol. 288, p. 824, 2000.
- [6] M. E. Goggin and P. W. Milonni, "Driven Morse oscillator: Classical chaos, quantum theory and photodissociation", *Phys. Rev. A*, vol. 37, no. 3, p. 796, 1988.
- [7] M. E. Goggin and P. W. Milonni, "Driven Morse oscillator: Classical chaos and quantum theory for two-frequency dissociation", *Phys. Rev. A*, vol. 38, no. 10, p. 5174, 1988.
- [8] A. Guldberg and G. D. Billing, "Laser-induced dissociation of hydrogen fluoride", *Chem. Phys. Lett.*, vol. 186, no. 2-3, p. 229, 1991.
- [9] S. Krempel, T. Eisenhammer, A. Hubler, G. Mayer-Kress and P. W. Milonni, "Optimal stimulation of a conservative nonlinear oscillator: classical and quantum-mechanical calculations", *Phys. Rev. Lett.*, vol. 69, no. 3, p. 430, 1992.
- [10] W. K. Liu, B. Wu, J. M. Yuan, "Nonlinear dynamics of chirped pulse excitation and dissociation of diatomic molecules", *Phys. Rev. Lett.*, vol. 75, no. 7, p. 1292, 1995.
- [11] A. L. Fradkov, A. M. Krivtsov, A. A. Efimov, "Speed-gradient control of a diatomic molecules dissociation", *Journal of Differential Equations and Control Theory*, no. 4, 2001. <http://osipenko.stu.neva.ru/journal>.
- [12] A. L. Fradkov, A. M. Krivtsov, A. A. Efimov, <http://ArXiv.org> LANL, E-print physics/0201020, 10 Jan, 2002.
- [13] A. L. Fradkov and A. Yu. Pogromsky, *Introduction to control of oscillations and chaos*, World Scientific Pub. Co, Singapore, 1998.
- [14] A. L. Fradkov, I. V. Miroshnik and V. O. Niki-forov, *Nonlinear and adaptive control of complex systems*, Dordrecht: Kluwer Academic Publishers, 1999.
- [15] *Laser Control and Manipulation of Molecules*, edited by A. D. Bandrauk, Y. Fujimura and R. J. Gordon, Oxford Univ. Press, 2002.
- [16] R. Walker and R. Preston, *J. Chem. Phys.*, vol. 67, p. 2017, 1977.
- [17] C. D. Schwieters and H. Rabitz, "Optimal control of nonlinear classical systems with application to unimolecular dissociation reactions and chaotic potential", *Phys. Rev. A*, vol. 44, no. 8, p. 5224, 1991.
- [18] H. Umeda and Y. Fujimura, "Applicability of a classical local control method to a quantum system", *Chem. Phys.*, vol. 274, pp. 231-241, 2001.
- [19] J. R. Stine and D. W. Noid, *Opt. Commun.*, vol. 31, p. 161, 1979.
- [20] A. Zewail, "Femtochemistry", *J. Phys. Chem. A*, vol. 104, p. 5660, 2000.
- [21] G.-C. Zhang, J.-L. Shen, J.-H. Dai and H.-J. Zhang, "Cooling charged particles in a Paul trap by feedback control", *Phys. Rev. A*, vol. 60, p. 704, 1999.