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Dissociation of Diatomic Molecule by Speed-Gradient Feedback Control

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Abstract

New method for dissociation of diatomic molecule based on nonperiodic excitation generated by speed-gradient feedback control mechanism is proposed. The speed-gradient algorithm does not depend on the shape of the potential energy of molecule. It is shown that the feedback control is more efficient than methods based on constant frequency and linear chirping excitations. Efficiency of the proposed method is illustrated by example of dissociation control for hydrogen fluoride molecule.

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1 Introduction

Dissociation of a diatomic molecule is a benchmark problem for a class of molecular control problems that has become popular during last decade [1, 2, 3]. Controlled dissociation of a diatomic molecule has been intensively studied by feedforward (nonfeedback) control [3, 4, 5, 6, 7, 8]. In the paper [4] 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 [5, 6] the case of two-frequency (two-laser) control field was investigated. It was shown that intensity of two-frequency field required for dissociation can be reduced compared to one-frequency case. In [8] the further reduction of the control field intensity has been demonstrated by means of chirping (frequency modulation) the laser frequency with constant chirping rate. The range of chirping rate values ensuring capture and dissociation has been determined.

New possibilities for changing of physical and chemical properties are provided by using feedback. In [3] methods based on geometric control theory (inverse control) were proposed for molecular systems. In the papers [9, 10] a general method for investigation of physical systems by means of feedback controlling actions was proposed. It was shown in [9] by example of the problem of escape from a potential well that feedback allows to reduce control intensity required for overcoming a potential barrier by several orders of magnitude. It appears that using speed-gradient method [11, 12] for design of feedback control action allows to achieve desired level of energy by excitation of intensity inversely proportional to the system dissipation degree. Particularly, for conservative systems it allows to reach any energy level by (ideally) arbitrarily small control action.

In this paper we apply the speed-gradient approach to the dissociation control problem for diatomic molecule. In [14] a new algorithm of the feedback controlling field frequency chirping was proposed based on dependence of the natural frequency of nonlinear molecule oscillations on its energy (frequency-energy FE-characteristics or FE-curve). On-line implementation of the algorithm requires measurement of molecule energy only. This can be easily generalized for an ensemble of molecules, replacing exact energy of the separate molecule in the control criterion by the average energy per single molecule. However, for control algorithm design the knowledge of the FE-curve is required.

The speed-gradient algorithm proposed in this paper does not depend on the

shape of the potential energy of molecule and does not require precalculation of the FE-curve. Instead, it requires measurement of the system momentum. Although for unimolecular systems such a possibility is problematic, for multi-molecular ensembles measuring of average phase may be realizable and sufficient for control.

2 Model of the controlled system

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 [6, 3]

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

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. E.g. for monochromatic control field $u(t) = E \cos(\omega t)$, where E and ω are strength and frequency of the external laser field. Substitution of (2) 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

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

For the case of harmonic excitation equations of motion is as follows:

$$m\ddot{r} = -\Pi'(r) + E\mu'(r) \cos(\omega t). \quad (4)$$

Let us use Morse form of the interatomic potential

$$\Pi(r) = D \left(1 - e^{-\alpha(r-a)}\right)^2 - D = D \left(e^{-2\alpha(r-a)} - 2e^{-\alpha(r-a)}\right), \quad (5)$$

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

$$f(r) = -\Pi'(r) = 2\alpha D \left(e^{-2\alpha(r-a)} - e^{-\alpha(r-a)}\right). \quad (6)$$

The dipole moment can be represented in the form [6, 13]

$$\mu(r) = A r e^{-\xi r^4} \quad \mu'(r) = A (1 - 4\xi r^4) e^{-\xi r^4}, \quad (7)$$

where A and ξ are the known constants. Thus the equation of motion 2 reads

$$m\ddot{r} = 2\alpha D \left(e^{-2\alpha(r-a)} - e^{-\alpha(r-a)} \right) + EA (1 - 4\xi r^4) e^{-\xi r^4} u(t). \quad (8)$$

For sufficiently small ξ the simplified expression for dipol potential can be used:

$$\mu(r) = Ar, \quad \mu'(r) = A, \quad (9)$$

In the vicinity of equilibrium $r \approx a$ equation (2) with harmonic excitation can be reduced to the equation of linear forced oscillations

$$m\ddot{r} = Cr + E\mu'(a) \cos(\omega t), \quad C \stackrel{\text{def}}{=} \Pi''(a) = 2\alpha^2 D, \quad (10)$$

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

$$\Omega_0 \stackrel{\text{def}}{=} \sqrt{C/m} = \alpha \sqrt{2D/m}. \quad (11)$$

3 Control of the dissociation process

In 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 (in our case decreasing) while the energy increases. The simplest control of this kind can be done by linear chirping:

$$\omega = \Omega_0 - \varepsilon t \quad (12)$$

where ε is a constant, which characterizes the speed of the frequency decrease. In this case equation of motion (2) takes the form

$$m\ddot{r} = -\Pi'(r) + E\mu'(r) \cos \varphi, \quad \dot{\varphi} = \omega(t) = \Omega_0 - \varepsilon t. \quad (13)$$

More effective dissociation can be achieved by taking advantage of the feedback control. In the paper [14] the method of feedback dissociation control was

proposed based on changing the frequency of excitation according to the oscillator energy so that at any amplitude of oscillations the excitation acts 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 curve* or *FE-curve*. It contains important information about dynamics of the molecular motion. The key idea of [14] is that if the curve $\Omega(W)$ is known and the energy $W = W(t)$ is observable then control algorithm

$$m\ddot{r} = -\Pi'(r) + E\mu'(r) \cos \varphi, \quad \dot{\varphi} = \Omega(W) \quad (14)$$

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

The relation $\Omega(W)$ in principle can be calculated if the potential $\Pi(r)$ known using the integral of energy:

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

where W is given 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 energy (the solutions of the equation $\Pi(r) = W$). If period T is known then frequency can be obtained as $\Omega = 2\pi/T$. However, integral (3) can not be calculated analytically for arbitrary potential. Moreover, in many cases the potential is known with very low accuracy.

An alternative way of introducing feedback is using speed-gradient (SG) method [11, 12] providing a general approach to design of control algorithms for nonlinear systems. It will be briefly outlined in the next section.

4 Speed-gradient algorithms and energy control

Let the controlled system be modeled as

$$\dot{x} = F(x, u), \quad (16)$$

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

$$Q(x(t)) \rightarrow 0 \text{ when } t \rightarrow \infty. \quad (17)$$

In order to achieve the goal (4) we may apply the SG-algorithm in the *finite* form

$$u = -\Psi(\nabla_u \dot{Q}(x, u)), \quad (18)$$

where $\dot{Q} = (\partial Q/\partial x)F(x, u)$ is the speed of changing $Q(x(t))$ along the trajectories of (4), vector $\Psi(z)$ forms a sharp 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 sharp angle condition. E.g. the choice $\Psi(z) = \gamma z, \gamma > 0$ yields the *proportional* (with respect to speed-gradient) feedback

$$u = -\gamma \nabla_u \dot{Q}(x, u), \quad (19)$$

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

$$u = -\gamma \text{sign}(\nabla_u \dot{Q}(x, u)). \quad (20)$$

The *integral* form of SG-algorithm

$$\frac{du}{dt} = -\gamma \nabla_u \dot{Q}(x, u), \quad (21)$$

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

The underlying idea of the choice (4) is that moving along the antigradient of the speed \dot{Q} provides 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 (4). However, to prove (4) some additional assumptions are needed, see [11, 12].

5 Speed-gradient control of dissociation

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 H_* , the energy related goal function $Q(q, p) = (H(q, p) - H_*)^2$ can be chosen, where H_* is the dissociation energy. Performing calculations as above, we arrive at simple feedback laws:

$$u = -E (H - H_*) \dot{r}, \quad (22)$$

$$u = -E \text{sign} (H - H_*) \cdot \text{sign} \dot{r}, \quad (23)$$

where $E > 0$, $\text{sign}(H) = 1$, for $H > 0$, $\text{sign}(H) = -1$ for $H < 0$ and $\text{sign}(0) = 0$. It can be proven (see [11, 12] for general statements) that the goal $H(x(t)) \rightarrow H_*$ in the system (2), (5) (or (2), (5)) 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 H_0 and H_* , the right hand side of (5) is bounded. Therefore, taking sufficiently small field intensity E we can achieve the given energy surface $H = H_*$ by means of *arbitrarily small* control.

The control algorithm (5)) can be further simplified if we eliminate energy (e.g., assuming that system energy do not exceed the dissociation threshold:

$$u = \gamma \text{sign} \dot{r}, \quad (24)$$

that looks like introducing negative Coulomb friction into the system.

Below simulation results for the system (2), (5) will be presented.

6 Simulation results

Let us consider the parameters, corresponding to hydrogen fluoride (HF) molecule [3, 6, 13]: $m = 1732$, $D = 0.2101$, $\alpha = 1.22$, $a = 1.75$, $A = 0.4541$, $\xi = 0.0064$, $E = 0.1$. All quantities are given in atomic units. The initial condition for excitation will be molecule equilibrium at the bottom of the potential well: $r = a$, $\dot{r} = 0$. The equation is integrated by central differences method with time step $dt = T_0/160$. For all calculations it is confirmed that integration with smaller time steps produce practically the same results.

The result of excitation at the resonance frequency is shown in Fig. 1a. The graph shows that the motion is quasiperiodic and maximum value of energy, which can be achieved by this method, is $-0.68D$. Since the natural frequency of the molecule is decreasing with the energy growth, more effective excitation can be performed at lower frequencies. It is even possible to dissociate the molecule if the excitation frequency is close to $0.841\Omega_0$ — see Fig. 2a. The figure shows that at $t \approx 13.5T_0$ the energy crosses the zero level, and at $t = 14.5T_0$ the energy becomes a positive constant. This practically means that the potential energy is negligible and atoms are moving in opposite directions with constant velocities — this is the total dissociation. However this result is not structurally stable, small variation in the excitation frequency can noticeably increase the dissociation time and even break the dissociation.

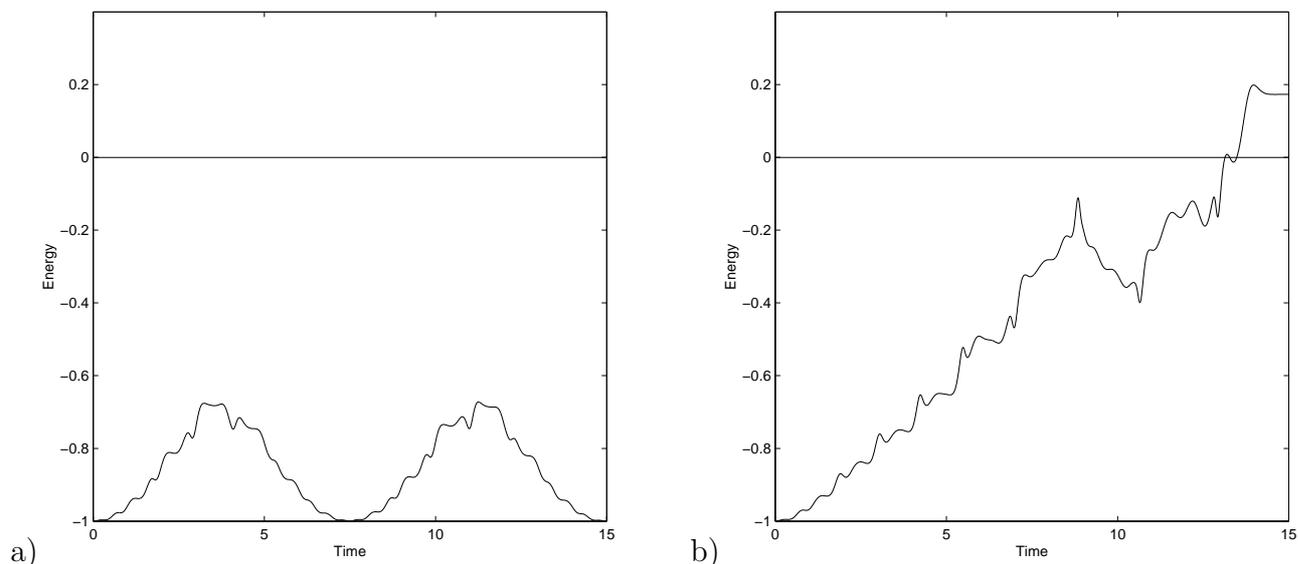


Figure 1: Excitation at constant frequency: a) resonance frequency $\omega = \Omega_0$, b) optimal frequency $\omega = 0.841\Omega_0$. Energy is measured in the units of the bond energy D , time is in the units of T_0 (natural period of linear oscillations).

Fig. 2a,b correspond to linear frequency chirping (3) at two different chirping rates. The dissociation is also achieved, but it is slower than in the previous case and the results are very sensitive to the variations of ε . Additional flexibility to the chirping process can be added by using the relation $\omega = \omega_0 - \varepsilon t$, where ω_0 is a constant less than Ω_0 . Optimal selection of both parameters is a pretty complicated task. In more details this problem is investigated in [8].

Below we will use the speed-gradient feedback control (5). Fig. 3a shows the energy as a function of time for the feedback control (5). At the initial stage the energy is growing faster than in other cases, but after the level about $W = -0.2D$ is reached, the efficiency of the excitation decreases so that dissociation is not realized. Probable cause for this phenomenon is that the sign of the multiplier $\mu'(r)$ in equation (2) due to formula (2) is changing for high energies, so that the excitation starts acting in the opposite phase. To solve this problem the following algorithm can be used: when the energy of the molecule reaches some certain value W_* then the sign of the excitation force is permanently changing to the opposite. The result of such excitation is shown in Fig. 3b. The dissociation is achieved at $t = 5.5T_0$, which is much faster than in all previous cases.

Thus for the selected level of control ($E = 0.1$ a.u.) the best result is obtained for feedback excitation. However excitation with shifted constant frequency gives the competitive result. The situation changes if we consider lower

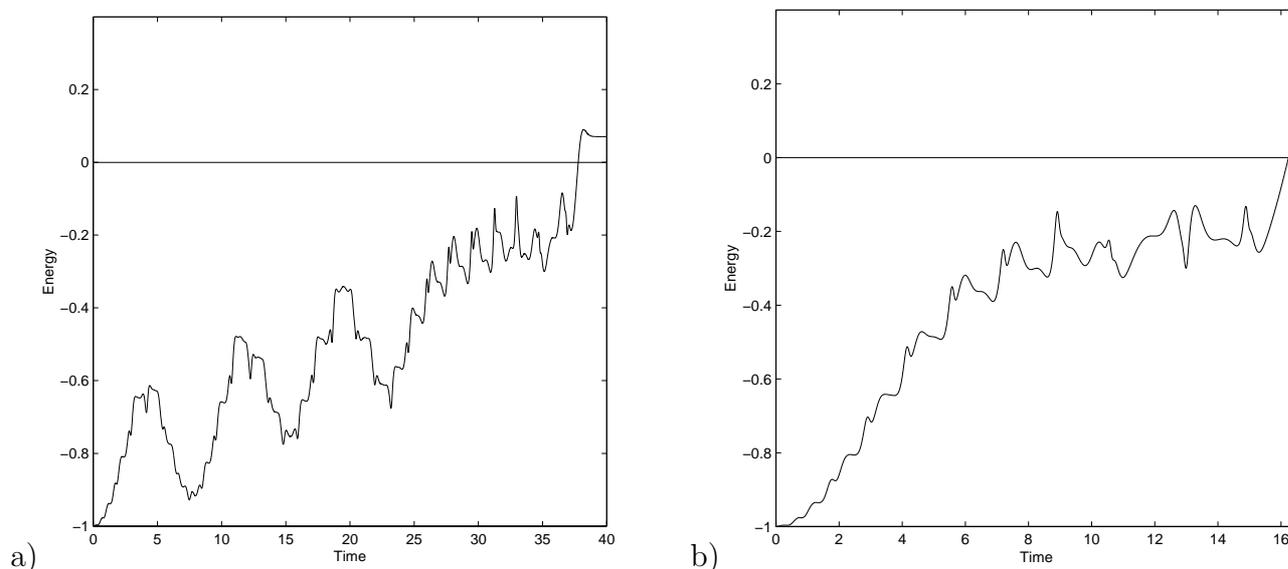


Figure 2: Excitation with linear frequency chirping: a) $\varepsilon = 0.0157 \frac{\omega_0}{T_0}$, b) $\varepsilon = 0.059 \frac{\omega_0}{T_0}$ (the chirping rate, which provides the fastest dissociation). Energy and time are measured in D and T_0 .

level of excitation. If this level is sufficiently small then excitation at any constant frequency can not provide the dissociation. On contrary, excitation with changing frequency can on principle give dissociation for any arbitrary small level of control. For illustration let us consider the 5 times smaller control then in previous calculations: $E = 0.02$ a.u. In this case dissociation at a constant frequency is impossible. Results of linear chirping and feedback control excitation are given in Fig. 4. For simplicity these calculations use approximation $\mu'(r) \approx \mu'(a)$. The graphs show that both methods provide dissociation, the linear chirping at $t = 89T_0$, and the feedback control at $t = 23.6T_0$.

Thus the feedback control based on the speed-gradient method provides more then three times faster dissociation then the best variant of the linear chirping. This method is also faster then the feedback method based on FE-characteristics [14]. On the other hand realization of the speed-gradient method may be more problematic, but for multi-molecular ensembles measuring of average phase may be realizable and sufficient for control.

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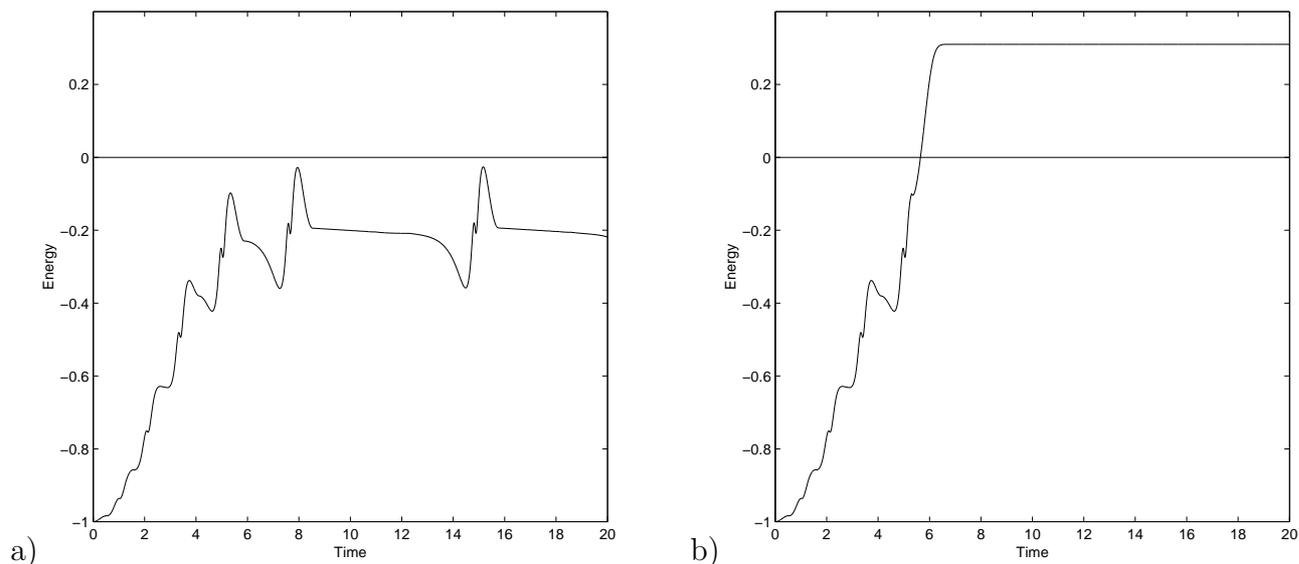


Figure 3: Excitation with feedback control: a) using the speed-gradient method; b) same, but with phase switch at $W = -0.1D$. Energy and time are measured in D and T_0 .

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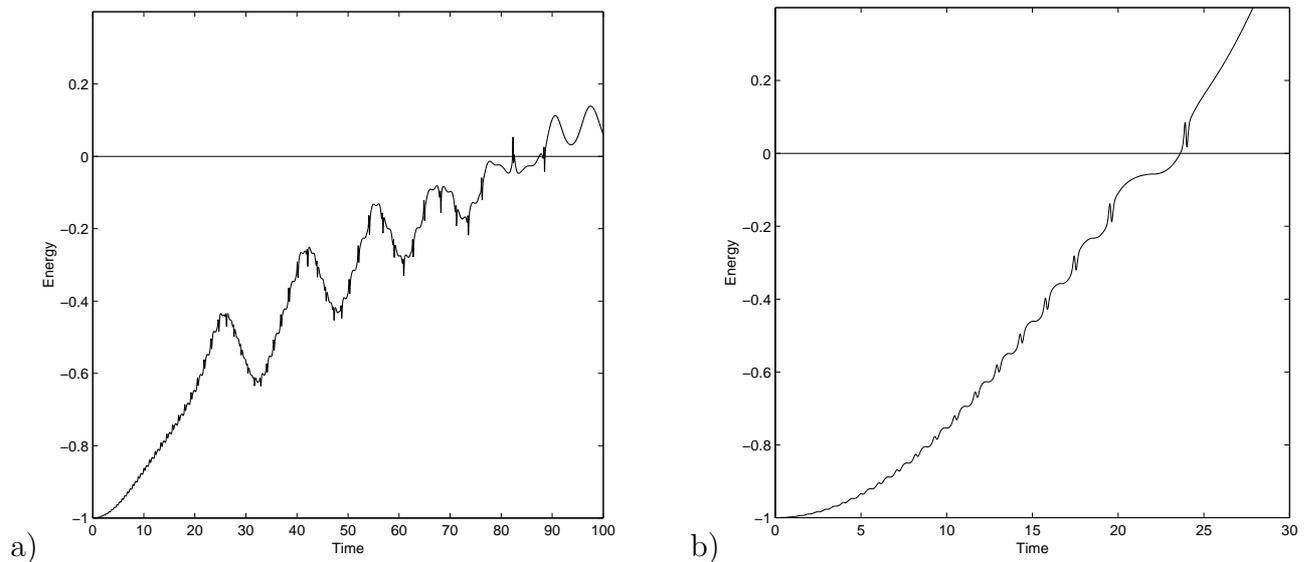


Figure 4: Excitation with lower level of control ($E = 0.02$ a.u.) and constant value of dipole moment a) linear chirping with $\varepsilon = 0.0091 \frac{\omega_0}{T_0}$, b) feedback control (using speed-gradient method). Energy and time are measured in D and T_0 .

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