===================== **DETERMINATE SYSTEMS** =====================

Control of the Observables
in the Finite-level Quantum Systems[1]

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Abstract—A new approach to designing the velocity gradient-based algorithms to control the observables of the quantum-mechanical systems was proposed. The aim of control was shown to be feasible under the nondegeneracy-type conditions, provided that the initial and target values lie in the same energy layer. The error of attaining the aim of control was shown to be proportional to that of defining the initial system state and the error of realization of the control action. For the problem of controlling predissociation of the hydrogen fluoride molecule, numerical results were presented. Design of the proposed algorithms features simplicity.

1. INTRODUCTION

The problems of controlling the processes of microcosm, including control of motion of atoms and molecules, have a rich history. Numerous works are devoted to the issues of control on the basis of quantum-mechanical models, but until recently the possibilities of control were considered in purely theoretical terms [1–6]. The main difficulties of controlling the processes at the atom-molecule level lie in the small dimensions of the controlled objects and high velocity of the processes going on in them. The molecules of chemical substances (monomers) have size of the order of nanometers ($1\,\mathrm{nm} = 10^{-9}\,\mathrm{m}$), and the characteristic times of natural oscillations of the atoms in a molecule have the order of femtoseconds ($1\,\mathrm{fsec} = 10^{-15}\,\mathrm{s}$). Design of instrumentation for measurement and control within this space-time scale is a challenge to science and technology. Until recently, there existed no technical facilities for control of such fast processes.

The situation changed at the late 1980's with the advent of superhigh-speed femtosecond lasers generating pulses of the order of tens or now even units of femtoseconds as well as the methods of computerized control of the form of laser pulses. A new line of chemical research, the so-called femtochemistry, arose. A. Zewail was awarded the 1999 Nobel Prize for the progress in this area [7]. The advances in other methods of using the femtosecond lasers gave rise to the term "femtosecond technologies" or "femptotechnologies." These technologies are used, in particular, to solve the problems of selective dissociation where one needs to break certain molecular bonds without affecting, wherever possible, the rest of them.

Several approaches to the control of molecular systems were suggested. M. Shapiro and P. Brumer [8] used control on the basis of interference of two laser beams of different frequencies, amplitudes, and phases (the pumping-damping scheme). D.J. Tannor and S.A. Rice [9] suggested two-pulse schemes of pumping-damping in the time domain. Methods of optimal control that are based, in particular, on the V.F. Krotov method [10] were later used in pulse optimization. H. Rabitz and his collaborators [11–14] considered various versions of optimal control under the classical and quantum descriptions of the dynamics of molecular motion. They put forward [12] the idea of realizing the adaptive laser control of chemical reactions by means of the methods of search optimization (genetic algorithms) whose feasibility was corroborated experimentally [15–17].

One of the simplest problems from this class is the typical problem of dissociation of the diatomic molecule [18–21] which is a convenient benchmark for comparing the advantages and disadvantages of different methods. M.E. Goggin and P.W. Milonni [18] carried out a numerical feasibility study of dissociation of the hydrogen fluoride (HF) molecule under the action of periodically varying field (monochromatic laser radiation). They used a similar method in [19] to study dissociation by the two-frequency (bichromatic) action and demonstrated that the intensity of the dissociating field can be substantially reduced. W.K. Liu, B. Wu, and J.M. Yuan [20] used *chirping*, that is, uniform variation of the frequency of external action, to estimate the intensity of a dissociating field. It was shown that the field intensity required for dissociation can be reduced even more.

Nonperiodic feedback action offers new possibilities for control of the molecular systems. The main problems here lie in measuring the system state and realizing the control actions over the time intervals comparable with the period of molecule natural oscillations. Various feedback algorithms, including those of optimal control, can be found in [13, 14, 21] and other works. Their common trait lies in that they are used to design the control action as a time function from the given model of the molecular system. In the computer experiments, one may assume that all the necessary signals are measured and the design algorithm is realized by the computer. As the result, the control signal will be generated as a time function, and its realization on the object is done already without measurements and feedback. Numerous uncertainties—the initial system state is not known precisely and the constructed control function is calculated inaccurately and realized with error—hinder the practical application of this method. Finally, the model of the molecule itself is imprecise because its parameters are not known precisely, and the choice itself between the classical and quantum descriptions is the matter of repeated discussions.

Recently, the interest to the control of quantum systems started to grow rapidly. According to the *Science Citation Index*, by the beginning of this century more than 500 papers were published annually in the cited journals. The reader can judge the state-of-the-art in this area by the papers published in the collected translations [22] and collected articles [23]. Studies on the quantum computers represent one of the important applications [24].

The present paper describes a new approach to a class of problems of control of the quantum systems, the problems of control of the observables which from the mathematical standpoint are classified with the problems of partial control. The approach relies on the method of velocity gradient [25] that is applied for the first time to the problems of control in complex spaces. Consideration is given to the case of systems obeying the Schrödinger equations in a finite-dimensional space. For the proposed algorithms, the applicability conditions were established. Effectiveness of this approach was demonstrated by the problem of dissociation of the diatomic molecule. The paper also proves that the algorithm remains operable under small deviations in the definition of the initial system state and errors of realization of the control action.

The algorithms obtained feature robustness because they are independent of the form of the potential of intermolecular interaction. They enable one to get dissociation with a smaller intensity of the control field than in the case of chirping and, as compared with the methods of optimal control, are easier to design and calculate.

2. CONTROL ALGORITHM: FORMULATION OF THE PROBLEM AND DESIGN

Let the dynamics of the controlled object obey the finite-dimensional Schrödinger equation with the control [22]

$$i\hbar\dot{\Psi}(t) = \left[H_0 + \sum_{k=1}^{r} u_k H_k\right]\Psi(t), \qquad \Psi(t) \in \mathbb{C}^n, \tag{1}$$

where $i = \sqrt{-1}$ is the imaginary unit, $\hbar$ is the Planck constant, u_k are the real-valued scalar control functions, and H_k are their corresponding terms in the complete Hamiltonian of the system. The operators H_k, $k = 0, \ldots, r$, are assumed to be self-conjugate. The phase space of this system is represented by the unit sphere of the n-dimensional complex space $\mathbb{C}^n$. The following goal of control (GC) is posed: it is required to construct functions $u_k(\Psi)$ such that they support the trend of the given observable Z to its goal value Z_g

$$(\text{GC}) \qquad \forall \Psi(t_0): \qquad \lim_{t \to +\infty} \Psi(t)^* Z \Psi(t) = Z_g, \tag{2}$$

where "*" stands for transposition and complex conjugation. The term "observable Z" usually refers to the operator in the state space which corresponds to some characteristic—energy, for example,—of the system. By means of one or another measurement one succeeds, as a rule, to get only a particular numerical value of the observable which is a random variable, and $\Psi(t)^* Z \Psi(t)$ has the sense of its mean value at time t.

To design the control algorithm, we make use of the method of velocity gradient in the finite form [25] and introduce with this aim the goal function

$$V(\Psi) = (\Psi^* Z \Psi - Z_g)^2. \tag{3}$$

According to the method of velocity gradient, the control algorithm follows the formula

$$u(\Psi) = -\gamma \nabla_u \dot{V}(\Psi), \tag{4}$$

where $\gamma > 0$ is the gain, ∇_u stands for taking the gradient with respect to the vector $u = (u_1, \ldots, u_r)$, and the point stands for the time derivative along the trajectories of system (1). This choice of the control function guarantees that the goal function will not grow along the system trajectories [25]. Since the tendency of the goal function to zero amounts to satisfying the goal of control (2), under some additional conditions this algorithm can satisfy the goal.

It follows from (1), (3), and (4) that

$$u_k(\Psi) = -\gamma \nabla_{u_k} \left\{ 2(\Psi^* Z \Psi - Z_g)(\dot{\Psi}^* Z \Psi + \Psi^* Z \dot{\Psi}) \right\}$$

$$= -\gamma \nabla_{u_k} \left\{ \frac{2i}{\hbar} (\Psi^* Z \Psi - Z_g) \Psi^* \left[H_0 Z - Z H_0 + \sum_{k=1}^{r} u_k (H_k Z - Z H_k) \right] \Psi \right\}.$$

Hence, we get the following control algorithm $(k = 1, \ldots, r)$

$$u_k(\Psi) = -\gamma \frac{2i}{\hbar} (\Psi^* Z \Psi - Z_g)(\Psi^* [H_0 Z - Z H_0 + (H_k Z - Z H_k)] \Psi). \tag{5}$$

Therefore, the feedback algorithm (5) to control observables is obtained by applying the method of velocity gradient to the quantum-mechanical model. We note that the proposed algorithm (5) can also be used to control the infinite-dimensional systems.

3. STUDIES OF THE CONTROL ALGORITHM

The main result of this study is formulated as the following statement.

Theorem 1. *Let the operator Z commute with the operator H_0 and the operators H_k, $k = 0, \ldots, r$, satisfy the following conditions:*

(A1) $z_k - z_m \neq 0$, $k \neq m$, $k, m = \overline{1, n}$, *where z_k are the eigenvalues of the observable Z arranged in the ascending order;*

(A2) *let* λ_k, $k = \overline{1,n}$, *be the eigenvalues of* H_0 *arranged in the ascending order, then* $(\lambda_k - \lambda_m) \neq (\lambda_r - \lambda_s)$, $(k,m) \neq (r,s)$, $k,m,r,s = \overline{1,n}$;

(A3) *for any pair* (k,m), *there exists a number* $l \in \{1, \dots, r\}$ *such that* $h_k H_l h_m \neq 0$, *where* h_k, $k = \overline{1,n}$, *stands for the eigenvectors* H_0 *of unit length.*

Then, for any initial condition Ψ_0 *such that* $z_k < \Psi_0^* Z \Psi_0 < z_{k+1}$, *where* $z_k < Z_g < z_{k+1}$, *the control algorithm* (5) *solves the problem of control* (2) *of the observable* Z *of system* (1).

Note 1. Validity of Theorem 1 and its proof will not change if $u = -F(\nabla_u \dot{V}(t))$, where the function $F(x)$ is continuous, $F(x) = 0 \iff x = 0$, and $F(x)x > 0$, is used as the control algorithm.

Note 2. Since control is continuous and the phase space is compact, by taking a sufficiently small gain γ one can attain the goal of control using an arbitrarily small control action.

Note 3. Despite the fact that there exists no proof that the goal of control can be attained for arbitrary initial conditions, in the numerical modeling of the models under consideration we always observed the trend of the observable to the goal value, except, of course, for the case where the pure system states played the role of the initial data.

Note 4. Condition (A1) means that different values of the observable Z correspond to different pure states. Condition (A2) means that for different pairs of pure states the frequencies of transitions between them are different as well. Condition (A3) means that for any two pure states there exists a nonzero probability of transitions between them for any (nonzero) control. For control of the molecule observables, the conditions imposed by Theorem 1 are not, therefore, unnecessarily restrictive. For example, they are satisfied for the model of the hydrogen fluoride molecule discussed in Section 6.

According to the scheme discussed in the Introduction, the experiment is based on a control in the form of the time function calculated by the computer-aided modeling of the mathematical model of the quantum system. Let us consider the behavior of the system designed in the presence of errors in defining the initial distribution and the error of realization of the control action.

We assume that the initial condition is known approximately rather than precisely: at the initial time t_0 the initial distribution $\Psi_0 = \Psi_* + \delta\Psi$, where Ψ_0 is the real initial condition, Ψ_* is the calculated initial condition, and $\delta\Psi$ is the mismatch between the real and assumed initial conditions. We assume also that control is realized with error: $u(t) = u_*(t) + \delta u(t)$, where $u(t)$ is the actual control, $u_*(t)$ is the calculated control, and $\delta u(t)$ is the mismatch between the actual and calculated controls. Let $\Psi(t, \Psi_0, u(t))$ be the solution of Eq. (1) with the initial condition Ψ_0 and control $u(t)$. The following statement enables one to estimate the error in attaining the goal of control under the given mismatches.

Theorem 2. *For any time* t, *errors in defining the initial distribution, and inaccuracies in realizing the control action, the deviation of the observable from the calculated value is as follows:*

$$|\Psi(t, \Psi_0, u(t))^* Z \Psi(t, \Psi_0, u(t)) - \Psi(t, \Psi_*, u_*(t))^* Z \Psi(t, \Psi_*, u_*(t))|$$
$$\leq (2|\delta\Psi| + |\delta\Psi|^2 + 2\Delta(t) + \Delta^2(t))\|Z\|, \tag{6}$$

$$\Delta(t) = \frac{1}{\hbar} \sum_{k=1}^{r} \|H_k\| \int_0^t |\delta u_k(t)| dt, \tag{7}$$

where by $|\cdot|$ *is meant the Hermitian norm of the vector in the complex space and by* $\|\cdot\|$, *the corresponding operator norm.*

Note 5. If $\int_0^{+\infty} |\delta u(t)| dt < +\infty$, then in (6) $\Delta = \frac{1}{\hbar} \sum_{k=1}^{r} \|H_k\| \int_0^{+\infty} |\delta u_k(t)| dt$ can be substituted for $\Delta(t)$.

Theorem 2 follows immediately from the two following statements that are proved in the Appendix.

Lemma 1. *Let $\delta u(t) \equiv 0$, that is, the control be realized without errors. Then, for any t there exists the following estimate of the deviation of the actual value of the observable from the calculated value:*

$$|\Psi(t, \Psi_0, u(t))^* Z \Psi(t, \Psi_0, u(t)) - \Psi(t, \Psi_*, u_*(t))^* Z \Psi(t, \Psi_*, u_*(t))| \leq 2\|Z\|\|\delta\Psi\|. \tag{8}$$

Lemma 2. *Let $\delta\Psi \equiv 0$, that is, the initial value be known precisely. Then, for any t there exists the following estimate of the deviation of the actual value of the observable from the calculated value:*

$$|\Psi(t, \Psi_0, u(t))^* Z \Psi(t, \Psi_0, u(t)) - \Psi(t, \Psi_*, u_*(t))^* Z \Psi(t, \Psi_*, u_*(t))| \leq (2\Delta(t) + \Delta^2(t))\|Z\|, \tag{9}$$

where $\Delta(t)$ follows (7).

4. NUMERICAL MODELING OF THE CONTROLLABLE QUANTUM-MECHANICAL SYSTEMS

The stage of numerical modeling of the controllable quantum systems is of great importance. According to the scheme of experiment discussed in the Introduction, the control function is calculated namely at the stage of numerical experiment.

If the original quantum-mechanical object has a finite-dimensional description, then modeling makes use of the well-developed methods for solution of the ordinary differential equation systems. For the infinite-dimensional quantum systems, the grid methods or that of Galerkin are used. The present paper makes use of the latter method which seems advantageous in terms of calculation burden. It allows one to carry out the main mass of calculations only once when calculating the parameters of the finite-dimensional system approximating the given system. Importantly, this approximation can be used for various control actions, which allows one to save calculations.

Consideration is given to the mathematical model of a quantum system whose dynamics obeys the controlled Schrödinger equation (1). The finite-dimensional approximation is taken over the eigenvectors of the complete Hamiltonian of the unperturbed quantum system (H_0). We denote by $h_1, \ldots, h_n$ the set of n orthonormal eigenvectors of the operator H_0 and by $\lambda_1, \ldots, \lambda_n$, their corresponding eigenvalues. Then, the approximating system is as follows:

$$i\hbar \frac{d\widehat{\Psi}(t)}{dt} = \widehat{H}_0 \widehat{\Psi}(t) + \sum_{k=1}^{r} u_k \widehat{H}_k \widehat{\Psi}(t), \qquad \widehat{\Psi}(t) \in \mathbb{C}^n, \tag{10}$$

where H_k, $k = 0, \ldots, r$, are the linear self-conjugate operators from $\mathbb{C}^n$ in $\mathbb{C}^n$ which obey the following relations:

$$\widehat{H}_0 \widehat{h}_k = \lambda_k \widehat{h}_k, \quad \forall k \in \{1, \ldots, r\},$$
$$\widehat{h}_p^* \widehat{H}_k \widehat{h}_q = h_p^* H_k h_q, \quad \forall p, q \in \{1, \ldots, n\}, \forall k \in \{1, \ldots, r\},$$

where $\widehat{h}_k$, $k = 1, \ldots, n$, are the eigenvectors of the operator $\widehat{H}_0$. For a suitable choice of the eigenvectors h_k and identical initial data, the dynamics of the coefficients of the pure states of systems (1) and (10) is reckoned to be approximately the same: $h_k^* \Psi(t) \approx \widehat{h}_k^* \widehat{\Psi}(t)$, $k = 1, \ldots, n$. This scheme is made specific for the model of the diatomic molecule.

5. FINITE-LEVEL APPROXIMATION OF THE QUANTUM-MECHANICAL MODEL OF THE HF MOLECULE

We make use of the mathematical model of the diatomic quantum-mechanical molecule obeying the controllable Schrödinger equation with the Morse potential $V(r)$:

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t} = H_0\Psi(r,t) + uH_1\Psi(r,t), \tag{11}$$

where

$$H_0 = \left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial r^2} + V(r)\right], \quad H_1 = A\mu(r),$$

$$V(r) = D\left(\exp\left(-2\alpha\frac{r-r_0}{r_0}\right) - 2\exp\left(-\alpha\frac{r-r_0}{r_0}\right)\right),$$

where $i = \sqrt{-1}$ is the imaginary unit, $\hbar$ is the Planck constant, $\Psi(r,t)$ is the wave function, $r \in (0, +\infty)$ is the distance between the molecule atoms, M is the molecule mass which in the case of the Hartree units is the reduced mass, $V(r)$ is the Morse potential, u is the control function of intensity of the external electromagnetic field, $\mu(r)$ is the molecular dipole moment, and D, α, and r_0 are the parameters of the Morse potential. According to [18, 19, 22], in the first approximation the molecular dipole moment can be assumed to be $\mu(r) = Ar$. In the Hartree units, the parameters of the HF molecule are as follows [18, 19]: $D = 0.2101$, $\alpha = 2.1350$, $r_0 = 1.75$, $M = 1732$, $A = 0.4541$, $\hbar = 1$.

The Morse potential is used to describe the oscillations of diatomic molecules. It is regarded as more physical than the Kratzer potential [27] and has the global minimum $-D = -0.2101$ at the system equilibrium point $r = r_0 = 1.75$. For a strong approach of the nuclei, $V(r)$ assumes positive values, then becomes negative owing to the strong Haitler–London attraction, and grows gradually describing the weaker Van der Waals forces (Fig. 1).

The eigenfunctions and their corresponding eigenvalues of the operator H_0 can be obtained analytically with a high degree of precision. The interested readers can familiarize themselves in [27] with a detailed derivation based on the reduction to the degenerate hypergeometric equation. All
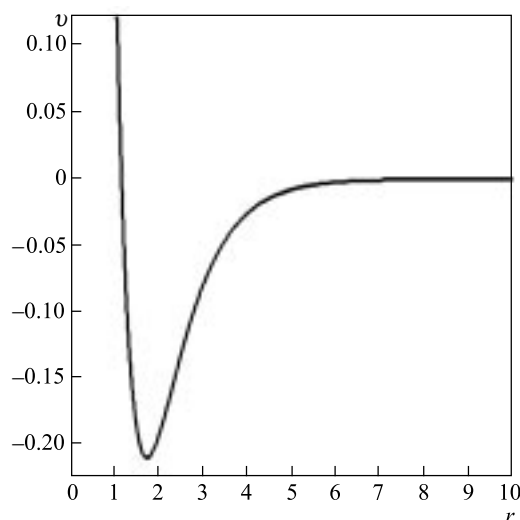
Fig. 1. Morse potential $V(r)$ for the hydrogen fluoride molecule. The Hartree units are used.

eigenvalues λ_k corresponding to the bound states ($\lambda_k < 0$) obey the following equations:

$$\lambda_k = -D + \frac{1}{2Mr_0^2}\left(2\alpha\sqrt{2MDr_0^2}\left(k+\frac{1}{2}\right) - \alpha^2\left(k+\frac{1}{2}\right)^2\right),$$

$$0 \leq k < \frac{\sqrt{2MDr_0^2}}{\alpha} - \frac{1}{2}.$$

Their corresponding eigenfunctions are as follows:

$$h_k(r) = B_k y^{-\frac{m_k}{2}} e^{\frac{1}{2}y}\frac{d^k}{dy^k}\left(y^{m_k+k}e^{-y}\right),$$

where

$$y = \frac{2\sqrt{2MDr_0^2}}{\alpha}\exp\left(-\alpha\frac{r-r_0}{r_0}\right), \qquad m_k = 2\frac{\sqrt{-2M\lambda_k r_0^2}}{\alpha},$$

and B_k is the normalizing factor. The coefficients B_k are calculated to within the sixth digit by the Lobatto method of adaptive quadrature [28] using the MATLAB procedure. Figure 2 shows examples of the eigenfunctions corresponding to the 2nd and 24th eigenvalues (22 in all).

Consideration is given to the finite-level approximation over all eigenfunctions corresponding to the bound states of the molecule:

$$i\frac{d\widehat{\Psi}(t)}{dt} = \widehat{H}_0\widehat{\Psi}(t) + u\widehat{H}_1\widehat{\Psi}(t), \qquad \widehat{\Psi}(t) \in \mathbb{C}^{22}, \tag{12}$$

where $\widehat{h}_k$, $k = 0, \ldots, 21$, are the orthonormal eigenvectors of the operator $\widehat{H}_0$ satisfying the relations

$$\widehat{h}_k^*\widehat{H}_0\widehat{h}_k = \lambda_k, \qquad k = 0, \ldots, 21,$$

$$\widehat{h}_p^*\widehat{H}_1\widehat{h}_q = A\int\limits_0^{+\infty} rh_p^*(r)h_q(r)dr, \qquad q, p = 0, \ldots, 21.$$

The matrix H_1 is calculated numerically, which requires considerable computer resources (for the considered example of the diatomic molecule and with regard for 23 energy levels, the time is 5 hours of Pentium 4).
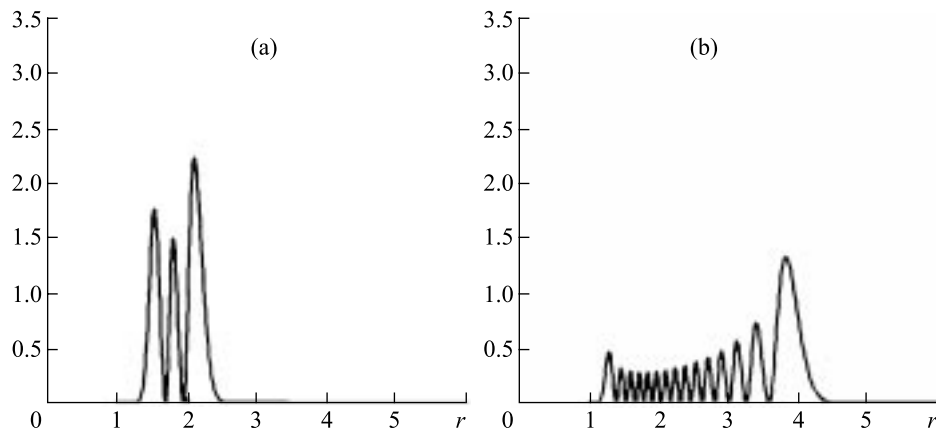

Fig. 2. Eigenfunctions corresponding to the (a) 2nd and (b) 14th eigenvalues. The Hartree units are used.

6. THE PROBLEM OF PREDISSOCIATION OF THE HF MOLECULE

Consideration is given to predissociation (driving to the given energy level) of the HF molecule. The initial state is assumed to be uniformly distributed between the 2nd and 3rd energy levels, which corresponds to the strongly connected state of the molecule. The observed energy $\widehat{H}_0$ is defined by the operator. The initial molecule energy is -0.1571. The goal value is set to -0.06 between the energies of the 10th and 11th levels, which corresponds to the state of molecule predissociation. It is required to construct the control function $u(t)$ stabilizing the molecule energy at the goal value. According to the scheme of Section 2, the control algorithm is as follows:

$$u_k(\Psi) = -\gamma \frac{2i}{\hbar}(\Psi^* \widehat{H}_0 \Psi + 0.06)\left(\Psi^* \left[\widehat{H}_1\widehat{H}_0 - \widehat{H}_0\widehat{H}_1\right]\Psi\right). \tag{13}$$

It follows from Theorem 1 that if the energy of initial state lies between the 10th and 11th levels, then this algorithm meets the aim of control. In the case at hand, the energy of the initial state lies between those of the 2nd and 3rd levels.
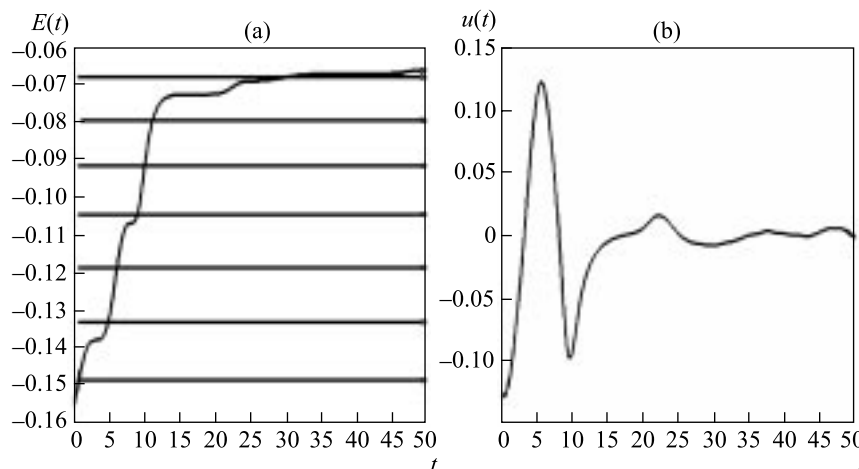
Fig. 3. (a) energy of the quantum system, (b) control function $u(t)$. The Hartree units are used. The time scale is in femtoseconds.

Figure 3b depicts a control pulse calculated from the quantum-mechanical model with the gain $\gamma = 200$. Figure 3a depicts energy profile, the horizontal lines corresponding to the energies of pure molecule states. The time of modeling was 50 femtoseconds. One can readily see that the proposed algorithm effectively meets the aim of control also for the initial data lying outside the domain indicated in the theorem.

7. CONCLUSIONS

The present paper is devoted to designing and studying the algorithms to control the observables for the quantum-mechanical systems. A new algorithm to control the observables on the basis of the methods of velocity gradient was proposed, and its efficiency was evaluated both theoretically and experimentally. The aim of control was shown to be reachable if the initial and goal values lie in the same energy level and satisfied are the nondegeneracy-type conditions—different values of the observed energy correspond to different pure states, their transition frequencies are different for different pairs of pure states, and for any two pure states and any nonzero control there exists a nonzero transition probability. Effectiveness of the proposed algorithm beyond these assumptions

was demonstrated by numerical modeling for the problem of predissociation (driving to the given energy level) of the hydrogen fluoride molecule. The algorithm sensitivity estimates are indicative of the fact that the error of calculation of the observable is proportional to the error in the initial data and to the error of realization of the control function. It is planned to study the possibility of extending the results obtained to the problems of control of more than one observable in polyatomic molecules.

APPENDIX

Proof of Theorem 1. Since the evolution operator of the closed-loop system (1), (5) is unitary and the initial state vector belongs to the unit sphere, the entire trajectory belongs to the unit sphere as well. Extendability of the solution to $\mathbb{R}$ is defined by the boundedness of the right-hand side of Eq. (1) over the entire phase space.

The proof of asymptotic stability of the goal energy value is based on the La Salle theorem [25]. The goal function $V(\Psi)$ is considered as the Lyapunov function. The derivative of the Lyapunov function

$$\dot{V}(\Psi) = \gamma \frac{4}{\hbar^2} (\Psi^* Z \Psi - Z_g)^2 \left(\sum_{k=1}^{r} \Psi^* [H_k Z - Z H_k]^2 \Psi \right) \le 0 \tag{A.1}$$

is nonpositive along the system trajectories. Consequently, by the La Salle theorem, any solution of the system tends to the maximum set which is invariant to a zero-control system and lies in $K = \{\phi : \dot{V}(\phi) = 0\}$.

$\dot{V}(\Psi)$ can be zero only in the two following cases:

$$\Psi^* Z \Psi - Z_g = 0, \tag{A.2}$$

$$\sum_{k=1}^{r} \Psi^* [H_k Z - Z H_k]^2 \Psi = 0. \tag{A.3}$$

We denote by K_1 and K_2 the subsets of the phase set where, respectively, the first and second equalities are satisfied ($K = K_1 \cup K_2$) and demonstrate that K_1 is invariant for the zero-control system (1). Since equality (A.2) is true for any vector of the phase space Ψ_1, the function

$$\Psi(t) = \exp(H_0(t - t_0))\Psi_1 \tag{A.4}$$

is the solution of the closed-loop system (1), (5) at any time instant t_0, and the corresponding trajectory belongs entirely to K_1, we see that the union of K_1 and the maximum invariant subset of K_2 will be the maximum invariant subset of the set K.

Let us consider K_2. Since membership of a trajectory in the set K_2 implies zero control along the entire trajectory, solution of system (1), (5) can be set down here in the explicit form as

$$\Psi(t) = \sum_{k=1}^{n} c_k \exp(-i\lambda_k t) h_k, \qquad \sum_{k=1}^{n} |c_k|^2 = 1. \tag{A.5}$$

Substitution of (A.5) in (A.3) which defines K_2 rearranges this equality in

$$\sum_{j=1}^{r} \sum_{k,m=1}^{n} \left(c_k^* c_m (z_k - z_m) e^{i(\lambda_k - \lambda_m)t} h_k^* H_j h_m \right) = 0. \tag{A.6}$$

According to condition (A2), the functions $\exp(i(\lambda_k - \lambda_m)t)$ are linearly independent. Consequently, their combination may be identically zero only if all coefficients of this linear combination are zero. It follows from conditions (A1), (A2), and (A3) that only one of the coefficients c_k, $k = \overline{1, n}$, may be other than zero. Consequently, the set of pure system states is the maximum invariant of the set K_2 (below $I(B)$ means the maximum invariant subset of B):

$$I(K_2) = \left\{ \Psi : \Psi = e^{ic}h_k, \quad k = \overline{1, n}, \quad c \in \mathbb{R} \right\}. \tag{A.7}$$

The goal function decreases monotonically, and by the theorem conditions the minimum value it assumes on the elements of the set $I(K_2)$ is other than zero and equal to

$$\min_{k=\overline{1,n}} (z_k - Z_g)^2. \tag{A.8}$$

Therefore, if the initial value of the goal function is smaller than this minimum, then the goal function tends to zero. The set K_1 is the maximum invariant of K where the goal function is zero; on this set the observable is equal to its goal value Z_g, which proves Theorem 1.

Proof of Lemma 1. For control in the form of the time function, the Schrödinger equation (1) becomes linear:

$$i\hbar\dot{\Psi}(t) = \left[H_0 + \sum_{k=1}^{r} u_k(t)H_k \right] \Psi(t), \qquad \Psi(t) \in \mathbb{C}^n. \tag{A.9}$$

By virtue of linearity, $\Psi(t, \Psi_0, u_*(t)) = \Psi(t, \Psi_*, u_*(t)) + \Psi(t, \delta\Psi, u_*(t))$. Consequently,

$$\begin{aligned}
&|\Psi(t, \Psi_0, u_*(t))^* Z\Psi(t, \Psi_0, u_*(t)) - \Psi(t, \Psi_*, u_*(t))^* Z\Psi(t, \Psi_*, u_*(t))| \\
&= |(\Psi(t, \Psi_*, u_*(t)) + \Psi(t, \delta\Psi, u_*(t)))^* Z(\Psi(t, \Psi_*, u_*(t)) + \Psi(t, \delta\Psi, u_*(t))) \\
&\qquad - \Psi(t, \Psi_*, u_*(t))^* Z\Psi(t, \Psi_*, u_*(t))| \\
&= |\Psi(t, \delta\Psi, u_*(t))^* Z\Psi(t, \Psi_*, u_*(t)) + \Psi(t, \Psi_*, u_*(t))^* Z\Psi(t, \delta\Psi, u_*(t)) \\
&\qquad + \Psi(t, \delta\Psi, u_*(t))^* Z\Psi(t, \delta\Psi, u_*(t))| \\
&= |\Psi(t, \delta\Psi, u_*(t))^* Z\Psi(t, \Psi_0, u_*(t)) + \Psi(t, \Psi_*, u_*(t))^* Z\Psi(t, \delta\Psi, u_*(t))| \\
&\leq |\Psi(t, \delta\Psi, u_*(t))| \, \|Z\| \, |\Psi(t, \Psi_0, u_*(t))| + |\Psi(t, \Psi_*, u_*(t))| \, \|Z\| \, |\Psi(t, \delta\Psi, u_*(t))| \leq 2\|Z\| \, |\delta\Psi|,
\end{aligned}$$

which provides the desired estimate and proves Lemma 1.

Proof of Lemma 2. The two systems

$$i\hbar\dot{x}(t) = H_0 x(t) + \sum_{k=1}^{r} u_k(t)H_k x(t) \quad \text{and} \tag{A.10}$$

$$i\hbar\dot{y}(t) = H_0 y(t) + \sum_{k=1}^{r} [u_k(t) + \delta u_k(t)]H_k y(t) \tag{A.11}$$

are considered. Equation (A.10) corresponds to the system without errors, and (A.11), to the system with error $\delta u(t)$ in control. Let $z(t)$ denote the mismatch between the solutions of these systems in time, provided that at the initial instant these solutions were coinciding: $z(t) = y(t) - x(t)$, $z(t_0) = 0$. Then,

$$i\hbar\dot{z}(t) = H_0 z(t) + \sum_{k=1}^{r} [u_k(t) + \delta u_k(t)]H_k z(t) + \sum_{k=1}^{r} \delta u_k(t)H_k x(t), \quad z(t_0) = 0. \tag{A.12}$$

Let $\mathcal{Z}(t)$ stand for the fundamental matrix of solutions of the uniform system of linear equations with variable coefficients corresponding to system (A.12). By substituting $z(t) = \mathcal{Z}(t)f(t)$ in (A.12), we obtain that the auxiliary function $f(t)$ satisfies the equation

$$i\hbar \mathcal{Z}(t)\dot{f}(t) = \sum_{k=1}^{r} \delta u_k(t) H_k x(t), \quad f(t_0) = 0.$$

Consequently,

$$z(t) = -\frac{i}{\hbar} \mathcal{Z}(t) \int_{t_0}^{t} \mathcal{Z}^{-1}(t) \sum_{k=1}^{r} \delta u_k(t) H_k x(t) dt.$$

By taking into account that $\|\mathcal{Z}(t)\| = \|\mathcal{Z}^{-1}(t)\| = 1$ and $\|x(t)\| = 1$, we conclude that

$$\|z(t)\| \le \frac{1}{\hbar} \sum_{k=1}^{r} \|H_k\| \int_{t_0}^{t} |\delta u_k(t)| dt. \tag{A.13}$$

The right-hand side of this expression is $\Delta(t)$ of Theorem 2.

Now, we estimate the variation of the observable Z under known variation of the phase vector:

$$|(x+\delta x)^* Z(x+\delta x) - x^* Z x| \le |\delta x^* Z x + x^* Z \delta x + \delta x^* Z \delta x| \le (2|\delta x| + |\delta x|^2)\|Z\|. \tag{A.14}$$

Expression (A.13) estimates the system phase vector under inaccuracies of control, and (A.14) estimates the observable for a known deviation of the phase vector. Together, they provide the desired estimate (9), which proves Lemma 2.

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