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TOPICAL ISSUE

Selective Control of the Observables in the Ensemble of Quantum Mechanical Molecular Systems[1]

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Abstract—A new approach to synthesize algorithms for selective control of the observables in quantum mechanical systems in the presence of additional constraints during the whole period of control is proposed. Analytic results of achieving the goal of control under some additional assumptions were obtained. It was demonstrated that the error in achieving the goal of control is proportionate to the error in prescribing the initial state of system and the error in realizing the control action. Numerical results for the problem of selective control for energy of hydrogen molecules (H_2) with different isotopes are represented. The proposed algorithms are easy to design.

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1. INTRODUCTION

The first monograph on the control of quantum mechanical processes was published in the USSR in 1984 [1]; it was a dusk study of several interesting problems. Practical realization of experiments on control of molecular dynamics became possible, when at the end of the 1980s there appeared ultrafast femtosecond lasers generating pulses of duration of about tens of femtoseconds (and nowadays, of about unities of femtoseconds, 1 fs $= 10^{-15}$ s) and also techniques for computer control of the form of laser pulses. The carried out experiments confirmed the possibility to use lasers for changing the natural character of chemical reactions by controlling them [2, 3]. Rapid development of this field (see Fig. 1) resulted in appearing a series of new problems; many of them are at the turn of physical chemistry and control theory [4–6].

One of the typical problems of this class is the problem of control of dissociation of a diatomic molecule. In [7–9] were obtained the results that proved the low probability of dissociation of diatomic molecules even when intensive monochromatic laser pulses are used. This effect is explained by anharmonicity of the molecular potential and nonlinearity of interaction with the control laser field. At the same time, it is known that if intensity of the laser exceeds $10^{13}\,\mathrm{W}\times\mathrm{c}^{-2}$, then the ionization process will dominate over the dissociation process. In [10], it was demonstrated that when two-frequency (bichromatic) action is used, intensity of the dissociating field can be considerably decreased. Investigations of application of algorithms with chirping, i.e., uniform change of frequency, showed the possibility of the further decrease in intensity of the field that is required for dissociation [11, 12]. In [13] on the basis of the fast gradient method was obtained an algorithm for computing the form of the dissociating field with the arbitrarily small amplitude.

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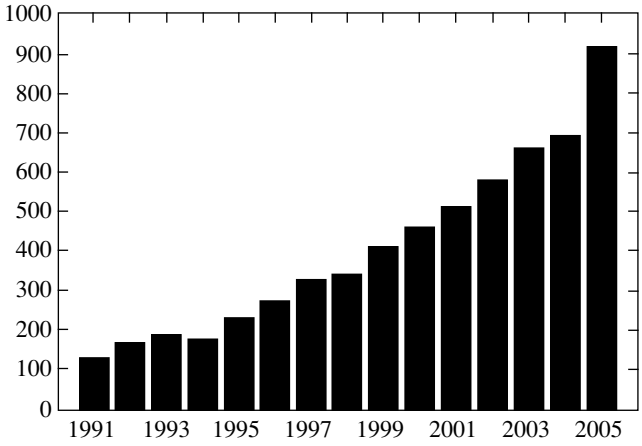

Fig. 1. The number of articles published in reviewed journals devoted to control in quantum systems (according to the journal "Science Citation Index").

Sizes of molecules of chemical agents (monomers) have the order of nanometers (1 nm $= 10^{-9}$ m), which is many orders less than the width of the laser field; thus, the selective action is impossible, and the control pulse simultaneously affects a larger number of molecular systems. As a result of this, a problem of selective control occurs, i.e., a problem of synthesizing the control pulse that transfers molecules of one type to the prescribed state and does not considerably change molecules of another type. In [15] were obtained necessary conditions for simultaneous controllability of several finite-dimensional quantum mechanical systems. However, these theorems of existence do not prompt the design of the control algorithm and do not allow investigating the property of controllability under additional constraints imposed on the control pulse.

This paper develops the results on the control of the observables obtained in [13, 14] for the case of several independent quantum mechanical systems. The approach is based on the fast gradient method [16] applied for the first time to problems of control in complex spaces with constraints. Sufficient conditions for applicability of the proposed algorithms are formulated. It was demonstrated that the achievement of the goal of control is possible by the arbitrarily amplitude-small control pulse. Efficiency of the approach is demonstrated by a numerical simulation in the problem of simultaneous control for energy of several diatomic hydrogen molecules (H_2) composed of different isotopes. Also were obtained estimates of achievement of the goal of control under small deviations in prescribing the initial state of system and in the presence of errors in realizing the control action.

2. FORMULATION OF THE PROBLEM

As mentioned in the introduction, laser control is not selective, and all molecules positioned in the domain of irradiation obtain the control pulse. Therefore, is posed the problem of synthesizing the control field that possesses the property of selective action, i.e, that excites molecules of one type and, if possible, does not considerably changing dynamics of others.

Several independent molecular systems are considered; their dynamics is described by the Schrödinger finite-dimensional control equation [15]:

$$i\hbar\dot{\phi}_n = H_n\phi_n + uS_n\phi_n, \quad n = 1, \ldots, N, \quad \phi \in \mathbb{C}^\nu, \quad \|\phi\| = 1, \tag{1}$$

where $i = \sqrt{-1}$; $\hbar$ is a Planck constant;[2] N is a number of the considered systems (different types of molecules placed in the domain of irradiation), u is a real-valued control function, intensity of the

[2] $\hbar = 5309\,\mathrm{cm}^{-1} \times \mathrm{fs}$.

electric component of laser field; the control action is identical for all systems. For the nth system $n = 1, \ldots, N$: H_n is a self-conjugate operator of the total energy of the unperturbed system; S_n is a self-conjugate operator of the dipole molecule moment; ϕ_n is a phase vector of the system.

The following problem of control is set for the known initial data. It is necessary to find the function $u(t)$ that ensures fulfillment of the following conditions:

$$\lim_{t\to+\infty} \phi_n^*(t) Z_n \phi_n(t) = g_n, \quad 1 \leqslant n \leqslant \mu, \tag{2}$$

$$\forall\, t \geqslant 0 : m_n < \phi_n^*(t) Z_n \phi_n(t) < M_n, \quad \mu + 1 \leqslant n \leqslant N. \tag{3}$$

Here "*" denotes transposition and complex conjugation for $n = 1, \ldots, N$: Z_n is a self-conjugate operator (the observable); g_n is a desired mean value of the observable Z_n; m_n, M_n are admissible boundaries of dynamics of the mean value of Z_n.

Usually the term "observable Z" denotes an operator in the space of states that corresponds to some characteristic of the system (e.g., energy). As a result of these or other observations, we can obtain a concrete numerical value of the observable. It is a random value, and $\phi(t)^* Z \phi(t)$ has the sense of its mean value at the instant t.

It is to be noted that fulfillment of constraint (3) is necessary during the whole period of control.

The typical example of the observable for the problem of control is the observed value of energy: $Z_n = H_n$, $n = 1, \ldots, N$. In this case, condition (2) implies that for $n = 1, \ldots, \mu$, the desired mean value of energy of the molecule of the nth type is g_n, and admissible boundaries for energies of others are m_n, M_n. If to choose $g_n \gg 0$ and $M_n \ll 0$, then the probability of dissociation of molecules of the type $1, \ldots, \mu$ will be high; and of the type $\mu + 1, \ldots, N$, low.

3. SYNTHESIS OF THE CONTROL ALGORITHM

According to [13], it is first proposed to design the control algorithm according to the feedback $u = u(\phi_1, \ldots, \phi_N)$, and then to perform a computer simulation of dynamics of the system with the known initial data and calculate the time profile of the control function:

$$u = u(\phi_1, \ldots, \phi_N) = u(\phi_1(t), \ldots, \phi_N(t)) = u(t). \tag{4}$$

It is to be noted that to prescribe the initial data, distribution of the molecular ensemble in the equilibrium state (i.e., Gibbs distribution), it is sufficient to know the value of temperature.

Synthesis of the control algorithm is based on the fast gradient method in the finite form [16] with the specific objective function Q:

$$Q(\phi_1, \ldots, \phi_N) = \sum_{n=1}^{\mu} a_n |\phi_n^* Z_n \phi_n - g_n|^{p_n} + \sum_{n=\mu+1}^{N} a_n |\phi_n^* Z_n \phi_n - m_n|^{-p_n} |\phi_n^* Z_n \phi_n - M_n|^{-p'_n}. \tag{5}$$

Here $a_n > 0$, $p_n, p'_n > 1$ are parameters of the algorithm. The first sum, the sum of degrees of deviations from the target value, is an ordinary technique in using the fast gradient method. The second sum with negative degrees of deviations from admissible boundaries is used for the first time in the fast gradient method and is introduced only to ensure fulfillment of conditions (3).

According to the fast gradient method, the control algorithm is computed by the formula

$$u(\phi_1, \ldots, \phi_N) = -\Gamma \nabla_u \dot{Q}(\phi_1, \ldots, \phi_N). \tag{6}$$

Here $\Gamma > 0$ is a gain coefficient, ∇_u implies the gradient over u, and the point is a time derivative due to systems (1). Such a choice of control ensures nonincrease of the objective function along

trajectories of the system; since at the domain boundary prescribed by constraints (3) the function is $Q(\phi_1,\dots,\phi_N)=+\infty$, then this boundary is never crossed. Since the tendency of the objective function to zero is equivalent to fulfillment of the goal of control (2), then the proposed algorithm can guarantee the fulfillment of the assigned goal under some additional conditions.

Let us compute the derivative of objective function (5) due to systems (1)

$$\dot{Q}(\phi_1,\dots,\phi_N)=\sum_{n=1}^{\mu}a_n p_n\Delta(g_n)^{p_n-1}L(Z_n)$$
$$-\sum_{n=\mu+1}^{N}a_n\left(p_n\Delta(m_n)^{-p_n-1}\Delta(M_n)^{-p'_n}+p'_n\Delta(m_n)^{-p_n}\Delta(M_n)^{-p'_n-1}\right)L(Z_n). \tag{7}$$

Here the following notation is introduced:

$$\Delta(g_n)=\phi_n^*Z_n\phi_n-g_n, \tag{8}$$
$$L(Z_n)=\frac{1}{i\hbar}\phi_n^*([Z_n,H_n]+u[Z_n,S_n])\phi_n, \tag{9}$$

where $[A,B]=(AB-BA)$ is a commutator of operators.

Substituting the obtained expression into (6), we obtain the sought feedback control algorithm

$$u(\phi_1,\dots,\phi_N)=-\frac{\Gamma}{i\hbar}\sum_{n=1}^{\mu}a_n p_n\Delta(g_n)^{p_n-1}\phi_n^*[Z_n,S_n]\phi_n$$
$$+\frac{\Gamma}{i\hbar}\sum_{n=\mu+1}^{N}a_n\Big(p_n\Delta(m_n)^{-p_n-1}\Delta(M_n)^{-p'_n}+p'_n\Delta(m_n)^{-p_n}\Delta(M_n)^{-p'_n-1}\Big)\phi_n^*[Z_n,S_n]\phi_n. \tag{10}$$

Remark 1. Parameters of the algorithm a_n, p_n, p'_n, and Γ can be used for numerical optimization and fulfillment of possible additional constraints imposed on the control function.

Remark 2. Proposed algorithm (10) can be also used to control infinite systems on condition that there exist all necessary derivatives and the formulation of the problem is correct.

4. STUDY OF THE CONTROL ALGORITHM

Lemma 1. *The Cauchy problem for system of Eqs.* (1) *with control* (10) *and the starting conditions satisfying constraints* (3) *has a unique solution that can be extended onto the whole real axis.*

The proof of the lemma is given in the Appendix.

Let λ_n^k, h_n^k, $k=1,\dots,\nu$, are eigenvalues and eigenvectors respectively of the operator H_n, $n=1,\dots,N$; and denote eigenvalues Z_n, $n=1,\dots,N$ by z_n^k, $k=1,\dots,\nu$. According to the terminology adopted in the modern theory of control of quantum mechanical systems [1–7], let us identify the state of the quantum system as "pure" if the phase vector corresponding to this state is an eigenvector for the energy operator (i.e., the states $e^{it}h_n^k$, $t\in\mathbb{R}$, are "pure" with respect to the nth system). In classic works on quantum mechanics [18, 19] these states are called stationary.

Theorem 1. *Let the following assumptions are fulfilled:*

(A1) $[Z_n,H_n]=0$, $n=1,\dots,N$;

(A2) $\lambda_n^k-\lambda_n^j\neq\lambda_m^r-\lambda_m^s$, $(n,k,j)\neq(m,r,s)$, $k,j,r,s=1,\dots,\nu$, $n,m=1,\dots,N$;

(A3) $(z_n^k - z_n^m)[(h_n^k)^* S_n h_n^m] \neq 0$, $n = 1, \ldots, \mu$, $k, m = 1, \ldots, \nu$;

(A4) *constraints* (3) *with* $t = 0$ *are fulfilled;*

(A5) $Q^{-1}([0, Q(\phi_1(0), \ldots, \phi_N(0))])$ *does not contain pure states of the systems* $1, \ldots, \mu$.

Then control algorithm (10) *ensures achievement of goal of control* (2) *and fulfillment of constraints* (3).

The proof of the theorem is given in the Appendix.

Remark 3. Since the control is continuous and the phase space is compact, then by choosing the sufficiently small gain coefficient Γ we can achieve the goal of control by means of an arbitrarily small control action.

Remark 4. Condition (A1) implies that in the absence of control the mean value of the observables Z_n, $n = 1, \ldots, N$, does not change. Conditions (A2) and (A3) are sufficient for simultaneous controllability of the systems $1, \ldots, \mu$. It is to be noted that the simultaneous controllability of all N systems is not required.

Remark 5. If to exclude condition (A5), then "sticking" of trajectories of systems in pure states is possible. However, this situation has never been observed during the numerical simulation in the models under study.

Let us study the behavior of the synthesized system in the presence of the error in prescribing the initial distribution and error in realizing the control action. Let us assume that the starting condition of the nth system is known approximately: at the initial instant t_0, the initial distribution is $\phi_n^0 = \phi_n^* + \delta\phi_n$ where ϕ_n^0 is a real starting condition, ϕ_n^* is a design starting condition, $\delta\phi_n$ is a residual between the real and design starting conditions. Let us also assume that the control is realized incorrectly: $u(t) = u_*(t) + \delta u(t)$. Here $u(t)$ is a realized control, $u_*(t)$ is a design control, and $\delta u(t)$ is a residual between the realized and design controls. Let $\phi_n(t, \phi_n^0, u(t))$ denotes the trajectory of the nth system with the starting condition ϕ_n^0 and control $u(t)$. The following statement allows estimating the error in achievement the goal of control under the prescribed residuals.

Theorem 2 ([13, p. 67]). *For any time t in the presence of errors in prescribing the initial distribution and inaccuracies in realizing the control action there exists the following estimate of deviations of the observed nth system from the computed value:*

$$\begin{aligned} &|\phi_n(t, \phi_n^0, u(t))^* Z_n \phi_n(t, \phi_n^0, u(t)) - \phi_n(t, \phi_n^*, u_*(t))^* Z_n \phi_n(t, \phi_n^*, u_*(t))| \\ &\qquad \leqslant (2|\delta\phi_n| + |\delta\phi_n|^2 + 2\Delta(t) + \Delta^2(t))\|Z_n\|, \qquad (11) \\ &\Delta(t) = \frac{1}{\hbar}\|S_n\| \int_0^t |\delta u_k(t)| dt, \end{aligned}$$

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

Remark 6. If $\int_0^{+\infty} |\delta u(t)| dt < +\infty$, then we can replace $\Delta(t)$ by $\Delta = \frac{1}{\hbar}\|S_n\| \int_0^{+\infty} |\delta u_k(t)| dt$

in (11).

5. FINITE-LEVEL APPROXIMATION OF THE QUANTUM MODEL OF THE MOLECULE H_2

We study a one-dimensional mathematical model of the diatomic quantum mechanical hydrogen molecule described by the controlled Schrödinger equation with the Morse potential $V(r)$:

$$i\hbar\frac{\partial\Psi(r,t)}{\partial t} = H\Psi(r,t) + uS\Psi(r,t), \tag{12}$$

where

$$H = \left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial r^2} + V(r)\right], \quad S = A\mu(r), \tag{13}$$

$$V(r) = D\left(\exp\left(-2\alpha\frac{r-r_0}{r_0}\right) - 2\exp\left(-\alpha\frac{r-r_0}{r_0}\right)\right). \tag{14}$$

Here $i = \sqrt{-1}$ is an imaginary unit; $\hbar$ is a Planck constant; $r \in (0, +\infty)$ is a distance between atoms of the molecule; $\Psi(r,t)$ is a wave function, at each instant the square of its module has the sense of density of distribution of the quantity r; H is an operator of the total energy of the free system; M is reduced mass of molecule; $V(r)$ is a Morse potential; u is intensity of the electric component of the external laser field; $\mu(r)$ is a molecular dipole moment; D, α, r_0 are parameters of the Morse potential. The molecular dipole moment in the first approximation can be let equal to $\mu(r) = Ar$; further we will consider that $A = 1$. Values of the parameters M and r_0 depend on the isotopic composition of molecule.

The Morse potential is often used to describe vibrations of diatomic systems. It is considered to be more physical than the Kratzer potential [20]. The Morse potential has the global minimum at the equilibrium point of the system $r = r_0$ equal to $-D$. If the approach of nuclei is strong, $V(r)$ assumes positive values and then it becomes negative due to the intensive Heitler–London attraction, and, finally, gradually increases describing weaker van der Waals forces (Fig. 2).

The eigenfunctions and eigenvalues of the operator H_0 corresponding to them can be obtained analytically with high accuracy by reducing the problem to the degenerate hypergeometric equation [20]. All eigenvalues of λ_k complying with bound states (i.e, states with the negative energy:

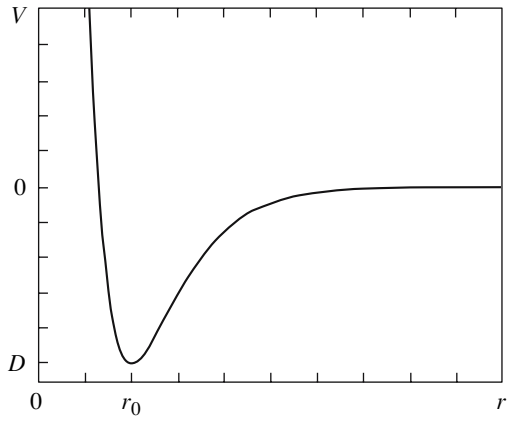

Fig. 2. Morse potential.

$\lambda_k < 0$) are prescribed by the following expressions

$$\lambda_k = -D + \frac{1}{2Mr_0^2}\left(2\alpha\sqrt{2MDr_0^2}\left(k+\frac{1}{2}\right) - \alpha^2\left(k+\frac{1}{2}\right)^2\right), \tag{15}$$

$$0 \leqslant k < \frac{\sqrt{2MDr_0^2}}{\alpha} - \frac{1}{2}, \quad k \in \mathbb{N}. \tag{16}$$

The eigenfunctions corresponding to them have the form

$$h_k(r) = B_k y^{-\frac{m_k}{2}} e^{\frac{1}{2}y} \frac{d^k}{dy^k}\left(y^{m_k+k}e^{-y}\right), \tag{17}$$

where

$$y = \frac{2\sqrt{2MDr_0^2}}{\alpha}\exp\left(-\alpha\frac{r-r_0}{r_0}\right), \quad m_k = 2\frac{\sqrt{-2M\lambda_k r_0^2}}{\alpha}, \tag{18}$$

and B_k are normalization coefficients. Let us make an important remark: according to (16), the set of eigenvalues corresponding to bound states is finite.

One of the methods to simplify the investigation of system (12) is the use of the finite-dimensional approximation. Tough the question of physical adequacy of this simplification is open, this approach is quite widespread [5]. In this paper, we consider the finite-level approximation over all eigenfunctions corresponding to bound states of the molecule

$$i\hbar\dot{\phi} = \widehat{H}\phi + uS\phi, \quad \phi \in \mathbb{C}^\nu, \tag{19}$$

where for the operator $\widehat{H}$ and its orthonormalized eigenvectors $\widehat{h}_k$, $k = 0, \ldots, \nu$, are fulfilled the following relations

$$\widehat{h}_k^* \widehat{H} \widehat{h}_k = \lambda_k, \quad k = 0, \ldots, \nu, \tag{20}$$

$$\widehat{h}_p^* \widehat{S} \widehat{h}_q = A \int_0^{+\infty} r h_p^*(r) h_q(r) dr, \quad q, p = 0, \ldots, \nu. \tag{21}$$

Computation of the matrix $\widehat{S}$ is fulfilled numerically and requires considerable computational resources (it is 4 h on Pentium 4 for the considered example of the diatomic molecule taking into consideration 14 energy levels).

Applying the method of a priori estimates [21], we can prove convergence of finite-dimensional approximations designed by the Bubnov–Galerkin method to the exact solution to Eq. (12) and obtain corresponding estimates of the approximation error. Unfortunately, the mathematically strict statement of this result would lead to the unwarrantable volume of this article and would distract readers' attention from the basic output.

6. PROBLEM OF SELECTIVE CONTROL OF ENERGY OF THE MOLECULES $^1H^1H$ AND $^1H^2H$

Two types of molecules $^1H^1H$ and $^1H^2H$ are considered; the upper index in the designation of atom denotes the number of neutrons belonging to it. To describe the dynamics of molecules, let us use approximation (19) of Eq. (12):

$$i\hbar\dot{\phi}_n = \widehat{H}_n\phi_n + u\widehat{S}_n\phi_n, \quad \phi_n \in \mathbb{C}^{17}, \quad n = 1, 2, \tag{22}$$

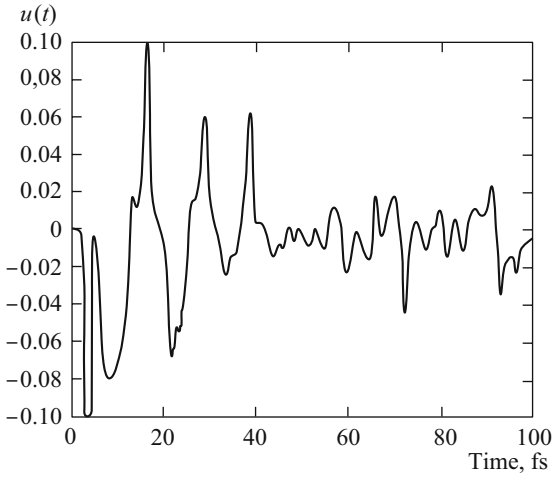

Fig. 3. Diagram of the objective function $u(t)$.

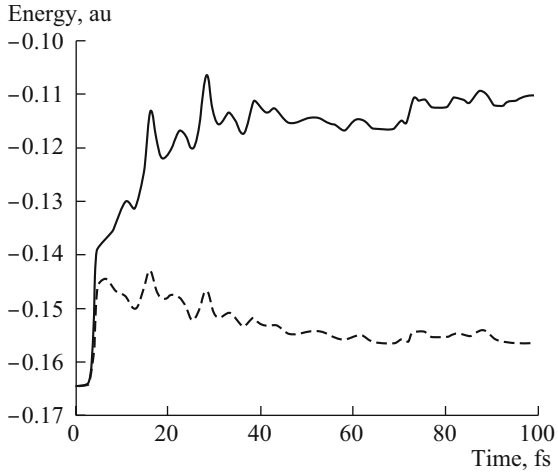

Fig. 4. Diagram of evolution of the mean values of the energies $\phi_1(t)H_1\phi_1(t)$ and $\phi_2(t)H_2\phi_2(t)$.

where $n = 1$ corresponds to ${}^1H^1H$, and $n = 2$, to ${}^1H^2H$. The following values of the parameters [20] of Eq. (12) were used (the Hartree atomic system of units)

$$\begin{array}{c|ccccccc} {}^1H^1H & \hbar = 1 & M = 918.5 & r_0 = 1.4014 & D = 0.1745 & \alpha = 1.44 & \nu = 17 \\ {}^1H^2H & \hbar = 1 & M = 1224.4 & r_0 = 1.2138 & D = 0.1745 & \alpha = 1.44 & \nu = 17 \end{array} .$$

As an initial state of the system, the Gibbs distribution corresponding to the temperature $T = 300^\circ K$ was taken:

$$\phi_n(0) = C\left(\exp\left(\frac{-\lambda_n^0}{kT}\right), \ldots, \exp\left(\frac{-\lambda_n^{\nu-1}}{kT}\right)\right)^{\mathrm{T}}, \quad n = 1, 2, \tag{23}$$

where k is a Boltzmann constant, and C is a normalization coefficient (in the Hartree atomic system of units $k = 1$, $T = 9.501 \times 10^{-4}$).

Was posed the problem of stabilization of the observable $\phi_1(t)^*\widehat{H}_1\phi_1(t)$ on the target value $g_1 = -0.09$ with the upper constraint on the dynamics $\phi_2(t)^*\widehat{H}_2\phi_2(t)$ equal to $M = -0.14$. The parameters of control algorithm (10) were as follows: $p_1 = 2$, $p_2 = 0$, $p_2' = 0.1$, $a_1 = 400$, $a_2 = 2$, the simulation time is $t_f = 4134.11$ (corresponds to 100 fs). Numerical optimization over the parameter Γ by the gradient-search method with the performance functional (H. Rabitz [17])

$$J(u) = \sum_{k=1}^{\mu}(\phi_k(t_f)^*H_k\phi_k(t_f) - g_k)^2 + \alpha\int_0^{t_f} u^2(t)dt, \tag{24}$$

where $\alpha = 0.02$ produced the value of $\Gamma = 4.8$. Substituting the values of parameters into control algorithm (10), we obtain

$$u(\phi_1, \phi_2) = -i\left(3840|\phi_1^*H_1\phi_1 + 0.09|\phi_1^*[H_1, S_1]\phi_1 + 0.96\frac{\phi_2^*[H_2, S_2]\phi_2}{|\phi_2^*H_2\phi_2 + 0.14|^{1,1}}\right). \tag{25}$$

The results of numerical computations are represented in Figs. 3 and 4. In Fig. 3 there is control function (25); in Fig. 4, evolution of the mean values of the energies. The energy of the molecule ${}^1H^1H$ tends to its target value, while the energy ${}^1H^2H$ does not cross the established boundary. The proposed algorithm can effectively fulfill the goal of control for the initial data placed out of the domain indicated in the theorem; sealing of trajectories in pure states is not observed.

7. CONCLUSIONS

The paper is devoted to elaborating and studying algorithms for selective control of the observables in quantum mechanical systems under constraints imposed on the whole period of control. A new control algorithm for the observables based on the fast gradient method with the new type of objective function is proposed. Theoretical and experimental estimates of its efficiency are represented. Conditions for achievement of the goal of control are formulated and proved. Efficiency of the proposed algorithm is demonstrated beyond the bounds of these conditions by numerical simulation for the problem of selective control for energy of hydrogen molecules (H_2) containing different isotopes. The obtained estimates of the algorithm sensitivity demonstrate that the error in computing the value of observable is proportionate to the error in the initial data and the error in realizing the control function.

APPENDIX

Proof of Lemma 1. Let us denote the domain where constraints (3) are fulfilled by Ω. The function $u(\phi_1, \dots, \phi_N)$ prescribed by expression (10) is continuous in the domain Ω; hence, the right-hand sides of systems (1) are also continuous. Thus, we conclude that the solution to the Cauchy problem exists on some time interval. Since the objective function $Q(\phi_1, \dots, \phi_N)$ does not increase along the trajectories of the system, then the unbounded approximation of trajectories to the boundary Ω is impossible (on the boundary we have $Q(\phi_1, \dots, \phi_N) = +\infty$). Hence, the right-hand sides of system (1) are bounded; thus, the solution can be extended onto the whole real axis.

Proof of Theorem 1. Let us consider an objective function $Q(\phi_1, \dots, \phi_N)$ as a Lyapunov function for system (1) with control (10). It possesses the following properties:

(B1) $Q(\phi_1, \dots, \phi_N) \geqslant 0$;

(B2) $\dot{Q}(\phi_1, \dots, \phi_N) = -\Gamma^{-1}u^2 \leqslant 0$ (see condition (A1) and expressions (6) and (7));

(B3) $\forall\, x \in \Omega : Q^{-1}(x)$ is a compact set.

Hence, we can apply the La Salle theorem [16], which affirms that the maximum invariant of the set of level 0 for the derivative of the objective function will be the limiting set for trajectories of the system under study due to the system $I(\dot{Q}^{-1}(0))$.

Let us select two important properties of the set $I(\dot{Q}^{-1}(0))$:

(C1) on it we have $u \equiv 0$ (i.e., $u^2 = -\Gamma u \nabla_u \dot{Q}(\phi_1, \dots, \phi_N) = -\Gamma \dot{Q}(\phi_1, \dots, \phi_N) = 0$);

(C2) on it we have $\dot{\Delta}(g_n) = \dot{\Delta}(m_n) = \dot{\Delta}(M_n) = 0$, (since $\dfrac{d}{dt}(\phi_n^* Z_n \phi_n) = \dfrac{1}{i\hbar} u \phi_n^* [Z_n, H_n] \phi_n = 0$).

By definition, $I(\dot{Q}^{-1}(0))$ consists of whole trajectories and, according to condition (C1), the control along them is equal to zero. Hence,

$$\phi_n(t) = \exp\left(\frac{1}{i\hbar} H_n t\right) \phi_n(0) = \sum_{k=1}^{\nu} \exp\left(\frac{1}{i\hbar} \lambda_n^k t\right) h_n^k x_n^k, \quad n = 1, \dots, N, \tag{A.1}$$

where for $n = 1, \dots, N$, $k = 1, \dots, \nu$: λ_n^k, h_n^k are respectively eigenvalues and eigenvectors of the operator H_n, and $x_n^k = (\phi_n(0), h_n^k)$ are expansion coefficients of the vector of the starting conditions $\phi_n(0)$ over h_n^k.

Let us consider expression (7) on the set $I(\dot{Q}^{-1}(0))$. Let us rewrite it, taking into consideration assumption (A1) and property (C2):

$$\dot{Q}(\phi_1, \dots, \phi_N) = \sum_{n=1}^{N} c_n \phi_n(t)^* [Z_n, S_n] \phi_n(t), \tag{A.2}$$

where c_n, $n = 1, \ldots, N$, are some constants, Let us substitute the expression for trajectories (A.1) into (A.2) and equate the last with zero:

$$\sum_{n=1}^{N} c_n \left(\sum_{k=1}^{\nu} \exp\left(\frac{1}{i\hbar}\lambda_n^k t\right) h_n^k x_n^k \right)^* [Z_n, S_n] \left(\sum_{k=1}^{\nu} \exp\left(\frac{1}{i\hbar}\lambda_n^k t\right) h_n^k x_n^k \right) \equiv 0. \tag{A.3}$$

Let us remove the brackets and pay attention to the fact that, according to (A1), the vectors h_n^k, $k = 1, \ldots, \nu$, are eigenvectors for the operators Z_n, $n = 1, \ldots, N$:

$$\sum_{n=1}^{N} \sum_{k,m=1}^{\nu} \left(c_n (x_n^k)^* x_n^m (z_n^k - z_n^m)[(h_n^k)^* S_n h_n^m] \exp\left(\frac{\lambda_n^m - \lambda_n^k}{i\hbar} t\right) \right) \equiv 0. \tag{A.4}$$

From condition (A2), it follows that exponents are linearly independent; hence, all coefficients in this linear combination are equal to zero. According to assumption (A3), we have in the condition of the theorem $(z_n^k - z_n^m)[(h_n^k)^* S_n h_n^m] \neq 0$ with $n = 1, \ldots, \mu$.

Hence, $c_n (x_n^k)^* x_n^m = 0$ with $n = 1, \ldots, \mu$, $k, m = 1, \ldots, \nu$, $k \neq m$. If there exists $c_n \neq 0$, then the nth system is in pure state, which is impossible due to condition (A5). Hence, all trajectories of the system tend to the set on which c_n are equal to zero with $n = 1, \ldots, \mu$, which is equivalent to the fulfillment of the goal of control. We are to demonstrate the fulfillment of constraints (3).

According to the choice of control, the objective function does not increase. It is equal to $+\infty$ on the boundary of the set Ω (where constraints (3) are fulfilled). Hence, the trajectories of the system starting in Ω (condition (A4)) will never leave it.

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