# Binding energy of bipartite quantum systems: Interaction, correlations, and tunneling

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We provide a physically motivated definition for the binding energy (or bond dissociation) of a bipartite quantum system. We consider coherently applying an external field to cancel out the interaction between the subsystems, to break their bond and separate them as systems from which no work can be extracted coherently by any cyclic evolution. The minimum difference between the average energies of the initial and final states obtained this way is defined as the binding energy of the system. We show that the final optimal state is a passive state. We discuss how the required evolution can be realized through a sequence of control pulses. The utility of our definition is illustrated through two examples. In particular, we also show how quantum tunneling can assist or enhance a bond-breaking process. This extends our definition to probabilistic events.

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## I. INTRODUCTION

Binding energy (BE) or bond-dissociation energy is a prevalent concept in various branches of science such as physical chemistry, condensed-matter physics, atomic physics, nuclear physics, and gravitation. Colloquially, e.g., in chemistry, BE is defined as the energy needed to fully decompose a composite material into its constituent elements (in a mole of material). Some further cases where BE can be relevant include ionization of an atom, alpha particle decay [1], or dissociation of molecules. In addition to advanced measurement techniques, there exist numerical methods in physical chemistry e.g., the finite-difference Poisson-Boltzmann electrostatic method—to theoretically compute BE for materials [2].

In *classical* systems, BE is attributed to the forces that bound elements of a composite system together [3]. However, with the recent advent of nanotechnology and engineering small-scale systems, it seems important to revisit the concept of BE for systems where *quantum* effects may prevail [4–7]. In particular, quantum coherence and quantum correlations have a role in physical and chemical evolutions since they contribute to energy exchange and thermodynamics of quantum systems [8–10]. Additionally, it has also been argued that quantum tunneling may be employed in some dynamical evolutions [1] or chemical reactions in order to reduce required initial energy in some bond-breaking processes [4].

Various technical tools have been developed in order to investigate control and manipulation of quantum systems. For example, optimal control theory (OCT) introduces techniques based on variational optimization and differential geometry to obtain optimal approaches to achieve a target in quantum systems [1,11-21], e.g., by *coherently* applying appropriate control fields such as lasers pulse trains [22,23].

Here we introduce a definition for the BE of a quantum bipartite system and propose methods to (optimally) break a bond in a composite system. We restrict ourselves to *unitary* processes during which a bond breaks due to *work extraction*. We consider several scenarios for breaking a bond by external control, and discuss optimal or close-to optimal control strategies. In particular, we focus on photodissociation where a bond breaks through absorption of photons generated by suitable laser pulse trains [24].

This paper is organized as follows. We start by briefly reviewing, in Sec. II, how control of a quantum system affects it. In Sec. III, we present and motivate a definition for BE. In Sec. IV, we obtain optimal state and coherent evolution for bond breaking. This section also includes discussions of an example of bond breaking in an atom-cavity system. We discuss the impact of quantum tunneling in bond breaking in Sec. V. The paper is summarized in Sec. VI. Two Appendixes, A and B, include some review material and detailed calculations related to an example discussed later in the paper.

## **II. CONTROLLING A QUANTUM SYSTEM**

Let us assume that we manipulate a quantum system (S) with an external control agent or apparatus (C), which is another classical or quantum system. The Hilbert space of the composite system is  $\mathcal{H}_{SC} = \mathcal{H}_S \otimes \mathcal{H}_C$ . It is known that the total Hamiltonian of this composite system is given by

$$H_{\mathsf{SC}}(\lambda, g; t) = H_{\mathsf{S}}(\lambda; t) + H_{\mathsf{C}} + H_{\mathsf{int}}(g; t).$$
(1)

Here  $H_{S}(\lambda;t)$  indicates the system Hamiltonian, which may depend explicitly on time as well as some other structural parameters  $\lambda$  (e.g., size of the box for particle in a box). The Hamiltonian of the controller is shown by  $H_{C}$ , which for simplicity we assume to be time independent. The interaction Hamiltonian  $H_{int}(g;t)$  is the main player in controlling system S, which itself may depend on time and some structural parameters g given by the physics of the two systems S and C and how they interact (e.g., an electron and an electric field)—see Fig. 1.

Note that, although the Hilbert space after the control is  $\mathcal{H}_{SC}$ , in general interaction of the system and the controller can yield a different control-induced decomposition as  $\mathcal{H}_{SC} = \mathcal{H}_{S_1} \otimes \mathcal{H}_{S_2} \otimes \ldots \mathcal{H}_{C'}$ , where new physical parties may be produced and the control system may also drastically



FIG. 1. Schematic of a system under control by another system.

vary. Evolution of each product or party  $(\ell \in \{S_1, \ldots, C'\})$  is then given by a dynamical equation obtained by reducing (tracing out) the total dynamical equation [25],

$$\frac{\partial \varrho_{\ell}(\lambda, g; t)}{\partial t} = -\frac{i}{\hbar} \Big[ H_{\ell}^{(\text{eff})}(\lambda, g; t), \varrho_{\ell}(\lambda, g; t) \Big] + L_{\ell}(\lambda, g; t).$$
(2)

Here the density matrix  $\varrho_{\ell} = \text{Tr}_{\bar{\ell}}[\varrho_{\text{SC}}]$ , with  $\bar{\ell} = \{\text{SC}\} - \{\ell\}$ , describes the quantum state of party  $\ell$ , and  $H_{\ell}^{(\text{eff})}$  is the *effective* Hamiltonian of party  $\ell$ . This effective Hamiltonian describes the *coherent* part of the dynamics. In addition to this part, there is an  $L_{\ell}$  which encompasses an *incoherent* (i.e., nonunitary) part of the dynamics of the party which incorporates correlations and interactions with other parties [25,26].

However, under some specific conditions the dynamics of a controlled system can still be described *coherently*. Consider the following conditions: (i) the applied control, e.g., a field, is sufficiently weak  $[||H_{int}(g)|| \ll ||H_S(\lambda) + H_C||$ , where  $|| \cdot ||$  is the standard operator norm]; (ii) the control-induced decomposition of the total Hilbert space is still the same as the decomposition before control; and (iii) the change in the control system **C** is not appreciable or of interest (thus it can be simply ignored), then the contribution of the incoherent term in the dynamics of system **S** may be negligible,  $||L_{\ell}(\lambda, g)|| \approx 0$ . Under such conditions, the action of the system Hamiltonian as

$$H_{\mathsf{S}}^{(\text{eff})}(\lambda, g; t) = H_{\mathsf{S}}(\lambda; t) + V(g; t), \tag{3}$$

where V is a Hamiltonian associated with the applied control field (acting on the space  $\mathcal{H}_S$ ). In this regime, varying the system Hamiltonian, by changing  $\lambda$  in the unperturbed system Hamiltonian  $H_S$  or by changing g in the applied field V, can yield a target dynamics for the system. As a remark, note that in some sense weakness of the control also implies weakness of V with respect to  $H_S$ .

It will be helpful to consider a simple physical example; interaction of light (e.g., a laser or electric field  $\hat{E}$ ) and matter (e.g., an atom) [27]. When the atom has only two energy levels, the field is single-mode almost at resonance with the atom ( $\omega \approx \epsilon_{es} - \epsilon_{gs}$ ), and it is sufficiently weak so that the dipole approximation suffices ( $H_{int} = -\hat{D} \cdot \hat{E}$ , with  $\hat{D}$  being the dipole moment operator of the atom), the total Hamiltonian of this atom-field system can be described by the Jaynes-Cummings model,

$$H_{\rm SC} = H_{\rm S} + H_{\rm C} + g(e^{-i\omega t}\hat{a} \otimes |\rm{es}\rangle\langle g\rm{s}| + e^{i\omega t}\hat{a}^{\dagger} \otimes |g\rm{s}\rangle\langle e\rm{s}|),$$
(4)

where  $H_{\rm S} = \sum_{i \in \{\rm es,gs\}} \epsilon_i |i\rangle \langle i|$  is the Hamiltonian of the atom (|gs\) and |es\) are the ground state and excited state, respectively), and  $H_{\rm C} = \hbar \omega (\hat{a}^{\dagger} \hat{a} + 1/2)$  is the field Hamiltonian, with  $\hat{a}$  being the bosonic annihilation operator of the field mode.

In the coherent regime, if the field is *classical*, we can say its action on the atom is given by the potential  $V(g, \omega; t) =$  $g(e^{i\omega t}|gs\rangle\langle es| + e^{-i\omega t}|es\rangle\langle gs|)$ , which induces transitions between the atomic energy levels and g is the coupling strength. Indeed, this approach is taken in elementary considerations of how an atom interacts with an electric field and yields the Rabi oscillation which presents the emission and absorption of the photon between atom and field periodically. Hence it mimics the binding energy between field source and atom [27,28].

### **III. BE OF BIPARTITE QUANTUM SYSTEMS**

Consider a composite bipartite system S, comprised of two parts A and B. The associated Hilbert spaces of the subsystems and the composite system are denoted by  $\mathcal{H}_A$ ,  $\mathcal{H}_B$ , and  $\mathcal{H}_S = \mathcal{H}_A \otimes \mathcal{H}_B$ . The free Hamiltonians of the subsystems A and B are given by  $H_A = \sum_{i=1}^{d_A} \epsilon_i^{(A)} |i\rangle_A \langle i|$  and  $H_B = \sum_{i=1}^{d_B} \epsilon_i^{(B)} |i\rangle_B \langle i|$ . The Hamiltonian of the composite system AB is assumed to be

$$H = H_{\rm free} + H_{\rm int},\tag{5}$$

where  $H_{\text{free}} = H_{\text{A}} + H_{\text{B}}$  is the free Hamiltonian of the composite system and  $H_{\text{int}}$  describes the interaction between the subsystems. We assume the spectral decomposition  $H_{\text{free}} = \sum_{\gamma=1}^{d} \epsilon_{\gamma} |\Phi_{\gamma}\rangle \langle \Phi_{\gamma}|$ , where  $d = d_{\text{A}}d_{\text{B}} = \dim(\mathcal{H}_{\text{S}}), \gamma \equiv (i, j)$ with  $i \in \{1, \dots, d_{\text{A}}\}$  and  $j \in \{1, \dots, d_{\text{B}}\}, \epsilon_{\gamma} \equiv \epsilon_i^{(\text{A})} + \epsilon_j^{(\text{B})}$ , and  $|\Phi_{\gamma}\rangle \equiv |i\rangle_{\text{A}}|j\rangle_{\text{B}}$  are the eigenstates of the free Hamiltonian (also known as the "bare states"). Similarly, we assume the spectral decomposition  $H = \sum_{\gamma} E_{\gamma}^{[\text{D}]} |\Phi_{\gamma}^{[\text{D}]}\rangle \langle \Phi_{\gamma}^{[\text{D}]}|$  (where  $|\Phi_{\gamma}^{[\text{D}]}\rangle$ 's are called "dressed states").

The instantaneous state of the composite system at any time  $\rho(t)$  can be represented as [29]

$$\varrho(t) = \varrho_{\mathsf{A}}(t) \otimes \varrho_{\mathsf{B}}(t) + \chi(t), \tag{6}$$

where  $\rho_A$  and  $\rho_B$  are the reduced density matrices of the subsystems, and  $\chi$  denotes correlations, classical or quantum, in the composite system. Note that  $\text{Tr}_A[\chi] = \text{Tr}_B[\chi] = 0$ . In addition, the ("average" or "internal") energy associated to the system is given by  $U(t) = \text{Tr}[H(t)\rho(t)]$ .

To dissociate parts A and B, a suitable time-dependent potential V(t) is applied which modifies the Hamiltonian as

$$H \to H(t) \equiv H(V(t)),$$
 (7)

such that V(0) = 0 and H(V(0)) = H and at the dissociation time  $t_f$  where again  $V(t_f) = 0$  the interaction part  $(H_{int})$  is turned off, i.e.,  $H(V(t_f)) = H_{free}$ . The energy change of the system during this process is given by

$$U(t_{\rm f}) - U(t_{\rm i}) = \text{Tr}[\rho(t_{\rm f})H(t_{\rm f})] - \text{Tr}[\rho(0)H(0)].$$
 (8)

Here  $\rho(t)$  depends on the applied external control field V(t) through the evolution equation

$$\frac{\partial \varrho(t)}{\partial t} = -\frac{i}{\hbar} [H(V(t)), \varrho(t)], \qquad (9)$$



FIG. 2. Schematic of coherent separation of a composite system (e.g., a molecule) into its subsystems by applying an external field V(t).

or equivalently through

$$\varrho(t) = \mathcal{U}(t)\varrho(0)\mathcal{U}^{\dagger}(t), \quad 0 \leq t \leq t_{\rm f}, \tag{10}$$

where the evolution is given by  $\mathcal{U}(t) = \mathbb{T} e^{-i \int_0^t H(V(s)) ds}$  and  $\mathbb{T}$  is the time-ordering operation. This evolution for a controllable composite system of dimension *d* belongs to the unitary group  $\mathbb{U}(d)$ . (See Fig. 2.)

Now, it is natural to define the BE as the *optimal* energy required to eliminate the interaction Hamiltonian of the composite system in a *coherent* manner, i.e.,

$$\Delta U_{\rm BE} = \min_{t_{\rm f}, V(t)} [\operatorname{Tr}[\varrho(t_{\rm f})H(t_{\rm f})] - \operatorname{Tr}[\varrho(0)H(0)]]$$
  
=  $\operatorname{Tr}[\varrho^{(\text{opt})}(t_{\rm f}^{(\text{opt})})H_{\rm free}] - \operatorname{Tr}[\varrho(0)(H_{\rm free} + H_{\rm int})].$ 
(11)

To lighten the notation, henceforth we denote the optimal time  $t_{\rm f}^{\rm (opt)}$  with  $t_{\rm f}$  and the optimal state  $\varrho^{\rm (opt)}(t_{\rm f})$  with  $\varrho(t_{\rm f})$ .

Several remarks are in order.

(i) The minimization over time is important because, if bond breaking takes too long, the composite system may experience decoherence or dissipation due to interactions with its ambient environment [30]. In such an open-system scenario one shall need to take into account environmental effects (decoherence or dissipation) into the formalism, e.g., use a relevant master equation for the dynamics of the composite system [25]. Thus, to avoid this issue and simplify our analysis, we consider that the evolution time of the system is considerably less than its coherence time [30]-hence the system can be considered quantum-mechanically closed. Although we confine our discussion to closed-system scenarios, we expect its extension to open systems to be straightforward. The time optimization for our scenario can be performed by employing Pontryagin's maximum principle [12], which in turn yields the optimal control field for the minimum time. We elaborate on this method in the next subsection.

(ii) The last term in Eq. (11) is the initial internal energy of the composite system, which is fixed and given; hence we only need to vary the final state and the Hamiltonian to find the BE—the energy needed for dissociation. Note that the sole result of this evolution should be effectively neutralizing the interaction Hamiltonian. That is, the final Hamiltonian should be equal to the free Hamiltonian of the system,  $H(t_f) = H_{free}$ . This yields that the average energy of the final state is

$$U(t_{\rm f}) = \operatorname{Tr}[\varrho_{\sf A}(t_{\rm f})H_{\sf A}] + \operatorname{Tr}[\varrho_{\sf B}(t_{\rm f})H_{\sf B}].$$
(12)

(iii) It is evident that the value of  $U(t_f)$  is independent of the correlations  $\chi$ . Thus, with this definition of the BE, non-interacting subsystems may still be correlated. Nevertheless, the optimization of Eq. (8) guarantees that the final state of

the system is a *passive state*, from which by definition it is impossible to extract any *work* in a *cyclic process* [7]. That is, all work-generating correlations have already been eliminated from the final state, and thus the residual correlations can only yield *heat*. To remove such leftover correlations one should employ strategies which may require sophisticated handling of the state in a nonunitary fashion.

## **IV. OPTIMIZATIONS**

### A. Optimal final state $\rho(t_f)$

As remarked in the previous section, the optimization (11) can be performed by varying  $\rho(t_f)$  over the achievable orbit of  $\rho(0)$  via unitary transformations. The kinematical extremum of  $U(t_f)$  is determined by the eigenvalues of  $H_{\text{free}}$  as well as the eigenvalues of  $\rho(t_f)$ .

We recall that the evolution of the state  $\rho(t)$  is unitary, given by Eq. (10), where  $\mathcal{U}(t) \in \mathbb{U}(d)$ . To have an extremum for the final energy  $U(t_f) = \text{Tr}[\rho(t_f)H_{\text{free}}]$ , it is necessary that the final density matrix  $\rho(t_f)$  commute with  $H_{\text{free}}$ ; that is,  $\rho(t_f)$ should be diagonal in the eigenbasis of  $H_{\text{free}}$  [7],

$$\varrho(t_{\rm f}) = \sum_{\gamma} p_{\gamma} |\Phi_{\gamma}\rangle \langle \Phi_{\gamma}|.$$
(13)

Here the probabilities  $p_{\gamma}$ 's are the eigenvalues of the initial density matrix  $\varrho(0)$ . The maximum and minimum values of  $U(t_f)$  belong to the finite set  $S = \{p \cdot \epsilon : p \in \Pi(p), \epsilon \in \Pi(\epsilon)\}$ , where  $\Pi(\mathbf{x})$  denotes the set of all permutations of  $\mathbf{x} = (x_1, x_2, \dots, x_d) \in \mathbb{R}^d$ . The maximum of the set *S* corresponds to the case where both vectors  $\mathbf{p}$  and  $\boldsymbol{\epsilon}$  are nondecreasing or nonincreasing, and its minimum is obtained when either of them are nondecreasing  $(x_{\gamma}^{\dagger} \leq x_{\gamma+1}^{\dagger}, \forall \gamma)$ , while the other one is nonincreasing  $(x_{\gamma}^{\downarrow} \geq x_{\gamma+1}^{\downarrow}, \forall \gamma)$ ,

$$\boldsymbol{p}^{\downarrow} \cdot \boldsymbol{\epsilon}^{\uparrow} = \boldsymbol{p}^{\uparrow} \cdot \boldsymbol{\epsilon}^{\downarrow} \leqslant \boldsymbol{p} \cdot \boldsymbol{\epsilon} \leqslant \boldsymbol{p}^{\downarrow} \cdot \boldsymbol{\epsilon}^{\downarrow}.$$
(14)

Thus minimizing the final energy  $U(t_f)$  leads to the *passive* state which is in the form of Eq. (13), where  $p_{\gamma} \ge p_{\gamma+1}$  with  $\gamma$ 's ordered such that  $\epsilon_{\gamma} \le \epsilon_{\gamma+1}$ ,  $\forall \gamma$ . As a result, we obtain

$$\Delta U_{\rm BE} = \sum_{\gamma} p_{\gamma} \epsilon_{\gamma} - U(0). \tag{15}$$

## **B.** Optimal evolution $\mathcal{U}(t)$

Here we discuss general unitary evolutions of arbitrary initial states towards desired final states by employing OCT techniques. We start with simple cases

(i) Maximally mixed initial state. Consider the initial state  $\rho(0) = \mathbb{I}/d$ . Because of the unitarity of the evolution, this state remains unchanged during the evolution.

(ii) *Pure initial state*. This initial state results in a pure passive state which is the ground state of the final dissociated system. If we denote the initial state of the composite system with  $|\Psi_{\alpha}\rangle$ , the corresponding unitary transformation to the ground state of the dissociated system ( $|\Phi_1\rangle$ ) becomes

$$\mathcal{U}^{(\alpha)}(t_{\rm f}) = |\Phi_1\rangle\langle\Psi_{\alpha}| + \sum_{\gamma=2}^d |\Phi_{\gamma}\rangle\langle\Psi_{\alpha(\gamma)}|, \qquad (16)$$

where  $|\Psi_{\alpha(\gamma)}\rangle$ 's are states orthonormal to  $|\Psi_{\alpha}\rangle$  and  $\alpha(\gamma)$  has a one-to-one and regular relation with  $\gamma$ . Since Eq. (16) is

independent of the transformation path it is not uniquely identified. The orthogonal vectors to  $|\Psi_{\alpha(\gamma)}\rangle$  are in a (d-1)dimensional subspace of the *d*-dimensional space; thus infinite sets of orthogonal sub-basis  $\{|\Psi_{\alpha(\gamma)}\rangle : \gamma = 2, ..., d-1\}$ can be found. The optimization process includes calculation of the unitary transformation  $\mathcal{U}(t)$  with minimum dissociation time  $t_{\rm f}$ .

(iii) *Thermal initial state*. In the dressed-state basis, this initial state is represented by

$$\varrho(0) = (1/Z^{[D]}) \sum_{\alpha} e^{-\beta E_{\alpha}^{[D]}} \left| \Phi_{\alpha}^{[D]} \right\rangle \! \left\langle \Phi_{\alpha}^{[D]} \right|, \tag{17}$$

where  $\beta = 1/(k_B T)$  is the inverse temperature (with  $k_B$  as the Boltzmann constant) and  $Z^{[D]} = \sum_{\alpha} e^{-\beta E_{\alpha}^{[D]}}$  is the partition function of the composite system in the dressed basis. The optimal final state becomes

$$\varrho(t_{\rm f}) = (1/Z^{\rm [D]}) \sum_{\gamma} e^{-\beta E_{\gamma}^{\rm [D]}} |\Phi_{\gamma}\rangle \langle \Phi_{\gamma}|$$
(18)

and the optimal unitary transformation is

$$\mathcal{U}^{(\alpha)}(t_{\rm f}) = \sum_{\gamma} |\Phi_{\gamma}\rangle \langle \Phi^{\rm [D]}_{\alpha(\gamma)} |.$$
(19)

It is evident that this state differs from the thermal state in the bare basis.

Since the BE and the corresponding unitary transformation are obtained, one only needs to obtain the optimal control potential in minimum time. A remark is in order here. After removing the interaction Hamiltonian  $H_{int}$ , we note that through OCT techniques the optimal unitary transformation for reaching a desired passive state can be determined by a proper laser pulse train—see Appendix A. However, as we later argue in Sec. V, in some particular dissociation processes related to a quantum tunneling and/or photoionization process, the laser pulse controlling can also lead to removing the interaction Hamiltonian. In fact, in the tunneling case, the dissociation is enhanced by the quantum tunneling effect.

The unitary transformations  $\mathcal{U}(t_f)$  are members of the unitary group  $e^{L}$  generated by Lie algebra  $\mathcal{L}$  defined by the Hamiltonian of the system. The dynamics of the evolution  $\mathcal{U}(t_f)$  obeys the Schrödinger equation and depends on a control potential V(t). The transformation  $\mathcal{U}(t_f)$  is reachable kinematically for some control potential. Here, we focus on attainable controls that can be realized by a suitable laser pulse train. In this method, the upper bound on the applied field V(t) is often limited by the laser power, and its lower bound is determined by the intensity modulator's extinction ratio  $(M_{ii}^{-}/M_{ii}^{+}$  as defined below). The rise-fall time of the potential switching is also limited by the frequency response of the laser intensity modulator  $(N_{ii}^{\pm})$ , which is the frequency which determines how fast one can change the laser intensity. Thus, for a pulse train which creates different dipole interactions between levels  $|\Phi_i^{[D]}\rangle$  and  $|\Phi_j^{[D]}\rangle$  (*V*<sub>*ij*</sub>), we have the following constraints:

$$M_{ii}^{-} \leqslant V_{ij}(t) \leqslant M_{ii}^{+}, \tag{20}$$

$$N_{ij}^{-} \leqslant \frac{1}{V_{ij}(t)} \frac{dV_{ij}(t)}{dt} \leqslant N_{ij}^{+}.$$
(21)

(See also our detailed discussion in Sec. VB.)

The cost function in this optimal control problem is the time minimization

$$t_{\rm f} = \int_0^{t_{\rm f}} dt, \qquad (22)$$

subject to the dynamical equation (9) and with some other constraints. Time minimization of this optimal process can be obtained by *Pontryagin's maximum principle*. This principle states that, at any instant of time, the optimal control must maximize the corresponding system "control Hamiltonian" H. This Hamiltonian is given by introducing conjugate variables  $\lambda_s, \lambda'_{s\neq 0}$ ;  $s \in \{0, (i, j)\}$  and  $i, j \in \{1, \ldots, d\}$  in the following form:

$$\mathbb{H} = \lambda_0 \mathbb{f}_0 + \sum_{i,j=1}^{d,d} (\lambda_{ij} \mathbb{f}_{ij} + \lambda'_{ij} \mathbb{R}_{ij}), \qquad (23)$$

where  $f_{ij}$ 's are the elements of the left-hand side of Eq. (9) in the dressed state basis,  $\mathbb{R}_{ij} = (1/V_{ij})dV_{ij}/dt$ , and  $\mathbb{f}_0$  is the integrand of the time functional (which here is simply 1) with  $\lambda_0$  as its "conjugate" variable in Pontryagin's theory. At first glance, according to Eq. (9), the elements of V(t) seem to be the relevant control parameters of the system. However, since practically jump with infinite tilt is impossible, rather than  $V_{ii}$ , the modulation bandwidth of the laser pulses  $\mathbb{R}_{ii}$ are the more suitable control parameters. Since the control Hamiltonian is *linear* vs the control parameters  $\mathbb{R}_{ij}$ , according to Pontryagin's maximum principle, the control  $\mathbb{R}_{ij}$ 's are of the bang-bang type [13]. More rigorously, one can see that  $\mathbb{H} = \mathbb{A} + \sum \lambda'_{ij} \mathbb{R}_{ij}$  is maximized when  $\mathbb{R}_{ij}$  acquires its maximum or minimum—depending on the sign of the  $\lambda'_{ij}$ 's. The explicit form of  $\mathbb{A}$  and  $\lambda'_{ij}$  can be readily derived by Eq. (23). Hence the optimal control problem is reduced to a two-point (initial and final) boundary value problem. This considerable reduction makes the control problem amenable to laser pulses to steer the system from its initial state to the target state in *minimum time* [31].

### C. Example: Atom cavity

We now consider an example where breaking the bond *releases* energy and the initial state of the system is pure; thus the correlation removing is plausible.

Consider a system consisting of a two-level atom and a cavity interacting with the Jaynes-Cummings Hamiltonian,

$$H = \frac{1}{2}\hbar\omega_{\mathsf{A}}\,\sigma_z + \frac{1}{2}\hbar\omega_{\mathsf{B}}\,\hat{a}^{\dagger}\hat{a} + g\,(\sigma_+\otimes\hat{a} + \sigma_-\otimes\hat{a}^{\dagger}),\quad(24)$$

where  $\sigma_z$  is the *z*-Pauli matrix,  $\sigma_{\pm} = \sigma_x \pm i\sigma_y$  (with  $\sigma_x$  and  $\sigma_y$  being the other Pauli matrices),  $\hat{a}$  ( $\hat{a}^{\dagger}$ ) is the annihilation (creation) operator of the cavity,  $\omega_A$  is the energy gap of the atom,  $\omega_B$  is the resonance frequency of the cavity, and *g* is the coupling strength. Note that the unexcited atom-cavity system experiences no interaction, hence no binding energy—a case which may appear in rare gas halogenide molecules [32]. Here we assume the atom-cavity molecule in the strong coupling regime and that only one photon contributes to the evolution [33]. Thus the eigenstates of this Hamiltonian (dressed states) are limited to { $|0, g_S\rangle, |\pm\rangle, |1, e_S\rangle$ , where

$$|+\rangle = \cos \phi |0, es\rangle + \sin \phi |1, gs\rangle,$$
 (25)

$$|-\rangle = -\sin\phi|0, es\rangle + \cos\phi|1, gs\rangle,$$
 (26)



FIG. 3. (a) By changing the position of the optical tweezer the atom is moved to a node in the cavity, where the interaction Hamiltonian is off. (b) By turning off the optical tweezer the atom leaks out of the cavity.

with  $tan(\phi/2) = 2g(\omega_A - \omega_B)$  [27]. The atom-cavity system prepared in either of the dressed states remains there forever unless the interaction is interrupted. Considering the initial system state to be the nonpassive state  $|+\rangle$  or  $|-\rangle$ , the atomcavity molecule dissociation occurs when both the interaction and the quantum correlation (here entanglement) are switched off. Assuming the atom is trapped in the cavity by an optical tweezer [34], by properly changing the optical tweezer's beam waist position with respect to the trapped atom's position, the atom can gain a desired velocity after switching off the optical tweezer and thus will exit the cavity [35]. As depicted in Fig. 3, along the cross section of the cavity center the coupling strength is almost constant. If one adjusts the velocity of the atom such that  $\phi(\tau) = n\pi$  for  $n \in \mathbb{N}$  ( $\tau = x/v$  is the flying time through the cavity and v is the velocity) for the initial states  $|+\rangle$   $(|-\rangle)$ , the final state of the atom-cavity becomes the bare state  $|0, es\rangle$  ( $|1, gs\rangle$ ), respectively [see Eqs. (25) and (26)]. This state still needs to be passivated. In the case of  $|1, gs\rangle$ , by employing a proper pulse on the atom, the passive state  $|0, gs\rangle$  can be generated [36]; in the case of  $|0, es\rangle$ , the photon can escape from the cavity by changing the cavity resonance frequency, e.g., by activation of a saturable absorber in the cavity. As a result, this scenario can lead to the final passive state, which is the requirement of the bond breaking of the atom-cavity system.

#### V. TUNNELING-INDUCED BOND BREAKING

## A. General considerations

In addition to active control by laser pulses, it has also been demonstrated that "quantum tunneling" may be an effective phenomena in controlling chemical reactions and molecular dissociation [4]. For example, photodissociation of the formaldehyde H<sub>2</sub>CO molecule by employing quantum tunneling effect has already been reported in Ref. [37]. This molecule absorbs a UV-Vis photon to get excited to its upper electronic level (called "S<sub>1</sub>"), then it experiences a nonradiative emission to the upper vibrational levels of the lower electronic state (called "S<sub>0</sub>"). Now, the electron has the chance to tunnel through the potential barrier and thus the molecule is decomposed to H<sub>2</sub> + CO. Another case in which quantum tunneling results in bond breaking is the  $\alpha$ -decay event—see Fig. 4 and Ref. [1].

In some molecules attractive and repulsive forces may result in a potential barrier and tunneling effect. Alternatively, one may employ an external field, such as electrostatic and





FIG. 4. Potential vs distance: a typical well with tunneling effect. A hallmark example is the " $\alpha$ -decay" event in particle physics [1].

optical radiation fields, to induce a potential barrier in a bipartite system to control decomposition rate of the system. For example, electron emission may be induced by tunneling from a conductor surface in a high electric field [38]. In this case, the required work for the potential reconfiguration should also be taken into account in the calculation of the BE.

Figure 4 shows a typical potential barrier. Energy levels of systems with finite-width barrier can be divided into three groups: (i) bound levels, for which the tunneling rate is zero, (ii) tunneling levels with finite tunneling rate, and (iii) unbounded levels, where the tunneling probability is one. Tunneling transitions in Fig. 4 are of the tunneling-decay group, where the decay transition is responsible for the depopulation of higher levels radiatively or nonradiatively. Depending on the ratio of the tunneling and decay rates of the level, the following behaviors can be discerned.

(i) In a bipartite system with long tunneling time relative to the decay rate, transition to bound states is faster than the tunneling-induced decomposition process. In this case, if tunneling does not occur, the multistep excitation to tunneling states should be performed as long as the decomposition can happen. For simplicity, here we only consider radiative transitions, which implies that there is no energy dissipation. Thus populating unbounded levels may energetically cost more than multistep excitation of the tunneling levels. Note that this condition is not dominant, because by modification of the width of the potential barrier the tunneling time can be arbitrarily reduced. Moreover, putting the molecule in a suitable cavity could increase the decay time.

(ii) When the tunneling rate is greater than the decay rate, dissociation of the molecule will be observed before the transition to the bound states.

Note that, in both cases, after the tunneling process the linear momentum of the excited state is precisely determined. Due to the uncertainty relation, the position can have large uncertainty; hence the interaction will practically vanish in the molecular dissociation process.



FIG. 5. (a) Potential step V(x) with well width a and height  $V_0$ , for  $x \ge a$ . There are four bound states ( $|k\rangle$ , k = 1, 2, 3, 4), and no tunneling occurs here. (b) Modified potential barrier where  $V(x) = V_0$  for  $a \le x \le b$  and  $V(x) = V'_0 < V_0$  for x > b. Here,  $a = 2.62 \times 10^{-10}$  m,  $b = 2.80 \times 10^{-10}$  m,  $V_0 = 80$  eV,  $V'_0 = 42$  eV,  $E_1 = 4.2$  eV,  $E_2 = 18.9$  eV,  $E_3 = 42$  eV, and  $E_4 = 72.3$  eV.

Since in this paper we have assumed the system to be subject to unitary evolutions, the initial and final states should have the same number of populated energy levels. Thus, if the number of the tunneling levels is less than the number of the populated levels in the initial state, one may need a multistep excitation process so that the tunneling can happen.

### **B.** Example

Consider an electron of mass  $m_e$  in the step potential depicted in Fig. 5(a). The energy levels E of this potential can be obtained readily by solving the equation  $\tan(\sqrt{2m_eEa}) = -\sqrt{E/(V_0 - E)}$  [19]. For specificity, we choose  $V_0 = 80$  eV and  $a = 2.62 \times 10^{-10}$  m, which gives only four bound states. We also take the initial state of the system in the following mixed state with no coherence:

$$\varrho_i = \alpha_1 |1\rangle \langle 1| + \alpha_2 |2\rangle \langle 2|, \qquad (27)$$

where  $\alpha_1 > \alpha_2 \ge 0$  and  $\alpha_1 + \alpha_2 = 1$ . For a quantum potential well in this shape quantum tunneling is not allowed in any energy level. Thus we apply an external control such that it only changes the potential for x > b by producing a finite-width barrier—to keep simplicity, we approximate this

modification as in Fig. 5(b). The barrier width is designed such that there exist two tunneling states in the system; we choose  $b = 2.8 \times 10^{-10}$  m and  $V'_0 = 42$  eV.

Note that, in some cases, the system should be excited to upper levels;  $\varrho_i \rightarrow \varrho'_i$ . Since the evolution is unitary, the excited state  $\varrho'_i$  has the same dimension as that of the initial one. Let us denote the number of no-tunneling and tunneling levels, respectively, with  $n_{\rm nt}$  and  $n_{\rm t}$ . When  $n_{\rm t} \ge n_{\rm nt}$ , the excited state  $\varrho'_i$  is diagonal with the same diagonal elements as in  $\varrho_i$ . When  $n_{\rm t} < n_{\rm nt}$ , the  $\varrho'_i$  can be written versus the upper  $n_{\rm t} - n_{\rm nt}$ no-tunneling levels and  $n_{\rm nt}$  tunneling levels. In such states the decomposition is a multistep procedure. Overall, this is the initial state  $\varrho_i$  that determines which scenario applies.

In our case,  $n_t = n_{nt}$  and  $\varrho'_i$  is written versus all tunneling state basis. To find the best configuration of the excited state  $\varrho'_i$ , the tunneling probability of each tunneling level is needed. This probability, given by  $P = e^{-2\int_a^b \sqrt{2m_e(V_0 - E)} dx}$  in the WKB approximation [19], for the first tunneling state []3 $\rangle$ in Fig. 5(a)] and the second tunneling state []4 $\rangle$  in Fig. 5(b)] can be obtained as  $P_3 = 0.15$  and  $P_4 = 0.40$ , respectively. The tunneling time of these two levels can also be calculated. Using the WKB method [19,39,40], we obtain  $\tau_3 = 0.65 \times 10^{-17}$  s for the level |3 $\rangle$  and  $\tau_4 = 1.31 \times 10^{-17}$  s for the level |4 $\rangle$ . In these calculations, the tunneling rate is defined as the inverse of the product P(2A/v) with v being the speed of the tunneling particle. As it is clear the tunneling time for both levels is relatively smaller than the decay time of the system (which is, e.g., of the order of nanosecond for hydrogen).

Although the tunneling probability from the upper tunneling level  $(|4\rangle)$  is higher, the tunneling time of the lower tunneling state  $(|3\rangle)$  is sufficiently short that we do not need to force the system to the upper tunneling level. With these considerations, the system should be excited to

$$\varrho_i' = \alpha_1 |3\rangle \langle 3| + \alpha_2 |4\rangle \langle 4|. \tag{28}$$

Note that with this choice less energy is needed to decompose the system. The corresponding unitary evolution is

$$\mathcal{U} = |3\rangle\langle 1| + |4\rangle\langle 2| + |1\rangle\langle 3| + |2\rangle\langle 4|.$$
<sup>(29)</sup>

Now, we want to drive the system in the optimal path which satisfies this unitary evolution and reaches the desired final state. To do so, we employ laser pulses based on OCT methods [24,41]. Specifically, we employ the group decomposition method of Ref. [31]-see also Appendix A for a review-and Pontryagin's method to determine the optimal control path in *minimum* time  $t_{\rm f}$ . In the group decomposition, the unitary operator is decomposed into a product of operators each of which is illustrative of a laser pulse [42]. Then, the phase and the energy of a sequence of pulses that drive the system through the optimal path to the desired state can be computed [Eq. (A8)]. Through the method of Ref. [31], one can construct the optimal pulse sequence by finding appropriate pulses each of which induces a transition to an upper level. Our numerical calculations shows that the pulse train for the evolution of  $\rho_i$  to  $\rho'_i$  should be applied in the following sequence:

$$\mathcal{U} = \mathcal{U}_{23}(t_4) \, \mathcal{U}_{34}(t_3) \, \mathcal{U}_{12}(t_2) \, \mathcal{U}_{23}(t_1), \tag{30}$$



FIG. 6. Envelope of the pulse sequence for the example introduced in Sec. V B: shape or envelope (A in the the SI units of kg m/s) vs time (t in the unit of ps). Due to Pontryagin's maximum principle, the finite rise-fall time of the pulse and its maximum reachable power [as explained in Eqs. (20) and (21)] are needed to calculate the optimal pulse trains and their duration. Here the maximum amplitude of each pulse and the modulation bandwidth (inverse of the rise-fall time) have been assumed, respectively,  $38.8 \times 10^4$  (in the SI units) and 40 GHz. See Appendix B for further details.

where  $\mathcal{U}_{ii+1}(t_k)$ , generated by a laser pulse with the shape  $f_i(t) = 2A_i(t)\cos(\omega_i t + \phi_i)$ , induces the dipole transition between the *i*th and (i + 1)th levels of the (composite) system in the time interval  $t \in [t_{k-1}, t_k]$  (the duration of the pulse). Details of the calculations of the shape and duration of the pulses can be found in Appendix B.

The laser pulse shapes are generated by intensity modulators where the slopes of intensity increasing or decreasing are limited by the intensity modulator bandwidth. The fall time is the stored energy divided by the rate of the energy dissipation. Since energy is proportional to the  $V_{ij}^2$  [or  $|A_k(t)|^2$ ], it is straightforward to see that  $1/\tau_{\text{fall}} = -(1/V_{ij})dV_{ij}/dt \ge$  $\Omega_{\text{modulator}}$ , where  $\Omega_{\text{modulator}}$  is the modulator bandwidth. Hence, to apply this restriction in the optimization process, the quantity  $-(1/V_{ij})dV_{ij}/dt$  should be considered as the control parameter in the Hamiltonian (23).

Moreover, the laser intensities are limited by the laser sources, which here we assume as 20 mW. Based on the conditions in Eqs. (20) and (21), the optimal potential  $V_{ij}(t)$  acquires its maximum and minimum values during the evolution through an exponent

$$\frac{1}{V_{ij}(t)}\frac{dV_{ij}(t)}{dt} = -\frac{1}{\Omega_{\text{modulator}}},$$
(31)

which yields some jumps with the rise and the fall times of the order  $\tau_{\text{fall}} = 1/(40 \text{ GHz}) = 25 \text{ ps}$ . Thus the pulse shapes can be approximated as squares. See Appendix B for details.

Figure 6 shows the result for the optimal pulse shapes and durations. By applying this pulse train, the system is totally in the tunneling levels (thus tunneling becomes possible). Since tunneling is a probabilistic phenomena, the system should spend sufficient time in the unbounded tunneling levels in comparison to the transition time from the tunneling levels to the lower levels in this state to experience tunneling; otherwise, the system decays to the stable states and dissociation does not occur. Although the essential time for dissociation is unspecified in this method, we use less energy than the PHYSICAL REVIEW A 101, 013403 (2020)

step size to decompose the composite system. However, this uncertainty in time is considerably small, as estimated above.

Remark. In closed-system scenarios, time minimization alone can yield specific shapes for control Hamiltonians [43], whereas the group decomposition technique alone does not fix necessarily the pulse shape (one can choose pulse shapes more conducive to practical considerations) [31]. In such cases, the dissociation energy becomes independent of the shape of the laser pulses. However, in more realistic cases when environmental effects might be present, time minimization is indeed crucial to ensure relevance of the calculated dissociation energy. This minimization, together with appropriate practical considerations, determines the pulse shape (as in Fig. 6). Note that finite lifetime and environmental noise mechanisms can result in the depopulation of the excited states. To partially mitigate this effect, extra laser pulses may be required, which in turn may give rise to an increase in the dissociation energy. A correct framework to investigate such open-system scenarios requires employment of an appropriate master equation rather than the Schrödinger equation. This extension can be important for practical purposes, but it is out of the scope of the current paper and is left as an open problem.

#### VI. SUMMARY

We have introduced a physically motivated and general definition for the binding energy of bipartite quantum systems. In the making, we have used an optimal time-dependent control potential to offset the interaction Hamiltonian and remove work-generating correlations between the subsystems. We have considered realization of the optimal potential through finite-intensity and finite-rate laser pulses which induce particular transitions in the system. We have noted that, for some systems, one may have further control in the form of making the interaction Hamiltonian time-dependent and then resetting it to zero. We have also extended the definition of the binding energy to probabilistic events, and through an example have demonstrated that the probabilistic dissociation may be induced by quantum tunneling.

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### APPENDIX A: MINIMUM DISSOCIATION TIME $t_{\rm f}$

Our calculation is based on the group factorization and Pontryagin's maximum principle. The Lie group decomposition of a unitary operator can be employed to obtain the optimal control signal. There exist several methods for group decomposition. Here we employ the planar rotation decomposition discussed in Ref. [31]. A laser pulse of the following form is applied to the system:

$$f_k(t) = 2A_k(t)\cos(\omega_k t + \phi_k), \qquad (A1)$$

in which  $A_k(t)$  is the pulse envelope and  $\omega_k$  is the frequency of the  $|\Phi_k^{[D]}\rangle \rightarrow |\Phi_{k+1}^{[D]}\rangle$  transition. The system interacts with the applied laser field through its dipole moment; thus the interaction Hamiltonian (under some conditions) is given by

$$H_{k}(t) = D_{kk}A_{k}(t) \Big[ e^{i(\omega_{k}t + \phi_{k})} \Big| \Phi_{k}^{[D]} \Big\rangle \Big| \Phi_{k+1}^{[D]} \Big| + \text{H.c.} \Big], \quad (A2)$$

where "H.c." denotes Hermitian conjugate, and

$$D_{ij} = -e \langle \Phi_i^{[D]} | \mathbf{x} | \Phi_j^{[D]} \rangle \tag{A3}$$

is the electric dipole moment of the electron transition  $|\Phi_i^{[D]}\rangle \rightarrow |\Phi_j^{[D]}\rangle$  caused by the laser pulse, with *e* being the electron charge and **x** the position operator.

Let us consider the following anti-Hermitian matrices as a basis for the su(d) Lie algebra:

$$\hat{S}_{m,n}^{R} = \left| \Phi_{m}^{[D]} \right\rangle \! \left\langle \Phi_{n}^{[D]} \right| - \left| \Phi_{n}^{[D]} \right\rangle \! \left\langle \Phi_{m}^{[D]} \right|, \tag{A4}$$

$$\hat{S}_{m,n}^{I} = i\left(\left|\Phi_{m}^{[D]}\right\rangle\!\!\left\langle\Phi_{n}^{[D]}\right| + \left|\Phi_{n}^{[D]}\right\rangle\!\!\left\langle\Phi_{m}^{[D]}\right|\right),\tag{A5}$$

$$\hat{S}_m = \left| \Phi_m^{[D]} \right\rangle \! \left\langle \Phi_m^{[D]} \right| - \left| \Phi_{m+1}^{[D]} \right\rangle \! \left\langle \Phi_{m+1}^{[D]} \right|, \tag{A6}$$

where  $1 \le m \le d - 1$  and  $m \le n \le d$ . It is straightforward to see that  $\hat{X}_k := \hat{S}_{k,k+1}^R$  and  $\hat{Y}_k := \hat{S}_{k,k+1}^I$ ,  $1 \le k \le d$ , suffice to generate the Lie algebra  $\mathcal{L}_0 \subset \mathfrak{su}(d)$ , which contain the generators  $\hat{X}_k$  and  $\hat{Y}_k$  for  $1 \le k \le d - 1$ . One can show that if the Lie algebra  $\mathcal{L}_0$  contains one of the pairs  $(\hat{X}_1, \hat{Y}_1)$  or  $(\hat{X}_d, \hat{Y}_d)$ , then it must contain all the other generators. Using this, starting from any level in an atom, one can go up or down step by step to reach the desired level.

The sequences in which the fields should be turned on and off are obtained by decomposition of  $\mathcal{U}(t)$  into a product of

generators of the dynamical Lie group,

$$\mathcal{U}(t) = \mathcal{U}_0(t) \mathcal{U}_K \mathcal{U}_{K-1} \dots \mathcal{U}_k \dots \mathcal{U}_1, \qquad (A7)$$

with  $\mathcal{U}_0(t) = e^{-itH/\hbar}$ . In the interaction picture and by applying the rotating-wave approximation, the interaction-picture Schrödinger equation becomes

$$\frac{\partial \mathcal{U}_{l}(t)}{\partial t} = \frac{1}{\hbar} \sum_{k=1}^{M} A_{k}(t) D_{kk} [\hat{X}_{k} \sin \phi_{k} - \hat{Y}_{k} \cos \phi_{k}] \mathcal{U}_{l}(t).$$

Then if we apply in the interval  $t_{k-1} \leq t \leq t_k$  a resonant pulse, then one can see that  $\mathcal{U}_I(t_k) = \mathcal{U}_k \mathcal{U}_I(t_{k-1})$ , where

$$\mathcal{U}_{k} = e^{C_{\sigma(k)}[\dot{X}_{\sigma(k)}\sin\phi_{k} - \dot{Y}_{\sigma(k)}\cos\phi_{k}]},\tag{A8}$$

with

$$C_{\sigma(k)} = (1/\hbar) D_{\sigma(k)\sigma(k)} \int_{t_{k-1}}^{t_k} A_{\sigma(k)}(t) dt$$
(A9)

and  $\sigma(k)$  being a mapping from the index set  $\{1, \ldots, K\}$  to the control index set  $\{1, \ldots, M\}$  that specifies the control  $A_k$  which is on in the time interval  $[t_{k-1}, t_k]$ . Here K is the optimal number of the dipole transitions and M is the number of possible dipole transitions in the (composite) system.

## APPENDIX B: OPTIMAL PULSES FOR THE EXAMPLE OF SEC. V B

As explained in the previous Appendix, we need to decompose the unitary evolution operator into a product of unitary operators each of which is illustrative of a laser pulse which interacts with the dipole moment associated to a specific pair of consecutive levels of the Hamiltonian of the composite system. Each pulse is a  $d \times d$  matrix (in the  $\{|\Phi_i^{[D]}\rangle\}_{i=1}^d$  basis) with a nontrivial  $2 \times 2$  block whose elements are specified by the dipole moments of the transitions  $|\Phi_k^{[D]}\rangle \rightarrow |\Phi_{k+1}^{[D]}\rangle$ ,



where  $C_{\sigma(k)}$  is given by Eq. (A9) and  $\phi_{\sigma(k)}$  is the phase of the pulse. This is the identity matrix except in the position of the nontrivial block.

To find the pulse sequence, we shall follow the steps of the algorithm introduced in Ref. [31]. Here the target unitary operator is given in Eq. (29), which can be written in the  $\{|k\rangle\}_{k=1}^{4}$  basis as

$$\mathcal{U} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}.$$
 (B2)

We now should find some unitary matrices of the form (B1) whose multiplication by  $\mathcal{U}$  results in the identity matrix,

 $W_K \dots W_2 W_1 \mathcal{U} = \mathbb{I}$ . In the first step, the last column of  $\mathcal{U}$  should be transformed to  $(0001)^T$  (*T* denotes transposition). This can be achieved by a pulse  $(W_1)$  inducing the transition between levels  $|2\rangle$  and  $|3\rangle$  followed by another pulse  $(W_2)$  between levels  $|3\rangle$  and  $|4\rangle$ . The transition between levels  $|2\rangle$  and  $|3\rangle$  can be shown by a block-diagonal matrix of the form

$$W_{1} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(C_{1}) & i e^{i\phi_{1}} \sin(C_{1}) & 0 \\ 0 & i e^{-i\phi_{1}} \sin(C_{1}) & \cos(C_{1}) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$
 (B3)

To find the unknown parameters  $C_1$  and  $\phi_1$ , we should use the column vector on which the pulse is applied. For example,



FIG. 7. Schematic of a generic pulse shape.

consider the last column of Eq. (B2), for which we have  $W_1(0\ 1\ 0\ 0)^T = (0\ 0\ 1\ 0)^T$ ; thence

$$(C_1, \phi_1) = (\pi/2, \pi/2).$$
 (B4)

The matrix  $W_2$  corresponding to the transition between levels  $|3\rangle$  and  $|4\rangle$  is in the form

$$W_2 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos(C_2) & i e^{i\phi_2} \sin(C_2) \\ 0 & 0 & i e^{-i\phi_2} \sin(C_2) & \cos(C_2) \end{pmatrix}.$$
 (B5)

We aim to find  $C_2$  and  $\phi_2$  such that  $W_2(a'_1 a'_2 a'_3 a'_4)^T = (0001)^T$ , where  $(a'_1 a'_2 a'_3 a'_4)^T = (0010)$  is the last column of  $W_1 \mathcal{U}$ . Thus we obtain

$$(C_2, \phi_2) = (\pi/2, \pi/2).$$
 (B6)

As a result, then the last column of  $W_2W_1U$  has become the desired vector  $(0\ 0\ 0\ 1)^T$ .

We now continue a similar procedure to transform the third column of  $W_2W_1 \mathcal{U}$ — $(1000)^T$ —to  $(0010)^T$ . This can be done with two pulses,  $W_3$  and  $W_4$ , respectively, inducing the transition from  $|1\rangle$  to  $|2\rangle$  and from  $|2\rangle$  to  $|3\rangle$ . The  $W_3$  matrix is in the form

$$W_{3} = \begin{pmatrix} \cos(C_{3}) & i e^{i\phi_{3}} \sin(C_{3}) & 0 & 0\\ i e^{-i\phi_{3}} \sin(C_{3}) & \cos(C_{3}) & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1 \end{pmatrix}.$$
 (B7)

The condition  $W_3(1000)^T = (0100)^T$  [where  $(0100)^T$  is the third column of  $W_2W_1\mathcal{U}$ ] gives

$$(C_3, \phi_3) = (\pi/2, \pi/2).$$
 (B8)

The matrix  $W_4$  is in the form of  $W_1$  [Eq. (B3)], where the condition  $W_4(0\,1\,0\,0)^T = (0\,0\,1\,0)^T$  [where  $(0\,1\,0\,0)^T$  is the third column of  $W_3W_2W_1\mathcal{U}$ ] yields

$$(C_4, \phi_4) = (\pi/2, \pi/2).$$
 (B9)

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TABLE I. Dipole moments (D) for the example of Sec. V B.

(×10 <sup>-30</sup> SI unit)
1.75
2.16
2.57
3.80
3.17
4.83

It is straightforward to see that  $W_4W_3W_2W_1 \mathcal{U} = \mathbb{I}$ ; thus the overall pulse sequence is  $\mathcal{U} = W_1^{\dagger}W_2^{\dagger}W_3^{\dagger}W_4^{\dagger}$  with  $C_k = \phi_k = \pi/2$ ,  $\forall k$ . To find each pulse duration, we note that, on the one hand, after learning the values of  $C_{\sigma(k)}$ 's the area covered by a pulse  $A_{\sigma(k)}$  in the envelope-time plot,

$$\operatorname{area}_{k} = \left| \int_{t_{k-1}}^{t_{k}} A_{\sigma(k)}(t) \, dt \right| = \hbar |C_{\sigma(k)}/D_{\sigma(k)\sigma(k)}|, \qquad (B10)$$

is also determined [see Eq. (A9) and Table I]. On the other hand, from Pontryagin's maximum principle we know that in each interval  $[t_{k-1}, t_k]$  the corresponding A(t) is an exponential segment which is related to the modulator bandwidth  $\Omega_{\text{modulator}}$ . If this bandwidth is sufficiently large, then the slope becomes sharp and can be well replaced by a sudden jump. That is, the pulse envelope A(t) starts at time  $t_{k-1}$  from zero and with an almost sudden jump reaches its maximum value  $A_{\text{max}}$ . Next there is a waiting time interval where the slope remains zero until at another instant  $t_k$  at which it drops to zero almost suddenly. This implies that the pulse shape is almost a square, where the exact value of  $\Delta t_{k\rightarrow k+1} = t_k - t_{k-1}$ is determined by the area condition (B10) as

$$\Delta t_{k-1 \to k} = \operatorname{area}_k / |A_{\max}|. \tag{B11}$$

Figure 7 depicts a generic example of the pulse.

Here is the detailed calculation of the time duration of each pulse. The power of the laser is considered to be  $P_{\text{laser}} = 20 \text{ mW}$ ; whence the amplitude of the laser pulse needs to satisfy

$$\frac{1}{2}\varepsilon_0 c |A_{\rm max}|^2 = \frac{P_{\rm laser}}{S_{\rm cross \ section}},\tag{B12}$$

where  $c = 3 \times 10^8$  m/s is the speed of light,  $\varepsilon_0 = 8.85 \times 10^{-12}$  (in the SI units) is the permittivity of the vacuum, and  $S_{\text{cross section}}$  is the cross section of the laser beam, which here is considered to be 100  $\mu$ m<sup>2</sup>. Hence we obtain  $A_{\text{max}} = 38.8 \times 10^4$  (in the SI units). The laser modulator bandwidth  $\Omega_{\text{modulator}} = 40$  GHz yields  $\tau_{\text{fall}} = 25$  ps, which is considerably short such that we can safely consider the pulses as square. Hence the pulse shapes are square. Now from Eq. (B11) and Table I, we obtain  $\Delta t_{1\rightarrow 2} \approx 244$  ps,  $\Delta t_{2\rightarrow 3} \approx 135$  ps, and  $\Delta t_{3\rightarrow 4} \approx 88$  ps, and the total duration of the laser pulse application is 601 ps—see Fig. 6.

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