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ABSTRACT

Two-level quantum systems are fundamental physical models that continue to attract growing interest due to their crucial role as a building block of quantum technologies. The exact analytical solution of the dynamics of these systems is central to control theory and its applications, such as that to quantum computing. In this study, we reconsider the two-state charge transfer problem by extending and using a methodology developed to study (pseudo)spin systems in quantum electrodynamics contexts. This approach allows us to build a time evolution operator for the charge transfer system and to show new opportunities for the coherent control of the system dynamics, with a particular emphasis on the critical dynamic region around the transition state coordinate, where the avoided crossing of the energy levels occurs. We identify and propose possible experimental implementations of a class of rotations of the charge donor (or acceptor) that endow the electronic coupling matrix element with a time-dependent phase that can be employed to realize controllable coherent dynamics of the system across the avoided level crossing. The analogy of these rotations to reference frame rotations in generalized semiclassical Rabi models is discussed. We also show that the physical rotations in the charge-transfer systems can be performed so as to implement quantum gates relevant to quantum computing. From an exquisitely physical–mathematical viewpoint, our approach brings to light situations in which the time-dependent state of the system can be obtained without resorting to the special functions appearing in the Landau–Zener approach.

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I. INTRODUCTION

Two-level quantum systems (namely, models that can describe a quantum system when only two of its states play a nonnegligible role in the dynamic problem study) are of paramount importance in a myriad of problems in physics^{1–7} and chemistry,^{7–13} with their nanotechnological applications. They are important at a fundamental level, as a dynamical problem in itself¹⁴ and as the main building block of quantum technologies.³ The practical relevance of the two-level approximation is further increased by recent experiments, which show, for example, the coherent evolution of molecules behaving like two-level systems inside suitable optical microcavities.¹¹

It was recognized long ago (e.g., see Ref. 1) that any two-level system that is not made of a 1/2 spin can be described as a fictitious spin 1/2 particle in a magnetic field. This representation may have far-reaching conceptual and practical implications for research in the field of charge transfer (CT), which have essentially

not been explored so far. For example, in a methodological perspective, the solution of two-state CT dynamic problems can benefit from methods generally used to solve the dynamics of spin systems or (pseudo)spin systems in quantum electrodynamics and quantum computing contexts, such as those of Barnes–Das Sarma,^{15–17} Messina–Nakazato,¹⁸ and other recently proposed ones.^{19,20}

Exact analytical solutions to two-level dynamics depending on the initial conditions are important in control theory, with implications for the implementation of quantum technologies,^{4,21} among which are quantum computing^{21–25} (where the qubit plays a central role and is described by a two-level quantum system¹⁰), quantum information creation/processing,^{4,5,26–31} quantum metrology,^{29,30,32} and quantum sensing.^{33–36} As is conveniently emphasized in Ref. 37, quantum computing requires not only having well-defined qubits but also being able to initialize and measure them precisely. This depends on the time evolution of qubits, whose control becomes critical at avoided crossings.^{3,38–42}

In CT systems, the diabatic states describing the initial and final localizations of the charge (which are, ideally, independent of nuclear coordinates⁴³) can be used as a basis to describe the state of the system. The two-electronic state model is used as a valid approximation to describe a myriad of CT systems near the avoided crossing of electronic energy levels, where the electronic transmission coefficient of the rate constant determines the occurrence of the CT and its rapidity.^{8,9,44–46} As the transition state coordinate that marks the avoided level crossing is approached, the coupling between the two electronic states is the main determinant of the excess-charge dynamics.^{9,47,48} Even at the avoided crossing, the vibronic coupling is to be considered in the case of proton-coupled electron transfer,⁴⁸ which is, however, out of the scope of the present study. The charge transition between the two diabatic states (whence a nonadiabatic evolution of the system) can generally occur near the transition state coordinate, where the minimum level splitting is twice the electronic coupling (Fig. 1), and is usually described with the Landau–Zener (LZ) formulation,^{9,48–53} where the coupling is approximated as a constant (independent of nuclear coordinates and without an explicit dependence on time),^{40,44,53} leading to descriptions of the dynamical problem in terms of Weber special functions.^{49–51,53} The formalism was extended to cases in which the coupling is nonzero over a finite time interval by Vitanov and Garraway.⁵⁴ In many cases, the dependence of the electronic coupling on nuclear degrees of freedom in flexible molecular systems does not allow the approximation of constant coupling.^{9,48,55–59} In different contexts relevant to molecular electronics, control theory, and quantum computing, the electronic coupling can be tuned to drive the dynamics of CT systems, or that of qubits in quantum electrodynamics and other quantum computing setups, using the phase of the coupling as a control parameter.^{39,41,60–72} This is also in the spirit of the well-known coupled-mode theory, where two modes are coupled in time and/or in space, and the coupling strength is endowed with a phase that depends on time or space.⁷³ The evolution of the relative phase between two states of a two-level system

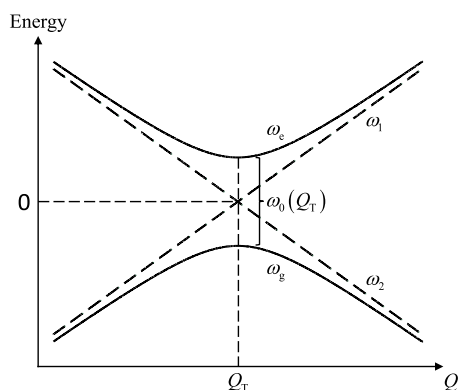


FIG. 1. Energy profile of the two-level system as a function of a parameter Q , which can be a nuclear reaction coordinate. The dashed lines represent the diagonal terms of $H(t)$, namely, the diabatic state energies $\omega_1(Q(t)) = \Omega(t)$ and $\omega_2(Q(t)) = -\Omega(t)$. The solid lines describe the instantaneous eigenvalues of the Hamiltonian $H(t)$, that is, the ground (ω_g) and excited (ω_e) adiabatic state energies, which are split near the transition state coordinate Q_T . Their minimum separation occurs at Q_T , where it is twice the modulus of the electronic coupling between the diabatic states $|1\rangle$ and $|2\rangle$ (ω_0).

(or, in general, the relative phases among quantum states of multicomponent, multilevel systems⁷⁴) driven by a given Hamiltonian, namely, the phase associated with their electronic coupling matrix element, is a determinant of the time evolution of the system that is increasingly taken into account in studies of the presence and function of quantum coherence in physical and chemical systems.^{74–76} In a recent quantum thermodynamics study,⁷⁷ a time-dependent interaction with an oscillatory phase between a qutrit and a qubit was used to conceive a heat engine operating between baths with positive and negative temperatures.⁷⁷ Reaching coherent control of coupled systems is a critical step to enable next-generation technologies for information processing based on quantum mechanical principles, as it has long been recognized in the field of quantum optics for example.^{66,78} The time dependence of the coupling, including its phase, as in some driven Landau–Zener problems,³ can also be related to detuning or other energy parameters that depend on the nature of the system.^{62,63,75,76,79} Particular attention to the coupling phase has been devoted in earlier studies, such as Ref. 80 or Ref. 38, where the two system levels were coupled by an oscillating field.

This is the general context of the present study, where we reconsider the CT dynamics in two-level systems from a perspective that connects it to approaches and dynamical problems in quantum optics, quantum control theory, and quantum computing. First, we identify physical conditions that consist of suitable rotations of the charge donor (and could be similarly applied to the acceptor) and allow us to change the phase of the electronic coupling between the diabatic states of CT two-level systems. Then, we formally extend the Messina–Nakazato method¹⁸ in such a way that it can be used to find the time evolution operator over arbitrary time ranges. The conditions on the coupling phase that characterize the possible solutions afforded by the method include the proposed experimental implementations of CT systems with time-dependent phases. These conditions are exploited here to achieve controllable coherent dynamics of CT two-level systems in their evolution across avoided crossings. Furthermore, these dynamics can be solved without resorting to special functions to represent the evolving state of the system. Finally, we show that the rotation of the charge donor (or acceptor) can be performed so that the evolution operator realizes a quantum gate useful to quantum computing at given time instants or asymptotically.

II. RESULTS AND DISCUSSION

A. Generating diabatic states with time-dependent coupling phase

In units such that $\hbar = 1$, the generally time-dependent Hamiltonian describing a quantum two-level system can be written in the following matrix form:

$$H(t) = \begin{pmatrix} \Omega(t) & V_{12}(t) \\ V_{12}^*(t) & -\Omega(t) \end{pmatrix} \equiv \begin{pmatrix} \Omega(t) & \frac{1}{2}\omega_0(t)e^{-i\phi(t)} \\ \frac{1}{2}\omega_0(t)e^{i\phi(t)} & -\Omega(t) \end{pmatrix} \quad (1)$$

(ω_0 is twice the modulus of the effective electronic coupling V_{12}) on the basis of eigenstates $|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ of the unperturbed Hamiltonian

$$H_0(t) = \begin{pmatrix} \Omega(t) & 0 \\ 0 & -\Omega(t) \end{pmatrix}, \quad (2)$$

which describes the system for zero electronic coupling V_{12} (note that $|1\rangle$ and $|2\rangle$ correspond to $|0\rangle$ and $|1\rangle$, respectively, in the usual qubit notation). Alternatively, using Pauli matrices and the matrices representing the related ladder operators $\sigma_{\pm} = \frac{1}{2}(\sigma_x \pm \sigma_y)$, we write the Hamiltonian in the equivalent forms (for example, cf. Refs. 1, 71, and 81),

$$\begin{aligned} H(t) &= \Omega(t)\sigma_z + \frac{\omega_0(t)}{2} [\cos \phi(t) \sigma_x + \sin \phi(t) \sigma_y] \\ &= \Omega(t)\sigma_z + \frac{\omega_0(t)}{2} [e^{-i\phi(t)} \sigma_+ + e^{i\phi(t)} \sigma_-]. \end{aligned} \quad (3)$$

The use of opposite diagonal elements does not reduce the generality of the 2×2 Hermitian matrix of Eq. (1) or (2). In fact, any other choice of the diagonal terms would amount to shift the energy zero by a time-dependent quantity, that is, to add a time-dependent matrix proportional to the identity matrix 1, thereby leading to an unimportant time-dependent overall phase factor in the time evolution operator.⁷⁶

In Eqs. (1)–(3), $\Omega(t)$ is real and, since here we are especially interested in CT systems, we refer to $|1\rangle$ and $|2\rangle$ as two diabatic electronic states, which describe the transferring excess charge (that is, an excess electron or electron hole) localized in one of two sufficiently separated electronic potential energy wells determined by the molecular system at stake. It is worth noting that Eq. (1) also describes the general matrix form of Hamiltonians widely used in quantum optics. For example, with a suitable specialization of the matrix elements in Eq. (1), one obtains the Hamiltonian matrix that describes the Jaynes–Cummings model in any of its dynamically invariant two-dimensional subspaces.⁸² Moreover, even in the cases (such as the present one) in which Eq. (1), or (3), does not describe a spin-1/2 particle, it is always possible to find a fictitious magnetic field such that this Hamiltonian represents a fictitious spin 1/2 subject to such a field.¹ In particular, if $\Omega(t) = \Omega_0$ and $\phi(t) = \omega t$, Eq. (3) gives the Hamiltonian of a spin 1/2 in a magnetic field composed of a constant component of modulus $2\Omega_0$ in the z direction and a component of modulus ω_0 rotating on the xy plane with the angular frequency $\phi(t) = \omega t$. This dynamic problem is exactly solvable (as is shown, for example, in Ref. 1) and belongs to the infinite class of problems solvable by the Messina–Nakazato (MN) method¹⁸ (*vide infra*).

In this study, the coupling generally depends on time, although we treat in more detail the cases in which its modulus is the constant $\omega_0/2$, while its phase ϕ changes over time. To clarify the

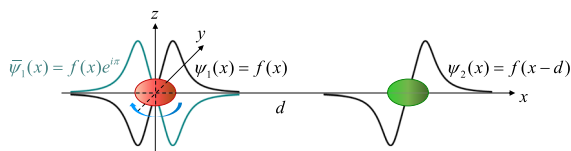


FIG. 2. A simple example of CT system in which the coupling phase can be made time dependent by a periodic switch of the orientation of molecule 1 along the x axis. $\psi_1(x)$ is an odd function of x .

meaning of this kind of electronic coupling and explore its actual implementation, we first consider the simple situation depicted in Fig. 2, where the diabatic wave function $\psi_1(\mathbf{r}) = \langle \mathbf{r} | 1 \rangle$ is an odd function of x , namely, $\psi_1(x) = f(x)$ with $f(x) = -f(-x)$, while $\psi_2(x) = f(x-d)$. Assuming a constant coupling strength between the two states, which varies as a function ξ of an effective distance d between the two localized distributions of the excess charge, the electronic coupling matrix element can be written as $V_{12} = \omega_0(d)/2$ with

$$\omega_0(d) = 2\xi(d) \int_{-\infty}^{\infty} f(x)f(x-d)dx \equiv 2\xi(d)S_{12}(d). \quad (4)$$

If the molecule, or other charge donor group or system, at the origin of the reference frame (hereafter called molecule 1, while the other molecular component involved in the CT is called molecule 2) is rotated by π around the z axis, its wave function becomes $\bar{\psi}_1 = f(-x) = -f(x)$ and the electronic coupling changes sign. Therefore, depending on the orientation of molecule 1 along the x axis, it is

$$V_{12}(d, \phi) = \frac{\omega_0(d)}{2} e^{-i\phi} \text{ with } \phi = 0, \pi. \quad (5)$$

This means that, if molecule 1 can be reoriented in response to a square wave signal, the phase of V_{12} changes as a square wave with amplitude π .

Next, consider that the initial charge distribution on molecule 1 is described by a hydrogen-like p orbital $\psi_1(r, \theta, \varphi) = f(r, \theta)e^{i\varphi}$ and $\psi_2(r', \theta', \varphi') = f(r', \theta')e^{i\varphi'}$ with $r' = |\mathbf{r} - \hat{\mathbf{x}}d|$. We also assume that molecule 1 is rotated clockwise around the z axis with an angular frequency ω and that this molecule can be described as a rigid rotor. This approximation means, in particular, that the effect of the rotation on the relative spatial distribution of $\psi_1(r, \theta, \varphi)$ can be neglected. This is a good approximation for any reasonable value of ω in many biomolecular systems in which the local electronic charge distribution is determined by very strong local fields.^{83–89} Then, the rotation of molecule 1 affects the Hamiltonian of the CT system in two ways: as a time-dependent term in $H_{11}(t)$, which describes the kinetic energy of the rigid rotor, and as a rotation of the molecular orbital on molecule 1 that changes the electronic coupling between the initial and final electronic states. The first effect is taken into account by setting the energy zero to the value $\frac{1}{2}[H_{11}(t) + H_{22}(t)]$ so that the diagonal elements of the Hamiltonian can still be written as in Eq. (1).¹ The second effect arises from the fact that the initial diabatic state is changed to $\bar{\psi}_1$ such that $\bar{\psi}_1(r, \theta, \varphi - \omega t) = \psi_1(r, \theta, \varphi)$, from which $\bar{\psi}_1(r, \theta, \varphi) = \psi_1(r, \theta, \varphi + \omega t) = f(r, \theta)e^{i(\varphi + \omega t)}$ and the electronic coupling acquires a time-dependent phase,

$$V_{12}(t) = \frac{\omega_0}{2} e^{-i\omega t}, \quad (6)$$

namely, $\phi(t) = \omega t$. In particular, one can also choose $\omega = \omega_0$, which, at the transition state coordinate, amounts to the separation between the adiabatic energy levels (see Fig. 1). Incidentally, the simplest, formally akin dynamical problem for spin systems consists of a spin-1/2 particle with a constant energy difference $2\Omega_0$ between the two spin states, subject to a magnetic field with a component that rotates with the resonance angular frequency $\omega = 2\Omega_0$; then, the coupling

matrix element acquires the phase $\phi(t) = 2\Omega_0 t = \int_0^t \Omega_0 dt'$ and the analytical solution of this dynamical problem is known.¹

Returning to the CT problem, the above context can be expanded in two ways: (i) considering that the diabatic states localized on the charge donor and acceptor groups are generally described by more complicated wave functions and (ii) rotating the donor at a time-dependent angular frequency $\omega(t)$. Here, we focus on point (ii), as we treat the CT dynamic problem at a fundamental level that applies to any system amenable to the two-state approximation.

We stress that $\phi(t) = 2\Omega_0 t$ represents an interesting physical condition also in the present context of CT, as well as in control theory methods.³⁹ Moreover, we generalize this condition considering the rotation of the charge donor (similar considerations apply to the rotations of the acceptor) with a variable angular frequency $\omega(t)$ such that $\phi(t) = \int_0^t \omega(t') dt'$ satisfies

$$\phi(t) = 2 \int_0^t \Omega(t') dt'. \quad (7)$$

The physical significance of this $\phi(t)$ is enhanced by the following arguments. In the unperturbed system represented by $H_0(t)$, which describes the limit of vanishing electronic coupling between the excess charge localizations on the donor and acceptor, $|1\rangle$ and $|2\rangle$ are the eigenstates of the Hamiltonian operator and evolve over time into the physically indistinguishable instantaneous diabatic states,

$$|\psi_1(t)\rangle = e^{-i\int_0^t \Omega(t') dt'} |1\rangle \quad (8a)$$

and

$$|\psi_2(t)\rangle = e^{i\int_0^t \Omega(t') dt'} |2\rangle, \quad (8b)$$

respectively. It is worth noting that, by definition, the charge localization in the diabatic states does not depend on their coupling and is already built in Eq. (2). This is the reason why $|\psi_j(t)\rangle$ ($j = 1, 2$) can be defined as the instantaneous diabatic states of the CT system. Moreover, since $|\psi_j(t)\rangle$ are both the evolved states starting from $|j\rangle$ ($j = 1, 2$) and the eigenstates of $H_0(t)$ at time t , the Berry phases associated with such states are $\beta_j(t) = (-1)^{j-1} \int_0^t \Omega(t') dt'$, as is easily derived from the expressions for $|\psi_j(t)\rangle$. If $\phi(t)$ satisfies condition (7), it represents the accumulated phase difference between states 2 and 1 evolved up to time t , or the corresponding difference in Berry phase between states 1 and 2. In the system described by the complete Hamiltonian $H(t)$ of Eq. (1), the electronic states (8a) and (8b) are no longer eigenstates of the Hamiltonian. These states are now coupled, and their coupling has a generally time-dependent phase,

$$\begin{aligned} \langle \psi_1(t) | H(t) | \psi_2(t) \rangle &= e^{2i\int_0^t \Omega(t') dt'} \langle 1 | H(t) | 2 \rangle \\ &= \frac{\omega_0(t)}{2} e^{-i[\phi(t) - 2\int_0^t \Omega(t') dt']}. \end{aligned} \quad (9)$$

Denoting $H_{\phi=0}(t)$ the Hamiltonian (1) with $\phi(t) = 0$ (namely, the Hamiltonian of the physical system without the rotation that produces a phase ϕ in the electronic coupling), Eq. (9) yields (also, cf. the particular pregnant cases treated in Refs. 1 and 90)

$$\langle \psi_1(t) | H(t) | \psi_2(t) \rangle = \frac{\omega_0(t)}{2} = \langle 1 | H_{\phi=0}(t) | 2 \rangle. \quad (10)$$

Namely, the physical rotation that generates the phase $\phi(t)$ of Eq. (7) in the electronic coupling exactly counterbalances the phase difference accumulated by the instantaneous diabatic states at each instant of time t , in such a way that the instantaneous electronic coupling between the instantaneous diabatic states equals the coupling between the time-independent diabatic states in the system without the rotation of the donor (D) or acceptor (A) molecular component. In particular, if the magnitude of the electronic coupling does not depend appreciably on time, Eq. (10) becomes

$$\langle \psi_1(t) | H(t) | \psi_2(t) \rangle = \frac{\omega_0}{2} = \langle 1 | H_{\phi=0} | 2 \rangle. \quad (11)$$

While $|j\rangle$ and $|\psi_j(t)\rangle$ describe the same physical state of the system and the transition probability from this state to $|k\rangle$ or $|\psi_k(t)\rangle$ ($k \neq j$) depends on $\omega_0^2(t)/4$, the state of the system at time t is

$$\begin{aligned} |\psi(t)\rangle &= C_1(t) e^{-i\int_0^t \Omega(t') dt'} |1\rangle + C_2(t) e^{i\int_0^t \Omega(t') dt'} |2\rangle \\ &= C_1(t) |\psi_1(t)\rangle + C_2(t) |\psi_2(t)\rangle, \end{aligned} \quad (12)$$

and its time evolution also depends on the relative phases of the expansion coefficients in the diabatic basis. In Sec. II B, we will solve the general dynamical problem ultimately described by such coefficients.

It is worth noting that we propose the rotation of part of the molecular system as a general scheme for future experimental implementations of situations in which the phase of the electronic coupling depends on time. Realistic experimental parameters to be used (in particular, the angular velocity of rotation) will clearly depend on the specific system and implementation considered. In general, the charge donor and acceptor can belong to two different molecules (as in intermolecular CT) or be parts of the same molecule (intramolecular CT). In both cases, we envisage that the rotation of one of the two molecular groups with respect to the other could be performed by a suitable interaction with the local environment or application of a local field (for example, an electric or a magnetic field suitably applied through STM⁹¹⁻⁹⁷ that causes the rotation of one of the two molecular components due to its local excess charge density or spin density). In the second case, the relative rotation of the charge donor and acceptor requires a proper flexibility at least of part of the molecular bridge between the two redox centers (as can be achieved, for example, in C-clamp molecular structures with CT function^{98,99}) and, for example, a periodic rotation in an alternating direction of the charge donor or acceptor may serve the purpose. Furthermore, the same general scheme may be applied to other nanostructures with two embedded redox centers, where a local field can be applied to one of the redox sites.

B. Time evolution operator

The general Hamiltonian (1) has a time-evolution operator that belongs to SU(2) (e.g., through parameterization in terms of Cayley–Klein parameters), and it is written as^{18,100,101}

$$U(t) = \begin{pmatrix} a(t) & b(t) \\ -b^*(t) & a^*(t) \end{pmatrix}, \quad (13)$$

where $|a(t)|^2 + |b(t)|^2 = 1$, and, since $U(0)$ is the identity operator, it is $a(0) = 1$ and $b(0) = 0$. Here, we will extend the MN method to obtain $U(t)$ in parametric form at any time t .

The most profitable implementation of the MN method to our two-level dynamic problem requires the construction of the real function,¹⁸

$$\Phi(\mu; t) = \frac{1}{2} \sqrt{1 + \mu^2} \int_0^t \omega_0(t') dt' \equiv \sqrt{1 + \mu^2} \kappa(t), \quad (14)$$

where we introduced the real positive parameter μ and a dimensionless “dynamical time,”^{18,82}

$$\kappa(t) = \frac{1}{2} \int_0^t \omega_0(t') dt' \quad (15)$$

(incidentally, it is worth noting that this quantity corresponds to half the pulse area in pulse techniques for quantum control, such as the robust inverse optimization method in Refs. 102 and 103). Then, with the present notation, the MN method gives

$$a(t) = \sqrt{\frac{\mu^2 + \cos^2 \Phi(\mu; t)}{1 + \mu^2}} e^{-i \left[\frac{\phi(t)}{2} + \vartheta(\mu; t) \right]} \quad (16a)$$

with

$$\vartheta(\mu; t) = \text{Arctan} \left[\frac{\mu}{\sqrt{1 + \mu^2}} \tan \Phi(\mu; t) \right] \quad (16b)$$

(in the notation, we stress the parametric dependence of Φ and ϑ on μ) and

$$b(t) = \frac{\sin \Phi(\mu; t)}{\sqrt{1 + \mu^2}} e^{-\frac{i}{2} [\phi(t) + \pi]}, \quad (17)$$

provided that the condition

$$\dot{\phi}(t) = 2\Omega(t) - \mu\omega_0(t) \quad (18)$$

is satisfied [for comparison, note that $\mu\omega_0$ is the detuning in studies of semiclassical Rabi systems⁷¹ and quantum control,¹⁰²

where Eq. (7) amounts to the resonance, or zero detuning, condition]. It is worth noting that, given condition (18), changing μ amounts to changing the rotation of the donor and thus the phase of the coupling in the Hamiltonian. The integration of Eq. (18) gives

$$\frac{\phi(t)}{2} = \int_0^t \Omega(t') dt' - \mu\kappa(t), \quad (19)$$

where, without loss of generality, it is assumed that $\phi(0) = 0$. In Ref. 18, Eq. (16b) is written as a relation between the tangents of ϑ and Φ , and the expressions for a and b implicitly assume that the sines of the two angles, as well as their cosines, have the same signs at any time. This fact can be easily derived by the inspection of Eqs. (14), (16), (18), and (20) in Ref. 18. Then, strictly speaking, the provided solution to the dynamic problem applies to a time interval in which $0 \leq \Phi(\mu; t) < \frac{\pi}{2}$ and $\vartheta(\mu; t)$ is defined by the principal value of the inverse tangent as in Eq. (16b).

The MN approach can describe the time evolution of the two-level system at all times by properly extending the definition of the angle ϑ . In particular, Arctan must be replaced by arctan in Eq. (16) so that ϑ becomes an increasing multivalued function of its argument in the range $[0, 2\pi[$. More precisely (see the Appendix),

- (i) As t increases, $\Phi(\mu; t)$ grows continuously according to Eq. (14), while $\tan \Phi(\mu; t)$ is clearly not defined at the times $t = t_{\pi/2}(\mu)$, $t_{3\pi/2}(\mu)$, etc., in which $\Phi(\mu; t) = \frac{\pi}{2}$, $\frac{3\pi}{2}$, etc.
- (ii) While $\Phi(\mu; t)$ takes on values in the interval $[0, 2\pi[$, and excluding the times $t_{\pi/2}(\mu)$ and $t_{3\pi/2}(\mu)$, ϑ is assigned values in the intervals $[0, \frac{\pi}{2}[$, $]\frac{\pi}{2}, \frac{3\pi}{2}[$, and $]\frac{3\pi}{2}, 2\pi[$ by replacing Arctan with arctan in Eq. (16b).
- (iii) At the time instants $t_{\pi/2}(\mu)$ and $t_{3\pi/2}(\mu)$, ϑ (which is a continuous and derivable function of time in the MN method¹⁸) is described, in terms of its relationship with Φ , by an analytic continuation: $\vartheta(\mu; t_{\pi/2}(\mu)) = \Phi(\mu; t_{\pi/2}(\mu)) = \frac{\pi}{2}$ and similarly for $t = t_{3\pi/2}(\mu)$.
- (iv) As $\Phi(\mu; t)$ grows above $[0, 2\pi[$, $\vartheta(\mu; t)$ can anyway be cyclically assigned values in the interval $[0, 2\pi[$ as prescribed by points (ii) and (iii).

Alternatively, and equivalently, ϑ can be defined as

$$\vartheta(\mu; t) = \begin{cases} \arctan \left[\frac{\mu}{\sqrt{1 + \mu^2}} \tan \Phi(\mu; t) \right] & \text{for } t \neq t_{(2n-1)\pi/2}(\mu) \\ (2n-1)\frac{\pi}{2} & \text{for } t = t_{(2n-1)\pi/2}(\mu) \end{cases} \quad (n \in \mathbb{N}), \quad (20)$$

which is the same as defining $\vartheta(\mu; t)$ as $\lim_{x \rightarrow t} \left\{ \arctan \left[\frac{\mu}{\sqrt{1 + \mu^2}} \tan \Phi(\mu; x) \right] \right\}$ at any time. In particular, for sufficiently large μ values, $\vartheta(\mu; t) \cong \arctan [\tan \Phi(\mu; t)] = \Phi(\mu; t) \forall t$. The same formalism holds for $t \leq 0$, but n is a

non-positive integer, and the arctan function is accordingly valued over the intervals $]-\frac{\pi}{2}, 0[$, $]-\frac{3\pi}{2} + n\pi, -\frac{\pi}{2} + n\pi[$. Note that the extended $\vartheta(\mu; t)$ is also derivable, as is necessary, since the derivative of the multivalued arctan function tends to zero on both sides of $t = t_{(2n-1)\pi/2}(\mu)$.

At this point, we can write the time evolution operator

$$U(t) = \begin{pmatrix} \sqrt{\frac{\mu^2 + \cos^2 \Phi(\mu; t)}{1 + \mu^2}} e^{-i[\frac{\vartheta(t)}{2} + \vartheta(\mu; t)]} & -i \frac{\sin \Phi(\mu; t)}{\sqrt{1 + \mu^2}} e^{-i\frac{\vartheta(t)}{2}} \\ -i \frac{\sin \Phi(\mu; t)}{\sqrt{1 + \mu^2}} e^{i\frac{\vartheta(t)}{2}} & \sqrt{\frac{\mu^2 + \cos^2 \Phi(\mu; t)}{1 + \mu^2}} e^{i[\frac{\vartheta(t)}{2} + \vartheta(\mu; t)]} \end{pmatrix}, \quad (21)$$

and, for any initial time t_0 (including $t_0 < 0$, depending on the time origin chosen),

$$U(t, 0) = U(t, t_0)U(t_0, 0) \rightarrow U(t, t_0) = U(t, 0)U^{-1}(t_0, 0) = U(t, 0)U^\dagger(t_0, 0). \quad (22)$$

Equation (21) will be next used to obtain the evolution of the system state.

C. Coherent control of CT dynamics at avoided crossings

For a system initially in the state

$$|\psi(0)\rangle = C_1(0)|1\rangle + C_2(0)|2\rangle, \quad (23)$$

the evolution operator (21) yields $|\psi(t)\rangle = U(t)|\psi(0)\rangle$ in the first form (12) with

$$C_1(t) = \left[\sqrt{\frac{\mu^2 + \cos^2 \Phi(\mu; t)}{1 + \mu^2}} e^{-i\vartheta(\mu; t)} C_1(0) - i \frac{\sin \Phi(\mu; t)}{\sqrt{1 + \mu^2}} C_2(0) \right] e^{i\mu\kappa(t)} \quad (24a)$$

and

$$C_2(t) = \left[-i \frac{\sin \Phi(\mu; t)}{\sqrt{1 + \mu^2}} C_1(0) + \sqrt{\frac{\mu^2 + \cos^2 \Phi(\mu; t)}{1 + \mu^2}} C_2(0) \right] e^{-i\mu\kappa(t)}. \quad (24b)$$

We first examine the two limiting cases of Eq. (24) with respect to the value of μ . For $\mu \gg 1$ (a large detuning regime⁷¹), Eq. (14) gives

$$\Phi(\mu; t) \cong \mu\kappa(t) \quad (25)$$

and Eqs. (24a) and (24b) become

$$\begin{cases} C_1(t) \cong C_1(0), \\ C_2(t) \cong C_2(0), \end{cases} \quad (26)$$

that is, the dynamics of the system is inhibited. It is worth noting that a quenching of the dynamics of the atomic population

inversion for $\mu \gg 1$ has recently been found for time-dependent Jaynes–Cummings models.⁸²

The study of the opposite limiting case, $\mu = 0$, amounts to an extension of the MN method, which, for simplicity, was originally set in the parameter range $1/\mu \in]0, \infty[$ (note that the parameter employed in Ref. 18 becomes $1/\mu$ in the present notation). ϑ must take on the values $n\pi$ or otherwise alternate between 0 and π , while $\Phi(\mu; t)$ grows with time and $\tan \Phi(\mu; t)$ correspondingly alternates between positive and negative values. In this way, $\tan \vartheta$ remains zero, while the cosines of ϑ and Φ have the same sign at all times. Furthermore, the temporal continuity of the solution to the dynamical problem requires that ϑ is properly defined also at the time instants in which $\tan \Phi(\mu; t)$ is not defined. Taking these considerations into account, the MN method is extended to the case $\mu = 0$ using (see the Appendix)

$$\vartheta(0; t) = \begin{cases} 0 & \text{for } t_{(-\frac{1}{2}+2n)\pi} \leq t < t_{(\frac{1}{2}+2n)\pi} \\ \pi & \text{for } t_{(\frac{1}{2}+2n)\pi} \leq t < t_{(\frac{3}{2}+2n)\pi} \end{cases} \quad (n \in \mathbb{Z}), \quad (27)$$

and therefore,

$$e^{\pm i\vartheta(0; t)} |\cos \Phi(0; t)| = \text{sgn} [\cos \kappa(t)] |\cos \kappa(t)| = \cos \kappa(t), \quad (28)$$

which ensures the continuity and the derivability of the evolution operator (21) for $\mu = 0$. In Eq. (27), the notation was simplified by writing $t_k \equiv t_k(0)$.

Through the differential equation $i\dot{U}(t, 0) = H(t)U(t, 0)$, it is easy to verify that inserting Eq. (28) into Eq. (21) leads to the correct evolution operator for the Hamiltonian (1) under condition (19) with $\mu = 0$, that is, Eq. (7). Incidentally, it is worth noting that Eq. (7) also describes the phase of the electronic coupling that appears in the interaction representation of two-level models, where, however, this phase results from the representation change, the two basis states are accordingly changed, and the diagonal elements of the Hamiltonian matrix consequently become zero.⁸⁰

Using Eq. (28), Eqs. (24a) and (24b) with $\mu = 0$ read

$$C_1(t) = \cos \kappa(t)C_1(0) + \sin \kappa(t)e^{-i\frac{\pi}{2}}C_2(0), \quad (29a)$$

$$C_2(t) = -\sin \kappa(t)e^{i\frac{\pi}{2}}C_1(0) + \cos \kappa(t)C_2(0). \quad (29b)$$

Note that Eqs. (29a) and (29b) describe an oscillatory behavior of the coefficients only when κ depends linearly on time.

Equations (14), (20), (24), (27), and (29) show that the expansion coefficients, C_1 and C_2 , depend on time only through the dynamic time κ . According to Eq. (12), this consideration applies

to all quantities that depend on the moduli of C_1 and C_2 . Let us add incidentally that universal properties in terms of the timescale κ also appear in the dynamical evolution of Jaynes–Cummings models.⁸² It is also worth noting that Eqs. (29a) and (29b) describe a rotation on the Bloch sphere of the system state, at a fixed azimuthal angle of $\pi/2$, and 2κ represents the polar angle on this sphere. Moreover, if the modulus of the electronic coupling takes a constant value ω_0 , Eq. (15) gives

$$\kappa(t) = \frac{\omega_0 t}{2}, \quad (30)$$

and the state expansion coefficients are also periodic over the real timescale. In this case,

$$C_1(t) = \cos \frac{\omega_0 t}{2} C_1(0) + \sin \frac{\omega_0 t}{2} e^{-i\frac{\pi}{2}} C_2(0) \quad (31a)$$

and

$$C_2(t) = -\sin \frac{\omega_0 t}{2} e^{i\frac{\pi}{2}} C_1(0) + \cos \frac{\omega_0 t}{2} C_2(0) \quad (31b)$$

describe a coherent Rabi oscillation between the two diabatic states.

Next, we analyze the physical meaning of parameter μ . We begin by showing that varying μ , one can generate physical situations ranging from a locked dynamics, in which the system is frozen in its initial state, as in Eq. (26), to a coherent oscillation, in which the system periodically reaches a maximum transition probability. Namely, we analyze the meaning of μ as a parameter related to the diabatic energy difference and coupling by Eq. (19) that can be used to control the dynamics of a two-level system (in the present case, the two energy levels correspond to two localized charge states of a CT system), with relevance to research on quantum control through nonadiabatic transitions.³

For simplicity, we assume that the system is initially in the localized state $|1\rangle$. This state virtually coincides with one of the two adiabatic electronic states if the nuclear coordinate Q is sufficiently far from Q_T (i.e., further to the left, or to the right, in the energy diagram of Fig. 1), while it is appreciably different from both adiabatic states near Q_T . $|1\rangle$ is not an instantaneous eigenstate of the Hamiltonian at any time, as it represents a transient diabatic state generated by the initial charge localization, e.g., as in Giese's experiments on hole transfer through DNA.¹⁰⁴ The probability of finding the system in state $|2\rangle$ at time t is derived from Eq. (24b) as

$$P_{1\rightarrow 2}(t) = |C_2(t)|^2 = \frac{\sin^2 \Phi(\mu; t)}{1 + \mu^2}. \quad (32)$$

Equation (32) is also derived in Ref. 71, within the context of generalized semiclassical Rabi models, where it is recognized that the main effect of μ is to attenuate the transition probability by $1 + \mu^2$. In fact, Eq. (32) expresses the quenching of the CT dynamics with increasing μ in agreement with Eq. (26). To grasp the more general and profound physical meaning of parameter μ within the CT context, we use Eqs. (15), (18), and (19) to write

$$\begin{aligned} \mu &= \frac{2\int_0^t \Omega(t') dt' - \phi(t)}{2\kappa(t)} = \frac{2\int_0^t [\Omega(t') - \frac{1}{2}\dot{\phi}(t')] dt'}{\int_0^t \omega_0(t') dt'} \\ &\equiv \frac{2\int_0^t \Omega_{\text{eff}}(t') dt'}{\int_0^t \omega_0(t') dt'} = \frac{2\langle \Omega_{\text{eff}} \rangle_t}{\langle \omega_0 \rangle_t}. \end{aligned} \quad (33)$$

In Eq. (33), we denoted $\langle \Omega_{\text{eff}} \rangle_t$ the average of Ω_{eff} over the time interval $[0, t]$. $\langle \omega_0 \rangle_t$ is the average magnitude of the coupling over the same time range. $2\Omega_{\text{eff}} \equiv 2\Omega - \dot{\phi}$ appears as an effective energy difference between the two diabatic electronic states. In fact, in the semiclassical Rabi model¹⁰⁵ and its generalizations,⁷¹ a similar quantity, named detuning, emerges as the energy difference between the two spin-1/2 levels in the effective Hamiltonian obtained by a suitable rotation of the reference frame, which thereby appears as the formal analog of the physical rotation within the CT system. In this Hamiltonian, which is also the starting point of recent robust approaches to optimal quantum control,^{102,103} the rotation leads to the appearance of the effective detuning in the diagonal elements, while only the modulus of the electronic coupling remains in the off-diagonal elements. In such contexts, the resonance condition (7) corresponds to zero detuning, while parameter μ generally appears as a constant of proportionality in the expression for the detuning.⁷¹ Moreover, for $\mu = 0$, as $\Phi = \kappa$ tends to $\pi/2$ (which corresponds to a pulse area of π in pulse techniques for quantum control), $P_{1\rightarrow 2}$ tends to unity (the so-called π -pulse transfer^{102,103,106}). In the present CT context, the diagonal elements of Hamiltonian matrix (1) describe the actual energy difference between the diabatic states, while the phase of the electronic coupling is physically generated (e.g., through the experimental schemes proposed in Sec. II A) to control the CT dynamics.

Let us first consider the case in which $\phi(t) = 0$. In this case, $\Omega_{\text{eff}}(t) = \Omega(t)$ and condition (19) for the dynamical evolution of the system described by Eq. (21) requires that the electronic coupling and energy splitting between the two diabatic electronic states change in the same way with time so that their ratio remains unchanged (otherwise, μ would depend on t at least in some time range). In particular, this condition holds for constant $\Omega(t) = \Omega_0$ and $\omega_0(t) = \omega_0$, which produce a standard Rabi oscillation. In fact, in this case, the insertion of Eqs. (14), (30), and (33) into Eq. (32) gives

$$\begin{aligned} P_{1\rightarrow 2}(t) &= \frac{1}{1 + \mu^2} \sin^2 \left(\sqrt{1 + \mu^2} \frac{\omega_0 t}{2} \right) \\ &= \frac{\omega_0^2}{4\Omega_0^2 + \omega_0^2} \sin^2 \left(\sqrt{4\Omega_0^2 + \omega_0^2} \frac{t}{2} \right), \end{aligned} \quad (34)$$

where $\mu = 2\Omega_0/\omega_0$. In CT theory, the ratio between the energy separation and the electronic coupling of the diabatic electronic states is a measure of the distance from the transition state coordinate Q_T , where the avoided crossing occurs, with the maximum entanglement between nuclear and electronic degrees of freedom.⁴⁸ Therefore, sustaining condition (19) (which amounts to a constant μ parameter and underlies the time evolution operator derived above) without acting on ϕ requires either to freeze the nuclear coordinates at some distance from Q_T (in particular, $\mu = 0$ for $Q = Q_T$) or to make in such a way that the modulus of the coupling changes proportionally to the diabatic state energy difference (the analogous condition in the case of a spin 1/2 under a time-dependent magnetic field, in

the rotating reference frame, is the proportionality of the perpendicular field intensity to the detuning^{1,18,71}). This last situation is compatible with the expression for the diabatic-state electronic coupling. Writing the adiabatic ground state as the linear combination $|\psi_g(Q(t))\rangle = a(Q(t))|1\rangle + b(Q(t))|2\rangle$ (note that here we assume that the rigorously diabatic, and hence coordinate-independent, set $\{|1\rangle, |2\rangle\}$ can properly describe the state of the system over the range of nuclear coordinates explored, although this is clearly an approximation, since infinitely many strictly diabatic states are generally required to this end^{43,48}), the magnitude of the effective electronic coupling has the following general expression:^{12,59,107}

$$|V_{12}| = \begin{cases} \left| \frac{pq}{p^2 - q^2} \Delta E_{12} \left(1 + \frac{p^2 + q^2}{2pq} S_{12} \right) \frac{1}{1 - S_{12}^2} \right| & (\Delta E_{12} \neq 0), \\ \frac{\Delta E_v}{2} & (\Delta E_{12} = 0), \end{cases} \quad (35)$$

where ΔE_v is the vertical adiabatic energy splitting, $p = \langle 1 | \psi_g \rangle$, $q = \langle 2 | \psi_g \rangle$, and, in the present case, $S_{12} = \langle 1 | 2 \rangle = 0$ and $\Delta E_{12} = 2\Omega$. Therefore, V_{12} and ΔE_{12} are related by a proportionality constant only if p and q do not change, or change by a same factor, with $Q(t)$. In principle, this can be consistently realized since p and q only depend on the ratio $\Delta E_{12} / \sqrt{\Delta E_{12}^2 + 4|V_{12}|^2}$.^{59,108} For example, the physical meaning of keeping p and q constant while varying V_{12} proportionally to ΔE_{12} is that the magnitude of the coupling needs to be increased (reduced) to maintain a given spreading of $|\psi_g(Q(t))\rangle$ over $|1\rangle$ and $|2\rangle$ as $|\Delta E_{12}|$ increases (decreases), and hence, the charge would tend to localize on one of the two sites (to equally delocalize over the two sites) otherwise. Changes in the size of the electronic coupling mean a breakdown of the Condon approximation, which can be realized by the involvement of inducing⁵⁵ nuclear modes.

Let us now consider the case in which $\phi(t) \neq 0$. In this case, μ takes on the meaning of an effective distance from Q_T , which can be fixed through a suitable rotation of the charge donor or acceptor that produces the necessary time-dependent phase $\phi(t)$ of the electronic coupling, prescribed by Eq. (19). When the modulus of the coupling has a constant value ω_0 , the denominator of μ in Eq. (33) depends linearly on time, and therefore, $\dot{\phi}(t)$ must differ from $2\Omega(t)$ by a constant to ensure that the numerator of μ is also a linear function of time, i.e., that $2\Omega_{\text{eff}}$ is a constant. Then, Eq. (32) describes a Rabi oscillation at a fixed effective distance from Q_T that is characterized by the effective diabatic energy difference $2\Omega_{\text{eff}}$, with an oscillation

amplitude of $\omega_0^2 / (4\Omega_{\text{eff}}^2 + \omega_0^2)$. In particular, if $\phi(t)$ satisfies condition (7), $\mu = 0$ and the CT system is effectively maintained in the Rabi oscillation with a unit amplitude characteristic of $Q = Q_T$, where the two diabatic states are degenerate.

When the modulus of the electronic coupling is not a constant, the insertion of Eqs. (14) and (15) into Eq. (32) shows that the time evolution of the CT system is no longer a Rabi oscillation. For example, for⁷¹

$$\omega_0(t) = 2\nu \text{sech}(vt) \quad (36)$$

and $\mu = 0$, the transition probability smoothly increases to unity as

$$P_{1 \rightarrow 2}(t) = \tanh^2(vt). \quad (37)$$

For

$$\omega_0(t) = \frac{2}{\sqrt{1 + \mu^2}} \dot{f}(t) \text{sech } f(t) \quad \text{with} \quad f(t) = vt + \eta \sin(vt), \quad (38)$$

using the chain rule for derivatives and the integral 2.423.9 of Ref. 109, it is easily seen that the transition probability grows to $1/(1 + \mu^2)$ while oscillating (see Fig. 3),

$$P_{1 \rightarrow 2}(t) = \frac{1}{1 + \mu^2} \tanh^2[vt + \eta \sin(vt)]. \quad (39)$$

In light of the above analysis, the quenching of the transition probability with increasing values of μ can be read as a quenching of nonadiabatic electronic transitions with increasing effective distance from the avoided crossing. In general, Eq. (18) or its integral form in Eq. (19) emerges as a condition on rotation ϕ for controlling the nonadiabatic dynamics of the two-level CT system, which can be implemented in an infinite number of ways. It is worth emphasizing that $P_{1 \rightarrow 2}(t)$ becomes the transition probability for two degenerate electronic states when $\mu = 0$, and this condition can also be achieved for nondegenerate charge-localized states if $\phi(t)$ satisfies condition (7). As we noticed, this rotation cancels the effect on the coupling of the phase difference accumulated by the instantaneous diabatic states due to their energy difference. In particular, if the absolute value of the electronic coupling does not depend on t , this means that the instantaneous diabatic states are coupled by $\omega_0/2$ at any time, as is described by Eq. (11), and thus, the transition probability per unit time can only depend on ω_0^2 . Looking at it in another way, we can interpret Eqs. (9) and (11) in the interaction representation,

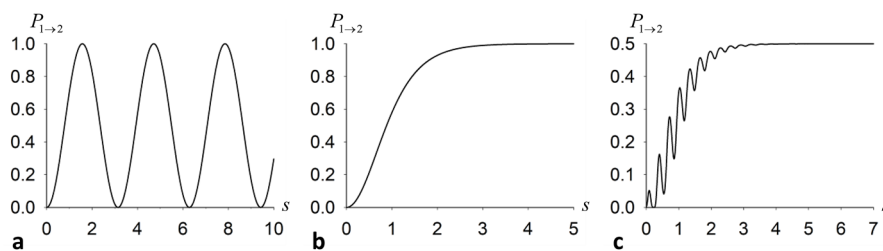


FIG. 3. Transition probability $P_{1 \rightarrow 2}$ as a function of $s = vt$, given by Eq. (32) for (a) $\mu = 0$ and $\omega_0(t) = \omega_0 \equiv 2\nu$, (b) $\mu = 0$ and $\omega_0(t)$ given by Eq. (36), and (c) $\mu = 1$ and $\omega_0(t)$ given by Eq. (38) with $\eta = 0.25$ and $\nu = 20\nu$. The initial condition is $\{C_1(0) = 1, C_2(0) = 0\}$.

where the two instantaneous diabatic states $|\psi_1(t)\rangle$ and $|\psi_2(t)\rangle$ are transformed to the time-independent initial diabatic states $|1\rangle$ and $|2\rangle$, respectively, while Eq. (9) and its complex conjugate describe the off-diagonal matrix elements of the perturbation Hamiltonian. The rotation ϕ in Eq. (7) removes the dependence of these matrix elements on the diabatic level splitting, which then is no longer a determinant of $P_{1\rightarrow 2}$.

D. Identifying interesting dynamical scenarios

Figure 3 shows just a few examples of the many opportunities provided by the above approach to define desired temporal evolutions of the CT system, which means controlling its dynamic evolution in the theory and in its feasible experimental implementations. In physical–mathematical terms, these opportunities are closely related to the implications of the approach presented for the solution of two-level dynamics through avoided crossings. Therefore, in this section, we treat some further examples of controllable dynamics by comparison with the traditional approach to the solution of the dynamical problem through the time-dependent Schrödinger equation, so as to highlight opportunities for simple identification of easily solvable evolutionary paths afforded by the use of the MN construction.

Inserting the Hamiltonian (1) and the state (12) into the Schrödinger equation, we obtain^{51,53}

$$i\dot{C}_1(t) = \frac{1}{2}\omega_0(t)e^{-i[\phi(t)-2\int_0^t\Omega(t')dt']}C_2(t), \quad (40a)$$

$$i\dot{C}_2(t) = \frac{1}{2}\omega_0(t)e^{i[\phi(t)-2\int_0^t\Omega(t')dt']}C_1(t). \quad (40b)$$

In the conventional Landau–Zener (LZ) problem, which should be more precisely called the Landau–Zener–Stückelberg–Majorana (LZSM) problem,³ the magnitude and phase of the electronic coupling are both assumed to be constant, and Eqs. (40a) and (40b) are decoupled by their further derivation and arrangement to give (for brevity, we do not indicate the obvious time dependence of C_1 and C_2 unless it is necessary to distinguish their values at $t = 0$ and $t \neq 0$)⁵³

$$\ddot{C}_1 - 2i\Omega(t)\dot{C}_1 + \frac{\omega_0^2}{4}C_1 = 0, \quad (41a)$$

$$\ddot{C}_2 + 2i\Omega(t)\dot{C}_2 + \frac{\omega_0^2}{4}C_2 = 0. \quad (41b)$$

These equations lead to expressions for C_1 and C_2 in terms of parabolic cylinder (Weber) functions,^{3,53,54,110} which are treated numerically or using asymptotic expansions and describe a nonperiodic time evolution of the system.

Condition (18) leads to equations different from (41a) and (41b), and, in physical terms, this implies that it opens new scenarios and offers new means to control the dynamics of the system, with great relevance to a plethora of dynamical problems relevant to quantum technologies, including quantum computing, in which quantum two-level systems play critical roles.^{2,3,38,40,79,111–121} To see this fact, we begin with deriving Eq. (40) with respect to time for

generally time-dependent electronic couplings. From Eq. (40a), we obtain

$$i\ddot{C}_1 = \frac{1}{2}\{\dot{\omega}_0(t)C_2 - i[\dot{\phi}(t) - 2\Omega(t)]\omega_0(t)C_2 + \dot{C}_2\omega_0(t)\} \times e^{-i[\phi(t)-2\int_0^t\Omega(t')dt']}, \quad (42)$$

and, by the insertion of Eqs. (40a) and (40b),

$$\begin{aligned} \ddot{C}_1 &= \frac{1}{\omega_0(t)}\dot{\omega}_0(t)\dot{C}_1 - i[\dot{\phi}(t) - 2\Omega(t)]\dot{C}_1 - \frac{\omega_0^2(t)}{4}C_1 \\ &= -i\left[\dot{\phi}(t) - 2\Omega(t) + i\frac{d}{dt}\ln\omega_0(t)\right]\dot{C}_1 - \frac{\omega_0^2(t)}{4}C_1 \end{aligned} \quad (43)$$

whence

$$\ddot{C}_1 - i\left[2\Omega(t) - \dot{\phi}(t) - i\frac{d}{dt}\ln\omega_0(t)\right]\dot{C}_1 + \frac{\omega_0^2(t)}{4}C_1 = 0, \quad (44a)$$

which is the generalization of Eq. (41a) for time-dependent electronic couplings. Similarly,

$$\ddot{C}_2 + i\left[2\Omega(t) - \dot{\phi}(t) + i\frac{d}{dt}\ln\omega_0(t)\right]\dot{C}_2 + \frac{\omega_0^2(t)}{4}C_2 = 0. \quad (44b)$$

By limiting the following analysis to cases in which the modulus of the coupling is a constant ω_0 while its phase is time dependent, we will identify some classes of situations emerging from (namely, controlled by) condition (7), or (18), and Eq. (44), in which the coherent dynamics of the system is described without resorting to special functions. When condition (7) is satisfied ($\mu = 0$), Eqs. (44a) and (44b) become

$$\ddot{C}_1 + \frac{\omega_0^2}{4}C_1 = 0, \quad \ddot{C}_2 + \frac{\omega_0^2}{4}C_2 = 0, \quad (45)$$

which lead to the expressions for the expansion coefficients C_1 and C_2 in Eqs. (31a) and (31b), obtained above using the extended MN approach. Under condition (18) ($\mu \neq 0$), we obtain, instead,

$$\ddot{C}_1 - i\mu\omega_0\dot{C}_1 + \frac{\omega_0^2}{4}C_1 = 0, \quad \ddot{C}_2 + i\mu\omega_0\dot{C}_2 + \frac{\omega_0^2}{4}C_2 = 0. \quad (46)$$

Setting $C_1(t) = e^{\eta t}$, with η independent of time, one obtains the quadratic equation

$$\eta^2 - i\mu\omega_0\eta + \frac{\omega_0^2}{4} = 0, \quad (47)$$

whose solutions are

$$\eta_{\pm} = \frac{i\omega_0}{2}\left(\mu \pm \sqrt{1 + \mu^2}\right). \quad (48)$$

The general solution of Eq. (46) can be written as

$$\begin{aligned} C_1(t) &= e^{\frac{i\omega_0 t}{2}}\left(C_{11}e^{\frac{i\omega_0 t}{2}\sqrt{1+\mu^2}} + C_{12}e^{-\frac{i\omega_0 t}{2}\sqrt{1+\mu^2}}\right), \\ C_2(t) &= e^{-\frac{i\omega_0 t}{2}}\left(C_{21}e^{\frac{i\omega_0 t}{2}\sqrt{1+\mu^2}} + C_{22}e^{-\frac{i\omega_0 t}{2}\sqrt{1+\mu^2}}\right), \end{aligned} \quad (49)$$

where C_{11} , C_{12} , C_{21} , and C_{22} are constants whose values are fixed through the initial conditions. For example, with the initial condition

$$C_1(0) = 1, \quad C_2(0) = 0, \quad (50)$$

Eqs. (40) and (49) give

$$\begin{aligned} C_1(t) &= \frac{1}{2} e^{i\mu \frac{\omega_0 t}{2}} \left[\left(1 - \frac{\mu}{\sqrt{1+\mu^2}} \right) e^{i\sqrt{1+\mu^2} \frac{\omega_0 t}{2}} \right. \\ &\quad \left. + \left(1 + \frac{\mu}{\sqrt{1+\mu^2}} \right) e^{-i\sqrt{1+\mu^2} \frac{\omega_0 t}{2}} \right] \\ &= e^{i\mu \frac{\omega_0 t}{2}} \left[\cos\left(\sqrt{1+\mu^2} \frac{\omega_0 t}{2}\right) - i \frac{\mu}{\sqrt{1+\mu^2}} \right. \\ &\quad \left. \times \sin\left(\sqrt{1+\mu^2} \frac{\omega_0 t}{2}\right) \right] \end{aligned} \quad (51a)$$

and

$$\begin{aligned} C_2(t) &= -\frac{1}{\sqrt{1+\mu^2}} e^{-i\mu \frac{\omega_0 t}{2}} \left[\frac{e^{i\sqrt{1+\mu^2} \frac{\omega_0 t}{2}} - e^{-i\sqrt{1+\mu^2} \frac{\omega_0 t}{2}}}{2} \right] \\ &= -\frac{i}{\sqrt{1+\mu^2}} \sin\left(\sqrt{1+\mu^2} \frac{\omega_0 t}{2}\right). \end{aligned} \quad (51b)$$

For $\mu = 0$, Eqs. (51a) and (51b) reduce to (31a) and (31b), while for $\mu \rightarrow \infty$, they reduce to (26).

It is worth noting that, once the molecular rotation satisfies condition (19), which depends on $\Omega(t)$ and the absolute value of the coupling, the time evolution of any property that only depends on the square moduli of the expansion coefficients in Eq. (12) shows a universal behavior, independent of the level energy $\Omega(t)$ and dependent on t only through the dynamical time κ . This is exemplified by the time evolutions predicted by Eq. (49), where $\kappa(t) = \omega_0 t/2$.

Finally, we reconsider the LZSM problem, where the coupling is generally assumed to be a constant (Condon approximation for the electronic coupling) and Eqs. (41a) and (41b) are at stake. Moreover, its treatment in Ref. 53 uses both the standard expression for the time-dependent level energy

$$\Omega(t) = \frac{\alpha t}{2} \quad (52)$$

and a more realistic expression for their experimental context given by

$$\Omega(t) = \frac{\alpha\tau}{2} \left(\frac{1}{1+e^{-4t/\tau}} - \frac{1}{2} \right). \quad (53)$$

Here, we assume ω_0 constant, but we use a time-dependent coupling phase ϕ that satisfies condition (19). Then,

$$\Phi(\mu; t) = \sqrt{1+\mu^2} \kappa(t) = \frac{1}{2} \sqrt{1+\mu^2} \omega_0 t. \quad (54)$$

Inserting Eqs. (52) and (53) into Eq. (19), we obtain

$$\phi(t) = 2 \int_0^t \Omega(t') dt' - 2\mu\kappa(t) = \frac{\alpha t^2}{2} - \mu\omega_0 t \quad (55)$$

and

$$\begin{aligned} \phi(t) &= \alpha\tau \int_0^t \left(\frac{1}{1+e^{-4t'/\tau}} - \frac{1}{2} \right) dt' - 2\mu\kappa(t) \\ &= -\frac{\alpha\tau}{2} t - \frac{\alpha\tau^2}{4} \int_0^{-4t/\tau} \frac{1}{1+e^x} dx - \mu\omega_0 t \\ &= \frac{\alpha\tau}{2} t + \frac{\alpha\tau^2}{4} \ln\left(1+e^{-4t/\tau}\right) - \mu\omega_0 t, \end{aligned} \quad (56)$$

respectively (in the last equation, we integrated by parts and used the fact that $x = \ln e^x$). At this point, the expansion coefficients that describe the evolving state of the system are given by Eqs. (20)–(22) with the insertion of the quantity in Eq. (54).

E. CT quantum gate

It is worth noting that, under suitable physical conditions (that is, for suitable physical parameters), the evolution operator matrix built above can realize some quantum gates or relevant linear combinations of quantum gates at given instants or at infinite time, which practically means after the conclusion of the passage through the avoided crossing of the two levels. For example, let us consider the time

$$t_0 = \frac{\pi}{\omega_0 \sqrt{1+\mu^2}}. \quad (57)$$

It is $\Phi(\mu; t_0) = \pi/2 = \vartheta(\mu; t_0)$. Requiring that $\phi(t_0) = -\pi$, and assuming that $\Omega(t) = \Omega_0$ and $\omega_0(t) = \omega_0$, relation (19) gives

$$\begin{aligned} -\frac{\pi}{2} &= \frac{\Omega_0 \pi}{\omega_0 \sqrt{1+\mu^2}} - \frac{\mu\pi}{2\sqrt{1+\mu^2}} \rightarrow \sqrt{1+\mu^2} \\ &= \mu - \frac{2\Omega_0}{\omega_0} \rightarrow \mu = 1 - \frac{\omega_0}{4\Omega_0}, \end{aligned} \quad (58)$$

which is possible for $\Omega_0 \geq \omega_0/4$ since μ cannot be negative. Then, we obtain

$$U(t_0) = \begin{pmatrix} \sqrt{\frac{\mu^2}{1+\mu^2}} & \frac{1}{\sqrt{1+\mu^2}} \\ -\frac{1}{\sqrt{1+\mu^2}} & \sqrt{\frac{\mu^2}{1+\mu^2}} \end{pmatrix}, \quad (59)$$

which has the form of one of the alternative unitary operations applied to an ancilla qubit in Ref. 122 to construct a quantum algorithm for simulating Hamiltonian dynamics based on linear combinations of unitary operators (that is, quantum gates).^{122–125} The operator (59) can be alternatively obtained at the end of the nonadiabatic passage. To this end, we consider, for example, the Gaussian-like time-dependent coupling magnitude,

$$\omega_0(t) = \frac{4}{\sqrt{\pi}\sigma} e^{-\frac{t^2}{\sigma^2}} \quad (t \geq 0), \quad (60)$$

which gives

$$\kappa(\infty) = \frac{2}{\sqrt{\pi}\sigma} \int_0^\infty e^{-\frac{t'^2}{\sigma^2}} dt' = 1, \quad (61)$$

where we used the shorthand notation $\kappa(\infty)$ for $\lim_{t \rightarrow \infty} \kappa(t)$. From $\Phi(\mu; \infty) = \sqrt{1 + \mu^2} = \pi/2 = \vartheta(\mu; \infty)$, we obtain $\mu = \sqrt{\frac{\pi^2}{4} - 1}$, and condition (18) with $\phi(\infty) = -\pi$ gives

$$-\frac{\pi}{2} = \int_0^t \Omega(t') dt' - \sqrt{\frac{\pi^2}{4} - 1} \rightarrow \int_0^t \Omega(t') dt' = \sqrt{\frac{\pi^2}{4} - 1} - \frac{\pi}{2}. \quad (62)$$

This condition can be satisfied for

$$\Omega(t) = \frac{\sqrt{\pi^2 - 4} - \pi}{\sqrt{\pi}\sigma} e^{-\frac{t^2}{\sigma^2}} \quad (t \geq 0) \quad (63)$$

(while negative values of Ω are allowed, positive values can also be readily obtained). Equation (59) follows again.

III. CONCLUDING REMARKS

We have proposed a new theoretical approach to the study of two-state CT systems that offers new opportunities for engineering and controlling the CT dynamics, with implications for its use in next-generation quantum technologies where two-level systems physically realize the fundamental unit of information. Our approach uses the MN method,¹⁸ which has been previously employed to investigate spin systems in time-dependent magnetic fields and quantum electrodynamics contexts. In this regard, our study aims to profitably merge methodological and conceptual ingredients from this research area with CT theory. Since the MN method was developed within an inverse-problem philosophy with the aim of generating solvable Hamiltonians for two-level quantum systems, it is particularly appropriate for engineering CT systems with desired dynamic evolutions of possible use for quantum information and computation tasks.

Through several examples, we show that suitable rotations of the charge donor or acceptor can be used to experimentally realize condition (7) on the phase of the electronic coupling between the initial and final (adiabatic) charge states and that this condition is a subset of a more general set of conditions represented by Eq. (19), which correspond to a vast class of exactly solvable Hamiltonian models with time evolution operators as in Eq. (21). The system evolutions described by these operators depend on a parameter, μ , which is here given a physical meaning in Eq. (33), as a measure of the system's ability to experience a nonadiabatic dynamics through the avoided level crossing region. The discussion of μ also gives us the opportunity to highlight similarities between the rotation in the charge-transfer system and the rotation of the reference frame in semiclassical Rabi models.

We extend the MN method in terms of its applicability to any time interval and then use it to solve the two-state charge transfer problem in some interesting cases. We emphasize that universal features of system dynamics emerge on a coupling-dependent dynamic timescale defined as in Eq. (15). As exemplified above, the MN approach to the solution of the CT dynamical problem clearly matches its traditional solution in terms of time-dependent Schrödinger equation, where both approaches are applicable. However, the MN approach highlights since the outset circumstances

in which this solution does not require the use of Weber's special functions, thus avoiding the related limitations in terms of further analytical elaborations.

We finally show that the CT time evolution operator in Eq. (21) offers opportunities to realize quantum gates. More generally, the theoretical framework of the present study is proposed as a natural approach to the engineering and analysis of CT systems (as well as other classes of two-level systems that are characterized by similar formal descriptions) with controllable coherent dynamics relevant to quantum information and computation applications.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Agostino Migliore: Conceptualization (lead); Formal analysis (lead); Funding acquisition (lead); Investigation (lead); Methodology (equal); Software (lead); Supervision (equal); Validation (equal); Visualization (lead); Writing – original draft (lead); Writing – review & editing (equal). **Antonino Messina:** Conceptualization (supporting); Formal analysis (supporting); Methodology (equal); Supervision (equal); Validation (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

APPENDIX: EXTENSION OF THE MN METHOD

Here, we derive Eqs. (20) and (27), which extend the MN method to all times and to the limit case $\mu = 0$, respectively. We first consider the extension of the method over time, starting from the analysis in Ref. 18. For the cases studied here and in the present notation, the magnitude of the coupling for nonzero μ is expressed, in Ref. 18, as the following function of θ :

$$\frac{\omega_0(t)}{2} = \frac{\mu}{\mu^2 + \sin^2 \vartheta(t)} \dot{\vartheta}(t), \quad (A1)$$

which gives (using the integral 2.562.1 on p. 177 of Ref. 126)

$$\begin{aligned} \Phi(\mu; t) &= \sqrt{1 + \mu^2} \int_0^{\vartheta(\mu; t)} \frac{\mu d\vartheta}{\mu^2 + \sin^2 \vartheta} \\ &= \arctan \left[\frac{\sqrt{1 + \mu^2}}{\mu} \tan \vartheta(\mu; t) \right], \end{aligned} \quad (A2)$$

from which

$$\tan \vartheta = \frac{\mu}{\sqrt{1 + \mu^2}} \tan \Phi. \quad (\text{A3})$$

In Ref. 18, $\Phi(\mu; t)$ is directly expressed as an integral, while $\vartheta(\mu; t)$ is obtained from Eq. (A3). At this point, it is necessary to note that the expression of $b(t)$ reported in Eq. (17) is obtained from Eqs. (14) and (16) of Ref. 18 in terms of $\sin \vartheta$ and then written in terms of $\sin \Phi$ by deriving the relationship between the two sines from Eq. (A3), with the assumption that they have the same sign. This sign choice, together with Eq. (A3), implies that $\cos \vartheta$ and $\cos \Phi$ also have the same sign. However, the standard definition of ϑ from Eq. (A3) consists of taking the principal value of the inverse trigonometric function as is done in Eq. (16b), and this results in jumps in the sign of $a(t)$, while $b(t)$ continuously varies with $\sin \Phi(\mu; t)$. In other terms, the original formalism applies from $t = 0$ to the time $t = t_{\pi/2}(\mu)$ at which $\Phi = \frac{\pi}{2}$, while the signs of $a(t)$ and $b(t)$ would be inconsistent after this time.

The extension of the method to $\Phi \in [0, 2\pi[$, and thus to any larger value of Φ , is easily performed by noting that Φ is defined by Eq. (14) as a continuously growing function of time and that the use of the multivalued arctan function in the expression for ϑ restores the continuity in the phase of $a(t)$ and maintains, at times $t > t_{\pi/2}(\mu)$, the consistency of the phase choice made by writing $b(t)$ as a function of $\sin \Phi$.

To conclude the temporal extension of the method, we must notice that, although ϑ tends to $\frac{\pi}{2}$ and $\frac{3\pi}{2}$ when Φ does, Eq. (A3) cannot be set at $t_{\pi/2}(\mu)$ and $t_{3\pi/2}(\mu)$ because the two trigonometric functions are not defined at these times. Therefore, if we want to express ϑ from its relationship with Φ , we need to use an analytic continuation as follows:

$$\vartheta(\mu; t_k) = \lim_{t \rightarrow t_k(\mu)} \left\{ \arctan \left[\frac{\mu}{\sqrt{1 + \mu^2}} \tan \Phi(\mu; t) \right] \right\} = k \quad (\text{A4})$$

for $k = \frac{\pi}{2}, \frac{3\pi}{2}$.

At this point, Eq. (20) immediately follows from the above.

Next, we consider the extension of the MN method to $\mu = 0$, where the variable ϑ is discretized. We need to express ϑ again as a multivalued trigonometric function,

$$\vartheta(\mu; t) = \arctan \left[\frac{\mu}{\sqrt{1 + \mu^2}} \tan \Phi(\mu; t) \right]. \quad (\text{A5})$$

For $0 < t < t_{\pi/2}(\mu)$, it is (note that μ tends to zero from the right)

$$\vartheta(0; t) = \lim_{\mu \rightarrow 0} \left\{ \arctan \left[\frac{\mu}{\sqrt{1 + \mu^2}} \tan \Phi(\mu; t) \right] \right\} = 0. \quad (\text{A6})$$

For $t_{\pi/2}(\mu) < t < t_{3\pi/2}(\mu)$, we use the next higher branch of arctan, thus obtaining $\vartheta(0; t) = \pi$, and so forth. In compact form, we can write

$$\vartheta(0; t) = \lim_{\mu \rightarrow 0^+} \vartheta(\mu; t) = \begin{cases} (n+1)\pi & \text{for } t_{(n+\frac{1}{2})\pi} < t < t_{(n+1)\pi} \\ n\pi & \text{for } t_{n\pi} \leq t < t_{(n+\frac{1}{2})\pi} \end{cases} \quad (n \in \mathbb{N}_0). \quad (\text{A7})$$

Extending to negative times,

$$\vartheta(0; t) = \begin{cases} 0 & \text{for } t_{(-\frac{1}{2}+2n)\pi} < t < t_{(\frac{1}{2}+2n)\pi} \\ \pi & \text{for } t_{(\frac{1}{2}+2n)\pi} < t < t_{(\frac{3}{2}+2n)\pi} \end{cases} \quad (n \in \mathbb{Z}). \quad (\text{A8})$$

At this point, the values can be assigned to ϑ for $t = t_{(\pm\frac{1}{2}+2n)\pi}$ as in Eq. (27), but they are, indeed, unimportant, because the complex exponential function with argument ϑ appears only multiplied by $|\cos \Phi(0; t)| = |\cos \kappa(t)|$ in the expression of a for $\mu = 0$.

Finally, Eq. (28) results from the fact that

$$\text{sgn}[\cos \kappa(t)] = \begin{cases} 1 = e^{\pm i\vartheta(0;t)} & \text{for } t_{(-\frac{1}{2}+2n)\pi} < t < t_{(\frac{1}{2}+2n)\pi} \\ 0 & \text{for } t = t_{(\pm\frac{1}{2}+2n)\pi} \\ -1 = e^{\pm i\vartheta(0;t)} & \text{for } t_{(\frac{1}{2}+2n)\pi} < t < t_{(\frac{3}{2}+2n)\pi} \end{cases} \quad (n \in \mathbb{Z}). \quad (\text{A9})$$

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