Maximum population transfer in a periodically driven two-level system

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We show that the evolution of a two-level quantum system in a sinusoidal driving field is remarkably regular for specific combinations of the field parameters. At these points, identified through analysis of the Floquet quasienergy spectrum, population transfer is optimal and takes place through a series of well defined steps of fixed duration. We also show how the corresponding evolution operator can be approximated at all times by a very simple analytical expression. Finally, we apply these results to designing a control protocol in a realistic molecular model, characterized by a complex multilevel structure.

Understanding the coherent control of quantum systems using time-dependent interacting fields is a goal of primary interest in many different areas, including chemical reactivity, nanotechnology, and quantum information processing. To this end, simple analytically solvable two-level systems (TLS) are often used since they can efficiently describe the dynamics. One popular choice is the Landau-Zener model, in which the driving field is assumed to vary linearly with time. Nonetheless, in many experimental situations sinusoidal, time-periodic control fields are easier to produce and manipulate, and are thus the preferred option. Beyond the well-known Rabi model (which accounts for the weak driving case), many approaches have been put forward in the literature in order to give a clear insight into this type of systems.

A striking phenomenon induced by time-periodic fields is the so-called coherent destruction of tunneling (CDT), first predicted by Grossman et al. and then observed experimentally. A particle in a symmetric double-well potential usually oscillates back and forth, if initially localized in one of the wells. However, if the depth of the wells oscillates in time, the tunneling rate may dramatically change. Actually, for certain combinations of the driving parameters, the rate vanishes, resulting in an effective localization of the particle in the initial well. As previously shown, this behavior takes place only when some Floquet quasienergies are degenerate.

In this Letter, we show that the Floquet spectrum of a TLS under a sinusoidal driving in the regime of intermediate frequencies (ω ≈ Δ, being ω the driving frequency and Δ the characteristic frequency of the system) has a second kind of “special points”, defined by the condition that the quasienergy separation is a local maximum, where: (i) population inversion is achieved after a time interval that only depends on the quasienergy difference, (ii) the evolution of the populations happens through a series of well-defined steps of fixed duration, in which the probability remains approximately constant, and (iii) the full time-dependent evolution operator U(t) can be obtained in a very simple analytical form, which provides a clear physical interpretation of (ii). Finally, let us remark that our result is of very general applicability, and then we present here, as an illustration, a relevant application to the control of the LiNC═LiCN isomerization, described by a realistic potential function.

We consider a hamiltonian of the form

\[ H(t) = (\Delta/2)\sigma_x + \varepsilon(t)\sigma_z, \]

where \( \sigma_x \) and \( \sigma_z \) are the usual Pauli operators. The instantaneous eigenvalues of \( H \) as a function of the control parameter \( \varepsilon \) show the usual avoided crossing (AC) structure, reaching a minimal separation of \( \Delta \) at \( \varepsilon = 0 \). We consider the driving field to be \( \varepsilon(t) = A \cos(\omega t) \), and define \( T = 2\pi/\omega \) as the period of \( H(t) \). When dealing with this type of systems, it is customary to factorize the evolution operator as \( U(t) = U_{1}(t)U_{2}(t) \), where \( U_{1}(t) = \exp[-i\gamma_{z}(t)\sigma_{z}/2] \) can be regarded as a transformation to a rotating frame, since \( \gamma_{z}(t) = 2 \int \varepsilon(\tau)d\tau = (2A/\omega)\sin(\omega t) \). The remaining factor is obtained by the transformed Schrödinger equation \( iU_{2}(t) = H_{2}(t)U_{2}(t) \), where \( H_{2}(t) = U_{1}^{\dagger}HU_{1} \)

\[ H_{2}(t) = (\Delta/2)\{\cos[\gamma_{z}(t)]\sigma_x + \sin[\gamma_{z}(t)]\sigma_y\}. \]

The time dependence in this expression can be averaged out over one period of the driving field in the high frequency regime, i.e. \( \omega \gg \Delta \), using the rotating wave approximation (RWA). This gives \( U_{2}(t) = \exp\left(-i\Delta_{0}^{'}t\sigma_x\right) \), with \( \Delta_{0}^{'} = \Delta_{0}(2A/\omega) \), being \( \Delta_{0} \) a Bessel function. For the values of \( 2A/\omega \) corresponding to the zeros of \( J_{0} \), the evolution operator \( U(t) \) is diagonal in the \( \sigma_z \) basis set, \( \{0\}, \{1\} \), which explains the occurrence of the CDT phenomenon. For any other value of the amplitude \( A \) the population inversion between these
When the RWA cannot be applied, a more general framework has to be used. In this case, Floquet theory \cite{Laub} shows that for a time-periodic hamiltonian a full set of orthonormal solutions for the corresponding Schrödinger equation exists, which are of the form $|\Psi_\alpha(t)\rangle = \exp(-i\epsilon_\alpha t)|\Phi_\alpha(t)\rangle$, with $\alpha = 0, 1$ for a TLS. The real-valued quantities $\{\epsilon_\alpha\}$ are called quasienergies, and the states $\{|\Phi_\alpha(t)\rangle\}$, which share the periodicity of $H(t)$, are called Floquet states. The quasienergies can be obtained in an easy way by diagonalizing $U(T)$, something that can be done by numerically computing the time evolution from $t = 0$ to $t = T$ of an adequate basis set. In this way, the eigenphases of $U(T)$ give the desired quasienergies, which in the case $\omega \gg \Delta$, discussed above, simply correspond to

$$\epsilon_{\pm} = \pm \Delta'/2.$$  \hspace{1cm} (4)

This expression implies that the spectrum contains an infinite set of degeneracies as $A/\omega$ increases, and also that expression \cite{3} can be rewritten as $T_F = \pi/|\epsilon_+ - \epsilon_-|$. When computed for lower frequencies, the quasienergies spectrum changes considerably for small amplitudes \cite{11}, as shown in Fig. 1 (top) for the case $\omega = \Delta$. However, the results still show the typical ribbon structure and expression \cite{4} remains a reasonable approximation for $A/\omega \gtrsim 3$. To assess the validity of expression \cite{3} in this regime, we simulate the evolution of the system starting from $|0\rangle$ for different values of amplitude, calculating the non-decay probability $P_{ND}(t) = |\langle 0|\psi(t)\rangle|^2$ at time $t = T_F$, in each case. The results that are shown in Fig. 1 (bottom) reflect a more complex behavior than that predicted by the high frequency model, in which $P_{ND}(T_F) = 0$ is expected for every value of $A$ corresponding to finite $T_F$. More interesting is the fact that the results of Fig. 1 reveal the existence of a new outstanding feature: the points for which $P_{ND} \approx 0$ pack around certain values of $A$, which correspond to the points of local maximum separation between quasienergies, i.e. the “peaks” of the spectrum. We have labeled these points by $n = 1, 2, \ldots$ in the figure. To analyze this behavior in more detail, we consider the time evolution of $P_{ND}(t)$ for different values of the driving amplitude. Some representative numerical results are shown in Fig. 2, where it can be seen that $P_{ND}$ shows a “ladder”-type structure, decreasing through a series of steps, in each of which the probability oscillates rapidly around a constant mean value. Moreover, as $n$ grows, the frequency of these oscillations increases, while the corresponding amplitude decreases. These steps occur whenever the field $\epsilon(t)$ reaches a maximum or a minimum, and then their amount can be estimated by the ratio $2\omega/\Omega$, with $\Omega = 2\pi/T_F$. This behavior can be accounted for using the transfer matrix approach \cite{5}. Also interesting is the fact that when $A$ is set outside the peaks, the rapid oscillations still take place, but the “stairs” become worse defined, and the probability ladder may not necessarily be decreasing at all times, as illustrated in Fig. 2 (b).

The singular behavior shown by the dynamics at the extrema of the quasienergy spectrum admits a (deeper) analytical explanation. Hamiltonian $H_2$ in eq. \cite{2} can be regarded as equivalent to the interaction of a spin-1/2 particle with a unit intensity magnetic field $B(t)$ rotating periodically but non-uniformly in the $x-y$ plane, such that the instantaneous Larmor frequency is $\Delta$. The components of this field can be expanded in Fourier series

$$B_x(t) \equiv \cos(\gamma_2(t)) = J_0(\nu) + 2 \sum_{n=1}^{\infty} J_{2n}(\nu) \cos(2n\omega t),$$  \hspace{1cm} (5)

$$B_y(t) \equiv \sin(\gamma_2(t)) = 2 \sum_{n=1}^{\infty} J_{2n-1}(\nu) \sin [(2n-1)\omega t].$$  \hspace{1cm} (6)

where $\nu = 2A/\omega$. If considered separately, the time integrals of both components give the accumulated phase throughout the evolution. As shown in Fig. 2 the contribution $\gamma_2(t) \equiv \frac{1}{\omega} \int_0^t B_x(s) \, ds$ shows the ladder structure found previously, as the result of integrating a constant term added to an oscillating series. On the other hand, integrating $B_y(t)$ shows that the leading term vanishes when $J_1(2A/\omega) = 0$, this resulting in a small phase contribution of the whole series. Also notice that, because

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Top: Quasienergy spectrum for the two level hamiltonian of eq. \cite{1} as a function of $A/\omega$. The boxed numbers $n = 1, 2, \ldots$ label the points of the spectrum in which the quasienergy separation is locally maximal. On top, we plot the analytical expression \cite{1}. Bottom: Non decay probability $P_{ND}(t)$, defined by eq. \cite{3}, calculated by numerical simulations of the system prepared in the initial state $|0\rangle$, as a function of $A/\omega$. Near the degeneracies, where $T_F$ vanishes, results are not displayed. In all cases, the resonant case (i.e. $\omega = \Delta$) is studied.}
\end{figure}
of the relation $J_0^\prime(x) = -J_1(x)$, the zeros of $J_0$ match the extrema of $J_0$, also giving the position of the spectrum peaks mentioned above, as long as approximation \[4\] holds. In this situation, $U_2(t)$ is well approximated by $U_2(t) = \exp \left[-\frac{i}{2} \gamma_x(t)\right] = \exp \left[-\frac{i}{2} \left[\Delta t + \delta(t)\right] \sigma_x\right]$ with

$$\delta(t) = \frac{\Delta}{\omega} \sum_n \frac{J_{2n}(2A/\omega)}{n} \sin(2\omega nt),$$

which is $T$-periodic and can be seen to vanish in the limit $\omega/\Delta$, as expected. Plots of $\delta(t)$ for different values of $n$ are displayed in Fig. 3. This model approximates very well the population dynamics when the field parameters are set at the extrema of the quasenergy spectrum. A representative example is shown in Fig. 2 and more cases are discussed in the Supplemental Material.

In this case the full evolution operator becomes

$$U = U_1U_2 = \exp \left[-i \gamma_z(t) \sigma_z/2\right] \exp \left[-i \gamma_x(t) \sigma_x/2\right],$$

and the particular time-dependence of $\gamma_z$ and $\gamma_x$ over one period of the driving field (see Fig. 3) allows to rationalize the resulting dynamics, as follows. Let us consider a partition of the driving period in six equal intervals, each one of length $T/6$. Then $\gamma_x(t)$ and $\gamma_z(t)$ can be approximated as a sequence of linear and constant pieces, both showing opposite behaviors during the interval. That is, from $t = T/6$ to $t = 2T/6$, $\gamma_z$ is almost constant and $\gamma_x$ increases with a positive slope; the resulting $U(t)$ being then well approximated by a $z$-rotation in Bloch sphere. From $t = 2T/6$ to $t = 3T/6$ (and also in the following interval) $\gamma_x$ shows low-amplitude oscillations around a steady value, while $\gamma_z$ decreases in time almost linearly; $U(t)$ will then produce rapid rotations around the $z$-axis rendering nearly constant populations. Similarly, we can continue with the rest of the intervals in the period. Finally, note that this discussion also accounts for the phenomenon of maximal/optimal population transfer at these points, shown in Fig. 1. Using this model, a simple calculation gives $P_{ND}(T_F) = \sin^2(\delta(T_F)/2)$, which is numerically seen never exceeding $10^{-2}$.

Let us discuss next the relevance of our results for problems in control theory \[17\]. For this purpose, we consider the LiNC/LiCN molecular system that has been extensively studied in connection with the theoretical issue of quantum chaos \[18\], and also in the simulation of the LiNC$\rightleftharpoons$LiCN isomerization reaction \[19\] in solution, where it was proven to provide the first unambiguous example of the elusive Kramer’ turnover \[20\]. This system can be adequately studied by a 2dof model, where the C-N stretch coordinate is kept frozen at its equilibrium distance, while the position of the Li is parametrized by the Li–CN stretch and the Li–C–N bending coordinates, $R$ and $\theta$, as indicated in Fig. 4(a), and the potential interactions are realistically described with \textit{ab initio} quantum mechanical calculations \[21\]. Our aim here is to design a
control protocol for the isomerization process, inducing the motion of the molecule from the most stable isomer, LiNC corresponding to \( \theta = 180^\circ \), to the less stable one, LiCN with \( \theta = 0 \). The idea is to apply a mixed dc electric field, \( \tilde{E}(t) = E(t) \), corresponding to the Hamiltonian:

\[
H(R, \theta, P_R, P_\theta, t) = H_{LiCN}(R, \theta, P_R, P_\theta) - \tilde{d}(R, \theta) \cdot \tilde{E}(t),
\]

where \( H_{LiCN} \) is the 2 dof rotationless hamiltonian of the molecule \( \phi_R \) and \( \tilde{d}(R, \theta) \) is the electric dipole operator \([13]\). Note that we assume that the isomerization process is fast compared with the rotation of the molecule. Further details on this model are given in the Supplemental Material.

In order to design an effective control strategy, we consider the electric field to be parallel to the C–N bond and compute the vibrational level spectrum as a function of the (static) electric field intensity \( E \), as previously proposed in \([14]\). Results are shown in Fig. 4. As a rule of thumb, positive-slope energy lines correspond to LiNC states (that is, those localized in the \( \theta = 180^\circ \) well), and the negative-slope lines to LiCN states (\( \theta \sim 0 \)). A careful analysis of the spectrum shows that most ACs in the low-energy region are very narrow and thus correspond to interactions too weak to be useful in the control process. However, there is an AC centered at \( E = E_{dc} \approx 2.39 \times 10^{-3} \) a.u., with a spectral gap of \( \Delta = 0.15 \) cm\(^{-1} \) which seems suitable for our purposes. Indeed, far for from the AC, the involved eigenstates, termed \([1]\) and \([2]\), show localization in opposite wells (see Fig. 4) as needed in the control process. We thus propose the use of an electric field of the form:

\[
E(t) = E_{dc} + A \cos(\omega t).
\]

It is important to emphasize here that high driving frequencies \( (\omega \gg \Delta) \) cannot be used in this case, since the quasienergy spectrum is a function of the ratio \( A/\omega \); high values of \( \omega \) would then imply the use of large amplitudes, which would in turn preclude the validity of the two-level approximation in a many level system showing multiple ACs, like ours. Indeed, we are in the intermediate frequency regime discussed before, so that our main results becomes relevant for this problem. Actually, defining \( \omega = \Delta \) make some expressions derived previously straightforwardly applicable \([24]\). As an illustration, we show in the bottom panel of Fig. 4 the evolution obtained starting from state \([1] \) \([23]\) for \( A = (1.23 \times 10^{-3}) \Delta \) (corresponding to \( n = 4 \)). As can be seen, the total control time is approximately \( 2.3 \times 2\pi/\Delta \approx 0.51 \) ps, which is well below the 400 ps reported in Ref. \([13]\), this meaning that the control mechanism proposed here is much more efficient.

In summary, we have shown the existence of set of special points in the quasienergy spectrum of a periodically-driven TLS, where the evolution of the populations takes place with maximum probability transfer. These points correspond to the maxima in the typical ribbon structure exhibited by the spectrum, localized between the degeneracies predicted by the occurrence of CDT. We have also shown that for these particular combinations of the driving parameters the full evolution operator for the system can be well approximated by a very simple analytical expression, which reveals that the system evolves in a Bloch sphere following a sequence of rotations around the \( x \) and \( z \) axes. This behavior reflects in the appearance of a series of steps in the time evolution of the populations, whose average takes the form of a decreasing “ladder”. It should be noted that these results correspond to the intermediate frequency regime \( (\omega \approx \Delta) \) where the RWA does not apply. Finally, we have made use of these conclusions to control the isomerization process in a tritomic molecule. Using this realistic model, we have shown that the regime described in this Letter is particularly relevant in many level systems showing multiple ACs, where the use of large-amplitude driving fields would make the simple two-level approximation invalid. We also believe that the results shown in this Letter could be of great interest to the vast ongoing research on driven superconducting qubits \([25]\), usually modelled.
also by Hamiltonian (1).

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[22] Note that the AC in model (1) is symmetrical; in the general case, the slopes of the diabatic branches must be taken into account (see more information in the Supplemental Material.)

[23] Note that preparing the system in state $|1\rangle$ can be done by exciting the molecule at zero field and then adiabatically tuning the field from $\mathcal{E} = 0$ to $\mathcal{E} = \mathcal{E}_{dc}$, as explained in [14].
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ANALYSIS OF THE TIME EVOLUTION

In Fig. S1 we show a series of plots where the population evolution is displayed, together with the corresponding Bloch sphere trajectories. The values of amplitudes used range from $A = 6.58\omega$ ($n = 4$) to $A = 8.21\omega$ ($n = 5$), including intermediate values between the peaks. When the amplitude of the field is set in the peaks of the spectrum (see cases a and b in the figure), it can be seen that the analytical expression in eq. (8) of the main text provides an excellent approximation not only to the temporal evolution of the populations, but also to the full trajectory of the state in Bloch sphere.

Figure S1. Time evolution of the non decay probability for the system starting in state $|0\rangle$, in the resonant ($\omega = \Delta$) regime. Thick lines show the results given by numerical simulations, while the black dashed curve is given by the analytical solution (see main text for more details). For comparison, we show the solution predicted in the high frequency regime (solid light gray line), and a cosine function with the frequency of the driving field, $\omega$ (dashed light gray line). Along with each plot, the corresponding Bloch sphere trajectory is shown; blue lines correspond to the numerical simulation, while the black curves shown in (a) and (b) are given by the analytical solution. Values of amplitude used: (a) $A = 6.58\omega$ ($n = 4$), (b) $A = 7.2\omega$, (c) $A = 7.64\omega$, (d) $A = 8.22\omega$ ($n = 5$).

THE LINC/LICN MOLECULAR SYSTEM

Theoretical model

As stated in the main text, we consider the CN vibrational mode to be decoupled from the motion of the Li atom, and we take the distance between the C and N atoms to be frozen at its equilibrium value, $r_e = 2.186$ a.u. Thus, the rotationless vibrational Hamiltonian function of the Li-NC$\leftrightarrow$Li-CN isomerizing system can be expressed as

$$H_{\text{LINC}} = \frac{P_R^2}{2\mu_1} + \frac{P_\theta^2}{2} \left( \frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r_e^2} \right) + V(R, \theta),$$

where $R$ and $\theta$ are Jacobi coordinates specifying the position of the Li atom with respect to the center mass of the CN moiety, as can be seen in Fig. 4 of the main text. $P_R$ and $P_\theta$ are the associate conjugate momenta,
Figure S2. Contour plot representation for relevant functions in configuration space \((R, \theta)\) for LiNC/LiCN isomerizing system.
(a) Potential energy surface \(V(R, \theta)\), with energy contour spacing \(\Delta E = 1000 \text{ cm}^{-1}\) from \(E = 0\). (b) Parallel to N→C bond component of the dipole moment \(d_||(R, \theta)\), with dipole contour spacing \(\Delta d_|| = 0.25 \text{ a.u.}\) from \(d_|| = 0\), where dashed contours correspond to negative values. (c) Perpendicular to N→C bond component of the dipole moment \(d_\perp(R, \theta)\), with dipole contour spacing \(\Delta d_\perp = 0.25 \text{ a.u.}\) from \(d_\perp = 0\). The minimum energy path connecting both energy wells has been superimposed as a grey thick dashed line in the three figures.

and \(\mu_1 = m_{\text{Li}}(m_C + m_N)/(m_{\text{Li}} + m_C + m_N)\) and \(\mu_2 = m_Cm_N/(m_C + m_N)\) are reduced masses, \(m_X\) being the corresponding atomic masses. The potential energy \(V(R, \theta)\) is given by an expansion in Legendre polynomials, fitting the corresponding \textit{ab initio} quantum calculations, taken from the literature \[S1\]. As it is shown in Fig. S2 (a), the potential energy surface has a global minimum at \(\theta = 180^\circ\) \((R = 4.349 \text{ a.u.)}\) and a relative minimum at \(\theta = 0\) \((R = 4.795 \text{ a.u.})\), corresponding to Li-NC and Li-CN isomers, respectively.

The LiCN molecule is a polar molecule, i.e., it has a permanent dipole moment, so that an additional potential energy term appear in the presence of an electric field \(\vec{E}\), leading to the effective Hamiltonian function

\[
H = H_{\text{LiCN}} - \vec{d}(R, \theta) \cdot \vec{E},
\]

where \(\vec{d}(R, \theta)\) is the dipole moment of the LiNC/LiCN molecular system. For the dipole moment, we have taken from the literature the \textit{ab initio} calculations fitted to an analytic expansion in associated Legendre functions of Brocks et al. \[S2\]. The parallel and perpendicular to N→C bond components of the dipole moment from this analytic expansion are depicted in Fig. S2.

Calculations

Using the discrete variable representation - distributed Gaussian basis (DVR-DGB) method introduced in Ref. \[S3\], we obtained the first 75 low lying eigenstates of Hamiltonian \[S2\], converged to 0.01 cm\(^{-1}\), for different values of the static electric field \(\mathcal{E}\) ranging from 0 to \(3 \times 10^{-3}\) a.u. We chose to work with the basis set given by the eigenstates at \(\mathcal{E} = 1.45 \times 10^{-3}\) a.u., corresponding to the position of the central AC involving the first positive and the first negative slope levels. Using this representation, the full energy spectrum of Fig. 4 in the main text was calculated, and it was verified that the results agreed with the spectrum obtained with the DVR-DGB method.

General model for an avoided crossing (AC)

The eigenvalues of the two-level hamiltonian

\[
H_{AC} = \left( \begin{array}{cc} \alpha_0 \varepsilon & \frac{\mathcal{E}}{2} \\ \frac{\mathcal{E}}{2} & -\alpha_1 \varepsilon \end{array} \right) = \Delta \sigma_z + \varepsilon \left( \frac{\alpha_0 - \alpha_1}{2} \sigma_x + \frac{\alpha_0 + \alpha_1}{2} \mathbb{1} \right)
\]

form an hyperbola in the \((\lambda, E)\) plane \((E \text{ being the energy})\), centered at \((0, 0)\), whose vertex represents an avoided crossing (AC) with an energy gap \(\Delta\). The coefficients \(\alpha_i\) \((i = 0, 1)\) are the slopes of the diabatic branches. The symmetric case is given by \(\alpha_0 = -\alpha_1 = 1\), as in eq. (1) in the main text. If we set \(\varepsilon = \varepsilon(t) = A \cos(\omega t)\), it can be
easily seen that by renormalizing the amplitude $A \to A' = \frac{\Delta \alpha}{2} A$ (where $\Delta \alpha \equiv \alpha_0 - \alpha_1$), all results drawn from the symmetric model can be extrapolated to this more general case. For example, the AC shown in Fig. 4 (b) in the main text has $\Delta \alpha = 1082.835$ cm$^{-1}$/a.u.

**Quasienergy spectrum**

In Fig. S3 we show the quasienergy spectrum of the molecular system as a function of $A'/\omega$, for different values of driving frequency $\omega$. Only the region of the spectrum corresponding to the AC of Fig. 4 (b) of the main text is displayed. It can be seen that the ribbon structure becomes clearly distorted as the frequency increases. This can be explained by the fact that, as the amplitude increases, the control parameter reaches zones of the energy spectrum (Fig. 4 of the main text) where more levels are involved, and thus the two-level approximation fails.

![Figure S3. Quasienergy spectrum for the molecular system, focused in the energy range of the avoided crossing under study. Values of frequency of the driving field used in each case: (a) $\omega = \Delta_M$, (b) $\omega = 10\Delta_M$, (c) $\omega = 20\Delta_M$.](image)

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