Universal Measure for the Impact of Adiabaticity on Quantum Transitions

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Adiabaticity is crucial for our understanding of complex quantum dynamics and thus for advancing fundamental physics and technology, but its impact cannot yet be quantified in complex but common cases where dynamics is only partially adiabatic, several eigenstates are simultaneously populated and transitions between noneigenstates are of key interest. We construct a universally applicable measure that can quantify the adiabaticity of quantum transitions in an arbitrary basis. Our measure distinguishes transitions that occur due to the adiabatic change of populated system eigenstates from transitions that occur due to beating between several eigenstates and can handle nonadiabatic events. While all quantum dynamics fall within the scope of the measure, we demonstrate its usage and utility through two important material science problems—energy and charge transfer—where adiabaticity could be effected by nuclear motion and its quantification will aid not only in unraveling mechanisms but also in system design, for example, of light harvesting systems.

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Introduction.—Adiabatic changes of quantum states via temporal manipulation of the Hamiltonian are essential for understanding and designing complex quantum dynamics. They are of key utility in adiabatic quantum computation [1–4], quantum optimization [5], chemical reactions [6–10], nuclear motion in photochemistry [11], and quantum state preparation [12–15], thus permeating quantum technologies. Despite this, no universal quantitative measure for adiabaticity existed so far, while they were proposed for entanglement [16], coherence [17], and non-Markovianity [18], for example.

When starting in one fixed initial quantum state, transforming that into a target state, the net change of state populations can be used. This can constrain whether evolution due to a changing Hamiltonian should be fully adiabatic, although this remains nontrivial to predict [19–21]. In more complex scenarios, the initial state will be a superposition of eigenstates and additionally dynamics will give rise to frequent nonadiabatic transitions between these. Then it becomes highly nontrivial to assess to what extent transitions *between noneigenstates* are reinforced by adiabatic evolution or would equally have occurred with a constant Hamiltonian, owing to interference between eigenstates. The problem arises across disciplines, for example, when analyzing quantum transport of an electronic excitation in a molecular aggregate [22–24] through molecular motion [25–31], vibrationally assisted intersystem crossing and charge transfer [32–37], carrier transport [38], electron transport at interfaces [39,40], or state generation and ionization in atomic physics [41,42].

We address this challenge by constructing a universal measure, to discriminate between transitions in an arbitrary basis that are caused by time-evolving eigenstates and those caused by beating between superimposed eigenstates. We derive the measure from the time-dependent Schrödinger equation (TDSE) based on general considerations valid for all quantum dynamics (QD) problems to ensure universal applicability. We then demonstrate its utility by applying it to two examples of high relevance to material science: energy and charge transport across molecules.

Problem statement.—Consider a time-dependent Hamiltonian $\hat{H}(t)$ with a discrete spectrum and let $\{|n\rangle\}$ be an arbitrary, time-independent, orthonormal basis of the Hilbert space, the diabatic basis. Meanwhile $|\varphi_k(t)\rangle$, an element of the adiabatic basis, is a solution of the instantaneous eigenproblem $\hat{H}(t)|\varphi_k(t)\rangle = U_k(t)|\varphi_k(t)\rangle$, with energy $U_k(t)$. The time-evolving state $|\Psi(t)\rangle$ can be expressed in either basis as $|\Psi(t)\rangle = \sum_n c_n(t)|n\rangle$ or $|\Psi(t)\rangle = \sum_k \tilde{c}_k(t)|\varphi_k(t)\rangle$, with expansion coefficients related by $c_n(t) = \sum_k d_n^{(k)}(t)\tilde{c}_k(t)$, where $d_n^{(k)}(t) = \langle n|\varphi_k(t)\rangle$ is the amplitude of $|n\rangle$ contained in eigenstate $|\varphi_k(t)\rangle$. For sufficiently slow variation of $\hat{H}(t)$ relative to inverse frequency gaps, the quantum adiabatic theorem guarantees that eigenstates are followed with constant populations, $\tilde{p}_k = \text{const}$. When this is *not* the case, we nonetheless seek to quantify to which extent a given transition in another basis $|n\rangle \to |n'\rangle$ has been aided or hindered by partial adiabatic state following, or was indifferent to it.

Suppose we seek the root cause of population changes in the basis $\{|n\rangle\}$ instead of $\{|\varphi_k(t)\rangle\}$, which could be because $\{|n\rangle\}$ is spatially localized to describe transport or represents the angular momenta of an atom in an electromagnetic field, as examples. These populations are

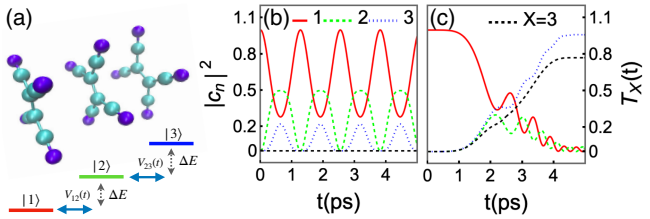

FIG. 1. Beating versus adiabatic transitions. (a) Nondegenerate, coupled, three-level system with basis $|n\rangle$, which could be a molecular trimer aggregate, with $|n\rangle$ representing, e.g., localized energy or charge on monomer n. (b) Quantum transitions due to beating. We show populations $p_n = |\langle n|\Psi(t)\rangle|^2$ in states $n = 1, 2, 3$ as per legend, for constant transition matrix elements $V_{\mathrm{nm}}(t) = V_0$, using $\Delta E = 3$ and $V_0 = 2$. The black dashed line in (b),(c) is the adiabatic transport measure $T_3(t)$. (c) Quantum transitions due to adiabatic changes in the Hamiltonian, while varying $V_{\mathrm{nm}}(t)$ as discussed in the text. ΔE and legend are as in (b).

$$p_n(t) = |c_n(t)|^2 = \sum_{k,k'} \tilde{c}^*_{k'}(t)\tilde{c}_k(t) d^{(k)}_n(t) d^{(k')*}_n(t). \quad (1)$$

Now there are three distinct contributions to changes in $p_n(t)$. (i) For a time independent Hamiltonian, we would have $d^{(k)}_n = \text{const}$ and $\tilde{c}_k(t) = \tilde{c}_k(0)\exp[-iU_k t/\hbar]$; nonetheless, populations p_n may vary in time due to *beating* from interference terms containing $e^{-i\Delta U_{kk'}t/\hbar}$ with $\Delta U_{kk'} = U_{k'} - U_k$. (ii) For a time dependent Hamiltonian, populations can change also due to variations of the $|\varphi_k(t)\rangle$ affecting the $d^{(k)}_n(t)$, clearly an *adiabatic* contribution, or (iii) there could be *nonadiabatic* changes in $|\tilde{c}_k(t)|$. All cases are illustrated in Fig. 1 for a three-level system with Hamiltonian

$$\hat{H}(t) = \sum_n E_n |n\rangle\langle n| + \sum_{nm;n\neq m} V_{nm}(t)|n\rangle\langle m|. \quad (2)$$

When only nearest neighbor couplings exist and are constant, $V_{n(n+1)}(t) = V_0$, with system initialized in $|1\rangle$, it eventually reaches state $|3\rangle$ due to beating, see Fig. 1(b). When couplings vary as $V_{12}(t) = \bar{V}_{12}\sin^2(\pi t/2t_{\max})$ and $V_{23}(t) = \bar{V}_{23}\cos^2(\pi t/2t_{\max})$ with $\bar{V}_{\mathrm{nm}} = 8$, the system reaches $|3\rangle$ mainly due to the temporal change of the Hamiltonian, Fig. 1(c). In generic complex QD both phenomena coexist, yet one often wishes to quantify to what extent adiabaticity contributes. For example, we might seek to optimize electron transfer at interfaces [35] or atomic state transfer to a certain angular momentum [41].

Measure for the adiabaticity of transitions.—To tackle this problem, we split the population change $\dot{p}_n(t)$ into

$$\dot{p}_n(t) = \sum_{k,k'}\Big[(\dot{\tilde{c}}^*_{k'}(t)\tilde{c}_k(t) + \tilde{c}^*_{k'}(t)\dot{\tilde{c}}_k(t))d^{(k)}_n(t)d^{(k')*}_n(t) + \tilde{c}^*_{k'}(t)\tilde{c}_k(t)\Big(\dot{d}^{(k)}_n(t)d^{(k')*}_n(t) + d^{(k)}_n(t)\dot{d}^{(k')*}_n(t)\Big)\Big]. \quad (3)$$

The last line already contains contributions to $\dot{p}_n(t)$ only from temporal changes of $|\varphi_k(t)\rangle$ and thus will be related to adiabatic state following. However, in scenarios where the $\tilde{c}_k(t)$ are not constant, this can be modified by contributions from the first line, see Supplemental Material [43]. For a time-independent Hamiltonian, we know that $\tilde{c}_k(t) = \tilde{c}_k(0)\exp[-iU_k t/\hbar]$, to reach

$$\dot{\tilde{c}}^*_{k'}(t)\tilde{c}_k(t) + \tilde{c}^*_{k'}(t)\dot{\tilde{c}}_k(t) = i\frac{\Delta U_{kk'}}{\hbar}\tilde{c}^*_{k'}(0)\tilde{c}_k(0)e^{-i\Delta U_{kk'}t/\hbar}, \quad (4)$$

quantifying the temporal changes of $p_n(t)$ due to beating between different eigenstates, where $\Delta U_{kk'} = U'_k - U_k$. In that case, only the phase of (4) is time dependent, not the modulus.

We now exploit this observation to isolate contributions from adiabatic population changes. Let us write the coefficient $\tilde{c}_k(t)$ in polar representation $\tilde{c}_k(t) = \tilde{a}_k(t)e^{i\tilde{b}_k(t)}$, with $\tilde{a}_k, \tilde{b}_k \in \mathbb{R}$, $\tilde{a}_k > 0$, such that $\dot{\tilde{c}}_k(t) = \dot{\tilde{a}}_k e^{i\tilde{b}_k(t)} + \tilde{a}_k(t)[i\dot{\tilde{b}}_k]e^{i\tilde{b}_k(t)}$. After insertion into (3), we remove the phase evolution ($\dot{\tilde{b}}_k \to 0$), with remainder

$$f_n(t) = \sum_{k,k'}\Big[\big(\dot{\tilde{a}}_{k'}e^{-i\tilde{b}_{k'}}\tilde{c}_k + \tilde{c}^*_{k'}\dot{\tilde{a}}_k e^{i\tilde{b}_k}\big)d^{(k)}_n d^{(k')*}_n + \tilde{c}^*_{k'}\tilde{c}_k\Big(\dot{d}^{(k)}_n d^{(k')*}_n + d^{(k)}_n \dot{d}^{(k')*}_n\Big)\Big], \quad (5)$$

where the time argument t of all functions on the rhs is suppressed. The real variable $f_n(t)$ measures the rate of change of the population in state n due to temporal changes in the eigenspectrum of the Hamiltonian only, by construction not containing any contribution from beating between multiple occupied eigenstates.

Equation (5) now enables the quantification of adiabaticity in complex scenarios. It significantly extends the construction of Ref. [35], proposed *ad hoc* in the context of physical chemistry, which omitted the first line of Eq. (5). This approach does not correctly handle strongly nonadiabatic jumps, as we show in Supplemental Material [43].

The best final assembly of a measure for the adiabatic contribution to transitions into a target state $|X\rangle$ will depend on the physical scenario of interest. Here, we shall use the net population adiabatically entering that state, $T_X(t) = \int_0^t dt' f_X(t')$, for demonstrations. Another proposal is described in Supplemental Material [43]. We verified in Fig. 1 that $T_X(t)$ can successfully discriminate adiabatic transitions from beating. It remains zero for beating in (b), and approaches the transferred target population $T_X(t) \to p_X$ for a strongly adiabatic transition, reaching $T_X(t) = p_X$ if the transition was exclusively adiabatic. The derivation above is quite general and hence valid for an arbitrary QD problem. In practice, the ingredients for the measure are either readily available in the model employed or can be

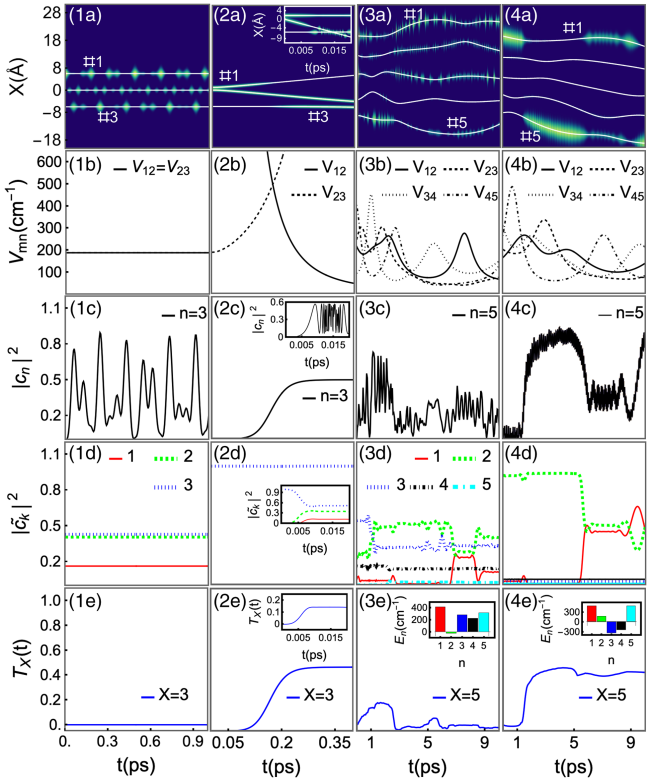

FIG. 2. Adiabaticity in complex dynamics of few level systems. The first row (1a)–(4a) shows the trajectories $X_n(t)$ of individual molecules (white lines) with the excitation probabilities of each molecule $p_n = |c_n|^2$ (diabatic populations) indicated by the width of color shading. This just forms one example which can cause Hamiltonian matrix elements to change as in (1b)–(4b). (1c)–(4c) show population p_X in the target state only. (1d)–(4d) show adiabatic populations $\tilde{p}_n = |\tilde{c}_n|^2$ and (1e)–(4e) the proposed adiabaticity measure for the target state T_X (solid line). The columns differ by initial state and parameters as discussed in the text. The insets in column 2 are for a similar scenario as the main panels but with faster changes and thus less adiabatic dynamics, those in (3e)–(4e) show basis state energy disorder.

built through suitable approximations. Hence, $T_X(t)$ is accessible in the context of all QD methodologies, making its scope universal. We will now benchmark the measure on a more complex set of examples, representing the problem we intend to address.

Quantum transitions during complex dynamics.—We consider transitions in few level systems in which the interaction matrix elements V_{nm} of the Hamiltonian (2) nontrivially vary with time. To be specific and realistic, we have an example in mind, in which state $|n\rangle$ describes energy localized with disorder E_n [22,49,50] on the nth monomer of a chain of N molecules. It can then migrate to other molecules through long range interactions $V_{nm} = \mu^2/|X_m(t) - X_n(t)|^3$. These in turn vary according to molecular positions $X_n(t)$, shown in Fig. 2 row (a), governed by an exemplary model for motion discussed in Supplemental Material [43]. However, the resultant changes in the Hamiltonian, shown in Fig. 2 row (b) could just as well have a completely different physical origin, and are all that enter subsequent results. We solve the TDSE to simulate QD from Eq. (2), with results shown in Fig. 2, rows (c)–(e). The first column (1a)–(1e) shows a case with unchanging Hamiltonian. The initial state is $|1\rangle$, which is not an eigenstate, and population quickly reaches $|3\rangle$ in the resultant beating, contribution (i) below Eq. (1). Per construction, the adiabaticity measure $T_3(t)$ remains zero, as can be seen in (1e). In the second column (2a)–(2e), interactions do change and the initial state is an eigenstate $|\psi(0)\rangle = (|n=1\rangle + |n=2\rangle)/\sqrt{2}$. The system reaches the output state solely due to the adiabatic quantum state following, contribution (ii), as in [51,52]. Hence, all population remains constantly in the initially occupied eigenstate, as shown in (2d). Once the excitation has reached the output state with probability $p = 1/2$ at about $t = 0.3$ ps, also the measure $T_3 = 1/2$, indicating that the transition has been entirely adiabatic. For the same scenario, but made less adiabatic by a faster change of the Hamiltonian, we see in the (2d) inset that the adiabatic population has dropped to 0.5 by the time $t = 0.01$ ps. The adiabatic measure in the inset of (2e) accordingly decreased, compared to the ideal adiabatic transition in the main panel.

The remaining two columns 3 and 4 show key cases for which the measure was developed: complex quantum dynamics with wildly changing Hamiltonian (see Supplemental Material [43] for a possible model of origin). We distribute E_n with probabilities $p_E(E_n) = (1/\sqrt{2\pi\sigma_E})e^{-E_n^2/(2\sigma_E^2)}$ showing the choice in row (e). In both columns, the system is initialized in $|1\rangle$, later reaching $|5\rangle$ with a significant probability, while adiabatic populations are constant only for finite intervals between significant changes. Thus, dynamics is merely partially adiabatic.

To manually assess how strongly adiabatic following has helped the system to make a transition into state $|5\rangle$ now requires careful inspection of populations in both adiabatic and diabatic bases. One then sees in column 4 that at the arrival, $t \approx 1.5$ ps, the population remains predominantly conserved within a single eigenstate, indicating a primarily adiabatic process. However, minute nonadiabaticity during the transition reduces the measure by ≈0.2. On the other hand the departure at $t = 5$ ps involved nonadiabatic splitting onto two eigenstates, contribution (iii), and subsequent beating between these states, resulting in no significant change in the measure at this later stage. The main contribution to population on site 5 in column 3 after 3 ps is from beating, since the initial adiabatic contribution has been adiabatically removed at $t = 3$ ps, according to T_5. Our measure now relieves us of the need for such detailed scrutiny of the dynamics, can be evaluated automatically, and thus allows ensemble averages.

Measure in a charge transfer problem, using ab initio many-body quantum dynamics.—To demonstrate the broad utility of the measure, we now move from single particle

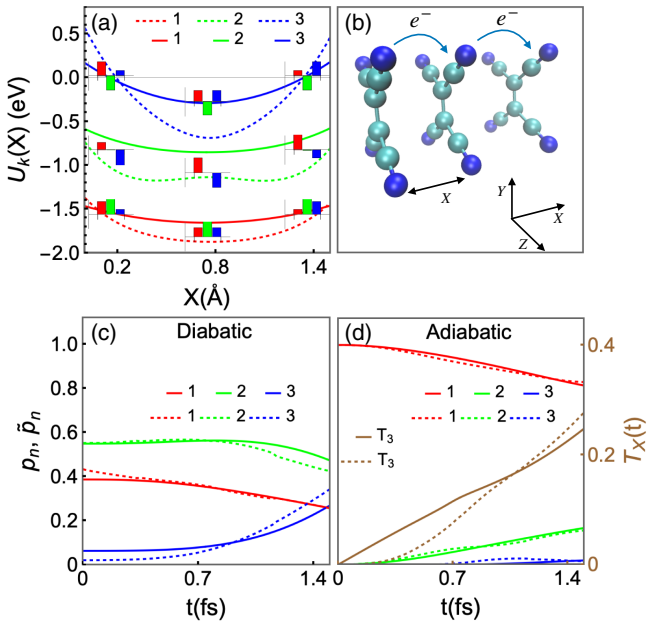

FIG. 3. Charge transport between molecules. (a) The lowest three energies $U_k(X)$, from DFT (dashed) and effective state model (solid) of the TCNE trimer shown in (b). (c) Diabatic populations $p_n = |c_n|^2$ and (d) adiabatic populations $\tilde{p}_n = |\tilde{c}_n|^2$ in the same style for both methods. The adiabaticity measure T_3 is finally shown in (d), right axis.

type models to full fledged *ab initio* many-body QD in a realistic system. We choose time-dependent density functional theory (TDDFT) [53–55], given its good compromise between accuracy, computational cost and size scalability. While a wave function is initially not directly available in TDDFT, we will demonstrate how all required quantities for the adiabaticity measure can be evaluated from simulations, such that the measure can be leveraged for much of quantum chemistry and material science. The same will be possible for other advanced quantum many-body methods, as long as one can extract or approximate the two inputs to the measure [$\tilde{c}_k$, $d_n^{(k)}$ in Eq. (5)].

We consider a prototypical charge transport example, in an artificially moved tetracyanoethylene (TCNE) trimer [56–60], shown in Fig. 3(b), onto which we place an additional electron. Within the *ab initio* framework, setting up the measure requires the adiabatic many-body states, their coefficients, and the charge-localized (diabatic) basis states. The ground-state wave function is obtained as a Slater determinant of the molecular orbitals calculated from density functional theory (DFT), while the excited states are constructed as linear combinations of excited singles [53,61]. For constructing diabats, we employ constrained density functional theory [62–64], which limits the additional electronic charge separately on individual TCNE molecules in our trimer. Both are implemented in NWCHEM [65]. Finally, the time-dependent adiabatic coefficients $\tilde{c}_k(t)$ are obtained by solving the TDSE $i\hbar(\partial/\partial t)\tilde{c}_k(t) = U_k(t)\tilde{c}_k(t) - i\hbar\sum_m \kappa_{km}(t)\tilde{c}_m(t)$, where $\kappa_{km}(t) = \langle\phi_k(t)|(\partial/\partial t)|\phi_m(t)\rangle$ are the nonadiabatic couplings. For this, we have used the trajectory surface hopping code SHARC [66,67] with disabled hopping, interfaced with ORCA [68,69]. More details on extraction of quantities from TDDFT can be found in Supplemental Material [43].

Charge transport on the trimer can be understood in the effective model (2), where $|n\rangle$ implies an excess electron localized on molecule number n, E_n are on-site energies, and V_{nm} electron transfer amplitudes. All Hamiltonian elements depend on the position $\mathbf{X}$ of the three monomers [43]. We fix the outer two molecules a distance $d = 7$ Å apart, and initially locate the middle molecule $X(t = 0) = 2.9$ Å from the first, such that V_{12} dominates. The trimer starts in its ground state ($k = 1$), with electron shared between sites number 1 and 2, thus $d_3^{(k=1)} \approx 0$.

We then move molecule number 2 toward $X(t_{\mathrm{fin}}) = 4.1$ Å until $t_{\mathrm{fin}} = 1.5$ fs with constant exaggerated velocity, such that the excess electron now becomes localized on molecules number 2 and 3. The charge on molecule number 3 hence increases. The extent to which this was aided by adiabatically following the ground state is captured by the measure T_3, see Fig. 3(d). Its value at t_{f} of $T_3(t_{\mathrm{f}})/|c_3(t_{\mathrm{f}})|^2 = 0.8 < 1$, also flags nonadiabatic effects. While this example was chosen for simplicity, the full power of the measure will unfold in *ab initio* simulations of complex dynamics such as shown in Fig. 2, columns 3 and 4. Here, we just demonstrated that the proposed measure can be integrated with TDDFT and thus leveraged for chemistry or material science.

Conclusions.—We quantified the extent to which adiabatic following of eigenstates is the root cause of quantum transitions in a noneigenbasis. The usage of our construction was demonstrated using clear-cut cases in which transitions are either fully due to adiabaticity or not at all. We then tackled examples that had defied earlier techniques: complex quantum dynamics with multiple populated eigenstates and imperfectly adiabatic dynamics, in which a manual assessment of the relevance of adiabaticity becomes very challenging and an automatic one impossible. We finally introduced a pipeline for the evaluation of the measure in TDDFT, as an example for a widely used and sophisticated technique for quantum many body dynamics. Quantification of the adiabatic contribution to a desired quantum process can now aid the design of quantum technologies and understanding of quantum dynamics, ranging from nuclear motion for dye-sensitized solar cells [70,71] or charge transfer to the acceptor [35] over the design of thin-film optical and optoelectronic devices [72] to state preparation in atomic physics [41,42]. More formally, our measure will enable the discussion of adiabaticity in the framework of quantum resource theory [73] or the separate quantification of geometric phase effects [74–76] in quantum transitions.

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