Nonadiabatic transition probabilities for quantum systems in electromagnetic fields: Dephasing and population relaxation due to contact with a bath

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Abstract: We contrast Dirac's theory of transition probabilities and the theory of nonadiabatic transition probabilities, applied to a perturbed system that is coupled to a bath. In Dirac's analysis, the presence of an excited state $| k_0 \rangle$ in the time-dependent wave function constitutes a transition. In the nonadiabatic theory, a transition occurs when the wave function develops a term that is not adiabatically connected to the initial state. Landau and Lifshitz separated Dirac's excited-state coefficients into a term that follows the adiabatic theorem of Born and Fock and a nonadiabatic term that represents excitation across an energy gap. If the system remains coherent, the two approaches are equivalent. However, differences between the two approaches arise when coupling to a bath causes dephasing, a situation that was not treated by Dirac. For two-level model systems in static electric fields, we add relaxation terms to the Liouville equation for the time derivative of the density matrix. We contrast the results obtained from the two theories. In the analysis based on Dirac's transition probabilities, the steady state of the system is not an equilibrium state; also, the steady-state population $\rho_{kk,s}$ increases with increasing strength of the perturbation and its value depends on the dephasing time T_2. In the nonadiabatic theory, the system evolves to thermal equilibrium with the bath. The difference is not simply due to the choice of basis, because the difference remains when the results are transformed to a common basis.

I. Introduction

In this work, we derive results for the probability of transition to an excited state for a quantum system in an applied electric field, when the system is coupled to a bath. The standard transition probability derived by Dirac[1,2] differs from the nonadiabatic transition probability first proposed by Landau and Lifshitz.[3] Dirac gave the transition probability as $| c_k(t) |^2$, in terms of the coefficient for the excited state $| k_0 \rangle$ in the basis of eigenfunctions of the unperturbed Hamiltonian H_0. Landau and Lifshitz instead gave the transition probability as $| b_k(t) |^2$, in terms of the coefficient for the instantaneous eigenstate $| k' \rangle$ of the full Hamiltonian, including the perturbation. If the wave function remains coherent, the differences are not physically significant. In that case, the differences simply reflect the choice of the basis set.

In this work, we test the robustness of the two forms of the transition probability for extension to cases where the quantum system loses coherence, a situation that is outside the scope of Dirac's theory[1,2] and also outside the scope of the nonadiabatic analysis given by Landau and Lifshitz.[3] We allow for dephasing and population relaxation due to contact between the system and a thermal bath. We treat two-level model systems in static electric fields by adding relaxation terms to the Liouville equation for the density matrix.[4] Then we contrast the results obtained by taking $| c_k(t) |^2$ as the transition probability and those obtained taking $| b_k(t) |^2$ as the transition probability. The loss of coherence of the wave function leads to physically meaningful differences between the two approaches. We show that the differences are not due simply to the choice of basis, by expressing the results in a common basis set. To our knowledge, the current work provides the first illustration of these differences.

The theory of quantum transition probabilities due to a time-dependent perturbation developed by Dirac has been used almost universally in perturbative treatments since his initial work.[1,2] Dirac expanded the solution of the time-dependent Schrödinger equation as a series in terms of the eigenstates $| k_0 \rangle$ of the unperturbed Hamiltonian, where $H_0 | k_0 \rangle = E_{k,0} | k_0 \rangle$. For a system that started in the ground state as t $\rightarrow -\infty$, the excited-state coefficients have the form $c_k(t) \exp(-iE_{k,0}\, t/\hbar)$. The values of $c_k(t)$ are determined by coupled first-order, linear differential equations.[1,2] Dirac stated that the transition probability is given by $|\, c_k(t)\, |^2$.

Landau and Lifshitz[3] separated $c_k(t)$ into two terms by integrating by parts in Dirac's equation for $c_k(t)$. The boundary term $a_k(t)$ characterizes the adjustment of the initial state to the perturbation by the incorporation of excited-state components, without actual excitation. The results obtained using $a_k(t)$ are identical to those from the adiabatic theorem of Born and Fock,[5] since inclusion of $a_k(t)$ preserves the adiabatic connection of the perturbed state to the initial state of the system, $|\, 0_0 \rangle$. The integral that remains after integration by parts gives the nonadiabatic coefficient $b_k(t)$. Working within linear response, Landau and Lifshitz[3] showed that the nonadiabatic probability amplitudes $b_k(t)$ are identical up to a phase to the coefficients for the instantaneous eigenstates $|\, k'(t) \rangle$ of the full, perturbed Hamiltonian $H_0 + H'(t)$ in the time-dependent wave function $|\, \Psi(t) \rangle$. Mandal and Hunt extended this result to nonlinear response.[6] The quantities $|\, b_k(t)\, |^2$, including both linear and nonlinear response, give the probability of transition to the instantaneous eigenstate $|\, k'(t) \rangle$, which is adiabatically connected to an excited state $|\, k_0 \rangle$ of the unperturbed Hamiltonian. The nonadiabatic theory represents an analysis in the basis of instantaneous eigenfunctions of the full Hamiltonian, rather than the unperturbed eigenbasis.

In Dirac's approach, if the excited state $|\, k_0 \rangle$ appears as a component in the wave function for a system that has started in the ground state as t $\rightarrow -\infty$, its appearance is regarded as a transition. A projection of the time-dependent wave function onto $|\, k_0 \rangle$ yields $c_k(t) \exp(-iE_{k,0}\, t/\hbar)$, so the transition probability is obtained as $|\, c_k(t)\, |^2$. In the analysis by Landau and Lifshitz, a transition is said to have occurred if the wave function contains a component that is not adiabatically connected to the initial state. Hence the probability of an excitation away from the perturbed ground state is given by $| b_k(t) |^2$.

In this work, we show that the difference in the definition of a transition may lead to numerical differences in the predictions about excited-state occupancies *within a single basis set*, when the quantum system relaxes due to contact with a bath. Experimentally detectable consequences of the difference between the two theories may also arise when the reaction to an experimental probe depends on the existence of an energy gap between a state of the perturbed system and the adiabatically perturbed starting state.

The effects of coupling to a bath are described by adding relaxation terms to the Liouville equation for the time-evolution of the density matrix[4] in the basis of the instantaneous eigenstates. The proper treatment of relaxation effects is more complicated in the basis $\{ | j_0 \rangle \}$ of eigenstates of H_0. If the relaxation terms are added to the Liouville equation in the $\{ | j_0 \rangle \}$ basis, the system does not evolve to equilibrium. The apparent value $\rho_{kk,s}$ of the excited-state population at steady state depends on the dephasing time T_2; and $\rho_{kk,s}$ increases rather than decreasing, as the perturbation strength increases. These features remain after transformation to a common basis set. Physically significant differences arise because the interactions with the bath convert a system from a pure state to a mixed state.

We use the term "nonadiabatic" refer to any quantum process that does not follow the adiabatic theorem.[5] Hence our analysis allows for rotationally and vibrationally nonadiabatic processes, in addition to electronically nonadiabatic processes.[7-9] In future applications to electronic transitions, we plan to use the nonadiabatic theory to characterize the initial excitation to an excited electronic potential surface, caused by an ultrafast laser pulse. We envision that the subsequent time-evolution of the molecule including nonadiabatic electronic transitions due to non-Born-Oppenheimer effects would be treated by existing theory, which accounts for first- and second-derivative nonadiabatic coupling.[10-13] Reviews of methods of treating nonadiabatic electronic transitions associated with nuclear motion have been provided by Tully,[14] Yarkony,[15] Yonehara, Hanasaki, and Takatsuka,[16] Curchod and Martínez,[17] Crespo-Otero and Barbatti,[18] Agostini and Curchod,[19] Wang *et al.*,[20] and Smith and Akimov.[21] Interestingly, representation-dependence also arises in surface-hopping calculations,[22-25] because of differences in the velocity-adjustment process in the adiabatic and nonadiabatic bases. This can be minimized, e.g., by use of global flux surface hopping[26] or surface hopping by consensus.[27] As in the current work, proper inclusion of decoherence is also important in surface-hopping calculations.[25,28,29]

Similarities exist between the notation used in this work and the notation used in the Förster[30-37] theory or in the Redfield-type theory of exciton transfer.[33,36,38-46] Here we focus on different physical phenomena, where interactions with a bath cause population relaxation and decoherence, without exciton transfer.

In earlier work, Mandal and Hunt have carried the nonadiabatic transition theory beyond the results given by Landau and Lifshitz.[3] We proved that the energy of a perturbed system separates cleanly into adiabatic and nonadiabatic terms, without cross-terms.[6] We proved that the power absorbed by a molecule from a time-dependent electromagnetic field is equal to the time-derivative of the nonadiabatic term in the energy, to second order.[47] We derived the n^{th} moments of the energy distribution as sums over excited states of $| b_k(t) |^2 (E_k - E_0)^n$, up to third order in the perturbation.[48] The equations for the moments in terms of $| c_k(t) |^2$ seem to lack a simple physical interpretation.[48]

Previously we have compared the functional forms of $| b_k(t) |^2$ and $| c_k(t) |^2$ in perturbations consisting of a harmonic wave in a Gaussian envelope,[49] a simple Gaussian pulse,[50] and a "plateau pulse" where the perturbing field remains constant for an interval.[50] In Section II of the current work, we provide analytical results for the Dirac coefficients, the adiabatic coefficients, and the nonadiabatic coefficients over the full time range of a transient electric field that rises via a half-Gaussian, remains constant for an interval, and then returns to zero via a falling half-Gaussian. Dirac's form of the transition probability $| c_k(t) |^2$ necessarily oscillates while the perturbing field is constant, while the nonadiabatic transition probability remains constant. We have shown earlier that it is possible to capture this difference "on the fly," by imposing a second perturbing field that overlaps in time with first pulse, while the field of the first pulse is constant.[51]

In Section III, we analyze the results in the limit as the widths of the half-Gaussians go to zero, and the field remains constant for an interval τ. Dirac's transition probability $| c_k(\tau) |^2$ shows oscillations, with a period that depends on the product of τ and the transition frequency ω_{k0}. Carried to all orders, these oscillations are sometimes described as Rabi oscillations[52-56] in a constant field. Here, we show that the nonadiabatic theory produces identical oscillations, even though no transitions occur while the field is acting, within this theory. Because of the oscillations, an increase in the duration τ of the constant field may increase the transition probability; but somewhat counter-intuitively, increasing the duration of the constant field may decrease the transition probability, and even reduce it to zero.

The analysis in Secs. II and III provides the groundwork for our treatment of the response to a perturbing field that is imposed suddenly and then remains constant. In these two sections, our analysis is limited to linear response. In Sec. IV, we treat the response to all orders in the perturbation, due to the sudden imposition of a constant field. We solve the Liouville equations for the density matrices[4] of two-level model systems in the perturbing field. The systems are otherwise isolated, so their wave functions remain coherent.

That assumption is removed in Sec. V, where we allow for dephasing and population relaxation. We determine the time evolution of the density matrix for a system that starts in the ground state of the unperturbed Hamiltonian and then is suddenly subject to a constant applied field. In the nonadiabatic transition theory, the perturbed eigenfunction basis is used, while in the extension of Dirac's theory, the unperturbed eigenfunction basis is used. Adding relaxation terms to the Liouville equation in the perturbed basis yields Redfield theory.[57-64] This approach is consistent with the assumption in Redfield's work that the full Hamiltonian of the system is diagonal in the basis set.[57,62] The system evolves to thermodynamic equilibrium in the long-time limit, when the density matrix is cast in the perturbed eigenfunction basis. More generally, Redfield commented, "If the system has a time-dependent Hamiltonian which varies slowly compared to the motion of the thermal bath, the same equation of motion is obeyed [i.e., the Redfield equation], and the system is relaxed by the bath toward a Boltzmann distribution with respect to its instantaneous Hamiltonian."[57]

In Sec. V, we also test a model for the time-evolution of the density matrix in the unperturbed eigenfunction basis, obtained by simply adding relaxation terms to the Liouville equation.[4,57-62] We find that the stationary solution of the Liouville equation plus relaxation terms is displaced from equilibrium, when expressed in the unperturbed basis. Transformation of the time-dependent results in the perturbed basis back into the unperturbed basis gives different results from the direct evolution in the unperturbed basis. For the two-level model systems, the differences depend on a host of parameters: the strength of the applied field, the transition dipole, the energy difference between the two unperturbed states, the temperature, and the values of the population relaxation time T_1 and the dephasing time T_2.[65,66] The elements of the relaxation matrix depend on the spectral density of the bath, see, e.g., Refs. 62, 67, and 68. We find the correct form of the time-evolution equations for the density matrix in the unperturbed basis, by transforming the Redfield equations in the perturbed basis back to the unperturbed basis.

More sophisticated treatments, going beyond the Redfield equation in the secular approximation, are possible. For example, nonsecular contributions to the relaxation matrix can be retained;[69-73] the effects of a finite bath size[74-76] and feedback from the system to the bath[77-79] can be included. Initial correlations between the quantum system and the bath can also be taken into account.[80-83] A closely related alternative treatment is based on the Lindblad equation,[84-89] the most general generator of Markovian dynamics in quantum systems.[89] That approach also ensures the positivity of the density operator.[84-86] Quantum systems interacting with thermal baths have been treated with multiple forms of the master equation,[75,76,90-94] including versions that are coarse-grained[72,95] or partially coarse-grained,[96] local,[73] nonlocal,[97] or global.[98] A time-dependent convex mix of the solutions of the local and global equations has been suggested.[99] Space[100] and time[101] correlations of the noise have been included explicitly in master-equation treatments. Generalized master equations have been developed to treat a quantum system in a quantum environment.[102,103] Equations of the Nakajima-Zwanzig type[104-106] contain a memory kernel[107-111] and an inhomogeneous term that accounts for the initial system-bath correlations.

Non-Markovian behavior has also been investigated;[112-115] for example, in the non-Markovian limit, time-correlated noise has been shown to lead to noncanonical dependence of the population distribution on temperature.[101] A stochastic Schrödinger equation corresponds to the Redfield equation with "slipped" initial conditions; the general version is non-Markovian, but if the bath is delta-correlated, a Markovian process results.[116] An exact reduced density matrix for the quantum harmonic oscillator, correct to second order in system-bath coupling has been obtained by nonequilibrium Green's function techniques and used to validate a modified Redfield solution.[117]

Alternative treatments of quantum systems in heat baths have been based on distribution functions in state space[118] or phase space.[119-122] The evolution of the reduced density matrix has also been addressed with tensor propagator[123] and projection operator[124] methods; the latter also yields a general Redfield approach to tunnelling in a molecule embedded in solvent.[125,126] Path integral methods[77,111,127-129] have been used to obtain influence functionals[127] and to analyze the time evolution of reduced density matrices.[77,111,128,129] In particular, quantum-classical path integral methods have made it possible to obtain numerically exact, fully quantum mechanical results for dynamics in systems with a large number of vibrational modes.[129]

The level of analysis that we have adopted is sufficient to show the differences between the results obtained within the nonadiabatic transition theory and the extended Dirac theory, after transformation to the same basis set. We anticipate that the differences will persist in a more detailed treatment based on a master equation or a generalized master equation.

In Section VI, we conclude by providing a brief summary and discussion of planned extensions of this work.

II. Transition probabilities for a system in a pure state, in a transient applied field

For a quantum system with an unperturbed Hamiltonian H_0 in a perturbation $\lambda H'(t)$, the time-dependent Schrödinger equation is

$$H(t) \mid \Psi(t) \rangle = [H_0 + \lambda H'(t)] \mid \Psi(t) \rangle = (i\hbar)\, \partial \mid \Psi(t) \rangle / \partial t \ . \tag{1}$$

Dirac[1,2] solved Eq. (1) by writing the solution as a series in the unperturbed eigenfunctions $\mid k_0 \rangle$, where $H_0 \mid k_0 \rangle = E_{k,0} \mid k_0 \rangle$,

$$\mid \Psi(t) \rangle = \sum_k c_k(t) \exp(-iE_{k,0}\, t/\hbar) \mid k_0 \rangle \ . \tag{2}$$

For a system that is initially in the unperturbed ground state $\mid 0_0 \rangle$ of H_0 as $t \to -\infty$, $c_k(t)$ satisfies

$$c_k(t) = (-i\lambda/\hbar) \int_{-\infty}^{t} \langle k_0 \mid H'(t') \mid 0_0 \rangle \exp[\, i\, (E_{k,0} - E_{0,0})\, t'/\hbar \,] \ dt' \ , \tag{3}$$

to first order in the perturbation.[1,2] Dirac expressed the probability of a transition to the excited state $\mid k_0 \rangle$ as $\mid c_k(t) \mid^2 = \mid \langle k_0 \mid \Psi(t) \rangle \mid^2$. In a modified approach, Landau and Lifshitz suggested integrating by parts in Eq. (3), to separate $c_k(t)$ into two terms,[3]

$$\begin{aligned} c_k(t) &= \langle k_0 \mid \lambda H'(t) \mid 0_0 \rangle \exp(i\omega_{k0}t)/(E_{0,0} - E_{k,0}) \\ &\quad + (\hbar\omega_{k0})^{-1} \int_{-\infty}^{t} \langle k_0 \mid \lambda\, \partial H'(t')/\partial t' \mid 0_0 \rangle \exp[i\, (E_{k,0} - E_{0,0})\, t'/\hbar]\, dt' \ , \end{aligned} \tag{4}$$

where $\hbar\omega_{k0} = (E_{k,0} - E_{0,0})$. The boundary term in Eq. (4) gives the first-order adiabatic coefficient $a_k(t)$, while the remaining integral represents nonadiabatic effects, which are characterized by the coefficient $b_k(t)$. The adiabatic term depends on the instantaneous value of the perturbation at time t, while the nonadiabatic term depends explicitly on the time-derivative of the perturbation at times $t' \leq t$. Landau and Lifshitz stated that $\mid b_k(t) \mid^2$ gives the probability of transition to an excited state, if the perturbation takes on a small constant value as $t \to \infty$. We have interpreted $\mid b_k^{(1)}(t) \mid^2$ more generally as the transition probability, even when the perturbation continues to vary in time.

In this section, we determine the response to a perturbation $H'(t)$ that is given by

$$H'(t) = \begin{cases} V \exp(-a t^2) & \text{for } t < 0 \\ V & \text{for } 0 \le t \le \tau \\ V \exp[-b(t-\tau)^2] & \text{for } t > \tau , \end{cases} \tag{5}$$

setting $\lambda = 1$ and using the width parameters a for the rising half-Gaussian and b for the falling half-Gaussian. We assume that the system occupies the ground state $| 0_0 \rangle$ of the unperturbed Hamiltonian H_0 as $t \to -\infty$. The application of $H'(t)$ introduces into $|\psi(t)\rangle$ components of excited-states $| k_0 \rangle$ with coefficients $c_k(t) \exp(-iE_{k,0}\, t/\hbar)$, where $c_k(t)$ satisfies

$$c_k(t) = (-i/\hbar) \int_{-\infty}^{t} \langle k_0 | V | 0_0 \rangle \exp(-a t'^2) \exp[\, i\,(E_{k,0} - E_{0,0})\, t'/\hbar \,]\, dt' \ , \tag{6}$$

for $t < 0$. From Eq. (6), in units with $\hbar = 1$,

$$c_k(t) = -(i/2)\,(\pi/a)^{1/2} \langle k_0 | V | 0_0 \rangle \exp[-\omega_{k0}^2/(4a)]\ \{1 + \mathrm{Erf}[(2at - i\omega_{k0})/(2a^{1/2})]\} \tag{7}$$

for $t < 0$. In Eq. (7) and below, Erf denotes the error function, defined as the integral of a normalized Gaussian function from zero to the argument of the function.[130] It is an entire function. We have followed the convention used in Mathematica,[131] which differs from the definition by Whittaker and Watson,[132] where the normalization factor is omitted.

While the field is rising, the nonadiabatic coefficient $b_k(t)$ is given by

$$b_k(t) = -2a\,\omega_{k0}^{-1} \int_{-\infty}^{t} \langle k_0 | V | 0_0 \rangle\, t' \exp(-a t'^2) \exp(i\omega_{k0} t')\, dt' \ . \tag{8}$$

Thus for $t < 0$, with $\hbar = 1$,

$$\begin{aligned} b_k(t) = {} & \langle k_0 | V | 0_0 \rangle\, \omega_{k0}^{-1} \exp[-\omega_{k0}^2/(4a)] \exp[-(2at - i\omega_{k0})^2/(4a)] \\ & - (i/2)\,(\pi/a)^{1/2} \langle k_0 | V | 0_0 \rangle \exp[-\omega_{k0}^2/(4a)]\ \{1 + \mathrm{Erf}[(2at - i\omega_{k0})/(2a^{1/2})]\} \ . \end{aligned} \tag{9}$$

For $t < 0$, the adiabatic coefficient can be obtained directly from the expression

$$\begin{aligned} a_k(t) &= \langle k_0 | H'(t) | 0_0 \rangle \exp(i\omega_{k0} t)/\omega_{0k} \\ &= -\langle k_0 | V | 0_0 \rangle \exp(-a t^2) \exp(i\omega_{k0} t)/\omega_{k0} \ , \end{aligned} \tag{10}$$

with $\hbar = 1$ as before. The adiabatic coefficient $a_k(t)$ can also be obtained as the difference between $c_k(t)$ from Eq. (7) and $b_k(t)$ from Eq. (9),

$$a_k(t) = -\langle k_0 \mid V \mid 0_0 \rangle\, \omega_{k0}^{-1} \exp[-\omega_{k0}^2/(4a)] \exp[-(2at - i\omega_{k0})^2/(4a)]\ . \tag{11}$$

Equations (10) and (11) give identical results for $t < 0$. At $t = 0$,

$$a_k(t = 0) = -\langle k_0 \mid V \mid 0_0 \rangle/\omega_{k0}\ , \tag{12}$$

$$b_k(t = 0) = \langle k_0 \mid V \mid 0_0 \rangle\, \omega_{k0}^{-1} - (i/2)\, (\pi/a)^{1/2} \langle k_0 \mid V \mid 0_0 \rangle \exp[-\omega_{k0}^2/(4a)]\, \{1 + \mathrm{Erf}[-i\omega_{k0}/(2a^{1/2})]\, \}, \tag{13}$$

and $c_k(t = 0) = -(i/2)\, (\pi/a)^{1/2} \langle k_0 \mid V \mid 0_0 \rangle \exp[-\omega_{k0}^2/(4a)]\, \{1 + \mathrm{Erf}[-i\omega_{k0}/(2a^{1/2})]\, \}$.

(14) The result for $b_k(t)$ at $t = 0$ is consistent with our previous results for the case when a perturbation is imposed via a rising half-Gaussian,[49]

$$\mathrm{Re}[b_k(t = 0)] = \langle k_0 \mid V \mid 0_0 \rangle\, \{1/\omega_{k0} - a^{-1/2}\, \mathrm{DawsonF}[(2a^{1/2})^{-1}\, \omega_{k0}]\, \}\ , \tag{15}$$

and $$\mathrm{Im}[b_k(t = 0)] = -\langle k_0 \mid V \mid 0_0 \rangle\, \{\, (1/2)(\pi/a)^{1/2} \exp[-\omega_{k0}^2/(4a)\,]\, \}\ . \tag{16}$$

In Eq. (15), DawsonF[x] denotes the Dawson integral F(x), defined as the integral of $\exp(y^2)$ integrated over y from zero to x, then multiplied by $\exp(-x^2)$.[133]

While the perturbation is constant, $b_k(t)$ remains constant at the value $b_k(t = 0)$, but $c_k(t)$ oscillates due to the oscillations in $a_k(t)$. So for times t in the range between 0 and τ,

$$a_k(t) = -\langle k_0 \mid V \mid 0_0 \rangle \exp(i\omega_{k0}t)/\omega_{k0}\ , \tag{17}$$

$$b_k(t) = \langle k_0 \mid V \mid 0_0 \rangle\, \omega_{k0}^{-1} - (i/2)\, (\pi/a)^{1/2} \langle k_0 \mid V \mid 0_0 \rangle \exp[-\omega_{k0}^2/(4a)]\, \{1 + \mathrm{Erf}[-i\omega_{k0}/(2a^{1/2})]\, \}, \tag{18}$$

and $$c_k(t) = \langle k_0 \mid V \mid 0_0 \rangle\, [1 - \exp(i\omega_{k0}t)]/\omega_{k0} - (i/2)(\pi/a)^{1/2} \langle k_0 \mid V \mid 0_0 \rangle \exp[-\omega_{k0}^2/(4a)]\, \{1 + \mathrm{Erf}[-i\omega_{k0}/(2a^{1/2})]\, \}\ . \tag{19}$$

Next we derive the results for the excited-state coefficients when the perturbation is turned off via a falling half Gaussian, beginning at time τ. We calculate the change $\Delta c_k(t)$ in the Dirac coefficient $c_k(t)$ relative to its value at $t = \tau$ from the relation,

$$\Delta c_k(t) = -i \int_\tau^t \langle k_0 \,|\, V \,|\, 0_0 \rangle \exp[-b(t' - \tau)^2] \exp(i\omega_{k0} t')\ dt' \tag{20}$$

for $t > \tau$. Then

$$\begin{aligned}\Delta c_k(t) = {}& (1/2) \langle k_0 \,|\, V \,|\, 0_0 \rangle \exp[i\tau\omega_{k0} - \omega_{k0}^2/(4b)]\, (\pi/b)^{1/2} \\ & \big(\mathrm{Erfi}[\omega_{k0}/(2b^{1/2})] + i\, \mathrm{Erf}\{[-2b\,(t - \tau) + i\omega_{k0}]/(2b^{1/2})\}\big) .\end{aligned} \tag{21}$$

From Eqs. (19) and (21), while the magnitude of the applied field is decreasing, $c_k(t)$ is given by

$$\begin{aligned}c_k(t) = {}& \langle k_0 \,|\, V \,|\, 0_0 \rangle\, [1 - \exp(i\omega_{k0}\tau)]/\omega_{k0} \\ & - (i/2)(\pi/a)^{1/2} \langle k_0 \,|\, V \,|\, 0_0 \rangle \exp[-\omega_{k0}^2/(4a)]\ \{1 + \mathrm{Erf}[-i\omega_{k0}/(2a^{1/2})]\ \} \\ & + (1/2) \langle k_0 \,|\, V \,|\, 0_0 \rangle \exp[i\tau\omega_{k0} - \omega_{k0}^2/(4b)]\, (\pi/b)^{1/2} \\ & \big(\mathrm{Erfi}[\omega_{k0}/(2b^{1/2})] + i\, \mathrm{Erf}\{[-2b\,(t - \tau) + i\omega_{k0}]/(2b^{1/2})\}\big) .\end{aligned} \tag{22}$$

In Eq. (22), $\mathrm{Erfi}[z]$ denotes the imaginary error function, which is related to the error function $\mathrm{Erf}[z]$ by $\mathrm{Erfi}[z] = -i\ \mathrm{Erf}[iz]$.[134] We have used the version of $\mathrm{Erfi}[z]$ implemented in Mathematica;[131] see also Ref. 134.

For $t > \tau$, the change $\Delta b_k(t)$ in the nonadiabatic coefficient $b_k(t)$ relative to its value at time τ satisfies

$$\Delta b_k(t) = -2b/\omega_{k0} \int_\tau^t \langle k_0 \,|\, V \,|\, 0_0 \rangle\, (t' - \tau) \exp[-b(t' - \tau)^2] \exp(i\omega_{k0} t')\ dt' . \tag{23}$$

Evaluation of the integral in Eq. (23) gives

$$\begin{aligned}\Delta b_k(t) = {}& (1/2) \langle k_0 \,|\, V \,|\, 0_0 \rangle \big\{2 \exp[-b\,(t - \tau)^2 + i\omega_{k0} t]/\omega_{k0} - 2 \exp(i\omega_{k0}\tau)/\omega_{k0} \\ & - i\, (\pi/b)^{1/2} \exp[i\omega_{k0}\tau - \omega_{k0}^2/(4b)]\ \mathrm{Erf}\{[2b(t - \tau) - i\omega_{k0}]/(2b^{1/2})\} \\ & + (\pi/b)^{1/2} \exp[i\omega_{k0}\tau - \omega_{k0}^2/(4b)]\ \mathrm{Erfi}[\omega_{k0}/(2b^{1/2})]\big\} .\end{aligned} \tag{24}$$

From Eqs. (18) and (24), we obtain the value of $b_k(t)$ while the applied field is declining as

$$\begin{aligned} b_k(t) = {} & \langle k_0 \mid V \mid 0_0 \rangle\, \omega_{k0}^{-1} - (i/2)\, (\pi/a)^{1/2} \langle k_0 \mid V \mid 0_0 \rangle \exp[-\omega_{k0}^2/(4a)]\ \{1 + \mathrm{Erf}[-i\omega_{k0}/(2a^{1/2})]\ \} \\ & + (1/2) \langle k_0 \mid V \mid 0_0 \rangle \Big\{ 2 \exp[-b\,(t-\tau)^2 + i\omega_{k0}t]/\omega_{k0} - 2 \exp(i\omega_{k0}\tau)/\omega_{k0} \\ & \qquad - i\, (\pi/b)^{1/2} \exp[i\omega_{k0}\tau - \omega_{k0}^2/(4b)]\ \mathrm{Erf}\{[2b(t-\tau) - i\omega_{k0}]/(2b^{1/2})\} \\ & \qquad + (\pi/b)^{1/2} \exp[i\omega_{k0}\tau - \omega_{k0}^2/(4b)]\ \mathrm{Erfi}[\omega_{k0}/(2b^{1/2})] \Big\}\ . \end{aligned} \tag{25}$$

Taking the limit as $t \to \infty$, we find

$$\begin{aligned} \lim_{t\to\infty} b_k(t) = {} & \langle k_0 \mid V \mid 0_0 \rangle \Big\{ [1 - \exp(i\omega_{k0}\tau)]/\omega_{k0} \\ & - (i/2)\, (\pi/a)^{1/2} \exp[-\omega_{k0}^2/(4a)]\ \{1 + \mathrm{Erf}[-i\omega_{k0}/(2a^{1/2})]\ \} \\ & - (i/2)\, (\pi/b)^{1/2} \exp[i\omega_{k0}\tau - \omega_{k0}^2/(4b)] \\ & + (1/2)\, (\pi/b)^{1/2} \exp[i\omega_{k0}\tau - \omega_{k0}^2/(4b)]\ \mathrm{Erfi}[\omega_{k0}/(2b^{1/2})] \Big\}\ , \end{aligned} \tag{26}$$

since $\lim_{t\to\infty} \exp[-b\,(t-\tau)^2 + i\omega_{k0}t]/\omega_{k0} = 0$ and $\lim_{t\to\infty} \mathrm{Erf}\{[2b(t-\tau) - i\omega_{k0}]/(2b^{1/2})\} = 1$. From Eq. (22) and $\lim_{t\to\infty} \mathrm{Erf}\{[-2b(t-\tau) - i\omega_{k0}]/(2b^{1/2})\} = -1$, similarly we find

$$\begin{aligned} \lim_{t\to\infty} c_k(t) = {} & \langle k_0 \mid V \mid 0_0 \rangle \Big\{ [1 - \exp(i\omega_{k0}\tau)]/\omega_{k0} \\ & - (i/2)\, (\pi/a)^{1/2} \exp[-\omega_{k0}^2/(4a)]\ \{1 + \mathrm{Erf}[-i\omega_{k0}/(2a^{1/2})]\ \} \\ & - (i/2)\, (\pi/b)^{1/2} \exp[i\tau\omega_{k0} - \omega_{k0}^2/(4b)] \\ & + (1/2)\, (\pi/b)^{1/2} \exp[i\tau\omega_{k0} - \omega_{k0}^2/(4b)]\ \mathrm{Erfi}[\omega_{k0}/(2b^{1/2})] \Big\}\ . \end{aligned} \tag{27}$$

The results for $b_k(t)$ and $c_k(t)$ in the limit as $t \to \infty$ are identical as expected, since $\lim_{t\to\infty} a_k(t) = 0$.

It is interesting to examine the long-time limiting results in the case where the perturbation is turned on and off very rapidly. In the limit as $a \to \infty$, we find

$$\begin{aligned} \lim_{a\to\infty} \lim_{t\to\infty} b_k(t) & = \lim_{a\to\infty} \lim_{t\to\infty} c_k(t) \\ & = \langle k_0 \mid V \mid 0_0 \rangle\, [1 - \exp(i\omega_{k0}\tau)]/\omega_{k0} \\ & \quad + (i/2)\, (\pi/b)^{1/2} \langle k_0 \mid V \mid 0_0 \rangle \exp[i\omega_{k0}\tau - \omega_{k0}^2/(4b)] \\ & \quad + (1/2) \langle k_0 \mid V \mid 0_0 \rangle\, (\pi/b)^{1/2} \exp[i\omega_{k0}\tau - \omega_{k0}^2/(4b)]\ \mathrm{Erfi}[\omega_{k0}/(2b^{1/2})]\ , \end{aligned} \tag{28}$$

and then taking the limit as $b \to \infty$ as well, we obtain

$$\lim_{b \to \infty} \lim_{a \to \infty} \lim_{t \to \infty} b_k(t) = \langle k_0 \mid V \mid 0_0 \rangle \, [1 - \exp(i\omega_{k0}\tau)]/\omega_{k0} \,. \quad (29)$$

Equation (29) is identical to the result in the sudden approximation.[135-142]

Different functional forms of $| b_k(t) |^2$ and $| c_k(t) |^2$ are observed, depending on the values of ω_{k0}, τ, a and b. Figures S.1−S.4 in the supplementary material[143] illustrate a few of these forms. In this case, the difference simply reflects the difference in the choice of the basis set.

III. Results in the sudden approximation

An oscillatory pattern in the probability of transition to an excited state $| k_0 \rangle$ of an unperturbed Hamiltonian is found for a system that is perturbed by a constant field that lasts for time τ. Figure 1 shows the scaled transition probability P_k, which is obtained by dividing $| c_k(t) |^2$ by the norm-square of the transition matrix element $| \langle k_0 | H' | 0_0 \rangle |^2$, for all times t after the perturbation has ended (in the absence of dephasing and population relaxation). For this plot, we have set $\hbar = 1$. The transition probability depends on the product $\omega_{k0}\tau$. The transition frequency ω_{k0} and the interval τ during which the field is applied are in arbitrary, but interrelated units; so for example, if τ is given in picoseconds, then ω_{k0} has units of 10^{12} s^{-1}.

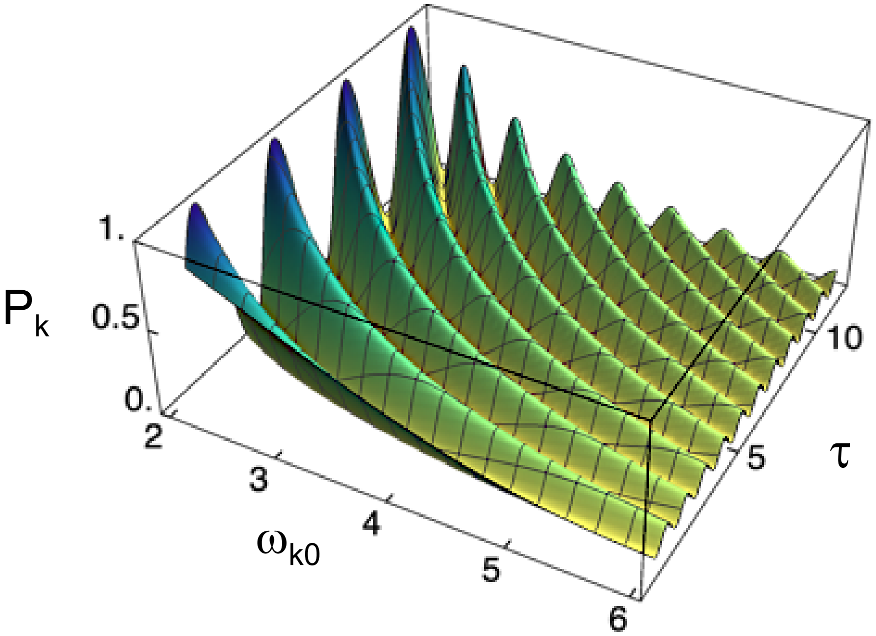

Figure 1. Scaled quantum transition probability $P_k \equiv | c_k(t) |^2 | \langle k_0 | H' | 0_0 \rangle |^{-2}$ after a perturbing field has been turned off, as a function of the transition frequency ω_{k0} and the duration of the constant field τ. Results from the sudden approximation.

The oscillations in the final occupancy of the excited state shown in Fig. 1 resemble Rabi oscillations,[52-56] although the calculations used to prepare Fig. 1 were limited to linear response. Our purpose in this section is to show that identical oscillations in P_k are predicted by $| b_k(t) |^2$, even though the value of $|b_k(t)|^2$ remains constant while the perturbing field is acting. Additionally, we explain why oscillations emerge in the nonadiabatic transition theory.

We use the sudden approximation[135-142] for this analysis. Equivalent results are obtained from the transition probabilities in Sec. II as the widths of a half-Gaussian rise of an applied field and of a half-Gaussian decay of the field both go to zero. The analytical results are simple in this limiting case. Despite its limitations, the sudden approximation is quite useful in elucidating the origin of the oscillations within the nonadiabatic transition theory.

We consider a perturbation that is turned on via a Heaviside theta function at t_0 and later is turned off equally abruptly, after an interval τ during which the field remains constant. Then

$$\langle k_0 | H'(t') | 0_0 \rangle = \langle k_0 | H' | 0_0 \rangle \{\theta(t' - t_0) - \theta[t' - (t_0 + \tau)]\} \tag{30}$$

and
$$\langle k_0 | \partial H'(t')/\partial t' | 0_0 \rangle = \langle k_0 | H' | 0_0 \rangle \{\delta(t' - t_0) - \delta[t' - (t_0 + \tau)]\} \ . \tag{31}$$

For convenience, we have set $\lambda = 1$. The second term in Eq. (4) gives $b_k(t)$, with the matrix element $\langle k_0 | \partial H'(t')/\partial t' | 0_0 \rangle$ from Eq. (31). We use Eq. (3) for $c_k(t)$ with $\langle k_0 | H'(t') | 0_0 \rangle$ from Eq. (30). When $t < t_0$, all three excited-state coefficients $a_k(t)$, $b_k(t)$, and $c_k(t)$ vanish. When $t_0 < t < t_0 + \tau$,

$$a_k(t) = -\langle k_0 | H' | 0_0 \rangle \exp(i\omega_{k0}t)/(\hbar\omega_{k0}) \ , \tag{32}$$

$$b_k(t) = \langle k_0 | H' | 0_0 \rangle \exp(i\omega_{k0}t_0)/(\hbar\omega_{k0}) \ , \tag{33}$$

and
$$c_k(t) = \langle k_0 | H' | 0_0 \rangle [\exp(i\omega_{k0}t_0) - \exp(i\omega_{k0}t)]/(\hbar\omega_{k0}) \ . \tag{34}$$

While the applied field is constant, the nonadiabatic transition probability is constant also, and

$$| b_k(t) |^2 = | \langle k_0 | H' | 0_0 \rangle |^2/(\hbar\omega_{k0})^2 \ . \tag{35}$$

The Dirac form of the transition probability oscillates,

$$| c_k(t) |^2 = | \langle k_0 | H' | 0_0 \rangle |^2 \{2 - 2 \cos[\omega_{k0}(t - t_0)]\}/(\hbar\omega_{k0})^2 \ . \tag{36}$$

If the wave function remains coherent, then after the field has been turned off,

$$b_k(t) = c_k(t) = \langle k_0 | H' | 0_0 \rangle \exp(i\omega_{k0}t_0) [1 - \exp(i\omega_{k0}\tau)]/(\hbar\omega_{k0}) \ , \tag{37}$$

and $| b_k(t) |^2 = | c_k(t) |^2 = | \langle k_0 | H' | 0_0 \rangle |^2 [2 - 2 \cos(\omega_{k0}\tau)]/(\hbar\omega_{k0})^2$. (38)

So the final transition probabilities are identical, as expected since $a_k(t) = 0$ for $t > t_0 + \tau$.

The final transition probability drops to zero if $\omega_{k0}\tau = 2n\pi$ for any integer n, while if $\omega_{k0}\tau = (2n + 1)\pi$, the final transition probability is maximized at

$$| b_k(t) |^2 = | c_k(t) |^2 = 4 | \langle k_0 | H' | 0_0 \rangle |^2/(\hbar\omega_{k0})^2 \ . \tag{39}$$

The maximum is four times the value of $| b_k(t) |^2$ while the applied field is constant. Figure 2 shows $| b_k(t) |^2$ and $| c_k(t) |^2$ for intervals τ of lengths $9\pi/\omega_{k0}$, $9.2\pi/\omega_{k0}$, $9.4\pi/\omega_{k0}$, $9.6\pi/\omega_{k0}$, $9.8\pi/\omega_{k0}$, and $10\pi/\omega_{k0}$, with $\omega_{k0} = 12\pi/5$ in all cases. For convenience, we have set $t_0 = 0$.

The coefficient $c_k(t)$ is continuous as a function of time throughout, while $a_k(t)$ and $b_k(t)$ are discontinuous at t_0 and $t_0 + \tau$. This is a consequence of taking the limits as the widths of the half-Gaussians for the rise and decay of the field both go to zero; equivalently, it is a consequence of the sudden approximation.[135-142] As shown in Sec. II, continuous functions $a_k(t)$ and $b_k(t)$ are obtained for any non-zero widths of the half-Gaussians.

Figures S.5 and S.6 in the supplementary material[143] show the real and imaginary parts of $a_k(t)$, $b_k(t)$, and $c_k(t)$ scaled by $\langle k_0 | H' | 0_0 \rangle$, for $\tau = 9\pi/\omega_{k0}$, $9.25\pi/\omega_{k0}$, $9.5\pi/\omega_{k0}$, $9.75\pi/\omega_{k0}$, and $10\pi/\omega_{k0}$, with $t_0 = 0$ to simplify the separation of the real and imaginary parts of the coefficients. Other choices of t_0 introduce overall phase factors into $a_k(t)$, $b_k(t)$, and $c_k(t)$ without affecting the transition probabilities. Independent of the duration of the plateau, the adiabatic coefficient $a_k(t)$ jumps to the value $a_k(t = 0^+) = -\langle k_0 | H' | 0_0 \rangle/(\hbar\omega_{k0})$ immediately after the field has been turned on. The imaginary part of $a_k(t)$ is zero at $t = 0^+$. Both the real and imaginary parts of $a_k(t)$ oscillate while the field is acting. When the field is turned off, $a_k(t)$ immediately drops to zero.

The coefficient $b_k(t)$ jumps to $b_k(t = 0^+) = \langle k_0 | H' | 0_0 \rangle/(\hbar\omega_{k0})$ immediately after the field has been turned on and remains constant while the constant field is acting. This is physically

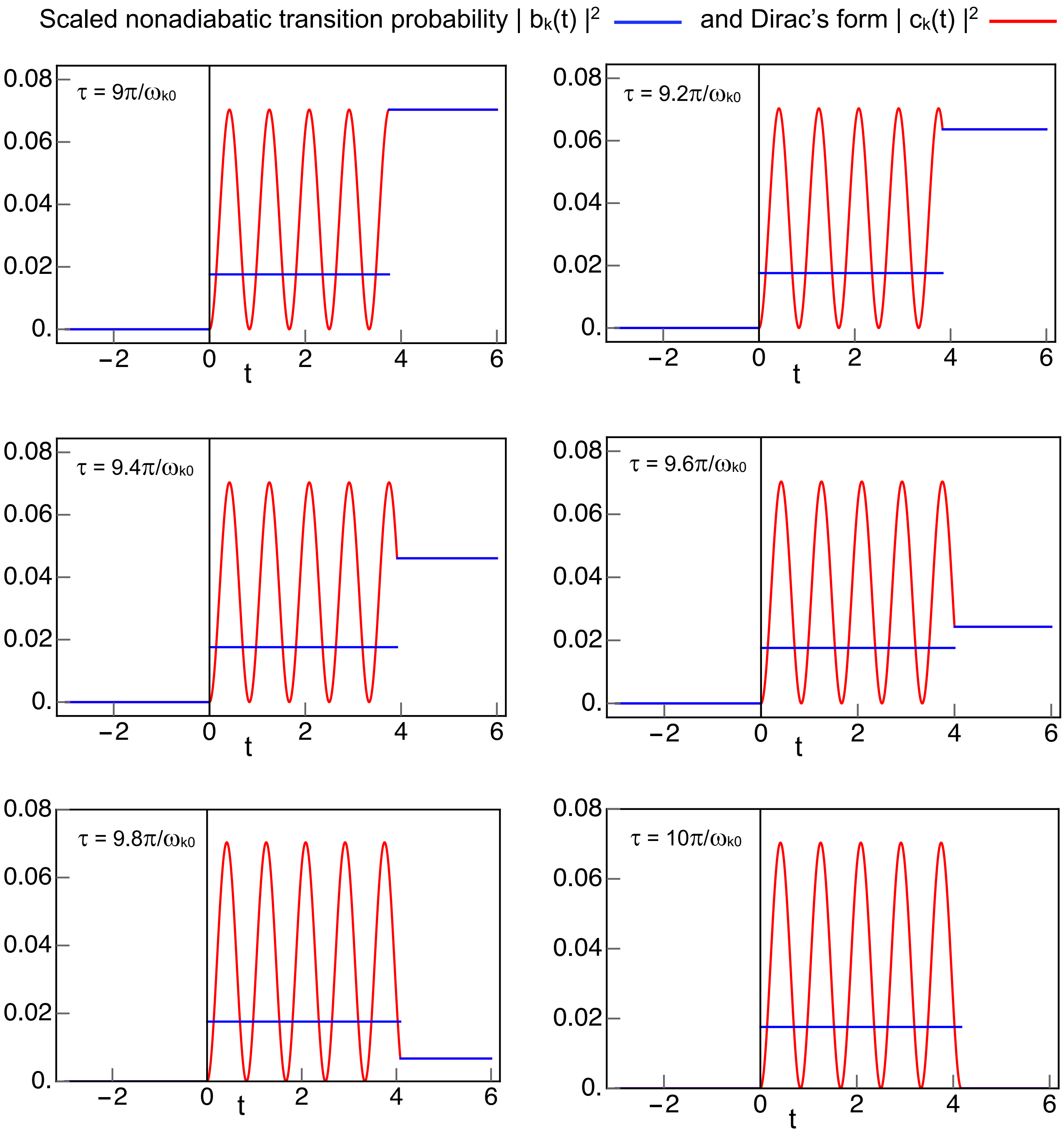

Figure 2. Nonadiabatic transition probability $| b_k(t) |^2$ and Dirac’s form of the transition probability $| c_k(t) |^2$ as functions of time, for various durations τ of the perturbation: $\tau = 9\pi/\omega_{k0}$, $9.2\pi/\omega_{k0}$, $9.4\pi/\omega_{k0}$, $9.6\pi/\omega_{k0}$, $9.8\pi/\omega_{k0}$, and $10\pi/\omega_{k0}$, with $\omega_{k0} = 12\pi/5$. Both transition probabilities are scaled as in Fig. 1.

reasonable, because $b_k(t)$ is the coefficient of the instantaneous eigenstate $| k' \rangle$ in the wave function, up to a phase. When the perturbation is first imposed and $c_k(t) = 0$, necessarily $b_k(t) \neq 0$ already, because the unperturbed and perturbed basis sets differ. Due to the choice $t_0 = 0$, $b_k(t)$ has no imaginary part while the field acts. When the field is turned off, $b_k(t)$ jumps to its final value, $\langle k_0 | H' | 0_0 \rangle [1 - \exp(i\omega_{k0}\tau)]/(\hbar\omega_{k0})$.

The pattern of the transition probabilities $| c_k(t) |^2$ after the field has been turned off—specifically, the oscillations in the transition probabilities—can be explained by considering the relationship between $a_k(t)$ and $b_k(t)$ in the limit as t approaches τ from below. If $\tau = (2n + 1)\pi/\omega_{k0}$, the imaginary parts of $a_k(t)$, $b_k(t)$, and $c_k(t)$ all vanish as $t \to \tau^-$. The real part of $a_k(t)$ satisfies

$$\lim_{t \to \tau-} a_k(t) = \langle k_0 | H' | 0_0 \rangle/(\hbar\omega_{k0}) \ . \tag{40}$$

Since $\lim_{t \to \tau-} b_k(t)$ is identical to the limit for $a_k(t)$ in Eq. (40), the values of $a_k(t)$ and $b_k(t)$ reinforce each other, so that

$$\lim_{t \to \tau} c_k(t) = 2\langle k_0 | H' | 0_0 \rangle/(\hbar\omega_{k0}) \ , \tag{41}$$

and the transition probability is maximized. In contrast, if $\tau = 2n\pi/\omega_{k0}$, again the imaginary parts of $a_k(t)$, $b_k(t)$, and $c_k(t)$ vanish in the limit as $t \to \tau^-$, but in this case,

$$\lim_{t \to \tau-} a_k(t) = -\langle k_0 | H' | 0_0 \rangle/(\hbar\omega_{k0}) \ . \tag{42}$$

Consequently we find $\lim_{t \to \tau} c_k(t) = 0$, leading to a minimum of the transition probability when the pulse duration satisfies $\tau = 2n\pi/\omega_{k0}$.

In intermediate cases with $\tau = (2n + 1/2)\pi/\omega_{k0}$ or $\tau = (2n + 3/2)\pi/\omega_{k0}$, the nonadiabatic transition probability changes by the same increment when the field is turned on and when it is turned off. Then for $t > \tau$,

$$| b_k(t) |^2 = | c_k(t) |^2 = 2 \, | \langle k_0 | H' | 0_0 \rangle |^2/(\hbar\omega_{k0})^2 \ . \tag{43}$$

For $t > \tau$, $a_k(t) = 0$, while $b_k(t)$ and $c_k(t)$ have both real and imaginary components that are nonzero. For $t > \tau$, from Eq. (37) with $t_0 = 0$,

$$b_k(t) = \langle k_0 \mid H' \mid 0_0 \rangle [1 - \cos(\omega_{k0}\tau) - i \sin(\omega_{k0}\tau)]/(\hbar\omega_{k0}) \ . \tag{44}$$

If $\omega_{k0}\tau = \text{Arccos}(1/2)$, $\cos(\omega_{k0}\tau) = 1/2$ and $\sin(\omega_{k0}\tau) = \pm (3/4)^{1/2}$. For either sign of $\sin(\omega_{k0}\tau)$,

$$\begin{aligned} | b_k(t) |^2 &= | \langle k_0 \mid H' \mid 0_0 \rangle |^2 [1/2 + i (3/4)^{1/2}][1/2 - i (3/4)^{1/2}]/(\hbar\omega_{k0})^2 \\ &= | \langle k_0 \mid H' \mid 0_0 \rangle |^2/(\hbar\omega_{k0})^2 \ , \end{aligned} \tag{45}$$

for $t > \tau$, as well as for $0 < t < \tau$. That is, if $\omega_{k0}\tau = \text{Arccos}(1/2)$, the transition probability $| b_k(t) |^2$ is identical while the field is acting and after the field has been turned off.

IV. Time evolution of the density matrix for a model two-level system in a constant field

In this section, we start by examining the time evolution of the density matrix for a model two-level system in a constant field, as characterized by the Liouville equation[4] in the basis of the unperturbed eigenstates by extension of Dirac's theory and separately in the basis of the perturbed eigenstates, as in the nonadiabatic transition theory. The analysis applies to a system that starts in the unperturbed ground state $| 0_0 \rangle$ at $t = 0$. The system is isolated aside from the effects of the applied field, which is held constant at times $t > 0$. Thus the system remains coherent in this case. The coefficient $c_0(t)$ for the ground eigenstate falls off gradually from its initial value $c_0(0) = 1$, while $c_k(t)$ rises gradually from its initial value $c_k(0) = 0$. We take the limiting case of a perturbation that is turned on via a rising half-Gaussian, as the width of the half-Gaussian goes to zero (consistent with the sudden approximation[135-142]). Since the eigenstate $| 0_0 \rangle$ is a superposition of the eigenstates $| 0' \rangle$ and $| k' \rangle$ of the perturbed Hamiltonian, the coefficient $b_{k'}(t)$ is already non-zero at $t = 0$, and $| b_{0'}(0) | < 1$.

The time-evolution of the density matrix for the two-level model system in the applied field is characterized by the Liouville equation,[4]

$$\partial\rho(t)/\partial t = -(i/\hbar)\,[H(t), \rho(t)] \;. \tag{46}$$

In the unperturbed state basis $\{| 0_0 \rangle , | k_0 \rangle\}$, where $H_0 | 0_0 \rangle = E_0 | 0_0 \rangle$ and $H_0 | k_0 \rangle = E_k | k_0 \rangle$, the initial conditions for the density matrix elements are $\rho_{00}(0) = 1$, and $\rho_{kk}(0) = \rho_{0k}(0) = \rho_{k0}(0) = 0$, since $\rho(0) = | 0_0 \rangle \langle 0_0 |$. The full Hamiltonian is the sum of the original unperturbed Hamiltonian H_0 and the perturbation H'. We assume that the diagonal elements of the perturbation vanish and that the off-diagonal elements of the Hamiltonian are real and equal. The off-diagonal elements are time independent for $t > 0$. We define h_{0k} as $H_{0k}/\hbar$ and use the relation $(E_k - E_0)/\hbar = \omega_{k0}$. Then the time-evolution equations for the density matrix elements in the unperturbed basis are

$$\partial\rho_{00}(t)/\partial t = -i\,h_{0k}\,\rho_{k0}(t) + i\,h_{0k}\,\rho_{0k}(t) \ , \tag{47}$$

$$\partial\rho_{kk}(t)/\partial t = -i\,h_{0k}\,\rho_{0k}(t) + i\,h_{0k}\,\rho_{k0}(t) \ , \tag{48}$$

$$\partial\rho_{k0}(t)/\partial t = -i\,\omega_{k0}\,\rho_{k0}(t) - i\,h_{0k}\,[\rho_{00}(t) - \rho_{kk}(t)] \ , \tag{49}$$

and $$\partial\rho_{0k}(t)/\partial t = i\,\omega_{k0}\,\rho_{0k}(t) - i\,h_{0k}\,[\rho_{kk}(t) - \rho_{00}(t)] \ . \tag{50}$$

At this point, it is useful to separate the real and imaginary terms in the differential equations, since the diagonal elements of the density matrix are purely real, and the off-diagonal elements are complex conjugates. Setting $\rho_{k0}(t) = p(t) + i\,q(t)$, we find

$$\partial\rho_{00}(t)/\partial t = 2\ h_{0k}\ q(t) \ , \tag{51}$$

$$\partial\rho_{kk}(t)/\partial t = -2\ h_{0k}\ q(t) \ , \tag{52}$$

$$\partial p(t)/\partial t = \omega_{k0}\ q(t) \ , \tag{53}$$

and $$\partial q(t)/\partial t = -\omega_{k0}\ p(t) + h_{0k}\ [\rho_{kk}(t) - \rho_{00}(t)] \ . \tag{54}$$

The solutions of Eqs. (51)-(54) are

$$\rho_{00}(t) = \{\gamma^2 - 2\ h_{0k}{}^2\ [1 - \cos(\gamma t)]\}/\gamma^2 \ , \tag{55}$$

$$\rho_{kk}(t) = 2\ h_{0k}{}^2\ [1 - \cos(\gamma t)]/\gamma^2 \ , \tag{56}$$

$$p(t) = h_{0k}\ \omega_{k0}\ [\cos(\gamma t) - 1]/\gamma^2 \ , \tag{57}$$

and $$q(t) = -h_{0k}\ \sin(\gamma t)/\gamma \ , \tag{58}$$

where the angular frequency γ is given by $\gamma = (4h_{0k}{}^2 + \omega_{k0}{}^2)^{1/2}$. The populations of the states $|\ 0_0\ \rangle$ and $|\ k_0\ \rangle$ oscillate with a period of $2\pi/\gamma$. The maximum value of $\rho_{kk}(t)$ is $4h_{0k}{}^2/\gamma^2$. To test the accuracy of our numerical work, we have compared the analytical values and numerical values of γ, the maximum value of $\rho_{kk}(t)$, the first time at which the maximum is reached, the minimum of $\rho_{kk}(t)$, and the first time at which the minimum is reached (after $t = 0$), for five different values of h_{0k}. The results are listed in Table 1 in the supplementary material. The level of agreement between the analytical and numerical values is very high in all cases.

Next we consider the time evolution of the density matrix for an isolated two-state system in the perturbed eigenfunction basis $\{|0'\rangle, |k'\rangle\}$. These states are the eigenstates of the full Hamiltonian, including the perturbation. In this basis,

$$\rho(t=0) = |0'\rangle\langle 0'|0_0\rangle\langle 0_0|0'\rangle\langle 0'| + |k'\rangle\langle k'|0_0\rangle\langle 0_0|0'\rangle\langle 0'|$$
$$+ |0'\rangle\langle 0'|0_0\rangle\langle 0_0|k'\rangle\langle k'| + |k'\rangle\langle k'|0_0\rangle\langle 0_0|k'\rangle\langle k'| \ . \qquad (59)$$

The transformation matrices between the basis sets $\{|0_0\rangle, |k_0\rangle\}$ and $\{|0'\rangle, |k'\rangle\}$ are independent of time in the current case. Explicit equations for the inner products in Eq. (59) are given in the supplementary material. All four elements of $\rho(t)$ in the perturbed eigenfunction basis are non-zero at $t = 0$. The off-diagonal elements satisfy $\rho_{0'k'}(t) = \rho_{k'0'}{}^*(t)$ at $t = 0$ and at all later times. The trace of the density matrix equals one, so $\rho_{0'0'}(t) = 1 - \rho_{k'k'}(t)$. For an isolated system, the density matrix is idempotent in either basis, because the system is always in a pure state.

The density matrix satisfies the Liouville equation, Eq. (46). Since the full Hamiltonian is diagonal in the basis $\{|0'\rangle, |k'\rangle\}$ with $E_{k'}$ and $E_{0'}$, the diagonal matrix elements of the commutator of H with ρ vanish. The off-diagonal elements are given by $[H(t), \rho(t)]_{k'0'} = (E_{k'} - E_{0'})\, \rho_{k'0'}(t)$ and the relation $\rho_{0'k'}(t) = \rho_{k'0'}{}^*(t)$. Hence the time derivatives of the density matrix elements in the basis $\{|0'\rangle, |k'\rangle\}$ satisfy

$$\partial\rho_{k'k'}(t)/\partial t = \partial\rho_{0'0'}(t)/\partial t = 0 \ , \qquad (60)$$

$$\partial\rho_{k'0'}(t)/\partial t = -(i/\hbar)\,(E_{k'} - E_{0'})\,\rho_{k'0'}(t) \ , \qquad (61)$$

and $$\partial\rho_{0'k'}(t)/\partial t = \partial\rho_{k'0'}{}^*(t)/\partial t \ . \qquad (62)$$

In this basis, the ground and excited-state populations remain constant at their initial values. The off-diagonal elements oscillate with the angular frequency γ, since $(E_{k'} - E_{0'})/\hbar = \gamma$, as shown in the supplementary material, and therefore

$$\rho_{k'0'}(t) = \rho_{k'0'}(0)\, \exp(-i\gamma t) \ . \qquad (63)$$

The components of the density matrices in the two basis sets $\{|\,0_0\,\rangle, |\,k_0\,\rangle\}$ and $\{|\,0'\,\rangle, |\,k'\,\rangle\}$ are plotted in Figures S.7 and S.8 in the supplementary material, for a case with $\omega_{k0} = 3.99086\ \mathrm{ps}^{-1}$ and $h_{0k} = 1.496573\ \mathrm{ps}^{-1}$. With these values of the parameters, $\rho_{00}(0) = 1$, $\rho_{kk}(0) = 0$, $\rho_{0'0'}(0) = 0.9$, and $\rho_{k'k'}(0) = 0.1$. While the plots in Figs. S.7 and S.8 look quite different, upon transformation of the results from the perturbed basis to the unperturbed basis, identical values are obtained for each of the matrix elements, as is expected for a pure state. In the supplementary material, we prove analytically that the values are identical, when expressed in the same basis. The oscillations in $\mathrm{Re}[\rho_{k'0'}(t)]$ and $\mathrm{Im}[\rho_{k'0'}(t)]$ give rise to the oscillations in $\rho_{00}(t)$ and $\rho_{kk}(t)$.

V. Effects of dephasing and population relaxation

In this section, we analyze the time evolution of the two-level system coupled to a bath. To include the effects of dephasing and population relaxation due to interactions with the bath, we use Redfield theory in the secular approximation as developed in Ref. 57. The full nonlinear response is included in the calculations in this section.

We assume that the system starts in the unperturbed ground state $| 0_0 \rangle$ at $t = 0$; then it is perturbed by a constant field that acts at times $t > 0$. It is further perturbed by interactions with a thermal bath at times $t > 0$. Redfield derived equations for the time-development of the system's density matrix due to the effects of the bath, using two different approaches,[57] the first involving random semiclassical perturbations of the system, and the second involving a full Hamiltonian for the system and bath, including an interaction term.

In the first approach, the Hamiltonian is expressed as the sum of the Hamiltonian of the unperturbed system and a Hermitian stochastic term G that characterizes interactions with the bath. Redfield analyzed the time evolution of the system's density matrix, with the assumption that G vanishes when averaged over the bath at any time.[57] The correlation time of the fluctuations of the bath is assumed to be short, relative to the time scale over which the density matrix elements of the system change appreciably. Redfield derived the density matrix as a function of time, to second order in the perturbation due to the bath, within the interaction representation.[57] Because the stochastic term in the Hamiltonian averages to zero and the correlation time is assumed to be short, the first-order terms are negligible. The second-order terms incorporate the bath effects, so that the time derivative of $\rho_{\alpha\alpha'}$ is given by the Liouville equation plus relaxation terms of the type $R_{\alpha\alpha',\beta\beta'}\, \rho_{\beta\beta'}$, summed over β and β'.[57] The relaxation matrix R depends on the spectral density of the fluctuations in the bath.[57] Consideration of the magnitudes of the elements $R_{\alpha\alpha',\beta\beta'}$ in the relaxation matrix shows that significant contributions to the time derivative of $\rho_{\alpha\alpha'}$ are obtained only from the secular terms, i.e., terms with $\alpha - \alpha' - \beta + \beta' = 0$.[57] Physically, this implies that the perturbations due to the bath connect states of the system that differ in energy by the approximate magnitude of the perturbation. Transformation back from the interaction representation to find the original density matrix of the system gives the Redfield equation in the form used in this work, Eq. (64) below.

Redfield also analyzed the effects of interactions in a second approach, allowing in principle for a full quantum mechanical description of the bath.[57] In this approach, the total Hamiltonian is the sum of the system Hamiltonian, the bath Hamiltonian, and a coupling term G, which is a sum of products of an operator for the system and an operator for the bath. The analysis in this case begins with the full density matrix for the system and the bath; the reduced density matrix for the system is obtained by taking the trace over the bath states.[57] The bath is assumed to be in a state of thermal equilibrium initially; at $t = 0$, the full density matrix is diagonal in the bath states, and the system is not entangled with the bath. When the system evolves according to the time-dependent Schrödinger equation, the full density matrix becomes mixed—it is no longer a simple product of the density matrix for the system and the density matrix for the bath.[57] However, if the fluctuations of the bath occur on a significantly shorter time scale than the variation of the reduced density matrix for the system, the bath effectively re-randomizes as the system evolves, remaining constantly in a state of thermal equilibrium.[57] This introduces an apparent irreversibility into this approach, whereas in the first approach, irreversibility resulted from the stochastic nature of G.[57]

We note that in the first approach, Redfield allowed for the possibility that the average of the stochastic perturbation is non-zero. In that case, he suggested redefining the system's

Hamiltonian to include the average of G over the bath.[57] Similarly, in the second approach, the *stationary* perturbations due to G modify the system's Hamiltonian into an effective Hamiltonian to second order.[57] In this work, we have taken the average of G to be zero within the first approach. In the second approach, this corresponds to assuming that the dynamical perturbations have a much larger effect than the stationary perturbations due to the bath. In any case, the energy difference between the unperturbed ground state $| 0 \rangle$ and the excited state $| k \rangle$ and the energy difference between the perturbed ground state $| 0' \rangle$ and the excited state $| k' \rangle$ shift identically through second order, when any stationary perturbation due to the bath is included in the system's Hamiltonian.

In both approaches, the relaxation matrix R is determined by the spectral density of the fluctuations in the bath.[57] In the first approach, however, the relaxation of the system to thermal equilibrium must be treated in an *ad hoc* manner, either by applying the time-evolution equation to the difference between the system's density matrix and the density matrix at thermal equilibrium,[57] or by modifying the elements of the relaxation matrix to satisfy detailed balance. In the second approach, the spectral densities take a quantum mechanical form that accounts explicitly for the thermal equilibrium of the bath, and thus automatically allows the system to evolve to thermal equilibrium at long times.[57] Calculations of the spectral densities from first principles require an accurate description of the bath dynamics, and that is beyond the scope of the current work (cf. Refs. 129 and 143). Instead, we draw on experimental results to obtain relaxation parameters that are physically realistic; as shown below, this yields differences between the analyses in the perturbed and unperturbed basis sets that range from ~2.5% to more than 88%. For the two-level model systems, connections between the population relaxation time T_1 and the dephasing time T_2 and the matrix elements in the Redfield theory[57] are made by the relationships $R_{k'k',0'0'} = -1/T_1$ and $R_{k'0',k'0'} = 1/T_2$.

We first examine the results for the density matrix using the Redfield equation in the perturbed basis, where the system's Hamiltonian is diagonal, as in Redfield's original analysis.[57] Use of the perturbed basis is consistent with the nonadiabatic transition theory. Separately, we examine the effects of adding relaxation terms directly to the Liouville equation[4] in the unperturbed basis, and we show that non-physical results are obtained in this case. The coupling to the bath destroys the coherence of the wave function. Due to the loss of coherence, predictions based on using $| b_k(t) |^2$ or $| c_k(t) |^2$ for the transition probability differ, even after the results have been transformed to a single basis. Comparison of the results in Sections IV and V shows that the differences between results in the two basis sets are fundamentally attributable to the relaxation terms.

In Redfield's theory, the time derivative of the reduced density matrix $\rho(t)$ for the system is given by the equation,[57]

$$\partial\rho(t)/\partial t = -(i/\hbar)\,[H(t), \rho(t)] - \mathsf{R} : \rho(t) \quad , \tag{64}$$

where R is the relaxation matrix that characterizes the coupling to the bath, and $[\mathsf{R} : \rho(t)]_{jk}$ denotes the sum of $R_{jk,mn}\, \rho(t)_{mn}$ over m and n. We assume that coupling to the bath environment is weak, and that R is static or very slowly changing over time.[57] Modifications for strong coupling are possible (see, e.g., Refs. 144 and 145), but they are not considered here.

In the secular approximation, the non-zero elements of the relaxation matrix are $R_{k'k',k'k'}$, $R_{0'0',0'0'}$, $R_{k'k',0'0'}$, $R_{0'0',k'k'}$, $R_{k'0',k'0'}$, and $R_{0'k',0'k'}$.[57] These matrix elements are system-, bath- and temperature-dependent. Allowing for coupling to the bath, the equations of motion for the density matrix elements in the perturbed basis become

$$\partial\rho_{k'k'}(t)/\partial t = - R_{k'k',k'k'}\, \rho_{k'k'}(t) - R_{k'k',0'0'}\, \rho_{0'0'}(t) \quad , \tag{65}$$

$$\partial\rho_{0'0'}(t)/\partial t = -\,R_{0'0',k'k'}\ \rho_{k'k'}(t)\ -\ R_{0'0',0'0'}\ \rho_{0'0'}(t)\ , \tag{66}$$

and $$\partial\rho_{k'0'}(t)/\partial t = -(i/\hbar)\ (E_{k'} - E_{0'})\ \rho_{k'0'}(t) - R_{k'0',k'0'}\ \rho_{k'0'}(t)\ , \tag{67}$$

with $\rho_{0'k'}(t)$ given by the complex conjugate of $\rho_{k'0'}(t)$.

The relationships $R_{k'k',k'k'} = -\,R_{0'0',k'k'}$ and $R_{k'k',0'0'} = -\,R_{0'0',0'0'}$ ensure that the sum of $\rho_{k'k'}(t)$ and $\rho_{0'0'}(t)$ remains constant in time, at one. After thermal equilibrium is reached with the bath, $\rho_{k'k'}(t)$ and $\rho_{0'0'}(t)$ individually remain constant in time; they are related by

$$(\rho_{0'0'}/\rho_{k'k'})^{eq} = \exp[(E_{k'} - E_{0'})/kT] = \xi\ , \tag{68}$$

with $\xi > 1$, since $|\,0'\,\rangle$ is the perturbed ground state. The requirement for $\rho_{k'k'}$ to remain constant in time when the two-level system is in thermal equilibrium with the bath implies that $R_{k'k',k'k'} = -\,\xi\ R_{k'k',0'0'}$, and therefore $R_{0'0',k'k'} = \xi\ R_{k'k',0'0'}$. Finally, $R_{0'0',0'0'} = -\,R_{k'k',0'0'} = \xi^{-1}\ R_{k'k',k'k'}$. Setting $R = -R_{k'k',0'0'}$ (i.e., $R > 0$), we obtain the solutions of the coupled equations for $\rho_{k'k'}(t)$ and $\rho_{0'0'}(t)$,

$$\rho_{k'k'}(t) = \{1 - [1 - \rho_{kk}(0)\ (1 + \xi)]\ \exp[-(1 + \xi)\ R\ t]\}/(1 + \xi) \tag{69}$$

and $$\rho_{0'0'}(t) = \{\xi + [1 - \rho_{kk}(0)\ (1 + \xi)]\ \exp[-(1 + \xi)\ R\ t]\}/(1 + \xi)\ . \tag{70}$$

Because we are considering the reduced density matrix for the system in contact with the bath, we take $R_{0'0',k'k'} = \xi\ R_{k'k',0'0'}$, rather than $R_{k'k',0'0'} = R_{0'0',k'k'}$, which would follow from Fermi's Golden Rule for an isolated system.[2,146] In the limit as $t \to \infty$, the ratio $\rho_{0'0'}(t)/\rho_{k'k'}(t) \to \xi$, as expected for thermal equilibrium. Since $0 < \exp[-(1 + \xi)\ R\ t] < 1$ for $t > 0$, we can set $x = \exp[-(1 + \xi)\ R\ t]$, with $x < 1$. Then at an arbitrary time $t > 0$, $\rho_{k'k'}(t) - \rho_{k'k'}(0)$ is given by

$$\rho_{k'k'}(t) - \rho_{k'k'}(0) = (1 - x)\ [1 - \rho_{k'k'}(0) - \rho_{k'k'}(0)\ \xi]/(1 + \xi)\ . \tag{71}$$

If the initial population of the excited state exceeds the population at thermal equilibrium, then we have $\xi > [1 - \rho_{k'k'}(0)]/\rho_{k'k'}(0)$, so $[1 - \rho_{k'k'}(0) - \rho_{k'k'}(0)\ \xi] < 0$. Then since $x < 1$ and $\xi > 1$, $\rho_{k'k'}(t)$ at later times is less than its initial value. If the initial population of the excited state is less than the value at thermal equilibrium, $[1 - \rho_{k'k'}(0) - \rho_{k'k'}(0)\ \xi] > 0$, and $\rho_{k'k'}(t)$ rises from its initial value.

From Eq. (67) in the perturbed eigenfunction basis, the time evolution of the off-diagonal element of the density matrix $\rho_{k'0'}(t)$ is decoupled from the evolution of the diagonal elements. Setting $R_{k'0',k'0'} = 1/T_2$, and solving for $\rho_{k'0'}(t)$, we obtain

$$\rho_{k'0'}(t) = \rho_{k'0'}(0) \exp[-i\omega_{k'0'}t - (t/T_2)] , \tag{72}$$

with $\rho_{0'k'}(t) = \rho_{k'0'}(t)^*$.

The results for the density matrix elements in the perturbed basis, with the inclusion of dephasing and population relaxation are plotted in Fig. 3. The rationale for the parameter choices used to produce Fig. 3 is explained in the supplementary material. They apply to a *hypothetical* two-level system with the parameters chosen to be appropriate for the J, M = 0, 0 and J, M = 1, 0 states of HCl in liquid argon at 84 K.[147] We have neglected the dependence of the dipole moment on the bath, and hence the dependence of the off-diagonal Hamiltonian matrix elements

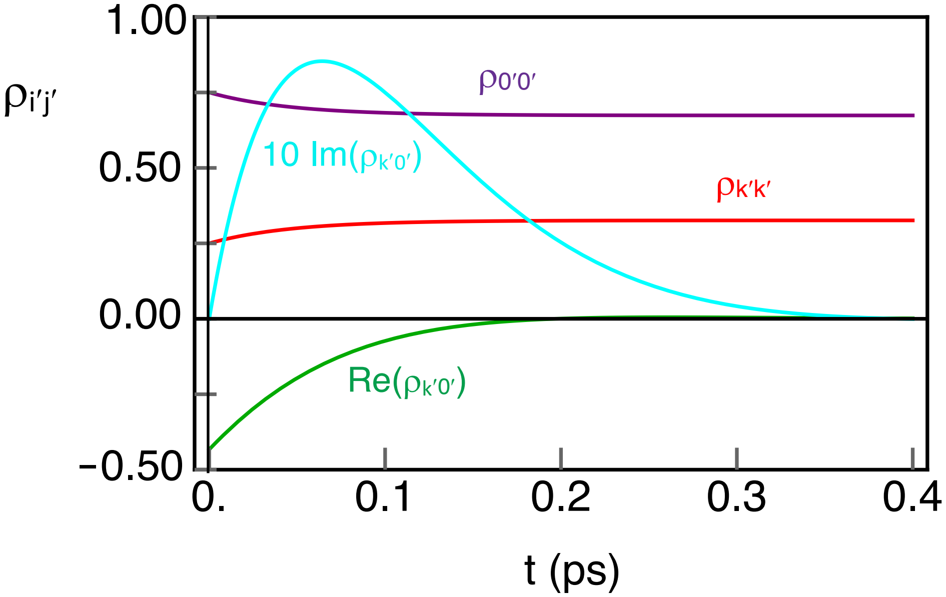

Figure 3. Density matrix elements in the perturbed basis for a hypothetical two-level system with parameter values ω_{k0} = 3.99086 ps^{-1}, h_{0k} = 1.496573 ps^{-1}, T_1 = 1/R = 0.141865 ps and T_2 = 0.0704659 ps. The imaginary part q(t) of the off-diagonal element of the density matrix $\rho_{k'0'}$ has been multiplied by a factor of 10 before plotting, to show its behavior more clearly.

h_{0k} and h_{k0} on the bath. This should be a reasonable approximation for very dilute HCl in liquid argon, the system we have used to obtain the parameters for the two-level model analyzed here.

Next we examine outcomes in the unperturbed basis, supposing that the relaxation terms can simply be added to the Liouville equation. We approximate the elements of the relaxation matrix as $R_{kk,kk} = -\xi_0 R_{kk,00}$, $R_{00,kk} = \xi_0 R_{kk,00}$, and $R_{00,00} = -R_{kk,00} = \xi_0^{-1} R_{kk,kk}$, where $(\rho_{00}/\rho_{kk})^{eq} = \xi_0$. Then the density matrix in the unperturbed eigenfunction basis would reach equilibrium in the absence of the perturbation H′. The difference between $E_k - E_0$ and $E_{k'} - E_{0'}$ produces the difference between ξ and ξ_0, and it is of second order in the perturbation. Replacing ξ_0 by ξ does not affect the qualitative features of the results. As before, $R = R_{00,00}$, $R_{0k,0k} = R_{k0,k0} = 1/T_2$, $h_{0k} = H_{0k}/\hbar$, and we set $(E_k - E_0)/\hbar = \omega_{k0}$. The time-evolution equations for the density matrix elements in the unperturbed basis are

$$\partial\rho_{00}(t)/\partial t = -i h_{0k}\, \rho_{k0}(t) + i h_{0k}\, \rho_{0k}(t) - R\, \rho_{00}(t) + \xi_0\, R\, \rho_{kk}(t)\ , \qquad (73)$$

$$\partial\rho_{kk}(t)/\partial t = -i h_{0k}\, \rho_{0k}(t) + i h_{0k}\, \rho_{k0}(t) - \xi_0\, R\, \rho_{kk}(t) + R\, \rho_{00}(t)\ , \qquad (74)$$

$$\partial\rho_{k0}(t)/\partial t = -i \omega_{k0}\, \rho_{k0}(t) - i h_{0k}\, \rho_{00}(t) + i h_{0k}\, \rho_{kk}(t) - (1/T_2)\, \rho_{k0}(t)\ , \qquad (75)$$

and

$$\partial\rho_{0k}(t)/\partial t = i \omega_{k0}\, \rho_{0k}(t) - i h_{0k}\, \rho_{kk}(t) + i h_{0k}\, \rho_{00}(t) - (1/T_2)\, \rho_{0k}(t)\ . \qquad (76)$$

After we express $\rho_{k0}(t)$ as a sum of its real and imaginary parts, as $\rho_{k0}(t) = p(t) + i\, q(t)$, we find

$$\partial\rho_{00}(t)/\partial t = 2\, h_{0k}\, q(t) - R\, \rho_{00}(t) + \xi_0\, R\, \rho_{kk}(t)\ , \qquad (77)$$

$$\partial\rho_{kk}(t)/\partial t = -2\, h_{0k}\, q(t) - \xi_0\, R\, \rho_{kk}(t) + R\, \rho_{00}(t)\ , \qquad (78)$$

$$\partial p(t)/\partial t = \omega_{k0}\, q(t) - (1/T_2)\, p(t)\ , \qquad (79)$$

and

$$\partial q(t)/\partial t = -\omega_{k0}\, p(t) + h_{0k}\, \rho_{kk}(t) - h_{0k}\, \rho_{00}(t) - (1/T_2)\, q(t)\ . \qquad (80)$$

The elements of the density matrix in the unperturbed basis are plotted in Fig. 4 below, for the hypothetical two-level system. The imaginary part q(t) of the off-diagonal element of the density matrix $\rho_{k'0'}$ has been multiplied by a factor of 10 before plotting and the real part p(t) has been multiplied by 25, to show the behaviors of both more clearly.

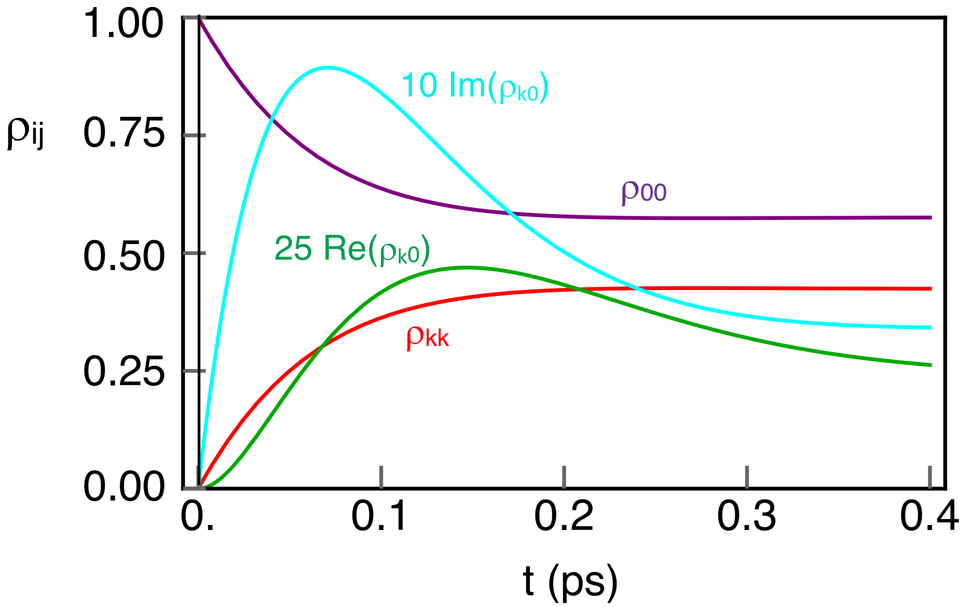

Figure 4. Density matrix elements in the unperturbed basis for the hypothetical two-level system with parameters as in Fig. 3.

Figure 5 shows the error in excited-state population ρ_{kk} calculated directly in the unperturbed basis for a stronger perturbation and shorter T_2, compared with ρ_{kk} found by transforming the density matrix in the perturbed basis into the unperturbed basis.

Equations (77)-(80) are coupled, first-order linear homogeneous equations, so they are analytically soluble in principle; however, the full analytical solutions are quite lengthy algebraically. The stationary solution (denoted by the subscript s) is comparatively simple though,

$$\rho_{00,s} = \{2\, h_{0k}^2/T_2 + \xi_0\, R\, [(1/T_2)^2 + \omega_{k0}^2]\}\eta^{-1}\ , \qquad (81)$$

$$\rho_{kk,s} = \{2\, h_{0k}^2/T_2 + R\, [(1/T_2)^2 + \omega_{k0}^2]\}\eta^{-1}\ , \qquad (82)$$

$$p_s = h_{0k}\, R\, (1 - \xi_0)\, \omega_{k0}\, \eta^{-1}\ , \qquad (83)$$

and $$q_s = h_{0k}\, R\, (1 - \xi_0)/(T_2)\, \eta^{-1}\ , \qquad (84)$$

where $\eta = 4\, h_{0k}^2\, (1/T_2) + R\, (1 + \xi_0)\, [\omega_{k0}^2 + (1/T_2)^2]$. In the unperturbed basis, Eqs (77)-(80) do not relax to equilibrium. At the stationary state, the ratio $\rho_{00,s}/\rho_{kk,s}$ differs from both ξ_0 and ξ. This ratio depends on T_2; but T_2 characterizes the dephasing time, so it includes the effects of purely adiabatic collisions, which should not alter the population ratio at steady state.

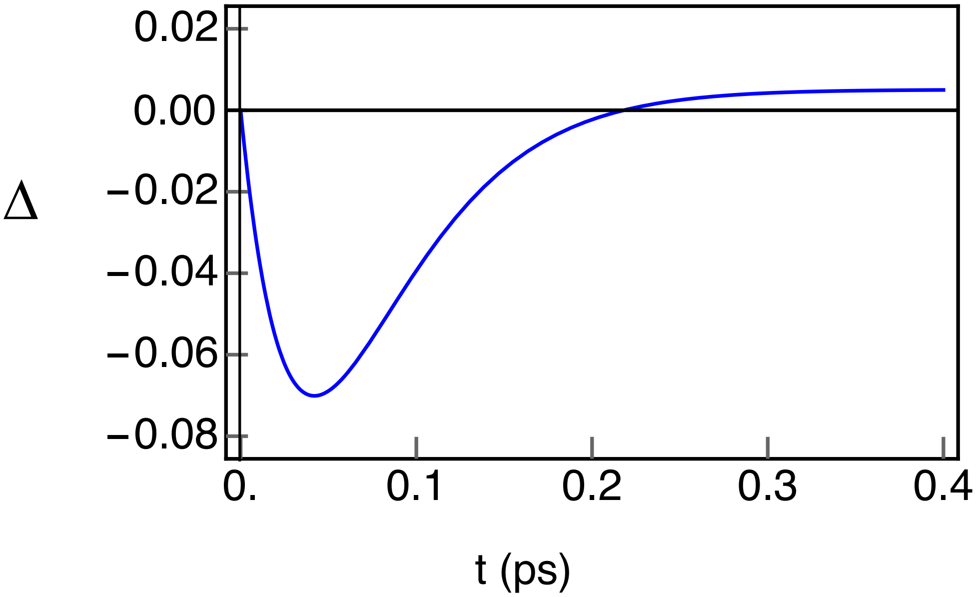

Figure 5. Difference Δ between $\rho_{kk}(t)$ calculated directly in the unperturbed basis and $\rho_{kk}(t)$ found by transformation of the density matrix in the perturbed basis, as a function of time. Parameters for the rotational transition J, M = 0,0 → 1, 0 of HCl in liquid argon at 84 K:[147] $\omega_{k0} = 3.99086$ ps^{-1}, $h_{0k} = 3.45619$ ps^{-1}, $\xi_0 = 1.43748$, $\xi = 2.06636$, $T_1 = 0.142$ ps, but with $T_2 = 0.0352$ ps.

The deviation of $\rho_{00,s}/\rho_{kk,s}$ from thermal equilibrium depends on the parameters h_{0k}, ω_{k0}, ξ_0 (or ξ), R, and T_2. The deviation from equilibrium is larger for strong fields (large h_{0k}/ω_{k0}) and for larger values of T_2, although large values of ξ_0 tend to suppress the deviation. After the coherences in the perturbed basis have decayed, coherences still remain in the unperturbed basis.

Figure 6 on the next page shows the steady-state population $\rho_{k'k',s}$ of state $|\, k' \rangle$ in the perturbed basis as a function of h_{0k}, the off-diagonal Hamiltonian matrix element divided by ħ. Values of $\rho_{k'k',s}$ obtained in the perturbed basis are plotted directly, while results obtained in the unperturbed basis from Eqs. (81)–(84) have been transformed into the perturbed basis before the comparison is made.

In generating Fig. 6, other parameters for the model two-level system have been adapted from information on rotational dephasing and population decay for HCl in liquid argon at T = 105 K.[147] The system is hypothetical, but the state $| 0_0 \rangle$ corresponds roughly to the ground rotational state of HCl, and the state $| k_0 \rangle$ corresponds to the first excited rotational state with J = 1 and M = 0. Other parameter values[147] used for this plot are $R = 7.93651\ \text{ps}^{-1}$, $T_2 = 0.0958$ ps, $\omega_{k0} = 3.99086\ \text{ps}^{-1}$, $\xi_0 = 1.33685$, $\xi = 1.437480$, $\gamma = 4.98858\ \text{ps}^{-1}$.

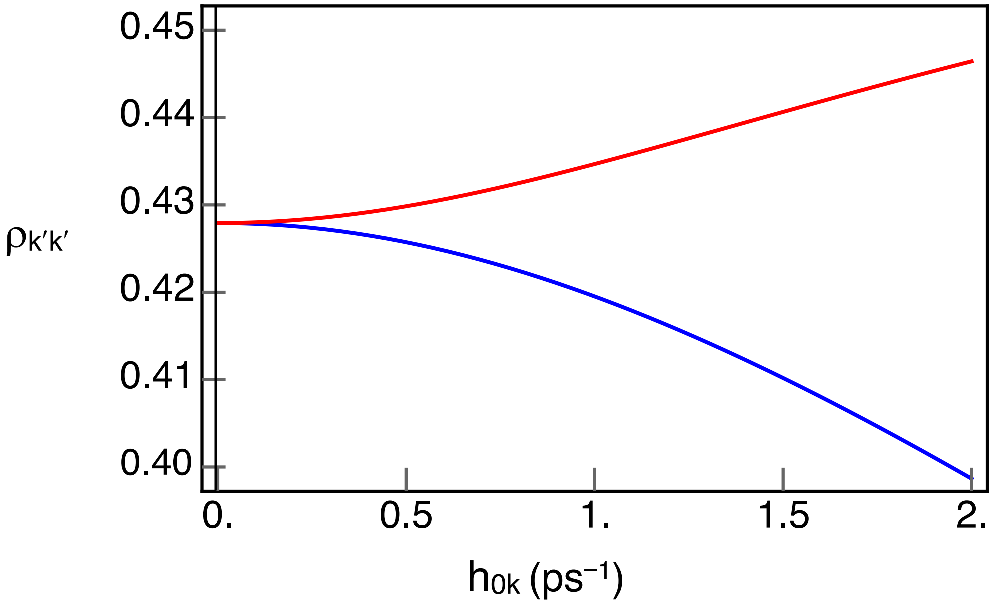

Figure 6. Stationary excited-state populations vs. h_{0k}. Blue curve: Population $\rho_{k'k',s}$ of the perturbed excited state obtained with the Redfield equation, from Eq. (69) in the long-time limit. Red curve: Population $\rho_{k'k',s}$ found from Eqs. (81)–(84) in the unperturbed basis after transformation into the perturbed basis.

In a two-level system, a perturbation pushes the ground and excited states further apart. Therefore, the population $\rho_{k'k'}$ should drop as h_{0k} increases. This pattern is observed for the direct calculation of $\rho_{k'k'}$ in the perturbed basis (shown as the blue curve in Fig. 6), but not for the calculation starting from Eqs. (81)–(84) in the unperturbed basis, followed by transformation into the perturbed basis (shown as the red curve). In the unperturbed basis, as in the original Dirac theory, when the excited state $| k_0 \rangle$ contributes to the adiabatic adjustment of the original ground state $| 0_0 \rangle$ to the perturbation, that counts as a transition. For this reason, increasing the strength of the perturbation h_{0k} appears to cause an increase in the population of the excited state, even after transformation of the results in Eqs. (81-84) into the perturbed basis.

Figure 7 on the next page shows the excited-state population $\rho_{k'k',s}$ as a function of the dephasing time T_2. For the results shown in this figure, we have set $h_{0k} = 2.0$ ps^{-1}, $\omega_{k0} = 3.99086$ ps^{-1}, $R = 3.0$ ps^{-1}, $\xi = 1.50838$, and $\xi_0 = 1.33685$. In the perturbed basis, $\rho_{k'k',s}$ is independent of the dephasing time, but the result for $\rho_{k'k',s}$ depends on T_2, if $\rho_{k'k',s}$ is obtained by transformation of the stationary solutions in Eqs. (81)-(84) into the perturbed basis.

In the supplementary material, we derive the differential equations in the unperturbed basis that correspond exactly to the Redfield equations[57] in the perturbed basis. They are

$$\gamma^2\, \partial\rho_{kk}/\partial t = (1/2)\, R\, (1 + \xi)\, \omega_{k0}^2\, [1 - 2\rho_{kk}(t)] - (1/2)\, \xi\, R\, \omega_{k0}\, \gamma + (1/2)\, R\, \omega_{k0}\, \gamma$$
$$+ (2/T_2)\, h_{0k}^2 [1 - 2\rho_{kk}(t)] - 2\, [R\, (1 + \xi) - (1/T_2)]\, h_{0k}\, \omega_{k0}\, p(t)$$
$$- 2\, \gamma^2\, h_{0k}\, q(t)\,, \tag{85}$$

$$\omega_{k0}\, \partial p/\partial t = \gamma^2\, q(t) - (1/T_2)\, h_{0k}\, [1 - 2\rho_{kk}(t)] - (1/T_2)\, \omega_{k0}\, p(t) + 2\, h_{0k}\, \partial\rho_{kk}/\partial t\,, \tag{86}$$

$$\partial q/\partial t = h_{0k}\, [\rho_{kk}(t) - \rho_{00}(t)] - \omega_{k0}\, p(t) - (1/T_2)\, q(t)\,, \tag{87}$$

and $\partial\rho_{00}/\partial t = -\partial\rho_{kk}/\partial t$. Interestingly, the differential equation for q(t), the imaginary part of the off-diagonal density matrix element ρ_{k0}, is identical to the differential equation produced by simply adding relaxation terms to the Liouville equation[4] in the unperturbed basis. The equations for $\partial\rho_{kk}/\partial t$ and $\partial p/\partial t$ are not the same as those obtained by adding relaxation terms to the Liouville equation, however. The stationary solutions of Eqs. (85)-(87) are

$$\rho_{kk,s} = (1/2) - \omega_{k0}\,(\xi - 1)/[2\gamma\,(\xi + 1)]\ , \tag{88}$$

$$p_s = h_{0k}\,(1 - \xi)/[\gamma\,(\xi + 1)]\ , \tag{89}$$

and $q_s = 0$, as derived in the supplementary material.

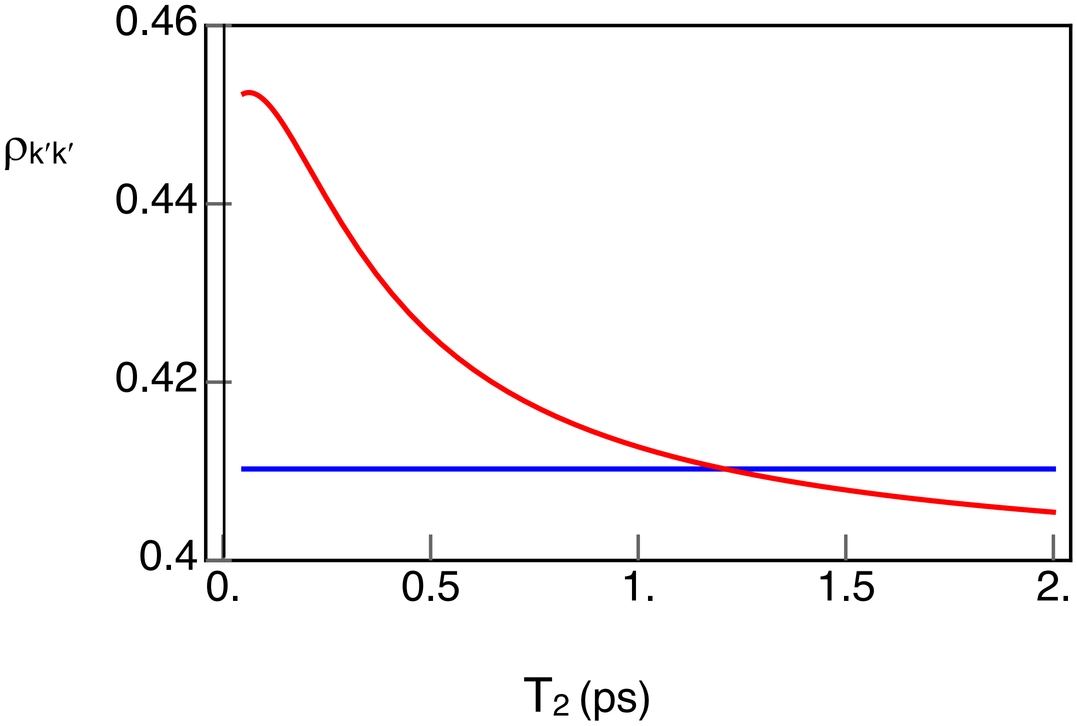

Figure 7. Stationary population $\rho_{k'k'}$ of the perturbed excited state vs. the dephasing time T_2 from 0.05 ps to 2.0 ps. Blue: $\rho_{k'k'}$ from the Redfield equations.[57] Red: $\rho_{k'k'}$ from Eqs. (81)-(84) in the unperturbed basis, followed by transformation to the perturbed basis.

The equilibrium solutions for the density matrix elements in the perturbed basis are $\rho_{k'k',s} = 1/(1 + \xi)$, $\rho_{0'0',s} = \xi/(1 + \xi)$, and $\rho_{k'0',s} = \rho_{0'k',s} = 0$. In the supplementary material,[143] we also prove that results identical to Eqs. (88) and (89) are derived by transforming the equilibrium solutions of the Redfield equations[57] in the perturbed basis into the unperturbed basis. Thus the stationary solutions of Eqs. (85)-(87) correspond to true thermal equilibrium with the bath. Equations (85)-(87) with $\partial\rho_{00}/\partial t = -\partial\rho_{kk}/\partial t$ are the correct differential equations for the density matrix elements for a two-level system coupled to a bath, when written in the unperturbed basis.

The comparisons in Figs. 5-7 show that the differences between the two solutions of the Liouville equation plus relaxation terms are physically significant, because the results have been expressed in a single basis in each case.

Additional considerations come into play if a physical phenomenon depends on the population of a state that is excited above the perturbed ground state, with a gap in the energies. Then the difference between $\rho_{k'k'}$ and ρ_{kk} becomes significant. We have evaluated $\rho_{00} - \rho_{kk}$ and $\rho_{0'0'} - \rho_{k'k'}$ for hypothetical two-level systems modeled with parameters appropriate for the rotational relaxation of hydrogen chloride,[147] fluoroacteylene,[148] cyanoacetylene,[149,150] carbonyl sulfide,[151-153] nitrous oxide,[154] and ethylene oxide.[155] We have selected these species because T_1 and T_2 have been determined experimentally for them, and differences between the two approaches are apparent in the results in these cases. The results are listed in Table 3 in the supplementary material. The percent differences between $\rho_{00} - \rho_{kk}$ and $\rho_{0'0'} - \rho_{k'k'}$ range from 2.54% to 88.72% with the parameters we have used.

It is important to note that for some physical systems, no detectable difference is expected between the results in the perturbed and unperturbed basis sets. For example, in many applications in the theory of nuclear magnetic resonance, there is no distinction between the two basis sets: Typically the eigenfunctions of the spin operator in the z direction are chosen as the unperturbed basis in zero field. The Hamiltonians for the spins perturbed by a static field in the z direction are diagonal in this basis, and the differences discussed here do not arise.

For vibrational relaxation, it may be very difficult to detect the differences between the results from Eqs. (65)-(67) in the perturbed basis, and those from direct addition of relaxation terms to the Liouville equation in the unperturbed basis, via Eqs. (73)–(76). Detectable differences would most likely require a strong perturbation that is capable of producing a high population in the perturbed excited state $| k' \rangle$. For nitrogen molecules, for example, an intense, inhomogeneous applied field would be required. While large values of T_1/T_2 tend to increase the discrepancies between results obtained in the perturbed and unperturbed basis sets, for N_2 the value of ξ_0 is so large that the differences are likely to be undetectable in normal circumstances.

VI. Summary and discussion

We have examined the differences between transition probabilities computed with the nonadiabatic theory,[3,6,47-51] which employs coefficients for the instantaneous eigenfunctions of the full Hamiltonian including the perturbation, *versus* those found with Dirac's standard theory,[1,2] which relies on coefficients for the eigenfunctions of the original, unperturbed Hamiltonian H_0. If a system remains coherent, the numerical differences simply reflect different choices of the basis set; but when interactions with a bath produce dephasing and population relaxation, the observed differences are physically significant.

Sections II and III lay the groundwork for our analysis of the density matrix for a two-level system in a field that is imposed suddenly and then remains constant. In Sec. IV, we have used the Liouville equation[4] for the time-dependent density matrix, incorporating response to all orders in the perturbation. Then in Sec. V, we introduced the effects of dephasing and population relaxation. In earlier work, we had proven that the differences between $| b_k(t) |^2$ and $| c_k(t) |^2$ could be detected experimentally by imposing a second perturbation after the coherences induced by the first perturbation had completely decayed.[51] In this work, we have considered a single external perturbation, but we have allowed for the full time-dependence of the reduced density matrix for a system coupled to a thermal bath.

We solved the Redfield equation[57] in the perturbed basis, for a model two-level system treated in the secular approximation. When the relaxation terms were added directly to the Liouville equation[4] in the unperturbed basis, we found that the density matrix did not evolve to thermal equilibrium. The stationary solutions for ρ_{00} and ρ_{kk} in the unperturbed basis depend on T_2, the dephasing time; but T_2 is affected by elastic collisions that cause pure dephasing with no change in population, so the stationary values of ρ_{00} and ρ_{kk} should be independent of T_2. We have demonstrated that the results from the analyses in the perturbed and unperturbed basis sets differ, after transformation to a single, common basis.

We also compared the stationary values of $\rho_{00} - \rho_{kk}$ with the equilibrium values of $\rho_{0'0'} - \rho_{k'k'}$ in the perturbed basis. The comparison shows the absolute differences in the predicted level of "excitation," for hypothetical model systems with parameters drawn from rotational relaxation of hydrogen chloride,[147] fluoroacteylene,[148] cyanoacetylene,[149,150] carbonyl sulfide,[151-153] nitrous oxide,[154] and ethylene oxide.[155]

The differences between the results allowing for relaxation in the perturbed and unperturbed basis sets are enhanced when the energy difference between the unperturbed ground and excited states is relatively small, when the perturbation is large, and when T_2 is small compared with T_1. The differences are not detectable in standard NMR experiments, because the perturbed and unperturbed basis sets are identical in that case. The differences are also likely to be quite small in vibrational relaxation, because the equilibrium ratio of $\rho_{0'0'}$ to $\rho_{k'k'}$ is typically very large.

In Sec. V and the supplementary material, we have shown how to account for relaxation effects accurately in the unperturbed basis. We obtained the appropriate time-evolution equations by transforming the Redfield equations[57] in the perturbed basis to the corresponding equations in the unperturbed basis. The time-evolution equation for the imaginary part of the off-diagonal density matrix element $\rho_{k0}(t)$ is the same as that obtained by adding the relaxation terms to the Liouville equation in the unperturbed basis, but the equation for the real part of the off-diagonal density matrix element differs, as do the equations for the time-dependence of $\rho_{00}(t)$ and $\rho_{kk}(t)$.

In future work, we plan extensions that are beyond the scope of this work. Working within the nonadiabatic transition framework, we plan to include multiple quantum states of specific quantum systems, starting with a thermal distribution over states (cf. Refs. 156-161). If a harmonic field is imposed after the stationary solution or thermal equilibrium has been reached, differences in the predicted power absorption should follow from the differences between $\rho_{00,s} - \rho_{kk,s}$ *versus* $\rho_{0'0'} - \rho_{k'k'}$ at equilibrium. We plan to consider the effects of the *gradual* imposition of a constant field, an oscillatory applied field,[55,162,163] or a chirped field.[164-166] We will also analyze spontaneous decay of excited states of atoms and molecules in a static electric field, following an initial excitation.

Treating the interactions between the system and the bath at a higher level would allow us to account for the effects of a perturbing field on the relaxation matrix elements[167] and for the effects of the bath on the off-diagonal matrix elements in the Hamiltonian; but the current level of treatment is sufficient to show the differences between the nonadiabatic theory and Dirac's transition theory and to reveal qualitative features of the differences. The nonadiabatic theory, which makes a distinction between the excited-state coefficient $b_k(t)$ and the full Dirac coefficient $c_k(t)$ may also be applicable to exciton transfer.[30-46] For a clear-cut demonstration of differences that may arise in the treatment of exciton transfer, accurate values of the transition matrix elements for large molecules would be needed, however. In studies of the response to ultrashort laser pulses that initiate electronically nonadiabatic transitions,[168] we anticipate that the distinction between $a_k(t)$ and $b_k(t)$ will affect the formation and motion of vibrational wave packets. The adiabatic terms $a_k(t)$ contribute to the probability amplitude for the molecule to remain on the perturbed electronic ground state, while the $b_k(t)$ terms characterize the formation of wave packets that evolve on the excited-state potential energy surfaces.

Supplementary Material

In the supplementary material, we provide the transformation matrix elements between the unperturbed and perturbed basis sets in a constant applied field. We prove that the analytic solutions of the Liouville equation[4] for a two-level model system are equivalent in the perturbed and unperturbed basis sets in the absence of coupling to a bath, as expected for a system that remains coherent. When decoherence arises due to contact with a bath for a system in a constant field, we prove that the results from the Redfield theory[57] in the perturbed basis differ from the results obtained by adding relaxation terms to the Liouville equation[4] in the unperturbed basis. We show that the density matrix in the unperturbed basis does not evolve to thermal equilibrium, the excited state population increases with increasing strength of the applied field, and the stationary populations depend on the dephasing time T_2. We transform the Redfield equations in the perturbed basis into the unperturbed basis, to identify the equivalent equations in that basis. Then we determine the stationary solutions of the equivalent equations in the unperturbed basis, and show that the results for the ground and excited-state populations, and for the off-diagonal elements of the density matrix are identical, when obtained from those stationary solutions of the newly derived equations in the unperturbed basis or by transformation of the thermal equilibrium results in the perturbed basis into the unperturbed basis. Figures S.1-S.4 in the supplementary material illustrate various forms of $| b_k(t) |^2$ and $| c_k(t) |^2$ that may develop when a constant field is applied and turned off either rapidly or gradually. Figure S.5 shows the real parts of $a_k(t)$, $b_k(t)$, and $c_k(t)$ as functions of time within the sudden approximation, when the perturbing field is held constant for intervals $\tau = 9\pi/\omega_{k0}$, $9.25\pi/\omega_{k0}$, $9.5\pi/\omega_{k0}$, $9.75\pi/\omega_{k0}$, and $10\pi/\omega_{k0}$. Figure S.6 shows the corresponding imaginary parts of the probability amplitudes $a_k(t)$, $b_k(t)$, and $c_k(t)$. Table 1 provides tests of the accuracy of the numerical results by comparison with the values of γ, the maximum excited-state population, the time at which the maximum is first reached, the minimum excited-state population, and the time at which the minimum is first reached. Table 2 lists the values of rotational state energies of HCl for J = 0-6, and the values of T_1 and T_2 as calculated by Velasco *et al.*[147] for HCl in liquid argon at 105 K. In Fig. S.7 and S.8, we show T_1 and T_2 as functions of E_J/kT at T = 105 K, from Ref. 147, along with the Mathematica fits to these plots. We have used these results to approximate T_1 and T_2 at 84 K, for use in Sec. V. Table 3 lists the values of $\rho_{00,s} - \rho_{kk,s}$ at steady state in the unperturbed basis, for comparison with $\rho_{0'0'} - \rho_{k'k'}$ at thermal equilibrium in the perturbed basis, for hypothetical two-level systems with parameters drawn from experimental results for HC≡CF,[148] HC≡CCN,[149,150] OCS,[151] $^{15}N_2O$,[154] and C_2H_4O,[155] and parameters from simulations on HCl in liquid argon.[147]

Author Declarations

The authors have no conflicts of interest to disclose.

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