How Fast Can a Quantum State Change with Time?

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Lower and upper bounds are derived for the decay and transitions of quantum states, evolving under a time-dependent Hamiltonian, in terms of the energy uncertainty of the initial and final state. The bounds are simultaneously a rigorous version of Fermi's golden rule and of the time-energy uncertainty relation. They are sharp, refer to short times, and are compared with recent long-time results for time-independent Hamiltonians. Illustrations for tunneling systems, laser-driven processes, and neutron interferometry in time-dependent magnetic fields are given.

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With the availability of very short and intense laser pulses (10^{-14} s, 10^{18} W/cm^2), a naturally arising question is how rapidly the state of a quantum system can change with time, given that we know the initial state and the Hamiltonian governing the time evolution. Recent examples for dynamics driven/probed by such laser fields are the suppression of ionization of atoms in strong laser fields [1]; wave-function shock waves [2]; observation of quantum jumps [3]; laser-enhanced/suppressed tunneling [4]; and the photoisomerization of rhodospin in 200 fs [5]. The 200 fs for rhodospin, during which a massive nuclear rearrangement occurs, make the molecule one of the fastest known quantum switches.

One answer to the question is the time-energy uncertainty relation stating that the time at which the state differs appreciably from the initial state is of order $\hbar/\Delta E$ or larger, where ΔE is the energy uncertainty of the initial state. The purpose of this paper is to cast this answer into a form suitable to treat driven systems, i.e., time-dependent Hamiltonians. It gives bounds for decay, revival, and transitions of a time-evolving state in terms of quantities that do not require integration of the Schrödinger equation. The bounds are remarkable because the oscillatory nature of time evolution makes such estimates in general difficult.

For any observable A and state φ (normalized vector in Hilbert space), the uncertainty $\Delta(A,\varphi)$ is defined by $\Delta(A,\varphi) := [\langle\varphi|A^2\varphi\rangle - \langle\varphi|A\varphi\rangle^2]^{1/2}$. The state of the system at time t is denoted by ψ_t and obeys the Schrödinger equation $i\hbar\dot{\psi}_t = H_t\psi_t$ with Hamiltonian H_t at time t and initial state ψ_0. For a perspective, four time-energy inequalities for t-independent Hamiltonians H are recalled. They are of the form

$$\Delta(H,\psi_0)\tau_j \geq \hbar\gamma_j \quad (j=1,\ldots,4), \tag{1}$$

where the τ_j's are different notions of lifetime of the state ψ_0 and the γ_j's are respective constants (Table I). Other inequalities exist in terms of chronometric observables [9], traversal times through potential barriers [10], and delay times in scattering [6,11]. They all may be viewed as offspring of the identity

$$\Delta(H_t,\psi_t) = \hbar\,||(1-|\psi_t\rangle\langle\psi_t|)\dot{\psi}_t||\,, \tag{2}$$

between energy uncertainty and the rate of change of ψ_t for an arbitrary driven system [12]: If one is large, so is the other. The norm in (2) measures the component of $\dot{\psi}_t$ orthogonal to ψ_t, i.e., the rate at which ψ_t leaves the subspace spanned by itself.

The core result of this paper extends (1) to *pointwise* bounds for the probability $|\langle\varphi|\psi_t\rangle|^2$ of finding a *driven* system in an *arbitrary* state φ. It is a rigorous, integrated form of Fermi's golden rule.

Theorem 1.—Let ψ_t obey the Schrödinger equation with Hamiltonian H_t and let φ be an arbitrary reference state ("target" state). Then

$$|\langle\varphi|\psi_t\rangle| \leq \sin(\delta+h_t)\,, \tag{3a}$$

$$|\langle\varphi|\psi_t\rangle| \geq \sin(\delta-h_t)\,, \tag{3b}$$

$$\delta := \arcsin|\langle\varphi|\psi_0\rangle|\,, \tag{4}$$

$$h_t := \hbar^{-1}\int_0^t \min\{\Delta(H_s,\varphi),\Delta(H_s,\psi_0)\}ds\,, \tag{5}$$

for $0 \leq t \leq T_\pm$, where $T_\pm$ is the smallest $t \geq 0$ for which the right-hand side of (3a) and (3b) reaches 1 and 0, respectively. Thus the population of the target state is limited by the cumulative energy uncertainty of the tar-

TABLE I. Lifetimes τ_j and constants γ_j in Eq. (1). The γ_j are sharp, i.e., for each j there exist H and ψ_0 with equality in (1).

j	τ_j	Meaning of τ_j	γ_j	Reference
1	$\inf_A \Delta(A,\psi_t)/\|(d/dt)\langle\psi_t\|A\psi_t\rangle\|$	Time for ψ_t to change appreciably	$\frac{1}{2}$	[6]
2	$\inf\{t\geq 0: \|\langle\psi_0\|\psi_t\rangle\|^2 = 1/2\}$	First half-lifetime of ψ_0	$\pi/4$	[7]
3	$\inf\{t\geq 0: \|\langle\psi_0\|\psi_t\rangle\|^2 = 0\}$	First death time of ψ_0	$\pi/2$	[7]
4	$\int_0^\infty \|\langle\psi_0\|\psi_t\rangle\|^2 dt$	Average lifetime of ψ_0	$3\times 5^{-3/2}\pi$	[8]

get or initial state, whichever is smaller; and $T_\pm$ is the earliest possible birth-death time of state φ. There are systems for which $|\langle\varphi|\psi_t\rangle|$ is nonstationary and equality holds in (3a) and (3b) over the entire interval $0 \le t \le T_\pm$.

Proof.—The density operator $\rho_t := |\psi_t\rangle\langle\psi_t|$ satisfies $i\hbar\dot\rho_t = [H_t, \rho_t]$. By taking the expectation value with respect to φ and using the inequality for the uncertainty product of two self-adjoint operators, one obtains for $p_t := |\langle\varphi|\psi_t\rangle|^2$ the relation

$$|\dot p_t| = |\langle\varphi|\dot\rho_t\varphi\rangle| = \hbar^{-1}|\langle\varphi|[H_t,\rho_t]\varphi\rangle|$$
$$\le 2\hbar^{-1}\Delta(H_t,\varphi)\Delta(\rho_t,\varphi) = 2\dot g_t(p_t - p_t^2)^{1/2}, \qquad (6)$$

where $g_t := \hbar^{-1}\int_0^t \Delta(H_s,\varphi)ds$ and $\rho_t^2 = \rho_t$ have been used in the last step [13]. Standard properties of differential inequalities [14] imply that $p_{-,t} \le p_t \le p_{+,t}$ $(t \ge 0)$ where $p_{\pm,t}$ is the maximal/minimal solution of the initial-value problem $\dot p_{\pm,t} = \pm 2\dot g_t(p_{\pm,t} - p_{\pm,t}^2)^{1/2}$, $p_{\pm,0} = p_0$ (the problem has a continuum of solutions). It is easy to verify that $p_{+,t} = \sin^2[\min(\delta + g_t, \pi/2)]$ and $p_{-,t} = \sin^2[\max(\delta - g_t, 0)]$. This proves the weak form of (3) where h_t is replaced by g_t. The proof of the strong form, (3) when $h_t < g_t$, is more involved and will be presented elsewhere (the proof is easy if the time evolution operator commutes with the Hamiltonian). Cases of equality in (3) are given below.

Discussion.—(a) If $\varphi = \psi_0$, the upper bound is trivial $(T_+ = 0)$ and the lower one reduces to

$$|\langle\psi_0|\psi_t\rangle| \ge \cos\left[\hbar^{-1}\int_0^t \Delta(H_s,\psi_0)ds\right], \qquad (7)$$

showing that the initial state cannot decay too fast and does not decay at all if it is an eigenstate of H_t (in which case $T_- = \infty$). Conversely if $\varphi \perp \psi_0$, the lower bound is trivial $(T_- = 0)$ and the upper one is $|\langle\varphi|\psi_t\rangle| \le \sin(h_t)$. It shows that a state orthogonal to the initial state cannot be populated too fast and recovers the elementary selection rule that φ can be populated only if φ and ψ_0 are simultaneously noneigenstates of H_t during some interval of time. Specifically, the transition is fast only if *both* have large energy uncertainty during that interval. The fast transition at large energy uncertainty is due, in a picture where ψ_0 and φ are localized on opposite sides of a potential barrier, to the admixture of excited states near the top of the barrier [4(a)]. Another corollary of (3) to the effect that ψ_t cannot change too fast is the following. If ψ_t returns to ψ_0 at time $t_1 > 0$ (revival time) after having decayed to a state orthogonal to ψ_0, then $t_1 \ge \inf\{t \ge 0: \int_0^t \Delta(H_s,\psi_0)ds = \pi\hbar\}$.

(b) The origin of the interval $0 \le t \le T_\pm$ is that the probability p_t may oscillate (quantum beats) and reach 1 or 0 in finite time. So if p_t varies monotonically, (3) cannot hold beyond the point where $\sin(\delta \pm h_t)$ reaches 1 or 0. The performance of (3) for the oscillatory case is illustrated in Fig. 1. It shows that the bounds (3) are saturated, both with respect to time range and sharpness, for tunneling states, i.e., for maximally *nonclassical* states.

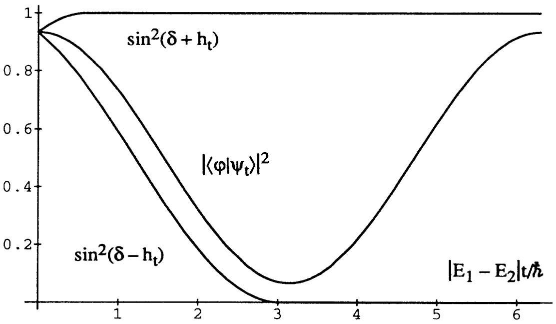

FIG. 1. Graph of $|\langle\varphi/\psi_t\rangle|^2$ and of the two bounds from Eqs. (3a) and (3b) for the t-independent Hamiltonian $H = E_1|\varphi_1\rangle\langle\varphi_1| + E_2|\varphi_2\rangle\langle\varphi_2|$ (two-level system with energies E_k and eigenstates φ_k), initial state $\psi_0 = (\varphi_1 + \varphi_2)/\sqrt{2}$, and target state $\varphi = (\varphi_1 + \sqrt{3}\varphi_2)/2$. The bounds are continued as 1 and 0 beyond $T_\pm$. Equality in (3a) and (3b) for $0 \le t \le T_\pm$ results, with this H and ψ_0, for the choices $\varphi = (\varphi_1 \mp \varphi_2)/\sqrt{2}$ and $\varphi = [\varphi_1 \mp i\,\mathrm{sgn}(E_1 - E_2)\varphi_2]/\sqrt{2}$. The case $\varphi = \psi_0$ also yields equality in (1), $j \ne 4$.

(c) For t-independent Hamiltonians H, the result (7) has been obtained earlier and gives the entries $j = 2,3$ in Table I [7]. In this case, (7) may be rewritten as

$$\langle\psi_0|\psi_t\rangle = \hat\mu(t) := \int_{-\infty}^{\infty} e^{-iEt/\hbar}d\mu(E), \qquad (8)$$

$$|\hat\mu(t)| \ge \cos(\sqrt{\mathrm{var}\mu}\, t/\hbar), \qquad (9)$$

where μ is the spectral measure (probability measure) of H with respect to ψ_0 and $\mathrm{var}\mu$ is its variance. Thus the short-time decay of the Fourier transform $\hat\mu(t)$ is limited by the first two moments of μ and is slow or fast depending on whether $d\mu/dE$ is narrowly peaked or broad. If the support of μ consists of a single point (i.e., ψ_0 is an eigenstate of H), there is no decay. If the support of μ consists of two points as in the two-level system in Fig. 1, the decay is fastest when the points have equal weight ("broad" $d\mu/dE$), giving equality in (9). Equation (9) may be regarded as a short-time counterpart of the well-known long-time decay of $\hat\mu(t)$ which is fast or slow depending on whether $d\mu/dE$ is smooth (continuous derivatives) or not. The general decay law for $t \to \infty$, such as when the support of μ is a Cantor set, is

$$(1/t)\int_0^t |\hat\mu(t')|^2 dt' \sim c(\sqrt{\mathrm{var}\mu}\, t/\hbar)^{-D_2}, \qquad (10)$$

where c is a constant and D_2 is the correlation dimension of μ, viewed as a fractal measure [15]. Thus the short/long-time decay is governed by the coarse/fine-structure correlations of μ. One can estimate the time of onset, t^*, of the asymptotic behavior (10) as follows. The bounds (9) and $|\hat\mu(t)| \le 1$ require that $f(x) \le c \le x^{D_2}$ for all $x \ge \sqrt{\mathrm{var}\mu}\, t^*/\hbar$ where $f(x) := x^{D_2}[\min\{2x,\pi\} + \sin(\min\{2x,\pi\})]/4x$. Analysis of this condition, based on whether c exceeds the maximum $f_{\max}$ of f or not, yields the results in Table II. They show that the bound (9) pushes the onset of the asymptotic regime to the distant future if $D_2 < 1$ and c drops below the critical value $f_{\max}$. Since every probability measure μ on $\mathbb{R}$ is the spectral measure of some pair (H, ψ_0), these results for $\hat{\mu}$ are general. It would be of interest to know if they extend to probability measures on $\mathbb{R}^d$ $(d=2,3,\ldots)$.

TABLE II. Bounds for the onset t^* and prefactor c of the long-time regime (10). The bounds for c are sharp.

	$t^* \geq x^* \hbar/\sqrt{\mathrm{var}\mu}$	c
$D_2=0$	$x^* = \max\{x \geq 0{:}f(x)=c\}$	$c \leq 1$
$0<D_2<1;\, c \leq f_{\max}$	$x^* = \max\{x \geq 0{:}f(x)=c\}$	$\cdots$
$0<D_2<1;\, c > f_{\max}$	$x^* = c^{1/D_2}$	$\cdots$
$D_2=1$	$x^* = c$	$c \geq 3\times 5^{-3/2}\pi$

(d) To illustrate (3) for a driven system, we take the hydrogen atom in a laser field [1]. Let ψ_0 be the eigenstate with quantum numbers n,l,m of the atomic Hamiltonian K. Let $H_t = k - e_0 \sin(\omega t)\mathbf{E}\cdot\mathbf{Q}$ with electron position $\mathbf{Q}$ and charge e_0, and electric-field amplitude $\mathbf{E}$ and frequency ω. No exact solution is known for ψ_t. Equation (7) in this case yields

$$|\langle\psi_0|\psi_t\rangle| \geq \cos\left[k_{n,l,m}|e_0\mathbf{E}|a_0\hbar^{-1}\int_0^t |\sin(\omega s)|ds\right], \tag{11}$$

$$k_{n,l,m} := (n/2)\{[5n^2+1-3l(l+1)][1+(1-4m^2)/(4l^2+4l-3)]\}^{1/2} \tag{12}$$

[16], where a_0 is Bohr's radius. This does not show suppression of ionization for large $|\mathbf{E}|$ and ω because it describes the probability of ψ_t remaining in the initial state, rather than in the subspace of all bound states. But it does show that for fixed n the initial state is particularly stable if l and $|m|$ are large, in agreement with Ref. [1(a)]. For example, $k_{n,n-1,n-1} = n\sqrt{(n+1)/2}$. The stability here has the simple interpretation that such a state has a small uncertainty in electric dipole moment. Equation (11) proves that the system remains well behaved as $\omega \rightarrow \infty$, in which case the time integral equals $2t/\pi$. For large ω, Eq. (11) exhibits resonances (plateaus) at $t=\pi/\omega, 2\pi/\omega, \ldots$ due to the zero energy uncertainty when the field vanishes. Such inflection points have been observed in numerical work [1(b)].

(e) If a state $\varphi \perp \psi_0$ experimentally is known to be populated with probability p' at time t', then (3) yields information about the two states. This is the converse of predicting transition probabilities from known φ and ψ_0. For example, let φ and ψ_0 be the two isomers of rhodospin [5], both eigenstates of the molecular Hamiltonian K; let $\mathbf{D}$ be the electric dipole moment operator for the electrons and nuclei; and assume $H_t = K - \sin(\omega t)\mathbf{E}\cdot\mathbf{D}$ for $0 \leq t \leq T$ and $H_t = K$ for $t > T$ where $\omega, \mathbf{E}$ are as above and T is the pulse duration. Reference [5] reports $p'=1$ at $t'=200$ fs with $T=35$ fs. This implies $h_{t'} \geq \pi/2$ by (3a), leading to

$$\Delta(\mathbf{E}\cdot\mathbf{D},\psi)\int_0^T |\sin(\omega s)|ds \geq \pi\hbar/2 \quad (\psi=\varphi,\psi_0). \tag{13}$$

Thus the experiment yields estimates of the dipole-moment fluctuations of the two states: A fast switch requires large fluctuations. If in addition $\Delta(\mathbf{E}\cdot\mathbf{D},\psi_0) \times \int_0^T |\sin(\omega s)|ds < \pi\hbar$, the revival-time corollary in (a) guarantees that no return to ψ_0 occurs (stable switching).

(f) Another example is the scalar Aharonov-Bohm effect [17] in which a neutron starts as a wave packet ψ_0, is split and recombined by Bragg diffraction (potential V), phase shifted in a solenoid (potential W_t), and registered (Fig. 2). Thus $H_t = \mathbf{P}^2/(2m) + V + W_t$ where $\mathbf{P}, m$ are momentum and mass of the neutron. When W_t is turned on at time t', the neutron must be inside the solenoid with probability p'. Typically, $t' \approx 10$ μs, $p' = \frac{1}{2}$, and the state "neutron inside the solenoid" may be taken as ψ_0 translated by $\mathbf{r}$. Thus $\varphi = \exp(-i\mathbf{r}\cdot\mathbf{P}/\hbar)\psi_0$. By hypothesis φ and ψ_0 are localized in disjoint regions with constant potential, so that the inequality $\sqrt{p'} \leq \sin(h_{t'})$ from (3a) reduces to the kinematical bound

$$\Delta(\mathbf{P}^2,\psi_0) \geq (2m\hbar/t')\arcsin\sqrt{p'}. \tag{14}$$

It estimates the localization of ψ_0 required for the neutron to be well localized in the solenoid at time t'. This localization leads to a spreading of the wave packet entering the solenoid and, by semiclassical arguments, to a fluctuation $\Delta t'$ of entry time t' of the form

$$\Delta t' \gtrsim (1/v) = [(2\hbar t'/m)\arcsin\sqrt{p'}]^{1/2}, \tag{15}$$

where v is the neutron velocity. Equation (15) gives $\Delta t' \gtrsim 10^{-3}$ μs for the present data and shows that the interference experiment is necessarily *macroscopic* (so that $\Delta t' \ll t'$). By analogy to $\Delta N \propto N^{1/2}$ for the fluctuation of particle number N in statistical mechanics, (15) may be regarded as a "fluctuation-dissipation theorem" for time. Here it is the probability that the neutron is at position $\mathbf{r}$ at time t' which "dissipates."

Examples (c)-(f) give a flavor of the applicability of Theorem 1: (c) estimates the onset of the power-law decay in systems with Cantor spectra; (d) yields analytic results for a continuously driven system that has been tract-

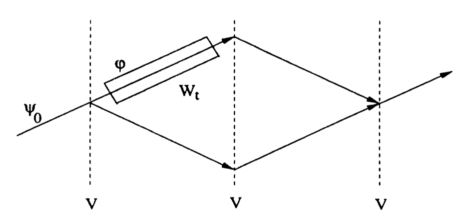

FIG. 2. Neutron interferometry in a pulsed scalar potential W_t (magnetic field interacting with the spin).

able only numerically so far; (e) treats a pulsed system and extracts, from the response, novel fluctuations results; and (f) shows that the "short times" in (3) may be quite long for macroscopic quantum systems.

Finally, one may ask how *slowly* a state can change with time for a given initial energy uncertainty ε. The answer is, arbitrarily slowly.

Theorem 2.—The maximum/minimum survival probability of the initial state for time t and energy uncertainty ε, expressed in terms of (8) for t-independent Hamiltonians, equals

$$\sup_{\mu,\sqrt{\text{var}\mu}=\varepsilon}|\hat{\mu}(t)| = 1\,, \tag{16}$$

$$\inf_{\mu,\sqrt{\text{var}\mu}=\varepsilon}|\hat{\mu}(t)| = \cos(\min\{\varepsilon t/\hbar,\pi/2\}) \tag{17}$$

for all $t,\varepsilon \geq 0$.

Sketch of proof.—Equation (16) obtains from a suitably chosen family of two-level systems. The short-time part of (17) is clear from (8) and the discussion in Fig. 1; the long-time part is realizable by suitable four-level systems.

Thus no matter how large ε is, the survival amplitude $\langle\psi_0|\psi_t\rangle$ may remain arbitrarily close to 1 for all t; and no matter how small ε is, the amplitude may reach 0 at any $t \geq \pi\hbar/2\varepsilon$. So with only δ and h_t available, the bounds (3) are the best possible ones.

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