The Physics of Spontaneous Emission and Quantum Mechanical Decay

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By using some very simple mathematical arguments, it is possible to prove that quantum mechanics forbids a strictly exponential form for the decay. Examining more closely the derivation of the approximate exponential decay from Fermi’s Golden rule reveals a clear physical interpretation of this strange result. Closely linked to this field is the topic of the quantum Zeno effect and how the observation affects state in quantum mechanics, and experimental confirmations of this.

INTRODUCTION

If one looks at the landmark successes of quantum mechanics, one of the most important results that quantum mechanics predicted was that atoms were stable. It is a famous classical result that electrons in orbit around a proton in classical mechanics continuously radiate energy, and eventually fall into the nucleus: the stability of atoms could not be explained in the context of classical mechanics.

In the formulation of quantum mechanics, instead of solving the classical equations of motion, we take the Hamiltonian as an operator, and define a wavefunction that this operator acts on:

\[ H_0 = \frac{p^2}{2m} + V(r) \]  

where \( V(r) \) is the Coulomb potential. The electrons are then eigenstates of energy: their energy is stationary in time, the electrons don’t radiate, and atoms are stable.

An important subtle difference in the quantum mechanical picture of the atom is that the everything is stationary in time. The electron is “moving” in the sense that it has kinetic energy, but every physical property of the atom is time independent. It is tempting to try to construct a physical picture in which the electron is rapidly “whizzing” around the nucleus and where what we are seeing is some kind of time average, but this picture would be physically inaccurate: in non-relativistic quantum mechanics, all of the physics of the atom is stationary on all timescales.

This poses a problem: quantum mechanics predicts that all of the eigenstates of the atom are time independent: excited states are also stationary in time–but we know that excited states decay!

This apparent paradox is solved by quantum field theory. In our treatment above, we have described the electric field of the nucleus as a fixed external potential. Quantum electrodynamics tells us that the electric field is not simply an external variable we enter in to our Hamiltonian as in (1), but that the electromagnetic field is itself also described by a quantum mechanical equation of motion, and that the problem we should be solving is for a Hamiltonian which includes both that atom and the field, plus a coupling between them. The stationary states are then the eigenstates of the combined atom-field Hamiltonian.

Physically, what this means is that the eigenstates we obtained by solving (1) are not true energy eigenstates. From a practical point of view, this is a small and nearly always negligible effect: the shift in the atomic energy levels, the Lamb shift, are corrections of the order \( \alpha^5 \). In contrast, from a philosophical point of view, these effects are indispensable. The effect of the coupling to the quantised field can be considered as a perturbation of our Hamiltonian:

\[ H = H_0 + V' \]  

where \( V' \) describes the change in the coupling of the atom to the field due to quantisation. If the system is initially prepared in an eigenstate of \( H_0 \), we can apply the time dependent perturbation theory (see [1] page 475) to obtain a transition rate between the atomic states from the golden rule:

\[ W = \frac{2\pi}{\hbar} |\langle k | V' | s \rangle|^2 \rho(E_s) \]  

where \( k \) is the final state, and \( s \) is the initial state, and \( \rho \) is the density of final states of the atom-field system, which we assume to form a continuum. Our excited states now have a mechanism by which they can decay, consistent with the physics we expect.

From this, one is lead to conclude that the decay is then exponential, the probability of finding the excited state \( s \) after a time \( t \) given by:

\[ P_S(t) = e^{-Wt} \]  

and one finds the familiar Breit-Wigner form for the spectrum of the excited state:

\[ \rho_{BW}(\varepsilon) = \frac{1}{\pi} \frac{W/2}{(\varepsilon - \varepsilon_s)^2 + W^2/4} \]

This Lorentzian line shape is found to agree very well with the natural lineshape of atomic transitions.

However, as we will see in the following sections, we can prove on very general grounds that the decay of a quantum mechanical system cannot be exponential! Of
course, the experiments are not wrong: what we will see is that at both very short and very long timescales the decay deviates from exponential, but that exponential behaviour is seen interpolating between the two.

**SHORT TIME BEHAVIOUR**

We start by giving a mathematical argument why quantum mechanical decay cannot be exponential on short timescales, and then proceed to describe the physics in subsequent section.

**Argument for Non-Exponential Decay at Short Times**

We will consider a system that is in a state $s$ at time $t = 0$. We will make only one assumption: we will assume that the energy of the initial state, $\langle s | H | s \rangle$ is finite. The evolution of the system is given by:

$$i\hbar \frac{\partial}{\partial t} \psi(t) = H \psi(t)$$

with $|\psi(0)\rangle = |s\rangle$. Defining $c_s(t) = \langle s | \psi(t) \rangle$, the surviving amplitude, gives:

$$i\hbar \dot{c}_s(t) = \langle s | H | s \rangle$$

At $t = 0$ with $a(0) = 1$, we get:

$$i\hbar \dot{a}(0) = \langle s | H | s \rangle = E_s$$

which is real and finite. Thus $\dot{a}(0)$ is purely imaginary. The probability of survival of the initial state is $P_s(t) = a(t)\ast a(t)$: taking the derivative and using $a(0) = 1$ gives:

$$\frac{dP_s}{dt} = \dot{a}(0) + \dot{a}^\ast(0) = 0$$

since $\dot{a}(0)$ is imaginary. Thus the slope of the decay must be zero at $t = 0$, which is clearly violated by exponential decay. Quantum mechanics predicts that the decay curve of an excited state is flat at small times. As we shall see later, this will lead to some interesting experimentally accessible effects. First, however, we will examine more closely the steps that earlier had lead us to exponential decay.

**A Re-examination of Exponential Behaviour: What Went Wrong?**

Exponential decay is a familiar result from classical statistics, which describes the decay of a system through an underlying stochastic process. The classical argument is as follows[1]: If we know that the system is in a state $s$ at a time $t$ and the probability of decay in a time interval is $W dt$, then the probability that it has not decayed is $(1 - W dt)$. Thus if the probability that it was in state $s$ was $P_s(t)$, then:

$$P_s(t + dt) = P_s(t) \times (\text{Prob. of no decay in } dt)$$

$$= P_s(t)(1 - W dt)$$

which leads to exponential decay.

The flaw in our argument can be traced to this last step: we have assumed that $P_s$ is changing entirely due to transitions out of state $s$, and have not accounted for the transitions from other states back into $s$. In quantum mechanics, the probability $P_s(t + dt)$ is given by the square modulus of the complex amplitude:

$$P_s(t + dt) = |c_s(t + dt)|^2$$

$$= |c_s(t) + \frac{dc_s}{dt} dt|^2$$

where

$$\frac{dc_s}{dt} = \frac{1}{\hbar} \sum_k V_{ks} c_{ks} e^{i\omega_{ks}t}$$

at first order in perturbation theory. In general, we have this equation to (10):

$$|c_s(t) + \frac{dc_s}{dt} dt|^2 \neq |c_s(t)|^2(1 + W dt)$$

The above can give approximate equality in certain situations. One such situation is the coupling of an initial state to a continuum of states densely packed around the final state. In our expression (12), we the have a sum over a large number of states. At $t = 0$, transitions from $s$ start feeding into the amplitudes of the final states $k$. At the same time, the states $k$ start to feed back into the amplitude of state $s$: however, each state feeds back with a different phase $e^{i\omega_{ks}t}$. For a continuous set of final energies, after some coherence time $T$, the phase factors will all be uncorrelated. There will be a net cancellation of the feedback of the states $k$ back into $s$, and the state $s$ will then decay exponentially as we predicted with classical statistics.

We see that for times less than the coherence time of the continuum, the evolution of the unstable excited state will be coherent. Treatments of coherent evolution such as Rabi oscillations are earmarked by an initial slope of zero, and we see that our physical interpretation is consistent with the mathematics of Section (II.A).

**Some Interesting Consequences: The Quantum Zeno Effect**

One may question the relevance of this short time behaviour on the physics of the problem: it is more that likely that the decoherence time of the continuum states
is very fast, and it seems unlikely that one would be able to observe the evolution of the system on these timescales.

Consider an experiment, however, where we make rapid successive measurements on the system. One of the postulates of quantum mechanics is that the process of making a measurement results in a collapse of the wavefunction onto one of the eigenstates: essentially, in performing a measurement, we are “preparing” the system again at \( t = 0 \). In the context of density matrices, the system is described by a diagonal density matrix. For a two level system, we would have:

\[
\rho(t = 0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}
\]

As time evolves, two things happen: first, \( \rho_{22} \) increases at the expense of \( \rho_{11} \), but we also develop coherence terms in the off diagonal elements. If at a later time \( t = \tau \) we make a measurement of the system (with an observable whose eigenstates are the 1,2 states), we “collapse” the system onto one of the two states:

\[
\rho(t = 0) = \rho_{11} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}
\]

or

\[
\rho(t = 0) = \rho_{22} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}
\]

If we have collapsed onto the 1 state, we have effectively “reset” the system to the initial state with a reduced initial amplitude. An important note is that the process of making the measurement sets the off-diagonal terms to zero: ie. it destroys the coherences. Making repeated measurements of the system at and interval \( \tau \) smaller than the decoherence time, the system would evolve as shown in Figure (1). We can see that the decay of state 1 is slower than if we had not been making the observations.

After \( n \) such observations, the probability that were are in the 1 state is given by:

\[
P_1(n\tau) = [\rho_{11}(\tau)]^n
\]

We note that for \( \tau < T \), we have inhibited the decay of the state. We would predict that for \( \tau \rightarrow 0 \) (continuous observation), that the system would be preserved indefinitely in the unstable excited state. The inhibition of quantum transitions through observation is referred to as the quantum Zeno effect, and has been confirmed by experiment.

**Experimental Evidence of the Quantum Zeno Effect**

In the previous section, we had discussed the possibility of inhibiting spontaneous emission by frequent observation. This was the original context in which the quantum Zeno effect was proposed. However, making successive observations on a system on timescales much faster than the decoherence time of the continuum is a very difficult experiment, and has yet to be achieved, to the author’s knowledge.

Note that the physics of the quantum Zeno effect is related to the collapse of the wavefunction on observation, and is not necessarily tied to a system that is decaying. The effect can be seen in any system where one makes observations at a rate much faster than the decoherence time. The longer the decoherence time, the easier the measurement.

Perhaps it is not surprising then that the experimental system where the quantum Zeno effect was first convincingly demonstrated was the inhibition of *coherent* transitions in a two level system with Rabi oscillations.

The experiment was performed by Itano et al. [2] at NIST Boulder in 1989. In idealised picture, the system they were studying was a three level atom as shown in Figure (2). Level 1 is the ground state, level 2 is an excited metastable state, and level 3 is an excited state with a strongly allowed transition to level 1. There are two external fields applied: there is a strong field on resonance with the 1,2 transition that drives the two states into coherent Rabi oscillations and there is a short pulsed field resonant on the 1,3 transition used the probe/observe the atom.

The idea is that we start with the system in the 1 state at time \( t = 0 \) and apply a \( \pi \) pulse on the driving field. If we make no intermediate observations, at the end of the driving pulse, the atom will be entirely in the 2 state.

We then start applying short probe pulses. If the atom is in the 1 state, if will be resonant on the 1,3 transition and it will scatter photons with it’s large resonant

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**FIG. 1:** The short time behaviour of \( P_1(t) \) for repeated measurements at times \( t_1, t_2, \) and \( t_3 \) made in the coherent evolution regime.
FIG. 2: A schematic of the idealised level structure used in the quantum Zeno effect experiment of Itano et al.

crossection. If the atom is in the 2 state when the probe pulse is sent, no photons will be scattered. If we observe scattered photons, we have measured the atom to be in the 1 state, while if we see no photons, we have measured the atom to be in the 2 state. Either way, we have successfully observed the state of the atom and have collapsed its wavefunction. Note that we don’t even need to detect the photons: the state of the atom has been recorded in the EM field, regardless if we try to look for the photons or not.

The prediction is that as we increase the number $n$ of probe pulses we send during the $\pi$ pulse, the probability of finding the atom in the 2 state at the end of the $\pi$ pulse will decrease, eventually going to zero for large $n$.

For the actual experiment, Be$^+$ ions placed in a magnetic field, and the transitions were between the Zeeman split 2s and 2p levels (see Figure 3). The results they obtained for $P_2$ for different $n$ are shown in Figure 4, and are consistent with the predictions of the quantum Zeno effect.

While these measurements do indeed confirm our physical picture of the wavefunction collapsing onto an eigenstate on observation, these do not address the non-exponential decay of spontaneous emission at small times. Some interesting theoretical proposals for studying the short time behaviour of spontaneous decay using the quantum Zeno effect to study atom in resonant cavities and waveguides, where the continuum coupling can be more carefully controlled have been suggested by [3].

LONG TIME BEHAVIOUR

In all of the previous sections, we have been discussing the consequences of non-exponential behaviour at small time scales. To obtain these results, we required no detailed information about the nature of the system we were studying. The only assumption we made was that the energy of the initial state was finite.

To obtain some general predictions about the behaviour quantum mechanical decay at large times, we must look at the problem from a slightly different angle. In the previous sections, we had determined the evolution of the wavefunction by treating the problem in the basis of the atomic Hamiltonian $H_0$ and using perturbation theory. We will now take a different approach and expand our unstable excited atomic state in energy eigenfunctions of the total Hamiltonian, which will denote by $\varepsilon$:

$$|\psi(t)\rangle = \int \sum (\varepsilon|s\rangle|\varepsilon\rangle e^{-i\varepsilon t/\hbar}$$ (14)

where we are integrating (summing) over the continuous (discreet) eigenstates of $H$. We then supposed that our quasi-stationary state is orthogonal to the discreet states: this is in keeping with our physical intuition that decay is linked to the continuum states in the problem. We then have:

$$c_s(t) = \langle s|\psi(t)\rangle = \int \rho(\varepsilon)e^{-i\varepsilon t/\hbar}$$ (15)

where we have defined $\rho(\varepsilon) = |\langle s|\varepsilon\rangle|^2$, the energy probability distribution of the initial state $s$. In this formalism, instead of calculating a set of interaction matrix elements, we calculate an energy distribution function, and instead of solving coupled equations, we integrate. We can see that to get exponential decay, we would put in the Briet-Wigner form:
\[ \rho = \rho_{BW} \rightarrow c_s(t) = e^{-Wt} \]

As we already know, although it may provide a good fit to the data, the Breit-Wigner distribution is not a physically correct energy distribution function since it does not reproduce coherent evolution at small times. Furthermore, it has an infinite variance, which is also somewhat unphysical.

It will not be covered in detail here (see reference [4] for an excellent discussion), we can predict deviations from exponential decay at asymptotically large times based on very general considerations on the energy distribution. For example, if the continuum has a ground state it can be shown that the probability at large times will decay as a power law, \( P_s(t) \sim t^{-p} \).

If the continuum has no ground state (for example, the coupling of an atom to a uniform electric field), the probability will decay faster than exponential, \( P_s(t) \sim e^{-t/t_p} \). Again, any interested readers would be recommended to examine reference [4].

Unfortunately, experimental observation of these effects is much more difficult than with the short time behaviour. For example, considering the decay of a charge pion, it is estimated in reference [5] that by the time this behaviour sets in, the surviving pion probability is less than \( 10^{-80} \).

**CONCLUDING REMARKS**

By very general arguments, we have shown that the evolution of a quantum mechanical system must be at some small time scale and will always begin with zero slope.

This contradicts the common and well accepted experimental fact that exponential decay is observed in a number of quantum systems. In going back and looking more carefully at a derivation of exponential decay in quantum mechanics, we have gained a deeper understanding of the way in which exponential decay arises through cancelling phase contributions from continuum states.

Possible ways to observe this very short time scale behaviour of decaying systems lead us to consider the quantum Zeno effect. While the quantum Zeno effect has been confirmed by experiments, it has not yet been applied convincingly in experiment for detecting the early coherent evolution of a state that would otherwise display exponential decay.

We concluded with a brief discussion of another way in which quantum mechanics disobeys exponential decay, this time as asymptotically long times, by imposing a different and independent set of physically motivated constraints on the properties of the quantum mechanical system. It would seem, however, that this decay regime is outside the realm of experiment.