LONG-TIME DEVIATIONS FROM EXPONENTIAL DECAY IN ATOMIC SPONTANEOUS EMISSION THEORY

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Long-term deviations from the purely exponential decay law are derived in both the Weisskopf–Wigner and Heisenber-picture approaches. For two-level systems the deviations are very small.

It has been known for some time that a quantum mechanical system whose energy spectrum is bounded from below cannot spontaneously decay from an excited state to a lower energy state with a purely exponential decay law [1]. The Paley–Wiener theorem [2] demands that the decay be slower than exponential at long times for such systems. The long-time deviations from an exponential decay have been investigated from a number of model systems [3–7]; notable amongs these is the work of Stroud [6] and Mostowski and Wódkiewicz [7] on different versions of the Weisskopf–Wigner model of atomic spontaneous emission. Stroud is rather unorthodox in his treatment of retardation; Mostowski and Wódkiewicz use the powerful but rather formal resolvent approach [8]. The purpose of this note is to demonstrate that the non-exponential 'tail' to the decay behaviour may be derived from the standard approach to the two-level Weisskopf–Wigner model [9]*, and also from the Heisenberg equation of motion approach [10].

We make the usual two-level approximation [TLA] and use the minimal substitution interaction Hamiltonian $\mathcal{H} = -(e/mc)\boldsymbol{p}\cdot\boldsymbol{R}$ (discarding the field zero-point energy, the A^2 term and making the dipole approximation) so that

$$\mathcal{H} = \tfrac{1}{2}\hbar\omega_0\sigma_3 - \mathrm{i}(\omega_0 d/\hbar c)\sum_\lambda [g_\lambda a_\lambda + g_\lambda^* a_\lambda^+][\sigma_+ - \sigma_-] + \sum_\lambda \hbar\omega_\lambda a_\lambda^+ a_\lambda \,, \tag{1}$$

where the coupling constant $g_\lambda \equiv (2\pi\hbar c^2/\omega_\lambda \mathcal{V})^{1/2}\hat{\epsilon}_\lambda\cdot\hat{d}$, and $\hat{d}$d is the two-level transition dipole matrix element $\langle +|e\boldsymbol{r}|-\rangle$, ω_0 the transition frequency, $\mathcal{V}$ the quantization volume and the other symbols have their usual meaning. The 'essential states' of the system are the excited state $|+\rangle$ and no photons present, and the ground state $|-\rangle$ and one photon present in $\mathcal{V}$:

$$|\Psi(t)\rangle = c_\mathrm{i}(t)|+\rangle|\{0_\lambda\}\rangle \exp(-\mathrm{i}E_+t/\hbar) + \sum_\lambda c_\mathrm{f}(\lambda,t)|-\rangle|\{1_\lambda\}\rangle \exp[(-\mathrm{i}E_- + \hbar\omega)t/\hbar] \,, \tag{2}$$

where $(E_+ - E_-) = \hbar\omega_0$. The choice of $|\Psi(t)\rangle$ is equivalent to a rotating wave approximation (RWA). The initial condition is $|\Psi(0)\rangle = |+\rangle|\{0_\lambda\}\rangle$, or $c_i(0) = 1$ and $c_\mathrm{f}(\lambda,0) = 0$. Using eq. (2) in the Schrödinger equation and using orthonormality, we obtain a set of coupled equations of motion for $c_\mathrm{i}(t)$ and $c_\mathrm{f}(\lambda,t)$. Using the Laplace transform approach of Källén we obtain

* Some of our results presented here were summarized in [10], where we were interested in non-Markovian memory effects in a two atom system.

$$c_i(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dy \exp(iyt)\,[y - iA(iy+\epsilon)]^{-1} , \tag{3}$$

where $iA(iy+\epsilon)$ is

$$iA(iy+\epsilon) \equiv -\frac{1}{\hbar^2} \lim_{\epsilon\to 0} \sum_{\lambda} \frac{|\langle -,\{1_\lambda\}|\mathcal{H}_{int}|+,\{0_\lambda\}\rangle|^2}{(\omega_\lambda - \omega_0 + y - i\epsilon)} , \tag{4}$$

and ϵ is a small positive number. Since we are discussing irreversible spontaneous emission we allow $\mathcal{V} \to \infty$; converting the mode sum to an integral and performing the polarization sums and angular integrals reduces (4) to

$$iA(iy+\epsilon) = \lim_{\epsilon\to\infty} \frac{\gamma}{2\pi\omega_0} \int_0^{\infty} \omega\, d\omega\, [\omega - \omega_0 + y - i\epsilon]^{-1} , \tag{5}$$

where $(\gamma/2)$ is one-half the Einstein A-coefficient for the transition. Using

$$\lim_{\epsilon\to 0} \frac{1}{x - i\epsilon} = \mathbf{P}\left(\frac{1}{x}\right) + i\pi\delta(x) , \tag{6}$$

in eq. (5), discarding a (divergent) self-mass and cutting off the frequency integrals at some high frequency Λ, leads to

$$iA(iy+\epsilon) = \frac{i\gamma}{2\omega_0}(\omega_0 - y)U(\omega_0 - y) + \frac{\gamma}{2\pi\omega_0}(\omega_0 - y)\ln\left(\frac{\Lambda}{\omega_0 - y}\right), \tag{7}$$

where U is the unit step-function and we have assumed $\Lambda \gg \omega_0 > y$. We have been careful not to allow negative energies [i.e. $(\omega_0 - y) < 0$] to participate in the emission in the derivation of eq. (7).

Of course if we now make the Weisskopf–Wigner 'pole' approximation in eq. (7) of eliminating the y-dependence of $iA(iy+\epsilon)$, then eq. (3) gives the standard exponential decay result

$$c_i(t) = \exp(-\gamma t/2)\exp(-i\Delta t) , \tag{8}$$

where $\Delta = \mathrm{Re}\,[iA(\epsilon)]$ is the TLA 'Lamb shift' of the upper level $|+\rangle$. The same result (8) is obtained if negative energies *are* allowed to participate in the emission and the lower limit of the frequency integral in eq. (5) for $iA(iy+\epsilon)$ is extended to $(-\infty)$. If instead we carry on with eq. (7) in eq. (3), and merely assume that $y < \omega_0 \ll \Lambda$ is the most important range of y's contributing to the integral, then we obtain

$$c_i(t) = \exp(-\gamma t/2) - \frac{\exp(i\omega_0 t)}{2\pi i} \int_0^{\infty} dx \left\{ \frac{\exp(-\Lambda x t)}{x - i(\omega_0/\Lambda) + i(\gamma x/2\omega_0) - \gamma x(\ln x - i\pi/2)/2\pi\omega_0} + \frac{\exp(-\Delta x t)}{x - i(\omega_0/\Lambda) - \gamma x(\ln x + i\pi/2)/2\pi\omega_0} \right\}, \tag{9}$$

where the first term is the usual exponential decay pole term, and the second arises from the additional effects of the threshold behaviour of the decay rate term $\mathrm{Im}\,[iA(iy+\epsilon)]$ and of the branch point from $\mathrm{Re}\,[iA(iy+\epsilon)]$. We may now drop the $x\ln x$ terms: they are never large enough to contribute to the integral because of the $\exp(-\Lambda x t)$ damping factor. Then eq. (9) can be written in terms of exponential integrals. Since we only expect to see deviations from an exponential decay for times $t \gg \gamma^{-1}$, the asymptotic expansion of the exponential integrals is adequate, and we obtain

$$c_i(t) \approx \exp(-\gamma t/2) + (\gamma/2\pi\omega_0)(1/(\omega_0 t)^2)\exp(i\omega_0 t) , \tag{10}$$

for times $t \gtrsim \gamma^{-1}$ in agreement with [6] and [7]. Note that eq. (10) is independent of the cutoff Λ. For sufficiently large times, the traditional Weisskopf–Wigner approach (with only the slight improvement of *relaxing* one approximation) predicts that the exponential decay 'law' is replaced by a slower decay as t^{-2} in agreement with the combined requirements of energy positivity and the Paley–Wiener theorem. The size of the non-exponential contribution is of probably unobservable magnitude in this TLA result.

To show that the Heisenberg equation-of-motion technique also leads to eq. (10) is also quite strightforward. The method of ref. [11] may be used provided the Markov approximation is *not* made. The Markov approximation is known to be equivalent to the Weisskopf–Wigner pole approximation in spontaneous emission theory [12]. The Heisenberg-picture approach makes use of quantities such as the dipole moment operators $\sigma_{\pm}$ and the inversion operator σ_3. The expectation values of these are bilinear in the Schrödinger state amplitudes but of course have a related time development. Heisenberg equations of motion can be derived from the Hamiltonian (1); the operator field mode equation of motion may be formally integrated and substituted into the equations of motion for the atomic variables, for example the raising operator σ_+, using normal ordering. To allow a fair comparison with the Weisskopf–Wigner results presented above, we will make the RWA throughout. The result for $\dot{\sigma}_+$ is

$$\dot{\sigma}_+ = \mathrm{i}\omega_0\sigma_+ + \sum_\lambda \left(\frac{\omega_0 d}{\hbar c}\right)\left\{g_\lambda^* \left[a_\lambda^+(0)\exp(\mathrm{i}\omega_\lambda t) + \left(\frac{\omega_0 d}{\hbar c}\right) g_\lambda \int_0^t \mathrm{d}t'\,\sigma_+(t')\exp(\mathrm{i}(\omega_\lambda + \mathrm{i}\epsilon)(t-t'))\right]\sigma_3(t)\right\}. \qquad (11)$$

We may avoid the usual Markov approximation by exploiting the very slow time-dependence of $\sigma_3(t)$ and replacing it by $\sigma_3(t')$ inside the integral. Then using the equal-time result $\sigma_+(t)\,\sigma_3(t) = -\sigma_+(t)$, and taking expectation value in the state

$$|\Psi(0)\rangle = |\Psi_a(0)\rangle \otimes |\{0_\lambda\}\rangle\,, \qquad (12)$$

where $|\psi_a(0)\rangle$ is some arbitrary* state of atomic excitation, we obtain the linear equation

$$\langle\dot{\sigma}_+(t)\rangle = \mathrm{i}\omega_0\langle\sigma_+(t)\rangle - \sum_\lambda |g_\lambda|^2\left(\frac{\omega_0 d}{\hbar c}\right)^2 \int_0^t \langle\sigma_+(t')\rangle\exp(\mathrm{i}(\omega_\lambda + \mathrm{i}\epsilon)(t-t'))\,. \qquad (13)$$

This may be solved by Laplace transforms to give

$$\langle\sigma_+(t)\rangle = \frac{\langle\sigma_+(0)\rangle}{2\pi\mathrm{i}} \int_{-\mathrm{i}\infty+\epsilon}^{\mathrm{i}\infty+\epsilon} \frac{\mathrm{d}s\,\exp(st)}{s + \mathrm{i}\omega_0 + \Delta(s)}\,, \qquad (14)$$

where

$$\Delta(s) = \sum_\lambda \left(\frac{\omega_0 d}{\hbar c}\right)^2 |g_\lambda|^2\left[\frac{1}{s + \mathrm{i}\omega_\lambda}\right]. \qquad (15)$$

If we put $s = \mathrm{i}y + \epsilon$, and observe that the 'pole' value of $\Delta(s)$ occurs at $y = -\omega_0$ instead of at $y = 0$, then the integral to be evaluated in eq. (15) becomes *identical* with that of eq. (3) in the Weisskopf–Wigner theory. We have then, for $t \gtrsim \gamma^{-1}$

$$\langle\sigma_+(t)\rangle = \langle\sigma_+(0)\rangle\left\{\exp(-\gamma t/2)\exp(-\mathrm{i}\omega_0 t) + \left(\frac{\gamma}{2\pi\omega_0}\right)\frac{1}{(\omega_0 t)^2}\right\}, \qquad (16)$$

in agreement with the predictions of eq. (10) as it should be. The reduction of the non-linear equation of motion for $\langle\dot{\sigma}_+(t)\rangle$ to a linear Volterra equation has also been studied by Wódkiewicz [13], who has formulated a quite general Liouville method to describe non-Markovian memory effects in spontaneous emission.

* $\langle\sigma_\pm(t)\rangle$ and hence the atomic dipole moment is zero if the atom is initially in the *fully* excited state. In this case we should compute the nonvanishing quantities $\langle\sigma_3(t)\rangle$ or $\langle\sigma_+(t+\tau)\sigma_-(t)\rangle$.

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