It is well known that an atom in an excited state is not in a stationary state — it will eventually decay to the ground state by spontaneously emitting a photon. The nature of this evolution is due to the coupling of the atom to the electromagnetic vacuum field. The idea of spontaneous emission goes back to Einstein when he studied Planck’s blackbody spectrum using the principle of detailed balance. The rate of spontaneous emission is still known as the “Einstein A coefficient”. Victor Weisskopf presented a method for analyzing this interesting problem in his thesis work, together with his advisor Eugene Wigner. We will follow their treatment here.

Consider a two-level atom. Initially the atom is prepared in its excited state $|e\rangle$ and the field is in vacuum state $|\{0\}\rangle$. We use

$$|\psi(0)\rangle = |e, \{0\}\rangle$$

to denote this initial state. Since this is not a stable state, the atom will decay to the ground state $|g\rangle$ and give off a photon in mode $(k, s)$. The state of the system after the decay is then $|g, 1_{ks}\rangle$. These state vectors form a complete set for expanding the time-dependent state of the system:

$$|\psi(t)\rangle = a(t)e^{-i\omega_0 t}|e, \{0\}\rangle + \sum_{k,s} b_{ks}(t)e^{-i\omega_k t}|g, 1_{ks}\rangle$$

where $\omega_0$ is the atomic transition frequency and $\omega_k = ck$ is the frequency of the photon.

The total Hamiltonian under the rotating wave approximation is $H = H_A + H_F + H_{\text{int}}$ with

$$H_A = \hbar \omega_0 \hat{\sigma}_{ee}$$
$$H_F = \sum_{k,s} \hbar \omega_k \hat{n}_{ks}$$
$$H_{\text{int}} = -\mathbf{d} \cdot \mathbf{E} = -\sum_{k,s} \hbar g_{ks} \hat{\sigma}_{eg} \hat{a}_{ks} + h.c.$$

where the atom-field coupling coefficient is

$$g_{ks} = i \sqrt{\frac{\omega_k}{2\hbar \epsilon_0 V}} (\mathbf{d} \cdot \mathbf{e}_{ks})$$

The Schrödinger equation reads

$$H|\psi(t)\rangle = i\hbar \frac{\partial}{\partial t}|\psi(t)\rangle = i\hbar (\hat{a} - i\omega_0 \hat{a}) e^{-i\omega_0 t}|e, \{0\}\rangle + i\hbar \sum_{k,s} \left( \hat{b}_{ks} - i\omega_k \hat{b}_{ks} \right) e^{-i\omega_k t}|g, 1_{ks}\rangle$$

By multiply through this equation by $\langle e, \{0\}|$ and $\langle g, 1_{ks}|$, respectively, we obtain

$$\dot{a}(t) = i \sum_{k,s} g_{ks} e^{-i(\omega_k - \omega_0)t} b_{ks}(t) \tag{1}$$
$$\dot{b}_{ks}(t) = ig_{ks} e^{i(\omega_k - \omega_0)t} a(t) \tag{2}$$

To solve these equations, we first formally integrate (2) as

$$b_{ks}(t) = ig_{ks} \int_0^t dt' e^{i(\omega_k - \omega_0)t'} a(t')$$

and put this back into (1), we have

$$\dot{a}(t) = -\sum_{k,s} |g_{ks}|^2 \int_0^t dt' e^{-i(\omega_k - \omega_0)(t-t')} a(t') \tag{3}$$

First let us concentrate on $\sum_{k,s} |g_{ks}|^2$. In the continuum limit (i.e., when the quantization volume $V \to \infty$), we have

$$\sum_{k,s} \to \sum_{k=1}^3 \int d^3 k D(k)$$

Spontaneous Emission: Weisskopf-Wigner Theory
where $D(k)$ is the density of states in $k$-space. Since $k = (2\pi n_1/L, 2\pi n_2/L, 2\pi n_3/L)$, there is one state in volume $(2\pi/L)^3 = (2\pi)^3/V$, hence the density of states is $D(k) = V/(2\pi)^3$. Then using the spherical coordinates $(k, \theta, \varphi)$, we have

$$
\sum_{k,s} \to \sum_{s=1}^{2} \frac{V}{(2\pi)^3} \int_0^\infty k^2dk \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi
$$

Thus

$$
\sum_{k,s} |g_{ks}|^2 = \sum_{k,s} \frac{\omega_k}{2\epsilon_0 V \hbar} \langle d \cdot \epsilon_{ks} \rangle^2 = \int_0^\infty dk k^2 \sum_{s=1}^{2} \frac{\omega_k}{2(2\pi)^3 \epsilon_0 \hbar} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi \ [\langle d \cdot \epsilon_{k1} \rangle^2 + \langle d \cdot \epsilon_{k2} \rangle^2]
$$

Here we assume that $d$ is real, but the final result is more general and works also for complex $d$. First let us evaluate the quantity inside the square bracket using a simple trick:

$$
\sum_{s=1}^{2} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi \ [\langle d \cdot \epsilon_{k1} \rangle^2 + \langle d \cdot \epsilon_{k2} \rangle^2] = \int_0^{2\pi} d\varphi \ [\langle d \cdot \epsilon_{k1} \rangle^2 + \langle d \cdot \epsilon_{k2} \rangle^2] = \left[\frac{1}{3} \langle d^2 \rangle^2 \right]
$$

Since the triplet $(\epsilon_{k1}, \epsilon_{k2}, \epsilon)$ with $\kappa = k/k$ forms an orthogonal set of unit vectors that we can use to expand any vector, so in particular

$$
d = \langle d \cdot \epsilon_{k1} \rangle \epsilon_{k1} + \langle d \cdot \epsilon_{k2} \rangle \epsilon_{k2} + \langle d \cdot \epsilon \rangle \epsilon
$$

and thus

$$
|d|^2 = \langle d \cdot \epsilon_{k1} \rangle^2 + \langle d \cdot \epsilon_{k2} \rangle^2 + \langle d \cdot \epsilon \rangle^2
$$

or

$$
\langle d \cdot \epsilon_{k1} \rangle^2 + \langle d \cdot \epsilon_{k2} \rangle^2 = |d|^2 - \langle d \cdot \epsilon \rangle^2
$$

We can choose the spherical axis in our integral in any direction that we like, so that we may as well choose it to lie along the direction parallel to $d$. So we have finally

$$
\langle d \cdot \epsilon_{k1} \rangle^2 + \langle d \cdot \epsilon_{k2} \rangle^2 = |d|^2 \left(1 - \cos^2 \theta\right) = |d|^2 \sin^2 \theta
$$

Now Eq. (4) can be easily evaluated to give

$$
\sum_{s=1}^{2} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi \ [\langle d \cdot \epsilon_{k1} \rangle^2 + \langle d \cdot \epsilon_{k2} \rangle^2] = \frac{8\pi}{3} |d|^2
$$

Therefore

$$
\sum_{k,s} |g_{ks}|^2 = \int_0^\infty dk k^2 \sum_{s=1}^{2} \frac{\omega_k}{2(2\pi)^3 \epsilon_0 \hbar} \int_0^{2\pi} d\varphi \ [\langle d \cdot \epsilon_{k1} \rangle^2 + \langle d \cdot \epsilon_{k2} \rangle^2] = \frac{|d|^2}{6\pi^2 \epsilon_0 \hbar c^3} \int_0^\infty \omega_k^2 \, d\omega_k
$$

where we have changed the integration over $k$ to over $\omega_k = \epsilon k$.

Next let us take a look at the time integral in (3):

$$
\int_0^t dt' \, e^{-i(\omega_k - \omega_0)(t-t')} \, a(t')
$$

The exponential oscillates with frequency $\sim \omega_0$. We assume that the excited state amplitude $a(t)$ varies with a rate $\Gamma \ll \omega_0$. Therefore $a(t)$ changes little in the time interval over which the remaining part of the integrand has non-zero value ($t' \sim t$), and we can replace $a(t')$ in the integrand by $a(t)$ and take it out of the integral. This is called the Weisskopf-Wigner approximation, which can be recognized as a Markov approximation: Dynamics of $a(t)$ depends only on time $t$ and not on $t' < t$, i.e., the system has no memory of the past. We will come back to Markov approximation in later lectures.
Now the time integral becomes
\[
\int_0^t dt' e^{-i(\omega_k - \omega_0)(t-t')} a(t') \approx a(t) \int_0^t d\tau e^{-i(\omega_k - \omega_0)\tau}
\]
with \( \tau = t - t' \). Since \( a(t) \) varies with a rate \( \Gamma \ll \omega_0 \), the time of interest \( t \gg 1/\omega_0 \), thus we can take the upper limit of the above integral to \( \infty \), and we have
\[
\int_0^\infty d\tau e^{-i(\omega_k - \omega_0)\tau} = \pi \delta(\omega_k - \omega_0) - i\mathcal{P} \left( \frac{1}{\omega_k - \omega_0} \right)
\]
where \( \mathcal{P} \) represents the Cauchy principal part.

Because of the \( i \) before it, the Cauchy principal part leads to a frequency shift. This is in fact one contribution to the Lamb’s shift. This shift diverges and has be dealt with through renormalization. Here we will neglect this part.

Put things together into (3), we finally have
\[
\dot{a}(t) = -\frac{\Gamma}{2} a(t)
\]
where
\[
\Gamma = \frac{\omega_0^3 |d|^2}{3\pi \varepsilon_0 \hbar c \omega_0^2}
\]
The excited state amplitude thus decays exponentially as
\[
a(t) = e^{-\Gamma t/2} a(0)
\]
\( \Gamma \) is then the population decay rate, also known as the Einstein A coefficient.

The Weisskopf-Wigner theory thus predicts an irreversible exponential decay of the excited state population with no revivals, in contrast to the JC model. In the latter, revival occurs due to the interaction with a single mode and the discrete nature of the possible photon numbers. In free-space spontaneous emission, the atom is coupled to a continuum of modes. Although under the action of each individual mode the atom would have a finite probability to return to the excited state, the probability amplitudes for such events interfere destructively when summer over all the modes.

Finally we can the lineshape of the emitted light. Using (2) we have
\[
\dot{b}_{ks}(t) = ig_{ks} e^{i(\omega_k - \omega_0)t} a(t) = ig_{ks} e^{i(\omega_k - \omega_0)t} e^{-\Gamma t/2}
\]
which can be integrated to give
\[
\lim_{t \to \infty} b_{ks}(t) = \frac{ig_{ks}}{\Gamma/2 - i(\omega_k - \omega_0)}
\]
and the corresponding probability is
\[
\lim_{t \to \infty} |b_{ks}(t)|^2 = \frac{|g_{ks}|^2}{\Gamma^2/4 + (\omega_k - \omega_0)^2}
\]
which is a Lorentzian form centered at \( \omega_0 \) with FWHM \( \Gamma \).

The angular dependence of the emitted light can be calculated from \( \sum_s |d \cdot \epsilon_{ks}|^2 \). If the dipole transition has \( \Delta m = 0 \), then \( d \) can be taken as real and can be chosen to lie along the polar axis (z-axis), as we have done above. Thus we have
\[
\lim_{t \to \infty} \sum_s |b_{ks}(t)|^2 \sim \sin^2 \theta
\]
which is the familiar linear dipole radiation pattern. If, on the other hand, the transition is \( \Delta m = \pm 1 \), then \( d \) is complex and can be taken as
\[
d = |d| \sqrt{2} (\hat{x} \pm i\hat{y})
\]
Using the same trick, we have
\[
\sum_s |d \cdot \epsilon_{ks}|^2 = |d|^2 - |\kappa \cdot d|^2 = |d|^2 \left( 1 - \frac{\sin^2 \theta}{2} \right) = |d|^2 \frac{1 + \cos^2 \theta}{2}
\]