

10. SPONTANEOUS EMISSION & MULTIPOLE INTERACTIONS

In this chapter we address two of the questions that remain as we build a theoretical description of atoms in a radiation field.

In Sec. 10.1 we discuss the origin of spontaneous emission, and

In Sec. 10.2 we explore the use of multipole expansions to understand why the electric dipole interaction dominates the atom-field coupling.

10.1 Why Excited Atoms Decay

A Principle Of Equal Probability

The common observation is that an excited atom tends to decay (e.g. $n=2 \rightarrow n=1$) with the spontaneous emission of a photon, but that the opposite process, spontaneous absorption ($n=1 \rightarrow n=2$), does not happen. We would like to understand why this is so on the basis of general principles.

Of course it is possible to say something like "atoms naturally seek their lowest energy level", but this is neither intellectually satisfying nor really correct. Rather we will approach the atom+field problem on the basis of a general statistical principle that can be applied to a wide variety of situations ranging from the simple throw of dice to the intricate coupling of an atom to a field. This principle can be summarized in a somewhat oversimplified manner as follows:

Suppose we have defined a physical system of interest. In our mind's eye we now consider a large number (an ensemble) of identical systems, all of which have been prepared in the same way.

Let the individual system have N different configurations ($k = 1, 2, 3, \dots, N$) in which it might be found under the conditions of preparation. We will assume that each system has an observable \mathbf{g} (with values g_k) that identifies the system's configuration. For the moment suppose that there is no *a priori* reason to prefer any one of the configurations over any another. Now do a sequence of measurements of the quantity \mathbf{g} on randomly selected members of the ensemble.

The principle asserts that (under these conditions) all values of g_k will occur with equal frequency.

This principle does not seem remarkable at first glance, but it underlies equilibrium statistical physics in a way that permits one to do real calculations. Its generalizations lead to the Liouville theorem and to the thermodynamic concepts of entropy and free energy. We bring it up here so that we can understand why spontaneous emission is common and why Einstein could ignore spontaneous absorption in his phenomenological description of radiative processes.

A Coupled Oscillator Model For The Atom + Field System

We now build on the oscillator representation of the electromagnetic field.

- OBJECTIVE:** To build a conceptual model based on coupled oscillators that replicates the important features of the atom in a radiation field.
- To show that an oscillator formalism can be used to represent the atom + field system in an intuitive way, and
- To show that this formalism provides a basis for understanding:
- (1) Why an atom in an excited state tends to decay to its ground state by spontaneous emission,
 - (2) Why the reverse process [spontaneous absorption] is not likely,
 - (3) That the Heisenberg uncertainty $\Delta E \times \Delta t \sim h$ (perhaps applied in the form $\Delta E \times \Delta t > h$ for the analysis of spectra) is *not* an additional postulate of quantum mechanics but instead follows as a consequence of this conventional model of the atom+field system.

Basics of Coupled Oscillators: Two entities having fairly similar oscillation frequencies find it relatively easy to exchange energy even if the coupling between them is weak. A simple example is provided by two pendulums of essentially equal length that are weakly coupled in some manner (for example by being hung from the same not-so-rigid support).

If one pendulum is set in motion while the other is at rest, the second gradually picks up oscillation amplitude while the first dies down; the energy then flows back from the second to the first and this slow cycle repeats over and over until mechanical losses cause the oscillations in both to die out.

This situation in classical mechanics has a close parallel in quantum mechanics that will prove useful for our model of the interaction of an atom (regarded as a micro-object with a dominant resonance frequency) with the matching Fourier components of the electromagnetic radiation field.

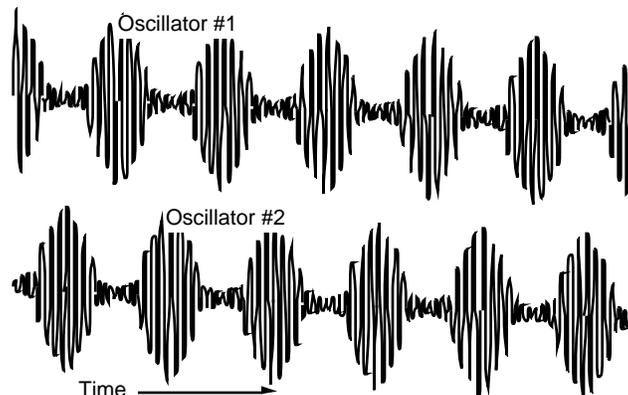


Fig 10.1 Coupled oscillator amplitudes: #1 initially excited, #2 initially at rest

The simplest atom+field model is one that uses a system with only two energy levels, separated by frequency ω , to represent the atom and a single, quantized harmonic oscillator (with equally spaced levels separated by the same frequency ω) to represent the field. The two oscillators systems are weakly coupled. We begin at time $t=0$ with the atom in its upper energy state and the field in its lowest state, and then gives its energy to the electromagnetic field after characteristic time T , but the field soon gives the energy back to the atom which returns to the excited state after time $2T$. The cycle then continues, with the back&forth flow of energy between field and atom, much as is shown in Fig. 10.1.

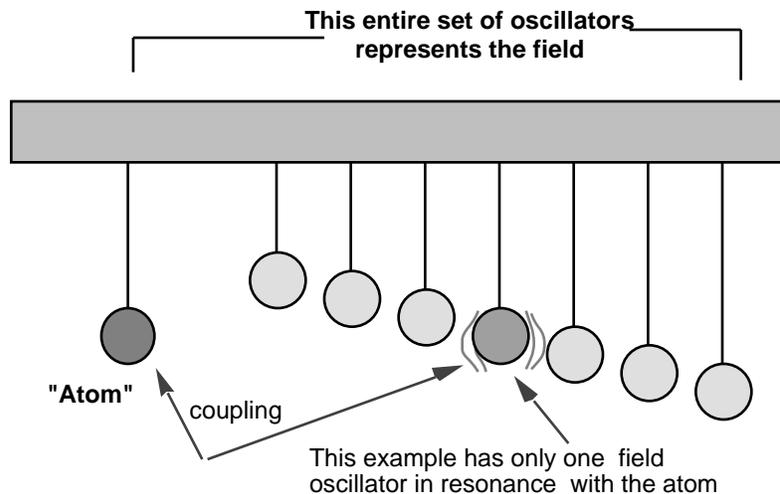


Fig. 10.2 Oscillator model for case where atom resonates with only one oscillator

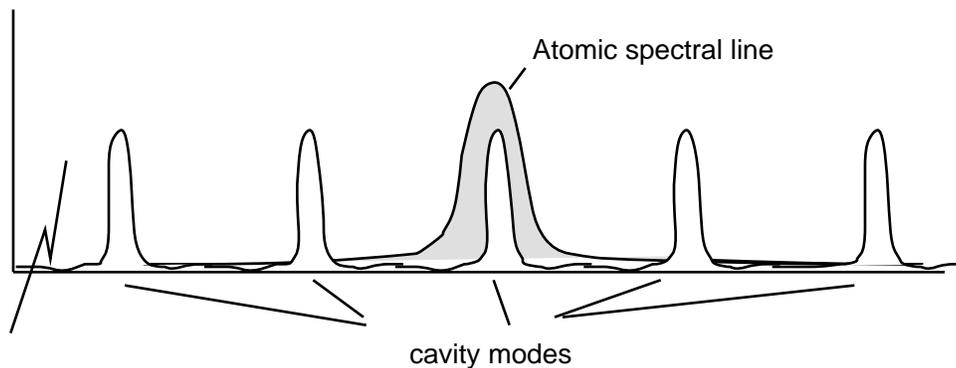


Fig. 10.3 Spectral diagram when atomic line is narrower than cavity mode spacing; atom resonates with only one cavity mode.

Although one can create the situation of Figs. (10.2) and (10.3) by placing an atom into a small resonant cavity of extraordinarily high Q , this model with only one active field mode does not show the usual behavior of the ordinary atom+field system. We need to allow for participation of more field modes.

More representative of actual situations is the model where the cavity is large enough so that many modes of the electromagnetic field are essentially resonant with the atomic transition. If there are M such modes, we can regard the composite system as one of $M+1$ weakly coupled oscillators, where all but one are in their lowest state at time $t=0$. The weak coupling allows the energy to be transferred from the initially excited oscillator to another oscillator in a characteristic time T . This passage of the excitation among the $M+1$ oscillators continues in random fashion, much as the passage of the little ball in a roulette wheel. M is often a rather large number and, as a consequence of this sharing of the quantum among all the field oscillators and the single atom, it is extremely unlikely that the atom will be again discovered in its excited state.

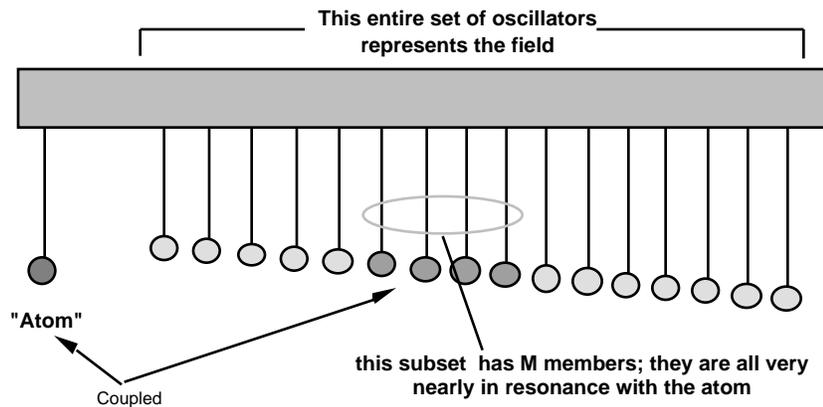


Fig. 10.4 Oscillator model for case where atom resonates with many cavity modes

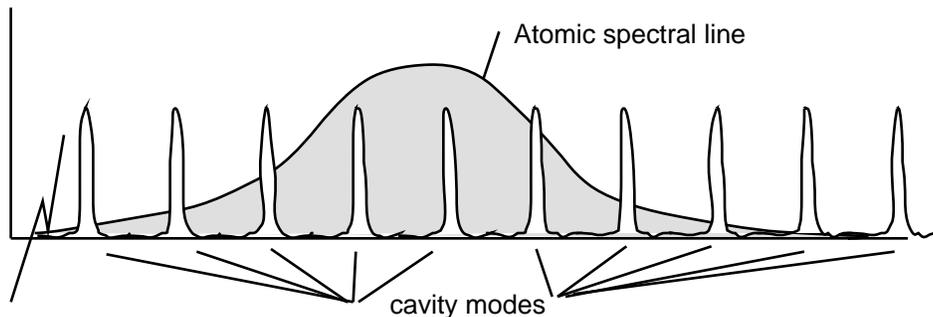


Fig. 10.5 Spectral diagram when atomic line spans many cavity modes

In presenting diagrams and analogies to illustrate the spirit of this model, we use the icon of a pendulum to represent an oscillator with one characteristic frequency. So a pendulum symbol will represent not only the 2-level atom but also a mode of the electromagnetic field. We suggest the variation in oscillator frequencies by drawing the pendulum cords of slightly different length.

(Note that we tacitly assume that the characteristic time for energy transfer between oscillators is much longer than the period ($2\pi/\omega$) of any of the oscillators.)

Can we predict the evolution of the system after t=0?

Suppose we begin at t=0 with the atom in an excited state but with no excitation in any mode of the field (all $n_k=0$). The system at time t=0 is approximately described by:

$$|t=0\rangle = |n^{atom}=1, n_k^{field}=0\rangle = |1,0,0,0,0,0,\dots\rangle \quad (10.1)$$

But this state is not stable because the quantum numbers of the modes will change at a rate that depends on the strength of the coupling between modes.

In principle, it would seem that the amplitude of each oscillator at time t is predictable from a knowledge of the amplitudes at time t=0. In practice, given the inevitable residual randomness in most experimental situations, one predicts that the initially-concentrated probability amplitude diffuses equally and rapidly so each oscillator finally has its own small share. . . Because there are so many field modes that are energetically accessible, the distribution of probability soon evolves to one that is heavily concentrated in the field and hardly at all in the atom:

$$|t=0\rangle = |1,0,0,0,0,0,0,\dots\rangle \quad t \gg \quad |t\rangle = | \dots, \dots, \dots, \dots, \dots, \dots, \dots \rangle \quad (10.2)$$

Density Of Modes

The overlap of the spectral line with many cavity modes provides the opportunity for excitation to wander away from the atom. The density of such modes (the number of cavity modes per frequency interval $d\nu$, reckoned at large mode numbers) goes up with the cube of the frequency in an ordinary, three-dimensional cavity. This provides a theoretical justification for the proportionality of the lifetime to ν^{-3} , as deduced by Einstein on thermodynamic grounds.

Harmonic Oscillator representation for field is not optional:

To model the atom we just needed an entity that would absorb/emit radiation at a relatively well defined frequency. In this discussion we are concerned almost entirely with the ground state and a single excited state of the atom, so we could have used any potential with at least one bound state for our atom model.

On the other hand, the choice of a harmonic oscillator representation is *essential* for our treatment of the field. We know that the energy per mode is directly proportional to the number of photons in the mode. Since all those photons have the same frequency, the mode energy levels are equally spaced. So our representative for a field mode must also have equally spaced energy levels, and this is found only in the simple harmonic oscillator. We have no alternative.

Spontaneous Absorption Is Unlikely

Under the hypothesized circumstances (with J.1 and only one quantum of available energy in the entire system) the atom, once de-excited via "spontaneous" decay, is very unlikely to be found again in its excited state. Therefore we regard "spontaneous" absorption (finding the atom in the excited state sometime after it had first decayed to the ground state) as a statistically insignificant process in our theory of atom-radiation interactions.

Stimulated Absorption is Probable if Field is Excited:

The argument presented so far has been based on the field being quiet ($n_k = 0$ for all k) at $t=0$, and this is not too bad an approximation when one has a modest intensity of field inside a cavity of decent size; the occupation number per mode is then very low.

However the description is significantly modified if any field modes near the atomic resonance are substantially excited, for example by shining a laser on the system. In that case the field has many photons in the relevant frequency range, and the atom has a good chance of acquiring a unit of that energy. One predicts theoretically (and confirms experimentally) that the an atom once in the ground state will be found in the excited state with a probability that depends on the intensity of the radiation at the relevant frequency.

This is the quantum theoretic basis for Einstein's phenomenological description [Eqs. (9.1) and (9.2)] of the rate of stimulated and spontaneous transitions between two atomic levels:

$$\frac{dN}{dt} = N_1(t) B_{12} \rho(\nu) \quad \text{and} \quad \frac{dN}{dt} = N_2(t) [A_{21} + B_{21} \rho(\nu)] \quad (10.3)$$

An excited atom is noticeable

The presence of an excited atom within an apparatus can be quite noticeable, whereas a radiation field with one quantum of energy has many more (but to the experimentalist, usually equivalent) ways of holding the quantum of energy than does the atom. So random process will usually end up with the atom de-excited and the field excited in one of its modes. In its way, this is analogous to playing a slot machine with many wheels instead of the usual three.... only one of all the possible configurations (each with its own minuscule probability) gets our attention.

10.2 Describing the Atom-Field Interaction with Multipoles

Suppose an atom finds itself in an electrical environment described by the scalar potential $V(x)$. This potential might be produced by a distant source of radiation or by a nearby set of electrodes connected to sources of voltage. Or in a collision experiment the field might be produced by an oncoming charged particle.

We want to describe the energy that arises from the atom's being exposed to this field. If the atom were considered as a classical system comprised of point charges q_n at locations x_n in this potential, the energy could be written as $\sum_n q_n V(x_n)$.

This can be generalized to an atom described as a classical, continuous distribution of charge $\rho(x)$. And we can write a similar form for an atom with a total charge e distributed with charge density $\rho(x)$.

$$W_{\text{Energy}} = \underbrace{\sum_n q_n V(x_n)}_{\text{Classical, with discrete charges}} + \underbrace{\int \rho(x) V(x) dx}_{\text{Classical, with continuous charge distribution } \rho(x)} + \underbrace{\int \rho(x) V(x) dx}_{\text{quantum mechanical, with charge distribution given by } \rho(x)} \quad (10.4)$$

It will be convenient to expand the externally-applied potential $V(x)$ in a Taylor series:

$$V(x) = V(x_0) + \frac{V'(x_0)}{1!} (x - x_0) + \frac{1}{2!} \frac{V''(x_0)}{x^2} (x - x_0)^2 + \dots \quad (10.5a,b)$$

$$= V_0 + \frac{V'}{x} x + \frac{1}{2!} \frac{V''}{x^2} x^2 + \dots$$

where the second form applies when we make the reasonable choice of taking $x = 0$ at the center of mass of the atom. The classical field-atom interaction energy is then:

$$W = \int \rho(x) \left[\overbrace{V_0}^{\text{constant}} + \frac{1}{x} \overbrace{V'}^{\text{constant}} x + \frac{1}{2!} \frac{V''}{x^2} \overbrace{x^2}^{\text{constant}} + \dots \right] dx \quad (10.6)$$

We consider a one-dimensional situation here in order to present the physics of the atom-field interaction with minimum of algebraic clutter. It is obvious that the theory will usually be needed in its three-dimensional form, and then often in spherical coordinates. We can discuss this more realistic case with greater ease somewhat later, after we have developed our use of spherical harmonics and the theory of angular momentum.

Note that the derivatives of V are evaluated at x=0 and therefore can be taken out from under the integrals.

$$\underbrace{W}_{\text{field-atom interaction energy}} = \underbrace{V_0 \int (x) dx}_{\text{netcharge on atom}} + \underbrace{\frac{V}{x} \int (x) x dx}_{\substack{\text{E-field at the origin} \\ \text{electric dipole moment of the atom}}} + \frac{1}{2!} \underbrace{\frac{\partial^2 V}{\partial x^2} \int (x) x^2 dx}_{\substack{\text{E-field gradient at origin} \\ \text{electric quadrupole moment of the atom}}} \quad (10.7)$$

This is the beginning (and the most important part) of a multipole expansion for the energy of interaction between a field and a charge distribution. The terms in this expansion (10.7) involve a separation of variables, so to speak, since they are products in which one term describes the field, the other, the atom:

characteristics of the field characteristics of the atom
 as given by the potential × as given by its
 and its gradients multipole moments

The first (monopole) term in the series describes the situation to first order as though a point charge were situated at the origin of coordinates. The subsequent terms then provide corrections and additions. In many cases it is sufficient to describe the system as though it had only a monopole interaction. But often (particularly if the net charge is zero) we are also forced to acknowledge the presence of the dipole interaction. We can usually (but not always) neglect the quadrupole interaction. The multipole moment description is very typical of physics, first using a coarse approximation and then adding more and more refinements to get better and better agreement between experiment and theory.

Example of Linear Multipole: In the figure below, we show an arbitrary distribution of charge (point charges of both signs) along the x-axis that can be represented by a superposition of the monopole, dipole and quadrupole moments. The monopole, dipole, and quadrupole should all be placed on the same x-axis to make this synthesis

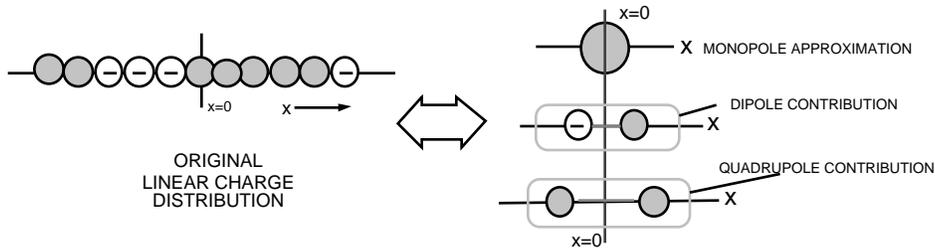


Fig 10.6 Charge distribution along a line and its resolution into multipole components

To first order, this is a point charge of +2. Upon closer inspection we find that the original distribution has properties of a dipole moment pointing to the left, and of a spreading of net of (+) charge as a quadrupole moment.

The equivalent to (10.7) written out using the quantum state functions to express the charge distribution is:

$$W = eV_0 \int |\psi|^2 dx + e \int \frac{V}{x} |\psi|^2 dx + e \frac{1}{2!} \int \frac{\partial^2 V}{\partial x^2} |\psi|^2 dx + \dots (10.8)$$

We see from expression (10.8) that:

- I. The monopole term $eV_0 \int |\psi|^2 dx$ has the same magnitude irrespective of the state of the atom since $\int |\psi|^2 dx = 1$ by normalization of the state function. In an electrically neutral atom, the interaction energy of the electrons is precisely offset by the energy from the interaction of the protons, so the monopole term will vanish.
- II. The dipole term vanishes unless
 - a) the state $\psi(x)$ is a superposition that contains terms of both (+) and (-) parity.
 - b) the electric field has a finite value at $x=0$

Comments

Applied Field induces a dipole moment: Isolated atoms have spherical symmetry and thus have no intrinsic electric dipole moment, however if one applies an external electric field, that field couples to and distorts the charge distribution; the field induces a dipole moment, and associated with this *polarization* of the atom there is a finite dipole interaction energy.

Dipole Interaction usually most important: If an atom is subjected to an oscillating field where the wave-length (λ) is much larger than the dimensions of the atom, then the field (even though oscillating in time) is essentially homogenous over the volume of the atom at any given instant. Thus the field $E = V/x$ is appreciable for situations involving ultraviolet, visible, infrared, and microwave radiation. (But the field gradient is very small: $E/x = \partial^2 V / \partial x^2 \sim 0$, so quadrupole processes are less important.) For this reason, atomic radiative processes at wavelengths longer than the extreme uv are almost completely governed by the dipole interaction. The formulation of the dipole interaction as given here enables us to can derive the selection rules and other statements about the relative probabilities for various radiative transitions.

Collision Experiment may Involve High-order multipoles: If the atom is subject to collisions from incoming charged particles, then the atom may experience an electric field that is not at all homogeneous. In that case, both the field and its gradients may be of substantial magnitude and, as a consequence, the quadrupole term of the multipole series may be relatively large.