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Chapter 7

Interaction of an Atom with an Electro-Magnetic Field

7.1 Introduction: Spontaneous and Stimulated Emission

Einstein's 1917 paper on the theory of radiation¹ provided seminal concepts for the quantum theory of radiation. It also anticipated devices such as the laser, and pointed the way to the field of laser-cooling of atoms. In it, he set out to answer two questions:

1) How do the internal states of an atom that radiates and absorbs energy come into equilibrium with a thermal radiation field? (In answering this question Einstein invented the concept of spontaneous emission)

2) How do the translational states of an atom in thermal equilibrium (i.e. states obeying the Maxwell-Boltzmann Law for the distribution of velocities) come into thermal equilibrium with a radiation field? (In answering this question, Einstein introduced the concept of photon recoil. He also demonstrated that the field itself must obey the Planck radiation law.)

The first part of Einstein's paper, which addresses question 1), is well known, but the second part, which addresses question 2), is every bit as germane for contemporary atom/optical physics. Because the paper preceded the creation of quantum mechanics there was no way for him to calculate transition rates. However, his arguments are based on general statistical principles and provide the foundation for interpreting the quantum mechanical results.

Einstein considered a system of N atoms in thermal equilibrium with a radiation field. The system has two levels² with energies E_b and E_a , with $E_b > E_a$, and $E_b - E_a = \hbar\omega$. The numbers of atoms in the two levels are related by $N_b + N_a = N$. Einstein assumed the Planck radiation law for the spectral energy density temperature. For radiation in thermal equilibrium at temperature T , the energy per unit volume in wavelength range $d\omega$ is:

$$\rho_E(\omega)d\omega = \frac{\hbar\omega^3}{\pi^2c^3} \frac{1}{\exp(\hbar\omega/kT) - 1} d\omega. \quad (7.1)$$

The mean occupation number of a harmonic oscillator at temperature T , which can be interpreted as the mean number of photons in one mode of the radiation field, is

¹A. Einstein, Z. Phys. **18**, 121 (1917), translated in *Sources of Quantum Mechanics*, B. L. Van der Waerden, Cover Publication, Inc., New York, 1967. This book is a gold mine for anyone interested in the development of quantum mechanics.

²An energy level consists of all of the states that have a given energy. The number of quantum states in a given level is its multiplicity.

$$\bar{n} = \frac{1}{\exp(\hbar\omega/kT) - 1}. \quad (7.2)$$

According to the Boltzmann Law of statistical mechanics, in thermal equilibrium the populations of the two levels are related by

$$\frac{N_b}{N_a} = \frac{g_b}{g_a} e^{-(E_b - E_a)/kT} = \frac{g_b}{g_a} e^{-\hbar\omega/kT}. \quad (7.3)$$

Here g_b and g_a are the multiplicities of the two levels. The last step assumes the Bohr frequency condition, $\omega = (E_b - E_a)/\hbar$. However, Einstein's paper actually derives this relation independently.

According to classical theory, an oscillator can exchange energy with the radiation field at a rate that is proportional to the spectral density of radiation. The rates for absorption and emission are equal. The population transfer rate equation is thus predicted to be

$$\dot{N}_b = -\rho_E(\omega)B_{ba}N_b + \rho_E(\omega)B_{ab}N_a = -\dot{N}_a. \quad (7.4)$$

This equation is incompatible with Eq. 7.3. To overcome this problem, Einstein postulated that atoms in state b must spontaneously radiate to state a, with a constant radiation rate A_{ba} . Today such a process seems quite natural: the language of quantum mechanics is the language of probabilities and there is nothing jarring about asserting that the probability of radiating in a short time interval is proportional to the length of the interval. At that time such a random fundamental process could not be justified on physical principles. Einstein, in his characteristic Olympian style, brushed aside such concerns and merely asserted that the process is analagous to radioactive decay. With this addition, Eq. 7.4 becomes

$$\dot{N}_b = -[\rho_E(\omega)B_{ba} + A_{ba}]N_b + \rho_E(\omega)B_{ab}N_a = -\dot{N}_a. \quad (7.5)$$

By combining Eqs. ??, ??, ?? it follows that

$$\begin{aligned} g_b B_{ba} &= g_a B_{ab} \\ \frac{\hbar\omega^3}{\pi^2 c^3} B_{ba} &= A_{ba} \\ \rho_E(\omega) B_{ba} &= \bar{n} A_{ba} \end{aligned} \quad (7.6)$$

Consequently, the rate of transition $b \rightarrow a$ is

$$B_{ba}\rho_E(\omega) + A_{ba} = (\bar{n} + 1)A_{ba}, \quad (7.7)$$

while the rate of absorption is

$$B_{ba}\rho_E(\omega) = \frac{g_b}{g_a} \bar{n} A_{ba} \quad (7.8)$$

If we consider emission and absorption between single states by taking $g_b = g_a = 1$, then the ratio of rate of emission to rate of absorption is $(\bar{n} + 1)/\bar{n}$.

This argument reveals the fundamental role of spontaneous emission. Without it, atomic systems could not achieve thermal equilibrium with a radiation field. Thermal equilibrium requires some form of dissipation, and dissipation is equivalent to having an irreversible

process. Spontaneous emission is the fundamental irreversible process in nature. The reason that it is irreversible is that once a photon is radiated into the vacuum, the probability that it will ever be reabsorbed is zero: there are an infinity of vacuum modes available for emission but only one mode for absorption. If the vacuum modes are limited, for instance by cavity effects, the number of modes becomes finite and equilibrium is never truly achieved. In the limit of only a single mode, the motion becomes reversible.

The identification of the Einstein A coefficient with the rate of spontaneous emission is so well established that we shall henceforth use the symbol A_{ba} to denote the spontaneous decay rate from state b to a . The radiative lifetime for such a transition is $\tau_{ba} = A_{ba}^{-1}$.

Here, Einstein came to a halt. Lacking quantum theory, there was no way to calculate A_{ba} .

7.2 Quantum Theory of Absorption and Emission

We shall start by describing the behavior of an atom in a classical electromagnetic field. Although treating the field classically while treating the atom quantum mechanically is fundamentally inconsistent, it provides a natural and intuitive approach to the problem. Furthermore, it is completely justified in cases where the radiation fields are large, in the sense that there are many photons in each mode, as for instance, in the case of microwave or laser spectroscopy. There is, however, one important process that this approach cannot deal with satisfactorily. This is spontaneous emission, which we shall treat later using a quantized field. Nevertheless, phenomenological properties such as selection rules, radiation rates and cross sections, can be developed naturally with this approach.

7.2.1 The classical E-M field

Our starting point is Maxwell's equations (S.I. units):

$$\begin{aligned}\nabla \cdot \mathbf{E} &= \rho/\epsilon_0 \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\ \nabla \times \mathbf{B} &= \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t} + \mu_0 \mathbf{J}\end{aligned}\tag{7.9}$$

The charge density ρ and current density \mathbf{J} obey the continuity equation

$$\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = 0\tag{7.10}$$

Introducing the vector potential \mathbf{A} and the scalar potential ψ , we have

$$\begin{aligned}\mathbf{E} &= -\nabla\psi - \frac{\partial \mathbf{A}}{\partial t} \\ \mathbf{B} &= \nabla \times \mathbf{A}\end{aligned}\tag{7.11}$$

We are free to change the potentials by a gauge transformation:

$$\mathbf{A}' = \mathbf{A} + \nabla\Lambda, \quad \psi' = \psi - \frac{\partial \Lambda}{\partial t}\tag{7.12}$$

where Λ is a scalar function. This transformation leaves the fields invariant, but changes the form of the dynamical equation. We shall work in the *Coulomb gauge* (often called the radiation gauge), defined by

$$\nabla \cdot \mathbf{A} = 0 \quad (7.13)$$

In free space, \mathbf{A} obeys the wave equation

$$\nabla^2 \mathbf{A} = \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} \quad (7.14)$$

Because $\nabla \cdot \mathbf{A} = 0$, \mathbf{A} is transverse. We take a propagating plane wave solution of the form

$$\mathbf{A}(r, t) = A \hat{\mathbf{e}} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) = A \hat{\mathbf{e}} \frac{1}{2} \left[e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \right], \quad (7.15)$$

where $k^2 = \omega^2/c^2$ and $\hat{\mathbf{e}} \cdot \mathbf{k} = 0$. For a linearly polarized field, the polarization vector $\hat{\mathbf{e}}$ is real. For an elliptically polarized field it is complex, and for a circularly polarized field it is given by $\hat{\mathbf{e}} = (\hat{\mathbf{x}} \pm i\hat{\mathbf{y}})/\sqrt{2}$, where the $+$ and $-$ signs correspond to positive and negative helicity, respectively. (Alternatively, they correspond to left and right hand circular polarization, respectively, the sign convention being a tradition from optics.) The electric and magnetic fields are then given by

$$\mathbf{E}(r, t) = \omega A \hat{\mathbf{e}} \sin(\mathbf{k} \cdot \mathbf{r} - \omega t) = -i\omega A \hat{\mathbf{e}} \frac{1}{2} \left[e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} - e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \right]. \quad (7.16)$$

$$\mathbf{B}(r, t) = k(\hat{\mathbf{k}} \times \hat{\mathbf{e}}) \sin(\mathbf{k} \cdot \mathbf{r} - \omega t) = -ikA(\hat{\mathbf{k}} \times \hat{\mathbf{e}}) \frac{1}{2} \left[e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} - e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \right]. \quad (7.17)$$

The time average Poynting vector is

$$\mathbf{S} = \frac{\epsilon_0 c^2}{2} (\mathbf{E} \times \mathbf{B}^*) = \frac{\epsilon_0 c}{2} \omega^2 A^2 \hat{\mathbf{k}}. \quad (7.18)$$

The average energy density in the wave is given by

$$u = \omega^2 \frac{\epsilon_0}{2} A^2 \hat{\mathbf{k}}. \quad (7.19)$$

7.2.2 Interaction of an electromagnetic wave and an atom

The behavior of charged particles in an electromagnetic field is correctly described by Hamilton's equations provided that the canonical momentum is redefined:

$$\mathbf{p}_{\text{can}} = \mathbf{p}_{\text{kin}} + q\mathbf{A} \quad (7.20)$$

The kinetic energy is $\mathbf{p}_{\text{kin}}^2/2m$. Taking $q = -e$, the Hamiltonian for an atom in an electromagnetic field in free space is

$$H = \frac{1}{2m} \sum_{j=1}^N (\mathbf{p}_j + e\mathbf{A}(r_j))^2 + \sum_{j=1}^N V(\mathbf{r}_j), \quad (7.21)$$

where $V(\mathbf{r}_j)$ describes the potential energy due to internal interactions. We are neglecting spin interactions.

Expanding and rearranging, we have

$$\begin{aligned} H &= \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m} + V(\mathbf{r}_j) + \frac{e}{2m} \sum_{j=1}^N (\mathbf{p}_j \cdot \mathbf{A}(\mathbf{r}_j) + \mathbf{A}(\mathbf{r}_j) \cdot \mathbf{p}_j) + \frac{e^2}{2m} \sum_{j=1}^N A_j^2(\mathbf{r}) \quad (7.22) \\ &= H_0 + H_{\text{int}} + H^{(2)}. \end{aligned}$$

Here, $\mathbf{p}_j = -i\hbar\nabla_j$. Consequently, H_0 describes the unperturbed atom. H_{int} describes the atom's interaction with the field. $H^{(2)}$, which is second order in \mathbf{A} , plays a role only at very high intensities. (In a static magnetic field, however, $H^{(2)}$ gives rise to diamagnetism.)

Because we are working in the Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$ so that \mathbf{A} and \mathbf{p} commute. We have

$$H_{\text{int}} = \frac{eA}{mc} \hat{\mathbf{e}} \cdot \mathbf{p} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t). \quad (7.23)$$

It is convenient to write the matrix element between states $|a\rangle$ and $|b\rangle$ in the form

$$\langle b|H_{\text{int}}|a\rangle = \frac{1}{2}H_{ba}e^{-i\omega t} + \frac{1}{2}H_{ba}e^{+i\omega t}, \quad (7.24)$$

where

$$H_{ba} = \frac{eA}{m} \hat{\mathbf{e}} \cdot \langle b|\mathbf{p} e^{i\mathbf{k}\cdot\mathbf{r}}|a\rangle. \quad (7.25)$$

Atomic dimensions are small compared to the wavelength of radiation involved in optical transitions. The scale of the ratio is set by $\alpha \approx 1/137$. Consequently, when the matrix element in Eq. 7.25 is evaluated, the wave function vanishes except in the region where $\mathbf{k} \cdot \mathbf{r} = 2\pi r/\lambda \ll 1$. It is therefore appropriate to expand the exponential:

$$H_{ba} = \frac{eA}{mc} \hat{\mathbf{e}} \cdot \langle b|\mathbf{p}(1 + i\mathbf{k} \cdot \mathbf{r} - 1/2(\mathbf{k} \cdot \mathbf{r})^2 + \dots)|a\rangle \quad (7.26)$$

Unless $\langle b|\mathbf{p}|a\rangle$ vanishes, for instance due to parity considerations, the leading term dominates and we can neglect the others. For reasons that will become clear, this is called the dipole approximation. This is by far the most important situation, and we shall defer consideration of the higher order terms. In the dipole approximation we have

$$H_{ba} = \frac{eA}{m} \hat{\mathbf{e}} \cdot \langle b|\mathbf{p}|a\rangle = \frac{-ieE}{m\omega} \hat{\mathbf{e}} \cdot \langle b|\mathbf{p}|a\rangle \quad (7.27)$$

where we have used, from Eq. 7.16, $A = -iE/\omega$. It can be shown (i.e. left as exercise) that the matrix element of \mathbf{p} can be transformed into a matrix element for \mathbf{r} :

$$\langle b|\mathbf{p}|a\rangle = -im\omega_{ab}\langle b|\mathbf{r}|a\rangle = +im\omega_{ba}\langle b|\mathbf{r}|a\rangle \quad (7.28)$$

This results in

$$H_{ba} = \frac{eE\omega_{ba}}{\omega} \hat{\mathbf{e}} \cdot \langle b|\mathbf{r}|a\rangle \quad (7.29)$$

We will be interested in resonance phenomena in which $\omega \approx \omega_{ba}$. Consequently,

$$H_{ba} = +e\mathbf{E}_0 \cdot \langle b|\mathbf{r}|a\rangle = -\mathbf{d}_{ba} \cdot \mathbf{E} \quad (7.30)$$

where \mathbf{d} is the dipole operator, $\mathbf{d} = -e\mathbf{r}$. Displaying the time dependence explicitly, we have

$$H'_{ba} = -\mathbf{d}_{ba} \cdot \mathbf{E}_0 e^{-i\omega t}. \quad (7.31)$$

However, it is important to bear in mind that this is only the first term in a series, and that if it vanishes the higher order terms will contribute a perturbation at the driving frequency.

H_{ba} appears as a matrix element of the momentum operator \mathbf{p} in Eq. 7.27, and of the dipole operator \mathbf{r} in Eq. 7.30. These matrix elements look different and depend on different parts of the wave function. The momentum operator emphasizes the curvature of the wave function, which is largest at small distances, whereas the dipole operator evaluates the moment of the charge distribution, i.e. the long range behavior. In practice, the accuracy of a calculation can depend significantly on which operator is used.

7.3 Quantization of the radiation field

We shall consider a single mode of the radiation field. This means a single value of the wave vector \mathbf{k} , and one of the two orthogonal transverse polarization vectors $\hat{\mathbf{e}}$. The radiation field is described by a plane wave vector potential of the form Eq. 7.15. We assume that \mathbf{k} obeys a periodic boundary or condition, $k_x L_x = 2\pi n_x$, etc. (For any \mathbf{k} , we can choose boundaries L_x, L_y, L_z to satisfy this.) The time averaged energy density is given by Eq. 7.19, and the total energy in the volume V defined by these boundaries is

$$U = \frac{\epsilon_0}{2} \omega^2 A^2 V, \quad (7.32)$$

where A^2 is the mean squared value of A averaged over the spatial mode. We now make a formal connection between the radiation field and a harmonic oscillator. We define variables Q and P by

$$A = \frac{1}{\omega} \sqrt{\frac{1}{\epsilon_0 V}} (\omega Q + iP), \quad A^* = \frac{1}{\omega} \sqrt{\frac{1}{\epsilon_0 V}} (\omega Q - iP). \quad (7.33)$$

Then, from Eq. 7.32, we find

$$U = \frac{1}{2} (\omega^2 Q^2 + P^2). \quad (7.34)$$

This describes the energy of a harmonic oscillator having unit mass. We quantize the oscillator in the usual fashion by treating Q and P as operators, with

$$P = -i\hbar \frac{\partial}{\partial Q}, \quad [Q, P] = i\hbar. \quad (7.35)$$

We introduce the operators a and a^\dagger defined by

$$a = \frac{1}{\sqrt{2\hbar\omega}} (\omega Q + iP) \quad (7.36)$$

$$a^\dagger = \frac{1}{\sqrt{2\hbar\omega}} (\omega Q - iP) \quad (7.37)$$

The fundamental commutation rule is

$$[a, a^\dagger] = 1 \quad (7.38)$$

from which the following can be deduced:

$$H = \frac{1}{2}\hbar\omega[a^\dagger a + aa^\dagger] = \hbar\omega \left[a^\dagger a + \frac{1}{2} \right] = \hbar\omega \left[N + \frac{1}{2} \right] \quad (7.39)$$

where the number operator $N = a^\dagger a$ obeys

$$N|n\rangle = n|n\rangle \quad (7.40)$$

We also have

$$\begin{aligned} \langle n-1|a|n\rangle &= \sqrt{n} \\ \langle n+1|a^\dagger|n\rangle &= \sqrt{n+1} \\ \langle n|a^\dagger a|n\rangle &= n \\ \langle n|aa^\dagger|n\rangle &= n+1 \\ \langle n|H|n\rangle &= \hbar\omega \left(n + \frac{1}{2} \right) \\ \langle n|a|n\rangle &= \langle n|a^\dagger|n\rangle = 0 \end{aligned} \quad (7.41)$$

The operators a and a^\dagger are called the annihilation and creation operators, respectively. We can express the vector potential and electric field in terms of a and a^\dagger as follows

$$A = \frac{1}{\omega\sqrt{\epsilon_0 V}}(\omega Q + iP) = \sqrt{\frac{2\hbar}{\omega\epsilon_0 V}}a \quad (7.42)$$

$$A^\dagger = \frac{1}{\omega\sqrt{\epsilon_0 V}}(\omega Q - iP) = \sqrt{\frac{2\hbar}{\omega\epsilon_0 V}}a^\dagger$$

$$\mathbf{E} = -i\sqrt{\frac{\hbar\omega}{2\epsilon_0 V}} \left[a\hat{\mathbf{e}}e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} - a^\dagger\hat{\mathbf{e}}^*e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \right] \quad (7.44)$$

In the dipole limit we can take $e^{i\mathbf{k}\cdot\mathbf{r}} = 1$. Then

$$\mathbf{E} = -i\sqrt{\frac{\hbar\omega}{2\epsilon_0 V}} \left[a\hat{\mathbf{e}} - a^\dagger\hat{\mathbf{e}}^* \right] \quad (7.45)$$

The interaction Hamiltonian is,

$$H_{\text{int}} = -ie\sqrt{\frac{\hbar\omega}{2\epsilon_0 V}}\mathbf{r} \cdot \left[a\hat{\mathbf{e}}e^{-i\omega t} - a^\dagger\hat{\mathbf{e}}^*e^{+i\omega t} \right], \quad (7.46)$$

where we have written the dipole operator as $\mathbf{d} = -e\mathbf{r}$.

7.4 Interaction of a two-level system and a single mode of the radiation field

We consider a two-state atomic system $|a\rangle, |b\rangle$ and a radiation field described by $|n\rangle$, $n = 0, 1, 2, \dots$. The states of the total system can be taken to be

$$|I\rangle = |a, n\rangle = |a\rangle |n\rangle, \quad |F\rangle = |b, n'\rangle = |b\rangle |n'\rangle. \quad (7.47)$$

We shall take $\hat{\mathbf{e}} = \hat{\mathbf{z}}$. Then

$$\langle F|H_{\text{int}}|I\rangle = ie z_{ab} \sqrt{\frac{2\pi\hbar\omega}{V}} \langle n'| a e^{-i\omega t} - a^\dagger e^{i\omega t} |n\rangle e^{-i\omega_{ab}t} \quad (7.48)$$

The first term in the bracket obeys the selection rule $n' = n - 1$. This corresponds to loss of one photon from the field and absorption of one photon by the atom. The second term obeys $n' = n + 1$. This corresponds to emission of a photon by the atom. Using Eq. 7.41, we have

$$\langle F|H_{\text{int}}|I\rangle = -ie z_{ab} \sqrt{\frac{2\pi\hbar\omega}{V}} (\sqrt{n} \delta_{n',n-1} e^{-i\omega t} - \sqrt{n+1} \delta_{n',n+1} e^{+i\omega t}) e^{-i\omega_{ab}t} \quad (7.49)$$

Transitions occur when the total time dependence is zero, or near zero. Thus absorption occurs when $\omega = -\omega_{ab}$, or $E_a + \hbar\omega = E_b$. As we expect, energy is conserved. Similarly, emission occurs when $\omega = +\omega_{ab}$, or $E_a - \hbar\omega = E_b$.

A particularly interesting case occurs when $n = 0$, i.e. the field is initially in the vacuum state, and $\omega = \omega_{ab}$. Then

$$\langle F|H_{\text{int}}|I\rangle = ie z_{ab} \sqrt{\frac{2\pi\hbar\omega}{V}} \equiv H_{FI}^0 \quad (7.50)$$

The situation describes a constant perturbation H_{FI}^0 coupling the two states $I = |a, n = 0\rangle$ and $F = |b, n' = 1\rangle$. The states are degenerate because $E_a = E_b + \hbar\omega$. Consequently, E_a is the upper of the two atomic energy levels.

The system is composed of two degenerate eigenstates, but due to the coupling of the field, the degeneracy is split. The eigenstates are symmetric and antisymmetric combinations of the initial states, and we can label them as

$$|\pm\rangle = \frac{1}{\sqrt{2}} (|I\rangle \pm |F\rangle) = \frac{1}{\sqrt{2}} (|a, 0\rangle \pm |b, 1\rangle). \quad (7.51)$$

The energies of these states are

$$E_{\pm} = \pm |H_{FI}^0| \quad (7.52)$$

If at $t = 0$, the atom is in state $|a\rangle$ which means that the radiation field is in state $|0\rangle$ then the system is in a superposition state:

$$\psi(0) = \frac{1}{\sqrt{2}} (|+\rangle + |-\rangle). \quad (7.53)$$

The time evolution of this superposition is given by

$$\psi(t) = \frac{1}{\sqrt{2}} (|+\rangle e^{i\Omega/2t} + |-\rangle e^{-i\Omega/2t}) \quad (7.54)$$

where $\Omega/2 = |H_{FI}^0|/\hbar = e z_{ab} \sqrt{\omega/(e\epsilon_0 V \hbar)}$. The probability that the atom is in state $|b\rangle$ at a later time is

$$P_b = \frac{1}{2}(1 + \cos \Omega t). \quad (7.55)$$

The frequency Ω is called the vacuum Rabi frequency.

The dynamics of a 2-level atom interacting with a single mode of the vacuum were first analyzed in Ref. [1] and the oscillations are sometimes called *Jaynes-Cummings* oscillations.

The atom-vacuum interaction H_{FI}^0 , Eq. 7.50, has a simple physical interpretation. The electric field amplitude associated with the zero point energy in the cavity is given by

$$\epsilon_o E^2 V = \frac{1}{2} \hbar \omega \quad (7.56)$$

Consequently, $|H_{FI}^0| = E d_{ab} = e z_{ab} E$. The interaction frequency $|H_{FI}^0|/\hbar$ is sometimes referred to as the vacuum Rabi frequency, although, as we have seen, the actual oscillation frequency is $2 \times H_{FI}^0/\hbar$.

Absorption and emission are closely related. Because the rates are proportional to $|\langle F | H_{\text{int}} | I \rangle|^2$, it is evident from Eq. 7.49 that

$$\frac{\text{Rate of emission}}{\text{Rate of absorption}} = \frac{n+1}{n} \quad (7.57)$$

This result, which applies to radiative transitions between any two states of a system, is general. In the absence of spontaneous emission, the absorption and emission rates are identical.

The oscillatory behavior described by Eq. 7.54 is exactly the opposite of free space behavior in which an excited atom irreversibly decays to the lowest available state by spontaneous emission. The distinction is that in free space there are an infinite number of final states available to the photon, since it can go off in any direction, but in the cavity there is only one state. The natural way to regard the atom-cavity system is not in terms of the atom and cavity separately, as in Eq. 7.47, but in terms of the coupled states $|+\rangle$ and $|-\rangle$ (Eq. 7.51). Such states, called *dressed atom* states, are the true eigenstates of the atom-cavity system.

7.5 Absorption and emission

In Chapter 6, first-order perturbation theory was applied to find the response of a system initially in state $|a\rangle$ to a perturbation of the form $H_{ba} e^{-i\omega t}$. The result is that the amplitude for state $|b\rangle$ is given by

$$a_b(t) = \frac{1}{i\hbar} \int_0^t H_{ba} e^{-i(\omega - \omega_{ba})t'} dt' = \frac{H_{ba}}{\hbar} \left[\frac{e^{-i(\omega - \omega_{ba})t} - 1}{\omega - \omega_{ba}} \right] \quad (7.58)$$

There will be a similar expression involving the time-dependence $e^{+i\omega t}$. The $-i\omega$ term gives rise to resonance at $\omega = \omega_{ba}$; the $+i\omega$ term gives rise to resonance at $\omega = \omega_{ab}$. One term is responsible for absorption, the other is responsible for emission.

The probability that the system has made a transition to state $|b\rangle$ at time t is

$$W_{a \rightarrow b} = |a_b(t)|^2 = \frac{|H_{ba}|^2 \sin^2[(\omega - \omega_{ba})t/2]}{\hbar^2 ((\omega - \omega_{ba})/2)^2} \quad (7.59)$$

In the limit $\omega \rightarrow \omega_{ba}$, we have

$$W_{a \rightarrow b} \approx \frac{|H_{ba}|^2}{\hbar^2} t^2. \quad (7.60)$$

So, for short time, $W_{a \rightarrow b}$ increases quadratically. This is reminiscent of a Rabi resonance in a 2-level system in the limit of short time.

However, Eq. 7.59 is only valid provided $W_{a \rightarrow b} \ll 1$, or for time $T \ll \hbar/H_{ba}$. For such a short time, the incident radiation will have a spectral width $\Delta\omega \sim 1/T$. In this case, we must integrate Eq. 7.59 over the spectrum. In doing this, we shall make use of the relation

$$\int_{-\infty}^{+\infty} \frac{\sin^2(\omega - \omega_{ba})t/2}{[(\omega - \omega_{ba})/2]^2} d\omega = 2t \int_{-\infty}^{+\infty} \frac{\sin^2(u - u_o)}{(u - u_o)^2} du \rightarrow 2\pi t \int_{-\infty}^{+\infty} \delta(\omega - \omega_{ba}) d\omega. \quad (7.61)$$

Eq. 7.59 becomes

$$W_{a \rightarrow b} = \frac{|H_{ba}|^2}{\hbar^2} 2\pi t \delta(\omega - \omega_{ba}) \quad (7.62)$$

The δ -function requires that eventually $W_{a \rightarrow b}$ be integrated over a spectral distribution function. $W_{a \rightarrow b}$ can also be written

$$W_{a \rightarrow b} = \frac{|H_{ba}|^2}{\hbar} 2\pi t \delta(E_b - E_a - \hbar\omega). \quad (7.63)$$

Because the transition probability is proportional to the time, we can define the transition rate

$$\begin{aligned} \Gamma_{ab} &= \frac{d}{dt} W_{a \rightarrow b} = 2\pi \frac{|H_{ba}|^2}{\hbar^2} \delta(\omega - \omega_{ba}) \\ &= 2\pi \frac{|H_{ba}|^2}{\hbar} \delta(E_b - E_a - \hbar\omega) \end{aligned} \quad (7.65)$$

The δ -function arises because of the assumption in first order perturbation theory that the amplitude of the initial state is not affected significantly. This will not be the case, for instance, if a monochromatic radiation field couples the two states, in which case the amplitudes oscillate between 0 and 1. However, the assumption of perfectly monochromatic radiation is in itself unrealistic.

Radiation always has some spectral width. $|H_{ba}|^2$ is proportional to the intensity of the radiation field at resonance. The intensity can be written in terms of a spectral density function

$$S(\omega') = S_0 f(\omega')$$

where S_0 is the incident Poynting vector, and $f(\omega')$ is a normalized line shape function centered at the frequency ω' which obeys $\int f(\omega') d\omega' = 1$. We can define a characteristic spectral width of $f(\omega')$ by

$$\Delta\omega = \frac{1}{f(\omega_{ab})} \quad (7.66)$$

Integrating Eq. 7.65 over the spectrum of the radiation gives

$$\Gamma_{ab} = \frac{2\pi |H_{ba}|^2}{\hbar^2} f(\omega_{ab}) \quad (7.67)$$

If we define the effective Rabi frequency by

$$\Omega_R = \frac{|H_{ba}|}{\hbar} \quad (7.68)$$

then

$$\Gamma_{ab} = 2\pi \frac{\Omega_R^2}{\Delta\omega} \quad (7.69)$$

Another situation that often occurs is when the radiation is monochromatic, but the final state is actually composed of many states spaced close to each other in energy so as to form a continuum. If such is the case, the density of final states can be described by

$$dN = \rho(E)dE \quad (7.70)$$

where dN is the number of states in range dE . Taking $\hbar\omega = E_b - E_a$ in Eq. 7.65, and integrating gives

$$\Gamma_{ab} = 2\pi \frac{|H_{ba}|^2}{\hbar} \rho(E_b) \quad (7.71)$$

This result remains valid in the limit $E_b \rightarrow E_a$, where $\omega \rightarrow 0$. In this static situation, the result is known as *Fermi's Golden Rule*.

Note that Eq. 7.67 and Eq. 7.71 both describe a uniform rate process in which the population of the initial state decreases exponentially in time. If the population of the initial state is $P(0)$, then

$$P(t) = P(0)e^{-\Gamma_{ba}t} \quad (7.72)$$

Applying this to the dipole transition described in Eq. 7.30, we have

$$\Gamma_{ab} = 2\pi \frac{E^2 d_{ba}^2}{\hbar^2} f(\omega) \quad (7.73)$$

The arguments here do not distinguish whether $E_a < E_b$ or $E_a > E_b$ (though the sign of $\omega = (E_b - E_a)/\hbar$ obviously does). In the former case the process is absorption, in the latter case it is emission.

7.6 Spontaneous emission rate

The rate of absorption for the transition $a \rightarrow b$, where $E_b > E_a$, is, from Eq. 7.46 and Eq. 7.65,

$$\Gamma_{ab} = \frac{4\pi^2}{\hbar V} |\hat{\mathbf{e}} \cdot \mathbf{d}_{ba}|^2 n\omega \delta(\omega_0 - \omega). \quad (7.74)$$

where $\omega_0 = (E_b - E_a)/\hbar$. To evaluate this we need to let $n \rightarrow n(\omega)$, where $n(\omega)d\omega$ is the number of photons in the frequency interval $d\omega$, and integrate over the spectrum. The result is

$$\Gamma_{ab} = \frac{4\pi^2}{\hbar V} |\hat{\mathbf{e}} \cdot \mathbf{d}_{ba}|^2 \omega_0 n(\omega_0) \quad (7.75)$$

To calculate $n(\omega)$, we first calculate the mode density in space by applying the usual periodic boundary condition

$$k_j L = 2\pi n_j, \quad j = x, y, z. \quad (7.76)$$

The number of modes in the range $d^3k = dk_x dk_y dk_z$ is

$$dN = dn_x dn_y dn_z = \frac{V}{(2\pi)^3} d^3k = \frac{V}{(2\pi)^3} k^2 dk d\Omega = \frac{V}{(2\pi)^3} \frac{\omega^2 d\omega d\Omega}{c^3} \quad (7.77)$$

Letting $\bar{n} = n(\bar{\omega})$ be the average number of photons per mode, then

$$n(\omega) = \bar{n} \frac{dN}{d\omega} = \frac{\bar{n} V \omega^2 d\Omega}{(2\pi)^3 c^3} \quad (7.78)$$

Introducing this into Eq. 7.75 gives

$$\Gamma_{ab} = \frac{\bar{n} \omega^3}{2\pi \hbar c^3} |\hat{\mathbf{e}} \cdot \mathbf{d}_{ba}|^2 d\Omega \quad (7.79)$$

We wish to apply this to the case of isotropic radiation in free space, as, for instance, in a thermal radiation field. We can take \mathbf{d}_{ba} to lie along the z axis and describe \mathbf{k} in spherical coordinates about this axis. Since the wave is transverse, $\hat{\mathbf{e}} \cdot \hat{\mathbf{D}} = \sin \theta$. However, there are 2 orthogonal polarizations. Consequently,

$$\int |\hat{\mathbf{e}} \cdot \mathbf{d}_{ba}|^2 d\Omega = 2 |\mathbf{d}_{ba}|^2 \int \sin^2 \theta d\Omega = \frac{8\pi}{3} |\mathbf{d}_{ba}|^2 \quad (7.80)$$

Introducing this into Eq. 7.79 yields the absorption rates

$$\Gamma_{ab} = \frac{4}{3} \frac{\omega^3}{\hbar c^3} |\mathbf{d}_{ba}|^2 \bar{n} \quad (7.81)$$

It follows that the emission rate for the transition $b \rightarrow a$ is

$$\Gamma_{ba} = \frac{4}{3} \frac{\omega^3}{\hbar c^3} |\mathbf{d}_{ba}|^2 (\bar{n} + 1) \quad (7.82)$$

If there are no photons present, the emission rate—called the rate of spontaneous emission—is

$$\Gamma_{ba}^0 = \frac{4}{3} \frac{\omega^3}{\hbar c^3} |\mathbf{d}_{ba}|^2 = \frac{4}{3} \frac{e^2 \omega^3}{\hbar c^3} |\langle b | \mathbf{r} | a \rangle|^2 \quad (7.83)$$

In atomic units, in which $c = 1/\alpha$, we have

$$\Gamma_{ba}^0 = \frac{4}{3} \alpha^3 \omega^3 |\mathbf{r}_{ba}|^2. \quad (7.84)$$

Taking, typically, $\omega = 1$, and $r_{ba} = 1$, we have $\Gamma^0 \approx \alpha^3$. The “ Q ” of a radiative transition is $Q = \omega/\Gamma \approx \alpha^{-3} \approx 3 \times 10^6$. The α^3 dependence of Γ indicates that radiation is fundamentally a weak process: hence the high Q and the relatively long radiative lifetime of a state, $\tau = 1/\Gamma$. For example, for the $2P \rightarrow 1S$ transition in hydrogen (the L_α transition), we have $\omega = 3/8$, and taking $r_{2p,1s} \approx 1$, we find $\tau = 3.6 \times 10^7$ atomic units, or 0.8 ns. The actual lifetime is 1.6 ns.

The lifetime for a strong transition in the optical region is typically 10–100 ns. Because of the ω^3 dependence of Γ^0 , the radiative lifetime for a transition in the microwave region—for instance an electric dipole rotational transition in a molecule—is longer by the factor $(\lambda_{\text{microwave}}/\lambda_{\text{optical}})^3 \approx 10^{15}$, yielding lifetimes on the order of months. Furthermore, if the transition moment is magnetic dipole rather than electric dipole, the lifetime is further increased by a factor of α^{-2} , giving a time of thousands of years.

7.7 Line Strength

Because the absorption and stimulated emission rates are proportional to the spontaneous emission rate, we shall focus our attention on the Einstein A coefficient:

$$A_{ba} = \frac{4}{3} \frac{e^2 \omega^3}{\hbar c^3} |\langle b | \mathbf{r} | a \rangle|^2 \quad (7.85)$$

where

$$|\langle b | \mathbf{r} | a \rangle|^2 = |\langle b | x | a \rangle|^2 + |\langle b | y | a \rangle|^2 + |\langle b | z | a \rangle|^2 \quad (7.86)$$

For an isolated atom, the initial and final states will be eigenstates of total angular momentum. (If there is an accidental degeneracy, as in hydrogen, it is still possible to select angular momentum eigenstates.) If the final angular momentum is J_a , then the atom can decay into each of the $2J_a + 1$ final states, characterized by the azimuthal quantum number $m_a = -J_a, -J_a + 1, \dots, +J_a$. Consequently,

$$A_{ba} = \frac{4}{3} \frac{e^2 \omega^3}{\hbar c^3} \sum_{m_a} |\langle b, J_b | \mathbf{r} | a, J_a, m_a \rangle|^2 \quad (7.87)$$

The upper level, however, is also degenerate, with a $(2J_b + 1)$ -fold degeneracy. The lifetime cannot depend on which state the atom happens to be in. This follows from the isotropy of space: m_b depends on the orientation of \mathbf{J}_b with respect to some direction in space, but the decay rate for an isolated atom can't depend on how the atom happens to be oriented. Consequently, it is convenient to define the *line strength* S_{ba} , given by

$$S_{ba} = S_{ab} = \sum_{m_b} \sum_{m_a} |\langle b, J_b, m_b | \mathbf{r} | a, J_a, m_a \rangle|^2 \quad (7.88)$$

Then,

$$A_{ba} = \frac{4}{3} \frac{e^2 \omega^3}{\hbar c^3} \frac{S_{ba}}{g_b} = \frac{4}{3} \frac{e^2 \omega^3}{\hbar c^3} \frac{S_{ba}}{2J_b + 1} \quad (7.89)$$

The line strength is closely related to the average oscillator strength \bar{f}_{ab} . \bar{f}_{ab} is obtained by averaging f_{ab} over the initial state $|b\rangle$, and summing over the values of m in the final state, $|a\rangle$. For absorption, $\omega_{ab} > 0$, and

$$\bar{f}_{ab} = \frac{2m}{3\hbar} \omega_{ab} \frac{1}{2J_b + 1} \sum_{m_b} \sum_{m_a} |\langle b, J_b, m_b | \mathbf{r} | a, J_a, m_a \rangle|^2 \quad (7.90)$$

It follows that

$$\bar{f}_{ba} = -\frac{2J_b + 1}{2J_a + 1} \bar{f}_{ab}. \quad (7.91)$$

In terms of the oscillator strength, we have

$$\bar{f}_{ab} = \frac{2m}{3\hbar} \omega_{ab} \frac{1}{2J_b + 1} S_{ab}. \quad (7.92)$$

$$\bar{f}_{ba} = -\frac{2m}{3\hbar} |\omega_{ab}| \frac{1}{2J_a + 1} S_{ab}. \quad (7.93)$$

7.8 Excitation by narrow and broad band light sources

We have calculated the rate of absorption and emission of an atom in a thermal field, but a more common situation involves interaction with a light beam, either monochromatic or broad band. Here “broad band” means having a spectral width that is broad compared to the natural line width of the system—the spontaneous decay rate.

For an electric dipole transition, the radiation interaction is

$$|H_{ba}| = e|\mathbf{r}_{ba}| \cdot \hat{\mathbf{e}}E/2, \quad (7.94)$$

where E is the amplitude of the field. The transition rate, from Eq. 7.80, is

$$W_{ab} = \frac{\pi}{2} \frac{e^2 |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 E^2}{\hbar^2} f(\omega_0) = \frac{\pi}{2} \frac{e^2 |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2 E^2}{\hbar} f(E_b - E_a) \quad (7.95)$$

where $\omega_0 = (E_b - E_a)/\hbar$ and $f(\omega)$ is the normalized line shape function, or alternatively, the normalized density of states, expressed in frequency units. The transition rate is proportional to the intensity I_0 of a monochromatic radiation source. I_0 is given by the Poynting vector, and can be expressed by the electric field as $E^2 = 8\pi I_0/c$. Consequently,

$$W_{ab} = \frac{4\pi^2}{c} \frac{e^2 |\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|^2}{\hbar^2} I_0 f(\omega_0) \quad (7.96)$$

In the case of a Lorentzian line having a FWHM of Γ_0 centered on frequency ω_0 ,

$$f(\omega) = \frac{1}{\pi} \frac{(\Gamma_0/2)}{(\omega - \omega_0)^2 + (\Gamma_0/2)^2} \quad (7.97)$$

In this case,

$$W_{ab} = \frac{8\pi e^2}{c\hbar^2 \Gamma_0} |\langle b|\hat{\mathbf{e}} \cdot \mathbf{r}|a\rangle|^2 I_0 \quad (7.98)$$

Note that W_{ab} is the rate of transition between two particular quantum states, not the total rate between energy levels. Naturally, we also have $W_{ab} = W_{ba}$.

An alternative way to express Eq. 7.95 is to introduce the Rabi frequency,

$$\Omega_R = \frac{2H_{ba}}{\hbar} = \frac{e|\hat{\mathbf{e}} \cdot \mathbf{r}_{ba}|E}{\hbar} \quad (7.99)$$

In which case

$$W_{ab} = \frac{\pi}{2} \Omega_R^2 f(\omega_0) = \Omega_R^2 \frac{1}{\Gamma_0} \quad (7.100)$$

If the width of the final state is due solely to spontaneous emission, $\Gamma_0 = A = (4e^2\omega^3/3\hbar c^3)|r_{ba}|^2$. Since W_{ab} is proportional to $|r_{ba}|^2/A_0$, it is independent of $|r_{ba}|^2$. It is left as a problem to find the exact relationship, but it can readily be seen that it is of the form

$$W_{ab} = X\lambda^2 I_0/\hbar\omega \quad (7.101)$$

where X is a numerical factor. $I/\hbar\omega$ is the photon flux—i.e. the number of photons per second per unit area in the beam. Since W_{ab} is an excitation rate, we interpret $X\lambda^2$ as the resonance absorption cross section for the atom, σ_0 .

At first glance it is puzzling that σ_0 does not depend on the structure of the atom; one might expect that a transition with a large oscillator strength—i.e. a large value of $|r_{ab}|^2$ —should have a large absorption cross section. However, the absorption rate is inversely proportional to the linewidth, and since that also increases with $|r_{ab}|^2$, the two factors cancel out. This behavior is not limited to electric dipole transitions, but is quite general.

There is, however, an important feature of absorption that does depend on the oscillator strength. σ_0 is the cross section assuming that the radiation is monochromatic compared to the natural line width. As the spontaneous decay rate becomes smaller and smaller, eventually the natural linewidth becomes narrower than the spectral width of the laser, or whatever source is used. In that case, the excitation becomes broad band.

We now discuss broad band excitation. Using the result of the last section, finding the excitation rate or the absorption cross section for broad band excitation is trivial. From Eq. 7.95, the absorption rate is proportional to $f(\omega_0)$. For monochromatic excitation, $f(\omega_0) = (2/\pi)A^{-1}$ and $W_{\text{mono}} = X\lambda^2 I_0/\hbar\omega$. For a spectral source having linewidth $\Delta\omega_s$, defined so that the normalized line shape function is $f(\omega_0) = (2/\pi)\Delta\omega_s^{-1}$, then the broad band excitation rate is obtained by replacing Γ_0 with $\Delta\omega_s$ in Eq. 7.101. Thus

$$W_B = \left(X\lambda^2 \frac{\Gamma_0}{\Delta\omega_s} \right) \frac{I_0}{\hbar\omega} \quad (7.102)$$

Similarly, the effective absorption cross section is

$$\sigma_{\text{eff}} = \sigma_0 \frac{\Gamma_0}{\Delta\omega_s} \quad (7.103)$$

This relation is valid provided $\Delta\omega_s \gg \Gamma_0$. If the two widths are comparable, the problem needs to be worked out in detail, though the general behavior would be for $\Delta\omega_s \rightarrow (\Delta\omega_s^2 + \Gamma_0^2)^{1/2}$. Note that $\Delta\omega_s$ represents the actual resonance width. Thus, if Doppler broadening is the major broadening mechanism then

$$\sigma_{\text{eff}} = \sigma_0 \Gamma_0 / \Delta\omega_{\text{Doppler}}. \quad (7.104)$$

Except in the case of high resolution laser spectroscopy, it is generally true that $\Delta\omega_s \gg \Gamma_0$, so that $\sigma_{\text{eff}} \ll \sigma_0$.

7.9 Higher-order radiation processes

The atom-field interaction is given by Eq. 7.25

$$H_{ba} = \frac{e}{mc} \langle b | \mathbf{p} \cdot \mathbf{A}(\mathbf{r}) | a \rangle \quad (7.105)$$

For concreteness, we shall take $\mathbf{A}(\mathbf{r})$ to be a plane wave of the form

$$\mathbf{A}(\mathbf{r}) = A \hat{\mathbf{z}} e^{ikz} \quad (7.106)$$

Expanding the exponential, we have

$$H_{ba} = \frac{eA}{mc} \langle b | p_z (1 + ikz + (ikz)^2/2 + \dots) | a \rangle \quad (7.107)$$

If dipole radiation is forbidden, for instance if $|a\rangle$ and $|b\rangle$ have the same parity, then the second term in the parentheses must be considered. We can rewrite it as follows:

$$p_z x = (p_z x - z p_x)/2 + (p_z x + z p_x)/2. \quad (7.108)$$

The first term is $-\hbar L_y/2$, and the matrix element becomes

$$-\frac{ieAk}{2m}\langle b|\hbar L_y|a\rangle = -iAk\langle b|\mu_B L_y|a\rangle \quad (7.109)$$

where $\mu_B = e\hbar/2m$ is the Bohr magneton.

The magnetic field, is $\mathbf{B} = -ikA\hat{\mathbf{y}}$. Consequently, Eq. 7.109 can be written in the more familiar form $-\vec{\mu} \cdot \mathbf{B}$ (The orbital magnetic moment is $\vec{\mu} = -\mu_B \mathbf{L}$: the minus sign arises from our convention that e is positive.)

We can readily generalize the matrix element to

$$H_{\text{int}}(M1) = \mathbf{B} \cdot \langle b|\mu_B \mathbf{L}|a\rangle \quad (7.110)$$

where $M1$ indicates that the matrix element is for a magnetic dipole transition.

The second term in Eq. 7.108 involves $(p_z x + z p_x)/2$. Making use of the commutator relation $[\mathbf{r}, H_0] = i\hbar \mathbf{p}/m$, we have

$$\frac{1}{2}(p_z x + z p_x) = \frac{m}{2i\hbar}([z, H_0]x + z[x, H_0]) = \frac{m}{2i\hbar}(-H_0 z x + z x H_0) \quad (7.111)$$

So, the contribution of this term to the matrix element in Eq. 7.107 is

$$\frac{ieA}{m} \frac{km}{2\hbar i} \langle b| -H_0 z x + z x H_0 |a\rangle = -\frac{eAk}{2c} \frac{E_b - E_a}{\hbar} \langle b|z x|a\rangle = \frac{ieE\omega}{2c} \langle b|z x|a\rangle \quad (7.112)$$

where we have taken $E = ikA$. This is an electric quadrupole interaction, and we shall denote the matrix element by

$$H_{\text{int}}(E2)' = \frac{ie\omega}{2c} \langle b|x z|a\rangle E \quad (7.113)$$

The prime indicates that we are considering only one component of a more general expression.

The total matrix element from Eq. 7.107 can be written

$$H_{\text{int}}^{(2)} = H_{\text{int}}(M1) + H_{\text{int}}(E2). \quad (7.114)$$

where the superscript (2) indicates that we are looking at the second term in the expansion of Eq. 7.107. Note that $H_{\text{int}}(M1)$ is real, whereas $H_{\text{int}}(E2)$ is imaginary. Consequently,

$$|H_{\text{int}}^{(2)}|^2 = |H_{\text{int}}(M1)|^2 + |H_{\text{int}}(E2)|^2 \quad (7.115)$$

The magnetic dipole and electric quadrupole terms do not interfere.

The magnetic dipole interaction,

$$H(M1) \sim \mathbf{B} \cdot \langle b|\vec{\mu}|a\rangle \quad (7.116)$$

is of order α compared to an electric dipole interaction because $\mu = \alpha/2$ atomic units.

The electric quadrupole interaction

$$H(E2) \sim e \frac{\omega}{c} \langle b|x z|a\rangle \quad (7.117)$$

is also of order α . Because transition rates depend on $|H_{ba}|^2$, the magnetic dipole and electric quadrupole rates are both smaller than the dipole rate by $\alpha^2 \sim 5 \times 10^{-5}$. For this reason they are generally referred to as *forbidden* processes. However, the term is used somewhat loosely, for there are transitions which are much more strongly suppressed due to other selection rules, as for instance triplet to singlet transitions in helium.

7.10 Selection rules

The dipole matrix element for a particular polarization of the field, $\hat{\mathbf{e}}$, is

$$\hat{\mathbf{e}} \cdot \mathbf{r}_{ba} = \hat{\mathbf{e}} \cdot \langle b, J_b, m_b | \mathbf{r} | a, J_a, m_a \rangle. \quad (7.118)$$

It is straightforward to calculate x_{ba}, y_{ba}, z_{ba} , but a more general approach is to write \mathbf{r} in terms of a spherical tensor. This yields the selection rules directly, and allows the matrix element to be calculated for various geometries using the Wigner-Eckart theorem, as discussed in various quantum mechanics text books.

The orbital angular momentum operator of a system with total angular momentum L can be written in terms of a spherical harmonic $Y_{L,M}$. Consequently, the spherical harmonics constitute spherical tensor operators. A vector can be written in terms of spherical harmonics of rank 1. This permits the vector operator \mathbf{r} to be expressed in terms of the spherical tensor $T_{1,M}(\mathbf{r})$.

The spherical harmonics of rank 1 are

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta; \quad Y_{1,+1} = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{+i\phi} \quad Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi} \quad (7.119)$$

These are normalized so that

$$\int Y_{1,m'}^* Y_{1,m} \sin \theta d\theta d\phi = \delta_{m',m} \quad (7.120)$$

We can write the vector \mathbf{r} in terms of components r_m , $m = +1, 0, -1$,

$$r_0 = r \sqrt{\frac{4\pi}{3}} Y_{1,0}, \quad r_{\pm} = r \sqrt{\frac{4\pi}{3}} Y_{1,\pm 1}, \quad (7.121)$$

or, more generally

$$r_M = r T_{1,M}(\theta, \phi) \quad (7.122)$$

Consequently,

$$\langle b, J_b, m_b | r_M | a, J_a, m_a \rangle = \langle b, J_b, m_b | r T_{1M} | a, J_a, m_a \rangle \quad (7.123)$$

$$= \langle b, J_b | r | a, J_a \rangle \langle J_b, m_b | r T_{1M} | J_a, m_a \rangle \quad (7.124)$$

The first factor is independent of m . It is

$$r_{ba} = \int_0^{\infty} R_{b,J_b}^*(r) r R_{a,J_a}(r) r^2 dr \quad (7.125)$$

where r_{ba} contains the radial part of the matrix element. It vanishes unless $|b\rangle$ and $|a\rangle$ have opposite parity. The second factor in Eq. 7.124 yields the selection rule

$$|J_b - J_a| = 0, 1; \quad m_b = m_a \pm M = m_a, m_a \pm 1 \quad (7.126)$$

Similarly, for magnetic dipole transition, Eq. 7.110, we have

$$H_{ba}(M1) = \mu_B B \langle b, J_b, m_b | T_{LM}(L) | a, J_a, m_a \rangle \quad (7.127)$$

It immediately follows that parity is unchanged, and that

$$|\Delta J| = 0, 1 \quad (J = 0 \rightarrow J = 0 \text{ forbidden}); \quad |\Delta m| = 0, 1 \quad (7.128)$$

The electric quadrupole interaction Eq. 7.113, is not written in full generality. Nevertheless, from Slichter, Table 9.1, it is evident that xz is a superposition of $T_{2,1}(\mathbf{r})$ and $T_{2,-1}(\mathbf{r})$. (Specifically, $xz = (T_{2,-1}(\mathbf{r}) - T_{2,1}(\mathbf{r}))/4$.)

In general, then, we expect that the quadrupole moment can be expressed in terms of $T_{2,M}(\mathbf{r})$. There can also be a scalar component which is proportional to $T_{0,0}(r)$.

Consequently, for quadrupole transition we have: parity unchanged

$$|\Delta J| = 0, 1, 2, \quad (J = 0 \rightarrow J = 0 \text{ forbidden}) \quad |\Delta m| = 0, 1, 2. \quad (7.129)$$

This discussion of matrix elements, selection rules, and radiative processes barely skims the subject. For an authoritative treatment, the books by Shore and Manzel, and Sobelman are recommended.

References for Chapter 7

- [1] E.T. Jaynes and F.W. Cummings, Proc. IEEE, **51**, 89 (1963).
- [2] A. Einstein, Z. Phys. **18**, 121 (1917), reprinted in English by D. ter Haar, *The Old Quantum Theory*, Pergammon, Oxford.