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Chapter 8

Resonance Line Shapes

In this chapter, we will discuss several phenomena which affect the line shape. Our motivation for this is simple: No resonance line is infinitely narrow. Unless we understand the line shape, we cannot extract spectroscopic information with high accuracy.

8.1 Ideal Line Shape for Rabi Resonance

The Rabi resonance transition probability,

$$P = \frac{\omega_R^2}{(\omega - \omega_0)^2 + \omega_R^2} \sin^2 \frac{\sqrt{(\omega - \omega_0)^2 + \omega_R^2} t}{2} \quad (8.1)$$

has the following properties:

- It is *exact*, it is not a perturbative result.
- P achieves a maximum value of 1 when the resonance condition is satisfied: $\omega = \omega_0$. At resonance P is periodic in the product $\omega_R t$.
- As $|\omega - \omega_0|$ is increased, P oscillates with increasing frequency but decreasing amplitude.

If the interaction time τ is fixed and the power is varied at resonance, then P achieves its maximum value when $\omega_R \tau = \pi$. Under these conditions the spin exactly “flips” under the influence of the applied field. If the frequency ω is then varied, P varies as a function of ω as shown in Fig. 8.1a (curve a). The resonance curve has a full width at half maximum (FWHM) of $\Delta\omega = 0.94\omega_R$, or, in units of Hz,

$$\Delta\nu_{\text{RABI}} = \frac{0.94\omega_R}{2\pi} = \frac{0.47}{\tau} \quad (8.2)$$

8.2 Line Shape for an Atomic Beam

In practice the conditions described by the simple Rabi formula are rarely met exactly. In most cases, 2-level resonance involves averaging over some combination of interaction times, field strengths, and possibly resonance frequency. Fig. 8.1a shows the situation for atomic beam resonance. In this case the experimental resonance curve depends on the distribution of interaction times due to the various speeds of atoms in the thermal atomic beam.

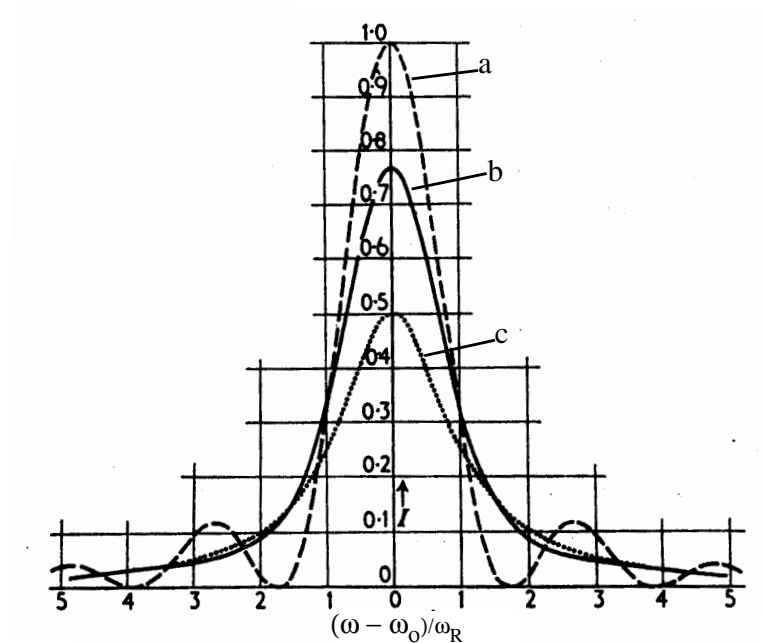


Figure 8.1. Calculated lineshapes: Probability of transition plotted as a function of $(\omega - \omega_0)/\omega_R$. Curve a) single velocity: $\omega_R\tau = \pi$. Curve b) thermal atomic beam average; $\omega_R\tau = 1.20\pi$, where $\tau = L/\alpha$. Curve c) heavily saturated resonance, $\omega_R\tau \gg \pi$. From Ramsey, *Molecular Beams*.

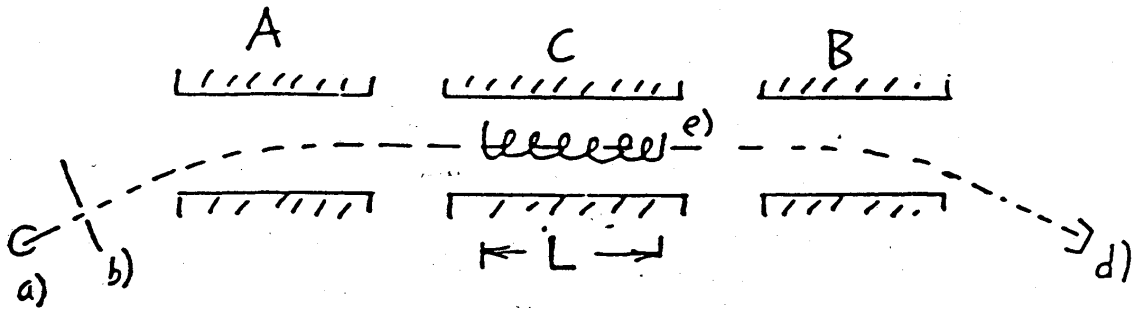


Figure 8.2. Elementary atomic beam resonance experiment. a) source of atoms; b) collimation slit for atomic beam; a) and b) Stern-Gerlach magnet for deflecting atoms. These are inhomogeneous magnets which exert a force $\mathbf{F} = \nabla(\vec{\mu} \cdot \mathbf{B}) = \gamma\hbar\nabla(J_z B) = \gamma\hbar m\nabla B$. Magnet A, the “polarizer”, selects a given value of m ; magnet B, the “analyzer”, allows the atoms to pass to the detector d only if m remains unchanged. Resonance is induced in uniform field c) by the oscillating field from the coil e). At the resonance a transition $m \rightarrow m'$ occurs; the atom can no longer pass through the analyzer, and the signal to the detector d) falls. If the length of the coil is L , then atoms moving with speed of ν interact with the oscillating field for time $t = L/\nu$.

In many cases the interaction time τ is not fixed, but is distributed according to a distribution of interaction times $f(t)$, where $\int_0^\infty f(t)dt = 1$. The observed quantity is the average transition probability which is given by

$$\langle P(\Delta\omega) \rangle = \int_0^\infty P(\Delta\omega, t)f(t)dt \quad (8.3)$$

where $\Delta\omega = \omega - \omega_0$.

In an atomic beam, for instance, the interaction time is L/v , where v is the speed. The distribution of speeds in an atomic beam can be found from the Maxwell-Boltzmann law and is

$$g(v) = \frac{2}{\alpha^4}v^3 \exp(v^2/\alpha^2) \quad (8.4)$$

where $\alpha = \sqrt{2k_B T/M}$ is the most probable velocity of atoms of mass M in a gas at temperature T (cf Ramsey, *Molecular Beams*, p.20). Thus, for a Maxwell-Boltzmann speed distribution the average transition probability is

$$\langle P \rangle_{\text{MB}} = 2 \int_0^\infty \exp(-y^2)y^3 \frac{\omega_R^2}{a^2} \sin\left(\frac{aL}{2\alpha y}\right) dy, \quad (8.5)$$

where $a^2 = \Delta\omega^2 + \omega_R^2$, and $y = v/\alpha$.

The integral must be evaluated numerically (Tables are given in Appendix D of Ramsey.) Results are shown in Fig. 1.8b. $\langle P \rangle$ has a maximum for $\omega_R L/\alpha = 1.200\pi$. In contrast, in a monochromatic beam the maximum occurs for $\omega_R t = \omega_R L/v = \pi$. The maximum transition probability is 0.75. The FWHM is

$$\Delta\nu_{\text{MB}} = 1.07 \frac{\alpha}{L} \quad (8.6)$$

If we regard L/α as the mean time for an atomic pass through the coil, then compared to the line width for a monoenergetic beam, Eq. 8.2, the effect of the velocity spread is to broaden the resonance curve by approximately two. Furthermore, all traces of periodic behavior have been erased.

8.3 Method of Separated Oscillatory Fields

The separated oscillatory field (SOF) technique is one of the most powerful methods of precision spectroscopy. As the name suggests, it involves the sequential application of the transition-producing field to the system under study with an interval in between. This technique was originally conceived by Norman Ramsey in 1948 for application in RF studies of molecular beams using two separated resonance coils through which the molecular beams passed sequentially. It represents the first deliberate exploitation of a quantum superposition state. Subsequently it has been extended to high frequencies where the RF regions were in the radiation zone (i.e. source-free), to two photon transitions, to rapidly decaying systems, and to experiments where the two regions were temporally (rather than spatially) separated. It is routinely used to push measurements to the highest possible precision (eg. in the Cs beam time standard apparatus). Ramsey shared the 1990 Nobel prize for inventing this method. The following figure shows a typical configuration.

The atomic beam resonance region is composed of two oscillatory field regions, each of length ℓ , separated by distance L . The resonance pattern reveals an interference fringe structure with characteristic width $\Delta\nu \approx \alpha/L$, where α is the most probable velocity for a

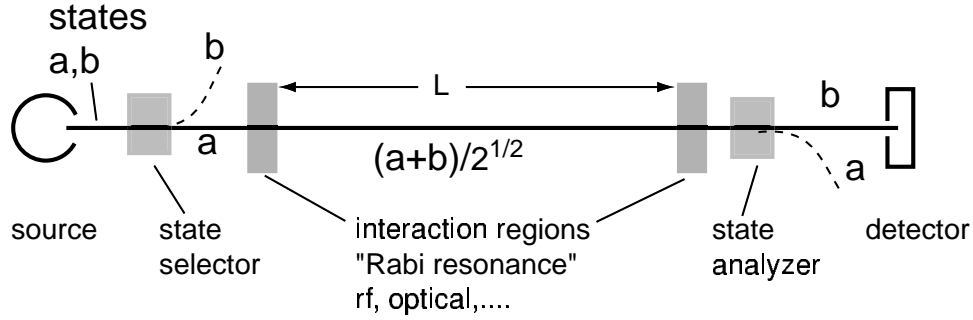


Figure 8.3. Separated oscillatory field atomic beam resonance. The two-state atom experiences a $\pi/2$ pulse in the first oscillatory field, and another $\pi/2$ pulse in the second field. In between, the atom moves freely for distance L . As viewed on the rotating system, on resonance the second field will have the correct phase on resonance, no matter how long it takes the atom to traverse distance L . Off-resonance, however, a phase difference accumulates with the increasing time. As a result, when the frequency is slowly swept, an interference pattern is generated whose frequency width is $\approx 1/T = v/L$, where v is the atom's velocity.

thermal distribution of atoms at temperature T (see the figure below). Of course a single coil of the same length would produce approximately the same resonance width.

The transition probability for the Ramsey method can be calculated by straightforward application of the formalism presented earlier. Details are described in Ramsey's *Molecular Beams*, Section V.4.2. The result is that the transition probability for a two-state system is

$$P = 4 \frac{\omega_R^2}{a^2} \sin^2(a\tau/2) \times \left[\cos(\delta\omega T/2) \cos(a\tau/2) - \left(\frac{\omega - \omega_0}{a} \right) \sin(\delta\omega T/2) \sin(a\tau/2) \right]^2 \quad (8.7)$$

where $a = \sqrt{(\omega - \omega_0)^2 + \omega_R^2}$, and $\delta\omega = \omega - \bar{\omega}_0$, where $\hbar\bar{\omega}_0$ is the average energy separation of the two states along the path between the coil. $\tau = \ell/\alpha$ and $T = L/\alpha$.

The first line in this expression is just 4 times the probability of transition for a spin passing through one of the OFs (oscillating fields). All interference terms (which must involve T) are contained in the second term. The quantity $\delta\omega T$ is the phase difference accumulated by the spin in the field-free region relative to the OF in the first OF region. If the phase in the second OF region differs from the phase in the first OF, the above results must be modified by adding the difference to $\delta\omega T$ in the above equations.

The SOF technique is based on an interference between the excitations produced at two separated fields - thus it is sensitive to the phase difference (coherence) of the oscillating fields. The method is most easily understood by consideration of the classical spin undergoing magnetic resonance in SOF's.

To maximize the interference between the two oscillating fields, we want there to be a probability of 1/2 for a transition in each resonance region. This is achieved by adjusting both field intensities (ω_R above) so that $a\tau = \pi/2$ (an interaction with this property is termed a " $\pi/2$ pulse" if the system is at resonance, in which case the spin's orientation is now along \hat{y} in the rotating coordinate system).

During the field-free time T , the spin precesses merrily about the constant field B_0 between the two oscillating-field regions. When it encounters the second OF, it receives a

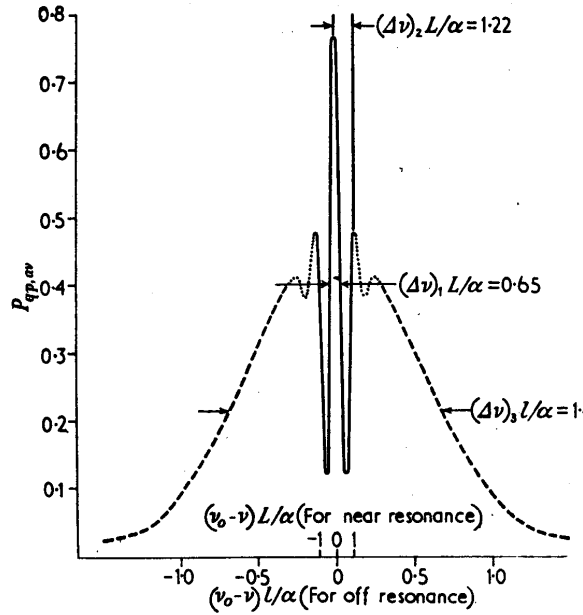


Figure 8.4. Transition probability by the separated oscillatory field method as a function of frequency. L is the distance between the excitation regions; α is the most probable velocity in the beam. Hence, L/α is approximately the average time of the measuring process. The “Ramsey fringe” is shown by the solid line: it is superimposed on the “Rabi pedestal”, dashed line, which is the resonance curve for a single end coil. (from N.F. Ramsey, *Molecular Beams*).

second interaction equal to the first. If the system is *exactly* on resonance, this second OF interaction will just complete the inversion of the spin. If, on the other hand, the system is off resonance just enough so that $\delta\omega\tau = \pi$ (but $\delta\omega\tau \ll 1$) then the spin will have precessed about \hat{z}_0 an angle π less far than the oscillating field. It will consequently lie in the $-\hat{y}'$ direction rather than in the \hat{y}' direction in the coordinate system rotating with the second OF, and as a result the second OF will precess the spin back to $+\hat{z}$, its original direction, and the probability of transition will be 0! A little more thought shows that the transition probability will oscillate sinusoidally with period $\Delta\omega = 2\pi/T$. The central maximum of this interference pattern is centered at ω_0 and its full width at half maximum (in ω -space) is π/T . The central maximum can be made arbitrarily sharp simply by increasing T . In fact, SOF can be used in this fashion to produce line widths for decaying particles which are narrower than the reciprocal of the natural line width! (This does not violate the uncertainty principle because SOF is a way of selecting only those few particles which have lived for time T .)

The separated oscillatory field method (the “Ramsey method”) has the following important properties compared to the single field method (“Rabi method”).

- The resonance frequency depends on the *mean* energy separation of the two states between the coils: instantaneous variations, for instance due to fluctuations in an applied field, either in space or in time, are averaged out.
- The Rabi method requires an applied oscillatory field having uniform phase: this is difficult to accomplish if the flight path is long compared to the wavelength. In

contrast, the Ramsey method requires only that the phase be constant across the short coils of length ℓ . Thus, Doppler effects are to a large extent eliminated.

- By the Rabi method the resonance linewidth due to a thermal beam is $1.07 \alpha/\ell$, whereas by the Ramsey method it is only $0.65 \alpha/\ell$. The linewidth is reduced almost by a factor of two.
- In the presence of radiative decay or some other loss mechanism the Ramsey method can be used to selectively observe long-lived atoms: atoms which have decayed are simply absent from the interference pattern. This makes it possible to observe a resonance line which is narrower than the “natural” linewidth, though one must pay a price in reduced intensity.
- Numerous experimental effects can be measured or reduced by modulating the relative phase of the two fields.
- The method is not restricted to atomic beams: the important point is that the applied fields interfere in *time*. The method can be applied to a fixed sample by applying the fields in some desired sequence of pulses.

8.4 Line Shape with Exponential Decay

If the atoms decay by spontaneous emission, or are otherwise removed from the field by some sort of random process, then the distribution of interaction times is described by an exponential

$$f(t) = \gamma e^{-\gamma t} \quad (8.8)$$

The mean interaction time is $\tau = \int t f(t) dt = 1/\gamma$. The average transition probability is

$$\langle P \rangle = \gamma \int \frac{\omega_R^2}{a^2} \sin^2(at/2) e^{-\gamma t} dt = \frac{1}{2} \frac{\omega_R^2}{\Delta\omega^2 + \gamma^2 + \omega_R^2} \quad (8.9)$$

$\langle P \rangle$ has the familiar Lorentzian shape. The full width at half maximum is

$$\Delta\nu_{\text{exp}} = \frac{1}{\pi} \sqrt{\gamma^2 + \omega_R^2} \quad (8.10)$$

At low power, $\omega_R \ll \gamma$, $\Delta\nu \approx \gamma/\pi$ and $\langle P \rangle \approx \omega_R^2/2\gamma^2$. As the power is increased, $\langle P \rangle$ approaches a limiting value of 0.5, and the line starts to broaden. Broadening of a resonance line due to high power is called *saturation*. In the saturation regime the line width is $\Delta\nu_{\text{exp}} = \omega_R/\pi$;

8.5 Perturbation Theory of Spectral Broadening

(Material in this section based in part on Abragam, *Principles of Nuclear Magnetism*, Section VIII-C.)

The ideal conditions for two-level resonance are rarely encountered, though they can be closely approximated in some atomic beam or atom trap experiments. In general, atomic spectroscopic measurements are affected by factors such as atomic motion—as in Doppler broadening or broadening due to motion in inhomogeneous applied fields—or in spectral broadening of the applied radiation. We describe here a general approach for dealing with

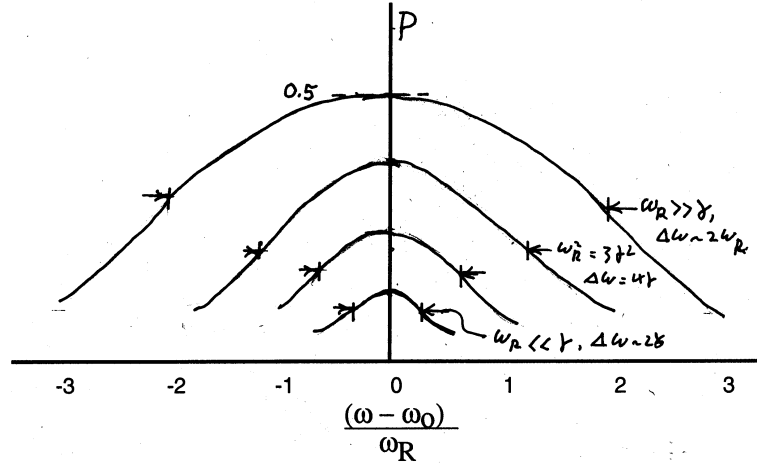


Figure 8.5. Sketch of resonance line shape with exponential damping, for various values of the ratio ω_R/γ .

such effects. The formalism can also be applied in a somewhat *ad hoc* fashion to include the effect of spontaneous emission.

We shall consider a two-level system: the extension to a many level system is straightforward. The physical situation deals with a system which is initially in a given quantum state. The problem is to calculate the effect of a time-varying interaction. Instead of obtaining an exact solution, as we did when we obtained the Rabi oscillations, we will work within first order perturbation theory.

The two-level system is described by

$$\Psi = Au_a e^{-i\omega_a t} + Bu_b e^{-i\omega_b t} \quad (8.11)$$

The Hamiltonian is taken as $H_0 + \hbar V$, where the perturbation V is assumed to have no diagonal matrix elements. Schrödinger's equation gives

$$\begin{aligned} i\dot{A} &= \langle a|V(t)|b\rangle e^{-i\omega_0 t} B \\ i\dot{B} &= \langle b|V(t)|a\rangle e^{+i\omega_0 t} A \end{aligned} \quad (8.12)$$

where $\omega_0 = \omega_b - \omega_a$. At $t = 0$ the system is in state $|a\rangle$, so that $A(0) = 1$, $B(0) = 0$. If W_{ba} is the *rate* at which the system evolves from state $|a\rangle$ to state $|b\rangle$, then

$$W_{ba} = \frac{d|B(t)|^2}{dt} = B^* \dot{B} + \dot{B}^* B = -iB^* \langle b|V(t)|a\rangle e^{+i\omega_0 t} A + c.c. \quad (8.13)$$

Integrating Eq. 8.12 yields,

$$B(t) = -i \int_0^t \langle b|V(t')|a\rangle e^{+i\omega_0 t'} A(t') dt' \quad (8.14)$$

To first order, $A(t') = A(0) = 1$. Introducing this result in Eq. 8.13 gives

$$W_{ba} = \int_0^t \langle a|V(t)|b\rangle \langle b|V(t')|a\rangle e^{-\omega_0(t-t')} dt' + c.c. \quad (8.15)$$

It is convenient to introduce the function

$$G_{ba}(t, t') \equiv \langle a|V(t)|b\rangle\langle b|V(t')|a\rangle. \quad (8.16)$$

In general, W_{ba} does not depend explicitly on t or t' , but only on their difference $\tau = |t' - t|$. In this case, Eq. 8.15 becomes

$$W_{ba} = \int_0^t G_{ba}(\tau)e^{-i\omega_0\tau}d\tau + c.c. = \int_{-t}^t G_{ba}(\tau)e^{-i\omega_0\tau}d\tau. \quad (8.17)$$

This formalism should give the same result as our earlier analysis in the limit of very short time, when first order perturbation theory should agree with an exact solution. Consider the case of a uniform oscillating field that generates a matrix element of the form

$$\langle b|V(t)|a\rangle = \frac{x}{2}e^{-i\omega t} \quad (8.18)$$

Then

$$G_{ba}(\tau) = \frac{|x|^2}{4}e^{+i\omega\tau}, \quad (8.19)$$

and

$$W_{ba} = \frac{|x|^2}{4} \int_{-t}^{+t} e^{-i(\omega_0 - \omega)\tau}d\tau = \frac{|x|^2}{2} \frac{\sin(\omega_0 - \omega)t}{(\omega_0 - \omega)} \quad (8.20)$$

In the limit of short time, $W_{ba} \rightarrow |x|^2 t/2$. To compare this with the Rabi resonance formula derived earlier

$$P = \frac{\omega_R^2}{(\omega - \omega_0)^2 + \omega_R^2} \sin^2 \frac{\sqrt{(\omega - \omega_0)^2 + \omega_R^2}}{2} t \quad (8.21)$$

In the limit $t \rightarrow 0$, $P \rightarrow \omega_R^2 t^2/4$, and $W_{ba} = dP/dt = \omega_R^2 t/2$. With the identification $x = \omega_R$, the results are the same.

The Correlation Function: In many cases the perturbation $V(t)$ varies from particle to particle, and our concern is to find the average response of the system. Denoting the system average of W by \overline{W} , we have

$$\overline{W_{ba}} = \int_0^t \overline{\langle a|V(t')|b\rangle\langle b|V(t)|a\rangle} e^{-i\omega_0 t'} dt' + c.c. \quad (8.22)$$

and Eq. 8.16 can be written

$$\overline{G_{ba}(\tau)} = \overline{\langle a|V(0)|b\rangle\langle b|V(\tau)|a\rangle}. \quad (8.23)$$

$\overline{G_{ba}(\tau)}$ is called the *correlation function* of $V(t)$. We shall henceforth drop the bar, with the understanding that a time average is always implied. The correlation function provides a consistent way to analyze effects of motion or other decorrelating factors such as spectral fluctuations in the driving field. After some characteristic time τ_c called the correlation time, $G_{ab}(\tau) \rightarrow 0$. Consequently, Eq. 8.17 becomes

$$W_{ba} = \int_{-\infty}^{\infty} G_{ba}(\tau)e^{-i\omega_0\tau}d\tau. \quad (8.24)$$

We now apply this formalism to an understanding of the shape of spectral lines. This is essential to interpreting the results of spectroscopy, and, more importantly, to controlling the underlying processes which affect it. In the following, we discuss a number of the more important processes that affect line shapes. We also omit some important processes, like pressure broadening. The formalism developed here can be extended to them, but the physics is a great deal more subtle.

8.5.1 Natural line width

Excited atoms spontaneously decay to their ground state, except under very special circumstances. A proper treatment of spontaneous emission requires treating the field quantum mechanically. Nevertheless, we can include its effect here in a phenomenological fashion. The population of atoms in an excited state B will decay in free space as

$$N_b(t) = N_b(0)e^{-\gamma_b t} \quad (8.25)$$

where $\tau_b = 1/\gamma_b$ is called the natural lifetime of the state. We can introduce spontaneous decay into the state vector by writing it as

$$\Psi_b(t) = u_b e^{-i(\omega_b - i\gamma_b/2)t} \quad (8.26)$$

i.e. by treating the energy as a complex quality. In this case, the population of atoms in state b varies as

$$N(t) = N_0 |\Psi_b(t)|^2 = N_0 e^{-\gamma_b t} \quad (8.27)$$

as we surmised. Making this *ansatz*, then the dipole matrix element due to an interaction with an oscillating field is

$$\langle a|V|b\rangle \rightarrow \frac{x}{2} e^{-\Gamma t/2} e^{i\omega t} \quad (8.28)$$

where $\Gamma = (\gamma_a + \gamma_b)$. (If a is the ground state of the system, then $\gamma_a = 0$ and $\Gamma = \gamma_b$.) We have

$$G_{ba}(\tau) = \frac{|x|^2}{4} e^{-\Gamma|\tau|/2} e^{i\omega\tau} \quad (8.29)$$

From Eq. 8.24, we have

$$W_{ba} = \frac{|x|^2}{4} \int_{-\infty}^{\infty} e^{-\Gamma|\tau|/2} e^{-i(\omega_0 - \omega)\tau} d\tau = \frac{|x|^2}{2} \frac{\frac{\Gamma}{2}}{\left(\frac{\Gamma}{2}\right)^2 + (\omega - \omega_0)^2} \quad (8.30)$$

The result, not unexpected, is a Lorentzian line. Note, however, that the linewidth Γ , does not depend on the power. In this first order treatment, saturation does not occur.

8.5.2 Doppler broadening

Consider a gas of atoms moving freely, irradiated by an electromagnetic wave $\mathbf{E} = \hat{\epsilon} E_0 e^{i(kz + \omega t)}$. If the interaction is electric dipole, then

$$\langle a|V|b\rangle = \frac{x}{2} e^{ikz} e^{i\omega t} \quad (8.31)$$

where x is the dipole matrix element. However, the situation here is quite general: x can represent any form of interaction with the wave. The important factor is the phase associated with position, e^{ikz} . If the atoms are moving, then

$$G_{ba} = \frac{|x|^2}{4} e^{i\omega(t'-t)} e^{ik(z(t')-z(t))} \quad (8.32)$$

Denoting the z -component of an atom's velocity by v , then $z(t') - z(t) = v\tau$, where $\tau = t' - t$. We need to evaluate

$$I = \overline{e^{ikv\tau}} \quad (8.33)$$

To take the system average, we use the well known Maxwell-Boltzmann distribution law for the velocity of an ideal gas particle

$$f(v_z) = \frac{1}{\alpha\sqrt{\pi}} e^{-v_z^2/\alpha^2} \quad (8.34)$$

where $\alpha = \sqrt{2k_B T/M}$ is the most probable speed of the gas. (T is the temperature, and M is the atomic mass.) Taking the average in Eq. 8.33 yields

$$I = \frac{1}{\alpha\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-ikv\tau} e^{-v^2/\alpha^2} dv \quad (8.35)$$

The result is

$$I = e^{-(k\alpha\tau)^2/4} \quad (8.36)$$

so that

$$G(t) = \frac{|x|^2}{4} e^{-(k\alpha\tau)^2/4} e^{i\omega\tau} \quad (8.37)$$

Eq. 8.24 becomes

$$\begin{aligned} W_{ba} &= \frac{|x|^2}{4} \int_{-\infty}^{\infty} e^{-(k\alpha\tau)^2/4} e^{i(\omega-\omega_0)\tau} d\tau \\ &= \frac{|x|^2}{2} \frac{1}{k\alpha} e^{-((\omega-\omega_0)/k\alpha)^2} \end{aligned} \quad (8.38)$$

The factor $k\alpha = \omega\alpha/c$ is the first order Doppler shift of an atom moving with the most probable speed α . The spectral line shape has the form of a Gaussian with a width (FWHM)

$$\Delta\omega_D = 2\sqrt{\ln 2} k\alpha = 2\sqrt{\ln 2} \omega \frac{\alpha}{c} \quad (8.39)$$

i.e. the linewidth is just approximately twice the first order Doppler shift. Typically, $\alpha/c \sim 10^{-5}$.

For an atom of mass 23 at a temperature of 500 K, absorbing radiation at 600 nm (sodium), the Doppler width is

$$\Delta\nu_D = \frac{1}{2\pi} \Delta\omega_D \sim 4 \text{ GHz} \quad (8.40)$$

Until the advent of lasers, Doppler broadening seriously limited the resolution of optical spectroscopy. In principle, it should also be a problem in microwave or radio-frequency spectroscopy since the fractional width, $\Delta\nu_D/\nu \sim \alpha/c \sim 10^{-5}$, is large compared to the resolution that can be achieved. However, as we shall demonstrate, it is essentially absent in laboratory experiments in those frequency regimes.

8.5.3 Dicke narrowing

If the atoms make many collisions while they absorb radiation, then their motion is governed by diffusion.

In the optical regime, when a radiating atom collides it can be seriously perturbed. In this case, known as the regime of pressure broadening, the correlation time is approximately the collision time. However, there are situations where atoms can make many collisions

without their dipole moments being affected. Typically, this occurs for atoms colliding with an inert gas called a buffer gas.

Robert Dicke first suggested the use of a buffer gas to reduce the Doppler effect. The situation under which this occurs is called Dicke narrowing.

For an atom moving diffusively, the probability of being at position z' , assuming that at $t = 0$ it was at z , is

$$P(z', z, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-(z'-z)^2/4Dt} \quad (8.41)$$

where D is the diffusion constant. Writing $z' - z = s$ we need to evaluate

$$G_{ba} = \frac{|x|^2}{4} e^{-iks} = \frac{|x|^2}{4} \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} e^{-s^2/4Dt} e^{-iks} ds = \frac{|x|^2}{4} e^{-k^2 Dt} \quad (8.42)$$

Then

$$W_{ba} = \frac{|x|^2}{4} \int_{-\infty}^{\infty} e^{-k^2 D|\tau|} e^{-i(\omega_0 - \omega)\tau} d\tau = \frac{|x|^2}{4} 2 \operatorname{Re} \left\{ \frac{1}{k^2 D + i(\omega_0 - \omega)^2} \right\} \quad (8.43)$$

$$= \frac{|x|^2}{2} \frac{k^2 D}{(k^2 D)^2 + (\omega_0 - \omega)^2} \quad (8.44)$$

This is a Lorentzian curve, with a line width $\Delta\omega_{\text{Dicke}} = 2k^2 D$. For an ideal gas, $D = \bar{v}\ell/3$, where ℓ is the mean free path and \bar{v} is the average speed. Taking $\bar{v} \approx \alpha$, and writing $k = 2\pi/\lambda = 1/\lambda$, we have

$$\Delta\omega_{\text{Dicke}} = \frac{2}{3} k\alpha \frac{\ell}{\lambda} \sim \Delta\omega_D \times \frac{\ell}{\lambda} \quad (8.45)$$

where $\Delta\omega_D$ is the Doppler line width. As the mean free path ℓ is made short compared to the wavelength, the Doppler broadening vanishes.

8.6 Lineshape of Confined Particles

Trapped particles offer the possibility of reaching the ultimate in spectroscopic precision: cooling the particle with lasers or electronics can reduce second order Doppler shifts at least to 10^{-17} (for 1 mK and atomic mass 10), proper design of the cavity can suppress spontaneous emission, and collisions can be virtually eliminated for single trapped particles in cryogenically pumped environments. The first order Doppler shift can be entirely eliminated also, in spite of the fact that v/c is not particularly small ($\approx 10^{-8}$ in the above example). Suppression of first order Doppler shift results from the spectrum of emission/absorption by a trapped particle—it consists of an unshifted central line with sidebands spaced apart by multiples of the frequency of oscillation. The amplitude of the sidebands may be reduced by lowering the amplitude of oscillation of the trapped particle, but it is also possible to address spectroscopically the unshifted central line—this approach underlies the Mössbauer effect as well as the use of buffer gases and specially coated containers to narrow spectra.

8.6.1 Spectrum of oscillating emitter

We now consider the lineshape (or equivalently the emission spectrum) of a harmonically bound particle. The absorption spectrum has the same shape, so we do not need to consider it separately. If the particle oscillates with amplitude x_0 at frequency ω_t , then the phase of

radiation emitted by the atom towards a detector situated at large x will contain the phase term

$$\phi(t) = -kx(t) - \omega_0 t = -kx_0 \sin \omega_t t - \omega_0 t \quad (8.46)$$

A wave with this phase will have an instantaneous frequency

$$\omega(t) = -\dot{\phi}(t) = kx_0 \omega_t \cos \omega_t t + \omega_0 = kv(t) + \omega_0 \quad (8.47)$$

consistent with the usual Doppler shift into the lab system, $\vec{k} \cdot \vec{v}$. In the parlance of electrical engineering, signals with the above phase and frequency correspond to phase and frequency modulation, respectively. We shall find the spectrum from the phase since the amplitude of the phase oscillation is the physically important *modulation index*, which is just the maximum phase shift relative to $\omega_0 t$.

$$\beta = kx_0 = x_0/\lambda \quad (8.48)$$

(This approach also avoids the common pitfall of assuming that the phase corresponding to frequency modulation is $-\omega(t)t$). Thus we must find the spectrum of a wave whose amplitude is proportional to

$$a(t) = \cos \phi(t) = \cos(\omega_0 t + \beta \sin \omega_t t) \quad (8.49)$$

Some algebra using identities (See e.g. M. Abramowitz and I.A. Stegun 9.1.42)

$$\cos(z \sin \theta) = J_0(z) + 2 \sum_{k=1}^{\infty} J_{2k}(z) \cos(2k\theta)$$

$$\sin(z \sin \theta) = 2 \sum_{k=0}^{\infty} J_{2k+1}(z) \sin[(2k+1)\theta]$$

gives

$$a(t) = \sum_{n=-\infty}^{\infty} (-1)^n J_n(\beta) \cos[(\omega_0 + n\omega_t)t] \quad (8.50)$$

Obviously the system does not have a continuous lineshape, rather the emission is either at ω_0 or sidebands which differ from ω_0 by a multiple of the trapping frequency, $n\omega_t$. (Physically this results from the exactly periodic nature of the motion.) The probability of emission at frequency $\omega_0 + n\omega_t$ is simply $J_n^2(\beta)$, hence the intensity spectrum of the emitted light is proportional to

$$I(\omega) \propto \sum_{n=-\infty}^{\infty} J_n^2(\beta) \delta(\omega - \omega_0 - n\omega_t) \quad (8.51)$$

An alternative and intuitively appealing derivation of these results is to consider the quantum number of the bound oscillating particle explicitly in the calculation. Then the initial state is an atom in state b trapped in quantum state n_i of the trap; after emission the atom is in state a in quantum state n_f of the trap. The frequency of the emitted photon determined from energy conservation,

$$\hbar\omega = \hbar\omega_{ba} - E_i^{\text{trap}} - E_f^{\text{trap}}$$

in general, and

$$\hbar\omega = \hbar(\omega_{ba} + n\omega_t) \quad (8.52)$$

for harmonic motion, where $n = n_i - n_f$. This expression needs no correction for recoil since the initial and final kinetic energies of the atom are explicitly accounted for in E_i^{trap} and E_f^{trap} . The transition rate is

$$R = \frac{4k^3}{3h} |\langle b | \hat{\epsilon}^* \cdot \vec{p} | \alpha \rangle|^2 |\langle \psi_f^{\text{trap}} | e^{-i\vec{k} \cdot \vec{r}} | \psi_i^{\text{trap}} \rangle|^2 \quad (8.53)$$

The second term is the confinement factor and depends on the phase variation of the outgoing wave and the trap eigenstates $|\psi_f\rangle$ and $|\psi_i\rangle$. If this matrix element is evaluated in the momentum representation $e^{-i\vec{k} \cdot \vec{r}}$ is a translation operator (by $-\hbar\vec{k}$) so this factor becomes $|\langle \phi_f(\vec{p} - \hbar\vec{k}) | \phi_i(\vec{p}) \rangle|^2$. In the case of a harmonic oscillator with $n_i, n_f \gg 1$, the confinement factor will yield the Bessel function expression consistent with Eq. 8.51.

The preceding view bears much similarity to electronic transitions in molecular spectroscopy in that an electronic transition occurs between two states with quantized vibrational motion. Indeed, the matrix element involving the trap states in Eq. 8.53 is analogous to the Frank-Condon factor in molecular spectroscopy (except $e^{ikr} \approx 1$ owing to the small size of molecules) This association emphasizes the generality of Eq. 8.53: it applies equally to non-harmonic traps, and even to traps (as for neutral atoms) in which the confinement potential differs for states a and b .

8.6.2 Tight confinement

The most dramatic effects associated with tightly confined radiators occur when the particles are confined to dimensions smaller than one wavelength of the emitted light (*tight confinement*). This is evident from the confinement matrix element in Eq. 8.53: if the spatial extent of the wavefunctions associated with ψ^{trap} is $x_0 \ll \lambda$, then $\vec{k} \cdot \vec{r} \ll 1$ and it is reasonable to expand $e^{-i\vec{k} \cdot \vec{r}} \approx 1 - i\vec{k} \cdot \vec{r}$. The first term will give the selection rule $i = f$ (since the ϕ_i are orthonormal) and hence $\omega = \omega_{ba}$ exactly. The second term will have matrix elements of order $x_0\lambda \ll 1$.

8.6.2.1 Recoilless emission

Emission with $i = f$ is called *recoilless emission* because the atom has the same momentum distribution after the emission as before. The momentum of the photon is provided (or taken up in the case of absorption) by the trap itself. This is analogous to the Mössbauer effect in which the momentum is taken up by the crystal as a whole. There the confinement matrix element with $f = i$ is called the *Debye-Waller* factor.

8.6.2.2 Trapping and Dicke narrowing

The concept of the confined particle can be generalized: It is not necessary to confine particles *harmonically* in order to achieve significant narrowing. In 1953 Dicke pointed out [1] that collisions could reduce the usual Doppler width substantially if two conditions were met: the mean free path must be much smaller than the wavelength, and the collisions must not destroy the coherence between the radiating states. This offers a different perspective on Dicke narrowing which we discussed already in Sec. 8.5.3.

The essence of Dicke's argument was that gas collisions could be viewed as a succession of traps each with a different frequency (he considered traps with steep walls rather than harmonic springs, but this is immaterial). All particles would have a recoilless line at $\omega =$

ω_{ba} , and the average over the traps with different frequencies would average the other lines into a broad spectrum with approximately the original Doppler width. He also discussed the case of random diffusion which we presented already in Sec. 8.5.3.

8.6.3 Weak confinement, classical regime

Now consider the case in which the particle is weakly confined so that the amplitude of oscillation is many wavelengths. In this case the maximum phase shift is large and the spectrum will contain many sidebands. We refer to this as the classical regime because the quantization of frequencies in the spectrum may be neglected while attention is concentrated on the overall lineshape. The viewpoint is completely justified for weak traps in which the trapping frequency is less than the spontaneous linewidth—then the sidebands are too close to be resolved and the spectrum will be continuous.

In this classical regime, the lineshape may be determined simply by examining the instantaneous frequency Eq. 8.47 and determining the fraction of the time it has each particular frequency. Consider the time interval 0 to π/ω_t , during which the frequency has each value only once, at the time

$$t(\delta) = \omega_t^{-1} \arccos[\delta/\omega_m] \quad (8.54)$$

where $\delta = \omega - \omega_0$ and $\omega_m = kx_0\omega_t$ is the maximum deviation of $\omega(t)$ from ω .

The probability density for emission between δ and $\delta + d\delta$ is

$$P(\delta)d\delta = |t(\delta + d\delta) - t(\delta)|(\pi/\omega_t) = \frac{\omega_t}{\pi} \left| \frac{dt}{d\delta} \right| d\delta. \quad (8.55)$$

Since the derivative of $\arccos(x)$ is $[1 - x^2]^{-1/2}$,

$$P(\delta) = \frac{(\omega_t/\pi)\omega_t^{-1}\omega_m^{-1}}{\left[1 - \left(\frac{\delta}{\omega_m}\right)^2\right]^{1/2}} = \frac{1}{\pi\omega_m} \cdot \left[1 - (\delta/\omega_m)^2\right]^{-1/2} \quad |\delta| \leq \omega_m \quad (8.56)$$

$$= 0 \quad |\delta| > \omega_m$$

One can compare the classical emission spectrum Eq. 8.56 with the Bessel function prediction of the quantized treatment Eq. 8.51. In addition to the obvious quantization, the Bessel function distribution projects slightly into the forbidden region ($\delta > \omega_m$) and also shows oscillations about the classical prediction.

8.7 Spectrum of Fluorescence from Dressed Atom

The additional levels which are found in the dressed atom are manifest in the spectrum of the spontaneous fluorescence from an atom which is strongly driven near its resonance frequency. If the driving field is weak ($\omega_R \ll \Gamma$, the spontaneous decay rate), then the system absorbs and emits only one photon at a time and must emit radiation at *exactly* the same frequency as the driving field in order to conserve energy (neglecting Doppler shift and atomic recoil by assuming an infinite mass of the atom). When the intensity is in the regime $\omega_R \gg \Gamma$, then several photons may be absorbed and emitted simultaneously and energy conservation restricts only the sum of the energies of the emitted photons. This implies, for example, that the spectrum of two simultaneous fluorescent photons must be

symmetrical about the driving frequency. The frequencies of peaks in the spectrum may be found from the positions of the dressed levels as discussed in 8.422. Their intensities may be found by solving rate equations for the populations of the dressed levels—this is done in some detail in 8.422.

When the driving field is at resonance, the level splittings are symmetric about the unperturbed levels and all four components of the fluorescence have the same intensity leading to a spectrum with twice the intensity in the central peak as in the side peaks. Off-resonance excitation produces a non-broadened δ -function spectral component at the driving frequency (Rayleigh component) in addition to the symmetric peaks about the driving frequency.

References for Chapter 8

- [1] R.H. Dicke, Phys. Rev. **89**, 472 (1953).