

# Chapter 7

## Corrections to Observed Atomic Resonance

All the atomic standards we shall be dealing with are based, in one form or another, on the resonant excitation of atoms or ions, by which they make transitions from one quantum state to another. From the observed resonance spectrum we must arrive at the intrinsic, or proper, frequency of the atoms' response, as it would be observed if they were at rest and free from any outside perturbation. Such perturbations will alter and broaden the resonance spectrum and put a limit on the degree of precision with which the intrinsic atomic frequency can be deduced.

It might be thought that a detailed knowledge of the frequency response curve, no matter how broad, should be sufficient for a theoretical analysis to obtain the true resonant frequency. In fact, this is not so; there will inevitably be sources of noise, some fundamental, some instrumental, present in any system, and the observed response curve will always suffer from a degree of uncertainty. The sharper the response curve, the less important becomes the noise in finding the resonance frequency. A quantitative expression of this fact obviously depends on the detailed shape of the resonance curve; for a Lorentzian line profile we find the following:

$$\frac{\varepsilon}{\Delta\nu} \approx 0.77 \frac{A_n}{A_0} \quad 7.1$$

where  $\varepsilon$  is the error in finding the line center,  $\Delta\nu$  is the line width, and  $A_0$ ,  $A_n$  are the mean *amplitudes* of the signal at resonance and the noise, respectively. The linear dependence on the ratio of amplitudes comes from the usual practice of defining, in effect, the position of the resonance line center in terms of the midpoint between the nearly linear portions on the two sides of the resonance curve at the inflection points. As a general rule, the 0.77 is ignored.

An understanding of the effects of the physical environment on the resonance line shape and position is crucial in finding ways to minimize these effects in practice, and in correcting for any displacement in frequency they may cause. Ultimately, the stability and reproducibility of the standards depend on how successfully this is accomplished. Such theories have also been developed from the inverse point of view: namely, for what they can reveal about the mechanisms that broaden

and/or shift the resonance frequency. The incredibly high degree of spectral resolution that has been reached has raised the level of significance of a number of subtle effects, some involving quantum theory, others Einstein's *Theory of Relativity*, about which more will be said later in this chapter.

## 7.1 Resonance Frequency Broadening

For resonances observed on a large group of atoms, it is useful to distinguish between line-broadening mechanisms according to whether *all* atoms have the *same* broadened spectrum, or the spectrum of the whole group is broadened because *each* atom has a slightly different frequency and the global spectrum merely reflects the distribution of frequencies among the particles. The former is called *homogeneous* broadening, as exemplified by broadening, common to all atoms, due to a finite radiative lifetime, while the latter is *inhomogeneous* broadening, as exemplified by a group in which each atom has a slightly different frequency because of its differing environment.

### 7.1.1 Homogeneous Broadening

The most common source of homogeneous broadening is the finite time of coherent interaction of the atom with the exciting field. This can be due to the finite radiative lifetime of a quantum state involved in the transition or to phase-randomizing collisions, as was postulated by Lorentz to explain optical dispersion in his *electron theory*. Unfortunately, as Lorentz realized, collisions could not solely explain the width of optical resonance lines; we now know that the radiative lifetimes in optical transitions are usually so short compared to average times between collisions, except at extreme pressures, that the observed broadening is evidence of the "natural" radiative lifetime, and not collisions. The situation is quite different, however, in the radio-frequency and microwave regions of the spectrum, where radiative lifetimes are extremely long. In this case collisions play a dominant role, and by making collisions rare, as in the ion standards, extremely narrow resonances are possible.

The spectral line shape that results from a finite radiative lifetime or collisions that only interrupt the phase is the same *Lorentzian* function  $L(\nu)$ , illustrated in Figure 7.1, that we introduced in connection with the response of a damped simple harmonic oscillator, namely

$$L(\nu) = \frac{1}{2\pi} \frac{\gamma}{(\nu_0 - \nu)^2 + \left(\frac{\gamma}{2}\right)^2}, \quad 7.2$$

where the factor  $1/(2\pi)$  is included so that  $\int L(\nu) d\nu = 1$ . In terms of the mean time between phase-randomizing collisions  $\Delta\tau$ , the expression for  $\gamma$  agrees with

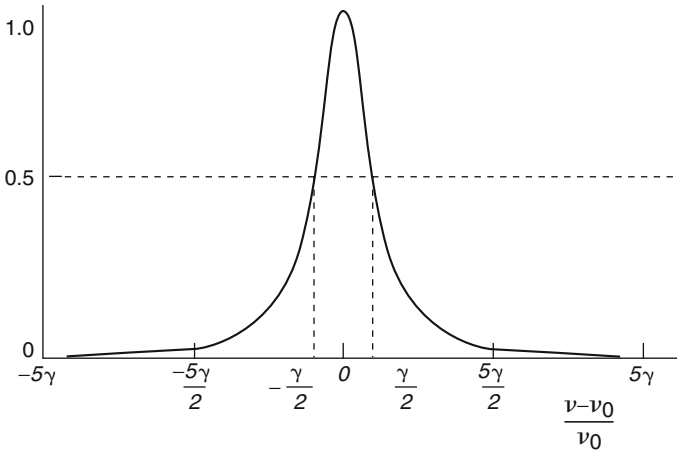


Figure 7.1 The Lorentzian resonance line shape

the approximate result we previously derived for the coherent buildup of oscillation in a resonant structure, namely  $\Delta \tau \gamma \approx 1$ , which, as already indicated, has a far more general application to the simultaneous measurement of frequency and time. As already mentioned, in the optical part of the spectrum, it is the radiative lifetime of quantum states that usually sets the line width, the so-called *natural line width*, typically in the megahertz range. For a driven oscillator the connection between phase-randomizing collisions and damping can be shown to arise from the energy dissipation that the continual interruption of phase produces even when each collision is perfectly elastic. The net effect is as though a resistive force were present; in fact, it was shown by Lorentz that  $\gamma = 2/\Delta\tau$ . In the absence of collisions, an undamped oscillator does not, on the average, continuously absorb energy from a driving field, nor does it dissipate energy if left alone.

### 7.1.2 Inhomogeneous Broadening

The inhomogeneous class of broadening applies to a large number of atoms or ions that have slightly varied resonance frequencies by virtue of, for example, non-uniformities in the distribution of some field that acts on them and displaces the energies of their quantum states. This is of particular concern in nuclear magnetic resonance on solid substances, where an important source of spectral line broadening is the inhomogeneity in the applied magnetic field intensity; in fact, in the original use of the term it was understood to refer to this particular case. The circumstance that makes spatial variations in the applied magnetic field particularly objectionable in solids is that each nucleus is constrained to vibrate with a small amplitude about a fixed lattice site, where the magnetic field may differ from

other lattice sites. However, our concern will be with quasi-free individual particles, which far from being constrained, are more or less free to move with their thermal velocity and only rarely collide with other objects. Under these conditions, the most important source of inhomogeneous broadening is the Doppler shift in the frequency of a moving source, a subject that requires us to think about the description of physical phenomena in terms of coordinate frames of reference in relative motion.

## 7.2 Thermal Doppler Broadening

### 7.2.1 Short Wavelength Limit

The term Doppler is of course familiar to everyone in the context of checking the speed of vehicles on our highways. It is, in general, the variation in the observed frequency of any wave whenever the observer and source of the wave are in relative motion. According to a principle enunciated by Christian Doppler in 1842, which applies equally to sound waves and light waves, frequencies observed with respect to reference frames in relative motion are shifted by what is now called the *Doppler effect*. It is a particularly important universal effect in the context of high-resolution spectroscopy because of the ever-present thermal agitation of atoms and molecules.

The frequency shift predicted classically is easily derived: Assume first that we use a frame of reference in which the source of the wave is stationary and the observer is moving relative to this frame in the direction of the source with a velocity  $V$ . We find  $\nu = (1 + V/c)\nu_0$ , showing that the frequency is increased fractionally by  $V/c$ . If the observer had been assumed to be moving away from the source, we would obviously have found  $\nu = (1 - V/c)\nu_0$ . In general, if the relative velocity vector makes an angle  $\theta$  with the direction of propagation of the wave, we can write the following for the classical change in the observed frequency:

$$\nu - \nu_0 = \frac{Vk \cos \theta}{2\pi}, \quad 7.3$$

where  $k = 2\pi/\lambda$  is the wave number. If we use a frame of reference in which the observer is stationary but the source of the waves has a velocity  $V$  in the direction of the observer, then we would find  $\nu = \nu_0/(1 - V/c)$ .

The Doppler effect is manifested in any type of wave motion. However, in anticipation of the fact that we are concerned here only with light waves, we have used the conventional symbol for the velocity of light,  $c$ . We notice that we have obtained different results depending only on whether we chose a frame of reference in which the source is at rest or the observer is at rest. If we had been considering only waves on the surface of water, the difference in the two results would not have been unexpected, since the water itself uniquely defines a frame of reference, and having the observer move in the water is not necessarily the same as having the source move. However in the case of light, the principle of relativity, one of the

pillars of Einstein's theory, denies the existence of any "absolute" frame of reference, and the two cases dealt with above must yield the exact same result. This is true in our classical derivation only if we neglect terms of order  $(V/c)^2$  and higher.

The Doppler broadening of spectral lines is familiar to spectroscopists working in the optical region of the spectrum because it is generally the limiting factor in the attempt to achieve high spectral resolution, and it is universally present. Under conditions where the wavelength of the wave is very much smaller than the average distance a particle travels between collisions, the Doppler shift in the resonance frequency of each atom will result in a spectral profile for the whole ensemble that simply reflects the distribution among the atoms of the frequency shifts associated with their individual thermal velocities. Such conditions commonly exist for light waves, since their wavelength is only on the order of  $0.5 \mu\text{m}$ , compared to mean free paths 100 times longer, at pressures below say 100 Pa. The exact line profile when collisions are not negligible is far more complicated; we will not concern ourselves with that, but in the next section we will consider the opposite extreme, where the wavelength is large compared with the average distance an atom is free to travel.

For atoms in thermal equilibrium at absolute temperature  $T$ , the components of the velocity of atoms along a given direction, taken to be the  $z$ -axis, are distributed among the atoms in accordance with the *Maxwell–Boltzmann* distribution, in which the number of atoms having a  $z$ -component of velocity in an infinitesimal range between  $V_z$  and  $(V_z + dV_z)$  is given by  $f(V_z)dV_z$ , where  $f(V_z)$  is the following function:

$$f(V_z) = N \sqrt{\frac{M}{2\pi kT}} \exp\left(-\frac{MV_z^2}{2kT}\right), \quad 7.4$$

where  $M$  is the atomic mass and  $k$  is the Boltzmann constant. Now suppose a monochromatic light beam of frequency  $\nu$  is directed along the  $z$ -axis through an ensemble of atoms whose resonance frequency would be  $\nu_0$ , measured in their rest frame of reference. We recall that an atom having a velocity component  $V_z$  will see (to first-order of approximation in  $V_z/c$ ) a Doppler shifted frequency  $\nu(1 - V_z/c)$ . Therefore, the light will be in resonance with such an atom not when  $\nu = \nu_0$ , but rather when  $\nu = \nu_0/(1 - V_z/c)$ , or to the same first-order approximation we have been assuming:  $\nu_0 \approx \nu(1 + V_z/c)$ . Therefore, the atoms, regarded as a whole, will behave as one entity with a broadened resonance line shape, obtained by rewriting the velocity distribution function as a *frequency* distribution function by using the fact that the number of atoms having a  $z$ -component of velocity in the range  $dV_z$  will equal those having a displaced frequency in the interval  $d\nu = (\nu_0/c)dV_z$ . Now, if we let  $g(\nu)$  represent the frequency distribution function, then

$$g(\nu)d\nu = \sqrt{\frac{\alpha}{\pi}} \exp\left[-\alpha\left(\frac{\nu - \nu_0}{\nu_0}\right)^2\right] \frac{d\nu}{\nu_0}; \quad \alpha = \frac{Mc^2}{2kT}. \quad 7.5$$

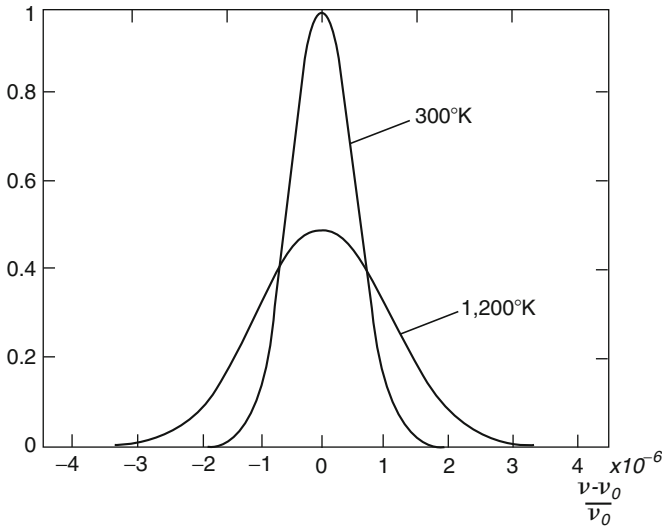


Figure 7.2 The Gaussian line shape for atoms in thermal equilibrium

Because this function has the form  $\exp(-x^2)$  it is called a *Gaussian line shape*, and plotted as a function of frequency, it has the well-known bell shape, shown in Figure 7.2 for Rb vapor at a temperature of 300°K.

### 7.2.2 Long Wavelength Limit: the Dicke Effect

Extremely narrow resonances, far below the Doppler width derived above, are actually observed at *microwave* frequencies on atoms diffusing in a buffer gas, in spite of their thermal agitation. This is due to what has been called the *Dicke effect* (Dicke, 1953). If we substitute in the formula for the first-order Doppler shift, namely  $\nu - \nu_0 = (V/c)\nu_0$ , the numerical values for a Rb atom diffusing through an inert buffer gas with an average thermal velocity of about  $10^4$  meters per second, we find a Doppler frequency shift in its microwave resonance at 6.8 GHz of about 200 kHz, or 10,000 times the frequency width of the resonance actually observed. Clearly, the conditions for “normal” Doppler broadening are not met.

The first theoretical analysis of the narrowing of Doppler widths through collisions in an inert gas was published by Dicke in 1953. To understand the conditions under which the Dicke effect is expected to be important, let us reexamine our assumptions in arriving at the formulas for the Doppler shifts in frequency. It was assumed that the observer and source continue indefinitely in their state of relative motion, with the observer crossing many undulations of the wave, that is, many wavelengths. To bring out the effects of not fulfilling this condition, consider the contrived example of an observer who is constrained to oscillate back and forth in

simple harmonic motion with finite amplitude. The question we have to address is: How does the magnetic field component, for example of the microwave, vary with time as seen by our peripatetic observer; from this we can arrive at the spectrum seen by him using Fourier analysis. Since the relative velocity of the observer is assumed to oscillate with a simple frequency, it follows that the Doppler effect will cause the observer to see a wave whose frequency oscillates about a fixed value. But this is nothing more than a frequency modulated (FM) wave, whose theory is familiar from its common use in radio broadcasting to provide static-free reception of high quality sound. There are three quantities aside from its amplitude that characterize a frequency modulated wave: first, its mean frequency; second, the frequency of modulation; and third, the maximum deviation of the frequency from its unmodulated value, that is, the depth of modulation. We will not reproduce here a derivation of the Fourier spectrum of such a wave, but merely state some of the salient results, some of which may not be altogether intuitive. The most striking is that the spectrum is discrete; it consists of a central line at the unmodulated frequency and *sidebands* consisting of equally spaced lines extending with diminished amplitude to infinity on both sides of the central undisplaced line, as shown in Figure 7.3.

The constant spacing of the lines is just the modulation frequency, so that each line is simply a multiple (harmonic) of the modulation frequency away from the central line. It might be thought that since the frequency “passes” through all values between the limits of modulation, that therefore the spectrum ought to contain all these frequencies; in fact, it does not. Curiously, the sideband amplitudes are not zero even for frequencies that extend beyond the “instantaneous” values the frequency passes through as it swings between its limits. However, if the modulation is infinitely slow, then the sidebands approach each other and will finally merge

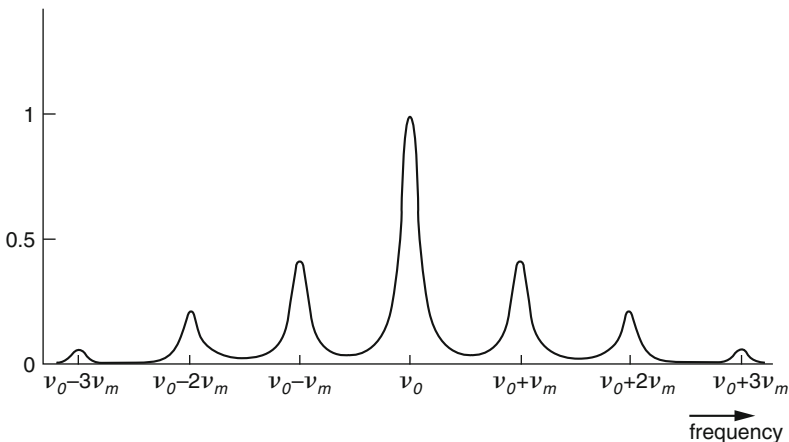


Figure 7.3 The Fourier spectrum of a frequency modulated wave

into a continuum. The amplitude distribution of this continuous spectrum reflects the relative amount of time the frequency spends at different values between the modulation limits.

The way that the amplitudes of the sidebands fall away as we go away from the central line depends on what is called the *modulation index*, which is defined as the ratio of the maximum frequency deviation to the modulation frequency. If the deviation is small in relation to the modulation frequency, that is, if the modulation index is small, then the sidebands will be weak and the central line will predominate.

Let us then compute the modulation index for our oscillating observer. From the Doppler formula, the maximum deviation is the following:

$$\Delta v = \frac{V_{\max}}{c} v_0 = \frac{2\pi v_m a}{c} v_0, \quad 7.6$$

where  $v_m$  is the frequency of the observer's to-and-fro motion, and  $a$  is his maximum distance traveled. It follows that the modulation index, which by definition is  $\Delta v/v_m$ , is given by the following:

$$\frac{\Delta v}{v_m} = \frac{2\pi a}{c} v_0 = 2\pi \frac{a}{\lambda_0}, \quad 7.7$$

where  $\lambda_0$  is the wavelength of the unmodulated wave. This last result contains the essential key to understanding the narrowing of the Doppler effect through collisions, because it tells us that as long as the observer, that is, the atom under study, moves only distances that are small compared to the wavelength, the modulation index will be small, and it will see mainly the undisplaced central frequency, with weak sidebands having an amplitude distribution and spacing determined by the parameters of its particular motion.

Quantitatively, the amplitude of the sideband at the frequency ( $v \pm nv_m$ ) is proportional to  $J_n(2\pi a/\lambda_0)$ , where as usual,  $J_n$  represents a Bessel function of order  $n$ . If the particle is constrained to oscillate with an amplitude below one wavelength, that is, if  $a/\lambda_0 < 1$ , then all the amplitudes rapidly approach zero for increasing  $n$  above zero, as can be seen from Figure 7.4. In this case the power resides principally in the undisplaced center frequency, which is itself free of the (first-order) Doppler effect. Although following Dicke, we chose a very special kind of confinement for our observer in the cause of mathematical lucidity, he went on to show that under broad conditions, a rigorous quantum treatment leads to essentially the same qualitative result; namely, whatever the detailed motion of the observer, as long as the motion does not continue uninterrupted for distances much greater than the wavelength, the Doppler spectrum has a sharp central line superimposed on a base that reflects the detailed motion of the observer. In the case of a Rb atom diffusing through a noble gas buffer, a given atom makes frequent random collisions with the gas atoms, collisions that are far more effective in deflecting a Rb atom in its path than in disturbing its internal quantum states. As a consequence, the atom executes a 3-dimensional "random walk" with a net average progress in any direction a slow function of time, a form of statistical confinement, we might say.



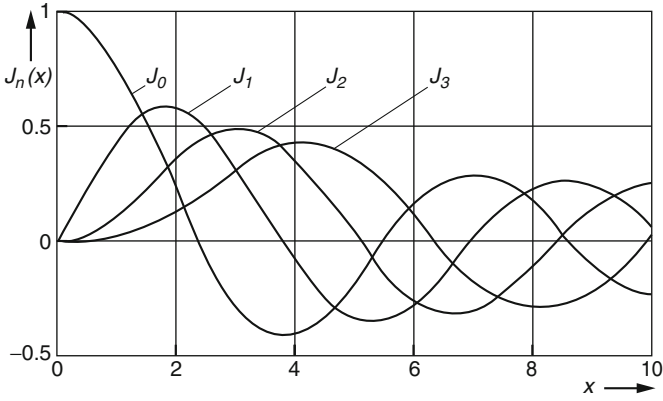


Figure 7.4 The Bessel function  $J_n(x)$  for  $n = 0, 1, 2, 3$

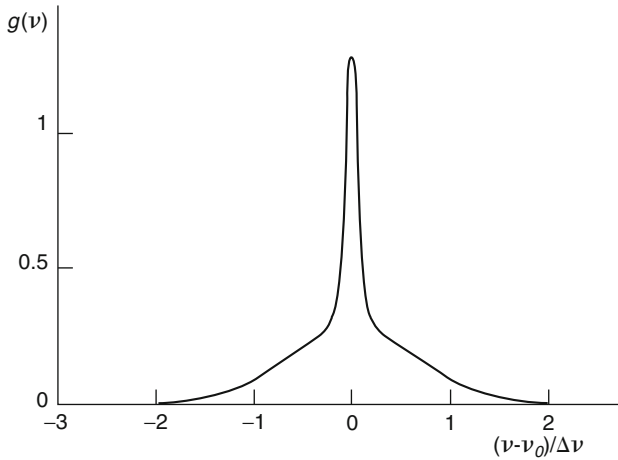


Figure 7.5 The Dicke effect; resonance line shape of an atom diffusing in a buffer gas

Figure 7.5 shows the average spectrum seen by particles of a gas in thermal equilibrium irradiated by a wave of a single frequency, whose spectrum seen by a stationary particle would be just the single central line. The base of the line has the shape expected of particles freely crossing many wavelengths of the wave, that is, the “normal” Doppler line shape. This Doppler base broadens out with increase in temperature, since the thermal velocities of the particles increase, but the central line remains unchanged.

## 7.3 Relativistic Effects

### 7.3.1 Einstein's Special Theory

A fundamental source of frequency broadening and shift in the observed resonance of an atomic system arises from the state of relative motion of the atoms and observer, a subject that underwent a revolution at the beginning of the 20<sup>th</sup> century. The origins of the radical theory published by A. Einstein in 1905 are found in the attempt to reconcile the way the laws of classical mechanics and electromagnetism are “seen” by observers in different states of motion. The equations of the classical theory of electromagnetism, the beautiful theory of Maxwell, are spectacularly successful in unifying the fields of optics, electricity, and magnetism and are one of the great triumphs of the 19<sup>th</sup> century. Unfortunately, under the classical coordinate transformation ( $x \rightarrow x + v_x t$ , etc.) corresponding to going from the coordinate axes of one observer to another in relative motion, they do not retain the same *form*. This would imply that the state of motion of different observers can be inferred by them by the way they see the fundamental laws of nature operate. This would in turn imply, for example, that a particular observer could be singled out as being “at absolute rest,” a possibility whose denial defines the *principle of relativity*. Now, the equations of classical mechanics (Newton's laws of motion), on the other hand can easily be shown to preserve their form under such a transformation of coordinates. Faith in Newtonian mechanics ran so deep that at first it was assumed that either Maxwell's theory was at fault or that for electromagnetic phenomena perhaps not all observers *are* equal; perhaps there *is* a special frame of reference. In fact, it had long been thought that light consists of waves in an all-pervading medium called the *ether*. If so, then for example, since the earth is in constant motion, presumably there should be experienced on the earth's surface an *ether drift*. Such a drift would cause light waves to appear to travel at different speeds depending the direction of propagation, just as the velocity of waves on a river relative to the shore would depend on their direction with respect to the flow. It was to test whether there was any detectable ether drift that the famous Michelson–Morley experiment was designed to do; none was found. Efforts to modify Maxwell's theory to explain this result were overtaken by a radical approach sought by Einstein to modify the coordinate transformations themselves. This was prompted by the work of Minkowski and Lorentz, who found and interpreted transformation equations (now known as the *Lorentz transformation*) under which Maxwell's equations do keep their mathematical form. We owe it to Minkowski for the interpretation of this transformation as an angular shift in the orientation of coordinate axes in four-dimensional space. Einstein's contribution was to take the Lorentz transformation as the correct one, and to modify Newton's equations of motion to preserve their form under *this* transformation. The ramifications of this theory go to all our fundamental concepts of space, time, energy, mass, etc. For us the most relevant result is the transformation of the time variable  $t$ . If one coordinate system has a constant velocity  $V$  along the

$x$ -axis of another system, the space and time coordinates in the two systems are related through the *Lorentz transformation* as follows:

$$x' = \frac{x - Vt}{\sqrt{1 - V^2/c^2}}, \quad y' = y, \quad z' = z, \quad t' = \frac{t - Vx/c^2}{\sqrt{1 - V^2/c^2}}. \quad 7.8$$

This shows explicitly through the presence of  $\sqrt{1 - V^2/c^2}$  in the denominators the physically radical departure from classical physics (and common experience) that the time scale itself varies according to the state of motion of the observer: Clocks will literally run at different rates! The clock reading  $t'$  will be ahead of the clock reading  $t$  in the system in which the spatial coordinate  $x$  is fixed. The latter clock therefore runs slower; hence the effect is called *time dilation*. It would not be in keeping with the spirit of the theory of relativity to say that the observed resonance frequency of a moving atom “only appears” to be lower; we must accept the fact that the time scale itself is not absolute, and a clock or atomic oscillation that defines time in a coordinate frame moving with respect to the observer simply runs slower. This radical break with the classical concept of time was not accepted lightly; it naturally stimulated strenuous efforts in the early establishment of the theory to find direct experimental evidence in the laboratory to support it.

Since the velocity of light is so large ( $2.99797 \times 10^8$  meters/sec) compared to velocities ordinarily encountered in the laboratory, the detection, let alone the measurement, of the dilation of the time scale is very difficult. For all ordinary velocities,  $V/c \ll 1$ , and the departure from the classical  $t' = t$  is extremely small; it is crucial that this be so, of course, since we know that Newtonian mechanics cannot be far from the truth. Nevertheless, the Lorentz transformation does represent a radical break from the classical concepts of space and time, but by now it has become such an integral part of modern physical theory, which has been validated experimentally at so many points, that the invariance of the velocity of light has been taken as a matter of definition: The standard meter is now defined as the distance traveled by light *in vacuo* in a certain (very small) fraction of a standard second. It is no longer in principle meaningful to measure the velocity of light, except as a determination of the meter. In spite of the fact that relativistic effects are extremely small, except for extreme velocities, in the case of atomic clocks, the precision has reached such a level that corrections for such effects are not negligible.

In the early years of the theory when the ramifications of it were being thought through, considerable debate centered on what became a famous “paradox”: the so-called *Twin Paradox* (See Figure 7.6). This “paradox,” which has long since been resolved, is the following: Imagine that identical twins decide that one of them will “slip the surly bonds of Earth” and journey at high speed in a spacecraft to a distant point in space and then return to rejoin his twin brother, who has remained on Earth, many years later. If, as relativity theory predicts, the returning twin finds that his Earthbound brother has noticeably aged more than he has, we are led to what appears to be a paradox; that is, it appears we can be led to contradictory conclusions even starting from equivalent premises. (If this were actually the case, then of course it would be a fatal flaw in the theory.) Thus it might be argued that from

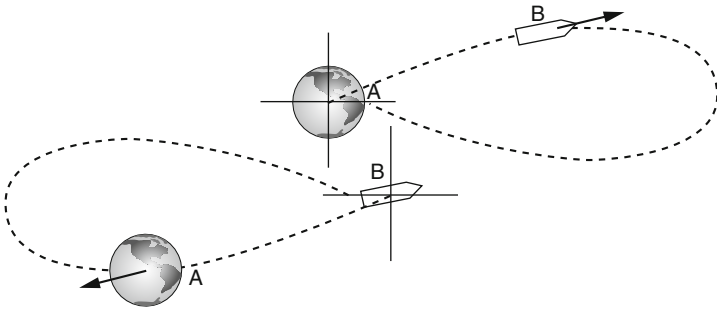


Figure 7.6 The “Clock Paradox”: the views of twins A and B

the point of view of the astronaut-twin, the Earthbound twin recedes at high speed and then returns along a trajectory that is the astronaut’s trajectory inverted with respect to their common starting point. The apparent symmetry between the trajectories as seen by the two twins would seem to predict that the astronaut would find that his Earthbound twin had aged less than he! This contradicts the earlier conclusion. If the symmetry assumed between the experiences of the two twins really exists, then there is only one logical conclusion: The twins must have aged precisely the same amount when they are reunited. This conclusion would, however, contradict a fundamental logical consequence of the underlying postulates of the theory of relativity. The argument has been made successfully, however, that the circumstances of the two twins are not symmetrical: One twin actually has to fire up his rocket engines, while the other does not, and this, after protracted analysis and debate, finally was accepted as providing the basis for resolving the “paradox.”

### 7.3.2 The Relativistic Doppler Effect

In the context of atomic resonance standards, even at relatively low atomic velocities an important correction to the resonance frequency is the *relativistic* Doppler effect, by which is meant the second-order term in an expansion of the following relativistically correct Doppler formula in powers of  $V/c$ .

$$\omega' = \frac{1 - \frac{V}{c} \cos \theta}{\sqrt{1 - \frac{V^2}{c^2}}} \omega. \quad 7.9$$

Since we are concerned only with cases in which  $V/c \ll 1$ , we can expand in powers of  $V/c$  retaining only the second-order term, the so-called “relativistic Doppler effect”:

$$\omega' = \omega \left( 1 - \frac{V}{c} \cos \theta + \frac{1}{2} \frac{V^2}{c^2} + \dots \right). \quad 7.10$$

There was intense interest during the early establishment of the theory in putting this result to the test in the laboratory. The most convincing early experiments were

those of Ives, published in 1938. The success of these experiments was largely due to the method developed of bringing out any second-order departure from the ever-present (even classically) linear Doppler effect. This he did by observing a particular line in the spectrum of light emitted by high-speed hydrogen atoms in such a way that he could simultaneously register on a photographic plate the spectrum as seen directly from the atoms and as reflected by a plane mirror to effectively reverse the observed velocity of the atoms. On the same photographic plate the spectrum of slow hydrogen atoms was also registered, providing a fiducial wavelength to compare with the two Doppler-shifted spectral lines on either side of it. Contrary to classical expectations, which are that the Doppler shift simply reverses sign with the velocity and that the two lines from the fast atoms must therefore be symmetrically situated about the center line, he found that the Doppler-shifted lines are both displaced slightly towards the red (lower frequencies) relative to the unshifted line.

### 7.3.3 Gravitational Red Shift: The Pound–Rebka Experiment

Einstein's *General Theory of Relativity* predicts that in a static gravitational field such as that of the earth (if we neglect its relatively slow rotation) the specific *proper* time scale that attaches to a particular point in the field differs from the coordinate time scale, which belongs to a general frame of reference defined far from the field region. This means that two *identical* oscillators placed at points in a gravitational field that differ in the value of the gravitational potential  $\Phi$  will oscillate at different frequencies. To a first approximation, the theory predicts a difference in frequency given as follows:

$$\nu_1 - \nu_2 = \frac{(\Phi_1 - \Phi_2)}{c^2} \nu_2. \quad 7.11$$

Thus if one oscillator is placed at height  $L$  above another oscillator at the surface of the earth, we should expect a difference in frequency between them amounting approximately to

$$\nu_1 - \nu_2 = \frac{gL}{c^2} \nu_2; \quad (L \ll R_E). \quad 7.12$$

where  $g$  is the acceleration of gravity at the surface of the earth, and  $R_E$  its radius. The gravitational potential is negative in the neighborhood of a gravitational mass; the proper frequency of an oscillator near such a mass is lower than at a point infinitely far from it, hence the name *gravitational red shift*. The effect is small: even for the gravitational field of the sun, the fractional shift is only about  $2 \times 10^{-6}$ . To observe shifts in the lines of the solar spectrum is unfortunately less than convincing as a test of the theory, since there are known to exist severe differences of environment between the sun and earth, in addition to the gravitational field.

In the earth's gravitational field the effect is far from insignificant when comparing clock rates aboard high-orbit satellites with ground-based stations. For example, a clock aboard a satellite in a circular orbit of radius (say) 26,000 km,

typical of the GPS satellites, would run *faster* than a ground-based clock by the fractional amount given by the following:

$$\frac{v - v_0}{v_0} = \frac{GM_E}{c^2 R}, \quad 7.13$$

where  $G$  is the gravitational constant,  $M_E$  is the mass of the earth, and  $R$  is the radius of the satellite orbit. If we substitute numerical values, we find a fractional difference of  $1.7 \times 10^{-10}$ , a large number in the context of atomic time keeping!

For a terrestrial experiment the effect is, of course, very much smaller; for  $L = 30$  m we get a fractional difference of only  $3 \times 10^{-15}$ ! Fortunately, an experimental breakthrough in  $\gamma$ -ray spectroscopy in 1958 by Mössbauer made it possible to reach the incredibly high level of spectral resolution that a terrestrial red shift experiment requires. It is only in recent years that atomic clocks have reached comparable resolution. In the  $\gamma$ -ray region of the spectrum there are nuclear transitions with long radiative lifetimes and narrow natural line widths. However, the photon momentum is sufficiently high that when it is emitted by a nucleus, part of the transition energy is taken up by the recoil of the nucleus. In fact, the consequent displacement in the photon energy makes it no longer able to be absorbed efficiently by another identical nucleus at rest. What Mössbauer discovered was that if the nuclei are constrained within a suitable crystal lattice in the right temperature range, the recoil is effectively taken up by the entire mass of the crystal, leading to essentially *recoilless* emission and absorption, and hence a degree of spectral resolution unheard of at the time. The  $\gamma$ -ray spectral resolution is so high that even the Doppler effect caused by a slow linear movement is sufficient to provide a sufficient sweep of its energy.

Pound and Rebka, in a classic experiment, exploited this new development in a terrestrial experiment to measure any frequency shift that might be exhibited by photons emitted at one point in a gravitational field and absorbed at another by identical nuclei. Initially, it proved difficult to reach conclusive results; little progress was possible until it was realized that temperature differences between the emitter and absorber can lead to significant second-order Doppler shifts, and that the temperatures must be stabilized and taken into account. Fluctuations as small as  $\pm 1^\circ\text{C}$  were computed to cause frequency shifts nearly as large as the gravitational shift. They used the Mössbauer effect in the resonance absorption of 14.4 keV  $\gamma$ -rays of  $\text{Fe}^{57}$ ; the sensitivity of their apparatus allowed them to observe the effect by placing the  $\text{Fe}^{57}$  source in the tower of the physics laboratory at Harvard University at a height of only about 20 m above the resonant absorber.

As with any other experiment designed to test a theory, the salient questions are: first, just how crucial is a positive result to the theory, and second, to what extent does a positive result preclude other theories? It is the uncertainty in answering the latter question that dictates a certain restraint in stating what the experiment actually proves. This is far from a simple matter: A careful analysis is required to strip away all the assumptions that are not in fact proved by the test. Of the elegant mathematical structure that is Einstein's theory of general relativity, this

particular test probably only proves that the *equivalence principle*, which states, in effect, that a gravitational field is indistinguishable from an appropriate coordinate transformation, is valid for photons. Falling under gravity is indistinguishable from motion with respect to a frame of reference accelerating upwards. Hence the photons develop a Doppler shift with respect to the accelerating frame of reference given by  $(V/c)v$ , where  $V = gL/c$ , and we have the same formula as before.

### 7.3.4 The Sagnac Effect

We should mention at this point an interesting relativistic effect on time measurement associated with the rotation of the earth. Since the coordinate system fixed in the earth is noninertial because its rotation with respect to “the fixed stars” constitutes an accelerated motion (not of speed, but direction), again the theory of *general relativity* is involved. According to the theory, if we imagine we have two identical, precise clocks at some point on the earth’s equator, and one remains *fixed* while the other is taken even *slowly* (with respect to the earth) along the equator all the way around until it reaches its starting point, then the times indicated on the two clocks will not agree. The difference  $\Delta\tau$  can be shown to be given by the following:

$$\Delta\tau = \pm \frac{2\Omega}{c^2} S, \tag{7.14}$$

where  $\Omega$  is the angular velocity of the earth ( $7.3 \times 10^{-5}$  rad/sec) and  $S$  is the area ( $\pi R_E^2 = 1.3 \times 10^{14} \text{m}^2$ ) enclosed by the path of the moving clock. The formula yields a significant time difference of about  $\pm 1/5$  microsecond, depending on the direction the moving clock takes around the equator. This effect is often referred to as the *Sagnac effect*, after the Frenchman G. Sagnac, who in 1911 detected by optical interference a difference in the time taken by a light wave to complete a round trip in the two possible directions around the mirror arrangement shown in Figure 7.7, when the latter is made to rotate.

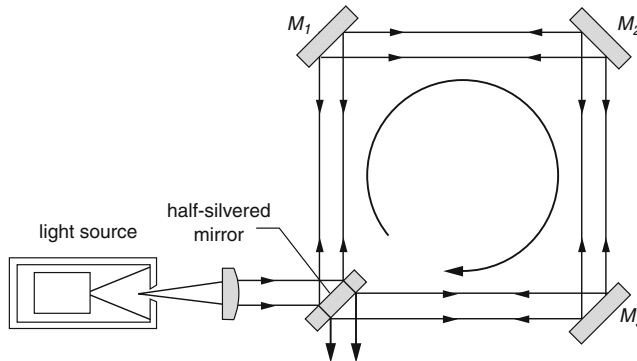


Figure 7.7 The mirror arrangement used by Sagnac to study the propagation of light in a rotating system

Since the velocity of light in free space is constant, this is usually interpreted as a difference in the effective optical path length due to the finite movement of the mirrors in the time it takes the light wave to go from one mirror to the next. In the reference frame of the mirrors themselves, however, it must be interpreted as *time itself* advancing at a changing rate as we go around from one mirror to the next.

## 7.4 Conclusion

There are a number of other mechanisms that can affect the spectral profile of an atomic resonance in the microwave and optical regions of the spectrum, but none as universal as the relativistic Doppler and gravitation red shifts. The atomic resonance used as standard in each of the different types of atomic clocks will have its own hierarchy of important factors affecting its width and position on the frequency scale. Thus we shall see in a later chapter that for the rubidium standard it is collisions with the buffer gas atoms and *light shifts* produced by the light used to observe the resonance that are dominant; for the hydrogen maser it is the *wall shift*, and so on. We will discuss these and other cases at greater length in the chapters dealing with specific standards. There is one subtle effect deserves mentioning here, though extremely small it may nevertheless become significant in the future in ultrahigh resolution optical clocks. It is the frequency shift due to the *recoil* of an atom or ion as it absorbs or emits a resonant photon. As we have already mentioned in connection with the *Mössbauer effect* and will again encounter when we come to discuss the *laser cooling* of atoms, photons carry momentum, and to conserve linear momentum the atom must recoil. Since the momentum of a single optical photon is exceedingly small, the kinetic energy an atom gains through the recoil is also minuscule and is expected to be near the outer limits of what is observable.