8.421 AMO I Lecture Notes

Contents

Preface

The original incarnation of these notes was developed to accompany the lectures in the MIT graduate courses in atomic physics. AMO I was created in the late 1960s as a one-term introductory course to prepare graduate students for research in atomic physics in the Physics department. Over the years Dan Kleppner and David Pritchard changed the contents of the course to reflect new directions of research, though the basic concepts remained as a constant thread. With the growth of interest in atom cooling and quantum gases, a second one-term course, AMO II, was designed by Wolfgang Ketterle in the late 1990s and presented with AMO I in alternating years. We still teach AMO I in the traditional way. These lecture notes combine the (g)olden notes of Dan and Dave. As part of the Joint Harvard/MIT Center for Ultracold Atoms summer school in Atomic Physics in 2002, John Doyle got involved and improved the notes. They have been circulated since and at some point were put into the form of an AMO Wiki. At this moment in time, I'd like to resurrect them in their traditional paper form, and only carefully add topics as I see fit.

Martin Zwierlein,

Spring 2022

Chapter 1
The Two-State System: Resonance

1.1 Introduction

The cornerstone of major areas of contemporary Atomic, Molecular and Optical Physics (AMO Physics) is the study of atomic and molecular systems through their resonant interaction with applied oscillating electromagnetic fields. The thrust of these studies has evolved continuously since Rabi performed the first resonance experiments in 1938. In the decade following World War II the edifice of quantum electrodynamics was constructed largely in response to resonance measurements of unprecedented accuracy on the properties of the electron and the fine and hyperfine structure of simple atoms. At the same time, nuclear magnetic resonance and electron paramagnetic resonance were developed and quickly became essential research tools for chemists and solid state physicists. Molecular beam magnetic and electric resonance studies yielded a wealth of information on the properties of nuclei and molecules, and provided invaluable data for the nuclear physicist and physical chemist. With the advent of lasers and laser spectroscopy these studies evolved into the creation of new species, such as Rydberg atoms, to studies of matter in ultra intense fields, to fundamental studies in the symmetries of physics, to new types of metrology. With the advent of laser cooling and trapping, these techniques led to the creation of novel atomic quantum fluids, from Bose-Einstein condensates to strongly interacting Fermi gases.

Resonance techniques may be used not only to learn about the structure of a system, but also to prepare it in a precisely controlled way. Because of these two facets, resonance studies have led physicists through a fundamental change in attitude - from the passive study of atoms to the active control of their internal quantum state and their interactions with the radiation field. The chief technical legacy of the early work on resonance spectroscopy is the family of lasers which have sprung up like the brooms of the sorcerer's apprentice. The scientific applications of these devices have been prodigious. They caused the resurrection of physical optics - what we now call quantum optics - and turned it into one of the liveliest fields in physics. They have had a similar impact on atomic and molecular spectroscopy. In addition, lasers have led to new families of physical studies such as single particle spectroscopy, multiphoton excitation, cavity quantum electrodynamics, and laser cooling and trapping. This chapter is about the interactions of a two-state system with a sinusoidally oscillating field whose frequency is close to the natural resonance frequency of the system. The term "two-level" system is sometimes used, but this is less accurate than the term two-state, because the levels could be degenerate, comprising several states. However, its misuse is so widespread that we adopt it anyway. The oscillating field will be treated classically, and the linewidth of both states will be taken as zero until near the end of the chapter where relaxation will be treated phenomenologically. The organization of the material is historical because this

happens to be also a logical order of presentation. The classical driven oscillator is discussed first, then the magnetic resonance of a classical spin, and then a quantized spin. The density matrix is introduced last and used to treat systems with damping - this is a useful prelude to the application of resonance ideas at optical frequencies and to the many real systems which have damping.
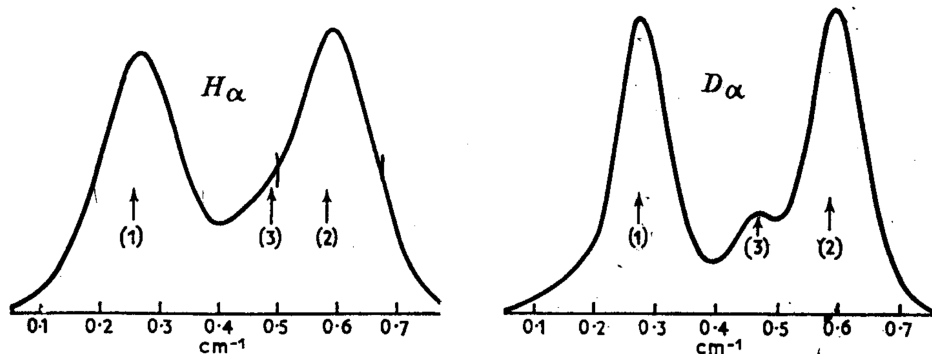
1.2 Resonance Studies and Q.E.D.

Figure 1. Spectral profile of the H_α line of atomic hydrogen by conventional absorption spectroscopy. Components 1) and 2) arise from the fine structure splitting. The possibility that a third line lies at position 3) was suggested to indicate that the Dirac theory might need to be revised. (From "The Spectrum of Atomic Hydrogen"-Advances. G.W. Series ed., World Scientific, 1988).

One characteristic of atomic resonance is that the results, if you can obtain them at all, are generally of very high accuracy, so high that the information is qualitatively different from other types. The hydrogen fine structure is a good example.

In the late 1930s there was extensive investigation of the Balmer series of hydrogen, $(n > 2 \rightarrow n = 2)$. The Dirac Theory was thought to be in good shape, but some doubts were arising. Careful study of the Balmer-alpha line $(n = 3 \rightarrow n = 2)$ showed that the line shape might not be given accurately by the Dirac Theory.

Pasternack, in 1939, suggested that the $2\,^2S_{1/2}$ and $2\,^2P_{1/2}$ states were not degenerate, but that the energy of the $2\,^2S_{1/2}$ state was greater than the Dirac value by $\sim .04\,\mathrm{cm}^{-1}$ (or, in frequency, $\sim 1200\,\mathrm{MHz}$). However, there was no rush to throw out the Dirac theory on such flimsy evidence.

In 1947, Lamb found a splitting between the $^2S_{1/2}$ and $^2P_{1/2}$ levels using a resonance method. The experiment is one of the classics of physics. Although his very first observa- tion was relatively crude, it was nevertheless accurate to one percent. He found

$$S_H = \frac{1}{h}\left[E(^2S_{1/2}) - E(^2P_{1/2})\right] = 1050(10)\,\mathrm{MHz} \qquad (1.1)$$

The inadequacy of the Dirac theory was inescapably demonstrated.

The magnetic moment of the electron offers another example. In 1925, Uhlenbeck and Goudsmit suggested that the electron has intrinsic spin angular momentum $s = 1/2$ (in units of $\hbar$) and magnetic moment

$$|\mu_e| = \frac{e\hbar}{2m} = \mu_B \tag{1.2}$$

where μ_B is the Bohr magneton (and $\mu_e = -\mu_B$ is negative). The evidence was based on studies of the multiplicity of atomic lines (in particular, the Zeeman structure). The proposal was revolutionary, but the accuracy of the prediction that $|\mu_e| = \mu_B$ was poor, essentially one significant figure. According to the Dirac theory, $|\mu_e| = \mu_B$, exactly. However, our present understanding is

$$\frac{|\mu_e|}{\mu_B} - 1 = 1.1596521884(43) \times 10^{-3} \qquad \text{(experiment, U. of Washington)} \tag{1.3}$$

This result is in good agreement with theory, the limiting factor in the comparison being possible doubts about the value of the fine structure constant.

The Lamb shift and the departure of $|\mu_e|$ from μ_B resulted in the award of the 1955 Nobel prize to Lamb and Kusch, and provided the experimental basis for the theory of quantum electrodynamics for which Feynman, Schwinger and Tomonaga received the Nobel Prize in 1965.

1.2.1   The language of resonance: a classical damped system

Because the terminology of classical resonance, as well as many of its features, are carried over into quantum mechanics, we start by reviewing an elementary resonant system. Consider a harmonic oscillator composed of a series RLC circuit. The charge obeys

$$\ddot{q} + \gamma\dot{q} + \omega_0^2 q = 0 \tag{1.4}$$

where $\gamma = R/L$, $\omega_0^2 = 1/LC$. Assuming that the system is underdamped (i.e. $\gamma^2 < 4\omega_0^2$), the solution for q is a linear combination of

$$\exp\left(-\frac{\gamma}{2}\right) \exp\left(\pm i\omega' t\right) \tag{1.5}$$

where $\omega' = \omega_0\sqrt{1 - \gamma^2/4\omega_0^2}$. If $\omega_0 \gg \gamma$, which is often the case, we have $\omega' \equiv \omega_0$. The energy in the circuit is

$$W = \frac{1}{2C}q^2 + \frac{1}{2}L\dot{q}^2 = W_0 e^{-\gamma t} \tag{1.6}$$

where $W_0 = W(t = 0)$. The decay time of the stored energy is $\tau = \frac{1}{\gamma}$. If the circuit is driven by a voltage $E_0 e^{i\omega t}$, the steady state solution is $q_0 e^{i\omega t}$ where

$$q_0 = \frac{E_0}{2\omega_0 L} \frac{1}{(\omega_0 - \omega + i\gamma/2)}. \tag{1.7}$$

(We have made the usual resonance approximation: $\omega_0^2 - \omega^2 \approx 2\omega_0(\omega_0 - \omega)$.) The average power delivered to the circuit is

$$P = \frac{1}{2}\frac{E_0^2}{R}\frac{1}{1 + \left(\frac{\omega - \omega_0}{\gamma/2}\right)^2} \tag{1.8}$$

$$x = (\omega - \omega_0)/(\gamma/2)$$
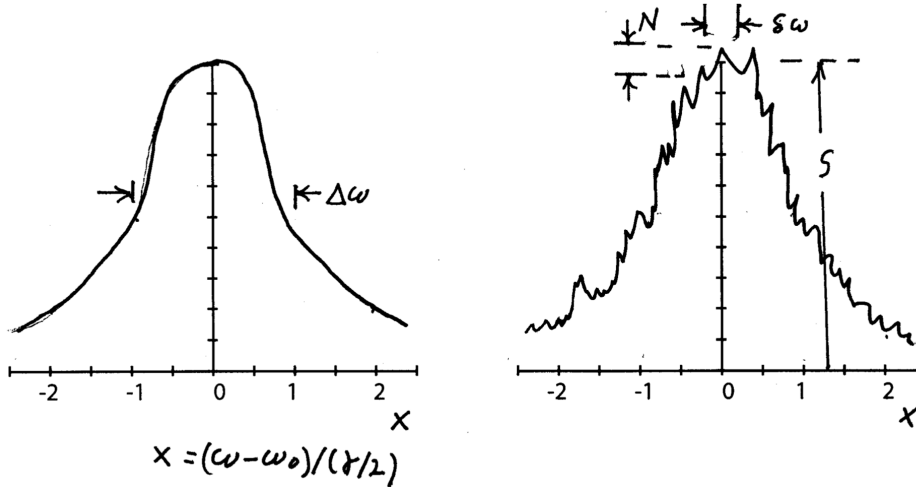
Figure 2. Sketch of a Lorentzian curve, the universal response curve for damped oscillators and for many atomic systems. The width of the curve (full width at half maximum) is $\Delta\omega = \gamma$, where γ is the decay constant. The time constant for decay is $\tau = \gamma$. In the presence of noise (right), the frequency precision with which the center can be located, $\delta\omega$, depends on the signal-to-noise ratio, S/N: $\delta\omega = \Delta\omega/(S/N)$.

The plot of P vs ω (Fig. 2) is universal resonance curve often called a "Lorentzian curve". The full width at half maximum ("FWHM") is $\Delta\omega = \gamma$. The quality factor of the oscillator is

$$Q = \frac{\omega_0}{\Delta\omega} \tag{1.9}$$

Note that the decay time of the free oscillator and the linewidth of the driven oscillator obey

$$\tau\Delta\omega = 1 \tag{1.10}$$

This can be regarded as an uncertainty relation. Assuming that energy and frequency are related by $E = \hbar\omega$ then the uncertainty in the energy is $\Delta E = \hbar\Delta\omega$ and

$$\tau\Delta E = \hbar \tag{1.11}$$

It is important to realize that the Uncertainty Principle merely characterizes the spread of individual measurements. Ultimate precision depends on the experimenter's skill: the Uncertainty Principle essentially sets the scale of difficulty for his or her efforts.

The precision of a resonance measurement is determined by how well one can "split" the resonance line. This depends on the signal to noise ratio (S/N)

(see Fig. 2). As a rule of thumb, the uncertainty $\delta\omega$ in the location of the center of the line is

$$\delta\omega = \frac{\Delta\omega}{S/N} \tag{1.12}$$

In principle, one can make $\delta\omega$ arbitrarily small by acquiring enough data to achieve the required statistical accuracy. In practice, systematic errors eventually limit the precision. Splitting a line by a factor of 10^4 is a formidable task which has only been achieved a few times, most notably in the measurement of the Lamb shift. A factor of 10^3, however, is not uncommon, and 10^2 is child's play.

1.3 Magnetic Resonance: Classical Spin in Time-Varying B-Field

1.3.1   The classical motion of spins in a static magnetic field

Note: angular momentum will always be expressed in a form such as $\hbar\boldsymbol{J}$, where the vector $\boldsymbol{J}$ is dimensionless. The interaction energy and equation of motion of a classical spin in a static magnetic field are given by

$$W = -\boldsymbol{\mu} \cdot \boldsymbol{B}, \tag{1.13}$$

$$\boldsymbol{F} = -\boldsymbol{\nabla}W = \boldsymbol{\nabla}(\boldsymbol{\mu} \cdot \boldsymbol{B}), \tag{1.14}$$

$$\text{torque} = \boldsymbol{\mu} \times \boldsymbol{B} \tag{1.15}$$

In a uniform field, $\boldsymbol{F} = 0$. The torque equation $(\mathrm{d}\hbar\boldsymbol{J}/\mathrm{d}t = \text{torque})$ gives

$$\frac{\mathrm{d}\hbar\boldsymbol{J}}{\mathrm{d}t} = \boldsymbol{\mu} \times \boldsymbol{B}. \tag{1.16}$$

Since $\boldsymbol{\mu} = \gamma\hbar\boldsymbol{J}$ (where γ is called the gyromagnetic ratio - not to be confused with the different meaning of γ in the previous section), we have

$$\frac{\mathrm{d}\boldsymbol{J}}{\mathrm{d}t} = \gamma\boldsymbol{J} \times \boldsymbol{B} = -\gamma\boldsymbol{B} \times \boldsymbol{J}. \tag{1.17}$$

To see that the motion of $\boldsymbol{J}$ is a pure precession about $\boldsymbol{B}$, imagine that $\boldsymbol{B}$ is along $\hat{\boldsymbol{z}}$ and that the spin, $\boldsymbol{J}$, is tipped at an angle θ from this axis, and then rotated at an angle $\phi(t)$ from the x-axis (i.e., θ and ϕ are the conventionally chosen angles in spherical coordinates). The torque, $-\gamma\boldsymbol{B}\times\boldsymbol{J}$, has no component along $\boldsymbol{J}$ (that is, along $\hat{\boldsymbol{r}}$), nor along $\hat{\boldsymbol{\theta}}$ (because the $\boldsymbol{J} - \boldsymbol{B}$ plane contains $\hat{\boldsymbol{\theta}}$), hence $-\gamma\boldsymbol{B} \times \boldsymbol{J} = -\gamma B|\boldsymbol{J}|\sin(\theta)\hat{\boldsymbol{\phi}}$. This implies that $\boldsymbol{J}$ maintains constant magnitude and constant tipping angle θ. Generally, for an infinitesimal change $\mathrm{d}\phi$ the component of $\mathrm{d}\boldsymbol{J}$ in the direction of $\hat{\boldsymbol{\phi}}$ is $|\boldsymbol{J}|\sin(\theta)\mathrm{d}\phi$, and so we can see that $\phi(t) = -\gamma Bt$. This solution shows that the moment precesses with angular velocity

$$\Omega_L = -\gamma B \tag{1.18}$$

where Ω_L is called the *Larmor frequency*.

For electrons, $\gamma_e = -2\pi \times 2.8\,\mathrm{MHz/G} \approx -2\mu_{\mathrm{B}}$, for protons, $\gamma_p = 2\pi \times 4.2\,\mathrm{kHz/G}$. Note that Planck's constant does not appear in the equation of motion: the motion is classical.

Note: G stands for gauss - it is part of the gaussian (cgs) system of units, and ubiquitous in atomic physics labs, as it is a much more typical laboratory field than the SI unit for magnetic field, 1 tesla. $10^4\,\mathrm{G} = 1\,\mathrm{T}$.

1.3.2   Rotating coordinate transformation

A second way to find the motion is to look at the problem in a rotating coordinate system. If some vector $\boldsymbol{A}$ rotates with angular velocity $\boldsymbol{\Omega}$, then

$$\frac{\mathrm{d}\boldsymbol{A}}{\mathrm{d}t} = \boldsymbol{\Omega} \times \boldsymbol{A}. \tag{1.19}$$

If the rate of change of the vector in a system rotating at $\boldsymbol{\Omega}$ is $(\mathrm{d}\boldsymbol{A}/\mathrm{d}t)_{\mathrm{rot}}$, then the rate of change in an inertial system is the motion *in* plus the motion *of* the rotating coordinate system.

$$\left(\frac{\mathrm{d}\boldsymbol{A}}{\mathrm{d}t}\right)_{\mathrm{inert}} = \left(\frac{\mathrm{d}\boldsymbol{A}}{\mathrm{d}t}\right)_{\mathrm{rot}} + \boldsymbol{\Omega} \times \boldsymbol{A}. \tag{1.20}$$

The operator prescription for transforming from an inertial to a rotating system is thus

$$\left(\frac{\mathrm{d}\cdot}{\mathrm{d}t}\right)_{\mathrm{rot}} = \left(\frac{\mathrm{d}\cdot}{\mathrm{d}t}\right)_{\mathrm{inert}} - \boldsymbol{\Omega} \times \cdot \tag{1.21}$$

Applying this to Eq. 1.17 gives

$$\left(\frac{\mathrm{d}\boldsymbol{J}}{\mathrm{d}t}\right)_{\mathrm{rot}} = \gamma\boldsymbol{J} \times \boldsymbol{B} - \boldsymbol{\Omega} \times \boldsymbol{J} = \gamma\boldsymbol{J} \times (\boldsymbol{B} + \boldsymbol{\Omega}/\gamma). \tag{1.22}$$

If we let

$$\boldsymbol{B}_{\mathrm{eff}} = \boldsymbol{B} + \boldsymbol{\Omega}/\gamma, \tag{1.23}$$

Eq. 1.22 becomes

$$\left(\frac{\mathrm{d}\boldsymbol{J}}{\mathrm{d}t}\right)_{\mathrm{rot}} = \gamma\boldsymbol{J} \times \boldsymbol{B}_{\mathrm{eff}}. \tag{1.24}$$

If $\boldsymbol{B}_{\mathrm{eff}} = 0$, $\boldsymbol{J}$ is constant in the rotating system. The condition for this is

$$\boldsymbol{\Omega} = -\gamma\boldsymbol{B} \tag{1.25}$$

as we have previously found in Eq. 1.18.

1.3.3   Larmor's theorem

Treating the effects of a magnetic field on a magnetic moment by transforming to a rotating coordinate system is closely related to Larmor's theorem, which asserts that the effect of a magnetic field on a free charge can be eliminated by a suitable rotating coordinate transformation.

Consider the motion of a particle of mass m, charge q, under the influence

of an applied force $\boldsymbol{F}_0$ and the Lorentz force due to a static field $\boldsymbol{B}$:

$$\boldsymbol{F} = \boldsymbol{F}_0 + q\boldsymbol{v} \times \boldsymbol{B}. \tag{1.26}$$

Now consider the motion in a rotating coordinate system. By applying Eq. 1.21 twice to $\boldsymbol{r}$, we have

$$\ddot{\boldsymbol{r}}_{\text{rot}} = \ddot{\boldsymbol{r}}_{\text{inert}} - 2\boldsymbol{\Omega} \times \boldsymbol{v}_{\text{rot}} - \boldsymbol{\Omega} \times (\boldsymbol{\Omega} \times \boldsymbol{r}). \tag{1.27}$$

$$\boldsymbol{F}_{\text{rot}} = \boldsymbol{F}_{\text{inert}} - 2m(\boldsymbol{\Omega} \times \boldsymbol{v}_{\text{rot}}) - m\boldsymbol{\Omega} \times (\boldsymbol{\Omega} \times \boldsymbol{r}), \tag{1.28}$$

where $\boldsymbol{F}_{\text{rot}}$ is the apparent force in the rotating system, and $\boldsymbol{F}_{\text{inert}}$ is the true or inertial force. Substituting Eq. 1.26 gives

$$\boldsymbol{F}_{\text{rot}} = \boldsymbol{F}_{0,\text{inert}} + q\boldsymbol{v} \times \boldsymbol{B} + 2m\boldsymbol{v} \times \boldsymbol{\Omega} - m\boldsymbol{\Omega} \times (\boldsymbol{\Omega} \times \boldsymbol{r}). \tag{1.29}$$

If we choose $\boldsymbol{\Omega} = -(q/2m)\boldsymbol{B}$, and take $\boldsymbol{B} = \hat{\boldsymbol{z}}B$, we have

$$\boldsymbol{F}_{\text{rot}} = \boldsymbol{F}_{0,\text{inert}} - m \left(\frac{qB}{2m} \right)^2 \hat{\boldsymbol{z}} \times (\hat{\boldsymbol{z}} \times \boldsymbol{r}). \tag{1.30}$$

The last term is usually small. If we drop it we have

$$\boldsymbol{F}_{\text{rot}} = \boldsymbol{F}_{0,\text{inert}} \tag{1.31}$$

The effect of the magnetic field is removed by going into a system rotating at the Larmor frequency $qB/2m$.

Although Larmor's theorem is suggestive of the rotating co-ordinate transformation, Eq. 1.22, it is important to realize that the two transformations, though identical in form, apply to fundamentally different systems. A magnetic moment is not necessarily charged- for example a neutral atom can have a net magnetic moment, and the neutron possesses a magnetic moment in spite of being neutral - and it experiences no net force in a uniform magnetic field. Furthermore, the rotating co-ordinate transformation is exact for a mag- netic moment, whereas Larmor's theorem for the motion of a charged particle is only valid when the $\propto B^2$ term is neglected.

1.3.4   Motion in a Rotating Magnetic Field

Exact resonance: Consider a moment $\boldsymbol{\mu}$ precessing about a static field $\boldsymbol{B}_0$, which we take to lie along the z axis. Its motion might be described by

$$\mu_z = \mu \, \cos\theta, \quad \mu_x = \mu \, \sin\theta \, \cos\omega_0 t, \quad \mu_y = -\mu \, \sin\theta \, \sin\omega_0 t \tag{1.32}$$

where ω_0 is the Larmor frequency, and θ is the angle the moment makes with $\boldsymbol{B}_o$.

Now suppose we introduce a magnetic field $\boldsymbol{B}_1$ which rotates in the x-y plane at the Larmor frequency $\omega_0 = -\gamma B_0$. The magnetic field is

$$\boldsymbol{B}(t) = B_1(\hat{\boldsymbol{x}} \, \cos\omega_0 t - \hat{\boldsymbol{y}} \, \sin\omega_0 t) \, + \, B_0 \, \hat{\boldsymbol{z}}. \tag{1.33}$$
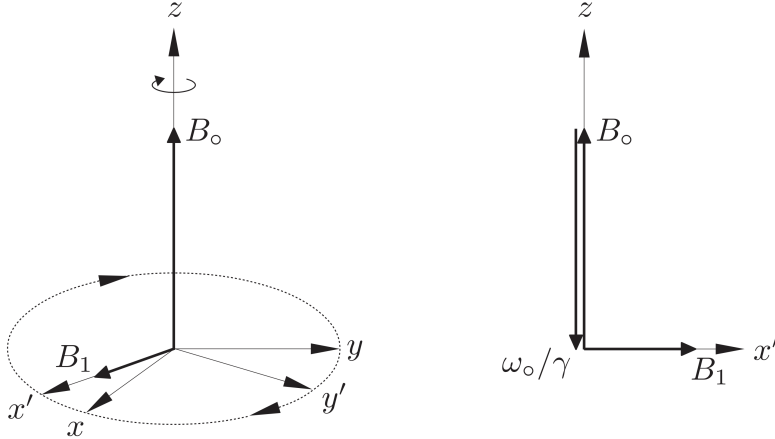
Figure 3. Rotating coordinate transformation to the primed system that is co-rotating with B_1 at ω, with x' chosen to lie along B_1. For the exact resonance case of $\omega = \omega_0$ considered here, the effective field around which the moment precesses is equal to B_1.

The problem is to find the motion of $\boldsymbol{\mu}$. The solution is simple in a rotating coordinate system (see Fig. 3). Let system $(\hat{\boldsymbol{x}}', \hat{\boldsymbol{y}}', \hat{\boldsymbol{z}}' = \hat{\boldsymbol{z}})$ precess around the z-axis at rate $-\omega_0$. In this system the field $\boldsymbol{B}_1$ is stationary (and $\hat{\boldsymbol{x}}'$ is chosen to lie along $\boldsymbol{B}_1$), and we have

$$\boldsymbol{B}_{\text{eff}}(t) = \boldsymbol{B}(t) - (\omega_0/\gamma)\ \hat{\boldsymbol{z}} = B_1\hat{\boldsymbol{x}}' + (B_0 - \omega_0/\gamma)\hat{\boldsymbol{z}} = B_1\hat{\boldsymbol{x}}'. \qquad (1.34)$$

The effective field is static and has the value of B_1. The moment precesses about the field at rate

$$\omega_R = \gamma B_1, \qquad (1.35)$$

often called the *Rabi* frequency, in honor of Rabi's invention of the resonance technique.

If the moment initially lies along the z axis, then its tip traces a circle in the $\hat{\boldsymbol{y}}' - \hat{\boldsymbol{z}}$ plane. At time t it has precessed through an angle $\phi = \omega_R t$. The moment's z-component is given by

$$\mu_z(t) = \mu\ \cos\omega_R t. \qquad (1.36)$$

At time $T = \pi/\omega_R$, the moment points along the negative z-axis: it has "turned over".

Off-resonant behavior: Now suppose that the field B_1 rotates at frequency $\omega \neq \omega_0$. In a coordinate frame rotating with B_1 the effective field is

$$\boldsymbol{B}_{\text{eff}} = B_1\hat{\boldsymbol{x}}' + (B_0 - \omega/\gamma)\hat{\boldsymbol{z}}. \qquad (1.37)$$

The effective field lies at angle θ with the z-axis, as shown in Fig. 4. The field is static, and the moment precesses about it at rate (called the *effective*

Rabi frequency)

$$\Omega_R = \gamma B_{\text{eff}} = \gamma\sqrt{(B_0 - \omega/\gamma)^2 + B_1^2} = \sqrt{(\omega_0 - \omega)^2 + \omega_R^2} \qquad (1.38)$$

where $\omega_0 = \gamma B_0, \omega_R = \gamma B_1$, as before.

Assume that $\boldsymbol{\mu}$ points initially along the +z-axis. Finding $\mu_z(t)$ is a straightforward problem in geometry. The moment precesses about B_{eff} at rate Ω_R, sweeping a circle as shown. The radius of the circle is $\mu \sin\theta$, where $\sin\theta = B_1/\sqrt{(B_0 - \omega/\gamma)^2 + B_1^2} = \omega_R/\sqrt{(\omega - \omega_0)^2 + \omega_R^2}$. In time t the tip sweeps through angle $\phi = \Omega_R t$. The z-component of the moment is $\mu_z(t) = \mu\cos\alpha$ where α is the angle between the moment and the z-axis after it has precessed through angle ϕ. As the drawing shows, $\cos\alpha$ is found from $A^2 = 2\mu^2(1 - \cos\alpha)$. Since $A = 2\mu \ \sin\theta \sin(\Omega_R t/2)$, we have $4\mu^2 \ \sin^2\theta \sin^2(\Omega_R t/2) = 2\mu^2(1 - \cos\alpha)$ and

$$\mu_z(t) = \mu\cos\alpha = \mu(1 - 2\sin^2\theta \sin^2\Omega_R t/2)$$

$$= \mu\left[1 - 2\frac{\omega_R^2}{(\omega - \omega_0)^2 + \omega_R^2}\sin^2\frac{1}{2}\sqrt{(\omega - \omega_0)^2 + \Omega_R t}\right]$$

$$\qquad (1.39)$$

$$= \mu\left[1 - 2(\omega_R/\Omega_R)^2 \sin^2(\Omega_R t/2)\right] \qquad (1.40)$$

The z-component of $\boldsymbol{\mu}$ oscillates in time, but unless $\omega = \omega_0$, the moment never completely inverts. The rate of oscillation depends on the magnitude of the rotating field; the amplitude of oscillation depends on the frequency difference, $\omega - \omega_0$, relative to ω_R. The quantum mechanical result will turn out to be identical.

1.3.5   Rapid Adiabatic Passage: Landau-Zener Crossing

Adiabatic rapid passage is a technique for inverting a spin population by sweeping the system through resonance. Either the frequency of the oscillating field or the transition frequency (e.g., by changing the applied magnetic field) is slowly varied. The principle is qualitatively simple in the rotating coordinate system.
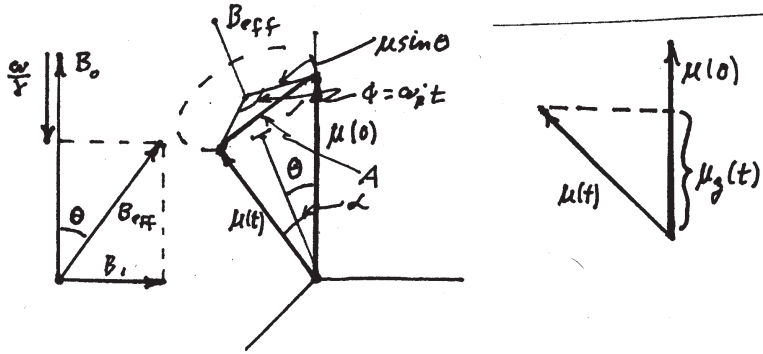

Figure 4. Constructions for viewing spin motion in a coordinate system rotating below the resonance frequency.
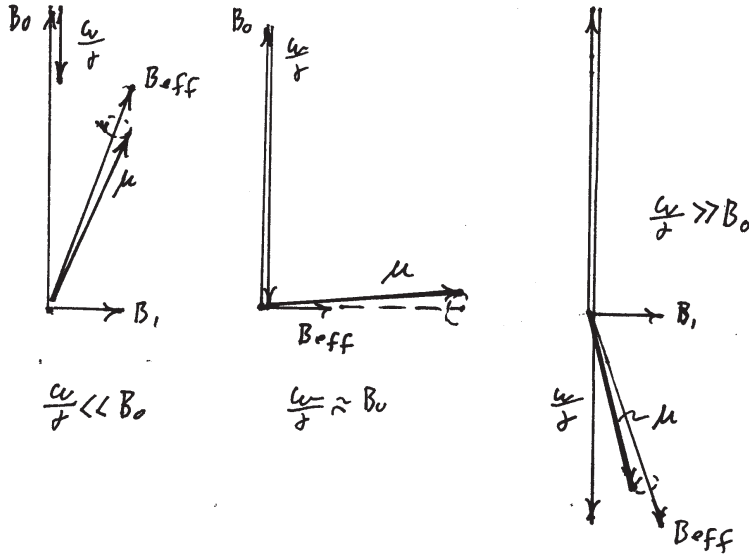
Figure 5. Motion of precessing moment in a rotating coordinate system whose frequency is swept from below resonance to above resonance.

The problem can also be solved analytically. In this section we give the qualitative argument and then, after having treated the quantum spin $1/2$, we will present the analytic quantum result. The solution is of quite general interest because this physical situation arises frequently, for example in inelastic scattering, where it is called a curve crossing.

Consider a moment $\boldsymbol{\mu}$ in the presence of a static magnetic field $\boldsymbol{B}_0$ and a perpendicular field $\boldsymbol{B}_1$ rotating at some frequency ω, originally far from resonance: $\omega \ll \gamma B_0$. In the frame rotating with $\boldsymbol{B}_1$ the magnetic moment "sees" an effective field $\boldsymbol{B}_{\text{eff}}$ whose direction is nearly parallel to $\boldsymbol{B}_0$. A magnetic moment $\boldsymbol{\mu}$ initially parallel to $\boldsymbol{B}_0$ precess around $\boldsymbol{B}_{\text{eff}}$, making only a small angle with $\boldsymbol{B}_{\text{eff}}$, as shown in Fig. 5.

If ω is *slowly* swept through resonance, $\boldsymbol{\mu}$ will continue to precess tightly around $\boldsymbol{B}_{\text{eff}}$, as shown in Figs. 5b,c. and will follow its direction adiabatically. In Fig. 5 the effective field now points in the $-\hat{\boldsymbol{z}}$ direction, because $\omega \gg \gamma B_0$. Since the spin still precesses tightly around $\boldsymbol{B}_{\text{eff}}$, its direction in the laboratory system has "flipped" from $+\hat{\boldsymbol{z}}$ to $-\hat{\boldsymbol{z}}$. The laboratory field $\boldsymbol{B}_0$ remains unchanged, so this represents a transition from spin up to spin down.

The requirement for $\boldsymbol{\mu}$ to follow the effective field $\boldsymbol{B}_{\text{eff}}(t)$ is that, at all times, the magnetic moment always precesses tightly around $\boldsymbol{B}_{\text{eff}}$. That means, within one precession period $2\pi/\Omega_R$, the angle θ that $\boldsymbol{B}_{\text{eff}}$ makes with $\hat{\boldsymbol{z}}$ must not have advanced more than a few degrees, i.e.

$$\Delta\theta = \dot{\theta} \cdot \Delta t = \dot{\theta}\frac{2\pi}{\Omega_R} \ll 2\pi \tag{1.41}$$

In other words, the Larmor frequency (the generalized Rabi frequency) $\Omega_R =$

γB_{eff} must be large compared to $\dot{\theta}$, the rate at which $\boldsymbol{B}_{\text{eff}}(t)$ is changing direction.

This requirement is most severe near exact resonance where $\theta = \pi/2$.

Using $B_{z,\text{eff}}(t) = B_0 - \omega(t)/\gamma$ we have in this case (from geometry)

$$| \dot{\theta}_{max} | = \frac{1}{B_1} \frac{dB_{z,\text{eff}}(t)}{dt} = \frac{1}{B_1} \frac{1}{\gamma} \frac{d\omega}{dt} \ll \gamma B_1, \qquad (1.42)$$

or using $\omega_R = \gamma B_1$,

$$\frac{d\omega}{dt} \ll \omega_R^2. \qquad (1.43)$$

In this example we have shown that a slow change from $\omega \ll \gamma B_0$ to $\omega \gg \gamma B_0$ will flip the spin; the same argument shows that the reverse direction of slow change will also flip the spin.

Note that since the change of ω in one Rabi period must be much smaller than the Rabi frequency itself, and since we need to sweep the detuning $\omega - \omega_0$ from much larger than ω_R to much smaller than $-\omega_R$ to complete the inversion, it is clear that the inversion will be slower than an on-resonance π-pulse.

In the examples below (Fig. 6), we see how the magnetic moment follows the changing magnetic field $\boldsymbol{B}_{\text{eff}}$ less and less faithfully as the ramp speed $\dot{\omega}$ is increased beyond ω_R^2. We will come back to the Landau-Zener problem after having introduced the quantum spin $1/2$ case.

1.3.6   Adiabatic Following in a Magnetic Trap

In a slight digression, an important example of adiabatic following of magnetic moments is given by the trapping of neutral atoms in magnetic traps. First, since Maxwell's equations forbid the existence of a magnetic field maximum in free space (there are no magnetic charges), we can only create magnetic field minima in free space, and therefore only trap atoms in so-called "low-field seeking" states, so for which the projection of the magnetic moment on the local magnetic field direction points opposite the field. For the atom to stay trapped, the magnetic moment must always be able to follow adiabatically the direction of the local magnetic field. Otherwise, "spin-flips", whereby the atoms flip their magnetic moments to be aligned with the field, lowering their energy and then leaving the trap (by seeking the high field right at the coils). A classic example is the quadrupole magnetic trap, formed by two parallel coils with currents running in anti-Helmholtz configuration. This results in a magnetic field zero right in the center between the coils, and a gradient field away from the zero:

$$\boldsymbol{B} = B' \begin{pmatrix} x \\ y \\ -2z \end{pmatrix}.$$

If an atom moves through the region close to the zero of magnetic field, the local Larmor frequency may become low compared to the rate of change of the field direction. For adiabatic following, the rate of change of the field angle should satisfy:
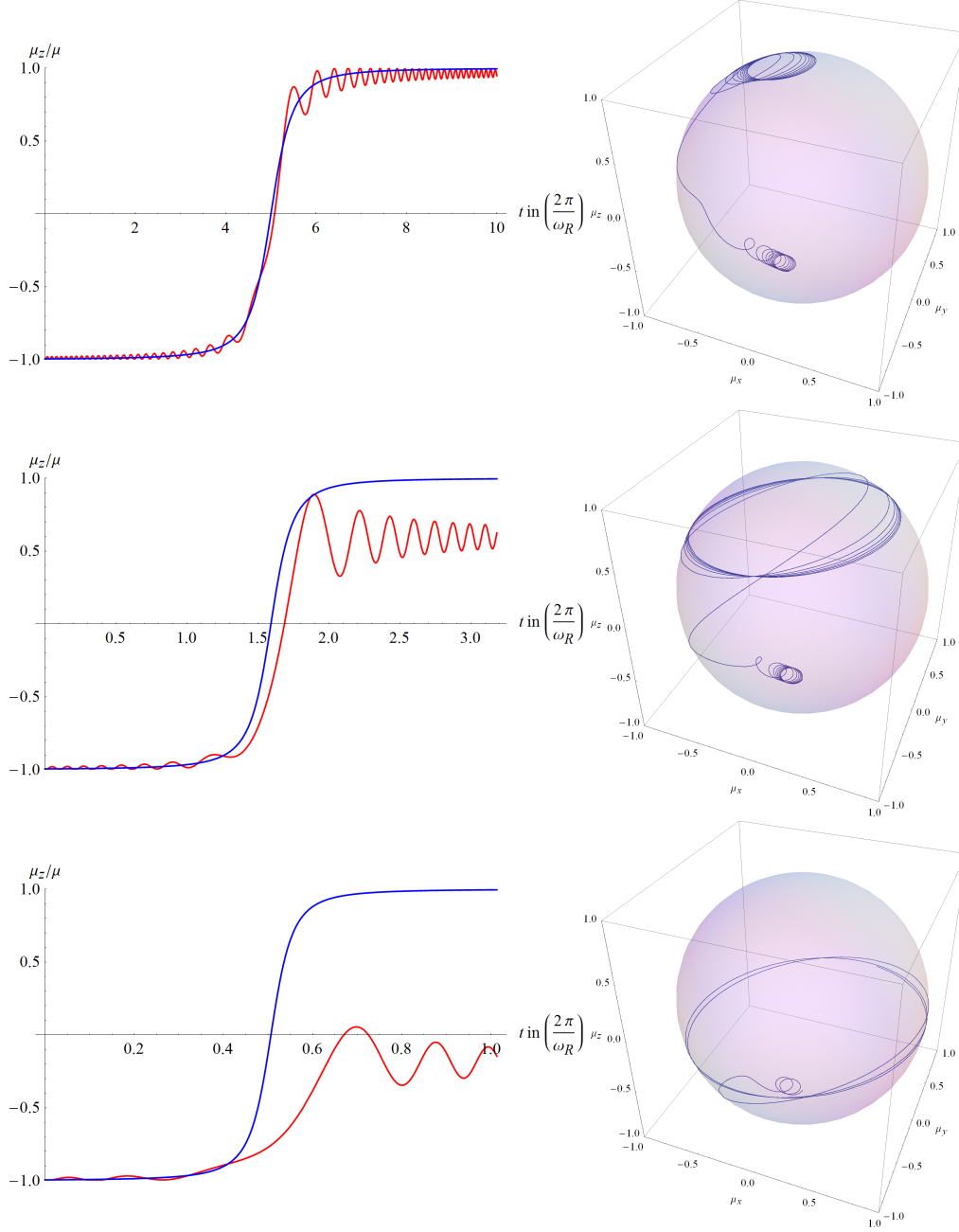
$$\dot{\theta} \ll \Omega_L$$

Figure 6. Top row: Adiabatic sweep. Start of sweep $\delta = -10\,\omega_R$, end of sweep $\delta = +10\,\omega_R$, sweep rate $\dot{\omega} = \frac{20\,\omega_R}{10\frac{2\pi}{\omega_R}} = \frac{1}{\pi}\omega_R^2$. Left: z-component of the magnetic moment versus time t measured in Rabi periods $2\pi/\omega_R$ (red curve). Blue is $\cos\theta = \frac{\delta(t)}{\sqrt{\delta(t)^2+\omega_R^2}}$, i.e. the cosine of the angle that $\boldsymbol{B}_{\text{eff}}$ makes with the z-axis. Right: Path traced out by the tip of the magnetic moment in real space (or, for a two-level system in quantum mechanics described by a pseudo-spin 1/2: the path traced out by the tip of the Bloch vector on the Bloch sphere. Middle row: sweep with imperfect adiabaticity. The sweep rate here is $\dot{\omega} = \pi \frac{20\,\omega_R}{10\frac{2\pi}{\omega_R}} = \omega_R^2$. Bottom row: non-adiabatic sweep. Sweep rate $\dot{\omega} = \pi^2 \frac{20\,\omega_R}{10\frac{2\pi}{\omega_R}} = \pi\omega_R^2$.
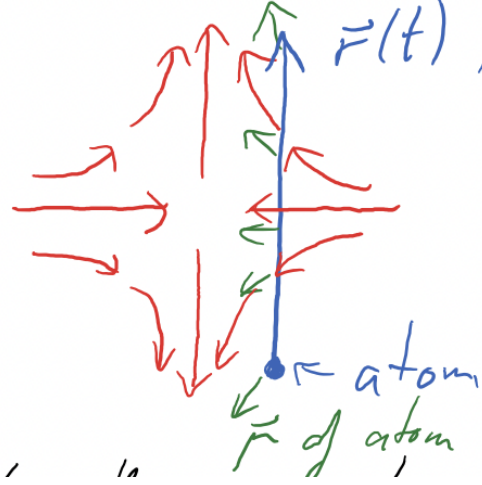
Figure 7. An atom moving in the quadrupole magnetic trap, with its magnetic moment attempting to follow the direction of the local magnetic field.

The field experienced by the atom changes as the atom is moving through space. We have (approximately, i.e. not worrying about factors on the order of two):

$$\dot{\theta} = \frac{\dot{B}}{B} = \frac{B'v}{B} = \frac{B}{r}.$$

Here, v is the atom velocity and r is the atom position. So, the adiabaticity condition is

$$\dot{\theta} \ll \Omega_L \implies \frac{v}{r} \ll \Omega_L = \gamma B = \gamma B' r.$$

So the "danger zone" where the atom may no longer be able to follow adiabatically, and therefore undergo spin flips, is the region of distances from the field zero smaller than

$$r = \sqrt{\frac{v}{\gamma B'}}.$$

This region is called the "Majorana hole". As the atom cloud is cooled (e.g. through radiofrequency evaporation), the velocity decreases like $\sqrt{T}$, the hole radius like $T^{1/4}$, but the cloud size $R \propto T/\mu B'$ decreases faster. So eventually, the cloud becomes comparable in size to the "Majorana hole" and severe losses in the number of trapped atoms are observed.

There are several solutions to this that were developed in order to keep atoms in a magnetic trap. Wolfgang Ketterle at MIT used a repulsive laser beam to "plug the hole". This is called the "plug trap". Eric Cornell at JILA added a time varying magnetic bias field that moves the magnetic field zero in a circular orbit of radius larger than the cloud size, and at a rate much faster than the atoms can follow (typically: 10 kHz, compared to the frequency of atomic motion of 100 Hz), but still much slower than the Larmor frequency (1 MHz), so that atoms stay trapped in a region of non-zero magnetic field (1 G) where their moments can adiabatically follow the rotating bias field. This was called the TOP (time orbiting potential) trap. These two completely different solutions

both led to the realization of Bose-Einstein condensation.

1.4 Resonance Of Quantized Spin

1.4.1   Expectation value of magnetic moment behaves classically

Before solving the quantum mechanical problem of a magnetic moment in a time varying field, it is worthwhile demonstrating that its motion is classical. By "its motion is classical" we mean the time evolution of the expectation value of the magnetic moment operator obeys the classical equation of motion. Specifically, we shall show that

$$\frac{d}{dt}\langle\hat{\boldsymbol{\mu}}\rangle = \gamma\langle\hat{\boldsymbol{\mu}}\rangle \times \boldsymbol{B}. \tag{1.44}$$

Proof: Recall the Heisenberg equations of motion for an operator $\hat{O}$:

$$\frac{d}{dt}\hat{O} = \frac{i}{\hbar}[\hat{H},\hat{O}] + \frac{\partial\hat{O}}{\partial t}. \tag{1.45}$$

If the operator is not explicitly time dependent the last term vanishes.

The interaction of $\hat{\boldsymbol{\mu}}$ with a static field $B_0\hat{\boldsymbol{z}}$ is

$$\hat{H} = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{B}_0 = -\gamma\hat{\boldsymbol{J}} \cdot \boldsymbol{B}_0 = -\gamma B_0\hat{J}_z, \tag{1.46}$$

Note that $\hat{\boldsymbol{J}}$ has dimensions of angular momentum. Thus

$$\frac{d\hat{\boldsymbol{\mu}}}{dt} = -i\gamma B_0[\hat{J}_z,\hat{\boldsymbol{\mu}}]/\hbar. \tag{1.47}$$

Using $\hat{\boldsymbol{\mu}} = \gamma\hat{\boldsymbol{J}}$, we can rewrite this as

$$\frac{d\hat{\boldsymbol{J}}}{dt} = -i\gamma B_0\left[\hat{J}_z,\hat{\boldsymbol{J}}\right]/\hbar. \tag{1.48}$$

The commutation rules for $\hat{\boldsymbol{J}}$ are $[\hat{J}_x,\hat{J}_y] = i\hbar\hat{J}_z$, etc., or $\hat{\boldsymbol{J}} \times \hat{\boldsymbol{J}} = i\hbar\hat{\boldsymbol{J}}$ (this is a shorthand way of writing $[\hat{J}_i,\hat{J}_j] = \epsilon_{ijk}\hat{J}_k$.) Hence

$$\frac{d\hat{J}_x}{dt} = \gamma B_0\hat{J}_y \tag{1.49}$$

$$\frac{d\hat{J}_y}{dt} = -\gamma B_0\hat{J}_x \tag{1.50}$$

$$\frac{d\hat{J}_z}{dt} = 0 \tag{1.51}$$

These describe the uniform precession of $\hat{\boldsymbol{J}}$ about the z-axis at a rate $-\gamma B_0$. In particular, taking the expectation value, we have:

$$\frac{d}{dt}\langle\hat{\boldsymbol{J}}\rangle = \gamma\langle\hat{\boldsymbol{J}}\rangle \times \boldsymbol{B} \tag{1.52}$$

and since $\hat{\boldsymbol{\mu}} = \gamma \hat{\boldsymbol{J}}$, this directly yields Eq. 1.44:

$$\frac{d}{dt}\langle\hat{\boldsymbol{\mu}}\rangle = \gamma\langle\hat{\boldsymbol{\mu}}\rangle \times \boldsymbol{B}. \tag{1.53}$$

Thus the quantum mechanical and classical equation of motion are identical. This fact underlies the great utility of classical magnetic resonance in providing intuition about resonance in quantum spin systems.

A few comments on this result:

- the result is valid for any angular momentum operator, so also for spin 1/2...

- ... and therefore for any two-level system that can be mapped onto an effective spin 1/2.

- it is valid for the case of several angular momenta within an atom coupled to a total angular momentum $\boldsymbol{F}$ (as long as the magnetic field $\boldsymbol{B}$ is not large enough to "break" the coupling).

- it is valid also for a system of N two-level systems symmetrically coupled to an external field. In this case, we have an effective angular momentum $L = N/2$. Spin precession in this case can be understood as Dicke superradiance, the constructive interference of N "aligned" particles.

1.4.2   The Rabi transition probability

For a spin 1/2 particle we can push the classical solution further and obtain the amplitudes and probabilities for each state. Consider [1] $\langle\mu_z\rangle/\hbar = \gamma\langle J_z\rangle = \gamma m$, where m is the usual "magnetic" quantum number. For a spin 1/2 particle m has the value $+1/2$ or $-1/2$. Let the probabilities for having these values be P_+ and P_- respectively. Then

$$\langle J_z\rangle = \frac{1}{2}P_+ - \frac{1}{2}P_-, \tag{1.54}$$

or, since $P_+ + P_- = 1$,

$$\langle J_z\rangle = \frac{1}{2}(1 - 2P_-), \tag{1.55}$$

$$\langle\mu_z\rangle = \frac{1}{2}\gamma\hbar(1 - 2P_-). \tag{1.56}$$

If $\boldsymbol{\mu}$ lies along the z axis at $t = 0$, then $\mu_z(0) = \gamma\hbar/2$, and we have

$$\mu_z(t) = \mu_z(0)(1 - 2P_-). \tag{1.57}$$

In this case, P_- is the probability that a spin in state $m = +1/2$ at $t = 0$ has made a transition to $m = -1/2$ at time t, $P_{\uparrow\to\downarrow}(t)$. So for the Rabi problem, the case of a static field $\boldsymbol{B}_0 = \omega_0\hat{\boldsymbol{z}}/\gamma$ and a rotating magnetic field $\boldsymbol{B}_1$ rotating

---

[1]We will in the following drop hats $\hat{\ }$ over operators for simplicity.

at frequency ω about the z-axis, switched on at time $t = 0$, we see immediately, comparing Eq. 1.57 with 1.39,

$$P_{\uparrow \to \downarrow}(t) = \frac{\omega_R^2}{\omega_R^2 + (\omega - \omega_0)^2} \sin^2\left(\frac{1}{2}\sqrt{\omega_R^2 + (\omega - \omega_0)^2}\, t\right)$$

$$\tag{1.58}$$

$$P_{\uparrow \to \downarrow}(t) = (\omega_R/\Omega_R)^2 \sin^2(\Omega_R t/2) \tag{1.59}$$

This result is known as the *Rabi transition probability*. It is important enough to memorize. We have derived it from a classical correspondence argument, but it can also be derived quantum mechanically. In fact, such a treatment is essential for a complete understanding of the system.

1.4.3   The Hamiltonian of a quantized spin $\frac{1}{2}$

Let us investigate the time dependence of the wave function for a quantized spin $\frac{1}{2}$ system with moment $\boldsymbol{\mu} = \gamma\hbar\boldsymbol{S}$ that is placed in a uniform magnetic field $\boldsymbol{B}_0 = \omega_0\hat{\boldsymbol{z}}/\gamma$ and, starting at $t = 0$, subject to a field $\boldsymbol{B}_R(t)$ which rotates in the $x - y$ plane with frequency ω. These fields are the same as the fields discussed in the preceding section on the motion of a classical spin and a time-varying field. The only difference is that now we are discussing their effect on a quantized system, so we must use Schrödinger's equation rather than the laws of classical Electricity and Magnetism to discuss the dynamics of the system.

The basis states are (using the standard column vector representation):

$$|g\rangle \equiv |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{1.60}$$

$$|e\rangle \equiv |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{1.61}$$

with state $|1\rangle$ lower in energy.

The unperturbed Hamiltonian is (note: we will take $\omega_0 = \gamma B_0$ to be positive, and $\boldsymbol{\mu}$ is an operator)

$$H_0 = -\boldsymbol{\mu} \cdot \boldsymbol{B}_0 = -\hbar S_z \omega_0$$
$$= -\frac{1}{2}\hbar\omega_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = -\frac{1}{2}\hbar\omega_0 \sigma_z \tag{1.62}$$

where σ_z is a Pauli spin matrix.

The energies are

$$E_1 = -\hbar\omega_0/2; \qquad \omega_1 = -\omega_0/2$$

$$E_2 = +\hbar\omega_0/2; \qquad \omega_2 = +\omega_0/2 \tag{1.63}$$

Suppose we have a spin initially aligned along $\hat{\boldsymbol{x}}$:

$$|\psi(t=0)\rangle = \frac{1}{\sqrt{2}}\left(|g\rangle + |e\rangle\right).$$

Then

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(e^{i\omega_0 t/2}\,|g\rangle + e^{-i\omega_0 t/2}\,|e\rangle\right) = \frac{1}{\sqrt{2}}e^{i\omega_0 t/2}\left(|g\rangle + e^{-i\omega_0 t}\,|e\rangle\right).$$

This corresponds to rotation about the equator of the Bloch sphere at a rate ω_0: the state of the spin $1/2$ rotates from being aligned along $\hat{\boldsymbol{x}}$ to being aligned along $-\hat{\boldsymbol{y}}$, then $-\hat{\boldsymbol{x}}$, then $\hat{\boldsymbol{y}}$ etc., so in the same sense as the classical magnetic moment.

We will now switch on the magnetic field $\boldsymbol{B}_R$ which rotates in the $x-y$ plane, with the goal of making it co-rotate with the spin when driven at $\omega = \omega_0$.

The perturbation Hamiltonian $H'(t)$ is written best in terms of $\omega_R = \gamma B_R$ where B_R is the magnetic field which rotates in the $x-y$ plane (in the magnetic resonance community the subscript R is often replaced by 1):

$$
\begin{aligned}
H'(t) &= -\boldsymbol{\mu}\cdot\boldsymbol{B}_R(t)\\
&= -\boldsymbol{\mu}\cdot(\omega_R/\gamma)[\hat{\boldsymbol{x}}\,\cos\,\omega t - \hat{\boldsymbol{y}}\,\sin\,\omega t]\\
&= -\omega_R[S_x\,\cos\omega t - S_y\,\sin\omega t]\\
&= -\frac{\hbar\omega_R}{2}\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\cos\omega t - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\sin\omega t\right]\\
&= -\frac{\hbar\omega_R}{2}\begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix}
\end{aligned}
\tag{1.64}
$$

where we used $\boldsymbol{\mu}\,\cdot\,\hat{\boldsymbol{x}} = \gamma S_x$. In the penultimate line we have replaced the operators S_x and S_y with $(\hbar/2)\,\sigma_x$ and $(\hbar/2)\,\sigma_y$ where σ_x and σ_y are Pauli spin matrices. The perturbation matrix element is just the entry $H'_{21}(t)$ in row 2 and column 1:

$$\langle 2\mid H'\mid 1\rangle = -\frac{\hbar\omega_R}{2}\,e^{-i\omega t} \tag{1.65}$$

We have thus derived the following Hamiltonian for the spin $\frac{1}{2}$ problem:

$$H = \frac{\hbar}{2}\begin{pmatrix} -\omega_0 & -\omega_R e^{+i\omega t} \\ -\omega_R e^{-i\omega t} & \omega_0 \end{pmatrix} \tag{1.66}$$

1.4.4   Quantum Mechanical Solution for Resonance in a Two-State System

As has been emphasized, a two-state system coupled by a periodic interaction is an archetype for large areas of atomic/optical physics. The quantum mechanical solution can be achieved by a variety of approaches, the most elegant of which is the dressed atom picture in which the atom and radiation field constitute a single quantum system and one finds its eigenstates. That approach will be introduced later. Here we follow a rather different approach, less elegant, but capable of being generalized to a variety or problems including multi-level resonance and

radiative decay in the presence of oscillating fields. The starting point is the interaction representation.

1.4.5   Interaction representation

We consider a complete set of eigenstates to a Hamiltonian $H_0, \psi =\mid 1 >, \mid 2 >$ ... , such that

$$H_0 \mid j >= E_j \mid j > . \tag{1.67}$$

The problem is to find the behavior of the system under an interaction $V(t)$, i.e. to find solutions to

$$i\hbar \frac{\partial \psi(t)}{\partial t} = (H_0 + V(t))\psi(t) \tag{1.68}$$

In the interaction representation we take

$$\psi(t) = \sum_j a_j(t) \mid j > e^{-iE_j t/\hbar}. \tag{1.69}$$

Schrödinger's equation yields

$$i\hbar \dot{a}_k = \sum_j < k \mid V \mid j > a_j e^{i(E_j - E_k)t/\hbar} = \sum_j V_{kj} a_j e^{i\omega_{jk}}. \tag{1.70}$$

Given any set of initial conditions, $a_j(0), j = 1, 2, 3...$, these equations can be integrated to find $\psi(t)$. Often, this is done iteratively, following a pertubative approach. For the two-state system, with V periodic, one can obtain an exact solution.

1.4.6   Two-state problem

We consider a two-state system

$$\psi = a_1 \mid 1 > + a_2 \mid 2 >, \tag{1.71}$$

with $\mid a_1 \mid^2 + \mid a_2 \mid^2 = 1$. We assume $E_2 > E_1$, and introduce $\hbar\omega_{12} = \hbar\omega_0 = E_2 - E_1$. Without loss of generality, we let $E_1 = -\hbar\omega_0/2$; $E_2 = \hbar\omega_0/2$. We take the interaction to be of the form $V_{11} = V_{22} = 0$, and

$$V_{12} = \frac{1}{2}\hbar\omega_R \left(e^{-i\omega t} \right), \tag{1.72}$$

Eq. 1.70 gives

$$i\dot{a}_1 = \frac{1}{2}\omega_R \left(e^{-i\omega t} \right) e^{+i\omega_0 t} a_2,$$
$$i\dot{a}_2 = \frac{1}{2}\omega_R \left(e^{i\omega t} \right) e^{-i\omega_0 t} a_1. \tag{1.73}$$

Introducing $\delta \equiv \omega - \omega_0$, Eqs. 1.73 becomes

$$i\dot{a}_1 = \frac{1}{2}\omega_R e^{-i\delta t}a_2,$$
$$i\dot{a}_2 = \frac{1}{2}\omega_R e^{i\delta t}a_1. \tag{1.74}$$

We can eliminate the explicit time dependence by making the substitution

$$a_1 = e^{-i\delta t/2}b_1,$$
$$a_2 = e^{+i\delta t/2}b_2. \tag{1.75}$$

Eqs. 1.74 become

$$\dot{b}_1 - i\frac{\delta}{2}b_1 = \frac{-i}{2}\omega_R b_2,$$
$$\dot{b}_2 + i\frac{\delta}{2}b_2 = \frac{-i}{2}\omega_R b_1. \tag{1.76}$$

These equations describe periodic behavior, so that it is natural to try solutions of the form

$$b_1 = \sum_j B_j e^{i\alpha_j t},$$
$$b_2 = \sum_j C_j e^{i\alpha_j t}. \tag{1.77}$$

Substituting these in Eq. 1.76 yields

$$\left(\alpha_j - \frac{\delta}{2}\right)B_j + \left(\frac{\omega_R}{2}\right)C_j = 0,$$
$$\left(\frac{\omega_R}{2}\right)B_j + \left(\alpha_j + \frac{\delta}{2}\right)C_j = 0. \tag{1.78}$$

for which the determinental equation yields two eigenfrequencies

$$\alpha_{1,2} = \pm\frac{1}{2}\sqrt{\omega_R^2 + \delta^2} = \pm\frac{1}{2}\Omega_R, \tag{1.79}$$

where Ω_R is the generalized Rabi frequency:

$$\Omega_R = \sqrt{\omega_R^2 + \delta^2}. \tag{1.80}$$

From Eqs. 1.78:

$$C_1 = -B_1\frac{\omega_R}{\Omega_R + \delta}, \qquad C_2 = B_2\frac{\omega_R}{\Omega_R - \delta}. \tag{1.81}$$

By combining this result with Eq. 1.76 and Eq. 1.77 we obtain

$$a_1(t) = e^{-i(\delta-\Omega_R)t/2}B_1 + e^{-i(\delta+\Omega_R)t/2}B_2$$

$$a_2(t) = -\left(\frac{\omega_R}{\Omega_R + \delta}\right)e^{i(\delta+\Omega_R)t/2}B_1 + \left(\frac{\omega_R}{\Omega_R - \delta}\right)e^{i(\delta-\Omega_R)t/2}B_2 \qquad (1.82)$$

The solution contains two arbitrary constants, B_1 and B_2, which permit fitting the boundary condition for the two amplitudes.

If the system is in state 1 at $t = 0$, then $a_1(1) = 1, a_2(0) = 0$, and

$$B_1 = \frac{1}{2}\frac{\Omega_R + \delta}{\Omega_R}, \qquad B_2 = \frac{1}{2}\frac{\Omega_R - \delta}{\Omega_R}$$

$$a_2(t) = \frac{1}{2}\frac{\omega_R}{\Omega_R}\left[-e^{i(\delta+\Omega_R)t/2} + e^{i(\delta-\Omega_R)t/2}\right]$$

$$= -i\frac{\omega_R}{\Omega_R}e^{i\delta t/2}\sin\left(\Omega_R t/2\right). \qquad (1.83)$$

The probability of being in state 2 at time t is,

$$P_2(t) = |a_2(t)|^2 = \frac{\omega_R^2}{\Omega_R^2}\sin^2\left[\frac{1}{2}\Omega_R t\right], \qquad (1.84)$$

which is identical to the classical result for the Rabi resonance formula, derived earlier.

If we introduce the parameter θ defined by

$$\cos\theta = \left(\frac{\Omega_R + \delta}{2\Omega_R}\right)^{1/2} = \left(\frac{1}{2}(1 + \frac{\delta}{\Omega_R})\right)^{1/2}$$

$$\sin\theta = \left(\frac{\Omega_R - \delta}{2\Omega_R}\right)^{1/2} = \left(\frac{1}{2}(1 - \frac{\delta}{\Omega_R})\right)^{1/2} \qquad (1.85)$$

Then we have

$$\psi(t) = a_1(t)\,|\,1\rangle + a_2(t)\,|\,2\rangle \qquad (1.86)$$

$$= [\cos^2\theta\,e^{-i(\delta-\Omega_R)t/2} + \sin^2\theta\,e^{-i(\delta+\Omega_R)t/2}]\,|\,1\rangle$$

$$+ [\cos\theta\sin\theta][e^{i(\delta+\Omega_R)t/2} - e^{i(\delta-\Omega_R)t/2}]\,|\,2\rangle$$

$$= e^{-i\,\delta\,t/2}\left[\cos\left(\frac{\Omega_R t}{2}\right) + i\frac{\delta}{\Omega_R}\sin\left(\frac{\Omega_R}{2}t\right)\right]|1\rangle$$

$$- i\,e^{+i\,\delta\,t/2}\frac{\omega_R}{\Omega_R}\sin\left(\frac{\Omega_R}{2}t\right)|2\rangle \qquad (1.87)$$

1.4.7   Solution via rotating frame

The preceding solution seems a bit "brute force" and required some ad hoc "tricks" like the substitution from the a to the b amplitudes. We will here see very clearly what is behind the mathematics: It is again frame rotation.

In the very same spirit of the classical solution, we want to rotate our spin $1/2$ into a frame in which the magnetic fields appear stationary. In this frame the Hamiltonian will be time independent and can be solved easily. Now just like the classical angular momentum L_z generated rotation of vectors about the z-axis, the spin angular momentum operator S_z generates rotation of spinors about the z-axis. The rotation operator for rotation about $\hat{z}$ by an angle θ is thus

$$T = e^{-i\hat{S}_z\theta}.$$

We can find this result from integration of infinitesimal rotations.

To keep aligned with the rotating magnetic field, we want $\theta = -\omega t$, then we have

$$T = e^{i\omega t\sigma_z/2} = \begin{pmatrix} e^{i\omega t/2} & 0 \\ 0 & e^{-i\omega t/2} \end{pmatrix}.$$

Our states transform by

$$|\psi\rangle = T\left|\tilde{\psi}\right\rangle.$$

We get a new term in the Schrödinger equation according to

$$i\hbar\frac{d}{dt}|\psi\rangle = i\hbar\dot{T}\left|\tilde{\psi}\right\rangle + Ti\hbar\frac{d}{dt}\left|\tilde{\psi}\right\rangle = H|\psi\rangle = HT\left|\tilde{\psi}\right\rangle.$$

So,

$$i\hbar\frac{d}{dt}\left|\tilde{\psi}\right\rangle = \left(T^\dagger HT - i\hbar T^\dagger\dot{T}\right)\left|\tilde{\psi}\right\rangle.$$

The Hamiltonian in the rotating frame is then

$$\tilde{H} = T^\dagger\left(H - i\hbar\frac{d}{dt}\right)T.$$

H_0 and T are both diagonal, so

$$T^\dagger H_0 T = H_0.$$

For H_1, T removes the time-dependence:

$$T^\dagger H_1 T = -\frac{\hbar\omega_R}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = -\frac{\hbar\omega_R}{2}\sigma_x.$$

This is what we set out to do, since we chose the frame to rotate with the field. The time derivative term is

$$T^\dagger\left(-i\hbar\frac{d}{dt}T\right) = \frac{\hbar\omega}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar\omega}{2}\sigma_z.$$

We thus see the $\hat{z}$ field effectively reduced in amplitude, as occured for our classical system. The new Hamiltonian is thus

$$\tilde{H} = -\frac{\hbar}{2}\begin{pmatrix} -\delta & \omega_R \\ \omega_R & \delta \end{pmatrix} \quad \text{with } \delta = \omega - \omega_0.$$

We can also write

$$\tilde{H} = \frac{\hbar\delta}{2}\sigma_z - \frac{\hbar\omega_R}{2}\sigma_x = \frac{1}{2}\boldsymbol{h}\cdot\boldsymbol{\sigma} \text{ for } \boldsymbol{h} = \begin{pmatrix} -\hbar\omega_R \\ 0 \\ \hbar\delta \end{pmatrix}.$$

The Hamiltonian is now time-independent, and represents the interaction of a spin 1/2 with a static magnetic field. The eigenvectors are thus simply the two states representing the spin aligned and anti-aligned with $\boldsymbol{h}$ ($+$ and $-$). The eigenvalues are

$$E_\pm = \pm\frac{1}{2}|\boldsymbol{h}| = \pm\frac{\hbar}{2}\sqrt{\omega_R^2 + \delta^2} = \pm\frac{\hbar\Omega_R}{2}.$$

We can obtain the eigenvectors from the original eigenvectors $|g\rangle \equiv |\uparrow\rangle$ and $|e\rangle \equiv |\downarrow\rangle$ which described a spin 1/2 aligned and anti-aligned with the z-axis, simply by rotating about the axis

$$\hat{\boldsymbol{z}} \times \boldsymbol{h} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \times \begin{pmatrix} -\hbar\omega_R \\ 0 \\ \hbar\delta \end{pmatrix} = -\begin{pmatrix} 0 \\ \hbar\omega_R \\ 0 \end{pmatrix} = \hbar\omega_R\,\hat{\boldsymbol{y}}$$

by the angle ϕ satisfying

$$\cos\phi = \hat{\boldsymbol{z}}\cdot\hat{\boldsymbol{h}} = \frac{\delta}{\Omega_R}.$$

Note that

$$\tan\phi = -\frac{\omega_R}{\delta}.$$

Rotation about the y-axis is generated by S_y, again through the exponential

$$R = e^{-i\phi S_y} = e^{-i\phi\sigma_y/2}.$$

This is equivalent to

$$R = \cos\frac{\phi}{2}\mathbb{I} - i\sin\frac{\phi}{2}\sigma_y = \begin{pmatrix} \cos\frac{\phi}{2} & -\sin\frac{\phi}{2} \\ \sin\frac{\phi}{2} & \cos\frac{\phi}{2} \end{pmatrix}.$$

We can thus find the eigenstates, properly aligned and anti-aligned with the direction of $\boldsymbol{h}$:

$$|+\rangle_h = R|\uparrow\rangle = \begin{pmatrix} \cos\phi/2 \\ \sin\phi/2 \end{pmatrix} = \cos(\phi/2)|\uparrow\rangle + \sin(\phi/2)|\downarrow\rangle \tag{1.88}$$

$$|-\rangle_h = R|\downarrow\rangle = \begin{pmatrix} -\sin\phi/2 \\ \cos\phi/2 \end{pmatrix} = -\sin(\phi/2)|\uparrow\rangle + \cos(\phi/2)|\downarrow\rangle \tag{1.89}$$

Note that $\cos(\phi/2) = \sqrt{\frac{1+\cos\phi}{2}} = \sqrt{\frac{\Omega_R+\delta}{2\Omega_R}}$ and $\sin(\phi/2) = \sqrt{\frac{1-\cos\phi}{2}} = \sqrt{\frac{\Omega_R-\delta}{2\Omega_R}}$.

Their time-evolution is simply, since $E_+ = -\frac{\hbar\Omega_R}{2}$ and $E_- = \frac{\hbar\Omega_R}{2}$:

$$| + (t)\rangle = e^{i\Omega_R t/2}|+\rangle_h \tag{1.90}$$

$$| - (t)\rangle = e^{-i\Omega_R t/2}|-\rangle_h \tag{1.91}$$

Now say we start with $|\psi(t=0)\rangle = |\uparrow\rangle$, that is

$$|\psi(t=0)\rangle = R^T |+\rangle = \cos(\phi/2)|+\rangle - \sin(\phi/2)|-\rangle$$

We immediately obtain the time evolution

$$
\begin{aligned}
|\psi(t)\rangle &= \cos\frac{\phi}{2}e^{+i\Omega_R t/2}|+\rangle - \sin\frac{\phi}{2}e^{-i\Omega_R t/2}|-\rangle \\
&= \cos\frac{\phi}{2}e^{+i\Omega_R t/2}\left(\cos(\phi/2)|\uparrow\rangle + \sin(\phi/2)|\downarrow\rangle\right) \\
&\quad - \sin\frac{\phi}{2}e^{-i\Omega_R t/2}\left(-\sin(\phi/2)|\uparrow\rangle + \cos(\phi/2)|\downarrow\rangle\right) \\
&= \cos\left(\frac{\Omega_R t}{2}\right)|\uparrow\rangle + i\sin\left(\frac{\Omega_R t}{2}\right)\cos\phi\,|\uparrow\rangle + i\sin\left(\frac{\Omega_R t}{2}\right)\sin\phi\,|\downarrow\rangle \\
&= \left(\cos\left(\frac{\Omega_R t}{2}\right) + i\frac{\delta}{\Omega_R}\sin\left(\frac{\Omega_R t}{2}\right)\right)|\uparrow\rangle - i\frac{\omega_R}{\Omega_R}\sin\left(\frac{\Omega_R t}{2}\right)|\downarrow\rangle.
\end{aligned}
$$

This is identical to what we had found before. We can also consider the time evolution operator directly

$$U(t) = e^{-i\tilde{H}t/\hbar} = \cos\left(\frac{\Omega_R t}{2}\right)\mathbb{1} + i\sin\left(\frac{\Omega_R t}{2}\right)\hat{\boldsymbol{h}}\cdot\boldsymbol{\sigma} \tag{1.92}$$

$$= \cos\left(\frac{\Omega_R t}{2}\right)\mathbb{1} + i\sin\left(\frac{\Omega_R t}{2}\right)\left(\frac{\delta}{\Omega_R}\sigma_z - \frac{\omega_R}{\Omega_R}\sigma_x\right). \tag{1.93}$$

from which the above result for $|\psi(t)\rangle = U(t)|\uparrow\rangle$ immediately follows. The probability of a spin flip is

$$p_\downarrow(t) = |\langle\downarrow|\psi(t)\rangle|^2 = \frac{\omega_R^2}{\Omega_R^2}\sin^2\left(\frac{\Omega_R t}{2}\right).$$

This is indeed just the same as the z-component of a classical magnetic moment.

1.4.8   Rapid adiabatic passage - Quantum treatment

We revisit the Landau Zener problem but now for a two-state system or equivalently a spin 1/2 system. The problem can be solved rigorously. Consider a spin 1/2 system in a magnetic field $\boldsymbol{B}_{\text{eff}}$ with energies

$$W_\pm = \pm\frac{1}{2}\hbar\gamma B_{\text{eff}}. \tag{1.94}$$

For a uniform field B_0 (with $B_1 = 0$), the effective field in the rotating frame

is $B_0 - \omega/\gamma$, and

$$W_\pm = \pm\frac{1}{2}\hbar(\omega_0 - \omega), \tag{1.95}$$

where $\omega_0 = \gamma B_0$. As ω is swept through resonance, the two states move along their changing eigenenergies. The energies change, but the states do not. There is no coupling between the states, so a spin initially in one or the other will remain so indefinitely no matter how ω changes relative to ω_0.

In the presence of a rotating field, B_1, however, the energy levels look quite different: instead of intersecting lines they form non-intersecting hyperbolas separated by energy $\hbar\omega_R$. If the system moves along these hyperbolas, then an $\uparrow$ spin will adiabatically convert into $\downarrow$ and a $\downarrow$ spin will turn into $\uparrow$.
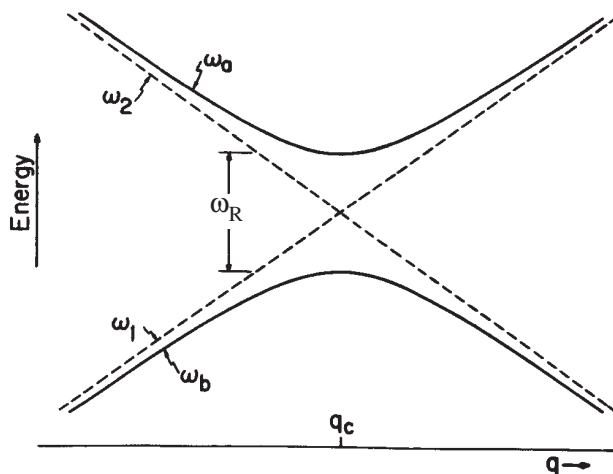
Figure 8. An avoided crossing. If the parameter q that governs the energy levels is swept slowly, the system can adiabatically change its state ("flip its spin"). If q is swept rapidly, it may instead jump across the gap and no spin flip occurs.

Whether or not the system follows an energy level adiabatically depends on how rapidly the energy is changed, compared to the minimum energy separation. To cast the problem in quantum mechanical terms, imagine two non-interacting states whose energy separation, ω, depends on some parameter q which varies linearly in time, and vanishes for some value q_c. Now add a perturbation having an off-diagonal matrix element V which is independent of q, so that the energies at q_c are $\pm V$, as shown in Fig. 8 ($\omega_R = 2V$). The probability that the system will "jump" from one adiabatic level to the other after passing through the "avoided crossing" (i.e., the probability of non-adiabatic behavior) is

$$P_{na} = e^{-2\pi\Gamma} \tag{1.96}$$

where

$$\Gamma = \frac{\mid V \mid^2}{\hbar^2} \left[\frac{d\omega}{dt} \right]^{-1} \qquad (1.97)$$

This result was originally obtained by Landau and Zener. The jumping of a system as it travels across an avoided crossing is called the Landau-Zener effect. Further description, and reference to the initial papers, can be found in [5]. Inserting the parameters for our magnetic field problem, we have

$$P_{na} = \exp\left\{ -\frac{\pi}{2} \frac{\omega_R^2}{d\omega/dt} \right\} \qquad (1.98)$$

Note that the factor in the exponential is related to the inequality in Eq. 1.43. When Eq. 1.43 is satisfied, the exponent is large and the probability of non-adiabatic behavior is exponentially small.

Incidentally the "rapid" in adiabatic rapid passage is something of a misnomer. The technique was originally developed in nuclear magnetic resonance in which thermal relaxation effects destroy the spin polarization if one does not invert the population sufficiently rapidly. In the absence of such relaxation processes one can take as long as one pleases to traverse the anticrossings, and the slower the crossing the less the probability of jumping.

1.4.9   Adiabatic passage - Detailed calculation

Our initial Hamiltonian in the rotating frame is (

$$H_0 = \frac{\hbar}{2} \begin{pmatrix} -\delta & 0 \\ 0 & \delta \end{pmatrix}.$$

The full Hamiltonian is

$$H = \frac{\hbar}{2} \begin{pmatrix} -\delta & \omega_R \\ \omega_R & \delta \end{pmatrix}.$$

This has eigenstates $|\pm\rangle$, which have energies separated by ω_R.

We start with $-\delta \ll \omega_R$, so the eigenstates are initially $|\uparrow\rangle$ and $|\downarrow\rangle$. If we change the system adiabatically, states connect smoothly according to the adiabatic theorem, so the system will go from $|\uparrow\rangle$ to $|\downarrow\rangle$. However, for a non-adiabatic change, the system may jump across the avoided crossing, staying in the same state. The probability of a non-adiabatic transition is

$$p_{na} = e^{-\frac{\pi}{2} \frac{\omega_R^2}{\dot{\omega}}}.$$

We thus see the previous adiabaticity criteria appear.

Now, let us derive this. Suppose we are in a perturbative limit, $p_{\text{flip}} \ll 1$.

Since the drive frequency changes, the Hamiltonian is

$$H = \frac{\hbar}{2} \begin{pmatrix} \omega_0 & \omega_R e^{-i\phi(t)} \\ \omega_R e^{+i\phi(t)} & -\omega_0 \end{pmatrix}.$$

In the frame rotating with the drive (in a time-dependent manner),

$$\tilde{H} = \frac{\hbar}{2} \begin{pmatrix} -\delta(t) & \omega_R \\ \omega_R & \delta(t) \end{pmatrix},$$

where $\delta(t) = \dot{\phi}(t) - \omega_0$. Suppose instead we rotate the frame at ω_0. We find

$$\bar{H} = \frac{\hbar}{2} \begin{pmatrix} 0 & \omega_R e^{-i(\phi(t) - \omega_0 t)} \\ \omega_R e^{+i(\phi(t) - \omega_0 t)} & 0 \end{pmatrix}.$$

The second Hamiltonian is actually easier to deal with. We know that

$$|\psi(t)\rangle = a(t) |\uparrow\rangle + b(t) |\downarrow\rangle$$

for eigenstates of this Hamiltonian. Acting with $\bar{H}$ on this,

$$\dot{a} = -i\frac{\omega_R}{2} e^{-i(\phi(t) - \omega_0 t)} b \text{ and } \dot{b} = -i\frac{\omega_R}{2} e^{+i(\phi(t) - \omega_0 t)} a.$$

Let us use a linear sweep, $\delta(t) = \dot{\phi} - \omega_0 = \alpha t$. So, $\phi(t) = \omega_0 t + \frac{1}{2}\alpha t^2$. Then

$$\dot{a} = -i\frac{\omega_R}{2} e^{-i\alpha t^2/2} b \text{ and } \dot{b} = -i\frac{\omega_R}{2} e^{+i\alpha t^2/2} a.$$

Suppose we start in $|\downarrow\rangle$, and have weak coupling, so at all times $b \approx 1$. Then

$$\dot{a} \approx -i\frac{\omega_R}{2} e^{-i\alpha t^2/2}.$$

So, a will only grow significantly when $\alpha t^2 \leq 1$. That is, the phase needs to be fairly constant for a to accumulate. This occurs for $\Delta t \sim \frac{1}{\sqrt{\alpha}} = \frac{1}{\sqrt{\dot{\omega}}}$ around the resonance. This implies that $a \approx \omega_R \Delta t \approx \frac{\omega_R}{\sqrt{\dot{\omega}}}$. The probability of a flip is thus

$$p_{\text{flip}} = |a|^2 \sim \frac{\omega_R^2}{\dot{\omega}},$$

which is proportional to what we expect. We can do the integral exactly since the $\dot{a}$ equation is Gaussian. We find

$$a(t) = -i\omega_R \int_0^\infty dt\, e^{-i\alpha t^2/2} = -ie^{-i\pi/4} \omega_R \sqrt{\frac{\pi}{2\alpha}}.$$

This gives a flip probability of

$$p_{\text{flip}} = |a|^2 = \frac{\pi}{2} \frac{\omega_R^2}{\dot{\omega}},$$

which is exactly the correct limit of the Landau-Zener formula.

We can perform the calculation also fully non-perturbatively. Note in passing that we could have solved the problem of a classical spin as well, as the result will have to be identical, but it is even more difficult than the quantum case as it involves three coupled equations instead of two.

Returning to the spin-1/2 system, we start with the coupled equations

$$\dot{a} = -i\frac{\omega_R}{2}e^{-i\alpha t^2/2}b \text{ and } \dot{b} = -i\frac{\omega_R}{2}e^{+i\alpha t^2/2}a.$$

We have boundary conditiosn $a(-\infty) = 0$, $b(-\infty) = 1$. Taking another derivative of a,

$$\ddot{a} = -i\frac{\omega_R}{2}e^{-i\alpha t^2/2}\dot{b} - i\alpha t\,\dot{a}.$$

So

$$\ddot{a} = -\frac{\omega_R^2}{4}a - i\alpha t\,\dot{a}.$$

We substitute $a = e^{-i\alpha t^2/4}c$, and find

$$\ddot{c} + \left(\frac{\omega_R^2}{4} - i\frac{\alpha}{2} + \frac{\alpha^2}{4}t^2\right)c = 0.$$

This is known as the Weber solution. We make it resemble a harmonic oscillator by introducing

$$z = \sqrt{\alpha}e^{-i\pi/4}t \implies dz = \sqrt{\alpha}e^{-i\pi/4}\,dt.$$

(the same substitution was actually necessary for the gaussian integral of the perturbative calculation). From this, our equation becomes

$$\frac{d^2c}{dz^2} + \left(i\frac{\omega_R^2}{4\alpha} + \frac{1}{2} - \frac{z^2}{4}\right)c = 0.$$

This can be compared to the Schrödinger equation for the harmonic oscillator

$$-\frac{\hbar^2}{2m}\psi'' + \frac{1}{2}m\omega^2x^2\psi = E\psi \implies \frac{d^2\psi}{d\tilde{x}^2} + \left(n + \frac{1}{2} - \frac{\tilde{x}^2}{4}\right)\psi = 0.$$

when expressing space in units of the harmonic oscillator length $x = \tilde{x}\sqrt{\hbar/m\omega}$, and writing energy $E = \hbar\omega(n + 1/2)$.

Here, we have $n = i\frac{\omega_R^2}{4\alpha}$. The parabolic cylinder functions are ultimately the solution, and accept complex arguments:

$$c(z) = \frac{\omega_R}{2\sqrt{\alpha}}e^{-\pi\omega_R^2/16\alpha}D_{-1-i\frac{\omega_R^2}{4\alpha}}(iz).$$

We eventually find

$$|a(\infty)|^2 = 1 - e^{-\pi\omega_R^2/2\alpha}.$$

This is exactly the spin-flip probably that we expect.

1.5 Density Matrix

1.5.1   General results

The *density matrix* provides a way of treating the time evolution of a quantized system which offers several advantages over the usual time dependent expansion,

$$| \psi(t) \rangle = \sum_n c_n(t) \, | \, \psi_n \rangle = \sum_n \langle \psi_n \, | \, \psi(t) \rangle \, | \, \psi_n \rangle \tag{1.99}$$

plus Schrödingerr equation. It provides a natural way to express coherences and to find the expectation value of operators which do not commute with the Hamiltonian, it treats *pure quantum states* and *statistical mixtures* on an equal footing, and it allows straightforward determination of the time evolution of the system even when it is affected by incoherent processes such as damping, addition or subtraction of atoms (from the system) or interactions with other quantized systems not accessible to measurement (eg. collisions).

An operator, A, with matrix elements

$$A_{nm} \equiv \langle \psi_n \, | \, A \, | \, \psi_m \rangle \tag{1.100}$$

has expectation value at time t

$$\langle A \rangle_t \equiv \langle \psi(t) \, | \, A \, | \, \psi(t) \rangle \tag{1.101}$$

$$= \sum_{mn} c_m^*(t) c_n(t) A_{nm} (\text{using Eq.} 1.99). \tag{1.102}$$

Clearly the correlation between the c_m and c_n coefficients is important - physically it reflects the coherence between the amplitude for being in states m and n. These correlations are naturally dealt with by the density operator

$$\rho(t) = \overline{| \, \psi(t) \rangle \langle \psi(t) \, |} \tag{1.103}$$

because its matrix elements are

$$\rho_{nm}(t) = c_m^*(t) c_n(t) \tag{1.104}$$

The bar here indicates an ensemble average over identically (but not necessarily completely) prepared systems. An ensemble average is essential to treat probabilities (eg. only the ensemble average of spin projections of atoms from an oven is zero although each atom will have $m = +1/2$ or $-1/2$ when measured), and an ensemble average is always implicit in using a density matrix. For notational simplicity, the averaging bar will be eliminated from here on.

The density matrix permits easy evaluation of expectation values: combining Eqs. 1.99 and Eq. 1.104 gives

$$\langle A \rangle_t = \sum_{nm} \rho_{nm} A_{mn} = Tr(\rho(t) A) \tag{1.105}$$

where Tr is the trace, i.e., the sum of the diagonal elements. Eq. 1.105

for $\langle A \rangle$ really involves two sums: the ensemble average in the preparation of the systems, and the usual quantum mechanical sum over the basis to find the expectation value.

The time evolution of the density matrix is determined by a first order differential equation which is obtained by applying Schrödingerr's equation to the time derivative of Eq. 1.103;

$$i\hbar\dot\rho = H\rho - \rho H \equiv [H, \rho]. \tag{1.106}$$

This reflects changes in ρ due solely to the interactions (eg. radiation, dc fields) included in the Hamiltonian - additional terms may be added to account for collisions, loss of atoms, damping, etc.

The density matrix operator also provides a convenient test for a properly normalized system (sum of all probabilities, $p_n = c_n^* c_n$, equal to unity)

$$Tr(\rho(t)) = 1, \tag{1.107}$$

and

$$Tr\rho^2 \leq Tr\rho. \tag{1.108}$$

where the equality implies a pure quantum state.

We always have in mind that ρ is to be used on a statistical ensemble of systems similarly prepared. If this preparation is sufficient to force the system into a pure state [so that Eq. 1.99 holds for each member of the ensemble], then the ensemble average is superfluous - if the preparation is insufficient, then there will be random phases between some of the $c_n's$ in Eq. 1.100 and some ensemble averages of $c_n^* c_m$ will have modulus less than $\mid c_n \mid\mid c_m \mid$. If no relative phase information is present in the ensemble the ensemble is termed a "mixture" (except it is pure if only one $\mid c_n \mid^2$ is non-zero).

1.5.2   Density matrix for two level system

The density matrix for a two level system is

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \text{ with } \rho_{12}^* = \rho_{21}^* \tag{1.109}$$

We shall consider a two level system in which $E_1 = \hbar\omega_0/2$ and $E_2 = -\hbar\omega_0/2$ where ω_0 is constant, and we shall subject it to an off-diagonal perturbation of arbitrary strength and time dependence: $\langle 1 \mid H' \mid 2 \rangle = (V_1 - iV_2)/2$. Thus

$$H_0 = \frac{\hbar}{2}\begin{pmatrix} \omega_0 & 0 \\ 0 & -\omega_0 \end{pmatrix} = \frac{\hbar\omega_0}{2}\sigma_z \tag{1.110}$$

and

$$H' = \frac{1}{2}\begin{pmatrix} 0 & V_1 - iV_2 \\ V_1 + iV_2 & 0 \end{pmatrix} = \frac{V_1}{2}\sigma_x + \frac{V_2}{2}\sigma_y \tag{1.111}$$

so

$$H = \frac{1}{2}\begin{pmatrix} \hbar\omega_0 & V_1 - iV_2 \\ V_1 + iV_2 & \hbar\omega_0 \end{pmatrix} = \frac{1}{2}[V_1\sigma_x + V_2\sigma_y + \hbar\omega_0\sigma_z] \tag{1.112}$$

is the full Hamiltonian (the σ's are Pauli spin matrices). This is a general enough system to encompass most two-level systems which are encountered in resonance physics.

Before solving for $\dot{\rho}$ (which we could do by grinding away using Eq. 1.106) we shall change variables in the density matrix:

$$\rho = \frac{1}{2}\begin{pmatrix} r_0 + r_3 & r_1 - ir_2 \\ r_1 + ir_2 & r_0 - r_3 \end{pmatrix} = \frac{1}{2}[r_0 I + r_1\sigma_x + r_2\sigma_y + r_3\sigma_z] \qquad (1.113)$$

There is no loss of generality in this substitution (it has 4 independent quantities just as ρ does), and it makes the physical constraints on ρ manifest, e.g.

$$Tr(\rho) = r_0 = 1 \qquad (1.114)$$

and $\rho_{12} = \rho_{21}^*$ obviously.

Now we have expressed both H and ρ in terms of Pauli spin matrices. We can now solve the equation of motion for $\rho(t)$,

$$i\hbar\dot{\rho} = [H, \rho], \qquad (1.115)$$

by using the cyclic commutation relations $[\sigma_j, \sigma_{j+1}] = 2i\sigma_{j+2}$ and then equating the coefficients of σ_x, σ_y, and σ_z, (rather than having to grind out the matrix products term by term):

$$\sigma_x : \dot{r}_1 = \frac{1}{\hbar}V_2 r_3 - \omega_0 r_2$$

$$\sigma_y : \dot{r}_2 = \omega_0 r_1 - \frac{1}{\hbar}V_1 r_3$$

$$\sigma_z : \dot{r}_3 = \frac{1}{\hbar}V_1 r_2 - \frac{1}{\hbar}V_2 r_1 \qquad (1.116)$$

These final results can be summerized by using the vector representation due [1]. Define

$$\boldsymbol{\omega} = \frac{1}{\hbar}V_1\hat{\boldsymbol{x}} + \frac{1}{\hbar}V_2\hat{\boldsymbol{y}} + \omega_0\hat{\boldsymbol{z}} \;\; \text{and} \;\; \hat{\boldsymbol{r}} = r_1\hat{\boldsymbol{x}} + r_2\hat{\boldsymbol{y}} + r_3\hat{\boldsymbol{z}} \qquad (1.117)$$

Using these definitions it is easy to see that Eq. 1.116,1.116, 1.116 become

$$\frac{d\boldsymbol{r}}{dt} = \boldsymbol{\omega} \times \boldsymbol{r} \qquad (1.118)$$

1.118 proves that the time evolution of the density matrix for our very general 2-level system is isomorphic to the behavior of a classic magnetic moment in a magnetic field which points along $\boldsymbol{\omega}$ (??. Our previous discussion showing that the quantum mechanical spin obeyed this equation also is therefore superfluous for spin 1/2 systems.)

One consequence of 1.118 is that $\boldsymbol{r}$ is always perpendicular to $\dot{\boldsymbol{r}}$ so that $|\boldsymbol{r}|$ does not change with time. This implies that if ρ is initially a pure state, ρ remains forever in a pure state no matter how violently $\boldsymbol{\omega}$ is gyrated, because

(recall $\sigma_i^2 = I$)

$$Tr\rho^2 = \frac{1}{2}(r_0^2 + r_1^2 + r_2^2 + r_3^2) = \frac{1}{2}(\mid \boldsymbol{r} \mid^2 + r_0^2) \qquad (1.119)$$

1.119 will be satisfied for all time since $\mid \boldsymbol{r} \mid^2$ doesn't change and, the state will remain pure. In general it is not possible to decrease the purity (coherence) of a system with a Hamiltonian like the one in 1.112. Since real coherences do, in fact die out, we shall have to add relaxation processes to our description in order to approach reality. The density matrix formulation makes this easy to do, and this development will be done in the next part of the section.

1.5.3   Phenomological treatment of relaxation: Bloch equations

Statistical mechanics tells us the form which the density matrix will ultimately take, but it does not tell us how the system will get there or how long it will take. All we know is that ultimately the density matrix will thermalize to

$$\rho^T = \frac{1}{Z}e^{-H_0/kT}, \qquad (1.120)$$

where Z is the partition function.

Since the interactions which ultimately bring thermal equilibrium are incoherent processes, the density matrix formulation seems like a natural way to treat them. Unfortunately in most cases these interactions are sufficiently complex that this is done phenomenologically. For example, the equation of motion for the density matrix 1.116 might be modified by the addition of a damping term:

$$\dot{\rho} = \frac{1}{i\hbar}[H, \rho] - (\rho - \rho^T)/T_e \qquad (1.121)$$

which would (in the absence of a source of non-equilibrium interactions) drive the system to equilibrium with time constant T_e.

This equation is not sufficiently general to describe the behavior of most systems studied in resonance physics, which exhibit different decay times for the energy and phase coherence, called T_1 and T_2 respectively.

- T_1 - decay time for population differences between non- degenerate levels, eg. for r_3 (also called the energy decay time)

- T_2 - decay time for coherences (between either degenerate or non-degenerate states), i.e. for r_1 or r_2.

The reason is that, in general, it requires a weaker interaction to destroy coherence (the relative phase of the coefficients of different states) than to destroy the population difference, so some relaxation processes will relax only the phase, resulting in $T_2 < T_1$. (caution: certain types of collisions violate this generality.)

The effects of thermal relaxation with the two decay times described above are easily incorporated into the vector model for the 2-level system since the z-component of the population vector $\boldsymbol{r}$ 1.117 represents the population difference

and r_x and r_y represent coherences (i.e. off-diagonal matrix elements of ρ): The results (which modify 1.119) are

$$\dot{\boldsymbol{r}}_z = \frac{1}{\hbar}(\boldsymbol{\omega} \times \boldsymbol{r})_2 - \left(r_z - r_z^T\right)/T_1 \tag{1.122}$$

$$\dot{\boldsymbol{r}}_{x,y} = \frac{1}{\hbar}(\boldsymbol{\omega} \times \boldsymbol{r})_{x,y} - \left(r_{x,y} - r_{x,y}^T\right)/T_2 \tag{1.123}$$

(r_z^T is determined from 1.120). For a magnetic spin system $\boldsymbol{r}$ corresponds directly to the magnetic moment $\boldsymbol{\mu}$. The above equations were first introduced by Bloch [4] in this context and are known as the Bloch equations.

The addition of phenomenological decay times does not generalize the density matrix enough to cover situations where atoms (possibly state-selected) are added or lost to a system. This situation can be covered by the addition of further terms to $\dot{\rho}$. Thus a calculation on a resonance experiment in which state-selected atoms are added to a two-level system through a tube which also permits atoms to leave (eg. a hydrogen maser) might look like:

$$\dot{\rho} = \frac{1}{i\hbar}[\rho, H] - \begin{pmatrix} (\rho_{11} - \rho_{11T})/T_1 & \rho_{12}/T_2 \\ \rho_{21}/T_2 & (\rho_{22} - \rho_{22T})/T_1 \end{pmatrix} \tag{1.124}$$
$$+ R\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} - \rho/T_{\text{escape}} - \rho/T_{\text{collision}}$$

R is the rate of addition of state-selected atoms

The last two terms express effects of atom escape from the system and of collisions (e.g. spin exchange) that can't easily be incorporated in T_1 and T_2.

The terms representing addition or loss of atoms will not have zero trace, and consequently will not maintain $\text{Tr}(\rho) = 1$. Physically this is reasonable for systems which gain or lose atoms; the application of the density matrix to this case shows its power to deal with complicated situations. In most applications of the above equation, one looks for a steady state solution (with $\dot{\rho} = 0$), so this does not cause problems.

1.5.4   Introduction: Electrons, Protons, and Nuclei

The two-level system is basic to atomic physics because it approximates accurately many physical systems, particularly systems involving resonance phenomena. All two-level systems obey the same dynamical equations: thus to know one is to know all. The archetype two level system is a spin-1/2 particle such as an electron, proton or neutron. The spin motion of an electron or a proton in a magnetic field, for instance, displays the total range of phenomena in a two level system. To slightly generalize the subject, however, we shall also include the motion of atomic nuclei. Here is a summary of their properties.

MASS

	electron	$m = 0.91 \times 10^{-31} kg$
	proton	$M_p = 1.67 \times 10^{-27}$ kg
	neutron	M_p
	nuclei	$M = AM_p$
		$A = N + Z =$ mass number
		Z = atomic number
		N = neutron number

CHARGE

	electron	-e $e = 1.60 \times 10^{-19}$ C
	proton	+e
	neutron	0
	nucleus	Ze

ANGULAR MOMENTUM

	electron	$S = \hbar/2$
	proton	$I = \hbar/2$
	neutron	$I = \hbar/2$
	nuclei	even A:$I/\hbar$ = 0, 1, 2, . . .
		odd A: $I/\hbar$ = 1/2, 3/2, . . .

STATISTICS

	electrons	Fermi-Dirac
	nuclei:	even A, Bose-Einstein
		odd A, Fermi-Dirac

ELECTRON MAGNETIC
MOMENT

$$\mu_e = \gamma_e S = -g_s \mu_B S/\hbar$$
$$\gamma_e = \text{gyromagnetic ratio} = e/m = 2\pi \times 2.80 \times 10^4 \text{MHzT}^{-1}$$
$$g_s = \text{free electron g-factor} = 2 \text{ (Dirac Theory)}$$
$$\mu_B = \text{Bohr magneton} = e\hbar/2m = 0.93 \times 10^{-24} \text{JT}^{-1} \text{ (erg/gauss)}$$

(Note that μ_e is negative. We show this explicitly by taking g_s to be positive, and writing $\mu_e = -g_s \mu_B S$)

NUCLEAR MAGNETIC
MOMENTS

$$\mu_{nuc} = \gamma_{nuc}\hbar I = g_{nuc}\mu_N I/\hbar$$
$$\gamma_I = \text{gyromagnetic ratio of the nucleus}$$
$$\mu_N = \text{nuclear magneton} = e\hbar/2Mc = \mu_B(m/M_p)$$

proton $\quad g_p = 5.6, \gamma_p = 2\pi \times 42.6 \text{ MHz T}^{-1}$

neutron $\quad g_n = -3.7$

References

[1] R.P. Feyman, F.L. Vernon, and R.W. Hellwarth, J. Appl. **28** 49 (1957).

[2] N.F. Ramsey, Phys. Rev. **76** 996 (1949).

[3] S.R. Lundeen and F.M. Pipkin, Phys. Rev. Lett. **34** , 1368 (1975).

[4] F. Bloch, Phys. Rev. **70** 460 (1946).

[5] Rubbermark et al., Phys. Rev. A **23**, 3107 (1981).

[6] A.H. Autler and C.H. Townes, Phys. Rev. **100**, 703, 1955.

[7] B.R. Mollow, Phys. Rev. A ??, 1522.

[8] B.R. Mollow, Phys. Rev. A **5**, 2217, 1972.

[9] R.E. Grove, F.Y. Wu, S. Ezekiel, Phys. Rev. A **15**, 227.

[10] R.M. Whitley and C.R. Stroud, Phys. Rev. A **14**, 1498.

[11] C. Delsart and J.C. Keller, J. Phys. B **9**, 2769.

[12] J.L. Picque and J. Pinard, J. Phys. B **9**, L77.

[13] F.Y. Wu, S. Ezekiel, M. Ducloy, B.R. Mollow, Phys. Rev. Lett. **38**, 1077.

Chapter 2
Atoms: Some Basics

This chapter comprises some miscellaneous topics in basic atomic physics. They do not form a unified exposition and the discussions are in some cases quite informal. The topics are intended to provide helpful reviews and to introduce a number of useful concepts.

2.1 Spectroscopic Notation

Neutral atoms consist of a heavy nucleus with charge Z surrounded by Z electrons. Positively charged atomic ions generally have structure similar to the atom with the same number of electrons except for a scale factor; negative ions lack the attractive Coulomb interaction at large electron-core separation and hence have few if any bound levels. Thus the essential feature of an atom is its number of electrons, and their mutual arrangement as expressed in the quantum numbers.

An isolated atom has two good angular momentum quantum numbers, J and M_J. (This is strictly true only for atoms whose nuclei have spin $I = 0$. However, J is never significantly destroyed by coupling to I in ground state atoms.) In zero external field the atomic Hamiltonian possesses rotational invariance which implies that each J level is degenerate with respect to the $2J + 1$ states with specific M_J (traditional atomic spectroscopists call these states "sublevels"). For each J,M_J an atom will typically have a large number of discrete energy levels (plus a continuum) which may be labeled by other quantum numbers.

If Russel-Saunders coupling ($L - S$ coupling) is a good description of the atom, then L and S, where

$$\mathbf{L} = \sum_{i=1}^{N} \boldsymbol{\ell}_i \tag{2.1}$$

$$\mathbf{S} = \sum_{i=1}^{N} \mathbf{S}_i \tag{2.2}$$

are nearly good quantum numbers and may be used to distinguish the levels. In this case the level is designated by a *Term* symbolized $^{2S+1}L_J$ where $2S+1$ and J are written numerically and L is designated with this letter code:

$$
\begin{array}{llllll}
L\text{:} & \text{O} & 1 & 2 & 3 & 4 & \text{...} \\
\text{Letter:} & S & P & D & F & G
\end{array}
$$

The Letters stand for Sharp, Principal, Diffuse, and Fundamental - adjectives applying to the spectral lines of one electron atoms. The term symbol is frequently preceded by the n value of the outermost electron, e.g. the $3^2S_{1/2}$ ground state of Na.

This discussion of the term symbol has been based on an external view of the atom. Alternatively one may have or assume knowledge of the internal structure - the quantum numbers of each electron. These are specified as the *configuration*, e.g.

$$1s^2 2s^2 2p^2, \tag{2.3}$$

a product of symbols of the form $n\ell^k$ which represents k electrons in the orbital n, ℓ. n is the principal quantum number, which characterizes the radial motion and has the largest influence on the energy. n and m are written numerically, but the *spdf* ... coding is used for ℓ. An example of the configuration for Ca is $1s^2 2s^2 2p^6 3s3d$ which is frequently abbreviated $3d$. In general each configuration leads to several terms which may be split apart by several eV. The above Ca configuration gives rise to $^1D_2$ and $^3D_{1,2,3}$ for example.

In classifying levels, the term is generally more important that the configuration because it determines the behavior of an atom when it interacts with E or B fields. Selection rules, for instance, generally deal with $\Delta J, \Delta L, \Delta S$. Furthermore the configuration may not be pure - if two configurations give rise to the same term (and have the same parity) then intra-atomic electrostatic interactions can mix them together. This process, called configuration interaction, results in shifts in the level positions and intensities of special lines involving them as well as in correlations in the motions of the electrons within the atoms.

2.2 One-Electron Atoms

In trying to understand some new phenomenon for the first time it is common sense (and good science) to study it in the simplest situation where it is manifest. With atoms it is evident that hydrogen is of paramount simplicity and, much of the "fundamental" physics which has been discovered in atoms has been discovered in hydrogen (but Na and other alkalis have taken over since tunable lasers arrived). In this chapter we shall use the phrase "one electron atom" to include not only atoms which are isoelectronic with H (e.g. He^+, Li^{++} ... etc.) but also atoms with one electron which is far less weakly bound than all the others so that the inner electrons may be considered collectively as a core whose interaction with the active electron may be adequately described by parameters such as a scattering length for low energy electrons, polarizability, etc.

2.2.1   The Bohr Atom

We briefly review the Bohr atom– a model that was soon obsolete, but which nevertheless provided the major impetus for developing quantum mechanics. Balmer's empirical formula of 1885 had reproduced Angstrom's observations of spectral lines in hydrogen to 0.1 Å accuracy, but it was not until 1913 that Bohr gave an explanation for this based on a quantized mechanical model of the atom. This model involved the postulates of the Bohr Atom:

- Electron and proton are point charges whose interaction is coulombic at all distances.

- Electron moves in circular orbit about the center of mass in *stationary states* with orbital angular momentum $L = n\hbar$.

These two postulates give the energy levels:

$$-E_n = \frac{1}{2}\left(\frac{m(e^2/4\pi\epsilon_o)^2}{\hbar^2}\frac{M}{M+m}\right)\Big/n^2 = hcR_H/n^2 \qquad (2.4)$$

where $m(e^2/4\pi\epsilon_o)^2/\hbar^2$ is the hartree[2], $M/(M+m)$ is the reduced mass factor, and R_H is the Rydberg in H: ($R_H = 1.09677576 \times 10^5$ cm^{-1}), and $hcR_H = 13.6$ eV.

- One quantum of radiation is emitted when the system changes between these energy levels.

- The wave number of the radiation is given by the Bohr frequency criterion:

$$\sigma_{n\to m} = (E_n - E_m)/(hc)$$

(Note that the wave number is a spectroscopic unit defined as the number of wavelengths per cm, $\sigma = 1/\lambda$. It is important not to confuse the wave number with the magnitude of the *wave vector* $\mathbf{k}$ which defines a traveling wave of the form $\exp i(\mathbf{k}\cdot\mathbf{r} - \omega t)$. The magnitude of the wave vector is 2π times the wave number.

The mechanical spirit of the Bohr atom was extended by Sommerfeld in 1916 using the Wilson-Sommerfeld quantization rule,

$$\oint p_i dq_i = n_i h \qquad (2.5)$$

where q_i and p_i are conjugate coordinate and momentum pairs for each degree of freedom of the system. This extension yielded elliptical orbits which were found to have an energy nearly degenerate with respect to the orbital angular momentum for a particular principal quantum number n. The dependency was lifted by a relativistic correction whose splitting was in agreement with the observed fine structure of hydrogen. (This was a great cruel coincidence in physics. The mechanical description ultimately had to be completely abandoned, in spite of the excellent agreement of theory and experiment.) Although triumphant in hydrogen, simple mechanical models of helium or other two-electron atoms failed, and real progress in understanding atoms had to await the development of quantum mechanics.

2.2.2   Radial Schrödinger equation for central potentials

Stationary solutions of the time dependent Schrödinger equation

$$i\hbar\frac{\partial\psi(\mathbf{r},\mathbf{t})}{\partial t} = H(\mathbf{r})\psi(\mathbf{r},\mathbf{t}) \qquad (2.6)$$

---

[2]There is often confusion about the capitalization of units named after people. The rule is that the unit is spelled lower case, but the abbreviation is upper case. Thus, 2.4 newton, or 2.4 N.

(H is the Hamiltonian operator) can be represented as

$$\psi(\mathbf{r}, t) = e^{-iE_n t/\hbar}\psi_n(\mathbf{r}), \tag{2.7}$$

where n stands for all quantum numbers necessary to label the state. This leads to the time-independent Schrödinger equation

$$[H(\mathbf{r}) - E_n]\psi_n(\mathbf{r}) = \mathbf{0} \tag{2.8}$$

A pervasive application of this equation in atomic physics is for the case of a spherically symmetric one-particle system of mass μ. In this case the Hamiltonian is

$$H \equiv \text{Kinetic Energy }+\text{ Potential Energy}$$

$$= p^2/2\mu + V(r) = \frac{-\hbar^2\nabla^2}{2\mu} + V(r)$$

$$= -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r) \quad (2.9)$$

where the kinetic energy operator ∇^2 has been written in spherical coordinates. Because V is spherically symmetric, the angular dependence of the solution is characteristic of spherically symmetric systems in general and may be factored out:

$$\psi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi) \tag{2.10}$$

$Y_{\ell m}$ are the *spherical harmonics* and ℓ is the eigenvalue of the operator for the orbital angular momentum, $\mathbf{L}$,

$$L^2 Y_{\ell m} = \ell(\ell+1)\hbar^2 Y_{\ell m} \tag{2.11}$$

and m is the eigenvalue of the projection of L on the quantization axis (which may be chosen at will)

$$L_z Y_{\ell m} = m\hbar Y_{\ell m} \tag{2.12}$$

With this substitution Eq. 2.10 the time independent radial Schrödinger equation becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_{n\ell}}{dr}\right) + \left[\frac{2\mu}{\hbar^2}[E_{n\ell} - V(r)] - \frac{\ell(\ell+1)}{r^2}\right]R_{n\ell} = 0 \tag{2.13}$$

This is the equation which is customarily solved for the hydrogen atom's radial wave functions. For most applications (atoms, scattering by a central potential, diatomic molecules) it is more convenient to make a further substitution.

$$R_{n\ell}(r) = y_{n\ell}(r)/r \tag{2.14}$$

which leads to

$$\frac{d^2 y_{n\ell}(r)}{dr^2} + \left[\frac{2\mu}{\hbar^2}[E_{n\ell} - V(r)] - \frac{\ell(\ell+1)}{r^2} \right] y_{n\ell}(r) = 0 \qquad (2.15)$$

with the boundary condition $y_{n\ell}(0) = 0$. This equation is identical with the time independent Schrödinger equation for a particle of mass μ in an effective one dimensional potential,

$$V^{\text{eff}}(r) = V(r) + L^2/(2\mu r^2) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \qquad (2.16)$$

The term $\hbar^2 \ell(\ell+1)/2\mu r^2$ is called the *centrifugal potential*, and adds to the actual potential the kinetic energy of the circular motion that must be present to conserve angular momentum.

2.2.3   Radial equation for hydrogen

The quantum treatment of hydrogenic atoms or ions appears in many textbooks and we present only a summary[3]. For hydrogen Eq. 2.15 becomes

$$\frac{d^2 y_{n\ell}(r)}{dr^2} + \left[\frac{2\mu}{\hbar^2} \left[E_n + \frac{e^2}{r} \right] - \frac{\ell(\ell+1)}{r^2} \right] y_{n\ell}(r) = 0 \qquad (2.17)$$

First look at this as $r \to 0$, the dominant terms are

$$\frac{d^2 y}{dr^2} - \frac{\ell(\ell+1)}{r^2} y = 0 \qquad (2.18)$$

for any value of E. It is easily verified that the two independent solutions are

$$y \sim r^{\ell+1} \text{ and } y \sim r^{-\ell} \qquad (2.19)$$

For $\ell \geq 1$ the only normalizable solution is $y \sim r^{\ell+1}$.

Question: What happens to these arguments for $\ell = 0$? What implications does this have for the final solution? Messiah has a good discussion of this.

We look next at the solution for $r \to \infty$ where we may investigate a simpler equation if $\lim_{r \to \infty} rV(r) = 0$. For large r:

$$\frac{d^2 y}{dr^2} + \frac{2\mu E}{\hbar^2} y = 0 \qquad (2.20)$$

If $E > 0$, this equation has oscillating solutions corresponding to a free particle. For $E < 0$ the equation has exponential solutions, but only the decaying

---

[3]The most comprehensive treatment of hydrogen is the classic text of Bethe and Salpeter, *The Quantum Mechanics of One- and Two-Electron Atoms*, H. A. Bethe and E. E. Salpeter, Academic Press (1957). Messiah is also excellent.

exponential is physically acceptable (i.e. normalizable)

$$R(r) = y(r)/r = \frac{1}{r}e^{-(-2\mu E/\hbar^2)^{\frac{1}{2}}r} \tag{2.21}$$

When $E < 0$, it is possible to obtain physically reasonable solutions to Eq. 2.15 (or indeed *any* bound state problem) only for certain discrete values of E, its eigenvalues. This situation arises from the requirement that the radial solution be normalizable, which requires that $\int_o^\infty y^2(r)dr = 1$, or alternatively, that $y(r)$ vanishes sufficiently rapidly at large r.

Eq. 2.17 is a prescription for generating a function $y(r)$ for arbitrary $E < 0$ given y and dy/dr at any point. This can be solved exactly in hydrogen. For other central potentials, one can find the eigenvalues and eigenstates by computation. One proceeds as follows: Select a trial eigenvalue, $E < 0$. Starting at large r a "solution" of the form of Eq. 2.21 is selected and extended in to some intermediate value of r, r_m. At the origin one must select the solution of the form $y_\ell \sim r^{\ell+1}$ Eq. (2.19); this "solution" is then extended out to r_m. The two "solutions" may be made to have the same value at r_m by multiplying one by a constant; however, the resulting function is a valid solution only if the first derivative is continuous at r_m, and this occurs only for a discrete set of $E_{n\ell}$. The procedure described here is, in fact, the standard Numerov-Cooley algorithm for finding bound states. Its most elegant feature is a procedure for adjusting the trial eigenvalue using the discontinuity in the derivative that converges to the correct energy very rapidly.

For the hydrogen atom, the eigenvalues can be determined analytically. The substitution

$$y_\ell(r) = r^{\ell+1}e^{-(-2\mu E/\hbar^2)^{1/2}r}v_\ell(r) \tag{2.22}$$

leads to a particularly simple equation. To make it dimensionless, one changes the variable from r to x

$$x = [2(-2\mu E)^{1/2}/\hbar]r \tag{2.23}$$

so the exponential in Eq. 2.22 becomes $e^{-1/2x}$), and defines

$$v = \frac{\hbar}{(-2\mu E)^{1/2}a_o} \tag{2.24}$$

where a_o is the Bohr radius:

$$\left[x\frac{d^2}{dx^2} + (2\ell + 2 - x)\frac{d}{dx} - (\ell + 1 - v)\right]v_\ell = 0 \tag{2.25}$$

This is a Laplace equation and its solution is a confluent hypergeometric series. To find the eigenvalues one now tries a Taylor series

$$v_\ell(x) = 1 + a_1x + a_2x^2 + \cdots \tag{2.26}$$

for v_ℓ. This satisfies the equation only if the coefficients of each power of x are

satisfied, i.e..

$$
\begin{aligned}
x^o &: \quad (2\ell + 2)a_1 - (\ell + 1 - v) = 0 \\
x^1 &: \quad 2(2\ell + 3)a_2 - (\ell + 2 - v)a_\ell = 0 \\
x^{p-1} &: \quad p(2\ell + 1 + p)a_p - (\ell + p - v)a_{p-1} = 0
\end{aligned}
\tag{2.27}
$$

The first line fixes a_1, the second then determines a_2, and in general

$$
a_p = \frac{(\ell + p - v)}{p(2\ell + 1 + p)} a_{p-1}
\tag{2.28}
$$

In general Eq. 2.27 will give a pth coefficient on the order of $1/p!$ so

$$
v_\ell(x) \sim \sum_{p=0} x^p/p! = e^x
\tag{2.29}
$$

this spells disaster because it means $y = r^{\ell+1}e^{-x/2}v_\ell(r)$ diverges. The only way in which this can be avoided is if the series truncates, i.e. if v is an integer:

$$
v = n = n' + \ell + 1 \qquad n = 0, 1, 2, \cdots
\tag{2.30}
$$

so that a_n, will be zero and v_ℓ will have n' nodes. Since $n' >= 0$, it is clear that you must look at energy level $n \geq \ell + 1$ to find a state with angular momentum ℓ (e.g. the $2d$ configuration does not exist). This gives the eigenvalues of hydrogen (from Eq. 2.24)

$$
E_n = -\frac{1}{2}\alpha^2\mu c^2/(n' + \ell + 1)^2 = -\frac{1}{2}\frac{\mu(e^2/4\pi\epsilon_o)^2}{\hbar^2}\frac{1}{n^2} = -\frac{hcR_H}{n^2},
\tag{2.31}
$$

which agrees with the Bohr formula.

2.3 One Electron Atoms with Cores: The Quantum Defect

2.3.1   Phenomenology

It is observed that the eigenvalues of atoms which have one valence electron have the same density (in energy space) as those of hydrogen, but not the same positions. If one defines an effective quantum number

$$
n* = (R/E_n)^{1/2}
\tag{2.32}
$$

such that

$$
T_n = -\frac{const}{n*^2}
\tag{2.33}
$$

then the formula can naturally reproduce the energy levels of a particular term (e.g. D). However, it was found that the n^* values for adjacent levels differ by almost exactly 1.000, especially after the first few terms. Thus the term energy can be written

$$
T_n = -\frac{const}{n^2 - \delta_\ell^2}
\tag{2.34}
$$

where the *quantum defect* δ_ℓ is defined by

$$\delta_\ell \equiv n - n^*. \tag{2.35}$$

Here, n is the principal quantum number of the valence electron for that term (if one does not know n, using the closest larger integer than n^* still leads to useful results), remains very constant with respect to n, but decreases rapidly with respect to L. A more accurate empirical formula for the term values of a series is the Balmer-Ritz formula

$$T_n = \frac{Z^2 R}{(n - \delta_\ell - \beta_\ell/n^2)^2} \tag{2.36}$$

A somewhat related concept in the study of x-ray lines was proposed by Moseley. When comparing spectra of isoelectronic ions, he found that a useful empirical formula was

$$T_n = \frac{(Z - \Delta Z)^2 R}{n^2} \tag{2.37}$$

in which the charge is adjusted, rather than n. ΔZ may be regarded as the amount of nuclear charge shielded by the core electrons, and an effective nuclear charge, $Z_e = Z - \Delta Z$ can be introduced.

2.3.2   Explanation

It must always be kept in mind that the quantum defect is a phenomenological result. To explain how such a simple result arises is obviously an interesting challenge, but it is not to be expected that the solution of this problem will lead to great new physical insight. The only new results obtained from understanding quantum defects in one electron systems are the connection between the quantum defect and the electron scattering length for the same system (Mott and Massey section III 6.2) which may be used to predict low energy electron scattering cross sections (ibid. XVII 9&10), and the simple expressions relating δ_L to the polarizability of the core for larger δ_L [1]. The principal use of the quantum defect is to predict the positions of higher terms in a series for which δ_L is known.

Explanations of the quantum defect range from the elaborate fully quantal explanation of Seaton [2] to the extremely simple treatment of Parsons and Weisskopf [3], who assume that the electron can not penetrate inside the core at all, but use the boundary condition $R(r_c) = 0$ which requires relabeling the lowest ns state 1s since it has no nodes outside the core. This viewpoint has a lot of merit because the exclusion principle and the large kinetic energy of the electron inside the core combine to reduce the amount of time it spends in the core. This is reflected in the true wave function which has n nodes in the core and therefore never has a chance to reach a large amplitude in this region.

To show the physics without much math (or rigor) we turn to the JWKB solution to the radial Schrödinger Equation (see Messiah Ch. VI). Defining the

wave number

$$k_\ell(r) = \sqrt{2m[E - V_{\text{eff}}(r)]}\hbar \quad \text{(remember } V_{\text{eff}} \text{ depends on } \ell) \tag{2.38}$$

then the phase accumulated in the classically allowed region is

$$\phi_\ell(E) = \int_{r_i}^{r_o} k_\ell(r)dr \tag{2.39}$$

where r_i and r_o are the inner and outer turning points. Bound state eigenvalues are found by setting

$$[\phi_\ell(E) - \pi/2] = n\pi \tag{2.40}$$

(The $\pi/2$ comes from the connection formulae and would be $1/4$ for $\ell = 0$ state where $r_i = 0$. Fortunately it cancels out.)

To evaluate $\phi(E)$ for hydrogen use the Bohr formula for $n(E)$,

$$\phi_H(E) = \pi(hcR_H/E)^{1/2} + \pi/2 \quad \text{(independent of } \ell) \tag{2.41}$$

In the spirit of the JWKB approximation, we regard the phase as a continuous function of E. Now consider a one-electron atom with a core of inner shell electrons that lies entirely within r_c. Since it has a hydrogenic potential outside of r_c, its phase can be written (where r_{oH}, r_{iH} are the outer and inner turning points for hydrogen at energy E):

$$\phi_\ell(E) = \int_{r_i}^{r_{oH}} k_\ell(r)dr = \int_{r_i}^{r_c} k_\ell(r)dr + \int_{r_c}^{r_{oH}} k_H(r)dr$$

$$= \int_{r_i}^{r_c} k(r)dr - \int_{r_{iH}}^{r_c} k_H(r)dr + \int_{r_{iH}}^{r_{oH}} k_H(r)dr$$

The final integral is the phase for hydrogen at some energy E, and can be written as $\phi_H(E) = (n*+1/2)\pi$. Designating the sum of the first two integrals by the phase $\delta\phi$, then we have

$$\delta\phi + (n*+1/2)\pi = (n + 1/2)\pi \tag{2.42}$$

or

$$n* = n - \delta\phi/\pi \tag{2.43}$$

Hence, we can relate the quantum defect to a phase:

$$\delta_\ell = \left[\int_{r_i}^{r_c} k(r)dr - \int_{r_{iH}}^{r_c} k_H(r)dr \right] \frac{1}{\pi} \tag{2.44}$$

since it is clear from Eq. 2.38 and the fact that the turning point is determined by $E + V_{\text{eff}}(r_i) = 0$ that δ_ℓ approaches a constant as $E \to 0$.

Now we can find the bound state energies for the atom with a core; starting with Eq. 2.40,

$$n\pi = \phi(E) - \pi/2$$

$$= \pi\delta_L(E) + \pi(hcR_H/E)^{1/2}$$

$$\Rightarrow E = hcR_H/[n - \delta_L(E)]^2 \equiv \frac{hcR_H}{[n - \delta_\ell^{(0)} + \delta_\ell^{(1)}hcR_H/n^2]^2} \qquad (2.45)$$

thus we have explained the Balmer-Ritz formula (Eq. 2.36).

If we look at the radial Schrödinger equation for the electron ion core system in the region where $E > 0$ we are dealing with the scattering of an electron by a modified Coulomb potential (Mott & Massey Chapter 3). Intuitively one would expect that there would be an intimate connection between the bound state eigenvalue problem described earlier in this chapter and this scattering problem, especially in the limit $E \to 0$ (from above and below). Since the quantum defects characterize the bound state problem accurately in this limit one would expect that they should be directly related to the scattering phase shifts $\sigma_\ell(k)$ (k is the momentum of the *free* particle) which obey

$$\lim_{k \to 0} \cot[\sigma_\ell(k)] = \pi\delta_\ell^o \qquad (2.46)$$

This has great intuitive appeal: $\pi\delta_\ell^o$ as discussed above is precisely the phase shift of the wave function with the core present relative to the one with V $=$ e^2/r. On second thought Eq. 2.46 might appear puzzling since the scattering phase shift is customarily defined as the shift relative to the one with $V = 0$. The resolution of this paradox lies in the long range nature of the Coulomb interaction; it forces one to redefine the scattering phase shift, $\sigma_\ell(k)$, to be the shift relative to a pure Coulomb potential.

2.3.3   Quantum defects for a model atom

Now we give a calculation of a quantum defect for a potential $V(r)$ which is not physically realistic, but has only the virtue that it is easily solvable. The idea is to put an extra term in the potential which goes as $1/r^2$ so that the radial Schrödinger equation (Eq. 2.15) can be solved simply by adjusting ℓ. The electrostatic potential corresponds to having all the core electrons in a small cloud of size r_n (which is a nuclear size) which decays as an inverse power of r.

$$\phi_\ell(r) = \frac{e}{r} + \frac{(Z-1)er_n}{2r^2}$$

$$\Rightarrow E(r) = \frac{e}{r^2} + \frac{(Z-1)er_n}{r^3}$$

$$\Rightarrow Q_{\text{inside}}(r) = e + \frac{(Z-1)er_n}{r}$$

$$\Rightarrow \rho(r) = \frac{dQ/dr}{4\pi r^2} = -(Z-1)er_n/4\pi r^4 \qquad (2.47)$$

At $r = r_n$, $Q_{\text{inside}}(r_n) = Ze$. We presume r_n is the nuclear size and pretend that it is so small we don't have to worry about what happens inside it.

When the potential V $(r) = -e\phi(r)$ is substituted in Eq. 2.17, one has

$$\frac{d^2y}{dr^2} + \left[\frac{2\mu}{\hbar^2}\left[E_n + \frac{e^2}{r}\right] - \frac{\ell(\ell+1) - A}{r^2}\right]y = 0 \qquad (2.48)$$

$$\text{where} \quad A = \frac{2\mu(Z-1)e^2r_n}{\hbar^2} \qquad (2.49)$$

If one now defines

$$\ell'(\ell'+1) = \ell(\ell+1) - A \qquad (2.50)$$

then $\ell' < \ell$ since $A > 0$, and one can write

$$\ell' = \ell - \delta_\ell \qquad (2.51)$$

Substituting Eq. 2.50 in Eq. 2.48 gives the radial Schrödinger equation for hydrogen, (Eq.2.15), except that ℓ' replaces ℓ; eigenvalues occur when (see Eq. 2.30)

$$v = n' + \ell' + 1 = n^* \qquad n' = 0, 1, 2, \cdots \qquad (2.52)$$

where n' is an integer. Using $n = n' + \ell + 1$ as before, we obtain the corresponding eigenvalues as

$$E_n = hcR_H/n^{*2} = hcR_H/(n - \delta_\ell)^2 \qquad (2.53)$$

The quantum defect is independent of E

$$\delta_\ell = \ell - \ell' = n - n^* \qquad (2.54)$$

Eq. 2.50 may be solved for δ_ℓ using the standard quadratic form. Retaining the solution which $\to 0$ as $Z \to 1$, gives

$$\delta_\ell = (\ell + 1/2) - \sqrt{(\ell+1/2)^2 - A} \approx \frac{A}{2\ell + 1} \text{ for } A << \ell + 1/2 \qquad (2.55)$$

This shows that $\delta_\ell \to 0$ as $\ell \to \infty$.

In contrast to the predictions of the above simple model, quantum defects for realistic core potentials decrease much more rapidly with increasing ℓ [for example as $(\ell + 1/2)^{-3}$] and generally exhibit $\delta_\ell^{(0)}$ close to zero for all ℓ greater than the largest ℓ value occupied by electrons in the core.

2.4 Metrology and Precision Measurement and Units

As scientists we take the normal human desire to understand the world to quantitative extremes. We demand agreement of theory and experiment to the greatest accuracy possible. We measure quantities way beyond the current level of theoretical understanding in the hope that this measurement will be valuable as a reference point or that the difference between our value and some other nearly equal or simply related quantity will be important. The science of measurement, called metrology, is indispensable to this endeavor because the accuracy of measurement limits the accuracy of experiments and their intercomparison. In fact,

the construction, intercomparison, and maintenance of a system of units is really an art (with some, a passion), often dependent on the latest advances in the art of physics (e.g. quantized Hall effect, cold atoms, trapped particle frequency standards).

As a result of this passion, metrological precision typically marches forward a good fraction of an order of magnitude per decade. Importantly, measurements of the same quantity (e.g. α or e/h) in different fields of physics (e.g. atomic structure, QED, and solid state) provide one of the few cross-disciplinary checks available in a world of increasing specialization. Precise null experiments frequently rule out alternative theories, or set limits on present ones. Examples include tests of local Lorentz invariance, and the equivalence principle, searches for atomic lines forbidden by the exclusion principle, searches for electric dipole moments (which violate time reversal invariance), and searches for a "fifth [gravitational] force".

A big payoff, often involving new physics, sometimes comes from attempts to achieve routine progress. In the past, activities like further splitting of the line, increased precision and trying to understand residual noise have led to the fine and hyperfine structure of H, anomalous Zeeman effect, Lamb shift, and the discovery of the 3K background radiation. One hopes that the future will bring similar surprises. Thus, we see that precision experiments, especially involving fundamental constants or metrology not only solidify the foundations of physical measurement and theories, but occasionally open new frontiers.

This chapter deals briefly with SI units (and its ancestor, the mks system), then systems of units which might appear more natural to a physicist, and then introduces atomic units, which will be used in this course.

2.4.1   Dimensions and Dimensional Analysis

Oldtimers were brought up on the mks system - meter, kilogram, and second. This simple designation emphasized an important fact: three dimensionally independent units are sufficient to span the space of all physical quantities. The dimensions are respectively ℓ - length, m-mass, and t-time. These three dimensions suffice because when a new physical quantity is discovered (e.g. charge, force) it always obeys an equation which permits its definition in terms of m,k, and s. Some might argue that fewer dimensions are necessary (e.g. that time and distance are the same physical quantity since they transform into each other in moving reference frames); we'll keep them both, noting that the definition of length is now based on the speed of light. Practical systems of units have additional units beyond those for the three dimensions, and often additional "as defined" units for the same dimensional quantity in special regimes (e.g. x-ray wavelengths or atomic masses).

Dimensional analysis consists simply in determining for each quantity its dimension along the three dimensions (seven if you use the SI system rigorously)

of the form

Dimension $(G) = [G] = m^{-1}l^3t^{-2}$, where $[x] \equiv$ dimensions of x.

Dimensional analysis yields an estimate for a given unknown quantity by combining the known quantities so that the dimension of the combination equals the dimension of the desired unknown. The art of dimensional analysis consists in knowing whether the wavelength or height of the water wave (both with dimension l) is the length to be combined with the density of water and the local gravitational acceleration to predict the speed of the wave.

2.4.2 SI units

A single measurement of a physical quantity, by itself, never provides information about the physical world, but only about the size of the apparatus or the units used. In order for a single measurement to be significant, some other experiment or experiments must have been done to measure these "calibration" quantities. Often these have been done at an accuracy far exceeding our single measurement so we don't have to think twice about them. For example, if we measure the frequency of a rotational transition in a molecule to six digits, we have hardly to worry about the calibration of the frequency generator if it is a high accuracy model that is good to nine digits. And if we are concerned we can calibrate it with an accuracy of several more orders of magnitude against station WWV or GPS satellites which give time valid to 20 ns or so.

Time/frequency is currently the most accurately measurable physical quantity and it is relatively easy to measure to 10^{-12}. In the SI (System International, the agreed-upon systems of weights and measures) the second is defined as 9,192,631,770 periods of the Cs hyperfine oscillation in zero magnetic field. Superb Cs beam machines at places like NIST-Boulder provide a realization of this definition at about 10^{-14}. Frequency standards based on laser- and evaporatively cooled atoms and ions are doing several orders of magnitude better owing to the longer possible measurement times and the reduction of Doppler frequency shifts. For example, recent experiments on degenerate samples of 100,000 fermionic ^{87}Sr trapped in an optical lattice at 100 nK are reaching fractional frequency uncertainty below 10^{-20} [?]. The expected clock stability is estimated at 3.1×10^{-18} in 1 second. In comparison, the age of the Universe is a few 10^{17} s. To give you an idea of the challenges inherent in reaching this level of precision, if you connect a 10 meter coaxial cable to a frequency source good at the 10^{-16} level, the frequency coming out the far end in a typical lab will be an order of magnitude less stable - can you figure out why?

The meter was defined at the first General Conference on Weights and Measures in 1889 as the distance between two scratches on a platinum-iridium bar when it was at a particular temperature (and pressure). Later it was defined more democratically, reliably, and reproducibly in terms of the wavelength of a certain orange krypton line. Most recently it has been defined as the distance

light travels in 1/299,792,458 of a second. This effectively defines the speed of light, but highlights the distinction between defining and realizing a particular unit. Must you set up a speed of light experiment any time you want to measure length? No: just measure it in terms of the wavelength of a He-Ne laser stabilized on a particular hfs component of a particular methane line within its tuning range; the frequency of this line has been measured to about a part in 10^{-11} and it may seem that your problem is solved. Unfortunately the reproducibility of the locked frequency and problems with diffraction in your measurement both limit length measurements at about 10^{-11}.

A list of spectral lines whose frequency is known to better than 10^{-9} is available on the homepage of the Bureau International de Poids et Mesures [4]. Also see the publication on the International System of Units (SI), 2019 by NIST [5], and the latest revision of the fundamental physical constants CODATA2018 NIST Reference on Constants, Units, and Uncertainty [6].

The third basic unit of the SI system is the kilogram, which until 2018 was the only fundamental SI base unit still defined in terms of an artifact - in this case a platinum-iridium cylinder kept in clean air at the Bureau de Poids et Measures in Severes, France. The dangers of mass change due to cleaning, contamination, handling, or accident are so perilous that this cylinder has been compared with the dozen secondary standards that reside in the various national measurement laboratories only two times in the last century. Clearly it was one of the major challenges for metrology to replace this artifact kilogram with an atomic definition. One way would have been to simply define Avogadro's number. While atomic mass can be measured to 10^{-11}, there is currently no sufficiently accurate method of realizing such a definition, however. (The unit of atomic mass, designated by m_u is 1/12 the mass of a ^{12}C atom.) The solution adopted by the 26th General Conference on Weights and Measures (CGPM) in 2018 was instead to define the Planck constant h to be exactly $6.626\,070\,15 \times 10^{-34}$ J s. So, h is no longer something we measure, it is defined.

There are four more base units in the SI system - the ampere, kelvin, mole, and the candela - for a total of seven. While three are sufficient (or more than sufficient) to do physics, the other four reflect the current situation that electrical quantities, atomic mass, temperature, and luminous intensity can be and are regularly measured with respect to auxiliary standards at levels of accuracy greater than those which can be expressed in terms of the above three base units. Thus measurements of Avogadro's constant, the Boltzmann constant, or the mechanical equivalents of electrical units play a role of interrelating the base units of mole (number of atoms of ^{12}C in 0.012 kg of ^{12}C), kelvin, or the new volt and ohm (defined in terms of Josephson and quantized Hall effects respectively). In fact independent measurement systems exist for other quantities such as x-ray wavelength (using diffraction from calcite or other standard crystals), but these other de facto measurement scales are not formally sanctified by the SI system.

---

[4]https://www.bipm.org/en/publications/mises-en-pratique/standard-frequencies
[5]https://doi.org/10.6028/NIST.SP.330-2019
[6]https://physics.nist.gov/cuu/Constants/

At the 26th CGPM a major step away from artifacts and towards universality was taken, in defining the values of Planck's constant, elementary charge, Boltzmann's constant, the Avogadro constant and to be complete, the luminous efficacy of monochromatic radiation of frequency 540×10^{12} Hz.

We can now simply say, quoting NIST publication 330 (see footnote above) "The International System of Units, the SI, is the system of units in which

- the unperturbed ground state hyperfine transition frequency of the cesium 133 atom $\Delta\nu_{\mathrm{Cs}}$ is 9 192 631 770 Hz,

- the speed of light in vacuum c is 299 792 458 m/s,

- the Planck constant h is 6.626 070 15 $\times 10^{-34}$ J s,

- the elementary charge e is 1.602 176 634 $\times 10^{-19}$ C,

- the Boltzmann constant k is 1.380 649 $\times 10^{-23}$ J/K,

- the Avogadro constant N_A is 6.022 140 76 $\times 10^{23}$ mol^{-1},

- the luminous efficacy of monochromatic radiation of frequency 540×10^{12} Hz, K_{cd}, is 683 lm/W,

where the hertz, joule, coulomb, lumen, and watt, with unit symbols Hz, J, C, lm, and W, respectively, are related to the units second, meter, kilogram, ampere, kelvin, mole, and candela, with unit symbols s, m, g, A, K, mol, and cd, respectively, according to Hz = s^{-1}, J = kgm^{2}s^{-2}, C = As, lm = cdm^{2}m^{-2} = cdsr, and W = kgm^{2}s^{-3}. The numerical values of the seven defining constants have no uncertainty."

This definition is nothing short of a paradigm shift, away from particular realizations of the unit, i.e. some metal bar in Paris, and more towards a permanent definition that will remain intact even as measurement capabilities advance. There are still differences in the various constants. The Planck constant h and the speed of light in vacuum c can be seen as fundamental, determining quantum effects and the properties of space-time. Choosing an atomic transition like $\Delta\nu_{\mathrm{Cs}}$ is less fundamental in character, and there are of course difficulties in implementing this definition in the lab, given field fluctuations and density-dependent shifts. At least, it is a universal reference, and for all we know constant in time, compared to e.g. a standard based on the rotation of the earth (which slows down over time).

The electric charge is connected to the strength of the electromagnetic force through the fine-structure constant α. For someone used to the *cgs* system, a hilarious apparent puzzle poses itself, as that person grew up learning $\alpha = \frac{e^2}{\hbar c}$. But now all constants appearing on the right of the equation are defined - so is α now no longer something we should measure, but it's forever fixed by the members of the CGPM 2018? Actually, no, but it gets first more confusing. In the SI system of units, remember that $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$, where ϵ_0 is the vacuum electric permittivity. Does that help? One might complain that it doesn't, since Maxwell taught us that $\epsilon_0\mu_0 = 1/c^2$, which is defined, and even people growing up with

the SI system learned that the vacuum magnetic permeability $\mu_0 = 4\pi \times 10^{-7}$.
Are we again concluding that α was suddenly defined in 2018? No, the hilarious
answer, to put it as a joke, is that "4π now has an error bar". More seriously, μ_0
is no longer exactly $4\pi \times 10^{-7}$! Performing more and more precise experiments
that connect electric charge to length, kilogram and second, for example the
"Watt balance" (Kibble balance) [7], will lead to a more precise value of μ_0 that's
just not quite $4\pi \times 10^{-7}$.

2.4.3   Metrology

The preceding discussion gives a rough idea of the definitions and realizations of
SI units, and some of the problems that arise in trying to define a unit for some
physics quantity (e.g. mass) that will work across many orders of magnitudes.
However, it sidesteps questions of the border between metrology and precision
measurements. (Here we have used the phrase "precision measurement" colloqui-
ally to indicate an accurate absolute measurement; if we were verbally precise,
precision would imply only excellent relative accuracy.)

The Boltzmann constant for example gives the ratio of energy scales defined
by the first three base units on the one hand and thermal energy that we call
one Kelvin. The Kelvin used to be defined by taking the triple point of water
as a fundamental fixed point and assigned to it the temperature 273.16 K. That
had practical difficulties. With k fixed, the triple point of water is now a thermal
energy that needs to be measured and that has an error bar. We are hardly learn-
ing any fundamental new physics from such a measurement, which is clearly of
metrological character. Similarly, measuring the hfs frequency of Cs would be a
metrological experiment in that it would only determine the length of the second.

If we measure the hfs frequency of H with high accuracy, this might seem like
a physics experiment since this frequency can be predicted theoretically. Unfor-
tunately theory runs out of gas at about 10^{-6} due to lack of accurate knowledge
about the structure of the proton (which causes a 42 ppm shift). Any digits
past this are just data collection until one gets to the 14th, at which point one
becomes able to use a H maser as a secondary time standard. This has stability
advantages over Cs beams for time periods ranging from seconds to days and so
might be metrologically useful – in fact, it is widely used in very long baseline
radio astronomy.

One challenge to using Nature's "quantized units" such as angular momen-
tum (h) and charge (e), and mass itself (which is quantized, although not so
simply), realized through Avogadro's constant (N_A^{-1} could have been thought of
as the mass quantum in grams) was that measurements of these "constants" in
the pre-2018 SI units are only accurate to about 10^{-8}, well below the accuracy
of the realization of the base units of the SI at the time. In 2018 one turned the
challenge around. Instead of defining, for example, the mass of the prototype kg

---

[7]The Kibble balance is a beam balance, with a test mass, coil and magnetic field on one
side and a counter balancing mass on the other. A feedback current passing through the coil
generates a force that balances the beam.

in Paris to be exactly 1 kg, and leaving h to be measured, now h is fixed and the mass of the prototype has to be measured - it now has an error bar.

To illustrate the intricacies one encounters, consider measurement of the Rydberg constant,

$$Ry_\infty = \frac{m_e e^4}{(4\pi)^3 \epsilon_0^2 \hbar^3 c} \tag{2.56}$$

a quantity which is an inverse length (an energy divided by $\hbar c$), closely related to the number of wavelengths per cm of light emitted by a H atom (the units are often given in spectroscopists' units, cm^{-1}, to the dismay of SI purists. Remember the conversion: $1\,\mathrm{cm}^{-1} \approx 30\,\mathrm{GHz}$). Clearly such a measurement determines a linear combination of the now defined fundamental quantities (and μ_0, which now has an error bar), which, as we said, were realized pre-2018 only to 10^{-8} accuracy. But Ry_∞ has recently been measured by several labs with results that agree to 10^{-11}. (In fact, the quantity that is measured is the Rydberg *frequency* for hydrogen, $c \times Ry_H$, since there is no way to measure wavelength to such precision.) This example illustrates a fact of life of precision experiments: with care you can trust the metrological realizations of physical quantities at accuracies to 10^{-7}; beyond that the limit on your measurement may well be partly metrological. In that case, what you measure is not in general clearly related to one single fundamental constant or metrological quantity. The importance of your experiment is determined by the size of its error bar relative to the uncertainty of all other knowledge about the particular linear combination of fundamental and metrological variables that you have measured.

2.5 Universal Units and Fundamental Constants

The sizes of the meter, kilogram and second were originally selected for convenience. They bear no relationship to things which most physicists would regard as universal or fundamental. Given the arbitrary scale of the "convenient units", physicists generally prefer to use systems of units that are natural for the problem at hand. We will now discuss Planck units, which seem most universal, and Atomic units fulfill this role when discussing atoms and their interactions with light. But let us start at the beginning by considering "are some of the fundamental constants listed by CODATA 2018 [8] more fundamental or universal?"

To begin, we assert that the three most universal constants are:

- c - the speed of light

- $\hbar$ - the quantum of action

- G - the gravitational constant

These quantities involve light, the quantum and gravitation. Since $\hbar$ can be related to measurements on light, these constants do not depend on the existence

---

[8]https://physics.nist.gov/cuu/Constants/

of quantized matter (only quantized radiation).

Next, we come to the atomic constants, whose magnitude is determined by the size of the quantized matter which we find all around us. Clearly, the most fundamental of these is:

e - the quantum of charge.

because it is the same (except for the sign) for all particles.

Even though the existence of quantized charge seems independent of the physics which underlies the construction of universal units, this is probably not the case because charge does not have independent units. In fact, the fine structure constant

$$\alpha \equiv \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} = (137.036\cdots)^{-1} \tag{2.57}$$

is arguably the only fundamental constant truly worthy of that name in atomic physics. High energy physicists regard α as the not so fundamental coupling strength of the electromagnetic interaction – At higher energies and correspondingly smaller distances, it gets larger as we approach the "bare charge" more closely. When we really understand E&M, QED, and the origins of quantized matter, we should be able to predict it. The fact that we have to measure it is a sign of our ignorance, but the good agreement of the many seemingly independent ways of measuring it in different subfields of physics shows that we begin to understand some things.

Other atomic constants like masses $(m_e, m_p, m_n, \cdots)$ and magnetic moments (u_e, u_p, u_n) seem to be rather arbitrary at our current level of physical knowledge except that certain relationships are given by QED ($\mu_e = -g_e e\hbar/(2m)$ with g_e a little more than 2) and quark models of the nucleons.

2.6 Atomic Units

Formulae in these notes will be displayed with the factors of $\hbar, e, m$ (m is the electron mass) etc., factored into atomic units to facilitate interpretation; numerical evaluations may be done using either atomic units or Gaussian-esu units. The system of atomic units (a.u.) is defined by setting $\hbar = m = e = 1$. Units for other physical quantities are formed by dimensionally suitable combinations of these units. When their use is frequent, they are given names (analogous to erg, dyne, etc., in cgs). In atomic units, the units of length and energy are the most important - they are called the Bohr (a_o) and Hartree (H) respectively. expressions for energy and length can generally be expressed in terms of H or a_o and powers of the dimensionless constant α.

2.7 The Fine Structure Constant

Quantity	Symbol	Value (to a few digits)	Name
*charge	e	$1.6 \times 10^{-19} C$	
*angular Momentum	$\hbar$	1.05×10^{-34} J s	
*mass	m	0.910×10^{-31} kg	
length	a_o	$\hbar^2/m(e^2/4\pi\epsilon_o)^2 = 0.53 \times 10^{-11}$ m	bohr
energy	H	$m(e^2/4\pi\epsilon_o)^2/\hbar^2 = 4.36 \times 10^{-18}$ J	hartree
		$\Rightarrow 27.2\text{eV} \Rightarrow 2\text{Ry} = 2.2 \times 10^7$ m^{-1}	
time	-	$\hbar^3/m(e^2/4\pi\epsilon_o)^2 = 2.42 \times 10^{-17}$ s	
velocity	-	$(e^2/4\pi\epsilon_o)/\hbar = \alpha_c = 2.2 \times 10^6$ m/s	
magnetic moment	μ_B	$e\hbar/2m = 1.4 \times 10^4$ MHz T^{-1}	Bohr magneton
electric field	-	$e/a_o^2 = 5.14 \times 10^{11}$ V/m	

*Charge, Angular Momentum and Mass are the *Basic Units*

$$\alpha = \frac{e^2}{4\pi\epsilon_o \hbar c} = (137.0606\cdots)^{-1} \tag{2.58}$$

is ubiquitous in atomic physics. The name, fine structure, reflects the appearance of this quantity (squared) in the ratio of the hydrogenic fine structure splitting to the Rydberg:

$$\frac{\Delta(\text{fine structure})}{\text{Rydberg}} = \alpha^2 \frac{Z^4}{n^3\ell(\ell+1)} \tag{2.59}$$

The fine structure constant will often crop up as the ratio between different physical quantities having the same dimensions. An impressive example of this is length: the "hydrogen wavelength" (1/Rydberg), Bohr radius, Compton wavelength, and classical radius of the electron are all related by powers of α.

References

[1] R.R. Freeman and D. Kleppner, Phys. Rev. A. (1967).

[2] M.J. Seaton, Proc. Phys. Soc. **88**, 801 (1966).

[3] R.G. Parsons and V.F. Weisskopf, Z. Phys. **202**, 492 (1967).

[4] E.R. Cohen and B.N. Taylor, Rev. Mod. Phys. **72**, No. 2 (2000).

[5] Bothwell, T., et al., Nature **602**, 420 (2022)