Chapter 1

Time dependent Schrodinger equation

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Quantum mechanics is interesting because states change. For example, a state can be subject to a rotation inside the Hilbert space. It may also be the case that a quantum state, which after all represents some physical reality, idly sits inside an environment which steers the quantum state to a new configuration. Therefore a quantum state at some time $|\psi(0)\rangle$, may evolve to give us some other state at a later time, $|\psi(t)\rangle$. If the state moves inside the Hilbert space and while doing so doesn't change its norm, then the dynamics is coherent and the time evolution can be described by a unitary operator

$$|\psi(t)\rangle = \hat{U}\,|\psi(0)\rangle$$

with $\hat{U}^\dagger = \hat{U}^{-1}$. The operator $\hat{U}(t)$ is also called a propagator since it moves the state in time.

While studying all of this, we can take some inspiration from Newton's law. Don't blame me for putting in a classical law into a book on quantum mechanics. Connections are always insightful. Newton's second law in one dimension reads

$$\frac{d^2x(t)}{dt^2} = \frac{f}{m} \tag{1.1}$$

and describes how an object of mass m changes its position $x(t)$ under the influence of a force f. One solves this equation to determine the evolution of the position. If f were a constant, the above equation produces the solution

$$x = x_o + \left.\frac{dx}{dt}\right|_{t=0} t + \frac{1}{2}\frac{f}{m}t^2. \tag{1.2}$$

Here x_o is the position at time $t = 0$, and $dx/dt|_{t=0}$ is the speed at this initial time. So these initial conditions help forecast the position at some later time. It is also possible to run time backwards, at least in the equations. Knowing the current position, constant force and mass, it is possible to predict the position at earlier times. This is the essence of Newton's deterministic law that works in almost all scenarios, unless of course you are working with quantum systems.

For quantum scenarios, you need an equation that is analogous to Newton's law and can determine state evolution. This is the time-dependent Schrodinger equation (TDSE), which just like its classical counterpart, cannot be derived. It can only be deduced from observations but its predictions work astoundingly well, at low energies. Even though it is a state evolution equation, it has remarkable and often apparently unsettling features when compared with Newton's equation. So let's now start our foray into understanding the TDSE.

1.1 Motivation for the time-dependent Schrodinger equation

1.1.1 Infinitesimal time evolutions

Consider an infinitesimal evolution which means that the unitary temporal operator acts only for a tiny period of time dt and write it in a manner similar to small angular rotations discussed earlier,

$$\hat{U}(dt) \approx \hat{\mathbf{1}} - i\hat{G}_t dt. \tag{1.3}$$

Compare this with the infinitesimal rotation operator along x

$$\hat{R}_x(d\theta) \approx \hat{\mathbf{1}} - i\hat{G}_x d\theta \tag{1.4}$$

wherein $\hat{G}_x$ is generating the rotation. Analogously $\hat{G}_t$ generates time evolution. The infinitesimal time evolution operator acts on an initial state $|\psi(0)\rangle$ to yield

$$\begin{aligned} \hat{U}(dt)\,|\psi(0)\rangle &\approx \left(\hat{\mathbf{1}} - i\hat{G}_t dt\right)|\psi(0)\rangle & (1.5)\\ &\approx |\psi(0)\rangle - i\hat{G}_t dt\,|\psi(0)\rangle\,. & (1.6)\end{aligned}$$

The inverse of $\hat{U}(dt)$ is really $\hat{U}^\dagger(dt)$. So putting the operator in Eq. (1.3) together with its inverse we obtain

$$\begin{aligned} \hat{U}^{-1}(dt)\hat{U}(dt) &= \hat{U}^\dagger(dt)\hat{U}(dt) & (1.7)\\ &\approx \left(\hat{\mathbf{1}} + i\hat{G}_t^\dagger dt\right)\left(\hat{\mathbf{1}} - i\hat{G}_t dt\right) & (1.8)\\ &= \hat{\mathbf{1}} + idt\left(\hat{G}_t - \hat{G}_t^\dagger\right) + O(dt^2) & (1.9)\\ &= \hat{\mathbf{1}}. & (1.10)\end{aligned}$$

In the second last equation, we reintroduced the equality sign by including the higher order terms $O(dt^2)$. For strict equality with $\hat{\mathbf{1}}$ all these terms must be equal to zero. The term $i\,dt\left(\hat{G}_t - \hat{G}_t^\dagger\right)$ must also be zero which implies $\hat{G}_t^\dagger = \hat{G}_t$. What kind of operator is this? No surprises, it's Hermitian. In complete analogy with the generator of rotation e.g. $\hat{G}_x = \hat{S}_x/\hbar$, the generator of temporal evolution can be defined as

$$\hat{G}_t = \frac{\hat{\mathcal{H}}}{\hbar}. \tag{1.11}$$

The constant $\hbar$ is just a number, a scaling factor and helps all the dimensions neatly fall in place while the operator $\hat{\mathcal{H}}$ is Hermitian

$$\hat{\mathcal{H}}^\dagger = \hat{\mathcal{H}} \tag{1.12}$$

and has a special name, the Hamiltonian.

A certain quantum state lives inside a physical environment. An elementary particle held fixed in a trap might see a stray electric field, magnetic field, there could be a nearby electron lurking around or the particle may be shone upon by a stream of photons. An electron inside an atom is always seeing protons inside the nucleus, electrons from the same or neighboring atoms, it might also be participating in some form of chemical bonding, or could be part of a molecular orbital. So there is little chance of witnessing a completely idealized isolated system. The Hamiltonian captures the interaction of the system with the environment and dictates to the system how to change with time. The environment can also be engineered. This is what a physics experimenter would do: create a composition of interactions that is meant to change the quantum state in a desired and hopefully predictable manner. This engineering means that some Hamiltonian may need to be sculpted.

1.1.2 The Schrodinger equation itself

This section uses the infinitesimal temporal propagation in Eq. (1.3) to deduce the time evolution operator over arbitrarily long but still finite time evolutions. Consider evolution for time $dt + t$. The operator $\hat{U}(t + dt)$ can be decomposed into two parts, evolution for a time t followed by shorter dt. The operators $\hat{U}(t)$ and $\hat{U}(dt)$ commute as it is immaterial how we section the time $t + dt$ into dt and t. Which comes first, dt or t doesn't really matter. Using Eq. (1.3) and Eq. (1.11) we obtain,

$$\begin{aligned}\hat{U}(t+dt) &= \hat{U}(dt)\hat{U}(t) && (1.13)\\ &\approx \left(\hat{\mathbf{1}} - i\frac{\hat{\mathcal{H}}}{\hbar}dt\right)\hat{U}(t) && (1.14)\\ &\approx \hat{U}(t) - i\frac{\hat{\mathcal{H}}}{\hbar}\hat{U}(t)dt. && (1.15)\end{aligned}$$

After some reshuffling,

$$\frac{\hat{U}(t+dt)-\hat{U}(t)}{dt} \approx -i\frac{\hat{\mathcal{H}}}{\hbar}\hat{U}(t) \tag{1.16}$$

and to turn the approximation into a strict equality, we take the limit that dt approaches zero:

$$\lim_{dt\to 0}\frac{\hat{U}(t+dt)-\hat{U}(t)}{dt} = -i\frac{\hat{\mathcal{H}}}{\hbar}\hat{U}(t). \tag{1.17}$$

The left hand side is a derivative of $\hat{U}(t)$ and this leads to the time-dependent Schrodinger equation

$$\frac{d\hat{U}(t)}{dt} = -i\frac{\hat{\mathcal{H}}}{\hbar}\hat{U}(t). \tag{1.18}$$

Bow in its glory and take a deep breath we have motivated the TDSE. But this is cunningly simple and looks much more concise than the time dependent Schrodinger equation we are all so familiar with,

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + U(x)\psi(x) = E\psi(x). \tag{1.19}$$

Don't worry. In later chapters, we will see how the form Eq. (1.18) leads to Eq. (1.19) when expressed appropriately.

The TDSE Eq. (1.18) has some properties we cannot miss. It is a differential equation in time. It has an imaginary unit i explicitly built in. It tells us how an operator $\hat{U}$ changes with time. So it's a complex valued differential equation for the time propagator. It's an operator equation.

Lets try to solve Eq. (1.18). Notice its similarity to a simple differential equation $dx(t)/dt = Ax(t)$ where A is a constant, whose solution is $x(t) = \exp(-At)$. Analogously the solution to the TDSE is proposed to be

$$\hat{U}(t) = e^{-i\frac{\hat{\mathcal{H}}}{\hbar}t}. \tag{1.20}$$

The solution provides the recipe of determining the propagation operator from the Hamiltonian. Exponentiate the Hamiltonian after multiplying it with $-it/\hbar$. The

Hamiltonian is Hermitian, but once multiplied with i, it becomes anti-Hermitian. The quantum state at initial time $|\psi(0)\rangle$ when acted upon by the unitary operator $\hat{U}(t)$, gives the state at later time $|\psi(t)\rangle$ and the time evolution is captured by the (solution of) TDSE

$$|\psi(t)\rangle = \hat{U}(t)\,|\psi(0)\rangle \quad \text{or} \tag{1.21}$$

$$|\psi(t)\rangle = e^{-i\frac{\hat{\mathcal{H}}}{\hbar}t}\,|\psi(0)\rangle\,. \tag{1.22}$$

These equations tell how the state evolves in time. You must remember them.

1.1 Show that if $\hat{\mathcal{H}}$ is Hermitian and constant, $U(t)$ is unitary.

1.2 Show that if $\hat{\mathcal{H}}$ is Hermitian and constant, $U(t)$ is unitary.

1.3 Show that $\exp\left(-i\frac{\hat{\mathcal{H}}}{\hbar}t\right)$ indeed solves the TDSE.

1.1.3 The Schrodinger and Heisenberg pictures

The operator equation (1.18) can also be expressed in a different form that takes away the focus from the time evolution of the operator to the time evolution of the state. Both pictures are perfectly valid, equivalent and equally useful in real calculations. For this, one can differentiate Eq. (1.22) to obtain

$$i\hbar\frac{d}{dt}\,|\psi(t)\rangle = \hat{\mathcal{H}}\,|\psi(t)\rangle\,. \tag{1.23}$$

which shifts our attention to evolving states inside of evolving operators. Eq. (1.18) and (1.23) are called the time-dependent Schrodinger equation in the Hiesenberg and Schrodinger pictures—the Schrodinger picture of the Schrodinger equation, tautologically refreshing! The solution to the Heisenberg version is (1.20) and the solution to the Schrodinger form is (1.22).

The hypothetical Hilbert space with a state evolving in time is shown in Figure 1.1. The state may change with time advertently or inadvertently. If the state is being changed by the environment that is beyond our control then it is inadvertent evolution and is commonly called decoherence, the bane of quantum computers. However physicists prefer to make deliberate changes to the state. In either case, the state changes with time. If we know the Hamiltonian that is governing the change we can predict the future state. The TDSE is therefore a deterministic equation and it is not shortchanged by the uncertainty principle. It is just like Newton's second law of motion. One major difference is the non-zero commutation between state variables. The Hamiltonian governs how the state changes with time, just as force determines the position of particle.

Note that in all foregoing discussion, the Hamiltonian is a constant of motion, it is independent of time. This forms the simplest kind, but in reality, the

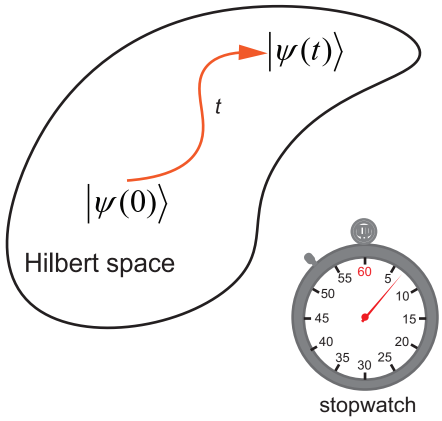

Figure 1.1: Temporal evolution of the state in Hilbert space under the action of unitary operator $\hat{U}$

Hamiltonian can also depend on time. This is more complicated but important enough that we cannot not overlook its possibility. Just be patient and read on till the end, yes the end, of this book.

1.2 More about the Hamiltonian

1.2.1 Energy eigenvalues and eigenvectors

The Hamiltonian is Hermitian so its eigenvalues are real and correspond to the measurement outcomes of some observable. In this section, we aim to understand the physical meaning of this observable. The infinitesimal version of the unitary operator $\hat{U}(dt)$ is given by

$$\hat{U}(dt) = \hat{\mathbf{1}} - i\frac{\hat{\mathcal{H}}}{\hbar}dt.$$

We resort to a dimensional analysis here. The operator $\hat{\mathbf{1}}$ is dimensionless, dt has dimensions of time, $\hbar$ has dimensions of energy×time, so $dt/\hbar$ has dimensions of 1/energy. This means that $\hat{\mathcal{H}}$ has dimensions of energy. Therefore, for non degenerate eigenvalues E_i's and their corresponding eigenstates $|E_i\rangle$, we can write the Hamiltonian as

$$\hat{H} = \sum_i E_i |E_i\rangle\langle E_i| \tag{1.24}$$

Now refer to Figure 1.2 which conceptualizes performing an experiment that aims at measuring the energy of a system. For an N-dimensional quantum system, the energy values can be labeled as $E_1, E_2, E_3, \ldots, E_N$. These are also the discrete measurement outcomes when energy is measured.

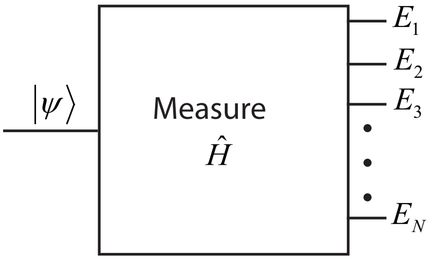

Figure 1.2: Measuring the energy can be symbolized by the Hamiltonian operator.

Also suppose $|E_1\rangle, |E_2\rangle, |E_3\rangle \ldots, |E_N\rangle$ are the eigenstates of the Hamiltonian with the corresponding eigenvalues. So $\hat{\mathcal{H}}$ acts on an eigenstate $|E_j\rangle$ and the result is same state with an energy eigenvalue E_j,

$$\hat{\mathcal{H}} |E_j\rangle = E_j |E_j\rangle . \tag{1.25}$$

Therefore upon measurement of energy, if the outcome is E_j, the new state created is $|E_j\rangle$. For a minute, consider all energy eigenvalues to be distinct. This implies that all the N eigenstates will be orthonormal and will form a basis for the N-dimensional Hilbert space in which the state lives. Therefore, any quantum state can also be expressed as a superposition of the eigenstates of a Hamiltonian

$$|\psi\rangle = \sum_{j=1}^{N} c_j |E_j\rangle , \tag{1.26}$$

and if we were to measure energy of a system in such a state, the probability of obtaining an outcome E_j and creating a state $|E_j\rangle$ will simply be $|c_j|^2$.

1.2.2 Stationary states

We now connect the TDSE with the concept of stationary states. Stationary states, by their very name, are states that don't evolve with time. These are truly eigenstates of the Hamiltonian. Suppose an electron is initially in the state $|E_1\rangle$ which is the ground state, which could be the lowest energy state of an electron residing on a quantum dot. It is also an eignestate of the Hamiltonian. From Eq. (1.22), so we have,

$$|\psi(t)\rangle = e^{-i\frac{\hat{\mathcal{H}}}{\hbar}t} |E_1\rangle = e^{-i\frac{E_1 t}{\hbar}} |E_1\rangle \tag{1.27}$$

indicating that the state will merely pick up a global phase which is immaterial as far as measurement is concerned. Refer to Figure 1.3. There is another interesting

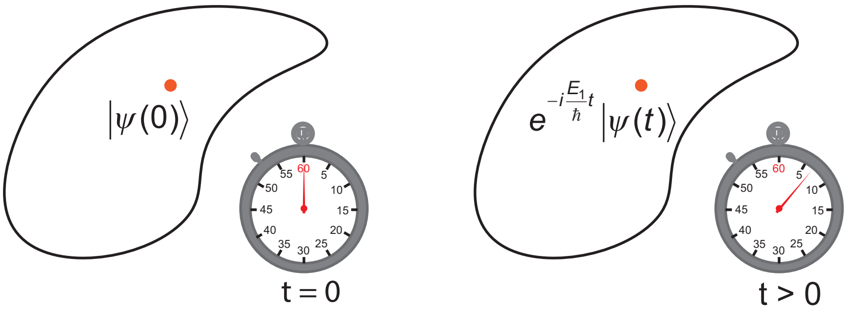

Figure 1.3: Temporal evolution of a stationary state

observation. The dimensions of $E_1/\hbar$ are 1/time which makes this into a frequency ω, allowing one to rewrite the global phase as

$$|\psi(t)\rangle = e^{-i\omega t}|E_1\rangle \tag{1.28}$$

as if the stationary state carries a tiny stopwatch with it which keeps on ticking with time and builds a phase $-\omega t$ and thus holds a record of time.

1.2.3 Superpositions of stationary states

On the other hand, a superposition of energy eignestates is not necessarily an eignestate of the Hamiltonian. Consider the initial state,

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}\big(|E_1\rangle + |E_2\rangle\big). \tag{1.29}$$

We know that the ket $|E_1\rangle$ alone is an eigenstate of the Hamiltonian, and so is $|E_2\rangle$ but their superposition is not a stationary state (unless $E_1 = E_2$). Can we predict what the state is going to be after time t? Yes, see this!

$$\begin{aligned} |\psi(t)\rangle &= \frac{1}{\sqrt{2}}\left(e^{-i\frac{E_1}{\hbar}t}|E_1\rangle + e^{-i\frac{E_2}{\hbar}t}|E_2\rangle\right) \\ &= \frac{e^{-i\frac{E_1}{\hbar}t}}{\sqrt{2}}\left(|E_1\rangle + e^{-i\frac{(E_2-E_1)}{\hbar}t}|E_2\rangle\right) \\ &= \frac{1}{\sqrt{2}}\left(|E_1\rangle + e^{-i\frac{(E_2-E_1)}{\hbar}t}|E_2\rangle\right) \end{aligned} \tag{1.30}$$

where in the last step, we have extinguished the immaterial global phase $e^{-i\frac{E_1}{\hbar}t}$. The state is changing with time and is not stationary.

Suppose our system has a dimensionality of 2, with the basis spanned by $|E_1\rangle$ and $|E_2\rangle$. Therefore, we can resort to the picture on the Bloch sphere. Our

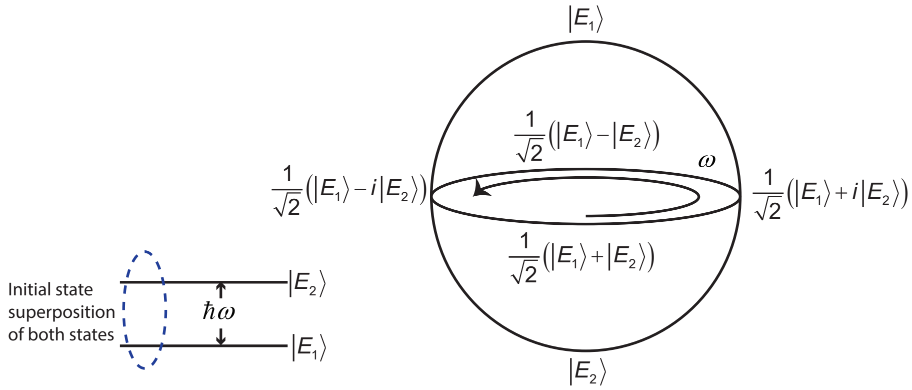

Figure 1.4: The evolution of the quantum state of a qubit which is not an eigenstate of the Hamiltonian.

initial state, Eq. (1.29) corresponds to superposition of the states $|E_1\rangle$ and $|E_2\rangle$, a situation that is shown in Figure 1.4 and we observe that the state is continually evolving with a characteristic frequency. The term $(E_2 - E_1)/\hbar$ in Eq. (1.30) has dimensions of frequency and is just the energy separation between quantum states $|E_1\rangle$ and $|E_2\rangle$. Let's identify the energy gap, also shown in the Figure, by $\hbar\omega$. We will show that in an interesting twist to the story, the rate at which the state is evolving is given by the energy difference between the components of the superposition divided by $\hbar$:

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(|E_1\rangle + e^{-i\omega t}|E_2\rangle\right). \tag{1.31}$$

At time $t = 0$, we have the initial state. At $\omega t = \pi/2$, the state becomes

$$\frac{1}{\sqrt{2}}\left(|E_1\rangle + i\,|E_2\rangle\right) \tag{1.32}$$

and at $\omega t = \pi$, it transforms to

$$\frac{1}{\sqrt{2}}\left(|E_1\rangle - |E_2\rangle\right) \tag{1.33}$$

which shows that by constantly changing the phase, new states are traversed along the equatorial plane of the Bloch sphere, also shown in Figure 1.4. This kind of time evolution is the hallmark of nuclear magnetic resonance (NMR) which is the subject of the next chapter.

1.4 A measurement of the energy is performed at time t. What are the possible outcomes and what are their probabilities? Do these probabilities change with time? What is the expectation value of the energy and does it change with time? In fact the next section focuses on expectation values.

1.3 Temporal evolution of expectation values

Suppose we have an observable A. This could be z-component of the angular momentum, energy, position, momentum, etc; basically something that is measured in a quantum experiment. Corresponding to the observable there is an operator $\hat{A}$ whose expectation value is $\langle \hat{A} \rangle (t) = \langle \psi(t) | \hat{A} | \psi(t) \rangle$. We like to see how the expectation value itself changes with time. Suppose we actually compute the time derivative of the expectation value:

$$\frac{d}{dt} \langle \psi(t) | \hat{A} | \psi(t) \rangle \tag{1.34}$$

$$= \left(\frac{d}{dt} \langle \psi(t) | \right) \hat{A} | \psi(t) \rangle + \langle \psi(t) | \frac{d}{dt} \hat{A} | \psi(t) \rangle + \langle \psi(t) | \hat{A} \left(\frac{d}{dt} | \psi(t) \rangle \right). \tag{1.35}$$

Let's also rewrite the TDSE (1.23) here,

$$\frac{d}{dt} | \psi(t) \rangle = \frac{-i}{\hbar} \hat{\mathcal{H}} | \psi(t) \rangle . \tag{1.36}$$

If we take the dual of this equation, the ket becomes a bra and $-i$ is replaced with i, while the adjoint of $\hat{\mathcal{H}}$ is $\hat{\mathcal{H}}$ itself, allowing us to write,

$$\frac{d}{dt} \langle \psi(t) | = \frac{i}{\hbar} \langle \psi(t) | \hat{\mathcal{H}}. \tag{1.37}$$

Inserting the preceding two equations into Eq. (1.35) produces

$$\begin{aligned} \frac{d}{dt} \langle \psi(t) | \hat{A} | \psi(t) \rangle &= \frac{i}{\hbar} \langle \psi(t) | \hat{\mathcal{H}} \hat{A} | \psi(t) \rangle + \langle \psi(t) | \frac{d}{dt} \hat{A} | \psi(t) \rangle + \langle \psi(t) | \hat{A} \left(\frac{-i}{\hbar} \hat{\mathcal{H}} | \psi(t) \rangle \right) \\ &= \frac{i}{\hbar} \langle \psi(t) | \left(\hat{\mathcal{H}} \hat{A} - \hat{A} \hat{\mathcal{H}} \right) | \psi(t) \rangle + \langle \psi(t) | \left(\frac{d}{dt} \hat{A} \right) | \psi(t) \rangle \\ &= \frac{i}{\hbar} \langle \psi(t) | \left[\hat{\mathcal{H}}, \hat{A} \right] | \psi(t) \rangle + \langle \psi(t) | \left(\frac{d}{dt} \hat{A} \right) | \psi(t) \rangle \end{aligned} \tag{1.38}$$

which spells out the time-derivative of expectation value of $\hat{A}$. In many cases, the explicit derivative of operator is zero because we are not switching from measuring one observable to another as time progresses, rather our observable keeps constant and only the state changes,

$$\frac{d}{dt} \hat{A} = 0 \tag{1.39}$$

which simplifies Eq. (1.38) to

$$\begin{aligned}
\frac{d}{dt}\langle\psi(t)|\,\hat{A}\,|\psi(t)\rangle &= \frac{i}{\hbar}\langle\psi(t)|\big[\hat{\mathcal{H}},\hat{A}\big]|\psi(t)\rangle + \cancel{\langle\psi(t)|\frac{d}{dt}\hat{A}|\psi(t)\rangle} \\
&= \frac{i}{\hbar}\langle\psi(t)|\big[\hat{\mathcal{H}},\hat{A}\big]|\psi(t)\rangle \qquad (1.40)\\
&= \frac{i}{\hbar}\langle\big[\hat{\mathcal{H}},\hat{A}\big]\rangle. \qquad (1.41)
\end{aligned}$$

The derivative of the expectation value of an observable is the expectation value of the commutator of the Hamiltonian with the observable. Hence, if the observable commutes with the Hamiltonian, then the time derivative of the observable's expectation value is zero, which means that the expectation value of the observable becomes a constant of motion. If $\hat{A}$ commutes with $\hat{\mathcal{H}}$, $\big\langle\hat{A}\big\rangle$ is a constant of motion. A concrete example is furnished by measuring the average energy of a unitarily evolving system. In this case the observable is the Hamiltonian which obviously commutes with itself. The average energy remains constant over time. This is the principle of conservation of energy.

1.4 An application: the solar neutrino problem

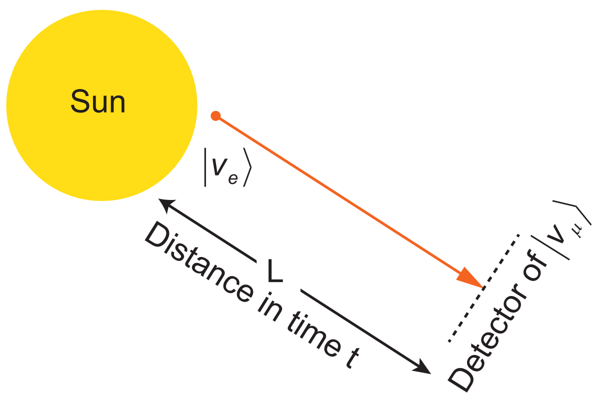

Figure 1.5: A conceptual diagram showing an electron neutrino created in the sun and being detected as muon neutrino.

The solar neutrino problem was a long outstanding problem in physics. Today, we know that neutrinos are highly relativistic particles with nonzero mass. Neutrinos can occur in two mutually orthogonal states labeled as $|\nu_e\rangle$ and $|\nu_\mu\rangle$ corresponding to the two 'flavors' of neutrinos — called the electron neutrino and muon neutrino respectively. These states are eigenstates of the weak interaction Hamiltonian.

Anyway when neutrinos propagate in free space, the only Hamiltonian of relevance is due to relativistic energy of the particles. The eigenstates of this Hamiltonian are generally called the mass eiegnstates, denoted by $|v_1\rangle$ and $|v_2\rangle$.

Hence states in the two dimensional Hilbert space can be described by the weak interaction eigenstates $\{|\nu_e\rangle, |\nu_\mu\rangle\}$ or by the mass eigenstates $\{|\nu_1\rangle, |\nu_2\rangle\}$. The relationship between the states is described by

$$|\nu_e\rangle = \cos\frac{\theta}{2}|\nu_1\rangle + \sin\frac{\theta}{2}|\nu_2\rangle \quad (1.42)$$

$$|\nu_\mu\rangle = \sin\frac{\theta}{2}|\nu_1\rangle - \cos\frac{\theta}{2}|\nu_2\rangle. \quad (1.43)$$

The angle $\theta/2$ is called the mixing angle. A similarity matrix $\hat{S}$ that takes a state vector from the $\{|\nu_e\rangle, |\nu_\mu\rangle\}$ (weak basis) to the $\{|\nu_1\rangle, |\nu_2\rangle\}$ (mass basis) is given by

$$\hat{S} = \begin{pmatrix} \langle\nu_1|\nu_e\rangle & \langle\nu_1|\nu_\mu\rangle \\ \langle\nu_2|\nu_e\rangle & \langle\nu_2|\nu_\mu\rangle \end{pmatrix} = \begin{pmatrix} \hat{S}_{11} & \hat{S}_{12} \\ \hat{S}_{21} & \hat{S}_{22} \end{pmatrix}. \quad (1.44)$$

where using Eqs (1.42) and (1.43), the matrix elements are

$$\hat{S}_{11} = \cos\frac{\theta}{2} \qquad \hat{S}_{12} = \sin\frac{\theta}{2}, \quad (1.45)$$

$$\hat{S}_{21} = \sin\frac{\theta}{2} \qquad \hat{S}_{22} = -\cos\frac{\theta}{2}. \quad (1.46)$$

Suppose an electron neutrino $|\psi(0)\rangle = |\nu_e\rangle$ is created on the sun. In its free propagation towards the earth, only the mass Hamiltonian is operative. The eigenvalues of this Hamiltonian are E_1 and E_2 for the eigenstates $|v_1\rangle$ and $|v_2\rangle$. Let's first write the time-dependent quantum state $|\psi(t)\rangle$ as neutrinos propagate in space, starting their journey from the sun and reaching earth. The initial quantum state of an electron neutrino created on the sun is

$$|\psi(0)\rangle = |\nu_e\rangle = \cos\frac{\theta}{2}|\nu_1\rangle + \sin\frac{\theta}{2}|\nu_2\rangle. \quad (1.47)$$

where we have made use of the similarity transform, Eq. (1.44). At time t, the state becomes

$$|\psi(t)\rangle = e^{-i\hat{\mathcal{H}}t/\hbar}|\psi(0)\rangle = e^{-i\hat{\mathcal{H}}t/\hbar}\left(\cos\frac{\theta}{2}|\nu_1\rangle + \sin\frac{\theta}{2}|\nu_2\rangle\right). \quad (1.48)$$

Here $\hat{\mathcal{H}}$ is the mass Hamiltonian with eigenstates $|\nu_1\rangle$ and $|\nu_2\rangle$ and eigenvalues E_1 and E_2, therefore Eq. (1.48) can be written as

$$|\psi(t)\rangle = \cos\frac{\theta}{2}e^{-iE_1t/\hbar}|\nu_1\rangle + \sin\frac{\theta}{2}e^{-iE_2t/\hbar}|\nu_2\rangle. \quad (1.49)$$

If $t = L/2$, where L is the sun-earth distance and v the speed of neutrons, then $|\psi(t)\rangle$ will denote the quantum state of neutrinos reaching the earth. Suppose the earth has a telescope which points toward the sun. The telescope is fitted with a detector can only count muon neutrinos $|\nu_\mu\rangle$. If we assume that no neutrinos are lost in between, the probability of detecting a muon neutrino on the terrestrial surface becomes

$$P(\mu, T) = \left|\langle\nu_\mu|\psi(t)\rangle\right|^2. \tag{1.50}$$

We first compute

$$\begin{aligned}\langle\nu_\mu|\psi(t)\rangle &= \left(\sin\frac{\theta}{2}\langle v_1| - \cos\frac{\theta}{2}\langle v_2|\right)\left(\cos\frac{\theta}{2}e^{-iE_1t/\hbar}|v_1\rangle + \sin\frac{\theta}{2}e^{-iE_2t/\hbar}|v_2\rangle\right)\\ &= \frac{1}{2}\sin\theta\left(e^{-iE_1t/\hbar} - e^{-iE_2t/\hbar}\right),\end{aligned} \tag{1.51}$$

which allows us to determine

$$\begin{aligned}P(\mu, T) &= \frac{1}{4}\sin^2\theta\left(e^{iE_1t/\hbar} - e^{iE_2t/\hbar}\right)\left(e^{-iE_1t/\hbar} - e^{-iE_2t/\hbar}\right)\\ &= \sin^2\theta\sin^2\left(\frac{(E_1 - E_2)T}{2\hbar}\right),\end{aligned} \tag{1.52}$$

We can express the probability in Eq. (1.52), $P(\mu, T)$ in terms of the masses of the two kind of neutrinos, instead of their energies. Since neutrinos are relativistic particles, the mass eigenstates have energies,

$$E_1 = \sqrt{(m_1c^2)^2 + (pc)^2} \tag{1.53}$$

$$E_2 = \sqrt{(m_2c^2)^2 + (pc)^2}, \tag{1.54}$$

where $m_{1,2}$ are masses of the mass eigenstates, c is the speed of light and p is their common momentum. For relativistic particles, $(pc) \gg (mc^2)$ and using Binomial expansion show we can rewrite the energy as,

$$E_1 = (pc)\sqrt{1 + \frac{(m_1c^2)^2}{(pc)^2}} \tag{1.55}$$

$$\approx pc + \frac{m_1^2c^3}{2p} \tag{1.56}$$

and

$$E_2 = pc + \frac{m_2^2c^3}{2p} \tag{1.57}$$

allowing us to write

$$P_{\mu,T} = \sin^2\theta\sin^2\left(\frac{c^2(m_1^2 - m_2^2)L}{4p\hbar}\right) \tag{1.58}$$

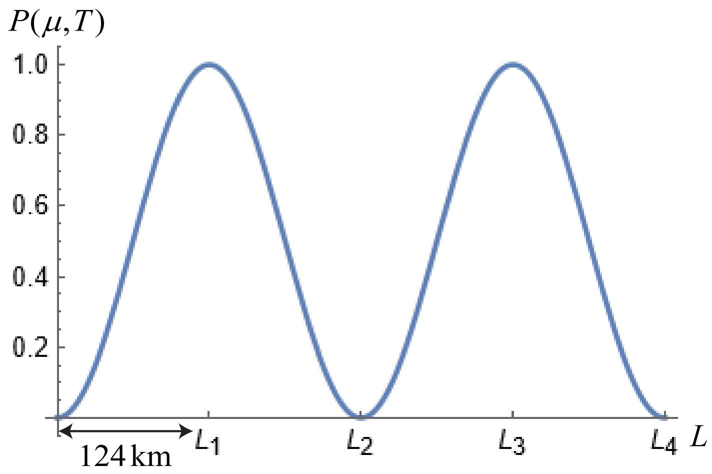

Figure 1.6: Neutrino Oscillations

where we have expressed this probability again in terms of L. This is a periodic function. Whenever the argument of the $\sin^2$ function changes by $\pi/2$ the probability goes from minimum to maximum, and vice versa. Therefore the oscillating length of neutrino ΔL, when it changes its identity is given by

$$\frac{c^2(m_1^2 - m_2^2)\Delta L}{4p\hbar} = \frac{\pi}{2}. \tag{1.59}$$

We can use $p = E/c$ and the masses $m_1^2 - m_2^2 = 8 \times 10^{-5}\ eV^2/c^2$ to obtain a numerical value too. For example, for neutrino of energy 8 MeV, ΔL comes out as 124 km. Figure 1.6 shows the probability curve as a function of L. The quantum state at the solar surface (L=0 km) is $|\nu_e\rangle$ given in Eq. (1.47) and at any other time $t \geq 0$, as in Eq. (1.49). At L_1 = 124 km and multiples thereof, it oscillates fully to the state

$$\nu_\mu = \sin\frac{\theta}{2}\,|\nu_1\rangle - \cos\frac{\theta}{2}\,|\nu_2\rangle \tag{1.60}$$

This is solar neutrino oscillation solved for you.

1.5 Application: Muon spin rotation

In this section we describe another interesting practical manifestation of Schrodinger's equation, the behavior of a muon's spin inside a magnetic field. The next chapter describes another illuminating application, called nuclear magnetic resonance which is really a more complete explanation of muon spin rotation (μSR). What are muons? Standing on the earth's surface, on average there is one muon that

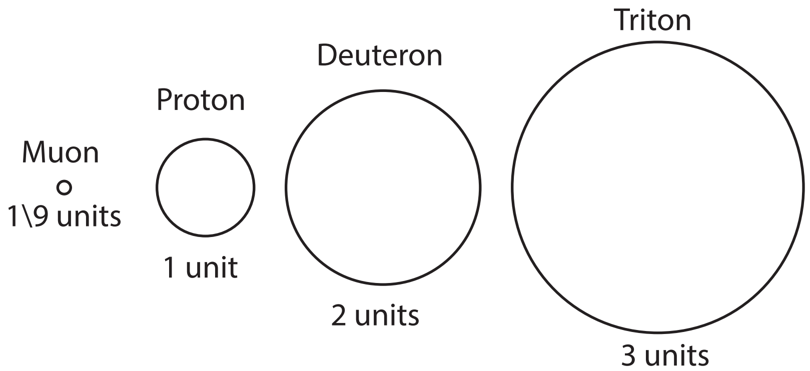

Figure 1.7: Mass of muon compared to nuclei

strikes 1 cm^2 of our bodies in a minute. The primary source of the muons are cosmic rays. Nuclear reaction taking place inside stars including our sun produce a plethora of particles which fan out in space and large number of them shower upon the earth's atmosphere producing secondary particles of which muons are an important component.

Suppose the proton has mass of one unit. A deuteron is one proton and neutron and has a mass of approximately two units. Tritium has one proton and two neutrons. The nucleus of Tritium is called Triton. Its mass would be three units. A positively charged muon can be considered to be a light proton whose mass is 1/9th of a proton or from another perspective, a heavy electron that is 273 times more massive than an electron. Refer to Figure 1.7 which depicts the relative masses of these particles. The muon is also a spin-1/2 particle just like an electron and so its quantum state can be drawn on a Bloch sphere similar to any two dimensional system. We use the muon spin to probe deep inside a material. The crystalline structure of materials is generally investigated using X-rays or neutrons but sometimes muons can also come in handy. The technique uses the spin of muons, whose time dynamics is governed by Schrodinger's equation and the method is called muon spin spectroscopy.

1.5.1 Smashing protons to produce pions which decay to give muons

We prepare muons in a giant colliders in which two protons are accelerated in counter propagating circular orbits and made to smash into one another. This is a catastrophic collision depicted in Figure 1.8 and results in creation of π^+, a proton and neutral neutron conserving the overall charge,

$$p^+ + p^+ \rightarrow \pi^+ + p^+ + n \tag{1.61}$$

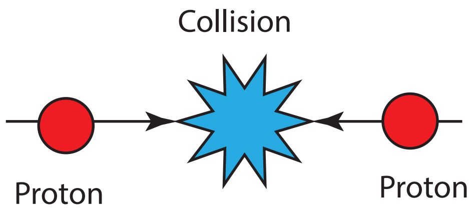

Figure 1.8: Cartoonic representation of Proton-proton collision

The Pion Π^+ is a spin zero particle and so it is a boson. As it is created it decays in about 26 nanosecond into a muon μ^+, a muon neutrino, ν_μ. Some pions decay before that but on average the half life is 26 nanoseconds,

$$\pi^+ \xrightarrow{26\,ns} \mu^+ + \nu_\mu. \tag{1.62}$$

The neutrino which was the subject of preceding section is uncharged and an extremely light particle. Both the parent pion and the daughter muon are positively charged, so charge is conserved in the particle reaction. The muon and the muon neutrino are both spin 1/2 particles and for spin to be conserved their spin points in the opposite direction, say $|\alpha\rangle$ and $|\beta\rangle$. The pion is is initially at rest, therefore the linear momentum p is zero and during the course of reaction it must be conserved. Therefore the daughter muon and neutrino go in opposite directions with momentum $\pm\hbar k$.

1.5.2 Relation between linear and angular momentum of a muon

The muon has a really interesting property that its spin angular momentum $\vec{S}$ points in direction opposite to its linear momentum. This has to do with violation of parity because the decay involves a weak nuclear force. We'll come to this concept in a minute. Now if we would to keep the total spin zero, the spin of muon neutrino $\vec{S}_{\nu_\mu}$ points in the direction opposite to its linear momentum and the spin of muon $\vec{S}_\mu$ also points opposite to its own linear momentum. The process showing the realative orientation of these linear and angular momentum is depicted in Figure 1.9.

1.5.3 Aah, the muon also decays!

Nothing is permanent. The muon also decays, producing three particles, a positron e^+, an electron neutrino ν_e and a muon anti-neutrino $\overline{\nu}_\mu$ which is an anti-particle for the neutrino. The decay time constant is about 2.2 μs.

$$\mu^+ \xrightarrow{2.2\,\mu s} e^+ + \nu_e + \overline{\nu}_\mu \tag{1.63}$$

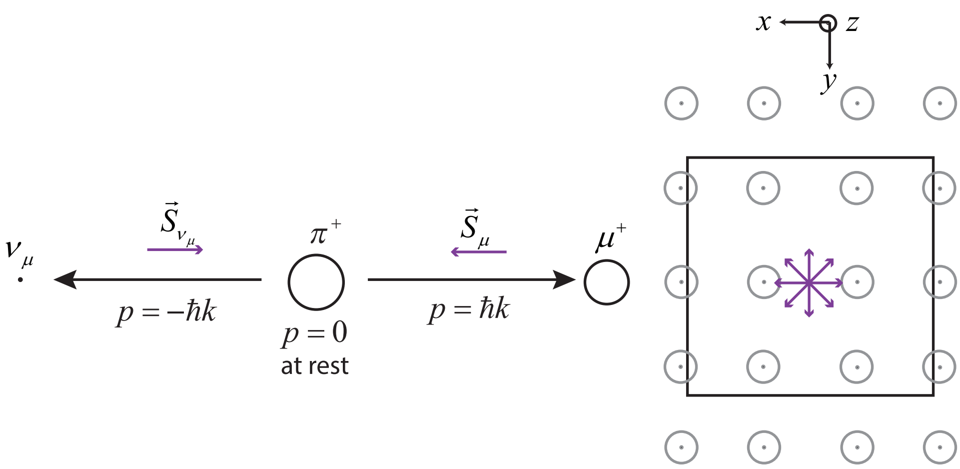

Figure 1.9: Solid placed inside the magnetic field pointing out of the paper. Spin angular momentum will precess

Which of these particles is the easiest to detect? Clearly the positron because it is charged. Neutrinos are elusive particles and hard to detect as they interact very weakly with matter (but still possible to detect as our previous section has shown). It is known that they can penetrate the entire mass of earth, entering one pole and leaving from the other. If we want to detect neutrinos, we have to do elaborate experiments under the Antarctic snow, waiting patiently for weeks and weeks to detect a single neutrino.

Muon decay is governed by the weak nuclear force so there are certain restrictions on the directions. Figure 1.11 illustrates the decay process with respect to parity violation. Now our plea to you is, don't take this depiction to be too literal. The spin angular momentum can be (let me emphasize) 'viewed' as the particle spinning in a particular direction. Using the right hand rule, the fingers curl in the direction of rotation and the thumb points in the direction of spin angular momentum $\vec{S}$. If the muon decays the positron will be emitted in the direction of the spin angular momentum of the muon. Therefore, if the muon spin points upward, the highest propensity of locating the daughter positron will also be upward. This is shown in Figure 1.10 (a). If this process is observed in a mirror, the direction of the spinning muon will reverse and therefore the spin angular momentum will also reverse, now pointing downward, (part (b) of the diagram). Parts (a) and (b) are mirror images or parts of a pair. Since the decay violates parity, only (a) is allowed and (b) is forbidden. A counter example of a process that does obey parity is the collision of gas molecules in a container, in which the mirror image is equally likely (parts (c) and (d) of the diagram). Most processes in nature obey parity, the process and its mirror image are equally likely but the decay of a muon leading to positrons being

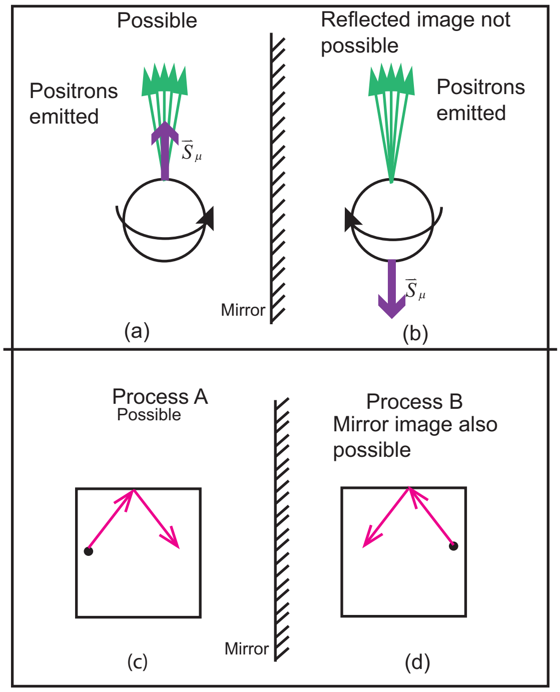

Figure 1.10: (a) and (b) Muon decay do not obey parity. (c) and (d) Movement of gas molecules inside the container obey parity.

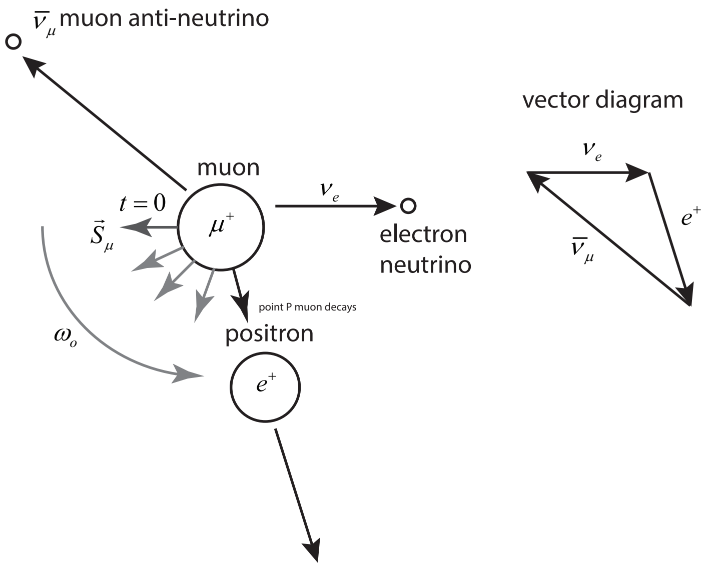

Figure 1.11: The decay of a muon showing the directions of the daughter particles: the positron, electron neutrino and muon anti neutrino.

emitted in a unique direction is a clear exception, and we use it to our advantage in muon spin resonance.

Along with the positron, a neutrino and an anti-neutrino will also be emitted. If the initial linear momentum of muon is zero, (it's at rest), the direction of the three daughter particles will be such that the resultant is zero. A vector diagram showing the possible directions of the daughter particles is shown in Figure 1.11.

1.5.4 The muon spin resonance experiment

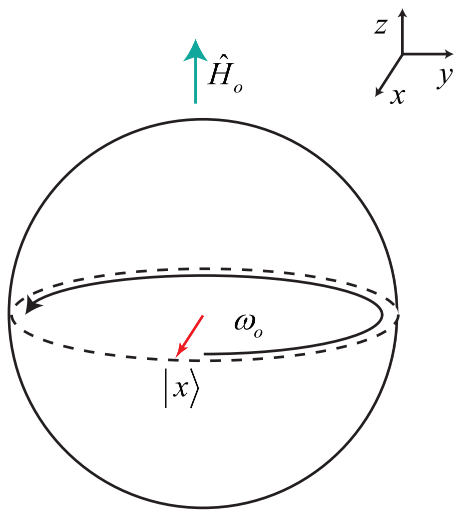

Figure 1.12: The spin angular momentum state vector precess with time

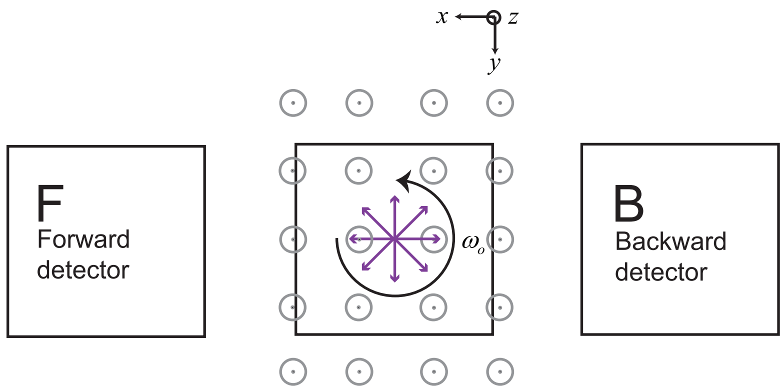

Figure 1.13: Forward and backward detectors used for registering positrons from the decaying, precession spin state of the muon.

Let's now put everything together. In a particle smashing experiment, pions are produced which decay into muons. The flux of muons is collimated into a beam and is called a spin polarized current of muons. All these muons have spin pointing in, say, the x-direction. Therefore the quantum state of each proton could be labeled as $|+x\rangle$. The beam is fired onto a solid target. The muons penetrate the solid and lose all their energy finally coming to rest with the quantum state still being $|+x\rangle$. This happens at time $t = 0$, and is shown in Figure 1.9

Now the material that captures the static muon is placed inside a magnetic field which is pointing say, outward and perpendicular to the spin, let's call it the z direction. Refer again to Figure 1.9 for the geometry. We will defer the details to the next chapter on magnetic resonance but a spin inside a z-pointing magnetic field will experience a Hamiltonian

$$\hat{\mathcal{H}}_o = \omega_o \hat{S}_z \tag{1.64}$$

where ω_o is called the Larmor frequency of muon inside magnetic field. We know that the eigenstate of the Hamiltonian are $|+z\rangle$ and $|-z\rangle$. The initial state is however $|+x\rangle$, not an eigenstate and hence the state will indeed evolve under the presence of the Hamiltonian. The initial state at $t = 0$ can be expressed though in terms of eigenstates as

$$|+x\rangle = \frac{|+z\rangle + |-z\rangle}{\sqrt{2}} \tag{1.65}$$

and its evolution will be determined by the TDSE

$$|\psi(t)\rangle = e^{-i\frac{\omega_o \hat{S}_z t}{\hbar}} |+x\rangle = e^{\frac{-i\omega_o t}{2}} \left(\frac{|+z\rangle + e^{i\omega_o t} |-z\rangle}{\sqrt{2}} \right). \tag{1.66}$$

The global phase factor $e^{(-i\omega_o t)/2}$ can be discarded. The state's motion is called precession and can be captured on the Bloch sphere as represented in Figure 1.12. The state precesses in the equatorial plane with frequency ω_o in the presence of the magnetic field. Even though we have assumed so, an external magnetic field is not even necessary. In many cases, the muon studded inside the solid will see local magnetic fields being produced by other spins belonging to the solid material. The local fields will cause the frequency ω_o to be a signature of the strength of local magnetic fields. Stronger the field, higher the ω_o. The crucial next stratagem is to detect something.

The muon decays to produce amongst three particles a positron which can be picked up by a detector. The emitted positron is predominately along the direction of the instantaneous spin state. For measurement we use forward (F) and backward (B) detectors pointing along $\pm x$-axes as shown in Figure 1.13. These detectors click when they register a positron fired by the decaying muon. The way we have come

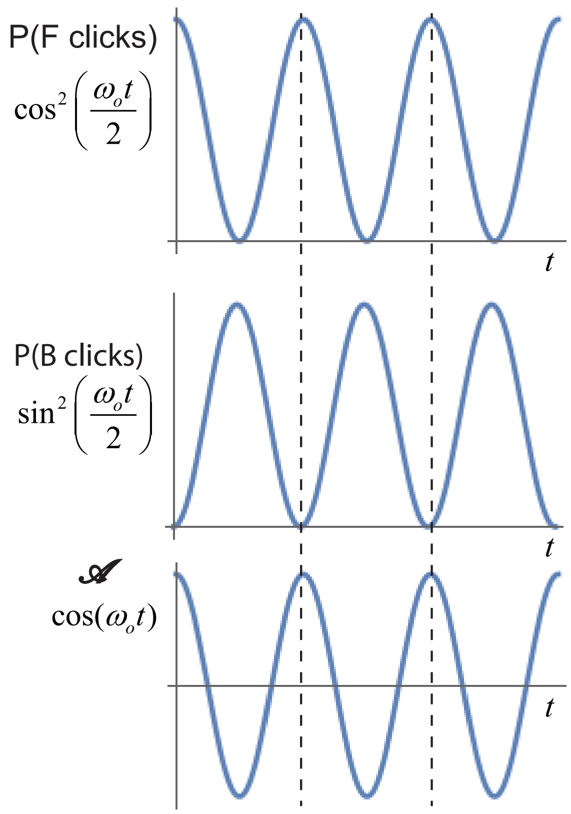

Figure 1.14: Probability versus time graphs, for positron detection in an μSR experiment

across projective measurements allows us to make sense of outcomes. If F fires, the positron collapses along the $+x$ direction, implying that the spin state of the muon after decay is $|+x\rangle$. If B fires, the muon state created is $|-x\rangle$. We can compute these probabilities in the usual way, i.e. by determining the overlap between the precessing state $|\psi(t)\rangle$ given in Eq. (1.66) and $|\pm x\rangle$. Here is how we go about doing precisely that,

$$\begin{aligned}\langle +x|\psi\rangle &= \left(\frac{1}{\sqrt{2}}\left(\langle +z| + \langle -z|\right)\right)\left(\frac{1}{\sqrt{2}}\left(|+z\rangle + e^{i\omega_o t}|-z\rangle\right)\right) \\ &= \frac{1}{2}\left(1 + e^{i\omega_o t}\right) \qquad (1.67)\\ P(\mathrm{F}) = |\langle +x|\psi\rangle|^2 &= \left(\frac{1}{2}\left(1 + e^{-i\omega_o t}\right)\right)\left(\frac{1}{2}\left(1 + e^{i\omega_o t}\right)\right) \\ &= \frac{1}{2}\left(1 + \cos\omega_o t\right) = \cos^2\left(\frac{\omega_o t}{2}\right) \qquad (1.68)\end{aligned}$$

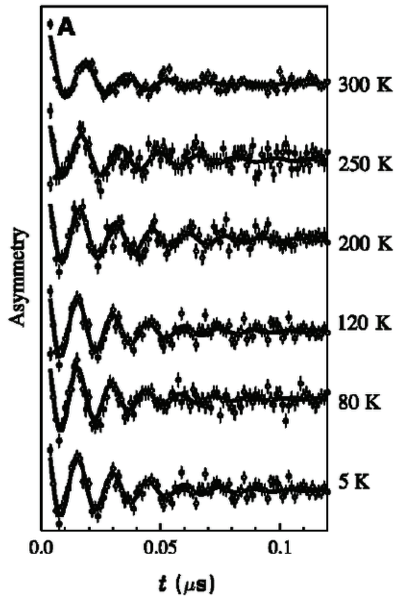

Figure 1.15: Asymmetry function obtained from the work "The Hydride Anion in an Extended Transition Metal Oxide Array: $LaSrCoO_3H_{0.7}$", M.A. Hayward et al., Science 295, 1882 (2002)

Similarly we have, $P(B) = \sin^2(\omega_o t)/2$, and if we subtract these probabilities, we would obtain an asymmetry function A given by

$$\mathscr{A} = \cos^2\left(\frac{\omega_o t}{2}\right) - \sin^2\left(\frac{\omega_o t}{2}\right) = \cos(\omega_o t) \tag{1.69}$$

The variables P(F), P(B) and $\mathscr{A}$ are plotted in Figure 1.14. Experimental schemes normally register the asymmetry function $\mathscr{A}$ with an important caveat. The curve also decays with time, which is clearly a signature of the decreasing fraction of muon as they decay. Figure 1.15 shows a typically achieved muon spin rotation signature.

1.5 What would be a suitable mathematical model for a decaying asymmetry function?

1.6 In Figure 1.15, why does the relative strength of the signal decrease at higher temperatures?

1.6 Questions

Q 1.1 The Hamailtonian of a three state system is:

$$\hat{\mathcal{H}} = \hbar\omega|1\rangle\langle 1| + 2\hbar\omega|2\rangle\langle 2| + 3\hbar\omega|3\rangle\langle 3|, \tag{1.70}$$

where $|1\rangle$, $|2\rangle$ and $|3\rangle$ form an othornormal basis. We also have two observables

$$\hat{A} = a\Big(|1\rangle\langle 2| + |2\rangle\langle 1| + 2|3\rangle\langle 3|\Big) \quad (1.71)$$

$$\hat{A} = b\Big(2|1\rangle\langle 1| + |2\rangle\langle 3| + |3\rangle\langle 2|\Big) \quad (1.72)$$

where a and b are real.

(a) If the state at time $t = 0$ is given by

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}|1\rangle - \frac{i}{\sqrt{2}}|3\rangle \quad (1.73)$$

what is the state at a later time t?

(b) For the initial state (1.73), what is $\langle\hat{B}\rangle$?

(c) Suppose at time $t = 0$ the state is $|1\rangle$. A measurement of A is made at $t = 0$ and the outcome is $2a$. After time t, B is measured. What are the possible measurement outcomes and what are their probabilities?

Chapter 2

Magnetic resonance

Dr. Sabieh Anwar
with Beenish Muazzam
April 14, 2025

We are now going to look at one of the most direct and beautiful applications of the Schrodinger equation. In fact the phenomenon of nuclear magnetic resonance (NMR) can be regarded as a test bed for quantum mechanics. The technique is also at the heart of many forms of quantum computers. It is a vivid proof that quantum mechanics actually works. Not only this, it results in an important radiological tool called magnetic resonance imaging (MRI) that helps scan the human body to detect disease and injury, presence of tumors and provides clues on how the brain works. NMR and MRI are applications of the TDSE.

If we are observing nuclei of atoms or molecules, such as protons, the isotopes carbon-13, nitrogen-15, fluorine-19 we are looking at the spin of the nuclei that are known spin-1/2 particles. The relevant spectroscopic technique is called NMR. However, if we look at electron spins we are dealing with electron spin resonance (ESR). We can build an effective understanding of these techniques using all that we've so far learnt from quantum mechanics.

The starting point is the time-dependent Schrodinger Equation (TDSE). Suppose we start with a quantum state at time zero $|\psi(0)\rangle$. The system is subject to a Hamiltonian $\hat{\mathcal{H}}$. With time, the state changes and after time t it has evolved into

$$|\psi(t)\rangle = e^{-i\frac{\hat{\mathcal{H}}}{\hbar}t}\,|\psi(0)\rangle\,. \tag{2.1}$$

Eq. (2.1) is the solution to the Schrodinger equation. If we know the Hamiltonian and know how much we have to wait, we can exactly predict what the future state is going to be. Measuring it is no doubt another business.

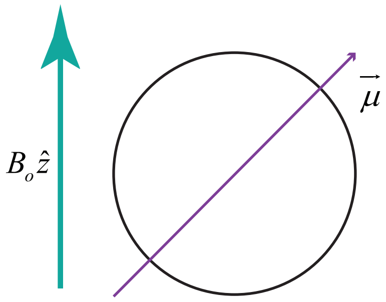

Figure 2.1: Magnetic moment of proton placed inside a uniform field

2.1 A spin-1/2 particle placed inside a uniform magnetic field

Consider a proton which is just a hydrogen nucleus. It's a spin-1/2 particle and hence a fermion. Therefore the Hilbert space is two-dimensional and is spanned by two basis states. One choice for the basis comprises the angular momentum eigenstates $|s = 1/2, m_s = 1/2\rangle = |+z\rangle$ and $|s = 1/2, m_s = -1/2\rangle = |-z\rangle$. For purpose of this chapter, let's relabel them as $|\alpha\rangle$ and $|\beta\rangle$ respectively.

2.1.1 Magnetic moment and energy of the particle

A proton has spin therefore it also has a magnetic moment which is a vector and denoted by $\vec{\mu}$. Figure 2.1 is a diagrammatic representation of a proton inside a uniform magnetic field, $B_o\hat{z}$, supposing that the field points in the z-direction in real space. This is a uniform field unlike the case of Stern-Gerlach style experiments discussed earlier. The energy of this magnetic dipole will change with the relative orientation of the magnetic moment and the field. The energy is given by

$$E = -\vec{\mu} \cdot \vec{B}. \tag{2.2}$$

When $\vec{\mu}$ and $\vec{B}$ are anti-parallel, the energy is maximum and when parallel, the energy is minimum. Therefore the magnetic moment lying parallel to the magnetic field yields the minimum energy $-\vec{\mu}B_o$. One can ask the binary question: is the moment parallel or anti-parallel to the field? These parallel and anti-parallel configurations are called orthogonal quantum states, and we've already chosen to denote them as $|\alpha\rangle$ and $|\beta\rangle$.

2.1.2 Relationship between magnetic moment and angular momentum

We have studied that the magnetic moment is proportional to an angular momentum. For the case of a pure spin $\vec{S}$ we have

$$\vec{\mu} = g\left(\frac{q}{2m}\right)\vec{S}. \tag{2.3}$$

For particles the value of the Lande-g factor determines the magnetic moment acquired. These values are shown in Table 2.1 for some important particles. Combining these with the charges ($q = +e$ for a proton and neutron and $q = -e$ for an electron) will determine the ratios between the magnetic moment and spin momentum. This ratio is also called the gyromagnetic ratio

$$\gamma = \frac{gq}{2m}. \tag{2.4}$$

Interestingly, even though the neutron is a neutral particle, it still possesses a non-zero magnetic moment. For purposes of calculation for a neutron, we use the charge on a proton in Eq. (2.3) to assign the value of g_n.

The value of the Lande-g factor is determined from experiment and is one of the most precisely known constants in all of fundamental physics, more accurately known that the charge of an electron or Planck's constant. In fact, one of the crowning achievements of the field of quantum electrodynamics was to predict the value of g.

2.1 How can one use a magnetic field gradient to determine the value of the gyromagnetic ratio of electrons? Think in terms of Stern and Gerlach's experiment.

Particle	Symbol	g-factor
electron	g_e	−2.00231930436182
muon	g_μ	−2.0023318418
neutron	g_n	−3.82608545
proton	g_p	+5.585694702

Table 2.1: Lande-g factor of common subatomic particles.

2.1.3 The Larmor frequency

Combining Eqs. (2.2) and (2.3) we can express the energy of the spin-1/2 particle in the magnetic field as

$$E = \frac{g_p q}{2m_p}\vec{S}\cdot\vec{B} = \frac{g_p q}{2m_p}S_z B_o \tag{2.5}$$

where we have used the fact that the field lies solely in the z direction.

For our proton, we have two possibilities when S_z is measured. These are $S_z = m_s\hbar = (\hbar/2, -\hbar/2)$. This results in two possibilities of the observed energy

$$E = \pm \frac{g_p q \hbar}{4m_p} B_o. \tag{2.6}$$

Since the energy is an observable, it must corresponds to a Hermitian operator, which has been identified as the Hamiltonian. Explicitly writing down the Hamiltonian (whose eigenvalues are the energy measurables given in Eq. (2.6)) by putting a hat on top of the angular momentum $\hat{S}_z$ yields,

$$\hat{\mathcal{H}} = \frac{g_p q}{2m_p} B_o \hat{S}_z = \gamma B_o \hat{S}_z. \tag{2.7}$$

We can find out the constant $\gamma = g_p q/2m$ by inserting the values of the various constants. The lumped pair of variables γB_o has dimensions of frequency, so let's denote it as ω_o and give it the name Larmor frequency

$$\omega_o = \gamma B_o. \tag{2.8}$$

For a proton $\gamma/2\pi$ is 42 MHz T^{-1} while for an electron it is 660 times larger, *i.e.*, 28 GHz T^{-1}. If we make a plot between B_o and ω_o, we obtain a straight line as shown in Figure 2.2. Higher the magnetic field, higher the Larmor frequency. In fact, when we talk about NMR machines, we identify them by their Larmor frequency. For example, a 200 MHz spectrometer implies an applied magnetic field of $200/42 = 4.8$ T. In summary, when we place a spin-1/2 particle such as a proton inside a magnetic field, a frequency ω_o sprouts out. We will shortly find out what this physically corresponds to.

Combining Eqs. (2.7) and (2.8), we can write the Hamiltonian as

$$\hat{\mathcal{H}} = \omega_o \hat{S}_z \tag{2.9}$$

which shows the direction of the applied field too, *i.e.* in the z direction. This is the tiny subscript with the spin angular momentum operator. If the field were applied across the x-direction, the Hamiltonian becomes $\omega_o \hat{S}_x$ and if it were applied in the xy plane at an angle of 45° between the x and y axes, it would become

$$\hat{\mathcal{H}} = \omega_o \frac{1}{\sqrt{2}} \left(\hat{S}_x + \hat{S}_y \right). \tag{2.10}$$

2.2 The earth's magnetic field is approximately 0.5 G (1 G= 10^{-4} T). What is a proton's Larmor frequency in the earth's field? The electron's?

2.3 Show that γB_o has dimensions of frequency.

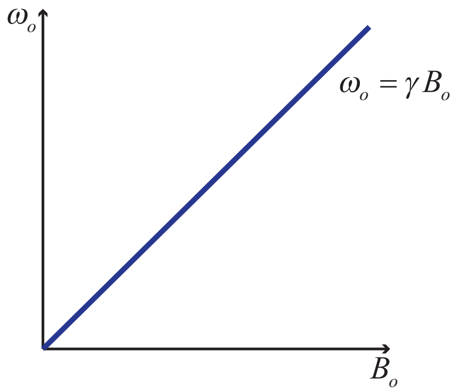

Figure 2.2: Relationship between magnetic field and frequency.

2.1.4 The Zeeman effect

In this section, we have some more things to say about the energy spectrum of the spin-1/2 particle inside a magnetic field B_o. The Hamiltonian Eq. (2.9) provides the key. The eigenstates $|\alpha\rangle$ and $|\beta\rangle$ of the Hamiltonian are also eigenstates of $\hat{S}_z$ with the energy eigenvalues are $m_s\hbar\omega_o$ with $m_s = \pm 1/2$. These eigenvalues are measurement outcomes of an energy measuring experiment. The outcomes are quantized.

The two energy outcomes allow us to think of the particle inside the magnetic field as a qubit with a quantized two-state energy spectrum. Conceptually we can draw the energy levels on an energy level diagram such as the one shown in Figure 2.3. The diagram puts the energy on the vertical scale. The separation between the energy levels is the energy gap and equal to $\hbar\omega_o$. For example if the field is 1 Tesla strong, the gap would correspond to a frequency of 42 MHz or an energy of 0.17 μeV. If the field is zero, there is no splitting between the energy levels. The energy levels are coincident because ω_o is zero. Coincident energy levels are degenerate. As we increase the magnetic field, the energy gap fans out as seen in Figure 2.3 gap generated by the magnetic field a magnetic field is called the Zeeman effect. This quantized energy level structure is ripe for a spectroscopy experiment. We know from school days that whenever systems make transitions between energy levels they absorb or emit radiation. Precisely this is what happens in an NMR experiment.

2.4 A proton is placed inside a magnetic field of strength 1 T. What is the energy gap between these levels in units of eV?

2.5 The thermal energy is of the order of $k_B T$. What is this energy at room temperature and how does it compare with the energy gap calculated above?

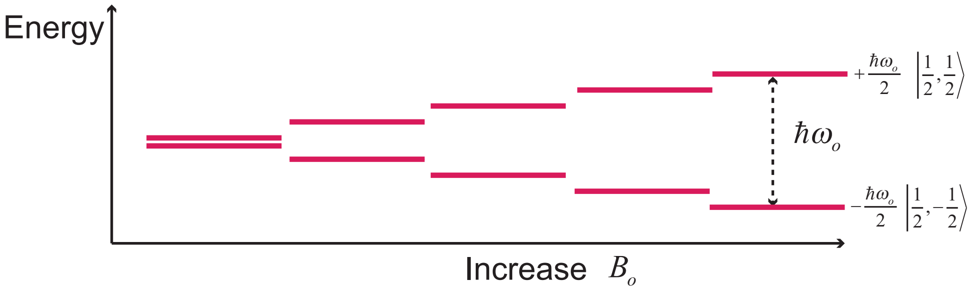

Figure 2.3: The Zeeman effect.

2.2 Evolution of quantum states

The two quantum level system that has emerged out of this discussion may change its state under the action of the Hamiltonian. We can freely draw its trajectory on a Bloch sphere which is a powerful tool for visualizing the state dynamics within the context of NMR as well. This is identical to our extended discussions revolving around the Bloch sphere and the example of μSR provided in the previous chapter.

2.2.1 Stationary states

The first example we consider is an initial state at time $|\psi(0)\rangle = |\alpha\rangle$ which lies on the north pole of the Bloch sphere. Does the state change with time? The Hamiltonian is given by Eq. (2.9). The state at some later time is

$$|\psi(t)\rangle = e^{-i\frac{\omega_o \hat{S}_z}{\hbar}t} |\alpha\rangle . \tag{2.11}$$

The unitary operator $e^{-i\frac{\omega_o \hat{S}_z}{\hbar}t}$ contains the exponent of a Hamiltonian acting on an eigenstate of the Hamiltonian. If we expand the exponent as a Maclaurin series we obtain a series of operators $\hat{S}_z$, $\hat{S}_z^2$, $\hat{S}_z^3$, ... Each one of these acts on the eigenstate producing an eigenvalue and returning the original state. For example, $\hat{S}_z |\alpha\rangle = \hbar/2 |\alpha\rangle$, $\hat{S}_z^2 |\alpha\rangle = (\hbar/2)^2 |\alpha\rangle$ and so on. Putting these terms back into the exponent gives us

$$|\psi(t)\rangle = e^{-i\frac{\hbar\omega_o}{2\hbar}t} |\alpha\rangle \tag{2.12}$$

and since the $\hbar$ cancels out, we obtain

$$|\psi(t)\rangle = e^{-\frac{i\omega_o t}{2}} |\alpha\rangle . \tag{2.13}$$

This is our state after some time t. The original state $|\alpha\rangle$ has not evolved. It only picks up a global phase which keeps growing with time, but since it is global, it remains largely inconsequential. It is as if the states carries a tiny clock with it which keeps on ticking but does not bother the state much. The state $|\alpha\rangle$ is stationary and remains affixed to its starting position on the Bloch sphere. Similarly, if we started off with $|\beta\rangle$ instead, it will also remain unchanged acquiring a global dynamical phase of $e^{\frac{i\omega_o t}{2}}$. Remember $\omega_o t$ is frequency into time so it is just a phase, a real scalar.

2.2.2 Precession of quantum states

This second example is our stepping stone for NMR. Suppose we have the same Hamiltonian Eq. (2.9) since the field is still kept along the z-direction. Our initial state is $1/\sqrt{2}\,(|\alpha\rangle + |\beta\rangle)$ which is not an eigenstate of the Hamiltonian, rather an equal superposition of the eigenstates. It lies on the x axis of the Bloch sphere,

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\rangle + |\beta\rangle\right).$$

As expected the state will change with time into

$$|\psi(t)\rangle = e^{-i\frac{\hat{\mathcal{H}}}{\hbar}t}\left(\frac{1}{\sqrt{2}}\left(|\alpha\rangle + |\beta\rangle\right)\right).$$

The propagator $e^{-i\frac{\omega_o \hat{S}_z t}{\hbar}}$, acts on both $|\alpha\rangle$ and $|\beta\rangle$ allowing us to write

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(e^{-i\frac{\omega_o \hat{S}_z t}{\hbar}}|\alpha\rangle + e^{-i\frac{\omega_o \hat{S}_z t}{\hbar}}|\beta\rangle\right).$$

Now $|\alpha\rangle$ and $|\beta\rangle$ are both eigenstates of $\hat{S}_z$ with eigenvalues $\pm\hbar/2$. We obtain

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(e^{-i\frac{\omega_o \hbar t}{2\hbar}}|\alpha\rangle + e^{i\frac{\omega_o \hbar t}{2\hbar}}|\beta\rangle\right)$$

and the $\hbar$'s cancel out to yield

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(e^{-i\frac{\omega_o t}{2}}|\alpha\rangle + e^{i\frac{\omega_o t}{2}}|\beta\rangle\right). \tag{2.14}$$

This is the state at some later time. To represent it on the Bloch sphere, we do a little trick. We factorize out the global phase. Pulling out the $e^{-i\frac{\omega_o t}{2}}$ factor, we have

$$|\psi(t)\rangle = e^{-i\frac{\omega_o t}{2}}\left(\frac{1}{\sqrt{2}}|\alpha\rangle + \frac{1}{\sqrt{2}}e^{i\omega_o t}|\beta\rangle\right). \tag{2.15}$$

Since $e^{-i\frac{\omega_o t}{2}}$ is a global phase its presence is immaterial. We observe, however, that there is an important relative phase between $|\alpha\rangle$ and $|\beta\rangle$ which captures the

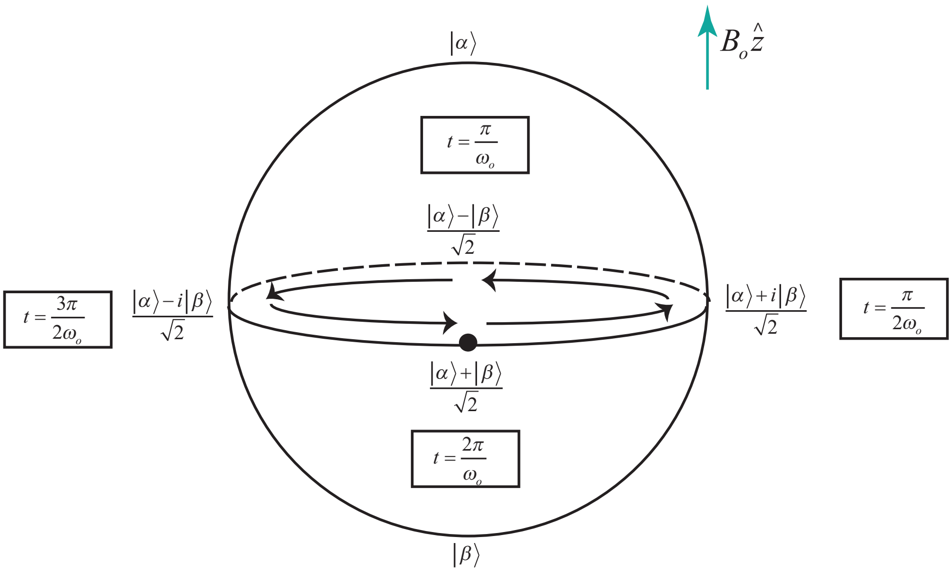

Figure 2.4: Representing precessional motion on the Bloch sphere.

state's evolution. At time $t = 0$, we recover the original state $\big(|\alpha\rangle + |\beta\rangle\big)/\sqrt{2}$. At a later time $t = \pi/2\omega_o$

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\rangle + e^{i\frac{\pi}{2}}|\beta\rangle\right) \tag{2.16}$$

$$= \frac{1}{\sqrt{2}}\left(|\alpha\rangle + i\,|\beta\rangle\right). \tag{2.17}$$

Where does that state lie on the Bloch sphere? Of course in the y-direction, indicating that the state has evolved into $|y\rangle$. Double the time elapsed to $t = \pi/\omega_o$ and the state will have gone into

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\rangle + e^{i\pi}|\beta\rangle\right) \tag{2.18}$$

$$= \frac{1}{\sqrt{2}}\left(|\alpha\rangle - |\beta\rangle\right) \tag{2.19}$$

which is at the far end of the Bloch sphere, generally labeled as $|-x\rangle$. This means that the state is rotating along the equator, $|x\rangle \to |y\rangle \to |-x\rangle \to |-y\rangle \to |x\rangle$ and so on. This rotation is called precession and its frequency is ω_o. Hence the Larmor frequency physically corresponds to a precessional frequency. When the magnetic field and the state vector are oriented in the fashion described, with the field along z and the initial state oriented perpendicularly, along x, or for that matter anywhere in the equatorial plane, it will go round and round with a frequency ω_o.

2.6 The time-dependent state is given by Eq. (2.15). What if this spin is captured at time t passes through a Stern Gerlach apparatus oriented along z? What are the probabilities of seeing an outcome on either of the two output channels of this apparatus?

2.2.3 Expectation values of precessing states

The time-dependent precessing spin vector in the equatorial plane is given by Eq. (2.15). What is the expectation value of the $\hat{S}_z(\mathrm{t})$ operator, denoted as $\left\langle \hat{S}_z \right\rangle (t)$? In other words, if we measure $\hat{S}_z$ what do we get and what is the average? We inject the quantum state into a Stern Gerlach apparatus oriented along z and we would like to find out the average outcome, remembering that the average *maynot* be equal to any of the outcomes, since the only possible outcomes are the eigenvalues of $\hat{S}_z$ which are $\pm\hbar/2$. The $\left\langle \hat{S}_z \right\rangle (t)$ acquires a more direct meaning if we there were a large number of spins with a spread of initial states centered around a likely value or a range of Larmor frequencies ω_o. This kind of situation is called an ensemble. So $\left\langle \hat{S}_z \right\rangle (t)$ is equal to the ensemble average at time t.

In fact, just by looking at the Bloch sphere picture can we predict the expectation value of the $\hat{S}_z$ operator? Zero it is, since the spin is always rotating in the equatorial plane with zero z component. We can also practice the calculation. Here we go.

$$\left\langle \hat{S}_z \right\rangle (t) = \langle \psi(t)| \hat{S}_z |\psi(t)\rangle \tag{2.20}$$

where we can use Eq. (2.17) for the precessing quantum state. The global phase $e^{-i\frac{\omega_o t}{2}}$ is immaterial because taking the dual changes all i's to $-i$'s resulting in the following

$$\begin{aligned}
\left\langle \hat{S}_z \right\rangle (t) &= \left(e^{i\frac{\omega_o t}{2}} \left(\frac{1}{\sqrt{2}} \langle\alpha| + \frac{1}{\sqrt{2}} e^{-i\omega_o t} \langle\beta| \right)\right) \hat{S}_z \left(e^{-i\frac{\omega_o t}{2}} \left(\frac{1}{\sqrt{2}} |\alpha\rangle + \frac{1}{\sqrt{2}} e^{i\omega_o t} |\beta\rangle \right)\right) \\
&= \left(\frac{1}{\sqrt{2}} \langle\alpha| + \frac{1}{\sqrt{2}} e^{-i\omega_o t} \langle\beta| \right) \hat{S}_z \left(\frac{1}{\sqrt{2}} |\alpha\rangle + \frac{1}{\sqrt{2}} e^{i\omega_o t} |\beta\rangle \right) \\
&= \frac{1}{2} \left(\langle\alpha| + e^{-i\omega_o t} \langle\beta| \right) \hat{S}_z \left(|\alpha\rangle + e^{i\omega_o t} |\beta\rangle \right). \qquad (2.21)
\end{aligned}$$

Inserting the spectral decomposition of $\hat{S}_z$ we obtain

$$\begin{aligned}
\left\langle \hat{S}_z \right\rangle (t) &= \frac{1}{2}\left(\langle\alpha| + e^{-i\omega_o t}\langle\beta|\right)\left(\frac{\hbar}{2}\left(|\alpha\rangle\langle\alpha| - |\beta\rangle\langle\beta|\right)\right)\left(|\alpha\rangle + e^{i\omega_o t}|\beta\rangle\right) \\
&= \frac{\hbar}{4}\left(\langle\alpha| + e^{-i\omega_o t}\langle\beta|\right)\left(|\alpha\rangle\langle\alpha| - |\beta\rangle\langle\beta|\right)\left(|\alpha\rangle + e^{i\omega_o t}|\beta\rangle\right) \\
&= \frac{\hbar}{4}\left(\langle\alpha| + e^{-i\omega_o t}\langle\beta|\right)\left(|\alpha\rangle\underbrace{\langle\alpha|\alpha\rangle}_{1} - e^{i\omega_o t}|\beta\rangle\underbrace{\langle\beta|\beta\rangle}_{1}\right) \\
&= \frac{\hbar}{4}\left(\langle\alpha| + e^{-i\omega_o t}\langle\beta|\right)\left(|\alpha\rangle - e^{i\omega_o t}|\beta\rangle\right) \\
&= \frac{\hbar}{4}\left(\underbrace{\langle\alpha|\alpha\rangle}_{1} - \underbrace{e^{-i\omega_o t}e^{i\omega_o t}}_{e^0=1}\underbrace{\langle\beta|\beta\rangle}_{1}\right) = 0. \qquad (2.22)
\end{aligned}$$

The expected value of $\hat{S}_z$ operator is indeed zero. The value is not only zero but also constant and that's because the variable we are trying to observe $\hat{S}_z$ commutes with the Hamiltonian $\omega_o\hat{S}_z$. We know that an observable that commutes with the Hamiltonian is a stationary observable Another perspective is that in this precessional motion, the z component of the spin angular momentum remains unchanged.

2.2.4 Measuring the magnetization

NMR works. This means there is a definite way of measuring expectation values. Consider the value $\left\langle \hat{S}_z \right\rangle$. This is an average component of the angular momentum. The average is taken over all the spins that reside inside the volume, a so called ensemble average. In a small test tube of water there would be quadzillions of such spins. Suppose we have N of them. Each spin creates a magnetic moment $\gamma\vec{S}$ so the magnetic moment vector from the entire sample is

$$\begin{aligned}
M_x &= \gamma N\langle\hat{S}_x\rangle & (2.23) \\
M_y &= \gamma N\langle\hat{S}_y\rangle & (2.24) \\
M_z &= \gamma N\langle\hat{S}_z\rangle. & (2.25)
\end{aligned}$$

Once the spin has been somehow tipped onto the state $|x\rangle$, it will precess with time with a form given by Eq. (2.15). Suppose we wanted to compute the expectation value.

$$\begin{aligned}\left\langle \hat{S}_x \right\rangle(t) &= \langle\psi(t)|\,\hat{S}_x\,|\psi(t)\rangle \\ &= \left(\frac{\langle\alpha| + e^{-i\omega_o t}\langle\beta|}{\sqrt{2}}\right)\hat{S}_x\left(\frac{|\alpha\rangle + e^{i\omega_o t}|\beta\rangle}{\sqrt{2}}\right) \\ &= \frac{1}{2}\left(\langle\alpha| + e^{-i\omega_o t}\langle\beta|\right)\hat{S}_x\left(|\alpha\rangle + e^{i\omega_o t}|\beta\rangle\right). \end{aligned} \tag{2.26}$$

Since $\hat{S}_x$ is equal to $\frac{\hbar}{2}\left(|\alpha\rangle\langle\beta| + |\beta\rangle\langle\alpha|\right)$ we proceed

$$\begin{aligned}\left\langle \hat{S}_x \right\rangle(t) &= = \frac{1}{2}\left(\langle\alpha| + e^{-i\omega_o t}\langle\beta|\right)\left(\frac{\hbar}{2}\left(|\alpha\rangle\langle\beta| + |\beta\rangle\langle\alpha|\right)\right)\left(|\alpha\rangle + e^{i\omega_o t}|\beta\rangle\right) \\ &= \frac{\hbar}{4}\left(\langle\alpha| + e^{-i\omega_o t}\langle\beta|\right)\left(|\alpha\rangle\langle\beta| + |\beta\rangle\langle\alpha|\right)\left(|\alpha\rangle + e^{i\omega_o t}|\beta\rangle\right) \\ &= \frac{\hbar}{4}\left(\langle\alpha| + e^{-i\omega_o t}\langle\beta|\right)\left(|\alpha\rangle\underbrace{\langle\beta|\alpha\rangle}_{0} + e^{i\omega_o t}|\alpha\rangle\underbrace{\langle\beta|\beta\rangle}_{1} + |\beta\rangle\underbrace{\langle\alpha|\alpha\rangle}_{1} + e^{i\omega_o t}|\beta\rangle\underbrace{\langle\alpha|\beta\rangle}_{0}\right) \\ &= \frac{\hbar}{4}\left(\langle\alpha| + e^{-i\omega_o t}\langle\beta|\right)\left(e^{i\omega_o t}|\alpha\rangle + |\beta\rangle\right). \end{aligned} \tag{2.27}$$

Next we perform the inner product resulting in

$$\left\langle \hat{S}_x \right\rangle(t) = \frac{\hbar}{4}\left(e^{i\omega_o t}\underbrace{\langle\alpha|\alpha\rangle}_{1} + e^{-i\omega_o t}\underbrace{\langle\beta|\beta\rangle}_{1}\right) = \frac{\hbar}{2}\cos\omega_o t \tag{2.28}$$

which shows a non-zero time-dependent value of the average x component of the spin angular momentum. Note that for single spins measured on their own, one-by-one, this is an average outcome and the real outcome measured may never coincide with this value. However for the collection of spins that we've called an ensemble, there is a distribution of states and precessional speeds and $\hbar/2\cos\omega_o t$ is indeed the observed ensemble average. The $\cos\omega_o t$ reflects precession and ω_o is the precessional (Larmor) frequency. We can also obtain the result in Eq. (2.28) by remembering that $\hat{S}_x = (\hbar/2)\sigma_x$, σ_x acts on $|\alpha\rangle$ giving $|\beta\rangle$ and acts on $|\beta\rangle$ to produce $|\alpha\rangle$. Furthermore, we can also do brute force matrix multiplication to obtain this result.

Here we would like to briefly address the meaning of this experiment. The spin angular momentum $\hat{S}_x$ belongs to a single spin whereas $\langle\hat{S}_x\rangle(t)$ is an average computed over the collection of spins in our sample. We can multiply this average with the number of spins N and obtain the x component of a macroscopic spin angular momentum: the giant momentum of our sample which is also proportional to the magnetic moment's x component, Eq. (2.23). An effective picture is to view the sample as comprising of a giant soup of many identical spin vectors each precessing as $\langle \hat{S}_x \rangle(t)$ and the overall sample spin is simply this spin vector amplified N times.

The spin vector is exactly equivalent to a tiny magnet, as claimed in Eq. (2.3). A dipole has a north pole and the south pole, the axis lies exclusively in the equatorial plane and further, it is precessing with the frequency ω_o. The rotating dipole also produces a rotating magnetic field. Suppose we place a pick-up coil, actually a solenoid, with many turns parallel to the x-axis and right outside but in close proximity with the sample. The arrangement seen from the top is shown in Figure 2.5. The precessing magnet is represented by the precessing arrow.

When the magnetic moment is parallel to the axis of the coil, it pierces a flux through the coil which is at its maximum. When the magnetic moment is perpendicular to the coil pointing in the y direction, very little flux pierces the coil. When the magnet is anti-parallel the flux piercing the coil is again maximum but now in the opposite direction. If we had a sensitive voltmeter or oscilloscope connected with the coil, it is going to register a voltage or E.M.F ε which is proportional the rate of change of flux Φ_m piercing the coil allowing one to write

$$\mathcal{E}_x(t) = -\frac{d\Phi_m}{dt} \tag{2.29}$$

which is simply Faraday's law of electromagnetism. Flux is a magnetic field $\vec{B}$ piercing the cross-sectional area of the coil allowing one to write

$$\mathcal{E}_x(t) = -\frac{d}{dt}\int \vec{B}_m \cdot d\vec{A}. \tag{2.30}$$

where B_m is the field due to the tiny magnets, distinct from the applied field B_o. Only that magnetic field will contribute to the flux which is parallel to the cross sectional area of the coil. So the magnetic field pointing along y will not give rise to any piercing flux. Since $d\vec{A} = dA_x$ (coil is oriented along x), the integrand in Eq. (2.30) is $B_x dA_x = \Phi_m$. We suppose that the magnetic field close to the sample is proportional to the magnetic moment of the sample, larger the magnetic moment, larger the field it will produce allowing us to write the entire integral $\int \vec{B}_m \cdot d\vec{A} = \int B_x \, dA_x = \Phi_m$ as $K\langle \mu_x \rangle$ where K is a proportionality factor containing the cross-sectional area, the conversion from magnetic moment to magnetic field, how closely coupled the pick-up coil is to the sample and its number of turns etc. It encapsulates the detection sensitivity of the pickup. Finally from Eqs. (2.3) and (2.4) we have

$$\mathcal{E}_x(t) = -KN\gamma\frac{d}{dt}\langle \hat{S}_x \rangle(t). \tag{2.31}$$

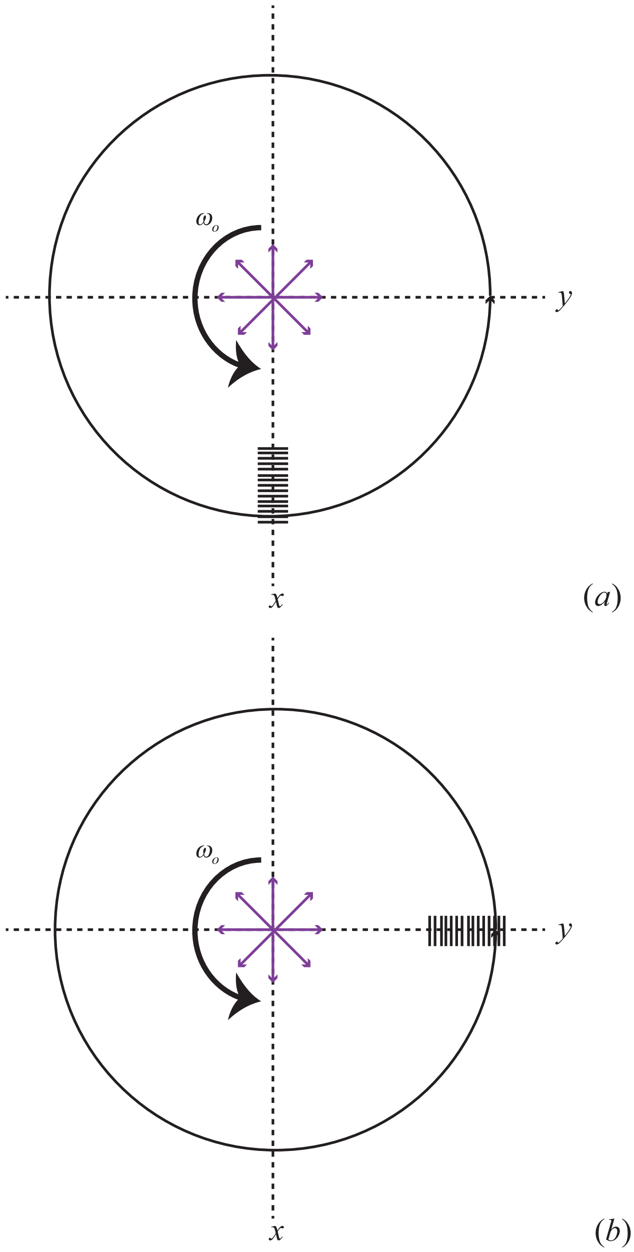

Figure 2.5: Top view of Bloch sphere showing the precessing magnetic moment. (a) Pickup coil along the x-axis and (b) pickup coil along the y-axis.

The number of spins N sneaks in because all spins are contributing to the voltage. We have already calculated $\langle \hat{S}_x \rangle(t)$ in Eq. (2.28). The induced E.M.F will therefore be

$$\mathcal{E}_x(t) = +KN\gamma\frac{\hbar}{2}\omega_o \sin\omega_o t. \tag{2.32}$$

The coil is actually measuring a voltage and if we connected this to an oscilloscope or similar data recording device we could see a sinusoidal signal whose amplitude depends on the geometric pick-up factor K, how large the sample is N and the Larmor frequency itself ω_o which in turn depends on how strong the magnetic field is (cf. Eq. (2.8)).

The Larmor frequency has a bigger role to play than what catches the eye. One, this is the frequency of the precessing spin. Two, it appears as a coefficient in the amplitude of the E.M.F. Three, it appears in disguise in the number of spins N participating in the production of the E.M.F and hence contributes one more time in the amplitude. From the questions in Section 2.1.4 we learned that the population difference between the Zeeman states α and β contributes to the strength of the NMR signal. In a state of equilibrium in a z pointing field, the $|\alpha\rangle$ spins each have a moment $\gamma\hbar/2$ and the $|\beta\rangle$ spins have a moment $-\gamma\hbar/2$ each. So a population difference is required to elicit a signal otherwise the oppositely pointing magnetic moments will cancel out. The population difference can be calculated from the Boltzmann factors

$$N = \frac{e^{\hbar\omega_o/(2k_BT)} - e^{-\hbar\omega_o/(2k_BT)}}{e^{\hbar\omega_o/(2k_BT)} + e^{-\hbar\omega_o/(2k_BT)}}. \tag{2.33}$$

You will recognize that the factors $\pm\hbar\omega_o/2$ represent the energies and the denominator above is called the partition function for the two-level system, the qubit. Quantum mechanics has met statistical mechanics! In the high temperature limit, $k_BT \gg \hbar|\omega_o|/2$, the exponents can be replaced by $1 \pm \hbar\omega_o/(2k_BT)$ and the approximate population difference becomes

$$N \approx \frac{\hbar\omega_o}{2k_BT}, \tag{2.34}$$

allowing one to re-write the generated E.M.F as

$$\mathcal{E}_x(t) = K\gamma\frac{\hbar^2}{4k_BT}\omega_o^2 \sin\omega_o t., \tag{2.35}$$

indicating a quadratic dependence of the amplitude of the signal on the Larmor frequency and hence the applied magnetic field B_o. That's why stronger magnets are considered superior, they can generate more signal for a given amount of sample. Alas, they are also considerably more expensive!

Suppose instead of using one coil along x, we have another coil along the y-axis as depicted in Figure 2.5 This is another measuring device. Here we are

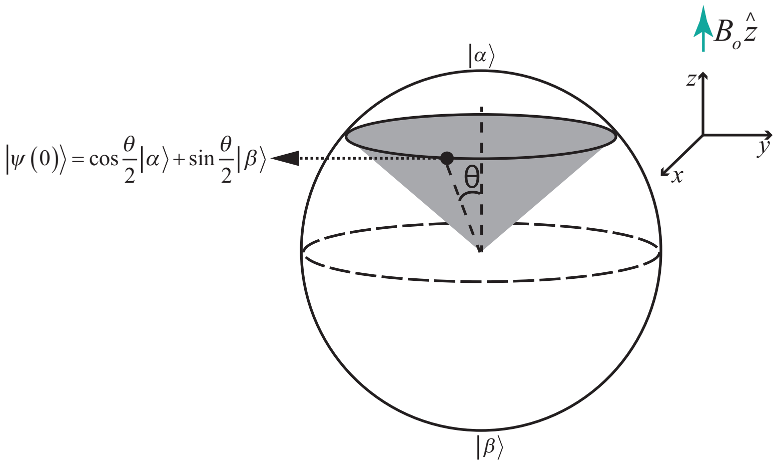

Figure 2.6: State in the x-z plane is precessing with frequency ω_o with a magnetic field applied in the z direction

using macroscopic coils to detect the magnetic moment emerging from various components of the spin angular momentum. If we were repeat the same calculation for $\langle \hat{S}_y \rangle (t)$, using the decomposition $\hbar/2\,(-i\,|\alpha\rangle\,\langle\beta| + i\,|\beta\rangle\,\langle\alpha|)$ the resulting expectation value will be

$$\langle \hat{S}_y \rangle (t) = \frac{\hbar}{2}\sin\omega_o t \tag{2.36}$$

which is $\pi/2$ out of phase with $\langle S_x \rangle (t)$ and its time derivative will determine the E.M.F produced

$$\mathcal{E}_y(t) = K\gamma\frac{\hbar^2}{4k_BT}\omega_o^2\cos\omega_o t. \tag{2.37}$$

2.2.5 Conical precession

Suppose the initial state is not along the equatorial plane but rather it is somewhere in the northern hemisphere (Figure 2.6) at an angle θ from $|z\rangle$. We also assume that the azimuthal phase is zero, the state lies in entirely the z-x plane. We will describe later, ways of getting there to begin with. The initial quantum state therefore is,

$$|\psi(0)\rangle = \cos\frac{\theta}{2}\,|\alpha\rangle + \sin\frac{\theta}{2}\,|\beta\rangle\,. \tag{2.38}$$

Again we apply the magnetic field along the z-direction, B_o resulting in our oft-repeated Hamiltonian $\omega_o S_z$. For finding the state at a later time, we repeat the same procedure as outlined in Section 2.2.2

$$\begin{aligned} |\psi(t)\rangle &= e^{-i\frac{\hat{\mathcal{H}}}{\hbar}t}\,|\psi(0)\rangle \\ &= e^{-i\frac{\hat{\mathcal{H}}}{\hbar}t}\left(\cos\frac{\theta}{2}\,|\alpha\rangle + \sin\frac{\theta}{2}\,|\beta\rangle\right) \\ &= \cos\frac{\theta}{2}\,|\alpha\rangle + e^{i\omega_o t}\sin\frac{\theta}{2}\,|\beta\rangle\,. \end{aligned} \tag{2.39}$$

The trajectory of this quantum state on the Bloch sphere is represented in Figure 2.6. Herein the azimuthal angle is $\omega_o t$ and changes linearly with time. However, the state preserves its angle θ. Geometrically, this means the state precesses in a cone with the Larmor frequency ω_o.

2.2.6 Rabi oscillations

In the previous examples, we applied a magnetic field along the z-axis. We switch gears and apply a field along y instead, $\vec{B} = B_1\hat{y}$. But let's that suppose the initial state is the ground state $|\alpha\rangle = |z\rangle$ instead. Out target is to tip the state to $(|\alpha\rangle + |\beta\rangle)/\sqrt{2} = |x\rangle$ so that we can make the spin subsequently undergo Larmor precession. In other words, we like to apply $\pi/2$ rotation about $\hat{S}_y$ which is the unitary operator $\exp\{-i(\pi/2)\,\hat{S}_y/\hbar\}$. The Hamiltonian is now proportional to $\hat{S}_y$. In complete correspondence with Eq. (2.9), we can write the Hamiltonian for the y-pointing field as

$$\hat{\mathcal{H}} = \omega_1\hat{S}_y \tag{2.40}$$

where $\omega_1 = \gamma B_1$ is some factor with dimensions of frequency and is completely analogous to Eq. (2.8). The evolving state is determined from the solution of the Schrodinger equation,

$$|\psi(t)\rangle = e^{-i\frac{\omega_1\hat{S}_y}{\hbar}t}\,|\alpha\rangle\,. \tag{2.41}$$

Now $|\alpha\rangle$ is not an eigenstate of $\hat{S}_y$. Therefore finding the evolving state is slightly more complicated. We employ a useful theorem we have proven earlier. Since the square of $\left(\frac{2\hat{S}_y}{\hbar}\right)$ is identity, we can write

$$\begin{aligned} |\psi(t)\rangle &= e^{-i\frac{\omega_1 t}{2}\left(\frac{2\hat{S}_y}{\hbar}\right)}\,|\alpha\rangle \\ &= \left(\cos\frac{\omega_1 t}{2}1 - i\sin\frac{\omega_1 t}{2}\sigma_y\right)|\alpha\rangle\,. \end{aligned} \tag{2.42}$$

As $\sigma_y = 2\hat{S}_y/\hbar = (-i\,|\alpha\rangle\,\langle\beta| + i\,|\beta\rangle\,\langle\alpha|)$, the above simplifies to

$$\begin{aligned}
|\psi(t)\rangle &= \cos\frac{\omega_1 t}{2}\,|\alpha\rangle - i\sin\frac{\omega_1 t}{2}\,(-i\,|\alpha\rangle\,\langle\beta| + i\,|\beta\rangle\,\langle\alpha|)\,|\alpha\rangle \\
&= \cos\frac{\omega_1 t}{2}\,|\alpha\rangle - i\sin\frac{\omega_1 t}{2}\left(-i\,|\alpha\rangle\,\underbrace{\langle\beta|\alpha\rangle}_{0} + i\,|\beta\rangle\,\underbrace{\langle\alpha|\alpha\rangle}_{1}\right) \\
&= \cos\frac{\omega_1 t}{2}\,|\alpha\rangle + \sin\frac{\omega_1 t}{2}\,|\beta\rangle\,. \qquad (2.43)
\end{aligned}$$

What is the trajectory of this state on the Bloch sphere? Refer to Figure 2.7. When $\omega_1 t$ is $\pi/2$, the state has evolved to

$$\left|\psi\left(t = \frac{\pi}{2\omega_1}\right)\right\rangle = \frac{|\alpha\rangle + |\beta\rangle}{\sqrt{2}} = |x\rangle \qquad (2.44)$$

and when we double the time, it goes to

$$\left|\psi\left(t = \frac{\pi}{\omega_1}\right)\right\rangle = \cos\frac{\pi}{2}\,|\alpha\rangle + \sin\frac{\pi}{2}\,|\beta\rangle = |\beta\rangle = |-z\rangle\,. \qquad (2.45)$$

Therefore the quantum state starts off at the north pole and moves toward south pole and circulates back to north pole. The motion persists as long as the field B_1 remains active. If we time the pulse (or the strength of the field ω_1) such that time equals $\pi/2\omega_1$, we will stop at the state $\big(|\alpha\rangle + |\beta\rangle\big)/\sqrt{2}$. If we time the pulse such that it is equal to π/ω_1, we will end up at $|\beta\rangle$. We can stop anywhere we desire. If we stop at $\big(|\alpha\rangle + |\beta\rangle\big)/\sqrt{2}$, the pulse is called the $\pi/2$ pulse and is used for tipping the spin vector from the equilibrium state to the equatorial plane. Such a pulse can also be thought of as an operation that creates a superposition. If we apply the π pulse, the original state is inverted from $|\alpha\rangle$ to $|\beta\rangle$. The rotational operator

$$\hat{R}_y(\omega_1 t) = e^{-i\frac{\omega_1 t \hat{S}_y}{\hbar}} \qquad (2.46)$$

is thus physically implemented through a magnetic field applied along a particular direction and switched on for a carefully chosen length of time.

Suppose we have the ability to distinguish between $|\alpha\rangle$ and $|\beta\rangle$ in some experiment. We want to determine the probability that we detect the state $|\alpha\rangle$ or $|\beta\rangle$. Clearly these probabilities are $\cos^2\omega_1 t/2$ and $\sin^2\omega_1 t/2$. These probabilities are shown in Figs 2.8 (a) and (b). The quantum state is oscillating between $|\alpha\rangle$ and $|\beta\rangle$ and this has been achieved by the application of a field perpendicular to the plane in the Bloch sphere containing the states of interest, $|\alpha\rangle$ and $|\beta\rangle$. These oscillations are of great interest in atomic physics experiments and are called Rabi oscillations.

2.7 Identify a constant of motion for Rabi oscillations described above.

2.8 How can one get to the state $\big(|\alpha\rangle + e^{i\pi/4}\,|\beta\rangle\big)/\sqrt{2}$ starting from $|\alpha\rangle$?

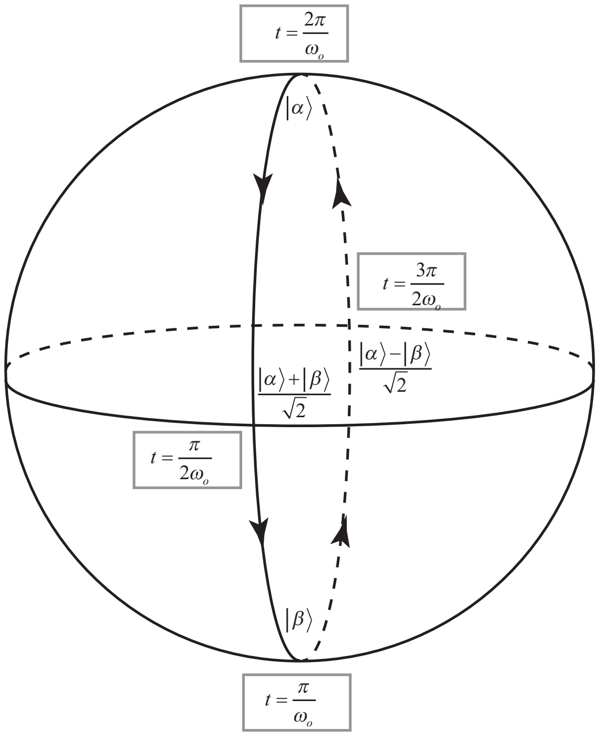

Figure 2.7: Rabi oscillations.

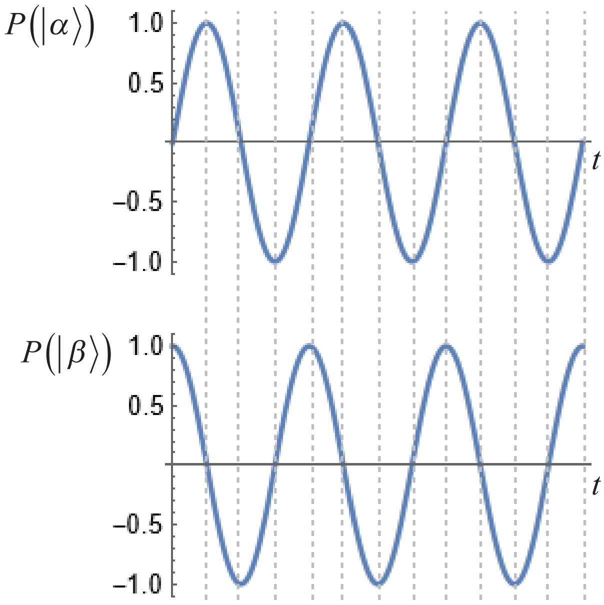

Figure 2.8: (a) Probability of state $|\alpha\rangle$ vs time. (b) Probability of state $|\beta\rangle$ vs time.

2.3 A complete NMR experiment

This section takes our discussion of a spin-1/2 particle placed inside magnetic fields oriented in different directions further and builds all necessary details for understanding the technology of NMR. It also shows that quantum mechanics is manifest in the form of a real-life application that actually saves lives.

In the previous section, we have looked at precession and Rabi flopping. What is the main difference between them? The only difference is the orientation of the applied static magnetic field, $B_o\hat{z}$ or $B_1\hat{y}$. In a real NMR equipment, the large $B_o\hat{z}$ field is always on so there is always the possibility of precession, rotation about the z axis. A small $B_1\hat{y}$ (or $B_1\hat{x}$) can be activated or de-activated at will. So there are lengths of time when the spins see an effective field which is a resultant of two fields. For example one can have

$$\vec{B} = B_o\hat{z} + B_1\hat{x} \tag{2.47}$$

with $B_1 \ll B_o$ if B_1 is applied along x. How will the state evolve in the presence of these fields applied together? This is the subject of the present section and will also help us complete our story of NMR as a practical and illustrative example of quantum evolution of states.

2.3.1 The NMR magnet

Here we consider the complete NMR experiment. A test tube containing water is taken. Each water molecule contains two protons (hydrogen nuclei) and therefore serves as the source of spin-1/2 particles. This tube is placed in upward direction along z and we define the x axis to be pointing out of the plane of paper while the y axis is toward the right. We apply a uniform magnetic field in the z direction. The best way to do this is by a solenoid connected to a current supply. We place the test tube coaxially inside the solenoid. The scheme is shown in Figure 2.9. If the field is to point vertically upwards along z, the current will be coming out of the coil on the left and going into the paper on the right. If the coil is very large compared to the size of the test tube, the magnetic field will be approximately uniform. In fact NMR manufacturers go extra lengths in making this field extremely homogeneous. If we like to create a large field, a large current is required since for a solenoid with n turns per unit length carrying a current I the axial magnetic field produced inside the coil is

$$B = \mu_o nI. \tag{2.48}$$

Large magnetic fields require large currents which cause the coils to heat up. This is the resistive I^2R heating. So how nice would it feel to have large currents yet no resistance. A superconductor is a material which precisely fit this criteria. In

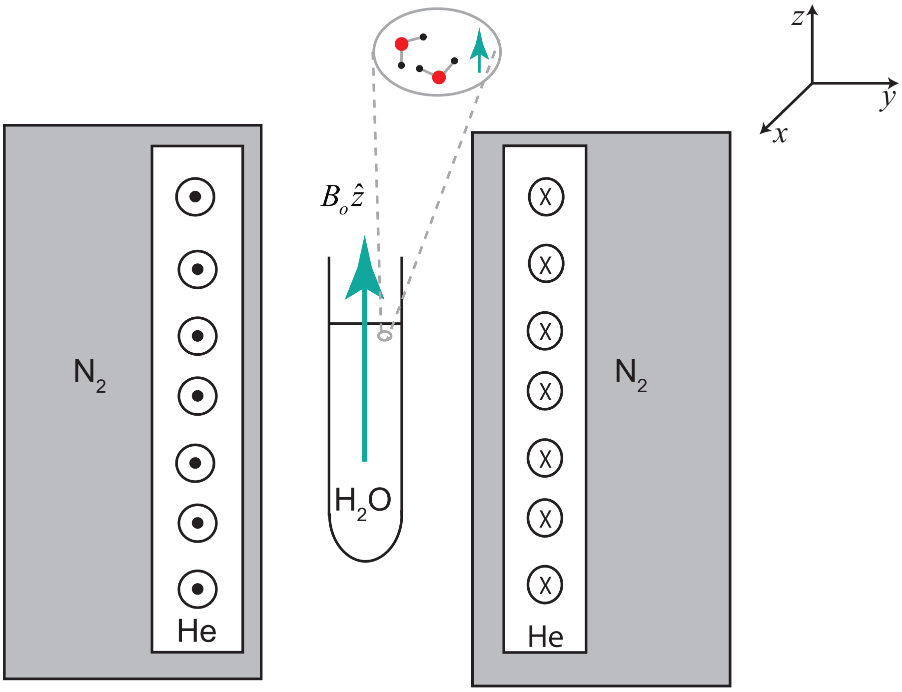

Figure 2.9: Magnetic field applied with the help of solenoid made of super conducting material. The superconducting coils are awash in liquid helium and surrounded by liquid nitrogen to soften the temperature gradient.

real NMR machines, this coil is made out of a superconducting material such as an alloy of niobium-tin or bismuth-strontium-calcium-copper-oxide (BSCCO). The only problem, besides manufacturing this material, is that it superconducts only at extremely low temperatures. We put the coil inside liquid helium which is kept in a large thermos like container. The temperature of boiling liquid helium is a mere 4 K. Once we cool the coil, connect the power supply to activate the supercurrent, then take away the power source we can expect a large supercurrent and hence a large B_o to persist until the coils are kept under liquid helium. Good! We are done with creating a large static field B_o and this field is never switched off. The spins persistently see a background Hamiltonian, that we all know too well by now

$$\hat{\mathcal{H}}_o = \omega_o \hat{S}_z. \tag{2.49}$$

where we have added subscript $'o'$ to indicate the background part. Spins, if they are not in a stationary state of the $\hat{S}_z$ operator will precess under the action of $\hat{\mathcal{H}}_o$.
2.9 What is the amount of current required through the main field producing coils in a 900 MHz NMR spectrometer? If the normally conducting coil had a finite resistance of just 100 Ω, how much power would be lost as heat? Heat loss

can be by-passed in a superconducting coil.

Our sample and the room is at room temperature but now we have a region at 4 K. This is a huge temperature gradient between room to Helium. So we put the liquid helium in another jacket containing liquid nitrogen at 77 K. Additionally, these cryogens are also surrounded by evacuated regions that minimize heat transfer preventing the continuous boil-off of the liquids.

2.3.2 Coils for NMR signal creation

In order to receive an E.M.F., the quantum state must precess about the z axis. We have seen from Sections 2.2.4 and 2.2.5 that the E.M.F is maximized when the spin vector has been brought fully to the equatorial plane. We have also learned that this requires a $\pi/2$ pulse applied to the $|\alpha\rangle$ state. A Hamiltonian $\omega_1 \hat{S}_x$ can achieve this if applied for the proper length of time. However, since the background Hamiltonian Eq. (2.49) cannot be silenced away at any instance the total Hamiltonian

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_o + \hat{\mathcal{H}}_1 = \omega_o \hat{S}_z + \omega_1 \hat{S}_x = \gamma(B_o \hat{S}_z + B_1 \hat{S}_x) \tag{2.50}$$

will be overwhelmed by the $\hat{S}_z$ part since $B_1 \ll B_o$, resulting in a rotation about an axis really close to the z axis. This isn't desired. Hence, we must use some other mechanism to achieve rotation about $\hat{S}_x$ only. One must remember that the x or y coils are not superconducting. They are at room temperature, so they must be kept as close as possible to the test tube. So they can carry only a small current producing a field B_1 that is perhaps a thousand times smaller than B_o. If B_m is constant, there will be hardly any luck in flipping the state vector away from $|\alpha\rangle$. So, we employ an oscillatory B_1 field that does the trick through the phenomena of resonance.

In electronics, we come across the transistor. A small base current is used to control the passage of a large current perhaps orders of magnitude larger in the main channel. The base current is like a control switch. Exactly, in the same fashion, in an NMR experiment, we use a small control signal (which is oscillatory) applied to a coil to control the rotation of the macroscopic spin vector which is normally under the influence of a much larger static magnetic field. The coil's axis is chosen to be along x and is placed really close to the sample. See Figure 2.11. The key is that the coil applies a time-varying sinusoidal magnetic field whose oscillatory frequency is, ideally, ω_o. In physics this process is called resonance. We will observe that with the help of a resonant magnetic field B_1 that is applied transverse to B_o

$$\vec{B}_1 = B_1 \cos(\omega_o t + \phi_p)\hat{x} \tag{2.51}$$

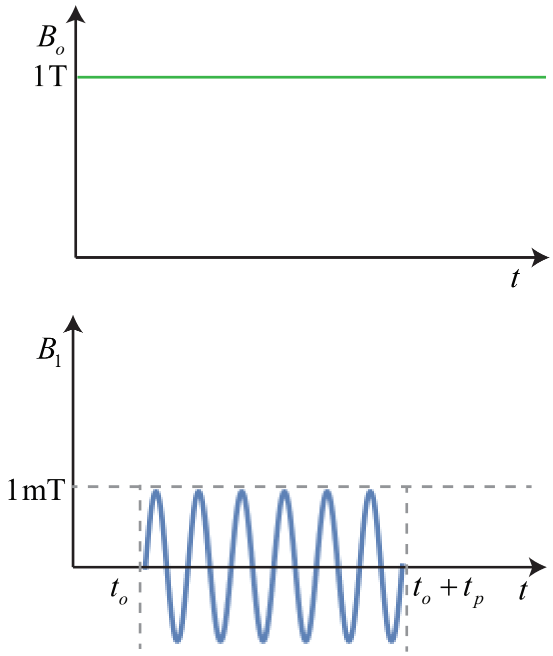

Figure 2.10: A timing diagram showing the fields B_o and B_1. The B_1 field is oscillatory and turned on only for a finite duration t_p.

we can drag the spin vector from $|z\rangle$ towards the equatorial plane; in this case, precisely to the $|-y\rangle$ state. In Eq. (2.51), $B_1 \ll B_o$ and ϕ_p is some phase. The rest of this section deals with the underlying quantum principle of this spin resonance phenomenon.

The magnetic field B_1 is produced by an alternating current applied to the room temperature x coil. Since it is not a superconductor, the range of the current is small allowing only small B_1's to be generated. Generally B_1 is in the mT regime. The oscillatory field is switched on only for a particular duration of time say t_p. Otherwise it remains off. Hence this is a 'pulse' of oscillatory field impinging upon the sample. The sequence of field's applied is shown in Figure 2.10.

2.10 What is the frequency ω_1 when $B_1 = 1$ mT?

2.11 Where does the axis of rotation lie for the rotation affected by a Hamiltonian given in Eq. (2.50) when $B_o = 1$ T and $B_1 = 1$ mT? When $B_o = 2$ mT and $B_1 = 1$ mT?

A computer controls all operations of the NMR process. A computer program instructs the hardware to generate a pulse of frequency ω_o, phase ϕ_p and duration t_p. Refer to Figure 2.11. Computers deal with digital data but the output is analog. This is achieved by a digital to analog converter (DAC) which produces an oscillating current. The current is amplified and then it goes to the coil. The coil is practically an inductor of inductance L with an extra capacitor C. Since the amount of B_1 field is small and hence precious, we like to transfer maximum power to the coil. The inductor and capacitor circuit has a resonant frequency $1/\sqrt{LC}$ and we adjust the capacitance such that $\omega_o = 1/\sqrt{LC}$. It is important to appreciate that $\omega_1 = \gamma B_1$ is a frequency distinct from the Larmor frequency ω_o. Additionally, in the resonance condition, the transmitted control field is of oscillating frequency ω_o and equals the Larmor frequency.

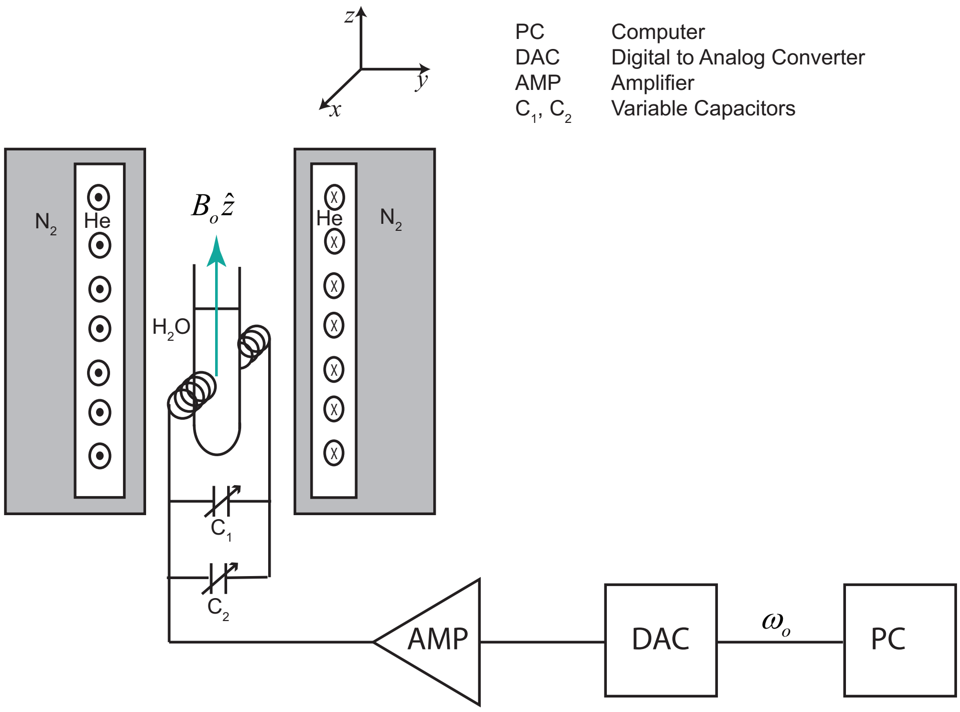

Figure 2.11: Oscillating magnetic field with Larmor frequency applied along the x-axis.

2.3.3 The control Hamiltonian

The Hamiltonian corresponding to the oscillatory x field Eq. (2.51) is

$$\hat{\mathcal{H}}_1(t) = \omega_1 \cos(\omega_o t + \phi_p)\hat{S}_x \tag{2.52}$$

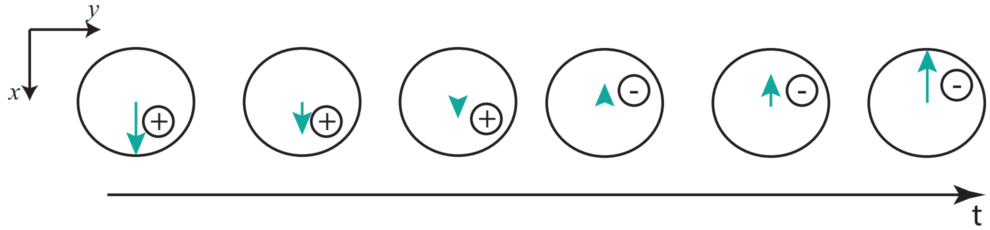

Figure 2.12: Top view of the vectorial field applied on the small coil. The field is sinusoidally reciprocating along the x-axis.

which depends upon time. If the state at time t is considered to evolve during a really small interval dt we can approximate the evolved state a tiny bit later as

$$\begin{aligned} |\psi(t+dt)\rangle &= \exp\Big(-i\big(\hat{\mathcal{H}}_o + \hat{\mathcal{H}}_1(t)\big)dt/\hbar\Big)|\psi(t)\rangle \\ &= \exp\Big(-i\big(\omega_o \hat{S}_z + \omega_1 \hat{S}_x(\cos(\omega_o t + \phi_p))\big)dt\Big)|\psi(t)\rangle\,. \end{aligned} \tag{2.53}$$

There are three complications with this calculation. First, the Hamiltonian inside the exponent is time-dependent. We don't know as yet how to solve problems of this kind. Second, the time-dependence necessitates the step-wise computation of the evolution as the Hamiltonian $\hat{\mathcal{H}}_1(t)$ is different on each step though this piecewise determination of the state is well suited for iterative computer programs. Third, the $\hat{S}_z$ and $\hat{S}_x$ in the exponent don't mutually commute so that the joint action of these Hamiltonians must be considered in one go. Suppose we have an operator $e^{i(\hat{A}+\hat{B})}$. Can we write this as $e^{i\hat{A}}$ multiplied by $e^{i\hat{B}}$? No, we cannot do this unless $\hat{A}$ and $\hat{B}$ commute. Let's now attempt to address some of these complications.

Here is an interesting observation. If we view down the z axis, which is looking down from the top (Figure 2.12), the x pointing field is sometimes positive and sometimes negative. The field varies cyclically, increasing positive, decreasing positive, increasing negative, decreasing negative and so on. Such a reciprocatory field can be termed as being x polarized. But we can decompose this motion into two different circular motions. Refer to Figure 2.13. We can visualize the reciprocating field as a sum of two counter rotating components. One component is going around at a frequency $+\omega_o$ in the anti-clockwise direction and another is a component going around with frequency $-\omega_o$ which is the clockwise direction (all viewed from the top). If we add both of these counter-rotating vectors the resultant is a reciprocating field in the x-direction. So we decompose the magnetic

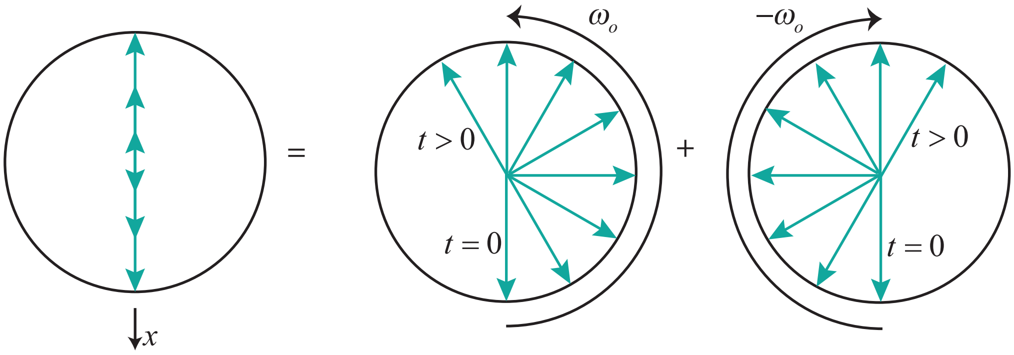

Figure 2.13: Top view of the rotating spin vector showing that reciprocating field along the x-axis is sum of two counter rotating fields.

field Eq. (2.51) as

$$\vec{B}_1(t) = \underbrace{\frac{B_1}{2}\cos(\omega_o t + \phi_p)\hat{x} + \frac{B_1}{2}\sin(\omega_o t + \phi_p)\hat{y}}_{\text{counter-clockwise component}} \tag{2.54}$$

$$+ \underbrace{\frac{B_1}{2}\cos(\omega_o t + \phi_p)\hat{x} - \frac{B_1}{2}\sin(\omega_o t + \phi_p)\hat{y}}_{\text{clockwise rotating component}}\,. \tag{2.55}$$

The Larmor frequency is $+\omega_o$. The counter-clockwise component also has a frequency $+\omega_o$ and is perfectly resonant with the natural precessional frequency of the spin. The clockwise component has a frequency $-\omega_o$ which is $2\omega_o$ away from the natural frequency. Hence it is a non-resonant component and will play an insignificant role in affecting the evolution of the spin. [1]The field only worthy of consideration up to the lowest order is therefore just the resonant component which carries one half of the amplitude and one fourth of the total energy supplied by the oscillating field. This results in the effective control Hamiltonian

$$\hat{\mathcal{H}}_1 = +\frac{\omega_1}{2}\left(\cos(\omega_o t + \phi_p)\hat{S}_x + \sin(\omega_o t + \phi_p)\hat{S}_y\right) \tag{2.56}$$

which is still time-dependent and rotating. It appears we have achieved nothing useful, only transformed a linearly polarized into a circularly polarized field. Let's explore the usefulness of this alteration.

There is a more appealing manner that portrays the Hamiltonian in Eq. (2.56) as a circularly rotating Hamiltonian. We propose that this Hamiltonian can be

[1]In fact, we have bypassed a large amount of technical details which are beyond the scope of this text.

simplified using the transformation

$$\cos(\omega_o t)\hat{S}_x + \sin(\omega_o t)\hat{S}_y = e^{-i\omega_o t\frac{\hat{S}_z}{\hbar}}\hat{S}_x e^{+i\omega_o t\frac{\hat{S}_z}{\hbar}}. \tag{2.57}$$

Inspecting this relation, we see that $\hat{S}_x$ is sandwiched between a rotation operator $e^{-i\omega t\frac{\hat{S}_z}{\hbar}} = \hat{R}_z(\omega_o t)$ and its inverse and therefore qualifies as a basis or similarity transformation. The operation rotates $\hat{S}_x$ in the equatorial plane through a time-dependent angle $\omega_o t$. The proof is simple.

We can express the rotation operator as

$$e^{-i\omega_o t\frac{\hat{S}_z}{\hbar}} = \cos\left(\frac{\omega_o t}{2}\right)\vec{\hat{1}} - i\sin\left(\frac{\omega_o t}{2}\right)\hat{\sigma}_z, \tag{2.58}$$

and using various properties of Pauli operators can make the L.H.S. of Eq. (2.57) become

$$\begin{aligned} L.H.S. &= \left(\cos\left(\frac{\omega t}{2}\right)\vec{\hat{1}} - \sin\left(\frac{\omega t}{2}\right)\hat{\sigma}_z\right)\left(\frac{\hbar}{2}\hat{\sigma}_x\right)\left(\cos\left(\frac{\omega t}{2}\right)\vec{\hat{1}} + \sin\left(\frac{\omega t}{2}\right)\hat{\sigma}_z\right) \\ &= \frac{\hbar}{2}\left(\cos^2\left(\frac{\omega t}{2}\right)\hat{\sigma}_x + \frac{i}{2}\sin(\omega t)[\hat{\sigma}_x, \hat{\sigma}_z] + \sin^2\left(\frac{\omega t}{2}\right)\hat{\sigma}_z\hat{\sigma}_x\hat{\sigma}_z\right), \end{aligned} \tag{2.59}$$

which upon using the identities $[\hat{\sigma}_x, \hat{\sigma}_z] = -2i\hat{\sigma}_y$, $\hat{\sigma}_z\hat{\sigma}_x\hat{\sigma}_z = -i\hat{\sigma}_z\sigma_y = -\hat{\sigma}_x$ and $\cos^2\beta/2 - \sin^2\beta/2 = \cos\beta$ comes out to be equal to the R.H.S. as desired. Therefore the total Hamiltonian can be finally written in the modified time-dependent form

$$\hat{\mathcal{H}} = \omega_o\hat{S}_z + \frac{\omega_1}{2}e^{-i\omega_o t\frac{\hat{S}_z}{\hbar}}\hat{S}_x e^{+i\omega_o t\frac{\hat{S}_z}{\hbar}}. \tag{2.60}$$

2.3.4 Rotating wave approximation

There is an extremely valuable transformation in quantum mechanics that can simplify many time-dependent Hamiltonians especially if they are rotating about an axis. Consider a view of the xy plane from above as shown in Figure 2.14. We draw a circle depicting the plane wherein the x axis is shown towards the bottom, the y-axis is towards the right and z-axis is pointing out of the plane of the paper.

The quantum state $|\psi(t)\rangle$ is precessing around the circle with frequency ω_o. Suppose the state at time zero, is $|\psi(0)\rangle$. At time t, this precessing state will evolve into

$$|\psi(t)\rangle = e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}}|\psi(0)\rangle \tag{2.61}$$

in complete correspondence with Eq. (2.13). The operator $e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}}$ in the expression above is simply a rotation about the z axis through an angle $\omega_o t$. Suppose the observer is also rotating with the state with the same frequency. In other words,

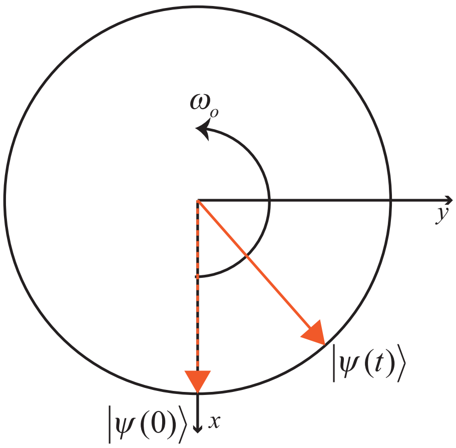

Figure 2.14: Top view showing the state precessing with frequency ω_o.

the state and the observer are tied together and co-rotating. The observer is in a rotating frame, observes the state and declares "the state isn't moving". This is exactly what is seen on an ultra-smooth train. Being inside the train, the coffee cup on the table in front of you appears static while for anyone outside on the platform, it whizzes past with an exceptionally high speed. Physically it's the same state in the static (also called the lab) frame and the rotating frames but the point-of-view and the representation may change. This is akin to a basis transformation.

We denote the description of the state in the rotating frame by putting a tilde sign on top $\left|\widetilde{\psi(t)}\right\rangle$. One can connect the pictures between the lab and rotating frames through

$$\left|\widetilde{\psi(t)}\right\rangle = e^{+i\frac{\omega_o t \hat{S}_z}{\hbar}} \left|\psi(t)\right\rangle \tag{2.62}$$

which together with Eq. (2.61) results in $\left|\widetilde{\psi(t)}\right\rangle = |\psi(0)\rangle$ which is absolutely correct because from the rotating observer's perspective nothing has changed since time $t = 0$.

The Schrodinger equation is an undeniable physical reality and the rule doesn't change when we disagree in choosing a reference frame. Therefore (in approximate condition) it must remain invariant across the lab and rotating frames. Putting tildes over the equation

$$i\hbar\frac{d}{dt}\left|\psi(t)\right\rangle = \hat{\mathcal{H}}\left|\psi(t)\right\rangle \tag{2.63}$$

should keep the physics intact, and the physicist happy at all times, allowing us to write

$$i\hbar\frac{d}{dt}\left|\widetilde{\psi(t)}\right\rangle = \tilde{\hat{\mathcal{H}}}\left|\widetilde{\psi(t)}\right\rangle. \tag{2.64}$$

The goal is to now find $\widetilde{\hat{\mathcal{H}}}$ for a given $\hat{\mathcal{H}}$ and expect that all the time dependence magically goes away, only if we as observers are rotating at the correct frequency.

Focus on the left hand side of the equation above and use the substitution Eq. (2.62)

$$\begin{aligned} L.H.S. &= i\hbar\frac{d}{dt}\left|\widetilde{\psi(t)}\right\rangle \\ &= i\hbar\frac{d}{dt}\left(e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\left|\psi(t)\right\rangle\right) \end{aligned} \tag{2.65}$$

indicating that we are required to find the derivative of a product of two time dependent functions, one is a phase factor and the other is the quantum state itself. We will just use the chain rule. Proceeding with the differentiation

$$\begin{aligned} L.H.S. &= i\hbar\left(\frac{d}{dt}\left(e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\right)\left|\psi(t)\right\rangle + e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\frac{d}{dt}\left(\left|\psi(t)\right\rangle\right)\right) \\ &= i\hbar\left(i\frac{\omega_o\hat{S}_z}{\hbar}\left(e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\right)\left|\psi(t)\right\rangle + e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\frac{d}{dt}\left(\left|\psi(t)\right\rangle\right)\right). \end{aligned} \tag{2.66}$$

and using the TDSE Eq. (2.63) allows us to simplify the second term above to

$$\begin{aligned} L.H.S. &= i\hbar\left(i\frac{\omega_o\hat{S}_z}{\hbar}\left(e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\right)\left|\psi(t)\right\rangle + e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\left(\frac{1}{i\hbar}\hat{\mathcal{H}}\left|\psi(t)\right\rangle\right)\right) \\ &= -\omega_o\hat{S}_z e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\left|\psi(t)\right\rangle + e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\hat{\mathcal{H}}\left|\psi(t)\right\rangle. \end{aligned} \tag{2.67}$$

The relationship between $|\psi(t)\rangle$ in the non rotating frame and in the rotating frame is given by Eq. (2.62) which upon time inversion becomes,

$$\left|\psi(t)\right\rangle = e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}}\left|\widetilde{\psi(t)}\right\rangle \tag{2.68}$$

modifying Eq. (2.67) to

$$\begin{aligned} L.H.S. &= -\omega_o\hat{S}_z\underbrace{e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}}}_{e^0=\hat{1}}\left|\widetilde{\psi(t)}\right\rangle + e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\hat{\mathcal{H}}e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}}\left|\widetilde{\psi(t)}\right\rangle \\ &= \left(-\omega_o\hat{S}_z + e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\hat{\mathcal{H}}e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}}\right)\left|\widetilde{\psi(t)}\right\rangle = \widetilde{\hat{\mathcal{H}}}\widetilde{|\psi(t)\rangle} \end{aligned} \tag{2.69}$$

which finally helps us identify the Hamiltonian in the rotating frame as

$$\widetilde{\hat{\mathcal{H}}} = e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\hat{\mathcal{H}}e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}} - \omega_o\hat{S}_z. \tag{2.70}$$

With this prescription, the lab frame Hamiltonian explicitly spelled out in Eq. (2.60) can be plugged into Eq. (2.70) with the following sequence of algebraic steps

$$\begin{aligned}
\widetilde{\hat{\mathcal{H}}} &= e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\hat{\mathcal{H}}e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}} - \omega_o\hat{S}_z \\
&= e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\left(\omega_o\hat{S}_z + \frac{\omega_1}{2}\left(e^{-i(\omega t+\phi_p)\frac{\hat{S}_z}{\hbar}}\hat{S}_x e^{+i(\omega t+\phi_p)\frac{\hat{S}_z}{\hbar}}\right)\right)e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}} - \omega_o\hat{S}_z \\
&= e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}\omega_o\hat{S}_z e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}} + \frac{\omega_1}{2}\left(e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}e^{-i(\omega t+\phi_p)\frac{\hat{S}_z}{\hbar}}\hat{S}_x e^{+i(\omega t+\phi_p)\frac{\hat{S}_z}{\hbar}}e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}}\right) - \omega_o\hat{S}_z \\
&= \frac{\omega_1}{2}\left(e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}e^{-i(\omega t+\phi_p)\frac{\hat{S}_z}{\hbar}}\hat{S}_x e^{+i(\omega t+\phi_p)\frac{\hat{S}_z}{\hbar}}e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}}\right) \\
&= \frac{\omega_1}{2}\left(\underbrace{e^{+i\frac{\omega_o t\hat{S}_z}{\hbar}}e^{-i\frac{\omega t\hat{S}_z}{\hbar}}}_{\hat{1}}e^{-i\frac{\phi_p\hat{S}_z}{\hbar}}\hat{S}_x e^{+i\frac{\phi_p\hat{S}_z}{\hbar}}\underbrace{e^{+i\frac{\omega t\hat{S}_z}{\hbar}}e^{-i\frac{\omega_o t\hat{S}_z}{\hbar}}}_{\hat{1}}\right) \\
&= \frac{\omega_1}{2}\left(e^{-i\frac{\phi_p\hat{S}_z}{\hbar}}\hat{S}_x e^{+i\frac{\phi_p\hat{S}_z}{\hbar}}\right). \qquad (2.71)
\end{aligned}$$

We notice that we could use the sandwich theorem spelled out in Eq. (2.57) to express the rotating frame Hamiltonian as

$$\widetilde{\hat{\mathcal{H}}} = \frac{\omega_1}{2}\left(\cos(\phi_p)\hat{S}_x + \sin(\phi_p)\hat{S}_y\right) \qquad (2.72)$$

which is brilliant because this now does not depend on time. This is some achievement.

2.3.5 Evolution of the quantum state pictured in the rotating frame

With the help of the Hamiltonian just derived we can easily find out the new quantum state since we have side stepped the time dependence. When I will draw the trajectory, you would appreciate what we have actually achieved through the rotating wave transformation. The evolving state is

$$\begin{aligned}
\left|\widetilde{\psi(t)}\right\rangle &= e^{-i\frac{\widetilde{\hat{\mathcal{H}}}t}{\hbar}}|\alpha\rangle \\
&= e^{-i\left(\frac{\omega_1}{2}\left(\cos(\phi_p)\hat{S}_x+\sin(\phi_p)\hat{S}_y\right)\right)\frac{t}{\hbar}}|\alpha\rangle. \qquad (2.73)
\end{aligned}$$

A careful analysis reveals what this operation is. Looking at the matrix exponent, we observe that we are doing a rotation about an axis which is in the equatorial plane at a phase ϕ_p with respect to the x-axis, as illustrated in Figure 2.15. We can choose the orientation of the axis from the phase ϕ_p which is as simple as changing a parameter on a computer program that powers the transmitter feeding in current into the x coils. Note that we can achieve this rotated axis without

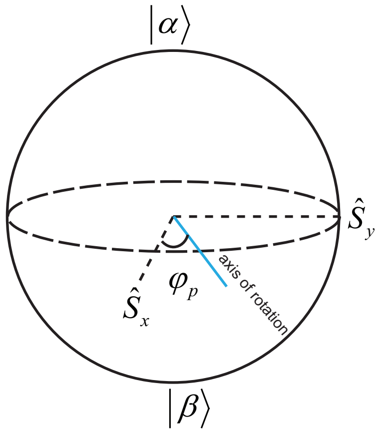

Figure 2.15: Axis of rotation depicted in the rotating frame

physically building a y coil. If ϕ_p is zero, then the axis of rotation is along the x-axis, because the term $\left(\sin(\phi_p)\hat{S}_y\right)$ goes to zero. Then we are doing the rotation about the x-axis. The trajectory as viewed from the rotating frame is shown in Figure 2.16. If $\phi_p = \pi/2$ we are implementing a rotation about the y axis. This allows us to implement the Rabi flopping scheme coercing the spin-1/2 system to oscillate between the Zeeman states $|\alpha\rangle$ and $|\beta\rangle$.

With an oscillatory B_1 field of controllable phase ϕ_p and intervals of evolution under the background B_o field, all of the Bloch sphere comes in our access. The parameters under our control are the phase ϕ_p, frequency of the oscillatory signal, timing and sequence of the control pulses and the strength of the pulses B_1.

In the rotating frame, we don't see precession rather the spin vector is only moving on longitudinal circles with a frequency ω_1. This motion is called nutation. As we shuttle back to the lab frame, we reintroduce precession. The observed motion in the lab frame is therefore a combination of precession and nutation and looks like a spiral. The nutation occurs at the slower ω_1 in the KHz regime while the precession ω_o in the MHz range, so the spin vector is likely to make thousands of turns as it nudges towards the equatorial plane as a result of the oscillatory field. We can summarize that the B_o and oscillatory B_1 field set at the resonant frequency, achieve respectively, rotations around the z axis, and an axes in the equatorial plane.

2.4 The NMR hardware

Refer to Figure 2.18 for a holistic view of the NMR experiment. Setting up all the physics ingredients, we are now in a position to draw a master plan of the NMR

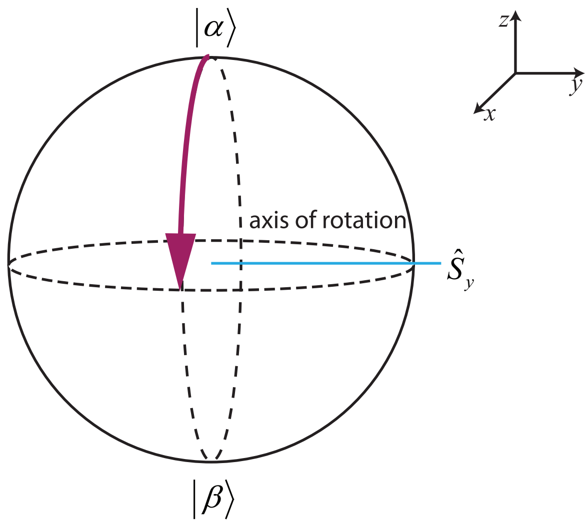

Figure 2.16: Trajectory of the state in the rotating frame

apparatus. A water containing test tube is placed inside a constant magnetic field applied along the z direction that is always on. A coil is placed close to the test tube of water and is oriented along the x-direction. A variable capacitor is placed in parallel with the coil, so that we can make it resonant with the Larmor frequency ω_o.

The NMR magnet and coils are coupled with a spectrometer. A computer program creates a pulse. This means that the program tells the spectrometer what t_p and B_1 are required for an oscillatory signal whose frequency is close to ω_o. The amplitude B_1 controls ω_1. We also notify the phase of the oscillatory signal ϕ_p which determines the axis of rotation. We enter all this information into the computer program. The digital information goes to a digital-to-analog converter (DAC) which converts it to a real analog current. It is amplified and goes through a device called duplexer into the resonant circuit. The duplexer is like a traffic crossing: it controls which signal goes where. The pulse into the coil and energy is pumped into the water spins, nutating the spins towards the equatorial plane. At this stage the coil is acting like a transmitting antenna. Once tilted into the equatorial plane, the spins precess and give rise to an E.M.F ε across the same coil. The generation of this E.M.F is described in Section 2.2.4.

At this stage we turn off the transmission circuit and use the same antenna to receive the NMR signal, the E.M.F which according to Eq. (2.35) is the time derivative of the expectation value of $\hat{S}_x$. We don't need an extra reception coil for picking up the E.M.F, it is just sufficient for the computer program to trigger the duplexer circuit to change the routing of the signal so that it goes into the reception route.

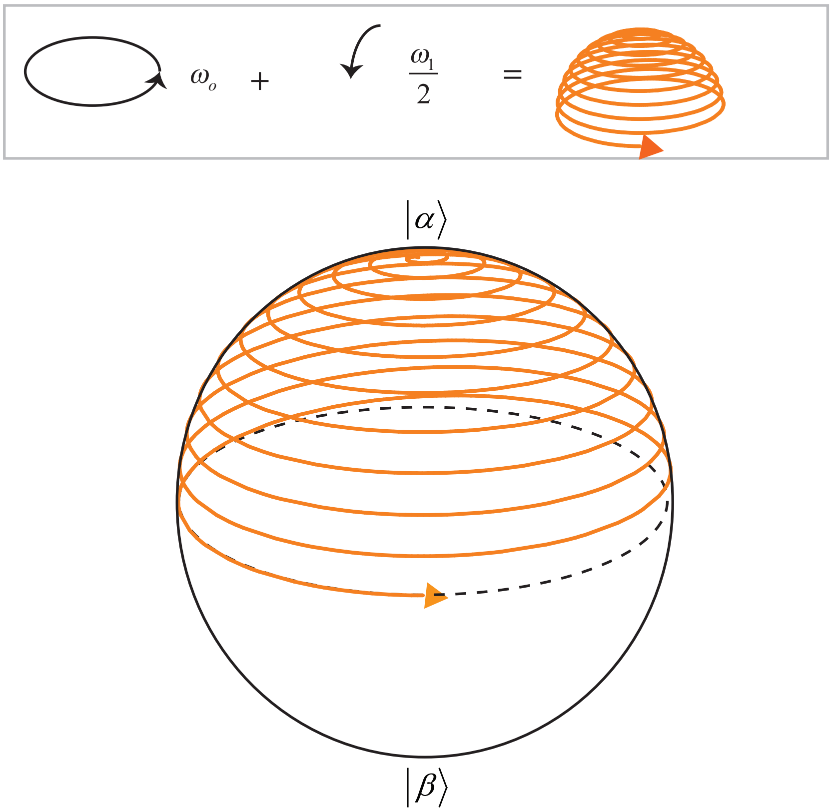

Figure 2.17: Precession with frequency ω_o and nutation with frequency ω_1 in lab frame. The downward motion is still exaggerated. While we only have shown $\approx$ 10 azimuthal rotation inside a $\pi/2$ rotation towards the equatorial plane, in real scenarios, the ratio of the number of azimuthal to polar rotation would be in the thousands.

The induced E.M.F. and the current it generates is a feeble signal and must be amplified again through a low noise mmplifier (LNA). The raw signal goes into some filters where the correct frequency is homed into. In essence, we obtain a sinusoidal signal of frequency ω_o indicative of the precession process. The signal enters the digital world through an analog-to-digital converter (ADC) which samples the NMR signal and the computer runs a Fourier transformation algorithm converting a time domain signal into the NMR spectrum which comprises a peak at the frequency ω_o.

This is not a book on NMR but on quantum mechanics so we stop here. For the application minded, I close this discussion by showing one NMR spectrum, *i.e.* of ethanol CH_3CH_2OH. The methylene (CH_2) protons and methyl (CH_3) protons produce spectral peaks as shown in Figure 2.19. Even though these groups

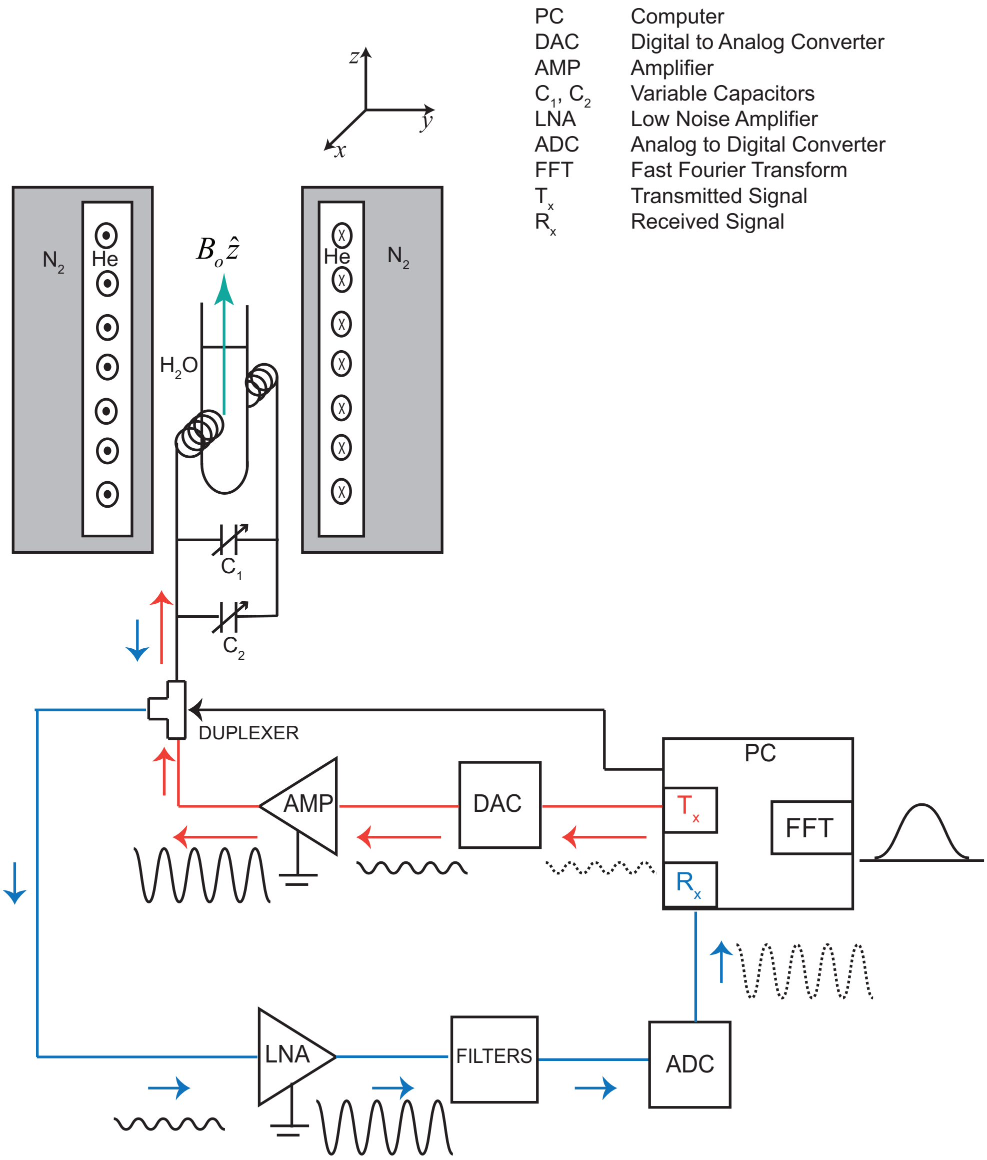

Figure 2.18: Compete NMR hardware

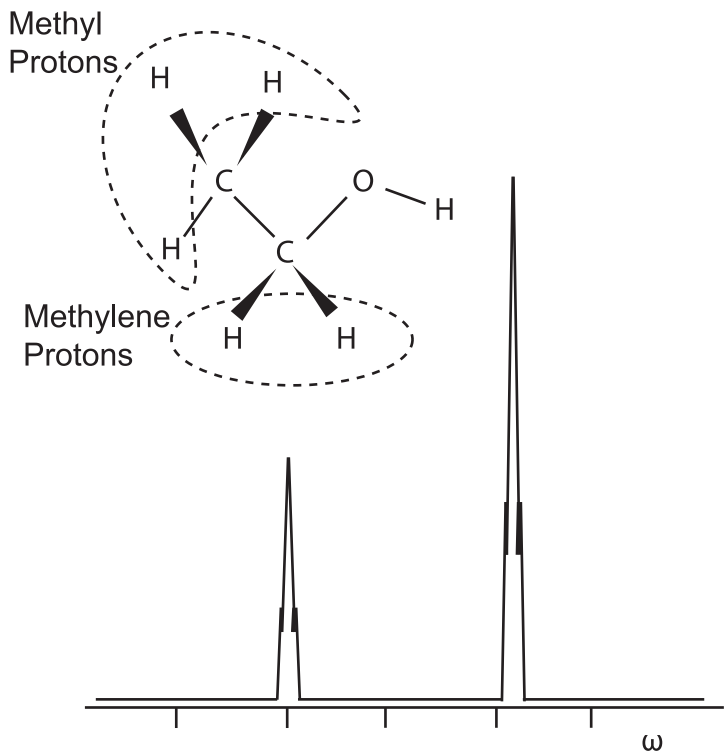

Figure 2.19: Proton spectrum of Ethanol

contain five protons and ideally each one of them has the same Larmor frequency, yet the two groups of protons show up at slightly different frequencies in the spectrum. That is because the precise precessional frequency depends upon the local environment of the spin inside the molecule and particularly what is the kind of configuration of the electrons that surround the spin. So the protons in CH_3 are in a different local environment from the protons in the CH_2 group (because the protons in the CH_2 group are two bond lengths away from the hydroxyl group and oxygen is an electronegative element). This affect is called chemical shift and determines the precise Larmor frequency of the nuclei inside the molecule. This affect is advantageous because depending on where the spin is inside the molecule, the Larmor frequency will slightly change. So by observing the spectrum carefully, we can make some headway in determining the internal structure of molecules. Ethanol is a small molecule but NMR allows determination of structures and dynamics of macroscopically large proteins as well.

Similarly, for NMR of muscle water, not only does the position of peak change depending on the environment, the width of the peak also changes. Healthy and malignant tissues will have variable linewidths in an NMR or MRI experiment. The peaks from water inside blood will be of different width and different shape from water peaks inside the cerebrospinal fluid or grey matter. All of these phenomena have led to advancing NMR and MRI as valuable techniques for the radiologist, for medical diagnostics and for research about the human brain, which many believe is the next most exciting frontier in human knowledge.

2.12 Using the Boltzmann distribution, what fraction of spins inside a collection of spins would be in the lower energy state $|\alpha\rangle$. Remember that inside an energy manifold, the fraction of spins with energy E_i is given by

$$p(E_i) = \frac{e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

2.13 How large a magnetic field is required at room temperature to keep ≈ 75 % of the spins in the ground energy level? How can this field be physically realized?

2.5 Some Problems

Q 2.1 We have an experimental arrangement that decides whether a quantum state is $|x\rangle$ or $|-x\rangle$. What is the probability that given the quantum state Eq. (2.15), the measured state is $|x\rangle = 1/\sqrt{2}\big(|\alpha\rangle + |\beta\rangle\big)$?

Q 2.2 What is the expectation value $\langle \hat{S}_y \rangle (t)$ for the precessing spin state in Eq. (2.15)? How is this related to the expectation value of $\hat{S}_x$ just computed?

Q 2.3 What is the expectation value $\langle \hat{S}_z \rangle(t)$ for the conically precessing quantum state? What is your physical intuition? And derive the result mathematically too. Is the value time-dependent and is $\langle \hat{S}_z \rangle(t)$ a constant of motion? Is $\langle \hat{S}_z \rangle(t)$ a constant of motion.

Q 2.4 Show that if $[\hat{A}, \hat{B}] = i\hat{C}$, the following sandwich theorem holds:

$$e^{-i\theta\hat{C}}\hat{A}e^{i\theta\hat{C}} = \cos\theta\ \hat{A} + \sin\theta\ \hat{B} \qquad \circlearrowright, \tag{2.74}$$

and that this helps explain the result in Eq. (2.57).

Q 2.5 Apply the rotating wave approximation to the clockwise rotating component of the oscillatory field given in Eq. (2.55) which is non-resonant with the Larmor frequency. What rotating frame Hamiltonian does it result in?

Q 2.6 Starting from $|\alpha\rangle$ we desire to take the quantum state of the spin-1/2 particle through the following sequence $\widetilde{|\alpha\rangle} \to \widetilde{|x\rangle} \to \widetilde{|y\rangle} \to \widetilde{|-y\rangle} \to \widetilde{|x\rangle}$. Here the kets with tilde are states in the rotating frame. Draw a timing sequence of magnetic fields and phases that need to be applied to achieve this choreography of the spin vector. Specialist call this sequence a spin echo.