CHAPTER

3

The Ups and Downs of Classical and Quantum Formulations of Magnetic Resonance

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3.1 INTRODUCTION

This chapter is triggered by misunderstandings that often appear when quantum mechanical (QM) descriptions of nuclear magnetic resonance (NMR) are interpreted. The errors are abundant in NMR introductions, including those in the literature on magnetic resonance imaging (MRI), and they provide examples of the Mental Traps described in Chapter 1. It will be argued that several of those Traps are responsible, and that even excellent and QM-savvy scientists are affected, which is apparent from much of the literature on NMR. The mathematical descriptions are typically accurate, but the accompanying explanations are often not. Misunderstandings make explanations nonintuitive and give rise to false expectations. It is here argued that many differences between classical and QM are a matter of formalism and that the two approaches are more similar than they initially appear. The connection between descriptions based on quantum and classical mechanics, and also important concepts such as eigenstates, superpositions, interference and entanglement, are discussed. The different roles of measurement for individual nuclei and ensembles are also covered. The dynamics involved in basic NMR are shown to be similar to those of coupled classical oscillators (e.g., pendulums), which gives insight into the resonance phenomenon itself as well as spectral features resulting from intramolecular, scalar J-coupling of atomic nuclei. It is discussed how classical and quantum mechanics give rise to similar expectations for the basic NMR phenomenon and why a classical intuitive understanding is central: classically described NMR provides an excellent basis not only for understanding phenomena like excitation, echoes, and relaxation but also for digging deeper and for understanding QM formulations. These aspects are of equal relevance for NMR in the context of chemical analysis and MRI. They are also relevant for electron spin resonance, which is not discussed explicitly in this chapter, although much of the discussion pertains to this also.

Neither the classical nor the quantum descriptions of NMR are covered in detail here, as that is done elsewhere, for example, in Chapter 2 and in Levitt's *Spin Dynamics: Basics of Nuclear Magnetic Resonance*[1] for the classical and quantum cases, respectively. Focus is instead shifted to the connection between the two, and to the Mental Traps that lie behind common misunderstandings in NMR introductions. This chapter, although self-contained, is largely a continuation of a paper[2] from 2008 entitled "Is quantum mechanics necessary for understanding magnetic resonance?" that addressed the equivalence of classical and quantum mechanics for describing the basic NMR phenomenon (and only that). Both that paper and the current chapter have sections aimed at a broad audience and sections with mathematical details needed to substantiate claims that may otherwise be considered controversial. The texts are largely complementary.

3.2 QUANTUM MECHANICS IN GENERAL

Some simplified characteristics of QM are widely known and are more or less implicitly brought forward in many NMR introductions:

1. Microscopic systems such as atoms can only exist in discrete states with specific energies.

2. Transitions between these discrete states happen in sudden "quantum jumps" and involve exchange of energy (emission or absorption). An atom in an excited state may, for example, spontaneously jump back to the ground state, in which case a photon with the difference energy is emitted.
3. The timing of such jumps is truly unpredictable.

These statements represent "old" QM as first proposed by Bohr[3] and they contradict both classical mechanics and the mature, general versions of QM that followed soon after the initial formulations. The claims above are often used to explain phenomena like optical emission spectra such as the discrete frequencies present in light from a sodium vapor lamp. Quantitative descriptions of optical spectra were indeed among the first victories of QM, as classical mechanics failed miserably when explanations for these experimental observations were sought. QM has since been developed into a general and quantitative theory (modern QM), applicable in theory to all observed phenomena. The general claims above need to be interpreted with care, since they are somewhat misleading simplifications of the general quantum theory.[4]

When the complexity of a physical problem has allowed for modern QM's full invocation, and when it has been applied properly, we were never let down. The predictions match experiments to the precision of the latter, and QM has proved its worth in countless situations. It is crucial for understanding atomic structure and has resulted in developments such as computers and lasers. The relative agreement between QM predictions and experiment has in certain situations been experimentally verified to be better than one part in a billion (10^{-9}), which shows that QM is amazingly accurate, when experimental conditions allow for sensitive testing.[5]

Though QM is typically called a theory, it has gained status of a set of physical laws, in the same sense as, for example, "Newton's laws" forming the basis for classical mechanics. This is appropriate since there have been no experimental data revealing fundamental limits of QM. In contrast, the limitations of classical mechanics are well established. Both have distinct properties that make their use advantageous in different contexts, typically QM for atomic scale systems and classical mechanics for macroscopic systems. Engaging in QM when building skyscrapers or when doing normal MRI makes little sense, for example, since classical and quantum descriptions are consistent for both.

Among the highlights of the theoretical QM framework are the Schrödinger and Liouville-von Neumann equations that describe how systems evolve over time, that is, they provide "equations of motion." When QM is combined with the theory of relativity that also has scientific status as a confirmed theory, spin appears as a natural but highly surprising characteristic of elementary particles. It is mind-boggling that all hydrogen nuclei (protons), for example, are equally magnetic and thus appear to rotate at exactly the same frequency. There are subtle properties of spin that makes it even more exotic, but that is of limited relevance for basic NMR. For now, we will just acknowledge that hydrogen nuclei largely behave as spinning, magnetic particles.

The rest of this chapter will focus on spin-½ nuclei such as hydrogen. Those are the simplest and the most important nuclei in the context of NMR. They constitute model systems suited for establishing the basic understanding, but there is more beyond. When not explicitly written, the scope is also limited to "normal" NMR with macroscopic samples. When NMR is done with isolated nuclei in atomic beams, quantum aspects become more important. Such experiments are not done in the context of chemical analysis or structure determination, but typically only in fundamental science. In this context, "macroscopic" does not need to be more than a thousand molecules, e.g., which is much less than a cell. Keeping the very exotic NMR situations out of the discussion is warranted since the focus here is on introductions to the basic NMR phenomenon, which is an important beginning, even for those who want to dig deeper. However, in order to discuss the connection between classical and quantum mechanics, measurements on isolated nuclei are also covered in this chapter.

3.3 MISCONCEPTIONS IN NMR INTRODUCTIONS

The paragraphs below provide a typical but problematic description of basic NMR in terms of QM. It should be printed in blinking red for warning, but we will have to go with reduced size text. Normal typesetting is used for the paragraphs that are largely free of problematic statements. As a practical exercise in critical thinking, you should consider carefully which sentences below should raise concerns because they are illogical or give limited predictive power. Since QM has nonintuitive elements, a certain amount of oddity in the explanation may be warranted.

A partially flawed introduction to NMR inspired by "old" QM:

> Due to proton spin, each hydrogen nucleus is weakly magnetic. In the absence of magnetic field, the nuclei are oriented randomly and the net magnetization of a macroscopic sample is zero. When the nuclei are exposed to a magnetic field, QM tells us that each spin will align either nearly parallel or antiparallel with the field as shown in Fig. 3.1. These orientations correspond to the up/down "eigenstates," which are the only possible states of the nuclei. The parallel orientation has the smallest energy, and is therefore the preferred state. A net magnetization of the sample is formed by the small surplus of nuclei in the parallel state (the ground state).

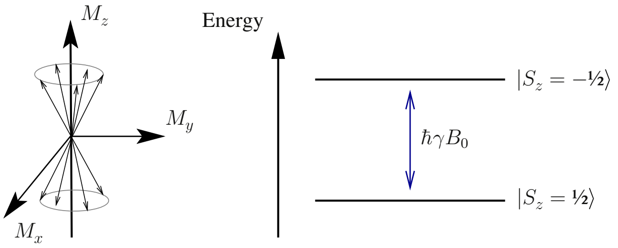

FIGURE 3.1 These graphs illustrate the energy eigenstates. The left side is often erroneously used to illustrate thermal equilibrium also: the low-energy "up" state $|S_z = ½\rangle$ (upper cone) with spin oriented mostly parallel to the applied B_0 field is slightly more populated than the "down" state $|S_z = -½\rangle$ (lower cone). This is a correct statement but the graphical representation is inappropriate. The corresponding energy levels are shown to the right. Radio waves with a photon energy matching the energy difference between the up and the down states can move population into the excited state from where it will relax back, sometimes while emitting radio waves (the NMR signal). There is truth in this, but mentioning of "radio waves" and "photons" is arguably bad practice in the context of NMR.[6] The graphs are not bad as illustrations of some of the up/down eigenstate properties, but the eigenstates are not central for understanding the basic NMR phenomenon.

QM indeterminism/uncertainty is reflected in Fig. 3.1 that shows the "up" and "down" eigenstates as spins precessing on one of two corresponding cones oriented parallel and antiparallel to the B_0 field directed along the z axis. These states are often labeled α and β as done in Chapter 2. Several different choices of quantization axis will be made in this chapter, and the eigenstates will therefore be denoted $|S_z = ½\rangle$ and $|S_z = -½\rangle$ in agreement with another popular convention discussed in detail later in the chapter. The figure illustrates reasonably well that the eigenstates cannot be perceived as purely longitudinal magnetization. It is a verified peculiarity of QM that all three components of the spin cannot have specific values simultaneously. Spin is classically represented as an angular momentum vector $\mathbf{S} = (S_x, S_y, S_z)$ along the spin axis. S_z is well-defined in the up/down states with values ±½, respectively, and the magnitude of **S** somewhat larger, $\sqrt{3}/2$ (angular momentum is given in units of Planck's reduced constant $\hbar$ throughout this chapter). The uncertainty of the transversal magnetization resulting from S_z being well defined is apparent in Fig. 3.1.

The problematic description of NMR continues:

> In equilibrium, the orientation of nuclei is as illustrated in Fig. 3.1 with most nuclei in the ground state (upper cone). In order to measure the magnetization, the nuclei need to be excited, which can be accomplished with a burst of radio waves moving population to the higher-energy state (lower cone). QM tells us that the photon energy associated with these radio waves need to be matched to the energy difference between the states. This is given by the Zeeman splitting (relative difference of energy levels proportional to the magnetic field). The radio wave frequency is therefore given by the gyromagnetic ratio times the magnetic field (the Larmor frequency). When the nuclei fall back to the ground state, they re-emit photons that are detected by the receiver coil. These quantum jumps are responsible for the NMR signal that is detected and analyzed.

You may consider this frequently heard explanation of NMR to be understandable, or even true, but it has serious problems. There are many elements of truth in it, but it contains misunderstood QM and leaves the reader with little predictive power. Considering that this is a common explanation of NMR, you should be skeptical of the claim of it being wrong (but also of it being right; cf. Trap #6). Here are a few questions for you to think about when evaluating the validity and usefulness of the provided explanation:

- Does QM really tell us that nuclear spin can only be parallel or antiparallel to an applied field? Does it apply to thermal equilibrium or more generally? How strong does the field need to be for this to apply? Is the earth magnetic field strong enough to give this very drastic effect, for example? Do the nuclei immediately jump into the up/down states when the field is applied, and if so, do they emit radio waves while doing so? What would the frequency of these be? If not, which states do they occupy in the brief period right before transition to the up/down states?
- If the preferred orientation is parallel to the field, why are nearly half the nuclei pointing opposite the field in thermal equilibrium, that is, the classically least favorable of all orientations? QM may tell us that they do, but it is surprising, considering that we never see compasses pointing opposite the magnetic field.*

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*In fact, you may think that you have seen exactly this. If a compass is brought rapidly into a strong magnetic field or enters in a way that prevents free needle movement all along, the needle may end up pointing opposite the expected direction since it is made of material that can be remagnetized. The magnetic moment of the needle may get inverted by a strong external field. This does not apply to nuclei since they are permanently magnetic. Do not fall into Mental Trap #25 or #39!

- What happens if the radio waves are not exactly on resonance? Nothing apparently, according to the above explanation, but that is actually incorrect. How close does the radio wave frequency need to be to the Larmor frequency? If anything, the explanation seems to indicate that the lifetime determines this, which is only true for very weak radio-frequency (RF) fields.
- If the NMR signal is the result of relaxation from the excited state back to the parallel ground state, then why does excitation by a 180° inversion pulse not result in subsequent emission of signal, which seems to be a consequence of the level diagram in Fig. 3.1 contradicting experiments? Such a pulse moves all ground-state population into the excited state and could therefore be expected to give the maximum signal considering the explanation above. You may correctly argue that such an inversion pulse would not create any transversal magnetization and therefore no signal. In the process, however, you have wisely extended the description above to include transversal magnetization as the source of signal. Sometimes, this is done as illustrated in Fig. 3.2 showing how transversal magnetization can arise, even when only the up/down states are available, as claimed in the explanation above.

Though not offering any proof, Fig. 3.2 at least indicates that the magnetization may be transversal while each nucleus is in one of the two eigenstates, which is often said to be of central importance in QM. The role of transversal magnetization was missing in the initial explanation, but the added claim of its importance seems to resolve the problem of the missing NMR signal after a 180° pulse that the level diagram in Fig. 3.1 introduces. It is time to ask yourself if you are now happy with the explanation above.

In fact, Fig. 3.2 raises new questions more serious than the one it was aimed at answering: Why are the nuclei affected differently by the radio waves? How do they “know” which way to point? Is the size of the magnetization changed by excitation, like it seems? If so, can this phenomenon be used to create magnetization? Don’t bother to find the answers, as the figure is misleading, considering that homogeneous magnetic fields cannot change relative spin directions of nuclei exposed to such fields. This is true for both the static field B_0 and the RF field B_1, so all they can do is to rotate the spin distribution in Fig. 3.1 around a vertical axis (precession around the field vector $\mathbf{B_0}$) or any other axis, depending on the characteristics of the applied fields (e.g., a transversal axis in the rotating frame of reference for a combination of B_0 and a resonant B_1 field).

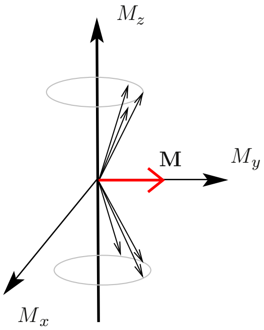

FIGURE 3.2 Illustration of how transversal magnetization could in principle be formed by nuclei in the conical eigenstates (Fig. 3.1) if the RF field somehow could reduce the angular spread. In reality, it is relatively easy to show using classical or quantum mechanics that homogeneous magnetic fields like B_0 and B_1 cannot change the relative orientation of nuclear spins, so the figure has no basis in reality. Instead, all spins are rotated equally during excitation, and the net magnetization consequently follows this rotation.

Even worse, the rest of the explanation above is also pretty bad for a number of reasons. One concern is the mentioning of "radio waves" in the explanation, which is problematic when understood as traveling waves as used for radio communication, for example. David Hoult, in particular, correctly insists that traveling waves play little role in NMR[6] and the term "radio waves" should therefore arguably not be used in this context. Detailed accounts of other problems are given in my introductory paper on myths in NMR,[2] including calculations based on QM and they will not be repeated. Here is a partial summary:

1. There is nothing in QM telling us that the nuclear spin can only be in the up or the down state. It can point in any direction, just like a classical dipole.
2. In thermal equilibrium, the most probable direction of the nuclear spin is indeed along the external magnetic field. But all the other directions are almost equally probable at relevant fields and temperatures. In equilibrium, the antiparallel orientation is the least probable of all states.
3. Neither photon energies nor the very concept of photons is needed in the explanations of normal NMR.[6–8] Photons are widely understood as particles or quanta of light, which is reasonably consistent with a more precise definition involving excitation of electromagnetic field modes.[7] Do not worry about what that really means, since field quantization is of little relevance to the basic NMR understanding. Even if you do QM calculations for NMR, you can typically treat the field classically with no loss of insight or accuracy.[6,8] An NMR description with simplified field quantization will nevertheless be used later in this chapter, since it gives insight into QM concepts from a classical perspective. For now, the RF field is treated classically, and a sinusoidal field is therefore characterized by the amplitude, phase, and frequency. The latter indeed has to be near the Larmor frequency to cause transitions. How near depends on the amplitude of the field, which is a natural consequence of the alternative NMR explanation discussed in Chapter 2, and not a consequence of the limited QM-inspired pseudoexplanation above, since amplitude translates into photon count.
4. As often done, it was stated in the flawed NMR explanation above that QM is responsible for the resonance condition, that is, the need of the RF to match the Larmor frequency (the Zeeman splitting) for transitions to occur. This is true but overly complicated since the text might equally well have stated that classical mechanics is responsible. Better yet, the explanation could have provided a simple argument that this is so. Since the principles of QM are believed to be generally valid, we can trivially claim that QM is responsible for everything we ever observe. With this in mind, a claim of QM being responsible for something has close to zero information content. Typically, when something is said to follow from QM, it is therefore implicitly meant that it is a nonclassical aspect, but this is not the case for the NMR resonance condition, which is exactly as you would expect it to be classically (including near-resonance effects as hinted above).
5. Abrupt transitions between states (quantum jumps) play no role in normal NMR. In particular, sudden changes in the quantum state caused by measurement are irrelevant (the so-called state reduction or collapse).

While the above QM-inspired description of NMR may sound simple and has elements of truth, it is misleading and even wrong in several important respects, as explained in detail elsewhere.[2,6] Of course, the validity of an explanation does not depend on whether it is simple or not, whereas the practical value of it may. What matters mostly is whether it gives the user insight and predictive powers. If more explanations are equally good in these respects, the simpler should be preferred, and unnecessary postulates avoided (see the principle of parsimony, Occam's razor, mentioned also in Chapter 1 in connection with Trap #24). To be of value, any explanation has to be reasonably correct, and the typical QM interpretation above does not qualify in this respect. It is largely misunderstood and reminiscent of early QM formulations.

In some contexts, it is important and necessary to describe NMR and field interactions quantum mechanically, but far from all, and important insights are missed if basic QM descriptions are not supplemented with analogous classical descriptions. Many will benefit from a quantum description, especially if it is preceded by a classical description providing intuitive insight. Even more are probably best left with a classical description alone, for example, the vast majority of people working with MRI where this is typically fully sufficient and leads to less confusion and misunderstanding than QM counterparts. A classical description can be relatively easy, intuitive, and even accurate, as it can be shown to be a direct consequence of QM. In that sense, it also qualifies as a QM explanation, despite the lack of typical QM formalism. Aimed with a classical understanding, many aspects of NMR will give more meaning, including a quantum description.

3.4 WHERE DID IT GO WRONG?

The correspondence between QM and classical NMR descriptions deserves explanation and is a focus of the remaining part of this chapter. Before engaging in that, it is worth considering why severe misunderstandings are present in much of the NMR literature many years after the phenomenon was first described. Has much of the scientific community really misunderstood the very basics of the quantum formulation that many rely on? Apparently, yes, but it is not unique to NMR[4] and the practical consequences are limited. The problems can largely be attributed to Mental Traps as discussed in Chapter 1. Even though not all the classic literature is flawed, a significant part is, and errors track back to the early days of QM and NMR (Traps #1, #7, #8, and #28). The wrong statements may sound simple and probable at first (Traps #4, #10, #22, and #42) but make NMR basics incomprehensible, which many fail to notice since the errors have little practical consequence. These are repeated by many authors and lecturers who do not have experience *interpreting* QM, including brilliant and widely recognized quantum-savvy scientists (Traps #6, #31, #42, and #43), who have failed to notice the mistakes (Traps #3 and #4) or have not bothered to explore alternatives. Although the errors are now recognized and avoided by many, they are still repeated without much reflection by unsuspecting authors. QM is correctly known to have very nonintuitive aspects, and though many have felt uncomfortable with the wrong explanations, most have been told—or have assumed—that this was a natural consequence of QM. Some find joy in the apparent necessity of exotic quantum physics for "truly understanding" NMR (Traps #23 and #24), although "truly misunderstanding" sometimes seems more accurate. Granted, QM is needed for NMR understanding beyond the very basics, and everybody is likely to make mistakes when interpreting QM, including the author of this chapter. QM indeed has oddities as described below, but none of relevance for the basic magnetic resonance phenomenon.

Other clear reasons for the abundant errors are misinterpretation of experimental results and mathematics. The QM formalism applied to NMR may seem to suggest that the eigenstates are more important than they really are (Traps #11, #12, and #13). The Stern-Gerlach experiment[9] discussed below may similarly be wrongly interpreted to show that nuclei can only be in one of two states (Traps #25 and #39), but the effect of measurement on the nuclei is ignored in that interpretation (Trap #26). The spiky appearance of NMR spectra may be wrongly interpreted as supporting this false conclusion (Trap #29). Both the mathematical and the physical aspects and sources of confusion are discussed in the following sections that supplement earlier work[2] by bringing the classical and the quantum descriptions closer together.

The reader may think of reasons for sticking to a wrong QM interpretation, for example, that it is based on benign approximations necessary to avoid lengthy or complicated descriptions. Such arguments reflect self-deceit in the case of introducing basic NMR. It takes little effort to avoid the mentioned errors and correct alternatives need to be neither lengthy nor complicated. For explaining spectral features, however, it can arguably be simpler to think in terms of sudden transitions between states rather than of slow transitions or coherent superpositions of such, but it should be with awareness that this is a substitute for the QM-predicted dynamics of normal NMR, which do not involve quantum jumps, as discussed later in this chapter (this relates closely to the issue of a model's legitimacy as discussed under Pillar 13 and Trap #18 in Chapter 1 and also to the ability to treat descriptions of NMR as models rather than "truths of nature" as mentioned in Chapter 2).

3.5 A LIMITED INTRODUCTION TO CLASSICAL AND QUANTUM MECHANICS

The fairly typical explanation of NMR opening this chapter was inspired by QM but got important aspects wrong. While the presented QM formalism is typically accurate, the problems concern interpretation. It can be argued that the mathematics speaks for itself, but only those sufficiently trained to make their own interpretations will likely benefit from unexplained formalism. Even the most hard-core NMR scientists make use of semiclassical mental representations when thinking about the basics since that has proved highly rewarding (see the role of metaphoric models in scientific thinking discussed in Chapter 1 under Pillars 10 and 11).

An attempt of explaining the QM foundation for NMR, while reconciling the classical and quantum descriptions, is now made. Only the needed parts are presented and only superficially so as to favor general readability. The mathematical description can be found in many books and will not be repeated here. The concepts of QM and classical mechanics are instead discussed in general and are related to NMR.

Initially, we focus on classical mechanics. A starting point is Newton's second law describing how forces influence particles. Generally, we need to supplement this with field descriptions, how they interact with particles, and how they evolve, for example, as expressed in the classical Maxwell equations. Taken together, all the classical equations necessary to describe system evolution will here be called "the classical equations of motion." A physical system can classically be described completely by all its characteristics including fields and the constituent particle's positions and velocities (the microstate). This will here be called the "classical configuration." Given such a complete description of an isolated system, the classical equations of motion can in principle tell us how the system will evolve forever after, as classical mechanics are deterministic. In practice, no physical system is completely isolated from the surroundings except the system of everything. This special case does not leave room for an external observer who can perform measurements on the system, so we largely keep that situation out of the discussion. Another practical issue is the obvious impossibility of measuring all system properties at a particular point in time with zero inaccuracy. This is needed since even minor uncertainty will generally make long-term system behavior unpredictable. These practical issues do not challenge the deterministic nature of classical mechanics: our experimental inabilities and limited knowledge of the configuration are irrelevant to that question. We can imagine a perfectly isolated system (e.g., the universe, even if infinite), and the classical equations of motion will deterministically describe how the system evolves forever, no matter whether observers know the classical configuration or not. If the isolation is imperfect, or our knowledge about the system incomplete, classical uncertainty about the system evolution increases over time, for example, as reflected in next week's weather forecast that is typically more uncertain than tomorrow's.

Classical mechanics is not generally valid, and we now focus on differences introduced with QM. The starting point for most QM derivations of NMR is the Schrödinger equation. It describes how any physical system, for example, nuclei in magnetic fields, evolves in periods where the system is left to itself. When written for a specific system, it constitutes "the QM equations of motion":

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle. \tag{3.1}$$

The skills needed to use this equation are not assumed known in the following, although occasional mathematics will appear. As an equation for the evolution of everything, it appears deceptively simple, but similarly to classical mechanics, the practical solving can be immensely complicated, especially when many particles and fields are involved. $\hat{H}$ is here the so-called Hamiltonian that describes interactions within the system, and it is taken to be piecewise constant throughout this text, that is, only changing at particular moments in time such as when the RF transmitter is turned on or off (this does not correspond to classical nuclear interactions within the system being piecewise constant). The state of the system is in QM represented by a time-dependent "state vector" $|\psi\rangle$ that is a complete characterization of the system state, that is, there is nothing more to know about it: from the state vector the result of any measurement of system properties can be calculated with maximum certainty (although not with full certainty as discussed below). The state vector is not a vector in real space, but in an abstract multidimensional state space with a dimensionality reflecting the degrees of freedom of the system. The notation $|X\rangle$ for a state with properties X is common and needed below. $|S_z = ½\rangle$ is, for example, the state vector for the spin-up state α since it has the z-component of the spin, S_z, equal to ½. Only properties of particular interest appear explicitly when this notation is used.

When the state vector and the character of all interactions of an isolated system are known, the Schrödinger equation deterministically describes how it evolves forever on. The state

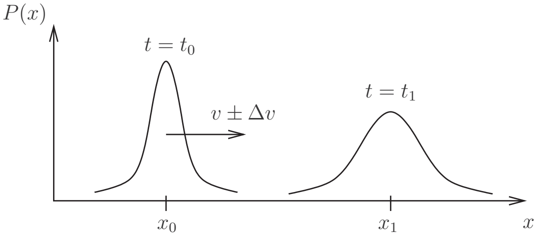

FIGURE 3.3 Consider a normal particle described by classical mechanics. Take it to move freely from approximately position x_0 at time t_0 with speed v along the x axis. The lack of precise knowledge of these quantities may, for example, be characterized by probability distributions with width Δx and Δv. In that case, the probability $P(x)$ of finding the particle at some position x at a later time t_1 will be distributed with a peak probability at $x_0 + v(t_1 - t_0)$ and with a position uncertainty increasing over time.

vector is a QM analog of the classical configuration in the sense that they both describe a system to the maximum extent. As mentioned for classical mechanics, it is practically impossible to isolate a system, but that does not change the fact that QM is deterministic in this sense: if the state vector is known at one point in time, it can be known forever on. In another sense, QM is truly indeterministic in contrast to classical mechanics. We will soon return to that point.

Readers having worked with state vectors or similar representations will know that they appear very different from classical configurations. First of all, they may be complex-valued, and "i" appearing in the Schrödinger equation is the complex unit, $i^2 = -1$. The complex unit does not appear in the classical equations of motion, but this apparent difference does not truly distinguish classical and quantum mechanics. Complex functions can generally conveniently be used to describe oscillatory systems, for example, precessing spins, electronics, or waves, whether they are classical or not.

Another deceptive difference comes from state vectors being close relatives of probability density functions. For a system of particles in normal 3-D space, for example, the state vector only provides probabilities that particles can be found at specific positions, having specific velocities, spin states, etc. In contrast, a classical configuration may be expressed in terms of exact particle positions and velocities, which are concepts that are revised in QM. This does not in itself imply any significant difference between classical and quantum mechanics. Indeed, classical mechanics can be expressed in terms of probability functions too, and it is often fruitful to do this. If the state of a system is known with some uncertainty, classical equations of motion can be formulated that describe deterministically how the system and the uncertainties evolve. An example is illustrated in Fig. 3.3.

3.6 INDETERMINISM VS. UNCERTAINTY AND THE ROLE OF MEASUREMENT

The main message so far is that even though the QM and classical equations of motion appear very different at first sight, they can both be expressed rigorously in terms of quantitative deterministic, probabilistic equations, and they will then appear much more similar. There are important fundamental differences regarding the role of measurement, however. These differences between quantum and classical mechanics are not important for the understanding of basic NMR, but they are an important source of QM misunderstanding and will be discussed here in the context of the previously introduced idealized isolated systems. To do a measurement on such a system, we will need to interact with it, independent of whether the system is described by QM or classical mechanics. In either case, there will be an effect on the system that we may want to minimize to limit the influence on future system evolution, but this minimal effect differs fundamentally. Important differences between QM and classical mechanics are as follows:

1. QM is probabilistic at the most fundamental level. In contrast to classical mechanics, it is not optional whether to express QM in terms of probabilities or specific configurations. Even if you have the most complete knowledge of the system (the state vector $|\psi\rangle$), you will still not be able to predict the outcome of every given experiment. But you will be able to accurately calculate the probabilities of different possible outcomes. Nature can thus be truly undecided about any outcome until it is measured, and this is called "quantum indeterminism." For example, a particle generally has no position until it is measured or confined—it is not just unknown. In contrast, classical mechanics can be expressed as a probabilistic theory, but with adequate information about a system, the uncertainties can in principle be arbitrarily small, leaving the result of experiment fundamentally predictable. As a side note, there are actually formulations of QM that are deterministic, but such nonlocal, hidden-variable formulations are more complicated than standard QM and have elements that are even more bizarre than indeterminism.[10] They rely on nonverifiable elements beyond normal QM and therefore fall for Occam's razor, but one of them could in principle be a correct explanation of mechanisms underlying QM.
2. Gaining knowledge about a classical system via measurement does not in itself change its evolution. The physical interaction between measurement apparatus and the system may, but classically there is no intrinsic change of system behavior associated with acquiring knowledge about it. In contrast, for a system described by QM any measurement by an external observer will force a reality onto the system that does not generally exist in advance (indeterminism is changed). During system evolution, the Schrödinger equation keeps all possible paths of system evolution open as $|\psi\rangle$ expresses the system properties in a probabilistic way (a probabilistic description accounts for all possible paths to all possible outcomes). However, according to QM, a particular path of system evolution is only selected when some interaction happens that limits the possible paths to just one, for example, a measurement. This reduction of indeterminism is superficially similar to measurement on a classical system characterized by uncertainty: A measurement reduces our uncertainty, but it does not necessarily change anything else, classically. The truly weird quantum aspect is that the Schrödinger equation allows for interference between different open paths. This may even result in cancellation of possibilities for events that could otherwise have happened. A particular event that can happen in two ways classically can be prevented by QM from happening at all due to cancellation of the two possibilities. Only if one of the two ways is eliminated, the event can happen, although classically it should have become less likely. The double-slit experiment is an often used example of this, illustrated in Fig. 3.4. As a direct result of changing interference via measurement, any part of the system may immediately after the measurement behave entirely differently. This is very nonintuitive but has been verified in many experiments. Even though the changes of system behavior can happen instantly over large distances, this

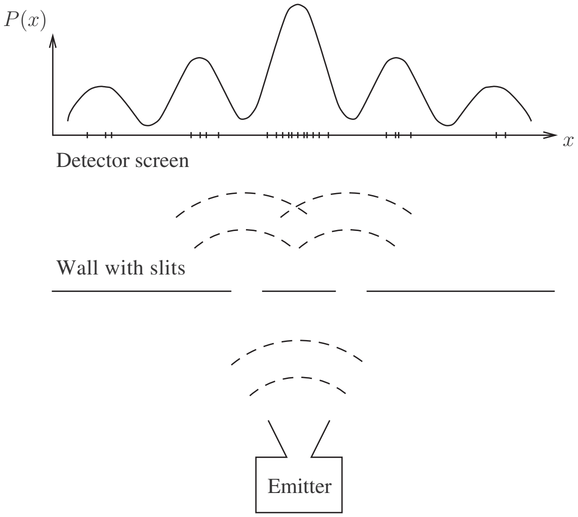

FIGURE 3.4 The famous double-slit experiment showing nonclassical aspects of QM. The emitter is adjusted to shoot electrons at a wall one by one. Some may pass through slits in the wall and hit the fluorescent screen behind it to produce small flashes of light upon impact. The marks on the x axis show example positions of these. If only one of the slits is open, the flashes will be distributed almost as expected classically, that is, symmetrically behind the open slit, although more spread out due to diffraction (the smaller the hole, the more do particles passing through the hole "forget" their direction). If both slits are open, however, an interference pattern may appear, that is, the distribution $P(x)$ of flashes on the screen will show a series of minima and maxima as indicated. In particular, there may be positions on the screen where no flash will ever be detected with both slits open, but where flashes may appear if one slit is blocked or equipped with a nonabsorbing electron detector. Flashes at such positions start appearing only when the canceling open paths through both slits are replaced with a single certain path, which eliminates interference. A similar pattern is seen for light, sounds, and other waves, and the distributions of flashes are consistent with electrons propagating as waves that interfere. However, the flashes on the screen each appear at just one distinct location, which shows that electrons are detected as particles, not waves. In fact, it is the probability amplitudes that propagate and interfere like waves as described by QM. The wave description was reasonably straightforward here, but it should be remembered that the waves of QM generally propagate in "configuration space," which is not a physical space but a mathematical construct. They should therefore not be thought of as "real."

does not allow for superluminal communication, for example. These mysterious "spooky actions at a distance" (Albert Einstein's words as discussed, e.g., by Bell[11]) are not violating the laws of relativity and will only show in the statistics when correlations between experimental results are calculated. They are classically most unexpected, but do not leave theoretical loose ends such as inconsistencies of the formalism.

3.7 THE ROLE OF EIGENSTATES IN SINGLE-PARTICLE MEASUREMENTS

Having established some fundamental differences between QM and classical mechanics, we now return to another difference that is fundamental and important, but nevertheless sometimes overestimated—the role of eigenstates. For the sake of simplifying arguments, we assume consistently in this chapter that there is no traditional measurement noise, and that our measurement apparatus is perfect and disturbs the probed system as little as theoretically possible.

It is often said that QM dictates that systems can only be in particular discrete states, for example, spin eigenstates. The situation is more complicated than that, however. For every measurement on a QM system, there are indeed only certain possible outcomes, which may or may not be discrete, that is, being separated numerically. These numerical outcomes are called "eigenvalues," and they correspond to specific states called "eigenstates." If a system is in an eigenstate for a particular kind of measurement, the corresponding eigenvalue will result, if the measurement is conducted. The mathematical representation of a particular measurement involves the corresponding "measurement operator." For a particle, for example, there is a mathematical position operator that represents a position measurement along a given direction, for example, the x axis. The eigenvalues of this are the possible results of a position measurement. Each eigenvalue x_0 is associated with at least one eigenstate $|x = x_0\rangle$ meaning that if the system is in this state at time t, that is, $|\psi\rangle = |x = x_0\rangle$, then a measurement of position at that point in time is guaranteed to give the value x_0. Once confined in this way, the particle will lose its memory of direction in accordance with the Heisenberg Uncertainty Principle. This gives rise to diffraction as described in the caption of Fig. 3.4.

A more pertinent example is now considered. Each proton has a magnetic moment, meaning that they magnetically appear like tiny spinning bar magnets with a north and a south pole. The direction of the magnetic moment coincides with the spin axis, since spin is responsible for the magnetic property: spin and magnetism are proportional. With a so-called Stern-Gerlach apparatus,[9] we can measure the magnetism of isolated nuclei along any particular axis, for example, the z axis. These nuclei are sent individually through the apparatus, and a component of nuclear magnetism is measured by their deflection in an inhomogeneous magnetic field oriented along the measurement axis. The measure of magnetism is trivially turned into a measure of the proportional spin component given in units of $\hbar$. It is found that the maximum measurement value of a proton spin component is ½ and that the minimum value is −½, for example, corresponding to +15° and −15° angular deflection of the particle trajectory for a particular Stern-Gerlach apparatus. These details of measurement and scaling are not important in the current context, but the results are.

If the nuclear spin happens to be oriented along the z axis chosen to coincide with the B_0 field (proton is in the up state), we will measure the value ½ for the spin S_z along this axis. Likewise, we will measure the value −½ when the spin is oriented opposite the measurement axis. If we send the same particle through two Stern-Gerlach devices to measure the direction of spin along the same direction twice, we will get the same result twice. From a classical perspective, there are no surprises so far, but they will soon appear.

If a nucleus happens to spin orthogonally to the measurement axis z, we will classically expect to measure 0. This value, however, is not an eigenvalue of the spin component measurement operator S_z, so this outcome will never appear. In fact, the only eigenvalues of spin along any axis are ±½, which is highly surprising from a classical perspective. Instead of measuring 0 when the spin and measurement directions are perpendicular, we will measure either +½ or −½ with equal probabilities, and in the process, the nucleus gets aligned with the measurement axis: the measurement forces it into the corresponding up/down eigenstates in a process often called "state reduction" or "collapse." This is technically a projection onto the subspace of eigenstates consistent with the measured eigenvalue. For a single proton, any prior indeterminism inconsistent with the measured value disappears when the measurement imposes a new reality onto the nucleus. However, new indeterminism of other variables than the one measured may well be introduced simultaneously. This is particularly true for the orthogonal spin components that become indeterminate, which can be verified by passing the particle through more Stern-Gerlach apparatus serially. Such results are highly surprising and nonclassical but have been verified in many different contexts.

It will be described below that nuclear spin can be oriented in any direction whether it is in a magnetic field or not. When its component in a particular direction is forming an angle θ with the measurement direction, the probabilities of measuring the only two possible outcomes are $\cos^2(\theta/2)$ and $\sin^2(\theta/2)$, so there is certainty of the outcome when the measurement direction is aligned with the spin direction (parallel or antiparallel).

3.8 ENTANGLEMENT

As mentioned earlier, it can be shown with Stern-Gerlach devices and similar experimental setups that measurements fundamentally change the state of the system. This can even have immediate consequences in far away regions, which is most obvious when "entanglement" is involved. This is another unique quantum aspect, and it is beyond the scope of this text to describe it in depth, but an example is given: consider a situation where two hydrogen nuclei with known and opposite spin orientations are brought together and left to interact magnetically, so that each precesses in the dipole field generated by the other. For the sake of argument, we will assume this to be the only interaction in this thought experiment. Afterward, we do not know either nucleus' spin orientation, but due to the conservation of angular momentum (including spin), we know for sure that they are still opposite. We have ended up with two nuclei whose spin states are perfectly correlated (opposite), but otherwise unknown. We say that the two nuclei are in an entangled state. We can bring the two nuclei far apart, and if we measure the component of spin of each along the same direction, we are guaranteed to get opposite results. There is yet no conflict with classical expectations, but there is an important difference that will soon show. The spin interaction may give rise to classical uncertainty, but in addition it can result in quantum indeterminism which may present itself similarly but is very different: the state of the nuclei after the interaction reflects that different possibilities of outcome are still open (not just unknown) even after the interaction has finished. If we repeat the spin preparation and measurement many times with the measurement done in varying directions for both particles, it will be found that the results violate classical expectations.[11] It will not show for individual measurements, but in the statistics when the results of repeated measurements performed for each nucleus are correlated. The reason is that the state collapse for one nucleus simultaneously also forces the other into an eigenstate even if it is far away. The statistics rule out that the outcome of the nuclear interaction is fixed before a measurement takes place, possibly much later and far away.[11] This makes little sense since our minds are shaped by the classical experience we have from everyday life, but nature offers such surprises when we move outside our classical comfort zone.

3.9 SUPERPOSITIONS

From the more exotic and fundamental differences between classical and quantum mechanics, we now return to the more practical that you will rapidly encounter when reading NMR introductions. A superficial difference between typical QM and classical descriptions becomes apparent when the state vector is expressed in terms of basis functions or eigenstates as typically done in the context of NMR. Such decompositions are often perceived as something specific to QM, which is not the case. The eigenstates of measurement operators do play a special role, but this role is often not visible from experiments on ensembles. Before discussing the classical analog of eigenstates, the role of these in QM descriptions will be discussed.

As described, noninteracting protons in a magnetic field each have two eigenstates for spin measured along any particular axis. Despite what some NMR introductions say, these are by no means the only possible states of the nuclei. In most texts that take the QM description of NMR seriously, you will find the state vector $|\psi\rangle$ written in terms of eigenstates, typically those associated with measurement of the spin component S_z:

$$|\psi\rangle = a|S_z = ½\rangle + b|S_z = -½\rangle, \tag{3.2}$$

where a and b are complex coefficients in this weighted sum of states called a superposition of S_z eigenstates. The probabilities of finding a particle characterized by state $|\psi\rangle$ in the up or down states are $|a|^2$ and $|b|^2$, respectively, for spin measurements along the z axis. Since $+½$ and $-½$ are the only two outcomes, the corresponding probabilities therefore must sum to 1: $|a|^2 + |b|^2 = 1$.

Does Eq. (3.2) imply that the particle in state $|\psi\rangle$ is in either the $|S_z = ½\rangle$ or the $|S_z = -½\rangle$ state? No. Before a measurement, all weighting factors a and b satisfying $|a|^2 + |b|^2 = 1$ are valid. Any such pair describes a spin state $|\psi\rangle$ according to the expression above. It can be shown that it is possible to write the coefficients a and b differently, so it becomes clear that any valid combination of these describe exactly one spin orientation in ordinary 3D space. Let θ and φ be the polar and azimuthal angles in normal spherical coordinates. A spin state expressing the closest QM analog to classical spin around the (θ,φ) direction can be written as

$$|\theta,\varphi\rangle = \cos(\theta/2)|S_z = ½\rangle + \sin(\theta/2)\exp(i\varphi)|S_z = -½\rangle. \tag{3.3}$$

$|\theta,\phi\rangle$ is here used as a shorthand for $|S_{\theta,\phi} = ½\rangle$, that is, spin along the (θ,φ) direction. The probability normalization condition $|a|^2 + |b|^2 = 1$ is clearly fulfilled for this superposition. The polar angle is seen to be reflected in the amplitude of the up and down states, whereas the azimuthal angle is their phase difference. It is a general feature of QM that the overall phase factor of any state vector is without physical significance ($|\psi\rangle$ and $\exp(i\chi)|\psi\rangle$ describe the same reality, whereas the relative phase of states in superpositions matters). The coefficient of $|S_z = ½\rangle$ was therefore chosen real in Eq. (3.3) without loss of generality, and the state $|\psi\rangle$ is seen to be fully characterized by the polar and the azimuthal angle only, just like a classical dipole with fixed amplitude. Although we can assign such specific angles to the spin state, there is still intrinsic indeterminism associated with orthogonal components of the spin. A spin cone similar to the upper part of Fig. 3.1 but oriented in the direction of (θ,φ) is a reasonable graphical representation of $|\theta, \phi\rangle$, but a unit vector with these spherical coordinates is in most ways a better visualization. This is the so-called Bloch vector that can be defined for any QM two-level system in an abstract parameter space.[12] In the case of basic spin ½ NMR, it is simply proportional to the magnetic moment in normal 3-D space. Generalizations to mixed states and to more levels can be made, but the discussion is limited to the Bloch vector of pure states for single spin ½ particles in this chapter. This vector offers a good graphical representation of $|\psi\rangle$ for several reasons:

(1) Unlike the vectors in the cone in Fig. 3.1, the Bloch vector has a definite physical meaning stated in Eq. (3.3), and it actually points up for the "up" state $|S_z = ½\rangle$ and down for the "down" state $|S_z = -½\rangle$ (θ=0° and 180°, respectively).

(2) It is the closest QM analog of a classical magnetic dipole, since it evolves like one when subject to magnetic fields.

(3) Apart from relaxation effects, it keeps these properties when generalized to statistical ensembles of weakly interacting nuclei. The description of magnetic resonance in Chapter 2 is therefore equally valid for QM and classical mechanics. Note that eigenstates played no role in the NMR introduction of Chapter 2, so they are not crucial for the understanding of the resonance phenomenon. As a shorthand, it is warranted to call the Bloch vector of a nucleus its magnetic moment in analogy with classical mechanics, but the differences should be remembered. Entanglement, for example, is not easily shown with Bloch vectors or cone figures, that is, that the Bloch vector of two nuclei may be correlated without having specific directions.

The problematic QM-inspired NMR explanation opening this chapter ignored superpositions, and it therefore invites rate equations for the populations of the eigenstates. It is tempting to introduce transition probabilities and write simple differential equations with reference to the energy level diagram in Fig. 3.1. Such rate equations are appropriate when T_2 is so short that it limits the possibility of coherence buildup, but they cannot describe coherent evolution essential to NMR. It is an important insight that rate equations offer no shortcut to the QM equations of motion that need to be based on the Schrödinger equation or equivalent forms, which describe vector dynamics similar to those of classical mechanics.[12]

3.10 THE MISSING ROLE OF EIGENSTATES IN ENSEMBLE MEASUREMENTS

If a measurement of the nucleus' individual spin along the z axis is performed, for example, with a Stern-Gerlach experiment as described above, this forces the nucleus into state $|S_z = ½\rangle$ or $|S_z = -½\rangle$. So it may be thought that a measurement of a sample's magnetization along the z direction forces each nucleus into one of its S_z eigenstates, but that is actually not true. Measurements of the total magnetization in other directions do not force individual spins into eigenstates either. The reason is that a complete ensemble consisting of many nuclei has spin eigenstates that are not eigenstates of any individual nuclear spin measurement. Whereas a series of measurements on individual nuclei force each into an eigenstate, it can be shown that a measurement on an entire spin ensemble changes the state of the individual nuclei only insignificantly.[2] The orientations of individual nuclei remain undetermined, both classically and in the special QM sense. In particular, a measurement of the total magnetization leaves the individual nuclei almost unaffected in entangled superpositions of the up and down states (the more nuclei, the less effect). Even if nuclei did get into single-nucleus eigenstates, they would soon interact with other nuclei, which results in more general superpositions.

3.11 THE ROLE OF EIGENSTATES IN MATHEMATICAL DESCRIPTIONS

Since we do not actually perform measurements along the longitudinal direction z in NMR, but rather along a transversal direction, for example, x, it may seem more natural to express the state $|\psi\rangle$ in terms of the eigenstates characteristic for measurement along that direction, $|S_x = ½\rangle$ and $|S_x = -½\rangle$. In analogy with the up/down nomenclature, these states could be called right/left eigenstates, as they have similar properties to the S_z eigenstates, but for a transversal spin component. Any spin state can be written as a superposition of these states, but with other coefficients: $|\psi\rangle = c|S_x = ½\rangle + d|S_x = -½\rangle$ where $|c|^2 + |d|^2 = 1$.

No matter which spin state a single nucleus is in, it can be written in terms of the two eigenstates associated with measurement along any particular axis. As illustrated above, we may or may not choose this "quantization axis" to coincide with the measurement axis. That choice is only a matter of mathematical convenience since $|\psi\rangle$ itself is not influenced by our mathematical description of it. The choice of quantization axis and corresponding eigenstates is something as mundane as selecting a basis or coordinate system for our mathematical descriptions. This is illustrated by a classical example. Suppose you want to describe the throw of a stone mathematically. When leaving the hand, the stone's velocity can be characterized by a vector $\mathbf{v}$ pointing in the direction of the throw. Ignoring air resistance, the stone is only affected by the gravitational downward pull, and the vertical velocity will therefore change linearly with time. In the horizontal direction there is no force, and the stone will move with constant velocity. The natural choice of basis defining the coordinate space is therefore unit vectors $\{\hat{\mathbf{x}}, \hat{\mathbf{y}}\}$ oriented in the horizontal and vertical directions, which makes the equations of motion simple to write down and solve. It is possible to choose any other rotated basis $\{\hat{\mathbf{x}}', \hat{\mathbf{y}}'\}$, but we then have to decompose the gravitational pull into x' and y' components to solve the equations of motion. The actual flight of the stone is unaffected of our choice of basis, but the mathematical description depends on it: $\mathbf{v} = v_x\hat{\mathbf{x}} + v_y\hat{\mathbf{y}} = v'_x\hat{\mathbf{x}}' + v'_y\hat{\mathbf{y}}'$.

Analogously, any spin component measurement (whether we perform it or not) has corresponding eigenstates that constitute a possible basis for calculations in NMR as exemplified by the two alternative decompositions $|\psi\rangle = a|S_z = ½\rangle + b|S_z = -½\rangle = c|S_x = ½\rangle + d|S_x = -½\rangle$. The basis $\{|S_z = ½\rangle, |S_z = -½\rangle\}$ and the basis $\{|S_x = ½\rangle, |S_x = -½\rangle\}$ are merely rotated with respect to each other. Each set of basis state vectors is orthogonal, in contrast to the spin orientations that the states represent: up and down are not orthogonal directions, but orthogonal eigenstates. These aspects are given some attention here since spin decompositions are often attributed more significance than they deserve. QM provides extreme oddities such as the "Schrödinger cat states," where more or less macroscopic systems appear to be in two states simultaneously.[10]

This may be the inspiration when spin superpositions are sometimes claimed to be mysterious in that individual nuclei can be in the $|S_z = ½\rangle$ and the $|S_z = -½\rangle$ states simultaneously. It is no more mysterious than a flying stone moving vertically and horizontally at the same time, which it does for a typical throw. QM does indeed include weird possibilities of several things apparently happening at once, for example, an electron passing through both slits in a double-slit experiment, but a simple decomposition of a nucleus' spin state reflects no such magic.

For descriptions of NMR the $S_x = \pm ½$ eigenstates may appear to be the natural choice since the transversal magnetization is measured. Nevertheless, the longitudinal axis is typically chosen as the quantization axis. For normal NMR the choice of basis is influenced more by relaxation processes and B_0 field interaction than by the measurement, since the latter is implicitly and correctly assumed to influence the nuclear states insignificantly. This choice is made since the up and down states are eigenstates not only of the spin measurement operator S_z, but also of the energy which is lowest when the nuclear spin and the magnetic field are aligned. As stated earlier, the nuclear spin can point in any direction, but only two states, $|S_z = ½\rangle$ and $|S_z = -½\rangle$, are associated with well-defined energies (this situation changes when an RF field is applied). The states with a well-defined energy play a special role in QM as they are stationary. Such a state $|\psi_E\rangle$ with energy E does not evolve into other states as long as the interaction remains unchanged. In the absence of measurement, only linear phase evolution occurs at a rate that is proportional to the energy of the eigenstate:

$$|\psi_E(t)\rangle = \exp(-iEt/\hbar)|\psi_E(t=0)\rangle. \tag{3.4}$$

This follows from solving the Schrödinger Eq. (3.1) for an energy eigenstate $|\psi_E(t=0)\rangle = |E\rangle$, where the Hamiltonian $\hat{H}$ and the energy E satisfy the eigenvalue equation $\hat{H}|E\rangle = E|E\rangle$.

This insight provides a relatively simple way to solve the equations of motion. Even if no energy measurement is made, we may still choose to express a general spin state $|\psi\rangle$ in terms of the energy eigenstates, which form a basis, $|\psi\rangle = \sum_E C_E|E\rangle$. If we, for example, want to find the time evolution of transversal magnetization excited to be along the x axis at time zero (i.e., $\theta = 90°$ and $\varphi = 0°$), Eq. (3.3) tells us that right after excitation the magnetization is in the state

$$|\psi(t=0)\rangle = |S_x = ½\rangle = \cos(90°/2)|S_z = ½\rangle + \sin(90°/2)|S_z = -½\rangle = 1/\sqrt{2}(|S_z = ½\rangle + |S_z = -½\rangle).$$

This is not an energy eigenstate but a weighted sum of such, and each term therefore evolves according to Eq. (3.4). The phase difference of the energy eigenstates will consequently evolve at a rate proportional to their energy difference. This frequency is the Larmor frequency ω_0, and by comparison to Eq. (3.3) we see that the azimuthal angle of the magnetization simply changes linearly with time:

$$|\psi(t)\rangle = \cos(90°/2)|S_z = ½\rangle + \sin(90°/2)\exp(-i\omega_0 t)|S_z = -½\rangle = |\theta = 90°, \phi = -\omega_0 t\rangle.$$

This is recognized as precession in the transversal plane, and it can be accurately visualized in terms of the Bloch vector or the similar classical dipole. In direct conflict with the incorrect NMR explanation opening this chapter, no transition between S_z eigenstates is involved, just independent phase evolution of each coefficient in the weighted sum of states.

Please note that the frequency of the periodic phase variation in Eq. (3.4) is not unique due to the zero-energy level being freely selectable. The frequency of each state should therefore not be confused with its precession frequency as sometimes done. Only phase differences are meaningful in QM state vector descriptions.

In summary, since NMR measurements on ensembles are affecting the state of individual nuclei insignificantly, the spin eigenstates are not essential for understanding the basic NMR phenomenon. They offer options for a choice of coordinate system when we wish to make mathematical descriptions. The choice can be practically important, and it may influence the way we interpret the experiments, but it must be remembered that with other choices of basis, other interpretations may be more natural. In particular, coherences and population differences are manifestations of the same quality but expressed in different bases.[2] This is important but beyond the scope of the current text. It should also be remembered that both classical and quantum mechanics can be formulated in different equivalent ways that each may invite both valid and invalid interpretations.[4,13]

3.12 VISUALIZATION OF SPIN DISTRIBUTIONS

Figures 2.9 and 2.14 in Chapter 2 show alternatives to the cones of Fig. 3.1. Such graphs (that are also available for download[14]) illustrate near-isotropic spin distributions that are of central importance for understanding thermal equilibrium and why it is sufficient to keep track of the net magnetization of spin isochromates, that is, collections of nuclei experiencing the same external fields.[2] With accompanying explanation, the graphs are easily understandable from a classical perspective, but it may be less clear which meaning they convey in a quantum context and whether the distributions will evolve as predicted classically, that is, precession around the immediate magnetic field that is the sum of $\mathbf{B}_0$ and $\mathbf{B}_1$. Unless you want arguments for the validity of the figures in a QM context, you can safely ignore the following two sections that are somewhat more technical than most.

Some familiarity with operators and particularly the density operator[1,7] is assumed below. This is defined as an ensemble average $\hat{\rho} = \overline{|\psi\rangle\langle\psi|}$ of the outer vector product of $|\psi\rangle$ with its own conjugate vector $\langle\psi|$. Except for the arbitrary phase, this outer product $|\psi\rangle\langle\psi|$ has the same information as the state vector itself, but unlike state vectors, it can be averaged in a meaningful way over ensembles of similar systems such as protons in a homogeneous sample. It can capture both classical uncertainty and quantum indeterminism and can compactly represent statistical properties of system behavior. When expressed in a basis, the diagonal elements of $\hat{\rho}$ provide the probabilities of finding the system in one of the basis states, should a measurement be performed. The off-diagonal elements represent coherences (correlations[1]) between the states. Expressed in the energy eigenstate basis, $\hat{\rho}$ is diagonal in thermal equilibrium with diagonal elements given by the Boltzmann factors (details follow).

Figure 3.1 showing cones is a reasonable representation of the eigenstates and therefore of the spin distribution after a series of spin measurements along the z axis have been conducted *on individual nuclei*. Each measurement will give a result ±½ and the measured nucleus will in the process be forced into the corresponding eigenstate of the S_z operator. Starting with an ensemble of nuclei in thermal equilibrium, there will be a slight surplus of measurements that leave the spin pointing in the direction of $\mathbf{B}_0$. However, Fig. 3.1 is not a good representation of thermal equilibrium undisturbed by measurement or after a measurement of a sample's net magnetization. As mentioned, showing Bloch vectors of individual nuclei is a better choice for visualization, but they are unknown since only average properties of spins in the ensemble are available, as expressed in the density operator $\hat{\rho}$. Furthermore, entanglement caused by nuclear interaction challenges the concept of individual Bloch vectors. We can nevertheless make a good graphical representation of a spin distribution by calculating the expected results of measurements over many directions approximately uniformly distributed. Figure 2.9 shows the resulting distribution as fairly isotropic but skewed towards north (higher density of arrows near this direction). The creation and interpretation of this figure are now discussed.

For each nucleus in a random subset of a nuclear ensemble, a simulated measurement is performed, resulting in an arrow showing the Bloch vector of each nucleus after measurement. This involves calculating the probability of measuring spin along a particular direction (θ,ϕ), $P(\theta,\phi)=\langle\theta,\varphi|\hat{\rho}|\theta,\varphi\rangle$. In accordance with the calculated probabilities, the Bloch vector is for each nucleus chosen semirandomly to point either along the measurement direction or directly against it. This is done since a measurement of spin $S_{\theta,\varphi}$ along direction (θ,ϕ) for a particular nucleus will bring it into the eigenstates $|\theta,\phi\rangle$ or $|\pi-\theta,\phi+\pi\rangle$ corresponding to finding the spin to be parallel or antiparallel to the $|\theta,\phi\rangle$ direction, where the latter state is calculated from Eq. (3.3):

$$|\pi-\theta,\varphi+\pi\rangle=\sin(\theta/2)|S_z=½\rangle-\cos(\theta/2)\exp(i\varphi)|S_z=-½\rangle.$$

Hence, each simulated measurement will assign a specific Bloch vector to a nucleus of the ensemble, and the directions will afterward be consistent with the general orientations of nuclei in the ensemble since the ensemble density matrix is unchanged by such measurements. The resulting distribution is sketched in Fig. 2.9 of Chapter 2 with the anisotropy of the distribution exaggerated to enhance visibility. The operator for spin measurement in direction (θ,ϕ) can be expressed in terms of its known eigenvalues and eigenstates, $S_{\theta,\varphi}=½|\theta,\varphi\rangle\langle\theta,\varphi|-½|\pi-\theta,\varphi+\pi\rangle\langle\pi-\theta,\varphi+\pi|$.

Using Eq. (3.3), this operator can be expressed in the basis $\{|S_z=½\rangle,|S_z=-½\rangle\}$. After having performed individual simulated spin measurements on a subset of the nuclei, these have well-defined Bloch vectors pointing in many directions but with an orientation distribution slightly skewed towards magnetic north. Since Bloch vectors are known to evolve like classical magnetic dipoles, it is valid QM to make animations, for example, showing how each vector is gradually rotated by magnetic fields.[14] The result of rotation of the distribution of Fig. 2.9 by a 90° excitation pulse will, for example, be as illustrated in Fig. 2.16. Nuclear interactions will only make the assignment of Bloch vectors dubious on a timescale T_2 that is typically long relative to timescales of field interactions (precession and excitation).

Considering that measurements change reality, it may be questioned, however, if it can be experimentally confirmed that the distribution rotates as indicated in the figures. Indeed, it can, since only measurements conducted in directions more or less orthogonal to the Bloch vector will change it randomly. If we subject the spin ensemble to known magnetic fields, we will know how each Bloch vector is rotated, and for each of the selected nuclei we can get confirmation by measuring the spin along the direction of the expected Bloch vector. The measurement result will be certain if the rotation was as expected. Conducting the actual experiment is not needed, since it has been shown before in many contexts that Bloch vectors of individual nuclei evolve as expected from QM, that is, in accordance with classical mechanics when left undisturbed by measurement or interaction. The conceptual or simulated experiments were merely introduced to provide a specific and experimentally verifiable quantum interpretation of Figs. 2.9 and 2.16.

Being gifted with healthy skepticism, you may have noticed there is still reason for concern, however, which is the topic of the next section providing further necessary arguments for Fig. 2.9 being a much better illustration of thermal equilibrium than Fig. 3.1.

3.13 THERMAL EQUILIBRIUM

Like the previous section, this one is likely of limited interest for the general reader. It discusses a crucial question, however: which reality can we reasonably assign to individual nuclei? The simulated measurements described in the previous section assign Bloch vectors to a subset of a spin ensemble so they get oriented consistently with the density matrix. Two objections can be raised, however. It suffices to discuss these for the case of thermal equilibrium (Fig. 2.9) where the concerns are most easily expressed:

1. The outlined method provides illustrations consistent with the density matrix, but very different and equally consistent illustrations can be made by other algorithms since the density matrix only expresses the statistical behavior of the nuclei, not the individual nuclei's orientation. In particular, the infamous Fig. 3.1 shows another spin distribution, which corresponds to the same density matrix and which therefore will give the same experimental predictions. So how can it be claimed that Fig. 2.9 is more precise than Fig. 3.1?
2. A related question concerns the fact that the simulated measurements may change the spin distribution: even if each spin was in either the up or the down state before doing simulated measurements, the prescribed method would result in a graph showing the chosen subsample as a near-uniform distribution.

It may seem that the illustration method was crafted to give the desired result. Indeed, it was to some extent, but it can be argued that this is also the only reasonable result. To get there, we first have to acknowledge that the individual nuclei do not actually have a direction in thermal equilibrium—there is only a tendency for them to have one. This is a nonclassical consequence of QM: suppose that each had some unknown direction at a particular moment of time, that is, that the diagonal density matrix was the result of classical lack of knowledge rather than indeterminism. Random interactions would soon cause entanglement, and as discussed earlier, this forces us to give up on the concept of nuclei having specific directions—they become undecided. So the classical uncertainty is very rapidly exchanged with quantum indeterminism, and we have to conclude that individual nuclei have no direction in thermal equilibrium. Nevertheless, they have a preferred direction when "asked" by measurement, as reflected in differences between the density matrix' diagonal elements.

Having acknowledged that individual nuclei have no direction (are "undecided") and that Figs. 2.9 and 3.1 give rise to the same density matrix, how can it be justified that Fig. 2.9 is any better than Fig. 3.1 as claimed here? The first argument is similar to the one given above:

If all nuclei were indeed in separate S_z eigenstates at some particular moment of time, their interactions would very rapidly bring them out of that state. There are many more configurations that are near isotropic than configurations that have each individual spin in the up or down state, so the entropy is much lower for the latter. Statistics tells us that nature evolves towards high-entropy states, so the spin configuration shown in Fig. 3.1 would rapidly evolve into a near-uniform distribution compatible with the density matrix. Such a distribution is shown in Fig. 2.9 that is calculated as outlined in the previous section.

A similar but somewhat more technical argument in favor of Fig. 2.9 involves calculation of the density matrix in the basis of product states for all nuclear spins, rather than for the single spin states. This basis is normally avoided since it has 2^N basis vectors where N is the number of nuclei in the ensemble. This is the basis of choice when we want to say something about individual nuclei, but the dimensionality of the problem correspondingly increases enormously. The basis vectors are each a product state $\prod_{i=1}^{N} \left| S_z^i = \pm ½ \right\rangle$ where S_z^i is the S_z spin component of nucleus i. The 2^N eigenvalue sign combinations each gives a basis vector. The product states are not exactly energy eigenstates due to nuclear interactions, but since these are very weak for normal NMR compared to the static field interaction, the exact energy eigenstates deviate only insignificantly.

The corresponding density matrix has dimension 2^N squared, and it is diagonal as before. The diagonal elements are each proportional to the Boltzmann factor $\exp(-E/kT)$ where E is the energy of the state corresponding to the particular diagonal element (the Boltzmann distribution expresses maximized entropy). A common normalization factor ensures that the sum of all diagonal elements is 1. The lowest energy state is, for example, the tensor product $\left|S_z^1 = ½\right\rangle \otimes \left|S_z^2 = ½\right\rangle \otimes \cdots \left|S_z^N = ½\right\rangle$ with energy $-N\hbar\omega_0$ relative to the highest energy state $\left|S_z^1 = -½\right\rangle \otimes \left|S_z^2 = -½\right\rangle \otimes \cdots \left|S_z^N = -½\right\rangle$. In thermal equilibrium at room temperature, the probabilities are nearly uniformly distributed over the 2^N states. This density matrix can be inappropriately interpreted to reflect that the probabilities of the ensemble being in each of these states are nearly equal.[15] It has already been demonstrated, however, that the nuclei are not each in any particular state (they are undecided), so instead, we have to interpret the density operator as the 2^N different states being almost equally populated, which is consistent with Fig. 2.9 and not at all with Fig. 3.1. We can conclude that the latter is not a valid representation of thermal equilibrium.

The fact that measurements, and therefore the observer, play such a prominent role in QM has been a subject of much debate. What qualifies as an observer? Does it need to be conscious, living, or macroscopic, for example? The latter option is the most reasonable.* If a "measurement" can be performed by interaction with anything macroscopic, like a bottle of water, for example, this opens an interesting possibility for potentially rescuing a QM interpretation that this text has been refuting: the random interactions between a nucleus and its surroundings could potentially amount to something similar to a measurement of S_z, so that the spin is brought into an eigenstate. May Fig. 3.1 thus be a reasonable representation of

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*Vaguely stated, measurement involves coupling to a system with essentially infinite degrees of freedom and states densely distributed over energies, which causes near-instant coherence loss and projection onto a subspace. This, however, does not eliminate the "measurement problem of QM," as it does not prevent the "Schrödinger cat states," that is, entanglement involving macroscopic entities.[10]

equilibrium magnetization after all? No. Even if such random interactions did have the same effect as measurements along the direction of the magnetic field, these would necessarily have to be weak/partial and be effective only on a timescale T_2 since coherent evolution would otherwise not be observable (we know it is). Those same nuclear interactions would make the cone picture of Fig. 3.1 inaccurate on the same timescale.

Although there are strong arguments for Fig. 2.9 and similar, they are still just particular illustrations of statistical distributions and of quantum realities, which arguably do not exist. The figure shows properties of nuclei that they do not have until it is enforced by simulated measurements (specific Bloch vector directions). However, these figures and the related and commonly used "semiclassical" vector diagrams showing, for example, excitation, dephasing, and echoes *do* capture the essential dynamics of QM for weakly interacting spin ½ ensemble dynamics. The Bloch vector diagrams leave NMR users and developers with a practically useful and intuitive understanding of basic NMR phenomena and methods. The remaining deviations from quantum reality are minor and of academic interest only. In contrast, the common cone figures will cause confusion, at best. The most important argument in favor of the Bloch vector diagrams is therefore pragmatism. Such graphs capture the essentials of the QM descriptions, unlike cone figures.

3.14 CLASSICAL EIGENSTATES, RESONANCE, AND COUPLINGS

The limited fundamental role of quantum eigenstates in NMR may be surprising considering that spectra are often explained as emission resulting from sudden quantum jumps between eigenstates. There are no jumps in normal NMR, however, and quantum eigenstates are convenient for describing NMR, but not a necessity. They share essential features with classical eigenstates that are useful for understanding aspects of NMR and QM qualitatively.

Vaguely stated, energy eigenstates in QM represent states where no observable quantity changes over time. They are therefore said to be stationary, but there is nevertheless linear phase evolution of the probability amplitude as described by Eq. (3.4). This periodic variation corresponds to a standing wave not reflected in any observable, when individual energy eigenstates are excited. The spin-up state, for example, may reasonably be thought of as a probabilistic representation of a single magnetic moment precessing with a specific polar angle (the "magic" angle, 55°) but with all azimuthal angles equally probable. This interpretation is reflected in the often seen Fig. 3.1 illustrating the eigenstates as cones that are symmetrical around the quantization axis (the cone opening angles were drawn much smaller than 110°, however, since otherwise the traditional up/down terminology would seem even less intuitive).

Classical systems also have resonances or modes of periodic oscillation. A pendulum will have a characteristic frequency, for example, and it is independent of amplitude when oscillations are small. Although energies are not quantized classically, frequencies often are. A guitar string will support a number of periodic oscillatory eigenmodes as shown in Fig. 3.5, each characterized by a standing wave pattern on the string. The corresponding classical probabilistic eigenstates represent a string known to oscillate with a particular frequency, but with unknown phase. Such modes are analogous to quantum eigenstates with all phases of the oscillation represented simultaneously, which is consistent with the probabilistic nature of eigenstates. Phase evolution corresponds to vibration of the string, but since all phases

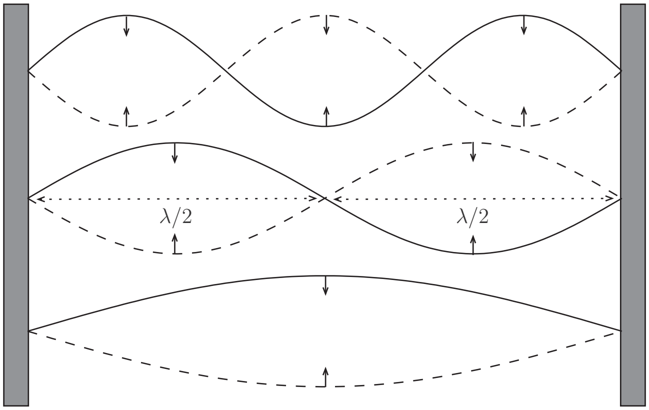

FIGURE 3.5 Three standing wave modes of oscillation are shown for an elastic string suspended between fixed points. The solid and dashed lines show the extreme positions of the string for a particular amplitude of oscillation. The vertical arrows indicate the direction of string motion when the string contracts from the extremes. The two dotted arrows each indicate half a wavelength, $\lambda/2$, for the middle pattern of oscillation. The three example modes represent repeated oscillation with only a single temporal frequency that increases from bottom to top. The time evolution can therefore be described by simple phase evolution on timescales that are short compared to the oscillation damping. Corresponding classical probabilistic states with unknown phase (even probability of all phases) are time-independent. Any possible motion of the string can be expressed as a superposition of eigenmode oscillations in accordance with Fourier theory.

are equally probable, this abstract classical state does not visibly change (it matches the blurred visual appearance of an oscillating guitar string, which only changes slowly on the timescale of damping).

It will be argued now that the evolution after excitation by plucking the guitar string is similar to that described earlier for quantum superpositions of energy eigenstates. Each stationary pattern of string movement is spatially characterized by the integer number of half wavelengths along the string and temporally by the frequency of oscillation as shown in Fig. 3.5. The two quantities increase together: high-pitched modes have a high number of half wavelengths along the string. That the string supports a number of eigenmodes does not imply that it can only oscillate in one of these standing wave patterns since any superposition of modes is in fact possible. Any possible string motion can be described as a superposition of the discrete eigenmode oscillations. When a guitar string is plucked sharply at one end, for example, a traveling wave will move along the string and be reflected a few times before it is completely dispersed.

Mathematically, such string motion can conveniently be described as excitation of a broad spectrum of the standing wave eigenmodes, a superposition $|\text{state}\rangle = \sum_{\text{mode}} C_{\text{mode}} |\text{mode}\rangle$. Each mode oscillates in accordance with its characteristic spectral-spatial pattern and independent of the other modes. The phase and amplitude of each mode are determined by the specifics of the string plucking. The particular movement of the string, such as a traveling wave, is expressed in the relative phases of the coefficients C_{mode}. Each mode's oscillation is damped on a timescale characteristic of the particular mode. In the absence of such damping, the excitation of each mode is constant since there are no transitions between the eigenmodes that are approximately uncoupled. There is just linear phase evolution happening at a rate given by each mode's frequency.

The advantage of this description is clear when the spectrum of the guitar sound is of interest. It will be peaked around the frequencies of the eigenmodes, and the phase of each peak is determined by the initial phase associated with the excitation. This classical description of the string oscillation is analogous to the description of precession made earlier, except that each nuclear spin supports only two eigenmodes, whereas a guitar string supports more. Similarly, the frequency spectra are related.

A more complicated system may exhibit a spectrum of resonances more interesting than the equally spaced harmonics of a string. A number of masses connected by springs, for example, may exhibit a spectrum of vibrational resonances with structure similar to that of a molecule where the nuclei are interacting magnetically, that is, a spectrum of a finite number of discrete peaks.

Focus is now shifted to a particular classical example that will give additional insight into eigenmodes, magnetic resonance, and spectral features: two coupled oscillators. A physical realization can, for example, be two pendulums that are well separated but both hanging down from a horizontal third string. If one pendulum is set in motion (excited) orthogonally to the connecting string, it will exert a weak force on the other pendulum via their common suspension. Energy may therefore be transferred between the pendulums, in particular if they are similar so they have the same natural oscillation frequency. The focus is on such similar pendulums in the following discussion.

If you do the experiment or search for "coupled pendulums" on the YouTube™ video community, for example, you may see the following: when one pendulum is set in motion, while the other is initially at rest, the amplitude of oscillation of the swinging pendulum gradually decreases, while the other begins to swing. After a while, the energy is completely transferred to the other pendulum, and simultaneously, the first one comes to a brief stop. It will soon regain oscillation, however, since energy is transferred back from the other pendulum. The energy will oscillate back and forth between the two pendulums at a frequency that can be much smaller than the pendulum oscillation frequency. This frequency is proportional to the coupling strength of the two pendulums that is characteristic of their common suspension.

The dynamics of this system is analogous to nuclear excitation, which may not be immediately clear, but follows from doing a quantization of the electromagnetic field. This is implicit whenever the concept of photons is engaged, but it is seldom spelled out for NMR, despite photons often being mentioned in that context. Field quantization will be done here to explain the role of eigenstates, even though photons are probably best left out of QM introductions for reasons that will soon be discussed.

To establish the correspondence between two coupled pendulums and nuclear excitation, we first think of the nucleus and the electromagnetic field as separate storages of energy. When a spin is aligned with the static field, it is in the ground state. During excitation, energy is transferred from the field to the nuclear spin, mediated by dipolar interaction. It will be transferred back if the RF field is kept on, so the tip angle exceeds 180° (yes, an RF pulse can remove spin energy). We can express the dynamics in terms of two weakly coupled combined states of the field and nucleus: the state $|S_z = ½, N+1\rangle$ has the nuclear spin in the ground state and $N+1$ photons in the field. The state $|S_z = -½, N\rangle$ has the nucleus in the excited state after absorbing one photon from the field, which is left with N photons. As before, any normalized superposition of the two states is possible.

Each photon carries an energy $\hbar\omega$ so the $|S_z = ½, N+1\rangle$ and $|S_z = -½, N\rangle$ states have the same energy (are "degenerate"), if the frequency of the electromagnetic field is matched to the Larmor frequency, that is, satisfies the resonance condition. Please note that both states are associated with almost equally strong electromagnetic fields with only one photon difference. These two states are only energy eigenstates in the absence of coupling between field and nucleus. Introducing coupling corresponds to placing the nucleus in the electromagnetic field. Rabi and coworkers realized this experimentally in 1937 when NMR was first detected in a molecular beam sent through a region with an oscillating magnetic field matched to the Larmor frequency.[16]

Once dipolar coupling between the $|S_z = ½, N+1\rangle$ and the $|S_z = -½, N\rangle$ states is introduced, they are no longer energy eigenstates. Couplings between degenerate states remove the degeneracy, and the new energy eigenstates are equal mixes of the former (superpositions with equal amplitude of the coefficients). It is convenient for the following discussion to adopt conventional naming: The states $|S_z = ½, N+1\rangle$ and $|S_z = -½, N\rangle$ specify the state of field and nucleus separately and they are therefore called "bare" states in contrast to the "dressed" states that are energy eigenstates after dipolar coupling is introduced, for example, when the nucleus enters the region with field (e.g., as in the Rabi molecular beam experiment[16]). The nuclei are "dressed" in the field.[7] The dressed states are equal mixes of the bare states, having well-defined energies with an energy separation proportional to the coupling strength between the bare states. This is itself proportional to the photon count N and therefore to the RF field amplitude B_1. Specifically, the energy difference between the dressed states is $\hbar\gamma B_1$ on resonance. When the system is in a superposition of dressed states, the phase difference between the components will therefore evolve at a frequency γB_1 in accordance with Eq. (3.4). As shown below, the components will sometimes add up to the bare state $|S_z = ½, N+1\rangle$ and sometimes to the bare state $|S_z = -½, N\rangle$. This oscillation back and forth is the nutation (or Rabi oscillation) happening during excitation.

In fact, the electromagnetic fields generated by NMR coils are far from being phase-free monochromatic photon states $|N\rangle$ that are closer to representing laser light and most appropriate for cavity electrodynamics.[7] The field inside an NMR coil is instead a superposition of modes of the electromagnetic field,[6,8] so results may be misleading if the above QM description is taken much further without representing the field realistically. This is an argument for not mentioning photons in NMR introductions—doing it right is far from simple, and it is not necessary as RF fields are typically better treated classically in this context.[6,8] This path will therefore not be followed far, but the relation to classical coupled oscillators (pendulums) will be shown, as well as the role of eigenstates, while staying with monochromatic electromagnetic fields.

3.15 THE EIGENMODE STRUCTURE FOR NUCLEAR EXCITATION

Energy eigenstates represent states of simple oscillation and their phases evolve proportionally to their energies. As such, each of the states $|S_z = ½, N+1\rangle$ and $|S_z = -½, N\rangle$ is represented as oscillators in the absence of coupling, and their phase evolves at the same rate since their energy is equal when the photon energy is matched to the Larmor frequency. We can take uncoupled pendulums as a mechanical analogy since they have the same characteristics and eigenstate structure. Each state corresponds to a pendulum. The physical nature of the systems and that of the oscillations are different, but similar dynamics occur and the mathematical description can be shared.

When coupling between the bare states is introduced, the energy eigenstates are changed. Two modes of oscillation are now stationary, that is, they represent states of simple oscillation. For the coupled pendulums, the eigenmodes are simple to imagine: If the two pendulums are started in synchrony, they will remain that way despite the coupling. Since they are similar and experience the same mutual interaction, a simple symmetry argument tells us that they will keep oscillating in synchrony. Similarly, if the two pendulums are released in an antisymmetrical state, they will remain oscillating with opposite phase. We therefore know the two patterns of simple oscillation for coupled pendulums (the eigenstates), symmetrical and antisymmetrical oscillation. The two eigenstates evolve at different frequencies, however, since the pendulums interact differently in the two situations: When the pendulums oscillate with opposite phase, they pull each other back towards equilibrium, which increases the oscillation frequency compared to in-phase oscillation. The energies of the eigenmodes of coupled pendulums (corresponding to dressed states) are therefore different, so the degeneracy of the eigenstates is removed. The corresponding normalized symmetrical and antisymmetrical QM dressed states are

$$|+\rangle = 1/\sqrt{2}(|S_z = ½, N+1\rangle + |S_z = -½, N\rangle)$$

$$|-\rangle = 1/\sqrt{2}(|S_z = ½, N+1\rangle - |S_z = -½, N\rangle).$$

All of this now comes together in a discussion of NMR excitation and, equivalently, pendulum motion. Initially, we will consider the uncoupled case starting from z-polarization, for example, a system in the bare state $|S_z = ½, N+1\rangle$. The state does not immediately change when the nucleus enters the electromagnetic field at time $t = 0$, but the energy eigenstates do. Expressed in terms of these, the state is

$$|\psi(t=0)\rangle = |S_z = ½, N+1\rangle = 1/\sqrt{2}(|+\rangle + |-\rangle) \tag{3.5}$$

A superposition of the symmetrical and antisymmetrical states is present as long as the RF field is on, but the phases of the coefficients will evolve at a rate determined by the energy of each eigenstate. The common phase is unimportant as it is not observable, but the energy difference $\hbar\gamma B_1$ mentioned above gives rise to an important phase difference $\gamma B_1 t$:

$$|\psi(t)\rangle = 1/\sqrt{2}(|+\rangle + \exp(-i\gamma B_1 t)|-\rangle).$$

A similar classical description can be made for the pendulums that each correspond to a bare state. To determine the dynamics after the pendulum associated with $|S_z = ½, N+1\rangle$ is set in motion, and coupling is introduced, it is convenient to express the initial state in terms of the symmetrical and antisymmetrical oscillation patterns as done above. Oscillation of just one pendulum can be interpreted as equal amounts of symmetrical and antisymmetrical oscillation, so the motion of the other pendulum cancels as expressed in Eq. (3.5). The components of the superposition will evolve with different frequencies, however, since antisymmetrical motion has a shorter period. Consequently, both pendulums will soon swing, until the time comes where all energy is completely transferred to the other pendulum. This follows from the analogous calculation for the NMR experiment where this characteristic time is $t = (\pi/\gamma B_1)$:

$$\begin{aligned} |\psi(t)\rangle &= 1/\sqrt{2}(|+\rangle + \exp(-i\gamma B_1 t)|-\rangle) \\ &= 1/2((|S_z = ½, N+1\rangle + |S_z = -½, N\rangle) + \exp(-i\gamma B_1 t)(|S_z = ½, N+1\rangle - |S_z = -½, N\rangle)) \\ &= 1/2((1 + \exp(-i\gamma B_1 t))|S_z = ½, N+1\rangle + (1 - \exp(-i\gamma B_1 t))|S_z = -½, N\rangle) \end{aligned}$$

$$|\psi(t = \pi/\gamma B_1)\rangle = |S_z = -½, N\rangle.$$

After yet another period $\pi/\gamma B_1$, the magnetization has been rotated a full round and is back in the longitudinal direction:

$$|\psi(t = 2\pi/\gamma B_1)\rangle = |S_z = ½, N+1\rangle.$$

This is all consistent with the motion of coupled pendulums where the energy also oscillates back and forth at a frequency determined by the coupling strength. Note that in the basis of dressed eigenstates there are no transitions whatsoever, only independent phase evolution of each component of the superposition of eigenstates. The bare states are only energy eigenstates when the dipolar field coupling is ignored. Expressed in terms of these, dipolar coupling causes smooth transitions, reflecting coherent evolution. There are no sudden jumps between states in any basis, even though such are often said to be the source of spectral features.

The previous example hopefully gave insight into the similarities of classical and quantum dynamics. It was covered in considerable detail to give a feel for eigenstates, both bare vs. dressed and quantum vs. classical. The close relation between NMR and pendulum motion is not incidental since energy eigenstates are indeed oscillatory, as are pendulum modes of oscillation. It was crucial to include the electromagnetic field in the quantum treatment to establish the connection, which can be done in several ways. The analogy extends further since the corresponding formulas remain consistent in the case where there is a frequency offset, that is, when the RF field is not applied exactly on resonance.

3.16 *J*-COUPLING

The coupled oscillator analogy can also give insight into effects of scalar *J*-coupling. This intramolecular interaction between nuclei is mediated by the electronic cloud. Considering the situation from a classical perspective can give insight into the nature of spectral features. This will be done with much less rigor compared to the description of magnetic resonance in the last section.

It is not surprising classically that nuclei interact magnetically via electrons that are also magnetic. *J*-coupling itself is a quantum effect, however, and from a classical perspective the size of the coupling is surprising, and the effect should not be observable in the spectra (nonclassical exchange interaction is responsible). Let us nevertheless take *J*-coupling for granted and consider what the effect on the spectra may be. We focus on the simplest situation where two nuclei after excitation have the same chemical shift but are *J*-coupled. This sounds much like the pendulum case, and we may classically expect similar behavior. When two similar classical oscillators are coupled, the eigenmodes of oscillation are changed. Symmetrical and antisymmetrical oscillation patterns result as described above. The degeneracy is removed by the coupling, and the energy separation of the eigenmodes is given by the coupling constant. Thus, two resonances exist around the uncoupled Larmor frequency with a frequency separation *J*. Exciting just one nucleus—or the antisymmetrical component—will be difficult in this case, however, since the nuclei have the same chemical shift.

If the starting point is changed to *J*-coupling of two nuclei with different chemical shifts, this corresponds to the coupling of two pendulums with different oscillation frequencies, for example, having different lengths of the strings. Each of the two eigenstates is split into a doublet separated by a frequency *J* when weak coupling is introduced. This sounds like NMR, but the sentence describes coupled pendulums, which have four eigenmodes in this case. When one of the pendulums is set in motion, this corresponds to a superposition of eigenmodes that each evolve at a different frequency. As in the previous case, the oscillations will be modulated with the difference frequencies, reflecting how energy is transferred between pendulums (or within the molecule for the case of NMR).

3.17 THE AFTERMATH

The coverage of *J*-coupling presented above is too simple. After all, the dynamics of just a single nucleus in an electromagnetic field was shown above to be accurately represented by two coupled oscillators. The much more complex system of two *J*-coupled nuclei is now represented by the same classical analogy, so obviously much was swept under the carpet using simplifying assumptions and vague statements. The main idea was not to give detailed insight into *J*-coupling, but to show that spectral features and peak splittings similar to those observed by NMR are not unexpected in classical systems. Spectral complexity is often taken as a sign of quantum mechanics' role in NMR, but this conclusion cannot be based on discrete spectral features alone (Trap #25). A simple system of masses connected by springs may have a qualitatively similar spectrum of resonances, for example, including peak splittings, amplitude modulation, and power broadening. QM is necessary for most NMR, however, to get not only the details right but also the larger picture, especially when coherent nuclear interactions are involved. This is exemplified by *J*-coupling itself being nonclassical and by NMR quantum computing implemented with coherently coupled nuclei, which clearly exposes nonclassical aspects of spin systems.[17] Even when a classical analogy or description can be made, it is typically not worth using it quantitatively, as the quantum formalism is analogous, and is known to give precise results. An exception is simple spin ½ NMR as used in almost all MRI, since the two descriptions are equal.

For relaxation, the situation is somewhat similar. Intuitive classical arguments will tell you much about relaxation mechanisms and the dependency on, for example, nuclear mobility, but it certainly will not tell you the whole story, and you must always be ready to question the validity of results obtained from classical arguments (Trap #19). QM and classical mechanics typically give qualitatively similar results, so when they do not agree, there is reason to expect a flaw in one of the derivations. Classical mechanics is therefore also a useful tool for sanity checking, including avoidance of Mental Traps.

The description of coupled oscillators was not included to suggest an alternative approach to explaining NMR. A brief introduction to classical NMR consistent with Chapter 2, for example, leading up to a good QM introduction is typically a better choice. Consistent classical and quantum vector descriptions need not be long or complicated and can advantageously be supplemented with animations and simulations.[14] The focus was on deeper NMR understanding and especially on making it clear that QM and classical descriptions of NMR can be quite similar. Some of the mistakes of typical QM interpretations were pointed out as well as Mental Traps responsible for their continued existence in literature describing basic NMR. Many aspects were obviously covered superficially, and assumptions and details were left out for the sake of focus and readability. Errors were likely also introduced or repeated. Science involves getting in and out of Mental Traps continuously.

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