
Spin Dynamics

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1. Matter

1.1 Spin

1.1.1 Angular Momentum

In classical mechanics, the angular momentum is

$$L = r \times p$$

that is,

$$L_x = yp_z - zp_y$$

and so on. The corresponding quantum operators are:

$$L_x = \frac{\hbar}{i} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

and so on.

L_x, L_y, L_z are incompatible observables :

$$[L_x, L_y] = i\hbar L_z$$

But, the square of total angular momentum $L^2 \equiv L_x^2 + L_y^2 + L_z^2$, commutes with L_x, L_y, L_z . Hence, we can find simultaneous eigenstates of L^2 and a component of L , say, L_z :

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m; \quad L_z f_l^m = \hbar m f_l^m$$

where

$$l = 0, 1/2, 1, 3/2, \dots; \quad m = -l, -l+1, \dots, l-1, l$$

1.1.2 Spin Angular Momentum

Spin is an intrinsic property of the particle and not produced by a rotation. The algebraic theory of spin is same as the theory of angular momentum, i.e.,

$$[S_x, S_y] = i\hbar S_z, \quad S^2 f_s^m = \hbar^2 s(s+1) f_s^m, \quad S_z f_s^m = \hbar m f_s^m$$

where,

$$s = 0, 1/2, 1, 3/2, \dots, \quad m = -s, -s+1, \dots, s-1, s$$

Particles with integer spin are called bosons. Particles with half-integer spin are called fermions.

Spin of a particle is simply its feature, like mass or charge. A particle always has a spin, even at absolute zero!

1.1.3 Combining Angular Momenta

Consider a system with two particles each having angular momentum given by quantum numbers J_1 and J_2 . The total angular momentum of entire system is:

$$J = \begin{cases} |J_1 - J_2| \\ |J_1 - J_2| + 1 \\ \vdots \\ |J_1 + J_2| \end{cases}$$

1.1.4 Addition of Spin-1/2 Particles

There are two possible states, $s = 1$ and $s = 0$.

There are three states with $s = 1$:

$$\begin{aligned} |1\ 1\rangle &= \uparrow\uparrow \\ |1\ 0\rangle &= \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1\ -1\rangle &= \downarrow\downarrow \end{aligned}$$

This is called the triplet combination.

For $s = 0$:

$$|0\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$$

1.1.5 The Pauli Principle

It states that no two fermions can have identical quantum states.

This originates from the fact that fermions are antisymmetric. (Spin-Statistics Theorem)

1.2 Nuclei

Everything in universe is made up of leptons, quarks and force particles.

Leptons are low-mass particles. Out of six leptons, one is electron, which have electric charge $-e$ and spin-1/2.

Quarks are relatively heavy particles, and all of them have spin-1/2. Three of them have electric charge $+2e/3$ and other three have $-e/3$.

Force particles mediate the action of different particles on each other. Photon, the particle manifestation of the electromagnetic field, is a force particle. It has no mass, no charge and spin = 1. Gluons and vector bosons are some other force particles.

1.2.1 Neutrons and Protons

They consist of three quarks, stuck together by gluons.

The neutron contains two quarks with charge $-e/3$ and one with charge $+2e/3$, making total electric charge zero. The neutron has spin-1/2, due to combination of quark spins.

The proton has two quarks with charge $+2e/3$ and one with charge $-e/3$, making total charge of the proton $+e$. It also has a net spin-1/2.

But, all three quarks spin can be in parallel, giving a total spin of 3/2. These particles are only known in high-energy physics. The spin-3/2 state of the proton is known as Δ^+ particle.

1.3 Nuclear Spin

The nuclear spin quantum number is conventionally denoted as I . The spins of nuclei are formed by combining the spins of protons and neutrons. The value of I in the lowest energy state is called the ground state nuclear spin.

Isotopes with even mass numbers have integer spin and isotopes with odd mass numbers have half-integer spin. Further, for isotopes with even mass numbers,

- If the number of protons and neutrons are both even, the ground state $I = 0$.
- If the numbers of protons and neutrons are both odd, the ground state spin is an integer > 0 .

1.3.1 Nuclear Zeeman Splitting

A nuclear state with spin I is $(2I + 1)$ -fold degenerate, but this degeneracy is broken when a magnetic field is applied. This splitting between the nuclear spin levels is called the nuclear Zeeman splitting. Nuclear Magnetic Resonance (NMR) is the spectroscopy (measuring of energies of transitions between quantized levels) of the nuclear Zeeman sublevels.

1.3.2 Zero-spin nuclei

Zero nuclear spin display no nuclear Zeeman effect. Organic substances contain many of these spinless isotopes, ^{12}C , ^{16}O , ^{32}S , etc. They are said to be NMR silent.

1.3.3 Spin-1/2 nuclei

These are of major importance in NMR. Such nuclei are spherical in shape. The alkali and alkaline earth metals possess no spin-1/2 isotopes at all. Few elements having spin-1/2 are: ^1H , ^{31}P , the rare isotopes of ^{13}C and ^{15}N , the abundant ^{19}F . The noble gases also contain two spin-1/2 isotopes, ^3He and ^{129}Xe .

1.3.4 Quadrupolar nuclei with integer spin

Nuclei with spin $I > 1/2$ are known as quadrupolar nuclei.

Quadrupolar nuclei with integer values of I are uncommon. The most abundant nucleus is

^{14}N . Deuterium (^2H) is also of great importance. There are no nuclei at all with ground state $I = 2$! The $I = 7$ isotope ^{176}Lu has the highest nuclear spin.

1.3.5 Quadrupolar nuclei with half-integer spin

They are common and particularly prominent for the alkali metals, the boron-to-thallium group, and the halogens.

1.4 Atomic and Molecular Structure

There are 3 sources of angular momentum in a hydrogen atom: the proton spin, the electron spin, the motion of the electron around the nucleus. Quantum states with zero electron orbital momentum are called s-orbitals ($l = 0$). Quantum states with ($l = 1$) are called p-orbitals.

1.4.1 Molecules

In most molecules, the only sources of angular momentum in the molecular ground state are the molecular rotation and the nuclear spins.

Molecules differing only in the mass numbers of the nuclei are called isotopomers. In many cases, even though the isotopomers are physically and chemically almost indistinguishable, one gives a large signal in NMR while another isotopomer gives none.

1.5 States of Matter

1.5.1 Liquids

There are two types of mobility in liquid phases:

- Translation Molecular Mobility: The molecules or atoms slide past each other and wander over large distances in a relatively short time.
- Rotational Molecular Mobility: The individual molecules rotate around their own centres of gravity.

We further distinct the liquid phase between isotropic and anisotropic phases.

In isotropic liquids, the translation and rotational mobilities of the molecules are the same in all directions.

The anisotropic liquids, also called liquid crystals, in which the molecules adopt a non-isotropic spatial configuration.

Anisotropic liquids behave very differently from isotropic liquids under NMR. This is because in an anisotropic liquid, the translation and rotational mobilities of the molecules depend on the direction.

1.5.2 Solids

Although the majority of solids are electrical insulators, with very limited electron mobility, in some cases electrons pair up to form bosons that form macroscopic, coherent quantum waves. This happens in superconductors.

Generally, the NMR spectra of solids are broader and more complex than in liquids.

2. Magnetism

The NMR spectroscopy operates with a magnetic field between 4T to 20T.

2.1 Macroscopic Magnetism

$$E_{\text{mag}} = -\boldsymbol{\mu} \cdot \mathbf{B}$$

An object that is free to move tends to align along an external magnetic field to minimise this magnetic energy.

Most objects display induced magnetism in the presence of an applied magnetic field, and it is often proportional to the applied magnetic field \mathbf{B} :

$$\mu_{\text{induced}} = \mu_0^{-1} V \chi \mathbf{B}$$

where χ is called the magnetic susceptibility of the material. It expresses how readily the material will develop a magnetic field in the presence of an external magnetic field. It can be positive or negative. Materials with a positive value are called paramagnetic, and they tend to pull the magnetic field into the material. Those with a negative value are called diamagnetic, and they tend to push the magnetic field out of the material.

2.2 Microscopic Magnetism

The major contribution to magnetism comes from the circulation of electric currents and the magnetic moments of the electrons. A small contribution is from the magnetic moments of the atomic nuclei, also.

Generally, the circulation of electric currents contributes a negative value to the susceptibility. This is due to because when an external magnetic field is applied, the electron orbital motion is induced opposite to the applied field. Whereas electron and nuclear magnetic moments contribute a positive value as they align with the applied magnetic field.

The electrons and nuclei both possess intrinsic magnetism; they have a magnetic moment, just like they simply have spin angular momentum. Spin and magnetic moment are proportional to each other:

$$\hat{\boldsymbol{\mu}} = \gamma \hat{\mathbf{S}}$$

where γ is the gyromagnetic ratio. For particles with a positive γ , the magnetic moment is parallel to the angular momentum. For particles with a negative γ , the magnetic moment is opposite to the angular momentum.

2.3 Spin Precession

The direction of the spin angular momentum is referred to as the spin polarization axis. For a sample in the absence of a magnetic field, the distribution of magnetic moments is isotropic. When a magnetic field is applied to such a sample, the spin polarization moves around the field. The magnetic moment moves on a cone, keeping a constant angle between the spin

magnetic moment and the field. This motion is called precession. The angle only depends on initial spin polarization. The extremes are, precession of zero angle in case the spin is initially polarized exactly along or against the field, and in case of initially perpendicular to the field, the spin polarization moves on a flat disc.

2.3.1 Larmor Frequency

$$\omega^0 = -\gamma B^0$$

where B^0 is the magnetic field at the site of the particle and γ is the gyromagnetic ratio. For nuclear spins, ω^0 is called the nuclear Larmor frequency.

2.4 Spin-Lattice Relaxation

When there is no magnetic field, the spins of the ^1H nuclei, in a sample of water, point randomly in all directions and hence the net magnetization is approximately zero. Now, when the field B_0 is suddenly applied, each spin undergoes Larmor precession. But, since the distribution of spin polarization is still isotropic, it does not contribute to the magnetism of the material. Though the water molecules undergo constant vigorous motion, the spin polarization is tied to space and not to the molecule's orientation. So even as the molecule moves, the spin vector keeps pointing in the same direction and continues its precession.

But the violent molecular surroundings do slightly influence the nuclear magnets. The local magnetic fields of electrons and nuclei fluctuate rapidly because of the thermal motion of the environment. This results in the total magnetic field from each spin fluctuating slightly in both magnitude and direction. These small fluctuations are important as they break the perfect isotropy and the spins can slowly align with B_0 , giving rise to a net macroscopic magnetization.

These tiny fluctuating molecular fields cause the cone angle to drift very gradually (in seconds), and hence a spin samples many different cone angles. If this wandering motion were perfectly random, the spin would stay isotropic and hence no net magnetization. But thermal fluctuations are biased by energy, i.e., it is slightly more probable that the nuclear spin is driven towards an orientation with low magnetic energy than towards high magnetic energy. Hence, the biased wandering motion leads eventually to a stable anisotropic distribution of nuclear spin polarizations, called thermal equilibrium. Though this distribution is stable, it is not static on a microscopic scale. Each spin keeps precessing and wandering, but on the macroscopic level, the average distribution gives a constant equilibrium magnetization. This means that the entire sample acquires a small net magnetic moment along the field, i.e., a longitudinal magnetic moment. This is the microscopic mechanism of nuclear paramagnetism.

Suppose that t_{on} is defined as the moment when the external magnetic field is applied, and the direction of the field is defined to be the z-axis. The build-up of longitudinal magnetization is:

$$M_z^{\text{nuc}}(t) = M_{\text{eq}}^{\text{nuc}}(1 - e^{-(t-t_{\text{on}})/T_1})$$

where T_1 is known as either the spin-lattice relaxation time constant or the longitudinal relaxation time constant.

If the magnetic field is suddenly switched off at a later time t_{off} ($t_{\text{on}} - t_{\text{off}} \gg T_1$, the nuclear spin magnetization relaxes back to zero again as:

$$M_z^{\text{nuc}}(t) = M_{\text{eq}}^{\text{nuc}} e^{-(t-t_{\text{off}})/T_1}$$

2.5 Transverse Magnetization and Transverse Relaxation

NMR spectroscopy measures the nuclear spin magnetization perpendicular to the magnetic field, rather than measuring it along the field.

In an equilibrium situation, there is no net magnetization perpendicular to the field, because, on average, the magnetization distribution in thermal equilibrium is cylindrically symmetrical around the z-axis.

Now, suppose that the polarization of every single spin is suddenly rotated by $\pi/2$ radians using an r.f. pulse (not explained yet). This will also rotate the entire nuclear magnetization distribution of the sample. Say the net spin polarization along the z-axis is therefore transferred to -y axis, i.e., along an axis perpendicular to the magnetic field. This net magnetic moment is referred to as transverse magnetization.

When the pulse is turned off, the individual spins precess on their cones as usual. But, since every single spin precesses, the bulk magnetic moment also precesses. The macroscopic nuclear magnetization rotates in the plane perpendicular to the main magnetic field with a frequency equal to the precession frequency of the individual spins.

$$M_y^{\text{nuc}} = -M_{\text{eq}}^{\text{nuc}} \cos(\omega^0 t) e^{-t/T_2}$$

$$M_x^{\text{nuc}} = M_{\text{eq}}^{\text{nuc}} \sin(\omega^0 t) e^{-t/T_2}$$

where, time constant T_2 is called transverse relaxation time constant or coherence dephasing time constant or coherence decay time constant, or spin-spin relaxation time constant.

These are the components of macroscopic magnetization at a time t after the pulse. This shows that the transverse magnetic moment precesses at the nuclear Larmor frequency, slowly decaying simultaneously. This is because of the slight fluctuations in the microscopic magnetic fields. The precessing nuclear magnets gradually get out of phase with each other. This process is irreversible, i.e., once the transverse magnetization is gone, it cannot be recovered. This is known as homogeneous decay in the jargon of NMR.

2.6 NMR Signal

If a wire coil is placed near this rotating magnetic field (after the r.f. pulse is applied and stopped), an oscillating electric current flows in the wire. The winding axis of the coil is perpendicular to the main magnetic field. The oscillating electric current induced is called the NMR signal or free-induction decay (FID).

So, a NMR spectrometer is a device capable of first magnetizing the nuclear spins with a large applied magnetic field, then rotating the spin polarizations by r.f. pulses to produce transverse magnetization, and finally, detecting the small oscillating currents induced by the precessing transverse spin magnetization.

3. NMR Spectroscopy

3.1 A Simple Spectrum

We know that after the r.f. pulse, the net magnetization lies in the perpendicular plane and precesses at the Larmor frequency ω_0 and decays with time constant T_2 .

$$M_y^{\text{nuc}} = -M_{\text{eq}}^{\text{nuc}} \cos(\omega^0 t) e^{-t/T_2}$$

$$M_x^{\text{nuc}} = M_{\text{eq}}^{\text{nuc}} \sin(\omega^0 t) e^{-t/T_2}$$

The computer applies a Fourier transform to convert our damped sinusoidal function from the time domain to the frequency domain. This will give us a peak at the frequency ω_0 . The Fourier transform generated a function of the form:

$$S(\omega) = \frac{\lambda}{\lambda^2 + (\omega - \omega_0)^2}$$

This is called an absorption Lorentzian. The parameter λ is called the coherence decay rate constant :

$$\lambda = \frac{1}{T_2}$$

The peakwidth of the half-height measured in rad s^{-1} is equal to 2λ .

So, a rapid decay of the transverse magnetization corresponds to a broad spectral peak, and a slow decay corresponds to a narrow spectral peak.

3.2 Isotopomeric Spectra

Consider a sample containing four isotopomers of tetramethylsilane, $\text{Si}(\text{CH}_3)_4$ (TMS). Each isotopomer emits a different NMR signal. Suppose the magnetic field is 9.3950 T, so that the Larmor frequency of the proton is exactly -400.000 MHz. ^{12}C , ^{28}Si , ^{30}Si are spinless and ^{13}C , ^{29}Si have spin 1/2. The Larmor frequency of the ^{13}C spins is -100.577 MHz, and of ^{29}Si spins is +79.460 MHz. The rest are silent as they have no spin and are not magnetic.

The total NMR spectrum of this sample contains 3 peaks produced from different molecules. The proton peak at -400.00 MHz. The ^{29}Si peak at +79.640 MHz, and the ^{13}C peak at -100.577 MHz.

3.3 Relative Spectral Frequencies

3.3.1 Case of Positive Gyromagnetic Ratio

It is not practically possible to examine the entire NMR spectrum at once. So, the NMR spectrometer has a set of independent frequency channels, each of which may be tuned to examine a single narrow frequency window.

For example, a two-channel spectrometer may be used to examine narrow frequency windows around the ^1H and ^{13}C Larmor frequencies. The bandwidth of each window is around 1 MHz or less, which is smaller than most separations between nuclear Larmor frequencies of

different isotopes. The centre frequency of each such window is under operator control and is called the reference frequency (ω_{ref}). The NMR spectrometer always determines frequency relative to this ω_{ref} . Hence, each spectrometer channel only detects the NMR signal from a single isotopic species.

$$\Omega^0 = \omega^0 - \omega_{\text{ref}}$$

By convention, signals with negative values of Ω^0 appear on the left-hand side and the positive values appear on the right-hand side of the spectrum.

3.3.2 Case of Negative Gyromagnetic Ratio

As spins with negative γ have positive Larmor frequencies ω^0 , the NMR signals generate even more confusion. For technical reasons, the spectra from spins with negative γ are always plotted with the frequency coordinate running backwards, i.e., with negative relative frequencies on the right and positive relative frequencies on the left.

3.4 Inhomogeneous Broadening

It is very difficult to generate a perfectly homogeneous magnetic field. The sample itself tends to distort the applied magnetic field because of its susceptibility.

An inhomogeneous magnetic field may be denoted $B^0(r)$, depending on the position in space. Hence, the Larmor frequency ω_0 is also spatially dependent:

$$\omega^0(\mathbf{r}) = -\gamma B^0(\mathbf{r})$$

Therefore, the total NMR spectrum is a superposition of very narrow peaks, each originating from a different location within the sample. This is called inhomogeneous broadening.

After a long time, it was realized that controlled inhomogeneous broadening can cause the NMR spectrum to depend on the shape of the sample and hence can become a means of examining the spatial structure of an object. This is called NMR imaging, also generally known in the medical world as magnetic resonance imaging (MRI).

3.5 Chemical Shifts

Even in a perfectly homogeneous magnetic field, nuclei don't give just one sharp NMR peak as was expected. This is because, on a microscopic scale, the magnetic field is slightly uneven or has "wrinkles" due to atomic structure. Due to these microscopic wrinkles, the precise Larmor frequency of a given nucleus depends on the atomic environment.

- Since electrons are magnetic, the nuclear Larmor frequency depends on the local electronic environment. This effect is called the chemical shift in diamagnetic materials, the Knight shift in metals and superconductors, and the paramagnetic shift in paramagnetic substances.
- The Larmor frequency also depends on interactions with nearby nuclear spins. This effect is called the nuclear spin-spin coupling.