

Spin resonance

“Spin resonance” refers to the enhancement of a spin flipping probability in a magnetic field, with fixed and oscillating components in different directions, when the spin is driven at a particular frequency. It was originally developed by Rabi and collaborators as a method of measuring nuclear magnetic moments, but applications of nuclear magnetic resonance (NMR) go far beyond that. It’s used to identify compounds and materials, in nondestructive testing, and in magnetometry. A well-known medical application is magnetic resonance imaging (MRI). Moreover, the mathematics is identical to that which governs to numerous other quantum systems, where the spin degree of freedom is replaced by some other discrete set of energy levels, e.g. the Raman coupling of hyperfine levels of atoms. The applications are numerous, so it’s worth taking a close look at this.

Basic idea

Most of the discussion we can do with a spin- j system with arbitrary j . A spin in a magnetic field $B_1\hat{x}$ has Hamiltonian $\gamma B_1 J_x$, where γ is *minus* the gyromagnetic ratio. (I choose to include an extra minus sign in γ to avoid a slew of annoying minus signs down the road.) Since J_x is the generator of rotations about the x axis, the spin will precess about the x -axis with angular frequency $\omega_1 = \gamma B_1$. This evolution conserves energy, as the Hamiltonian is time independent. If we impose also a strong magnetic field $B_0\hat{z}$ in the z -direction, then the spin states with different projection on the z -axis no longer have the same energy, so it shouldn’t be possible to rotate them into each other with a time-independent Hamiltonian.

Indeed, we know what happens: the spin precesses about the net magnetic field $B_0\hat{z} + B_1\hat{x}$. If $B_0 \gg B_1$, the spin barely changes direction. If it starts out aligned with the \hat{z} direction, it initially tries to precess about \hat{x} , but as soon as it acquires a component perpendicular to \hat{z} , that starts to precess about \hat{z} . So we could make the spin flip over, in the presence of a strong $B_0\hat{z}$, if we were to make the direction of the applied field B_1 co-rotate with the precession about \hat{z} , applying the time-dependent field

$B_1(\cos \omega t \hat{x} + \sin \omega t \hat{y})$. If the frequency ω is matched to the precession frequency $\omega_0 = \gamma B_0$, it's plausible that the spin will flop over from up to down and back again in the z -direction, while it is rotating about \hat{z} . Evolving between these states of different energy is now possible because the Hamiltonian has become time-dependent. If ω isn't matched perfectly to ω_0 , we expect the flopping amplitude will be related to $\omega - \omega_0$ and will diminish as this difference grows.

Schrödinger equation in the rotating frame

Now let's formulate this precisely. The time-dependent Hamiltonian for the spin in the field $\vec{B} = B_0 \hat{z} + B_1(\cos \omega t \hat{x} + \sin \omega t \hat{y})$ is given by

$$H(t) = \omega_0 J_z + \omega_1(\cos \omega t J_x + \sin \omega t J_y), \quad (1)$$

with $\hbar = 1$, $\omega_0 = \gamma B_0$, and $\omega_1 = \gamma B_1$. (“Spin state” here refers to the state of the spin- j system, so it has $2j + 1$ components.) Since $[H(t'), H(t'')] \neq 0$, the state $|v(t)\rangle = \exp(-i \int_0^t dt' H(t'))|v(0)\rangle$ is *not* a solution to the Schrödinger equation. Typically, we must resort to perturbation theory when a time-dependent Hamiltonian doesn't commute with itself at different times, but in the present case we can find the exact solution by “transforming to the rotating frame”, since in the corotating frame the spin simply precesses about the rotating x -axis.

To see how this works, and to find the Hamiltonian in the rotating frame, we write the lab frame state as

$$|\text{lab}\rangle = e^{-i\omega t J_z} |\text{rot}\rangle, \quad (2)$$

and plug into the Schrodinger eqn. (1), finding¹

$$i\partial_t |\text{rot}\rangle = [-\omega J_z + e^{i\omega t J_z} H(t) e^{-i\omega t J_z}] |\text{rot}\rangle. \quad (3)$$

Although the Hamiltonian on the right hand side of (3) is not yet manifestly time independent, our expectation that the time dependence vanishes in the rotating frame is in fact borne out, since the second term on the right hand side is actually independent of t . To see this, just take its derivative and use the commutation relations of the components of \vec{J} . Thus, putting $t = 0$, we see that (3) is equivalent to

$$i\partial_t |\text{rot}\rangle = [(\omega_0 - \omega) J_z + \omega_1 J_x] |\text{rot}\rangle. \quad (4)$$

¹The term ωJ_z can be thought of as the coupling to a fictitious magnetic field B_f with a fictitious gyromagnetic ratio γ_f , such that $\gamma_f B_f = -\omega$, analogous to what occurs in classical mechanics when working in a rotating frame of reference.

Thus $|\text{rot}\rangle$ indeed satisfies the Schrodinger eqn with a time-independent Hamiltonian, and the solution is

$$|\text{rot}(t)\rangle = e^{-i\Omega t \hat{n} \cdot \vec{J}} |\text{rot}(0)\rangle, \quad (5)$$

where

$$\Omega \hat{n} = (\omega_0 - \omega) \hat{z} + \omega_1 \hat{x}, \quad \Omega = \sqrt{(\omega_0 - \omega)^2 + \omega_1^2}. \quad (6)$$

The evolution is a time-dependent rotation about the axis \hat{n} , with angular frequency Ω .

Resonance and Rabi oscillations

If we tune the frequency of the applied field ω to the precession frequency $\omega_0 = \gamma B_0$ we kill off the J_z term in (4), leaving only the J_x term. In this case, the spin precesses about the x -axis, with the frequency gamma B_1 , flopping from up to down in the z -direction and back again. (In the lab frame, it is also precessing about the z -axis while it flops.) If $B_0 \gg B_1$ then we have to tune ω very close indeed, so the resonance is sharper. So the resonance is a sensitive probe of γB_0 .

The exact form of the rotation matrices for any spin was worked out by Majorana, but is a bit complicated. Let's just write the result here for spin-1/2. Then $J_z/\hbar = \sigma_z/2$ and $J_x/\hbar = \sigma_x/2$, so

$$|\text{rot}(t)\rangle = [\cos(\Omega t/2) - i \sin(\Omega t/2) \hat{n} \cdot \vec{\sigma}] |\text{rot}(0)\rangle. \quad (7)$$

If the spin starts out $|+z\rangle$ at $t = 0$, then the probability of finding it down at time t is

$$\text{Prob}(\text{down}, t) = |\langle -z | \text{lab}(t) \rangle|^2 \quad (8)$$

$$= |\langle -z | e^{-i\omega t J_z} | \text{rot}(t) \rangle|^2 \quad (9)$$

$$= |\langle -z | \text{rot}(t) \rangle|^2 \quad (10)$$

$$= \frac{\omega_1^2 \sin^2(\Omega t/2)}{(\omega_0 - \omega)^2 + \omega_1^2}. \quad (11)$$

This is the *Rabi oscillation* formula. The probability of “down” oscillates in time with frequency Ω . On resonance, at $\omega = \omega_0$, it oscillates between zero and unity. Otherwise it only partially oscillates. For example, if $\omega = 0$, it oscillates because the spin precesses about a tilted axis \hat{n} . Classically, of course, the spin vector only dips down a bit in this case, but quantum

mechanically this means there is a nonzero probability to actually find the spin in the down state. The maximum probability of the down state is

$$P_{\max}(\text{down}, \omega) = \frac{\omega_1^2}{(\omega_0 - \omega)^2 + \omega_1^2}. \quad (12)$$

The smaller the ratio $\omega_1/\omega_0 = B_1/B_0$, the more sharply peaked is this function of ω .

Rabi's "Molecular beam magnetic resonance" method

In a 1938 PRL (I.I. Rabi et al, Phys. Rev. Lett. 53, 318 (1938); see also the full paper Phys. Rev. 55, 526 (1939)) Rabi and collaborators describe a method to measure nuclear gyromagnetic ratios, called the molecular beam magnetic resonance (MBMR) method. For nuclear spins, which are of the order of a "nuclear magneton", $\omega_0 = \gamma B \sim 1.5 \text{ MHz } (B/1000 \text{ gauss})$. The spin flopping resonance thus happens in an RF field for laboratory strength magnetic fields. They fixed an oscillating RF field of frequency ω and varied B_0 until they observed the resonant spin flip. (The beam consisted of diatomic molecules (LiCl, LiF, NaF, and Li₂) in a configuration with zero electronic magnetic moment. The beam was deflected by magnetic field gradients and deflected back to a focus, provided no spin flip occurred in the middle. The drop in intensity of the beam was the signal that spin flip had occurred. They claimed an absolute precision of 0.5 % (limited by magnetic field calibration), and a relative precision for different moments of 0.1%. See the article for details.) This told them they had reached $\omega = \omega_0 = \gamma B_0$, so they had found $\gamma = \omega/B_0$. They independently knew the nuclear spin I (which is always \hbar times an integer or half-integer), so from γ they obtained the nuclear magnetic moment, $\mu = \gamma I$.

Rotating wave approximation

Rather than drive with a rotating B_1 field, one can use a linearly polarized field:

$$B_1 \cos \omega t \hat{x} = \frac{1}{2} B_1 (\cos \omega t \hat{x} - \sin \omega t \hat{y}) + \frac{1}{2} B_1 (\cos \omega t \hat{x} + \sin \omega t \hat{y}). \quad (13)$$

If the first term is co-rotating with the precession about \hat{z} , the second one is counter-rotating. Near resonance, the second term is way off-resonance and just produces high frequency wiggles. The complete neglect of this term is called the rotating wave approximation.

General two-state interpretation

Note we have solved a general time-dependent two-state problem, even if it isn't spin: Consider the general Hamiltonian

$$H = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2| + be^{i\omega t}|2\rangle\langle 1| + b^*e^{-i\omega t}|1\rangle\langle 2|. \quad (14)$$

The parameter b controls the coupling between the two states, which have energies E_1 and E_2 in the absence of the coupling. This system can be identified with the spin in the magnetic field, by identifying $|1\rangle$ and $|2\rangle$ with the up and down spin states in the z direction, $|\pm z\rangle$, and rewriting it as

$$H = \frac{1}{2}(E_1 + E_2)I + \frac{1}{2}(E_1 - E_2)\sigma_z + \text{Re}(be^{i\omega t})\sigma_x - \text{Im}(be^{i\omega t})\sigma_y. \quad (15)$$

The first term, proportional to the identity, just produces an overall phase in the time evolution of the quantum state. The x & y terms are like what we had before, but since $b = |b|e^{i\delta}$, the rotating field is shifted in time. The solution is therefore nearly identical, and in particular if the state is initially $|1\rangle$, then the probability of finding it $|2\rangle$ at time t is given by

$$\text{Prob}(2, t) = |\langle 2|v(t)\rangle|^2 = \frac{|b|^2 \sin^2(\Omega t/2)}{(\omega_0 - \omega)^2 + |b|^2}, \quad (16)$$

with $\omega_0 = (E_1 - E_2)/2$ and $\Omega = \sqrt{(\omega_0 - \omega)^2 + |b|^2}$.

This oscillation provides a basic technique for quantum state manipulation. Suppose the coupling parameter b in the Hamiltonian is under experimental control, and can be turned on and off at will. Then by adjusting the time that it is on, one can choose the amount of rotation of $|1\rangle$ into $|2\rangle$. For example, a “ π pulse”, on resonance with $\Omega t = \pi$, sends $|1\rangle$ to $|2\rangle$, while a “ $\pi/2$ pulse” sends $|1\rangle$ to an equal superposition of $|1\rangle$ and $|2\rangle$.

NMR

If solutions or bulk samples of matter are placed in a magnetic field, and exposed to an RF field, one will observe a resonant absorption of energy from the field when $\omega = \omega_0$. This is called nuclear magnetic resonance (NMR). In a solution, the magnetic field seen by the nuclei is not just the imposed field B_0 . The induced electronic currents in the chemical environment of the nucleus partly shield the nucleus from B_0 , so each nucleus sees a field B_0^* that depends on its chemical environment. This is called the chemical shift. Only the nuclei with $\gamma B_0^* = \omega$ will be resonant at a given ω . This can be used to distinguish different chemical compounds, or superfluid textures in

helium-3, or types of tissue in the human body, etc. In the last application, magnetic resonance imaging (MRI), the power absorption is measured at many frequencies, and with the applied RF field at many angles relative to the body. All this data is “inverted” to reconstruct a three dimensional map of the distribution of chemical environments in the body, i.e., the tissue types.

The energy difference between the nuclear spin states in, say, a 1 Tesla (= 10^4 gauss) field is miniscule:

$$\Delta E = \Delta(-M \cdot B) = \Delta(-\gamma B J) \sim \hbar \gamma B \sim (2/3 \text{ eV} - 10^{-15} \text{ s})(15 \text{ MHz}) = 10^{-8} \text{ eV}. \quad (17)$$

Compared to body temperature, $\sim 1/40$ eV, this is tiny: the ratio is of order 10^{-6} . So only one in 10^6 of the nuclei are aligned with the field. This is enough, however, since there are so many nuclei at body density.

A method of MRI has been developed for imaging lungs and other body cavities, or tissues that are not well resolved by ordinary MRI, using hyperpolarized gas. The idea is to orient the nuclear spins by some method, then to use the hyperpolarized gas to accomplish imaging or sensing. The most commonly used gas is xenon-129, and it is most commonly polarized via “spin-exchange optical pumping.” The nuclear spin polarization is accomplished via exchange interactions in collisions with rubidium atoms that have had their valence electron spin-polarized by circularly polarized laser light. Once polarized the noble gas nuclei interact very weakly with their environment. (Xenon-129 has spin-1/2, which precludes any electric quadrupole moment, which helps to minimize interactions and thus preserve the spin polarization.) The polarized gas can be stored in a bottle, and polarized xenon can even be frozen, for later use. No large magnetic field is required to align the spins once they are in the body to be imaged, since they are not in thermal equilibrium with their environment (though I think a strong field still gives better resolution for the power absorption resonance). A recent review article is available at <http://onlinelibrary.wiley.com/doi/10.1002/chem.201603884/full>, and it’s posted to our supplements page.