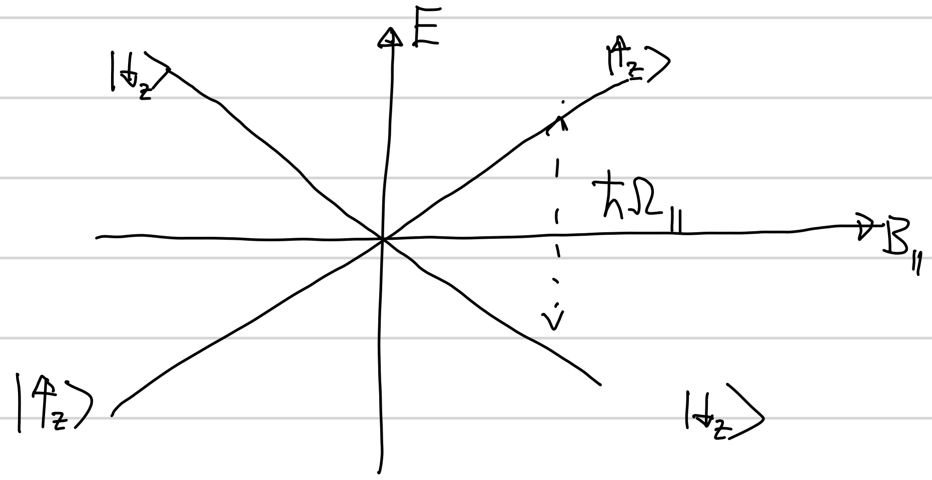
Physics 492: Quantum Mechanics II
Lecture 15: Introduction to Perturbation theory

Avoided Crossing:

Consider again a spin in a magnetic field. The Hamiltonian is
$$\hat{H} = -\hat{\vec{\mu}}\cdot\vec{B} = \mu_B \hat{\vec{\sigma}}\cdot\vec{B}$$

If we take the magnetic field in the z-direction: $\vec{B} = B_{\parallel}\vec{e}_z$, $\hat{H} = \frac{\hbar\Omega_{\parallel}}{2}\hat{\sigma}_z$
where $\hbar\Omega_{\parallel} = 2\mu_B B_{\parallel}$; $\Omega_{\parallel}$ is the Larmor frequency for precession of the spin parallel to the z-axis. The eigenvectors are $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$ with corresponding eigenvalues
$$E_{\uparrow} = \frac{\hbar\Omega_{\parallel}}{2}, \quad E_{\downarrow} = -\frac{\hbar\Omega_{\parallel}}{2}$$

If we plot the eigenvalues as a function of $B_{\parallel}$



At $B_{\parallel}=0$, the two energy levels become degenerate (corresponding to spherical symmetry). This energy level diagram shows a crossing.

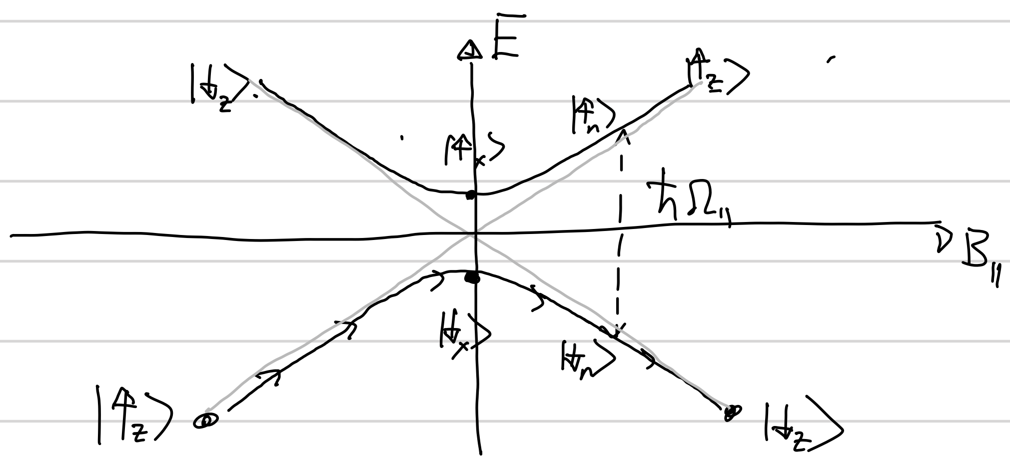
Now let us add a small magnetic field in the x-direction, $\vec{B} = B_{\parallel}\vec{e}_z + B_{\perp}\vec{e}_x$
$$\Rightarrow \hat{H} = 2\mu_B\vec{B}\cdot\hat{\vec{\sigma}} = \frac{\hbar\vec{\Omega}}{2}\cdot\hat{\vec{\sigma}}$$

There is a trick to diagonalizing this Hamiltonian. We know that the eigenvectors of $\vec{e}_n\cdot\hat{\vec{\sigma}} \equiv \hat{\sigma}_n$ where $\vec{e}_n$ is a unit vector in 3D are $|\uparrow_n\rangle$ and $|\downarrow_n\rangle$ (spin up and down along $\vec{e}_n$) with corresponding eigenvalues $+1$ and -1.

Let us write $\hat{H} = \frac{\hbar\Omega}{2}\hat{\sigma}_n$ where $\vec{B} = |\vec{B}|\,\vec{e}_n$, $|\vec{B}| = \sqrt{B_\parallel^2 + B_\perp^2}$

$$\vec{e}_n = \frac{\vec{B}}{|\vec{B}|} = \frac{B_\perp}{|\vec{B}|}\vec{e}_x + \frac{B_\parallel}{|\vec{B}|}\vec{e}_z \equiv \sin\theta\,\vec{e}_x + \cos\theta\,\vec{e}_z$$

Then the eigenvectors are $|\uparrow_n\rangle$ and $|\downarrow_n\rangle$ (spin up and down along $\vec{e}_n$) with corresponding eigenvalues $\pm\frac{\hbar\Omega}{2} = \pm\frac{\hbar}{2}\sqrt{B_\parallel^2 + B_\perp^2}$. Let us fix $B_\perp$ as a small number and plot the new energy eigenvalues, as a function of $B_\parallel$



Note: At $B_\parallel = 0$, the energy levels are no longer degenerate because there is a small magnetic field in the x-direction. This type of energy level diagram is known as an avoided crossing; the breaking of the symmetry lifts the degeneracy, and the levels avoid crossing. We have left in this diagram the asymptotes when $B_\perp = 0$. If $|B_\parallel| \gg |B_\perp|$ we asymptote to the original eigenvectors and eigenvalues. But when $|B_\perp| \gg |B_\parallel|$ the two original levels $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$ are strongly "mixed" (actually superposed). When $B_\parallel = 0$, the eigenvectors are $|\uparrow_x\rangle = \frac{1}{\sqrt{2}}(|\uparrow_z\rangle + |\downarrow_z\rangle)$ and $|\uparrow_x\rangle = \frac{1}{\sqrt{2}}(|\uparrow_z\rangle - |\downarrow_z\rangle)$, equal 50-50 superpositions of $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$

Peturbation

We can think of the magnetic field along x and a "perturbation" that affects the nature of the eigenvectors and eigenvalues when $\vec{B}$ is along the z-axis.

Let us write $\hat{H} = \hat{H}_0 + \hat{H}_1$ where $\hat{H}_0 = \frac{\hbar\Omega_\parallel}{2}\hat{\sigma}_z$ and $\hat{H}_1 = \frac{\hbar\Omega_\perp}{2}\hat{\sigma}_x$

When $\Omega_\perp \ll \Omega_\parallel$ this is a weak perturbation, otherwise it is a strong perturbation.

Let us more closely examine the case of weak perturbation.

The eigenvalues $E_{\substack{\uparrow\\\downarrow}} = \pm\frac{\hbar}{2}\sqrt{\Omega_{\parallel}^2 + \Omega_{\perp}^2} = \pm\frac{\hbar\Omega_{\parallel}}{2}\sqrt{1+\frac{\Omega_{\perp}^2}{\Omega_{\parallel}^2}} \approx \pm\frac{\hbar\Omega_{\parallel}}{2}\left(1+\frac{\Omega_{\perp}^2}{2\Omega_{\parallel}^2}\right)$

$$\Rightarrow E_{\substack{\uparrow\\\downarrow}} \approx \pm\frac{\hbar\Omega_{\parallel}}{2} \pm \frac{\hbar\Omega_{\perp}^2}{4\Omega_{\parallel}} = E^{(0)}_{\substack{\uparrow\\\downarrow}} + \Delta E^{(1)}_{\substack{\uparrow\\\downarrow}}$$

Here I have written $E^{(0)}_{\pm} = \pm\frac{\hbar}{2}\Omega_{\parallel}$ as the eigenvalues of $\hat{H}_0 = \frac{\hbar\Omega_{\parallel}}{2}\hat{\sigma}_z$
the energy levels are "perturbed" by the addition of $\hat{H}_1 = \frac{\hbar\Omega_{\perp}}{2}\hat{\sigma}_x$

A systematic perturbation expansion follows in what is known as "perturbation theory."
We won't study that in full detail here, but the result is

$$\Delta E^{(1)}_{\uparrow} = \frac{|\langle\downarrow_z|\hat{H}_1|\uparrow_z\rangle|^2}{E^{(0)}_{\uparrow} - E^{(0)}_{\downarrow}} = \frac{\left(\frac{\hbar\Omega_{\perp}}{2}\right)^2|\langle\downarrow_z|\hat{\sigma}_x|\uparrow_z\rangle|^2}{\hbar\Omega_{\parallel}} = \frac{\hbar\Omega_{\perp}^2}{4\Omega_{\parallel}}$$

$$\Delta E^{(1)}_{\downarrow} = \frac{|\langle\uparrow_z|\hat{H}_1|\downarrow_z\rangle|^2}{E^{(0)}_{\downarrow_z} - E^{(0)}_{\uparrow_z}} = \frac{\left(\frac{\hbar\Omega_{\perp}}{2}\right)^2|\langle\uparrow_z|\hat{\sigma}_x|\downarrow_z\rangle|^2}{-\hbar\Omega_{\parallel}} = -\frac{\hbar\Omega_{\perp}^2}{4\Omega_{\parallel}}$$

Note: The shift in energy here is second order in the perturbation. This is because the perturbing magnetic field was perpendicular to $\vec{B}_{\parallel}$. If we had added a small magnetic field in the $\vec{e}_z$ $\vec{B} \to (B_{\parallel} + \Delta B_{\parallel})\vec{e}_z$ so $\hat{H}_1 = 2\mu_B\Delta B_{\parallel}\hat{\sigma}_z$, then $E \to \pm\frac{\hbar}{2}(\Omega_{\parallel} + \Delta\Omega_{\parallel}) = E^{(0)}_{\substack{\uparrow\\\downarrow}} + \Delta E^{(1)}_{\substack{\uparrow\\\downarrow}}$ where $\Delta E^{(1)}_{\substack{\uparrow\\\downarrow}} = \substack{\langle\uparrow_z|\hat{H}_1|\uparrow_z\rangle \\ \langle\downarrow_z|\quad|\downarrow_z\rangle}$. We obtain the perturbation by the expected value of $\hat{H}_1$ in the state of interest.

The eigenstates are also perturbed by the additional B-field. For the case we considered $|\uparrow_n\rangle = \cos\frac{\theta}{2}|\uparrow_z\rangle + \sin\frac{\theta}{2}|\downarrow_z\rangle$ where $\tan\theta = \frac{B_{\perp}}{B_{\parallel}}$
For a weak perturbation $|B_{\perp}| << |B_{\parallel}|$ $|\uparrow_n\rangle \approx |\uparrow_z\rangle + \frac{\theta}{2}|\downarrow_z\rangle$

$|\uparrow_n\rangle \approx |\uparrow_z\rangle + \frac{B_{\perp}}{2B_{\parallel}}|\downarrow_z\rangle$. The perturbation weakly mixes some $|\downarrow_z\rangle$ character into $|\uparrow_z\rangle$. Similarly $|\downarrow_n\rangle \approx |\downarrow_z\rangle - \frac{B_{\perp}}{2B_{\parallel}}|\uparrow_z\rangle$.

Degenerate Perturbation theory:

When to two energy levels of $\hat{H}_0$ are degenerate, as for $B_{\parallel}=0$, the effect of the perturbation has a much more profound effect on the energy eigenstates. We need to fully diagonalize $\hat{H}$ in the degenerate subspace (here the 2D Hilbert space). The result is equal superposition of $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$.

Adidabatic evolution:

Suppose now we change $\vec{B}$ as a function of time so that we sweep $B_{\parallel}$ from $-\infty$ to $+\infty$: $\vec{B}(t) = B_{\perp}\vec{e}_x + B_{\parallel}(t)\vec{e}_z$. Let us imagine we started in the ground state at $t=-\infty$, $|\psi(-\infty)\rangle = |\downarrow_z\rangle$. How does the state evolve as a function of time? The exact solution follows from the time-dependent Schrödinger equation $\frac{\partial}{\partial t}|\psi(t)\rangle = -\frac{i}{\hbar}\hat{H}(t)|\psi\rangle$ where $\hat{H}(t) = -\hat{\vec{\mu}}\cdot\vec{B}(t)$

Solving this exactly is impossible, in general. Note because $\hat{H}$ is time-dependent we cannot write the time evolution operator $\hat{U}(t) = e^{-i\hat{H}(t)t/\hbar}$. Generally solving for the time evolution is a very challenging task we $\hat{H}$ is time dependent. However, we can sometimes solve this approximately. In particular, we known how to solve for the instaneous eigenstates of the

$$\hat{H}(t)|\uparrow_{\vec{n}(t)}\rangle = \frac{\hbar\Omega(t)}{2}|\uparrow_{n(t)}\rangle,\quad \hat{H}(t)|\downarrow_{n(t)}\rangle = -\frac{\hbar\Omega(t)}{2}|\downarrow_{n(t)}\rangle$$

$$\Omega(t) = \sqrt{\Omega_{\parallel}^2(t)+\Omega_{\perp}^2}\qquad |\uparrow_{n(t)}\rangle = \cos\frac{\theta(t)}{2}|\uparrow_z\rangle + \sin\frac{\theta(t)}{2}|\downarrow_z\rangle,\qquad \tan\theta(t) = \frac{\Omega_{\parallel}(t)}{\Omega_{\perp}(t)}$$

Adiadatic theorem of Quantum Mechanics

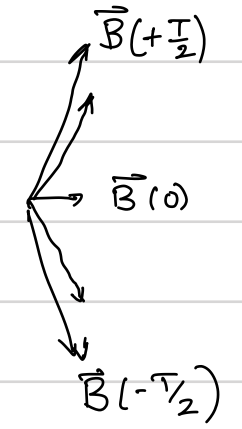
If at some time t_0 the system is prepared is an eigenstate of $\hat{H}(t_0)$, $|\psi(t_0)\rangle = |E_\alpha(t_0)\rangle$ where $\hat{H}(t_0)|E_\alpha(t_0)\rangle = E_\alpha(t_0)|E_\alpha(t_0)\rangle$, then if $\hat{H}(t)$ changing "adidabatically" which means the rate of change of $\hat{H}(t)$ is slow in some well defined sense, then at a later time $t>t_0$ $|\psi(t)\rangle = |E_\alpha(t)\rangle$. In other words $|\psi\rangle$ stays in the "local eigenstate" of the Hamiltonian. For example, if the system started in the ground state of $\hat{H}(t_0)$ it would evolve in time to the ground state of $\hat{H}(t)$.

Let us examine adiabatic evolution in the context of the spin-½ interacting with the time-dependent magnetic field. Let us take

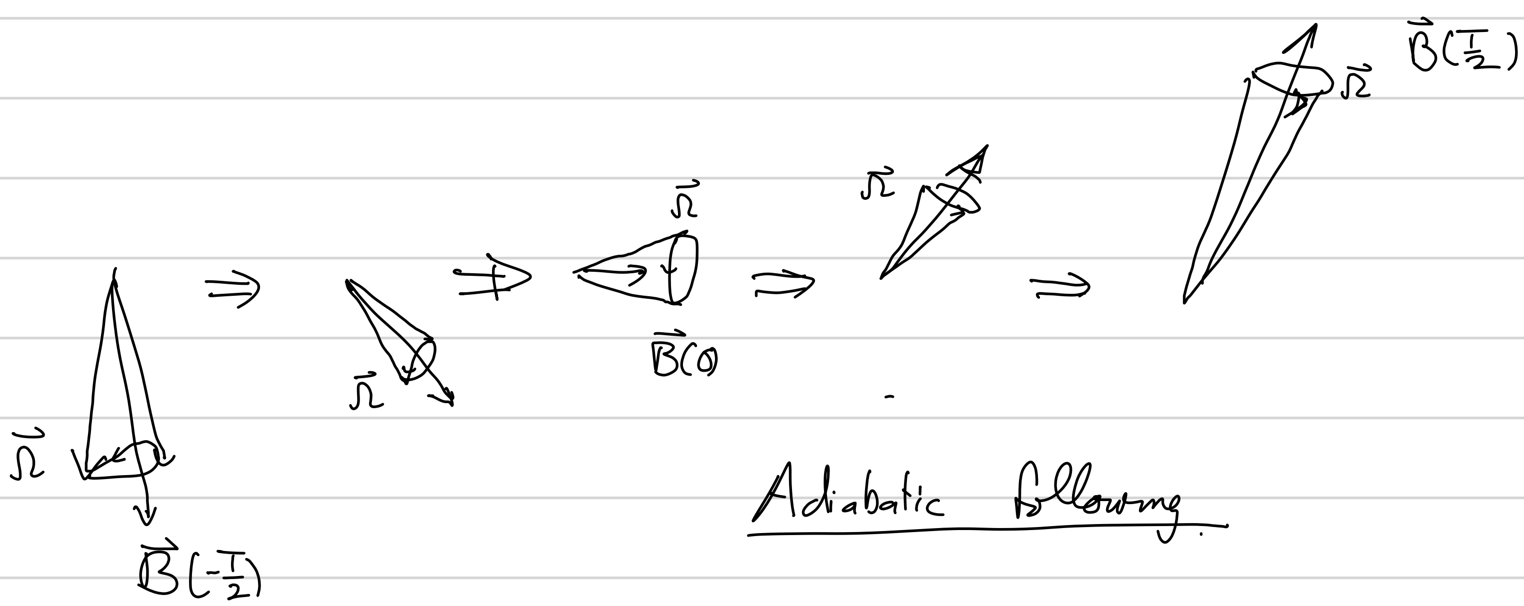
$$\vec{B}(t) = B_\perp \vec{e}_x + B_\parallel(t)\,\vec{e}_z\,, \quad \text{where we sweep linearly} \quad -B_0 \le B_\parallel \le +B_0$$

$$B_\parallel(t) = \frac{B_0}{2}\, t/T \qquad \text{Choose } |B_0| \gg |B_\perp|$$

The magnetic field will change in direction and magnitude:



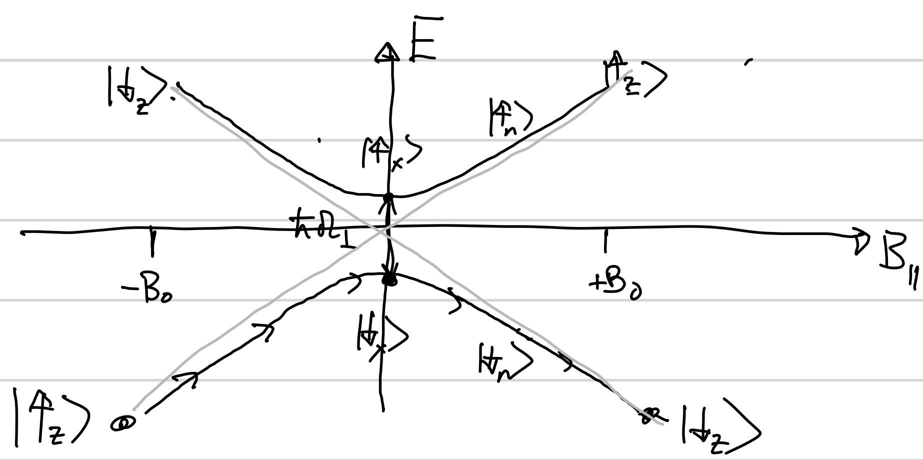
As the magnetic field changes the spin direction (and thus spin state) changes. Let us suppose the magnetic dipole moment pointing in the negative-z direction (corresponding to $|\uparrow_z\rangle$ for a negative charge). The magnetic diple moment will precess around $\vec{B}(-\frac{T}{2}) = B_\perp \vec{e}_x + B_0\vec{e}_z \approx B_0\vec{e}_z$ at Larmor frequency $\frac{2\mu_B}{\hbar}\sqrt{B_\perp^2+B_0^2} \approx \frac{2\mu_B B_0}{\hbar}$. As time progresses, the magnetic field rotates. If the rate of rotation is small compared to the rate of Larmor precession, then the spin will "adiabatically follow" the direction of the spin.



Adiabatic following

Geometrically, this requires $|\dot{\Theta}| \ll \frac{2\mu_B |\vec{B}(t)|}{\hbar}$ where $\Theta(t)$ is the direction of the magnetic field.
Because the Larmor frequency is smallest at $t=0$ where $\vec{B}(t) = B_\perp \vec{e}_x$, this is the point in the sweep where the magnetic field most change most slowly in order for the field to follow. So we require $|\dot{\Theta}|_{t=0} \ll \frac{2\mu_B B_\perp}{\hbar} = \Omega_\perp$

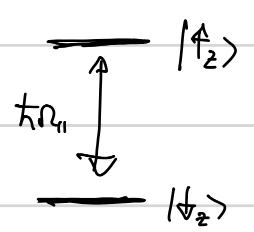
This vector picture of spin Larmor precession captures the adiabatic following curve:



We start the system in the ground state when $B_\parallel = -B$ $|\psi\rangle \approx |\uparrow_z\rangle$.
As we adiabatically sweep $\vec{B}$-field the system stays in the ground state.
At $t=0$, $\vec{B}$ is along the x-direction, the ground state is $|\downarrow_x\rangle$. If we continue to sweep the "avoided" crossing we will transfer the spin to $|\uparrow_z\rangle$.
The rate of adiabatic transfer depends on the minimum gap $\Omega_\perp$. This sets the scale of rate of precession from $|\uparrow_z\rangle$ to $|\downarrow_z\rangle$.

Magnetic Resonance and time-dependent perturbation

If we place a spin in a strong magnetic field in the z-direction, we Zeeman split the levels



The Bohr energy in $E_\uparrow - E_\downarrow = \hbar\Omega_\parallel$. If we apply a weak transverse field in the x-direction, as we saw we will slightly "perturb" the energy level. A weak field will generally not greatly affect the system. There is one exception to the rule: Resonance. If the perturbing field is time-dependent, and it oscillates will a frequency ω near the Bohr frequency $\frac{E_\uparrow - E_\downarrow}{\hbar}$, we can drive the probability amplitude from one energy level to another. For example, if it starts in the ground state, it can end up in the excited state, i.e. absorption. This is what you have studied previously in modern physics in a phenomenological manner.

Consider then the following Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_1(t), \qquad \hat{H}_0 = -\hat{\vec{\mu}} \cdot \vec{B}_{\parallel}, \quad \hat{H}_1 = -\hat{\vec{\mu}} \cdot \vec{B}_{\perp}(t)$$

$$\text{where } \vec{B}_{\parallel} = B_{\parallel} \vec{e}_z, \qquad \vec{B}_{\perp}(t) = B_{\perp} (\cos\omega t \, \vec{e}_x + \sin\omega t \, \vec{e}_y)$$

$\hat{H}_0$ is the Hamiltonian associated with the static strong field.
$\hat{H}_1(t)$ is the time-dependent perturbation.

$$\Rightarrow \hat{H} = \frac{\hbar\Omega_{\parallel}}{2} \hat{\sigma}_z + \frac{\hbar\Omega_{\perp}}{2} (\cos\omega t \, \hat{\sigma}_x + \sin\omega t \, \hat{\sigma}_y)$$

Here I have take the time-dependent perturbing field as rotating in x-y plane at angular frequency ω.

Let us consider the solution to the T.D.S.E. $\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\hbar}\hat{H}(t)|\psi(t)\rangle$
In the absence of the perturbation, we know how to solve this.
If at the initial time $|\psi(0)\rangle = c_\uparrow |\uparrow_z\rangle + c_\downarrow |\downarrow_z\rangle$, then at a later time $|\psi(t)\rangle = c_\uparrow e^{-\frac{i\Omega_{\parallel} t}{2}} |\uparrow_z\rangle + c_\downarrow e^{\frac{i\Omega_{\parallel} t}{2}} |\downarrow_z\rangle$. Now consider the solution with the perturbation. We make the Ansatz guided by the unperturbed form

$$|\psi(t)\rangle = c_\uparrow(t) e^{-\frac{i\Omega_{\parallel} t}{2}} |\uparrow_z\rangle + c_\downarrow(t) e^{-\frac{i\Omega_{\parallel} t}{2}} |\downarrow_z\rangle$$

Here we know $c_\uparrow(t)$ and $c_\downarrow(t)$ will change slowly compared to $\Omega_{\parallel}$ (the unperturbed frequency).

With this Ansatz, we can solve the T.D.S.E

$$\frac{\partial}{\partial t}|\psi\rangle = \frac{-i}{\hbar}\hat{H}(t)|\psi\rangle \Rightarrow$$

Matrix representation

$$\frac{d}{dt}\begin{bmatrix} c_\uparrow(t)\, e^{-\frac{i\Omega_\parallel t}{2}} \\ c_\downarrow(t)\, e^{\frac{i\Omega_\parallel t}{2}} \end{bmatrix} = \frac{-i}{\hbar}\begin{bmatrix} \frac{\hbar\Omega_\parallel}{2} & \frac{\hbar\Omega_\perp}{2} e^{-i\omega t} \\ \frac{\hbar\Omega_\perp}{2} e^{i\omega t} & \frac{\hbar\Omega_\parallel}{2} \end{bmatrix}\begin{bmatrix} c_\uparrow(t)\, e^{-\frac{i\Omega_\parallel t}{2}} \\ c_\downarrow(t)\, e^{\frac{i\Omega_\parallel t}{2}} \end{bmatrix}$$

$$\Rightarrow -i\frac{\Omega_\parallel}{2} c_\uparrow(t) e^{-\frac{i\Omega_\parallel t}{2}} + \dot{c}_\uparrow(t)\, e^{-\frac{i\Omega_\parallel t}{2}} = -i\frac{\Omega_\parallel}{2} c_\uparrow(t) e^{-\frac{i\Omega_\parallel t}{2}} - i\frac{\Omega_\perp}{2} c_\downarrow(t)\, e^{-i\omega t + \frac{i\Omega_\parallel t}{2}}$$

$$+i\frac{\Omega_\parallel}{-2} c_\downarrow(t) e^{+\frac{i\Omega_\parallel t}{2}} + \dot{c}_\downarrow(t)\, e^{+\frac{i\Omega_\parallel t}{2}} = +i\frac{\Omega_\parallel}{2} c_\downarrow(t)\, e^{+\frac{i\Omega_\parallel t}{2}} - i\frac{\Omega_\perp}{2} c_\uparrow(t)\, e^{i\omega t - \frac{i\Omega_\parallel t}{2}}$$

$$\Rightarrow \quad \dot{c}_\uparrow(t) = -i\frac{\Omega_\perp}{2} c_\downarrow(t)\, e^{-i(\omega-\Omega_\parallel)t}$$
$$\dot{c}_\downarrow(t) = -i\frac{\Omega_\perp}{2} c_\uparrow(t)\, e^{i(\omega-\Omega_\parallel)t}$$

Let us suppose now the perturbing field is tuned to resonance

$$\omega = \frac{E_\uparrow - E_\downarrow}{\hbar} = \Omega_\parallel$$

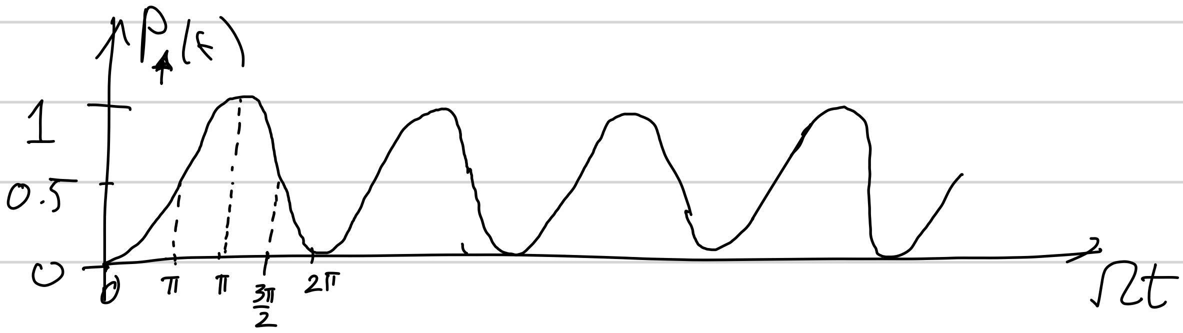
$$\Rightarrow \quad \dot{c}_\uparrow(t) = -i\frac{\Omega_\perp}{2} c_\downarrow(t)$$
$$\dot{c}_\downarrow(t) = +i\frac{\Omega_\perp}{2} c_\uparrow(t)$$

We can now solve these coupled differential equations. The solutions are

$$c_\uparrow(t) = c_\uparrow(0)\cos\left(\frac{\Omega t}{2}\right) - i\, c_\downarrow(0)\sin\left(\frac{\Omega t}{2}\right)$$
$$c_\downarrow(t) = c_\downarrow(0)\cos\left(\frac{\Omega t}{2}\right) + i\, c_\uparrow(0)\sin\left(\frac{\Omega t}{2}\right)$$

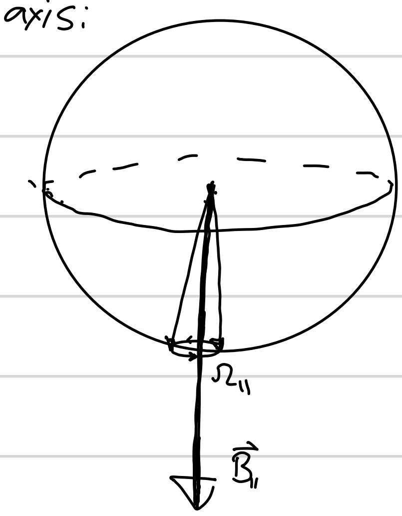
Thus, for example, if at time $t=0$ the spin is in the ground state $|\psi(0)\rangle = |\downarrow_z\rangle$ then $c_\uparrow(0) = 0$, $c_\downarrow(0) \simeq 1$. The probability to find the spin in the excited state, spin-up along z, $|\uparrow_z\rangle$ is

$$P_\uparrow(t) = |C_\uparrow(t)|^2 = \left|-i\sin\left(\frac{\Omega t}{2}\right)\right|^2 = \sin^2\left(\frac{\Omega t}{2}\right) = \frac{1-\cos\Omega t}{2}$$

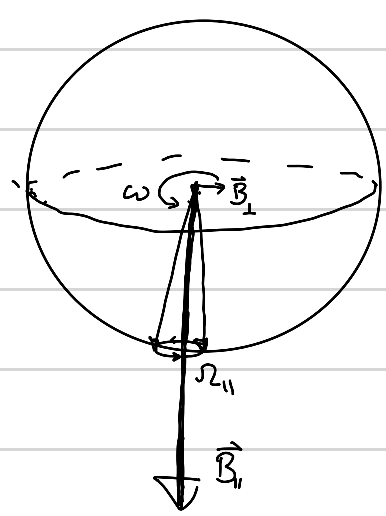


The this oscillation of population from ground to excited is known as "Rabi flopping" who first studied this in microwave spectroscopy. The resonant flipping of the spin here is known a spin magnetic resonance. In the case of nucleon spins this is known as nuclear magnetic resonance or NMR. It is the physical basis of magnetic resonance imagining MRI.

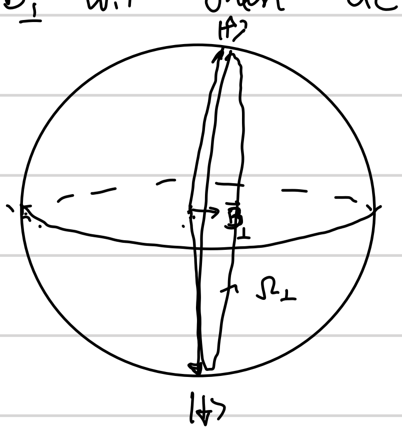
We can understand this result using the geometry of the Bloch sphere. In the presence of the strong field, the spin precesses around the z-axis if it is slight off axis:



Now we add the small transverse field rotating in the x-y plane



If we go into a frame corotating with the transverse field, the transverse field is static. If $\Omega_{\parallel} = \omega$, in this frame the spin is not precessing around $\vec{B}_{\parallel}$. The effect of $\vec{B}_{\perp}$ will then accummulate, and the spin will precess around $B_{\perp}$



In the rotating frame, the spin Larmor precesses about x-axis and frequency $\Omega_{\perp}$.

Mathematically, the rotation of the spin on the Bloch Sphere is combination of two SU(2) rotation

$$\hat{U} = \underbrace{e^{-i\frac{\Omega_{\perp} t}{2}\hat{\sigma}_x}}_{\text{Precession of x-axis}} \underbrace{e^{-i\frac{\omega t}{2}\hat{\sigma}_z}}_{\text{Rotating frame}} \doteq \begin{bmatrix} \cos\frac{\Omega_{\perp} t}{2} & -i\sin\frac{\Omega_{\perp} t}{2} \\ -i\sin\frac{\Omega_{\perp} t}{2} & \cos\frac{\Omega_{\perp} t}{2} \end{bmatrix} \begin{bmatrix} e^{-i\frac{\omega t}{2}} & 0 \\ 0 & e^{+i\frac{\omega t}{2}} \end{bmatrix}$$

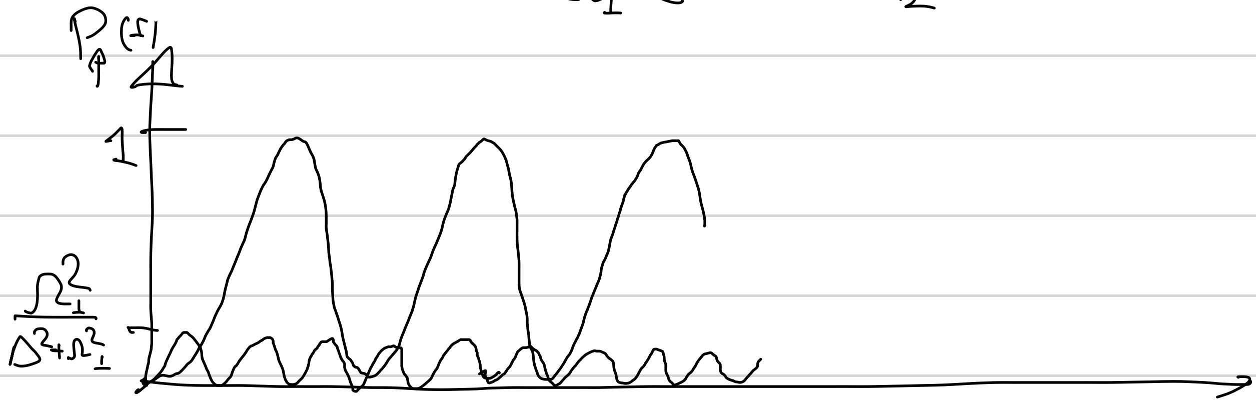
Given $|\psi(0)\rangle = c_{\uparrow}(0)\,|\uparrow_z\rangle + c_{\downarrow}(0)\,|\uparrow_z\rangle$

$$|\psi(t)\rangle = \hat{U}(t)\,|\psi(0)\rangle = e^{-i\omega t}\left(c_{\uparrow}(0)\cos\frac{\Omega_{\perp} t}{2} - i\,c_{\downarrow}(0)\sin\left(\frac{\Omega_{\perp} t}{2}\right)\right)|\uparrow_z\rangle$$
$$+ e^{+i\omega t}\left(c_{\downarrow}(0)\cos\frac{\Omega_{\perp} t}{2} - i\,c_{\uparrow}(0)\sin\left(\frac{\Omega_{\perp} t}{2}\right)\right)|\downarrow_z\rangle$$

Note, the evolution here is <u>coherent</u>. The spin does not "jump" from ground to excited state. the state vector continuously evolves in time, rotating on the Bloch sphere from $|\downarrow_z\rangle$ to $|\uparrow_z\rangle$. When $\Omega_{\perp} t = \pi$, we flip the spin. This is known as a "π-pulse." If the duration if half as long, $\Omega_{\perp} t = \frac{\pi}{2}$, (a "$\frac{\pi}{2}$-pulse"), we coherents prepare a 50-50 <u>superposition</u> of $|\downarrow_z\rangle$ and $|\uparrow_z\rangle$. This is an example of "coherent control."

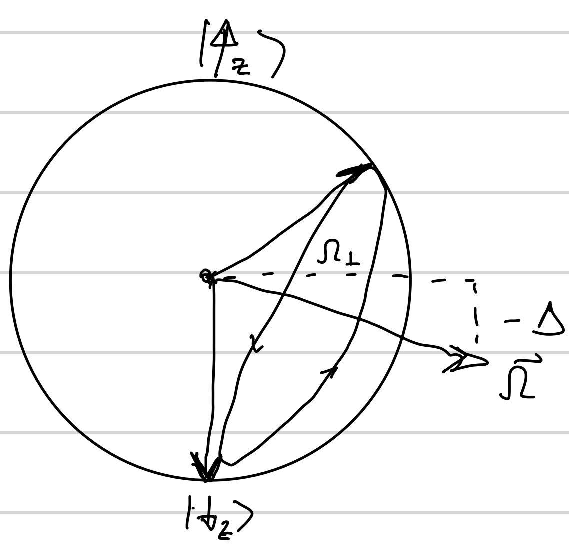
Suppose now that $\omega \neq \Omega_{\parallel}$; the perturbing field is "detuned" from resonance $\Delta \equiv \omega - \Omega_{\parallel}$. In that case the TISE can also be solved exactly. Given the intial condition $|\psi(0)\rangle = |\downarrow_z\rangle$, the solution for the probability is

$$P_{\uparrow}(t) = \frac{\Omega_\perp^2}{\Omega_\perp^2 + \Delta^2} \sin^2\left(\frac{\sqrt{\Omega_\perp^2+\Delta^2}}{2} t\right) \qquad \text{(see homework)}$$



In this case the "torque vector" in in the x-z plane $\vec{\Omega} = -\Delta \vec{e}_z + \Omega_\perp \vec{e}_x$

The precession is faster than when $\Delta = 0$, but the probability to be in the excited state never gets to 1.



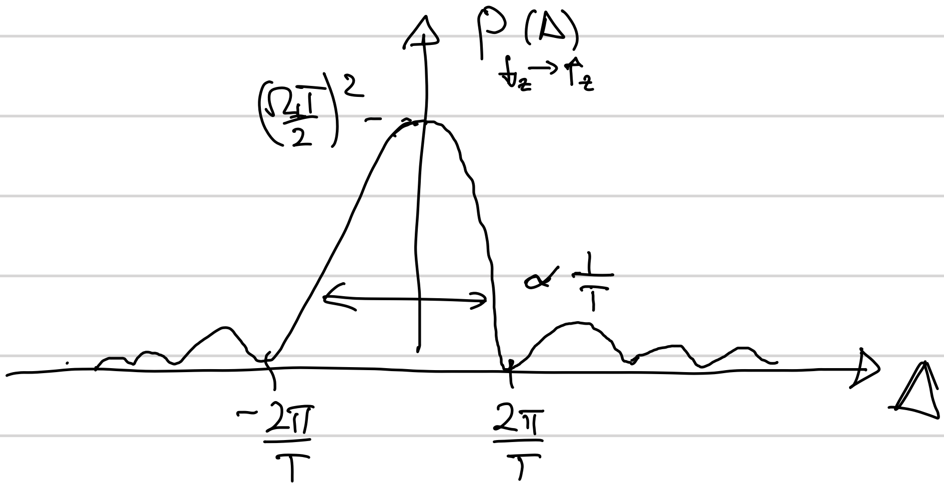
Time - Energy Uncertainty

Let us fix the final time as $t = T$, and plot the probability to make the transition from $|\downarrow_z\rangle \Rightarrow |\uparrow_z\rangle$: $P_{\downarrow_z \to \uparrow_z} = \frac{\Omega_\perp^2}{\Omega_\perp^2+\Delta^2} \sin^2\left(\frac{\sqrt{\Omega_\perp^2+\Delta^2}}{2} T\right)$.

We take the time such that $\Omega_\perp T = \pi$

so that on resonance, the spin flip is exact. We are ultimately interested in long times so $\Omega_\perp = \frac{\pi}{T} \ll \Delta$, so $P_{\downarrow_z \to \uparrow_z} \approx \left(\frac{\Omega_\perp T}{2}\right)^2 \frac{\sin^2\left(\frac{\Delta T}{2}\right)}{\left(\frac{\Delta T}{2}\right)^2} = \left(\frac{\Omega_\perp T}{2}\right)^2 \mathrm{sinc}^2\left(\frac{\Delta T}{2}\right)$

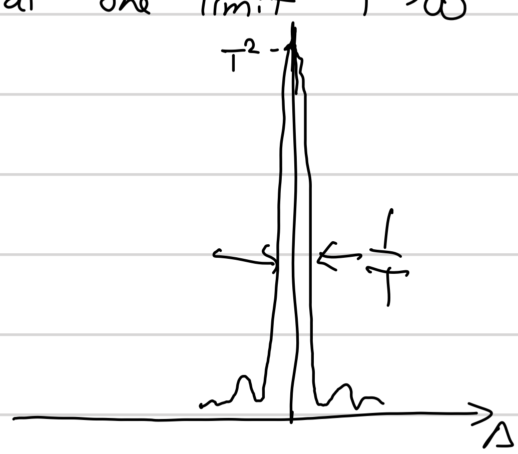
For a fixed T, Plot this as a function of Δ



This curve exhibits a form of "<u>time-energy uncertainty principle</u>"
We can imagine trying to measure the resonance frequency Ω_{11} by tuning the perturbing field's frequency ω and measuring the fraction of spins that get excited. Our ability to determine $\Delta = 0$ is determined by the width of this curves; the narrower the curve the more "certain" we are about the resonance frequency and the broader the curve, the more "uncertain" we are. If we can $\Delta E = \hbar \Delta$, $\Delta t = T \Rightarrow \Delta E \, \Delta t \sim \hbar$. This is the time-energy uncertainty. The nature of this uncertainty is not quite other uncertainty principles we have encountered, the $\Delta x \Delta p \geq \frac{\hbar}{2}$ that rigorously follows from the operator algebra. In turns out that there is no "time operator" $\hat{t}$. Nonetheless, the time-energy uncertainty principle follows from wave-particle duality. the "wavy nature" of matter implies that we can exactly measure its energy unless we have infinite time.

<u>Fermi's Golden Rule</u>

Let us now look at the limit $T \to \infty$



The sinc^2 curve gets narrower and higher. As $T \to \infty$, this become a delta function.

Formally, as $x \to \infty$ $\quad \mathrm{sinc}^2(ax) \to \pi\,\delta(ax) = \frac{\pi}{a}\delta(x)$

Thus, as $T \to \infty$ $\quad \mathrm{sinc}^2\left(\frac{\Delta T}{2}\right) \to \frac{2\pi}{T}\,\delta(\Delta)$

$\Rightarrow$ as $T \to \infty$ $\quad P_{\downarrow_z \to \uparrow_z} \to \frac{\Omega_\perp^2 T^2}{4}\,\frac{2\pi}{T}\,\delta(\Delta) = \left(\frac{\Omega_\perp}{2}\right)^2 2\pi T\,\delta(\Delta)$

We define the rate of transition

$$R_{\downarrow_z \to \uparrow_z} = \frac{dP}{dT} = \left(\frac{\Omega_\perp}{2}\right)^2 2\pi\,\delta(\Delta) = \left(\frac{\Omega_\perp}{2}\right)^2 2\pi\,\delta\left(\omega - \left(\frac{E_\uparrow - E_\downarrow}{\hbar}\right)\right)$$

$$\boxed{R_{\downarrow_z \to \uparrow_z} = \left(\frac{\hbar\Omega_\perp}{2}\right)^2 \frac{2\pi}{\hbar}\,\delta(E_\uparrow - E_\downarrow - \hbar\omega)}$$

This is a form of "Fermi's Golden Rule" which determines the rate of absorption. The general form

$$\boxed{R_{i \to f} = \frac{2\pi}{\hbar}\left|\langle E_f|\hat{H}_1^{(+)}|E_i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)}$$

where $|E_i\rangle$ and $|E_f\rangle$ are the intial and final energy levels, and the perturbing Hamiltonian has the form

$$\hat{H}_1(t) = \hat{H}_1^{(+)} e^{-i\omega t} + \hat{H}_1^{(-)} e^{+i\omega t}$$

For our spin-½ system $\hat{H}_1(t) = \frac{\hbar\Omega_\perp}{2}\hat{\sigma}_+ e^{-i\omega t} + \frac{\hbar\Omega_\perp}{2}\hat{\sigma}_- e^{-i\omega t}$

$|E_i\rangle = |\downarrow_z\rangle$, $\quad |E_f\rangle = |\uparrow_z\rangle \Rightarrow \langle E_f|\hat{H}_1|E_i\rangle = \frac{\hbar\Omega_\perp}{2}\langle\uparrow_z|\hat{\sigma}_+|\downarrow_z\rangle = \frac{\hbar\Omega_\perp}{2}$

The delta function in the rate is reflection of energy-conservation. Of course this delta function only makes sense within an integral. Typically, ω has some spectrum or E_f has a "linewidth", which gives a find rate. Fermi's Golden Rule is ubiquitous in physics, but its application often misses the important coherent evolution we saw in Rabi flopping.