CW Solid effect and Integrated SE

Contents

Background

The Hamiltonian of is

$$H = H_z + H_{SI} + H_{rf}$$

$$H_z = \Omega_S S_z + \Omega_I I_z$$

$$H_{SI} = d\left(\vec{S}\cdot\vec{I} - 3\big(\vec{S}\cdot\,\hat{r}\big)\big(\,\vec{I}\cdot\hat{r}\big)\right)$$

$$H_{rf} = 2\Omega_\mu \cos\omega t\ \ S_x = \Omega_\mu S_x\big(e^{i\omega t} + e^{-i\omega t}\big)$$

$$d = \left(\frac{\mu_0}{4\pi}\right)\frac{\gamma_e\gamma_p\hbar}{r^3}$$

We assume the effective hyperfine coupling take this form:

$$H_{SI} = AS_zI_z + BS_zI_x$$

To be more concrete, if we write down the complete H_{SI}

$$H_{SI} = \overrightarrow{B_S}\cdot\overrightarrow{B_I} = \left(\frac{\mu_0}{4\pi}\right)\gamma_e\gamma_p\hbar\,\vec{S}\cdot\big(\vec{I}\cdot\nabla\big)\frac{\vec{r}}{r^3} = d\,\vec{S}\cdot T\cdot\vec{I}$$

$$T=\begin{pmatrix}1-\frac{3x^2}{r^2} & -\frac{3xy}{r^2} & -\frac{3xz}{r^2}\\ -\frac{3xy}{r^2} & 1-\frac{3y^2}{r^2} & -\frac{3yz}{r^2}\\ -\frac{3xz}{r^2} & -\frac{3yz}{r^2} & 1-\frac{3z^2}{r^2}\end{pmatrix}=\begin{pmatrix}1-3\cos^2\phi\sin^2\theta & -\frac{3}{2}\sin 2\phi\sin^2\theta & -\frac{3}{2}\cos\phi\sin 2\theta\\ -\frac{3}{2}\sin 2\phi\sin^2\theta & 1-3\sin^2\phi\sin^2\theta & -\frac{3}{2}\sin\phi\sin 2\theta\\ -\frac{3}{2}\cos\phi\sin 2\theta & -\frac{3}{2}\sin\phi\sin 2\theta & 1-3\cos^2\theta\end{pmatrix}$$

By setting $\phi = 0$

$$T=\begin{pmatrix}1-3\sin^2\theta & 0 & -\frac{3}{2}\sin 2\theta\\ 0 & 1 & 0\\ -\frac{3}{2}\sin 2\theta & 0 & 1-3\cos^2\theta\end{pmatrix}$$

$$H_{SI}=d\left((1-3\sin^2\theta)S_xI_x-\frac{3}{2}\sin 2\theta\, S_xI_z+S_yI_y-\frac{3}{2}\sin 2\theta\ S_zI_x+(1-3\cos^2\theta)S_zI_z\right)$$

If there is no S_x or S_y, i.e. to electron polarization always on S_z, then,

$$H_{SI}=d\left(-\frac{3}{2}\sin 2\theta\ S_zI_x+(1-3\cos^2\theta)S_zI_z\right)=AS_zI_z+BS_zI_x$$

$$A=\left(\frac{\mu_0}{4\pi}\right)\frac{\gamma_e\gamma_p\hbar}{r^3}(1-3\cos^2\theta)$$

$$B=-\left(\frac{\mu_0}{4\pi}\right)\frac{\gamma_e\gamma_p\hbar}{r^3}\frac{3}{2}\sin 2\theta$$

Notices that the y-component is cancelled when we set $\phi = 0$, since the $(\vec{I}\cdot\nabla)\frac{\vec{r}}{r^3}$, which mean is the directional derivative along y-axis is zero when setting $r_y = 0$, i.e. $T_{23} = 0$. Or to say, the y-component of the derivative along the z-direction from I spin is zero.

Density Matrix and Polarization

The density matrix is defined by the state ket

$$\rho = |\chi\rangle\langle\chi|$$

Where

$$|\chi\rangle = \sum a_{m_s}|m_s\rangle$$

For spin half system

$$|\chi\rangle = a_+|+\rangle + a_-|-\rangle$$

$$\rho = |a_+|^2|+\rangle\langle+| + a_+a_-^*|+\rangle\langle-| + a_+^*a_-|-\rangle\langle+| + |a_-|^2|-\rangle\langle-| = \begin{pmatrix}|a_+|^2 & a_+a_-^*\\ a_+^*a_- & |a_-|^2\end{pmatrix}$$

The density matrix can be decomposed into operator,

$$\rho = \frac{|a_+|^2 + |a_-|^2}{2} I + \frac{|a_+|^2 - |a_-|^2}{2} \sigma_z + a_+ a_-^* \sigma_+ + a_+^* a_- \sigma_-$$

Where σ are Pauli's spin matrix.

The total population and the normalization condition require

$$Tr(\rho) = 1$$

the trace of a matrix is independence of unitary transform. Therefore, the trace is the same for any coordinate system. Since this property, the trace also called characteristic of a matrix.

Unitary transform matrix has property:

$$U^{-1} = U^T$$

The transformation of density matrix follows the transformation of the state ket, thus,

$$\rho' = U \rho U^{-1}$$

by equality

$$Tr(ABC) = \sum_{ijk} A_{ij} B_{jk} C_{ki} = \sum_{jki} B_{jk} C_{ki} A_{ij} = Tr(BCA)$$

$$Tr(\rho') = Tr(U\rho U^{-1}) = Tr(\rho U^{-1} U) = Tr(\rho)$$

The trace of density matrix keeps unchanged. Especially, when the density matrix is commuted with the unitary operator, the density matrix is unchanged. i.e.

$$\rho \propto I\, , S_z$$

The equation of motion of the density matrix is:

$$\frac{d}{dt}\rho = -i[H, \rho]$$

For time-independent Hamiltonian, the solution is

$$\rho(t) = e^{-iHt} \rho(0) e^{iHt}$$

and the polarization is

$$P_e(t) = Tr\big(S_z \rho(t)\big)$$
$$P_I(t) = Tr\big(I_z \rho(t)\big)$$

Interaction Picture

To solve this Hamiltonian and find the transition condition, we can use a transform similar to the interaction picture.

Recall the interaction picture:

$$H = H_0 + V(t)$$

where H_0 is time independent and $V(t)$ is the time-dependent part. Using transform:

$$U = e^{iH_0 t}$$

the ket will be transformed as:

$$|\psi_i\rangle = U|\psi\rangle$$

the corresponding Hamiltonian is by the Schrödinger equation:

$$\frac{d|\psi_i\rangle}{dt} = \frac{dU}{dt}|\psi\rangle + U\frac{d|\psi\rangle}{dt} = iH_0|\psi_i\rangle - iUHU^{-1}|\psi_i\rangle$$

$$UHU^{-1} = H_0 + V_i$$

$$\frac{d|\psi_i\rangle}{dt} = -iV_i|\psi_i\rangle$$

$$H_i = V_i = UVU^{-1}$$

for other operator $Q = \sum |q_i\rangle q_i \langle q_i|$, since the ket are transformed in same say, thus, the operator in interaction picture is:

$$Q_i = UQU^{-1}$$

since H_0 is a hermitian operator, thus the transform is unitary.

Notice that this transform is valid for time-independent Hamiltonian.

Titled Rotating truncate frame

The Hamiltonian in lab frame is:

$$H = \Omega_S S_z + \Omega_I I_z + AS_z I_z + BS_z I_x + \Omega_\mu S_x\left(e^{i\omega t} + e^{-i\omega t}\right)$$

The rotating frame operator is

$$U_R = e^{-iS_z \omega t}$$

The rotating frame Hamiltonian is:

$$H_R = U_R H U_R^{-1} + \omega S_z$$

After a change in rotation frame along with the oscillating frame, the high frequency term will be truncated. The Hamiltonian becomes a constant.

$$H_R = (\Omega_S + \omega)S_z + \Omega_\mu S_x + \Omega_I I_z + A S_z I_z + B S_z I_x$$

The titled operator is

$$U_T = e^{i\theta S_y}$$

Where

$$\tan\theta = \frac{\Omega_\mu}{\Omega_S + \omega}$$

Then,

$$U_T S_z U_T^{-1} = \cos\theta\, S_z - \sin\theta\, S_x$$

$$U_T S_x U_T^{-1} = \sin\theta\, S_z + \cos\theta\, S_x$$

Then,

$$(\Omega_S + \omega)S_z + \Omega_\mu S_x \rightarrow \Omega_{eff} S_z$$

$$\Omega_{eff} = \sqrt{(\Omega_S + \omega)^2 + \Omega_\mu^2}$$

$$A S_z I_z + B S_z I_x \rightarrow A\cos\theta\, S_z I_z - A\sin\theta\, S_x I_z + B\cos\theta\, S_z I_x - B\sin\theta\, S_x I_x$$

Substitute

$$S_x = \frac{S_+ + S_-}{2}$$

$$I_x = \frac{I_+ + I_-}{2}$$

$$\begin{aligned} H_{IS}^T &= A S_z I_z + B S_z I_x \\ &= A\cos\theta\, S_z I_z - \frac{A}{2}\sin\theta\,(S_+ + S_-)I_z \\ &+ \frac{B}{2}\cos\theta\, S_z(I_+ + I_-) \\ &- \frac{B}{4}\sin\theta\,(S_+ I_- + S_- I_+) - \frac{B}{4}\sin\theta\,(S_+ I_+ + S_- I_-) \end{aligned}$$

$$H_T = \Omega_{eff} S_z + \Omega_I I_z + H_{IS}^T$$

The titled rotated truncated hyper-fine Hamiltonian is the reason for spin transfer.

Interaction picture

In order to see the effect of each term, we have to do 1 more transform:

$$U_H = e^{-i(\Omega_{eff}S_z+\Omega_I I_z)t} = e^{-i\Omega_{eff}S_z t}e^{-i\Omega_I I_z t}$$

This time-dependence transform will change the Hamiltonian to

$$\frac{d}{dt}|\psi\rangle_H = -iV|\psi\rangle_H$$

$$V = U_H(H_{IS}^T)U_H^{-1}$$

For spin-half particle,

$$e^{-i\Omega_{eff}S_z t} = \cos\left(\frac{\Omega_{eff}}{2}t\right)E + 2i\sin\left(\frac{\Omega_{eff}}{2}t\right)S_z$$

$$e^{-i\Omega_I I_z t} = \cos\left(\frac{\Omega_I}{2}t\right)E + 2i\sin\left(\frac{\Omega_I}{2}t\right)I_z$$

And by

$$[S_z, S_\pm] = \pm S_\pm$$

$$[I_z, I_\pm] = \pm I_\pm$$

Thus,

$$U_H S_z I_z U_H^{-1} = S_z I_z$$

$$U_H S_z I_\pm U_H^{-1} = S_z I_\pm e^{\pm i\Omega_I t}$$

$$U_H S_\pm I_z U_H^{-1} = S_\pm I_z e^{\pm i\Omega_{eff} t}$$

$$U_H S_\pm I_\pm U_H^{-1} = S_\pm I_\pm e^{\pm i(\Omega_I+\Omega_{eff})t}$$

$$U_H S_\pm I_\mp U_H^{-1} = S_\pm I_\mp e^{\pm i(\Omega_{eff}-\Omega_I)t}$$

In order to make $V = U_H(H_{IS}^T)U_H^{-1}$ be time independent, so that the density matrix can be computed by

$$\rho(t) = e^{-iVt}\rho_0 e^{iVt}$$

And the spin transfer, which mean the term,

$$-\frac{B}{4}\sin\theta\,(S_+I_- + S_+I_-)$$

Survive and not truncated by high frequency, We can choose ω and Ω_μ, such that,

$$\Omega_{eff} = \Omega_I$$

Or

$$\sqrt{(\Omega_S+\omega)^2+\Omega_\mu^2}=\Omega_I$$

Which is the Hartmann – Hahn condition. And the Hamiltonian

$$V = A\cos\theta\, S_z I_z - \frac{B}{4}\sin\theta\,(S_+ I_- + S_- I_+)$$

Notices that, the spin flip operator are sine function, that corresponding to the spin flip rate, as the Hamiltonian are related the time propagator. In the basis of $|m_s, m_I\rangle$

$$e^{-iVt} = \begin{pmatrix} e^{i\frac{A}{4}\cos\theta t} & 0 & 0 & 0 \\ 0 & e^{-i\frac{A}{4}\cos\theta t}\cos\left(\frac{B}{4}\sin\theta\, t\right) & ie^{-i\frac{A}{4}\cos\theta}\sin\left(\frac{B}{4}\sin\theta\, t\right) & 0 \\ 0 & i\,e^{-i\frac{A}{4}\cos\theta}\sin\left(\frac{B}{4}\sin\theta\, t\right) & e^{-i\frac{A}{4}\cos\theta}\cos\left(\frac{B}{4}\sin\theta\, t\right) & 0 \\ 0 & 0 & 0 & e^{i\frac{A}{4}\cos\theta} \end{pmatrix}$$

A summary

we made 3 unitary transforms:

$$U_R, U_T, U_H$$

After every time-dependent unitary transform, the high frequency terms were truncated.

The polarization in lab frame is

$$P_e = Tr(2S_z\rho)$$

$$P_I = Tr(2I_z\rho)$$

The operator ρ, S_z and I_z also have to transform too

$$S_z \to S_z \to \cos\theta\, S_z - \sin\theta\, S_x \to \cos\theta\, S_z - \sin\theta\,\left(S_x\cos(\Omega_{eff}t) - S_y\sin(\Omega_{eff}t)\right) \to \cos\theta\, S_z$$

$$I_z \to I_z \to I_z$$

and for the special case, $\theta = \frac{\pi}{2}$,

$$S_z \to 0$$

Thus, we see that, only the component of the electron polarization will take part in the spin transfer.

The transformation of density matrix, in general form of initial polarization $P_e = P_{e0}$ and $P_I = P_{I0}$ along z-axis, and no polarization along transverse axis, in the basis $|m_s, m_I\rangle$, takes the form:

$$\rho_0 = \frac{1}{4}1 + \frac{P_{e0}}{2}S_z + \frac{P_{I0}}{2}I_z + P_{e0}P_{I0}S_zI_z$$

Thus, after the transforms:

$$\rho_0 \to \frac{1}{4}1 + \frac{P_{e0}}{2}\cos\theta\, S_z + \frac{P_{I0}}{2}I_z + P_{e0}P_{I0}\cos\theta\, S_zI_z$$

the dynamic of the density matrix in interaction picture is:

$$\rho = e^{-iVt}\rho_0 e^{iVt}$$

Thus, the polarization is:

$$P_e = 2Tr(S_z\rho) = 2Tr\left(\cos\theta\, S_z \cdot e^{-iVt}\left(\frac{1}{4}1 + \frac{P_{e0}}{2}\cos\theta\, S_z + \frac{P_{I0}}{2}I_z + P_{e0}P_{I0}\cos\theta\, S_zI_z\right)e^{iVt}\right)$$

$$P_I = 2Tr(S_z\rho) = 2Tr\left(I_z \cdot e^{-iVt}\left(\frac{1}{4}1 + \frac{P_{e0}}{2}\cos\theta\, S_z + \frac{P_{I0}}{2}I_z + P_{e0}P_{I0}\cos\theta\, S_zI_z\right)e^{iVt}\right)$$

The result is

$$P_e = P_{e0}\cos^2\theta\cos^2\left(\frac{B}{4}\sin\theta\, t\right) + P_{I0}\cos\theta\sin^2\left(\frac{B}{4}\sin\theta\, t\right)$$
$$P_I = P_{e0}\cos\theta\sin^2\left(\frac{B}{4}\sin\theta\, t\right) + P_{I0}\cos^2\left(\frac{B}{4}\sin\theta\, t\right)$$

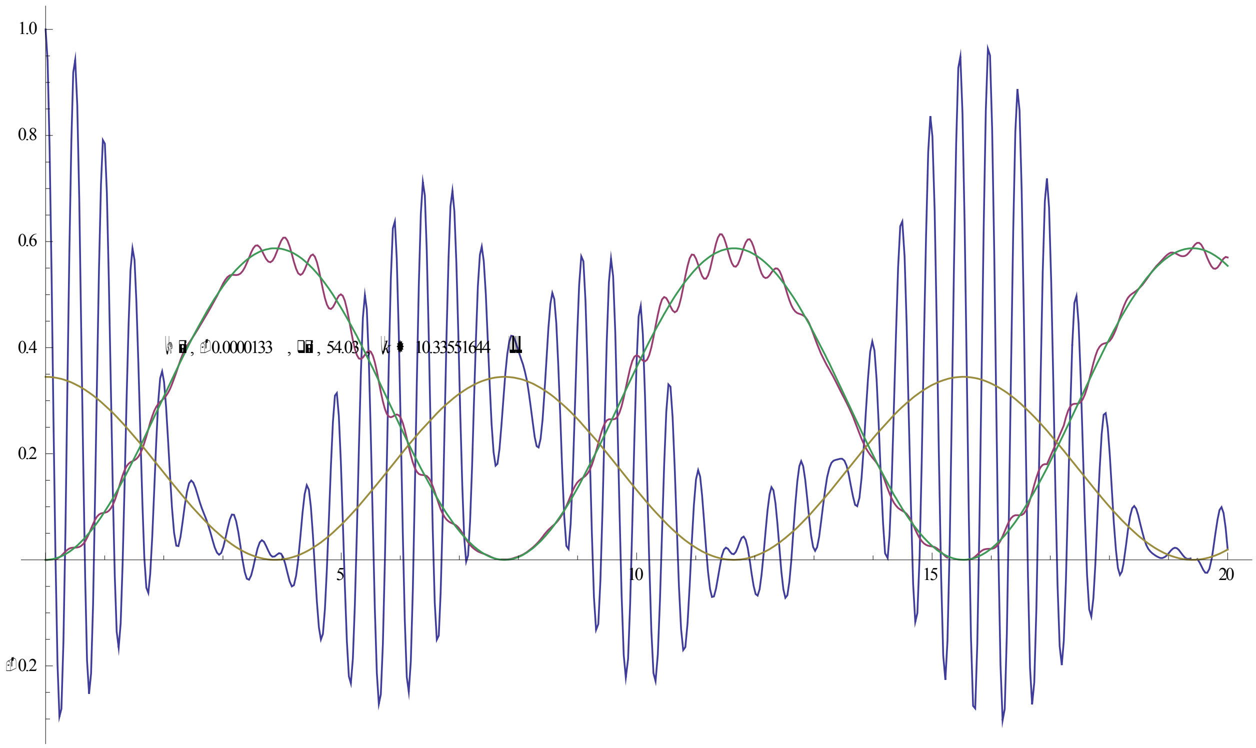
We can see that, the larger the θ, the smaller the usable electron polarization, however, the smaller the θ, the longer time for polarization transfer.

And from the equation, the proton polarization is bounded by

$$P_I(\max) = P_{e0}\cos\theta$$

If we compare the result to the direct computation with real data at rotating frame Hamiltonian:

$$H_R = (\Omega_S + \omega)S_z + \Omega_\mu S_x + \Omega_I I_z + AS_zI_z + BS_zI_x$$



The blue line is the electron polarization, which is 1 at initial, the red line is the proton polarization, 0 at beginning. The yellow and green line are the smoothen electron and proton polarization, which is given by the equations above.

Some Notes on Hartmann-Hahn Condition

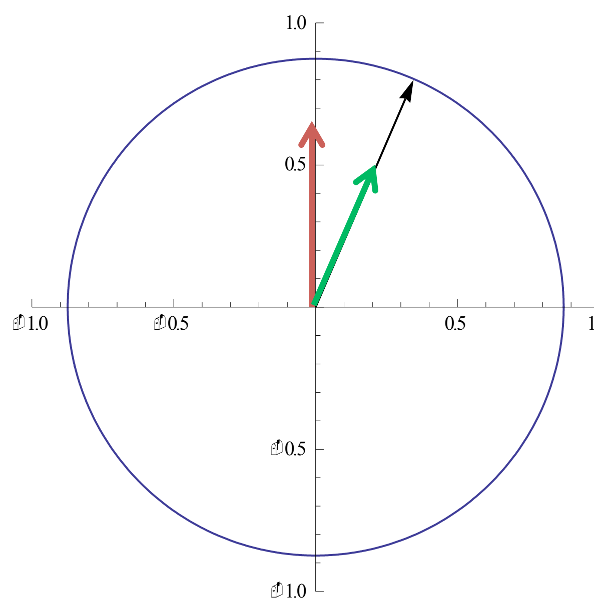
The Hartmann-Hahn condition is :

$$(\Omega_S + \omega)^2 + \Omega\mu^2 = \Omega_I^2$$

If we write the Larmor frequency in term of external magnetic field, since the electron gyromagnetic ratio is negative, so,

$$(\gamma_e H - \omega)^2 + \Omega_\mu^2 = \gamma_p^2 H^2$$

There are 2 pictorial views of this equation.



Fixing Magnetic field

we draw a circle with radius $\gamma_p H$, thus, the solution for the microwave power and frequency is related by

$$\Omega_\mu = \pm\sqrt{\gamma_p^2 H^2 - (\gamma_e H - \omega)^2}$$

The x-axis is the size of Ω_μ and the y-axis is the size of $(\gamma_e H - \omega)$. If we changing the power, and in order to meet the condition, the angle

$$\tan\theta = \frac{\Omega_\mu}{\Omega_S + \omega} = \frac{\Omega_\mu}{\gamma_e H - \omega} = \frac{\Omega_\mu}{\sqrt{\gamma_p^2 H^2 - \Omega_\mu^2}}$$

And the $\cos\theta$, which is the factor that bounded the Maximum usable polarization in Solid effect is:

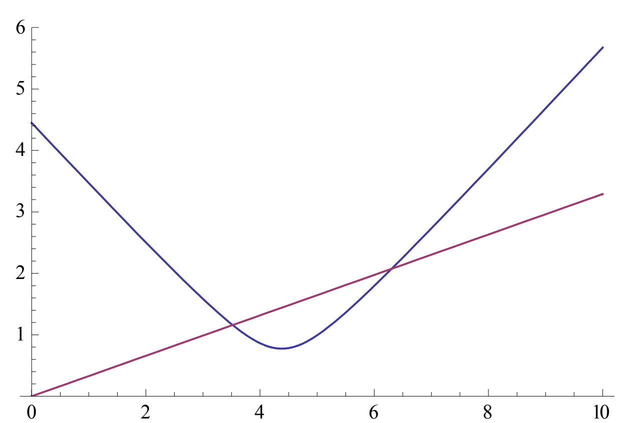
$$\cos\theta = \sqrt{1 - \left(\frac{\Omega_\mu}{\gamma_p H}\right)^2}$$

In the figure, we draw the red arrow as electron polarization, and the green arrow is the usable polarization. Therefore, smaller the microwave power is better. However, as mentioned before, the proton polarization is:

$$P_I = P_{e0}\cos\theta\sin^2\left(\frac{B}{4}\sin\theta\, t\right) + P_{I0}\cos^2\left(\frac{B}{4}\sin\theta\, t\right)$$

The time for polarization build up depends on $\sin\theta = \frac{\Omega_\mu}{\gamma_p H}$. So, smaller angle results in longer time.

Fixed microwave setting



Another way to view the condition is by fixed the microwave frequency and power. if we make the x-axis is the magnetic field, the y-axis is the effective rotation frequency. Recall,

$$y = \Omega_{eff} = \sqrt{(\gamma_e H - \omega)^2 + \Omega_\mu^2}$$

The minimum is $y_{min} = \Omega_\mu$, the center of symmetry is $H = \frac{\omega}{\gamma_e}$. There are 2 curves, one was shown in above, and the other is

$$y = \gamma_p H$$

There are 2 solutions for the 2 curves intercept each other.

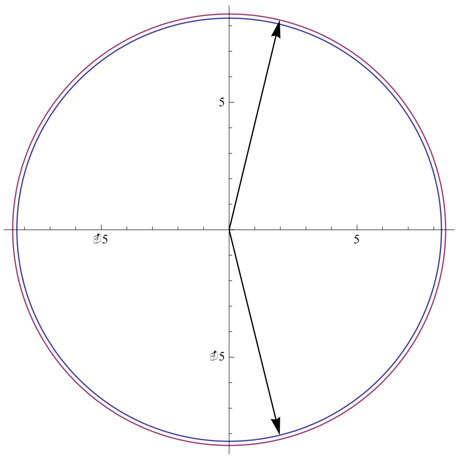
$$H = \frac{\frac{1}{\gamma_p}}{1-\frac{1}{\gamma^2}}\left(\frac{\omega}{\gamma} \pm \sqrt{\frac{\omega^2}{\gamma^2} - \left(1-\frac{1}{\gamma^2}\right)\Omega_\mu^2}\right)$$

For

$$\omega \geq \sqrt{\gamma^2 - 1}\Omega_\mu \sim \gamma\Omega_\mu$$

where

$$\gamma = \frac{\gamma_e}{\gamma_p} \sim 660 \gg 1$$



For the smaller root, the value

$$\gamma_e H_- - \omega = \frac{1}{1-\frac{1}{\gamma^2}}\left(\frac{\omega}{\gamma^2} - \gamma\sqrt{\frac{\omega^2}{\gamma^2} - \left(1-\frac{1}{\gamma^2}\right)\Omega_\mu^2}\right) \sim$$

$$-\gamma\sqrt{\frac{\omega^2}{\gamma^2} - \Omega_\mu^2} < 0$$

So, the smaller root gives us a negative polarization and the larger root gives us a positive polarization, with similar magnitude. Thus, if the field sweep is crossing the 2 roots, there will be no polarization. If we compare the root in the other picture, the 2 circles for the 2 difference value of H is almost the same. And the angle of each is:

$$\tan\theta_+ = \frac{\Omega_\mu}{\gamma_e H_+ - \omega} = \frac{\Omega_\mu}{\frac{1}{1-\frac{1}{\gamma^2}}\left(\frac{\omega}{\gamma^2} + \gamma\sqrt{\frac{\omega^2}{\gamma^2} - \left(1-\frac{1}{\gamma^2}\right)\Omega_\mu^2}\right)} \sim \frac{\Omega_\mu}{\left(\frac{\omega}{\gamma^2} + \gamma\sqrt{\frac{\omega^2}{\gamma^2} - \Omega_\mu^2}\right)}$$

$$\tan\theta_- = \sim \frac{\Omega_\mu}{\left(\frac{\omega}{\gamma^2} - \gamma\sqrt{\frac{\omega^2}{\gamma^2} - \Omega_\mu^2}\right)}$$

So, the best way to deal with the fluctuation of magnetic field, we make the separation as large as possible by setting,

$$\omega \gg \sqrt{\gamma^2 - 1}\Omega_\mu$$

We can do this by enlarge the frequency or by smaller the microwave power. in either case, the angle is getting smaller.

Integrated Solid Effect

To be continuous…