**Modern methods in experimental physics**:
site-directed spin labeling EPR

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# Solution Problem Set 5

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## Excitation of forbidden transitions with a $\pi/2$ pulse

a. To transform the operator $\hat{S}_x$ to the eigenframe of the spin Hamiltonian one needs to perform the unitary transformation with $U_{EB} = \exp\left(-i\left(\eta 2\hat{S}_z\hat{I}_y + \xi\hat{I}_y\right)\right)$ which can be reduced to $U_{EB} = \exp\left(-i\left(\eta 2\hat{S}_z\hat{I}_y\right)\right)$ since operators $\hat{S}_x$ and $\hat{I}_y$ commute. According to this transformation we get:

$$\hat{S}_x \quad \xrightarrow{\eta 2\hat{S}_z\hat{I}_y} \quad \left(\hat{S}_x\cos\eta + 2\hat{S}_y\hat{I}_y\sin\eta\right) \tag{1}$$

The equilibrium density matrix $\hat{\sigma}_0 = -\hat{S}_z$ does not change when transformed into this frame, because $\hat{S}_z$ commutes with all terms in the transformation matrix.

b. Application of the $(\pi/2)\hat{S}_x$ pulse is described in the lab frame by:

$$-S_z \quad \xrightarrow{\alpha S_x} \quad -S_z\cos\alpha + S_y\sin\alpha = S_y = \hat{\sigma}_1(\alpha = \pi/2)$$

Expression for $\hat{\sigma}_1$ in the eigenframe of the spin Hamiltonian is obtained under the unitary transformation with $U_{EB} = \exp\left(-i\left(\eta 2\hat{S}_z\hat{I}_y + \xi\hat{I}_y\right)\right)$. We get:

$$\hat{S}_y \quad \xrightarrow{\eta 2\hat{S}_z\hat{I}_y} \quad \hat{S}_y\cos\eta - 2\hat{S}_x\hat{I}_y\sin\eta$$

c. For computing the evolution during the FID period, we use $\hat{H}_0 = \frac{\omega_+}{2}\hat{I}_z + \frac{\omega_-}{2}2\hat{S}_z\hat{I}_z$. During the computation we use for brevity the following notations: $\beta_+ = \frac{\tau\omega_+}{2}$ and $\beta_- = \frac{\tau\omega_-}{2}$. With that:

$$\hat{S}_y\cos\eta - 2\hat{S}_x\hat{I}_y\sin\eta \quad \xrightarrow{\beta_+\hat{I}_z} \quad \hat{S}_y\cos\eta - 2\hat{S}_x\hat{I}_y\sin\eta\cos\beta_+ + 2\hat{S}_x\hat{I}_x\sin\eta\sin\beta_+$$

$$\xrightarrow{\beta_- 2\hat{S}_z\hat{I}_z} \quad \hat{S}_y\cos\eta\cos\beta_- - 2\hat{S}_x\hat{I}_z\cos\eta\sin\beta_- -$$

$$-2\hat{S}_x\hat{I}_y\sin\eta\cos\beta_+ + 2\hat{S}_x\hat{I}_x\sin\eta\sin\beta_+$$

d. The back transformation to the original Cartesian (laboratory) frame is done with the operator $U^{-1} = U^{\dagger}$. Only the first and third term from (c) give rise to detectable terms in the laboratory frame. The transformation of these terms is (note that we omit for the moment the coefficients of the operators):

$$\hat{S}_y \xrightarrow{-\eta 2\hat{S}_z\hat{I}_y} \hat{S}_y \cos\eta + 2\hat{S}_x\hat{I}_y \sin\eta$$

$$-2\hat{S}_x\hat{I}_y \xrightarrow{-\eta 2\hat{S}_z\hat{I}_y} -2\hat{S}_x\hat{I}_y \cos\eta + \hat{S}_y \sin\eta$$

Here we used the fact that both of these terms commute with $\hat{I}_y$. Therefore only one term in the operator $U^{-1}$ plays a role for the coordinate transformation. As a result the FID signal along $-y$ direction can be detected:

$$\langle -S_y \rangle = \cos^2\eta\cos\beta_- + \sin^2\eta\cos\beta_+ = \cos^2\eta\cos\frac{\tau\omega_-}{2} + \sin^2\eta\cos\frac{\tau\omega_+}{2} \quad (2)$$

e. The Fourier transform of $\cos\omega_0\tau$ gives rise to two delta-functions $\delta(\omega - \omega_0)$ and $\delta(\omega + \omega_0)$. The stick representation of such a spectrum is shown in Fig.2, considering $\omega_-$ as negative and $\omega_+$ as positive.

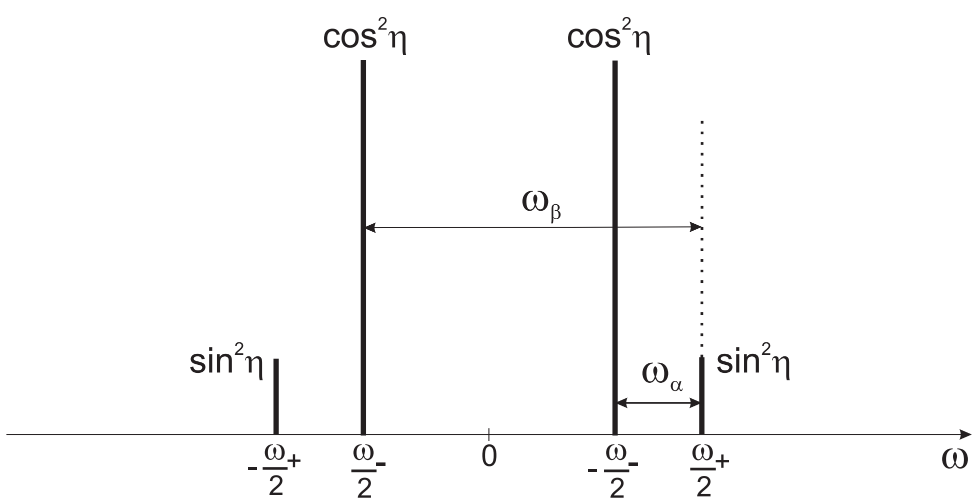


Figure 1: Fourier transform of the free induction decay after a $\pi/2$ pulse.