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Spectral line of stimulated emission in magnetic resonance

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Abstract

A two-level magnetic system is modelled by means of a 1/2-angular momentum with arbitrary orientation and its interaction with a periodic external magnetic field is considered (Rabi-like problem). Drawing on Schwinger's treatment of a similar problem, we apply the results to the emitted radiation and the absorbed power. It is shown that, owing to the continuous oscillations of the magnetization, the emission is one stimulated by the driving field, the coherent signal being enhanced.

Introduction. Magnetic resonance research focuses on the parametrization of the energy levels, which provides information about the magnetic moments and electronic and magnetic structure of the local molecular environment. The spectral line of the response receives comparatively little attention, it being given by well-known transition probabilities in the first-order of the perturbation theory. However, it provides direct access to measurable quantities like the absorbed power or the emitted magnetic field, which require the calculation of the magnetization.

As it is well known, in typical experiments of magnetic resonance we consider two energy levels separated by a frequency ω_0, populate the upper level by means of electromagnetic radiation with frequency $\omega \simeq \omega_0$ and detect the response. The excitation is peformed by a time-dependent magnetic field $\mathbf{H} = \mathbf{H}_1 \cos \omega t$, where $\mathbf{H}_1$ is the amplitude and t denotes the time. In the standard treatment $\mathbf{H}$ is viewed as a small perturbation to the free hamiltonian, whose energy levels are not changed by perturbation, in the first order of the perturbation theory. The response is provided either by the absorbed power or by free-induction decay, including various versions of the latter, like the spin echo procedure. In free-induction decay the dis-excitation processes are spontan statistical processes, and the response, which is governed by the loss (damping) parameter, is spontan emission of incoherent radiation. It exhibits the characteristic shape of a spectral line.[1]-[15]

We present in this paper a different approach to magnetic resonance, where the time-dependent interaction, introduced adiabatically in a long time, changes the free energy levels and generates oscillations in magnetization. Since we are interested in one spectral line at one time, it is sufficient to consider a two-level magnetic system. The continuous emission of radiation is a stimulated, coherent emission, which enhances the response. We examine here to what extent the response signal is enhanced by stimulated emission in realistic situations. The calculations are based on Schwinger's treatment of Rabi's problem,[16]-[18] and are performed up to second-order powers of the coupling constant.

Zeeman splitting and transverse excitation. We assume a free hamiltonian

$$\mathcal{H}_0 = \frac{1}{2}\hbar\omega_0 J_z \quad , \tag{1}$$

where $\hbar$ is Planck's constant and J_z is the z-component of the Pauli matrices $\mathbf{J} = (J_x,\, J_y,\, J_z)$; the frequency $\omega_0 = 2\gamma H_0$ can be viewed as being due to the Zeeman splitting caused by a static magnetic field H_0, applied along the negative z-axis, γ being a gyromagnetic factor. We consider an interaction hamiltonian

$$\mathcal{H}_i = -\hbar\gamma H J_x e^{\alpha t} \quad , \tag{2}$$

where $H = H_1 \cos\omega t$; we assume that frequency ω is close to the frequency ω_0; the interaction is introduced adiabatically through the factor $e^{\alpha t}$, $\alpha \to 0^+$. This factor may account for the energy loss; it corresponds to the transverse relaxation time in nuclear magnetic resonance, where the Bloch approximation scheme, which disentagles the transverse components from the longitudinal component of the magnetization, allows the introduction of a second, longitudinal, relaxation time. It is convenient to introduce the coupling parameter $g = g_0 e^{\alpha t}\cos\omega t$, $g_0 = 2\gamma H_1/\omega_0$ and write the interaction hamiltonian as

$$\mathcal{H}_i = -\frac{1}{2}\hbar\omega_0 g J_x \;; \tag{3}$$

we assume $g_0 \ll 1$. The two hamiltonians $\mathcal{H}_{0,i}$ given by equations (1) and (2) describe a typical nuclear magnetic resonance for a two-level magnetic system.

The eigenvalues of the full hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_i$ are $E_{1,2} = \pm\frac{1}{2}\hbar\omega_0\lambda$, $\lambda = \sqrt{1+g^2}$ (Rabi frequencies[16, 17]), and the eigenvectors, up to second-order powers of the coupling constant g, are

$$\begin{gathered} \psi_1 = a\varphi_{1/2} - b\varphi_{-1/2} \;,\; \psi_2 = b\varphi_{1/2} + a\varphi_{-1/2} \;, \\ a = 1 - g^2/8 \;,\; b = g/2 \;; \end{gathered} \tag{4}$$

noteworthy, these eigenvectors (which are orthonormal) depend on the time through the coupling constant g. The wavefunction is a superposition of the form

$$\psi(t) = C_1(t) e^{-\frac{i\omega_0}{2}\int^t dt'\lambda(t')}\psi_1(t) + C_2(t) e^{\frac{i\omega_0}{2}\int^t dt'\lambda(t')}\psi_2(t) \quad , \tag{5}$$

where $\lambda = \sqrt{1+g^2} \simeq 1 + g^2/2$ and $C_{1,2}(t)$ are time-dependent coefficients to be determined. The lower limit of the time integration in equation (5) is $-\infty$ for the interacting term in λ (the term $g^2/2$) and an arbitrary time for the free term; this contribution of the free term is a constant phase factor which may be included in $\psi_{1,2}$, such that we recover the non-interacting temporal phase factors $e^{\mp\frac{i}{2}\omega_0 t}$ in the limit $g \to 0$. The Schrodinger equation $i\hbar\partial\psi/\partial t = \mathcal{H}\psi$ leads to

$$\dot{C}_1 + \tfrac{1}{2}\dot{g}e^{i\omega_0 t}C_2 = 0 \;,\; \dot{C}_2 - \tfrac{1}{2}\dot{g}e^{-i\omega_0 t}C_1 = 0 \;; \tag{6}$$

such systems of coupled equations for the coefficients of the wavefunction have been introduced by Schwinger in his solution to Rabi problem.[18] In Ref. [18] the system of equations (6) is solved for a gyrating magnetic field, where the coefficients $C_{1,2}$ reduce to constants. The solution of the system of equations (6) is

$$C_1 = \left(1 - \tfrac{1}{2}|A|^2\right)C_1^0 - AC_2^0 \;,\; C_2 = A^* C_1^0 + \left(1 - \tfrac{1}{2}|A|^2\right)C_2^0 \quad , \tag{7}$$

where

$$A = \frac{1}{2}\int_{-\infty}^{t} dt'\,\dot{g}e^{i\omega_0 t'} \tag{8}$$

and $C^0_{1,2}$ are the initial values of the coefficients $C_{1,2}$ at time $t \to -\infty$. For $\Delta\omega = \mid \omega - \omega_0 \mid \ll \alpha \ll \omega_0$ the leading term in equation (8) is

$$A \simeq -\frac{i}{4} g_0 \omega_0 \frac{\alpha}{(\Delta\omega)^2 + \alpha^2} \to -\frac{i\pi}{4} g_0 \omega_0 \delta(\Delta\omega) \ , \ \ \alpha \to 0 \tag{9}$$

(where δ is the Dirac delta function). We assume a thermal equilibrium for the initial states, such that the initial populations of the energy levels are given by

$$\begin{gathered} w^0_1 = |C^0_1|^2 = \tfrac{1}{2}(1-p) \ , \ \ w^0_2 = |C^0_2|^2 = \tfrac{1}{2}(1+p) \ , \\ p = \tanh(\beta\hbar\omega_0/2) \ \ , \end{gathered} \tag{10}$$

β being the inverse of the temperature; since the frequency ω_0 is in the radio-frequency range, we may use $p \simeq \beta\hbar\omega_0/2 \ll 1$ for a wide range of temperatures. The populations of the two states after introducting the interaction are

$$w_{1,2} = |(\psi_{1,2}(t), \psi(t))|^2 = |C_{1,2}(t)|^2 \simeq w^0_{1,2} \pm \tfrac{1}{16} \tfrac{p g_0^2 \omega_0^2}{(\Delta\omega)^2 + \alpha^2} \ \ ; \tag{11}$$

we can see that the upper level acquires a net over-population due to the interaction. If we keep the factor $e^{\alpha t}$ in A (equation (9)), we can compute the transition rate, which is identical with the result of the first-order perturbation calculation. The leading contributions to the mean value $\overline{\mathbf{J}} = (\psi(t), \mathbf{J}\psi(t))$ of the angular momentum $\mathbf{J}$ in the state $\psi(t)$ are

$$\begin{gathered} \overline{J}_x \simeq \tfrac{1}{2} p g_0 \omega_0 \tfrac{\alpha}{(\Delta\omega)^2+\alpha^2} \sin\omega_0 t \ , \ \ \overline{J}_y \simeq -\tfrac{1}{2} p g_0 \omega_0 \tfrac{\alpha}{(\Delta\omega)^2+\alpha^2} \cos\omega_0 t \ \ , \\ \overline{J}_z \simeq \tfrac{1}{8} \tfrac{p g_0^2 \omega_0^2}{(\Delta\omega)^2+\alpha^2} \ \ ; \end{gathered} \tag{12}$$

these results are identical with those obtained by solving the Bloch equations of motion for magnetization.[3]

The interaction induces a magnetic moment $\mathbf{m} = \hbar\gamma\overline{\mathbf{J}}$ and a magnetization $\mathbf{M} = n\mathbf{m}$, where n is the concentration of the two-level systems in the sample. The current density $\mathbf{j}_m = c \cdot curl\mathbf{M}$ (where c denotes the speed of light in vacuum) generates a dipolar magnetic field

$$\mathbf{H}_m \simeq v \frac{3\mathbf{r}(\mathbf{r}\mathbf{M}) - r^2\mathbf{M}}{r^5} \tag{13}$$

at the position $\mathbf{r}$ from the sample, where v is the sample volume. We can see that this response is proportional to the number $N = vn$ of two-level systems in the sample and oscillates with the resonance frequency ω_0 ($\omega \simeq \omega_0$). The mean power absorbed (and dissipated) per unit volume is

$$P = \overline{\mathbf{H}\dot{\mathbf{M}}} = \frac{1}{8} p g_0^2 n \hbar \omega_0^3 \frac{\alpha}{(\Delta\omega)^2 + \alpha^2} \ \ ; \tag{14}$$

it exhibits the characteristic shape of a spectral line, as $M_{x,y} = n\hbar\gamma\overline{J}_{x.y}$ and $\mathbf{H}_m$ do.

Arbitrary orientation. In electron spin resonance (paramagnetic resonance) or the nuclear quadrupole resonance the ω_0-splitting is produced by the local molecular environment, which may have an arbitrary orientation. Therefore, we assume a free hamiltonian

$$\mathcal{H}_0 = \frac{1}{2}\hbar\omega_0 \mathbf{n}\mathbf{J} \ \ , \tag{15}$$

where $\mathbf{n} = (\sin\theta\cos\varphi,\, \sin\theta\sin\varphi,\, \cos\theta)$ is the unit vector defined by the angles θ, φ of the spherical coordinates; if the orientation is random, we may average over these angles. The eigenvalues of $\mathcal{H}_0$ are $\pm\hbar\omega_0/2$ and the eigenvectors are given by the 1/2-spin rotation matrix

$$\begin{aligned} \varphi_1^0 &= \cos\tfrac{\theta}{2}\cdot\varphi_{1/2} + e^{i\varphi}\sin\tfrac{\theta}{2}\cdot\varphi_{-1/2} \ , \\ \varphi_2^0 &= -\sin\tfrac{\theta}{2}\cdot\varphi_{1/2} + e^{i\varphi}\cos\tfrac{\theta}{2}\cdot\varphi_{-1/2} \ , \end{aligned} \tag{16}$$

where $\varphi_{\pm 1/2}$ are the eigenvectors of J_z ($J_z\varphi_{\pm 1/2} = \pm\varphi_{\pm 1/2}$). The interaction hamiltonian

$$\mathcal{H}_i = -\hbar\gamma H J_z e^{\alpha t} = -\frac{1}{2}\hbar\omega_0 g J_z \tag{17}$$

is provided by a magnetic field $H = H_1\cos\omega t$ directed along the z-axis.

The full hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_i$ can be diagonalized straightforwardly; its eigenvalues are $E_{1,2} = \pm\frac{1}{2}\hbar\omega_0\lambda$,

$$\lambda = \sqrt{1 - 2g\cos\theta + g^2} \simeq 1 - g\cos\theta + \frac{1}{2}g^2\sin^2\theta \tag{18}$$

(Rabi frequencies[16, 17]), and its eigenvectors are given by

$$\begin{aligned} \psi_1 &= \cos\tfrac{\theta}{2}\left[1 - g\sin^2\tfrac{\theta}{2} + g^2\sin^2\tfrac{\theta}{2}\left(1 - \tfrac{5}{2}\cos^2\tfrac{\theta}{2}\right)\right]\varphi_{1/2} + \\ &+ e^{i\varphi}\sin\tfrac{\theta}{2}\left[1 + g\cos^2\tfrac{\theta}{2} + g^2\cos^2\tfrac{\theta}{2}\left(1 - \tfrac{5}{2}\sin^2\tfrac{\theta}{2}\right)\right]\varphi_{-1/2} \ , \\ \psi_2 &= -\sin\tfrac{\theta}{2}\left[1 + g\cos^2\tfrac{\theta}{2} + g^2\cos^2\tfrac{\theta}{2}\left(1 - \tfrac{5}{2}\sin^2\tfrac{\theta}{2}\right)\right]\varphi_{1/2} + \\ &+ e^{i\varphi}\cos\tfrac{\theta}{2}\left[1 - g\sin^2\tfrac{\theta}{2} + g^2\sin^2\tfrac{\theta}{2}\left(1 - \tfrac{5}{2}\cos^2\tfrac{\theta}{2}\right)\right]\varphi_{-1/2} \ , \end{aligned} \tag{19}$$

where contributions up to the g^2-order are included. Also, it is useful to give the interacting eigenvectors $\psi_{1,2}$ in terms of the free (non-interacting) eigenvectors $\varphi_{1,2}^0$,

$$\psi_1 = a\varphi_1^0 + b\varphi_2^0 \ , \ \ \psi_2 = -b\varphi_1^0 + a\varphi_2^0 \ , \tag{20}$$

where

$$a = 1 - \tfrac{1}{8}g^2\sin^2\theta \ , \ \ b = \tfrac{1}{2}g\sin\theta\,(1 + g\cos\theta) \ . \tag{21}$$

The time-dependent interacting wavefunction has the same form as in equation (5); the Schrodinger equation $i\hbar\partial\psi/\partial t = \mathcal{H}\psi$ leads to Schwinger's system of equations

$$\begin{aligned} \dot{C}_1 - \dot{g}\sin\theta\left(\tfrac{1}{2} + g\cos\theta\right)e^{i\omega_0\int^t dt'\lambda(t')}C_2 = 0 \ , \\ \dot{C}_2 + \dot{g}\sin\theta\left(\tfrac{1}{2} + g\cos\theta\right)e^{-i\omega_0\int^t dt'\lambda(t')}C_1 = 0 \ . \end{aligned} \tag{22}$$

In estimating the time integrals $\int^t dt'\lambda(t')$ we encounter terms corresponding to transitions $\omega = 0, \pm\omega_0/2, \pm\omega_0$; limiting ourselves to $\omega \simeq \omega_0$, the system of equations (22) becomes

$$\dot{C}_1 + \beta C_2 = 0 \ , \ \ \dot{C}_2 - \beta^* C_1 = 0 \ , \tag{23}$$

where

$$\beta = \frac{i}{4}g_0\sin\theta\cdot(\omega + i\alpha)e^{-i(\omega-\omega_0)t+\alpha t} \ . \tag{24}$$

The solution of this system of equations is

$$C_1 = \left(1 - \tfrac{1}{2}\left|A\right|^2\right) C_1^0 + AC_2^0 \ , \ \ C_2 = -A^* C_1^0 + \left(1 - \tfrac{1}{2}\left|A\right|^2\right) C_2^0 \ \ , \tag{25}$$

where

$$A = -\frac{i}{4} g_0 \omega_0 \sin\theta \frac{\alpha}{(\Delta\omega)^2 + \alpha^2} \ \ . \tag{26}$$

We use $C_{1,2}^0 = \sqrt{(1 \mp p)/2}$, where p is given by equation (10), corresponding to thermal equilibrium. The populations of the two states are

$$w_{1,2} \simeq w_{1,2}^0 \pm \tfrac{1}{16} \sin^2\theta \tfrac{p g_0^2 \omega_0^2}{(\Delta\omega)^2 + \alpha^2} \tag{27}$$

and the leading contributions to the mean value of the angular momentum in the state $\psi(t)$ are

$$\begin{gathered} \overline{J}_+ = \overline{J}_x + i\overline{J}_y \simeq 2p\left|A\right|(i - g\cos\theta\sin\omega_0 t) e^{-i(\widetilde{\omega}_0 - \varphi)t} - \\ -2p\left|A\right|(1 + \cos\theta)(\sin\widetilde{\omega}_0 t - g_0 \cos\theta \sin\omega_0 t \cos\widetilde{\omega}_0 t) e^{i\varphi} + \\ +2p\left|A\right| g \sin^2\theta \sin\widetilde{\omega}_0 t + 2p\left|A\right|^2 \sin\theta \cdot e^{i\varphi} \ \ , \end{gathered} \tag{28}$$

and

$$\begin{gathered} \overline{J}_z \simeq 2p\left|A\right|\sin\theta\left(\sin\widetilde{\omega}_0 t - g_0\cos\theta\sin\omega_0 t\cos\widetilde{\omega}_0 t\right) + \\ +p\left|A\right| g\sin 2\theta \sin\widetilde{\omega}_0 t + 2p\left|A\right|^2 \cos\theta \ \ , \end{gathered} \tag{29}$$

where $\widetilde{\omega}_0 = \omega_0(1 + \frac{1}{4} g_0^2 \sin^2\theta)$ and $\overline{J}_- = \overline{J}_x - i\overline{J}_y == \overline{J}_+^*$. We may use ω_0 instead of $\widetilde{\omega}_0$ in the above equations, leave aside the time-independent contributions and the terms oscillating with frequency $2\omega_0$, and get

$$\begin{gathered} \overline{J}_x \simeq 2p\left|A\right|\left[\sin(\omega_0 t - \varphi) - \tfrac{1}{4} g_0 \cos\theta \sin(\omega_0 t + \varphi) - (1 + \cos\theta)\sin\omega_0 t\cos\varphi\right] \ \ , \\ \overline{J}_y \simeq 2p\left|A\right|\left[\cos(\omega_0 t - \varphi) + \tfrac{1}{4} g_0 \cos\theta \cos(\omega_0 t + \varphi) - (1 + \cos\theta)\sin\omega_0 t\sin\varphi\right] \ \ , \\ \overline{J}_z \simeq 2p\left|A\right|\sin\theta\sin\omega_0 t \ \ ; \end{gathered} \tag{30}$$

the mean power absorbed per unit volume is

$$P = \overline{\mathbf{H}\dot{\mathbf{M}}} = \frac{1}{8} p g_0^2 n\hbar\omega_0^3 \sin^2\theta \frac{\alpha}{(\Delta\omega)^2 + \alpha^2} \ \ . \tag{31}$$

If we take the average over angles φ and θ, we get $\overline{J}_{x,y} = 0$ and

$$\overline{J}_z = \frac{1}{3} p g_0 \omega_0 \frac{\alpha}{(\Delta\omega)^2 + \alpha^2} \sin\omega_0 t \ \ . \tag{32}$$

Making use of these results, we can compute immediately the emitted field, which exhibits the coherent character of a stimulated emission.

Conclusion. In conclusion, we have solved the Schrodinger equation for a two-level magnetic system subject to a time-dependent external magnetic field with arbitrary orientation up to the second order in the coupling constant. The mean power absorbed per unit volume and the emitted radiation have been estimated. It is shown that the emitted radiation has the character of a coherent radiation, stimulated by the driving external field, due to the continuous oscillations of the magnetization.

As it is well-known, the coherent response increases the signal by a factor of the order $\sqrt{N}$, where N is the number of the two-level systems in the sample. However, in realistic situations important decoherence factors appear, which reduce appreciably this enhancement. First, we have used in the discussion above quantum-mechanical wavefunctions, while the sample was supposed to be at thermal equilibrium. The thermal bath is an important decoherence factor. For instance, at room temperature the energy levels are affected by an uncertainty of the order $T = 300K \simeq 4\times10^{-14}erg$, which is much higher than the two-level separation energy $\hbar\omega_0 \simeq 10^{-21}erg$ for $\omega_0 = 1MHz$. On the other hand, the magnetic momenta may be ordered along a distance of the order $1\mu m$, which further reduces the number of coherent two-level systems. All these reduction factors apply to the number N of two-level systems.

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