

Fourier Transform for a Single Nucleus of Spin $\frac{1}{2}$ in the Presence of a Strong rf Field*

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(Received 5 July 1972)

The problem of the Fourier transform of the response to a $\pi/2$ pulse of a single nucleus of spin $\frac{1}{2}$ interacting with a strong rf field is examined theoretically using the density-matrix master equation. In this experiment the nuclear spins are polarized in the rotating frame along a direction different from the laboratory z axis. It is shown that the resulting Fourier-transform spectrum differs in intensities from the steady-state double-resonance spectrum—in contrast with the usual single-resonance case. This phenomenon is understood physically in terms of a rotating-frame model.

In recent times the Fourier-transform technique has become the most popular way of obtaining NMR spectra in view of its several advantages over conventional steady-state techniques.¹ The basic principle involved in this method, in its simplest form, uses the fact that the NMR line shape and the response (free-induction signal) of the spin system to a $\pi/2$ pulse form a Fourier-transform pair.^{2,3} This method has been applied with success for several single-resonance problems,^{4,5} i. e., the only magnetic field that is present besides the pulsing radio-frequency (rf) field is the static field \vec{H}_0 . Though this method has been applied to double-resonance situations as in proton decoupled C¹³ Fourier NMR spectra,⁶ the situation is still quite similar to that of a single-resonance problem since the C¹³ nuclei are still polarized along the laboratory z axis. In this paper we have considered a more general situation where the nuclear spins under study are polarized in the rotating frame along an effective field direction, different from the laboratory z axis. Such a situation can easily be realized by applying a strong rf field $2H_2 \cos \omega_2 t$ along the x axis in the laboratory frame,⁷ as is usually done in the steady-state double-resonance experiments. In the following we shall outline the theory for obtaining the Fourier-transform spectrum, and apply it in particular to the single-spin- $\frac{1}{2}$ problem.

We shall consider the most simple experimental situation where the rf field \vec{H}_2 itself is pulsed. The signals would be most conveniently detected by referencing the detector at ω_2 , using a detection system as described by Redfield and Gupta.⁸ We first allow the nuclear spin system to interact with the static magnetic field $H_0 \hat{k}$ and \vec{H}_2 , and attain a steady state. In the rotating frame at angular frequency ω_2 the steady state is described by the spin density matrix $(\sigma_0 + \bar{\chi})$, where $\bar{\chi}$ describes the deviation from the thermal equilibrium density matrix σ_0 caused by \vec{H}_2 . (In this paper a tilde denotes quantities in the rotating frame.) The density matrix can be calculated using a set of simultaneous

equations.⁹ After the steady state is reached, \vec{H}_2 is simultaneously pulsed to an amplitude H_p and phase shifted by $\pi/2$ for a pulse duration τ , where H_p is much larger than all other fields in the rotating frame and τ is much shorter than the relaxation times. At the end of the pulse, \vec{H}_2 returns to its original amplitude and phase.

The time evolution of the density matrix $\sigma(t)$ is conveniently described by $\tilde{\eta}(t)$, defined by

$$\tilde{\sigma}(t) = \sigma_0 + \bar{\chi} + \tilde{\eta}(t) \quad (1)$$

and

$$\begin{aligned} \tilde{\eta}(0) = & \exp(-i\gamma H_p \tau \sum_i I_y(i)) \\ & \times (\sigma_0 + \bar{\chi}) \exp(i\gamma H_p \tau \sum_i I_y(i)) - (\sigma_0 + \bar{\chi}), \quad (2) \end{aligned}$$

where t is chosen to be zero at the end of the pulse. The density matrix $\tilde{\eta}(t)$ satisfies the Redfield equation¹⁰

$$\frac{d\tilde{\eta}_{\alpha\alpha'}}{dt} = -i[H^R, \tilde{\eta}]_{\alpha\alpha'} + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} \tilde{\eta}_{\beta\beta'}, \quad (3)$$

where the basis set α, β is chosen so that H^R is diagonal. In Eq. (3),

$$H^R = 2\pi \left(\sum_i A_i I_z(i) + \sum_{i < j} J_{ij} I(i) \cdot I(j) \right) + (D_{2+} + D_{2-}),$$

where $A_i = v_{0i} + (\omega_2/2\pi)$, $D_{2\pm} = \pi \sum_i v_{2i} I_z(i)$, and the magnetic field strengths v_{ki} are expressed in Hz by $v_{ki} = -\gamma_i H_k/2\pi$, $k=0, 2$.⁹ Solution of Eq. (3) in conjunction with the trace relation, $\text{Tr} \tilde{\eta} = 0$, determines $\tilde{\sigma}(t)$.

The magnetization in the laboratory frame is proportional to $\text{Tr}[\tilde{\sigma}(t) \vec{I}_y]$, and is the sum of a steady-state signal due to $(\sigma_0 + \bar{\chi})$ and a free-induction signal due to $\tilde{\eta}(t)$. The steady-state signal will produce a δ -function response at $\omega = \omega_2$ in the Fourier transform (as well as in the steady-state experiment), and should be subtracted from the total signal before carrying out the Fourier transformation. Assuming that this subtraction has been done, the Fourier spectrum is given by¹

$$S(\omega)^{\text{FT}} = K \int_0^\infty \text{Tr}[\tilde{\eta}(t) \vec{I}_y] e^{i\omega t} dt. \quad (4)$$

Single-Spin- $\frac{1}{2}$ Problem

We shall consider the response to a $\pi/2$ pulse. Further, we shall assume that the relaxation is through external isotropic random fields.^{11,12} H^R is diagonal in the basis $|1\rangle = \alpha \cos\theta + \beta \sin\theta$, $|2\rangle = \beta \cos\theta - \alpha \sin\theta$, with eigenvalues $E_1 = \pi(A^2 + v_2^2)^{1/2}$ and $E_2 = -\pi(A^2 + v_2^2)^{1/2}$, where $\tan 2\theta = v_2/A$. In this basis,⁹

$$\sigma_0 = \frac{1}{2} - \frac{(2\pi q v_0) \pi}{E_1 - E_2} \begin{pmatrix} A & -v_2 \\ -v_2 & -A \end{pmatrix}, \quad (5)$$

and the matrix elements of $\bar{\chi}$ are $\bar{\chi}_{11} = \bar{\chi}_{22} = 0$, $\text{Re}\bar{\chi}_{12} = -(2\pi q v_0) (\pi v_2) T_2^2 (E_1 - E_2) / [1 + T_2^2 (E_1 - E_2)^2]$, and $\text{Im}\bar{\chi}_{12} = -(2\pi q v_0) (\pi v_2) T_2 / [1 + T_2^2 (E_1 - E_2)^2]$, where $q = \hbar/2kT$, $T_2^{-1} = 2f\tau_c$, f is the mean-square amplitude of the random fields, and τ_c is the correlation time. Solving Eq. (3) for isotropic random fields and evaluating $\bar{\eta}(0)$ from Eq. (2) for a $\pi/2$ pulse we get

$$\bar{\eta}_{11}(t) = \bar{\eta}_{11}(0) e^{-t/T_2}, \quad (6)$$

$$\bar{\eta}_{12}(t) = \bar{\eta}_{12}(0) e^{-i(E_1 - E_2)t} e^{-t/T_2}$$

and

$$\bar{\eta}_{11}(0) = [(2\pi q v_0) \pi (A - v_2) / (E_1 - E_2)] - \text{Re}\bar{\chi}_{12}, \quad (7)$$

$$\bar{\eta}_{12}(0) = -[(2\pi q v_0) \pi (A + v_2) / (E_1 - E_2)] - \text{Re}\bar{\chi}_{12}.$$

Now as a further simplification, we assume that the irradiation strength is strong enough to satisfy the Bloch approximation^{9,13} ($|E_1 - E_2| \gg T_2^{-1}$). Under this condition, Eqs. (7) simplify to $\bar{\eta}_{11}(0) = -\bar{\eta}_{12}(0) = (2\pi q v_0) (\cos 2\theta) / 2$.

We now obtain the Fourier-transform spectrum $S(\omega)^{\text{FT}}$ by evaluating Eq. (4). The imaginary part of Eq. (4) is usually identified with the steady-state NMR absorption spectrum, and is given by

$$S^{\text{FT}}(\omega) = K_F (1 + \cos 2\theta) f(\omega - \omega_2 + E_1 - E_2) - K_F (1 - \cos 2\theta) f(\omega - \omega_2 - E_1 + E_2) - 2K_F \sin 2\theta f(\omega - \omega_2), \quad (8)$$

where $f(\omega) = (2\pi q v_0) \cos 2\theta T_2 / (1 + T_2^2 \omega^2)$ and $K_F = K/8$. The $\cos 2\theta$ term in $f(\omega)$ corresponds to the population difference between levels 1 and 2. The real part of (4) maybe obtained from (8) by replacing $f(\omega)$ with $g(\omega) = -(2\pi q v_0) \cos 2\theta T_2^2 \omega / (1 + T_2^2 \omega^2)$. The Fourier-transform signal given by Eq. (8) corresponds to three resonances. The feature at $\omega = \omega_2$ corresponds to resonance absorption produced by \bar{H}_e . In addition, there occur two features inverted with respect to each other; S_+^{FT} at $\omega = \omega_2 + E_2 - E_1$ and S_-^{FT} at $\omega = \omega_2 - E_2 + E_1$. The intensity ratio of these features is given by

$$S_+^{\text{FT}}/S_-^{\text{FT}} = -(1 + \cos 2\theta) / (1 - \cos 2\theta). \quad (9)$$

Equations (8) and (9) are to be compared with the

steady-state double-resonance absorption-mode spectrum detected at the exciting frequency ω_1 , which is given under the Bloch approximation as⁹

$$S^{\text{SS}}(\omega_1) = K_S (1 + \cos 2\theta)^2 f(\omega_1 - \omega_2 + E_1 - E_2) - K_S (1 - \cos 2\theta)^2 f(\omega_1 - \omega_2 - E_1 + E_2), \quad (10)$$

where K_S is a constant. The Fourier-transform spectrum in Eq. (8) differs from the steady-state double-resonance spectrum in Eq. (10) in several respects. There is a new Lorentzian absorption shape at ω_2 in the Fourier spectrum which is absent in Eq. (10). Furthermore, the features at $\omega_1 = \omega_2 \pm (E_2 - E_1)$ in the steady-state spectrum have the intensity ratio⁹

$$S_+^{\text{SS}}/S_-^{\text{SS}} = -(1 + \cos 2\theta)^2 / (1 - \cos 2\theta)^2. \quad (11)$$

Therefore, the Fourier-transform spectrum of a single spin $\frac{1}{2}$ in the presence of a strong rf field is not proportional to the steady-state double-resonance spectrum.

The differences are explained by viewing the motion of the magnetization \vec{M} in the rotating frame. Before the pulse, \vec{M} is stationary in the rotating frame.¹⁴⁻¹⁶ If the Bloch approximation is valid \vec{M} is aligned along the effective field \vec{H}_e , where \vec{H}_e is oriented in the $\bar{x}z$ plane at an angle 2θ with respect to the z axis. The $\pi/2$ pulse rotates \vec{M} away from its steady-state orientation. As \vec{M} relaxes back to its steady state, it precesses about \vec{H}_e with a frequency $E_1 - E_2$.¹⁷ The signal which is detected is due to the projection of \vec{M} onto the laboratory xy plane. The projection yields two counter rotating components producing signals proportional to $\frac{1}{2}(\cos 2\theta + 1) \cos(\omega_2 - E_1 + E_2)t$ and $\frac{1}{2}(\cos 2\theta - 1) \cos(\omega_2 + E_1 - E_2)t$. In addition, the recovering component of \vec{M} along \vec{H}_e produces a signal proportional to $\sin 2\theta \cos \omega_2 t$. This explains the intensity ratio¹⁸ in Eq. (9) as well as the Lorentzian shape at ω_2 .

In steady-state double resonance, the weak observing rf field \vec{H}_1 is decomposed⁷ into two counter rotating fields proportional to $\frac{1}{2}(\cos 2\theta \pm 1) (\cos \omega' t \hat{i}_e \mp \sin \omega' t \hat{j}_e)$, where $\omega' = \omega_1 - \omega_2$ and \hat{i}_e and \hat{j}_e are unit vectors defining the plane normal to \vec{H}_e , and fixed in the rotating frame. The signals giving rise to S_+^{SS} and S_-^{SS} therefore already have amplitudes proportional to $(1 + \cos 2\theta)$ and $(1 - \cos 2\theta)$ before their projection on to the laboratory xy plane. This projection as described in previous paragraph, results in signals given in Eq. (10) and the intensity ratio in Eq. (11).

It is thus seen that the Fourier spectrum for a spin system interacting with a strong rf field is not proportional to the steady-state double-resonance spectrum if the nuclei under study are not polarized along the laboratory z axis. It is also interesting to note that by this technique one can observe the signals that are very close to and at the irradiating

frequency. This is difficult with conventional steady-state double-resonance experiments because

of the presence of a strong beat pattern near the irradiation.

*Work supported by the National Science Foundation under Research Grant No. GP-28921.

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Analytic Self-Consistent-Field Wave Functions for Transition-Metal Atoms

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(Received 20 July 1972)

Analytic Hartree-Fock-Roothaan calculations have been carried out for the states arising from the $3d^n 4s^2$ configurations for neutral transition-metal atoms and from the $3d^n$ configurations for the doubly ionized ions. The atomic orbitals have been expanded in terms of linear combinations of Slater-type functions, 21 of them for the neutral atoms and 18 for the doubly ionized ions.

A little more than a decade ago Watson^{1,2} performed a rather large number of analytic restricted Hartree-Fock calculations on atoms and ions belonging to the first transition series. He obtained analytic self-consistent-field (SCF) wave functions for the various states arising from the electronic configurations that he studied. Subsequently other investigators (e.g., see Refs. 3-7) have reported results of similar calculations based on the selection of various basis sets of different sizes. The primary purpose of the present paper is to present additional refinements of the previous calculations with a basis set of reasonable size. Specifically the computations carried out here are for the various term energies for states arising from the $3d^n 4s^2$ configurations for neutral atoms (I) and from the $3d^n$ configurations for the doubly ionized ions (II). The actual calculations were performed in double precision on an IBM 360/67. The atomic SCF program is a modification of the scheme set forth by Roothaan and Bagus.⁸

The initial or primitive basis set employed consists of the usual Slater-type functions (STO's) of the form

TABLE I. Comparison of excited-state energies (in a.u.) of Mn obtained from orbital exponents optimized for the ground state with those from reoptimized orbital exponents.

State	Reoptimization neglected	Reoptimization done
⁴ G	-1149.7224	-1149.7226
⁴ F	-1149.6264	-1149.6271
⁴ D	-1149.6876	-1149.6880
⁴ P	-1149.7007	-1149.7010
² I	-1149.6626	-1149.6631
² H	-1149.6164	-1149.6171
² G	-1149.5511	-1149.5518
² F	-1149.6099	-1149.6106
² D	-1149.5131	-1149.5137
² P	-1149.4121	-1149.4125
² S	-1149.5593	-1149.5596