Different averaging methods in magnetic-resonance theory

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The causes of the discrepancy between J. Waugh's mean Hamiltonian theory based on the Magnus expansion, in the one hand, and the averaging method, on the other, are considered. It is shown that the contributions to the line width from the main line and from the satellite are not separated; in a number of cases this is the cause of the discrepancy between the Waugh theory and the experimental data. The general results are illustrated for the case of a two-level system located in a linearly polarized alternating field (the Bloch-Siegert shift).

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In connection with the development of multipulse methods of narrowing NMR lines in solids, much interest is attached in recent years to problems in which the Hamiltonian of the spin system is a rapidly oscillating function of time. This situation is generally typical of magnetic resonance. The time dependence of the Hamiltonian is usually eliminated by transforming to a rotating coordinate system. In this system, to a certain approximation, the behavior of the spin system is described by a time-independent effective Hamiltonian. The situation in multipulse experiments is more complicated. It is therefore meaningful to pose the general mathematical problem of the behavior of a spin system acted upon by rapidly oscillating external actions. Problems of this kind arise not only in magnetic resonance, but also in other branches of physics such as in optics.

There are at present three different theoretical approaches to the study of such problems: Waugh's mean-Hamiltonian theory,[1,2] based on the Magnus expansion,[3] the canonical-transformation method developed in the papers of Provotorov and co-workers,[4,5] and our approach[6] based on the Krylov-Bogolyubov-Mitropol'skiĭ averaging method[7] and on the canonical variant of this method.[8]

The starting point in all three approaches is the Liouville equation for the statistical operator

$$i\frac{d\rho}{dt}=[V(t)+H,\rho],\tag{1}$$

where $V(t)$ is the Hamiltonian of the rapidly oscillating external action (in particular, the Hamiltonian of a multipulse sequence), and H is the Hamiltonian of the spin-spin interactions. With the aid of the unitary transformation

$$\tilde\rho(t)=L(t)\rho(t)L^{-1}(t),$$

where

$$idL/dt=-L(t)V(t),\tag{2}$$

Eq. (1) is transformed into

$$id\tilde\rho/dt=[\tilde H(t),\tilde\rho],\tag{3}$$

where $\tilde H(t)$ is a periodic function of the time with period t_c. A condition usually satisfied in multipulse experiments is $t_c\|H\|\ll 1$, where $\|H\|$ is the "magnitude" of the Hamiltonian in frequency units).

The results obtained by Provotorov *et al.*[4,5] and in the canonical variant of the averaging method[8] are in the main in agreement. At the same time the mean Hamiltonians calculated by Waugh's method and by the averaging method differ already in second order,[6] and in a number of cases this difference leads to fundamentally different physical results. The purpose of the present paper is to find the causes of this discrepancy and to investigate to greater detail its consequences.

The gist of the approach proposed by Waugh is the following: if we introduce an evolution operator defined by

$$\tilde\rho(t)=U(t)\tilde\rho(0)U^{-1}(t),\tag{4}$$

$$dU/dt=-i\tilde H(t)U(t),\tag{5}$$

the solution of Eq. (5), using the Magnus expansion,[3] can be written in the form

$$U(t)=\exp(F_1(t)+F_2(t)+\dots),\tag{6}$$

where

$$F_1(t)=-i\int_0^t\tilde H(t')dt',\tag{7}$$

$$F_2(t)=-\frac{1}{2}\int_0^t dt_1\int_0^{t_1}dt_2[\tilde H(t_1),\tilde H(t_2)].\tag{8}$$

Since $\tilde H(t)$ is a periodic function of time, it can be expanded in a Fourier series

$$\tilde H(t)=\sum_{n=-\infty}^{\infty}H_n e^{i\omega_n t},\quad \omega_n=2\pi n/t_c,$$
$$H_n=\frac{1}{t_c}\int_0^{t_c}dt\tilde H(t)e^{-i\omega_n t}.\tag{9}$$

Substituting (9) in (7) and (8) and integrating, we obtain the following representations for F_1 and F_2:

$$F_1(t)=-itH_0-\sum_{n\neq 0}\frac{e^{i\omega_n t}-1}{\omega_n}H_n,\tag{10}$$

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$$F_2(t)=-it\sum_{n\neq 0}\frac{1}{2\omega_n}[H_n,H_{-n}]-it\sum_{n\neq 0}\frac{1}{2\omega_n}[H_0,H_n]$$

$$+it\sum_{n\neq 0}\frac{1}{2\omega_n}e^{i\omega_n t}[H_n,H_0]$$

$$-\sum_{n\neq 0}\frac{1}{2\omega_n{}^2}[H_n,H_0](e^{i\omega_n t}-1)-\sum_{n,m\neq 0}\frac{1}{2\omega_m\omega_n}[H_n,H_m](e^{i\omega_n t}-1)$$

$$+\sum_{n\neq 0,n\neq m}\frac{1}{2\omega_n(\omega_n+\omega_m)}[H_n,H_m](\exp\{i(\omega_n+\omega_m)t\}-1). \tag{11}$$

For instants of time that are multiples of t_c we can represent $U(t)$ in the form

$$U(t)=\exp\{-it(\bar{H}^{(1)}+\bar{H}^{(2)}+\ldots)\}_{t=Nt_c}. \tag{12}$$

It is seen therefore that $\tilde{\rho}(t)$ takes the form of the solution of the Liouville equation (3) with a time-independent Hamiltonian

$$\rho(t)=\exp(-i\bar{H}t)\rho(0)\exp(i\bar{H}t), \tag{13}$$

$$\bar{H}=\bar{H}^{(1)}+\bar{H}^{(2)}+\ldots, \tag{14}$$

where

$$\bar{H}^{(1)}=H_0, \tag{15}$$

$$\bar{H}^{(2)}=\sum_{n\neq 0}\frac{1}{2\omega_n}[H_n,H_{-n}]+\sum_{n\neq 0}\frac{1}{\omega_n}[H_0,H_n]. \tag{16}$$

The Hamiltonian (14) is usually called the mean Hamiltonian.

We note now that if (11) were to contain only terms linear in t and oscillating terms, we could expand (6) in the case of long times in powers of the oscillating terms. Since, however, (11) contains terms of the type $t\exp(i\omega_n t)$, no such expansion is possible.

Terms of this type are well known in nonlinear mechanics (they are called secular terms). Their appearance is evidence that ordinary perturbation theory in inapplicable. One of the convenient methods that makes it possible to get rid of terms of this type is the Krylov-Bogolyubov-Mitropol'skiĭ averaging method. As applied to mangetic-resonance problems, this method was developed in our earlier papers.[6,8] In this approach the solution of Eq. (3) is sought in the form

$$\tilde{\rho}(t)=\xi(t)+\rho^{(1)}(t,\xi)+\rho^{(2)}(t,\xi)+\ldots, \tag{17}$$

where $\xi(t)$ is a slowly varying part of the density matrix, and $\rho^{(1)},\rho^{(2)}$, etc. contain the rapid oscillations. The equation for ξ is closed (i.e., it does not contain the time explicitly), and in second order it can be represented in the form[6]

$$id\xi/dt=[\bar{H}',\xi], \tag{18}$$

where

$$\bar{H}'=H_0+\sum_{n\neq 0}\frac{1}{2\omega_n}[H_n,H_{-n}]. \tag{19}$$

In the corresponding order, Eq. (17) takes the form

$$\tilde{\rho}(t)=\xi(t)-\sum_{n\neq 0}\frac{1}{\omega_n}[H_n,\xi(t)]e^{i\omega_n t}, \tag{20}$$

where

$$\xi(t)=\exp(-i\bar{H}'t)\xi(0)\exp(i\bar{H}'t), \tag{21}$$

while $\xi(0)$ takes according to (20) the form

$$\xi(0)=\rho(0)+\sum_{n\neq 0}\frac{1}{\omega_n}[H_n,\rho(0)].$$

We have thus for $\tilde{\rho}(t)$

$$\tilde{\rho}(t)=e^{-i\bar{H}'t}\Big(\rho(0)+\sum_{n\neq 0}\frac{1}{\omega_n}[H_n,\rho(0)]\Big)e^{i\bar{H}'t}$$

$$-\sum_{n\neq 0}\frac{1}{\omega_n}[H_n,e^{-i\bar{H}'t}\rho(0)e^{i\bar{H}'t}]e^{i\omega_n t}. \tag{22}$$

Expression (22), unlike (13), is valid for arbitrary instants of time. If we put here $t=Nt_c$, and use a power expansion of (13)

$$\sum_{n\neq 0}\frac{1}{\omega_n}[H_0,H_n]$$

(it can be seen from (14)–(16) and (19) that

$$\bar{H}=\bar{H}'+\sum_{n\neq 0}\frac{1}{\omega_n}[H_0,H_n]),$$

then (22) and (13) coincide. When calculating the mean values of the observable quantities in (17) and accordingly in (22), however, it is necessary to discard the rapidly oscillating terms. Indeed, in multipulse NMR experiments, as well as in certain other NMR procedures, one measures the damping with time of the transverse magnetization, followed by taking the Fourier transform of this signal. In the language of Fourier transforms, the slowly varying part $\xi(t)$ in the expansion (17) for $\tilde{\rho}(t)$ corresponds to the main line, and the rapidly oscillating terms correspond to the satellites. Thus, in the averaging method we should use in the calculation of the mean values the formula

$$\langle A'(t)\rangle=\mathrm{Sp}\Big\{\tilde{A}(t)e^{-i\bar{H}'t}\Big(\rho(0)+\sum_{n\neq 0}\frac{1}{\omega_n}[H_n,\rho(0)]\Big)e^{i\bar{H}'t}\Big\}, \tag{23}$$

where $\bar{H}'$ is given by (19), and $\tilde{A}(t)=L(t)AL^{-1}(t)$.

At the same time, Waugh's theory yields

$$\langle A(t)\rangle=\mathrm{Sp}\{Ae^{-i\bar{H}t}\rho(0)e^{i\bar{H}t}\} \tag{24}$$

(we have used here the fact that $L(Nt_c)=1$ is cyclic).

The time dependence in (23) and (24) is determined by the different mean Hamiltonians. It is easily seen that they are connected by a unitary transformation. Indeed, we stipulate that

$$U\bar{H}'U^{-1}=\bar{H}$$

with appropriate accuracy in terms of the small parameter $t_c\|H\|$. This condition is satisfied by U in the form

$$U=\exp\Big\{-\sum_{n\neq 0}\frac{1}{\omega_n}H_n\Big\}. \qquad (25)$$

With the aid of this unitary operator it is easy to find the connection between the mean values (23) and (24). Indeed,

$$\langle A'(t)\rangle=\mathrm{Sp}\Big\{U\bar{A}U^{-1}Ue^{-i\bar{H}'t}U^{-1}U\Big(\rho(0)+\sum_{n\neq 0}\frac{1}{\omega_n}[H_n,\rho(0)]\Big)U^{-1}Ue^{i\bar{H}'t}U^{-1}\Big\}$$
$$=\mathrm{Sp}(U\bar{A}U^{-1}e^{-i\bar{H}t}\rho(0)e^{i\bar{H}t}]=\langle\bar{A}(t)\rangle+\sum_{n\neq 0}\frac{1}{\omega_n}\mathrm{Sp}([H_n,\bar{A}]e^{-i\bar{H}t}\rho(0)e^{i\bar{H}t}). \qquad (26)$$

The presence of the last term in (26), as follows from the foregoing reasoning, is due to the fact that in Waugh's mean-Hamiltonian theory there is no separation of the contributions made to the width by the main line and by the satellites. The term

$$\sum_{n\neq 0}\frac{1}{\omega_n}[H_0,H_n]$$

in the averaging method causes the presence of satellites, whereas in Waugh's theory it is included in the mean Hamiltonian. This is indeed the reason why Waugh's theory leads in a number of cases to incorrect physical results.

By way of example illustrating the general results above, we consider the calculation of the so-called Bloch-Siegert shift.[9] It is known that when a two-level system is in a resonant linearly polarized field, its frequency is shifted. The Hamiltonian of such a system is of the form

$$H=\omega_0 I_z+2\omega_1\cos\omega_0 t I_x, \qquad (27)$$

where ω_0 is the eigenfrequency and ω_1 the amplitude of the alternating field in frequency units. If we change to a rotating coordinate frame, the Hamiltonian (27) takes the form

$$H=\omega_1 I_x+{}^1/_2\omega_1(I^+e^{i2\omega_0 t}+I^-e^{-i2\omega_0 t}). \qquad (28)$$

Since $\omega_0\gg\omega_1$, this problem can be analyzed on the basis of the mean-Hamiltonian theory. As shown in Ref. 6, if we use the Waugh mean Hamiltonian (14), we obtain an incorrect sign of the Bloch-Siegert shift, whereas the averaging method yields the correct result.

We examine now this question in greater detail. We shall assume that at the initial instant of time a preparatory pulse directed the magnetization along the x axis, i.e., the density matrix is of the form

$$\rho(0)=\frac{1}{\mathrm{Sp}(1)}\{1+aI_x\},\qquad a=\frac{\mathrm{Sp}(1)\langle I_x(0)\rangle}{\mathrm{Sp}(I_x^2)}. \qquad (29)$$

(This choice of initial conditions makes it easy to determine the magnitude and the sign of the frequency shift.) We calculate with the aid of Waugh's method and with the aid of our method the time dependence of the mean squared value of the z component of the magnetization (it will be seen from the final results that its behavior leads readily to conclusions concerning the magnitude and sign of the frequency shift). Using (13), (15), and (16) we can easily see that the Waugh theory yields

$$\langle I_z(t)\rangle=\frac{\omega_1}{4\omega_0}\langle I_x(0)\rangle(\cos\omega_e t-1),\qquad \omega_e=\Big[\omega_1^2+\Big(\frac{\omega_1^2}{4\omega_0}\Big)^2\Big]^{1/2}. \qquad (30)$$

Obviously, $\langle I_z(t)\rangle\leqslant 0$. This means that the frequency shift equals $\omega_1^2/4\omega_0$ and is negative, whereas it is well known[9] that it is positive.

We now calculate $\langle I_z(t)\rangle$ by the averaging method. Using (19) and (23) we obtain

$$\langle I_z(t)\rangle=\frac{\omega_1}{4\omega_0}\langle I_x(0)\rangle(\cos\omega_e t+1). \qquad (31)$$

In this case $\langle I_z(t)\rangle\geqslant 0$, and the Bloch-Siegert shift is of the correct sign.

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