Application of average Hamiltonian theory to the NMR of solids

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The question of the validity of the average Hamiltonian theory is discussed. This is derived from consideration of the Floquet theorem for periodic systems. A perturbation scheme is developed and shown to give an average Hamiltonian equivalent to that obtained from the Magnus expansion. The convergence condition is shown to depend on the existence of resonances. These results are applied to a discussion of pulse spin-locking experiments.

INTRODUCTION

In the development of high-resolution NMR spectroscopy the average Hamiltonian theory (AHT) has evolved as a powerful method of analysis.[1–3] It rests on the principle that under suitable conditions the evolution of a spin system driven by a time-dependent external field can be described by the average effect of the field over one cycle of its oscillation. The external field, if carefully selected, can be used to selectively average out undesirable parts of the internal spin interactions. The aim is to remove portions of the interaction which cause line broadening while at the same time to retain those parts which yield useful spectroscopic information. For this, AHT has been widely successful.[1–3]

Recently, in the literature, conflicting opinions have appeared as to the validity of the average Hamiltonian approach. The objections arise from results obtained from multiple-pulse experiments.[4–10] One group of these, carried out by Erofeev and Schumm,[6] and also by Erofeev *et al.*,[7] provides new data on the behavior of a spin system under pulse spin-locking conditions. In the experiment the fluorine nuclei in CaF_2 are subject to a periodic train of pulses polarized along the x axis of the rotating frame, each with a flip angle of θ. Erofeev *et al.*[6,7] find two main results. The first is that after a time period of a few T_2 there appears a quasistationary magnetization dependent on θ, the pulse spacing, and the detuning from the line center. In a theoretical analysis of these results, Ivanov, Provotorov, and Fel'dman[8,9] maintain, as part of their conclusion, that the average Hamiltonian theory cannot predict the quasistationary state. In fact that is incorrect as will be shown below. Subsequently the pulse spin-locking experiment has been repeated by Suwelack and Waugh.[10] They use an average Hamiltonian formalism to compute the behavior of the quasistationary magnetization. Both sets of results will be discussed in detail in Sec. V.

The second finding by Erofeev *et al.*[6,7] poses a more serious question as to the validity of AHT. The quasistationary magnetization is found to have a slow exponential decay. Such long-time decays are found more generally in dipole systems evolving under external fields.[11,12] AHT predicts that the spin system should appear to evolve under a time-independent Hamiltonian and hence, by the general arguments of spin thermodynamics, should reach a stationary state.[13] This holds true for times $t < T_{1\rho}$ when spin-lattice relaxation is negligible. However, contrary to this, a variety of experiments show that the quasistationary state does not persist; rather, it decays over a time scale less than $T_{1\rho}$. This decay has been attributed by Cantor[12] to the failure of the Magnus expansion under certain conditions. This will be discussed below and a different reason will be given.

It is important to settle these questions. One concern is that some of the criticisms made about the theory are due to misunderstandings of exactly what conclusions can be drawn from an average Hamiltonian analysis and under what conditions the theory may be applied. Secondly, various other fields make use of similar theories. For example, the description of multiphoton processes in molecules has been studied within the framework[14] as has the interaction of molecules and intense laser fields.[15] In addition, ever more complicated pulse sequences are being applied to spin systems in order to selectively excite multiple quantum transitions.[16]

In Sec. II the criteria for the existence of an exponential solution to the Schrödinger equation are reviewed. As this assumption is not really necessary for the average Hamiltonian concept, a different approach is taken in Sec. III using Floquet theory[17,18] and is shown to give an expression equivalent to the Magnus expansion. Section IV covers the convergence conditions for the average Hamiltonian and in Sec. V the pulsed spin-locking experiment is treated.

II. MAGNUS EXPANSION

The usual derivation of the average Hamiltonian is based on the following: It is known that the evolution operator for a time-independent system is in the form of an exponential operator. Hence, it is assumed that even in the time-dependent case, the Schrödinger equation,

$$\frac{dU(t)}{dt} = -i\mathscr{H}(t)U(t) , \quad (1)$$

with initial condition $U(0)=1$ has a solution given by

$$U(t)=e^{-iH(t)} , \quad (2)$$

where $H(t)$ is a continuous function of time. The analysis then proceeds by a series expansion of $H(t)$ into

$$H(t)=H^{(0)}(t)+H^{(1)}(t)+H^{(2)}(t)+ \cdots . \quad (3)$$

Various methods have been used to solve for the $H^{(n)}(t)$: first by Magnus[19] and later by Wilcox[20] and Haeberlen.[2] For reference the first two terms are given here[21]:

$$H^{(0)}(t)=\int_0^t \mathscr{H}(t_1)dt_1 , \quad (4a)$$

$$H^{(1)}(t)=\frac{-i}{2}\int_0^t \int_0^{t_2} [\mathscr{H}(t_2),\mathscr{H}(t_1)]dt_1 dt_2 . \quad (4b)$$

Next, Eq. (1) is specialized to the case where the Hamiltonian is periodic, i.e., $\mathscr{H}(t+\tau)=\mathscr{H}(t)$. With this, the integration of Eq. (4) in the interval $[0,\tau]$ is the same as for $[n\tau,(n+1)\tau]$. Thus once the solution is obtained for one cycle it can be extended to times $N\tau$ for $N=1,2\ldots$ simply by setting $U(N\tau)=\{\exp[-H(\tau)]\}^N$. In the literature, $H(\tau)$ is divided by τ to provide a time-independent effective Hamiltonian. The zeroth-order term, $\overline{H}^{(0)}=(1/\tau)H^{(0)}(\tau)$, is called the average Hamiltonian, while $\overline{H}^{(1)}=(1/\tau)H^{(1)}(\tau)$ is the first-order correction.

Though the effective Hamiltonian approach provides a considerable simplification in the calculation, there is now the restriction that the system can only be observed once every cycle, i.e., only at $t=N\tau$. A point sometimes overlooked is this trade-off of the loss of information about the state of the system, at times other than multiples of the period, in exchange for a simpler description of the evolution operator.[8,9] Note however, that often it is exactly the extra information within the cycle which causes the line broadening in the resulting spectra.

The above arguments have two weaknesses which should be kept distinct. Each could lead to a failure of AHT. The first is the assumption that $H(t)$ exists for all t. In his original paper Magnus[19] shows that although $H(t)$ always exists for t close enough to zero it is not necessarily global. In fact for $H(t)$ to be well defined for all t rather stringent restrictions must be placed on $\mathscr{H}(t)$. Reference 12 contains a discussion of the implications of this.

The second weakness has to do with the convergence properties of the series expansion Eq. (3) of $H(t)$. Often the rough criterion is used that, as $H^{(n)}(t)$ contains n-fold products of $\mathscr{H}(t)$, and whereas each integration produces a factor of τ, the relative size of the term goes like (Ref. 1–3) $(\langle\mathscr{H}^2\rangle^{1/2}\tau)^n$. Hence, the series should converge for $\langle\mathscr{H}^2\rangle^{1/2}\tau<1$. While this is a sometimes useful guideline it is not rigorous and can be misleading. Within this question of convergence lies the reason for the failure of the AHT to correctly predict the long-time decay observed in the pulse experiments. We will return to this point later.

First we consider the existence of $H(t)$. Equation (2) can be thought of simply as a transformation of variables from $U(t)\rightarrow H(t)$. As such, $e^{-iH(t)}$ should satisfy the differential Eq. (1). To differentiate the exponential operator we make use of a formula due to Wilcox[20]:

$$\frac{d}{dt}\exp[-iH(t)]=-i\int_0^1 e^{-iuH}\frac{dH}{dt}e^{-i(1-u)H}du . \quad (5)$$

Let Eq. (5) be multiplied through from the right by e^{iH}. The left-hand side of the result is by definition, $-i\mathscr{H}(t)$. Next, the integration is carried out by first taking matrix elements of both sides of Eq. (5) in the basis $|\psi_i\rangle$ of the operator $H(t)$. After integrating over u, a system of nonlinear differential equations for the matrix elements of $H(t)$ is found

$$-i\langle\psi_i\,|\,\mathscr{H}(t)\,|\,\psi_j\rangle=\frac{\exp[-i(\omega_i-\omega_j)]-1}{\omega_i-\omega_j}\times\left\langle\psi_i\left|\frac{dH}{dt}\right|\psi_j\right\rangle . \tag{6}$$

The initial condition is $H(0)=0$. Note that the eigenvalues ω_i are defined by

$$H(t)\,|\,\psi_i(t)\rangle=\omega_i(t)\,|\,\psi_i(t)\rangle ,$$

and are time dependent.

The criterion for a solution of Eq. (6) is as follows: If there exists a neighborhood of the point $[t_0,H(t)]$ at which

$$(\{\exp[-i(\omega_i-\omega_j)]-1\}/(\omega_i-\omega_j))^{-1}$$

is continuously differentiable then there exists a solution, satisfying the initial condition, for values of t sufficiently close to t_0.[22] This will not be satisfied at those points where[19]

$$\omega_i-\omega_j=n2\pi,\quad n=\pm1,\pm2,\ldots . \tag{7}$$

At such points a solution to Eq. (6) does not exist and hence, the assumption of an exponential solution to Eq. (1) is not valid. When $t=0$, because

$$\lim_{x\to0}\frac{e^x-1}{x}=1 ,$$

the convergence criterion is satisfied. Hence, there is always a well-defined solution $H(t)$, for times t close enough to zero. Since $\mathscr{H}(t)$ is Hermitian, the eigenvalues of $H(t)$ are all purely real. Thus, except in special circumstances, as t increases a value $t_{\max}$ is reached for which Eq. (7) holds and there is a singularity in $H(t)$. Only for the trivial case when $dH(t)/dt$ commutes with $H(t)$, or equivalently when $\mathscr{H}(t)$ commutes with itself at different times, is the solution to Eq. (6) global.

We see from this that the existence problem arises from the insistence that the solution take an exponential form. This induces a transformation of a linear system of differential equations into a nonlinear system and admits the possibility of singularities in the solution.

III. FLOQUET THEORY

The problem with the Magnus solution is that it tries to impose a structure on the evolution operator which is too restrictive. On the other hand, AHT makes use of it for the special case of periodic Hamiltonians and for the special times $t=N\tau$. Hence, it would be advantageous to begin from a more suitable point.

Given a periodic Hamiltonian with period τ, a group of symmetry operators $\mathscr{P}_{N\tau}$ can be defined which commute with $\mathscr{H}(t)$ and have the property of transforming solutions at time t to those at time $t+N\tau$, i.e., $\mathscr{P}_{N\tau}:U(t)\to U(t+N\tau)$. Hence, $U(t+N\tau)$ and $U(t)$ are both solutions of Eq. (1) with the same initial condition and are therefore related by a unitary transformation which itself does not depend on time, thus

$$U(t+\tau)=U(t)e^{-i\hat{H}\tau} . \tag{8}$$

The caret serves to distinguish the Floquet Hamiltonian from the effective Hamiltonian, $\overline{H}$, obtained via the Magnus expansion. Note that the order of the operators in (8) is important. Reverse the order and Eq. (1) will no longer be satisfied. From Eq. (8) the evolution operator can be written in the form[17,18,22]

$$U(t)=P(t)e^{-i\hat{H}t} , \tag{9}$$

with $P(t)$ defined as $P(t)=U(t)e^{i\hat{H}t}$. It is easily verified that $P(t)$ is periodic with period τ. At times $t=N\tau$, the propagator is thus $U(N\tau)=e^{-\hat{H}N\tau}$. Exactly as propounded by the average Hamiltonian theory, the system, when observed stroboscopically appears to evolve under a time-independent Hamiltonian. However, thus far there is no connection with the Magnus form usually used.

To continue, substitute Eq. (9) into the Schrödinger equation. This gives

$$\frac{dP(t)}{dt}=-i\mathscr{H}(t)P(t)+iP(t)\hat{H} , \tag{10}$$

with $P(0)=1$. Unlike Eq. (6), encountered for the exponential solution, this is a linear system. A perturbation scheme is obtained by invoking the following expansions:

$$P(t)=\sum_n\lambda^nP_n(t) , \tag{11a}$$

$$\hat{H}=\sum_n\lambda^n\hat{H}_n , \tag{11b}$$

and with the substitution $\mathscr{H}\to\lambda\mathscr{H}$. The factor λ has been introduced to keep track of the various orders and is set to 1 in the end. Next, Eqs. (11a) and (11b) are inserted into Eq. (10) and the coefficients of λ^n on each side compared. This yields the main result

$$P_n(t) = -i\int_0^t \left[\mathscr{H}(t')P_{n-1}(t') - \sum_{k=1}^{n-1} P_k(t')\hat{H}_{n-k} - \hat{H}_n\right] dt' , \tag{12a}$$

$$\hat{H}_n = \frac{1}{\tau}\int_0^\tau \left[\mathscr{H}(t')P_{n-1}(t') - \sum_{k=1}^{n-1} P_k(t')\hat{H}_{n-k}\right] dt' . \tag{12b}$$

The $\hat{H}_n$ are obtained with the additional requirement that each $P_n(t)$ be periodic with period τ. Note also the existence of the two zeroth-order terms $P_0 = 1$ and $\hat{H}_0 = 0$.

A different perturbation solution has been given by Barone, Narcowich, and Narcowich.[18] That version, however, results in a set of integral operator equations which are more difficult to solve than the present equations. Our result is simpler since, unlike Barone *et al.*,[18] we remove any large static part of the Hamiltonian by transformation to an interaction picture before proceeding with the perturbation solution, Eq. (12).

A quick glance at Eq. (12) and a comparison with Eq. (4) does not reveal much to support any similarity to the Magnus expression. In fact, it is not clear that $\hat{H}_n$ is even Hermitian for each order, though the sum must be. We consider first the $n = 1$ case. Then, as the only lower order involved is $P_0 = 1$, Eq. (12b) yields

$$\hat{H}_1 = (1/\tau)\int_0^\tau \mathscr{H}(t')dt' .$$

This is identical to the average Hamiltonian $\bar{H}^{(0)} = (1/\tau)H^{(0)}(\tau)$ as given by Eq. (4a).

To facilitate the comparison of higher order terms, expand

$$\mathscr{H}(t) = \sum_\alpha \mathscr{H}_\alpha e^{i\alpha\omega t} , \tag{13a}$$

and

$$P_n(t) = \sum_\alpha P_{n,\alpha} e^{i\alpha\omega t} \tag{13b}$$

in a Fourier series and define $\omega = 2\pi/\tau$. When these are substituted into Eq. (12) the forms

$$\hat{H}_n = \sum_\alpha \mathscr{H}_{-\alpha} P_{n-1,\alpha} - \sum_{k=1}^{n-1} P_{k,0}\hat{H}_{n-k} , \tag{14a}$$

$$P_n(t) = \sum_{\alpha+\beta\neq 0}\sum \frac{1-\exp[i(\alpha+\beta)\omega t]}{(\alpha+\beta)\omega}\mathscr{H}_\alpha P_{n-1,\beta} - \sum_{k=1}^{n-1}\sum_{\beta\neq 0} \frac{1-\exp(i\beta\omega t)}{\beta\omega} P_{k,\beta}\hat{H}_{n-k} , \tag{14b}$$

are obtained which in many circumstances may be simpler to use than the counterparts in Eq. (12).

For the present we examine $\hat{H}_2$. First the term

$$P_1(t) = \sum_{k\neq 0} \frac{1}{k\omega}(1-e^{ik\omega t})\hat{H}_k$$

is determined, and the appropriate frequency components are inserted into Eq. (14a). After a straightforward calculation we arrive at

$$\hat{H}_2 = \sum_{k=1}^{\infty} \frac{1}{k\omega}([\mathscr{H}_k,\mathscr{H}_{-k}] + [\mathscr{H}_0,\mathscr{H}_k] - [\mathscr{H}_0,\mathscr{H}_{-k}]) . \tag{15}$$

If the expressions (13) are substituted into Eq. (4b) and the integral evaluated over $[0,\tau]$, a result identical to Eq. (15) is obtained for $\bar{H}^{(1)}$. Thus, the two expansions are equal for each of the first two orders.

The direct comparison of higher orders becomes impossible rather quickly. Hence, a different approach is taken to show that the two series (11b) and (3) are equal term by term for the case in which the latter is evaluated at $t = \tau$. Under conditions when the Floquet and exponential solutions both exist they must be equal. Taking the logarithm of each gives

$$-i\sum_k \lambda^k H^{(k-1)}(t) = \ln\left[\sum_k \lambda^k P_k(t)\right] - i\sum_k \lambda^k \hat{H}_k t , \tag{16}$$

where the summation over k is from 1 to ∞. At $t = \tau$ the periodicity condition ensures $P(\tau) = 1$, whereby the two series are identical.[21] The factor λ is used if necessary to ensure that $H(t)$ will exist. This will not change the form of any of the terms in either series [for example, Eqs. (12b), (4a), etc.]. Thus, since the Floquet solution (9) is global, the existence of the average Hamiltonian with the form (4) or (12) is proved. With this, the correspondence between the two series is

$$\hat{H}_n = \bar{H}^{(n-1)} . \tag{17}$$

It is interesting to compare the two forms. First, the form of the nth-order term is more easily obtained from the Floquet version than the Magnus expansion. Once in hand, it is also more easily evaluated by the former method. A second point is that the expansion of $P(t)$ is evaluated concurrently with $\hat{H}$. This can be used to follow the evolution of the system within each cycle. Hence, the restriction of stroboscopic observation necessary in the Magnus case no longer applies. An interesting possibility is to sample fast, but at a submultiple of τ, say at τ/p. The data can then be divided into two groups: the points at $Np\tau$ and those within each cycle. The first group gives the usual information obtained from the average Hamiltonian, while complementary information is obtained from the second. In this way the extra information is decoupled rather than present as line broadening.

IV. CONVERGENCE OF THE EFFECTIVE HAMILTONIAN SERIES

The expansion of $P(t)$ and $\hat{H}$ given by Eqs. (11a) and (11b) constitute formal series solutions to the differential equation (10) and the auxiliary condition that $P(t)$ is periodic. The term "formal" signifies that these series satisfy the differential equation. However, it is still necessary to prove that the series converge in order for them to equal the actual unique solutions. The discussion of this proceeds in three parts: The first part is devoted to showing the convergence of the effective Hamiltonian in the mathematical sense. Part two elucidates by example those conditions which must be satisfied in order to truncate the series for $P(t)$ and $\hat{H}$ after the first few terms. For practical calculations this will be of the most interest. Finally, in the last part an alternative expansion for $P(t)$ and $\hat{H}$ is given.

For any discussion of convergence, when the size of succeeding terms is to be determined, the concept of a norm must be introduced. Two examples are the trace norm

$$||A||=(\mathrm{Tr}A^{\dagger}A)^{1/2} \tag{18}$$

and the supremum norm

$$||A||=\sup_{\langle x|x\rangle\neq 0}\frac{\langle x|A|x\rangle}{\langle x|x\rangle} . \tag{19}$$

At this point a particular formula for the norm does not have to be chosen; it is only necessary to know that a norm can be defined on the space of operators which contains $\mathscr{H}(t)$.

The determination of the convergence of the series (12a) and (12b) directly provides difficulties because the two series are interdependent. A more indirect method proceeds as follows: From Eq. (9) and the periodicity of $P(t)$, we have

$$U(\tau)=e^{-i\hat{H}\tau} . \tag{20}$$

Next, $U(t)$ is determined by the method of Picard approximations.[22] A sequence of functions is defined by

$$U_0(t)=1 ,$$
$$U_{n+1}(t)=1-i\int_0^t \lambda\mathscr{H}(t)U_n(t)dt . \tag{21}$$

The factor λ is introduced as an expansion parameter. Note that the iterative sequence (21) therefore produces a power-series solution for $U(t)$ in terms of the parameter λ. For the present discussion of convergence, we take λ as a measure of the size of the Hamiltonian; thus, $||\lambda\mathscr{H}(t)||=\lambda$. By induction, the norms of the differences of successive terms in (21) are

$$||U_n(t)-U_{n-1}(t)||\leq\frac{\lambda^n t^n}{n!} , \tag{22}$$

whereby (21) produces a convergent sequence for the propagator $U(t)$. The periodicity of the Hamiltonian is accounted for by expansion of $\mathscr{H}(t)$ into a Fourier series as given by Eq. (13a). Evaluated at $t=\tau$, this gives

$$U_2(\tau)=1-i\lambda\mathscr{H}_0\tau+\frac{\lambda^2\tau}{i\omega}\sum_{k=1}^{\infty}\frac{1}{k}([\mathscr{H}_a,\mathscr{H}_{-a}]-[\mathscr{H}_a,\mathscr{H}_0]+[\mathscr{H}_{-a},\mathscr{H}_0])-\frac{\lambda^2\tau^2}{2}\mathscr{H}_0^2 \tag{23}$$

for the propagator to second order. To make the connection to the effective Hamiltonian series,

$$\exp\left[-i\tau\sum_1^{\infty}\lambda^n\hat{H}_n\right] ,$$

is also expanded in a power series in terms of λ:

$$\exp\left[-i\tau\sum_1^{\infty}\lambda^n\hat{H}_n\right]=1-i\lambda\tau\hat{H}_1-i\lambda^2\tau\hat{H}_2-\frac{\lambda^2\tau^2}{2}\hat{H}_1^2+\cdots . \tag{24}$$

Equating coefficients of λ^n in Eq. (24) and the power series for $U(\tau)$ then determines the various terms $\hat{H}_n$. From Eqs. (23) and (24) it can be seen easily that $\hat{H}_1$ and $\hat{H}_2$ are in fact given by $\mathscr{H}_0$ and Eq. (15), respectively. The convergence of $U_n(t)$ implies, via Eq. (20), that the series for $\exp(-i\hat{H}\tau)$ converges. Thus, the power series $\hat{H}=\sum_1^{\infty}\lambda^n\hat{H}_n$ must also converge.

We turn now to practical considerations of convergence to be applied to specific problems. The discussion is pursued on a qualitative level. A suitable norm must be chosen and the value λ describing the size of the Hamiltonian determined. Additionally, due to the difficulties in evaluating the higher-order terms $P_n(t)$, it is desirable to truncate the series after the first few terms; generally two or three are kept.

The considerations which are important for the rapid convergence of Eq. (11) can be motivated by an example. Let $\mathscr{H}(t)$ be the Hamiltonian for a spin in a static magnetic field with an rf field applied perpendicular to it:

$$\mathscr{H}(t) = -\omega_0 I_z + \omega_1 \cos(\omega t + \phi) I_x \ . \tag{25}$$

Application of Eq. (14a) yields after some calculation

$$\overline{H}^{(0)} = -\omega_0 I_z \ , \tag{26a}$$

$$\overline{H}^{(1)} = \frac{\omega_0 \omega_1}{\omega} \sin\phi I_y \ , \tag{26b}$$

$$\overline{H}^{(2)} = \frac{-\omega_0^2 \omega_1}{\omega^2} \cos\phi I_x + \frac{1}{2}\frac{\omega_0 \omega_1^2}{\omega^2}\left(1 - \tfrac{1}{2}\cos 2\phi\right) I_z \ , \tag{26c}$$

for the first three terms of the effective Hamiltonian. Note that the more conventional notation, $\overline{H}^{(0)}$ is used here. From Eq. (18) the norms of these are given by

$$|\omega_0| \, \| I_z \| \ ,$$

$$\left| \frac{\omega_0 \omega_1}{\omega} \sin\phi \right| \| I_z \| \ ,$$

and

$$\left[\frac{\omega_0^4 \omega_1^2}{\omega^4} \cos^2\phi \| I_x \|^2 + \frac{1}{4}\frac{\omega_0^2 \omega_1^4}{\omega^4}\left(1 - \tfrac{1}{2}\cos 2\phi\right)^2 \| I_z \|^2 \right]^{1/2} ,$$

respectively. The single bars denote an absolute value. Except for the trigonometric terms, the size of the norm develops as a double power series in $(\omega_0/\omega)^n$ and $(\omega_1/\omega)^m$. Therefore, in order that the size of the terms decreases monotonically, it is required that $|\omega_0/\omega| < 1$ and $|\omega_1/\omega| < 1$. The important thing to notice from this is that Eq. (26) will not converge rapidly at resonance or below, i.e., with $\omega \le \omega_0$. As an aside, the I_z term in $\overline{H}^{(2)}$ is essentially the off-resonance Bloch-Siegert shift. Although, in the present case it is obtained in the lab frame, and hence, is only valid when ω is above resonance.

We now make the situation more complicated by adding a quadrupole term, $R_{20}^{q} T_{20}$ (see Ref. 2, for notation). The zeroth- and first-order terms are corrected by adding to them $R_{20}^{q} T_{20}$ and

$$i(\omega_1 R_{20}^{q})/\omega \sin\phi [T_{20}, I_x] \ ,$$

respectively. By applying the trace norm and following the reasoning used above, the conditions $|\omega_0/\omega| < 1$, $|\omega_1/\omega| < 1$, and $|R_{20}^{q}/\omega| < 1$ are obtained for rapid convergence. However, due to the lifting of the degeneracies by the quadrupole interaction, the resonance frequencies are now at

$$\omega = \omega_0 + 3/\sqrt{6} R_{20}^{q} (2m_z + 1) \ ,$$

with m_z as the quantum number of the lower state. For a spin system with large total spin angular momentum the rapid convergence conditions can easily be met, while at the same time there is a resonance between two levels with large m_z (e.g., $I = 10$, $m_z = 9$, and ω_0, ω_1, and $R_{20}^{q} < \omega = \omega_0 + 23.3 R_{20}^{q}$). This leads to a contradiction as, physically, we know that the field will cause transitions between the resonant levels. Also the previous analysis, when applied to the pseudo-spin-$\frac{1}{2}$ system consisting of only the two resonant levels, leads to the conclusion that the effective Hamiltonian series will not converge.

The problem stems from the oversimplifications made above in conjunction with the use of the trace norm. This norm is perfectly satisfactory when applied to $\overline{H}^{(n)}$ as required for $n \to \infty$. However, the drawback of the trace norm for determining if the series can be truncated is that it averages out the structure of the operators in $\mathscr{H}(t)$. In essence, the condition $|\omega_0/\omega| < 1$, etc., ensures only that the frequency of the field is above the root mean square (rms) of the transition frequencies. This deficiency leaves open the possibility of resonances with those transition frequencies which lie above the rms value.

The following conclusion can now be drawn: In the collective picture of a dipole-coupled spin system, the dipole Hamiltonian has the same structure as the quadrupole interaction of the example above. In addition the total spin angular momentum quantum number for a macroscopic collection of spins is very large. Though the lowest harmonic of the rf field is chosen to be much larger than $\langle \mathscr{H}^2 \rangle^{1/2}$, there are a few levels in the wings of the dipole line which will be resonant with the driving field. Absorption of energy by this small number of levels will slowly heat the spins. Therefore, the quasistationary magnetization will slowly decay.

In light of the above, a better norm would be the supremum norm given by Eq. (19). An equivalent version of this norm can be written as $\|\mathscr{H}\| = |\lambda_{\max}|$, that is, the eigenvalue of $\mathscr{H}(t)$ with the largest magnitude. This norm will ensure that the frequency of the driving field is above any absorption frequencies of the physical system. An example of a dipolar system for which this is true is the usual truncated dipolar Hamiltonian in the rotating frame. The oscillating terms in this reference frame are at twice the Larmor frequency which is well above the full width of the dipolar interaction. We can say that the art of the average Hamiltonian theory is to find the right interaction frame in which the series is convergent.

To conclude this section, a brief outline of an alternate expansion of the Floquet solution is given. The assumption is made that $\mathscr{H}(t)$ is bounded by a constant M: that is, $\sup\|\mathscr{H}(t)\|=M$, for $0<t<\tau$. The expansion consists of forming an iterative sequence of Picard approximations[22] defined by

$$P_0(t)=1\ ,$$
$$P_{n+1}(t)=1-i\int_0^t[\mathscr{H}(t')P_n(t') - P_n(t')\hat{H}]dt'\ . \tag{27}$$

Note that here the $P_n(t)$ represent a sequence of approximations to the solution $P(t)$ and are not the terms in a series expansion for $P(t)$, as elsewhere in this work. The nth-order approximation to $\hat{H}_n$ is determined from the condition that $P_n(\tau)=1$, whereby

$$\hat{H}_n=\left[\int_0^\tau P_n(t)dt\right]^{-1}\int_0^\tau \mathscr{H}(t)P_n(t)dt\ . \tag{28}$$

By an inductive procedure it can be shown that in this case

$$\|P_n(t)-P_{n-1}(t)\|\le\frac{(2M)^n t^n}{n!}\ . \tag{29}$$

Because the right-hand side of (29) is the nth term in a series which converges for all t, the sequence (27) will converge to the solution of Eq. (10). It is easily verified that in this case too, the lowest-order term is the average Hamiltonian, $\bar{H}^{(0)}$. Higher-order terms are, however, more difficult to calculate owing to the inverse required in Eq. (28).

V. APPLICATION TO THE PULSE SPIN-LOCKING EXPERIMENT

We now consider in detail the pulse spin-locking experiment. The Hamiltonian in the rotating frame is

$$\mathscr{H}_R(t)=-\omega_1(t)I_x+\Delta I_z+H_{20}^d\ . \tag{30}$$

The pulse sequence is represented by

$$\omega_1(t)=\theta\sum_{k=1}^{\infty}\delta(t-(2k-1)\tau) = \frac{\theta}{2\tau}\sum_{-\infty}^{\infty}(-1)^n e^{in\pi t/\tau}\ , \tag{31}$$

where θ is the flip angle of each pulse and 2τ is the period. Δ is the resonance offset and H_{20}^d is the truncated, homonuclear dipole Hamiltonian. Note that in (31) the Fourier-series representation of the pulse sequence is also given. The methods of Sec. III are applied to calculate the effective Hamiltonian to second order, giving

$$\begin{aligned}\bar{H}=H_{20}^d+\Delta I_z-\frac{\theta}{2\tau}I_x &-\frac{\theta\tau}{12}([[I_x,H_{20}^d],H_{20}^d] - 2i\Delta[I_y,H_{20}^d]+\Delta^2 I_x)\\ &-\frac{\theta^2}{12}([[H_{20}^d,I_x],I_x]+\Delta I_z)\ .\end{aligned} \tag{32}$$

(Note that $\bar{H}^{(1)}=0$.)

The calculation can be done by various means: (a) integration of (12), (b) use of the Fourier expansion in (14), or (c) application of the Baker-Campbell-Hausdorff theorem[19] to the evolution operator over one cycle:

$$U(2\tau)=\exp[-i(H_{20}^d+\Delta I_z)\tau]\exp(i\theta I_x) \times\exp[-i(H_{20}^d+\Delta I_z)\tau]\ . \tag{33}$$

The evolution operator in (c) is obtained by piecewise integration of Eq. (1) from 0 to τ, insertion of the pulse, and integration from τ to 2τ. As (32) can be seen to be a power series in θ and $(H_{20}^d+\Delta)\tau$, the usual convergence condition is just $|\theta|<1$ and $\|H_{20}^d+\Delta\|\tau<1$.

The initial density matrix after the $\pi/2$ preparation pulse is $\rho(0)\sim 1-\beta_i\omega_0 I_x$. By the arguments of spin thermodynamics, this will evolve to $\rho_{st}\sim 1-\beta_{st}\bar{H}$. Conservation of energy yields

$$\frac{\beta_{st}}{\beta_i}=\frac{\omega_0 \mathrm{Tr} I_x\bar{H}}{\mathrm{Tr}\bar{H}^2}\ ,$$

whereby the quasistationary magnetization is

$$\frac{M_{\rm st}}{M_i}=\frac{\left[\dfrac{\theta}{2\tau}\right]^2\left[1+\dfrac{\tau^2}{2}H_L^2+\dfrac{\tau^2}{6}\Delta^2\right]^2}{\left[\left[\dfrac{\theta}{2\tau}\right]^2+\left[1-\dfrac{\theta^2}{4}+\dfrac{\theta^4}{12}\right]H_L^2+\left[1-\dfrac{\theta^2}{12}+\dfrac{\theta^4}{144}\right]\Delta^2+\dfrac{3}{16}\theta^2\tau^2H_L^4+\dfrac{1}{144}\theta^2\tau^2\Delta^4+\dfrac{1}{8}\theta^2\tau^2\Delta^2H_L^2\right]}\;. \tag{34}$$

The definition

$$H_L^2=M_2/3=\mathrm{Tr}(H_{20}^d)^2/\mathrm{Tr}I_z^2$$

has been made in (34) with M_2 as the second moment of the dipolar line shape. In addition, we have used the assumption of a Gaussian line shape in Eq. (34) to write $M_4=27\ H_L^4$ where M_4 is the fourth moment.

Plots of $M_{\rm st}/M_i$ vs θ are shown in Fig. 1. The comparison with the results of Refs. 6–9 is good. Figure 2 shows the variation of $M_{\rm st}/M_i$ with detuning. Qualitatively, the correct behavior is predicted, though in this case there is disagreement on some features with Refs. 7 and 9. These features are not so evident in the experimental results[7] so that the AHT result compares more favorably with the latter than with the theory of Ivanov *et al.*[9] The conclusion, though, is that AHT can in fact be used to predict the quasistationary state.

As noted above, the failure of the quasistationary state to persist is due to the small number of levels resonant with the pulses which can absorb energy. The preceding treatment ignores this possibility and is therefore unable to account for the decay. The number of such levels is just proportional to $g(\pi/\tau)$, where

$$g(\omega)=\sum{}'\,|\langle\lambda_i\,|I_x|\,\lambda_j\rangle|^2$$

is the absorption line shape.[23] The prime indicates that only those states which satisfy $\lambda_i-\lambda_j=\omega$, are included.

To obtain an idea of the rate of absorption we can apply the Fermi Golden Rule to Eq. (30). The result for the rate W is

$$W=\left[\frac{\theta}{2\tau}\right]^2|\langle\lambda_i\,|I_x|\,\lambda_j\rangle|^2\rho(\lambda_i-\lambda_j=\pi/\tau)\;, \tag{35}$$

where $\rho(\omega)$ is the density of transitions at frequen-

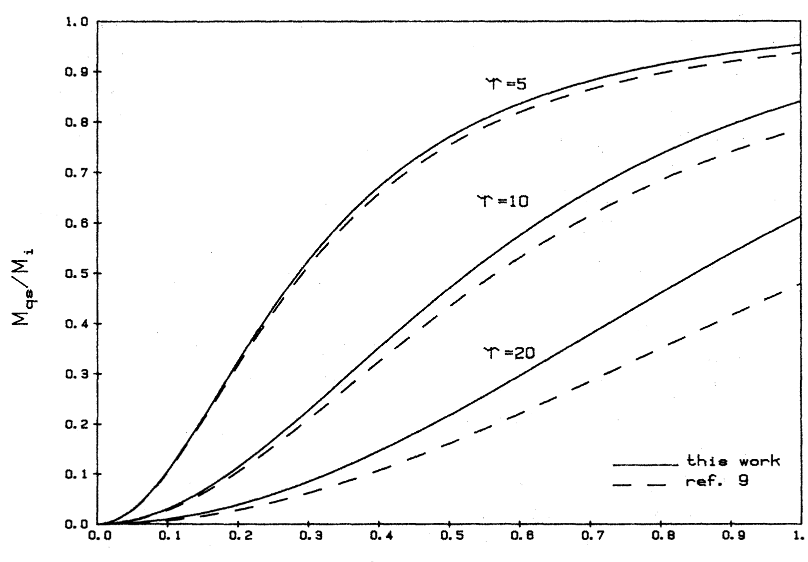

FIG. 1. Quasistationary magnetization vs pulse angle θ for various values of τ (in μsec). The solid curve is from Eq. (34). The dashed curve is obtained from Eq. (37) of Ref. 9 for comparison (Ref. 24) (parameters: $H_L=29\,500$ rad/sec, $\Delta=0$).

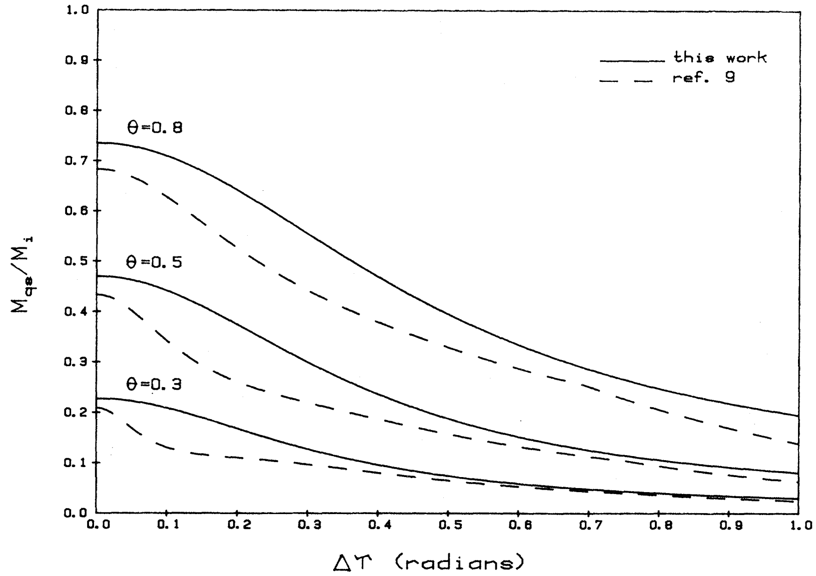

FIG. 2. Quasistationary magnetization vs detuning Δ for various values of θ (in radians). The solid line is from Eq. (34). The dashed curve is obtained from Eq. (37) of Ref. 9 for comparison (parameters: $H_L = 29\,500$ rad/sec, $\tau = 10^{-5}$ sec).

cy ω. By definition, the last two factors in (35) are $g(\pi/\tau)$, so that

$$W = \left[\frac{\theta}{2\tau}\right]^2 g(\pi/\tau) .$$

Qualitatively, this argument explains the observed decay rate.[12] Ivanov *et al.*[9] improve on this approach by a complicated infinite series of unitary transformations to an interaction frame in which the application of the time-dependent perturbation theory is more rigorous. However, a similar result is obtained.

Let us proceed to see why the average Hamiltonian method works at all. Instead of taking the collective approach, consider the sample to be an ensemble of tightly coupled spins I. Then, for the majority of spin pairs, the frequency of the driving field is much higher than any possible transition frequencies and the series of average Hamiltonian plus first few correction terms converges rapidly. For the very small number of spins which do not obey the convergence criterion (32) is not a correct representation of $\bar{H}$. Consider, for the moment, that there are no interactions between these two groups of spins. The magnetization, because it is a macroscopic observable, is an average over the ensemble of spins. Therefore only a small fractional error in M_{st}/M_i will be provided by the group of spins for which $\bar{H}$ is incorrect. This is the reason for the correct predictions of AHT in the short-time regime. However, we must remember that the two groups of spins defined above are actually tightly coupled. Energy from the absorbing group of spins will slowly leak through the remainder of the spin system. In the long-time regime, then, the system can be observed to evolve away from what is predicted by the average Hamiltonian approach.

In principle, AHT can be used to predict the correct final state, except that a better reference frame is needed—one with $\pi/\tau > |\lambda_{max}|$. This is what Suwelack and Waugh[10] have attempted to do. Their choice of interaction frame is an example of the kind of subtle problem that can be encountered in the use of AHT.

Starting with Eq. (30), except that they chose $\Delta = 0$, the unitary transformation

$$V(t) = \exp[-i\phi(t)I_z]\exp\left[i\frac{\pi}{2}I_y\right] ,$$

is made with the time-dependent rotation angle defined as

$$\phi(t) = \int_0^t [\omega_1(t') - \bar{\omega}_1]dt' ,$$

and $\bar{\omega}_1 = \theta/2\tau$. The interaction-frame Hamiltonian in this "switched" frame is

$$\mathscr{H}_S = -\bar{\omega}_1 I_z - \tfrac{1}{2}H_{20}^d + \sqrt{3/8}H_{22}^d e^{i2\phi(t)} + \sqrt{3/8}H_{2-2}^d e^{-i2\phi(t)} . \quad (36)$$

The H_{2m}^d are the various spherical tensor components of the dipolar Hamiltonian. The zeroth-order average Hamiltonian can be obtained from either Eqs. (4a), (12), or (14) and is

$$\bar{H}^{(0)} = -\bar{\omega}_1 I_z - \tfrac{1}{2} H_{20}^d + \sqrt{3/8}\, c_0 (H_{22}^d + H_{2-2}^d) . \quad (37a)$$

Here, $c_0 = \sin\theta/\theta$ is the zero-frequency Fourier component of $\exp[2i\phi(t)]$. In Ref. 10 it is the c_0 term which leads to the θ dependence of the quasistationary magnetization.

Now, however, let us continue and consider the first-order correction,

$$\bar{H}^{(1)} = \tfrac{1}{2}\sqrt{3/8}\left[1 - \frac{\sin\theta}{\theta}\right][I_z, H_{22}^d - H_{2-2}^d] + \frac{1}{4\bar{\omega}_1}\sqrt{3/8}\left[1 - \frac{\sin\theta}{\theta}\right][H_{20}^d, H_{22}^d - H_{2-2}^d] - \frac{3}{16\bar{\omega}_1}\left[1 - \frac{2\sin\theta}{\theta} + \frac{\sin 2\theta}{2\theta}\right][H_{22}^d, H_{2-2}^d] . \quad (37b)$$

Notice that the first term in $\bar{H}^{(1)}$ is really the same "size" as $\bar{H}^{(0)}$. In fact, it exactly cancels the c_0-dependent term in $\bar{H}^{(0)}$ leaving an effective zeroth-order Hamiltonian

$$\bar{H}_{\text{eff}}^{(0)} = -\bar{\omega}_1 I_z + H_{20}^{dx} ,$$

where H_{20}^{dx} is just the truncated dipole Hamiltonian rotated 90° about the y axis. In reality, even this is not the correct zeroth-order expression, as consideration of second and higher orders shows that each will contain terms which look like "zeroth order." This difficulty arises because the choice of interaction frame only partially removes the pulse term in the Hamiltonian. The result is that the oscillating components of the interaction-frame Hamiltonian will have the same frequency as the eigenvalues of the rf term which are left in $\mathscr{H}_S$.

Next, we consider a method by which an average Hamiltonian can be obtained for the case $\theta > 1$. Note that for Eq. (34) to hold, θ must be less than 1. To do so we transform to the "toggling" frame via

$$V(t) = \exp[i\psi(t) I_z] \exp\left[i \frac{\pi}{2} I_y\right] ,$$

with

$$\psi(t) = \int_0^t \omega_1(t')\,dt' .$$

In this representation the interaction frame Hamiltonian is

$$\mathscr{H}_T = \Delta \sum_{-1}^{1} D_{m0}^1\left[0, \frac{\pi}{2}, 0\right] I_m e^{im\psi(t)} + \sum_{-2}^{2} D_{m0}^2\left[0, \frac{\pi}{2}, 0\right] H_{2m}^d e^{im\psi(t)} . \quad (38)$$

The D_{m0}^L are the Wigner rotation matrices.[2] Note that, because of the function $\psi(t)$, the interaction-frame Hamiltonian is not generally periodic. It is so only when $n\theta = m\,2\pi$, whereupon the period is $(m\,2\pi/\theta)2\tau$. Strictly, the AHT can only be applied in these instances. A Fourier expansion of $\exp[im\psi(t)]$ shows that for $|\theta| < \pi$, there is no zero-frequency component. Thus, $\bar{H}^{(0)}$ is simply

$$\bar{H}^{(0)} = -\tfrac{1}{2} H_{20}^d . \quad (39a)$$

To calculate $\bar{H}^{(1)}$ is not quite so simple. As the details are not important to the present discussion, only the result is given here:

$$\bar{H}^{(1)} = \frac{\tau}{4} \frac{1+\cos\theta}{\sin\theta} (\Delta^2 I_z - i\Delta[H_{20}^d, I_y]) + \frac{\tau}{4}\cot\theta\left(-\sqrt{3/8}[H_{20}^d, H_{22}^d - H_{2-2}^d] + \tfrac{3}{4}[H_{22}^d, H_{2-2}^d]\right) . \quad (39b)$$

This will generally be valid in the regime $1 < |\theta| < \pi$ and $\|H_{20}^d\|\tau < 1$. The initial density matrix has the form $\rho(0) \sim 1 - \beta_i \omega_0 I_z$. If only $\bar{H}^{(0)}$ is considered, we note that there are two constants of the motion: the energy and I_z. Thus, the equilibrium density matrix can be given the form[13]

$$\rho_{\text{st}} \sim 1 - \alpha_{\text{st}} \omega_0 I_z - \beta_{\text{st}} \bar{H} .$$

Equating the expectation values of I_z and energy at $t = 0$ to those at equilibrium leads us to the quasistationary magnetization $M_{\text{st}}/M_i = 1$. This agrees with Ivanov *et al.*[8] Again, there will be a few levels which are resonant so that this quasistationary state will decay.

VI. CONCLUSION

The main objective of this paper was to consider the validity of the average Hamiltonian approach for solving the time-dependent Schrödinger equation. The existence of an average Hamiltonian in the case where $\mathscr{H}(t)$ is periodic is a direct result of the Floquet theorem. A source of difficulty arises in providing a convergent solution to $\bar{H}$. In this connection the important result is the failure of the perturbation expansion under conditions which allow resonances. This is well known in the case of a two-level system driven by a resonant field; so the transformation to the rotating frame is made. It was less clear what to do for a system with a large spread of transition frequencies. Those systems with large homonuclear dipole interactions fall into this class. The rigorous result is that all these transitions must lie below the oscillation frequency of the time-dependent part of the Hamiltonian. This is not satisfied for the pulse spin-locking experiment considered. However, this poses no contradiction to the general validity of AHT. In this particular instance the requirements for the convergence were not satisfied exactly. The small number of offending levels in this experiment forms a bottleneck for the absorption process, thereby providing for a slow decay of the quasistationary magnetization.

Finally we note that a crucial aspect which will determine the success of the theory in a particular application is the judicious choice of reference frame in which to calculate the average Hamiltonian.

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