Coherent averaging in the frequency domain

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(Received 18 January 2012; accepted 15 May 2012; published online 1 June 2012)

Quantum-mechanical evolution of systems with periodic time-modulated Hamiltonians is often described by effective interactions. Such average Hamiltonians, calculated as few terms of an expansion in powers of the interaction, are sometimes difficult to relate to experimental observations. We propose a frequency-domain approach to this problem, which offers certain advantages and produces an approximate solution for the density matrix, better linked to measurable quantities. The formalism is suitable for calculating the intensities of narrowed spectral peaks. Fast magic-angle-spinning NMR spectra of solids are used to experimentally illustrate the method. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4723682>]

I. INTRODUCTION

The problem of evolution under a periodically modulated Hamiltonian $H(t)$ can be met in many areas of physics. When the modulation frequency Ω is large compared to the magnitude of interactions: $\Omega \gg |H|$, it seems natural to describe the long-time evolution by an effective interaction that accounts for an averaged action of $H(t)$ over the modulation period. In classical mechanics, non-trivial effective interactions result from non-linear equations of motion. In quantum mechanics, they are a consequence of commutation relations. Some anisotropic internal interactions can be averaged out by application of external fields or even by the mechanical motion of the sample. Such averaging can be utilized in spectroscopy for simplifying spectra and narrowing individual spectral lines. Dynamical decoupling can be helpful in quantum information processing for suppressing interaction between qubits and environment,¹ improving control² and quantum gates fidelity.³ Average Hamiltonians can also be used for constructing artificial interactions. A recent example for trapped neutral atoms in an addressable optical lattice can be found in Ref. 4.

Originally, experimental capabilities of altering internal interactions by their fast modulation have been limited by systems of coupled nuclear spins manipulated by NMR techniques. With advancement of instrumentation, the list of systems and techniques expanded and continues to grow. Various theoretical approaches to coherent averaging have been formulated over the last four decades. To name some, they are the average Hamiltonian theory (AHT),^{5,6} canonical transformation technique,⁷ method of non-equilibrium statistical operator,⁸ and Floquet theory.⁹

For a periodically modulated Hamiltonian $H(t)$ with the modulation period $t_c = 2\pi/\Omega$, the average Hamiltonian H_{av} is defined by a unitary evolution operator $U(0, t_c)$ as

$$U(0, t_c) = \exp(-i H_{av} t_c). \quad (1)$$

Then, the evolution at longer times $t = Nt_c$ can be calculated as

$$U(0, Nt_c) = U(0, t_c)^N = \exp(-i H_{av} t_c)^N = \exp(-i H_{av} Nt_c). \quad (2)$$

For many-body dynamics, H_{av} cannot be calculated exactly. In AHT, the average Hamiltonian H_{av} is calculated as a series in powers of interaction. Only few terms of such expansion can usually be calculated explicitly. The canonical transformation technique is an iterative procedure for building periodic unitary transformation, which eliminates, at each step, the major oscillating term in the Hamiltonian. The goal is to find a periodic transformation to a frame, where the Hamiltonian is time-independent. For a finite system, the existence of such frame is guaranteed by the Floquet-Lyapunov theorem: for a linear system of ordinary differential equations with periodic coefficients, there exists a linear periodic transformation of coordinates, which turns this system into a system with constant coefficients. Conceptually similar Floquet theory is also based on this theorem. Usually, the result of calculations in the Floquet theory is presented in a form of effective Hamiltonian. Equivalence of different effective Hamiltonians has been discussed in Ref. 10. The average Liouvillian theory¹¹⁻¹³ can be developed in a similar way. In this article, we use the term AHT very broadly to name a class of theories, which derive results as expansions in powers of the interaction. For a Hamiltonian $H(t)$ in an interaction frame, in the case when a simple time average $\langle H(t) \rangle = 0$, higher order terms describing the residual interactions appear when $H(t)$ does not commute with itself at different moments of time.

For many-body systems, the AHT replaces one unsolvable problem, with the original time-dependent Hamiltonian, by another unsolvable problem with time-independent effective interactions. Nevertheless, effective Hamiltonian is a very efficient tool for estimating various contributions and analyzing how the result scales with changing experimental parameters. AHT has been widely used for designing NMR pulse sequences, which eliminate certain terms of the effective

interactions. Some examples, picked from a vast literature on the subject, can be found in Refs. 14–16. Such use of the AHT is straightforward. However, an application of the lowest order non-zero multi-spin term for quantitative description of the residual spectral lines is far from being trivial. Some of the difficulties are listed below.

- (1) What quantity should be used to describe the “size” $|H_{av}|$ of the Hamiltonian H_{av} ? A simple choice would be a square root of the second moment, but the line shapes observed in all line-narrowing experiments resemble Lorentzian (for a true Lorentzian shape the second and higher moments are infinite). In other words, the time-domain signals are near exponential. The question of explaining an exponential decay of signals in a line-narrowing experiment has been raised by Lee and Goldburg^{17,18} and it still remains unanswered. If the low-order approximation to the average Hamiltonian describes the true line shape, then the magnitude of this truncated Hamiltonian is related to square root of the second moment of the line shape rather than the line width. These two are very different for the Lorentzian-like line shapes. Alternatively, if the truncated average Hamiltonian contributes only to a central part of the spectral line, the question of the line shape and height remains open.
- (2) Experimentalists commonly use peak heights rather than line widths to quantify the quality of decoupling. Peak heights are easier to measure, especially when there are several overlapping peaks. It is often observed that, under improved decoupling, peak heights grow faster than the line width decreases, i.e., the peak height is not inversely proportional to the line width. Therefore, an interpretation in terms of a single scaled effective Hamiltonian may be inaccurate. Peak heights are given by integrated time-domain signals and strongly depend on the behavior of these signals at long times $t \rightarrow \infty$. Omitted terms of the average Hamiltonian, even when they have relatively small effect at intermediate times, may critically change the behavior of time-domain signals at $t \rightarrow \infty$.
- (3) A formal requirement for neglecting the higher order terms $\Omega \gg |H|$, where Ω is the modulation frequency, is not achievable in experimental applications, like homo- or hetero-nuclear spin decoupling, or magic-angle spinning (MAS) of the sample in the cases when the residual line width can be interpreted in terms of the AHT. At the same time, a significant line-narrowing can be observed in experiments at $\Omega \approx |H|$. As an example, in the MAS experiment below, 5 kHz spinning produces a narrowed line for adamantane that has the line width of 13 kHz under a static condition. Therefore, the role of the higher order terms remains unclear, and it is desirable to reformulate the theory so that it could utilize, in approximations, a parameter which appears as a result of actual averaging rather than the formal condition $\Omega \gg |H|$.

It seems more rational to build approximations not for the Hamiltonian but directly for the density matrix or the resol-

vent. In this study, we show how a theory can be formulated to provide an approximate solution for the density matrix in frequency domain, which can be more directly related to experimentally measured quantities. Of course, similar to most applications of the AHT, we are not trying to solve explicitly the problem of many-body dynamics. The goal is only to predict how the results of an experiment change when some of the experimental parameters change.

II. THEORY

For a time-independent Hamiltonian H , the time evolution of a quantum-mechanical operator x and its spectrum can be calculated as

$$\langle x(t) \rangle = \langle x | \rho_t(t) \rangle, \quad |\rho_t(t)\rangle = \exp(Lt) |\rho_{in}\rangle, \quad (3a)$$

$$\begin{aligned} \langle x(\omega) \rangle &= \text{Re} \langle x | \rho_\omega(\omega) \rangle, \quad \rho_\omega(\omega) = \int_0^\infty dt \exp(-i\omega t) |\rho_t(t)\rangle \\ &= (i\omega - L)^{-1} |\rho_{in}\rangle, \end{aligned} \quad (3b)$$

where $|\rho_t\rangle$ and $|\rho_\omega\rangle$ are the density matrix in time and frequency domains, $|\rho_{in}\rangle$ is the initial density matrix, $L = -i[H, \dots]$ is the Liouvillian super-operator, and the binary product is defined as $\langle A | B \rangle = \text{Tr}(A^+ B)$. The super-operator $(i\omega - L)^{-1}$ in Eq. (3b) is called the (super)-resolvent. Some technical details on using super-operators and super-resolvents can be found in the literature.¹⁹ For mathematical simplicity, in Eq. (3b) and below, we assume that the Liouvillian contains small damping ε : $L' = L - \varepsilon$, which is set to zero at the end of all calculations by taking the limit $\varepsilon \rightarrow 0$. Expansions of Eqs. (3a) and (3b) in powers of L are

$$\langle x(t) \rangle = \sum_{k=0}^{\infty} (t^k / k!) \langle x | L^k | \rho_{in} \rangle, \quad (4a)$$

$$\langle x(\omega) \rangle = \text{Re} (1/i\omega) \sum_{k=0}^{\infty} \langle x | (L/i\omega)^k | \rho_{in} \rangle. \quad (4b)$$

Equation (4a) is the familiar moment expansion²⁰ (expansion in the moments $M_k = \langle x | L^k | \rho_{in} \rangle$ of the spectrum $\langle x(\omega) \rangle$). Equation (4b) can be obtained by iterative application of the identity

$$(A - B)^{-1} = A^{-1} + (A - B)^{-1} B A^{-1} \quad (5)$$

to the resolvent $(i\omega - L)^{-1}$ in Eq. (3b) by using $A = i\omega$ and $B = L$. Equation (4b), with the order of the terms as written, is valid even when the terms L and $i\omega$ do not commute. The first term of the expansion (4b) is $\text{Re} (1/i\omega) = \delta(\omega)$, according to our convention of using small damping ε . The terms of the same power of L in Eqs. (4a) and (4b) are formally related by a Fourier transform.

Now we will derive Eq. (3b) in a way, suitable for a time-dependent Liouvillian $L(t)$. In particular, we assume that the Hamiltonian and, therefore, the Liouvillian, are periodic functions of time with the period $2\pi/\Omega$,

$$L(t) = \sum_n L_n \exp(in\Omega t). \quad (6)$$

The equation of motion

$$(d/dt)|\rho_t(t)\rangle = L(t)|\rho_t(t)\rangle = \sum_n L_n \exp(in\Omega t)|\rho_t(t)\rangle \quad (7)$$

after a Fourier transform becomes

$$\begin{aligned} & \int_0^\infty dt \exp(-i\omega t) (d/dt)|\rho_t(t)\rangle \\ &= \int_0^\infty dt \exp(-i\omega t) \sum_n L_n \exp(in\Omega t)|\rho_t(t)\rangle, \\ & i\omega|\rho_\omega(\omega)\rangle - |\rho_{in}\rangle = \sum_n L_n|\rho_\omega(\omega - n\Omega)\rangle. \end{aligned} \quad (8)$$

By introducing the operator of frequency shift T as $T|\rho_\omega(\omega)\rangle = |\rho_\omega(\omega - \Omega)\rangle$, one can rewrite Eq. (8) in a more compact form,

$$(i\omega - L)|\rho_\omega(\omega)\rangle = |\rho_{in}\rangle, \text{ or } |\rho_\omega(\omega)\rangle = (i\omega - L)^{-1}|\rho_{in}\rangle, \quad (9)$$

where

$$L = \sum_n L_n T^n. \quad (10)$$

With the new Liouvillian (10), Eq. (9) has exactly the same form as Eq. (3b) derived for the case of time-independent Liouvillian. At $\Omega \rightarrow 0$, $T \rightarrow 1$, $L = \sum_n L_n T^n \rightarrow \sum_n L_n = L(0)$, and Eqs. (9) and (10) and (3b) coincide.

Now we have the exact Eqs. (9) and (10) valid at arbitrary values of Ω . Let us think how useful the expansions in powers of L can be? Suppose that such a calculation, based on finite number of terms, has resulted in an expression which provides an accurate description of the spectrum $I(\omega) = \langle x(\omega) \rangle$. Among other things, this would mean that $I(0)$ has been reasonably estimated. However, one can see that Eq. (4b) and a similar expansion of Eq. (9) have poor behavior in the limit $\omega \rightarrow 0$. This inability of predicting $I(0)$ creates a doubt that a finite number of terms of average Hamiltonian or Liouvillian is sufficient for describing the true shape of the spectrum.

As a more practical alternative for estimating $I(0)$, we will reverse the problem and make an attempt to calculate $I(0)$ directly. By applying the first of Eqs. (9), without inversion, repeatedly to $|\rho_\omega(\omega)\rangle$, $|\rho_\omega(\omega + \Omega)\rangle$, $|\rho_\omega(\omega - \Omega)\rangle$, ..., one obtains a set of coupled algebraic equations for $|\rho_\omega(\omega + n\Omega)\rangle$. In what follows, it is convenient using the shorter notations: $|\rho_\omega(n\Omega)\rangle = |\rho_n\rangle$. The quantity of interest will be $I(0) = \text{Re} \langle x|\rho_\omega(0)\rangle = \text{Re} \langle x|\rho_0\rangle$. The first of Eq. (9) will, therefore, generate an infinite set of coupled equations for $|\rho_n\rangle$. As a base for an approximation, we will use the actual performance of averaging. Under efficient averaging, the intensity of the central band is much higher than that of the satellites: $I(0) \gg I(\pm\Omega) \gg I(\pm2\Omega) \gg \dots$. In this case, neglecting the terms $|\rho_n\rangle$ with $|n| > 1$ would be a reasonable approximation. With this truncation and $L_0 = 0$, the set of equations (9) and (10) for $|\rho_n\rangle$ becomes

$$\begin{aligned} -L_1|\rho_{-1}\rangle - L_{-1}|\rho_1\rangle &= |\rho_{in}\rangle \\ i\Omega|\rho_1\rangle - L_1|\rho_0\rangle &= |\rho_{in}\rangle \\ -i\Omega|\rho_{-1}\rangle - L_{-1}|\rho_0\rangle &= |\rho_{in}\rangle. \end{aligned} \quad (11)$$

The solution of Eqs. (11) for $|\rho_0\rangle$ is

$$|\rho_0\rangle = [L_1, L_{-1}]^{-1}(i\Omega - L_1 + L_{-1})|\rho_{in}\rangle. \quad (12)$$

Therefore, the amplitude of the spectrum $I(0) = \text{Re} \langle x|\rho_0\rangle$ is a sum of linear in Ω term, described by the ‘‘average Liouvillian’’ $L_{AV} = -[L_1, L_{-1}]/i\Omega$, and the term which does not depend on Ω . Within the same approximation, one can also calculate $|\rho_1\rangle + |\rho_{-1}\rangle$,

$$|\rho_1\rangle + |\rho_{-1}\rangle = (i\Omega)^{-1}(L_1 - L_{-1})|\rho_0\rangle, \quad (13)$$

where $|\rho_0\rangle$ is given by Eq. (12). Then, the height of the first satellite $I(\Omega) = \text{Re} \langle x|\rho_1\rangle$ is a sum of the term, which does not depend on Ω , and the term proportional to $1/\Omega$. One would, therefore, expect that, at large Ω , $I(\Omega)$ does not depend on Ω .

The conventional second-order average Liouvillian is

$$\begin{aligned} L_{AV}^{(2)} &= (\Omega/2\pi) \int_0^{2\pi/\Omega} dt' \int_0^{t'} dt'' L(t')L(t'') \\ &= -\sum_{n>0} [L_n, L_{-n}]/(in\Omega). \end{aligned} \quad (14)$$

It can be also obtained by using the Liouvillian in Eq. (10) in the expansion in Eq. (4b) as following. The second-order ($k = 2$) term in Eq. (4b), after inserting the Liouvillian in Eq. (10), performing the frequency shifts $T\omega \rightarrow \omega - \Omega$, and using the condition $\omega \ll \Omega$, becomes the first-order term in $L_{AV}^{(2)}$.

Compared to Eq. (14), Eq. (12) contains only the term with $n = 1$. A more important difference is in the way how this Liouvillian is used. The inverse ‘‘average Liouvillian’’ $L_{AV} = -[L_1, L_{-1}]/i\Omega$ in Eq. (12) enters directly the solution for the density matrix and the amplitude of the spectrum $I(0)$.

So far, we assumed that $L_0 = 0$. In experiments, there are always some contributions to L_0 . They can be small, but never zero. When coherent averaging is used for improving the spectral resolution, L_0 contains valuable spectral information. The addition of the terms with L_0 to Eqs. (11) leads to a more complicated form of the solution for $|\rho_0\rangle$. However, this solution simplifies at $\Omega \gg |L_0|$ (the case $\Omega \approx |L|$ but $\Omega \gg |L_0|$ is relevant in many practical cases):

$$(-L_0 - L_{AV})|\rho_0\rangle = (1 - (L_1 - L_{-1})/i\Omega)|\rho_{in}\rangle. \quad (15)$$

Therefore, in this case, the evolution is governed by a simultaneous action of L_0 and L_{AV} . Well expectedly, in the limit $\Omega \rightarrow \infty$ the evolution is described by L_0 alone.

III. EXPERIMENTAL EXAMPLE

In NMR spectroscopy, due to low frequencies and easily controlled radio-frequency fields, the methods based on periodic modulation became widely used. The periodic modulation of internal interactions can be achieved by application of continuous or pulsed radio-frequency field and/or by mechanical rotation of the sample. Various pulse sequences have been proposed for averaging out undesired interactions (homo- and hetero-nuclear decoupling) to improve spectral resolution and simplify spectra. In practice, the performance of multi-pulse sequences, as a function of the modulation frequency Ω , can be compared to theoretical predictions in a very narrow range of Ω . The reason is that the effect of various experimental imperfections (radio-frequency field inhomogeneity, phase, amplitude, and shape errors) increase at increasing Ω . Mechanical spinning of the sample, without any

FIG. 1. Dependence of the experimentally measured increase in the ^1H NMR peak height on MAS rate in powder samples of : (●) glycine, (○) glucose, (+) valine-leucine dipeptide line 1 (CH_3), (×) valine-leucine dipeptide line 2, (Δ) adamantane. All experiments were carried out on 600 MHz Varian/Agilent solid-state NMR spectrometer using a 1 mm ultrafast-spinning double-resonance MAS probe. A single-pulse excitation with a recycle delay of 5 s and 4 scans were used.

interference from radio-frequency pulses, presents a better case for comparison with a theory. Recent advances in instrumentation has led to greatly increased spinning rates (50 kHz and above). Such ultra-fast spinning rates are comparable to the strength of proton-proton dipolar interactions in organic solids and cause a significant ^1H NMR line-narrowing.

Figure 1 presents an experimental example for ^1H NMR spectra recorded under fast MAS of the samples. It shows an increase of the central ^1H NMR peak height for several powder samples as a function of MAS rate. According to Eq. (12), we expect a linear dependence on Ω when Ω is sufficiently high to make spinning bands small compared to the central peak. The heights of the peaks in Fig. 1 are normalized individually for each sample so that the height increase (measured height minus the height for the static sample) at 50 kHz MAS rate is assigned to be one. For the L-valyl-L-leucine dipeptide, there are two well-resolved peaks at 50 kHz MAS. The height of the spectrum at fixed frequencies of these two peaks was measured at all spinning rates for this sample.

For typical organic samples, the line width (full width at half height) changes from 20–30 kHz under static conditions to about 1 kHz under 50 kHz MAS. As an example, for glycine and hexamethylbenzene (not shown) the line width under 50 kHz MAS drops from 22.7 kHz to 1.15 kHz and from 14.2 kHz to 0.67 kHz, respectively. Due to extremely small sample size and, as a result, comparable broad background signal from the probe itself, we were not able to accurately compare the absolute peak heights (except for narrower signal of adamantane, where the peak height increased 39 times under 50 kHz MAS). However, this background signal from the probe did not affect our results, where we present only an increase of the peak height, which comes solely from Ω -dependent signal of the sample.

The results for all samples except adamantane look similar. In adamantane, intra-molecular dipolar couplings are averaged out by fast molecular rotations, resulting in 13 kHz

residual static line width, so that 5 kHz spinning causes significant line-narrowing, and we already expect a linear dependence on Ω .

The linear dependence on Ω is expected only when neglecting L_0 . As one would expect from Eq. (15), the slopes for all samples should decrease at very high spinning rates, when Ω -independent L_0 is no longer negligible. L_0 may include various line-broadening factors, like distribution of isotropic chemical shifts, imperfect shims and any inaccuracy in the magic angle set-up. Another contribution to line broadening comes from spin-lattice relaxation, not included in theoretical treatment. One more source of experimental errors is the sample and probe heating at high spinning rates and detuning of the probe due to this heating. We did not compensate possible detuning in our experiments.

One may try to explain the linear dependence of the peak height on Ω by using the second-order average Liouvillian in Eq. (14). Under the assumption that this average Liouvillian accurately describes the entire shape of the central spectral band, one would expect that the line shape remains the same, except scaling, its width is proportional to $1/\Omega$, and, therefore, the peak height is proportional to Ω . However, in practice this assumption does not work well, and the observed peak heights are not inversely proportional to the line widths. As an example, Ref. 21 presents an experimental study of the line width dependence on MAS rate for a variety of samples. In most cases, the dependences for the line width are much more irregular than the data presented in Fig. 1.

IV. CONCLUSION

For quantum-mechanical problems with periodic modulation in space, it is convenient using the k -space or momentum space. In the same way, the frequency/energy domain is well suited for analyzing the problems with periodic modulation in time. The theoretical methods of coherent averaging in time domain, which use expansions in powers of interaction, use a formal requirement $\Omega \gg |L|$ for neglecting higher-order terms. In practice, high degree of averaging is often achieved at $\Omega \approx |L|$. In this paper, we proposed the approximation, based on actual performance of averaging, i.e., using smallness of satellites compared to the central peak.

The resolvent $(i\omega - L)^{-1}$ in Eqs. (3b) and (9), which describes the solution for the density matrix in frequency domain, has the same form for the time-independent and periodically time-modulated Liouvillians, except that the Liouvillian in Eq. (9) contains the frequency-shift operators (Eq. (10)). As we discussed above, the AHT is related to the expansion (4b) of the resolvent in powers of $(L/i\omega)$. For the central region of the spectral peak, at $\omega \rightarrow 0$, such an expansion is useless. Alternatively, one can expand the resolvent in powers of the inverse interaction $(i\omega/L)$. To do so, one can iteratively use the identity (5) with $A = -L$ and $B = -i\omega$. The result is

$$(i\omega - L)^{-1} = -(1/L) \sum_{k=0}^{\infty} (i\omega/L)^k. \quad (16)$$

The approximate solution for the density matrix, derived in this paper, is related to the expansion in the inverse powers of interaction in Eq. (16) as following. By using the first two terms of the expansion (16), inserting the Liouvillian $L = L_1 T + L_{-1} T^{-1}$, neglecting the terms $|\rho_\omega(\omega \pm 2\Omega)\rangle$, and taking the limit $\omega \rightarrow 0$, one obtains Eq. (12).

In conclusion, for many-body systems the non-zero average Hamiltonians obtained from expansions in powers of the interaction are not easily related to experimentally measurable heights of narrowed spectral peaks. The role of higher-order terms also remains unclear. As a more practical alternative, one may focus on calculating the amplitude of the spectrum of the observable (in spectroscopy, it is a measurable height of a spectral peak). In this case, the result can be obtained as a solution for the density matrix and directly related to experimental observations. While for a time-independent Hamiltonian the limit $\omega \rightarrow 0$ in Eq. (3b) does not provide any new insights, for periodically modulated Hamiltonians and generalized Eqs. (9) and (10) it can lead to meaningful approximations like in Eq. (12). One can also use the expansion (16) for obtaining more details on the shapes of narrowed spectral peaks.

ACKNOWLEDGMENTS

A.K.K. was a visiting Professor at the University of Michigan during his sabbatical leave. This study was supported by research funds from National Institutes of Health

(NIH) (GM084018, GM095640, and RR023597 to A.R.) and the instrumentation grant from Chemistry Research Instrumentation Funding (CRIF)-National Science Foundation (NSF).

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