A continuous approach to Floquet theory for pulse-sequence optimization in solid-state NMR

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We present a framework that uses a continuous frequency space to describe and design solid-state NMR experiments. The approach is similar to the well-established Floquet treatment for NMR, but is not restricted to periodic Hamiltonians and allows the design of experiments in a reverse fashion. The framework is based on perturbation theory on a continuous Fourier space, which leads to effective, i.e., time-independent, Hamiltonians. It allows the back calculation of the pulse scheme from the desired effective Hamiltonian as a function of spin-system parameters. We show as an example how to back calculate the rf irradiation in the MIRROR experiment from the desired chemical-shift offset behaviour of the sequence.

I. INTRODUCTION

Time-dependent Hamiltonians are very common in (solid-state) NMR due to sample rotation, e.g., magic angle spinning (MAS)1–3 or even rotations about multiple axes as implemented in double rotation (DOR)4 or dynamic-angle spinning (DAS)5 and the application of pulse sequences that can be described by interaction-frame transformations.6–8 Calculating the time evolution of the density operator under a time-dependent Hamiltonian is usually done numerically using time-slicing methods where we assume that the Hamiltonian is time constant for small enough time periods, \( \tau \). However, in many cases an analytical solution to the Liouville-von Neumann equation is advantageous especially if predictions of the response of the sequence on spin-system parameters are of interest. Since the late 1960s, various methods have been developed to approximate such time-dependent Hamiltonians using time-independent representations. This can be achieved using average Hamiltonian theory (AHT)6,8–10 Floquet theory11–15 or other less-established methods like the Fer expansion16,17 or the Floquet-Magnus expansion18,19 or the path-sum method20. Average Hamiltonian theory6,8–10 can be used for periodic Hamiltonians and is based on the Magnus expansion21. It generates a series of time-independent average Hamiltonians that approximate the time evolution of the density operator over the basic time period with increasing accuracy. Limitations of AHT are the stroboscopic observations at integer multiples of the basic time period, e.g., the difficulty to describe spinning side bands in MAS spectra, and the difficulty to describe Hamiltonians with multiple incommensurate frequencies that appear, for example in homonuclear22 or heteronuclear23 decoupling experiments. Despite these limitations, AHT is one of the most used techniques in NMR to develop and optimize pulse sequences. In Floquet theory11–15 the finite-dimensional time-dependent spin-Hilbert space Hamiltonian is replaced by an infinite-dimensional but time-independent Floquet Hamiltonian. Both representations are equivalent and describe the identical time evolution of the density operator. Floquet theory can be used to describe periodic time-dependent Hamiltonians without the requirement of stroboscopic sampling, i.e., side bands under MAS are predicted correctly15 and also multiple incommensurate time dependencies can be included using multi-mode Floquet theory13,15. Using the time-independent Floquet Hamiltonian makes no approximations but it is not always easy to get physical insights from the infinite-dimensional matrices. Therefore, operator-based Floquet theory24–29 that is based on the van Vleck perturbation treatment13,15 in the Floquet space was developed. Such a treatment allows the analytical block diagonalization of the Floquet Hamiltonian and a subsequent projection back into the spin-Hilbert space, generating a series of effective Hamiltonians that describe the time evolution of the density operator. Floquet theory and especially the operator-based implementation has become an important tool for the understanding of magnetic-resonance experiments and also for the design of new experiments.30–32

In this publication, we present a modified version of Floquet theory that is based on a continuous frequency space and not a discrete Fourier series. We show that the modified approach allows the description of sequences of limited length and also allows, in some cases, a simpler back calculation of pulse-sequence parameters.

II. THEORY

A. Standard Floquet theory

The formalism presented in this article is similar to the formulation of Floquet theory used in magnetic resonance. Therefore we first want to give a short review of the Floquet treatment and subsequently present the new formalism. A more detailed derivation can be found in the literature.13,14,15

The time dependence of the density operator is given by the Liouville-von Neumann equation

\[ \dot{\sigma}(t) = -i [\mathcal{H}(t), \sigma(t)] \tag{1} \]

with the solution

\[ \sigma(t) = U(t) \sigma(0) U^{-1}(t) \tag{2} \]
where the propagator is formally given by

$$U(t) = \mathcal{T} \exp \left( -i \int_0^t \mathcal{H}(\tau) d\tau \right) \tag{3}$$

and $\mathcal{T}$ is the Dyson time-ordering operator. An equivalent formulation and a good starting point for the derivation of Floquet theory is the differential equation in the propagator

$$\dot{U}(t) = -i \mathcal{H}(t) U(t) \tag{4}$$

Floquet theory for magnetic resonance is based on the assumption that the Hamiltonian is periodic and, therefore, the Schrödinger equation is a periodic differential equation. We can incorporate the periodicity of the Hamiltonian explicitly by expanding it in a Fourier series as reported by expanding it in a Fourier series as reported by extending operator-based Floquet theory to multiple frequencies instead of the Fourier harmonics. Typically van Vleck perturbation theory is applied on the Floquet Hamiltonian to obtain effective Hamiltonians. The procedure can be found in the literature and leads to the first and second-order Hamiltonians

$$\mathcal{H}^{(1)} = \mathcal{H}^{(0)} \tag{12}$$

and

$$\mathcal{H}^{(2)} = \frac{1}{2} \sum_{n \neq 0} \frac{[\mathcal{H}(n), \mathcal{H}(-n)]}{n\omega} \tag{13}$$

Extending operator-based Floquet theory to multiple frequencies is straightforward. The details can be found in several reviews.

### B. Frequency-domain formulation

Let us consider an arbitrary time-dependent Hamiltonian that is not necessarily periodic in time. In this case we cannot use the Floquet theorem nor a Fourier series to solve Eq. (1), since both require periodicity. However, we can use similar methods such as the Fourier transform to obtain an algebraic equation from Eq. (4). Instead of a Fourier series expansion, we apply the Fourier transformations to each matrix element of the Hamiltonian $\mathcal{H}(t)$ and the propagator $U(t)$. This will lead to a similar description, where the Fourier transformed operators take the role of the Fourier coefficients in the Floquet approach. In addition, Fourier transformation leads to a continuous spectrum of frequencies instead of the Fourier harmonics.

For the derivation of the generalized framework we again start from the differential equation Eq. (4). As a first step we use the Fourier transformation (element wise) to define a
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In Eq. (4) and using the convolution theorem leads to the frequency-domain Hamiltonian and propagator as

$$\mathcal{H}(t) = \mathcal{F}^{-1}\{\mathcal{H}(\Omega)\} = \tau \int_{-\infty}^{\infty} \mathcal{H}(\Omega) e^{i\Omega t} d\Omega$$  \hspace{1cm} (14)$$

$$\mathcal{H}(\Omega) = \mathcal{F}\{\mathcal{H}(t)\} = \frac{1}{2\pi \tau} \int_{0}^{\tau} \mathcal{H}(t) e^{-i\Omega t} dt$$ \hspace{1cm} (15)$$

$$U(t) = \mathcal{F}^{-1}\{\hat{U}(\Omega)\} = \tau \int_{-\infty}^{\infty} \hat{U}(\Omega) e^{i\Omega t} d\Omega$$ \hspace{1cm} (16)$$

$$\hat{U}(\Omega) = \mathcal{F}\{U(t)\} = \frac{1}{2\pi \tau} \int_{0}^{\tau} U(t) e^{-i\Omega t} dt$$ \hspace{1cm} (17)$$

The Fourier transformation is normalized such that it leads to a correspondence with the standard Floquet approach. Thus, the presented theory is a generalization of standard Floquet theory and reproduces all of its results. Notice that the normalization also has to ensure \( \mathcal{F}\{f(x)\} \equiv f(x) \).

The 'wide' hats on \( \hat{U}(\Omega) \) and \( \mathcal{H}(\Omega) \) indicate that these are frequency-domain operators. The underlying frequency domain is continuous, orthonormal, and complete, hence conceptually similar to the position or momentum basis used, for example, to describe a free particle. Inserting the expressions in Eq. (4) and using the convolution theorem leads to

$$i \mathcal{F}^{-1}\{\hat{\Omega}\} = -i \mathcal{F}^{-1}\{\mathcal{H}(\Omega)\} \mathcal{F}^{-1}\{\hat{U}(\Omega)\}$$

$$= -i \mathcal{F}^{-1}\{\mathcal{H}(\Omega) \hat{U}(\Omega)\}$$ \hspace{1cm} (18)$$

where * symbolizes the convolution operation in frequency space. Applying Fourier transformation to Eq. (18) results in the time-independent equation

$$\Omega \hat{U}(\Omega) = -\mathcal{H}(\Omega) \hat{U}(\Omega)$$ \hspace{1cm} (19)$$

Since convolution with the delta function is an identity operation we can write Eq. (19) as

$$\Omega \delta(\Omega) \hat{U}(\Omega) = -\mathcal{H}(\Omega) \hat{U}(\Omega)$$ \hspace{1cm} (20)$$

and express it as a single integral

$$\int_{-\infty}^{\infty} [\mathcal{H}(\Omega) \mathcal{H}(\Omega - \Omega') \hat{U}(\Omega') d\Omega' = 0$$ \hspace{1cm} (21)$$

Since this has to be fulfilled for every possible \( \hat{U}(\Omega') \) the kernel has to vanish

$$[\mathcal{H}(\Omega) \mathcal{H}(\Omega - \Omega') \hat{U}(\Omega') = 0$$ \hspace{1cm} (22)$$

Notice, that this is an eigenvalue equation of \( \hat{U}(\Omega') \) with the eigenoperator

$$\mathcal{H}_F = \Omega \delta(\Omega - \Omega') + \mathcal{H}(\Omega - \Omega')$$ \hspace{1cm} (23)$$

Similar to the standard Floquet treatment, we can express this Hamiltonian in the orthonormal product basis \( \Omega, \mu = |\Omega \rangle \otimes |\mu \rangle \). As before the states \( \mu \) denote the basis states of the spin Hilbert space, but \( \Omega \) are the basis states of the continuous Fourier space. Notice that the operators \( \mathcal{H}(\Omega - \Omega') \) and \( \Omega \) in \( \mathcal{H}_F \) live in different subspaces, i.e. the spin and the frequency space, respectively. Hence the Hamiltonian in the product basis takes the form

$$\langle \Omega, \mu | \Omega', \nu \rangle = \delta(\Omega - \Omega') \otimes \delta_{\mu \nu} + 1 \otimes \mathcal{H}_{\mu \nu}(\Omega - \Omega')$$ \hspace{1cm} (24)$$

where \( \mathcal{H}_{\mu \nu}(\Omega) = \langle \mu | \mathcal{H}(\Omega) | \nu \rangle \) are the matrix elements of the spin-system Hamiltonian at frequency \( \Omega \).

In full analogy to the Floquet description (Eq. (10)), \( \mathcal{H}_F \) can be formulated in a basis-free operator form as

$$\mathcal{H}_F = \int D(\Omega) \otimes \mathcal{H}(\Omega) d\Omega + \hat{\Omega} \otimes 1$$ \hspace{1cm} (25)$$

with the frequency operator

$$\hat{\Omega} |\Omega \rangle = \Omega |\Omega \rangle \quad \leftrightarrow \quad \hat{\Omega} = \int \Omega' |\Omega' \rangle \langle \Omega' | d\Omega'$$ \hspace{1cm} (26)$$

and the frequency-shift operator

$$\hat{D}(\Omega_0) |\Omega \rangle = |\Omega + \Omega_0 \rangle$$ \hspace{1cm} (27)$$

$$\hat{D}(\Omega_0) = \int_{\Omega_0}^{\Omega_0} \langle \Omega' + \Omega_0 | \langle \Omega' | d\Omega'$$ \hspace{1cm} (28)$$

The equivalence of Eq. (25) and Eq. (23) is shown in the supplementary information (SI). Notice that we introduced the frequency operator \( \hat{\Omega} \), which is similar to a position operator, but acting on the frequency space. It takes the place of the number operator \( F_\tau \) in standard Floquet theory. The frequency-shift operator \( \hat{D}(\Omega) \) is conceptually similar to the usual translation operator in the position space. It takes the place of the generalized ladder operators \( F_n \) in standard Floquet theory. Both of this operators act exclusively on the frequency domain.

As in the standard Floquet treatment used in solid state NMR we utilize a frequency basis together with the spin basis to represent the Hamiltonian. In contrast to the standard Floquet theory we use a continuous frequency basis, which enables the description of an arbitrary time-modulated Hamiltonian. Nonetheless, we obtained a similar description, employing a continuous Fourier basis and Fourier transformations instead of the discrete Fourier basis and Fourier series as in the Floquet approach. Since we do not have a discrete Fourier basis, we do not obtain a representation of the Hamiltonian as a matrix of constant coefficients, but as a frequency dependent matrix function. However, the commutation relations are similar to those of the Floquet approach and allow for a similar treatment for example using van Vleck perturbation theory.[30][32]

1. Generalization to multiple time-dependent modulations

In principle, with the continuous frequency basis, there is no need to describe multiple time-dependent modulations using different frequency dimensions as is required in standard
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Floquet theory. All time-dependent modulations could be lumped into a single dimension. However, to understand resonance conditions between different processes, e.g., magic-angle spinning and radio-frequency irradiation of the spins, it is advantageous to separate these processes in different dimensions represented by multiple frequency bases. Let us generalize the approach presented in the previous section to \( n \) time-dependent modulations of the Hamiltonian. As before we can describe the Hamiltonian in a frequency domain by using Fourier transformation, resulting in the expression

\[
\mathcal{H}(t) = \tau^n \int \cdots \int \mathcal{H}(\Omega_1, \Omega_2, \ldots, \Omega_n) e^{i \Omega_1 t} e^{i \Omega_2 t} \cdots e^{i \Omega_n t} d\Omega_1 d\Omega_2 \cdots d\Omega_n
\]  

(29)

Now the underlying basis is the direct product basis of \( n \) frequency bases and one spin basis \( \{\Omega_1, \Omega_2, \ldots, \Omega_n, \mu\} \). This approach is similar to multimodal Floquet theory, but is not limited to periodic modulations of the Hamiltonian. From Eq. (29) we directly obtain the resonance condition

\[
\Omega_1^{(0)} + \Omega_2^{(0)} + \cdots + \Omega_n^{(0)} = 0
\]  

(30)

Following the same procedure as in the single mode case we obtain a time-independent Hamiltonian of the form

\[
\mathcal{H}_F = \int \cdots \int \mathcal{H}(\Omega_1, \Omega_2, \ldots, \Omega_n) d\Omega_1 d\Omega_2 \cdots d\Omega_n
\]  

(31)

where \( \mathcal{H}_F(\Omega_1, \Omega_2, \ldots, \Omega_n) \) is the corresponding frequency-translation operator and \( \Omega_j \) the frequency operator. It is important to emphasize that in practice most likely two frequency domains will be sufficient, a spatial modulation, for example due to sample rotation, and a modulation of the spin system due to rf-field irradiation. In this case the bimodal approach will be sufficient. However, for rf-field irradiation addressing different spin species, like proton, nitrogen or electron spins, a higher modal approach might offer advantages. In principle, one can also combine the frequency-domain approach in one dimension (e.g., rf irradiation) with the traditional Floquet approach in a different dimension (e.g., sample rotation) where the Fourier series is a perfect description of the time-dependent Hamiltonian (vide infra).

C. Van Vleck perturbation theory and effective Hamiltonian

In the following, we apply van Vleck perturbation theory \(^{30,32}\) to the Floquet Hamiltonian defined in Eq. (25) with the goal of obtaining effective Hamiltonians of different orders. The detailed derivation can be found in the SI and follows the treatment in Ref. \(^{28}\). As usual we split the Hamiltonian into two parts

\[
\mathcal{H}_F = \mathcal{H}_F^{(0)} + \varepsilon \mathcal{H}_F^{(1)}
\]  

(32)

and apply the van Vleck transformation given by

\[
e^\varepsilon \mathcal{H}_F e^{-\varepsilon} = \sum_{m=0}^{\infty} \frac{[S, \mathcal{H}_F]_m}{m!} = \sum_{n=1}^{\infty} e^{\varepsilon} \Lambda_F^{(n)}
\]  

(33)

where the nested commutator is defined as \([S, \mathcal{H}_F]_m = [S, [S, \mathcal{H}_F]_{m-1}] \) with \([S, \mathcal{H}_F]_0 = \mathcal{H}_F \). We choose \( S \), such that \([\Lambda_F, \mathcal{H}_F] = 0 \) and proceed by expanding \( S \) as a series

\[
S = \sum_{n=1}^{\infty} \varepsilon^n S^{(n)}
\]  

(34)

and inserting it into Eq. (33), which leads to

\[
[S^{(n)}, \mathcal{H}_F^{(0)}] = \Lambda_F^{(n)} - \Phi_F^{(n)}
\]  

(35)

with

\[
\sum_{j=1}^{\infty} \varepsilon^{j} \Phi_F^{(j)} = \sum_{m=2}^{\infty} \frac{\varepsilon^{m} S^{(1), \mathcal{H}_F^{(0)}}}{m!} + \sum_{m=1}^{\infty} \frac{\varepsilon^{m} S^{(1), \mathcal{H}_F^{(1)}}}{m!}.
\]  

(36)

Adopting the approach from Primas \(^{31,32}\) we obtain the formal solution of Eq. (162) as

\[
S^{(n)} = \Gamma_F^{-1}(\Pi(\Phi_F^{(n)}) - \Phi_F^{(n)})
\]  

(37)

\[
\Lambda_F^{(n)} = \Pi(\Phi_F^{(n)})
\]  

(38)

where \( \Pi(X) \) is the projection operator and \( \Gamma_F^{-1} \) the inverse commutation operator defined in the SI. Let us calculate the first and second-order effective Hamiltonians for the single-mode case:

\[
\mathcal{H}_F^{(0)} = \tilde{\Omega}
\]  

(39)

\[
\mathcal{H}_F^{(1)} = \int \tilde{D}(\Omega) \tilde{\mathcal{H}}(\Omega) d\Omega = \Phi_F^{(1)}
\]  

(40)

For the first-order effective Hamiltonian we evaluate Eq. (159) leading to

\[
\mathcal{H}^{(1)} = (\Omega | \Lambda_F^{(1)} | \Omega) = \tilde{\mathcal{H}}(0) = \frac{1}{2\pi} \tau \int_0^\tau \mathcal{H}(t) \, dt
\]  

(41)

For the second-order Hamiltonian we use Eqs. (153-159) resulting in

\[
\mathcal{H}^{(2)} = \frac{1}{2} P \mathcal{V} \int \frac{[\tilde{\mathcal{H}}(\Omega), \tilde{\mathcal{H}}(-\Omega)]}{\Omega} d\Omega
\]  

(42)

We use the Cauchy principal value (PV) for the regularization of the integral, which avoids the integration over the singularity using limits. The main difference of Eq. (42) to Floquet theory is that the integral over the frequency-domain Hamiltonian, instead of a sum of Fourier coefficients of the Hamiltonian. This disparity stems from the fact that the underlying Fourier
space is continuous in contrast to the discrete space we use to describe periodic Hamiltonians. The derivation of the effective Hamiltonians for multiple frequency dimensions is quite similar and leads to the first and second-order effective Hamiltonian
\[ \hat{\mathcal{H}}^{(1)} = \int \hat{\mathcal{H}}(\Omega_1, -\Omega_1^0) d\Omega_1 \] (43)
and
\[ \hat{\mathcal{H}}^{(2)} = \frac{1}{2} PV \int d\Omega_1 \int d\Omega_1^0 \int d\Omega_2 \frac{[\hat{\mathcal{H}}(\Omega_1, \Omega_2), \hat{\mathcal{H}}(\Omega_1^0, -\Omega_1, -\Omega_1^0 - \Omega_2)]}{\Omega_1 + \Omega_2} \] (44)
where we used the resonance condition
\[ \Omega_2^0 = -\Omega_1^0 \] (45)
In fact, we can retrieve the effective Hamiltonians obtained from Floquet theory, considering a periodic Hamiltonian. Periodicity with period \( t_m \), causes quantization in the frequency domain with the frequency \( \omega_m = 2\pi / t_m \). Therefore the frequency-domain Hamiltonian is only non-zero at the harmonics \( n \omega_m \). Expressing this fact by a Dirac comb we obtain
\[ \hat{\mathcal{H}}(t) = \int_{-\infty}^{\infty} \hat{\mathcal{H}}(\Omega) e^{i\Omega t} d\Omega = \sum_{n=0}^{\infty} \delta(\Omega - n \omega_m) \hat{\mathcal{H}}(\Omega) e^{i\Omega t} d\Omega = \sum_{n=0}^{\infty} \hat{\mathcal{H}}(n \omega_m) e^{i n \omega_m t} = \sum_{n=0}^{\infty} \hat{\mathcal{H}}^{(n)} e^{i n \omega_m t} \] (46)
where we can identify the Fourier coefficients of the Hamiltonian as \( \hat{\mathcal{H}}(n \omega_m) = \hat{\mathcal{H}}^{(n)} \). This is simply the transition of the Fourier transformation to a Fourier series for a periodic function. As a consequence imposing a periodic boundary condition on the Hamiltonian leads to the results from Floquet theory.

As mentioned already above, it is possible to use a mixed approach, describing periodic modulations with a discrete Fourier space and non-periodic modulations on a continuous Fourier space. We can use the same approach with the delta comb as in Eq. (46) to arrive at
\[ \hat{\mathcal{H}}(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \delta(\Omega_1 - n \omega_m) \hat{\mathcal{H}}(\Omega_1, \Omega_2) e^{i\Omega_1 t} e^{i\Omega_2' t} d\Omega_1 d\Omega_2 = \sum_{n} \hat{\mathcal{H}}(n \omega_m, \Omega_2) e^{i n \omega_m t} e^{i \Omega_2' t} d\Omega_2 = \sum_{n} \hat{\mathcal{H}}^{(n)}(\Omega_2) e^{i n \omega_m t} e^{i \Omega_2' t} d\Omega_2 \] (47)
This approach is useful to analyze general solid-state NMR experiments under MAS, where the sample spinning is described as a periodic modulation, but the rf-field irradiation can be arbitrary. Such mixed approaches can be used for any number of modes, where for example the periodic modulation due to the chemical shift offset is treated as a third mode. The first and second-order effective Hamiltonians for the mixed approach with two frequencies as in Eq. (47) have the form
\[ \hat{\mathcal{H}}^{(1)} = \sum_{n_0} \hat{\mathcal{H}}^{(n_0)}(\Omega_0) \] (48)
and
\[ \hat{\mathcal{H}}^{(2)} = \frac{1}{2} \sum_{n} \sum_{n_0} PV \int d\Omega \frac{[\hat{\mathcal{H}}^{(n_0)}(\Omega), \hat{\mathcal{H}}^{(n_0-n)}(\Omega_0 - \Omega)]}{\Omega + n \omega_m} \] (49)
with the resonance conditions defined by \( \Omega_0 + n_0 \omega_m = 0 \). Similar to standard Floquet theory, the propagation with an effective Hamiltonian is mediated by
\[ \mathcal{U}(t) = \exp(-i \hat{\mathcal{H}}^{(1)} t) \] (50)
In contrast to standard Floquet Theory, the effective Hamiltonian is only valid for one specific duration, since the time dependence is implicitly in \( \hat{\mathcal{H}}^{(1)} \). However, if the duration of the irradiation scheme is changed or the scheme is applied repeatedly, the effective Hamiltonian is weighted by a function, which depends on the duration or repetitions. In section II(E2) we derive this function and discuss its effects.

D. Calculation of the frequency-domain interaction-frame trajectory

As already mentioned, sample spinning in NMR leads to a periodic modulation of the Hamiltonian and can be described by a discrete Fourier series with the Fourier coefficients typically limited to the range -1 to 2. Radio-frequency irradiation is also often periodic in time, but typically an interaction-frame transformation is required to ensure the convergence of the effective Hamiltonian series. We split the Hamiltonian into two parts
\[ \hat{\mathcal{H}}(t) = \hat{\mathcal{H}}(t) + \hat{\mathcal{H}}_{\text{CS}}(t) + \hat{\mathcal{H}}_{\text{rf}}(t) = \hat{\mathcal{H}}_{\text{iso}}(t) + \hat{\mathcal{H}}_{\text{I}}(t) \] (51)
where \( \hat{\mathcal{H}}_{\text{lo}} \) describes the spin-system Hamiltonian, \( \hat{\mathcal{H}}_{\text{rf}}(t) \) is the rf-field Hamiltonian and \( \hat{\mathcal{H}}_{\text{CS}}(t) \) the isotropic chemical-shift Hamiltonian. We can choose how to divide the total Hamiltonian into \( \hat{\mathcal{H}}_{\text{lo}} \) and \( \hat{\mathcal{H}}_{\text{I}} \), either we can set \( \hat{\mathcal{H}}_{\text{rf}}(t) = \hat{\mathcal{H}}_{\text{rf}}(t) \) and \( \hat{\mathcal{H}}_{\text{lo}}(t) = \hat{\mathcal{H}}_{\text{lo}}(t) + \hat{\mathcal{H}}_{\text{CS}}(t) \) resulting in an interaction-frame transformation by the rf irradiation only. In this case, the interaction-frame transformation is the same for all spins. Alternatively we can set \( \hat{\mathcal{H}}_{\text{rf}}(t) = \hat{\mathcal{H}}_{\text{CS}}(t) + \hat{\mathcal{H}}_{\text{rf}}(t) \) and \( \hat{\mathcal{H}}_{\text{lo}}(t) = \hat{\mathcal{H}}_{\text{lo}}(t) \) resulting in an interaction-frame transformation by the time-dependent effective field of each spin. In this case we have again two options. We can either include only the isotropic chemical shift into the interaction-frame transformation or we can include the isotropic and the
anisotropic chemically shift. With this choice, the interaction-frame trajectory of each spin will be distinct if the chemical shifts are different. The selection of the most convenient interaction frame will depend on the system and problem at hand. In the following we use an interaction frame generated by a general rf-field modulation including the chemical shift offset. In this case the unitary interaction-frame transformation of the Hamiltonian for each spin is a general complex rotation. Again, each spin will have its unique unitary transformation and, therefore, its unique frame, except if they are chemical equivalent. In the usual rotating frame defined by the Zeeman Hamiltonians, the Hamiltonian used for the interaction-frame transformation has the form

$$\mathcal{H}_i(t) = \omega_1(t) [\cos(\phi(t))I_x + \sin(\phi(t))I_y] + \omega_2(t)I_z$$

$$\theta(t)I$$

(52)

with

$$\hat{\theta}(t) = \begin{pmatrix} \theta_x(t) \\ \theta_y(t) \\ \theta_z(t) \end{pmatrix} = \begin{pmatrix} \omega_1(t) \cos(\phi(t)) \\ \omega_1(t) \sin(\phi(t)) \\ \omega_2(t) \end{pmatrix}$$

(53)

$$|\theta(t)| = \sqrt{\omega_1^2(t) + \omega_2^2(t)}$$

(54)

where \(\omega_1(t)\) is the amplitude and \(\phi(t)\) the phase of the rf-field and \(\omega_2(t)\) the chemical shift offset. The direction of \(\hat{\theta}(t)\) specifies the axis of rotation, its length \(|\theta(t)|\) is the angular velocity at time \(t\). The interaction-frame transformation is given by

$$U(t) = \mathcal{T} \exp\left(-i \int_0^t \mathcal{H}_i(t') dt'\right)$$

(55)

where \(\mathcal{T}\) is the Dyson time-ordering operator\(^{35}\). The evolution of the initial spin operators \(I = (I_x, I_y, I_z)^T\) can be written with a single rotation matrix with elements \(a_{\mu\nu}(t)\) as

$$I_\mu(t) = U^\dagger(t) I_\mu U(t) = \sum_\nu a_{\mu\nu}(t) I_\nu$$

(56)

This also can be expressed in the frequency domain using Fourier transform leading to

$$I_\mu(t) = \mathcal{F}^{-1}\{\hat{I}_\mu(\omega)\} = \sum_\nu \hat{a}_{\mu\nu}(\omega) I_\nu$$

(57)

$$\hat{I}_\mu(\omega) = \mathcal{F}\{I_\mu(t)\} = \sum_\nu \hat{a}_{\mu\nu}(\omega) I_\nu$$

(58)

where \(\hat{a}_{\mu\nu}(\omega) = \mathcal{F}\{a_{\mu\nu}(t)\}\). In the following we present an efficient route to calculate \(a_{\mu\nu}(t)\). Notice that the map

$$I_\mu \mapsto U(t) I_\mu U^\dagger(t)\text{ and } I_\mu \mapsto (-U(t)) I_\mu (-U^\dagger(t))$$

leads to the same rotation of \(\mathbb{R}^3\), hence two elements of \(SU(2)\) are mapped onto one element of \(SO(3)\). In more technical terms this means that there exists a 2:1 surjective homomorphism from \(SU(2)\) to \(SO(3)\). However Eq. (55) yields to only one of the two \(SU(2)\) elements, since it is impossible to get \(-U(t)\) from a given \(U(t)\) with the Hamiltonian of the form given in Eq. (52). Therefore, the operator defined in Eq. (55) is always a member of \(SU(2)/Z_2\) which is isomorphic to \(SO(3)\), i.e. \(SU(2)/Z_2 \cong SO(3)\). This fact will be important for the back-calculation, when we infer the rf-irradiation from rotation matrices. A second important point is, that in general, \(\mathcal{H}_i(t)\) does not commute with itself at different times. For this reason we divide the irradiation into time intervals, small enough to assume that the Hamiltonian commutes with itself during the interval. However, the intervals do not necessary have to be of the same size and can be adjusted to fit the problem at hand. The propagator of the \(j\)th interval corresponds to \(U_j\) and has a complex \(2 \times 2\) matrix representation given in the SI. Equipped with this matrix representation we calculate the coefficients of the rotation matrices \(a_{\mu\nu}^{(j)}\) corresponding to \(U_j\) as

$$U_j^\dagger I_\mu U_j = \sum_\nu a_{\mu\nu}^{(j)} I_\nu$$

(59)

Using \(a_{\mu\nu} = 2 \text{Tr}(I_\mu U_j U_j^{-1})\), leads to\(^{36}\)

$$a_{xx} = \left[ (\theta_x^2 + \theta_y^2) \cos(|\theta|) + \theta_z^2 \right] / (4|\theta|)$$

$$a_{xy} = \left[ -\theta_x \theta_y (\cos(|\theta|) - 1) - \theta_z |\theta| \sin(|\theta|) \right] / (4|\theta|)$$

$$a_{xz} = \left[ \theta_z (|\theta| \sin(|\theta|) + \theta_z (\cos(|\theta|) - 1)) / (4|\theta|) \right]$$

$$a_{yy} = \left[ (\theta_x^2 + \theta_y^2) \cos(|\theta|) + \theta_z^2 \right] / (4|\theta|)$$

$$a_{yz} = \left[ -\theta_x \theta_y (\cos(|\theta|) - 1) + \theta_z |\theta| \sin(|\theta|) \right] / (4|\theta|)$$

$$a_{zz} = \left[ \theta_z (|\theta| \sin(|\theta|) - \theta_z (\cos(|\theta|) - 1)) / (4|\theta|) \right]$$

(60)

(61)

(62)

where we omitted the indices \(j\) and \(\theta\) on \(a_{\mu\nu}\) for the sake of simplicity. Equivalent expressions can also be found for the alternate basis with \(\mu, \nu \in \{+, -, \cdot\}\). The interaction-frame trajectory at time \(t_j\) is given by

$$a(t_j) = a_j a_{j-1} \cdots a_1$$

(63)

Note, that the rotation matrices \(a_j\) describe the rotation during a single time step while the matrix \(a(t_j)\) describes the total rotation up to the time point \(t_j\). The expressions for the elements \(a_{\mu\nu}(t_j)\) in dependence on the parameter \(\omega_1\), \(\omega_2\), and \(\phi\) can be found in the SI. As mentioned before, the elements \(\hat{a}_{\mu\nu}(\omega)\) are obtained by Fourier transformation of the elements \(a_{\mu\nu}(t)\)

$$\hat{a}_{\mu\nu}(\omega) = \mathcal{F}\{a_{\mu\nu}(t)\} = \frac{1}{2\pi} \int_0^\pi a_{\mu\nu}(t) e^{i\omega t} dt$$

(64)

The mathematical properties of \(a_{\mu\nu}(t)\) and \(\hat{a}_{\mu\nu}(\omega)\) can be summarized as follows:

$$a_{\mu\nu}(t) \in \mathbb{R} \iff \hat{a}_{\mu\nu}(\omega) = \hat{a}_{\mu\nu}(-\omega)$$

(65)

$$\sum_\chi a_{\mu\chi}(t) a_{\nu\chi}(t) = \delta_{\mu\nu} \iff \sum_\chi \hat{a}_{\mu\chi}(\omega) \ast \hat{a}_{\nu\chi}(\omega) = \delta_{\mu\nu} \delta(\Omega)$$

(66)
E. Properties of the interaction-frame trajectory

In the following section the properties of the time and frequency-domain interaction-frame trajectory are explored. We will show that any finite irradiation can be expressed in term of its periodic version, on one hand reducing the computational effort, on the other hand isolating the effect of the finite duration. Furthermore we will show that for any cyclic irradiation the calculation of the frequency-domain interaction-frame trajectory can be reduced to the calculation of a single segment, further lessening the computational efforts significantly. Finally we will discuss the case of irradiation along a single axis, which always enables the expression of the frequency-domain interaction-frame trajectory in a closed form.

1. General properties of the interaction-frame trajectory

From the Plancherel theorem we obtain the general property

$$\frac{1}{2\pi\tau} \int_{-\infty}^{\infty} |\tilde{a}_{\mu\nu}(\Omega)|^2 d\Omega = \tau \int_{0}^{\tau} |\tilde{a}_{\mu\nu}(t)|^2 dt \quad (67)$$

In contrast to standard Floquet Theory, the duration of the irradiation scheme is incorporated implicitly in the frequency-domain interaction-frame trajectory. However any finite $a_{\mu\nu}(t)$ defined on $t \in [0, T]$ can be made periodic ($t \in \mathbb{R}$) using the modulo function

$$\tilde{a}_{\mu\nu}(t) = a_{\mu\nu}(t \mod T) \quad (68)$$

where we indicate the periodized function using a tilde. For a periodic interaction-frame trajectory the frequency-domain interaction-frame trajectory is related to the Fourier coefficients

$$\tilde{a}_{\mu\nu}(\Omega) = \sum_{n=-\infty}^{\infty} a_{\mu\nu}(n) \delta(\Omega - n 2\pi/T) \quad (69)$$

This relation is the bridge between standard Floquet theory, which utilizes Fourier series and continuous Floquet theory, which uses the Fourier transform. This correspondence only exists for the periodic case where standard Floquet theory is valid. Vice versa, a periodic function $\tilde{a}_{\mu\nu}(t)$ can be made finite by multiplication with the appropriate rectangular window function $\Pi(t)$

$$a_{\mu\nu}(t) = \tilde{a}_{\mu\nu}(t) \cdot \Pi(t/T - 1/2) \quad (70)$$

$$\Pi(t/T - 1/2) = \begin{cases} 1 & 0 \leq t \leq T \\ 0 & \text{else} \end{cases} \quad (71)$$

Eq. (70) and the convolution theorem lead to they frequency-domain interaction-frame trajectory

$$\tilde{a}_{\mu\nu}(\Omega) = \tilde{a}_{\mu\nu}(\Omega) \ast \mathcal{F} \{ \Pi(t/T - 1/2) \}$$

$$\tilde{a}_{\mu\nu}(\Omega) = \tilde{a}_{\mu\nu}(\Omega) \ast \frac{\sin(\Omega T/2)}{\pi \Omega T} \ast e^{-i\Omega \tau} \quad (72)$$

Notice, that Eq. (72) can be efficiently implemented numerically via discrete Fourier transformation (DFT), since $\tilde{a}_{\mu\nu}(\Omega)$ is periodic. Furthermore, the slope of $\tilde{a}_{\mu\nu}(\Omega)$ is dictated by $T$, as $\tilde{a}_{\mu\nu}(\Omega)$ has sharp frequency components, see Eq. (69). As a consequence sharp edges of $\tilde{a}_{\mu\nu}(\Omega)$ cannot be realized by any irradiation with finite duration. We can go a step further and decompose $\tilde{a}_{\mu\nu}(t)$ into a product and subsequently use the convolution theorem

$$\tilde{a}_{\mu\nu}(\Omega) = \mathcal{F} \{ \Pi(t/T) \} \ast \prod_{\mu,\nu} a^{(n)}_{\mu\nu}(\Omega)$$

$$\tilde{a}_{\mu\nu}(\Omega) = \mathcal{F} \{ \Pi(t/T) \} \ast \tilde{a}^{(1)}_{\mu\nu}(\Omega) \ast \tilde{a}^{(2)}_{\mu\nu}(\Omega) \ast \ldots \ast \tilde{a}^{(n)}_{\mu\nu}(\Omega) \quad (73)$$

This trick will be useful to construct pulse schemes, since we can decompose the desired $\tilde{a}_{\mu\nu}(\Omega)$ with convolutions and calculate the necessary $a^{(j)}_{\mu\nu}$ for each part. Finally we obtain the desired trajectory $a_{\mu\nu}(t)$ by calculating the product $\prod_{\mu,\nu} a^{(j)}_{\mu\nu}$. The ability to describe sequences of different length and the consequences of finite recoupling sequences is one of the advantages of the new method. Independent of the basis of the spin operator, $a_{\mu\nu}(t)$ are the elements of a rotation matrix, hence

$$\sum_{z} a_{\mu\nu}(t) a_{\nu z}(t) = \delta_{\mu\nu} \Leftrightarrow \sum_{z} \tilde{a}_{\mu\nu}(\Omega) \ast \tilde{a}_{\nu z}(\Omega) = \delta_{\mu\nu} \delta(\Omega) \quad (74)$$

The presented properties of the interaction-frame trajectory hitherto always hold. However some symmetries of $a_{\mu\nu}(t)$ and $\tilde{a}_{\mu\nu}(\Omega)$ depend on the basis of the spin operator. In the hermitian basis $\{I, I_1, I_2\}$ the interaction-frame trajectory is real and therefore the elements of the frequency-domain interaction-frame trajectory are hermitian functions

$$\tilde{a}^*_{\mu\nu}(t) = \tilde{a}_{\mu\nu}(t) \quad (75)$$

$$\tilde{a}^*_{\mu\nu}(-\Omega) = \tilde{a}_{\mu\nu}(\Omega) \quad (76)$$

In contrast in the basis $\{I_+1, I_1-I_2\}$ complex conjugation flips the sign of the indices, resulting in

$$a_{\mu\nu}^+(t) = a_{\mu\nu}^{-}(t) \quad \text{and} \quad a_{\mu\nu}^{-+(t)} = a_{\mu\nu}^{+\pm}(t) \quad (77)$$

$$a_{\mu\nu}^{\pm \pm}(\Omega) = a_{\mu\nu}^{\pm \pm}(-\Omega) \quad \text{and} \quad a_{\mu\nu}^{\pm \pm}(\Omega) = a_{\mu\nu}^{\pm \pm}(-\Omega) \quad (78)$$

$$a_{\mu\nu}^{\pm}(t) = a_{\mu\nu}^{\pm}(t) \quad \text{and} \quad a_{\mu\nu}^{\pm}(\Omega) = a_{\mu\nu}^{\pm}(\Omega) \quad (79)$$

2. Repetitive irradiation - nonzero effective field

Many pulse schemes in NMR are repetitive, i.e., consist of repeating segments. In general a repetitive irradiation does not generate a cyclic interaction-frame trajectory but will lead to an effective field after each segment. In this section we consider a pulse scheme of duration $T$, consisting of $N$ repeating segments of duration $\tau$. The interaction-frame trajectory of
such an irradiation can be written as

\[
a_{\mu\nu}(t) = \begin{cases} 
  a_{\mu\nu}(t) & 0 \leq t \leq \tau \\
  \sum_{\chi} a_{\mu\chi}(t-\tau)a_{\chi\nu}(\tau) & \tau \leq t \leq 2\tau \\
  \sum_{\chi} a_{\mu\chi}(t-2\tau)a_{\chi\nu}(2\tau) & 2\tau \leq t \leq 3\tau \\
  \vdots & \vdots \\
  \sum_{\chi} a_{\mu\chi}(t-(N-1)\tau)a_{\chi\nu}((N-1)\tau) & (N-1)\tau \leq t \leq N\tau 
\end{cases}
\]

Notice that \( a_{\mu\nu}(N\tau) = [a^N(\tau)]_{\mu\nu} \) where \( a(\tau) \) is the matrix with the elements \( a_{\mu\nu}(t) \). The rotation matrix \( a(\tau) \) represents the rotation of the spin due to the effective field. As shown in detail in the SI, we obtain for a frequency-domain interaction-frame trajectory

\[
\hat{a}_{\mu\nu}(\Omega) = \frac{1}{2\pi N\tau} \sum_{n=1}^{N} \sum_{\chi} \int_{(n-1)\tau}^{n\tau} a_{\mu\chi}(t-(n-1)\tau) \times a_{\chi\nu}((n-1)\tau)e^{-i\Omega t}dt
\]

(81)

with

\[
g_{\mu\nu}^{(N)}(\Omega) := \frac{1}{N} \sum_{n=0}^{N-1} e^{-in\Omega t} a_{\mu\nu}(n\tau)
\]

(83)

and

\[
\hat{a}_{\mu\nu}(\Omega) = \frac{1}{2\pi \tau} \int_{0}^{\tau} a_{\mu\nu}(t)e^{-i\Omega t}dt
\]

(84)

\[
= \mathcal{F}\{a_{\mu\nu}(\tau)\Pi(t/\tau-1/2)\}
\]

(85)

\[
= \mathcal{F}\{a_{\mu\nu}(t)\} + \mathcal{F}\{\Pi(t/\tau-1/2)\}
\]

(86)

As a result the \( \hat{a}_{\mu\nu}(\Omega) \) can be calculated efficiently using DFT, since \( a_{\mu\nu}(t) \) can be reduced to the periodized trajectory of a single segment.

3. Cyclic interaction-frame trajectory - zero effective field

As shown previously, a cyclic interaction-frame trajectory \( a(\tau) \) can be rewritten using modulo and a rectangular window function as

\[
a_{\mu\nu}(t) = a_{\mu\nu}(t \mod \tau) \Pi\left(\frac{t-T/2}{T}\right)
\]

(87)

The effective field for a cyclic interaction-frame trajectory after a segment is always zero, i.e., the interaction frame ends at the same point where it started. As a consequence \( a(N\tau) = I \), which leads to

\[
g_{\mu\nu}^{(N)}(\Omega) = \frac{1}{N} \sum_{n=0}^{N-1} e^{-in\Omega t}
\]

(88)

Notice that in the case of a periodic interaction-frame trajectory, i.e., an infinite repetition of the basic pulse scheme, the relation in Eq. \( \text{(87)} \) connects the standard Floquet theory with continuous Floquet theory.

4. Single irradiation axis

In many pulse schemes in NMR, rf irradiation is always along the same axis. Therefore, the axis of rotation does not change during the pulse scheme if we do not include the chemical-shift offset into the interaction-frame calculation. In this case, the phase of the rf-field Hamiltonian can be kept constant whereas the amplitude \( \phi_1 \) can be positive or negative and allows rotations in both directions. A special feature of the resulting rf-field Hamiltonian is that it commutes with itself at different times and, therefore, an analytical expression for the frequency trajectory \( a_{\mu\nu}(\Omega) \) can be found. Without loss of generality, we consider the case where \( \phi = 0 \) and, therefore, \( \mathcal{H}_I \) only generates rotation around the x-axis. It is convenient to transform in a tilted frame, where the z-axis is aligned with the rotation axis of the rf-field. The propagator resulting from \( \mathcal{H}_I \) together with the tilted-frame transformation is

\[
U(t) = e^{-i\int_{0}^{t} \phi_1(t)dt} e^{i\frac{\Omega t}{2} \hat{I}_y}
\]

(89)

In most cases we only have to calculate the evolution of the spin operator along the static magnetic field, which typically is along the z-axis

\[
I_z(t) = U(t)I_zU(t)
\]

\[
= \frac{1}{2} \begin{pmatrix}
  I^+ & e^{-i\int_{0}^{t} \phi_1(t)dt} \\
  e^{-i\int_{0}^{t} \phi_1(t)dt} & I^-
\end{pmatrix} 
\]

\[
= \frac{1}{2} (a_{z+}(t)I^+ + a_{z-}(t)I^-)
\]

\[
= \frac{\tau}{2} \int_{-\infty}^{\infty} (a_{z+}(\Omega)I^+ + a_{z-}(\Omega)I^-) e^{i\Omega t} d\Omega
\]

(90)

As a result, we get a relation between \( \phi_1(t) \) and \( \hat{a}_{z\pm}(\Omega) \)

\[
a_{z\pm}(t) = e^{\pm i\int_{0}^{t} \phi_1(t)dt} = \tau \int_{-\infty}^{\infty} \hat{a}_{z\pm}(\Omega) e^{i\Omega t} d\Omega
\]

(91)

\[
\hat{a}_{z\pm}(\Omega) = \frac{1}{2\pi \tau} \int_{-\infty}^{\infty} e^{\pm i\int_{0}^{t} \phi_1(t)dt} e^{-i\Omega t} dt
\]

(92)

We can solve Eq. \( \text{(91)} \) to obtain a solution for \( \phi_1(t) \)

\[
\phi_1(t) = \pm i \frac{d}{dt} \ln \left( \mathcal{F}^{-1}\{\hat{a}_{z\pm}(\Omega)\} \right)
\]

\[
= \pm \mathcal{F}^{-1}\{\Omega \hat{a}_{z\pm}(\Omega)\} \left( \mathcal{F}^{-1}\{\hat{a}_{z\pm}(\Omega)\} \right)
\]

(93)
In addition, from the convolution theorem we obtain

$$\tilde{a}_{\mu\nu}^{(j)}(\Omega) * \tilde{a}_{\mu\nu}^{(2)}(\Omega) * \cdots * \tilde{a}_{\mu\nu}^{(n)}(\Omega) = \mathcal{F}\left\{ \prod_{j=1}^{n} \tilde{a}_{\mu\nu}^{(j)}(t) \right\} = \mathcal{F}\left\{ \exp\left(-i \int_0^t \sum_{j=1}^{n} \omega_1^{(j)}(t) dt \right) \right\}$$

(94)

This means that, if we decompose the desired shape \( \tilde{a}_{\mu\nu}(\Omega) \) as a convolution, we can just add the corresponding \( \omega_1(t) \) to obtain the desired rf-field profile.

F. Calculation of the effective-field Hamiltonian from the frequency-domain interaction-frame trajectory

In this section we reverse the previous procedure and calculate the rf-field Hamiltonian from \( \tilde{a}_{\mu\nu}(\Omega) \). As a first step we simply apply the inverse Fourier transform

$$a_{\mu\nu}(t) = \tau \int_{-\infty}^{\infty} \tilde{a}_{\mu\nu}(\Omega) e^{i\Omega t} d\Omega$$

(95)

In the next step we want to construct \( U(t) \) from \( a(t) \). As mentioned previously the \( U(t) \) given in Eq. (55) are members of \( SU(2)/Z_2 \), which is isomorphic to \( SO(3) \). Hence we can map each rotation matrix \( \mathbf{a}_j \) uniquely to \( U_j \). For the construction, we use unit quaternions\(^{13,19}\) since they can represent complex as well as real rotations. More precisely, we reformulate the rotation matrices as unit quaternions and subsequently represent them with spin matrices in order to read out the pulse parameter.

A unit quaternion is given by \( q_j = u + jv + kw + lz \) with \( jk = -1 \) and \( u^2 + v^2 + w^2 + z^2 = 1 \). With the Euler-Rodriguez formula\(^{5,40}\) we express its components with the elements of the corresponding rotation matrix

$$u = \frac{1}{2} \sqrt{1 + \text{tr}(a)}$$

(6)

$$v = \frac{1}{4a} (a_{xy} - a_{yz})$$

(7)

$$w = \frac{1}{4a} (a_{yz} - a_{zx})$$

(8)

$$z = \frac{1}{4a} (a_{zx} - a_{xy})$$

(9)

Notice, that there are different options to calculate a unit quaternion from the corresponding rotation matrix. It is important for the numerical evaluation to choose the option, where the denominator is not close to zero, in order to increase the precision. We can always represent a unit quaternion as

$$q_j = \cos \left( \frac{\theta |\delta t|}{2} \right) + \frac{1}{|\theta|} \left( j \theta_x + k \theta_y + l \theta_z \right) \sin \left( \frac{\theta |\delta t|}{2} \right)$$

(100)

where \( \bar{\theta}(t) \) is defined in Eq. (53). The norm of \( \bar{\theta}(t) \) is the angular velocity and the direction specifies the rotation axis. Next, we rewrite the unit quaternions to assemble \( U_j \) in its exponential form. Therefore, we represent the quaternion units with the spin matrices

$$j = 2iI_x, \quad k = 2iI_y, \quad l = 2iI_z$$

(101)

which leads to the desired representation

$$q_j = \exp (-i \bar{\theta} I \delta t) = \exp (-i X_{\bar{\theta}} \delta t)$$

(102)

Together with the definition of \( \bar{\theta} \) in Eq. (53) we obtain

$$u = \frac{1}{2} \sqrt{1 + \text{tr}(a)} = \cos \left( \frac{\theta |\delta t|}{2} \right)$$

(103)

$$v = \frac{1}{4u} (a_{xy} - a_{yz}) = \frac{\omega_1}{|\theta|} \cos(\phi) \sin \left( \frac{\theta |\delta t|}{2} \right)$$

(104)

$$w = \frac{1}{4u} (a_{yz} - a_{zx}) = \frac{\omega_1}{|\theta|} \sin(\phi) \sin \left( \frac{\theta |\delta t|}{2} \right)$$

(105)

$$z = \frac{1}{4u} (a_{zx} - a_{xy}) = \frac{\omega_1}{|\theta|} \sin \left( \frac{\theta |\delta t|}{2} \right)$$

(106)

The solution of these equations for the pulse parameter \( \omega_1, \phi, \omega_2 \) are

$$|\theta| \delta t = 2 \arccos (u)$$

(107)

$$\omega_1 = \frac{|\theta| w}{\sin(\phi) \sin \left( \frac{|\theta| \delta t}{2} \right)}$$

(108)

$$\phi = \arctan \left( \frac{w}{v} \right)$$

(109)

$$\omega_2 = \frac{|\theta| z}{\sin \left( \frac{|\theta| \delta t}{2} \right)}$$

(110)

which can be also expressed using \( a_{\mu\nu} \) as
Continuous Floquet Theory in NMR

FIG. 1. Schematic diagram of continuous Floquet theory for magnetic resonance. The information of the interaction-frame transformation \( U(t) \) is encoded in the frequency-domain interaction-frame trajectory \( \hat{a}(\Omega) \) which is calculated from the interaction-frame trajectory \( a(t) \). Subsequently \( \hat{a}(\Omega) \) is combined with the effective Hamiltonian.

\[
|\theta|\delta t = \arccos \left( \frac{1}{2} \sqrt{1 + \text{tr}(a)} \right) \\
\phi = \arctan \left( \frac{a_{xz} - a_{zx}}{a_{zy} - a_{yz}} \right) \\
\omega_1 = -\frac{\text{arcsec} \left( 2 (\text{tr}(a) + 1)^{-\frac{1}{2}} \right) (a_{xz} - a_{zx} + a_{yz} - a_{zy})^2 \csc \left( 2 \text{arcsec} \left( 2 (\text{tr}(a) + 1)^{-\frac{1}{2}} \right) \right)}{\delta t \left[ (\text{tr}(a) + 1) (3 - \text{tr}(a)) \right]^{\frac{1}{2}}} \\
\omega_2 = \frac{2 (a_{xy} - a_{yx}) \text{arcsec} \left( 2 (\text{tr}(a) + 1)^{-\frac{1}{2}} \right)}{\delta t \left[ (\text{tr}(a) + 1) (3 - \text{tr}(a)) \right]^{\frac{1}{2}}} 
\]

(111)  
(112)  
(113)  
(114)

Eq. (112-114) express the phase, rf-field amplitude and offset as function of the interaction frame trajectory \( a_{\mu\nu}(t) \). In order to obtain the complete sequence, these equations have to be evaluated at every time step of \( a_{\mu\nu}(t) \).

III. THE DESIGN OF BAND-SELECTIVE MIRROR EXPERIMENTS

In this section we apply continuous Floquet theory to design the rf irradiation for a tunable PDS-based sequence called AM-MIRROR. The sequence can be designed for broadband or band-selective polarization transfer even at fast MAS frequencies by creating side-bands in the zero-quantum spectrum. Using the continuous frequency-space Floquet formalism, we show how to calculate the irradiation scheme to achieve tailored zero-quantum side-bands without any need of numerical optimization, which is in general not possible with the standard Floquet approach.
A. Theoretical preliminaries

To analyze the MIRROR experiment it is sufficient to consider a $S_2I$ spin system with irradiation on the I spin. In the standard rotating frame such a Hamiltonian has the form

$$\mathcal{H}(t) = \mathcal{H}_S(t) + \mathcal{H}_{\text{rf}}(t)$$

with

$$\mathcal{H}_S(t) = \sum_{n=-2}^{2} \omega^{(n)} S_{1S_2} e^{i\omega t} (S_{1S_2} - \hat{S}_1 \hat{S}_2)$$

$$+ \sum_{p=1}^{2} \sum_{n=-2}^{2} \omega^{(a)}_{p} S_p e^{i\omega t} 2I_p S_{pc}$$

$$+ \sum_{p=1}^{2} \omega^{(0)}_{p} S_{pc}$$

and

$$\mathcal{H}_{\text{rf}}(t) = \omega_{\text{rf}}(t) I_x$$

Here, consider only isotropic the chemical shifts of the S spins, but not of the I spins. Furthermore we assume an amplitude-modulated rf-irradiation in the x-direction ($\phi = 0, 180^\circ$). For simplicity, we tilt the frame of reference to align the z-axis with rf-irradiation axis as in section II E 4. In addition, we transform into an interaction frame with the isotropic chemical shift of the S spins. As usual we also transform into an interaction frame with the rf irradiation on the I spins leading to a total interaction-frame transformation defined by:

$$U(t) = \exp\left(-i \int_0^t \omega(t') dt' \right) \exp\left(-i \frac{\pi}{2} I_y \right)$$

$$\exp\left(i \sum_{p=1}^{2} \omega^{(0)}_p t S_{pc} \right)$$

Since the S-spin chemical shift and the MAS spinning lead to a continuous rotation around a single axis, the interaction-frame Hamiltonian $\tilde{H}(t) := U(t) H(t) U^\dagger(t)$ can be written as:

$$\tilde{H}(t) = T \sum_{n=-2}^{2} \sum_{\ell=1}^{2} \int_0^\infty \tilde{H}^{(n,\ell)}(\Omega) e^{i\omega t} e^{i\delta \omega_{\text{iso}}} e^{i\Omega_0} d\Omega$$

from where we can read out the MIRROR resonance condition

$$\Omega_0 + n_0 \omega_x + \ell_0 \Delta \omega_{\text{iso}} = 0$$

and

$$\Omega_0, n_0, \ell_0 \in \mathbb{R} \times \{-2, -1, \ldots, 2\} \times \{-1, 0, 1\}$$

The dominant second-order effective Hamiltonian is

$$\tilde{H}_{SS\otimes IS} = \frac{1}{4} \sum_{n,v=-2}^{2} \int_{-\infty}^{\infty} \left( \omega^{(v)}_{S_1S_2} (\omega^{(n-v)}_{S_1S_2} - \omega^{(n-v)}_{S_1S_2}) + \omega^{(v)}_{S_1S_2} (\omega^{(n-v)}_{S_1S_2} - \omega^{(n-v)}_{S_1S_2}) \right) \left( \tilde{a}_{z+}(\Omega) \widehat{I}_z^{+} + \tilde{a}_{z-}(\Omega) \widehat{I}_z^{-} \right) S_1 \widehat{S}_2^z d\Omega$$

where

$$\tilde{a}_{z\pm}(\Omega) := \tilde{a}_{z\pm}(\Omega) \pm i \tilde{a}_{xy}(\Omega)$$

In the following we are going to use Eq. (93) which enables the calculation of the rf-field amplitude.

B. Targeting single $\Delta \omega_{\text{iso}}$

The first example is the recoupling of a single chemical-shift difference $\Delta \omega_{\text{iso}}$ given by

$$\tilde{a}_{z+}(\Omega) = \frac{i}{\Delta \omega_{\text{iso}}} \delta(\Omega - \Delta \omega_{\text{iso}})$$

Inserting it in Eq. (91) leads to

$$e^{i \int_0^t \omega(t') dt'} = \int_{-\infty}^{\infty} \delta(\Omega - \Delta \omega_{\text{iso}}) e^{i\Omega t} d\Omega = e^{i\Delta \omega_{\text{iso}} t}$$

hence

$$\omega_{\text{rf}}(t) = \Delta \omega_{\text{iso}}$$

Alternatively we can use Eq. (93)

$$\omega_{\text{rf}}(t) = \frac{\mathcal{F}^{-1}\{\Omega \delta(\Omega - \Delta \omega_{\text{iso}})\}}{\mathcal{F}^{-1}\{\delta(\Omega - \Delta \omega_{\text{iso}})\}} = \frac{\Delta \omega_{\text{iso}} e^{-i\Delta \omega_{\text{iso}} t}}{e^{-i\delta(\Omega - \Delta \omega_{\text{iso}})}} = \Delta \omega_{\text{iso}}$$

This solution is not physical, since it would require irradiation of a infinite duration. As we will show below, the optimal rf-field amplitude for a given duration $T$ is in our case

$$\omega_{\text{rf}}(t) = \begin{cases} \Delta \omega_{\text{iso}} & 0 \leq t \leq T \\ 0 & \text{else} \end{cases}$$

Using Eq. (92), we obtain

$$\tilde{a}_{z+}(\Omega) = \frac{i}{2\pi T} \frac{1 - e^{iT(\Omega - \Delta \omega_{\text{iso}})}}{\Delta \omega_{\text{iso}} - \Omega}$$
Note that this is a sinc function where the time origin was shifted to the beginning of the time period and not at the center. The singularity at $\Omega = \Delta \omega_{iso}$ is removable, which can be seen from its expansion

$$\tilde{a}_c^+(\Omega) = \frac{i}{2\pi} \sum_{m=1}^{\infty} \frac{e^{-i\Omega mT}}{m!} (\Delta \omega_{iso} - \Omega)^{m-1}$$

(130)

We can easily calculate the global maximum of $|\tilde{a}_c^+(\Omega)|$ with Eq. (130), which is located at $\Omega = \Delta \omega_{iso}$

$$|\tilde{a}_c^+(\Delta \omega_{iso})| = \frac{1}{2\pi}$$

(131)

Notice, that the global maximum is independent of the duration of the pulse scheme, because of the chosen normalization.

C. Targeting multiple isolated $\Delta \omega_{iso}$

The simplest example of targeting multiple frequencies is to target 2 frequencies

$$\tilde{a}_c^+(\Omega) = \frac{1}{2} \left( \delta(\Omega - \Delta \omega_{iso}^{(1)}) + \delta(\Omega - \Delta \omega_{iso}^{(2)}) \right)$$

(132)

Inserting it into Eq. (93) leads to

$$\omega_i(t) = \Delta \omega_{iso}^{(1)} + \Delta \omega_{iso}^{(2)}$$

(133)

This irradiation is not possible for 2 reasons. First, we would again require irradiation of infinite duration as before. The second problem is that two waves with the same phase just add up in amplitude, i.e. $\Delta \omega_{iso}^{(1)} + \Delta \omega_{iso}^{(2)} = \Delta \omega_{iso}^{(3)}$. As a result, we would just target one frequency, namely $\Delta \omega_{iso}^{(3)}$. Notice, that this is the only existing solution for the given $\tilde{a}_c^+(\Omega)$. Therefore we have no choice than to split the irradiation into parts that target the two frequencies separately and successively in time

$$\omega_i(t) = \begin{cases} \Delta \omega_{iso}^{(1)} & 0 \leq t \leq \tau_1 \\ \Delta \omega_{iso}^{(2)} & \tau_1 < t \leq T \end{cases}$$

(134)

We again can use Eq. (92) and obtain

$$\tilde{a}_c^+(\Omega) = \tilde{a}_c^{(1)}(\Omega) + \tilde{a}_c^{(2)}(\Omega)$$

$$= \frac{i}{2\pi T} \left( 1 - e^{-i\tau_1(\Omega - \Delta \omega_{iso}^{(1)})} \right) \frac{\Delta \omega_{iso}^{(1)} - \Omega}{(\Delta \omega_{iso}^{(1)} - \Omega)}$$

$$+ \frac{i}{2\pi T} \left( e^{-i\tau_1(\Omega - \Delta \omega_{iso}^{(2)})} - e^{-iT(\Omega - \Delta \omega_{iso}^{(2)})} \right) e^{i(\tau_1\Delta \omega_{iso}^{(1)} - T\Delta \omega_{iso}^{(2)})}$$

(135)

Notice, that only the phase factor of the second term $\tilde{a}_c^{(2)}(\Omega)$ depends on the first part of the irradiation, but not its absolute value. Similar to the case of a single chemical shift we find

$$|\tilde{a}_c^{(1)}(\Delta \omega_{iso}^{(1)})| = \frac{\tau_1}{2\pi T}$$

(136)

$$|\tilde{a}_c^{(2)}(\Delta \omega_{iso}^{(2)})| = \frac{T - \tau_1}{2\pi T}$$

(137)

which approximates well the height of the two highest maxima of $|\tilde{a}_c^+(\Omega)|$, becoming more accurate the bigger $|\Delta \omega_{iso}^{(2)} - \Delta \omega_{iso}^{(1)}|$, because the overlap between $a^{(1)}(\Omega)$ and $a^{(2)}(\Omega)$ decreases. We can generalize this findings to $N$ chemical shifts as

$$\omega_i(t) = \begin{cases} \Delta \omega_{iso}^{(1)} & 0 \leq t \leq \tau_1 \\ \Delta \omega_{iso}^{(2)} & \tau_1 < t \leq \tau_2 \\ \vdots \\ \Delta \omega_{iso}^{(N)} & \tau_{N-1} < t \leq \tau_N \end{cases}$$

(138)

leading to

$$\tilde{a}_c^+(\Omega) = \frac{i}{2\pi T} \sum_{n=0}^{N} \left( e^{-i\tau_{n-1}(\Omega - \omega_n)} - e^{-i\tau_n(\Omega - \omega_n)} \right)$$

$$e^{i(\tau_1\omega_0 + \tau_2\omega_1 + \cdots + \tau_{n-1}(\omega_{n-2} - \omega_{n-1}) \omega_n - \omega_0))}$$

(139)

where we set $\tau_N = T$ and $\tau_0 = 0 = \omega_0$. Like before, the maxima of the absolute value of each term is given by

$$|\tilde{a}_c^{(n)}(\Delta \omega_{iso}^{(n)})| = \frac{\tau_{n+1} - \tau_n}{2\pi T}$$

(140)

It might be possible to construct an arbitrary function from general stepwise function by taking the limits carefully. The same limit can be applied directly on Eq. (139), if the integral in Eq. (91) is dominant integrable and hence we can change the order of the limit and the integral operation.
To obtain $\omega(t)$ we set $\hat{a}_{\pm}(t)$ to be a rectangular function with width $b$, normalized according to Eq. (97), as

$$\hat{a}_{\pm}(t) = \sqrt{\frac{2\pi}{b}} \Pi(\Omega/b)$$

From Eq. (93) follows

$$\omega(t) = \frac{\mathcal{F}^{-1}\{\Omega \Pi(\Omega/b)\}}{\mathcal{F}^{-1}\{\{\Omega(\Omega/b)\}\}} = i \left( \frac{b}{2} \cot \left( \frac{b t}{2} \right) - \frac{1}{t} \right)$$

Notice that $\omega(t)$ is independent of a constant factor of $\hat{a}_{\pm}(t)$. As before we have the problem of infinite duration in order to obtain the desired shape exactly.

In contrast to the previous theoretical rf-field amplitudes, we get a time-dependent function, which has poles and is purely imaginary. Motivated by Eq. (138) and Eq. (139), we use a linear function

$$\omega(t) = \frac{(\Delta\omega_{iso}^{(2)} - \Delta\omega_{iso}^{(1)})}{T} t + \Delta\omega_{iso}^{(1)}$$

Inserting it in Eq. (92), yields

$$\hat{a}_{\pm}(t) = \sqrt{\frac{\pi}{2 T}} e^{\frac{1}{2} \pi^2} e^{-\frac{T (\Delta\omega_{iso}^{(1)} - \Delta\omega_{iso}^{(2)})^2}{2 (\Delta\omega_{iso}^{(1)} - \Delta\omega_{iso}^{(2)})^2}}$$

$$\text{erf} \left( \frac{(1 + i) \sqrt{T (\Delta\omega_{iso}^{(2)} - \Delta\omega_{iso}^{(1)})}}{\sqrt{(\Delta\omega_{iso}^{(1)} - \Delta\omega_{iso}^{(2)})^2}} \right) - \text{erf} \left( \frac{(1 + i) \sqrt{T (\Delta\omega_{iso}^{(1)} - \Delta\omega_{iso}^{(2)})}}{\sqrt{(\Delta\omega_{iso}^{(1)} - \Delta\omega_{iso}^{(2)})^2}} \right)$$

$$\sqrt{(\Delta\omega_{iso}^{(1)} - \Delta\omega_{iso}^{(2)})}$$

(D) Targeting a range of $\Delta\omega_{iso}$

Taking a closer look on Eq. (143) and Eq. (144), we notice that Eq. (143) consists of 2 parts. The first term causes a rectangular like shape, the second term shifts this shape to the desired position. An intuitive picture offers Eq. (91) when we consider an interaction-frame rotation with an uniformly changing frequency $a_{\pm}(t) = e^{i(m t+c)}$. The frequencies $\omega(t) = m t + c$ are visible in its Fourier transform. Sweeping uniformly through a range of nutation frequencies slowly once, will drive more resonances than to sweep the same range several times, even if the overall time is the same. This is because a repeated sweep, also includes other, much slower, frequency components, due to the repetition.

Figure 2 shows $\frac{1}{T} \left( |\hat{a}_{\pm}(t)|^2 + |\hat{a}_{\pm}(t)|^2 \right)$ for different irradiation schemes. (A) Step-wise irradiation (Eqs. (134) and (135)) with $\Delta\omega_{iso}^{(1)} = 5$ and $\Delta\omega_{iso}^{(2)} = 10$ with $T = 2 \tau_1 = 20 ms$. (B) Same as (A) but with $\tau_1 = 3/4 T$. (C) Ramped irradiation described by Eq. (143) and Eq. (144), ranging from $7.5 kHz \leq \omega_1 \leq 12.5 kHz$. For the red curves, the duration has been set to $T = 20$, repeating the shape once. For the blue curves the duration has been set to $T/10$ and repeated $10$ times. For the green curves the duration has been $T/10$ and repeated once, but subsequently scaled up $10$ times. The integral of the red and blue curve is equal, since the duration of the irradiation is the same. As a consequence of the repetition, the blue curve is discretized by the modulation frequency $\nu_m = 0.5 kHz$.

E. Comparison to numerical simulation

An alternate description of such PSD-type experiments which does not rely on effective Hamiltonians, was provided by Veshtorf , where the rate constants $k_D$ under MAS can be calculated as

$$k_D = \sum_{n=-2}^{2} |\omega_{n}^{(n)}|^2 \text{Re}(J_0(\Delta\omega_{iso} - n\omega_1))$$

Here $\omega_{n}^{(n)}$ is defined as in Eq. (116) and $J_0(\omega)$ is the ZQ line. Notice, that $k_D$ is proportional to $J_0(n\omega_1)$, which can be manipulated by the irradiation and is dependent on the MAS.
frequency, similarly to $a_{c+}(\Omega)$. However the zero-quantum line and $a_{c+}(\Omega)$ are quantities that stem from fundamentally different theoretical descriptions. Nevertheless both quantities ultimately describe the evolution of the ZQ operator and dictate the ZQ transfer selectivity and efficiency. Figure 3 shows a comparison of the ZQ line and $1/(4\pi)(|a_{c+}(\Omega)|^2 + |a_{c-}(\Omega)|^2)$ for different irradiation schemes. The plots of the ZQ line are the results of numerical time-slicing simulation of a CH$_2$ spin system using the C++ library GAMMA\cite{7}. The mixing time was set to 20 ms and the MAS frequency to 50 kHz. The $a_{c\pm}(\Omega)$ were calculated from Eq. (135) and (144) using the same mixing time as in the numerical simulation. As mentioned before the two quantities stem from different descriptions, but the agreement, especially of the width and position, is very good, underlying their physical similarities.

IV. CONCLUSION

We presented a generalization of operator-based Floquet theory to non-periodic Hamiltonians. Instead of a discrete frequency space, which is sufficient for the description of pe-
Continuous Floquet Theory in NMR

DATA AVAILABILITY

AUTHORS DECLARATION

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CONFLICT OF INTEREST

The authors have no conflicts of interest to disclose.

DATA AVAILABILITY

The simulated data will be uploaded to a public repository after acceptance of the paper.

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In the following we apply Van Vleck perturbation theory on the single-mode Floquet Hamiltonian. As usual we split the Hamiltonian into two parts

\[ H_F = H_F^{(0)} + \varepsilon H_F^{(1)} \]  

(146)

Next we apply a unitary transformation called van Vleck transformation on Eq. (146) which is defined as

\[ \Lambda_F = U H_F U^\dagger = H_F^{(0)} + W_F \]  

(147)

where we choose \( U = e^S \) such that \([\Lambda_F, H_F^{(0)}] = 0\). This commutation relation is fulfilled if \([U, H_F^{(0)}] = 0\). We define the nested commutator as \([S, H_F^{(0)}]_m = [S, [S, H_F^{(0)}]_{m-1}]\) with \([S, H_F^{(0)}]_0 = H_F^{(0)}\). In this notation the Baker-Campbell-Hausdorff formula takes the form

\[ \Lambda_F = \sum_{m=0}^{\infty} \frac{[S, H_F^{(0)}]_m}{m!} = H_F^{(0)} + \sum_{n=1}^{\infty} \varepsilon^n \Lambda_F^{(n)} \]  

(148)

where we identify

\[ W_F = \sum_{n=1}^{\infty} \varepsilon^n \Lambda_F^{(n)} = \sum_{m=1}^{\infty} \frac{[S, H_F^{(0)}]_m}{m!} \]  

(149)

This is an important equation, because it connects the Hamiltonian \( H_F \) and the operator \( S \) with the perturbation series. We now proceed with inserting the expansion

\[ S = \sum_{l=1}^{\infty} \varepsilon^l S^{(l)} \]  

(150)
as well as Eq. (146) in Eq. (149), which leads to

\[
\sum_{n=1}^{\infty} n^n \Lambda_F^{(n)} = \sum_{m=1}^{\infty} \frac{\left[ \sum_{l=1}^{\infty} \epsilon^l S^{(l)}, \mathcal{H}_F^{(0)} + \mathcal{E} \mathcal{H}_F^{(1)} \right]_m}{m!} = \sum_{m=1}^{\infty} \frac{\left[ \sum_{l=1}^{\infty} \epsilon^l S^{(l)}, \mathcal{H}_F^{(0)} \right]_m + \left[ \sum_{l=1}^{\infty} \epsilon^l S^{(l)}, \mathcal{E} \mathcal{H}_F^{(1)} \right]_m}{m!} = \sum_{m=1}^{\infty} \frac{\left[ \sum_{l=1}^{\infty} \epsilon^l S^{(l)}, \mathcal{H}_F^{(0)} \right]_m}{m!} + \sum_{m=2}^{\infty} \frac{\left[ \sum_{l=2}^{\infty} \epsilon^l S^{(l)}, \mathcal{H}_F^{(0)} \right]_m + \left[ \sum_{l=1}^{\infty} \epsilon^l S^{(l)}, \mathcal{E} \mathcal{H}_F^{(1)} \right]_m}{m!}
\]

(151)

As a result, we arrive at the equation

\[
[S^{(l)}, \mathcal{H}_F^{(0)}] = \Lambda_F^{(l)} - \Phi_F^{(l)}
\]

(152)

with

\[
\sum_{j=1}^{\infty} \epsilon^j \Phi_F^{(j)} = \sum_{m=2}^{\infty} \frac{\left[ \sum_{l=1}^{\infty} \epsilon^l S^{(l)}, \mathcal{H}_F^{(0)} \right]_m}{m!} + \sum_{m=1}^{\infty} \frac{\left[ \sum_{l=1}^{\infty} \epsilon^l S^{(l)}, \mathcal{E} \mathcal{H}_F^{(1)} \right]_m}{m!}
\]

(153)

Utilizing mathematical induction over \( m \) we can prove following identities

\[
\sum_{m=1}^{\infty} \left[ \sum_{l=1}^{\infty} \epsilon^l S^{(l)}, \mathcal{H}_F^{(1)} \right]_m = \sum_{m=1}^{\infty} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \cdots \sum_{n_m=1}^{\infty} \epsilon^{1+n_1+n_2+\cdots+n_m} [S^{(n_1)}, [S^{(n_2)}, \ldots, [S^{(n_m)}, \mathcal{H}_F^{(1)}] \ldots]]
\]

(154)

\[
\sum_{m=2}^{\infty} \left[ \sum_{l=1}^{\infty} \epsilon^l S^{(l)}, \mathcal{H}_F^{(0)} \right]_m = \sum_{m=2}^{\infty} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \cdots \sum_{n_m=1}^{\infty} \epsilon^{1+n_1+n_2+\cdots+n_m} [S^{(n_1)}, [S^{(n_2)}, \ldots, [S^{(n_m)}, \mathcal{H}_F^{(0)}] \ldots]]
\]

(155)

which lead to a more explicit form of \( \sum_{j=1}^{\infty} \epsilon^j \Phi_F^{(j)} \)

\[
\sum_{j=1}^{\infty} \epsilon^j \Phi_F^{(j)} = \sum_{m=2}^{\infty} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \cdots \sum_{n_m=1}^{\infty} \frac{\epsilon^{1+n_1+n_2+\cdots+n_m}}{m!} [S^{(n_1)}, [S^{(n_2)}, \ldots, [S^{(n_m)}, \mathcal{H}_F^{(0)}] \ldots]]
\]

(156)

Although this expression is quite complicated, it allows relatively easy and efficient calculation of \( \Phi_F^{(l)} \). To find a solution of Eq. (152) for \( S^{(l)} \) we adapt the approach of Primas and use projection operator defined as

\[
\Pi(X) = \int P(u)X P(u) \, du \quad \mathcal{H}_F^{(0)} = \int_{-\infty}^{\infty} \kappa(u)P(u) \, du
\]

(157)

By applying the projection operator \( \Pi(X) \) on Eq. (152) we obtain

\[
\Pi([S^{(l)}, \mathcal{H}_F^{(0)}]) = \Pi(\Lambda_F^{(l)} - \Phi_F^{(l)})
\]

(158)

Since \([\Lambda_F, \mathcal{H}_F^{(0)}] = 0\), hence \([U, \mathcal{H}_F^{(0)}] = 0\), we have

\[
0 = \Pi([S^{(l)}, \mathcal{H}_F^{(0)}]) = \Pi(\Lambda_F^{(l)} - \Phi_F^{(l)}) = \Lambda_F^{(l)} - \Phi_F^{(l)} \implies \Lambda_F^{(l)} = \Pi(\Phi_F^{(l)})
\]

(159)

By introducing the commutation operator

\[
\Gamma_F(X) = [X, \mathcal{H}_F^{(0)}], \quad \Gamma_F^{-1}(X) = \int \int \frac{P(u)X P(v)}{\kappa(u) - \kappa(v)} \, du \, dv
\]

(160)
we can rewrite Eq. (152) as
\[
\Gamma_F(S^{(l)}) = \Pi(\Phi_F^{(l)}) - \Phi_F^{(l)}
\]
and finally arrive at the formal solution
\[
S^{(l)} = \Gamma_F^{-1}(\Pi(\Phi_F^{(l)}) - \Phi_F^{(l)})
\]
(162)
The solution has the same form as found by Primas but with differ in the operators \(\Pi(X)\) and \(\Gamma_F(X)\) given in Eq. (157) and Eq. (160), respectively. Ultimately we have all the ingredients to derive each term of the perturbation series.

A. Equivalence of the representations of the Floquet Hamiltonian (Eq. (23) and Eq. (25) of the main text)

The following shows that Eq. (23) and Eq. (25) of the main text is equivalent:
\[
\langle \chi, \mu | \mathcal{H} | \xi, \nu \rangle = \langle \chi, \mu | \int D(\Omega) \otimes \hat{\mathcal{H}}(\Omega) \, d\Omega + \hat{\Omega} \otimes 1 | \xi, \nu \rangle
\]
\[
= \langle \chi, \mu | \int D(\Omega) \otimes \hat{\mathcal{H}}(\Omega) | \xi, \nu \rangle \, d\Omega + \langle \chi, \mu | \hat{\Omega} \otimes 1 | \xi, \nu \rangle
\]
\[
= \int \langle \chi | D(\Omega) | \xi \rangle \otimes \langle \mu | \hat{\mathcal{H}}(\Omega) | \nu \rangle \, d\Omega + \langle \chi | \hat{\Omega} | \xi \rangle \otimes \langle \mu | 1 | \nu \rangle
\]
\[
= \int \langle \chi | \xi + \Omega \rangle \otimes \langle \mu | \hat{\mathcal{H}}(\Omega) | \nu \rangle \, d\Omega + \xi \langle \chi | \xi \rangle \otimes \langle \mu | \nu \rangle
\]
\[
= \delta(\chi - \xi - \Omega) \otimes \hat{\mathcal{H}}_{\mu \nu}(\Omega) \, d\Omega + \xi \delta(\chi - \xi) \otimes \delta_{\mu \nu}
\]
\[
= 1 \otimes \hat{\mathcal{H}}_{\mu \nu}(\chi - \xi) + \xi \delta(\chi - \xi) \otimes \delta_{\mu \nu}
\]
(163)

B. Derivation of the first and second-order effective Hamiltonian for a single-mode problem

Next we are going to use the previous results to calculate the first and second-order effective Hamiltonian. For the sake of simplicity, we just present the single mode case, because it already captures the whole procedure. A generalization to the \(n\)-modal case in retrospect is straight forward, therefore we will just state the results afterwards. The goal is to derive the first three terms of the perturbation series, i.e. \(\langle \Omega | \mathcal{H}_F^{(0)} + \Lambda_F^{(1)} + \Lambda_F^{(2)} | \Omega' \rangle\). In essence, the only equations we need are Eq. (156) (or Eq. (153)), Eq. (159) and Eq. (162). For the single mode case the Hamiltonians are
\[
\mathcal{H}_F^{(0)} = \hat{\Omega}
\]
(164)
\[
\mathcal{H}_F^{(1)} = \int \hat{D}(\Omega) \otimes \hat{\mathcal{H}}(\Omega) \, d\Omega = \Phi_F^{(1)}
\]
(165)

In the subsequent derivation the projection operator will be often applied on the translation operator, which results in a delta distribution
\[
\Pi(\hat{D}(\Omega)) = \delta(\Omega)
\]
(166)
The projection of \(\Phi_F^{(1)}\) simply leads to
\[
\Lambda_F^{(1)} = \Pi(\Phi_F^{(1)}) = \Pi \left( \int \hat{D}(\Omega) \otimes \hat{\mathcal{H}}(\Omega) \, d\Omega \right) = \int \delta(\Omega) \otimes \hat{\mathcal{H}}(\Omega) \, d\Omega = \hat{D}(0) \otimes \hat{\mathcal{H}}(0)
\]
(167)
Inserting it into the Eq. (162) gives
\[
S^{(1)} = \Gamma_F^{-1} \left( \Pi(\Phi_F^{(1)}) - \Phi_F^{(1)} \right) = \Gamma_F^{-1} \left( \hat{D}(0) \otimes \hat{\mathcal{H}}(0) - \int \hat{D}(\Omega) \otimes \hat{\mathcal{H}}(\Omega) \, d\Omega \right) = -PV \int \frac{\hat{D}(\Omega) \otimes \hat{\mathcal{H}}(\Omega)}{\Omega} \, d\Omega
\]
(168)
Notice that we use Cauchy principal value (PV) for the regularization of the integral defined as
\[
PV \int_a^c f(x) = \lim_{\epsilon \to 0^+} \left[ \int_a^{b-\epsilon} f(x) \, dx + \int_{b+\epsilon}^c f(x) \, dx \right]
\]
(169)
Using this regularization technique is justified, since we subtract $\tilde{D}(0) \otimes \tilde{H}(0)$, which is the kernel of the integral at the critical value $\Omega = 0$ and therefore can be exclude it from the integration. Equipped with the expression for $S^{(1)}$ we move to the second order

$$
\Phi_{F}^{(2)} = [S^{(1)}, H_F^{(1)}] + \frac{1}{2} [S^{(1)}, [S^{(1)}, H_F^{(0)}]]
$$

(170)

$$
= - \text{PV} \int \frac{[\tilde{H}(\Omega), \tilde{H}(0)] \tilde{D}(0)}{\Omega} d\Omega + \frac{1}{2} \text{PV} \int \frac{[\tilde{H}(\Omega), \tilde{H}(\Omega')] \tilde{D}(\Omega + \Omega')}{\Omega} d\Omega d\Omega'
$$

(171)

which results in

$$
\Lambda_{F}^{(2)} = \Pi \left( \Phi_{F}^{(2)} \right) = \frac{1}{2} \text{PV} \int \frac{[\tilde{H}(\Omega), \tilde{H}(-\Omega)] \tilde{D}(0)}{\Omega} d\Omega
$$

(172)

Finally we express the Hamiltonian in the product basis

$$
\tilde{H}^{(0)} + \tilde{H}^{(1)} + \tilde{H}^{(2)} = \langle \Omega, \mu | \tilde{H}^{(0)} + \Lambda_{F}^{(1)} + \Lambda_{F}^{(2)} | \Omega', \nu \rangle
$$

(173)

with

$$
\tilde{H}^{(0)} = \tilde{\Omega} \quad \tilde{H}^{(1)} = \int_{-\infty}^{\infty} \tilde{H}(\Omega) d\Omega \quad \tilde{H}^{(2)} = \frac{1}{2} \text{PV} \int \frac{[\tilde{H}(\Omega), \tilde{H}(-\Omega)]}{\Omega} d\Omega
$$

(174)

As expected this results are similar to the corresponding equations known from Floquet theory. The main difference is that we have an integral and a translation operator instead of a sum and a ladder operator.

One of the main differences in the higher modal cases is the appearance of resonance conditions between the modes. For the n-modal case the resonance conditions are

$$
\Omega_{1}^{(0)} + \Omega_{2}^{(0)} + \cdots + \Omega_{n}^{(0)} = 0
$$

(175)

The derivation of the effective Hamiltonians is quite similar and leads to the first and second-order effective Hamiltonian, for the bimodal case

$$
\tilde{H}^{(1)} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \tilde{H}(\Omega_{1}, \Omega_{2}) d\Omega_{1} d\Omega_{2}
$$

(176)

$$
\tilde{H}^{(2)} = \int d\Omega_{1} \int \Omega_{1}^{(0)} d\Omega_{1} \int d\Omega_{2} \int \Omega_{2}^{(0)} \frac{[\tilde{H}(\Omega_{1}, \Omega_{2}), \tilde{H}(\Omega_{1}^{(0)} - \Omega_{1}, \Omega_{2}^{(0)} - \Omega_{2})]}{\Omega_{1} + \Omega_{2}}
$$

(177)

VII. CALCULATION OF THE FREQUENCY-DOMAIN INTERACTION-FRAME TRAJECTORY

A. Propagator

The propagator of the $j$th time slice $U_{j}$ (Eq. (59)), has the complex $2 \times 2$ matrix representation

$$
U_{j} = \exp(-i \tilde{\mathcal{H}} \delta t) = \frac{1}{|\theta| \delta t} \begin{pmatrix}
|\theta| \cos \left( \frac{|\theta| \delta t}{2} \right) + i \theta \sin \left( \frac{|\theta| \delta t}{2} \right) & |\theta| \cos \left( \frac{|\theta| \delta t}{2} \right) \left( \theta_{y} + i \theta_{z} \right) \\
|\theta| \sin \left( \frac{|\theta| \delta t}{2} \right) \left( -\theta_{y} + i \theta_{z} \right) & |\theta| \cos \left( \frac{|\theta| \delta t}{2} \right) - i \theta \sin \left( \frac{|\theta| \delta t}{2} \right)
\end{pmatrix}
$$

(178)

where we dropped the index $j$ of $\theta$ for sake of simplicity. This representation is used for derivation of Eq. (61) in the main text.
B. The frequency-domain interaction-frame trajectory for a cyclic pulse scheme

The interaction-frame trajectory of a cyclic pulse scheme with a basic element of duration $\tau$ and an overall duration $N\tau$ can be written as

$$a_{\mu\nu}(t) = \begin{cases} 
  a_{\mu\nu}(t) & 0 \leq t \leq \tau \\
  \sum_{\chi} a_{\mu\chi}(t-\tau)a_{\chi\nu}(\tau) & \tau \leq t \leq 2\tau \\
  \sum_{\chi} a_{\mu\chi}(t-2\tau)a_{\chi\nu}(2\tau) & 2\tau \leq t \leq 3\tau \\
  \vdots & \vdots \\
  \sum_{\chi} a_{\mu\chi}(t-(N-1)\tau)a_{\chi\nu}((N-1)\tau) & (N-1)\tau \leq t \leq N\tau 
\end{cases}$$

(179)

Fourier transformation leads to

$$\tilde{a}_{\mu\nu}(\Omega) = \frac{1}{2\pi N\tau} \left( \sum_{\chi} \int_0^\tau a_{\mu\nu}(\tau)e^{-i\Omega\tau}d\tau + \int_\tau^{2\tau} a_{\mu\chi}(t-\tau)a_{\chi\nu}(\tau)e^{-i\Omega\tau}d\tau + \int_{2\tau}^{3\tau} a_{\mu\chi}(t-2\tau)a_{\chi\nu}(2\tau)e^{-i\Omega\tau}d\tau + \cdots \sum_{\chi} \int_{(N-1)\tau}^{N\tau} a_{\mu\chi}(t-(N-1)\tau)a_{\chi\nu}((N-1)\tau)e^{-i\Omega\tau}d\tau \right)$$

(180)

$$= \frac{1}{2\pi N\tau} \sum_{\chi} \sum_{n=1}^N \int_0^{n\tau} a_{\mu\chi}(t-(n-1)\tau)a_{\chi\nu}((n-1)\tau)e^{-i\Omega\tau}d\tau$$

(181)

$$= \frac{1}{2\pi N\tau} \sum_{\chi} \sum_{n=1}^N e^{-i\Omega(n-1)\tau} \int_0^{\tau} a_{\mu\chi}(t')a_{\chi\nu}((n-1)\tau)e^{-i\Omega't'}dt'$$

(182)

$$= \frac{1}{2\pi N\tau} \sum_{\chi} \int_0^{\tau} a_{\mu\chi}(t')e^{-i\Omega't'}dt' \sum_{n=0}^{N-1} e^{-i\Omega n\tau} a_{\chi\nu}(n\tau)$$

(183)

$$= \sum_{\chi} \tilde{a}_{\mu\chi}(\Omega) g^{(N)}_{\chi\nu}(\Omega)$$

(184)

and therefore

$$g^{(N)}_{\mu\nu}(\Omega) := \frac{1}{N} \sum_{n=0}^{N-1} e^{-in\Omega\tau}a_{\mu\nu}(n\tau)$$

(185)

Notice that $a_{\mu\nu}(n\tau) = [a^{\mu}(\tau)]_{\mu\nu}$ where $a^{\mu}(\tau)$ is the matrix with the elements $a_{\mu\nu}(\tau)$. Furthermore we have

$$\tilde{a}_{\mu\nu}(\Omega) = \frac{1}{2\pi \tau} \int_0^{\tau} a_{\mu\nu}(t)e^{-i\Omega t}dt$$

(186)

$$= \mathcal{F}\{a_{\mu\nu}(t)\Pi(t/\tau-1/2)\}$$

(187)

$$= \mathcal{F}\{a_{\mu\nu}(t)\} * \mathcal{F}\{\Pi(t/\tau-1/2)\}$$

(188)

and

$$\mathcal{F}\{\tilde{a}_{\mu\nu}(t)\} = \tilde{a}_{\mu\nu}(\Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} a_{\mu\nu}(t \mod \tau)e^{-i\Omega t}dt$$

(189)

Notice that $\tilde{a}_{\mu\nu}(\Omega)$ is just calculated using FFT. As described in the main text, the special case of a cyclic interaction-frame trajectory occurs when $a^{\mu}(\tau) = 1$. 

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