Closed solution to the Baker-Campbell-Hausdorff problem: Exact effective Hamiltonian theory for analysis of nuclear-magnetic-resonance experiments

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(Received 6 April 2001; published 23 January 2002)

A closed solution to the Baker-Campbell-Hausdorff problem is described. The solution, which is based on the Cayley-Hamilton theorem, allows the entanglement between exponential operators to be described by an exact finite series expansion. Addressing specifically the special unitary Lie groups SU(2), SU(3), and SU(4), we derive expansion formulas for the entangled exponential operator as well as for the effective Hamiltonian describing the net evolution of the quantum system. The capability of our so-called exact effective Hamiltonian theory for analytical and numerical analysis is demonstrated by evaluation of multiple-pulse methods within liquid- and solid-state nuclear-magnetic-resonance spectroscopy. The examples include composite pulses for inversion, decoupling, and dipolar recoupling, as well as coherence-order- and spin-state-selective double- to single-quantum conversion, homonuclear dipolar decoupling, finite rf excitation for quadrupolar nuclei, heteronuclear coherence transfer, and gates for quantum computation.

DOI: 10.1103/PhysRevE.65.021108 PACS number(s): 82.56.Lz

I. INTRODUCTION

In many branches of modern physics, it is of substantial interest to describe the effect of complex time-dependent processes in terms of a single operator that is representative of the overall evolution of the system. The resulting operator may provide direct physical insight into the evolution of the system, which is useful for evaluation and systematic design of complex experiments. Considering unitary evolution in quantum physics as an attractive example, relevant, e.g., in coherent spectroscopy [1–4] and quantum computing [5–7], information about the effective Hamiltonian or propagator may require entanglement of the product of noncommuting exponential operators into a single unitary operator with the same effect. Depending on the time dependence of the underlying Hamiltonians, the effective Hamiltonian may be derived using the Baker-Campbell-Hausdorff (BCH) [8] or Magnus [9] expansion [or combinations of these, such as the semicontinuous BCH (SCBCH) expansion [10]] which allow the entangled operator to be expressed in terms of an infinite series of commutators between the operators subject to entanglement [11]. Through systematic ordering of the expansion elements of the effective Hamiltonian according to size, entanglements of this type [10,12] have, for example, proved to be an indispensable tool for the evaluation and systematic design of multiple-pulse experiments in nuclear-magnetic-resonance (NMR) spectroscopy ever since the pioneering work by Haeberlen and Waugh [1,12–17].

Despite its proven success, it is relevant to consider some difficulties and limitations of effective Hamiltonian theory based on the BCH, Magnus, and SCBCH expansions. First, the quality and usefulness of the effective Hamiltonian critically rely on the convergence of the commutator series to concentrate the most important dynamics into the first few orders. Under favorable conditions this may be accomplished by transforming the description into an appropriate interaction frame, removing dominant terms from the external manipulations not necessarily being important for evaluation purposes. This strategy may be applied in several steps provided the relevant parts of the Hamiltonian are sufficiently well separated in terms of magnitude. Unfortunately, however, this does not cover the most general case where the magnitudes of various of the desired, undesired, relevant, and irrelevant terms may be similar. An example could be solid-state NMR of powder samples, where the orientation dependence may scale the impact of anisotropic interactions continuously from zero up to a size significantly larger than the available rf field strengths and sample spinning frequencies [13–15]. Another case could be rf irradiation subject to resonance offsets, which in cases relevant in practice may be larger than the available or desired rf field strengths. Second, even for quite simple experiments it may be difficult to calculate the effective Hamiltonian to high order due to the complexity of the involved commutators along with the need for time-ordered integration which is complicated in cases of discontinuous time dependence [10]. In this context we note that very often the most complicating time dependence is introduced by the transformation into an interaction frame with the aim of stimulating faster convergence. These complications are unfortunate considering the recognized value of high-order evaluations in systematic design of pulse sequences that efficiently eliminate undesired components of the internal Hamiltonian [10,16–25]. Third, considering the difficulties in achieving appropriate convergence and derivation of high-order terms of the effective Hamiltonian, it is typical to assist the analytical evaluations by numerically exact calculations based on the Hamiltonian in the normal rotating frame rather than in the interaction frame constructed to simplify the analytical evaluations. Although a match between the two descriptions may be obtained by performing the analytical evaluations stroboscopically at the

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points where the interaction and normal rotating frames coincide, this often leaves the scientist with an undesirable gap between analytical formulas providing physical insight with low precision and digitalization and numerical simulations providing high precision but no direct physical insight.

In this paper we address the above-mentioned problems and introduce a closed solution to the BCH problem in the normal rotating frame. The solution is based on the Cayley-Hamilton theorem [26,27], which allows reformulation of the infinite BCH expansion into a finite series expansion of exponential operators as recently demonstrated in relation to the special unitary (SU) and general linear (GL) groups [28–31]. In this paper this analysis is extended to provide an analytically exact description of the exponent to characterize the effective fields associated with the entangled operator. This forms the basis for our so-called exact effective Hamiltonian theory (EEHT). Furthermore, with specific formulas derived for SU(2), SU(3), and SU(4), this work extends earlier attempts using a related quaternion algebra formalism [32] to describe the effective fields encountered in the SU(2) case [33,34].

II. THEORY

In this section we derive the basic formulas required for analytical entanglement of the product of two exponential operators as a finite power series depending on the exponents of the two operators. This involves expansion of the individual exponential operators into a finite power series using the Cayley-Hamilton theorem followed by coupling of the two series into an overall propagator. By expansion of the logarithm to the entangled operator we derive the effective Hamiltonian that is representative for the overall evolution.

A. Expansion of the exponential operator

Confronted with the standard definition of the exponential operator as an infinite series

$$e^{iA}=\sum_{k=0}^{\infty}\frac{(iA)^k}{k!} \tag{1}$$

and the interest in a closed solution to the BCH entanglement problem [8]

$$e^{iC}=e^{iA}e^{iB}, \tag{2}$$

it is desirable to establish an alternative definition of the exponential containing a finite number of terms. This may be accomplished using the Cayley-Hamilton theorem [26], which states that any $n\times n$ matrix A is a solution to its own characteristic polynomial, i.e.,

$$p(A)=A^n+c_{n-1}A^{n-1}+\cdots+c_1A+c_0\mathbb{1}=0 \tag{3}$$

with the characteristic polynomial defined as

$$p(\lambda)=\det(A-\lambda\mathbb{1})=\lambda^n+c_{n-1}\lambda^{n-1}+\cdots+c_1\lambda+c_0. \tag{4}$$

This implies that it is possible to express matrices A^m for any power $m\geqslant n$ in terms of the matrices $\{\mathbb{1},A,\ldots,A^{n-1}\}$ with coefficients determined by the characteristic polynomial. This result is of great interest for the decomposition in Eq. (2), but also in more general terms considering the large number of mappings used in quantum physics which typically are characterized via their infinite power expansions. Using the Cayley-Hamilton theorem these mappings may be reduced to closed series of finite order. In the following sections we shall take advantage of the expansion in Eq. (3) to express the exponential and logarithmic mappings in terms of the eigenvalues for the operators in their arguments.

Using Eq. (3), the matrix exponential in Eq. (1) may be rewritten as [30]

$$e^{iAt}=x_0(t)\mathbb{1}+ix_1(t)A-x_2(t)A^2+\cdots+i^{n-1}x_{n-1}(t)A^{n-1}, \tag{5}$$

where we explicitly emphasized the time (or rotation angle, depending on the units of A) dependence in the exponential to facilitate practical application typically involving dynamical propagators. Under appropriate consideration of the multiplicity (m) of the eigenvalues (λ) of iA, the coefficients take the form

$$x_j(t)=f_{j,1}(\lambda_1,m_1)e^{\lambda_1 t}+\cdots+f_{j,n}(\lambda_n,m_n)e^{\lambda_n t}. \tag{6}$$

The coefficients to the exponentials in Eq. (6) may be expressed as

$$f_{j,i}(\lambda_i,m_i)=a_{j,i,0}+a_{j,i,1}t+\cdots+a_{j,i,m_i-1}t^{m_i-1} \tag{7}$$

with the $a_{j,i,k}$ coefficients obtained by solution of the coupled equations

$$\begin{aligned}
&x_0(0)=1,x_0'(0)=0,x_0''(0)=0,\ldots,x_0^{(n-1)}(0)=0,\\
&x_1(0)=0,x_1'(0)=1,x_1''(0)=0,\ldots,x_1^{(n-1)}(0)=0,\\
&\qquad\vdots\\
&x_{n-1}(0)=0,x_{n-1}'(0)=0,x_{n-1}''(0)=0,\ldots,x_{n-1}^{(n-1)}(0)=1
\end{aligned} \tag{8}$$

defining the initial conditions for the problem [30].

To illustrate the simplicity of the procedure for expansion of an exponential operator, we consider e^{itI_x} for a two-level system. The roots to the characteristic polynomial for iI_x,

$$p(\lambda)=\lambda^2+i\lambda\,\mathrm{Tr}\{I_x\}-\det I_x=\lambda^2+\frac{1}{4},\quad I_x=\frac{1}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}, \tag{9}$$

may be identified as the nondegenerate eigenvalues $\lambda_1=i/2$ and $\lambda_2=-i/2$. Using the Cayley-Hamilton theorem, it is straightforward to derive known identities of the type $I_x^2=\mathbb{1}/4$. With the eigenvalues established, the general expressions for the $x_i(t)$ coefficients are

$$\begin{aligned}
x_0(t)&=a_{0,1,0}e^{it/2}+a_{0,2,0}e^{-it/2},\\
x_1(t)&=a_{1,1,0}e^{it/2}+a_{1,2,0}e^{-it/2}.
\end{aligned} \tag{10}$$

Considering the initial conditions in Eq. (8), the coefficients need to be $a_{0,1,0}=a_{0,2,0}=\frac{1}{2}$ and $a_{1,1,0}=-a_{1,2,0}=-i$, leading to

$$e^{itI_x}=\cos\frac{t}{2}\mathbb{1}+2i\sin\frac{t}{2}I_x \tag{11}$$

in agreement with previous findings based on an eigenvector or infinite series approach.

B. Coupling of two exponential operators

Using the finite series expansion, it is possible to derive a closed solution to the coupling of the two exponentials in Eq. (2) for which the traditional solution depends on an infinite commutator series

$$e^{iA}e^{iB}=e^{iA+iB-[A,B]/2-i([A,[A,B]]+[[A,B],B])/12+\cdots} \tag{12}$$

known as the BCH expansion [8]. Using Eq. (5) the entanglement may be written

$$\begin{aligned}e^{iA}e^{iB}=&(x_0^A\mathbb{1}+ix_1^AA-x_2^AA^2+\cdots+i^{n-1}x_{n-1}^AA^{n-1})\\&\times(x_0^B\mathbb{1}+ix_1^BB-x_2^BB^2+\cdots+i^{n-1}x_{n-1}^BB^{n-1}),\end{aligned} \tag{13}$$

with the definitions $x_0^A=x_0^A(1),\ldots,x_{n-1}^A=x_{n-1}^A(1)$ and similarly for the x_i^B coefficients. This expression has the obvious advantage of being closed and thereby applicable for exact description of the quantum dynamics. With the number of terms increasing by n^2, this advantage applies in particular for smaller values of n, where it proves possible to establish quite simple expressions for the exponential product and the exponent C [cf. Eq. (2)]. We note that evaluation of the product in Eq. (13) becomes particularly simple in cases where A and B are related through a similarity transformation. In this case the eigenvalues and thereby the x_i coefficients become identical for A and B.

As an example, we address the coupling of two exponentials in su(2) for which the exponents A and B are related through a similarity transformation. Using Eq. (13) with $n=1$ and $x_i=x_i^A(1)=x_i^B(1)$, this leads to

$$e^{iA}e^{iB}=x_0^2\mathbb{1}+ix_0x_1(A+B)-x_1^2AB, \tag{14}$$

which compares favorably with the infinite series approach in Eq. (12). Considering that su(2) is spanned by a three-dimensional basis, full generality is maintained by considering propagators of the type

$$e^{iA}=e^{i(a_xI_x+a_yI_y+a_zI_z)},\quad e^{iB}=e^{i(b_xI_x+b_yI_y+b_zI_z)}. \tag{15}$$

The eigenvalues of $i(a_xI_x+a_yI_y+a_zI_z)$ may be determined as

$$\lambda=\pm i\frac{\sqrt{a_x^2+a_y^2+a_z^2}}{2}\equiv\pm i\delta, \tag{16}$$

leading to the coefficients $x_0=\cos\delta$ and $x_1=(\sin\delta)/\delta$, and thereby

$$e^{iA}=\cos\delta\mathbb{1}+i\frac{\sin\delta}{\delta}(a_xI_x+a_yI_y+a_zI_z). \tag{17}$$

Finally, using Eq. (14) we arrive at the closed expression for the entanglement of two operators related through a similarity transformation:

$$\begin{aligned}e^{iA}e^{iB}=&\left\{\cos^2\delta-\frac{\sin^2\delta}{4\delta^2}(a_xb_x+a_yb_y+a_zb_z)\right\}\mathbb{1}\\&+i\frac{\sin\delta\cos\delta}{\delta}\{(a_x+b_x)I_x+(a_y+b_y)I_y\\&+(a_z+b_z)I_z\}-i\frac{\sin^2\delta}{\delta^2}\{(a_yb_z-a_zb_y)I_x\\&+(a_zb_x-a_xb_z)I_y+(a_xb_y-a_yb_x)I_z\}.\end{aligned} \tag{18}$$

C. The entangled Hamiltonian

While the entangled propagator may be useful for obtaining analytical formulas for the overall propagator and the propagated density operator, physical insight into the effective fields of the experiment requires determination of the exponent. Relying on the traditional BCH expansion, this information may be obtained through the exponent in the right-hand side of Eq. (12). As above, however, this approach has the distinct disadvantage of an infinite commutator series description which in practice often calls for an undesirable compromise between accuracy and complexity.

Using the Cayley-Hamilton theorem, it is possible to derive a finite series description of the effective Hamiltonian. This may be achieved on the basis of the infinite expansion of the logarithmic mapping

$$\ln(e^{iA}e^{iB})=-\sum_{k=1}^{\infty}\frac{1}{k}X^k, \tag{19}$$

with

$$X=\mathbb{1}-e^{iA}e^{iB}. \tag{20}$$

By expanding the X^m elements with $m\geqslant n$ (n denotes the dimension of the Lie algebra, or physically the number of energy levels) in terms of lower-order elements using the Cayley-Hamilton theorem followed by substitution of the exponential product in Eq. (20) by the finite series expansion in Eq. (13), the logarithmic function may be expanded as

$$\ln(e^{iA}e^{iB})=g_0\mathbb{1}+g_1X+\cdots+g_{n-1}X^{n-1}. \tag{21}$$

The g_i coefficients may be determined from the eigenvalues of X as described below for the cases of su(2), su(3), and su(4). This provides the desired finite series expansion of the effective Hamiltonian for the entangled operation, which henceforth will be referred to as exact effective Hamiltonian theory to emphasize its role as an exact alternative to the very popular, but approximate, BCH expansion as well as average Hamiltonian theory (AHT) so far used alone or in combination with SCBCH to evaluate the effective fields of

entangled operations. Finally, we should note that the analytical expansions in Eqs. (13) and (21) form an attractive alternative to a direct evaluation of their matrix representations, which typically will lead to much less transparent formulas and will in addition to eigenvalues also require establishment of the eigenvectors for the operators involved.

1. The su(2) case

For a two-level system, the operator X may be expanded as

$$X^2 = a_0 X + b_0 \mathbb{1} \tag{22}$$

with the coefficients defined via the characteristic polynomial to X,

$$p(\lambda) = (\lambda - \lambda_1)(\lambda - \lambda_2) = \lambda^2 - a_0 \lambda - b_0 \tag{23}$$

using $a_0 = \lambda_1 + \lambda_2$ and $b_0 = -\lambda_1 \lambda_2$, with λ_1 and λ_2 being the eigenvalues of X. Thus, using Eqs. (13) and (20) we obtain

$$\begin{aligned} \ln(e^{iA} e^{iB}) &= g_0 \mathbb{1} + g_1 X \\ &= (g_0 + g_1)\mathbb{1} - g_1 (x_0^A \mathbb{1} + i x_1^A A)(x_0^B \mathbb{1} + i x_1^B B). \end{aligned} \tag{24}$$

The $g_i = g_i(\lambda_1, \lambda_2)$ coefficients may be derived by comparison of the general expressions in Eqs. (19) and (24). This is most conveniently accomplished using

$$X^{2+i} = a_i X + b_i \mathbb{1}, \tag{25}$$

which along with Eq. (22) leads to the recursion relations $a_{i+1} = a_i a_0 + b_i$ and $b_{i+1} = a_i b_0$ with $i > 0$. Equipped with these definitions, Eq. (19) may be rewritten as

$$\ln(e^{iA} e^{iB}) = -\left(1 + \sum_{k=0}^{\infty} \frac{1}{k+2} a_k\right) X - \left(\sum_{k=0}^{\infty} \frac{1}{k+2} b_k\right) \mathbb{1}, \tag{26}$$

with g_1 and g_0 identified as the coefficients of X and $\mathbb{1}$, respectively. With the definition $m = \lambda_1 - \lambda_2$, it can be shown that the coefficients a_k and b_k are subject to the relations

$$m a_k = \lambda_1^{k+2} - \lambda_2^{k+2}, \quad m b_k = -\lambda_2 \lambda_1^{k+2} + \lambda_1 \lambda_2^{k+2}. \tag{27}$$

Thus, using the definitions of g_0 and g_1 in Eq. (26), we obtain

$$\begin{aligned} m g_0 &= \sum_{k=0}^{\infty} \frac{\lambda_1^{k+2} \lambda_2 - \lambda_1 \lambda_2^{k+2}}{k+2} \\ &= -\lambda_2 \ln(1 - \lambda_1) + \lambda_1 \ln(1 - \lambda_2), \end{aligned} \tag{28}$$

$$\begin{aligned} m g_1 &= -\left((\lambda_1 - \lambda_2) + \sum_{k=0}^{\infty} \frac{\lambda_1^{k+2} - \lambda_2^{k+2}}{k+2}\right) \\ &= \ln(1 - \lambda_1) - \ln(1 - \lambda_2), \end{aligned} \tag{29}$$

which upon insertion into Eq. (24) leads to the desired general finite series expression for the effective field of the entangled operator.

2. The su(3) case

Using the same approach for a three-level system we obtain

$$X^{3+i} = a_i X^2 + b_i X + c_i \mathbb{1} \tag{30}$$

with $a_0 = \lambda_1 + \lambda_2 + \lambda_3$, $b_0 = -\lambda_1 \lambda_2 - \lambda_1 \lambda_3 - \lambda_2 \lambda_3$, and $c_0 = \lambda_1 \lambda_2 \lambda_3$ defined via

$$p(\lambda) = (\lambda - \lambda_1)(\lambda - \lambda_2)(\lambda - \lambda_3) = \lambda^3 - a_0 \lambda^2 - b_0 \lambda - c_0 \tag{31}$$

and the coefficients for $i > 0$ determined by the recurrence formulas $a_{i+1} = a_i a_0 + b_i$, $b_{i+1} = a_i b_0 + c_i$, and $c_{i+1} = a_i c_0$. As in the su(2) case, the logarithmic function may be expressed by the expansions

$$\begin{aligned} \ln(e^{iA} e^{iB}) &= g_0 \mathbb{1} + g_1 X + g_2 X^2 \\ &= -\left(\frac{1}{3} c_0 + \sum_{k=1}^{\infty} \frac{1}{k+3} c_k\right) \mathbb{1} \\ &\quad - \left(1 + \sum_{k=0}^{\infty} \frac{1}{k+3} b_k\right) X \\ &\quad - \left(\frac{1}{2} + \sum_{k=0}^{\infty} \frac{1}{k+3} a_k\right) X^2 \end{aligned} \tag{32}$$

with the coefficients related to the eigenvalues of X by

$$m a_k = \lambda_1^{k+3}(\lambda_2 - \lambda_3) + \lambda_2^{k+3}(\lambda_3 - \lambda_1) + \lambda_3^{k+3}(\lambda_1 - \lambda_2), \tag{33}$$

$$m b_k = \lambda_1^{k+3}(\lambda_3^2 - \lambda_2^2) + \lambda_2^{k+3}(\lambda_1^2 - \lambda_3^2) + \lambda_3^{k+3}(\lambda_2^2 - \lambda_1^2), \tag{34}$$

$$\begin{aligned} m c_k &= \lambda_1^{k+3}(\lambda_2^2 \lambda_3 - \lambda_2 \lambda_3^2) + \lambda_2^{k+3}(\lambda_1 \lambda_3^2 - \lambda_1^2 \lambda_3) \\ &\quad + \lambda_3^{k+3}(\lambda_1^2 \lambda_2 - \lambda_1 \lambda_2^2), \end{aligned} \tag{35}$$

with $m = (\lambda_1 - \lambda_2)(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)$. This allows the g_i coefficients to be determined from Eq. (32), i.e.,

$$\begin{aligned} m g_0 &= (\lambda_2^2 \lambda_3 - \lambda_3^2 \lambda_2) \ln(1 - \lambda_1) + (\lambda_3^2 \lambda_1 - \lambda_1^2 \lambda_3) \ln(1 - \lambda_2) \\ &\quad + (\lambda_1^2 \lambda_2 - \lambda_1 \lambda_2^2) \ln(1 - \lambda_3), \end{aligned} \tag{36}$$

$$\begin{aligned} m g_1 &= (\lambda_3^2 - \lambda_2^2) \ln(1 - \lambda_1) + (\lambda_1^2 - \lambda_3^2) \ln(1 - \lambda_2) \\ &\quad + (\lambda_2^2 - \lambda_1^2) \ln(1 - \lambda_3), \end{aligned} \tag{37}$$

$$\begin{aligned} m g_2 &= (\lambda_2 - \lambda_3) \ln(1 - \lambda_1) + (\lambda_3 - \lambda_1) \ln(1 - \lambda_2) \\ &\quad + (\lambda_1 - \lambda_2) \ln(1 - \lambda_3), \end{aligned} \tag{38}$$

which in combination with Eqs. (13), (20), and (32) enable expression of the effective field in an exact finite series expansion. This applies in the typical case with nondegenerate

eigenvalues. The corresponding formulas applying for the special case where two of the three eigenvalues are degenerate are compiled in the Appendix.

3. The su(4) case

In a analogous manner, the su(4) expansion may be derived using

$$X^{4+i}=a_iX^3+b_iX^2+c_iX+d_i\mathbb{1} \tag{39}$$

with the coefficients related to the characteristic polynomial

$$p(\lambda)=\lambda^4-a_0\lambda^3-b_0\lambda^2-c_0\lambda-d_0 \tag{40}$$

using $a_0=\lambda_1+\lambda_2+\lambda_3+\lambda_4$, $b_0=-\lambda_1\lambda_2-\lambda_1\lambda_3-\lambda_1\lambda_4-\lambda_2\lambda_3-\lambda_2\lambda_4-\lambda_3\lambda_4$, $c_0=\lambda_1\lambda_2\lambda_3+\lambda_1\lambda_2\lambda_4+\lambda_1\lambda_3\lambda_4+\lambda_2\lambda_3\lambda_4$, $d_0=-\lambda_1\lambda_2\lambda_3\lambda_4$, as well as $a_{i+1}=a_ia_0+b_i$, $b_{i+1}=a_ib_0+c_i$, $c_{i+1}=a_ic_0+d_i$, and $d_{i+1}=a_id_0$ for $i>0$. The infinite and finite expansions for the logarithmic functions may be expressed as

$$\begin{aligned}\ln(e^{iA}e^{iB})&=g_0\mathbb{1}+g_1X+g_2X^2+g_3X^3\\&=-\left(\sum_{k=0}^{\infty}\frac{1}{k+4}d_k\right)\mathbb{1}-\left(1+\sum_{k=0}^{\infty}\frac{1}{k+4}c_k\right)X\\&\quad-\left(\frac{1}{2}+\sum_{k=0}^{\infty}\frac{1}{k+4}b_k\right)X^2\\&\quad-\left(\frac{1}{3}+\sum_{k=0}^{\infty}\frac{1}{k+4}a_k\right)X^3,\end{aligned} \tag{41}$$

where the g_i coefficients in the general nondegenerate case take the form

$$\begin{aligned}mg_0&=\ln(1-\lambda_1)[\lambda_2^3(-\lambda_3^2\lambda_4+\lambda_3\lambda_4^2)+\lambda_3^3(-\lambda_4^2\lambda_2+\lambda_2^2\lambda_4)\\&\quad+\lambda_4^3(-\lambda_2^2\lambda_3+\lambda_2\lambda_3^2)]+\ln(1-\lambda_2)[\lambda_1^3(\lambda_4\lambda_3^2-\lambda_3\lambda_4^2)\\&\quad+\lambda_3^3(\lambda_1\lambda_4^2-\lambda_4\lambda_1^2)+\lambda_4^3(\lambda_3\lambda_1^2-\lambda_3^2\lambda_1)]+\ln(1-\lambda_3)\\&\quad\times[\lambda_1^3(-\lambda_4\lambda_2^2+\lambda_4^2\lambda_2)+\lambda_2^3(-\lambda_1\lambda_4^2+\lambda_1^2\lambda_4)\\&\quad+\lambda_4^3(\lambda_1\lambda_2^2-\lambda_1^2\lambda_2)]+\ln[1-\lambda_4)[\lambda_1^3(-\lambda_2\lambda_3^2+\lambda_3\lambda_2^2)\\&\quad+\lambda_2^3(-\lambda_1^2\lambda_3+\lambda_1\lambda_3^2)+\lambda_3^3(\lambda_2\lambda_1^2-\lambda_2^2\lambda_1)],\end{aligned} \tag{42}$$

$$\begin{aligned}mg_1&=\ln(1-\lambda_1)[\lambda_2^3(\lambda_3^2-\lambda_4^2)+\lambda_3^3(\lambda_4^2-\lambda_2^2)+\lambda_4^3(\lambda_2^2-\lambda_3^2)]\\&\quad+\ln(1-\lambda_2)[\lambda_1^3(-\lambda_3^2+\lambda_4^2)+\lambda_3^3(-\lambda_4^2+\lambda_1^2)\\&\quad+\lambda_4^3(-\lambda_1^2+\lambda_3^2)]+\ln(1-\lambda_3)[\lambda_1^3(\lambda_2^2-\lambda_4^2)\\&\quad+\lambda_2^3(\lambda_4^2-\lambda_1^2)+\lambda_4^3(-\lambda_2^2+\lambda_1^2)]+\ln(1-\lambda_4)\\&\quad\times[\lambda_1^3(\lambda_3^2-\lambda_2^2)+\lambda_2^3(\lambda_1^2-\lambda_3^2)+\lambda_3^3(-\lambda_1^2+\lambda_2^2)],\end{aligned} \tag{43}$$

$$\begin{aligned}mg_2&=\ln(1-\lambda_1)[\lambda_2^3(-\lambda_3+\lambda_4)+\lambda_3^3(-\lambda_4+\lambda_2)\\&\quad+\lambda_4^3(-\lambda_2+\lambda_3)]+\ln(1-\lambda_2)[\lambda_1^3(\lambda_3-\lambda_4)\\&\quad+\lambda_3^3(\lambda_4-\lambda_1)+\lambda_4^3(\lambda_1-\lambda_3)]+\ln(1-\lambda_3)\\&\quad[\lambda_1^3(-\lambda_2+\lambda_4)+\lambda_2^3(-\lambda_4+\lambda_1)+\lambda_4^3(\lambda_2-\lambda_1)]+\ln(1\\&\quad-\lambda_4)[\lambda_1^3(-\lambda_3+\lambda_2)+\lambda_2^3(-\lambda_1+\lambda_3)\\&\quad+\lambda_3^3(\lambda_1-\lambda_2)],\end{aligned} \tag{44}$$

$$\begin{aligned}mg_3&=\ln(1-\lambda_1)[\lambda_2^2(\lambda_3-\lambda_4)+\lambda_3^2(\lambda_4-\lambda_2)+\lambda_4^2(\lambda_2-\lambda_3)]\\&\quad+\ln(1-\lambda_2)[\lambda_1^2(-\lambda_3+\lambda_4)+\lambda_3^2(-\lambda_4+\lambda_1)\\&\quad+\lambda_4^2(-\lambda_1+\lambda_3)]+\ln(1-\lambda_3)[\lambda_1^2(\lambda_2-\lambda_4)\\&\quad+\lambda_2^2(\lambda_4-\lambda_1)+\lambda_4^2(-\lambda_2+\lambda_1)]+\ln(1-\lambda_4)\\&\quad\times[\lambda_1^2(\lambda_3-\lambda_2)+\lambda_2^2(\lambda_1-\lambda_3)+\lambda_3^2(-\lambda_1+\lambda_2)]\end{aligned} \tag{45}$$

using $m=(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)(\lambda_1-\lambda_4)(\lambda_2-\lambda_3)(\lambda_2-\lambda_4)(\lambda_3-\lambda_4)$. Specific solutions for the three cases of degenerate eigenvalues (i.e., $\lambda_1=\lambda_2$, $\lambda_1=\lambda_2$, and $\lambda_3=\lambda_4$, and $\lambda_1=\lambda_2=\lambda_3$ degeneration) are given in the Appendix.

D. General principles for experiment design revisited

The EEHT formalism may provide exact analytical insight into the working of entangled operations, which may be very useful for evaluation and systematic design of experimental methods. In this regard the EEHT expansion may serve as a powerful alternative to the commonly used BCH and Magnus expansion based average Hamiltonian and SCBCH methods. Thus, before proceeding to specific examples it appears relevant to comment on the relation of design principles from these earlier methods to the exact formalism. These principles include in particular the so-called $2m+1$ rule [10,21] and the use of reflection symmetric pulse sequence elements to eliminate all even order [35] terms in the effective Hamiltonian [10,18,19].

The first thing to notice is, obviously, that the order concept and accompanying convergence principles have no meaning in relation to an exact expansion. It may, however, be relevant to use the exact entanglement of two propagators as an alternative to the SCBCH formulation in cases where an ordered expansion exists for the individual operators. Without looking at the details of the expansions, it is evident that the same relations apply for the two formalisms independently of the reference frame being an interaction frame in the former case or the laboratory frame in the latter. This follows from the interaction frame equation of motion

$$\frac{d\tilde{U}}{dt}=-i\tilde{H}\tilde{U} \tag{46}$$

with the interaction frame propagator ($\tilde{U}$) related to the laboratory frame propagator (U) as

$$U=U_T\tilde{U}, \tag{47}$$

where U_T denotes a unitary propagator mediating transformation between the two frames. With the assumption that U_T is exact and does not contain the interaction that we want to find an order expansion for, any ordered expansion of the Hamiltonian applying in the interaction frame applies

equally well in the laboratory frame. This is ascribed to the fact that the coupling of U_T and $\widetilde{U}$, e.g., conducted by the BCH expansion, will not change the original ordering in $\tilde{U}$, with the consequence that the $2m+1$ and reflection symmetry principles can be adopted directly into the formalism described here.

In more specific terms, the $2m+1$ rule states that, if a unitary transformation e^{iA} can be represented by an effective Hamiltonian where the first m orders vanish and this exponential is coupled with another propagator e^{iB} fulfilling the same condition, then all terms of the effective Hamiltonian up to order $2m+1$ can be established by simple sums of terms of the same order for the two blocks individually. To qualitatively identify this rule within the EEHT formalism, we consider two propagators that are defined through the order expansions of the exponents

$$e^{iA}=e^{i\Sigma_{i=1}^{\infty}H_A^{(i)}t}, \quad e^{iB}=e^{i\Sigma_{i=1}^{\infty}H_B^{(i)}t} \tag{48}$$

with the assumption that $H_A^{(1)}=H_B^{(1)}=\cdots=H_A^{(m)}=H_B^{(m)}=0$. Taking su(2) as a particularly simple case, it is evident that the operational part of the effective Hamiltonian for the entangled operation, as represented by Eq. (24), contains linear A and B terms and bilinear AB terms. The former terms have nonvanishing terms only of order larger than $m+1$ while the latter have nonvanishing terms of order larger than $2m+2$.

III. APPLICATIONS TO NMR SPECTROSCOPY

In this section we demonstrate how the EEHT formalism may be applied to analyze pulse sequences commonly used in liquid- and solid-state NMR. This involves the establishment of analytically exact formulas, which may be used directly for numerical simulations and analytical evaluation, or may be Taylor expanded to provide more easily accessible physical insight. This is valuable for analysis of experimental results, error analysis, and systematic design of optimum pulse sequences for practical applications. The first series of examples address composite pulses in the su(2) case with focus on inversion [36], so-called WALTZ decoupling [17,37], and chemical shift truncation in the basic building blocks of the sevenfold-symmetric C7 [38] and the more recent permuation offset stabilized C7(POST-C7) [24] pulse sequences proposed for dipolar recoupling in solid-state NMR. The second series of examples address pulse sequences for pairs of spins 1/2 leading to a four-level system which may be analyzed directly in su(4) or in many practically relevant cases transformed into a su(2) or su(3) description in a coupled representation. Thus, the first two examples, (i) INADEQUATE CR [39–41] (i.e., incredible natural abundance double quantum transfer composite refocusing) pulse sequence for coherence-order and spin-state selective (COS^3) conversion of double-quantum coherence into single-quantum coherence and (ii) magic-sandwich (MS) [42] and the high-order-truncating MSHOT-3 [22,23] pulse sequences for homonuclear dipolar decoupling, both concern su(3). The decomposition of a su(4) problem into two su(2) problems is addressed by analysis of the effect of finite rf pulses on spin $I=3/2$ nuclei influenced by large quadrupolar couplings. Finally, the su(4) case is demonstrated by INEPT (i.e., insensitive nuclei enhanced by polarization transfer) type heteronuclear coherence transfer [43,44] and gates for quantum computation [45].

At this point it is relevant to note that the overall procedure for establishment of the effective Hamiltonian, including determination of the entangled operator and finding the g_i coefficients from the X operator, may readily be implemented in symbolic mathematics programs such as MATHEMATICA [46].

A. Composite pulse sequence elements for two-level systems: su(2)

Considering that the following examples address offresonance compensation in composite pulses of the type 90_x-180_y-90_x, 90_x-180_{-x}-270_x, 360_x-360_{-x}, and 90_{-x}-360_x-270_{-x}, which with one exception are all composed of three rotations involving one or more $90_{\pm x}$ rotations, it proves useful to calculate *a priori* the influence of an offset-perturbed propagator

$$U=e^{-i(a_xI_x+a_zI_z)} \tag{49}$$

on the three orthogonal basis operators I_x, I_y, and I_z. Here a_x may denote a nominal flip angle of the pulse, e.g., $a_x=\omega_{rf}\tau_{\pi/2}=\pi/2$ with ω_{rf} being the angular nutation frequency of the rf pulse with a duration $\tau_{\pi/2}$ corresponding to a $\pi/2$ rotation. Likewise, a_z may represent the offset rotation angle depending on the resonance offset angular frequency (ω_o) and the pulse duration, e.g., $a_z=\omega_o\tau_{\pi/2}$. The transformations may be written

$$UI_xU^{\dagger}=(1-2a_z^2q_2^2)I_x+a_zq_1I_y+2a_xa_zq_2^2I_z, \tag{50}$$

$$UI_yU^{\dagger}=-a_zq_1I_x+q_3I_y+a_xq_1I_z, \tag{51}$$

$$UI_zU^{\dagger}=2a_xa_zq_2^2I_x-a_xq_1I_y+(1-a_x^2q_2^2)I_z, \tag{52}$$

with $q_1=\sin(\sqrt{a_x^2+a_z^2})/\sqrt{a_x^2+a_z^2}$, $q_2=\sin(\sqrt{a_x^2+a_z^2}/2)/\sqrt{a_x^2+a_z^2}$, and $q_3=\cos(\sqrt{a_x^2+a_z^2})$.

These relations will be used extensively in the following since they reduce the entanglements to coupling of two propagators followed by a similarity transformation of the type given in Eqs. (50)–(52). The latter is possible since $Ue^{-iH\tau}U^{\dagger}=e^{-iUHU^{\dagger}\tau}$.

1. A composite inversion pulse

The offset dependence of the $C_{121}=90_x$-180_y-90_x composite inversion pulse may be analyzed using the propagator

$$e^{-i(\pi I_x+2a_zI_z)/2}e^{-i(\pi I_y+2a_zI_z)}e^{-i(\pi I_x+2a_zI_z)/2}$$
$$=Ue^{-i(\pi I_y+2a_zI_z)}e^{-i(\pi I_x+2a_zI_z)}U^{\dagger}, \tag{53}$$

with U defined in Eq. (49) using $a_x=\pi/2$ and a_z related to the resonance offset and the rf field strength as $a_z=\omega_o\tau_{\pi/2}=\omega_o\pi/(2\omega_{rf})$. Here and henceforth the subscripts to the pulse sequence elements C and the Hamiltonians reflect the

pulses involved in units of $\pi/2$ flip angles and with roman and italic numbers indicating the x and y phases, respectively.

With $n=2$ the two central exponential operators in Eq. (53) may be evaluated using Eqs. (5)–(8),

$$e^{-i(\pi I_q+2a_zI_z)}=c_1\mathbb{1}-i2s_1(\pi I_q+2a_zI_z), \tag{54}$$

where $q=x,y$, $s_1=\sin(\sqrt{4a_z^2+\pi^2}/2)/\sqrt{4a_z^2+\pi^2}$, and $c_1=\cos(\sqrt{4a_z^2+\pi^2}/2)$. This allows X for the two-pulse element to be expressed as

$$\begin{aligned}X&=\mathbb{1}-e^{-i(\pi I_y+2a_zI_z)}e^{-i(\pi I_x+2a_zI_z)}\\&=(8a_z^2+\pi^2)s_1^2\mathbb{1}+i\pi(4a_zs_1^2+s_2)(I_x+I_y)\\&\quad+i(-2\pi^2s_1^2+4a_zs_2)I_z\end{aligned} \tag{55}$$

with $s_2=\sin(\sqrt{4a_z^2+\pi^2})/\sqrt{4a_z^2+\pi^2}$. Using this expression the eigenvalues of X may be calculated as

$$\begin{aligned}\lambda&=(8a_z^2+\pi^2)s_1^2\\&\quad\pm\frac{1}{2}\sqrt{-2\pi^2(4a_zs_1^2+s_2)^2-4(\pi^2s_1^2-2a_zs_2)^2},\end{aligned} \tag{56}$$

which may be inserted into Eqs. (28) and (29) to obtain the g_0 and g_1 coefficients for the entangled effective Hamiltonian:

$$-iH_{22}^{eff}\tau_{2\pi}=\ln(e^{-i(\pi I_y+2a_zI_z)}e^{-i(\pi I_x+2a_zI_z)})=g_0\mathbb{1}+g_1X, \tag{57}$$

of the offset-perturbed 180_y-180_x pulse sequence element ($\tau_{2\pi}=2\pi/\omega_{rf}$). Finally, using Eq. (53) the effective Hamiltonian for the 90_x-180_y-90_x composite pulse may be written

$$-iH_{121}^{eff}\tau_{2\pi}=g_0\mathbb{1}+g_1UXU^\dagger=b_x^{121}I_x+b_y^{121}I_y+b_z^{121}I_z, \tag{58}$$

where the coefficients readily may be established using Eqs. (50)–(52).

Although Eq. (58) gives a relatively simple and analytically exact expression for the effective Hamiltonian of the composite pulse, it may be useful to extract physical insight from a standard Taylor expansion around $a_z=0$, which up to eighth order leads to

$$\begin{aligned}b_x^{121}&=\frac{i(4+\pi)a_z^2}{\pi}+\frac{i(32-16\pi+\pi^2)a_z^4}{\pi^4}\\&\quad-\frac{2i(480-192\pi+27\pi^2+6\pi^3+\pi^4)a_z^6}{3\pi^6}+O(a_z^8),\end{aligned} \tag{59}$$

$$\begin{aligned}b_y^{121}&=-i\pi-\frac{2i(4-\pi)a_z^2}{\pi^2}+\frac{i(96-28\pi+4\pi^2+\pi^3)a_z^4}{2\pi^4}\\&\quad-\frac{2i(488-150\pi-6\pi^2-3\pi^3)a_z^6}{3\pi^6}+O(a_z^8),\end{aligned} \tag{60}$$

$$\begin{aligned}b_z^{121}&=-2ia_z+\frac{2i(-8+6\pi+\pi^2)a_z^3}{\pi^3}\\&\quad+\frac{i(160-60\pi+6\pi^2+\pi^3)a_z^5}{\pi^5}\\&\quad-\frac{4i(968-342\pi+21\pi^2+3\pi^3+\pi^4)a_z^7}{3\pi^7}+O(a_z^8).\end{aligned} \tag{61}$$

The effective Hamiltonian may be compared directly with the Hamiltonian of a standard 180_y inversion pulse

$$-iH_2^{eff}\tau_\pi=-i(\pi I_y+2a_zI_z), \tag{62}$$

either directly from the formula or graphically as in Fig. 1. In the graphical representation, the exact values of b_x, b_y, and b_z for the effective rotation angles of the pulse are plotted directly against $\omega_o/\omega_{rf}=2a_z/\pi$ or in a normalized fashion in a three-dimensional (3D) spherical plot. We note that the coefficients of the effective Hamiltonian (rather than the effective rotation) may be obtained by scaling with the inverse pulse duration, which effectively halves the coefficients of the composite pulse relative to the single-pulse case. In all representations, it is evident that the improved off-resonance compensation for the desired π_y rotation is obtained by reduction of the I_z contribution to the effective Hamiltonian. This is achieved at the expense of the introduction of a symmetric I_x rotation and an antisymmetric destructive contribution to the I_y rotation. For small off-resonance effects these contributions are not problematic since phase errors do not influence the inverted signal component.

2. A WALTZ decoupling element

The propagator for the WALTZ-type $C_{1\bar{2}3}=90_x$-180_{-x}-270_x element [17,37] may be written

$$\begin{aligned}&e^{-i(\pi I_x+2a_zI_z)/2}e^{-i(-\pi I_x+2a_zI_z)}e^{-i(3\pi I_x+6a_zI_z)/2}\\&\quad=Ue^{-i(-\pi I_x+2a_zI_z)}e^{-i(2\pi I_x+4a_zI_z)}U^\dagger,\end{aligned} \tag{63}$$

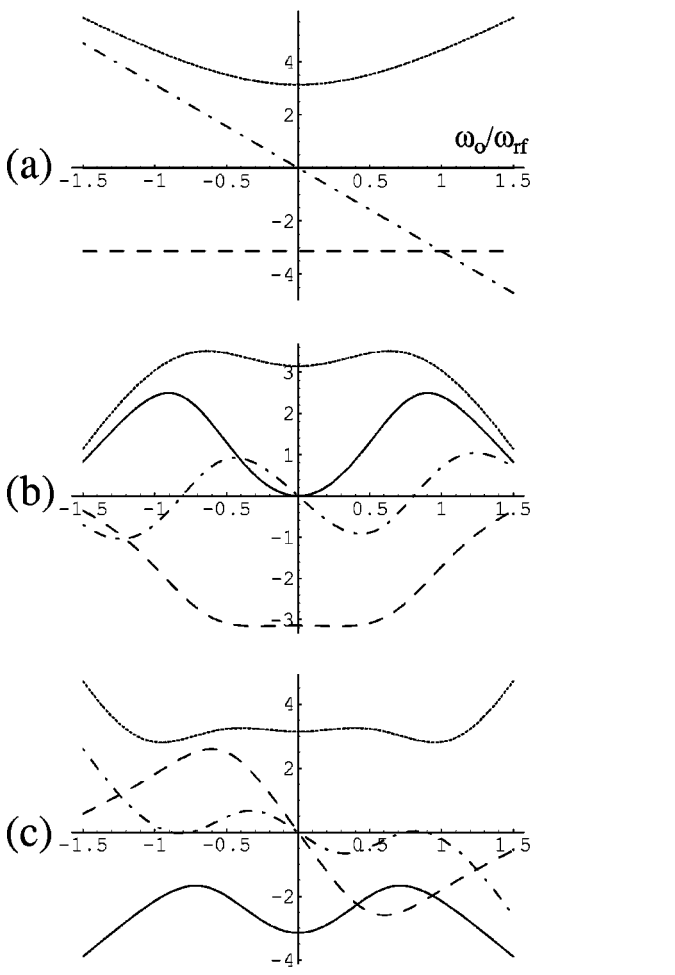
for which we derive

$$e^{-i(-\pi I_x+2a_zI_z)}=c_1\mathbb{1}+i2s_1(\pi I_x-2a_zI_z), \tag{64}$$

$$e^{-i(2\pi I_x+4a_zI_z)}=(2c_1^2-1)\mathbb{1}-is_2(2\pi I_x+4a_zI_z) \tag{65}$$

using Eqs. (5)–(8). This leads to

$$\begin{aligned}X&=\mathbb{1}-e^{-i(-\pi I_x+2a_zI_z)}e^{-i(2\pi I_x+4a_zI_z)}=(1-\pi^2c_2-4a_z^2c_3)\mathbb{1}\\&\quad+2i\pi s_1I_x+8ia_z\pi s_1s_2I_y+4ia_zs_3I_z\end{aligned} \tag{66}$$



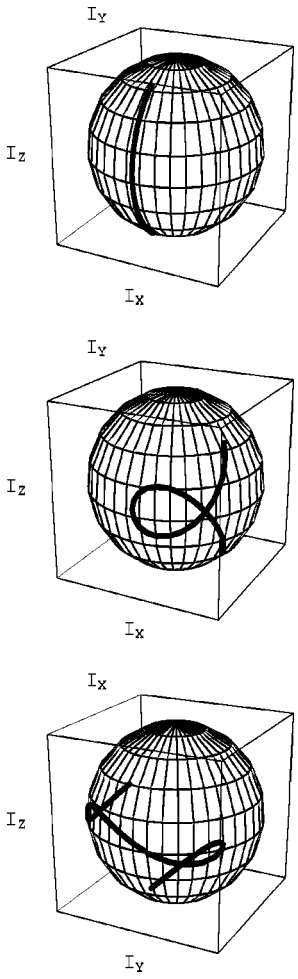


FIG. 1. Graphs showing the offset dependence for the b_i coefficients of the effective Hamiltonian $-iH_{eff}\tau = b_x I_x + b_y I_y + b_z I_z$, for the (a) 180_y ($b_i = a_i, \tau = \tau_\pi$), (b) 90_x-180_y-90_x ($\tau = \tau_{2\pi}$), and (c) 90_x-180_{-x}-270_x ($\tau = \tau_{3\pi}$) inversion pulses. The solid, dashed, and dot-dashed lines (left column) represent the imaginary components of b_x, b_y, and b_z, respectively, while the dotted line represents the norm $|b| = \sqrt{|b_x|^2 + |b_y|^2 + |b_z|^2}$. The spherical trajectories (right column) represent the imaginary part of $b_i/|b|$ as a function of ω_o/ω_{rf} ranging from -1.5 to 1.5.

for the two-pulse element using $c_2 = c_1/(4a_z^2 + \pi^2)$, $c_3 = \cos(3\sqrt{4a_z^2 + \pi^2}/2)/(4a_z^2 + \pi^2)$, and $s_3 = \sin(3\sqrt{4a_z^2 + \pi^2}/2)/\sqrt{4a_z^2 + \pi^2}$. The eigenvalues for X are

$$\lambda = 1 - 4a_z^2 c_3 - c_2\pi^2 \pm \sqrt{-\pi^2 s_1^2(1 + 16a_z^2 s_2^2) - 4a_z^2 s_3^2}, \tag{67}$$

which allows straightforward calculation of g_0 and g_1 using Eqs. (28) and (29). The effective Hamiltonian of the $C_{1\bar{2}\bar{3}}$ WALTZ element may be expressed as

$$-iH_{123}^{eff}\tau_{3\pi} = U \ln(e^{-i(-\pi I_x + 2a_z I_z)} e^{-i(2\pi I_x + 4a_z I_z)}) U^\dagger = g_0 \mathbb{1} + g_1 U X U^\dagger = b_x^{1\bar{2}\bar{3}} I_x + b_y^{1\bar{2}\bar{3}} I_y + b_z^{1\bar{2}\bar{3}} I_z \tag{68}$$

with $\tau_{3\pi} = 3\pi/\omega_{rf}$.

The analytical expression in Eq. (68) may readily be expanded using Eqs. (50)–(52) to provide exact formulas for numerical simulations and analytical evaluations. It may alternatively be instructive to examine the coefficients

$$b_x^{1\bar{2}\bar{3}} = -i\pi + \frac{8ia_z^2}{\pi} - \frac{8ia_z^4}{\pi^2} + \frac{8i(-44 + 5\pi)a_z^6}{\pi^5} + O(a_z^8), \tag{69}$$

$$b_y^{1\bar{2}\bar{3}} = -4ia_z + \frac{8ia_z^3}{\pi^2} + \frac{2i(52 + \pi^2)a_z^5}{\pi^4} + \frac{8i(-134 + 7\pi^2)a_z^7}{\pi^6} + O(a_z^8) \tag{70}$$

$$b_z^{1\bar{2}\bar{3}} = -2ia_z + \frac{4i(4 + \pi)a_z^3}{\pi^2} - \frac{20ia_z^5}{\pi^3} - \frac{2i(1056 + 60\pi + \pi^3)a_z^7}{3\pi^6} + O(a_z^8) \tag{71}$$

resulting from an eighth order Taylor expansion of Eq. (68).

On the basis of these formulas, it is straightforward to rationalize why the WALTZ element is more compensated with respect to off-resonance effects than the composite pulse (and the standard π pulse) described above. The effective Hamiltonian of the composite pulse contains a I_z component which is linearly dependent on the offset and a I_x component with a quadratic offset dependence. This implies that even for small offsets the effective rotation axis is turned away from the transverse plane toward I_z with the result of decreasing inversion capacity. For WALTZ, the undesired longitudinal component is still linearly dependent on the offset but this is partly compensated by an even more dominant linear contribution to I_y. The latter component, though being

orthogonal to the desired I_x rotation, tends to keep the effective rotation axis close to the transverse plane, leading to a more broadbanded inversion. This aspect is clearly evident from the 3D plots in Fig. 1 comparing the imaginary part of the normalized $b_i/\sqrt{|b_x|^2+|b_y|^2+|b_z|^2}$ coefficients ($i=x,y,z$) for the three discussed inversion pulses.

3. C7 and POST-C7 dipolar recoupling elements

To proceed with a solid-state NMR example, we consider the $C_{44}^{\bar{}}$ and $C_{\bar{1}43}^{\bar{}}$ building blocks of the C7 [38] and POST-C7 [24] pulse sequences, respectively, used for broadband γ-encoded [47] dipolar recoupling in magic-angle-spinning NMR. These elements serve to eliminate undesired effects from resonance offsets while allowing dipolar recoupling upon concatenation into a C7 multiple-pulse cycle. Thus, to illustrate how the EEHT formalism can be used in systematic design of sequences with efficient offset compensation we calculate analytically the effective Hamiltonians for the C_4, $C_{44}^{\bar{}}$, and $C_{\bar{1}43}^{\bar{}}$ elements in su(2) followed by a comparative evaluation.

For the basic $C_4=360_x$ building block the propagator [Eq. (17)] and the effective Hamiltonian are straightforwardly derived as

$$e^{-i(\pm 2\pi I_x+4a_zI_z)}=c_4\mathbb{1}+is_4(\pm 2\pi I_x+4a_zI_z), \tag{72}$$

$$-iH_2^{eff}\tau_\pi=-i(2\pi I_x+4a_zI_z) \tag{73}$$

with $s_4=\sin(\sqrt{4a_z^2+\pi^2})/\sqrt{4a_z^2+\pi^2}$ and $c_4=\cos(\sqrt{4a_z^2+\pi^2})$. Using Eq. (18) for the $C_{44}^{\bar{}}=360_x\text{-}360_{-x}$ element we obtain

$$\begin{aligned}X&=\mathbb{1}-e^{-i(2\pi I_x+4a_zI_z)}e^{-i(-2\pi I_x+4a_zI_z)}\\&=8a_z^2s_4^2\mathbb{1}-8ia_z\pi s_4^2I_y+8ia_zs_4c_4I_z.\end{aligned} \tag{74}$$

The eigenvalues for X are given by

$$\lambda=8a_z^2s_4^2\pm 4a_zs_4\sqrt{-\pi s_4^2-c_4^2}, \tag{75}$$

which defines the g_0 and g_1 coefficients [Eqs. (28) and (29)] for the effective Hamiltonian

$$-iH_{44}^{eff}\tau_{4\pi}=g_0\mathbb{1}+g_1X=b_y^{44}{}^{\bar{}}I_y+b_z^{44}{}^{\bar{}}I_z \tag{76}$$

with

$$b_y^{44}{}^{\bar{}}=-8ia_z\pi s_4^2g_1,\quad b_z^{44}{}^{\bar{}}=8ia_zs_4c_4g_1, \tag{77}$$

and $\tau_{4\pi}=4\pi/\omega_{rf}$. The robustness of the $C_{44}^{\bar{}}$ pulse sequence element toward resonance offsets may alternatively be evaluated to high order using the Taylor expansions

$$b_y^{44}{}^{\bar{}}=\frac{i32a_z^5}{\pi^3}-\frac{i192a_z^7}{\pi^5}-\frac{i32(-87+4\pi^2)a_z^9}{3\pi^7}+O(a_z^{10}), \tag{78}$$

$$b_z^{44}{}^{\bar{}}=\frac{-i16a_z^3}{\pi^2}+\frac{i48a_z^5}{\pi^4}+\frac{i32(-15+4\pi^2)a_z^7}{3\pi^6}-\frac{i16(-35+24\pi^2)a_z^9}{\pi^8}+O(a_z^{10}). \tag{79}$$

We note that by insertion of $a_z=\pi\omega_o/(2\omega_{rf})$ and scaling by $(i\tau_{4\pi})^{-1}$ the low-order components are identical to those obtained earlier to fourth order [24] using the SCBCH expansion [10]. This demonstrates the general feature that EEHT followed by a straightforward Taylor expansion may provide an easy route to high-order evaluations, which may be quite tedious to establish using commutator based expansions such as SCBCH, potentially in combination with the high-order Magnus expansion formula of Bialynicki-Birula *et al.* [48].

Recently, we demonstrated that the off-resonance compensation may be improved considerably by replacing the $C_{44}^{\bar{}}$ element by the perturbed three-pulse $C_{\bar{1}43}^{\bar{}}=90_{-x}\text{-}360_x\text{-}270_{-x}$ element leading to the POST-C7 sequence [24]. The advantage of this replacement appears directly from the formulas given above, which reveal that the prefactor to the dominant I_z term is associated with an offset dependence that is two orders of magnitude larger than that for the dominant I_y term. Considering that the longitudinal components are not eliminated by the z rotations involved in the sevenfold symmetric C7 pulse sequence [24,38], it may be beneficial to interchange the I_y and I_z terms by a $-90°$ x-phase rotation of the above propagator or a permutation leading to the $C_{\bar{1}43}^{\bar{}}$ sequence element. (We note that the even more intuitive $-90°$ y-phase rotation, which would allow elimination of both I_z and I_y components, is unattractive since it changes the scaling factor of the dipolar interaction to a very low value.) In practice, this operation is also influenced by off-resonance effects, implying that the propagators for the two pulse sequence elements are related through

$$U_{\bar{1}43}^{\bar{}}=U_PU_{44}^{\bar{}}U_P^\dagger,\quad U_P=e^{-i[-(\pi/2)I_x+a_zI_z]}. \tag{80}$$

Thus, the $C_{\bar{1}43}^{\bar{}}$ POST-C7 element may be characterized by the effective Hamiltonian

$$\begin{aligned}-iH_{\bar{1}43}^{eff}\tau_{4\pi}&=U_PH_{44}^{eff}U_P^\dagger\tau_{4\pi}\\&=g_0\mathbb{1}+g_1U_PXU_P^\dagger=b_x^{\bar{1}43}{}^{\bar{}}I_x+b_y^{\bar{1}43}{}^{\bar{}}I_y+b_z^{\bar{1}43}{}^{\bar{}}I_z\end{aligned} \tag{81}$$

which may readily be expanded using the X eigenvalues for the $C_{44}^{\bar{}}$ element and the transformation formulas in Eqs. (50)–(52).

The Taylor expanded coefficients

$$b_x^{\bar{1}43}{}^{\bar{}}=\frac{-32ia_z^4}{\pi^3}+\frac{32i(7+\pi)a_z^6}{\pi^5}+\frac{64i(-57-12\pi+4\pi^2)a_z^8}{3\pi^7}+O(a_z^{10}), \tag{82}$$

$$b_y^{\bar{1}43\bar{}}=\frac{16ia_z^3}{\pi^2}-\frac{80ia_z^5}{\pi^4}-\frac{8i(-132+7\pi^2)a_z^7}{3\pi^6}+\frac{8i(-558+113\pi^2)a_z^9}{3\pi^8}+O(a_z^{10}), \tag{83}$$

$$b_z^{\bar{1}43\bar{}}=\frac{-16i(4+\pi)a_z^5}{\pi^4}+\frac{64i(7+2\pi)a_z^7}{\pi^6}+\frac{8i(-912-282\pi+64\pi^2+5\pi^3)a_z^9}{3\pi^8}+O(a_z^{10}) \tag{84}$$

clearly reveal the improved broadband behavior of the permuted element, since the longitudinal component now depends on the offset to fifth order rather than third order as was the case for the original $C_{44}^{\bar{}}$ element. It is also evident that this improvement is achieved at the expense of increased offset dependence on b_x and b_y, which, however, is unproblematic since these components are eliminated to high order by the C7 supercycle. These aspects become clearly evident from Fig. 2 showing the b_i coefficients as functions of the offset parameter $\omega_o/\omega_{rf}=2a_z/\pi$. Comparison of the plots for C7 and POST-C7 clearly demonstrates the change of the residual offset dependence of the effective Hamiltonian from being longitudinal dominated to being transverse dominated and thereby amenable to *z*-rotational decoupling upon concatenation into the C7 supercycle.

As stated earlier, one of the most powerful strategies in the design of pulse sequences with improved error compensation is to concatenate symmetry related elements to form reflection symmetric pulse sequences that eliminate all even order terms in the effective Hamiltonian. This effect follows directly from the AHT formalism and, as discussed above, also the EEHT formalism. To give a practical example, it may be relevant to ask the following question: Based on EEHT, why is the $C_{44}^{\bar{}}$ element more offset compensated than the C_{44} element and what is the origin of this? From the EEHT analysis it is evident that the I_z contribution from X amounts to $8ia_zs_4c_4$ for both sequence elements [see Eq. (77)]. This implies that the different offset compensation has to be associated with differences in the g_1 coefficients. That this indeed is the case appears clearly from Fig. 2(c), showing significantly smaller g_1 values for $C_{44}^{\bar{}}$ than for C_{44}. This is, obviously, related to differences in the eigenvalues for the relevant X operators that determine g_1. For $C_{44}^{\bar{}}$ the eigenvalues are closer to zero as compared with C_{44} as can be seen from Fig. 2(d).

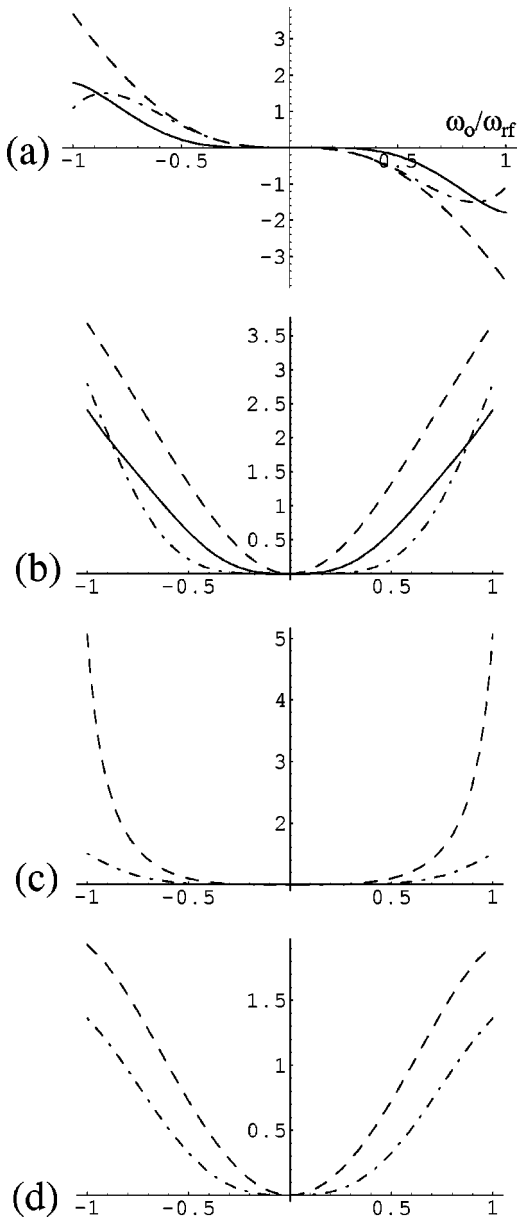


FIG. 2. Graphical representation of (a) the imaginary part of b_z, (b) the transverse norm $\sqrt{|b_x|^2+|b_y|^2}$, (c) the exact $-g_1$ coefficients, and (d) the norm of the eigenvalues for the C_{44} (dashed line), $C_{44}^{\bar{}}$ (dot-dashed line), and $C_{\bar{1}43\bar{}}$ (solid line) elements of the C7 and POST-C7 dipolar recoupling pulse sequences. It is noted that $C_{44}^{\bar{}}$ and $C_{\bar{1}43\bar{}}$ behave identically in (c) and (d).

B. Four-level problems analyzed in su(2), su(3), and su(4)

Obviously, NMR pulse sequences are not restricted to the simple su(2) single-spin-1/2 case although a large number of sequences, for example, used for excitation, inversion, and decoupling, may be described within this system. To demonstrate the power of the EEHT approach for deriving exact finite series descriptions of the propagators and Hamiltonians for two-spin-1/2 and single-spin-3/2 four-level systems, we address five examples, among which the three first upon appropriate transformation may be analyzed in su(2) or su(3), while the latter two require analysis in su(4).

1. Composite INADEQUATE CR refocusing described in su(3)

As the first example, we demonstrate how the effective field of a quite complex spin-pair liquid-state NMR experiment may be described using EEHT. Specifically, we consider the coherence- and spin-state-selective (COS^3) double- to single-quantum transfer mixing sequence of the most re-

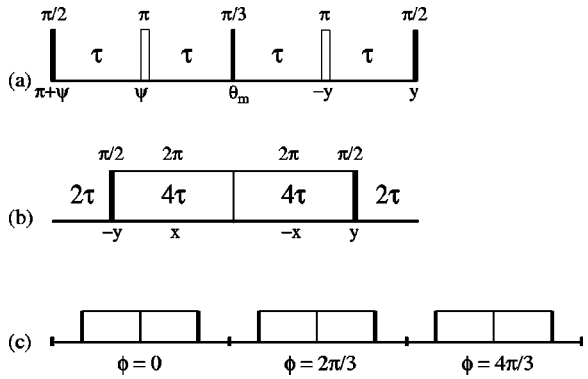


FIG. 3. Timing schemes for the (a) INADEQUATE CR mixing [$\tau=1/(4J)$ and $\psi=2\theta_m+\pi/2$ with $\theta_m=\tan^{-1}\sqrt{2}$], (b) MS [$\tau=\pi/(2\omega_{rf})$], and (c) MSHOT-3 pulse sequences. For MSHOT-3 the basic building block is the MS sequence; however, the phase of the rf field is shifted in each individual block according to the value of ϕ.

cent variant of the liquid-state NMR INADEQUATE CR experiment [Fig. 3(a)] [39,40], derived using analytical unitary bounds on quantum dynamics [41]. For this experiment we need to couple three exponential operators constituting the overall propagator for the mixing sequence [41]

$$U_{CR}=e^{i\theta_m(2I_yS_z+2I_zS_y)}e^{-i\pi(2I_xS_y+2I_yS_x)/6}e^{i\theta_m(I_y+S_y)}, \tag{85}$$

where $\theta_m=\tan^{-1}\sqrt{2}$. This is most conveniently accomplished in a symmetrized basis reflecting invariance toward permutation of the two spins [40,49] obtained using

$$A^{sym}=TAT^{\dagger},\quad T=\begin{bmatrix}1&0&0&0\\0&q&q&0\\0&0&0&1\\0&q&-q&0\end{bmatrix}, \tag{86}$$

where $q=1/\sqrt{2}$ and T represents the unitary transformation relating the standard Zeeman and the symmetrized base. In this so-called strong-coupling basis, the relevant mixing process may be treated as a su(3) problem [40].

As before, the first step is to establish analytical expressions for the individual exponential operators on the basis of the eigenvalues for the exponent. The eigenvalues for $i\theta_m(2I_yS_z+2I_zS_y)$ and $i\theta_m(I_y+S_y)$ in su(3) both equal $\{0,-i\theta_m,i\theta_m\}$, leading to the expansion coefficients

$$x_0=1,\quad x_1=\sqrt{\frac{2}{3}}\frac{1}{\theta_m},\quad x_2=\frac{1}{\theta_m^2}\left(1-\frac{1}{\sqrt{3}}\right). \tag{87}$$

Likewise, the eigenvalues for $-i\pi(2I_xS_y+2I_yS_x)/6$ are $\{0,-i\pi/6,i\pi/6\}$, leading to

$$x_0=1,\quad x_1=\frac{3}{\pi},\quad x_2=-\frac{18(\sqrt{3}-2)}{\pi^2}. \tag{88}$$

Thus, using Eq. (5) the three relevant exponential operators may be written as

$$e^{i\theta_m(2I_yS_z+2I_zS_y)}=\frac{3+\sqrt{3}}{6}\mathbb{1}+i\sqrt{\frac{2}{3}}(2I_yS_z+2I_zS_y)-\left(1-\frac{1}{\sqrt{3}}\right)2I_xS_x, \tag{89}$$

$$e^{-i\pi(2I_xS_y+2I_yS_x)/6}=\frac{2+\sqrt{3}}{4}\mathbb{1}-\frac{i}{2}(2I_xS_y+2I_yS_x)-\frac{1}{2}(2-\sqrt{3})2I_zS_z, \tag{90}$$

$$e^{i\theta_m(I_y+S_y)}=\frac{3+\sqrt{3}}{6}\mathbb{1}+i\sqrt{\frac{2}{3}}(I_y+S_y)-\left(1-\frac{1}{\sqrt{3}}\right)2I_yS_y, \tag{91}$$

which through multiplication gives a closed analytical expression for the propagator of the INADEQUATE CR experiment in the Zeeman base.

To find the effective Hamiltonian for the full mixing sequence, we shall further need

$$X=\mathbb{1}-U_{CR}=\frac{1}{2}\mathbb{1}-\frac{i}{\sqrt{2}}(I_y+S_y)+\frac{1}{2}(I_z+S_z)+I_xS_x+I_yS_y-i\sqrt{2}(I_yS_z+I_zS_y), \tag{92}$$

$$X^2=-i\sqrt{2}(I_y+S_y+2I_zS_y+2I_yS_z). \tag{93}$$

The eigenvalues of X in su(3) may be calculated to be $\{0,1-i,1+i\}$, which using Eqs. (36)–(38) leads to $g_0=0$, $g_1=0$, and $g_2=-\pi/4$.

Upon insertion into Eq. (21) extended to coupling of three propagators, we find the following effective Hamiltonian for the INADEQUATE CR mixing sequence:

$$-iH^{eff}\tau_{CR}=\ln(U_{CR})=-\frac{\pi}{4}X^2=i\frac{\sqrt{2}\pi}{4}(I_y+S_y+2I_zS_y+2I_yS_z)=\frac{\sqrt{2}\pi}{4}\begin{bmatrix}0&1&1&0\\-1&0&0&0\\-1&0&0&0\\0&0&0&0\end{bmatrix}, \tag{94}$$

where $\tau_{CR}=1/J$ is the overall duration of the pulse sequence, depending on the homonuclear J coupling required to ac-

complish the bilinear rotations in Eq. (85). Using Eq. (86), this effective Hamiltonian is readily identified as a selective π pulse,

$$(-iH^{eff}\tau_{CR})^{sym}=i\pi I_y^{1,2}, \tag{95}$$

influencing the two lowest energy levels in the su(3) base as discussed in Ref. [40].

2. MS and MSHOT-3 homonuclear dipolar decoupling described in su(3)

Using a similar approach, it is also straightforward to establish the effective Hamiltonians for the magic-sandwich [42] and the higher-order truncating MSHOT-3 [22] pulse sequences [Figs. 3(b) and 3(c)] earlier proposed for homonuclear dipolar decoupling in solid-state NMR.

For a homonuclear dipolar coupled two-spin-1/2 system, the action of the MS pulse sequence may be described by the four propagators

$$U_1=e^{-i2a_D\sqrt{6}T_{20}},\quad U_2=e^{-i\pi(I_y+S_y)/2},$$
$$U_3=e^{-i[2\pi(I_x+S_x)+4a_D\sqrt{6}T_{2,0}]},$$
$$U_4=e^{-i[-2\pi(I_x+S_x)+4a_D\sqrt{6}T_{2,0}]}, \tag{96}$$

using the irreducible spherical tensor operator $T_{2,0}=(2I_zS_z-I_xS_x-I_yS_y)/\sqrt{6}$ and where $a_D=\pi\omega_D/(2\omega_{rf})$ expresses the dependency on the angular frequencies for the dipolar coupling (ω_D) and the rf field amplitude. The homonuclear dipolar coupling Hamiltonian is defined as $H_D=\sqrt{6}\omega_D T_{2,0}$. The four propagators reflect free precession under the influence of H_D, an ideal $(\pi/2)_y$ bracketing pulse (a typical simplifying assumption [42,22], which is not required but used to avoid excessively long expressions), and two nonideal 2π pulses of phase x and $-x$ under the influence of H_D in accordance with Fig. 3(b).

The individual propagators may be calculated using Eqs. (5)–(7), and the operator X for the concatenated sequence established as

$$X=\mathbb{1}-U_1U_2U_4U_3U_2^{\dagger}U_1. \tag{97}$$

Upon transformation into the coupled basis using Eq. (86), the eigenvalues for X are derived as

$$\lambda_1=0,\quad \lambda_{2,3}=\frac{18a_D^2s_\alpha^2\mp3\sqrt{2}a_Ds_\alpha\sqrt{-9a_D^2-8\pi^2-9a_D^2c_{2\alpha}}}{\alpha^2} \tag{98}$$

with the definitions $\alpha=\sqrt{9a_D^2+4\pi^2}$, $s_x=\sin x$, and $c_x=\cos x$. With the eigenvalues determined, it is straightforward to determine the effective Hamiltonian for the MS sequence using Eq. (32) and Eqs. (36)–(38), i.e.,

$$-iH^{eff}\tau_{MS}=\frac{[\lambda_2^2\ln(1-\lambda_3)-\lambda_3^2\ln(1-\lambda_2)]X-[\lambda_3\ln(1-\lambda_2)-\lambda_2\ln(1-\lambda_3)]X^2}{\lambda_2\lambda_3(\lambda_2-\lambda_3)} \tag{99}$$

using $\tau_{MS}=12\tau=6\pi/\omega_{rf}$. In terms of standard irreducible spherical tensor operators [22], the exact effective Hamiltonian takes the form

$$-iH^{eff}\tau_{MS}=b_{T_{2,2}}^{MS}T_{2,2}+b_{T_{2,-2}}^{MS}T_{2,-2} \tag{100}$$

with $T_{2,\pm2}=\frac{1}{2}I_1^{\pm}I_2^{\pm}$,

$$b_{T_{2,2}}^{MS}=\frac{-\sqrt{2}a_D\alpha^2[\ln(1-\lambda_2)-\ln(1-\lambda_3)]s_\alpha(i\alpha c_\alpha+2\pi s_\alpha)}{s_\alpha a_D\alpha^2\sqrt{-9a_D^2-8\pi^2-9a_D^2c_{2\alpha}}}, \tag{101}$$

and $b_{T_{2,-2}}^{MS}=(-b_{T_{2,2}}^{MS})^*$ where * denotes complex conjugation.

While the exact expressions in Eqs. (100) and (101) are valuable for exact calculations, it is easier to extract physical insight into the decoupling performance by making a Taylor expansion around $a_D=0$. To tenth order this leads to

$$b_{T_{2,2}}^{MS}=\frac{-27ia_D^3}{2\pi^2}-\frac{243(-3i+4\pi)a_D^5}{32\pi^4}+\frac{729[-15i+4(9+4i\pi)\pi]a_D^7}{256\pi^6}+\frac{6561\{105i+4\pi[-87+8\pi(-9i+2\pi)]\}a_D^9}{8192\pi^8}+O(a_z^{10}). \tag{102}$$

We note that the lowest-order terms are identical to those derived earlier using the SCBCH expansion [10].

As recently demonstrated, the decoupling performance of the MS pulse sequence may be improved significantly by concatenating two phase alternated MS sequences or in practice more efficiently by concatenating three MS sequences mutually phase shifted by $2\pi/3$, leading to the so-called MSHOT-3 pulse sequence in Fig. 3(c) [22]. The rationale behind these pulse sequences becomes evident from Eq. (100), revealing that the residual dipolar coupling terms are

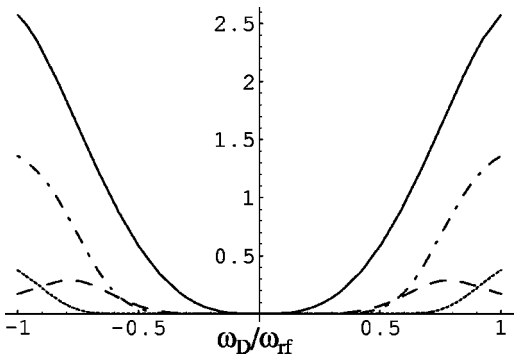


FIG. 4. Graphical representation of the norm for the exact $b_{T_{2,0}}$ (MSHOT-3, dotted line), $b_{T_{2,2}}$ (MS, solid line; MSHOT-3, dot-dashed line), and $b_{T_{1,0}}$ (MSHOT-3, dashed line) coefficients for the residual dipolar coupling from homonuclear MS and MSHOT-3 decoupling as a function of ω_D/ω_{rf}.

proportional to $T_{2,\pm 2}$ and thereby may be eliminated by the proposed z rotations. More insight may be obtained using the EEHT formalism, which based on the formulas derived for the MS sequence leads to the following effective Hamiltonian for the MSHOT-3 sequence:

$$-iH^{eff}\tau_{MSHOT\text{-}3}=b_{T_{1,0}}^{MSHOT\text{-}3}T_{1,0}+b_{T_{2,0}}^{MSHOT\text{-}3}T_{2,0}+b_{T_{2,2}}^{MSHOT\text{-}3}T_{2,2}+b_{T_{2,-2}}^{MSHOT\text{-}3}T_{2,-2} \tag{103}$$

with $T_{1,0}=I_z+S_z$ and $b_{T_{2,-2}}^{MSHOT\text{-}3}=(-b_{T_{2,2}}^{MSHOT\text{-}3})^*$. In this case the exact formulas are quite long, so we restrict ourselves to presentation of the coefficients in a tenth order Taylor expansion around $a_D=0$, i.e.,

$$b_{T_{1,0}}^{MSHOT\text{-}3}=\frac{i729\sqrt{3}}{32\pi^4}a_D^6-\frac{19683i\sqrt{3}}{256\pi^6}a_D^8+O(a_D^{10}), \tag{104}$$

$$b_{T_{2,2}}^{MSHOT\text{-}3}=-\frac{19683(i+\sqrt{3})}{64\pi^6}a_D^9+O(a_D^{10}), \tag{105}$$

$$b_{T_{2,0}}^{MSHOT\text{-}3}=O(a_D^{10}). \tag{106}$$

By comparison of Eq. (102) and Eqs. (104)–(106), it is evident that MSHOT-3 reduces the offset dependence by three orders of magnitude relative to MS. This finding is supported by Fig. 4, showing the exact coefficients for MS and MSHOT-3 schemes as functions of ω_D/ω_{rf}.

3. Finite rf pulse excitation for I = 3/2 quadrupolar nuclei described in su(2)

A problem very often encountered in AHT based analytical descriptions of solid-state NMR experiments is that the magnitude of the external part of the Hamiltonian is not separated by one or more orders of magnitude from the magnitude of internal parts of the Hamiltonian. In such cases, it is impossible to establish an interaction representation that ensures rapid convergence of the average Hamiltonian. This has motivated the introduction of analytical expressions in limiting cases, such as the ''weak'' and ''strong'' rf field cases, while leaving the intermediate cases to numerical simulations. A typical example could be rf excitation in the case of a powder of spin $I>1/2$ nuclei influenced by a strong quadrupolar coupling interaction, which because of its orientation dependence scales from being much smaller to much larger than the available rf field strength.

Addressing this specific example, we will demonstrate the use of the Cayley-Hamilton expansion to establish an exact operator exponential for the propagator of an x-phase rf pulse with amplitude ω_{rf} on an $I=3/2$ spin influenced by a quadrupolar coupling interaction with amplitude ω_Q, as expressed by the Hamiltonian

$$H=\omega_{rf}I_x+\omega_Q(3I_z^2-I^2). \tag{107}$$

Such propagators can subsequently be concatenated and the effective Hamiltonian established with the EEHT formalism (not shown). Since both terms of the Hamiltonian are symmetric with respect to the m quantum number, the su(4) problem may conveniently be transformed into two su(2) problems using the similarity transformation [50]

$$A^T=TAT^\dagger,\quad T=\begin{bmatrix} q & 0 & 0 & q \\ 0 & q & q & 0 \\ 0 & -q & q & 0 \\ -q & 0 & 0 & q \end{bmatrix} \tag{108}$$

with $q=1/\sqrt{2}$. Within this frame H^T and the corresponding propagator block diagonalize into two independent SU(2) representations, allowing definition of

$$H_{upper}^T\tau=\frac{\omega_{rf}\tau}{2}\mathbb{1}+\sqrt{3}\omega_{rf}\tau I_x+(6\omega_Q\tau-\omega_{rf}\tau)I_z, \tag{109}$$

$$H_{lower}^T\tau=-\frac{\omega_{rf}\tau}{2}\mathbb{1}+\sqrt{3}\omega_{rf}\tau I_x-(6\omega_Q\tau+\omega_{rf}\tau)I_z, \tag{110}$$

where the basis operators I_x, I_z, and $\mathbb{1}$ now belong to a two-level system. Accordingly, the exponentials may readily be calculated using Eq. (17), i.e.,

$$e^{-iH_{upper}^T\tau}=e^{-i\omega_{rf}\tau/2}\left(\cos\delta^-\mathbb{1}-i\frac{\sin\delta^-}{\delta^-}[\sqrt{3}\omega_{rf}\tau I_x+(6\omega_Q\tau-\omega_{rf}\tau)I_z]\right), \tag{111}$$

$$e^{-iH_{lower}^T\tau}=e^{i\omega_{rf}\tau/2}\left(\cos\delta^+\mathbb{1}-i\frac{\sin\delta^+}{\delta^+}[\sqrt{3}\omega_{rf}\tau I_x-(6\omega_Q\tau+\omega_{rf}\tau)I_z]\right) \tag{112}$$

with $\delta^{\pm}=\tau\sqrt{9\omega_Q^2+\omega_{rf}^2\pm 3\omega_Q\omega_{rf}}$. These expressions are exact and may be used for analytical and numerical evaluations independently of the relative sizes of ω_{rf} and ω_Q.

4. Heteronuclear coherence transfer described in su(4)

All heteronuclear NMR experiments are based on the transfer of magnetization or coherence from one nuclear spin species to another, with the aim, e.g., of establishing correlations between signals from directly bonded heteronuclei. This may be accomplished by in-phase transfers of the type $I_x\rightarrow S_x$, e.g., using refocused INEPT [43,44]. This experiment is characterized by the propagator

$$U=e^{-i\pi 2I_zS_z/2}e^{-i\pi(I_x+S_x)/2}e^{-i\pi 2I_zS_z/2}, \tag{113}$$

with the $2I_zS_z$ rotations accomplished by J-coupling evolution with the precession period (τ) for the first and third propagators related to the heteronuclear J coupling as $\pi J\tau=\pi/2$.

In order to appreciate the overall effect of this pulse sequence element it may be relevant to calculate the effective Hamiltonian. This may readily be accomplished using the su(4) formalism outlined in the previous section. First, the eigenvalues of $X=\mathbb{1}-U$ are found to be $\{1-i,1-i,1+i,1+i\}$. Second, the g_i coefficients are calculated using Eqs. (A11)–(A14) in the Appendix, assuming that we have two pairs of identical eigenvalues in this case. This leads to $g_0=\pi-1$, $g_1=1-3\pi/2$, $g_2=(3\pi-2)/4$, and $g_3=-\pi/4$, allowing the effective Hamiltonian of the experiment to be expressed as

$$\begin{aligned}-iH_{eff}\tau&=g_0\mathbb{1}+g_1X+g_2X^2+g_3X^3\\&=-\frac{i\pi}{2}(I_x+S_x+2I_zS_z+2I_yS_y).\end{aligned} \tag{114}$$

5. Gates for quantum computing described in su(4)

Obviously, the EEHT formalism is not restricted to NMR and certainly not only to NMR pulse sequences aimed at molecular structure determination. It is well established that coherent spectroscopy, and in particular NMR, may play an important role in the development of quantum computing. In a NMR implementation quantum gates may be realized using pulse sequences that exploit internal nuclear spin interactions as well as external rf fields to tailor the Hamiltonian to an appropriate shape. It may, however, be difficult to see *a priori* which specific pulse sequences correspond to a particular quantum gate and what are the functions on the level of the overall Hamiltonian and propagator. Such information may readily be obtained using the analytical tools established in this paper. Specifically we address the fundamental controlled NOT (CNOT) and SWAP gates operating on four-level systems. Before proceeding to these examples, we should note that the relevant propagators in these cases have the determinant -1, implying that they belong to the unitary group U(4) rather than the special unitary group SU(4) addressed so far. In our context, however, this only gives the additional problem that it is possible to have four identical eigenvalues different from zero for the propagator, which has not been accounted for in the formulas presented so far. In all other respects the formulas presented apply equally well for U(4).

In NMR the controlled-NOT gate may be implemented using the propagator [45]

$$\begin{aligned}U_{\mathrm{CNOT}(IS)}&=e^{-i\pi/4}e^{i(\pi/2)I_x}e^{i(\pi/2)I_z}e^{-i(\pi/2)2I_zS_x}\\&=\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&0&1\\0&0&1&0\end{bmatrix},\end{aligned} \tag{115}$$

which leads to

$$X=\mathbb{1}-U_{\mathrm{CNOT}(IS)} \tag{116}$$

with the eigenvalues $\lambda_1=\lambda_2=\lambda_3=0$, and $\lambda_4=2$. With three degenerate eigenvalues, the g_i coefficients for the effective Hamiltonian may be established as $g_3=-\frac{1}{2}-i\pi/8$, $g_2=\frac{1}{2}$, $g_1=0$, and $g_0=0$ using Eqs. (A15)–(A18). Equipped with these the effective Hamiltonian may be derived as

$$\begin{aligned}\ln(U_{\mathrm{CNOT}(IS)})&=\frac{1}{2}X^2-\left(\frac{1}{2}+\frac{i\pi}{8}\right)X^3\\&=i\frac{\pi}{2}\left(I_z+S_x-2I_zS_x-\frac{1}{2}\mathbb{1}\right),\end{aligned} \tag{117}$$

where the $(i\pi/4)\mathbb{1}$ term can be neglected for practical purposes.

Similarly the effective Hamiltonian for the controlled-NOT gate $U_{\mathrm{CNOT}(SI)}$ defined as

$$\begin{aligned}U_{\mathrm{CNOT}(SI)}&=e^{i(\pi/4)}e^{-i(\pi/2)I_y}e^{-i(\pi/2)(I_z+S_z)}e^{i(\pi/2)2I_zS_z}e^{i(\pi/2)I_y}\\&=\begin{bmatrix}1&0&0&0\\0&0&0&1\\0&0&1&0\\0&1&0&0\end{bmatrix}\end{aligned} \tag{118}$$

can be found. For this gate, the eigenvalues of $X=\mathbb{1}-U_{\mathrm{CNOT}(SI)}$ are identical to those found in the $U_{\mathrm{CNOT}(IS)}$ case, implying that the entangled Hamiltonian may be derived as

$$\ln(U_{\mathrm{CNOT}(SI)})=i\frac{\pi}{2}\left(I_x+S_z-2I_xS_z-\frac{1}{2}\mathbb{1}\right). \tag{119}$$

From these two simple gates, the so-called SWAP gate can be constructed as

$$U_{\mathrm{SWAP}}=U_{\mathrm{CNOT}(SI)}U_{\mathrm{CNOT}(IS)}U_{\mathrm{CNOT}(SI)}=\begin{bmatrix}1&0&0&0\\0&0&1&0\\0&1&0&0\\0&0&0&1\end{bmatrix}. \tag{120}$$

The eigenvalues and thereby the g_i coefficients are identical to those for CNOT(IS). Thus, the effective Hamiltonian can be found as

$$\ln(U_{\mathrm{SWAP}}) = g_0\mathbb{1} + g_1 X + g_2 X^2 + g_3 X^3$$

$$= i\frac{\pi}{2}\left(2S_xI_x + 2I_yS_y + 2S_zI_z - \frac{1}{2}\mathbb{1}\right), \quad (121)$$

which in NMR terminology corresponds to an isotropic mixing sequence [51] when we ignore the irrelevant term proportional to unity.

IV. CONCLUSION

In conclusion, we have presented a closed solution to the BCH problem which allows for exact description of the entanglement between two or more exponential operators in terms of the effective propagator and the effective Hamiltonian describing the overall evolution of the system. The solution is based on the Cayley-Hamilton theorem, which enables translation of the typical infinite series expansions for the exponential and logarithmic mappings into finite series expansions containing n terms for the n^2-dimensional Lie group, e.g., an n-level system. Addressing specifically the special unitary groups, we have derived explicit formulas for SU(2), SU(3), and SU(4) in cases of nondegenerate and degenerate eigenvalues. In these cases, it is typically feasible to determine the required eigenvalues for the individual and concatenated propagators and establish relatively simple exact expressions for the entangled operators. These formulas may be used directly for analytical evaluations, for numerical simulations, or may in favorable cases be Taylor expanded to provide impact-ordered expressions identical to those obtained earlier using infinite series expansion approaches.

As demonstrated by several examples, the EEHT formalism may represent an attractive alternative to the commonly used infinite series Magnus expansion based AHT and SCBCH formalisms, which have had their major use on two- to four-level problems. As a distinct advantage the EEHT formalism is exact and allows the analysis to be performed directly in the laboratory frame without the need for complicating transformations into appropriate interaction frames. Thus the EEHT formalism spans the gap between the approximate analytical and exact numerical descriptions often used for evaluation and design of experimental methods in coherent spectroscopy. Although the present paper exclusively address examples within NMR spectroscopy, it is envisaged that the EEHT formalism through its general nature may have a considerable potential for analytical/numerical analysis within other areas in chemistry and physics. In particular, applications within optical spectroscopy, coherent control, and quantum computing may be foreseen.

ACKNOWLEDGMENTS

Support from Carlsbergfondet, the Danish Natural Science Foundation, and the Danish Research Council through the Danish Biotechnology Instrument Centre is acknowledged.

APPENDIX

In this Appendix we will in condensed form give the g_i coefficients for the finite expansion of the entangled Hamiltonian in the su(3) and su(4) cases with degeneracy of eigenvalues.

In the su(3) case with $\lambda_1 = \lambda_2$, the a_k and g_i coefficients may be expressed as

$$ma_k = (k+2)\lambda_1^{k+3} - (k+3)\lambda_1^{k+2}\lambda_3 + \lambda_3^{k+3}, \quad (A1)$$

$$mb_k = -(k+1)\lambda_1^{k+4} + (k+3)\lambda_1^{k+2}\lambda_3^2 - 2\lambda_1\lambda_3^{k+3}, \quad (A2)$$

$$mc_k = (k+1)\lambda_1^{k+4}\lambda_3 - (k+2)\lambda_1^{k+3}\lambda_3^2 + \lambda_1^2\lambda_3^{k+3}, \quad (A3)$$

and

$$mg_0 = \frac{(\lambda_1-1)(2\lambda_1-\lambda_3)\lambda_3\ln(1-\lambda_1) + \lambda_1[\lambda_3(\lambda_3-\lambda_1) - (\lambda_1-1)\lambda_1\ln(1-\lambda_3)]}{(1-\lambda_1)}, \quad (A4)$$

$$mg_1 = \frac{\lambda_1^2 - \lambda_3^2 - 2(\lambda_1-1)\lambda_1\ln(1-\lambda_1) + 2(\lambda_1-1)\lambda_1\ln(1-\lambda_3)}{(1-\lambda_1)}, \quad (A5)$$

$$mg_2 = \frac{-\lambda_1 + \lambda_3 + (\lambda_1-1)\ln(1-\lambda_1) - (\lambda_1-1)\ln(1-\lambda_3)}{(1-\lambda_1)} \quad (A6)$$

using $m=(\lambda_1-\lambda_3)(\lambda_2-\lambda_3)$.

In the su(4) case with $\lambda_1=\lambda_2$ degenerate eigenvalues the coefficients may be written as

$$mg_0=\frac{1}{(1-\lambda_1)}(\lambda_1(\lambda_1-\lambda_3)\lambda_3(\lambda_1-\lambda_4)(\lambda_3-\lambda_4)\lambda_4+(-1+\lambda_1)\{\lambda_3\lambda_4(-\lambda_3+\lambda_4)[3\lambda_1^2+\lambda_3\lambda_4-2\lambda_1(\lambda_3+\lambda_4)]\times\ln(1-\lambda_1)+\lambda_1^2[(\lambda_1-\lambda_4)^2\lambda_4\ln(1-\lambda_3)-(\lambda_1-\lambda_3)^2\lambda_3\ln(1-\lambda_4)]\}), \tag{A7}$$

$$mg_1=\frac{1}{(1-\lambda_1)}(-(\lambda_1-\lambda_3)(\lambda_1-\lambda_4)(\lambda_3-\lambda_4)\{\lambda_1^3+(\lambda_2-\lambda_3)(\lambda_2-\lambda_4)-\lambda_1^2(1+\lambda_3+\lambda_4)+\lambda_1[2(\lambda_3+\lambda_4)+\lambda_2(-\lambda_2+\lambda_3+\lambda_4)]\}+(-1+\lambda_1)\lambda_1[-2\lambda_3^3+2\lambda_4^3+3\lambda_1(\lambda_3-\lambda_4)(\lambda_3+\lambda_4)\ln(1-\lambda_1)-(\lambda_1-\lambda_4)^2(\lambda_1+2\lambda_4)\ln(1-\lambda_3)+(\lambda_1-\lambda_3)^2(\lambda_1+2\lambda_3)\ln(1-\lambda_4)]), \tag{A8}$$

$$mg_2=\frac{-1}{2(1-\lambda_1)}((\lambda_1-\lambda_3)(\lambda_1-\lambda_4)(\lambda_3-\lambda_4)\{\lambda_1^3+\lambda_2^2-2(\lambda_3+\lambda_4)-\lambda_2(\lambda_3+\lambda_4)-\lambda_1^2(1+\lambda_3+\lambda_4)+\lambda_1[-2+\lambda_3+\lambda_4+\lambda_2(-\lambda_2+\lambda_3+\lambda_4)]\}+2(-1+\lambda_1)\{[-\lambda_3^3+3\lambda_1^2(\lambda_3-\lambda_4)+\lambda_4^3]\ln(1-\lambda_1)-(\lambda_1-\lambda_4)^2(2\lambda_1+\lambda_4)\ln(1-\lambda_3)+(\lambda_1-\lambda_3)^2\times(2\lambda_1+\lambda_3)\ln(1-\lambda_4)\}), \tag{A9}$$

$$mg_3=\frac{1}{3(\lambda_1-1)}((\lambda_1-\lambda_3)(\lambda_1-\lambda_4)(\lambda_3-\lambda_4)\{3+\lambda_1^3+\lambda_2^2-\lambda_2(\lambda_3+\lambda_4)-\lambda_1^2(1+\lambda_3+\lambda_4)+\lambda_1[\lambda_3+\lambda_4+\lambda_2(-\lambda_2+\lambda_3+\lambda_4)]\}+3(-1+\lambda_1)(\lambda_3-\lambda_4)(-2\lambda_1+\lambda_3+\lambda_4)\ln(1-\lambda_1)+3(-1+\lambda_1)[(\lambda_1-\lambda_4)^2\ln(1-\lambda_3)-(\lambda_1-\lambda_3)^2\ln(1-\lambda_4)]\}, \tag{A10}$$

with $m=(\lambda_1-\lambda_3)(\lambda_1-\lambda_4)(\lambda_2-\lambda_3)(\lambda_2-\lambda_4)(\lambda_3-\lambda_4)$.

In the su(4) case with $\lambda_1=\lambda_2$ and $\lambda_3=\lambda_4$ degeneracy we obtain

$$mg_0=\frac{-1}{(\lambda_1-1)(\lambda_3-1)}((\lambda_1-\lambda_3)\{-\lambda_1(\lambda_1-\lambda_3)\lambda_3\times[(\lambda_1-1)\lambda_1+(\lambda_3-1)\lambda_3]+(\lambda_1-1)(\lambda_3-1)\times[(3\lambda_1-\lambda_3)\lambda_3^2\ln(1-\lambda_1)+\lambda_1^2(\lambda_1-3\lambda_3)\ln(1-\lambda_3)]\}), \tag{A11}$$

$$mg_1=\frac{-1}{(\lambda_1-1)(\lambda_3-1)}((\lambda_1-\lambda_3)\{-\lambda_1^4-\lambda_1^3(\lambda_3-1)+3\lambda_1^2\lambda_3+\lambda_1(\lambda_3-3)\lambda_3^2+(\lambda_3-1)\lambda_3^3+6(\lambda_1-1)\lambda_1(\lambda_3-1)\lambda_3(\ln(1-\lambda_1)-\ln(1-\lambda_3))]\}), \tag{A12}$$

$$mg_2=\frac{-1}{(\lambda_1-1)(\lambda_3-1)}[(\lambda_1-\lambda_3)\{\lambda_1^2(2\lambda_1-3)+(3-2\lambda_3)\lambda_3^3+3(\lambda_1-1)(\lambda_3-1)(\lambda_1+\lambda_3)\times[\ln(1-\lambda_3)-\ln(1-\lambda_1)]\}], \tag{A13}$$

$$mg_3=\frac{\lambda_1-\lambda_3}{(\lambda_1-1)(1-\lambda_3)}\{(\lambda_3-\lambda_1)(\lambda_1+\lambda_3-2)+2(\lambda_1-1)\times(\lambda_3-1)[\ln(1-\lambda_1)-\ln(1-\lambda_3)]\} \tag{A14}$$

with $m=(\lambda_1-\lambda_3)(\lambda_1-\lambda_4)(\lambda_2-\lambda_3)(\lambda_2-\lambda_4)$.

Finally, in the su(4) case with $\lambda_1=\lambda_2=\lambda_3$ degeneracy we obtain

$$mg_0=\frac{-1}{2(\lambda_1-1)^2}\{-\lambda_1(\lambda_1-\lambda_4)\lambda_4[\lambda_1(-4+5\lambda_1-3\lambda_4)+2\lambda_4]+2(-1+\lambda_1)^2[\lambda_4(3\lambda_1^2-3\lambda_1\lambda_4+\lambda_4^2)\times\ln(1-\lambda_1)-\lambda_1^3\ln(1-\lambda_4)]\}, \tag{A15}$$

$$mg_1=\frac{1}{2(\lambda_1-1)^2}((\lambda_1-\lambda_4)(2\lambda_1^4+4\lambda_1(\lambda_2-\lambda_4)(\lambda_3-\lambda_4)+2(\lambda_2-\lambda_4)(-\lambda_3+\lambda_4)-\lambda_1^3(9+4\lambda_4)+\lambda_1^2[-2\lambda_2\lambda_3+2(\lambda_2+\lambda_3)\lambda_4+3(2+\lambda_4)]\}+6(-1+\lambda_1)^2\lambda_1^2\times[\ln(1-\lambda_1)-\ln(1-\lambda_4)]), \tag{A16}$$

$$mg_2=\frac{1}{2(\lambda_1-1)^2}((\lambda_1-\lambda_4)\{\lambda_1^4-2\lambda_1^3(1+\lambda_4)+(\lambda_2-\lambda_4)\times(-\lambda_3+\lambda_4)+\lambda_1^2[9-\lambda_2\lambda_3+(4+\lambda_2+\lambda_3)\lambda_4]+\lambda_1[2\lambda_2\lambda_3-2(\lambda_2+\lambda_3)\lambda_4-3(2+\lambda_4)]\}+6(-1+\lambda_1)^2\lambda_1[-\ln(1-\lambda_1)+\ln(1-\lambda_4)]), \tag{A17}$$

$$mg_3=\frac{1}{6(\lambda_1-1)^2}[(\lambda_1-\lambda_4)(6-2\lambda_2\lambda_3+\lambda_1\{-9+4\lambda_2\lambda_3+2\lambda_1[(-1+\lambda_1)^2-\lambda_2\lambda_3]\}+3\lambda_4-2(-1+\lambda_1)^2(2\lambda_1-\lambda_2-\lambda_3)\lambda_4)+6(-1+\lambda_1)^2\times\ln(1-\lambda_1)-6(-1+\lambda_1)^2\ln(1-\lambda_4)] \tag{A18}$$

with $m=(\lambda_1-\lambda_4)(\lambda_2-\lambda_4)(\lambda_3-\lambda_4)$.

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