Suppression of higher-order nuclear dipole-dipole interactions in multipulse NMR spectroscopy of solids

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Simple recurrence relationships are obtained for a time-independent effective Hamiltonian governing the behavior of spin systems in rapidly oscillating magnetic fields. A geometric representation is proposed for multipulse sequences which average the dipole-dipole interaction between nuclear spins. New classes of multipulse sequences performing such averaging are proposed. Geometric "images" of sequences are used to estimate the resolution attainable with their aid in NMR spectra of solids.

An increase in the resolution of NMR in solids attained recently[1,2] by the development of multipulse methods[1] has provided means of obtaining valuable information on the structure of solids,[3] and on the nature of hydrogen bonds[4] or protons[5] in solids, on the composition, degree of crystallinity, and motion in polymers,[6] and so on (see Ref. 2).

High-resolution multipulse NMR spectroscopy of solids is based on the simple physical idea of averaging the anisotropic dipole-dipole (DD) interactions of nuclear spins by a periodic sequence of high-power resonance hf pulses. Interaction of a spin system with such a pulse sequence induces periodic changes in the spin orientations relative to the z axis, along which a static field H_0 is applied. Although there is no change in the relative orientation of the spins, the secular part of the DD interactions varies (relative to the z axis) and these interactions rapidly oscillate in time if the pulse repetition frequency obeys $\Omega \gg \omega_{\text{loc}}{}^2 = \text{Tr}(\hat{\mathscr{H}}_{dz}{}^2)/\text{Sp}(\hat{S}_z{}^2)$, where $\hat{\mathscr{H}}_{dz}$ is the Hamiltonian of the secular part of the DD interactions and $\hat{S}_z$ is the operator representing the projection of the total spin along the z axis). The degree of averaging of the DD interactions increases on reduction in the parameter $\varepsilon = \omega_{\text{loc}}/\Omega$, which however cannot be small under multipulse experimental conditions (values $\varepsilon = 0.1$–0.5 are reported in Refs. 1, 2, and 7). Therefore, a sequence of pulses should be organized so that the residual (nonaveraged) DD interactions are of the order of ε^k, where k is an integer ($k > 1$). For example, in the case of the first sequence used for the averaging of the DD interactions and known as WHH-4 (Ref. 1) this integer is $k = 2$, and for one of the most effective averaging sequences called BR-52 (Ref. 8), we have $k = 4$.

A BR-52 pulse sequence applied to a CaF_2 single crystal ($H_0 \| 111$) made it possible to reduce[8] the DD interactions of the spins of the ^{19}F nuclei by a factor of about 1000, whereas in other experiments the resolution was sufficient for the tasks mentioned above.[2–6]

The resolution attainable in NMR spectra of solids is much poorer than that attainable for liquids, which limits applications of NMR spectroscopy in studies of the structure and dynamic processes in solids. Considerable progress in improving the resolution of NMR spectra has been made recently by the development of combined methods in which a multipulse sequence is used jointly with rotation of a sample at a "magic" angle,[9,10] with two-dimensional[11] and multiphoton[12] spectroscopy, and with heteronuclear correlation spectroscopy.[13] Nevertheless, improvement of the resolution of NMR spectroscopy of solids is still an urgent task.

It should be pointed out that nonaveraged DD interactions are not the only factor which limits the resolution of the spectra. Other factors which affect the resolution include imperfections of multipulse sequences,[2] inhomogeneity and instability of the magnetic field H_0, shape of the sample, etc. (see, for example, Ref. 7). However, whereas these factors can be eliminated or reduced considerably by improving the apparatus and the method used in the experiments, the residual DD interactions governed largely by the properties of the investigated substance are the fundamental cause which limits the resolution of NMR spectra in a solid.

In the case of multipulse experiments the residual DD interactions are governed by a time-independent effective Hamiltonian which describes completely the dynamics of spin systems in rapidly oscillating magnetic fields.[14] This Hamiltonian is expanded as a series in terms of the parameter ε mentioned above[14] and the smaller the magnitude of the first nonvanishing term of this series, the smaller are the residual DD interactions. Therefore, in selecting multipulse sequences which average the DD interactions it is necessary to ensure vanishing of as many as possible of the initial terms of the effective Hamiltonian by a suitable selection of the pulse sequence parameters. It is necessary to analyze terms of higher orders in ε and this can be done only by recurrence formulas describing the effective Hamiltonian terms of a given order in ε as functions of lower-order terms.

Methods suitable for the derivation of such formulas are given in Refs. 15 and 16, but the recurrence relationships for the terms of the effective Hamiltonian are not derived. These relationships are given in a recent paper.[17] However, the absence of the commutator structure in the case of the effective Hamiltonian terms in Ref. 17 makes it difficult to use the formulas given there in many-body problems.

We shall propose simple recurrence relationships which link the effective Hamiltonian terms and describe the behavior of spin systems in rapidly oscillating magnetic fields. Such recurrence formulas and the symmetry properties will be used to develop a geometric approach to the design of multipulse sequences which average the DD interactions by six orders in respect of the parameter ε. The geometric approach will be used to analyze the main multi-

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pulse sequences used to obtain high-resolution NMR spectra of solids and new multipulse sequences averaging the DD interactions and reducing them by four to six orders of magnitude in respect of the parameter ε will be proposed. Geometric "images" of multipulse sequences will be used in a comparative estimate of the resolution of NMR spectra obtained using various multipulse methods.

1. RECURRENCE FORMULAS FOR THE EFFECTIVE HAMILTONIAN OF A SYSTEM OF INTERACTING SPINS IN A RAPIDLY OSCILLATING MAGNETIC FIELD

We shall consider a system of nuclear spins ($s = 1/2$) and describe the interaction between them by a Hamiltonian $\hat{\mathscr{H}}_{in}$. In a coordinate system rotating at the Larmor frequency the spins experience a rapidly oscillating field of frequency $\Omega \gg \omega_{\text{loc}}$ and the local field $\omega_{\text{loc}}/\gamma$ (γ is the gyromagnetic ratio) is governed by the interaction $\hat{\mathscr{H}}_{in}$. The equation for the density matrix ρ of the spin system considered using rotating coordinates can be written as follows (for $\hbar = 1$)[14]:

$$id\rho/dt = [\hat{\mathscr{H}}(\bar{t}/\varepsilon),\ \rho(\bar{t})], \tag{1}$$

where the dimensionless time is $\bar{t} = t\omega_{\text{loc}}$ (t is the real time), $\varepsilon = \omega_{\text{loc}}/\Omega \ll 1$, and $\hat{\mathscr{H}}(\bar{t}/\varepsilon)$ is the Hamiltonian $\hat{\mathscr{H}}_{in}$ considered in the interaction representation in respect of the alternating field.[14] We shall drop the bar over the dimensionless time. The effective Hamiltonian $\hat{\mathscr{H}}^{\text{eff}}$ independent of time and accurate to within terms of the order of ε^k ($k = 0, 1, 2, \ldots$) can be obtained[14] by the transformation $\hat{F}_k = \hat{F}_k(t/\varepsilon, \varepsilon)$ of the density matrix

$$\rho = \hat{F}_k^{+}(t/\varepsilon, \varepsilon)\rho_k\hat{F}_k(t/\varepsilon,\ \varepsilon), \tag{2}$$

which conserves the form of Eq. (1) and reduces it to

$$i\,d\rho_k/dt = \left[\sum_{m=0}^{k}\varepsilon^m\hat{\mathscr{H}}_m + \bar{D}^{(k)}(t/\varepsilon, \varepsilon), \rho_k\right]$$

$$= [\hat{\mathscr{H}}^{(k)} + \bar{D}^{(k)}(t/\varepsilon, \varepsilon), \rho_k], \tag{3}$$

where

$$k = 0, 1, 2, \ldots$$

and the Hermitian operators $\hat{\mathscr{H}}_m$ ($m = 0, 1, \ldots, k$) are independent of time and $\hat{D}^{(k)}(t/\varepsilon, \varepsilon)$ are rapidly oscillating terms of order ε^k. To find $\hat{F}_k$ and $\hat{\mathscr{H}}_k$ ($k = 0, 1, 2, \ldots$), we shall first carry out[18] the $\langle . \rangle$ operation as follows:

$$\langle\varphi\rangle = \int_0^t(\varphi - \bar{\varphi})\,d\tau - \overline{\int_0^t(\varphi - \bar{\varphi})\,d\tau}, \tag{4}$$

where $\bar{\varphi}$ is the time-average value. It should be noted that $\hat{D}^{(k)}(t/\varepsilon, \varepsilon)$ can be represented in the form

$$\bar{D}^{(k)} = \hat{d}_k(t/\varepsilon,\ \varepsilon) + \varepsilon^{k+1}\hat{\eta}_k(t/\varepsilon) + \varepsilon^{k+2}\hat{\psi}_k(t/\varepsilon,\ \varepsilon),\quad k = 0, 1, 2, \ldots, \tag{5}$$

and $\hat{d}_k(t/\varepsilon, \varepsilon)$ has the following structure:

$$\hat{d}_k(t/\varepsilon,\ \varepsilon) = \varepsilon^k\hat{f}_k(t/\varepsilon), \tag{6}$$

where $\hat{d} = 0$. It follows from Eq. (4) that the structure of $\langle\hat{d}_k\rangle$ is as follows:

$$\langle\hat{d}_k\rangle = \varepsilon^{k+1}\hat{\varphi}_k(t/\varepsilon). \tag{7}$$

The recurrent process governing the terms in the effective Hamiltonian $\hat{\mathscr{H}}^{\text{eff}}$ and the transformation $\hat{F}_k$ ($k = 0, 1, 2, \ldots$) can now be described as follows:

$$\hat{F}_0 = E,\quad \hat{\mathscr{H}}^{(0)} = \hat{\mathscr{H}}_0 = \overline{\hat{\mathscr{H}}(t/\varepsilon)},\quad \hat{d}_0 = \hat{D}_0^{(0)}(t/\varepsilon, \varepsilon) \tag{8}$$

(E is a unit operator),

$$\hat{F}_1 = \exp(i\langle\hat{d}_0\rangle),\quad \hat{\mathscr{H}}_1 = (i/2\varepsilon)\overline{[\langle\hat{d}_0\rangle, \hat{d}_0]},$$

$$\hat{d}_1 = i[\langle\hat{d}_0\rangle, \hat{\mathscr{H}}_0] + {}^1/_2\,i([\langle\hat{d}_0\rangle, \hat{d}_0] - \overline{[\langle\hat{d}_0\rangle, \hat{d}_0]}). \tag{9}$$

We shall assume that $\hat{F}_k$ and $\hat{\mathscr{H}}_k$ are already known and then, applying the formula for $\hat{D}^{(k)}(t/\varepsilon, \varepsilon)$ (Ref. 14) which can be written in the form

$$\bar{D}^{(k)}(t/\varepsilon,\ \varepsilon) = \hat{F}_k\hat{\mathscr{H}}(t/\varepsilon)\hat{F}_k^{+} + i(d\hat{F}_k/dt)\hat{F}_k^{+} - \hat{\mathscr{H}}^{(k)}, \tag{10}$$

we obtain

$$\hat{F}_{k+1} = \exp(i\langle\hat{d}_k\rangle)F_k,\quad \hat{\mathscr{H}}_{k+1} = \overline{\hat{\eta}_k},\quad k = 1, 2, \ldots. \tag{11}$$

We shall also give a recurrence formula convenient in the subsequent calculations:

$$\hat{d}_{k+1} = i[\langle\hat{d}_k\rangle, \hat{\mathscr{H}}_0] + \varepsilon^{k+1}(\hat{\eta}_k - \bar{\hat{\eta}}_k),\quad k = 1, 2, \ldots. \tag{12}$$

The formulas (8)–(11) allow us to find successively the operators $\hat{\mathscr{H}}_0$, $\hat{\mathscr{H}}_1$, $\hat{\mathscr{H}}_2$, ... and thus to determine the time-independent effective Hamiltonian $\hat{\mathscr{H}}^{\text{eff}}$ which will be used later to study multipulse sequences that average the DD interactions. The proof of the recurrence relationships (8)–(11) is given in the Appendix 1. Using Eqs. (8)–(11), we obtain expressions for some of the first terms in $\hat{\mathscr{H}}^{\text{eff}}$ taking from each term the time average (the bar is omitted):

$$\varepsilon^2\hat{\mathscr{H}}_2 = -\frac{1}{2}[\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, \hat{\mathscr{H}}_0]] - \frac{1}{3}[\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, \hat{d}_0]], \tag{13}$$

$$\varepsilon^3\hat{\mathscr{H}}_3 = -\frac{i}{6}[\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, \hat{\mathscr{H}}_0]]] + i[\langle\hat{d}_1\rangle, \varepsilon\hat{\mathscr{H}}_1] + \frac{i}{2}[\langle\hat{d}_1\rangle, \hat{d}_1] - \frac{i}{8}[\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, d_0]]], \tag{14}$$

$$\varepsilon^4\hat{\mathscr{H}}_4 = \frac{1}{24}[\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, \hat{\mathscr{H}}_0]]]] - \frac{1}{2}[\langle d_1\rangle, [\langle\hat{d}_1\rangle, \hat{\mathscr{H}}_0]] + i[\langle\hat{d}_2\rangle, \varepsilon\hat{\mathscr{H}}_1] - \frac{i}{2}[\langle\hat{d}_1\rangle, [\langle\hat{d}_0\rangle[\langle\hat{d}_0\rangle, \hat{\mathscr{H}}_0]]] + \frac{1}{30}[\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, d_0]]]] - \frac{i}{3}[\langle\hat{d}_1\rangle, [\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, \hat{d}_0]]], \tag{15}$$

$$\varepsilon^5\hat{\mathscr{H}}_5 = \frac{1}{6}[\langle\hat{d}_1\rangle, [\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, \mathscr{H}_0]]]] + \frac{i}{120}[\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, [\langle d_0\rangle, [\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, \hat{\mathscr{H}}_0]]]]] + i[\langle\hat{d}_3\rangle, \varepsilon\hat{\mathscr{H}}_1] - \frac{1}{2}[\langle\hat{d}_1\rangle, [\langle\hat{d}_1\rangle, \varepsilon\hat{\mathscr{H}}_1]] + i[\langle\hat{d}_2\rangle, \varepsilon^2\hat{\mathscr{H}}_2] + \frac{1}{2}[\langle\hat{d}_2\rangle, \hat{d}_2] - \frac{1}{3}[\langle\hat{d}_1\rangle, [\langle d_1\rangle, \hat{d}_1]]$$

$$+\frac{1}{8}[\langle\hat{d}_1\rangle,[\langle d_0\rangle,[\langle d_0\rangle,[\langle\hat{d}_0\rangle,\hat{d}_0]]]]$$

$$+\frac{1}{144}[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,\hat{d}_0]]]]], \quad (16)$$

$$\varepsilon^6\hat{\mathcal{H}}_6=-\frac{1}{2}[\langle\hat{d}_2\rangle,[\langle\hat{d}_2\rangle,\hat{\mathcal{H}}_0]]$$

$$-\frac{i}{6}[\langle\hat{d}_1\rangle,[\langle\hat{d}_1\rangle,[\langle\hat{d}_1\rangle,\hat{\mathcal{H}}_0]]]$$

$$+\frac{1}{6}[\langle\hat{d}_2\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,\hat{\mathcal{H}}_0]]]]$$

$$+\frac{i}{24}[\langle\hat{d}_1\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,\hat{\mathcal{H}}_0]]]]]$$

$$+\frac{1}{4}[\langle\hat{d}_1\rangle,[\langle\hat{d}_1\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,\hat{\mathcal{H}}_0]]]]$$

$$-\frac{1}{720}[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,\hat{\mathcal{H}}_0]]]]]]$$

$$+i[\langle\hat{d}_4\rangle,\varepsilon\hat{\mathcal{H}}_1]-[\langle\hat{d}_2\rangle,[\langle\hat{d}_1\rangle,\varepsilon\hat{\mathcal{H}}_1]]+i[\langle\hat{d}_3\rangle,\varepsilon^2\hat{\mathcal{H}}_2]$$

$$-\frac{1}{2}[\langle\hat{d}_2\rangle,[\langle\hat{d}_1\rangle,\hat{d}_1]]$$

$$+\frac{1}{8}[\langle\hat{d}_2\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,\hat{d}_0]]]]$$

$$+\frac{1}{6}[\langle\hat{d}_1\rangle,[\langle\hat{d}_1\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,\hat{d}_0]]]]$$

$$+\frac{i}{30}[\langle\hat{d}_1\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,\hat{d}_0]]]]]$$

$$-\frac{1}{840}[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,[\langle\hat{d}_0\rangle,\hat{d}_0]]]]]]. \quad (17)$$

The method used in calculations which give Eqs. (13)–(17) is described in the Appendix 2. It should be pointed out that none of the methods used previously[1,14–17] has succeeded in deriving terms of the effective Hamiltonian higher than of the fourth order in ε. The recurrence relationships (8)–(11) make it possible to calculate quite simply also $\hat{\mathcal{H}}_7$, $\hat{\mathcal{H}}_8$, etc.

2. DESIGN OF MULTIPULSE SEQUENCES FOR AVERAGING THE DIPOLE–DIPOLE INTERACTIONS OF NUCLEAR SPINS

We shall now consider a system of nuclear spins ($s = 1/2$) linked by the dipole-dipole interactions and subjected to a periodic (with a period $t_c = 2\pi/\Omega$) sequence of

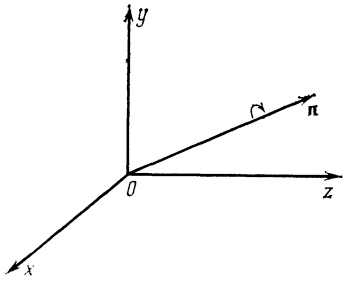

FIG. 1. Axes x, y, and z of a rotating coordinate system; n is the "magic" axis.

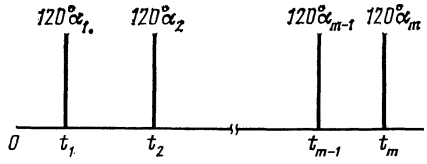

FIG. 2. Sequence of 120° pulses applied along the magic axis n in the process of averaging of dipole-dipole interactions ($\alpha_i = \pm 1$, $i = 1, 2, \ldots$).

resonance hf δ pulses which rotate the spins by $\pm 90°$ about the axes x and y in a rotating system of coordinates. Our task is to select the relative phases of the pulses and the time intervals between them so as to ensure vanishing of the largest possible number N of the initial terms of the expansion of the effective Hamiltonian $\hat{\mathcal{H}}^{\text{eff}}$ in terms of ε, i.e., to ensure that $\hat{\mathcal{H}}_i = 0$ ($i = 1, 2, \ldots, N$). Since the only interaction between spins is assumed to be of the DD nature, it follows that rotations by $+90°$ and $-90°$ about the x (or y) axis are equivalent. We can therefore assume that the investigated sequences consist of pulses rotating the spins by $\pm 120°$ about the "magic" axis n (Ref. 1) that makes the same angles with the semiaxes x, y, and z (Fig. 1). Such pulse sequences can be realized experimentally[19] and, therefore, the solution of the problem facing us should make it possible also to find sequences of 120° pulses which rotate the spins about the n axis in a rotating coordinate system and which average effectively the DD interactions. We shall assume that during each period t_c such a system is acted upon by m pulses which arrive at moments t_i ($i = 1, 2, \ldots, m$) and each of them rotates the spins by $120° \alpha_i$, where $\alpha_i = \pm 1, i = 1, 2, \ldots, m$ (see Fig. 2). In this case the interaction Hamiltonian is $\hat{\mathcal{H}}_{\text{in}} = \hat{\mathcal{H}}_{dz}$, where $\hat{\mathcal{H}}_{dz}$ is the secular (relative to the z axis) part of the DD interactions. Since the secular part $\hat{\mathcal{H}}_{dz}$ vanishes along the magic axis n[1], we can write down

$$\hat{\mathcal{H}}_{dz} = \hat{\mathcal{H}}_n{}^1 + \hat{\mathcal{H}}_n^{-1} + \hat{\mathcal{H}}_n{}^2 + \hat{\mathcal{H}}_n^{-2}, \quad (18)$$

where $\hat{\mathcal{H}}_n{}^{\pm 1}$ and $\hat{\mathcal{H}}_n{}^{\pm 2}$ are the nonsecular part of the DD interactions relative to the n axis and we obtain the relationships

$$[\hat{S}_n, \hat{\mathcal{H}}_n{}^m] = m\hat{\mathcal{H}}_n{}^m, \quad m = 0, \pm 1, \pm 2; \quad (19)$$

here, $\hat{S}_n$ is the operator representing the projection of the total spin along the n axis. Adopting the representation of the interaction of pulses,[14] we find that the Hamiltonian $\hat{\mathcal{H}}(t/\varepsilon)$ in Eq. (1) can be described by

$$\hat{\mathcal{H}}(t/\varepsilon) = a(t/\varepsilon)\hat{\mathcal{H}}_n{}^1 + a^*(t/\varepsilon)\hat{\mathcal{H}}_n^{-1} + a^2(t/\varepsilon)\hat{\mathcal{H}}_n{}^2 + \{a^2(t/\varepsilon)\}^*\hat{\mathcal{H}}_n^{-2}, \quad (20)$$

where

$$a(t/\varepsilon) = \exp\left\{-i\frac{2\pi}{3}\sum_{i=0}^{r(t/\varepsilon)}\alpha_i\right\}, \quad (21)$$

whereas $r(t/\varepsilon)$ is the number of pulses which reach the system in a time interval t. It follows from Eq. (21) that $a(t/\varepsilon) = \{a^2(t/\varepsilon)\}$ and, therefore, $\hat{\mathcal{H}}(t/\varepsilon)$ can be represented in the form

$$\hat{\mathcal{H}}(t/\varepsilon) = a(t/\varepsilon)\hat{P}_1 + a^*(t/\varepsilon)\hat{P}_{-1}, \quad (22)$$

where

$$\hat{P}_1=(\hat{P}_{-1})^+=\hat{\mathcal{H}}_n{}^1+\hat{\mathcal{H}}_n{}^2. \tag{23}$$

It should be pointed out that if we use the above geometric representation, we find that the Hamiltonian in the problem of derivation of pulse sequences which average the DD interaction can be obtained also in the form of Eq. (22) which is simpler than for the simplest pulse sequence representing multipulse spin locking.[1] We have to find now such a function $a(\tau=t/\varepsilon)$ that all the terms in the expansion of the effective Hamiltonian vanish up to a selected order N.

3. GEOMETRIC REPRESENTATION OF MULTIPULSE SEQUENCES FOR AVERAGING THE DIPOLE-DIPOLE INTERACTIONS

Design of multipulse sequences averaging the DD interactions may be simplified greatly by the geometric approach described below. We shall establish the relationship between multipulse sequences and contours in a complex plane. We shall assume that the period of the function $a(\tau)$ is $T(T\geqslant t_c)$. We shall consider multipulse sequences satisfying the condition

$$\int_0^T a(\tau')\,d\tau'=0. \tag{24}$$

Then, the function

$$z(\tau)=\int_0^\tau a(\tau')\,d\tau', \quad 0\leqslant\tau\leqslant T \tag{25}$$

represents in the plane of a complex variable z a closed oriented broken line $[z(0)=z(T)=0]$, which we shall call the contour. The segments of this broken line meet at angles of $\pm 120°$ and the lengths of the segments are equal to the intervals between the pulses. Conversely, each oriented broken line with neighboring segments meeting at angles of $\pm 120°$ corresponds to a multipulse sequence which can be reconstructed as follows. The kinks correspond to the pulses and a pulse rotates spins about the magic axis n by an angle $-120°$ ($\alpha_i=-1$) if the segment of the broken line rotates by 120° anticlockwise (Fig. 3a); the ratio of the lengths of the segments of the broken line is equal to the ratio of the lengths of the intervals between the pulses. We can then readily use hf pulses which rotate the spins about the axes x and y in a rotating coordinate system. We shall select the required contours to solve the problem because they can be explained geometrically, and then use these contours to reconstruct multipulse sequences.

We shall now show that for any sequence averaging the DD interactions in zeroth order in ε because of the condition (24) we can obtain a sequence averaging the DD interactions up to terms of the order of ε^3 inclusive. We shall do this by considering the contour $W(\tau)$ $[W(0)=W(T)=0]$ corresponding to an arbitrary sequence which satisfies Eq. (24). We shall now plot $W(\tau)$ with its central symmetry relative to the point 0 (Figs. 3a and 3b) and reverse the direction of travel along the contour. We shall take the new contour to be a combination of two contours (initial and transformed) with the following sequenc of travel along the contour: first, the initial contour is traversed and then its image. We shall call this operation the antisymmetric imaging and we shall denote it by S. Then, the contour $z(\tau)=SW(\tau)$ satisfies the condition

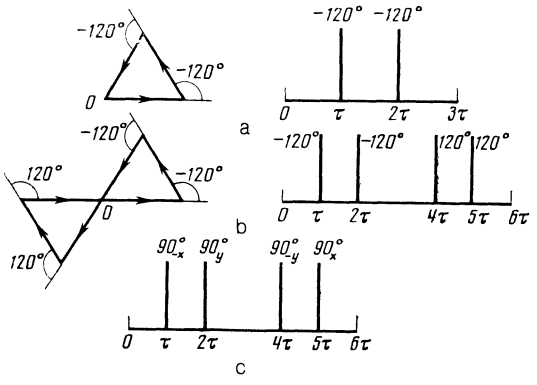

FIG. 3. Contours in the complex plane and multipulse sequences averaging the dipole-dipole interactions. The arrows indicate the direction of traverse of the contours. a) Contour $W(\tau)$ and two-pulse sequence averaging $\hat{\mathcal{H}}_0$; b) contour $z(\tau)=SW(\tau)$ and four-pulse sequence causing $\hat{\mathcal{H}}_0$ and $\hat{\mathcal{H}}_1$ to vanish; c) sequence b but with 90° x and y pulses.

$$\dot{z}(\tau)=\dot{z}(2T-\tau). \tag{26}$$

Continuing the function $a(\tau)=i(\tau)$ periodically with a period $\tilde{T}=2T$, we find from Eq. (26) that $a(\tau)$ is an even function. Applying the Wang-Ramshaw theorem,[20] we obtain

$$\hat{\mathcal{H}}_{2k+1}=0, \quad k=0, 1, \ldots . \tag{27}$$

In particular, if the initial contour $W(\tau)$ is a regular triangle (Fig. 3a), then the contour $z(\tau)=SW(\tau)$ (Fig. 3b) corresponds to a sequence of pulses which averages the DD interaction to within terms of order ε inclusive. If we consider pulses that rotate the spins about the x and y axes in a rotating coordinate system, we find that the contour of Fig. 3b corresponds to the sequence known as WHH-4 (Ref. 1)—see Fig. 3c.

We shall consider another transformation of the initial contour. We shall rotate it twice about the point 0 (Fig. 4a) by an angle of 120° ($-120°$). Then, we shall combine three contours [initial, that rotated by 120° ($-120°$) and by 240° ($-240°$) relative to the initial one] which will be traversed in the order just indicated. We shall call this the rotation operator and denote it by P_θ. Then the new contour $z(\tau)=P_\theta W(\tau)$ will satisfy the conditions

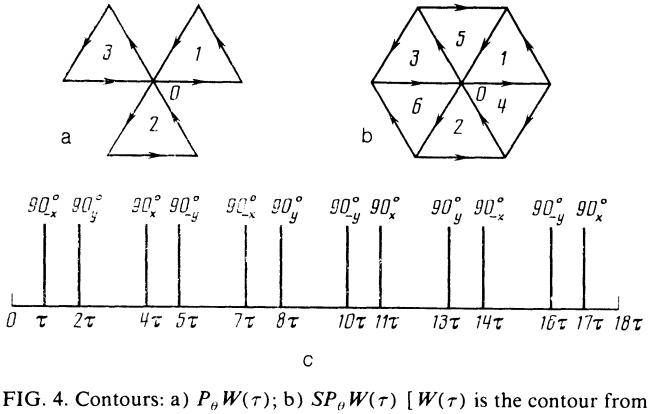

FIG. 4. Contours: a) $P_\theta W(\tau)$; b) $SP_\theta W(\tau)$ [$W(\tau)$ is the contour from Fig. 3a]. The arrows and numbers indicate the direction of traverse of contours. c) Twelve-pulse sequence of Burum and Rhim[8] which causes vanishing of $\hat{\mathcal{H}}_0$, $\hat{\mathcal{H}}_1$, $\hat{\mathcal{H}}_2$, and $\hat{\mathcal{H}}_3$.

$$\begin{aligned} \dot{z}(\tau)&=W(\tau), \quad 0\leqslant\tau<T,\\ \dot{z}(\tau)&=\theta W(\tau-T), \quad T\leqslant\tau<2T,\\ \dot{z}(\tau)&=\theta^2 W(\tau-2T), \quad 2T\leqslant\tau\leqslant 3T,\\ \theta&=e^{\pm 2\pi i/3}. \end{aligned} \tag{28}$$

The corresponding function $a(\tau)=\dot{z}(\tau)$ continued periodically with a period $\tilde{T}=3T$ gives $\hat{\mathscr{H}}_2=0$, which follows directly from Eq. (13). Applying now the principle of decoupling of the pulse cycles,[8] we find that the contour $z(\tau)=SP_\theta W(\tau)$ corresponds to a pulse sequence ensuring that $\hat{\mathscr{H}}_i=0$ $(i=1,2,3)$. The same result is obtained for the contour $z(\tau)=P_\theta SW0(\tau)$. Therefore, using any sequence with $\hat{\mathscr{H}}_0=0$ we can design multipulse sequences which average the DD interaction to within terms of the order of ε^3 inclusive. In particular, when the contour $W(\tau)$ is a regular triangle, the contour $z(\tau)=SP_\theta\cdot W(\tau)$ (Fig. 4b) corresponds to a 12-pulse sequence of Burum and Rhim[8] (Fig. 4c) for which we have $\hat{\mathscr{H}}_i=0$ $(i=0,1,2,3)$. This sequence can be used as the basis of 24- and 52-pulse sequences[8] which average effectively the DD interaction when inhomogeneities of magnetic fields and imperfections of the pulses are important.[1] The contour $z(\tau)=P_\theta SW(\tau)$ (Fig. 5a) differs in this case from the contour of Fig. 4b only by the direction of traverse and it corresponds to a new five-pulse sequence (Fig. 5b).

A condition analogous to those given in Eq. (28) has been used in the design of sequences described in Ref. 8, where it is shown[1,8] that combination of three WHH-4 sequences can cause vanishing of $\hat{\mathscr{H}}_2$. The above analysis allows us to conclude that this result applies to a wide class of multipulse sequences with 90° pulses.

The above method of design of multipulse sequences is of general validity, but it is of course not the only one possible. By way of example, we shall consider a contour $W(\tau)$ satisfying not only the conditions of Eq. (24), but also

$$\overline{W^*W^2(\tau)}=0. \tag{29}$$

Then, we can use Eq. (13) to show readily that $\hat{\mathscr{H}}_2=0$. Now, allowing for Eqs. (24), (27), and (29) and for the principle of decoupling of pulse cycles,[8] we find that the sequence corresponding to the contour $z(\tau)=SW(\tau)$ causes vanishing of $\hat{\mathscr{H}}_0$, $\hat{\mathscr{H}}_1$, $\hat{\mathscr{H}}_2$, and $\hat{\mathscr{H}}_3$. The condition of Eq.

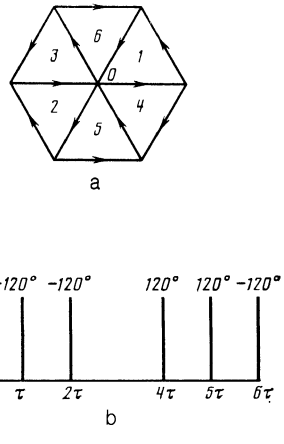

FIG. 5. a) Contour $P_\theta SW(\tau)$ [$W(\tau)$ is the contour from Fig. 3a]. The arrows and numbers show the direction of traverse. b) Five-pulse sequence causing vanishing of $\hat{\mathscr{H}}_0$, $\hat{\mathscr{H}}_1$, $\hat{\mathscr{H}}_2$, and $\hat{\mathscr{H}}_3$.

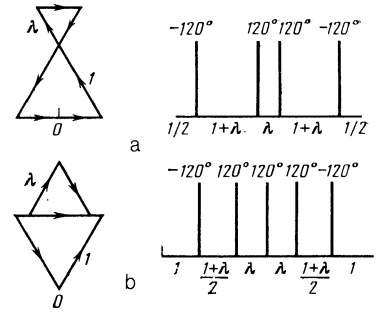

FIG. 6. a) Contour $W(\tau)$ for $\lambda=1/2$ and Evans cycle[1]. b) Contour $W(\tau)$ for $\lambda=\sqrt{3}-1$ and five-pulse cycle which ensures that $\hat{\mathscr{H}}_0=\hat{\mathscr{H}}_1=0$.

(29) is satisfied, for example, by the contours in Figs. 6a and 6b consisting of equilateral triangles with lengths of the sides equal to unity and different values of λ. The sequence in Fig. 6a is the Evans cycle[1] representing the main element of a 16-pulse sequence[21] which averages the DD interactions under the same conditions as the sequences described in Ref. 8. The five-pulse sequence of Fig. 6b is suggested for the first time.

We have considered so far multipulse sequences which average the DD interactions by no more than four orders of ε. The difficulty encountered in the design of sequences averaging the DD interactions to within terms of the order of ε^4 or higher is the fact that we can no longer use the principle of pulse decoupling.[8] However, an analysis based on the use of Eq. (15) allows us to conclude that if the contour $W(\tau)$ of Fig. 6a satisfies the condition

$$\overline{W^*(\tau)W^4(\tau)}=0, \tag{30}$$

which is obeyed if λ (Fig. 6a) is a root of the equation

$$4\lambda^5+20\lambda^4+30\lambda^3+15\lambda^2-1=0, \quad \lambda\approx 0.2118, \tag{31}$$

then the contour $z(\tau)=SP_\theta W(\tau)$ corresponds to a 28-pulse sequence (Figs. 7a and 7b) which ensures that $\hat{\mathscr{H}}_0$, $\hat{\mathscr{H}}_1$, $\hat{\mathscr{H}}_2$, $\hat{\mathscr{H}}_3$, $\hat{\mathscr{H}}_4$, and $\hat{\mathscr{H}}_5$ all vanish.

4. GEOMETRIC APPROACH TO ESTIMATION OF THE RESOLUTION OF MULTIPULSE NMR EXPERIMENTS

How many terms of the effective Hamiltonian $\hat{\mathscr{H}}^{\text{eff}}$ can be made to vanish by multipulse sequences derived by methods developed in the preceding section? We can answer this question by assuming that we have been able to design a sequence corresponding to a contour $W(\tau)$ defined as follows (Fig. 8):

$$\begin{aligned} W(\tau)&=e^{i\frac{2\pi}{T}\tau}, \quad 0\leqslant\tau<T,\\ W(\tau)&=e^{-i\frac{2\pi}{T}\tau}, \quad T\leqslant\tau\leqslant 2T. \end{aligned} \tag{32}$$

It then follows from Eqs. (22) and (25) that the contour $W(\tau)$ corresponds to a sequence which is described by a Hamiltonian with the following property

$$\hat{\mathscr{H}}(2T-\tau)=-\hat{\mathscr{H}}(\tau), \quad 0\leqslant\tau\leqslant T. \tag{33}$$

It is clear from Eq. (33) that at the moments $2Tn$ (n is a natural number) the initial state of the system is restored completely (spin echo) and the envelope of response of the system to a multipulse interaction is completely independent of the DD interactions, i.e., $\hat{\mathscr{H}}^{\text{eff}}\equiv 0$. Therefore, our hypo-

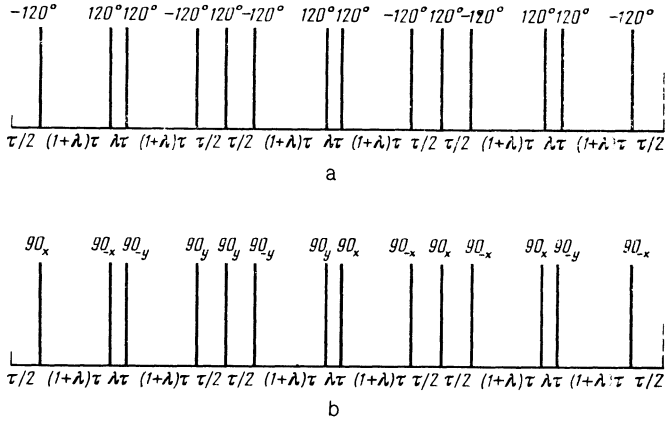

FIG. 7. Twenty-eight-pulse sequences causing vanishing of $\hat{\mathscr{H}}_0$, $\hat{\mathscr{H}}_1$, $\hat{\mathscr{H}}_2$, $\hat{\mathscr{H}}_3$, $\hat{\mathscr{H}}_4$, and $\hat{\mathscr{H}}_5$: sequence of 120° pulses; b) sequence of 90° $x$and y pulses. Half the sequence periods are shown. The second halves are obtained by changing the phases of all the pulses by 180°. Sequences a and b correspond to the contour $SP_\theta W(\tau)$ [$W(\tau)$ is the contour from Fig. 6a with $\lambda = 0.2118$].

thetical sequence averages the DD interactions in all orders of the parameter ε. We now note that the broken line with neighboring segments meeting at angles of $\pm$ 120° can be used to approximate the contour $W(\tau)$ of Fig. 8 with any desired accuracy. Therefore, we can design multipulse sequences of 120° pulses rotating the spins about the magic axis and causing vanishing of any finite number m of terms in the effective Hamiltonian $\hat{\mathscr{H}}^{\text{eff}}$. However, we can then estimate the resolution attainable using such sequences by estimating the residual term $\hat{D}^{(m)}(\tau, \varepsilon)$ [see Eq. (5)]. In general, such an estimate is difficult to obtain, so that we shall limit ourselves to the following qualitative discussion. We shall assume that we can find the average Hamiltonian $\hat{\mathscr{H}}_0$. The residue $\hat{D}^{(0)}(\tau,\varepsilon) = d_0$ may be of the same order of magnitude as $\hat{\mathscr{H}}_0$, but d_0 is a rapidly oscillating function of time so that the maximum value of $\langle \hat{d}_0 \rangle$ should be small. In other words, the smaller the amplitude of the spin echo which is governed by the value of $\langle \hat{d}_0 \rangle$, the closer is the average motion described by the Hamiltonian $\hat{\mathscr{H}}_0$ to the motion of the system of spins described by the initial Hamiltonian $\hat{\mathscr{H}}(\tau)$ in Eq. (1). It follows from Eq. (7) that $\langle \hat{d}_0 \rangle \sim \varepsilon$, so that in the limit $\varepsilon \to 0$ the effective Hamiltonian $\hat{\mathscr{H}}^{\text{eff}}$ can describe as accurately as necessary the dynamics of the investigated system.[18] However, there is in practice always a minimum time $\tau_{\min}$ between the successive pulses, which limits the value of ε. Consequently, the Hamiltonian $\hat{\mathscr{H}}^{\text{eff}}$ describes the evolution of the system only approximately and it can be used to estimate the resolution of multipulse experiments by a more careful analysis of the quantity $\langle \hat{d}_0 \rangle$. Although we have $\langle \hat{d}_0 \rangle = 0$ [see Eq. (4)], at certain moments the value of $\langle \hat{d}_0 \rangle$ can be quite large. We shall estimate $\langle \hat{d}_0 \rangle$ from the maximum value of the function $|\langle a(\tau) \rangle|$ [$\max|\langle a(\tau) \rangle|$]. However, $\max|\langle a(\tau) \rangle|$ is the "diameter" of the figure described by the contour corresponding to the pulse sequence in question. Therefore, the more compact the figure bounded by the contour used to reconstruct the sequence, the greater the resolution which can be achieved using this sequence. For example, the value of $\max|\langle a(\tau) \rangle|$ for the contours in Figs. 4b and 5a is less than for the contours $SW(\tau)$, where $W(\tau)$ are the contours in Figs. 6a and 6b. Therefore, the sequences in Figs. 4c and 5b can in principle ensure a higher resolution of NMR spectra than the sequences in Figs. 6a and 6b, in spite of the fact that all these sequences cause vanishing of the same terms in the Hamiltonian $\hat{\mathscr{H}}^{\text{eff}}$.

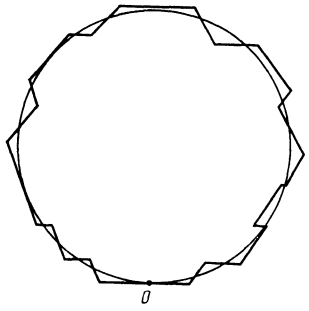

FIG. 8. Contour $W(\tau)$ described by Eq. (32) and the approximating broken line with adjacent segments making an angle of $\pm$ 120° with one another.

If the diameters of the figures bounding the contours corresponding to two different sequences are the same, then the resolution of the corresponding multipulse experiments can be found by considering the terms in the effective Hamiltonian $\hat{\mathscr{H}}_k$ and the residues $\hat{d}_k$ of higher orders.

In the introductory part of this paper we pointed out that, in addition to the residual DD interactions, the resolution of NMR spectra is influenced also by other factors. Although their influence on the resolution in NMR spectroscopy of solids is not discussed above, it can be investigated by methods described here together with methods given in Refs. 1 and 8.

APPENDIX 1

We shall show that the recurrence relationships (8)–(11) ensure consecutive generation of terms of the effective Hamiltonian $\hat{\mathscr{H}}^{\text{eff}}$. We shall do this by showing that rapidly oscillating terms $\hat{D}^{(k+1)}(t/\varepsilon, \varepsilon)$ are of order ε^{k+1}.

Using Eqs. (10) and (11) in the case when $k > 1$, we obtain

$$\begin{aligned}
&\hat{D}^{(k+1)}\left(\frac{t}{\varepsilon}, \varepsilon\right) = \bar{F}_{k+1}\hat{\mathscr{H}}\left(\frac{t}{\varepsilon}\right)\dot{\bar{F}}_{k+1} + i\frac{d\dot{\bar{F}}_{k+1}}{dt}\dot{\bar{F}}_{k+1}\\
&-\hat{\mathscr{H}}^{(k+1)} = \exp(i\langle \hat{d}_k \rangle)\,\bar{F}_k\hat{\mathscr{H}}\left(\frac{t}{\varepsilon}\right)\dot{\bar{F}}_k \exp(-i\langle \hat{d}_k \rangle)\\
&+ i\frac{d}{dt}[\exp(i\langle \hat{d}_k \rangle \bar{F}_k)]\,\dot{\bar{F}}_k \exp(-i\langle \hat{d}_k \rangle) - \hat{\mathscr{H}}^{(k+1)}\\
&= \exp(i\langle \hat{d}_k \rangle)\left[\bar{D}^k\left(\frac{t}{\varepsilon}, \varepsilon\right) + \hat{\mathscr{H}}^{(k)}\right]\exp(-i\langle d_k \rangle)\\
&+ i\frac{d}{dt}(\exp(i\langle \hat{d}_k \rangle))\exp(-i\langle \hat{d}_k \rangle) - \hat{\mathscr{H}}^{(k+1)}; \qquad k = 1, 2, \ldots .
\end{aligned} \tag{A.1.1}$$

Separating in Eq. (A.1.1) the rapidly oscillating and time-independent terms of order ε^{k+1}, we can establish with the aid of Eq. (11) that all the constant terms up to the $(k+1)$th order inclusive and all the rapidly oscillating terms up to the k th order inclusive are canceled out in the final expression for $\hat{D}^{(k+1)}$ in Eq. (A.1.1). Therefore, $\hat{D}^{(k+1)}(t/\varepsilon, \varepsilon) \sim \varepsilon^{(k+1)}$, which was the relationship that had to be proved.

APPENDIX 2

We shall illustrate the derivation of Eqs. (13)–(17) by obtaining the expression for $\hat{\mathscr{H}}_4$ of Eq. (15), which requires determination of terms of order ε^4 in $\hat{D}^{(3)}(t/\varepsilon, \varepsilon)$. It follows from Eq. (A.1.1) that such terms are contained only in

$$\begin{aligned}&\exp(i\langle\hat{d}_2\rangle)[\hat{D}^{(2)}(t/\varepsilon, \varepsilon)+\hat{\mathscr{H}}^{(2)}]\exp(-i\langle\hat{d}_2\rangle)\\ &\approx\hat{D}^{(2)}(t/\varepsilon, \varepsilon)+i[\langle\hat{d}_2\rangle, \hat{D}^{(2)}(t/\varepsilon, \varepsilon)]+\hat{\mathscr{H}}^{(2)}+i[\langle\hat{d}_2\rangle, \hat{\mathscr{H}}^{(2)}].\end{aligned} \tag{A.2.1}$$

Terms of the fourth order in Eq. (A.2.1) can occur only in $\hat{D}^{(2)}(t/\varepsilon, \varepsilon)$ and $i[\langle\hat{d}_2\rangle, \varepsilon\hat{\mathscr{H}}_1]$. An analysis of terms of order ε^4 contained in $\hat{D}^{(2)}(t/\varepsilon, \varepsilon)$ requires again the use of Eq. (A.1.1) with $k=1$. We then find that the required terms occur only in the expression

$$\begin{aligned}&\exp(i\langle\hat{d}_1\rangle)[\hat{D}^{(1)}(t/\varepsilon, \varepsilon)+\hat{\mathscr{H}}^{(1)}]\exp(-i\langle\hat{d}_1\rangle)\\ &\approx\hat{D}^{(1)}(t/\varepsilon, \varepsilon)+i[\langle\hat{d}_1\rangle, \hat{D}^{(1)}(t/\varepsilon, \varepsilon)]+\hat{\mathscr{H}}^{(1)}\\ &\quad+i[\langle\hat{d}_1\rangle, \hat{\mathscr{H}}^{(1)}]-{}^1/_2[\langle\hat{d}_1\rangle, [\langle\hat{d}_1\rangle, \hat{\mathscr{H}}^{(1)}]].\end{aligned} \tag{A.2.2}$$

Contributions of the fourth order come from the first two terms and from the last term in Eq. (A.2.2). The task is therefore to find terms of the second and fourth orders in ε that occur in $\hat{D}^{(1)}(t/\varepsilon, \varepsilon)$. This is a general result in the sense that the problem of calculation of the effective Hamiltonian of any order reduces, in the final analysis, to finding terms of specific order in $\hat{D}^{(1)}(t/\varepsilon, \varepsilon)$. Using Eq. (10) we can apply the method of complete mathematical induction to show readily that a term of the k-th order in $\hat{D}^{(1)}(t/\varepsilon, \varepsilon)$ is as follows:

$$\begin{aligned}&\frac{i^k}{k!}[\langle\hat{d}_0\rangle, [\langle d_0\rangle, [\ldots[\langle\hat{d}_0\rangle, \hat{\mathscr{H}}_0+\hat{d}_0]\ldots]\\ &+\frac{i^{k+2}}{(k+1)!}[\langle\hat{d}_0\rangle, [\langle\hat{d}_0\rangle, [\ldots[\langle\hat{d}_0\rangle\hat{d}_0]\ldots].\end{aligned} \tag{A.2.3}$$

(The dots in the square brackets mean that the commutation is performed k times.) We can derive Eq. (15) directly using Eqs. (A.2.3) and including the contributions mentioned above. Equations (13), (14), (16), and (17) can be derived similarly.

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