# Theory of Resonance Absorption of Energy by a Rotating Solid

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The theory of both nuclear resonance energy absorption and the relaxation of a coherent magnetization transverse to an applied external magnetic field is developed for nuclei in a mechanically rotating solid. The consequences of the formalism in the simple case of a solid composed of effectively isolated nuclear pairs is presented. For the more general nuclear lattice, a procedure for isolating and experimentally measuring the "exchange" interaction between the nuclei in the solid is proposed. Finally, the moments of the energy absorption line shape for the rotating solid are investigated and the second and fourth moments are explicitly calculated.

A SYSTEM of nuclear spins regularly disposed at lattice sites sitting in an external magnetic field and interacting among themselves via spin dependent forces constitutes a many-body system which can be explored both experimentally and theoretically by relatively simple techniques. The theoretical study of the resonance absorption of energy in a static lattice was initiated by Van Vleck[1] just after the introduction of magnetic resonance techniques[2,3] for exploring the structure of solids. A procedure alternative to resonance absorption measurements is available—the study of the time dependence of the coherently induced magnetization transverse to the applied magnetic field. This latter method gives essentially the same information as resonance absorption studies for the case of the static lattice.[4,5]

In this paper we set ourselves the task of determining both the nuclear spin absorption spectrum and the behavior of the transverse magnetization of a mechanically rotating lattice. Preliminary work on the transverse magnetization in a rotating solid has already been carried out by Lowe.[6] In addition, some of the results which are obtained in Sec. II below have been given independently by Andrew and Newing[7] in their study of internal pair rotation in a solid. However, our procedure is based on rigorous quantum mechanical principles and so differs from the previously given local magnetic field calculation.

The conditions under which the calculation will be carried out are:

(a) Rigid lattice. The absolute value of the separation of any pair of nuclei is invariant. The rigid lattice is to be contrasted with the static lattice wherein the vector separation of any two nuclei is an invariant. An ionic crystal such as $CaF_2$ will provide a sufficiently rigid lattice structure.

(b) Large external magnetic field. The nuclear spins are bathed in an external magnetic field which is large compared to the magnetic field seen by one nucleus due to all the other nuclei. As a consequence of this condition, the energy levels determined by the Zeeman energy of the spins in an external magnetic field, i.e., the Zeeman levels of the solid as a whole, are well defined. The internuclear interaction then splits the Zeeman levels of the solid into many sublevels but does not to any detectable extent mix Zeeman levels. With magnetic fields of a few thousand gauss, this condition prevails for all the solids on which nuclear paramagnetic resonance can be performed.

(c) Neglect of spin-lattice interaction. The spin-lattice interaction is assumed weak compared to the spin-spin interactions and, *a fortiori*, to the spin interaction with the external field.[8]

In the language of magnetic resonance phenomena, we demand that $T_2 \ll T_1$, where $T_1$ and $T_2$ are the phenomenological relaxation times introduced by Bloch[9] to describe the spin-spin and spin-lattice interactions, respectively. For $CaF_2$, for example, $T_2 \cong 40$ $\mu$sec and $T_1 \cong 20$ sec (room temperature).

(d) "High" magnetic temperature. The Zeeman levels of the solid in an external magnetic field of $10^4$ gauss are almost equally populated for temperatures above $10^{-3}$ °K. The assumption of a high lattice temperature will simply mean that the difference in Boltzmann populations of the magnetic levels is very small.

(e) Neglect of nuclear electric quadrupole and magnetic octupole moments. The intrinsic electric and magnetic properties of the nuclei, other than electric

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1 J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).
2 E. M. Purcell, H. C. Torrey, and R. Pound, Phys. Rev. **69**, 37 (1946).
3 F. Bloch, N. Hansen, and M. Packard, Phys. Rev. **69**, 127 (1946).
4 R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).
5 I. Lowe and R. Norberg, Phys. Rev. **107**, 46 (1957).
6 I. Lowe, Phys. Rev. Letters **2**, 285 (1959).
7 E. Andrew and R. Newing, Proc. Phys. Soc. (London) **72**, 959 (1958).

8 Of course, we do include the modification of the dipole interaction of the nuclear spins by the mechanical rotation of the lattice which can be looked upon as a type of lattice-spin interaction.
9 F. Bloch, Phys. Rev. **70**, 460 (1946).

charge and magnetic moment, are assumed to have no effect on the resonance process.

To motivate the study of resonance absorption in a rotating lattice, it need only be observed that the part of the magnetic dipole interaction Hamiltonian which operates within a Zeeman level between two nuclei in an external magnetic field is anisotropic, and varies both in sign and magnitude when the internuclear vector is reorientated with respect to the magnetic field. Hence, the possibility arises of controlling the magnetic dipole interaction strength by partial or complete rotational averaging. By using the mechanical rotation as a switch for regulating the strength of the dipole interaction, other isotropic internuclear interactions in the solid can be relatively enhanced and so more easily studied. The order of magnitude of spinning frequencies ($\Omega$) required is readily surmised: $\Omega \cong 1/T_2$. For $CaF_2$, $\Omega \cong 2.4\times 10^4$ rad/sec.

In Sec. I, we develop the general formalism for computing the nuclear resonance absorption line shape and apply the results in Sec. II to the simple example of a nuclear pair imbedded rigidly in a rotating lattice. The problem of the relaxation of transverse magnetization in a rotating solid is treated in Sec. III. In the limit of ultra-high frequency (uhf) rotation ($\Omega \gg 1/T_2$), the consequences of rotation are especially simple and form the subject matter of Sec. IV, where a method for measuring the isotropic "exchange-type" internuclear interaction is proposed. Finally, the conventional procedure of calculating the absorption line moments is pursued in Sec. V, for the nonstatic lattice.

In a future paper, a comparison between theory and experiment will be given as well as the detailed numerical evaluation of the theoretical expressions for the specific solids of interest.

## I. GENERAL FORMALISM. THE RESONANCE ABSORPTION LINE

The atomic nuclei which reside at the lattice sites of a rotating solid can be considered as essentially structureless entities except for an intrinsic charge and an intrinsic magnetic moment. An intrinsic electric quadrupole moment or magnetic octupole moment is excluded by assumption. Our interest is in the energy levels of the aggregate of nuclei in the solid, more specifically, those energy levels which depend on the orientation of the individual nuclear spins.

Consonant with the restrictions which are assumed to prevail and which were outlined in the Introduction, the only interactions to which the nuclear spins will be subjected are:

(a) The interaction with an external field $\mathbf{H}$ which is describable by the Hamiltonian associated with the Zeeman energy[10]:

$$\mathcal{H}_z = -\gamma \sum \mathbf{I}_i \cdot \mathbf{H}, \tag{I.1}$$

[10] Units with $\hbar=1$ are employed.

where $\gamma$ = magnetogyric ratio of nucleus. In the following we have tacitly assumed that all the nuclear $\gamma$ are equal but this restriction is easily lifted.

(b) The internuclear interaction ($\mathcal{H}_i$), which we need not specify here except to note that $\mathcal{H}_i(t)$ will be explicitly time dependent if the lattice is mechanically rotating. Since the Zeeman levels are assumed to determine the gross structure of the energy levels of the solid as a whole, $\mathcal{H}_i$ is a small perturbation on $\mathcal{H}_z$ and consequently its effect is to split the highly degenerate Zeeman levels into a fine structure and to mix but negligibly the distinct Zeeman levels. $\mathcal{H}_i(t)$ can then be truncated so as to commute with $\mathcal{H}_z$:

$$[\mathcal{H}_z, \mathcal{H}_i(t)] = 0 \quad [\text{truncation of } \mathcal{H}_i(t)]. \tag{I.2}$$

We also note that, in general,

$$[\mathcal{H}_i(t_1), \mathcal{H}_i(t_2)] \neq 0 \quad \text{if } t_1 \neq t_2. \tag{I.3}$$

(c) The rf magnetic field interaction which is of the form:

$$\mathcal{H}_{\mathrm{rf}}(t) = -\gamma \sum \mathbf{I}_i \cdot \mathbf{H}_{\mathrm{rf}}(t), \quad \mathbf{H}_{\mathrm{rf}}(t) = \mathbf{H}_{\mathrm{rf}} \cos\omega t. \tag{I.4}$$

$H_{\mathrm{rf}} \equiv |\mathbf{H}_{\mathrm{rf}}|$ = amplitude of exciting rf magnetic field.

The rf field is taken to be so weak that the first-order perturbation effect of $\mathcal{H}_{\mathrm{rf}}(t)$ alone is important, i.e., the saturation of the resonance is precluded.

Let $\psi(t)$ denote the probability amplitude describing the state of the nuclear spins. Then the Schrödinger equation of motion is

$$i\partial\psi(t)/\partial t = [\mathcal{H}_z + \mathcal{H}_i(t) + \mathcal{H}_{\mathrm{rf}}(t)]\psi(t). \tag{I.5}$$

To solve (I.5), we make the following sequence of canonical transformations:

(i) $\psi(t) \equiv \exp(-i\mathcal{H}_z t)\psi'(t)$,

(ii) $\psi'(t) \equiv W(t)\psi''(t)$,

where $i\partial W(t)/\partial t = \mathcal{H}_i(t)W(t)$; $W(0)=1$,

(iii) $\psi''(t) \equiv U(t)\psi'''(t)$,

where

$$i\partial U(t)/\partial t = \mathcal{H}_{\mathrm{rf}}'(t)U(t); \quad U(0)=1,$$

$$\mathcal{H}_{\mathrm{rf}}'(t) \equiv W^\dagger(t)\exp(i\mathcal{H}_z t)\mathcal{H}_{\mathrm{rf}}(t)\exp(-i\mathcal{H}_z t)W(t), \tag{I.6}$$

so that

$$\begin{aligned} \psi(t) &= \exp(-i\mathcal{H}_z t)W(t)U(t)\psi(0), \\ W(t) &= 1 - i\int_0^t \mathcal{H}_i(t')W(t')dt', \\ U(t) &= 1 - i\int_0^t \mathcal{H}_{\mathrm{rf}}'(t')U(t')dt'. \end{aligned} \tag{I.7}$$

In view of the postulated weakness of the rf excitation $U(t)$ can well be approximated by the first iterate of

the integral equation which it obeys:

$$U(t)\rightarrow 1-i\int_0^t \mathcal{H}_{\mathrm{rf}}'(t')dt'. \tag{I.8}$$

$\mathcal{H}_{\mathrm{rf}}(t)$ induces transitions between the Zeeman levels when $\omega$ is in the neighborhood of the Larmor frequency. If the original state of the solid at time $t=0$ is specified by the total quantum number $m$ and the sublevel index $\alpha$, then the probability of having made the transition to the level with quantum number $m'$ and $\alpha'$ at time $T$ is

$$\begin{aligned}[P(T)]_{m\alpha\rightarrow m'\alpha'}&\\ &=|\langle m'\alpha'|\exp(-i\mathcal{H}_zT)W(T)U(T)|m\alpha\rangle|^2\\ &=|\langle m'\alpha'|W(T)U(T)|m\alpha\rangle|^2.\end{aligned} \tag{I.9}$$

The final state can either have higher or lower energy than the initial depending on whether the rf field induced emission or absorption. (Spontaneous emission is always negligible.)

For a solid in thermal equilibrium the net probability of the solid having absorbed energy at time $T$ is the probability of a Boltzmann populated level jumping to a higher level minus the probability of a Boltzmann populated level jumping to a lower level:

$$\begin{aligned}P(\omega,T)=\sum_{\substack{m\alpha,\,m'\alpha'\\ m'>m}}\Bigg\{&|\langle m'\alpha'|W(T)U(T)|m\alpha\rangle|^2\frac{e^{-\beta E_{m\alpha}}}{Z}\\ &-|\langle m\alpha|W(T)U(T)|m'\alpha'\rangle|^2\frac{e^{-\beta E_{m'\alpha'}}}{Z}\Bigg\},\end{aligned} \tag{I.10}$$

$$Z\equiv\sum e^{-\beta E_{m\alpha}},\quad \beta=(kT)^{-1}.$$

The dependence of $E_{m\alpha}$ on $\alpha$ and $E_{m'\alpha'}$ on $\alpha'$ can be neglected at any realizable temperature in the cases which we shall consider. Now $W(t)$ can be removed from the expression (I.10) by noting that

$$\sum_{\alpha'} W^\dagger(T)|m'\alpha'\rangle\langle m'\alpha'|W(T)=\sum_{\alpha'}|m'\alpha'\rangle\langle m'\alpha'|, \tag{I.11}$$

which is a simple consequent of the unitarity of $W(t)$ in the subspace defined by $m'$ since $[W(t),\gamma\sum l_i^z]=0$.

In the limit of sufficiently high temperature (room temperature in most experimental situations) the Boltzmann factor can be expanded and only the first nonvanishing term retained:

$$\begin{aligned}P(\omega,T)&=\kappa\sum_{\substack{m\alpha,\,m'\alpha'\\ m\neq m'}}|\langle m'\alpha'|U(T)|m\alpha\rangle|^2\\ &=\kappa\,\mathrm{Tr}\left[\int_0^T dt\int_0^T dt'\,\mathcal{H}_{\mathrm{rf}}'(t)\mathcal{H}_{\mathrm{rf}}'(t')\right],\end{aligned} \tag{I.12}$$

where $\beta(E_{m'\alpha'}-E_{m\alpha})\cong\beta\omega_L$; $\langle m\alpha|\mathcal{H}_{\mathrm{rf}}'(t)|m\beta\rangle=0$, $\omega_L=$ Larmor frequency $=\gamma|\mathbf{H}|$, and $\kappa=(\beta\omega_L)/(2Z)$. In the future, all constants, unimportant for our purposes, will be designated by $\kappa$.

The following identities are useful:

(i) $W(t')W^\dagger(t)=W(t')W^{-1}(t)=W(t',t)$,

where

$$W(t',t)=1-i\int_t^{t'}\mathcal{H}_i(t'')W(t'',t)dt'',$$

(ii) $$\begin{aligned}\exp[i\mathcal{H}_z(t'-t)]\gamma\sum l_i^xH_{\mathrm{rf}}\exp[-i\mathcal{H}_z(t'-t)]&\\ =H_{\mathrm{rf}}\{\gamma\sum l_i^x\cos[\gamma H(t'-t)]&\\ +\gamma\sum l_i^y\sin[\gamma H(t'-t)]\},&\end{aligned}$$

(iii) $\mathbf{H}_{\mathrm{rf}}=H_{\mathrm{rf}}\hat{x}$; $\mathbf{H}=H\hat{z}$;

$$\begin{aligned}\mathrm{Tr}\{&\sum\gamma l_i^x\cos[\gamma H(t'-t)]W^\dagger(t',t)\\ &\times\sum\gamma l_i^y\sin[\gamma H(t'-t)]W(t',t)\}=0.\end{aligned} \tag{I.13}$$

The last expression in (I.13) is valid only if $W(t',t)$ is invariant under a unitary transformation which rotates all the spins about the $x$ axis through $\pi$ radians. For all the explicit forms of $\mathcal{H}_i(t)$ which generate $W(t)$ this will be true. With the use of (I.13), $P(\omega,T)$ simplifies to

$$\begin{aligned}P(\omega,T)=\kappa\int_0^T dt\int_0^T dt'&\left\{\frac{\cos[\omega(t'-t)]+\cos[\omega(t'+t)]}{2}\right\}\\ &\times\cos\gamma H(t'-t)\ \mathrm{Tr}\{\gamma\sum l_i^xW^\dagger(t',t)\gamma\\ &\times\sum l_i^xW(t',t)\}.\end{aligned} \tag{I.14}$$

Introducing the new variables $\tau\equiv t'-t$:

$$\begin{aligned}P(\omega,T)=\kappa\int_0^T dt\int_{-t}^0 d\tau&\{\cos[\omega\tau]+\cos[\omega(\tau+2t)]\}\\ &\times\cos[\gamma H\tau]\ \mathrm{Tr}[L_xW^\dagger(t+\tau,t)L_xW(t+\tau,t)]\\ +\kappa\int_0^T dt'\int_0^{t'} d\tau&\{\cos[\omega\tau]+\cos[\omega(-\tau+2t')]\}\\ &\times\cos[\gamma H\tau]\ \mathrm{Tr}[L_xW^\dagger(t',t'-\tau)L_xW(t',t'-\tau)],\\ L_x\equiv\sum l_i^x,&\end{aligned} \tag{I.15}$$

and the transition probability per unit time $\Gamma(\omega)$ in the limit as $T\rightarrow\infty$ finally assumes the form[11]:

$$\begin{aligned}\Gamma(\omega)\equiv\lim_{T\rightarrow\infty}\frac{dP(\omega,T)}{dT}=\kappa\int_{-\infty}^{+\infty}&\cos[\omega\tau]\cos[\gamma H\tau]\\ \times\lim_{T\rightarrow\infty}\mathrm{Tr}[&L_xW^\dagger(T,T-\tau)\\ &\times L_xW(T,T-\tau)]d\tau,\\ \lim_{T\rightarrow\infty}W(T,T-\tau)=&\lim_{T\rightarrow\infty}W(T+\tau,\tau).\end{aligned} \tag{I.16}$$

[11] The limiting procedure which has been employed in deriving Eq. (I.16) can be justified physically by noting that the observed $\Gamma(\omega)$ should not depend on the orientation of the spinning crystal about the rotation axis at $t=0$. In later sections, we shall exhibit that the limit prescription is actually equivalent to averaging over the azimuthal angle of the spinning crystal at any instance, in particular, at $t=0$ and that after such an averaging, the trace of Eq. (I.16) no longer depends on $T$. Of course, a powdered (microcrystalline) sample automatically incorporates an azimuthally averaged ensemble.

It should be noted that we can drop the term in the integrand containing $\cos[(\omega+\gamma H)\tau]$ since only the resonance line about $\omega=\gamma H$ is of interest and indeed the experimental observable phenomenon. Also the term containing $\cos 2\omega T$ and $\sin 2\omega T$ oscillates to zero in the limit $T\to\infty$ for $\omega\sim\gamma H$ simply because the trace can give rise to no term coherent with such a fast oscillation. Thus the resonance energy absorbed at frequency $\omega$ is proportional to

$$\Gamma(\omega)=\kappa\int_{-\infty}^{+\infty}\cos[(\omega-\gamma H)\tau]R(\tau),$$

$$R(\tau)\equiv\lim_{T\to\infty}\operatorname{Tr}[L_x W^\dagger(t_2,t_1)L_x W(t_2,t_1)],\qquad t_2=T;\quad t_1=T-\tau, \tag{I.17}$$

$$W(t_2,t_1)=1-i\int_{t_1}^{t_2}\mathcal{H}_i(t)W(t,t_1)dt.$$

If the Fourier transform of (I.17) is taken, we find:

$$\frac{R(\tau)+R(-\tau)}{2}=\frac{1}{2\pi\kappa}\int_{-\infty}^{+\infty}e^{-i(\omega-\gamma H)\tau}\Gamma(\omega)d\omega, \tag{I.18}$$

$\kappa$ can now be specified by requiring $\int_{-\infty}^{+\infty}\Gamma(\omega)d\omega=1$:

$$\kappa=[2\pi R(0)]^{-1},\quad R(0)=\operatorname{Tr}[(\sum l_i^x)^2]. \tag{I.19}$$

From (I.18) the moments of the normalized resonance absorption curve about the Larmor frequency $\omega_L=\gamma H$ follows:

$$M_n=\frac{(-)^{n/2}}{R(0)}\frac{d^nR(\tau)}{d\tau^n}\bigg|_{\tau=0}\qquad(n\text{ even}),$$

$$M_n=0\qquad(n\text{ odd}), \tag{I.20}$$

$$M_n\equiv\int_{-\infty}^{+\infty}(\omega-\gamma H)^n\Gamma(\omega)d\omega.$$

In particular, $M_0=1$ by (I.19).

Formulas (I.17) and (I.20) are the required generalization of the Van Vleck procedure for the case of a rotating lattice.

## II. APPLICATION OF THE GENERAL FORMALISM. THE ROTATING NUCLEAR PAIR

As a specific example of the foregoing formalism, we treat the problem of a rotating solid containing nuclear pairs which to a first approximation can be considered as isolated. The background magnetic field associated with nuclei more distant than the nuclear pair partner will give rise to secondary effects on the line structure. In the static lattice the theoretical and experimental line shape of such nuclear pairs has been successfully treated by Pake.[12] The following discussion will be limited to a pair of identical spin-$\frac{1}{2}$ nuclei.

[12] G. Pake, J. Chem. Phys. **16**, 327 (1948).

The Hamiltonian for the spin pair in an external magnetic field is

$$\mathcal{H}_z=-\gamma(\mathbf{I}_1+\mathbf{I}_2)\cdot\mathbf{H}, \tag{II.1}$$

where $\gamma=$ magnetogyric ratio and $\mathbf{H}=$ external magnetic field, while the internuclear Hamiltonian is taken in the most general form[13]:

$$\begin{aligned}\mathcal{H}_i(t)&=c_1\mathbf{I}_1\cdot\mathbf{I}_2+c_2\mathbf{I}_1\cdot\hat{r}(t)\mathbf{I}_2\cdot\hat{r}(t)\to c_1\mathbf{I}_1\cdot\mathbf{I}_2\\&\quad+c_2[\mathbf{I}_1\cdot\hat{H}\mathbf{I}_2\cdot\hat{H}\cos^2\theta(t)\\&\qquad+\tfrac{1}{2}(\mathbf{I}_1\cdot\mathbf{I}_2-\mathbf{I}_1\cdot\hat{H}\mathbf{I}_2\cdot\hat{H})\sin^2\theta(t)]\\&=\mathbf{I}_1\cdot\mathbf{I}_2[c_1+\tfrac{1}{2}c_2\sin^2\theta(t)]\\&\qquad-\tfrac{1}{2}c_2\mathbf{I}_1\cdot\hat{H}\mathbf{I}_2\cdot\hat{H}[1-3\cos^2\theta(t)],\end{aligned} \tag{II.2}$$

where $\hat{H}=$ unit vector in the direction of $\mathbf{H}$ and $\cos\theta(t)=\hat{r}(t)\cdot\hat{H}$. In effect, the Zeeman levels are so far separated that any part of $\mathcal{H}_i(t)$ which would mix Zeeman levels is negligible so that $\mathcal{H}_i(t)$ has been truncated in the above manner. A more detailed presentation of the truncation process is given in Appendix A. The explicit time dependence associated with a rotating lattice has also been indicated in (II.2).

For a pure dipole interaction $c_1=-\frac{1}{3}c_2=\gamma^2/r^3$ and (II.2) takes the form:

$$\mathcal{H}_i=\frac{-\gamma^2}{2r^3}[\mathbf{I}_i\cdot\mathbf{I}_2-3\mathbf{I}_1\cdot\hat{H}\mathbf{I}_2\cdot\hat{H}][1-3\cos^2\theta(t)] \tag{II.3}$$

(pure dipole interaction).

The truncated Hamiltonian (II.2) is diagonal in the representation of the four-dimensional spin space characterized by the total spin $L$ and the projection of the total spin along $\hat{H}$, i.e., $\mathbf{L}\cdot\hat{H}$:

$$\begin{aligned}&\mathcal{H}_i|L=1,M=\pm1\rangle\\&\quad=[\tfrac{1}{4}(c_1+\tfrac{1}{2}c_2\sin^2\theta)-\tfrac{1}{8}c_2(1-3\cos^2\theta)]\\&\qquad\qquad\times|L=1,M=\pm1\rangle,\\&\mathcal{H}_i|L=1,M=0\rangle\\&\quad=[\tfrac{1}{4}(c_1+\tfrac{1}{2}c_2\sin^2\theta)+\tfrac{1}{8}c_2(1-3\cos^2\theta)]\\&\qquad\qquad\times|L=1,M=0\rangle,\\&\mathcal{H}_i|L=0,M=0\rangle\\&\quad=[-\tfrac{3}{4}(c_1+\tfrac{1}{2}c_2\sin^2\theta)+\tfrac{1}{8}c_2(1-3\cos^2\theta)]\\&\qquad\qquad\times|L=0,M=0\rangle,\end{aligned} \tag{II.4}$$

Transitions out of the state $|L=0,M=0\rangle$ are impossible via an exciting rf field (since $\mathbf{L}|L=0,M=0\rangle=0$) and so for the following calculations the state $|L=0,M=0\rangle$ lies dormant. In addition, because $\mathbf{I}_1\cdot\mathbf{I}_2$ can thus effectively take on only its triplet state value 1, the subsequent calculation proves to be independent of $c_1$.

In view of this remark, only the explicit time dependence of $[1-3\cos^2\theta(t)]$ is needed. In terms of the

[13] That (II.2) is the most general expression for the interaction Hamiltonian of two spin-$\frac{1}{2}$ particles is readily proved by observing that only three vectors ($\mathbf{r}$, $\mathbf{I}_1\mathbf{I}_2$) are available with which to form a rotationally invariant Hamiltonian. Furthermore, the vector $\mathbf{r}$ must occur an even number of times if the particles are to be reflectionally equivalent. All invariant dot products thus formed reduce to one of the types constituting the expression (II.2).

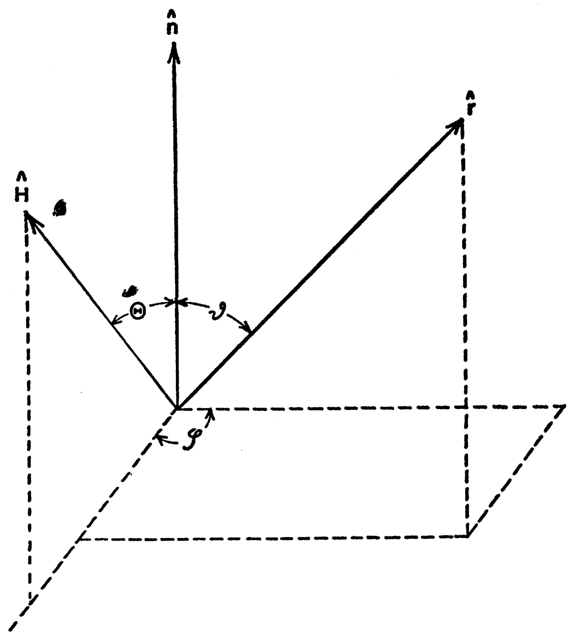


FIG. 1. The orientation of $\hat{H}$ and $\hat{r}$ relative to the rotation axis directed along the unit vector $\hat{n}$.

angles of the internuclear vector $(\vartheta,\varphi)$ and the magnetic field $(\Theta,\Phi)$ relative to the rotation axis taken as the polar axis (Fig. 1):

$$
\begin{aligned}
\{1-3[\hat{r}(t)\cdot\hat{H}]^2\} &= -2P_2(\cos\theta) = a+b\cos(\Omega t+\varphi) \\
&\qquad + c\cos 2(\Omega t+\varphi), \\
a &= -(8\pi/5)Y_{2,0}(\vartheta,\,\Omega t+\varphi)Y_{2,0}(\Theta,\Phi) \\
&= -\tfrac{1}{2}(1-3\cos^2\vartheta)(1-3\cos^2\Theta), \\
b &= -(8\pi/5)[Y_{2,1}(\vartheta,\,\varphi=0)-Y_{2,-1}(\vartheta,\,\varphi=0)] \\
&\qquad \times Y_{21}(\Theta,\,\Phi=0) = -\tfrac{3}{2}\sin 2\Theta\sin 2\vartheta, \\
c &= -(8\pi/5)[Y_{2,2}(\vartheta,\,\varphi=0)+Y_{2,-2}(\vartheta,\,\varphi=0)] \\
&\qquad \times Y_{2,2}(\Theta,\,\Phi=0) = -\tfrac{3}{2}\sin^2\vartheta\sin^2\Theta,
\end{aligned}
\tag{II.5}
$$

where $\Omega$=rotation frequency. Note that in the rotating solid each pair rotates about an axis which can be taken through any member of the nuclear pair.

The general expression for the shape of the normalized absorption line is

$$
\begin{aligned}
\Gamma(\omega) &= \frac{1}{2\pi\,\mathrm{Tr}L_x^2}\int_{-\infty}^{+\infty} d\tau\,\cos[(\omega-\gamma H)\tau] \\
&\qquad \times \lim_{T\to\infty}\mathrm{Tr}[W^\dagger(t_2,t_1)L_xW(t_2,t_1)L_x], \\
&\qquad t_2=T;\quad t_1=T-\tau, \\
W(t_2,t_1) &= 1-i\int_{t_1}^{t_2}\mathcal{H}_i(t)W(t,t_1)dt.
\end{aligned}
\tag{II.6}
$$

For the two-particle case,

$$
[\mathcal{H}_i(t'),\mathcal{H}_i(t'')]=0, \tag{II.7}
$$

and so the integral equation for $W(t_2,t_1)$ can be solved exactly:

$$
\begin{aligned}
W(t_2,t_1) &= \exp\left[-i\int_{t_1}^{t_2}\mathcal{H}_1(t)dt\right] \\
&= \exp\left[-i\int_{t_1}^{t_2}\mathbf{l}_1\cdot\mathbf{l}_2[c_1+\tfrac{1}{2}c_2\sin^2\theta(t)]dt\right. \\
&\qquad \left. +ig(t_2,t_1)\mathbf{l}_1\cdot\hat{H}\mathbf{l}_2\cdot\hat{H}\right], \\
g(t_2,t_1) &= \tfrac{1}{2}c_2\int_{t_1}^{t_2}\{a+b[\cos(\Omega t+\varphi)] \\
&\qquad +c\cos[2(\Omega t+\varphi)]\}dt \\
&= \tfrac{1}{2}c_2\{a\tau+(2b/\Omega)\sin(\Omega\tau/2) \\
&\qquad \times\cos[\Omega(\sigma/2+\varphi/\Omega)] \\
&\qquad +(c/\Omega)\sin\Omega\tau\cos[2\Omega(\sigma/2+\varphi/2)]\}, \\
&\qquad \sigma\equiv t_2+t_1,\quad \tau\equiv t_2-t_1.
\end{aligned}
\tag{II.8}
$$

From (II.8) and using $\mathbf{l}_1\cdot\mathbf{l}_2=1$,

$$
\begin{aligned}
&\mathrm{Tr}[W^\dagger(t_2,t_1)L_xW(t_2,t_1)L_x] \\
&= \mathrm{Tr}\{\exp[-ig(t_2,t_1)\mathbf{l}_1\cdot\hat{H}\mathbf{l}_2\cdot\hat{H}]L_x \\
&\qquad \times\exp[+ig(t_2,t_1)\mathbf{l}_1\cdot\hat{H}\mathbf{l}_2\cdot\hat{H}]L_x\} \\
&= \tfrac{1}{2}\,\mathrm{Tr}\{\exp[ig(t_2,t_1)\mathbf{l}_1\cdot\hat{H}\mathbf{l}_2\cdot\hat{H}]L_+ \\
&\qquad \times\exp[ig(t_2,t_1)\mathbf{l}_1\cdot\hat{H}\mathbf{l}_2\cdot\hat{H}]L_-\} \\
&= \sum_{M=1,0}\langle M|\exp[-ig(t_2,t_1)\mathbf{l}_1\cdot\hat{H}\mathbf{l}_2\cdot\hat{H}]|M\rangle \\
&\qquad \times\langle M-1|\exp[ig(t_2,t_1)\mathbf{l}_1\cdot\hat{H}\mathbf{l}_2\cdot\hat{H}]|M-1\rangle \\
&= \sum_{M=1,0}\exp\left[ig(t_2,t_1)\left(\frac{2-4M}{4}\right)\right] \\
&= 2\cos[g(t_2,t_1)/2].
\end{aligned}
\tag{II.9}
$$

The limit $T\to\infty$ must now be effected and to this end we employ the expansion[14]:

$$
\exp(i\alpha\cos\beta)=\sum_{n=-\infty}^{n=+\infty}J_n(\alpha)\exp\left[in\left(\beta+\frac{\pi}{2}\right)\right], \tag{II.10}
$$

where $J_n(\alpha)$=Bessel function of the first kind of order $n$ and argument $\alpha$. The limiting process amounts to retaining only the nonoscillatory terms in

$$
\begin{aligned}
T' &= (\sigma/2+\varphi/\Omega) \\
\lim_{T'\to\infty}\exp[in\Omega T'] &= \delta_{n0},
\end{aligned}
\tag{II.11}
$$

[14] P. M. Morse and H. Feshbach, *Methods of Mathematical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, Chap. 5, p. 620.

and so after (II.10) and (II.11) is applied to Eq. (II.9):

$$\lim_{T'=0} \exp[ig(t_2,t_1)/2]$$

$$=\exp[i(c_2a\tau)/4]\sum_{m=-\infty}^{m=+\infty} J_{-2m}\left[\frac{c_2b}{2\Omega}\sin(\Omega\tau/2)\right] \times J_m\left[\frac{c_2c}{4\Omega}\sin(\Omega\tau)\right]\exp\left[-im\frac{\pi}{2}\right]$$

$$=\exp[i(c_2a\tau)/4]\left\{J_0\left[\frac{c_2b}{2\Omega}\sin(\Omega\tau/2)\right]J_0\left[\frac{c_2c}{4\Omega}\sin(\Omega\tau)\right] +2i\sum_{m=1}^{\infty}(-)^m J_{4m-2}\left[\frac{c_2b}{2\Omega}\sin(\Omega\tau/2)\right] \times J_{2m-1}\left[\frac{c_2c}{4\Omega}\sin(\Omega\tau)\right] +2\sum_{m=1}^{\infty}(-)^m J_{4m}\left[\frac{c_2b}{2\Omega}\sin(\Omega\tau/2)\right] \times J_{2m}\left[\frac{c_2c}{4\Omega}\sin(\Omega\tau)\right]\right\}. \quad \text{(II.12)}$$

With the use of (II.9) and (II.12), (II.6) is now

$$\Gamma(\omega)\equiv\frac{1}{2\pi\,\mathrm{Tr}(L_x^2)}\int_{-\infty}^{+\infty} d\tau\,\cos[(\omega-\gamma H)\tau]R(\tau),$$

$$R(\tau)=2\cos\alpha\tau\left\{J_0\left[\beta\frac{2}{\Omega}\sin\left(\frac{\Omega}{2}\tau\right)\right]J_0\left[\delta\frac{1}{\Omega}\sin(\Omega\tau)\right] +2\sum_{m=1}^{\infty}(-)^m J_{4m}\left[\beta\frac{2}{\Omega}\sin\left(\frac{\Omega\tau}{2}\right)\right] \times J_{2m}\left[\frac{\delta}{\Omega}\sin(\Omega\tau)\right]\right\}$$
$$-2\sin\alpha\tau\left\{2\sum_{m=1}^{\infty}(-)^m J_{4m-2}\left[\beta\frac{2}{\Omega}\sin\left(\frac{\Omega\tau}{2}\right)\right] \times J_{2m-1}\left[\frac{\delta}{\Omega}\sin(\Omega\tau)\right]\right\}, \quad \text{(II.13)}$$

$$\alpha\equiv c_2a/4=-\tfrac{1}{8}c_2(1-3\cos^2\vartheta)(1-3\cos^2\Theta),$$

$$\beta\equiv c_2b/4=-\tfrac{3}{8}c_2\sin2\vartheta\sin2\Theta,$$

$$\delta\equiv c_2c/4=-\tfrac{3}{8}c_2\sin^2\vartheta\sin^2\Theta.$$

It is worth mentioning that the limiting processes $\Omega\to 0$ and $T'\to\infty$ do not commute since, if $T'\to\infty$ is performed first, an average over the azimuthal angle about the rotation axis is irrevocably effected.

We shall now briefly discuss the implications of (II.13) under three aspects.

### A. Right-Angle Spinning

By this, we mean that the angle between the magnetic field and the spinning axis is $\pi/2$. Consequently, $\beta=0$ and $J_n[\beta(2/\Omega)\cos(\frac{1}{2}\Omega\tau)]=\delta_{n0}$. The integral in (II.13) can be carried out by using

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty}\cos r\varphi J_0(2Z\sin\varphi)d\varphi =\sum_{m=-\infty}^{m=+\infty}\delta(r-2m)[J_m(Z)]^2, \quad \text{(II.14)}$$

which can be proved by taking the Fourier transform of the addition theorem for Bessel functions.[15] The final result for the line shape is

$$\Gamma(\omega)=\frac{1}{2\pi\,\mathrm{Tr}(L_x^2)}\int_{-\infty}^{+\infty}d\tau\,\cos[(\omega-\gamma H)\tau] \times\cos\alpha\tau\{2J_0(\delta\Omega^{-1}\sin\Omega\tau)\}$$
$$=\frac{1}{2\pi\,\mathrm{Tr}(L_x^2)}\int_{-\infty}^{+\infty}d\tau\{\cos[(\omega-\gamma H-\alpha)\tau] +\cos[(\omega-\gamma H+a)\tau]\}J_0(\delta\Omega^{-1}\sin\Omega\tau)$$
$$=\frac{1}{\mathrm{Tr}(L_x^2)}\left\{\sum_{m=-\infty}^{m=+\infty}[\delta(\omega-\gamma H-\alpha-2m\Omega) +\delta(\omega-\gamma H+\alpha-2m\Omega)][J_m^2(\delta/2\Omega)].\right\} \quad \text{(II.15)}$$

Andrew and Newing[7] have also computed the line shape by the semiclassical method of treating the local internuclear field seen by the nuclei to be frequency modulated by the rotation of the pair. The above method leads to the same expression as obtained by these authors for the particular case of the spinning axis perpendicular to the internuclear axis.

The line shape $\Gamma(\omega)$ consists of the "Pake-split" lines at $\omega=\gamma H\pm\alpha$ and satellite lines around each of these "Pake-split" lines at regular intervals of spacing $2\Omega$. At certain critical rotation frequencies, namely those frequencies which are associated with a root of a Bessel function, certain lines will vanish. For example, the lines at $\omega=\gamma H\pm\alpha$ will disappear when $J_0[\delta/(2\Omega)]=0$. The critical frequencies $\Omega_n$ are determined by $\delta/(2\Omega_n)=x_n$, where $x_n$ is a root of $J_0(x)$:

$$\Omega_n=\delta/(2x_n),$$
$$x_1=2.405,\quad x_2=5.520,\quad x_3=8.654,\quad \text{etc.} \quad \text{(II.16)}$$

### B. High-Frequency Spinning

The arguments of the Bessel function in Eq. (II.13) all depend on the parameters $\beta/\Omega$ and $\delta/\Omega$ which become small compared to unity as the "energy" $\Omega$ becomes large compared to the energies $\beta$ and $\delta$. Con-

[15] Reference 14, Vol. 2, Chap. 10, p. 1322.

sequently, for sufficiently large rotation frequencies, $\Gamma(\omega)$ is expressible as a rapidly converging series in $\Omega^{-1}$.

It will be noted that $\Gamma(\omega)$ of (II.13) can always be written in the following form:

$$\begin{aligned}\Gamma(\omega)=&\frac{1}{2\pi\,\mathrm{Tr}(L_x^2)}\int_{-\infty}^{\infty}d\tau\{\cos[(\omega-\gamma H-\alpha)\tau]\\&+\cos[(\omega-\gamma H+\alpha)\tau]\}\sum_{n=0}^{\infty}a_n\cos n\Omega\tau\\&+\{\sin[(\omega-\gamma H-\alpha)\tau]-\sin[(\omega-\gamma H+\alpha)\tau]\}\\&\times\sum_{n=0}^{\infty}b_n\sin n\Omega\tau\\=&\frac{1}{\mathrm{Tr}(L_x^2)}\{a_0[\delta(\omega-\gamma H-\alpha)+\delta(\omega-\gamma H+\alpha)]\\&+\sum_{n=-\infty}^{n=+\infty}\tfrac{1}{2}a_n[\delta(\omega-\gamma H-\alpha-n\Omega)\\&+\delta(\omega-\gamma H-\alpha+n\Omega)+\delta(\omega-\gamma H+\alpha-n\Omega)\\&+\delta(\omega-\gamma H+\alpha+n\Omega)]\\&+\sum_{n=1}^{\infty}\tfrac{1}{2}b_n[\delta(\omega-\gamma H-\alpha-n\Omega)\\&-\delta(\omega-\gamma H-\alpha+n\Omega)-\delta(\omega-\gamma H+\alpha-n\Omega)\\&+\delta(\omega-\gamma H+\alpha+n\Omega)]\},\end{aligned}\tag{II.17}$$

$$a_n\equiv\frac{\Omega}{\pi}\int_0^{2\pi/\Omega}\cos(n\Omega\tau)R_1(\tau)d\tau;$$

$$a_0\equiv\frac{\Omega}{2\pi}\int_0^{2\pi/\Omega}R_1(\tau)d\tau;$$

$$b_n\equiv\frac{\Omega}{\pi}\int_0^{2\pi/\Omega}\sin(n\Omega\tau)R_2(\tau)d\tau,$$

where

$$\begin{aligned}R_1(\tau)=&J_0\left[\beta\frac{2}{\Omega}\sin\left(\frac{\Omega\tau}{2}\right)\right]J_0\left[\delta\frac{1}{\Omega}\sin\Omega\tau\right]\\&+2\sum_{m=1}^{\infty}(-)^mJ_{4m}\left[\beta\frac{2}{\Omega}\sin\left(\frac{\Omega\tau}{2}\right)\right]J_{2m}\left[\frac{\delta}{\Omega}\sin(\Omega\tau)\right],\\R_2(\tau)=&2\sum_{m=1}^{\infty}(-)^mJ_{4m-2}\left[\beta\frac{2}{\Omega}\sin\left(\frac{\Omega\tau}{2}\right)\right]\\&\times J_{2m-1}\left[\delta\frac{1}{\Omega}\sin(\Omega\tau)\right].\end{aligned}$$

For small arguments:

$$J_n(z)=\frac{1}{n!}\left(\frac{z}{2}\right)^n\left[1-\frac{z^2}{4(n+1)}+\frac{z^4}{32(n+2)(n+1)}+\cdots\right],\tag{II.18}$$

so that up to but not including terms of sixth order in $\Omega^{-1}$, the only contributing $a$ and $b$ coefficients turn out to be

$$\begin{aligned}a_0=&\left[1-\left(\frac{\beta^2+(\delta/2)^2}{2\Omega^2}\right)+\frac{3}{32}\left(\frac{\beta^4+(\delta/2)^2}{\Omega^4}\right)+\frac{1}{4}\frac{\beta^2(\delta/2)^2}{\Omega^4}\right],\\a_1=&\left[\beta^2/(2\Omega^2)-\beta^4/(8\Omega^4)-\frac{\beta^2(\delta/2)^2}{8\Omega^4}\right],\\a_2=&\left[\frac{\beta^4}{32\Omega^4}+\frac{(\delta/2)^2}{2\Omega^2}-\frac{(\delta/2)^4}{8\Omega^4}-\frac{\beta^2(\delta/2)^2}{4\Omega^4}\right],\\a_3=&\left[\frac{1}{8}\frac{\beta^2(\delta/2)^2}{\Omega^4}\right],\quad b_1=\left[-\frac{1}{4}\frac{\beta^2\delta}{\Omega^3}\right],\\a_4=&\left[\frac{1}{32}\frac{(\delta/2)^4}{\Omega^4}\right],\quad b_2=\left[\frac{1}{8}\frac{\beta^2\delta}{\Omega^3}\right].\end{aligned}\tag{II.19}$$

With the use of the $a_n$ and $b_n$ of (II.19), Eq. (II.17) gives the line shape for high rotation frequencies.

### C. Moments of the Line

It is a simple matter to calculate the $n$th moment $M_n$ of the line about the Larmor frequency $\gamma H$:

$$M_n=\frac{1}{\mathrm{Tr}(L_x^2)}(-)^{n/2}\left.\frac{d^nR(\tau)}{d\tau^n}\right|_{\tau=0},\tag{II.20}$$

or the even and odd moments $(M', M'')$ about the Pake lines at $\gamma H\pm\alpha$:

$$\begin{aligned}M_n'=&\frac{2}{\mathrm{Tr}(L_x^2)}(-)^{n/2}\left.\frac{d^nR_1(\tau)}{d\tau^n}\right|_{\tau=0},\qquad n\text{ even}\\M_n'=&0,\qquad n\text{ odd}\\M_n''=&-\frac{2}{\mathrm{Tr}(L_x^2)}(-)^{(n+1)/2}\left.\frac{d^nR_2(\tau)}{d\tau^n}\right|_{\tau=0},\qquad n\text{ odd}\\M_n''=&0,\qquad n\text{ even}.\end{aligned}\tag{II.21}$$

Furthermore, the two sets of moments are directly related:

$$M_n=\sum_m\binom{n}{m}(M_m'+M_m'')\alpha^{n-m},\qquad\binom{n}{m}\equiv\frac{n!}{m!(n-m)!}.\tag{II.22}$$

Again because of the fact that $J_n(z)$ is expansible according to (II.18) and the series for sin $z$ starts with $z$, only a finite number of terms in $R_1(\tau)$ and $R_2(\tau)$ will contribute to the $n$th moment. The first few moments

are:

$$
\begin{aligned}
&M_0'=1,\\
&M_2'=\tfrac{1}{2}(\beta^2+\delta^2),\\
&M_4'=[\tfrac{3}{8}\beta^4+\tfrac{3}{8}\delta^4+\tfrac{3}{2}\beta^2\delta^2]+[\tfrac{1}{2}\beta^2+2\delta^2]\Omega^2, \quad \text{(II.23)}\\
&M_1''=0,\\
&M_3''=\tfrac{3}{4}(\beta^2\delta/\Omega^3)\Omega^3.
\end{aligned}
$$

Equation (II.23) shows that $M_4'$ diverges as $\Omega\rightarrow\infty$. It is thus apparent that the method of moments is useful only for rotation "energies" small compared to the interparticle interaction energy and so is a procedure complementary to that of the high-frequency spinning limit.

Generalization of these results to interacting pairs of higher spin can be made quite straightforwardly. Moreover, many of the features of the spinning nuclear pair are still exhibited by the $n$-body system formed by spins disposed at the lattice sites of a rotating microscopic sample to which we direct our attention below.

## III. RELAXATION OF TRANSVERSE MAGNETIZATION IN A ROTATING SOLID

In the exploration of nuclear and internuclear magnetic properties, the relaxation history of a macroscopic magnetization transverse to the external magnetic field $\mathbf{H}$ provides a second possible experimental approach. The first desideratum, of course, is to induce coherently a macroscopic magnetization transverse to $H$. Experimentally, this is accomplished by irradiating the sample (for a precisely determined time) with an rf pulse oscillating with the Larmor frequency $\omega=\gamma H$ perpendicular to the magnetic field. We briefly summarize the process of transversalization.

Since the nuclear magnetization is in thermal equilibrium with its ambient before the pulse is applied, the magnetization $\mathbf{M}(t)$ is

$$
\begin{aligned}
&\mathbf{M}(t)=\gamma\,\mathrm{Tr}\rho\mathbf{L}=\gamma\hat{H}\,\mathrm{Tr}\rho\mathbf{L}\cdot\hat{H},\\
&\quad\rho=\textstyle\sum_{m\alpha}|m\alpha\rangle\rho_{m\alpha}\langle m\alpha|\\
&\qquad\quad=\exp[\beta\gamma\mathbf{L}\cdot\mathbf{H}]/\mathrm{Tr}(\exp[\beta\gamma\mathbf{L}\cdot\mathbf{H}]), \qquad \text{(III.1)}\\
&\quad\beta=(kT)^{-1}.
\end{aligned}
$$

The form of the density matrix $\rho$ given in (III.1) originates under the assumption that the internuclear forces are weak compared to the forces exerted by the external field $H$ and so can be neglected in determining the sample magnetization.

When the rf pulse is turned on for the time interval from $t_0$ to $t_1$, the density matrix becomes time-dependently driven by the Hamiltonian:

$$
\begin{aligned}
\mathcal{H}(t)&=\mathcal{H}_z+\mathcal{H}_i(t)+\mathcal{H}_p(t),\\
\mathcal{H}_p(t)&=-\gamma H_p[\hat{\imath}\cos\omega(t-t_0)-\hat{\jmath}\sin\omega(t-t_0)]\cdot\mathbf{L},
\end{aligned}
\qquad \text{(III.2)}
$$

where $\mathcal{H}_z$ and $\mathcal{H}_i(t)$ have the same significance as in Sec. I. The properties with which the magnetic pulse $H_p\{\hat{\imath}\cos[\omega(t-t_0)]-\hat{\jmath}\sin[\omega(t-t_0)]\}$ are invested are:

(i) $\omega=\gamma H$; when the pulse has the Larmor frequency $\gamma H$, the magnetic field $\mathbf{H}_p(t)$ follows the nuclear spin and forces it to precess about itself.

(ii) $|H_p|/|H_i|\gg1$; the magnetic field of the pulse dominates the internuclear magnetic field $H_i$. (III.3)

(iii) $\Delta t=(\pi/2)/(\gamma H_p)$; a pulse of duration $\Delta t$ will turn the magnetization through $\pi/2$ radians.

The equation of motion of the density matrix is

$$
\rho(t_2)=U(t_2,t_0)\rho(t_0)U^\dagger(t_2,t_0);\quad U(t_2,t_0)=U(t_2,t_1)U(t_1,t_0),
$$

$$
\begin{aligned}
&\text{(i)}\quad U(t_1,t_0)=\exp[-i\mathcal{H}_z(t_1-t_0)]T(t_1,t_0),\\
&\qquad T(t_1,t_0)=1-i\int_{t_0}^{t_1}\exp[i\mathcal{H}_z(t-t_0)]\mathcal{H}_p(t)\\
&\qquad\qquad\times\exp[-i\mathcal{H}_z(t-t_0)]T(t,t_0)dt, \qquad \text{(III.4)}\\
&\text{(ii)}\quad U(t_2,t_1)=\exp[-i\mathcal{H}_z(t_2-t_1)]W(t_2,t_1)\quad(\text{for } t_2>t_1),\\
&\qquad W(t_2,t_1)=1-i\int_{t_1}^{t_2}\mathcal{H}_i(t)W(t,t_1)dt,
\end{aligned}
$$

where $t_0$= time of application of rf pulse and $t_1$= time of removal of rf pulse.

In the evolution of the dynamical system from $t_0$ to $t_1$ described by $U(t_1,t_0)$ the motion induced by $\mathcal{H}_i(t)$ has been treated as negligible in view of the properties (III.3). It will be noted that the dismemberment of $\mathcal{H}_i(t)$ [Eq. (I.2)] has been taken for granted in (III.4). (The amputated terms will produce small amplitude terms rotating at multiples of the Larmor frequency.)

Again because of the conditions (III.3), the integral equation for $T(t_1,t_0)$ leads to a simple form for $T(t_1,t_0)$:

$$
T(t_1,t_0)=\exp[i(\pi/2)L_x]. \qquad \text{(III.5)}
$$

A few elementary manipulations result in a more closed form for $\mathbf{M}(t_2)$:

$$
\begin{aligned}
\mathbf{M}(t_2)=(\gamma/Z)\,\mathrm{Tr}[U(t_2,t_1)\exp(+\beta\gamma H\mathbf{L}\cdot\hat{n})&\\
\times U^\dagger(t_2,t_1)\mathbf{L}],&\qquad \text{(III.6)}\\
\hat{n}=\hat{\jmath}\cos\gamma H(t_1-t_0)+\hat{\imath}\sin\gamma H(t_1-t_0).&
\end{aligned}
$$

At time $t_2=t_1$, the intuitively expected magnetization is realized:

$$
\begin{aligned}
\mathbf{M}(t_1)=+\{\hat{\imath}\sin[\gamma H(t_1-t_0)]&\\
+\hat{\jmath}\cos[\gamma H(t_1-t_0)]\}|\mathbf{M}(t_0)|,&\qquad \text{(III.7)}
\end{aligned}
$$

while at later times:

$$
\begin{aligned}
\mathbf{M}(t_2)=(\gamma/Z)\{\hat{\imath}\sin[\gamma H(t_2-t_0)]&\\
+\hat{\jmath}\cos[\gamma H(t_2-t_0)]\}\,\mathrm{Tr}[\exp(+\beta\gamma HL_x)&\\
\times W^\dagger(t_2,t_0)L_xW(t_2,t_0)],&\qquad \text{(III.8)}\\
W(t_2,t_1)\cong W(t_2,t_0).&
\end{aligned}
$$

Free use of the rotational invariance of $W(t_2,t_1)$ against rotation of the spins about the $z$ axis through any angle and about the $x$ and $y$ axis through $\pi$ radians has been made to create the form (III.8). Furthermore, the Boltzmann factor is always close to unity:

$$\mathbf{M}(t_2)=(\gamma/Z)\beta\gamma H\{\hat{\imath}\sin[\gamma H(t_2-t_0)] + \hat{\jmath}\cos[\gamma H(t_2-t_0)]\} \times \mathrm{Tr}[L_xW^\dagger(t_2,t_0)L_xW(t_2,t_0)], \quad \text{(III.9)}$$

$$W(t_2,t_0)=1-i\int_{t_0}^{t_2}\mathcal{H}_i(t)W(t,t_0)dt.$$

Comparison of (III.9) and (I.17) reveals the relationship between the temporal behavior of the transverse magnetization and the Fourier transform of the line shape in a rotating lattice.

To understand the origin and meaning of the limiting procedure of (I.17) and its absence in (III.9), one only need note that in the pulsed experiment, the results will depend upon the orientation of the crystal about the rotation axis at the instant of the application of the rf pulse, whereas no such selective situation occurs in the investigation of the absorptive line shape. Thus the limiting procedure is essentially an averaging over the azimuthal angle about the rotation axis.

To conclude the discussion of the behavior of an induced transverse magnetization in a rotating solid, again the specific example of the rotating spin-$\frac{1}{2}$ nuclear pair will be explored. Almost all of the requisite calculations have been presented in Sec. II.

The trace of (III.9) which gives the modulation envelope of the Larmor precessing magnetization was calculated in (II.9):

$$\mathrm{Tr}[L_xW^\dagger(t_2,t_0)L_xW(t_2,t_0)]=2\cos[g(t_2,t_0)/2],$$
$$g(t_2,t_0)=\tfrac{1}{2}c_2[a\tau+2(b/\Omega)\sin(\Omega\tau/2)\cos\Omega(\sigma/2+\varphi/\Omega) + (c/\Omega)\sin(\Omega\tau)\cos 2\Omega(\sigma/2+\varphi/\Omega)], \quad \text{(III.10)}$$
$$\tau=t_2-t_0,\quad \sigma=t_2+t_0=\tau+2t_0.$$

Expression (III.10) depends both on the time $\tau$ elapsed since the application of the pulse and on the switch-on time of the pulse $t_0$ in accord with our previous remarks. However, by taking the azimuthal average over $\varphi$, (III.10) becomes independent of $t_0$:

$$\langle\mathrm{Tr}[L_xW^\dagger(t_2,t_0)L_xW(t_2,t_0)]\rangle \equiv\frac{1}{2\pi}\int_0^{2\pi}\mathrm{Tr}[L_xW^\dagger(t_2,t_0)L_xW(t_2,t_0)]d\varphi$$
$$=2\cos\alpha\tau R_1(\tau)-2\sin\alpha\tau R_2(\tau), \quad \text{(III.11)}$$
$$\alpha=-\tfrac{1}{8}c_2(1-3\cos^2\vartheta)(1-3\cos^2\Theta),$$
$$\beta=-\tfrac{3}{8}c_2\sin 2\vartheta\sin 2\Theta,$$
$$\delta=-\tfrac{3}{8}\sin^2\vartheta\sin^2\Theta,$$

$R_1(\tau)$ and $R_2(\tau)$ are defined by (II.17).

The average over $\varphi$ is accomplished in exactly the same way in which the limit $T'\to\infty$ was carried out (II.10), (II.12) except that instead of (II.11), we use

$$\frac{1}{2\pi}\int_0^{2\pi}\exp[in\varphi']d\varphi'=\delta_{n0},\quad \varphi'\equiv\varphi+\Omega\sigma/2. \quad \text{(III.12)}$$

Experimentally for a single rotating crystal, the azimuthal averaging can be realized by averaging the experimental $\mathbf{M}(\tau,t_0)$ over all data taken by applying many randomly timed pulses:

$$\langle\mathbf{M}(\tau)\rangle\equiv\frac{1}{2\pi}\int_0^{2\pi}\mathbf{M}(\tau,t_0)d\varphi=\frac{\Omega}{2\pi}\int_{t_0=0}^{t_0=2\pi/\Omega}\mathbf{M}(\tau,t_0)dt_0. \quad \text{(III.13)}$$

If a powdered sample is used, not only is the azimuthal average automatically involved but also an averaging over the $\cos\vartheta$ of (III.11).

As an example of the magnetic behavior of the pulsed rotating solid, we give the modulation envelope (III.11) up to and including terms of order $\Omega^{-4}$:

$$\langle\mathrm{Tr}[L_xW^\dagger(t_2,t_0)L_xW(t_2,t_0)]\rangle =\sum_{n=0}^{\infty}a_n\{\cos[(\alpha+n\Omega)\tau]+\cos[(\alpha-n\Omega)\tau]\} +\sum_{n=0}^{\infty}b_n\{\cos[(\alpha+n\Omega)\tau-\cos[(\alpha-n\Omega)\tau]\}, \quad \text{(III.14)}$$

with the $a_n,b_n$ of (II.19). Finally, if the crystal is in powdered form and the angle included between the direction of the spinning axis and the external magnetic field direction is $\Theta=\cos^{-1}(\frac{1}{3})^{\frac{1}{2}}$, the explicit form assumed by (III.14) is:

$$\langle\langle\mathrm{Tr}[L_xW^\dagger(t_2,t_0)L_xW(t_2,t_0)]\rangle\rangle \equiv\tfrac{1}{2}\int_0^{\pi}\langle\mathrm{Tr}[L_xW^\dagger(t_2,t_0)L_xW(t_2,t_0)]\rangle\sin\vartheta d\vartheta =2\sum_{n=0}^{4}\langle a_n\rangle\cos n\Omega\tau,$$

$$\langle a_n\rangle\equiv\tfrac{1}{2}\int_0^{\pi}a_n\sin\vartheta d\vartheta, \quad \text{(III.15)}$$

$$a_0=1+\frac{1}{3\times2^3}\left(\frac{c_2}{\Omega}\right)^2+\left(\frac{227}{315}\right)\left(\frac{1}{2^{10}}\right)\left(\frac{c_2}{\Omega}\right)^4,$$
$$a_1=\frac{1}{30}\left(\frac{c_2}{\Omega}\right)^2-\left(\frac{17}{315}\right)\left(\frac{1}{2^6}\right)\left(\frac{c_2}{\Omega}\right)^4,$$
$$a_2=\left(\frac{1}{15}\right)\left(\frac{1}{2^4}\right)\left(\frac{c_2}{\Omega}\right)^2+\left(\frac{1}{45}\right)\left(\frac{1}{2^8}\right)\left(\frac{c_2}{\Omega}\right)^4,$$
$$a_3=\left(\frac{1}{315}\right)\left(\frac{1}{2^6}\right)\left(\frac{c_2}{\Omega}\right)^4,\quad a_4=\left(\frac{1}{315}\right)\left(\frac{1}{2^{10}}\right)\left(\frac{c_2}{\Omega}\right)^4.$$

Observation of the oscillatory envelope (III.15) leads to the value of $c_2$ defined by (II.2).

## IV. MAGNETIC PROPERTIES IN THE uhf ROTATION LIMIT

As the foregoing belaboring of the rotating nuclear pair indicates, the effect of rotation is to feed out the strength of the center line of the rf energy absorption curve to satellite lines which move out of the range of observation in the limit of ultrahigh rotation frequencies. We deal now with the properties of the residual center line for the general lattice of $N$ nuclei. It is, however, important that the rotation frequency and its first few harmonics be still much smaller than the Larmor frequency since spin-lattice relaxation effects would otherwise be expected to become nonnegligible.

The Hamiltonian which is assumed to represent the internuclear interaction is

$$\mathcal{H}_i(t)=\sum_{ij} A_{ij}(\mathbf{I}_i\cdot\mathbf{I}_j-3\mathbf{I}_i\cdot\hat{H}\mathbf{I}_j\cdot\hat{H})[1-3\cos^2\theta_{ij}(t)] +\sum_{ij} B_{ij}\mathbf{I}_i\cdot\mathbf{I}_j,$$

$$A_{ii}=B_{ii}=0 \quad \text{for all } i, \qquad \text{(IV.1)}$$

$$A_{ij}=A_{ji};\quad B_{ij}=B_{ji},$$

$$\cos\theta_{ij}(t)=\frac{\mathbf{r}_j(t)-\mathbf{r}_i(t)}{|\mathbf{r}_j(t)-\mathbf{r}_i(t)|}\cdot\hat{H},$$

where $\mathbf{r}_l(t)$=radius vector to $l$th nucleus. If the only internuclear force springs from the magnetic dipole interaction, then

$$A_{ij}=-\gamma^2/4r_{ij}^3,\quad B_{ij}=0. \qquad \text{(IV.2)}$$

The form of (IV.1) explicitly representing the rotating lattice is

$$\mathcal{H}_i(t)=h_0+h_1(t)+h_2(t),$$

$$h_0=\sum a_{ij}(\mathbf{I}_i\cdot\mathbf{I}_j-3\mathbf{I}_i\cdot\hat{H}\mathbf{I}_j\cdot\hat{H})+B_{ij}\mathbf{I}_i\cdot\mathbf{I}_j,$$

$$h_1=\sum l_{ij}\cos(\Omega t+\varphi_{ij}-\Phi)(\mathbf{I}_i\cdot\mathbf{I}_j-3\mathbf{I}_i\cdot\hat{H}\mathbf{I}_j\cdot\hat{H}),$$

$$h_2=\sum c_{ij}\cos 2(\Omega t+\varphi_{ij}-\Phi)(\mathbf{I}_i\cdot\mathbf{I}_j-3\mathbf{I}_i\cdot\hat{H}\mathbf{I}_j\cdot\hat{H}),$$

$$a_{ij}=A_{ij}(1-3\cos^2\vartheta_{ij})[(3\cos^2\Theta-1)/2], \qquad \text{(IV.3)}$$

$$b_{ij}=-\tfrac{3}{2}A_{ij}\sin 2\Theta\sin 2\vartheta_{ij},$$

$$c_{ij}=-\tfrac{3}{2}A_{ij}\sin^2\vartheta_{ij}\sin^2\Theta,$$

$$a_{ij}=a_{ji};\quad b_{ij}=-b_{ji},\quad c_{ij}=c_{ji};$$

$$\varphi_{ij}=\varphi_{ji}+\pi,\quad \vartheta_{ij}=(\pi-\vartheta_{ji}).$$

Figure 1 of Sec. II indicates the significance of the angles in (IV.3); viz., $\vartheta_{ij}$, $\varphi_{ij}$ are the polar angles of the internuclear vector $\mathbf{r}_j-\mathbf{r}_i$; $\Theta$, $\Phi$, the polar angles of the magnetic field relative to the rotation axis chosen as polar axis.

Certain properties of (IV.3) are of immediate note. The Hamiltonian $\mathcal{H}_i(t)$ does not commute with itself for all times:

$$[\mathcal{H}_i(t_2),\mathcal{H}_i(t_1)]\neq 0 \quad \text{for all times } t_2 \text{ and } t_1, \qquad \text{(IV.4)}$$

a fact preventing a simple formal solution of the integral equation for $W(t_2,t_1)$ of (I.17). Furthermore, $\mathcal{H}_i(t)$ has one term $h_0$, which is not explicitly time dependent.

From (I.17):

$$R(\tau)=\lim_{T\to\infty}\mathrm{Tr}[L_xW^\dagger(t_2,t_1)L_xW(t_2,t_1)],$$

$$W(t_2,t_1)=1-i\int_{t_1}^{t_2}[h_0+h_1(t)+h_2(t)]W(t,t_1)dt. \qquad \text{(IV.5)}$$

Now in the limit $\Omega\to\infty$, $h_1(t)$ and $h_2(t)$ oscillate infinitely fast and generate the unique asymptotic solution:

$$W(t_2,t_1)=e^{-ih_0(t_2-t_1)}=e^{-ih_0\tau},$$
$$R(\tau)=\mathrm{Tr}[L_xe^{ih_0\tau}L_xe^{-ih_0\tau}], \qquad \text{(IV.6)}$$

because by the operator generalization of the Riemann-Lebesgue lemma[16]

$$\lim_{\Omega\to\infty}\int_{t_1}^{t_2}[h_1(t)+h_2(t)]e^{-ih_0(t-t_1)}dt\to 0, \qquad \text{(IV.7)}$$

the validity of which rests upon the property that the matrix elements of $e^{-ih_0(t_2-t_1)}$ oscillates with a frequency of the order of magnitude $a_{ij}$ and so cannot be coherent with an arbitrarily large $\Omega$ frequency. We observe that in the limit of ultra-high rotation frequencies the residual resonance energy absorption line shape is again simply related to the Fourier transform of the function prescribing the temporal relaxation of any transverse magnetization. A comparison of the Hamiltonian $\mathcal{H}_s$ describing the static lattice and $h_0$:

$$\mathcal{H}_s=\sum A_{ij}(\mathbf{I}_i\cdot\mathbf{I}_j-3\mathbf{I}_i\cdot\hat{H}\mathbf{I}_j\cdot\hat{H})(1-3\cos^2\theta_{ij}) +\sum B_{ij}\mathbf{I}_i\cdot\mathbf{I}_j,$$

$$h_0=\sum\lambda(\Theta)A_{ij}(\mathbf{I}_i\cdot\mathbf{I}_j-3\mathbf{I}_i\cdot\hat{H}\mathbf{I}_j\cdot\hat{H})(1-3\cos^2\vartheta_{ij}) +\sum B_{ij}\mathbf{I}_i\cdot\mathbf{I}_j, \qquad \text{(IV.8)}$$

$$\lambda(\Theta)\equiv(3\cos^2\Theta-1)/2;\quad -\tfrac{1}{2}\le\lambda\le 1$$

reveals a strong resemblance between the two.

Suppose that $B_{ij}$ is either zero or negligible in comparison to the dipole-dipole interaction strength $A_{ij}$ and denote the experimentally observed lattice relaxation function for the static solid by $G_s(\tau)$:

$$G_s(\tau)\equiv R(t)_{\text{experimental}},$$
$$G_s(\tau)=\mathrm{Tr}[L_x\exp(i\mathcal{H}_s\tau)L_x\exp(-i\mathcal{H}_s\tau)]. \qquad \text{(IV.9)}$$

The exact relaxation function $G_r(\tau)$ for the rotating lattice in the ultra-high rotation frequency limit is then

[16] T. Apostol, *Mathematical Analysis* (Addison Wesley Publishing Company, Inc., Reading, Mass., 1957), Chap. 15, p. 469.

predicted:

$$G_r(\lambda,\tau)=G_s[\lambda(\Theta)\tau],\quad G_s(\tau)=G_r(\lambda=1,\tau),\qquad \text{(IV.10)}$$

where $\vartheta_{ij}=\theta_{ij}$. (IV.10) follows from the observation that $\mathcal{H}_s$ and $h_0$ always occur in the combination $\mathcal{H}_s\tau$ and $h_0\tau$ in $R(\tau)$. Given the experimentally observed function $G_r(\tau)$ at one angle $\Theta$, its form at all angles follows if the internuclear interaction is predominantly of the dipole type. It is important to note that exactly the same statements (IV.10) can be made for a powdered sample.

As the angle between the axis of rotation and the magnetic field is gradually increased from zero, the function $G_s(\tau)$ is dilated by change of scale along the time axis. In addition, the moments of the rf absorption line $\Gamma(\omega)$ as a function of $\Theta$ change in a predictable manner:

$$\begin{aligned}&M_n(\Theta)=M_n[\lambda(\Theta)]^n,\\ &M_n=M_n(\Theta=0)\ \text{(static lattice moments)}\\ &\qquad\text{(pure dipole interaction).}\end{aligned}\qquad \text{(IV.11)}$$

A method for determining the strength of the "exchange interaction" coefficient $B_{ij}$ will now be outlined. The variation of the angle $\Theta$ is an experimental method for weakening the effective strength of the dipole interaction coefficient, or view another way, of strengthening the effective "exchange interaction" coefficient, $B_{ij}$. In fact, the dipole interaction is effectively zero for $\Theta=\cos^{-1}(\frac{1}{3})^{\frac{1}{2}}$. Supposing now that for $\lambda(\Theta)=1$ the dipole interaction completely dominates the line shape, we can increase $\Theta$ until $G_r(\tau)$ is no longer given by (IV.10). At this point the exchange interaction will dominate (since the dipole interaction strength has been decreased in magnitude by as much as was necessary). Now a knowledge of the second and fourth moment of the residual resonance absorption line enables the calculation of the relative magnitude of $B_{ij}$ to $A_{ij}$, a possibility first indicated by Van Vleck and Gorter[17] in their treatment of nuclei interacting with strong exchange interactions. We defer until the next section the calculation of the moments of the line for rotating lattice.

At the angle $\Theta=\cos^{-1}[(\frac{1}{3})^{\frac{1}{2}}]$:

$$\begin{aligned}G_r(\tau)=\mathrm{Tr}\{L_x\exp[i\textstyle\sum B_{ij}\mathbf{l}_i\cdot\mathbf{l}_j\tau]L_x\\ \times\exp[-i\textstyle\sum B_{ij}\mathbf{l}_i\cdot\mathbf{l}_j\tau]\}=\mathrm{Tr}L_x^2,\end{aligned}\qquad \text{(IV.12)}$$

and so $T_2$ becomes "infinite" $(=T_1)$, a phenomenon which can be experimentally investigated. Finally, attention should be directed to another criterion for $B_{ij}=0$, the independence of $G_r(\lambda,\tau)$ on the sign of $\lambda$:

$$\begin{aligned}G_r(\lambda,\tau)=\mathrm{Tr}\{L_x\exp[i\textstyle\sum\lambda A_{ij}(\mathbf{l}_i\cdot\mathbf{l}_j-3\mathbf{l}_i\cdot\hat{H}\mathbf{l}_j\cdot\hat{H})]L_x\\ \exp[-\textstyle\sum\lambda A_{ij}(\mathbf{l}_i\cdot\mathbf{l}_j-3\mathbf{l}_i\cdot\hat{H}\mathbf{l}_j\cdot\hat{H})]\}\\ =G_r(-\lambda,\tau)\ \text{(pure dipole interaction).}\end{aligned}\qquad \text{(IV.13)}$$

[17] C. Gorter and J. Van Vleck, Phys. Rev. **72**, 1128 (1947).

In summary, the lattice at ultra-high mechanical rotation frequencies $\Omega/A_{ij}\gg1$; $\Omega/B_{ij}\gg1$ provides a means of controlling the relative strengths of the dipole and "exchange" internuclear interactions and thereby studying the effects and magnitude of each.

## V. ROTATIONAL MODIFICATION OF THE ABSORPTION LINE MOMENTS

Because the attainment of mechanical rotation frequencies necessary to produce the limiting situations discussed in Sec. IV is still, for some resonating solids, a refractory experimental project, the consequences of crystal rotations of intermediate frequencies ($\sim10^4$ cps) are of practical significance.

In order to write $R(\tau)$ of (I.17) in a more readily evaluable form, we observe that

$$\begin{aligned}&\mathrm{Tr}[A^{-1}L_xAL_x]\\ &\quad=\mathrm{Tr}L_x^2+\frac{1}{2!}\frac{d^2}{d\alpha^2}\mathrm{Tr}[A^{-1}e^{iL_x\alpha}Ae^{-iL_x\alpha}]|_{\alpha=0},\end{aligned}\qquad \text{(V.1)}$$

where $A=$arbitrary operator, and so

$$\begin{aligned}&R(\tau)=\lim_{T\to\infty}\Big\{\mathrm{Tr}(L_x^2)+\frac{1}{2!}\frac{d^2}{d\alpha^2}\mathrm{Tr}[W^\dagger(t_2,t_1)\\ &\qquad\qquad\times W'(t_2,t_1)]|_{\alpha=0}\Big\},\\ &W(t_2,t_1)=1-i\int_{t_1}^{t_2}\mathcal{H}_i(t)W(t,t_1)dt,\\ &W'(t_2,t_1)=1-i\int_{t_1}^{t_2}\mathcal{H}_i'(t)W'(t,t_1)dt,\\ &\mathcal{H}_i'(t)\equiv e^{iL_x\alpha}\mathcal{H}_i(t)e^{-iL_x\alpha},\\ &t_2=T+\tau;\quad t_1=T,\end{aligned}\qquad \text{(V.2)}$$

The remaining problem is the evaluation of

$$\mathrm{Tr}[W^\dagger(t_2,t_1)W'(t_2,t_1)].$$

To this end, we first find $\mathcal{H}_i'(t)$ from $\mathcal{H}_i(t)$ of (IV.1):

$$\begin{aligned}\mathcal{H}_i'(t)&=e^{iL_x\alpha}\mathcal{H}_i(t)e^{-iL_x\alpha}\\ &=\mathcal{H}_i(t)-3\textstyle\sum A_{ij}[1-3\cos^2\theta_{ij}(t)]\\ &\quad\times(l_i^yl_j^y-l_i^zl_j^z)\sin^2\alpha\\ &\quad-3\textstyle\sum A_{ij}[1-3\cos^2\theta_{ij}(t)]l_i^zl_j^z\sin2\alpha,\end{aligned}\qquad \text{(V.3)}$$

$$\begin{aligned}A_{ij}&(1-3\cos^2\theta_{ij}(t))\\ &=a_{ij}+b_{ij}\cos(\Omega t+\varphi_{ij}-\Phi)\\ &\quad+c_{ij}\cos2(\Omega t+\varphi_{ij}-\Phi),\end{aligned}$$

$a_{ij}$, $b_{ij}$, and $c_{ij}$ are defined in (IV.3). Use has been made of

$$e^{iL_x\alpha}\mathbf{l}_i\cdot\mathbf{l}_je^{-iL_x\alpha}=\mathbf{l}_i\cdot\mathbf{l}_j,$$

$$\begin{aligned}e^{iL_x\alpha}l_1^zl_j^ze^{-iL_x\alpha}&=(l_i^z\cos\alpha+l_i^y\sin\alpha)(l_j^z\cos\alpha+l_j^y\sin\alpha)\\ &=l_i^zl_j^z+(l_i^yl_j^y-l_i^zl_j^z)\sin^2\alpha\\ &\quad+(l_i^zl_j^y+l_i^yl_j^z)\sin\alpha\cos\alpha.\end{aligned}\qquad \text{(V.4)}$$

It does not appear possible to solve the integral equation for $W(t_2,t_1)$ and $W'(t_2,t_1)$ in closed form. However, as we demonstrate below, if the integral equation be solved by iteration, only the first $n$ iterates contribute to the $n$th moment. Hence, an iterate solution is sufficient for the calculation of absorptive line moments:

$$W(t_2,t_1)=\sum_{n=0}^{\infty}(-i)^n I_n(t_2,t_1),$$

$$I_n(t_2,t_1)=\int_{t_1}^{t_2} ds_1\int_{t_1}^{s_1} ds_2\cdots\int_{t_1}^{s_{n-1}} ds_n\, \mathcal{H}_i(s_1)\times\mathcal{H}_i(s_2)\cdots\mathcal{H}_i(s_n),\qquad I_0=1, \tag{V.5}$$

and

$$W'(t_2,t_1)=\sum_{n=0}^{\infty}(-i)^n I_n'(t_2,t_1),$$

$$I_n'(t_2,t_1)=\int_{t_1}^{t_2} ds_1\int_{t_1}^{s_1} ds_2\cdots\int_{t_1}^{s_{n-1}} ds_n\, \mathcal{H}_i'(s_1)\times\mathcal{H}_i'(s_2)\cdots\mathcal{H}_i'(s_n),\qquad I_0'=1. \tag{V.6}$$

The substitution of (V.5) and (V.6) into

$$\mathrm{Tr}[W^\dagger(t_2,t_1)W'(t_2,t_1)]$$

yields

$$\mathrm{Tr}W^\dagger(t_2,t_1)W'(t_2,t_1)=\sum_{n=0}^{\infty}(-i)^n\{\sum_{r=0}^{n}(-)^r\,\mathrm{Tr}[I_r^\dagger I_{n-r}']\}. \tag{V.7}$$

That all the odd-order terms, i.e., $n$ odd, are zero is now to be demonstrated. For $n$ odd:

$$\begin{aligned}\frac{d^2}{d\alpha^2}\sum_{r=0}^{n}(-)^r\,\mathrm{Tr}[I_r^\dagger I_{n-r}']|_{\alpha=0}
&=\frac{1}{2}\frac{d^2}{d\alpha^2}\sum_{r=0}^{n}(-)^r\,\mathrm{Tr}[I_r^\dagger I_{n-r}'-I_{n-r}^\dagger I_r']|_{\alpha=0}\\
&=\frac{1}{2}\frac{d^2}{d\alpha^2}\sum_{r=0}^{n}(-)^r\{[\mathrm{Tr}(I_r^\dagger I_{n-r}')]-[\mathrm{Tr}(I_r^\dagger I_{n-r}')]^*\}|_{\alpha=0}\\
&=i\frac{d^2}{d\alpha^2}\sum_{r=0}^{n}(-)^r\,\mathrm{Im}\,\mathrm{Tr}[I_r^\dagger I_{n-r}']|_{\alpha=0},\end{aligned} \tag{V.8}$$

where we have used

$$\frac{d^2}{d\alpha^2}\mathrm{Tr}[I_{n-r}^\dagger e^{iL_x\alpha}I_r r^{-iL_x\alpha}]|_{\alpha=0}=\frac{d^2}{d\alpha^2}\mathrm{Tr}[I_{n-r}^\dagger e^{-iL_x\alpha}I_r e^{iL_x\alpha}]|_{\alpha=0}. \tag{V.9}$$

Now $(d^2/d\alpha^2)\,\mathrm{Tr}(I_r^\dagger I_{n-r}')|_{\alpha=0}$ is real because $\mathcal{H}_i$ and $\mathcal{H}_i'$ can be chosen as real if the ordinary representation of the angular momentum operators is chosen, viz., $l_i^x$ and $l_i^z$ has real, $l_i^y$ pure imaginary matrix elements. The proof of the reality of the trace in such a representation rests upon the observation that although $l_i^y$ is pure imaginary, it always occurs an even number of times in the traces of form (V.8). [The term

$$-3\sum A_{ij}(1-3\cos^2\theta_{ij}(t))l_i^y l_j^z\sin 2\alpha$$

must itself occur an even number of times in any nonvanishing trace of the form (V.8) because its coefficient $\sin 2\alpha$ is an odd function of $\alpha$.] Thus the odd-order terms in $n$ of (V.7) vanish.

For the even $n$ terms of (V.7), one can effectively write

$$\sum_{r=0}^{n}(-)^r\,\mathrm{Tr}[I_r^\dagger I_{n-r}']\to 2\sum_{r=1}^{\frac{1}{2}n-1}(-)^r\,\mathrm{Tr}[I_r^\dagger I_{n-r}']+(-)^{\frac{1}{2}n}\,\mathrm{Tr}[I_{n/2}^\dagger I_{n/2}'] \tag{V.10}$$

by reasoning similar to that given above for the odd $n$ terms and the observation that

$$(d^2/d\alpha^2)[\mathrm{Tr}I_n']=(d^2/d\alpha^2)[\mathrm{Tr}I_n]=0.$$

A second general property of (V.7) to which allusion has already been made is

$$\frac{d^m}{dt_2^m}\sum_{r=0}^{n}(-)^r\,\mathrm{Tr}[I_r^\dagger(t_2,t_1)I_{n-r}'(t_2,t_1)]|_{t_2=t_1}=0\qquad\text{for } m<n, \tag{V.11}$$

the theorem being a consequence of

$$\begin{aligned}&\frac{d^m}{dt_2^m}I_n(t_2,t_1)|_{t_2=t_1}=0\quad\text{for } m<n,\\
&\frac{d^m}{dt_2^m}I_n'(t_2,t_1)|_{t_2=t_1}=0\quad\text{for } m<n,\\
&\frac{d^m}{dt^m}ab=\sum_{l=0}^{m}\binom{m}{l}\frac{d^l a}{dt^l}\frac{d^{m-l}b}{dt^{m-l}}.\end{aligned} \tag{V.12}$$

If the following definition is adopted:

$$\mathrm{Tr}[W^\dagger(t_2,t_1)W'(t_2,t_1)]\equiv\sum_{n=0}^{\infty}S_n,$$

$$\begin{aligned}S_n&=\{(-i)^n\sum_{r=0}^{n}(-)^r\,\mathrm{Tr}[I_r^\dagger I_{n-r}']\}\\
&=\{2\sum_{r=1}^{\frac{1}{2}n-1}(-)^r\,\mathrm{Tr}[I_r^\dagger I_{n-r}']+(-)^{n/2}\,\mathrm{Tr}[I_{n/2}^\dagger I_{n/2}']\}(-)^{n/2},\quad n\text{ even}\\
S_n&=0,\quad n\text{ odd},\end{aligned} \tag{V.13}$$

then $d^2S_0/d\alpha^2|_{\alpha=0}=0$ and the first nonvanishing $S$ is $S_2$:

$$S_2=+\mathrm{Tr}[I_1^\dagger I_1'],$$

$$I_1=\int_{t_1}^{t_2}\mathcal{H}_i(s)ds=\int_{t_1}^{t_2}\{\sum A_{ij}(\mathbf{l}_i\cdot\mathbf{l}_j-3\mathbf{l}_i\cdot\hat{H}\mathbf{l}_j\cdot\hat{H})$$

$$\times(1-3\cos^2\theta_{ij}(s))+\sum B_{ij}\mathbf{l}_i\cdot\mathbf{l}_j\}ds,\quad \text{(V.14)}$$

$$I_1'=\int_{t_1}^{t_2}\mathcal{H}_i'(s)ds\to\int_{t_1}^{t_2}\{-3\sum A_{ij}[1-3\cos^2\theta_{ij}(s)]$$

$$\times(l_i^yl_j^y-l_i^zl_j^z)\sin^2\alpha\}ds.$$

Here $\mathcal{H}_i'(s)$ has been replaced by its only member which does not vanish upon operating with $d^2/d\alpha^2$ and evaluating the result at $\alpha=0$. The traces in $S_2$ are evaluated without difficulty:

$$\mathrm{Tr}[\mathbf{l}_i\cdot\mathbf{l}_j(l_m^yl_n^y-l_m^zl_n^z)]=0,$$

$$\mathrm{Tr}[l_i^zl_j^z(l_m^yl_n^y-l_m^zl_n^z)]_{i\neq j,m\neq n}$$
$$=-(2l+1)^{N-2}[\tfrac{1}{3}(l+1)(2l+1)]^2[\delta_{im}\delta_{jn}+\delta_{in}\delta_{jm}].\quad \text{(V.15)}$$

Appendixes C and D contain several remarks on the evaluation of traces which are encountered in (V.15) and in $S_4$.

Both $I_1$ and $I_1'$ contain the integral:

$$\int_{t_1}^{t_2}A_{ij}[1-3\cos^2\theta_{ij}(t)]dt$$
$$=\int_{t_1}^{t_2}[a_{ij}+b_{ij}\cos(\Omega t+\varphi_{ij}-\Phi)$$
$$+c_{ij}\cos 2(\Omega t+\varphi_{ij}-\Phi)]dt$$
$$=a_{ij}(t_2-t_1)+(2b_{ij}/\Omega)\sin[\tfrac{1}{2}\Omega(t_2-t_1)]$$
$$\times\sin[\tfrac{1}{2}\Omega(t_2+t_1)+\varphi_{ij}-\Phi]$$
$$+(c_{ij}/\Omega)\sin[\Omega(t_2-t_1)]$$
$$\times\sin\{2[\tfrac{1}{2}\Omega(t_2+t_1)+\varphi_{ij}-\Phi]\}.\quad \text{(V.16)}$$

With $t_2=T+\tau$, $t_1=T$:

$$\lim_{T\to\infty}A_{ij}\int_{t_1}^{t_2}[1-3\cos^2\theta_{ij}(t)]dt$$
$$\times A_{mn}\int_{t_1}^{t_2}[1-3\cos^2\theta_{mn}(t)]dt\quad \text{(V.17)}$$
$$=a_{ij}a_{mn}\tau^2+2(b_{ij}b_{mn}/\Omega^2)\cos(\varphi_{ij}-\varphi_{mn})\sin^2(\tfrac{1}{2}\Omega\tau)$$
$$+\tfrac{1}{2}(c_{ij}c_{mn}/\Omega^2)\cos[2(\varphi_{ij}-\varphi_{mn})]\sin^2\Omega\tau,$$
$$\tau=t_2-t_1.$$

We now have $R(\tau)$ approximated for small times $\tau$ by:

$$R(\tau)=\mathrm{Tr}L_x^2-2\sum 3^2[l(l+1)/3]^2(2l+1)^N$$
$$\times[a_{ij}^2\tau^2+2(b_{ij}^2/\Omega^2)\sin^2(\tfrac{1}{2}\Omega\tau)$$
$$+\tfrac{1}{2}(c_{ij}^2/\Omega^2)\sin^2\Omega\tau],$$
$$\mathrm{Tr}L_x^2=Nl(l+1)(2l+1)^N/3,$$

where $N$ = number of nuclear spins,

$$a_{ij}=A_{ij}(1-3\cos^2\vartheta_{ij})(3\cos^2\Theta-1)/2,$$
$$b_{ij}=-\tfrac{3}{2}A_{ij}\sin 2\vartheta_{ij}\sin 2\Theta,\quad \text{(V.18)}$$
$$c_{ij}=-\tfrac{3}{2}A_{ij}\sin^2\vartheta_{ij}\sin^2\Theta.$$

Although only a power series development of $R(\tau)$ up to $\tau^2$ is needed to find the second moment of the absorption line, the terms oscillatory in $\Omega$ have purposely been kept in (V.18). The expected invariance of the azimuthally averaged second moment against motional narrowing is a consequence of the expansion:

$$\left(\frac{2}{\Omega}\right)^2\sin^2(\tfrac{1}{2}\Omega\tau)=\tau^2-\frac{1}{3!}\left(\frac{\Omega}{2}\right)^2\tau^4+\cdots,$$
$$\left(\frac{1}{\Omega}\right)^2\sin^2\Omega\tau=\tau^2-\frac{1}{3!}\Omega^2\tau^4+\cdots,\quad \text{(V.19)}$$

because the coefficient of $\tau^2$ is independent of $\Omega$. By putting in the form (V.18), the uhf rotation limit is again exhibited:

$$\lim_{\Omega\to\infty}R(\tau)=\mathrm{Tr}[L_x^2]-2\sum 3^2[l(l+1)/3]^2$$
$$\times(2l+1)^Na_{ij}^2\tau^2,\quad \text{(V.20)}$$
$$\lim_{\Omega\to\infty}\frac{\sin^2(\tfrac{1}{2}\Omega\tau)}{\Omega^2}=0,$$

in agreement with the more general results of Sec. IV [in particular with (IV.11)]. Note that in the uhf rotation limit the second moment of the observable residual line is decreased by the motion while the sum of the second moment of the unobservable distant satellite lines and that of the residual line add up to the azimuthally averaged static lattice value.

As in the case of magnetic resonance in a static lattice, the evaluation of $S_4$ involves a large number of essentially trivial manipulations. From (V.13), we find:

$$S_4=-2\,\mathrm{Tr}(I_3^\dagger I_1')+\mathrm{Tr}(I_2^\dagger I_2'),$$

$$I_2^\dagger=\int_{t_1}^{t_2}ds_1\int_{t_1}^{s_1}ds_2\,\mathcal{H}_i(s_2)\mathcal{H}_i(s_1),$$

$$I_2'=\int_{t_1}^{t_2}ds_1\int_{t_1}^{s_1}ds_2\,\mathcal{H}_i'(s_1)\mathcal{H}_i'(s_2),\quad \text{(V.21)}$$

$$I_3^\dagger=\int_{t_1}^{t_2}ds_1\int_{t_1}^{s_1}ds_2\int_{t_1}^{s_2}ds_3\,\mathcal{H}_i(s_3)\mathcal{H}_i(s_2)\mathcal{H}_i(s_1),$$

$$I_1'=\int_{t_1}^{t_2}ds_1\,\mathcal{H}_i'(s_1).$$

We delimit considerations of $S_4$ to the specific case:

$$\begin{aligned} B_{ij}&=0, \quad \text{[see Eq. (IV.1)]} \\ \Theta&=\pi/2, \quad \text{[see Eq. (IV.3)]}. \end{aligned} \tag{V.22}$$

The more general case results in expressions which are almost identically algebraically constructed but multiplicatively increased in length. Besides, the choice of $\Theta=\pi/2$ implies $b_{ij}=0$ and hence as far as the formal calculation is concerned the rotation frequency is effectively doubled since now $\Omega$ always enters with a coefficient of 2.

With the restrictions (V.22) in mind, we introduce the following symbols:

$$f_{ij}(T,\tau)\equiv\int_{t_1}^{t_2} A_{ij}[1-3\cos^2\theta_{ij}(s_1)]ds_1,$$

$$f_{ij,kl}(T,\tau)\equiv A_{ij}A_{kl}\int_{t_1}^{t_2} ds_1\int_{t_1}^{s_1} ds_2[1-3\cos^2\theta_{ij}(s_2)][1-3\cos^2\theta_{kl}(s_1)], \tag{V.23}$$

$$f_{ij,kl,mn}(T,\tau)\equiv A_{ij}A_{kl}A_{mn}\int_{t_1}^{t_2} ds_1\int_{t_1}^{s_1} ds_2\int_{t_1}^{s_3} ds_3[1-3\cos^2\theta_{ij}(s_3)][1-3\cos^2\theta_{kl}(s_2)][1-3\cos^2\theta_{mn}(s_1)],$$

$$A_{ij}[1-3\cos^2\theta_{ij}(t)]=a_{ij}+b_{ij}\cos(\Omega t+\varphi_{ij}-\Phi)+c_{ij}\cos2(\Omega t+\varphi_{ij}-\Phi),$$

with $a_{ij}$, $b_{ij}$, and $c_{ij}$ defined in (IV.3). The forms of the $f$'s are simple, but tedious to calculate. In terms of these $f$'s, $S_4$ can be rewritten as

$$\begin{aligned} S_4=&\sum f_{ij,kl}f_{mn,rs}\,\mathrm{Tr}[(\mathbf{l}_k\cdot\mathbf{l}_l-3\mathbf{l}_k{}^z\mathbf{l}_l{}^z)(\mathbf{l}_i\cdot\mathbf{l}_j-3l_i{}^zl_j{}^z)e^{iL_x\alpha}(\mathbf{l}_m\cdot\mathbf{l}_n-3l_m{}^zl_n{}^z)(\mathbf{l}_r\cdot\mathbf{l}_s-3l_r{}^zl_s{}^z)e^{-iL_x\alpha}] \\ &-2\sum f_{ij,kl,mn}f_{rs}\,\mathrm{Tr}[(\mathbf{l}_m\cdot\mathbf{l}_n-3l_m{}^zl_n{}^z)(\mathbf{l}_k\cdot\mathbf{l}_l-3l_k{}^zl_l{}^z)(\mathbf{l}_i\cdot\mathbf{l}_j-3l_i{}^zl_j{}^z)e^{iL_x\alpha}(\mathbf{l}_r\cdot\mathbf{l}_s-3l_r{}^zl_s{}^z)e^{-iL_x\alpha}], \end{aligned} \tag{V.24}$$

and further:

$$\lim_{T\to\infty}\frac{1}{2!}\frac{d^2}{d\alpha^2}S_4\bigg|_{\alpha=0}=\sum\lim_{T\to\infty}(f_{ij,kl}f_{mn,rs})T^{(1)}{}_{ij,kl,mn,rs}-2\sum\lim_{T\to\infty}(f_{ij,kl,mn}f_{rs})T^{(2)}{}_{ij,kl,mn,rs}, \tag{V.25}$$

where $T^{(1)}{}_{ij,kl,mn,rs}$ and $T^{(2)}{}_{ij,kl,mn,rs}$ are tensors formed from the traces over the angular momentum operators:

$$\begin{aligned} T^{(1)}{}_{ij,kl,mn,rs}=&36\,\mathrm{Tr}[(\mathbf{l}_k\cdot\mathbf{l}_l-3l_k{}^zl_l{}^z)(\mathbf{l}_i\cdot\mathbf{l}_j-3l_i{}^zl_j{}^z)l_m{}^yl_n{}^zl_r{}^yl_s{}^z] \\ &-3\,\mathrm{Tr}[(\mathbf{l}_k\cdot\mathbf{l}_l-3l_k{}^zl_l{}^z)(\mathbf{l}_i\cdot\mathbf{l}_j-3l_i{}^zl_j{}^z)(\mathbf{l}_m\cdot\mathbf{l}_n-3l_m{}^zl_n{}^z)(\mathbf{l}_i\cdot\mathbf{l}_s-3l_r{}^zl_s{}^z)], \end{aligned} \tag{V.26}$$

$$T^{(2)}{}_{ij,kl,mn,rs}=-\tfrac{3}{2}\,\mathrm{Tr}[(\mathbf{l}_m\cdot\mathbf{l}_n-3l_m{}^zl_n{}^z)(\mathbf{l}_k\cdot\mathbf{l}_l-3l_k{}^zl_l{}^z)(\mathbf{l}_i\cdot\mathbf{l}_j-3l_i{}^zl_j{}^z)(\mathbf{l}_r\cdot\mathbf{l}_s-3l_r{}^zl_s{}^z)].$$

The somewhat lengthy result of evaluating $T^{(1)}{}_{ij,kl,mn,rs}$ and $T^{(2)}{}_{ij,kl,mn,rs}$ is relegated to Appendix D. If only the terms which contribute to the fourth moment be kept, the limits contained in (V.25) are

$$\begin{aligned} \lim_{T\to\infty} f_{ij,kl}f_{mn,rs}=&a_{ij}a_{kl}a_{mn}a_{rs}(\tau^4/4)+a_{ij}a_{kl}c_{mn}c_{rs}\tfrac{1}{2}\cos[2(\varphi_{ij}-\varphi_{kl})]\tau^2(\sin^2\Omega\tau)/4\Omega^2 \\ &+c_{ij}a_{kl}c_{mn}a_{rs}\cos[2(\varphi_{kl}-\varphi_{mn})](\tau/2\Omega)^2\sin^2\Omega\tau+c_{ij}a_{kl}a_{mn}c_{rs}\tfrac{1}{2}\cos[2(\varphi_{ij}-\varphi_{rs})](\tau/2\Omega)^2\sin^2\Omega\tau \\ &+a_{ij}c_{kl}c_{mn}a_{rs}\tfrac{1}{2}\cos[2(\varphi_{kl}-\varphi_{rs})](\tau/2\Omega)^2\sin^2\Omega\tau \\ &+c_{ij}c_{kl}c_{mn}c_{rs}\tfrac{1}{2}\cos[2(\varphi_{kl}+\varphi_{ij}-\varphi_{mn}-\varphi_{rs})](\sin^2\Omega\tau/4\Omega\tau)^2, \end{aligned} \tag{V.26a}$$

$$\lim_{T\to\infty} f_{ij,kl,mn}f_{rs}=a_{ij}a_{kl}a_{mn}a_{rs}\frac{\tau^4}{6}+c_{ij}c_{kl}a_{mn}a_{rs}\cos[2(\varphi_{ij}-\varphi_{kl})]\frac{\tau}{\Omega}\left[\frac{\tau}{2\Omega}-\frac{\sin 2\Omega\tau}{4\Omega^2}\right]$$

$$+c_{ij}a_{kl}c_{mn}a_{rs}\cos[2(\varphi_{mn}-\varphi_{ij})]\frac{\tau}{2\Omega}\left[\frac{\sin 2\Omega\tau}{4\Omega^2}-\frac{\tau}{2\Omega}\right]$$

$$+a_{ij}c_{kl}c_{mn}a_{rs}\cos[2(\varphi_{mn}-\varphi_{kl})]\frac{\tau}{2\Omega}\left[\frac{\tau}{4\Omega}-\frac{\sin 2\Omega\tau}{8\Omega^2}\right]$$

$$+c_{ij}a_{kl}a_{mn}c_{rs}\cos[2(\varphi_{ij}-\varphi_{rs})]\frac{\sin\Omega\tau}{4\Omega^2}\left[\frac{\tau\cos\Omega\tau}{2\Omega}-\frac{1}{2\Omega^2}\sin\Omega\tau+\frac{\tau^2}{2}\sin\Omega\tau\right]$$

$$+a_{ij}c_{kl}a_{mn}c_{rs}\cos[2(\varphi_{kl}-\varphi_{rs})]\frac{\sin\Omega\tau}{8\Omega^3}\left[\frac{2}{\Omega}\sin\Omega\tau-2\tau\cos\Omega\tau\right]$$

$$+a_{ij}a_{kl}c_{mn}c_{rs}\cos[2(\varphi_{mn}-\varphi_{rs})]\frac{\sin\Omega\tau}{32\Omega^2}\left[4\tau^2\sin\Omega\tau+\frac{4\tau}{\Omega}\cos\Omega\tau-\frac{4}{\Omega^2}\sin\Omega\tau\right]$$

$$+c_{ij}c_{kl}c_{mn}c_{rs}\frac{\sin\Omega\tau}{8\Omega^2}\Bigg\{\cos[2(\varphi_{ij}+\varphi_{kl}-\varphi_{mn}-\varphi_{rs})]\left[\frac{\tau\cos\Omega\tau}{4\Omega}-\frac{1}{8\Omega^2}\sin\Omega\tau-\frac{1}{8\Omega^2}\sin\Omega\tau\cos 2\Omega\tau\right]$$

$$+\cos[2(\varphi_{mn}+\varphi_{kl}-\varphi_{ij}-\varphi_{rs})]\left[\frac{\tau}{4\Omega}\cos\Omega\tau-\frac{1}{8\Omega^2}\cos\Omega\tau\sin 2\Omega\tau\right]$$

$$+\cos[2(\varphi_{mn}+\varphi_{ij}-\varphi_{kl}-\varphi_{rs})]\left[-\frac{\tau}{2\Omega}\cos\Omega\tau+\frac{\sin\Omega\tau}{2\Omega^2}\right]\Bigg\}. \quad \text{(V.26b)}$$

Equations (V.26a) and (V.26b) again demonstrate how the asymptotic limit is recovered for large $\Omega$. In addition, it will be observed that the final expression for

$$\lim_{T\to\infty}\left(\frac{1}{2!}\frac{d^2}{d\alpha^2}S_4\right)$$

is independent of $\Phi$, the arbitrary phase angle of crystal orientation. That such should be the case is a consequence of the equivalence of averaging over $\Phi$ and of taking the limit $T\to\infty$. Putting together (V.25), (V.26), the expressions of Appendix E, and the previous result (V.18) yields $R(\tau)$ correct up to terms in $\tau^4$:

$$R(\tau)=\mathrm{Tr}L_x^2-2\sum 3^2\left(\frac{l(l+1)}{3}\right)^2(2l+1)^N$$
$$\times\left[a_{ij}^2\tau^2+2\frac{b_{ij}^2}{\Omega^2}\sin^2(\tfrac{1}{2}\Omega\tau)+\frac{1}{2}\frac{c_{ij}^2}{\Omega^2}\sin^2\Omega t\right]$$
$$+\lim_{T\to\infty}\frac{1}{2!}\frac{d^2}{d\alpha^2}S^4\bigg|_{\alpha=0}. \quad \text{(V.27)}$$

Note that the fourth moment which is calculated by the prescription of (I.20) receives contributions also from (V.18).

The method of calculation of the moments presented in this section will, in a subsequent paper, be used to evaluate the moments for specific crystal structures in order to compare the results with the data to be presented.

## CONCLUSION

By high-speed mechanical rotation of a resonated solid, new possibilities for the measurement of the magnetic properties of matter arise. For example, the "exchange type" interactions between nuclei in solids can be measured by the method proposed in Sec. IV. The prediction of the effect of spinning on the resonant absorption line (Sec. V) also invites detailed experimental verification. Perhaps the experiment most simply suited to an exhaustive comparison with theory is a resonance experiment on a quasi-isolated nuclear pair rigidly bound in a solid lattice.

Further research along the line of resonance in rotating solids is indicated. Among the problems remaining are the generalization of the formalism to the case of nuclei possessed of a quadrupole moment and the effect of rotation upon $T_1$ especially in solids in a low external magnetic field.

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## APPENDIX A. TRUNCATION OF THE DIPOLE INTERACTION HAMILTONIAN AND THE uhf ROTATION LIMIT

An operator expression of the type $\mathbf{l}_i\cdot\hat{r}\;\mathbf{l}_2\cdot\hat{r}$ can be mutated into a form where its properties under rotation are more transparent:

$$\mathbf{l}_1\cdot\hat{r}\;\mathbf{l}_2\cdot\hat{r}=(4\pi/3)^2\sum_{mm'}\mathcal{Y}_{1m}(\mathbf{l}_1)\mathcal{Y}_{1m}{}^*(\mathbf{r})\mathcal{Y}_{m'}(\mathbf{l}_2)\mathcal{Y}_{1m'}{}^*(\mathbf{r}),\tag{A.1}$$

where $\mathcal{Y}_{1m}(\mathbf{A})$ = spherical harmonic polynomial in the components of $\mathbf{A}=(A_x,A_y,A_z)$ taken in the coordinate system with the $z$ axis along the applied external magnetic field. By introducing the definitions,

$$\begin{aligned}Z_{LM}(\mathbf{l}_1,\mathbf{l}_2)&\equiv\sum_{mm'}C_{mm'M}{}^{11L}\mathcal{Y}_{1m}(\mathbf{l}_1)\mathcal{Y}_{1m'}(\mathbf{l}_2),\\ Z_{LM}(\mathbf{r})&\equiv\sum_{mm'}C_{mm'M}{}^{11L}\mathcal{Y}_{1m}(\mathbf{r})\mathcal{Y}_{1m}(\mathbf{r}),\end{aligned}\tag{A.2}$$

where $C_{mm'M}{}^{11L}\equiv$ Clebsch-Gordan coefficient, we find

$$(\mathbf{l}_1\cdot\hat{r})(\mathbf{l}_2\cdot\hat{r})=(4\pi/3)^2\sum_{LM}Z_{LM}{}^*(\mathbf{r})Z_{LM}(\mathbf{l}_1\mathbf{l}_2).\tag{A.3}$$

Now $Z_{LM}(\mathbf{l}_1\mathbf{l}_2)$ when operating on a state with magnetic quantum number $M'$ generates a state with magnetic quantum number $M'+M$ (Wigner-Eckart theorem[18]). Hence truncation of the operator $\mathbf{l}_1\cdot\hat{r}\;\mathbf{l}_2\cdot\hat{r}$ occurring in the dipole interaction amounts to retaining only $M=0$ terms in (A.3):

$$\begin{aligned}\mathbf{l}_1\cdot\hat{r}\;\mathbf{l}_2\cdot\hat{r}&\rightarrow(4\pi/3)^2\textstyle\sum_L Z_{L0}(\mathbf{r})Z_{L0}(\mathbf{l}_1\mathbf{l}_2)\\ &=\tfrac{1}{3}\mathbf{l}_1\cdot\mathbf{l}_2r^2+\tfrac{1}{6}(\mathbf{l}_1\cdot\mathbf{l}_2-3l_1{}^zl_2{}^z)r^2(1-3\cos^2\theta),\\ Z_{L0}{}^\dagger(\mathbf{r})&=Z_{L0}(\mathbf{r}),\\ Z_{00}(\mathbf{r})Z_{00}(\mathbf{l}_1\mathbf{l}_2)&=\tfrac{1}{3}(3/4\pi)^2\mathbf{l}_1\cdot\mathbf{l}_2r^2,\\ Z_{10}(\mathbf{r})Z_{10}(\mathbf{l}_1\mathbf{l}_2)&=0,\\ Z_{20}(\mathbf{r})Z_{20}(\mathbf{l}_1\mathbf{l}_2)&=\tfrac{1}{6}(3/4\pi)^2r^2(1-3\cos^2\theta)(\mathbf{l}_1\cdot\mathbf{l}_2-3\mathbf{l}_1{}^z\mathbf{l}_2{}^z).\end{aligned}\tag{A.4}$$

The reason why rotation of the lattice can control the truncated dipole interaction strength rests upon the decomposition of the form $-[(1-3\cos^2\theta)/2]=P_2(\cos\theta)$:

$$P_2(\cos\theta)=(4\pi/5)\textstyle\sum_m Y_{2m}(\vartheta,\varphi)Y_{2m}{}^*(\Theta,\Phi),\tag{A.5}$$

where the angles have been defined in (II.5) and Fig. 1. Rotation of the lattice causes $\varphi$ to oscillate very rapidly and so

$$\begin{aligned}P_2(\cos\theta)\rightarrow(4\pi/5)Y_{20}(\vartheta,\varphi)Y_{20}(\Theta,\Phi)\\ =P_2(\cos\vartheta)P_2(\cos\Theta),\end{aligned}\tag{A.6}$$

since only the $m=0$ terms of (A.5) are independent of $\varphi$. $P_2(\cos\Theta)$ is essentially the factor which controls the strength of the effective dipole interaction.

## APPENDIX B. ALGEBRA OF DIRECT PRODUCTS

The spin degrees of freedom of $N$ spin-$l$ nuclei lead to the consideration of a $(2l+1)N$-dimensional space representing the possible total spin states of the $N$ nuclei. Of the many possible bases spanning this space, the one which is useful for our purposes is the base of of ket vectors $|m_1m_2\cdots m_N\rangle$ formed from the direct product of the base vectors of the individual $(2l+1)$-dimensional spin spaces characterized by a magnetic quantum number $m$:

$$\begin{aligned}|m_1m_2\cdots m_N\rangle&\equiv|m_1\rangle\otimes|m_2\rangle\otimes\cdots\otimes|m_N\rangle,\\ m_i&=l,\,l-1,\,\cdots,\,-l+1,\,-l.\end{aligned}\tag{B.1}$$

The direct product $A_i\otimes B_j$ of two operators $A_i$ operating in the $n_i$-dimensional spin space of particle $i$ and $B_j$ operating in the $j$-dimensional spin space of particle $j$ is defined by

$$\langle m_i'm_j'|A_i\otimes B_j|m_im_j\rangle=\langle m_i'|A_i|m_i\rangle\langle m_j'|B_j|m_j\rangle,\tag{B.2}$$

often written simply as $A_iB_j$. Some useful properties of the direct product of two operators are:

$$\begin{aligned}&\text{(i)}\quad \mathrm{Tr}A_i\otimes B_j=\mathrm{Tr}A_i\,\mathrm{Tr}B_j,\\ &\text{(ii)}\quad \mathrm{Det}A_iA_j=(\mathrm{Det}A_i)^{n_j}(\mathrm{Det}B_j)^{n_i},\\ &\text{(iii)}\quad [A_i\otimes B_j]^{-1}=A_i^{-1}\otimes B_j^{-1},\\ &\text{(iv)}\quad [A_i\otimes B_j][C_i\otimes D_j]=(A_iC_j)\otimes(B_jD_j),\\ &\text{(v)}\quad [S_i\otimes T_j][A_i\otimes B_j][S_i^{-1}\otimes T_j^{-1}]\\ &\qquad=(S_iA_iS_i^{-1})\otimes(T_jB_jT_j^{-1}).\end{aligned}\tag{B.3}$$

Both traces and determinants are to be taken in whatever space the operator following the symbols Tr and Det are defined. If the operator $A_i$ is to be evaluated in the direct product space of the operators $A_i$ and $B_j$, its unambiguous form is $A_i\otimes 1_j$, where $1_j$ is the unit operator in the $j$ space. But for $N$ spin-$l$ particles $\mathrm{Tr}[(l_i{}^x)^2]$ usually means:

$$\begin{aligned}\mathrm{Tr}[(l_i{}^x)^2]&=\mathrm{Tr}[1_1\otimes 1_2\otimes\cdots\otimes(l_i{}^x)^2\otimes\cdots\otimes 1_n]\\ &=\mathrm{tr}[(l^x)^2][\mathrm{tr}1]^{N-1},\end{aligned}\tag{B.4}$$

where tr signifies a trace taken in the $(2l+1)$-dimensional spin space.

Property (B.3.v) is of special significance—the direct product of unitary transformations is a unitary transformation. Thus:

$$U\equiv 1_1\otimes 1_2\otimes\cdots\otimes U_j\otimes\cdots\otimes 1_N,\tag{B.5}$$

[18] M. Rose, *Quantum Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), Chap. 5, p. 85.

where $U_j$=unitary transformation in the space of the $j$th particle, is a unitary transformation. Because the trace is invariant under a unitary transformation (in particular, the rotation operator about any axis is a unitary transformation) and because of (B.5), we can rotate a single nuclear spin or any number of nuclear spins about any axis with impunity, i.e., without changing the value of the trace. Just this property has been used extensively in evaluating the traces of Sec. V.

### APPENDIX C. TRACE EVALUATION

To illustrate the techniques which proved useful in the evaluation of the traces, a few specific examples will prove sufficient.

First, the equality:

$$\mathrm{Tr}\mathbf{l}_i\cdot\mathbf{l}_j\, l_m^y l_n^y = \mathrm{Tr}\mathbf{l}_i\cdot\mathbf{l}_j\, l_m^z l_n^z \tag{C.1}$$

follows by subjecting the first trace to a unitary transformation rotating all the nuclear spins about the $x$ axis through $\pi/2$ radians and observing that $\mathbf{l}_i\cdot\mathbf{l}_j$ is rotationally invariant. Also if $i\neq j$, $m\neq n$:

$$\mathrm{Tr}l_i^z l_j^z l_m^z l_n^z = [\delta_{im}\delta_{jn}+\delta_{in}\delta_{jm}][\mathrm{tr}(l^x)^2]^2 \tag{C.2}$$

for, if $i$ does not equal $m$ or $n$, a unitary transformation of the $i$th particle about the $z$ axis converts the trace to its negative. Hence $i$ must be equal to $m$ or $n$. Similarly, $j$ must be equal to the remaining unpaired index. (C.1) and (C.2) provide the necessary traces for the second moment calculation.

As an example of the more extensive calculations required to evaluate the fourth moment, consider

$$\begin{aligned}
&T_1 \equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}\,\mathrm{Tr}[l_i^x l_j^x l_k^x l_l^x l_m^y l_n^y l_r^z l_s^z],\\
&A_{ij}=A_{ji};\quad B_{kl}=B_{lk};\quad C_{mn}=C_{nm};\quad D_{rs}=D_{sr},\\
&A_{ii}=B_{kk}=C_{mm}=D_{rr}=0,
\end{aligned}\tag{C.3}$$

By an argument similar to that following (B.2):

$$T_1 = 2\sum A_{ij}B_{kl}C_{mn}D_{mn}\,\mathrm{Tr}l_i^x l_j^x l_k^x l_l^x l_m^y l_n^y l_m^z l_n^z \tag{C.4}$$

for, if $r$ were not equal to either $m$ or $n$, a unitary transformation of the $r$th particle about the $x$ axis by $\pi$ radians would change the trace to its negative regardless of whether $i=r$, $j=r$, $k=r$, or $l=r$ or not. Now, because of the symmetry of the indices of $A_{ij}$, $B_{kl}$, $C_{mn}$, $D_{rs}$:

$$\sum_{kl} = \sum_{k=m,l=m} + 2\sum_{k=m,l\neq m} + \sum_{k\neq m,l\neq m} = 2\sum_{k=m,l\neq m} + \sum_{k\neq m,l\neq m}, \tag{C.5}$$

and

$$\begin{aligned}
T_1 = {}& 4\sum A_{ij}B_{kl}C_{kn}D_{kn}\,\mathrm{Tr}l_i^x l_j^x l_k^x l_l^x l_k^y l_n^y l_k^z l_n^z\\
&+2\sum_{kl\neq m} A_{ij}B_{kl}C_{mn}D_{mn}\\
&\times \mathrm{Tr}l_i^x l_j^x l_k^x l_l^x l_m^y l_n^y l_m^z l_n^z.
\end{aligned}\tag{C.6}$$

Continuing in this manner, we soon arrive at the result:

$$T_1 = -4(2l+1)^r \sum_{ijk} A_{ij}B_{ik}C_{jk}D_{jk} \times \Big[\Big(\sum_{m=-l}^{m=+l} m^2\Big)\Big/(2l+1)\Big]^3. \tag{C.7}$$

One more observation proved to be labor-saver:

$$\begin{aligned}
T_2 &\equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}\,\mathrm{Tr}l_i^x l_j^x l_k^x l_l^x l_m^x l_n^x l_r^x l_s^x\\
&= \frac{1}{3!}\Big(\sum_{kl} B_{kl}\frac{\partial}{\partial A_{kl}}\Big)\Big(\sum_{mn} C_{mn}\frac{\partial}{\partial A_{mn}}\Big)\\
&\qquad\times\Big(\sum_{rs} D_{rs}\frac{\partial}{\partial A_{rs}}\Big)T_2',
\end{aligned}\tag{C.8}$$

$$T_2' = \sum A_{ij}A_{kl}A_{mn}A_{rs}\,\mathrm{Tr}l_i^x l_j^x l_k^x l_l^x l_m^x l_n^x l_r^x l_s^x.$$

The form $T_2'$ is much simpler to evaluate than $T_2$ because of its complete symmetry in the indices $(ij)$, $(kl)$, $(mn)$, and $(rs)$. When $T_2'$ is evaluated, the polarization operator

$$\frac{1}{3!}\Big(\sum B_{kl}\frac{\partial}{\partial A_{kl}}\Big)\Big(\sum C_{mn}\frac{\partial}{\partial A_{mn}}\Big)\Big(\sum D_{rs}\frac{\partial}{\partial A_{rs}}\Big)$$

generates the expression $T_2$.

Finally, we append a table of "little" traces:

$$\begin{aligned}
&\text{(i)} && \mathrm{tr}(l^x)^2 = \sum_{m=-l}^{m=+l} m^2 = l(l+1)(2l+1)/3,\\
&\text{(ii)} && \mathrm{tr}(l^x)^4 = \sum_{m=-l}^{m=+l} m^4\\
& && = [l(l+1)(2l+1)(3l^2+3l+1)]/15,\\
&\text{(iii)} && \mathrm{tr}[(l^x)^2(l^y)^2] = [\mathrm{tr}(\mathbf{l}^2)^2 - 3\,\mathrm{tr}(l^x)^4]/6,\\
&\text{(iv)} && \mathrm{tr}[l^x l^y l^z] = [\mathrm{tr}l^x l^y l^z + \mathrm{tr}l^y l^x l^z + i\,\mathrm{tr}(l^z)^2]/2\\
& && = [(\mathrm{tr}l^x l^y l^z) - (\mathrm{tr}l^y l^x l^z)^*\\
& && \quad + i\,\mathrm{tr}(l^z)^2]/2 = \tfrac{1}{2}i\,\mathrm{tr}(l^x)^2,\\
&\text{(v)} && \mathrm{tr}l^x l^y l^x l^y = \mathrm{tr}l^x l^x l^y l^y + i\,\mathrm{tr}l^x l^y l^z.
\end{aligned}\tag{C.9}$$

### APPENDIX D. THE TRACES $T^{(1)}{}_{ij,kl,mn,rs}$ AND $T^{(2)}{}_{ij,kl,mn,rs}$

As already indicated in Sec. V, the evaluation of the fourth moment of the nuclear absorption line shape requires a knowledge of the following:

$$\begin{aligned}
S^{(a)}{}_{ij,kl,mn,rs} &\equiv \mathrm{Tr}[(\mathbf{l}_i\cdot\mathbf{l}_j - 3l_i^z l_j^z)\\
&\qquad\times(\mathbf{l}_k\cdot\mathbf{l}_l - 3l_k^z l_l^z)(l_m^y l_n^z l_r^y l_s^z)],\\
S^{(b)}{}_{ij,kl,mn,rs} &\equiv \mathrm{Tr}[(\mathbf{l}_i\cdot\mathbf{l}_j - 3l_i^z l_j^z)(\mathbf{l}_k\cdot\mathbf{l}_l - 3l_k^z l_l^z)\\
&\qquad\times(\mathbf{l}_m\cdot\mathbf{l}_n - 3l_m^z l_n^z)(\mathbf{l}_r\cdot\mathbf{l}_s - 3l_r^z l_s^z)],
\end{aligned}\tag{D.1}$$

in terms of which $T^{(1)}$ and $T^{(2)}$ are immediately obtained:

$$\begin{aligned} T^{(1)}{}_{ij,kl,mn,rs} &= 36S^{(a)}{}_{kl,ij,mn,rs} - 3S^{(b)}{}_{kl,ij,mn,rs}, \\ T^{(2)}{}_{ij,kl,mn,rs} &= -\tfrac{3}{2}S^{(b)}{}_{mn,kl,ij,rs}, \end{aligned} \tag{D.2}$$

$S^{(a)}$ and $S^{(b)}$ in turn can be expressed in terms of seven fundamental traces $S^{(i)}$ which we give below:

$$\begin{aligned} S^{(a)}{}_{ij,kl,mn,rs} &= 5S^{(1)}{}_{ij,kl,mn,rs} + S^{(2)}{}_{ij,kl,mn,rs} \\ &\quad - 4S^{(3)}{}_{ij,kl,mn,rs} - S^{(4)}{}_{kl,ij,mn,rs} \\ &\quad - S^{(4)}{}_{ij,kl,mn,rs}, \\ S^{(b)}{}_{ij,kl,mn,rs} &= 18\{S^{(5)}{}_{ij,kl,mn,rs} + S^{(6)}{}_{kl,mn,rs,ij} \\ &\quad + S^{(6)}{}_{ij,kl,mn,rs} + S^{(7)}{}_{ij,kl,mn,rs}\}. \end{aligned} \tag{D.3}$$

The $S^{(i)}$ are found to be

$$\begin{aligned} S_1 &\equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}S^{(1)}{}_{ij,kl,mn,rs} \\ &\equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}\,\mathrm{Tr}[l_i{}^x l_j{}^x l_k{}^x l_l{}^x l_m{}^x l_n{}^y l_r{}^x l_s{}^y] \\ &= \frac{1}{2!}\sum_{uv} B_{uv}\frac{\partial}{\partial A_{uv}}S_1', \end{aligned}$$

$$\begin{aligned} S_1' = {}& 4\sum A_{ij}{}^2 C_{ij}D_{ij}[\mathrm{tr}(l^x)^2(l^y)^2][\mathrm{tr}(l^x)^4](2l+1)^{N-2} \\ &+4\sum_{j\neq k} A_{ij}{}^2 C_{ik}D_{ik}[\mathrm{tr}(l^x)^2(l^y)^2] \\ &\qquad\times[\mathrm{tr}(l^x)^2]^2(2l+1)^{N-3} \\ &+8\sum_{j\neq k} A_{ij}A_{ik}C_{ij}D_{ik}[\mathrm{tr}(l^x)^2(l^y)^2] \\ &\qquad\times[\mathrm{tr}(l^x)^2]^2(2l+1)^{N-3} \\ &+4\sum_{j\neq k} A_{ij}{}^2 C_{ik}D_{ik}[\mathrm{tr}(l^x)^4][\mathrm{tr}(l^x)^2]^2(2l+1)^{N-3} \\ &+8\sum_{i\neq k,\, j\neq l} A_{ij}A_{jk}B_{kl}D_{il}[\mathrm{tr}(l^x)^2]^4(2l+1)^{N-4} \\ &+2\sum_{(ij)\neq(kl)} A_{ij}{}^2 C_{kl}D_{kl}[\mathrm{tr}(l^x)^2]^4(2l+1)^{N-4}, \end{aligned}$$

$$\begin{aligned} S_2 &\equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}\,\mathrm{Tr}[l_i{}^z l_j{}^z l_k{}^z l_l{}^z l_m{}^x l_n{}^y l_r{}^x l_s{}^y] \\ &\equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}S^{(2)}{}_{ij,kl,mn,rs} \\ &= \frac{1}{2!}\sum_{uv} B_{uv}\frac{\partial}{\partial A_{uv}}S_2', \end{aligned}$$

$$\begin{aligned} S_2' = {}& 4\sum A_{ij}{}^2 C_{ij}D_{ij}[\mathrm{tr}(l^z)^2(l^y)^2] \\ &\qquad\times[\mathrm{tr}(l^z)^2(l^x)^2](2l+1)^{N-2} \\ &+8\sum_{j\neq k} A_{ij}{}^2 C_{ik}D_{ik}[\mathrm{tr}(l^x)^2]^2 \\ &\qquad\times[\mathrm{tr}(l^z)^2(l^x)^2](2l+1)^{N-3} \\ &+2\sum_{(ij)\neq(kl)} A_{ij}{}^2 C_{kl}D_{kl}[\mathrm{tr}(l^x)^2]^4(2l+1)^{N-4} \\ &+8\sum A_{ij}A_{kl}C_{jk}D_{jk}[\mathrm{tr}(l^z)^2][\mathrm{tr}(l^z l^y l^x)] \\ &\qquad\times[\mathrm{tr}(l^z l^x l^y)](2l+1)^{N-3}, \end{aligned}$$

$$\begin{aligned} S_3 &\equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}S^{(3)}{}_{ij,kl,mn,rs} \\ &= \sum A_{ij}B_{kl}C_{mn}D_{rs}\,\mathrm{Tr}[l_i{}^x l_j{}^x l_k{}^y l_l{}^y l_m{}^x l_n{}^y l_r{}^x l_s{}^y] \\ &= 4\sum A_{ij}B_{ij}C_{ij}D_{ij}[\mathrm{tr}l^x l^y l^x l^y] \\ &\qquad\times[\mathrm{tr}l^x l^y l^y l^x](2l+1)^{N-2} \\ &\quad+4\sum_{j\neq k} A_{ij}B_{ik}C_{ik}D_{ij}[\mathrm{tr}l^x l^y l^x l^y] \\ &\qquad\times[\mathrm{tr}(l^x)^2](2l+1)^{N-3} \\ &\quad+4\sum_{i\neq k} A_{ij}B_{jk}C_{ij}D_{jk}[\mathrm{tr}(l^x)^2] \\ &\qquad\times[\mathrm{tr}l^x l^y l^y l^x](2l+1)^{N-3} \\ &\quad+4\sum_{i\neq l,\, j\neq k} A_{ij}B_{kl}C_{ik}D_{jl}[\mathrm{tr}(l^x)^2]^4(2l+1)^{N-4}, \end{aligned}$$

$$\begin{aligned} S_4 &\equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}S^{(4)}{}_{ij,kl,mn,rs} \\ &= \sum A_{ij}B_{kl}C_{mn}D_{rs}\,\mathrm{Tr}[l_i{}^x l_j{}^x l_k{}^z l_l{}^z l_m{}^x l_n{}^y l_r{}^x l_s{}^y] \\ &= 4\{-\sum A_{ij}B_{jk}C_{jk}D_{ik} + \sum A_{ij}B_{ik}C_{jk}D_{ik} \\ &\quad+\sum A_{ij}B_{ij}C_{ik}D_{jk}\}[\mathrm{tr}(l^x)^2][\mathrm{tr}l^x l^y l^z] \\ &\qquad\times[\mathrm{tr}l^x l^y l^z](2l+1)^{N-3}, \end{aligned}$$

$$\begin{aligned} S_5 &\equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}S^{(5)}{}_{ij,kl,mn,rs} \\ &= \sum A_{ij}B_{kl}C_{mn}D_{rs}\,\mathrm{Tr}[l_i{}^x l_j{}^x l_k{}^x l_l{}^x l_m{}^x l_n{}^x l_r{}^x l_s{}^x] \\ &= \frac{1}{3!}\left(\sum_{kl} B_{kl}\frac{\partial}{\partial A_{kl}}\right)\left(\sum_{mn} C_{mn}\frac{\partial}{\partial A_{mn}}\right) \\ &\qquad\times\left(\sum_{rs} D_{rs}\frac{\partial}{\partial A_{rs}}\right)S_5', \end{aligned}$$

$$\begin{aligned} S_5' = {}& 8\sum A_{ij}{}^4[\mathrm{tr}(l^x)^4]^2(2l+1)^{N-2} \\ &+48\sum_{k\neq j} A_{ij}{}^2 A_{ik}{}^2[\mathrm{tr}(l^x)^2]^2[\mathrm{tr}(l^x)^4](2l+1)^{N-3} \\ &+12\sum_{(kl)\neq(ij)} A_{ij}{}^2 A_{kl}{}^2[\mathrm{tr}(l^x)^2]^4(2l+1)^{N-4} \\ &+48\sum_{i\neq l} A_{ij}A_{ik}A_{jl}A_{kl}[\mathrm{tr}(l^x)^2]^4(2l+1)^{N-4}. \end{aligned}$$

$$\begin{aligned} S_6 &\equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}S^{(6)}{}_{ij,kl,mn,rs} \\ &= \sum A_{ij}B_{kl}C_{mn}D_{rs}\,\mathrm{Tr}[l_i{}^x l_j{}^x l_k{}^x l_l{}^x l_m{}^y l_n{}^y l_r{}^y l_s{}^y] \\ &= 8\sum A_{ij}B_{ij}C_{ij}D_{ij}[\mathrm{tr}l^x l^x l^y l^y]^2(2l+1)^{N-2} \\ &\quad+16\sum_{i\neq k} A_{ij}B_{ij}C_{ik}D_{ik}[\mathrm{tr}l^x l^x l^y l^y] \\ &\qquad\times[\mathrm{tr}(l^x)^2]^2(2l+1)^{N-3} \\ &\quad+4\sum_{(ij)\neq(kl)} A_{ij}B_{ij}C_{kl}D_{kl}[\mathrm{tr}(l^x)^2]^4(2l+1)^{N-4}, \end{aligned}$$

$$\begin{aligned} S_7 &\equiv \sum A_{ij}B_{kl}C_{mn}D_{rs}S^{(7)}{}_{ij,kl,mn,rs} \\ &= \sum A_{ij}B_{kl}C_{mn}D_{rs}\,\mathrm{Tr}[l_i{}^x l_j{}^x l_k{}^y l_l{}^y l_m{}^x l_n{}^x l_r{}^y l_s{}^y] \\ &= 8\sum A_{ij}B_{ij}C_{ij}D_{ij}[\mathrm{tr}l^x l^y l^x l^y]^2(2l+1)^{N-2} \\ &\quad+16\sum_{j\neq k} A_{ij}B_{ij}C_{ik}D_{ik}[\mathrm{tr}l^x l^x l^y l^y] \\ &\qquad\times[\mathrm{tr}(l^x)^2]^2(2l+1)^{N-3} \\ &\quad+4\sum_{(ij)\neq(kl)} A_{ij}B_{ij}C_{kl}D_{kl}[\mathrm{tr}(l^x)^2]^4(2l+1)^{N-4}. \end{aligned}$$