We present a theory for the temperature-dependent nuclear magnetic shielding tensor of molecules with arbitrary electronic structure. The theory is a generalization of Ramsey’s theory for closed-shell molecules. The shielding tensor is defined as a second derivative of the Helmholtz free energy of the electron system in equilibrium with the applied magnetic field and the nuclear magnetic moments. This derivative is analytically evaluated and expressed as a sum over states formula. Special consideration is given to a system with an isolated degenerate ground state for which the size of the degeneracy and the composition of the wave functions are arbitrary. In this case the paramagnetic part of the shielding tensor is expressed in terms of the $g$ and $A$ tensors of the EPR spin Hamiltonian of the degenerate state. As an illustration of the proposed theory, we provide an explicit formula for the paramagnetic shift of the central lanthanide ion in endohedral $\text{Ln@C}_{60}$, with $\text{Ln}=\text{Ce}^{3+}$, $\text{Nd}^{3+}$, $\text{Sm}^{3+}$, $\text{Dy}^{3+}$, $\text{Er}^{3+}$ and $\text{Yb}^{3+}$, where the ground state can be a strongly spin-orbit coupled icosahedral sextet for which the paramagnetic shift cannot be described by previous theories.

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I. INTRODUCTION

Nuclear magnetic shielding measured in NMR spectroscopy is caused by the electrons’ response to an externally applied magnetic field. In closed-shell molecules this response consists of an induced magnetic field caused by electronic orbital currents, the electron spin playing no role other than forcing appropriate orbital permutation symmetries in the many-body wave function. This, at least, is true when spin-orbit coupling is ignored. Ramsey, in Ref. [1], presented the quantum mechanical theory of the shielding tensor for molecules in this regime.

In open-shell molecules however, there is a second contribution to the shielding, arising from the permanent magnetic moment associated with the spin of the unpaired electrons. This contribution is known as the ‘paramagnetic shift’. More generally, a paramagnetic shift arises from a degenerate electronic state. When the degeneracy is weakly split in a magnetic field, the magnetic polarization of each thermally populated state can be described in terms of permanent non-compensating spin (and orbital) currents, inducing a net response field at the nucleus, each state contributing in proportion to its thermal population. A general equation for the isotropic paramagnetic shift was first derived by Kurland and McGarvey. Moon and Patchkovskii derived a formula for the paramagnetic shielding tensor in an arbitrary Kramers doublet and expressed this formula in terms of the $g$ and $A$ tensors of the EPR spin Hamiltonian. Later Pennanen and Vaara extended the Moon and Patchkovskii theory of paramagnetic shifts to cases which deviate from a pure spin degeneracy in the lowest order of perturbation theory in the spin-orbit coupling.

Although the work of Pennanen and Vaara represents the first comprehensive effort towards a completely general theory of NMR chemical shielding for electronically degenerate states in the weak spin-orbit coupling regime, their approach exposes a few issues: (i) It is developed using perturbation theory on the thermodynamic internal energy $U$, which appears to require different perturbation expansions of a same energy level, according to whether the level is either a weighted addend, or an exponent of the thermal weight, in the Boltzmann sum-over-states. (ii) It considers Zeeman and hyperfine spin Hamiltonians linear in the spin operators, which is strictly correct only if the degeneracy is no larger than threefold. (iii) It does not provide a formulation of the problem for an arbitrary electronic degeneracy, such as can be found for example in strongly spin-orbit coupled systems. (iv)
Finally, the inclusion of low-lying excited states resulting from weak splitting of a degeneracy, as described by a zero field splitting Hamiltonian for pure spin states, is not described in the most general way.

We have recently published a communication in which especially points (iii) and (iv) were thoroughly discussed and generalized. In the present paper we wish to present a theory which offers a rigorous solution to point (i). We do this by taking no more than Ramsey’s original assumptions and applying them to a system where the electrons are in thermal equilibrium. Thus we are led to identifying the shielding tensor with a second derivative of the Helmholtz free energy, as in Eq. (3). Then, without needing further assumptions, we use perturbation theory on the free energy to derive the expression for the shielding tensor, Eq. (10). In the second part of the paper, we show that this expression lends itself easily to a reformulation of the paramagnetic shielding in a degenerate state in terms of the spin Hamiltonian $g$ and $A$ parameters (Eq. (16)), which provides a general solution to point (ii).

II. NON-DEGENERATE GROUND STATE: SHIELDINGS AS ENERGY DERIVATIVES

In the following we shall be concerned exclusively with nuclear shielding in the ‘solid state limit’ by which is meant that the molecular nuclei are fixed in space with respect to the static external magnetic field.

In this section we want to recall the essential points of Ramsey’s theory for a molecule in a non-degenerate ground state. He observed that the nuclear magnetic moment $\mu$ can be treated as a classical vector because it is much slower in its dynamics than the electrons. The idea is that as the nuclear moments go about their rotating motion the electron cloud follows adiabatically; at every moment the electrons are in the ground state that corresponds to the instantaneous orientation of the nuclear moments. Hence the components of $\mu$ become external parameters in the electronic Born–Oppenheimer Hamiltonian, as are the nuclear positions and the applied field $B$. The ground state energy will naturally be a function of $\mu$ and $B$, and can be expanded in a Taylor series as

$$E(\mu, B) = E_0 + \sum_{ij} B_i \sigma_{ij} \mu_j + \text{higher order terms}. \quad (1)$$

Here $E_0$ is the electronic energy in the absence of nuclear moments and external field. Note
that the energy contains no terms of odd degree, which is a consequence of the assumption that $E_0$ is a non-degenerate eigenvalue of a time-even Hamiltonian. The second term in (1) has the form of a Zeeman interaction between the nuclear moment $\mu$ and the induced field $-B \cdot \sigma$. The $3 \times 3$ matrix $\sigma$ is the magnetic shielding tensor of the nucleus. We consider $\sigma$ to be field independent, but note that field-dependent corrections to the shielding can be found among the higher order terms of (1). It follows from Eq. (1) that $\sigma_{ij}$ can be obtained from perturbation theory (up to second order) on $E_0$. Thus, in Ramsey’s theory,

$$\sigma_{ij} = \frac{\partial^2 E}{\partial B_i \partial \mu_j} \bigg|_0$$

For reasons of simplicity we have assumed that there is only one magnetic nucleus in the molecule. When there is more than one, Eq. (1) is readily adjusted to expand the energy $E(\mu_1, \mu_2, \ldots, B)$ in all the nuclear moments. Each nucleus will have its own shielding tensor.

III. ARBITRARY ELECTRONIC SPECTRUM: SHIELDINGS AS FREE ENERGY DERIVATIVES

A. Separation of slow and fast dynamical variables: Free energy as an effective Hamiltonian for nuclear spins

We have seen that in the case of a non-degenerate isolated ground state the shielding tensor is obtained from the electronic energy. In this section we want to extend the theory to include molecules which have several thermally populated electronic energy levels, so that temperature comes into play. We want to find an expression for the shielding tensor that is universally valid, regardless of the particular electronic spectrum of the molecule. We start again from the physical assumptions of Ramsey: the nuclear magnetic moments are classical vectors, they interact with the electrons, and the electron cloud is at all instants in a state of equilibrium governed by the applied magnetic field and the instantaneous orientation of the nuclear moments. This equilibrium state is not simply the ground state, because we have to allow for the molecule to possess multiple electronic states between which rapid transitions occur. As the timescale of these transitions is much shorter than the timescale of the nuclear spin dynamics, the electron system can at all times preserve thermal equilibrium at constant temperature $T \equiv 1/\beta$. That is, the state of the system is described by a Boltzmann distribution over the energy levels $E_n(\mu, B)$, eigenvalues of the
electronic Hamiltonian \( H(\mu, B) \). As the energy levels depend on \( \mu \), so do the partition function and all other thermodynamic functions. Note that \( \mu \) is not treated as a dynamic variable of the thermodynamic system (which consists of the electrons only) but as an external parameter that modifies the energy levels of the system.

Our next task is to establish which equation should replace Eq. (1). Recall that Eq. (1) gives the electronic energy as a function of nuclear moments and external field. For the present purpose however, a better interpretation is to regard this energy as the effective Hamiltonian \( H_{\text{eff}} \) for the system of nuclear moments in the external field \( B \). There is no longer any explicit reference to the electrons but the influence of the electrons on the motion of the nuclear moments enters the effective Hamiltonian in such quantities as the shielding tensor, the nuclear spin-spin coupling, etc. For the class of molecules to which Eq. (1) applies (non-degenerate, isolated ground state) we can thus write: \( H_{\text{eff}}(\mu; B) = E(\mu, B) \). Note that in the effective Hamiltonian, \( \mu \) is a dynamical variable, whereas \( B \) remains an external parameter (hence the semicolon). In the more general case of electrons in thermal equilibrium the effective Hamiltonian is temperature-dependent and is given by the electronic Helmholtz free energy \( F = U - TS \), where \( F, U, \) and \( S \) are parametric functions of \( \mu \) and \( B \), and of temperature:

\[
H_{\text{eff}}(\mu; B) = F(\mu, B) = F_0 + \sum_{ij} B_i \sigma_{ij} \mu_j + \text{higher order terms.} \tag{2}
\]

Here we have expanded \( F \) in a Taylor series in analogy with the expansion of the ground state energy in Eq. (1). One way to see that \( F \) acts as the effective Hamiltonian for the nuclear moments is by considering the work done on the system by changing an external parameter (\( \mu_i \), say) at constant temperature. This amount of work is given by the concomitant negative change in \( H_{\text{eff}} \). The only thermodynamic function that has this property is the Helmholtz free energy. Hence, up to an irrelevant constant, the effective Hamiltonian is given by \( F \).

B. Analytical derivatives of the Helmholtz free energy

The shielding tensor component \( \sigma_{ij} \) is the coefficient of \( B_i \mu_j \) in the effective nuclear Hamiltonian. In Ramsey’s theory \( \sigma_{ij} \) is temperature independent and can be obtained from Rayleigh–Schrödinger perturbation theory on the ground state energy, Eq. (1). In the general theory \( \sigma_{ij} \) is temperature dependent and can be obtained from perturbation theory.
on the free energy. From Eq. (2) we have

$$\sigma_{ij} = \frac{\partial^2 F}{\partial B_i \partial \mu_j} \bigg|_0 .$$  \hspace{1cm} (3)

We write the electronic Hamiltonian $H(\mu, B) = H_0 + V(\mu, B)$. Here $H_0$ is the electronic Born–Oppenheimer Hamiltonian in the absence of nuclear magnetic moments and external magnetic field, and $V(\mu, B)$ collects all interactions of the electrons with $\mu$ and $B$. The expressions of these terms are well known and can be found for example in Abragam.\(^\text{12}\) Their detailed form is not important for our discussion.

In the calculation of $\sigma_{ij}$, only those terms of $V$ will contribute that are linear in $\mu$ or linear in $B$ or bilinear in $\mu$ and $B$. Thus we write $V$ as the sum of four parts:

$$V_z = -\textbf{m} \cdot \textbf{B} = -\sum_i m_i B_i,$$

$$V_{hf} = \mathcal{F} \cdot \mu = \sum_i \mathcal{F}_i \mu_i,$$

$$V_D = \textbf{B} \cdot \textbf{D} \cdot \mu = \sum_{ij} B_i D_{ij} \mu_j,$$

$$V' = \text{terms of higher order in } \textbf{B} \text{ and } \mu.$$  \hspace{1cm} (4)

Here $V_z$ is the electronic Zeeman Hamiltonian, with $\textbf{m} = -(\textbf{L} + g_e \textbf{S})$; $V_{hf}$ is the hyperfine coupling, and $\mathcal{F}$ may be further divided into orbit, spin dipole, and Fermi contact terms;\(^\text{12}\) $V_D$ is the diamagnetic nuclear–magnetic field coupling; $V'$ contains all those terms that are not needed to calculate the shielding tensor, and will be discarded from now on. In general, $V_{hf}$ and $V_D$ must be summed over all magnetic nuclei, each with its own $\mathcal{F}$ and $\mathcal{D}$, as these depend on the position of the nucleus which they represent. It is important to keep in mind that $\textbf{m}$, $\mathcal{F}$, and $\mathcal{D}$ are electron operators, whereas $\mu$ and $B$ are classical external parameters. Furthermore, $\textbf{m}$ and $\mathcal{F}$ are time-odd, whereas $\mathcal{D}$ is time-even.

For the derivation\(^\text{13}\) of a perturbation expansion of $F$ it will be convenient to introduce a parameter $\lambda$ in the Hamiltonian to denote the combined order in $\mu$ and $B$:

$$H = H_0 + \lambda V_1 + \lambda^2 V_2, \text{ with } V_1 = V_z + V_{hf} \text{ and } V_2 = V_D.$$  \hspace{1cm} (5)

The free energy is given by

$$F = -\frac{1}{\beta} \ln \text{Tr} \rho, \text{ where } \rho = e^{-\beta H}$$
Now $ρ$ can be expressed as a power series in $λ$:

$$ρ = ρ_0 + λρ_1 + λ^2ρ_2 + \ldots$$

(6)

Here $ρ_0 = e^{-βH_0}$ and $ρ_1$ and $ρ_2$ are first and second order corrections. A power series for $F$ can now be obtained as follows:

$$F = -\frac{1}{β} \ln(Tr \ ρ_0 + λ \ Tr \ ρ_1 + λ^2 \ Tr \ ρ_2 + \ldots)$$

$$= -\frac{1}{β} \ln Tr \ ρ_0 - \frac{1}{β} \ ln \left(1 + \lambda \frac{Tr \ ρ_1}{Tr \ ρ_0} + \lambda^2 \frac{Tr \ ρ_2}{Tr \ ρ_0} + \ldots\right)$$

$$= F_0 - \frac{λ}{β} \frac{Tr \ ρ_1}{Tr \ ρ_0} + \frac{λ^2}{β} \left[\frac{1}{2} \left(\frac{Tr \ ρ_1}{Tr \ ρ_0}\right)^2 - \frac{Tr \ ρ_2}{Tr \ ρ_0}\right] + \ldots$$

(7)

We know however that the free energy is an even function of the time-odd fields $B$ and $μ$ and therefore odd powers of $λ$ must not occur in the expansion of $F$. Hence $Tr \ ρ_1 = 0$ and

$$F = F_0 - \frac{λ^2}{β} \frac{Tr \ ρ_2}{Tr \ ρ_0} + \ldots$$

To proceed, an expression for $ρ_2$ is needed. $ρ$ satisfies the Schrödinger equation $\frac{∂ρ}{∂β} = -Hρ$. By substituting Eqs. (5) and (6) and collecting terms of equal power in $λ$, a recurrence relation for $ρ_i$ is found:

$$\frac{∂ρ_1}{∂β} = -H_0 ρ_1 - V_1 ρ_0,$$

$$\frac{∂ρ_2}{∂β} = -H_0 ρ_2 - V_1 ρ_1 - V_2 ρ_0,$$

etc. These are linear differential equations of the form $\frac{dy}{dx} = ay + bx(x)$, whose general solutions are given by $y = e^{ax} \int_0^x e^{-at} b(t) dt$. Thus we find

$$ρ_1 = -\int_0^β e^{(w-β)H_0} V_1 e^{-wH_0} dw$$

$$ρ_2 = -\int_0^β e^{(w-β)H_0} V_2 e^{-wH_0} dw + \int_0^β \int_0^w e^{(w-β)H_0} V_1 e^{(w'-w)H_0} V_1 e^{-w'H_0} dw' \ dw.$$

Taking the trace of $ρ_2$, we use $Tr(AB) = Tr(BA)$ to rearrange and simplify the integrands. Write $ρ_2 = ρ_2^{(1)} + ρ_2^{(2)}$, then

$$Tr \ ρ_2^{(1)} = -\int_0^β Tr[e^{-βH_0} V_2] dw = -β \langle V_2 \rangle_0 Tr \ ρ_0,$$

where

$$\langle V_2 \rangle_0 = \frac{Tr(V_2ρ_0)}{Tr ρ_0}$$
is the thermal average of $V_2$ in the canonical ensemble corresponding to $H_0$. For the second part of $\rho_2$ we have

$$\text{Tr} \rho_2^{(2)} = \int_0^\beta \int_0^w \text{Tr}[e^{-\beta H_0} e^{(w-w')H_0} V_1 e^{(w'-w)H_0} V_1] dw' dw.$$

The integrand depends on $w - w'$ only, suggesting a change of variables $u = w, v = w - w'$. This gives

$$\text{Tr} \rho_2^{(2)} = \int_0^\beta \int_0^u \text{Tr}[e^{-\beta H_0} e^{vH_0} V_1 e^{-vH_0} V_1] dv du.$$

A second change of variables $u \rightarrow \beta - u, v \rightarrow \beta - v$ shows that this integral is also equal to $\int_0^\beta \int_u^\beta$ of the same integrand. Hence

$$\text{Tr} \rho_2^{(2)} = \frac{1}{2} \int_0^\beta \int_0^\beta \text{Tr}[e^{-\beta H_0} e^{vH_0} V_1 e^{-vH_0} V_1] dv du$$

$$= \frac{\beta}{2} \left\langle \int_0^\beta e^{vH_0} V_1 e^{-vH_0} V_1 dv \right\rangle_0 \text{Tr} \rho_0.$$ 

At this point $\lambda$ is no longer needed and we set $\lambda = 1$, so that Eq. (7) becomes

$$F = F_0 + \langle V_2 \rangle_0 - \frac{1}{2} \left\langle \int_0^\beta e^{wH_0} V_1 e^{-wH_0} V_1 dw \right\rangle_0 + \ldots.$$ 

We substitute $V_1$ and $V_2$ according to Eqs. (5) and (4) and then take the second derivative as in Eq. (3) to obtain the shielding

$$\sigma_{ij} = \left. \frac{\partial^2 F}{\partial B_i \partial \mu_j} \right|_0 = \langle D_{ij} \rangle_0 + \left\langle \int_0^\beta e^{wH_0} m_i e^{-wH_0} F_j dw \right\rangle_0.$$ 

In deriving this expression we have used that, for any two operators $A$ and $B$,

$$\left\langle \int_0^\beta e^{wH_0} A e^{-wH_0} B dw \right\rangle_0 = \left\langle \int_0^\beta e^{wH_0} B e^{-wH_0} A dw \right\rangle_0,$$

which can be shown by a change of integration variable $w \rightarrow \beta - w$.

To evaluate the integral in Eq. (8), the ensemble averaging is carried out before the integration. Let $|n \nu\rangle$ be the eigenstates of $H_0$ with eigenvalue $E_n(0,0)$, hereafter simply written $E_n$. The index $\nu$ labels an arbitrary orthonormal basis of states with the same energy $E_n$. The integral then becomes

$$\int_0^\beta \left\langle e^{wH_0} m_i e^{-wH_0} F_j \right\rangle_0 dw =$$

$$\frac{1}{Q_0} \sum_{n\nu, m\mu} \langle n \nu | m \mu \rangle \langle m \mu | F_j | n \nu \rangle e^{-\beta E_n} \int_0^\beta e^{w(E_n - E_m)} dw.$$
where \( Q_0 = \text{Tr} \rho_0 = \sum_n e^{-\beta E_n} \) denotes the partition function of \( H_0 \). The remaining integral can now be evaluated and this gives

\[
\int_0^\beta \langle e^{\omega H_0} m_i e^{-\omega H_0} F_j \rangle_0 \, d\omega = \frac{1}{Q_0} \sum_n e^{-\beta E_n} \left[ \beta \sum_{\nu, \nu'} \langle n \nu | m_i | n \nu' \rangle \langle n \nu' | F_j | n \nu \rangle \right.
\]

\[
+ \left. \sum_{m \neq n} \sum_{\nu, \mu} \frac{\langle n \nu | m_i | m \mu \rangle \langle m \mu | F_j | n \nu \rangle + \text{c.c.}}{E_m - E_n} \right].
\]

(9)

Finally, combining Eqs. (8) and (9), we find a sum over states formula for the nuclear shielding tensor,

\[
\sigma_{ij} = \frac{1}{Q_0} \sum_n e^{-\beta E_n} \left[ \beta \sum_{\nu, \nu'} \langle n \nu | m_i | n \nu' \rangle \langle n \nu' | F_j | n \nu \rangle \right.
\]

\[
+ \sum_{\nu} \langle n \nu | D_{ij} | n \nu \rangle \left. \right] + \sum_{m \neq n} \sum_{\nu, \mu} \frac{\langle n \nu | m_i | m \mu \rangle \langle m \mu | F_j | n \nu \rangle + \text{c.c.}}{E_m - E_n} \]

(10)

Incidentally, the complex conjugate (c.c.) is not strictly needed and may be replaced by a factor of 2 in front of the last sum, because this sum is always real. The present expression bears an evident similarity to the Van Vleck equation for the magnetic susceptibility.\(^{14}\) One only has to substitute \( m_j \) for \( F_j \) and the diamagnetic susceptibility term for \( D_{ij} \) to obtain the Van Vleck equation. The origin of this similarity is readily understood when one notices that the susceptibility tensor, just like the shielding tensor, occurs in a term of the free energy expansion Eq. (2), viz. in the term that is quadratic in the external field: \( \sum_{ij} B_i \chi_{ij} B_j \). The calculation of \( \chi_{ij} \) then proceeds along exactly identical lines and yields the Van Vleck equation.

Eq. (10) can be cast in a more transparent form using projection operators. Let \( P_n = \sum_\nu \langle n \nu | n \nu \rangle \) be the projector on level \( n \) (which is possibly degenerate), and \( Q_n = 1 - P_n \) its complement, then we can write

\[
\sigma_{ij} = \frac{1}{Q_0} \sum_n e^{-\beta E_n} \text{Tr} \left[ \beta P_n m_i P_n F_j P_n + P_n D_{ij} P_n \right.
\]

\[
+ \left. P_n m_i \frac{Q_n}{H_0 - E_n} F_j P_n + P_n F_j \frac{Q_n}{H_0 - E_n} m_i P_n \right].
\]

This formula shows that the shielding tensor can be seen as a Boltzmann average over the electronic energy levels of the unperturbed molecule, of a quantity (the trace of the operator in brackets) that is associated with each level. This quantity has a temperature-dependent
part and a temperature-independent part. The temperature-dependent part,

\[ \beta \text{Tr}(P_n m_i P_n F_j P_n), \]

which we shall call the Curie term, can only be non-zero if \( E_n \) is degenerate. This is because if \( E_n \) is not degenerate, the eigenstate \(|n\rangle\) is real (w.r.t. time-reversal) and expectation values of time-odd operators on a real state vanish (i.e, \( P_n m_i P_n = P_n F_j P_n = 0 \) if \( E_n \) is not degenerate). Physically, the Curie term arises from the polarization in the applied field of the permanent magnetic moment of the degenerate level. The temperature-independent part of the quantity in brackets consists of two terms, the ‘diamagnetic’ term (\( \sim D \)) and the ‘paramagnetic’ term. These terms are known from the Ramsey theory for shielding in a non-degenerate ground state. When the state is degenerate, the Curie term appears on top of the Ramsey terms, shifting the chemical shift from the value it would have if the state were not degenerate. This shift, coming from the Curie term, is known as the paramagnetic shift.

As Eq. (10) was derived for a system with an arbitrary electronic spectrum, it must obviously also be valid for a ‘closed shell’ system, i.e., for a system with a non-degenerate, isolated ground state. In that case, Eq. (10) reduces to

\[ \sigma_{ij} = \langle 0 | D_{ij} | 0 \rangle + \sum_{n \neq 0} \frac{\langle 0 | m_i | n \nu \rangle \langle n \nu | F_j | 0 \rangle + \text{c.c.}}{E_n - E_0} \]  

(11)

which is indeed the Ramsey expression, which can also be obtained starting from Eq. (1) and applying perturbation theory (first order in \( D \) and second order in \( F \) and \( m \)) on the ground state energy. The equivalence of the two approaches, one starting from the ground state energy \( E \), the other from the free energy \( F \), follows from the fact that the entropy is zero (as only the ground state is occupied), and therefore \( F = E \). We would like to note that although Eq. (11) has the same form as the original Ramsey expression\(^{11}\), it is more general than the latter in that the ground state \(|0\rangle\) in Ramsey’s paper was assumed to be a pure spin singlet state, which allowed him to ignore the spin-dependent parts of \( F \) and \( m \). The present treatment imposes no restrictions on \(|0\rangle\) other than those stated before, viz. that \(|0\rangle\) is the non-degenerate ground state of a time-even Hamiltonian \( H_0 \) (which, incidentally, excludes odd electron systems). \( H_0 \) may include spin-orbit coupling and in cases where this is an important effect the spin-dependent terms, the spin Zeeman term in \( m \) and the
spin-dipolar and Fermi contact hyperfine terms in $\mathbf{F}$, must be included in the calculation of $\sigma_{ij}$ from Eq. (11).

It should be noted that the procedure outlined above for the shielding tensor can be used to obtain expressions for any desired term in the nuclear effective Hamiltonian. It is, for example, straightforward to obtain nuclear spin-spin coupling tensors by using the appropriate $V$ terms in the Hamiltonian and carrying out the subsequent derivation as before. Thus, in analogy with Eq. (8), the coupling tensor between two nuclei $K$ and $L$ is found to be

$$J_{ij}^{KL} = \left. \frac{\partial^2 F}{\partial \mu_i^K \partial \mu_j^L} \right|_0 = \langle D_{ij}^{KL} \rangle_0 + \left. \left\langle \int_0^\beta e^{wH_0} F_i^K e^{-wH_0} F_j^L dw \right\rangle_{0} \right.,$$

where $D_{ij}^{KL}$ is the diamagnetic nucleus-nucleus coupling term.

**IV. SHIELDING TENSOR IN A DEGENERATE ISOLATED GROUND STATE**

We now consider a case of particular interest: a system with a degenerate ground state of multiplicity $\omega$. We assume that the system is in thermal equilibrium at a temperature such that no excited states are thermally populated. The main results of this section were published in Ref. 10. Here and in the appendices we provide a thorough discussion of the details of their derivation.

Applying our general equation (10) to the case of a degenerate and isolated ground state we find

$$\sigma_{ij} = \frac{1}{\omega} \left[ \frac{\beta}{\nu} \sum_{\nu,\nu'} \langle 0 \nu | m_i | 0 \nu' \rangle \langle 0 \nu' | F_j | 0 \nu \rangle \right. + \sum_{\nu} \langle 0 \nu | D_{ij} | 0 \nu \rangle + \sum_{m \neq 0} \sum_{\nu,\mu} \frac{\langle 0 \nu | m_i | m \mu \rangle \langle m \mu | F_j | 0 \nu \rangle + c.c.}{E_m - E_0} \right].$$

The last two terms are familiar from the Ramsey expression Eq. (11) (and reduce to the latter when $\omega = 1$), but here they are averaged over the states of the manifold. The first term is the Curie term which, as we have noted before, is unique to degenerate states and causes a paramagnetic shift, inversely proportional to temperature. As much of the following discussion will focus on this term we repeat it explicitly:

$$\sigma^p_{ij} = \frac{\beta}{\omega} \sum_{\nu,\nu'} \langle 0 \nu | m_i | 0 \nu' \rangle \langle 0 \nu' | F_j | 0 \nu \rangle. \quad (12)$$
The sum in Eq. (12) is evidently the trace of the product of two matrices, respectively the representations of the electronic magnetic moment and the hyperfine field on the nucleus in a basis of the degenerate manifold. Being a trace of a matrix product, it is invariant under unitary transformations of the basis, which is of course required for an observable property. This means that we are free to choose whichever orthonormal basis we want to calculate $\sigma_{ij}^p$ using Eq. (12).

Both matrices in Eq. (12) are known from the theory of electron paramagnetic resonance (EPR) spectroscopy. They represent respectively the Zeeman effect and the hyperfine coupling in the degenerate manifold. And thus we arrive at the well-known result that the paramagnetic shielding tensor can be obtained completely from EPR parameters, and, vice versa, NMR experiments on paramagnetic molecules provide information on the EPR parameters. The precise expression of this correspondence will be derived in section [IV.B] but let us start with an example, the simplest case of degeneracy, a Kramers doublet.

### A. Kramers doublet

In a Kramers doublet the Zeeman and hyperfine interactions can be conveniently expressed by means of a spin Hamiltonian

$$H_S = \mu_B S \cdot g \cdot B + S \cdot A \cdot I$$

operating within a fictitious spin-1/2 doublet. What this means is that the matrix elements of $V_z + V_{hf}$ (Eq. (1)) within the true wave functions of the Kramers doublet are the same as the matrix elements of $H_S$ within the fictitious spin doublet. For example, if we denote the basis states of the Kramers doublet by $|0a\rangle$ and $|0b\rangle$ and let $|0a\rangle$ correspond to the fictitious spin state $|\frac{1}{2}\rangle$ and $|0b\rangle$ to $|\frac{1}{2}\rangle$, then we have

$$\langle 0a|m_x|0b\rangle = -\mu_B\langle \frac{1}{2}\rangle |\sum_i S_i g_{ix}| - \frac{1}{2}\rangle = -\mu_B (g_{xx} - ig_{yx})/2,$$

$$\langle 0a|F_x|0b\rangle = \frac{1}{g_I \mu_N} \langle \frac{1}{2}\rangle |\sum_i S_i A_{ix}| - \frac{1}{2}\rangle = \frac{1}{g_I \mu_N} (A_{xx} - iA_{yx})/2,$$

and so on. Here $g_I$ is the nuclear $g$-factor and we have used $\mu = g_I \mu_N I$, where $I$ is the nuclear spin vector in units of $\hbar$. Using the spin Hamiltonian of the Kramers doublet, Eq. (12) becomes

$$\sigma_{ij}^p = -\frac{\mu_B \beta}{2g_I \mu_N} \sum_{k,l} g_{ki} A_{lj} \text{Tr}(S_k S_l).$$
The trace of the product of two cartesian spin components is given by
\[ \text{Tr}(S_k S_l) = \delta_{kl} \frac{S(S+1)(2S+1)}{3}. \]

And with \( S = 1/2 \), we find that the paramagnetic shielding tensor for a Kramers doublet can be expressed as follows.
\[ \sigma^p = -\frac{\mu_B \beta}{4g_I \mu_N} g^T A. \]  

This equation was first obtained by Moon and Patchkovskii using a different method. Note how the two interactions that combine to give rise to a paramagnetic shift are separated in Eq. (14): \( g \) represents the Zeeman splitting in the external field and is a property of the molecule as a whole, independent of the nuclear moments; \( A \) represents the hyperfine interaction between the electrons and the nucleus whose shielding tensor we wish to calculate. The ratio \( A/g_I \) however is independent of the nuclear species and depends only on the position of the nucleus in the molecule.

**B. Degeneracy of arbitrary multiplicity**

The example of the Kramers doublet showed how the paramagnetic shielding can be obtained from EPR \( g \)- and \( A \)-tensors. In this section we extend this treatment to degenerate ground states of any multiplicity and derive a formula for \( \sigma^p \) which is the generalization of Eq. (14).

The starting point is again Eq. (12). We have seen that the matrices of \( m_i \) and \( F_i \) in a Kramers doublet can be reproduced by operator equivalents, linear in the spin components, working in a fictitious spin doublet. An expansion of this kind is an application of a general theorem to the effect that any \( n \times n \) matrix can be reproduced by a unique spin operator, polynomial in the spin components \( S_i \). Mathematical details about the construction and properties of this spin operator are given in Appendix. The main result is that the matrix of an operator \( X \) in a basis \( \{ \psi_i \}_{i=1...n} \) can be reproduced by a spin operator \( X_S \) in a fictitious spin multiplet \( \{|S M\}\} \) whose dimension equals \( n \), i.e., \( 2S + 1 = n \). Specifically,

\[ X_S = \sum_{k=0}^{2S} \sum_{q=-k}^{k} (-1)^q Q_q^{(k)} S_q^{(k)}. \]

where \( Q_q^{(k)} \) are complex coefficients, unique for given operator \( X \) and basis functions \( \psi_i \). The \( S_q^{(k)} \) are irreducible tensor operators, which are basically products of \( k \) spin components
The formula for the paramagnetic shielding, Eq. (12), depends on six matrices, one for each cartesian component of the magnetic moment \( \mathbf{m} \) and the hyperfine field \( \mathcal{F} \). We now apply the spin-decomposition to each of these matrices and write the corresponding spin operators

\[
\sigma_{ij}^p = -\mu_B \sum_{k=0}^{2S} \sum_{q=-k}^{k} (-1)^q S^{(k)}_{-q} g_{qi}^{(k)}
\]

(15)

where the \( Q \)-numbers have been renamed \( g_{qi}^{(k)} \) for the magnetic moment and \( A_{qi}^{(k)} \) for the hyperfine field, in accordance with the usual notation in EPR spectroscopy. Note that in the present formalism the “\( g \)-factors” and “\( A \)-factors” are complex numbers whose complex conjugates are given by

\[
g_{qi}^{(k)*} = (-1)^q g_{-qi}^{(k)}, \quad A_{qi}^{(k)*} = (-1)^q A_{-qi}^{(k)}.
\]

These relations make the operators in Eq. (15) Hermitian (See Appendix, Eq. (A.8)). The spin Hamiltonian

\[
H_S = -\sum_i m_{i,S} B_i + g_I\mu_N \sum_i \mathcal{F}_{i,S} I_i
\]

(13)

gives a complete description of an EPR experiment in the degenerate manifold. It is the generalization of Eq. (13) to a manifold of arbitrary degeneracy.

We can now proceed to express the paramagnetic shielding tensor in terms of the EPR parameters. In Eq. (12), we replace the matrix elements in real space by the corresponding, and identical, matrix elements in fictitious spin space:

\[
\sigma_{ij}^p = \frac{\beta}{\omega} \sum_{M,M'} \langle SM|m_{i,S}|SM'\rangle \langle SM'|\mathcal{F}_{j,S}|SM\rangle
\]

\[
= \frac{\beta}{2S+1} \text{Tr}(m_{i,S}\mathcal{F}_{j,S})
\]

\[
= -\frac{\mu_B}{g_I\mu_N} \frac{\beta}{2S+1} \sum_{kq} (-1)^{q+q'} g_{qi}^{(k)} A_{q'j}^{(k')} \text{Tr}\left(S_{-q}^{(k)} S_{-q'}^{(k')}\right)
\]

The trace simplifies using Eqs. (A.7) and (A.4) and we get

\[
\sigma_{ij}^p = -\frac{\mu_B}{g_I\mu_N} \frac{\beta}{2S+1} \sum_{k=0}^{2S} \sum_{q=-k}^{k} g_{qi}^{(k)*} A_{qj}^{(k)} \frac{\langle S||S^{(k)}||S\rangle^2}{2k+1}.
\]

(16)
This expression is the generalization of Eq. (14). Note that, whereas the spin Hamiltonian parameters are basis dependent (see Appendix), this is not so for the contraction of the parameters appearing in Eq. (16). The tensor $\sigma^p$ is thus an invariant property of the degenerate manifold, as expected. Another such invariant is the magnetic susceptibility tensor, which is proportional to the same contraction but with $g^{(k)}_{ij}$ substituted for $A^{(k)}_{ij}$. For the twofold degenerate Kramers doublet this particular contraction is in fact well known as the $G$ tensor: $G = g^T g$, with $g$ as in Eq. (13).\footnote{15}

An example of the application of Eq. (16) to the cubic quartet electronic ground state of certain paramagnetic lanthanide ion impurities in CaF$_2$ crystals can be found in Ref. 10. In the next section we apply the formula to the icosahedral sextet that can arise in endohedral metallofullerene Ln@C$_{60}$.

1. Example: paramagnetic shielding in the icosahedral sextet

The highest degeneracy that can be generated by point group symmetry is sixfold and corresponds to the $W'$ irreducible spin representation of the icosahedral double group $I^*$.\footnote{19} A ground state of this symmetry type may arise from the crystal field splitting of the $J$ ground multiplet of the rare earths Ce$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Dy$^{3+}$, Er$^{3+}$, and Yb$^{3+}$, when placed in an environment of icosahedral symmetry.\footnote{20} We consider the paramagnetic shielding at the central nucleus.

The high symmetry reduces the number of free parameters in the spin Hamiltonian drastically. To make maximum use of the symmetry it is best to have the cartesian axes coincide with the twofold axes of a $D_2$ subgroup of $I$. This way the $x$, $y$, and $z$ directions are equivalent,\footnote{21} and the shielding tensor is isotropic and diagonal: $\sigma^p = \sigma^p I$. The fictitious spin representation of $W'$ has $S = 5/2$. A vector operator equivalent working in this space has to transform as the $T_1$ irreducible representation of the icosahedral group.\footnote{16} This means that the linear combinations of tensor operators in Eq. (15) must transform as the cartesian component of $T_1$. Symmetry adaptations of spherical harmonics were published by Qiu and Ceulemans.\footnote{21} Using their tables one finds that $T_1$ occurs in the subduction of $k = 1$ and $k = 5$. The spin operators with $k = 1$ are just the cartesian spin components $S_x$, $S_y$, and $S_z$.\footnote{15}
The corresponding operators for $k = 5$ are as follows (Ref. 21, Table 5.

\[ \beta_{n,m} = \frac{1}{2} \left( \pm n + m \sqrt{5} \right) \]

\[ T_x = \sqrt{5} \beta_{-1,3} \left( S_5^{(5)} - S_{-5}^{(5)} \right) - \frac{3 \sqrt{3} \beta_{-1,1}}{16 \sqrt{2}} \left( S_3^{(5)} - S_{-3}^{(5)} \right) - \frac{\sqrt{3} \beta_{7,1}}{16} \left( S_1^{(5)} - S_{-1}^{(5)} \right) \]

\[ T_y = i \sqrt{5} \beta_{-1,3} \left( S_5^{(5)} + S_{-5}^{(5)} \right) - i \frac{3 \sqrt{3} \beta_{-1,1}}{16 \sqrt{2}} \left( S_3^{(5)} + S_{-3}^{(5)} \right) + i \frac{\sqrt{3} \beta_{7,1}}{16} \left( S_1^{(5)} + S_{-1}^{(5)} \right) \]

\[ T_z = \sqrt{35} \frac{16}{16} \left( S_4^{(5)} + S_{-4}^{(5)} \right) + \frac{\sqrt{21}}{8} \left( S_2^{(5)} + S_{-2}^{(5)} \right) - \frac{3}{8} \sqrt{2} S_0^{(5)} \]

These expressions are normalized in the sense that the squares of the coefficients sum up to one. It remains now to choose a reduced matrix element for $S^{(5)}$. Eq. (16) adopts a simplified form if we choose

\[ \frac{\langle S || S^{(5)} || S \rangle^2}{11} = \frac{\langle S || S^{(1)} || S \rangle^2}{3} = \frac{(2S + 1) S (S + 1)}{3} = \frac{35}{2}, \]

for $S = 5/2$. The second equality follows from our choice of $S^{(1)}$ as in Eq. (A.2).18

A completely general spin Hamiltonian for Zeeman and hyperfine coupling (with the central nucleus) in the icosahedral sextet thus contains just four parameters and is given by

\[ H_S = \mu_B (gS + g'T) \cdot B + (AS + A'T) \cdot I. \]

The expression for the paramagnetic shielding follows now readily from Eq. (16):

\[ \sigma^p = - \frac{35}{12} \frac{\mu_B}{g_{12}} \beta (gA + g'A'). \]

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Appendix: Spin operator equivalents

We consider the following problem. Given an arbitrary, complex square matrix of dimension $2S + 1$, to construct a spin operator, polynomial in the components of $S$, whose matrix representation in the fictitious spin manifold $| SM \rangle$ is the same as the given matrix. The main results in this appendix are not new and were published by Griffith.16,17,22 For convenience, we collect them here in a coherent presentation, and expound in more detail on the derivations.
1. Orthogonal matrix expansion

The first non-trivial case is that of a complex $2 \times 2$ matrix. This corresponds to fictitious spin $S = 1/2$. It is not hard to see that any such matrix can be expanded as

$$a \mathbf{l} + b \sigma_x + c \sigma_y + d \sigma_z,$$

where $\mathbf{l}$ is the $2 \times 2$ unit matrix and the $\sigma_i$ are the Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$  

The four complex quantities $a, b, c, d$ are uniquely determined by a set of four linear equations, one for each element of the given matrix. The corresponding spin operator is given by

$$a + 2bS_x + 2cS_y + 2dS_z. \quad (A.1)$$

We have seen an example in section [V.A] where matrices of Zeeman and hyperfine coupling in a Kramers doublet were represented by a spin Hamiltonian (Eq. (13)), which is an application of Eq. (A.1), (with $a = 0$, as the matrices considered there are traceless).

When we move to matrices of dimension $n \times n$ ($n \geq 3$), the operator equivalent in Eq. (A.1) is no longer adequate to reproduce an arbitrary matrix. This is most easily seen from the requirement that the number of parameters in the spin operator must be at least $n^2$ (i.e., the number of elements in the arbitrary matrix), whereas there are only four of them in Eq. (A.1). The most obvious way to increase the number of parameters is to include terms of quadratic, cubic, and higher degrees in the spin components $S_i$, until the required number of parameters is reached. This procedure suffers from a drawback though, which is that linear dependencies arise among the terms. For example, there are nine quadratic terms: $S_x^2, S_xS_y, S_yS_z, \ldots$, but four linear combinations of them are already contained among the terms of lower degree (i.e., in Eq. (A.1)). These are $S_x^2 + S_y^2 + S_z^2 = \mathbf{S}^2 = S(S + 1)$, $S_xS_y = -S_yS_x = iS_z$, $S_yS_z - S_zS_y = iS_x$, and $S_zS_x - S_xS_z = iS_y$. The five remaining linear combinations are linearly independent from terms of lower degree and can be added to Eq. (A.1) to obtain a spin operator with nine parameters in total, which allows to expand any $3 \times 3$ matrix.

This procedure may be repeated for higher degrees and one will always find that, among the $3^k$ spin products of degree $k$, only $2k + 1$ are independent from the products of lower
degree. These \(2k+1\) operators form an irreducible tensorial set of rank \(k\). To prove this we make use of the general theory of irreducible tensor operators (ITO) and angular momentum, as can be found for example in Zare. 18

Let \(S_q^{(k)}(q = -k, \ldots, k)\) denote the irreducible tensor operators of rank \(k\) constructed from the products of \(k\) spin components \(S_i\). \(S_0^{(0)}\) is simply a constant, which may be taken to be 1. The three components of \(S^{(1)}\) are (up to a common, real factor of choice, see below)

\[
S_0^{(1)} = S_z, \quad S_{\pm 1}^{(1)} = \frac{1}{\sqrt{2}}(\mp S_x - iS_y).
\]  

(A.2)

The tensors of higher rank are obtained as follows. \(S^{(2)}\) is found by coupling \(S^{(1)}\) with itself into a rank-2 ITO. Next, \(S^{(3)}\) is found by coupling \(S^{(2)}\) with \(S^{(1)}\) into a rank-3 ITO, and so on. This process may be repeated several times to obtain the ITO of desired rank. We thus define our \(S_q^{(k)}\) by Eq. (A.2) and the following recursion relation.

\[
S_q^{(k)} = N_k(-1)^q \sum_{q_1,q_2} \begin{pmatrix} k - 1 & 1 & k \\ q_1 & q_2 & -q \end{pmatrix} S_{q_1}^{(k-1)} S_{q_2}^{(1)}.
\]  

(A.3)

The multiplicative constant \(N_k\) may be chosen freely for each \(k\) but we require it to be real, in order for the tensor operator to obey certain simple relations under Hermitian and time conjugation, to be explained in Section 3 below. The large bracket is a 3\(j\) symbol. 18

We write \(S_q^{(k)}\) for the matrix representation of \(S_q^{(k)}\) in the basis \(|SM\rangle\). The Wigner–Eckart theorem tells us that the matrix elements factor into a 3\(j\) symbol and a reduced matrix element as follows:

\[
\langle S M | S_q^{(k)} | S M' \rangle = (-1)^{S-M} \langle S || S^{(k)} || S \rangle \left( \begin{array}{cc} S & k \\ -M & q \end{array} \right) \left( \begin{array}{cc} S & k \\ -M & q \end{array} \right) \left( \begin{array}{cc} S & k \\ -M & q \end{array} \right) \left( \begin{array}{cc} S & k \\ -M & q \end{array} \right) \left( \begin{array}{cc} S & k \\ -M & q \end{array} \right) \left( \begin{array}{cc} S & k \\ -M & q \end{array} \right) \left( \begin{array}{cc} S & k \\ -M & q \end{array} \right).
\]

Note that the triangle condition implies that the matrices are zero for all \(k > 2S\). We can now show that the \(S_q^{(k)}(k = 0, 1, \ldots, 2S)\) form a basis for the vector space \(\mathbb{C}^{n \times n}\) \((n = 2S+1)\) of all complex \(n \times n\) matrices. First, observe that the set consists of \(\sum_{k=0}^{2S}(2k+1) = (2S+1)^2 = n^2\) matrices, in agreement with the dimension of \(\mathbb{C}^{n \times n}\). Second, the matrices constitute a linearly independent set, which can be shown as follows. Define an inner product between two matrices by imagining each matrix to be reorganized as a vector by sticking the rows together and then taking the usual scalar product in \(\mathbb{C}^{n^2}\):

\[
(A, B) = \sum_{ij} A_{ij}^* B_{ij} = \text{Tr}(A^\dagger B).
\]
We have now
\[
\left(S^{(k)}_q, S^{(k')}_{q'}\right) = \text{Tr} \left(S^{(k)\dagger}_q S^{(k')}_{q'}\right) = \sum_{MM'} \langle S M | S^{(k)}_q | S M' \rangle^* \langle S M | S^{(k')}_{q'} | S M' \rangle
\]
\[
= \sum_{MM'} \left( \begin{array}{cc}
S & k \\
M' & -M
\end{array} \right) \left( \begin{array}{cc}
S & k' \\
M' & -M
\end{array} \right)^{\dagger} \langle S || S^{(k)}_q || S \rangle^* \langle S || S^{(k')}_{q'} || S \rangle \\
= \frac{|\langle S || S^{(k)}_q || S \rangle|^2}{2k + 1} \delta_{kk'} \delta_{qq'},
\] (A.4)
which shows that the $S^{(k)}_q$ are orthogonal and therefore linearly independent. Note that the derivation leading to Eq. (A.4) makes nowhere use of the specific form one may choose for the $S^{(k)}_q$, such as the one in Eq. (A.3) for example. Rather, the result follows straight from the Wigner–Eckart theorem, which is by definition true for all ITO’s.

It follows that any given $n \times n$ matrix $X$ has a unique expansion in spin matrices $S^{(k)}_q$ of the ITOs $S^{(k)}_q$ in the basis $|S M\rangle$ ($2S + 1 = n$). The expansion coefficients are obtained by orthogonal projection, using Eq. (A.4).

\[
X = \sum_{k=0}^{2S} \sum_{q=-k}^{k} (-1)^q Q^{(k)}_q S^{(k)}_q
\] (A.5)
\[
Q^{(k)}_q = \alpha(k)(-1)^q \text{Tr} \left(S^{(k)\dagger}_q X\right), \quad \alpha(k) = \frac{2k + 1}{|\langle S || S^{(k)}_q || S \rangle|^2}
\]

2. The choice of basis

We have established that to every square matrix $X$ there corresponds a unique set of coefficients $Q^{(k)}_q$ such that Eq. (A.5) is true. These coefficients define the spin operator which reproduces $X$ in the fictitious spin manifold:

\[
X_S = \sum_{k=0}^{2S} \sum_{q=-k}^{k} (-1)^q Q^{(k)}_q S^{(k)}_{-q}.
\] (A.6)

However, when $X$ is the matrix representation of a true operator $X$, the spin equivalent $X_S$ representing $X$ is not at all unique. Given an orthonormal basis $(\psi_1, \ldots, \psi_n)$ and

\[
X_{ij} = \langle \psi_i | X | \psi_j \rangle,
\]
any unitary transformation of this basis results in an equally valid representation of $X$, given by a transformed matrix $X \rightarrow U^\dagger X U$. The transformed matrix may in turn be expanded...
according to Eq. (A.5), yielding a new set of coefficients $Q^{(k)}_q$ and hence a new operator equivalent $X_S$. Clearly, an infinite number of different spin operators can thus be generated and they all represent the same physical situation. Choosing a basis can be seen as establishing an association between the true states and the fictitious spin states: $\psi(M) \leftrightarrow |SM\rangle$. A different association leads to a different spin operator, and a suitable choice often leads to a simplified spin operator.  

3. Implications of Hermiticity and time reversal

The matrices we wish to represent by spin operators are usually Hermitian and they often have a symmetry related to time reversal as well. These two properties will naturally impose some restrictions on the spin operator equivalent. Under Hermitian conjugation ($\dagger$) and Kramers’s time reversal operation ($\ast$) the $S^{(k)}_q$ transform as follows:

$$\begin{align*}
S^{(k)}_q \dagger &= (-1)^q S^{(k)}_{-q} \\
S^{(k)}_q \ast &= (-1)^{q-k} S^{(k)}_{-q},
\end{align*}$$

(A.7)

which can be verified from Eqs. (A.2) and (A.3), using induction on $k$.

a. Hermiticity. Suppose now that $X$ is an Hermitian matrix, e.g., the matrix representation of an Hermitian operator in an orthogonal basis of wave functions. There exists a unique operator $X_S$, of the form (A.6), whose matrix in $|SM\rangle$ equals $X$. The Hermiticity of $X$ then implies

$$\langle SM'|X_S|SM\rangle = \langle SM|X_S^\dagger |SM'\rangle^* = \langle SM'|X_S^\dagger |SM\rangle,$$

for all $M, M'$, which can only be true if $X_S^\dagger = X_S$. Thus the Hermiticity of an operator in true space translates into the Hermiticity of the equivalent spin operator, and this is independent of the choice of basis in true space. The fact that an Hermitian true operator must be represented by an Hermitian spin operator may seem obvious, but we mention it explicitly because the behavior of the true operator under time conjugation does not automatically lead to the same behavior of the spin operator, as we shall see below. From Eqs. (A.6) and (A.7) follow the conditions on the coefficients $Q^{(k)}_q$ that make $X_S$ Hermitian:

$$X_S^\dagger = X_S \iff Q^{(k)*}_q = (-1)^q Q^{(k)}_{-q}.$$

(A.8)
b. Time reversal. The operation of time reversal works on states and on operators. We consider the implications hereof on the spin operator equivalent. Let $X$ be the operator working in a set of $n$ states. We assume that this set is closed under time reversal. This means that there exists a unitary matrix $A$ such that

$$
\psi_i^* = \sum_{j=1}^{n} \psi_j A_{ji}.
$$

(A.9)

If $\psi_i$ describes a system of $n_e$ electrons then we know that $(\psi_i^*)^* = (-1)^{n_e} \psi_i$, and therefore $AA^* = (-1)^{n_e}$. From this and the fact that $A$ is unitary follows $A = (-1)^{n_e}A^T$, that is, $A$ is symmetric for even and antisymmetric for odd number of electrons. In spin space, the time reversal operator is given by $K_S = Y_S K_0$, where $Y_S$ is the operator for a rotation through $\pi$ about the $y$ axis and $K_0$ takes the complex conjugate of numbers, but leaves the basis kets $|SM\rangle$ unchanged.

$$
|SM\rangle^* \equiv K|SM\rangle = Y_S|SM\rangle = (-1)^{S-M}|S-M\rangle.
$$

(A.10)

We shall consider the case where the operator $X$ has a definite parity under time reversal: $X^* = \epsilon X$, with $\epsilon = \pm 1$. Using Eq. (A.9) we have for the matrix elements of $X$

$$
X_{ij}^* = \langle \psi_i | X | \psi_j \rangle^* = \langle \psi_i^* | X^* | \psi_j^* \rangle = \epsilon \sum_{k,l} A_{ki}^* X_{kl} A_{lj},
$$

(A.11)

or, in matrix notation,

$$
X^* = \epsilon A^\dagger X A.
$$

On the other hand, for the matrix elements of $X_S$ we find, using Eq. (A.10)

$$
\langle S M'|X_S|S M\rangle^* = \langle S M'|Y_S^\dagger X_S^* Y_S|S M\rangle
$$

(A.12)

We now define $A_S$ as the spin operator whose matrix representation in $|SM\rangle$ is $A$. Then we can derive from Eqs. (A.11) and (A.12) and the requirement that $X_S$ reproduces the matrix $X$ that

$$
\langle S M'|Y_S^\dagger X_S^* Y_S|S M\rangle = \epsilon \langle S M'|A_S^\dagger X_S A_S|S M\rangle,
$$

and therefore

$$
X_S^* = \epsilon Y_S A_S^\dagger X_S A_S Y_S^\dagger.
$$

(A.13)

This result shows that, in general, the fact that the true operator $X$ has a definite time parity $\epsilon$ does not automatically imply that the same is true for the fictitious spin operator.
$X_S$. In particular, the behavior of $X_S$ under time conjugation is seen to depend, through $A_S$, on the choice of basis in the manifold of true states.

Is it nevertheless possible, by a suitable choice of basis, to obtain that $X_S^* = \epsilon X_S$? This would require, from Eq. (A.13), that $A_S = Y_S$. Then we would have

$$(-1)^{n_e} = AA^* = Y_S Y_S^* = Y_S^2 = (-1)^{2S},$$

(A.14)

where the third equality follows from the reality of the matrix elements of $Y_S$, see Eq. (A.10), and the last equality follows from the fact that $Y_S^2$ is a rotation through an angle of $2\pi$, which multiplies a spin ket by $+1$ if $S$ is integer and by $-1$ if $S$ is half-integer. We conclude from Eq. (A.14) that in cases where $n_e + 2S$ is odd, we cannot in general obtain that $X_S^* = \epsilon X_S$.

Let us first then consider the other case, $n_e + 2S$ even. Recall that the fictitious spin quantum number $S$ is determined by the degeneracy of the manifold $n = 2S + 1$. Thus, $n_e + 2S$ is even for odd degeneracy in an even electron system and for even degeneracy in an odd electron system. For these cases it is always possible to find a basis $\psi(M)$ in true space satisfying $\psi(M)^* = (-1)^{S-M} \psi(-M)$. With this choice we have $A = Y_S$ and thus a spin operator which has the same time parity as the true operator: $X_S^* = \epsilon X_S$. If $X_S$ is also Hermitian we find, using Eqs. (A.6), (A.7) and (A.8),

$$X_S^\dagger = X_S \text{ and } X_S^* = \epsilon X_S \iff Q_q^{(k)} = 0 \text{ for } \begin{cases} \epsilon = +1 \text{ and } k \text{ odd} \\ \epsilon = -1 \text{ and } k \text{ even} \end{cases}$$

(A.15)

This result is equivalent to the well-known rule that a spin Hamiltonian can contain only even powers of the spin if it represents a time-even operator and only odd powers of the spin if it represents a time-odd operator. However, this rule is only valid for a particular choice of basis, namely one which transforms under time reversal in exactly the same way as the associated spin basis.

It remains now to discuss the case $n_e + 2S$ odd. Although this case is far less common than the previous one, it is worth including because the rule mentioned in the previous paragraph does not apply here. First note that we may limit the discussion to even electron systems having even degeneracy because odd electron systems always belong to the previous case, by Kramers’s theorem. We have already proven that it will never be possible to have the spin operator satisfy $X_S^* = \epsilon X_S$, no matter which basis is chosen. Nevertheless, as shown
by Griffith\textsuperscript{22} a simplification of the spin operator similar to Eq. (A.15) obtains if the basis consists of time conjugate pairs. Given a real basis \( \psi_i \) \( (\psi^*_i = \psi_i) \) (and this is always possible for even-electron systems), construct a new basis \( \psi(M) \) as follows:

\[
\psi(\pm S) = \frac{1}{\sqrt{2}} (\psi_1 \pm i\psi_2),
\]

\[
\psi(\pm (S - 1)) = \frac{1}{\sqrt{2}} (\psi_3 \pm i\psi_4),
\]

and so on. Then evidently \( \psi(M)^* = \psi(-M) \), and it is easily verified that this corresponds to \( A_S = (-1)^{-S_z - S_Y} S \). From Eq. (A.13) follows the time-reversal behavior of \( X_S \):

\[
X_S^* = \epsilon (-1)^S_z X_S (-1)^{-S_z} \tag{A.16}
\]

Formally, \( X_S \) undergoes a rotation through \( \pi \) about the \( z \) axis followed by multiplication with \( \epsilon \). To translate Eq. (A.16) into a rule on the coefficients we use that \( (-1)^{S_z} (S^{(k)}_q)^{-S_z} = (-1)^{q} \) and find\textsuperscript{22}

\[
X_S^\dagger = X_S \text{ and } X_S^* = \epsilon (-1)^{S_z} X_S (-1)^{-S_z} \iff Q^{(k)}_q = 0 \text{ for } \begin{cases} 
\epsilon = +1 \text{ and } k - q \text{ odd} \\
\epsilon = -1 \text{ and } k - q \text{ even}
\end{cases}
\]

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