Magnetic resonance in systems with equivalent spin-1/2 nuclides. Part 1

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Abstract

Electron paramagnetic resonance (EPR) spectra of $S = 1/2$ systems XL_n with n equivalent nuclei having spin $I = 1/2$ have been simulated for microwave frequencies in the L-, X-, and W-bands. It has been shown that for $n > 2$ nuclei, the EPR spectra have a more complicated form than anticipated from the usual oversimplified analysis, which predicts $n + 1$ lines with intensity ratios given by the coefficients of the binomial expansion. For the XL_n system with $n = 3$, the EPR spectra in fact consist of six lines. The exact solution of the spin-hamiltonian for this case has been obtained, which gives four levels in zero magnetic field. For $n > 2$ systems, the degeneracy of the energy levels cannot be completely removed by the Zeeman electronic and nuclear interactions. For $n > 4$, certain spin states cannot occur, consistent with the (generalized) Pauli exclusion principle. Discussion of the underlying theory, invoking exchange degeneracy and the appropriate permutation group theory, is included in some detail. Analogous considerations hold for NMR spectroscopy of non-radicals.
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1. Introduction

There are numerous examples in the literature and textbooks describing the electron paramagnetic resonance (EPR) spectra of $S = 1/2$ systems in which there occur several equivalent (isochronous) nuclides with spin $I = 1/2$. Many of these appear oversimplified [49, pp. 58–59; 40, pp. 12–13; 22, pp. 44–45; 4, pp. 81–83; 50, pp. 120–121; 45, pp. 21–23; 19, pp. 50–57]. In reality, they can be far more complicated than is commonly realized, and we wish herein to address ourselves to this situation, from the viewpoint of spin theory. As models, we shall consider paramagnetic $S = 1/2$ chemical species XL_n, where the nucleus of a single central atom is spinless, and where attached atoms L each have nuclear spin

of 1/2. Thus, the spin-hamiltonian operator $^{op}H_s$ is relatively simple, containing no quadrupole or higher-spin terms.

The emphasis herein is not on the occurrence and nature of the higher-order contributions to the hyperfine splittings, which are well known [(e.g., see 19, pp. 45–47; 49, pp. 72–73)], but rather is on the occurrence of certain energy degeneracies, as well as the absences of certain spin states, occurring in some situations. Thus, the emphasis herein is on group-theoretical results. Part 2 of the present work [NW05] will present details of transition energies and intensities.

We shall begin by considering species with XL_3, studied by EPR spectroscopy since the 1950s, and typified by the free radicals $^{12}C^1H_3$ and $^{28}Si^1H_3$, or their fluorinated equivalents. We shall ignore low-temperature considerations, i.e., quantum-statistical effects [33,37,23,27,29, 53,30], and shall focus on freely rotating (thus isotropic) systems.

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A Zeeman energy-level diagram for $n = 3$ is shown in Fig. 1, and a closer-up view of these levels at appropriate magnetic field B showing possible EPR transitions is given in Fig. 2. Here (with four spins of 1/2 each) there are 16 spin states and hence, in principle, $2^n(2^{n+1} - 1) = 120$ magnetic-resonance transitions could occur. We note that 12 of these are significant for pure EPR, yielding six distinct lines.

It should also be said that the considerations of the present paper apply equally well to liquid-phase or gas-phase pure nuclear magnetic resonance (NMR) spectroscopy, e.g., the AX_3 (and AB_3) case such as affor-
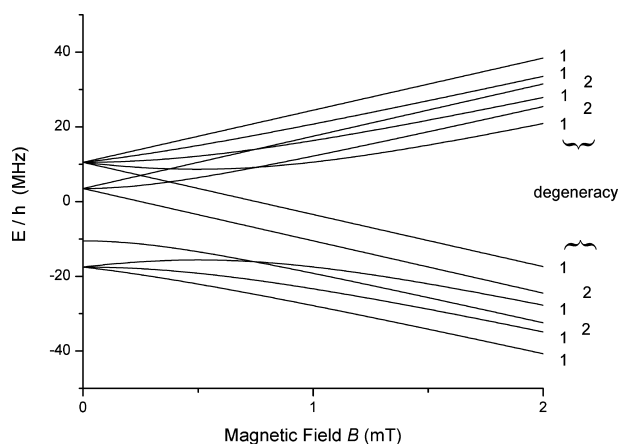

Fig. 1. The Zeeman energy-level diagram for the hypothetical isotropic species XL_3 having one unpaired electron ($g = 2.0030$) and three equivalent $I = 1/2$ nuclides (using g_n for ^{1}H). Here $A/g_e\beta_e$ was taken to be $+0.500$ mT ($A/h = 14.0$ MHz). The field-independent degeneracies are at the right. The appropriate labels for the states at $B = 0$ are, in order of increasing energy: $F = 1, 0, 1, 2$.
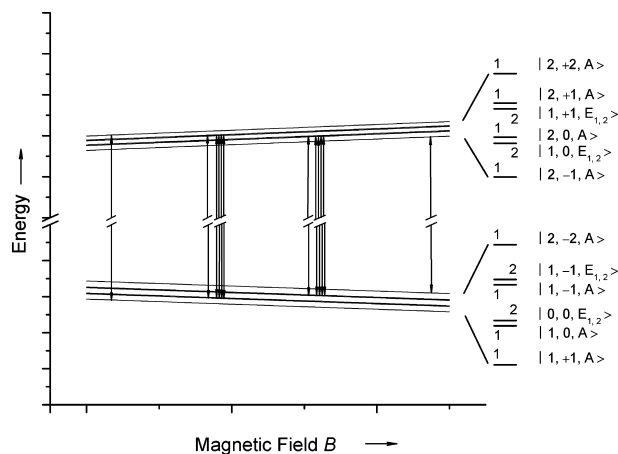

Fig. 2. Schematic of the typical energy levels of species XL_3 and the 12 primary EPR transitions between them, depicted for the X-band region (9.40 GHz). The digits in the first column at right are the degeneracies. The labels at the far right for the states are: Zero-field F, M_F, Irred. Repr. of Permutation Group P_3. The lines occur at 334.55, 335.05 (4 + 1 transitions), 335.55 (4 + 1 transitions) and 336.05 mT, with $A/g_e\beta_e$ taken to be $+0.500$ mT, and $g = 2.0030$. The relative intensities, provided by program EPR–NMR, are 0.250, 0.250 + 0.387 (set of four), 0.250 + 0.705 (set of four), and 0.250. Clearly, the conditions imposed here are not yet very close to the high-field limit.

ded by ^{15}NH$_3$ [41, pp. 101, 196; 24] as well as ^{31}PH$_3$ and ^{31}PF$_3$ [20], and also by ^{11}BF$_3$ [25]. Examples of AX_4 are furnished by ^{15}NH$_4^+$ in water [43, p. 89] and by gaseous ^{13}CH$_4$ [25].

2. Experimental

The production of various energy-level diagrams, and generation of required magnetic resonance spectra, was carried out by use of our in-house FORTRAN program called EPR–NMR [36]. This program performs exact numerical diagonalizations of the H_s matrices, thus taking into account all higher-order energy contributions, and generates relative intensities as well as all magnetic resonance line positions.

3. The chemical systems

3.1. Next, we examine some examples of XL_3 species

The methyl free radical has been much studied, very fruitfully since it is far from a simple system. Its equilibrium geometric configuration has symmetry D_{3h}, i.e., it is planar [9]. Its spin-hamiltonian parameters when the molecule is freely rotating are $g = 2.0024$ [26] and $A/g_e\beta_e = -2.31$ mT for ^{1}H [14; PF87, p. 52]; these parameters depend slightly on temperature [55] and solvent matrix. They do not exhibit appreciable anisotropy even at 4 K [37].

When observed at sufficiently high temperatures, ^{12}C^{1}H$_3$ are said to yield a four-line EPR spectrum (nominal intensity ratios 1:3:3:1). In reality, it only approaches this nominal perfection at sufficiently high magnetic fields. At (say) X-band, the middle two lines are in fact in some systems actually split into two, due to higher-order hyperfine effects, as discussed in the literature [1,14,39,46,8,18,16] and below.

The free radical CF_3 too has been much studied [32,42,15,16]. Its parameters are anisotropic, with $g = $ ca. 2.0036, and $|A|/g_e\beta_e = $ ca. 14.5 mT for ^{19}F. Its 'geometry' is pyramidal. The relatively large magnitude of A, as compared to that of CH_3, produces relatively easy-to-detect splittings of the central lines of the 'quartet.'

Other XL_3 species include SiH_3 [37,19, p. 188], SiF_3 [50, p. 144], and SF_3 [45, p. 66], as well as NH_3^+ [54].

3.2. The system XL_4

In Fig. 3, we show the Zeeman-energy-level scheme for XL_4. We see that there are 32 spin states, with field-independent degeneracies: six states of three, two states of two, and 10 non-degenerate.

Chemical examples include CH_4^+ [19, p. 375] and PH_4 [10], and of course the elusive NH_4 radical.
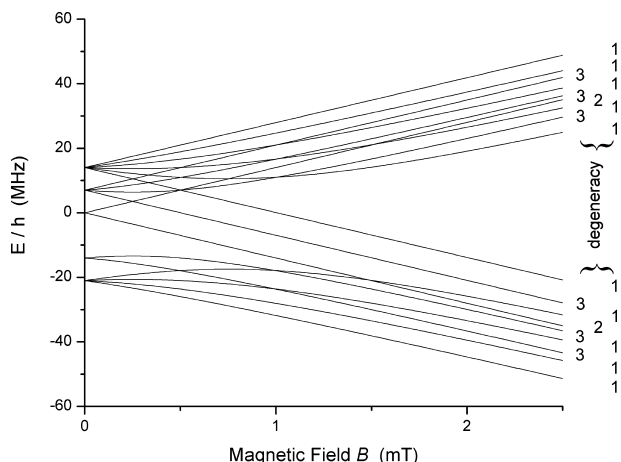
Fig. 3. The Zeeman energy-level diagram for the hypothetical isotropic species XL_4 having one unpaired electron ($g = 2.0030$) and four equivalent $I = 1/2$ nuclides (using g_n for ^{1}H). Here, $A/g_e\beta_e$ was taken to be $+0.500$ mT ($A/h = 14.0$ MHz). The field-independent degeneracies are given at the right.

3.3. The system XL_5

Here there are 64 spin states, with field-independent degeneracies: four states of 5, eight states of 4, 12 non-degenerate.

Chemical examples are SF_5 [45, p. 68] and PF_5^- [38], but these do not exhibit equivalence of all five fluoride ions.

3.4. The system XL_6

Finally, we encounter the important system XL_6, for which there are very numerous examples: e.g., L = F with X = Cl, Br, I, and, Mo, W, Y, Xe, As, Sb, S, and Se, Te, and Bi, Pb, Tl, and of course U, Np, occurring as neutral or ionic species, many carrying a single unpaired electron. In some of these species, at sufficiently low temperatures, there tends to be distortion to yield molecules with D_4 symmetry, having two uniaxial equivalent fluorides differing from the four equivalent co-planar fluorides placed normal to the axis (which thus exhibit exchange degeneracy). At higher temperatures, all six fluoride anions move sufficiently so as to become equivalent (time-average octahedral symmetry), leading to greater exchange symmetry. Thus, in the limit as the mean life-time of the three ground-state D_4 configurations goes to zero, $XL_4L'_2$ becomes XL_6. As an example, we cite the X = halogen species [6].

4. The spin systems

The XL_n systems feature $(2S + 1)(2I + 1)^n$ spin states. The states can be labeled with the total spin angular-momentum operator $^{op}\mathbf{S} + \sum_{i=1,n} {}^{op}\mathbf{I}_i \equiv {}^{op}\mathbf{F}$ for each system, and the corresponding primary quantum numbers F. The number of ways in which a spin value F may

be realized out of an assembly of $N \equiv n + 1$ spins 1/2 is [28, pp. 214–215] given by $k(F) \equiv (2F + 1) N!/\{[(N/2) + F + 1]![(N/2) - F]!\}$; compare with Eq. (5).

Using the formula for $k(F)$, taking $n = 3$ as an example, one finds that there is one way only to construct a state with $F = 2$, three with $F = 1$, and two with $F = 0$.

At the limit $B = 0$ of the external magnetic field, the 16 states of XL_3 occur at energies $-5A/4$ (one $F = 1$ state), $-A/4$ (two $F = 0$ states), $+A/4$ (two $F = 1$ states), and $+3A/4$ (one $F = 2$ state), as shown in Fig. 1 (and see Appendix A in Part 2 of the present work). In the above, A is the isotropic hyperfine coupling energy parameter [see Eq. (1b) and Footnote[1]]. The quantum number F is not valid for non-zero magnetic fields B, and hence is not meaningful as a state label (Fig. 2) when $n > 1$ except via parentage (tracing back to $B = 0$); however, its projection M_F is available for all B. Note the extra degeneracies (exchange degeneracies [3, p. 391; 34, pp. 431, 507–508]), occurring besides the M_F degeneracy $2F + 1$ present at $B = 0$ (the latter only is lifted by $B > 0$).

It may be of some interest to note that in the unphysical case $A = 0 \neq g_n$, field-independent degeneracy occurs even for XL_2 (two doublets), which is lifted by the hyperfine interaction. For XL_3, $A = 0$ implies presence of two triplets.

For XL_4, there are 32 states (Fig. 3) featuring zero-field energies $-3A/2$ ($F = 3/2$), $-A(F = 1/2)$, $0(F = 1/2)$, $+A/2(F = 3/2)$, and $+A(F = 5/2)$. Among the B-field-independent degeneracies, there are six triply degenerate sets.

The high-field electron spin resonance spectra of systems with equivalent nuclei should generally be interpreted in terms of spin-hamiltonian

$$^{op}H_s = {}^{op}H^Z + {}^{op}H^{hf} \tag{1a}$$

$$= \left(g\beta_e \mathbf{B}^T \cdot {}^{op}\mathbf{S} - g_n\beta_n \mathbf{B}^T \cdot \sum_{i=1,n} {}^{op}\mathbf{I}_i \right)$$

$$+ A{}^{op}\mathbf{S}^T \cdot \sum_i {}^{op}\mathbf{I}_i. \tag{1b}$$

Here operator $^{op}H^Z$ represents the Zeeman interactions of the unpaired electron, and also of the nuclear spins respectively, with the external magnetic field **B**, while $^{op}H^{hf}$ [second term in (1a)] describes the hyperfine coupling between the electron and the nuclear spins. Super-

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[1] Assignment of the correct sign to hyperfine coupling parameters is not an entirely trivial matter [27,2,49]. Changing the sign of A reverses the order in which the energy levels occur (e.g., in Fig. 1), which is most easily visible at or near $B = 0$. The order of the EPR peaks is reversed, i.e., the low-field end versus the high-field end, but this is not discernible experimentally unless the nuclear Zeeman term in H_s yields effects of the same order-of-magnitude as the hyperfine term. In principle, the sign can be obtained by observing the relative population of the spin states at or near $B = 0$, i.e., line intensities. It is possible to predict the sign of A from theory, especially if accurate calculations of core-polarization effects are feasible.

script T denotes spatial matrix transposition. The nuclear spin–spin interactions have been neglected in (1a), but see Part 2 of the present work.

It is sufficient for our present purposes to consider the EPR spectrum of a system with n equivalent nuclei in the high-field case (since usually parameter A is sufficiently small, this is the most common experimentally observed situation). It is then usual to approximate $(^{op}\mathbf{S}^T \cdot \sum_i {}^{op}\mathbf{I}_i)$ by term $(^{op}S_z \, {}^{op}I_z)$, where $^{op}I_z$ is taken to be $\sum_i {}^{op}I_i$ is the total z component operator of the nuclear spin angular momentum. Furthermore, we neglect the nuclear Zeeman term as small compared to the electronic Zeeman energy. As a result, the EPR spectrum is the well-known multiplet of equally spaced lines described by transitions between the energy levels $E(S_z, I_z) = g\beta_e B S_z + A S_z I_z$. In this approximation, the unpaired electron with a given value $M_S (= S_z)$ experiences nuclear magnetic spin $(M_I)_i (= I_z)$.

In the high-B region, i.e., above all the level crossings (B above ca. $4|A|/g_e\beta_e$; where g_e is the free-electron Zeeman splitting factor, and β_e is the Bohr magneton; Figs. 1 and 3), the states can be labeled by sets of the secondary quantum numbers M_S and M_I, where the spin quantization is best taken along $\mathbf{B}$, and where $M_S + \sum_{i=1,n} (M_I)_i = M_F$.

For $n = 3$, at sufficiently large B fields, the states can be taken as "degenerate" manifolds with 1:3:3:1 relative energies for each of $M_S = -1/2$ and $+1/2$. The field-swept EPR allowed transitions then consist nominally of four equally spaced absorptions, with relative intensities 1:3:3:1. The spacing is $A/g_e\beta_e$ in magnetic-field units. This four-line spectrum is depicted frequently in the literature, e.g., [49, p. 59], and thus constitutes 'common knowledge' for virtually all EPR spectroscopists.

However, the reality often differs appreciably from this ideal spectrum, at usual microwave frequencies (X-band: 9–10 GHz). This is caused by line shifts and splittings that can be represented by 2nd-order and higher perturbation energy expressions, which go to zero as B goes towards infinity; for example, see [13,47]. The spectra will be described in more detail below, along with specific chemical examples.

To enter the realm of NMR spectroscopy, we have simulated [36] a 300 MHz spectrum (very similar to the EPR spectrum, say, of CH_3) for the hypothetical chemical species $H(H)_3$ [see Footnote[2] for some details],

where the three ^{1}H nuclides were taken to be equivalent. Here, the relevant spin–spin coupling parameter J was chosen to be 10 Hz, and the full lorentzian linewidth 0.06 Hz. We note that the theory setout herein for EPR converts to NMR by replacing $g\beta_e$ with $g_n\beta_n$, and A with nuclear spin–spin coupling parameter J, and (of course) $^{op}\mathbf{S}$ with $^{op}\mathbf{I}$.

Returning to EPR, for the case of $n = 3$, the first-approximation theory gives four distinct energy levels for each value S_z, which correspond to $M_I = +3/2$ (singlet), $M_I = +1/2$ (triply degenerate), $M_I = -1/2$ (triply degenerate) and $M_I = -3/2$, and the EPR spectrum which consists of four-lines with relative intensities 1:3:3:1. However, the calculated energy-level diagram (see Figs. 1 and 2) does not show triply degenerate states, but rather these levels are split into a singlet and a quartet each.

This behavior can be qualitatively explained using group-theoretical analysis. The XL_n system is invariant with respect to any permutation of equivalent nuclei. The spin-hamiltonian (1) must remain unaltered under these permutations. Then each of the individual state functions or sets of degenerate functions must transform in the same way, as one of the symmetry species of the appropriate permutation group P_n [51], and states that belong to different symmetry species cannot "interact" with one another, i.e., both cannot appear as components in the same energy eigenvector.

As stated above, for XL_3, the three nuclei with spin 1/2 yield total spin z components M_I of $+3/2$, $+1/2$, $-1/2$, and $-3/2$. One then finds:

(a) For $M_I = \pm 3/2$, there is only one state 'function' each (which is the product of three nuclear single-spin kets):

$$^{+3/2}| > \equiv | + + + >, \tag{2a}$$

$$^{-3/2}| > \equiv | - - - >; \tag{2b}$$

(b) For $M_I = \pm 1/2$, there are three basic product functions each:

$$^{+1/2}|>_{j=1,2,3} = |+ + ->, |+ - +>, \text{ and } |- + +>, \tag{3a}$$

$$^{-1/2}|>_{j=1,2,3} = |- - +>, |- + ->, \text{ and } |+ - ->. \tag{3b}$$

The latter two sets of functions each form a reducible representation of the symmetry group P_3. The deconvolution of such representations into irreducible ones, for the groups P_n (with $n = 3, 4, 5, 6$) is described in Section 5.

5. Group theory of the general XL_n problem

We need to deal with the symmetric (permutation) groups P_n relevant to the nuclear-spin system consid-

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[2] According to Program Spartan '04 Windows [44] using the 6-311 + G** basis set for diamagnetic species H_4, the following results are valid. For a system XL_3 featuring a central atom $X = H$ attached covalently to three coplanar atoms $L = H$ would exhibit system symmetry D_{3h} with predicted energy -2.1632 a.u. relative to the total energy of the bare protons and electrons, all infinitely far apart (bond lengths 1.857 Å). A tetrahedral system XL_4, with X empty and four ligands $L = H$, would have energy -1.7256 a.u. ($X - L$ distances 1.516 Å, bond $L - L$ lengths 2.475 Å). For comparison, the energy calculated with Spartan for the H_2 molecule is -1.1325 a.u. (observed -1.1664 a.u.).

ered. The order of each such group is $n!$ and each has n_c classes (see Table 1), and thus n_c irreducible representations (species). However, with spin systems such as ours, the number of species actually needed may be less than n_c (see Table 1). Some states are excluded, consistent with the operation of the generalized Pauli principle [52, p. 128]. The details are set by the fact that all the nuclei involved have spin 1/2.

The number n_α of irreducible representations (symmetry species) Γ^α can be obtained ([21, p. 105; 28, p. 334]) from the group-theory formula

$$n_\alpha = (1/\gamma) \sum_C \gamma_c \chi_c \chi_c^\alpha, \tag{4}$$

applicable for determination of the number of times any given symmetry species is contained in any given group representation. Here, γ is the number ($n!$) of operations in the group, γ_c is the number of operations in each class [C], χ_c are the characters for the various classes of per-

mutations, and χ_c^α are the species characters as tabulated for each group [21, pp. 185–188]. Symbol α labels the symmetry species.

The number $\kappa(M_I)$ of ways in which the nuclear spins can be arranged to give particular value of M_I is

$$\kappa = n!/\{[(n/2) + M_I]![(n/2) - M_I]!\}, \tag{5}$$

so that the degeneracy of the energy levels is determined by this number, as are the relative intensities of the EPR lines. Thus, for XL_3, $\kappa = 1$ & 3 for $|M_I| = 3/2$ & 1/2.

For our purposes, following Wigner's lead [52; Chapter 13; also see 35, vol. 2, Appendix D, #18], we note that the system of n equivalent nuclei can be represented as having n variables each of which can only assume either of two values. Then the relevant space consists of 2^n points, and we can have 2^n linearly independent functions. Denote by u_i and v_i, respectively, the states of the ith individual spin corresponding, respectively, to the eigenvalues $+1/2$ and $-1/2$ of I_z. An orthogonal

Table 1
Reduced character tables of permutation groups P_n

Group P_2

	1 (1^2)	1 (2)	
$^+D_{(0)}$	1	1	A_1
$^-D_{(0)}$	1	−1	A_2

Group P_3

	1 (1^3)	3 (2,1)	2 (3)	
$^+D_{(0)}$	1	1	1	A_1
$^-D_{(0)}$	1	−1	1	A_2
$^+D_{(1)}$	2	0	−1	E

Group P_4

	1 (1^4)	6 (2,1^2)	3 (2^2)	8 (3,1)	6 (4)	
$^+D_{(0)}$	1	1	1	1	1	A_1
$^-D_{(0)}$	1	−1	1	1	−1	A_2
$^+D_{(1)}$	3	1	−1	0	−1	T_1
$^-D_{(1)}$	3	−1	−1	0	1	T_2
$^+D_{(2)}$	2	0	2	−1	0	E

Group P_5

	1 (1^5)	10 (2,1^3)	15 (2^2,1)	20 (3,1^2)	20 (3,2)	30 (4,1)	24 (5)
$^+D_{(0)}$	1	1	1	1	1	1	1
$^-D_{(0)}$	1	−1	1	1	−1	−1	1
$^+D_{(1)}$	4	2	0	1	−1	0	−1
$^-D_{(1)}$	4	−2	0	1	1	0	−1
$^+D_{(2)}$	5	1	1	−1	1	−1	0
$^-D_{(2)}$	5	−1	1	−1	−1	1	0

Group P_6

	1 (1^6)	15 (2,1^4)	45 (2^2,1^2)	15 (2^3)	40 (3,1^3)	120 (3,2,1)	40 (3^2)	90 (4,1^2)	90 (4,2)	144 (5,1)	120 (6)
$^+D_{(0)}$	1	1	1	1	1	1	1	1	1	1	1
$^-D_{(0)}$	1	−1	1	−1	1	−1	1	−1	1	1	−1
$^+D_{(1)}$	5	3	1	−1	2	0	−1	1	−1	0	−1
$^-D_{(1)}$	5	−3	1	1	2	0	−1	−1	−1	0	1
$^+D_{(2)}$	9	3	1	3	0	0	0	−1	1	−1	0
$^-D_{(2)}$	9	−3	1	−3	0	0	0	1	1	−1	0
$^+D_{(3)}$	5	1	1	−3	−1	1	2	−1	−1	0	0

The rows list the irreducible representations required in our problem. The columns represent the group classes, giving the number γ_c of elements in each. Below this number, the class, having α 1-cycles, β 2-cycles, γ 3-cycles, etc. (see Footnote 3), is designated by ($1^\alpha, 2^\beta, 3^\gamma, \ldots$; the superscript is suppressed when equal to 1). Also included on the right are some commonly used symbols for the irreducible representations. The pre-superscript $\pm$ on the species symbol $D_{(q)}$ ($q = 0, 1, \ldots, n' \leqslant n$) indicates a member of an associated pair (see text).

basis is obtained by taking all possible products of n of these u and v state vectors (kets). Thus, the product

$$\zeta_M = u_1 u_2 \cdots u_{n-k} v_{n-k+1} \cdots v_n \quad (\text{where } k = 0, 1, \ldots, n) \tag{6}$$

not only is a function within this basis but also is an eigenstate of the component I_z of the total nuclear spin operator; the corresponding eigenvalue is $M_I = (n/2) - k$. In this notation, the function ζ_M when $k = 0$ is the product of all n kets u_i and contains no kets v_i, and similarly ζ_M when $k = n$ is the product of all n kets v_i. The number of functions which correspond to any given M_I (all those with the same k) is binomial coefficient $C_n^{(k)} = n!/[k!(n-k)!]$. It is convenient to group all functions ζ_M with identical M_I values into single rows, arranging the 2^n functions in a set of rows labeled with increasing k values.

If the operator $^{op}P(R)$, corresponding to any given permutation R of the n nuclei, is applied to one of the functions ζ_M, it produces a new function which can be expressed as a linear combination of the 2^n basis functions. The coefficients will give a 2^n-dimensional representation of the symmetric group P_n. This representation $\Delta(R)$ is not irreducible, except in the trivial $n = 1$ case. Because the functions considered are defined in such narrowly limited space, one finds that $\Delta(R)$ does not contain all the irreducible representations of the symmetric group and, therefore, that generally it can be reduced more easily than a completely arbitrary representation. The irreducible representations are described in detail by Wigner [52, pp. 128–139]. It turns out that, if the operator $^{op}P(R)$ is applied to one of the functions ζ_M, where R is any arbitrary permutation, the result is again a product of spin kets with the same value of M_I. If one wishes to express in terms of the basic product functions those $C_n^{(k)}$ functions which result from applying $^{op}P(R)$ to all the functions having the same number k, only the functions with this value of k need be used. These functions, therefore, provide a representation $\Delta^{(k)}(R)$ of the symmetric group, with dimension $C_n^{(k)}$. Since each function in the kth row is transformed by a permutation into another function in the kth row, $\Delta^{(k)}(R)$ has one element in each row equal to 1 and all other elements equal to 0. The representation $\Delta(R)$ therefore decomposes into representations $\Delta^{(0)}(R)$, $\Delta^{(1)}(R)$,..., and $\Delta^{(n)}(R)$. It is clear that $\Delta^{(k)}(R)$ is not necessarily an irreducible representation, since linear combinations which transform under $^{op}P(R)$ according to $\Delta^{(k-1)}(R)$ can be formed from the kth row, and this would not be possible in an irreducible representation. In Wigner's book [52, pp. 131–133], it is shown that, for $k \leqslant n/2$, the $C_n^{(k-1)}$ functions form a linearly independent set. Furthermore, the representation $\Delta^{(k)}(R)$ divides into two representations, $\Delta^{(k-1)}(R)$ and $\Delta_{(k)}(R)$, with dimensions $C_n^{(k-1)}$ and $C_n^{(k)} - C_n^{(k-1)}$, respec-

tively. The representation $\Delta^{(k-1)}(R)$ divides into $\Delta^{(k-2)}(R)$ and $\Delta_{(k-1)}(R)$, and so on. Finally, $\Delta^{(k)}(R)$ divides into $D_{(0)}$ & $D_{(1)}$ &$\cdots$& $D_{(k)}$. The function in the kth row which transforms according to species $D_{(0)}$ is the 'sum' of all functions in this row.

As shown in Wigner [52, p. 127], if there is an irreducible representation $D_{(k)}$, then another representation, the representation $D_{(k)assoc}$ associated with $D_{(k)}$, can be formed from $D_{(k)}$ by leaving unchanged all matrices which correspond to the even permutations, and multiplying all others (odd permutations) by -1. Pairs of associated species will henceforth be denoted by $^{\pm}D_{(k)}$. The above considerations hold for $k \leqslant n/2$. For $k > n/2$, the $C^{(k)}$ functions in which $n - k$ variables assume $M_S = -1/2$ and k variables have $M_S = +1/2$ transform exactly like the functions belonging with $k < n/2$.

It is worthy of note that decomposition into irreducible representations for each permutation group P_n can be done using Eq. (4), which allows one to determine the number of times any given symmetry species is contained in any given group representation. The characters of the species were determined using a procedure described by Wigner [52, pp. 138–139], and given in Table 1. In these tables, the elements of the permutation groups are grouped into classes, and the number γ_c of operations in each class [C] is indicated. The description of the classes can be found elsewhere [21, pp. 23–28] (also see Table 2).

As a simplest example, we can consider XL_2 [For some other details, see [49, pp. 465–468], and set out the appropriate table

$$\Delta^{(0)} = D_{(0)},$$
$$\Delta^{(1)} = D_{(0)},$$
$$\Delta^{(2)} = D_{(0)}.$$

Here symbol $D_{(0)}$ in all three rows represents $^{+}D_{(0)}$ for the triplet of states all symmetrical under particle L interchange, and $D_{(0)}$ in the middle row also represents $^{-}D_{(0)}$ for the single antisymmetrical state.

For the system XL_3, the relevant symmetry group is P_3, which consists of the six permutations grouped into three classes as shown by brackets (see Table 1 and Footnote[3]):

[(1)] (identity element), [(123), (132)], [(12), (23), (13)]. Typically for $n > 2$ [35, vol. 2, Appendix D, #18], when considering pairwise interchange of the nuclei L, one finds

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[3] In a frequently used notation for permutations, these are resolved into cycles [21, pp. 13–24; 31, pp. 538–541]. A cycle is a permutation which replaces every element by the element following it, except that the last element of the set is replaced by the first element. All permutations which have the same cycle structure form a conjugate class in group P_n. The degree of the cycle is the number of letters within the parentheses. Note that a symbol (1^α) denotes α cycles of degree 1, while a symbol such as $(ac)(b)$ (for $n = 3$) signifies simultaneous presence of two cycles in a class.

Table 2
The resolution of the representations $\Delta^{(p)}$ $(p = 0, 1, \ldots, n)$ of the symmetric groups P_n into irreducible representations $D_{(q)}$ $(q = 0, 1, \ldots, n' \leqslant n)$

$n = 2$
$\quad \Delta^{(0)} = D_{(0)}$
$\quad \Delta^{(1)} = D_{(0)}$
$\quad \Delta^{(2)} = D_{(0)}$

$n = 3$
$\quad \Delta^{(0)} = D_{(0)}$
$\quad \Delta^{(1)} = D_{(0)} \,\&\, D_{(1)}$
$\quad \Delta^{(2)} = D_{(0)} \,\&\, D_{(1)}$
$\quad \Delta^{(3)} = D_{(0)}$

$n = 4$
$\quad \Delta^{(0)} = D_{(0)}$
$\quad \Delta^{(1)} = D_{(0)} \,\&\, D_{(1)}$
$\quad \Delta^{(2)} = D_{(0)} \,\&\, D_{(1)} \,\&\, D_{(2)}$
$\quad \Delta^{(3)} = D_{(0)} \,\&\, D_{(1)}$
$\quad \Delta^{(4)} = D_{(0)}$

$n = 5$
$\quad \Delta^{(0)} = D_{(0)}$
$\quad \Delta^{(1)} = D_{(0)} \,\&\, D_{(1)}$
$\quad \Delta^{(2)} = D_{(0)} \,\&\, D_{(1)} \,\&\, D_{(2)}$
$\quad \Delta^{(3)} = D_{(0)} \,\&\, D_{(1)} \,\&\, D_{(2)}$
$\quad \Delta^{(4)} = D_{(0)} \,\&\, D_{(1)}$
$\quad \Delta^{(5)} = D_{(0)}$

$n = 6$
$\quad \Delta^{(0)} = D_{(0)}$
$\quad \Delta^{(1)} = D_{(0)} \,\&\, D_{(1)}$
$\quad \Delta^{(2)} = D_{(0)} \,\&\, D_{(1)} \,\&\, D_{(2)}$
$\quad \Delta^{(3)} = D_{(0)} \,\&\, D_{(1)} \,\&\, D_{(2)} \,\&\, D_{(3)}$
$\quad \Delta^{(4)} = D_{(0)} \,\&\, D_{(1)} \,\&\, D_{(2)}$
$\quad \Delta^{(5)} = D_{(0)} \,\&\, D_{(1)}$
$\quad \Delta^{(6)} = D_{(0)}$

Here the pre-superscript $\pm$ on symbols D (compare Table 1) have been suppressed.

no antisymmetrical state(s). However, the species $^{+}D_{(0)}$ (alias $|A_1\rangle$; see Table 1) is symmetrical for all three such interchanges. The other species show no symmetry, i.e., are neither symmetrical or antisymmetrical. The detailed functions will be given explicitly in Part 2 of this work.

The three nuclei, each with spin 1/2, yield total z components M_I of $+3/2$, $+1/2$, $-1/2$, $-3/2$. One then finds:

(a) For $M_I = \pm 3/2$, there is only one state function each (which is the product of three single-spin kets, labeled $k = 0$ and 3, respectively [Eqs. (2a) and (2b)]. Each of them forms the irreducible representation $D_{(0)}$. Obviously there is only one state with $M_I = +3/2$ and one with $M_I = -3/2$.

(b) For $M_I = \pm 1/2$, there are three basic nuclear spin product functions each, as given above [Eqs. (3a) and (3b)]. The latter two sets of functions (they correspond to $k = 1$ and 2) each form a reducible representation $\Delta^{(1)}$ of the symmetry group P_3. This representation decomposes into two irreducible representations, $D_{(0)}$ and $D_{(1)}$, having dimensions 1 and 2 (Table 2). We can see that the three prod-

uct functions with $M_I = +1/2$ can be combined to give one linear combination in the completely symmetric species $D_{(0)}$, and one degenerate pair in species $D_{(1)}$. The three nuclear spin states with $M_I = -1/2$ can be combined in the same manner, in complete analogy to those with $M_I = +1/2$. One can summarize the occurrence of the irreducible representations for $n = 3$ via Table 2.

It follows from the above that the energy levels which correspond to $M_I = +1/2$ and $-1/2$ are not triply degenerate (as often intimated in the literature) but rather are split into a singlet and a doublet each, by the hyperfine and Zeeman interactions, as shown in Figs. 1 and 2. Consequently, the EPR spectrum consists of six lines. However, the splitting of each of the two middle lines can be observed only when the hyperfine parameter $A/g_e\beta_e$ is not too small compared to $g\beta_eB_0$; here B_0 is the position of the center of the field-swept spectrum.

An alternative labeling of the 16 states is using quantum numbers F and M_F, plus the irreducible representation of permutation group P_3 (see Fig. 2). Note that the transitions 1, 2, 3, and 6 labelled according to increasing field line positions are between states of type A, while 3 is for type E between states labeled with different F values, while 5 is also of type E but occurring between states of the same F. Thus, there is an inherent asymmetry: for the experimental spectrum, see [15; 49, Fig. 3.16 on p. 73].

5.1. Systems XL_n with n greater than three can be considered in the same fashion

Thus for $n = 4$ equivalent nuclei, the relevant permutation group is P_4, and application of group-theoretical consideration to this 16-state nuclear-spin system (Fig. 3) reveals that the decomposition of representations $\Delta(R)$ takes the form given in Table 2. Here, the dimensions of irreducible representations $D_{(0)}$, $D_{(1)}$, and $D_{(2)}$ are 1, 3, and 2, respectively (Table 1). The values of κ are 1 & 4 & 6 for $|M_I| = 2$ & 1 & 0. The state with $M_I = +2$ $(k = 0)$ forms a singlet state of species $D_{(0)}$; the four states with $M_I = +1$ $(k = 1)$ can be combined to give one linear combination in the completely symmetric species $D_{(0)}$ plus species $D_{(1)}$ (triplet state); the six $M_I = 0$ $(k = 2)$ nuclear states yield a singlet, a triplet and a doublet. Similarly, the four states $M_I = -1$ $(k = 3)$ lead to a singlet and a triplet, and $M_I = -2$ $(k = 4)$ gives a singlet.

For $n = 5$ equivalent nuclei, the representation $\Delta(R)$ within permutation group P_5 decomposes as shown in Table 2. Here, $D_{(0)}$ denotes the irreducible representation of dimension one, $D_{(1)}$ of dimension four, and $D_{(2)}$ of dimension five. It shows that the state with $M_I = +5/2$ $(k = 0)$ forms a singlet, the five states $M_I = +3/2$ $(k = 1)$ give one singlet and one quadruplet.

The 10 $M_I = +1/2$ ($k = 2$) nuclear states give one singlet, one quadruplet, and one quintet. Once again, the $M_I < 0$ states behave analogously.

For $n = 6$ equivalent nuclei (XL_6), one obtains the pattern shown in Table 2. The dimensions of the irreducible representations $D_{(0)}$, $D_{(1)}$, $D_{(2)}$, and $D_{(3)}$ are 1, 5, 9, and 5, respectively (see Table 1).

Note that, for $n > 4$, the number of allowed irreducible representations of symmetric groups P_n is less than the number of classes in the group, as one can see from Table 1. As stated above, this phenomenon results from operation of the Pauli exclusion principle. As described, one notes that the described treatment does not need to invoke all the irreducible representations of the symmetric group P_n. This is related to the fact that a spin-1/2 particle can assume only two possible spin variables, and, consequently, only representations, along with their associated representations, corresponding to the partition of n into sums of the numbers 1 and 2 (see Appendix A) can occur.

Obviously, and extension of the present work to allow ligand symbol L to represent groups of equivalent nuclei would be of interest, but is not tackled herein.

6. Recoupling theory

There is an alternative approach to the problem discussed herein, as pointed out by a knowledgeable referee. This invokes "re-coupling" of the angular momenta vector (spin) operators present, using theory set out in the literature [5,12]. An example seems appropriate here.

For XL_3, one can recouple the three ($I = 1/2$) nuclear spins to yield four states belonging to $I_{\text{total}} = 3/2$, and two states with $I_{\text{total}} = 1/2$. With addition of the electron spin, one achieves new total angular momentum quantum numbers, $F' = 2$ and 1. Since there is available [7,48,11] an exact energy solution for a single unpaired electron and a single nuclear of arbitrary spin, these two manifolds can be be solved exactly, yielding (of course) the same energies as via our present method (i.e., Figs. 1 and 3). The energy solutions occur in pairs, i.e., as functions of $M_{F'}$ but not of F', containing $\pm\sqrt{}$ terms. Always, one of the pairs for $M_{F'} = \pm F'$ is an unphysical solution. Thus, for $F' = 2$, there will be eight valid solutions, and for $F' = 1$ there will be four. There are two identical $F' = 1$ manifolds (hence, double degeneracy), so that a total of 16 energies occur, matching the previous results in this paper, for XL_3. In Fig. 1, the levels in the region $0 < B < 0.25$ mT, in the order of increasing energies, can be labeled with $F' = 2, 2, 2, 1, 1, 2, 2, 2, 1, 1, 2, 2$. We note that M_F is identical with $M_{F'}$ and that, in these two separate $n = 1$ systems, F' is a good quantum number for all B. It is planned to present further discussion in Part 2 of this work.

7. Conclusions

We have investigated in some detail the theory underlying the energy-level schemes of chemical entities XL_n having equivalent ligands, and have clarified the nature of certain effects found in their magnetic-resonance spectra, which cause complications spoiling the commonly expected simplicity of such spectra. The effects of permutation between equivalent particles have been found to be important, and are discussed in terms of exchange degeneracy and the underlying group theory. It is found that, for $n > 4$, some irreducible representations of the symmetric group P_n do not occur, due to the operation of the generalized Pauli principle. Exact solutions have been found for the spin-hamiltonian energies, and are given in Part 2 of the present work, as are details of transition energies and relative spectral intensities.

Appendix A

The permutations of symmetric group P_n operate on a total of n symbols. Suppose that we resolve the permutations into independent cycles and let the number of 1-cycles be v_1, of 2-cycles be $v_2, \ldots$, of n-cycles be v_n. The group is said to have the cycle structure $(1^{v1}, 2^{v2}, \ldots, n^{vn})$. Since the total number of symbols is n, we must have

$$v_1 + 2v_2 + \cdots + nv_n = n.$$

All those permutations of P_n, which have the same cycle structure form a class in this group, and each solution for positive integers $v_1, v_2, \ldots, v_n$ yields a class in P_n. If we let

$$v_1 + v_2 + v_3 + \cdots + v_n = \lambda_1,$$
$$v_2 + v_3 + \cdots + v_n = \lambda_2,$$
$$\cdots$$
$$v_n = \lambda_n,$$

then

$$\lambda_1 + \lambda_2 + \cdots + \lambda_n = n \text{ and } \lambda_1 \geqslant \lambda_2 \geqslant \cdots \geqslant \lambda_n \geqslant 0.$$

The splitting-up of positive integer n into a sum of n integers is called creating a partition of n. Each class in P_n corresponds to a certain partition of n, and thus the problem of finding the number n_c of classes of conjugate elements in P_n is transformed to the problem of partitioning n.

A given partition $\{\lambda_1, \lambda_2, \ldots, \lambda_n\}$ may be represented by a helpful diagram Y_λ, called a Young tableau [17, 21, and 35, vol. 2, Appendix D, #14], made up of n squares arranged in n rows placed one above the other, the first line having λ_1 squares, the second λ_2 squares, …, the nth λ_n squares. Two partitions which are obtained from each other by interchange of all rows and columns are called 'associated.' Since the number of irreducible representations of the symmetric group P_n is equal to the number of its classes and therefore to the number of partitions of n, each irreducible representation of P_n may be uniquely characterized by a Young diagram. Then any two associated irreducible representations $^+D_{(k)}$ ($k =$ one of $0, 1, \ldots, n$) correspond to associated Young diagrams.

For the system of n spin-1/2 equivalent particles, the single-particle ket can occur in either one of only two forms. The Young diagram for such a system can have at most two rows, and only partitions into sizes (λ) 1 and 2 are possible. Because of this, not all n_c irreducible representations of the symmetric group P_n can occur for this system, for arbitrary n.

Moreover, each type of Young diagram corresponds to the total spin I of a system comprised of n equivalent spins. The Young diagram with $n - k$ squares in one line and k squares in another corresponds to a total spin $I = (n/2) - k$.

For $n = 2$, there are two partitions, $\{2\}$ and $\{1, 1\}$, which can be represented by the Young diagrams with one row of two squares in line ($I = 1$), and two rows with one square each ($I = 0$). The three linearly independent symmetrical states are connected with $I = 1$ and belong to irreducible representation $^+D_{(0)}$, and the one antisymmetrical state, connected with $I = 0$, belongs to irreducible representation $^-D_{(0)}$ of the symmetric group P_2.

For the systems with $n > 2$, the number of possible types of Young diagrams is equal to number partitions n into values 1 and 2. This number is $(n/2) + 1$ for even n, and $(n + 1)/2$ for odd n. These diagrams correspond to states with total spin $I = (n/2), (n/2) - 1, \ldots, 0$ (for an even number of particles) or $(1/2)$ (for an odd number of particles). The states with total spin I belong to irreducible representation $^+D_{(k)}$ with $k = (n/2) - I$. It is clear that the spin functions (kets) of n spin-1/2 particles can be antisymmetrized only with respect to two particles, but not with respect to all n particles.

It can be shown that there is no independent linear combination of spin states in a system with $n > 2$, which corresponds to an antisymmetrical irreducible representation $^-D_{(k)}$. Since $^+D_{(k)}$ and $^-D_{(k)}$ are associated, the

Young diagrams which correspond to them also must be associates. Thus, if the Young diagram with length $n - k$ of the first line corresponds to the irreducible representation $^+D_{(k)}$, then the Young diagram which correspond to $^-D_{(k)}$ must contain $n - k$ lines, the smallest number of lines is expected at $k = n/2$ for n even or $(n + 1)/2$ for n odd?, but this number will be larger than two, except of two cases: when $n = 3$, $k = 1$, and $n = 4$, $k = 2$. The Young diagrams in these two cases are self-associated and the correspondent irreducible representation $^-D_{(1)}$ is equivalent to $^+D_{(1)}$ for group P_3, and $^-D_{(2)}$ is equivalent to $^+D_{(2)}$ for P_4.

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