

The Origin of Mirror Symmetry in High-Resolution NMR Spectra

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Abstract

A connection between the symmetry of high-field NMR spectra, including higher-order spectra, and the properties of the spin system has been established. It is shown that for a spectrum to be symmetric about the mid-resonance frequency (ν_0), two conditions must be satisfied: 1) the resonance frequencies of the spins must be symmetrically positioned about ν_0 , and 2) there must exist at least one spin ordering with a monotonic increase (or decrease) of resonance frequencies such that the spectrum is invariant under the reflection of the J -coupling matrix about its anti-diagonal (one way to satisfy this condition is for the J -coupling matrix to be explicitly persymmetric). The results were validated by calculating theoretical spectra for 3-, 4-, 5-, and 6-spin systems.

Keywords

symmetric NMR spectra, spin systems theory, NMR spectra simulation

1. Introduction

This study investigates the spectral properties of the high-field (or ‘high-resolution’ in the classical sense) spin Hamiltonian under the condition $\nu \gg J$. However, for weak magnetic fields, comparable to or below the Earth's field, the following reasoning becomes inapplicable.

Some high-resolution high-field NMR spectra exhibit symmetry, which can be reasonably categorized into two types: (1) the symmetry of a first-order multiplet about its resonance frequency, and (2) the symmetry of the entire spectrum of a spin system about its spectral center of mass (mirror-symmetric spectrum), as observed, for example, in AB (Pople et al., 1959, p.122; Hoffman et al., 1971, p.57; Gunter, 2013, p.166), A_nB_n (Corio, 1966; p.254), and $AA'XX'$ (Pople et al., 1959, p.142; Hoffman et al., 1971, p.110; Gunter, 2013, p.197) spin systems. The first type of symmetry is readily explained by the fact that the coupled nuclei exist in different spin states which contribute equally to the spectral density on either side of the resonance frequency, regardless of the nuclei spin quantum numbers.

The second type of symmetry is an intrinsic property of the entire spin system. For instance, the spectra of AB (AX), A_nB_n (A_nX_n) and $AA'BB'$ ($AA'XX'$) spin systems exhibit symmetry about their mid-resonance frequency, $\nu_0=(\nu_A+\nu_B)/2$. At first glance, one might expect the spectrum of the $AA'A''XX'X''$ spin system with C_3V symmetry (as in 1,3,5-trifluorobenzene, see Figure 1) to also be mirror-symmetric, however, this is not observed in practice (Cheshkov and Sinitsyn, 2020).

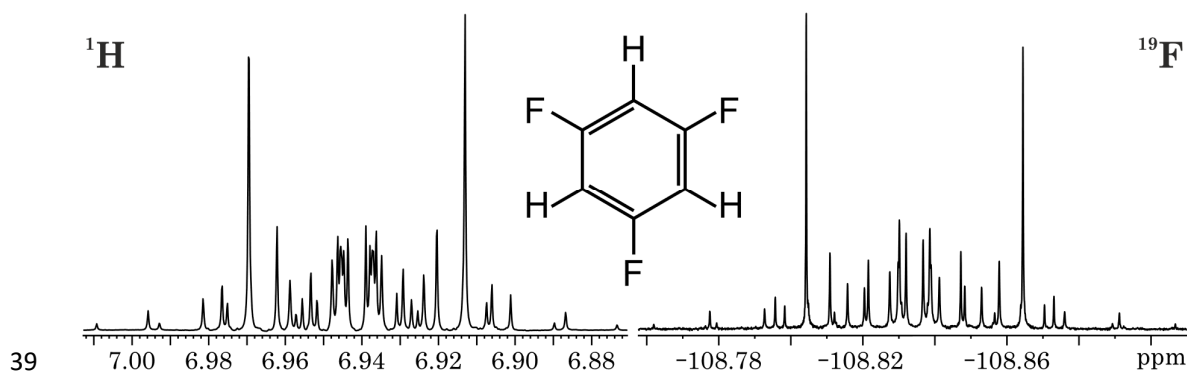
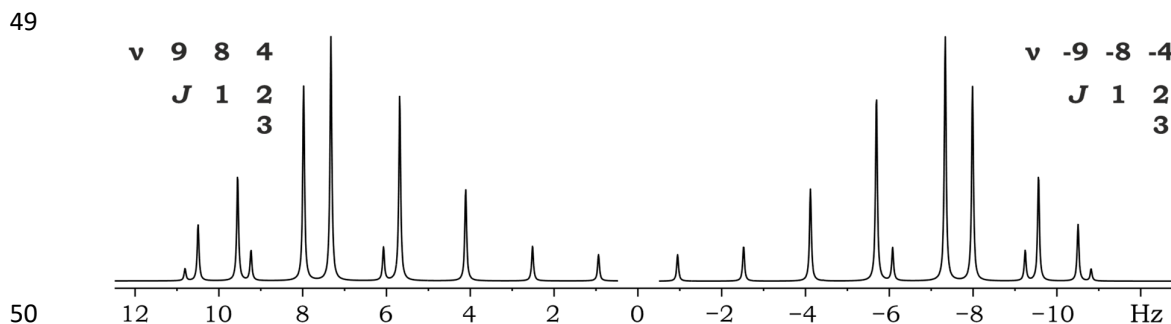


Figure 1. ¹H (300.13 MHz) and ¹⁹F (282.40 MHz) spectra of 1,3,5-trifluorobenzene.

41 In general, high-resolution NMR spectra do not exhibit symmetry about the mid-
42 resonance frequency. It is worth considering how this type of spectrum symmetry can arise.

43 2. Theory

44 Figure 2 shows the spectra of two ABC spin systems with different signs of resonance
45 frequencies. It is readily apparent that the spectra of these spin systems are mirror images of
46 each other. Inverting the order of the resonance frequencies while maintaining the differences
47 between them produces a reflected spectrum, which can be thought of as reversing the direction
48 of the frequency axis.



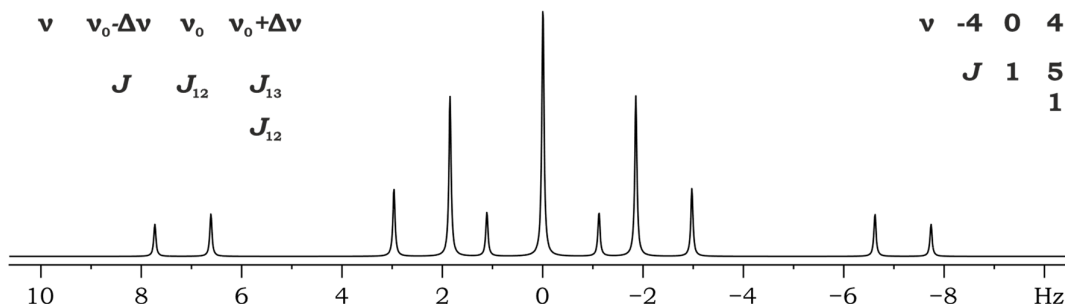
51 Figure 2. Spectra of two ABC spin systems, with different signs of resonance frequencies.

52 To demonstrate how this spectral symmetry can be achieved for a single spin system, the
53 parameter matrices of the considered ABC spin systems are rewritten in the order of their
54 resonance frequencies:

| | | | | | |
|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| v₁ | v₂ | v₃ | -v₃ | -v₂ | -v₁ |
| 9 | 8 | 4 | -4 | -8 | -9 |
| | J₁₂ | J₁₃ | | J₂₃ | J₁₃ |
| | 1 | 2 | | 3 | 2 |
| | | J₂₃ | | | J₁₂ |
| | | 3 | | | 1 |

55 It can be shown that reversing the sequence of resonance frequencies results in a
56 reflection of the *J*-coupling matrix about its anti-diagonal, while the coupling constants on the
57 anti-diagonal itself remain unchanged. If for a certain spin system, the parameter matrix is

58 constructed in such a way that the resonance frequencies are symmetric about the mid-
 59 resonance frequency (ν_0) and the J -coupling matrix is symmetric about the anti-diagonal, i.e.
 60 persymmetric (and thus bisymmetric), then reversing the order of the resonance frequencies
 61 will not alter the spectrum (Figure 3). Moreover, the spectrum itself will be symmetric about
 62 ν_0 . Thus, a persymmetric J -coupling matrix remains invariant under a reversal of the spin order.
 63 The anti-diagonal itself contains the coupling constants between spin pairs that are
 64 interchanged upon order reversal, i.e., the first and the last, the second and the penultimate, and
 65 so forth. The resonance frequencies of these spin pairs must be symmetrically arranged about
 66 the mid-resonance frequency ν_0 , in other words, they must be "equilibrated".



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Figure 3. Mirror-symmetry spectrum of ABC spin system.

69 3. Results and discussion

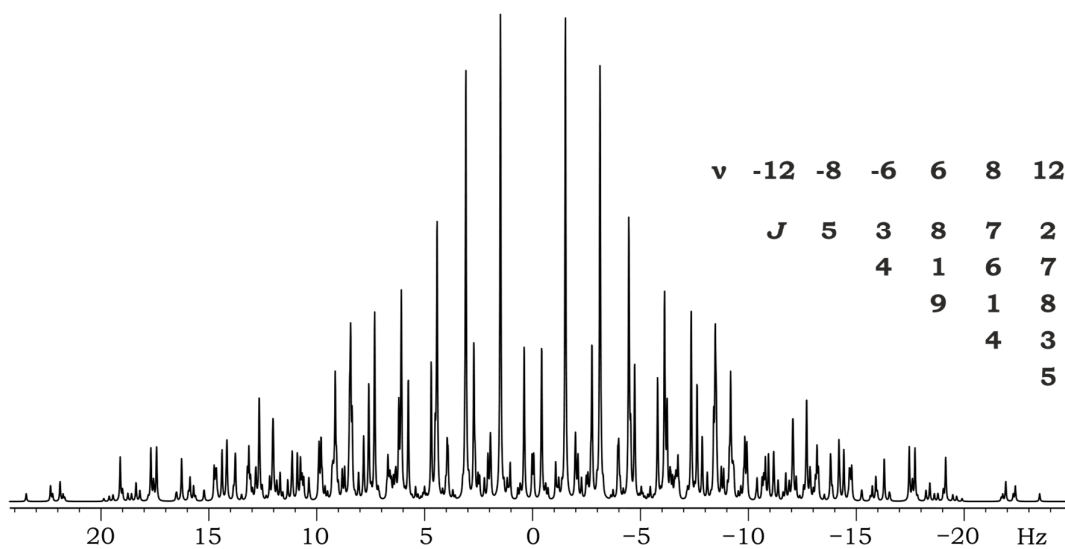
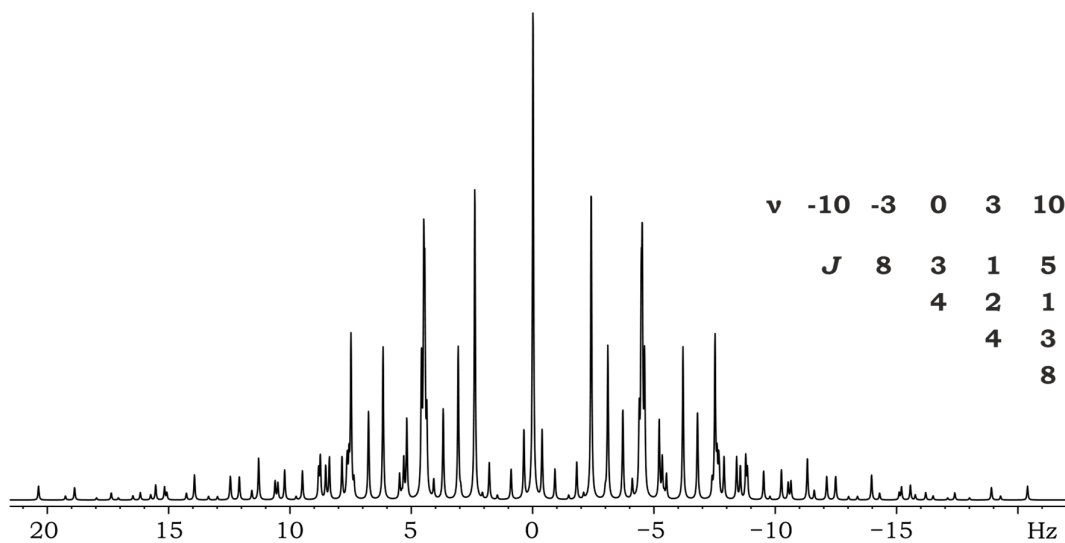
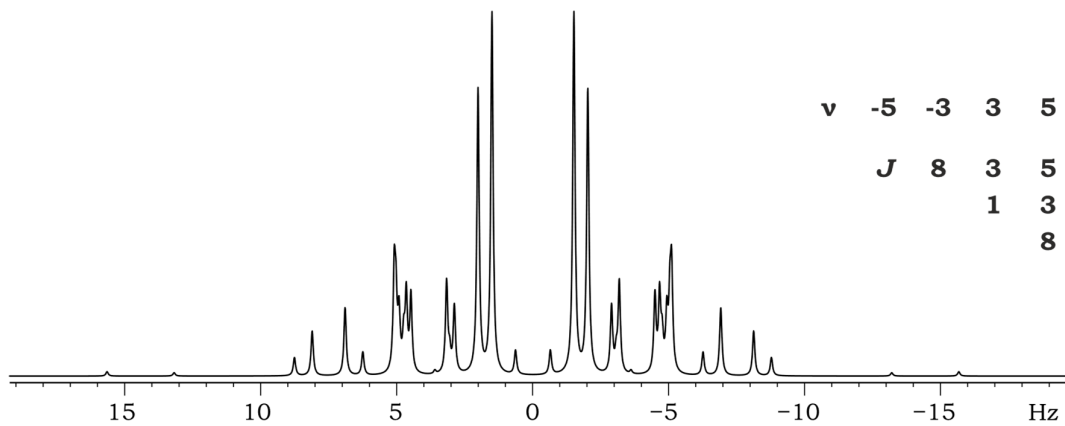
70 Below, in Figure 4, we present several theoretically calculated mirror-symmetric spectra
 71 for spin systems with different numbers of spins (4, 5, and 6). All these spin systems possess
 72 parameter values that meet the conditions outlined above.

73 3.1. Spectral Mirror Symmetry of AA'XX' (AA'BB') and A_nX_n (A_nB_n) Spin Systems

74 It is well-established that o-dichlorobenzene (ODCB) exhibits a mirror-symmetric
 75 ¹H NMR spectrum, corresponding to an AA'XX' spin system (Figure 5).

76 From the algebraic properties of the AA'XX' spin system Hamiltonian, it follows that the
 77 spectrum is independent of the signs of the differences within the coupling constant pairs
 78 $\{J_{AA'}, J_{XX'}\}$ and $\{J_{AX}, J_{AX'}\}$. Consequently, the spectrum is invariant under permutation of the
 79 values within these pairs. Crucially, interchanging $J_{AA'}$ and $J_{XX'}$ is equivalent to interchanging
 80 the resonance frequencies ν_A and ν_X . Since the spectrum is determined by two resonance
 81 frequencies and remains invariant under their permutation (i.e., the reversal of the resonance-
 82 frequency order), it must possess mirror symmetry.

83 The existence of three independent permutations within parameter pairs gives rise to
 84 eight distinct combinations of spin-system parameters corresponding to the same NMR
 85 spectrum (Fig. 5). Four of these combinations can be represented as a result of spin reordering
 86 (Fig. 5, a, c, f, h), while the others contain "non-physical" permutations of parameter values.
 87 Notably, none of these J -coupling matrices possess symmetry with respect to the anti-diagonal.
 88 However, J -coupling matrix e#Fig.5) is the anti-diagonal reflection of matrix d#Fig.5). This
 89 observation leads to more general criteria for mirror symmetry:



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Figure 4. Some examples of theoretically calculated mirror-symmetric spectra for 4, 5 and 6-spin systems.

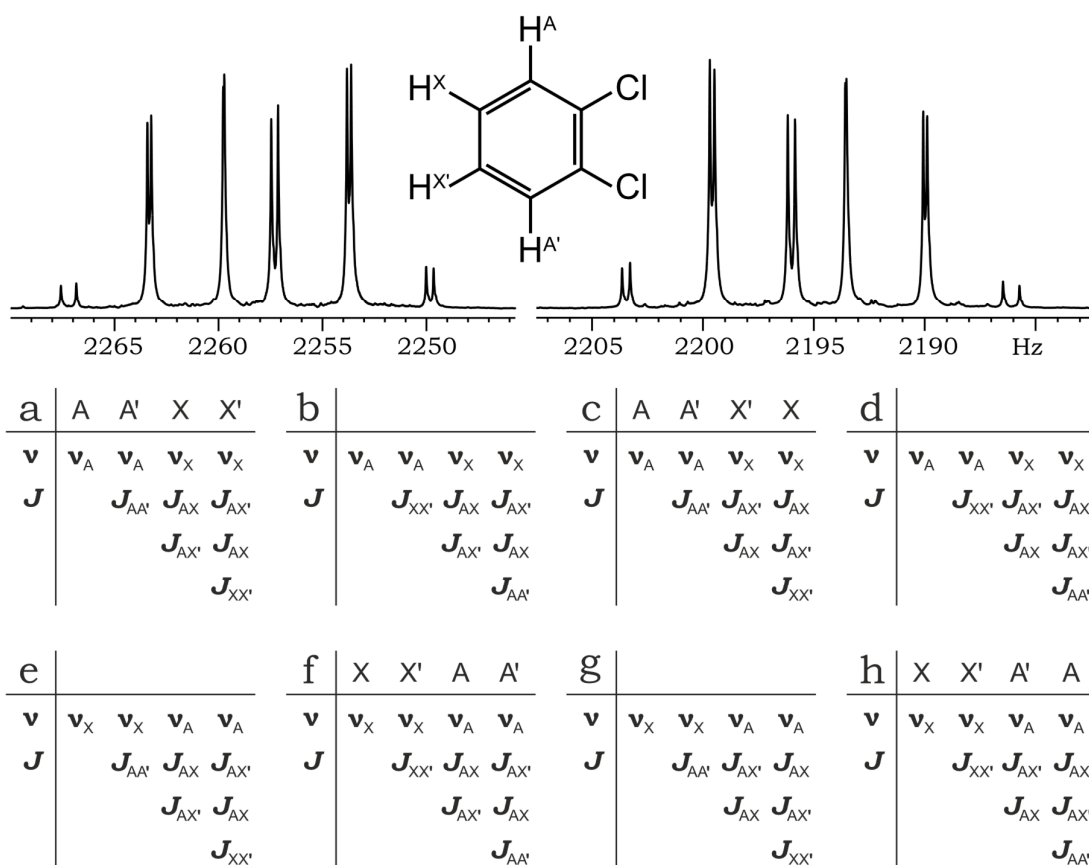


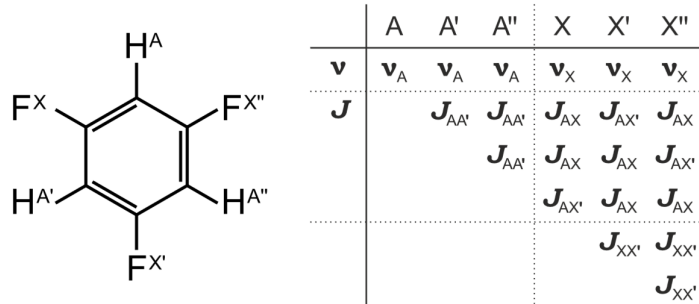
Figure 5. ODCB chemical structure with spin labeling,
 1H NMR spectrum (300.13 MHz), and spin system matrices.

If the resonance frequencies are symmetric about the mid-resonance frequency (ν_0) and if there exists a spin ordering in which resonance frequencies are monotonically ordered increasingly (or decreasingly) and in this order the spectrum is invariant under the reflection of the J -coupling matrix about its anti-diagonal, then the spectrum will be mirror-symmetric. Alternatively: the spectrum is mirror-symmetric if it is invariant under the reflection of all resonance frequencies about their mid-resonance frequency.

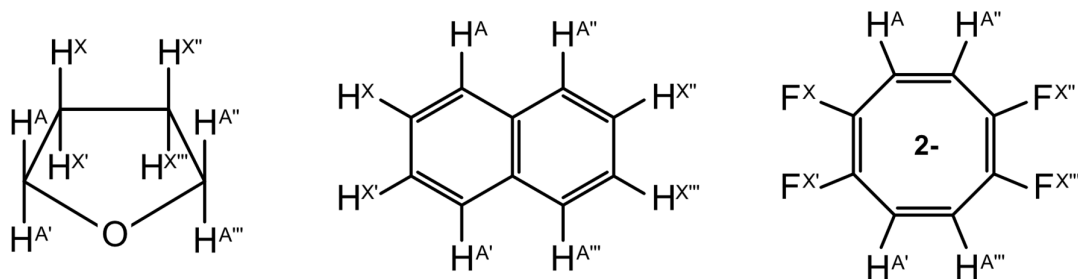
The coupling constants that map onto each other above and below the anti-diagonal can either be equal or form "balanced pairs" (actually, balance each other). In fact, in the $AA'XX'$ ($AA'BB'$) spin system, the constants $J_{AA'}$ and $J_{XX'}$ should be considered as "equivalent" under anti-diagonal reflection. Therefore, when analyzing symmetric spin systems with chemically equivalent but magnetically non-equivalent spin groups, one must first identify all such balanced pairs of coupling constants and treat them as equivalent in assessing the symmetry of the J -coupling matrix.

Another family of mirror-symmetric spectra originates from spin systems with two groups of magnetically equivalent nuclei A_nX_n (A_nB_n), the mirror symmetry of which was proved by Corio (Corio, 1966, p.254). In general, the J -coupling matrix in such systems lacks persymmetry because the coupling constant between the A nuclei can differ from the coupling

D_3 -symmetric $[A'X']_3$ spin system of 1,3,5-trifluorobenzene

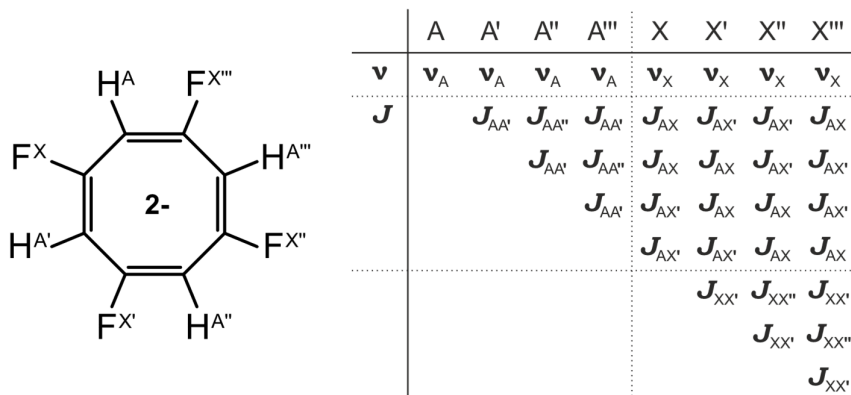


C_{2v} -symmetric $[A'X']_4$ spin systems



| | A | A' | A'' | A''' | X | X' | X'' | X''' |
|-------|---------|-----------|------------|-------------|------------|------------|------------|-------------|
| ν | ν_A | ν_A | ν_A | ν_A | ν_X | ν_X | ν_X | ν_X |
| J | | $J_{AA'}$ | $J_{AA''}$ | $J_{AA'''}$ | J_{AX} | $J_{AX'}$ | $J_{AX''}$ | $J_{AX'''}$ |
| | | | $J_{AA''}$ | $J_{AA'''}$ | J_{AX} | J_{AX} | $J_{AX''}$ | $J_{AX''}$ |
| | | | | $J_{AA''}$ | $J_{AX''}$ | $J_{AX''}$ | J_{AX} | $J_{AX'}$ |
| | | | | | $J_{AX''}$ | $J_{AX''}$ | J_{AX} | J_{AX} |
| | | | | | | $J_{XX'}$ | $J_{XX''}$ | $J_{XX''}$ |
| | | | | | | | $J_{XX''}$ | $J_{XX''}$ |
| | | | | | | | | $J_{XX'}$ |

D_4 -symmetric $[A'X']_4$ spin system



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Figure 6. Some examples of symmetric $[A'X']_n$ ($[A'B']_n$) spin systems.

117 constant between the X (or B) nuclei. However, the theoretical spectrum is independent of
118 coupling between magnetically equivalent nuclei. The spectrum depends only on the inter-
119 group couplings, which are all equal to the same value J_{AX} (J_{AB}). Thus, the part of the
120 J -coupling matrix that contains these coupling constants and defines the spectrum does indeed
121 possess persymmetry.

122 3.2. Spectral Asymmetry of Some Symmetric $[A'X']_n$ ($[A'B']_n$) Spin Systems

123 Five representative examples of highly symmetric $[A'X']_n$ spin systems are shown in
124 Figure 6. The condition of resonance frequency balance requires ordering spins by their
125 resonance frequencies in ascending or descending order. However, within groups of chemically
126 equivalent spins an additional ordering is required. The chemical equivalence of spin groups,
127 determined by spin permutation symmetry, results in the topological equivalence of the
128 coupling networks of the $[A']_n$ and $[X']_n$ subsystems. Therefore, the most symmetric form of
129 the J -coupling matrix can be achieved by a consistent ordering of chemically equivalent spins
130 from different groups such that the equality $J_{AX} = J_{A'X'} = J_{A''X''} = J_{A'''X'''}$ holds. For
131 1,3,5-trifluorobenzene and the 1,3,5,7-tetrafluorosubstituted cyclooctatetraene dianion, this
132 ordering coincides with the molecular canonical topological order. Accordingly, in all examples
133 of J -coupling matrices presented in Fig. 6, the chemically equivalent spins were ordered using
134 the described scheme.

135 In all considered spin systems, the J -coupling matrices exhibit high symmetry, with the
136 inter-group coupling blocks being persymmetric. Unlike the AA'BB' case, due to the algebraic
137 properties of the Hamiltonian, there is no balancing of topologically equivalent homonuclear
138 coupling constant pairs in these systems. Specifically, the constant pairs $\{J_{AA'}, J_{XX'}\}$, $\{J_{AA''},$
139 $J_{XX''}\}$, and $\{J_{AA'''}, J_{XX'''}\}$ do not form balanced pairs. Consequently, the spectra are not invariant
140 under the permutation of constant values within these pairs nor under the permutation of ν_A
141 and ν_X , and therefore do not possess mirror symmetry, despite the high symmetry of the spin
142 systems themselves.

143 Nevertheless, in the case of 1,3,5-trifluorobenzene, the high symmetry of the $[A'X']_3$ spin
144 system results in symmetric signal patterns for the $^1\text{H}(A)$ signal about ν_A and for the $^{19}\text{F}(X)$
145 signal about ν_X separately.

146 4. Conclusion

147 The properties that a spin system must possess for its high-field NMR spectrum to be
148 symmetric about the mid-resonance frequency ν_0 have been identified. We believe these
149 findings are of fundamental importance to the theory of spin system spectra.

150 All theoretical spectra were simulated using the ANATOLIA NMR software (Cheshkov
151 et al., 2018). For an in-depth theoretical analysis of spectral mirror symmetry, see
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158 **8. References**

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