Combinatorial Methods in ESR Spectroscopy

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Combinatorial methods based on the Pólya theory of counting and multinomial expansions are applied to the prediction of the number of hyperfine lines and their intensity patterns arising from the electronic spin and nuclear spin couplings. It is shown that these methods are very useful for predicting the ESR spectral patterns of radicals containing a large number of multinuclear spins. © 1991 Academic Press, Inc.

Combinatorial techniques have been shown to be useful in almost all spectroscopies and symmetry-related applications (1–10). A comprehensive review of various applications of combinatorial methods to nuclear spin statistics in molecular spectroscopy (6), NMR (5, 7), NQR (8), dynamic NMR (11), and other related areas can be found in Ref. (1). Combinatorial techniques have been proven to be useful in the enumeration of NMR signals and in the construction of NMR signal intensity patterns. Furthermore, such combinatorial techniques have also been computerized (2, 12).

In this investigation we develop combinatorial techniques and apply them to an important problem in ESR spectroscopy. An interesting and common problem in ESR is the prediction of the hyperfine structure arising from the interaction of the open-shell electronic spin of a radical with the nuclear spins in the radical. It is shown in this article that combinatorial techniques based on Pólya’s theorem and multinomial expansion methods can be applied to predict both the number of lines in the ESR hyperfine structure and the intensity patterns of the hyperfine lines. The next section outlines the nature of the problem in the prediction of hyperfine structure. A subsequent section describes the various combinatorial methods that we employ. The last section comprises applications of the combinatorial methods to ESR.

ESR HYPERFINE INTERACTIONS

It is well known that the hyperfine structure in the ESR spectrum arises from the interaction of an open-shell electronic spin of the radical with various nuclear spins in the molecule. The hyperfine interaction term in the Hamiltonian can be represented in general as (19)

\[ H_{HF} = S \cdot \sum_{i} A_{i} \cdot I_{i}, \]  

[1]

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where $S$ is the spin vector of the unpaired electron, $A_i$ is the hyperfine constant, and $I_i$ is the spin of the $i$th nucleus.

If $m_i$ is the projection of the $i$th nuclear spin along the $z$ axis, then the projection of the above term along this axis is simplified into

$$\mathcal{H}_{HF} = \sum_i A_i m_i,$$

where $A_i$ is the hyperfine coupling constant between the open-shell electron and the $i$th nuclear spin.

In general for a nucleus with spin $I_i$ there are $2I_i + 1$ possible projections along the $z$ axis defined by $m_i = I_i, I_i - 1, \ldots, -I_i + 1, -I_i$. For example, the possible projections for a proton nucleus are $-\frac{1}{2}$ and $+\frac{1}{2}$ while for a nitrogen nucleus the possible projections are $-1, 0$, and $+1$. Different nuclear projections would then correspond to different hyperfine lines since the eigenvalue of $\mathcal{H}_{HF}$ depends on the projection if the applied field coincides with the projection.

All equivalent nuclei in a molecule would couple with the electronic spin equally and hence would have the same hyperfine constant. For example, a radical containing four equivalent protons with the hyperfine constant $A_p$ and three equivalent nitrogen nuclei with the hyperfine constant $A_N$ would have the hyperfine Hamiltonian

$$\mathcal{H}_{HF} = A_p (m_{f_1} + m_{f_2} + m_{f_3} + m_{f_4}) + A_N (m'_{f_5} + m'_{f_6} + m'_{f_7}).$$

[3]

A system which consists of two equivalence classes of protons, each class consisting of, say, two protons, would have a Hamiltonian of the form

$$\mathcal{H}_{HF} = A_p (m_{f_1} + m_{f_2}) + A_p (m_{f_3} + m_{f_4}),$$

[4]

where $A_p$ is the hyperfine constant for the protons in the first equivalence class with the electron while $A_p$ is the hyperfine constant for the protons in the second equivalence class with the electron.

The nuclei belonging to the same equivalence class will make identical contributions to the hyperfine structure of the ESR spectrum (19) since the hyperfine constants of these nuclei are the same. The effect of this would be enhancement of the intensity of a particular line in the hyperfine structure pattern due to the coupling of any nucleus in an equivalence class with the electron.

A nucleus in an equivalence class with the spin quantum number $I_i$ would have $2I_i + 1$ spin projections as shown above. Thus if an equivalence class consists of $n_i$ nuclei then the number of possible spin functions for the nuclei in this class is $(2I_i + 1)^{n_i}$. For example, in a radical which contains a set of four equivalent protons the number of possible spin functions is $2^4$. Since the hyperfine interaction energies of nuclear spin functions with the same total $M_f$ (total $z$ projection) are equal, nuclear spin functions with the same total $M_f$ will contribute to the same line in the hyperfine pattern. Alternatively, if two nuclear spin functions have different total $M_f$ values then they will correspond to different lines in the hyperfine patterns. Hence the hyperfine structure and the intensities of various lines depend on the equivalence classes of nuclei and possible spin functions in each equivalence class. In the next section, we show how to enumerate both equivalence classes and spin functions in various nuclear equivalence classes and how to connect this information with the hyperfine structure.
ENUMERATION OF NUCLEAR EQUIVALENCE CLASSES

As shown in the previous section for rigorous prediction of hyperfine structure of any radical, first the nuclear equivalence classes of all nuclei in the radical which possesses nonzero spins must be enumerated. This is accomplished through the use of Pólya’s theorem and multinomial expansion techniques described later.

Let $D$ be a set of nuclei of the same kind ($\text{H}, \text{^{13}C}$, etc.) in the radical. For example, for $p$-benzosemiquinone radical, $D$ would be the set of four protons present in the radical. Let $R$ be a set containing just two elements. Let $G$ be the point group or the permutation-inversion group of the radical. Since $G$ is the set of all permutational and composite permutation-inversion operations a $g \in G$ induces permutations on elements in $D$. Consider a set $F$ of all maps from $D$ to $R$. Every $g \in G$ acts on the elements of $F$ as follows:

$$gf(d) = f(g^{-1}d) \quad \text{for every} \quad d \in D. \quad [5]$$

Two maps $f_i$ and $f_j \in F$ are equivalent if

$$f_i(d) = f_j(gd) \quad \text{for every} \quad d \in D. \quad [6]$$

All maps in $F$ that are equivalent are grouped into the same equivalence class. Consequently, the group $G$ partitions $F$ into equivalence classes. Let us restrict ourselves to those maps in $F$ which have the following structure, since these are the relevant maps for ESR hyperfine structure patterns. Let the elements of the set $R$ be denoted by $\alpha_1$ and $\alpha_2$. Label the elements of $D$ as $d_1, d_2, \ldots, d_n$, with $n = |D|$. Consider a subset $F_w$ of $F$ with every $f_i \in F_w$ defined as

$$f_i(d_j) = \alpha_1 \quad \text{if} \quad i \neq j, \quad d_j \in D,$$

$$= \alpha_2 \quad \text{if} \quad i = j. \quad [7]$$

It can be seen that two nuclei $d_i$ and $d_j$ are magnetically equivalent if $f_i$ is equivalent to $f_j$. Thus the equivalence classes of $F_w$ are the magnetic equivalence classes of nuclei in the set $D$. Hence all nuclei in a class would have the same ESR hyperfine constant.

If one assigns a weight $w(r)$ to an element $r \in R$ to count the number of times any $r \in R$ occurs in a function, then the weight of any function $f \in F$ can be defined as the product of the weight of its images. Symbolically, the weight of $f$, $W(f)$, is

$$W(f) = \prod_{d \in D} w(f(d)). \quad [8]$$

Since any $f_i \in F_w$ takes all $d_j \in D$ to $\alpha_1$ except when $i = j$, the weight of any $f_i$ in $F_w$ is $w$, if 1 is the weight associated with $\alpha_1$ and $w$ is the weight assigned to $\alpha_2$.

Pólya (13) proved a theorem which generates the equivalence classes of $F$ from a structure known as the cycle index of a group which is defined below. See also Refs. (14–17) for several illustrative examples. Suppose any $g \in G$ generates $b_1$ cycles of length 1, $b_2$ cycles of length 2, etc. when it acts on $D$; then we can associate a cycle representation $x_1^{b_1}x_2^{b_2}\cdots$ with $g$. The cycle index of $G$, $P_G$, is defined as

$$P_G(x_1, x_2, \ldots) = \frac{1}{|G|} \sum_{g \in G} x_1^{b_1}x_2^{b_2}\cdots. \quad [9]$$
Pólya showed that a generating function (GF) for the equivalence classes of \( F \) is given by the following substitution in the cycle index:

\[
GF = P_G(x_k \rightarrow \sum_{r \in R} (w(r))^k).
\]  

The coefficient of \( w \) in \( GF \) gives the number of equivalence classes of nuclei in \( D \). This is illustrated later when actual ESR hyperfine patterns of radicals are considered.

**Enumeration and Construction of Nuclear Spins**

Once the nuclear equivalence classes are enumerated, we proceed with the enumeration of nuclear spin functions. Let the given radical contain a nuclear equivalence class pattern comprising \( n_1 \) nuclei with spin \( I_1 \) in the first class, \( n_2 \) nuclei with spin \( I_2 \) in second class, \ldots, \( n_m \) nuclei with spin \( I_m \) in the \( m \)th class. Any nucleus in the first set, for example, would have \( 2I_1 + 1 \) possible spin projections along the \( z \) axis. For example, if the first set is composed of protons then there would be two possible spin projections. Hence the total number of all possible spin projections in the first set is \((2I_1 + 1)^{n_1}\). The number of possible spin projections of all nuclei in all classes is then given by

\[
\prod_I (2I + 1)^{n_i}.
\]

For convenience we need to associate a symbol with each spin projection. For example, the standard convention is to use \( \alpha \) (\( m_f = +\frac{1}{2} \)) and \( \beta \) (\( m_f = -\frac{1}{2} \)) as symbols for the two projections of the hydrogen nucleus. Similarly for the three spin projections of the nitrogen nucleus we use the symbols \( \lambda \) (\( m_f = 1 \)), \( \mu \) (\( m_f = 0 \)), and \( \nu \) (\( m_f = -1 \)).

Spin projections of different equivalence classes are not equivalent in the sense that they will not give rise to the same hyperfine interaction energies. Hence to differentiate these we use suffixes 1, 2, \ldots in the order of occurrence for a given type of nucleus, for example, consider a system containing multinuclear equivalence classes of the type \( \{ P_1, P_2 \}, \{ P_3, P_4 \}, \{ N_1, N_2 \} \), where \( P \) stands for proton and \( N \) stands for nitrogen. Then the nuclear projections for any nucleus in the first class are \( \alpha_1 \) and \( \beta_1 \); those in the second class, \( \alpha_2 \) and \( \beta_2 \); and those in the third class, \( \lambda_1, \mu_1, \) and \( \nu_1 \). Let us denote \( p_i = 2I + 1 \) for convenience. Then possible spin functions of \( n_i \) nuclei in an equivalence class with nuclear spin \( I \) with projection represented by, say, \( f_1, f_2, \ldots, f_{p_i} \) are enumerated by the multinominal expansion

\[
F = (f_1 + f_2 + \cdots + f_{p_i})^{n_i}.
\]

The coefficient of a term \( f_1^\alpha f_2^\beta \cdots f_{p_i}^\gamma \), such that \( \sum_{\gamma=1}^{p_i} \alpha_i = n_i \), gives the number of possible spin functions spanned by \( n_i \) nuclei, among which \( a_1 \) nuclei have spin projection \( f_1 \), \( a_2 \) nuclei have spin projection \( f_2 \), \ldots, \( a_{p_i} \) have spin projection \( p_i \).

To illustrate, consider a simple example containing one class with four nitrogen atoms. Since \( I = 1 \) for the nitrogen atom, there are three spin projections for each nucleus, which we denote by \( \lambda, \mu, \) and \( \nu \), respectively. The generating function for possible nuclear spin functions for a radical containing one class of four nitrogen nuclei is then given by [13]:

\[
F = (\lambda + \mu + \nu)^4.
\]
Upon expansion the above expression yields

\[ F = \lambda^4 + 4\lambda^3\mu + 4\lambda^3\nu + 6\lambda^2\mu^2 + 6\lambda^2\nu^2 + 12\lambda\mu\nu + 12\lambda\mu^2\nu + 12\lambda\mu\nu^2 + 4\mu^3\lambda + 4\mu^3\nu + 6\mu^2\nu^2 + \nu^4 + 4\nu^3\lambda + 4\nu^3\mu. \]  \[14\]

The coefficient of a typical term \(\lambda^{a_i}\mu^{a_2}\nu^{a_3}\) enumerates the number of spin functions containing \(a_1\) \(\lambda\)'s, \(a_2\) \(\mu\)'s, and \(a_3\) \(\nu\)'s. For example, there are 12 possible spin functions containing two \(\lambda\)'s, one \(\mu\), and one \(\nu\).

The number of terms in a typical multinomial expansion, such as the one shown above, is given by the number of composition of \(n_i\) into \(p_i\) parts \((18)\). This is given by

\[ \binom{n_i + p_i - 1}{n_i}. \]

For the above example of four nitrogen nuclei, \(n_i = 4\) and \(p_i = 3\) since \(p_i = 2I_i + 1\). Thus the number of terms in the expansion for the above example is

\[ \binom{4 + 3 - 1}{4} = \binom{6}{4} = 15. \]

A simpler example would be a radical containing four equivalent protons. For this system the following simple expression is obtained:

\[ F = (\alpha + \beta)^4 = \alpha^4 + 4\alpha^3\beta + 6\alpha^2\beta^2 + 4\alpha\beta^3 + \beta^4. \]  \[15\]

If the given radical contains \(n_1\) nuclei in the first class with spin \(I_1\), \(n_2\) nuclei with spin \(I_2\), \ldots, \(n_m\) nuclei with spin \(I_m\), then the total number of possible spin functions is given by

\[ F = F_1F_2\cdots F_m, \]  \[16\]

where

\[ F_i = (f_1 + f_2 + \cdots + f_{p_i})^{n_i}, \]  \[17\]

where \(f_1, f_2, \ldots, f_{p_i}\) are the possible projections of a nucleus in the \(i\)th class and \(p_i = 2I_i + 1\).

Consider a radical containing three equivalent nitrogen atoms and three equivalent protons as an example. The generating function for this case is given by

\[ F = (\alpha + \beta)^3(\lambda + \mu + \nu)^3 = (\alpha^3 + 3\alpha^2\beta + 3\alpha\beta^2 + \beta^3)(\lambda^3 + 3\lambda^2\mu + 3\lambda\mu^2 + \mu^3 + 3\mu^2\nu + 3\mu\nu^2 + \nu^3 + 6\lambda\mu\nu). \]  \[18\]

Thus there are three nitrogen spin functions with two spins with \(m_F = 1\) \((\lambda)\) and one with \(m_F = 0\) \((\mu)\). That is, the coefficient of \(\lambda^2\mu\) gives the number of possible spin functions containing two \(\lambda\)'s and one \(\mu\). The total \(M_F\) value corresponding to \(\lambda^2\mu\) is simply the sum of individual \(m_F\)'s and hence it is 2. Table 1 shows the various terms
### Table 1

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>$M_f$</th>
<th>Term(s) in the generating function corresponding to this $M_f$</th>
<th>Individual coefficient</th>
<th>Sum of coefficients with the same $M_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogens</td>
<td>3</td>
<td>$\lambda^3$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Nitrogens</td>
<td>2</td>
<td>$\lambda^2 \mu$</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Nitrogens</td>
<td>1</td>
<td>$\lambda \mu^2$</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Nitrogens</td>
<td>0</td>
<td>$\mu^3$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Nitrogens</td>
<td>$-1$</td>
<td>$\lambda \mu \nu$</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Nitrogens</td>
<td>$-2$</td>
<td>$\nu^2 \lambda$</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Nitrogens</td>
<td>$-3$</td>
<td>$\nu \lambda^2$</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Protons</td>
<td>$\frac{1}{2}$</td>
<td>$\alpha^3$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Protons</td>
<td>$\frac{1}{2}$</td>
<td>$\alpha^2 \beta$</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Protons</td>
<td>$-\frac{1}{2}$</td>
<td>$\alpha \beta^2$</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Protons</td>
<td>$-\frac{1}{2}$</td>
<td>$\beta^3$</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

In the nitrogen and protonic generating functions, the coefficients in $F$, and the total contribution to a given value of $M_f$, from Table 1, it can be inferred that the 27 spin functions of three equivalent nitrogens distribute into seven classes of functions such that all functions in the same class have the same total $M_f$. The seven classes contain 1, 3, 6, 7, 6, 3, and 1 functions, respectively, on the basis of the sum of coefficients with the same $M_f$ (Table 1). Similarly, the spin functions of three equivalent protons are partitioned into 1, 3, 3, and 1 functions.

Since all nuclear spin functions of equivalent nuclei with the same $M_f$ values have the same eigenvalues of $\mathcal{H}_{HF}$, they contribute to the same line in the hyperfine structure of the ESR spectrum. Consequently, three equivalently coupled nitrogen atoms of a radical give rise to a 1:3:6:7:6:3:1 hyperfine pattern. Note that the lines are arranged in the order of $M_f$ since the eigenvalues of $\mathcal{H}_{HF}$ are proportional to $M_fA_N$, where $A_N$ is the hyperfine constant. Similarly, the intensity pattern of three equivalent protons, as in a methyl radical, is given by 1:3:3:1 (Table 1).

If there are two types of nuclei, such as protons and nitrogens as in the present case, then the intensity pattern is generated by a composition of the two intensity patterns depending on which hyperfine constant dominates (19).

If $A_P > A_N$ then the spacing between the hyperfine lines arising from protons will be larger than the spacing between the lines attributed to nitrogens. This means that the nitrogen lines with the intensity ratio 1:3:6:7:6:3:1 would be closer and form a group. This group of lines will then be split apart further by the protonic nuclear spins into widely spaced groups with a ratio of 1:3:3:1 in this case. The result of this composite hyperfine pattern would be $(1:3:6:7:6:3:1):(3:9:18:21:18:9:3):(3:9:18:21:18:9:3):(1:3:6:7:3:1)$, as shown in Fig. 1, where the lines within parentheses would be closely...
Fig. 1. Hyperfine pattern resulting from interactions of three equivalent protons and three equivalent nitrogens if $A_p > A_n$. See Eq. [18] for the generating function for this case.

spaced as in Fig. 1 since $A_p > A_n$. Note the symmetry in the intensities within a group and the whole hyperfine structure in Fig. 1. This is discussed later.

If $A_n > A_p$, then the protonic lines would be closer with a ratio of 1:3:3:1. These lines will then be split apart in seven groups with a ratio of 1:3:6:7:6:3:1, resulting in an intensity ratio of $(1:3:3:1):(3:9:9:3):(6:18:18:6):(7:21:21:7):(6:18:18:6):(3:9:9:3):(1:3:3:1)$. Hence from the generating functions the hyperfine pattern and the intensities of various lines can be predicted.

It can be seen that the number of possible total $M_T$ values for a system containing $m$ nuclei with the spin quantum number $I$ is given by

$$n_{HF} = \prod_{i=1}^{n} (2I, m_i + 1).$$  

[20]

Thus for a radical which contains $m_1$ equivalent nuclei with spin $I_1$, $m_2$ nuclei with spin $I_2$, ..., $m_n$ nuclei with spin $I_n$, the number of hyperfine lines is given by

$$n_{HF} = \prod_{i=1}^{n} (2I, m_i + 1).$$  

[20]

The intensity ratios are obtained by the total generating function $F$, which is expressed as a product of individual generating functions, as illustrated by the example in Table 1.

APPLICATIONS

In this section we apply the methods developed in the earlier sections to several systems containing both protons distributed into equivalence classes and nitrogen atoms.

Consider the heteronuclear radical in Fig. 2. In most of the aromatic radicals, the unpaired electron resides in a $p_z$ orbital and hence is delocalized over the entire
nuclear framework. The cycle index for the protons of the radical in Fig. 2 is given by

\[ P = \frac{1}{2} [x_1^6 + x_2^3]. \]  

[21]

Note that the point group of the radical in Fig. 2 is \( C_{2h} \) but it generates only two nuclear permutation operations. The generating function for the equivalence classes of protons is given by

\[ F = \frac{1}{2} [(1 + w)^6 + (1 + w^2)^3]. \]  

[22]

The coefficient of \( w \) in the above expression can be seen to be 3, yielding three equivalence classes of protons distributed as \( \{1,4\}, \{2,5\}, \{3,6\} \).

The nitrogen nuclei yield a cycle index and generalizing function given by

\[ P = \frac{1}{2} [x_1^4 + x_2] \]  

[23]

\[ F = \frac{1}{2} [(1 + w)^2 + (1 + w^2)]. \]  

[24]

The coefficient of \( w \) in the above expression can be seen to be 1. Consequently, both the nitrogen atoms are equivalent.

Since there are three classes of protons, the nuclear spins of protons in different classes are differentiated with suffixes. The total generating function is thus given by

\[ F = (\alpha_1 + \beta_1)^2(\alpha_2 + \beta_2)^2(\alpha_3 + \beta_3)^2(\lambda + \mu + \nu)^2. \]  

[25]

Upon simplification the above expression yields

\[ F = (\alpha_1^2 + 2\alpha_1\beta_1 + \beta_1^2)(\alpha_2^2 + 2\alpha_2\beta_2 + \beta_2^2)(\alpha_3^2 + 2\alpha_3\beta_3 + \beta_3^2) \times (\lambda^2 + \mu^2 + \nu^2 + 2\lambda\mu + 2\lambda\nu + 2\mu\nu). \]  

[26]

When sorted in accordance with the total \( M \)-values the coefficients in the expression corresponding to the nitrogen atoms yield a hyperfine pattern of 1:2:3:2:1. Table 2 shows how this pattern is split further apart into various groups if \( A_p > A_N \). Note that in that table the coefficients of various protonic nuclear spin functions are sorted but \( \alpha_1^2, \alpha_2^2, \alpha_3^2, \beta_1^2, \beta_2^2, \beta_3^2 \) for example, is treated different from \( \alpha_1\alpha_2^2, \alpha_1\beta_3^2, \alpha_2\beta_1^2, \alpha_2\beta_3^2, \alpha_3\beta_1^2, \alpha_3\beta_2^2 \) since the nuclei in the first and third sets are not equivalent. The resulting hyperfine pattern for \( A_p > A_N \) is

\[
\]

The underlying symmetry of the overall hyperfine pattern and within a group of the pattern arises from the symmetry of the binomial distribution and the fact that the nuclear spin eigenvalues simply change signs when spins \( \alpha \) and \( \beta \) are interchanged (similarly when \( \lambda \) and \( \nu \) are interchanged for the nitrogen atom).
Consider a radical which consists of four protons and three nitrogens such that the four protons are divided into two classes while the nitrogen atoms are equivalent. The generating function for this case is given by

\[ F = (\alpha_1 + \beta_1)^2(\alpha_2 + \beta_2)^2(\lambda + \mu + \nu)^3. \]  

\[ \text{[27]} \]

**TABLE 2**

Combinations of the Hyperfine Pattern of Three Classes of Protons, Each Containing Two Nuclei and One Class of Three Nitrogen Atoms (Fig. 1), Assuming \( A_2 > A_3 \)

<table>
<thead>
<tr>
<th>Protonic GF term</th>
<th>Coefficient</th>
<th>Intensity pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_1 \alpha_2 \alpha_3 )</td>
<td>1</td>
<td>1:2:3:2:1</td>
</tr>
<tr>
<td>( \alpha_1 \alpha_3 \alpha_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
</tr>
<tr>
<td>( \alpha_1 \beta_2 \beta_3 )</td>
<td>1</td>
<td>1:2:3:2:1</td>
</tr>
<tr>
<td>( \alpha_1 \beta_2 \beta_3 \alpha_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
</tr>
<tr>
<td>( \alpha_2 \alpha_3 \beta_3 \alpha_3 )</td>
<td>4</td>
<td>4:8:12:8:4</td>
</tr>
<tr>
<td>( \alpha_2 \beta_2 \beta_3 \alpha_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
</tr>
<tr>
<td>( \alpha_1 \beta_2 \beta_3 \beta_3 )</td>
<td>1</td>
<td>1:2:3:2:1</td>
</tr>
<tr>
<td>( \alpha_2 \beta_2 \beta_3 \beta_3 \alpha_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
</tr>
<tr>
<td>( \alpha_1 \beta_2 \alpha_3 \beta_3 \alpha_3 )</td>
<td>4</td>
<td>4:8:12:8:4</td>
</tr>
<tr>
<td>( \alpha_1 \beta_2 \alpha_3 \beta_3 \beta_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
</tr>
<tr>
<td>( \alpha_1 \beta_3 \alpha_2 \beta_3 \beta_3 )</td>
<td>4</td>
<td>8:16:24:16:8</td>
</tr>
<tr>
<td>( \alpha_1 \beta_3 \alpha_2 \beta_3 \beta_3 \alpha_3 )</td>
<td>8</td>
<td>8:16:24:16:8</td>
</tr>
<tr>
<td>( \alpha_1 \beta_3 \alpha_2 \beta_3 \beta_3 \beta_3 )</td>
<td>4</td>
<td>4:8:12:8:4</td>
</tr>
<tr>
<td>( \alpha_1 \beta_3 \alpha_2 \beta_3 \beta_3 \beta_3 \alpha_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
</tr>
<tr>
<td>( \alpha_1 \beta_3 \alpha_2 \beta_3 \beta_3 \beta_3 \beta_3 )</td>
<td>4</td>
<td>4:8:12:8:4</td>
</tr>
<tr>
<td>( \alpha_1 \beta_3 \alpha_2 \beta_3 \beta_3 \beta_3 \beta_3 \alpha_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
</tr>
<tr>
<td>( \beta_1 \alpha_2 \alpha_3 \beta_3 )</td>
<td>1</td>
<td>1:2:3:2:1</td>
</tr>
<tr>
<td>( \beta_1 \alpha_2 \alpha_3 \beta_3 \alpha_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
</tr>
<tr>
<td>( \beta_1 \alpha_2 \alpha_3 \beta_3 \beta_3 )</td>
<td>1</td>
<td>1:2:3:2:1</td>
</tr>
<tr>
<td>( \beta_1 \alpha_2 \alpha_3 \beta_3 \beta_3 \alpha_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
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<tr>
<td>( \beta_1 \alpha_2 \alpha_3 \beta_3 \beta_3 \beta_3 )</td>
<td>4</td>
<td>4:8:12:8:4</td>
</tr>
<tr>
<td>( \beta_1 \alpha_2 \alpha_3 \beta_3 \beta_3 \beta_3 \alpha_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
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<td>( \beta_1 \alpha_2 \alpha_3 \beta_3 \beta_3 \beta_3 \beta_3 )</td>
<td>1</td>
<td>1:2:3:2:1</td>
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<tr>
<td>( \beta_1 \alpha_2 \alpha_3 \beta_3 \beta_3 \beta_3 \beta_3 \alpha_3 )</td>
<td>2</td>
<td>2:4:6:4:2</td>
</tr>
<tr>
<td>( \beta_1 \alpha_2 \alpha_3 \beta_3 \beta_3 \beta_3 \beta_3 \beta_3 )</td>
<td>1</td>
<td>1:2:3:2:1</td>
</tr>
</tbody>
</table>
On the basis of the sorting of coefficients in the \((\lambda + \mu + \nu)^3\) term (Table 1), the intensity pattern due to three equivalent nitrogen atoms is 1:3:6:7:6:3:1. Consequently, the expansion of the first two terms together with the nitrogen pattern gives rise to \((A_P > A_N)\) the hyperfine pattern
\[
\]
The total number of lines for the above example can be independently verified as
\[
N = (2 \times \frac{1}{2} \times 2 + 1)(2 \times \frac{1}{2} \times 2 + 1)(2 \times 1 \times 3 + 1) = 63. \quad [28]
\]
A radical containing three equivalent protons and three equivalent nitrogen atoms yields the function
\[
F = (\alpha + \beta)^3(\lambda + \mu + \nu)^3
= (\alpha^3 + 3\alpha^2\beta + 3\alpha\beta^2 + \beta^3)(\lambda + \mu + \nu)^3. \quad [29]
\]

Consider the \(p\)-anthrosemiquinone radical shown in Fig. 3 as another example which illustrates both of the combinatorial techniques considered here. The cycle index of the proton nuclei is given by
\[
P = \frac{1}{2}[x_1^8 + 3x_2^4]. \quad [30]
\]
Thus the generating function for the proton nuclei is given by
\[
F = \frac{1}{2}[(1 + w)^8 + 3(1 + w^2)^4]. \quad [31]
\]
The coefficient of \(w\) in the above expression is 2, yielding two classes of protons, namely, \(\{1, 4, 5, 8\}\) and \(\{2, 3, 7, 6\}\). The generating function for nuclear spin functions in this case is
\[
(\alpha_1 + \beta_1)^4(\alpha_2^4 + \beta_2^4). \quad [32]
\]

\[\text{Fig. 3. The } p\text{-anthrosemiquinone radical. See Table 3 for the distribution of intensity pattern.}\]
The Generating Function Coefficients and the Hyperfine 
Pattern of p-Anthroseminone Radical (Fig. 3)

<table>
<thead>
<tr>
<th>Term in GF</th>
<th>Coefficient</th>
<th>Contribution to the intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha\beta_1\beta_2$</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$\alpha\beta_1\beta_2\beta_3$</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>$\alpha\beta_1\beta_2\beta_3$</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$\alpha\beta_2\alpha\beta_3$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\alpha\beta_2\alpha\beta_3$</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$\alpha\beta_2\alpha\beta_3\beta_4$</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>$\alpha\beta_2\alpha\beta_3\beta_4$</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>$\alpha\beta_2\alpha\beta_3\beta_4$</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>$\alpha\beta_2\alpha\beta_3\beta_4$</td>
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<td>4</td>
</tr>
<tr>
<td>$\alpha\beta_2\alpha\beta_3\beta_4$</td>
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<td>6</td>
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<tr>
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<td>24</td>
</tr>
<tr>
<td>$\alpha\beta_2\alpha\beta_3\beta_4$</td>
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<td>36</td>
</tr>
<tr>
<td>$\alpha\beta_2\alpha\beta_3\beta_4$</td>
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<td>24</td>
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<tr>
<td>$\alpha\beta_2\alpha\beta_3\beta_4$</td>
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<tr>
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<tr>
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<tr>
<td>$\beta_1\beta_2\beta_3$</td>
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<td>4</td>
</tr>
<tr>
<td>$\beta_1\beta_2\beta_3$</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The resulting coefficients and hyperfine pattern are shown in Table 3. The number of hyperfine lines is given by

\[(2 \times \frac{1}{2} \times 4 + 1)(2 \times \frac{1}{2} \times 4 + 1) = 25.\]  

CONCLUSION

In this investigation we described the combinatorial techniques based on the Pólya theory of counting and multinomial expansions to enumerate the number of hyperfine lines and their intensity patterns. A general method was developed and applied to many cases. It was shown that this combinatorial method is very powerful for the prediction of the hyperfine structure of ESR spectra.
REFERENCES