

# Polynomial Coefficients. Application to Spin-Spin Splitting

by  $N$  Equivalent Nuclei of Spin  $I > 1/2$

(Short Title: Spin-Spin Splitting by  $N$  Equivalent Nuclei of Spin  $I > 1/2$ )

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**Abstract.** The NMR intensity pattern of a nucleus split by  $N$  identical nuclei of spin  $1/2$  is given by the binomial coefficients. These are conveniently obtained from Pascal's Triangle, equivalent to the chemist's branching diagram. Much less well known is the pattern from splitting by  $N$  identical nuclei of spin  $I > 1/2$ . This was originally presented in terms of multinomial coefficients, but polynomial coefficients are more convenient. These describe the number of ways that  $N$  objects can be distributed to  $2I+1$  numbered boxes. They arise in the polynomial expansion and are conveniently obtained from generalizations of Pascal's Triangle. Examples and predictions are given.

**Keywords.** NMR, EPR,  $^2\text{H}$ ,  $^{14}\text{N}$ ,  $^{35}\text{Cl}$ ,  $^{11}\text{B}$ , spin-spin splitting, multiplet pattern

## Binomial Coefficients

It is well known that the NMR intensity pattern of a nucleus that is split by  $N$  identical nuclei of spin  $I = 1/2$  is an  $(N+1)$ -line multiplet with relative intensities given by the binomial

coefficients,  $C_r^N$ , in eq 1.<sup>[1]</sup> The separation between successive lines is the coupling constant  $J$ . The binomial coefficients arise from the binomial expansion (eq 2).<sup>[2]</sup> Eq. 3 then gives the probability of throwing  $N$  coins and obtaining  $r$  heads and  $N-r$  tails, or equivalently, the probability that  $r$  nuclei out of  $N$  are of spin  $+1/2$  and  $N-r$  nuclei are of spin  $-1/2$ . The binomial coefficients are conveniently obtained from Pascal's Triangle (Fig. 1), where each coefficient is the sum of the two coefficients above it, according to eq 4. Chemists more customarily present this figure as a branching diagram,<sup>[3,4]</sup> developed from splittings by successive nuclei, as shown in Fig. 2 for splitting by the three protons of an adjacent methyl group, with a separation between successive lines equal to the coupling constant  $J$ . Another example, from Fig. 1, is the intensity pattern of the central CH of isopropyl alcohol,  $(\text{CH}_3)_2\text{CHOH}$ , split by the six adjacent methyl protons into a seven-line multiplet with relative intensities 1:6:15:20:15:6:1. These correspond to the successive values 3, 2, 1, 0, -1, -2, -3 of the spin quantum number  $M_I = 1/2N-r$ .

$$C_r^N = \quad (1)$$

$$(1+x)^N = \sum_{r=0}^N C_r^N x^r \quad (2)$$

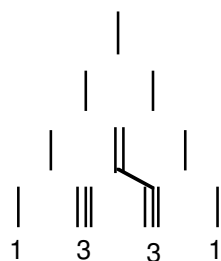
$$P(r) = C_r^N (1/2)^N \quad (3)$$

$$C_r^{N+1} = C_{r-1}^N + C_r^N \quad (4)$$

$$(N=0) \quad 1$$

(N=1)	1	1									
(N=2)	1	2	1								
(N=3)	1	3	3	1							
(N=4)	1	4	6	4	1						
(N=5)	1	5	10	10	5	1					
(N=6)	1	6	15	20	15	6	1				
(N=7)	1	7	21	35	35	21	7	1			
(N=8)	1	8	28	56	70	56	28	8	1		
(N=9)	1	9	36	84	126	126	84	36	9	1	
(N=10)	1	10	45	120	210	252	210	120	45	10	1

Figure 1. Pascal's Triangle.

Figure 2. Splitting by three adjacent nuclei of spin  $1/2$ .

### Multinomial Coefficients

Much less well known is the NMR or EPR pattern from splitting by  $N$  identical nuclei of spin  $I > 1/2$ . In particular, the EPR spectrum of tetracyanoethylene radical anion,  $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2^-$ , was puzzling, showing a nine-line multiplet with relative intensities

1:4:10:16:19:16:10:4:1.<sup>[5]</sup> This is an example of splitting by four identical  $^{14}\text{N}$  nuclei, of spin  $I = 1$ , but these are clearly not the familiar binomial coefficients. Further unfamiliar sequences were presented for the relative intensities of both a 19-line EPR multiplet due to splitting by six equivalent chlorines of  $I = 3/2$  (but without distinguishing  $^{35}\text{Cl}$  from  $^{37}\text{Cl}$ , which have magnetic moments and coupling constants that are nearly, but not exactly, the same),<sup>[6]</sup> and a 25-line EPR multiplet due to splitting by eight equivalent  $^{11}\text{B}$  atoms, also of  $I = 3/2$ .<sup>[7]</sup> In neither case was the method for obtaining the intensity pattern disclosed.

A brief explanation for such patterns was presented in terms of multinomial coefficients.<sup>[8]</sup> Multinomial coefficients, describing the number of ways that  $N$  objects can be distributed to  $2I+1$  boxes, with  $n_0$  objects in box #0,  $n_1$  objects in box #1,  $n_2$  objects in box #2, etc., subject to the constraint of eq 5, are given in eq 6.<sup>[9]</sup> These arise in the multinomial expansion (eq 7), although the usual treatment replaces  $2I$  by the parameter  $n-1$ ,<sup>10</sup> whereas we allow for the possibility that  $I$  is a half-integer. Then, if  $N$  coins are tossed into  $(2I+1)$  equally likely boxes, the probability of the distribution  $\{n_i\}$ , with  $n_0$  coins in box #0,  $n_1$  coins in box #1,  $n_2$  coins in box #2, etc., is given by eq 8. Eq 8 reduces to eq 3 for  $I = 1/2$ . These multinomial coefficients are well-known to mathematicians, but their applicability to NMR is little known to chemists.

$$\sum_{i=0}^{2I} n_i = N \quad (5)$$

$$M_{\{n_i\}}^N = \quad (6)$$

$$\left(\sum_{i=0}^{2I} x_i\right)^N = (x_0 + x_1 + x_2 + \dots + x_{2I})^N = M_{\{n_i\}}^N \prod_{i=0}^{2I} x_i^{n_i} \quad (7)$$

$$P(\{n_i\}) = M_{\{n_i\}}^N \quad (8)$$

It is necessary to use sums of multinomial coefficients to describe the relative intensities  $P_r^N$  of the  $2NI+1$  peaks in an NMR or EPR multiplet due to splitting by  $N$  nuclei of spin  $I$ . Those intensities are given in eq 9, where the summation is only over those distributions  $\{n_i\}$  where  $\sum in_i = r$  and where the spin quantum number  $M_I$ , equal to  $r - NI$ , ranges from  $-NI$  to  $+NI$ .

$$P_r^N = \sum M_{\{n_i\}}^N \quad (9)$$

### Polynomial Coefficients

This formulation, in terms of sums of multinomial coefficients, is awkward. Consequently, that early presentation,<sup>[8]</sup> which also focused on moments of the distribution, is not useful. It is more convenient to recognize the  $P_r^N$  as polynomial coefficients. These describe the number of ways that  $N$  objects can be distributed to  $2I+1$  boxes, numbered from  $-I$  to  $+I$ , such that the sum of the box numbers is  $r$ . They are called polynomial coefficients because they also arise in the expansion of a polynomial (eq 10). For example, the expansion of  $(1+x+x^2)^4$  is  $1 + 4x + 10x^2 + 16x^3 + 19x^4 + 16x^5 + 10x^6 + 4x^7 + x^8$ , which reproduces the relative intensities above in the EPR spectrum of tetracyanoethylene radical anion. These polynomial coefficients are likewise well-known to mathematicians, but their applicability to NMR and EPR

is little known to chemists.

$$\left(\sum_{r=0}^{2I} x^r\right)^N = (1 + x + x^2 + \dots + x^{2I})^N = \sum_{r=0}^{2NI} P_r^N x^r \quad (10)$$

The polynomial coefficients are conveniently obtained from generalizations of Pascal's Triangle,<sup>[11]</sup> where each coefficient is the sum of the  $2I+1$  coefficients above it. Thus, for  $I = 1$  each coefficient is the sum of the three coefficients above it, according to eq 11 and as illustrated in Fig. 3. An example is the intensity pattern of the  $^{13}\text{C}$  NMR of methanol- $d_3$ , split by the 3 adjacent deuteriums, of  $I = 1$ , which is a seven-line multiplet with relative intensities 1:3:6:7:6:3:1, as can also be seen from the chemists' branching diagram, shown in Fig. 4. Another example is the seven-line  $^1\text{H}$  NMR multiplet of  $\text{TpIrD}_3\text{H}$  (Tp = hydridotrispyrazol-1-ylborato), split by three deuteriums.<sup>[12]</sup> Again, the separation between successive lines is the coupling constant  $J$ . For  $I = 3/2$  each coefficient is the sum of the four coefficients above it in a generalized Pascal's triangle, according to eq 12 and as illustrated in Fig. 5. An example is the  $^1\text{H}$  NMR spectrum of fluxional  $\text{B}_3\text{H}_8^-$ , which shows a 10-line pattern from splitting by three equivalent  $^{11}\text{B}$  of  $I = 3/2$ ,<sup>[13]</sup> with relative intensities 1:3:6:10:12:12:10:6:3:1 (although these ratios were not provided).

$$P_r^{N+1} = P_{r-2}^N + P_{r-1}^N + P_r^N \quad (11)$$

$$P_r^{N+1} = P_{r-3}^N + P_{r-2}^N + P_{r-1}^N + P_r^N \quad (12)$$

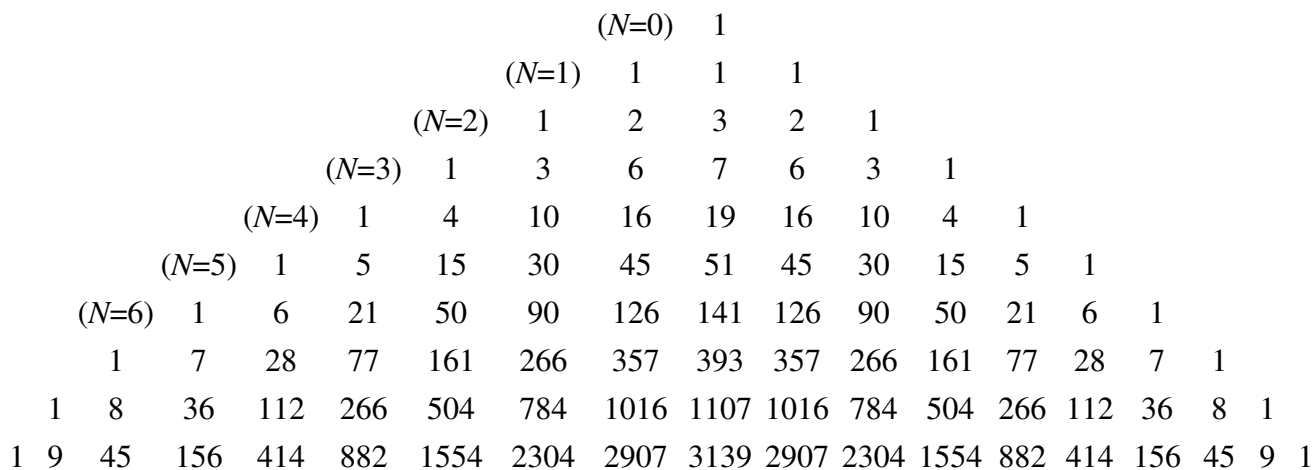


Figure 3. Pascal's Triangle Generalized to  $I = 1$ .

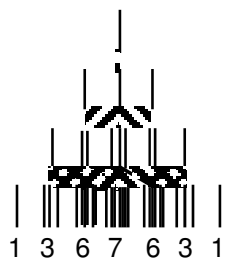


Figure 4. Splitting by three adjacent nuclei of spin 1.

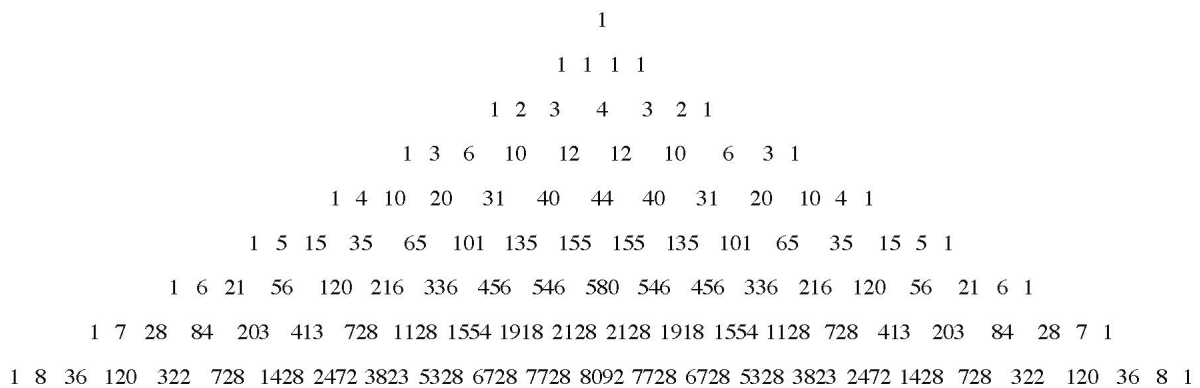


Figure 5. Pascal's Triangle Generalized to  $I = 3/2$ .

A more elaborate pattern is the 19-line multiplet from splitting by nine identical nuclei of

$I = 1$ , with relative intensities 1:9:45:156:414:882:1554:2304:2907:3139:2907:2304:1554:882:414:156: 45:9:1, as in the last line displayed in Figure 3. This can be predicted for the  $^1\text{H}$  NMR spectrum of isobutane- $d_9$   $\text{HC}(\text{CD}_3)_3$ , which was characterized only as an incompletely deuterated material.<sup>[14]</sup> Still more elaborate is the  $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of  $(\text{CD}_3\text{CH}_2)_4\text{P}^+$ , which is as yet unknown but which can be predicted to show a 25-line multiplet with relative intensities 1:12:78:352:1221:3432:8074:16236:28314:43252:58278:69576:73789:69576, etc. Other predictions for splitting by many nuclei of spin  $I = 1$  or  $3/2$  can be drawn from Figures 3 and 5, but they are more likely to appear in EPR spectra.

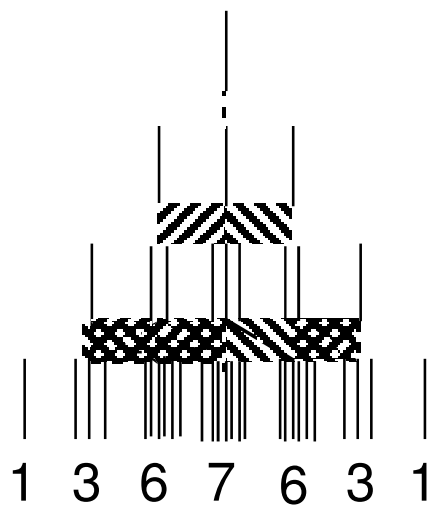
### Summary

Beyond the familiar binomial coefficients, which specify the relative intensities for splitting by  $N$  identical nuclei of spin  $1/2$ , there are little-known polynomial coefficients applicable to  $N$  nuclei of spin  $I > 1/2$ . These describe the number of ways that  $N$  objects can be distributed to  $2I+1$  boxes, numbered from  $-I$  to  $+I$ , such that the sum of the box numbers is  $r$ . Besides, they are the coefficients in the expansion of the polynomial  $(1 + x + x^2 + \dots + x^{2I})^N$ , and they are readily obtained by generalizations of Pascal's triangle.

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### TOC Graphic





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