Pascal's triangle, non-adjacent numbers, and D-dimensional atomic orbitals

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The topics in chemico-physical poblems which are related to Pascal's triangle and asymmetrical Pascal's triangle are collected and their mathematical relations are discussed. The selected topics are: ESR hyperfine splitting, spin–spin coupling of NMR, topological indices of linear and cyclic hydrocarbons, and the number of degeneracy of the atomic orbitals of D-dimensional hydrogen atom. The relation between the Pascal's and asymmetrical Pascal's triangles is also discussed.

1. Introduction

In this report as many and as diversified aspects and roles of the Pascal's triangle and related topics in physico-chemical problems will be introduced as possible (extensive bibliographies on Pascal's triangle and related papers are given in [3]). In some sense the relation among seemingly unrelated subjects through these mathematical concepts and formulations might be accidental. However, some connections among them seem to be too close to be neglected. The present author dares to expose these raw materials in the hope that there might induce fruitful discussion and trigger unexpected discovery on the hidden secret relations among these topics.

2. Definitions of the Pascal's triangle

Expand $(a + b)^n$ into a polynomial in terms of $a^{n-k}b^k$, and one gets the set of binomial coefficients $B(n, k)$ as in figure 1 such that

$$(a + b)^n = \sum_{k=0}^{n} B(n,k)a^{n-k}b^k, \quad B(n,k) = \binom{n}{k} = \frac{n!}{k!(n-k)!}. \tag{1}$$

The triangular array of $B(n, k)$ has been called Pascal's triangle (PT). Although there have been known a number of documentations on this triangle prior to Pascal [3], in this paper no attempt has been taken to change this traditional naming. On the other
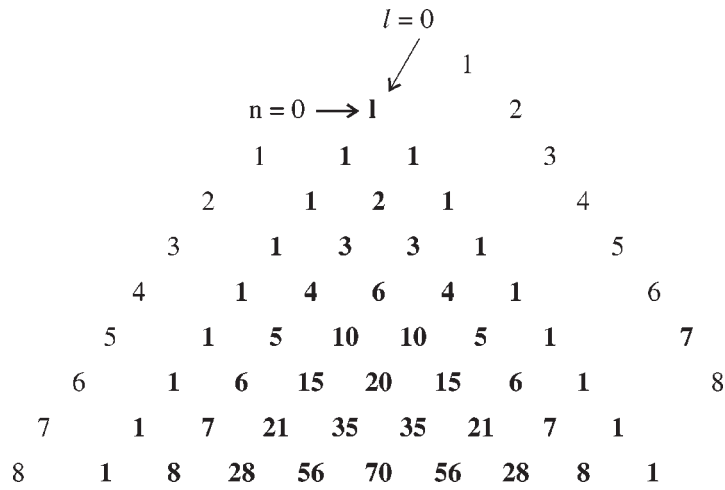
$l = 0$

1

n = 0 → 1   2

1   1   1   3

2   1   2   1   4

3   1   3   3   1   5

4   1   4   6   4   1   6

5   1   5   10   10   5   1   7

6   1   6   15   20   15   6   1   8

7   1   7   21   35   35   21   7   1

8   1   8   28   56   70   56   28   8   1

Figure 1. Binomial coefficients and Pascal's triangle.

$l = 0$

1

n = 0 → 1   2

1   2   1   3

2   2   3   1   4

3   2   5   4   1   5

4   2   7   9   5   1   6

5   2   9   16   14   6   1   7

6   2   11   25   30   20   7   1   8

7   2   13   36   55   50   27   8   1

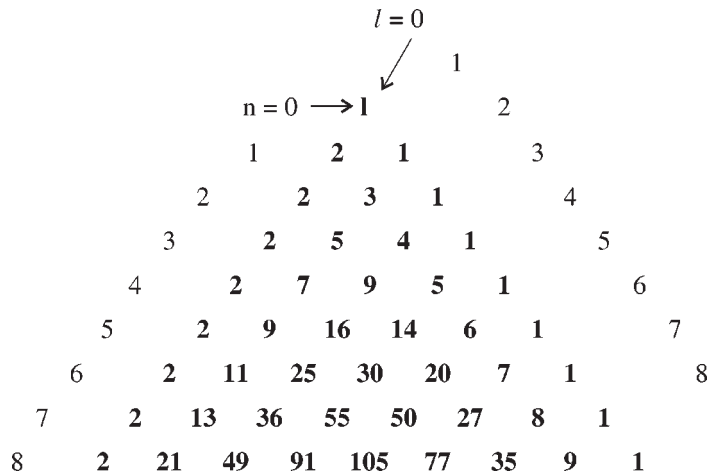8   2   21   49   91   105   77   35   9   1

Figure 2. Asymmetrical Pascal's triangle.

hand, asymmetric Pascal's triangle (APT, see figure 2) [10] and its another version are proposed. APT is constructed by starting from the triangular arrray of

$$1$$
$$2 \quad 1 .$$

It is interesting to note that this triangle can be constructed just by adding a pair of PT's which are staggered by one row along one of the slants of the original PT. In other words, its general term $A(n, k)$ is expressed by

$$A(n, k) = B(n, k) + B(n - 1, k) = \binom{n}{k} + \binom{n - 1}{k}$$

$$= \begin{cases} \frac{2n-k}{n} \binom{n}{k}, & n \neq 0, \\ 1, & n = 0 \end{cases} \quad (k = 0, 1, \ldots, n). \tag{2}$$

As will be shown in this paper APT is also found in various problems in chemistry.

3. ESR hyperfine splitting and spin–spin coupling of NMR

Suppose a set of an electron spin and a group of N equivalent proton spins are subjected under a strong magnetic field. The magnitude of the magnetic interaction among them depends on the distribution of the directions of these spins, which is monitored by a microwave radiation of an appropriate frequency during the sweep of the magnitude of the applied magnetic field. One can then observe the so-called hyperfine splittings of ESR. The mechanism of the observed $(N+1)$-plet electron spin resonance pattern with binomial intensity distribution is well-known as illustrated in figure 3 (the
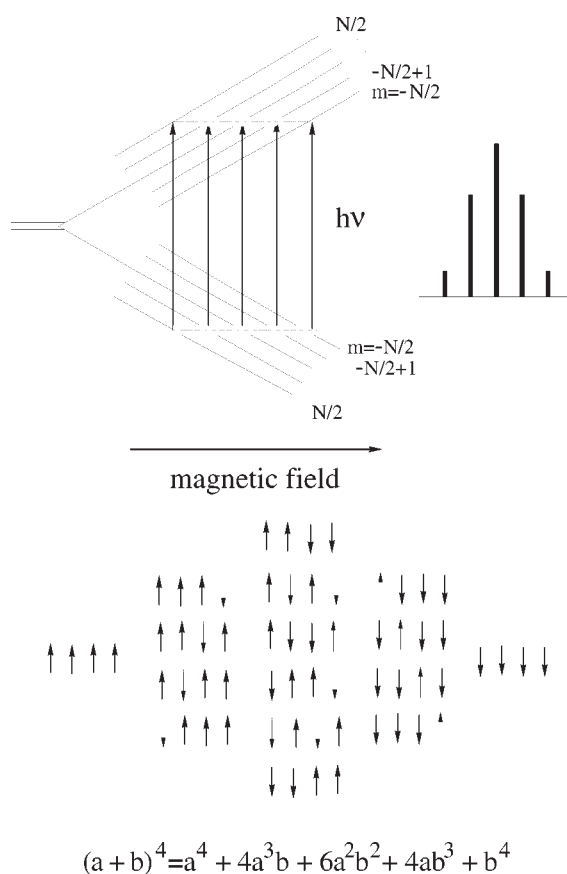

$$(a+b)^4 = a^4 + 4a^3b + 6a^2b^2 + 4ab^3 + b^4$$

Figure 3. Mechanism of ESR hyperfine splitting caused by the interaction of an electron spin with the set of N equivalent proton spins.

mechanism of these magnetic interactions are usually explained in the textbooks of physical chemistry such as [2]).

If a proton spin instead of an electron spin interacts with the group of N equivalent proton spins, the spin–spin interaction takes place to yield multiplet signals in NMR. A typical example is shown in highly resolved NMR spectrum of ethanol giving triplet CH_3 and quartet CH_2 proton signals, as a result of mutual interaction between these two groups of proton spins in different magnetic environments.

Although the magnitudes of these two magnetic interactions differ from each other due to the intrinsic difference in the magnitudes of the electron and proton spins, the essence of the mechanism of these magnetic resonances is the same as is clear in the following pair of statements.

- Interaction of an electron spin with N equivalent proton spins yields $(N + 1)$-plet ESR hfs signals.
- Interaction of a proton spin with N equivalent proton spins yields $(N + 1)$-plet NMR spin–spin interaction signals.

4. Non-adjacent numbers and topological index Z_G

In 1971 the present author coined the term "topological index" by defining the Z-index for characterizing the topological nature of the isomeric graphs corresponding to saturated hydrocarbon isomers [6]. Besides this feature this index has been shown to be closely related to a number of problems, such as bond order [14,15] and aromatic charracter [1,4,16] of unsaturated hydrocarbons, coding and identification of graphs [7], etc. [11]. For deriving the value of the Z-index one has to define the set of the non-adjacent numbers, $p(G, k)$'s, as k-matching number, namely, the number of ways for choosing k disjoint edges (bonds) from a given graph G with N vertices. The largest number of k is denoted as $m = [N/2]$. For even N, $p(G, m)$ is the perfect matching number, or the Kekulé number, $K(G)$.

With the set of $p(G, k)$'s, the Z-counting polynomial $Q_G(x)$ for G is defined as

$$Q_G(x) = \sum_{k=0}^{m} p(G, k)x^k. \tag{3}$$

The Z-index is the sum of $p(G, k)$ numbers to be expressed as

$$Z_G = \sum_{k=0}^{m} p(G, k) = Q_G(1). \tag{4}$$

Consider a series of path graphs, $\overline{N}$, with N consecutively connected vertices, or the graphs corresponding to the carbon atom skeletons of normal paraffins leading to
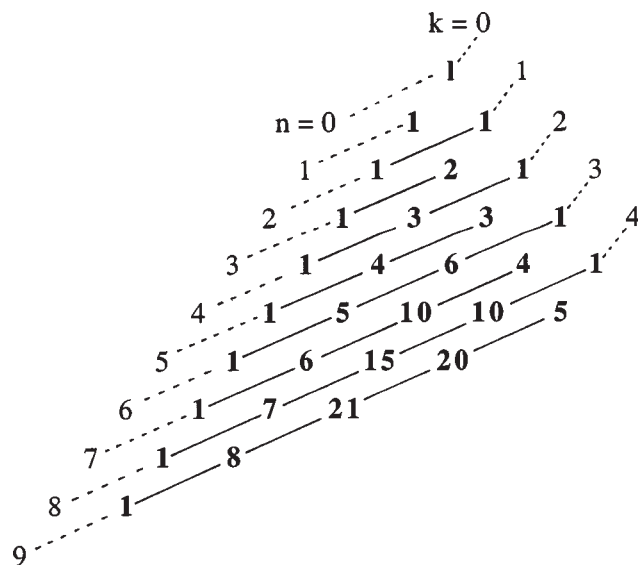
Figure 4. Diagram showing the relation between the $p(G, k)$ numbers of a whole family of $\overline{N}$ graphs ($N = 0, 1, 2, \ldots$) and the Pascal's triangle. Each parallel line indicates the set of $p(G, k)$'s for a particular $\overline{N}$.

polyethylene, or of linear polyenes leading to polyacetylene. It has been known that the $p(G, k)$ number of $\overline{N}$, is expressed by

$$p(\overline{N}, k) = \binom{N - k}{k} = B(N - k, k) \quad (k = 0, 1, 2, \ldots, [N/2]), \tag{5}$$

from which it is straightforwardly deduced that the whole family of $p(\overline{N}, k)$ numbers for $\overline{N}$'s form the PT as in figure 4.

Our new findings is that the whole families of $p(N^0, k)$ numbers for N^0, cylce graph (derived from branchless cyclic alkanes or annulenes) also span completely the APT as shown in figure 5. The notations $\overline{N}$ and N^0 have been proposed in [6].

It has already been known that the coefficients of the second and first kinds of Chebyshev polynomials are directly connected to $p(\overline{N}, k)$ and $p(N^0, k)$'s, respectively [5,9].

It is also to be noted here that the respective sums of the $p(\overline{N}, k)$ and $p(N^0, k)$ for each entry of $\overline{N}$ and N^0 are nothing else but the famous Fibonacci and Lucas numbers [6,8], which are defined respectively as

$$F_N = F_{N-1} + F_{N-2}, \quad F_0 = F_1 = 1 \quad \text{(Fibonacci)} \tag{6}$$

and

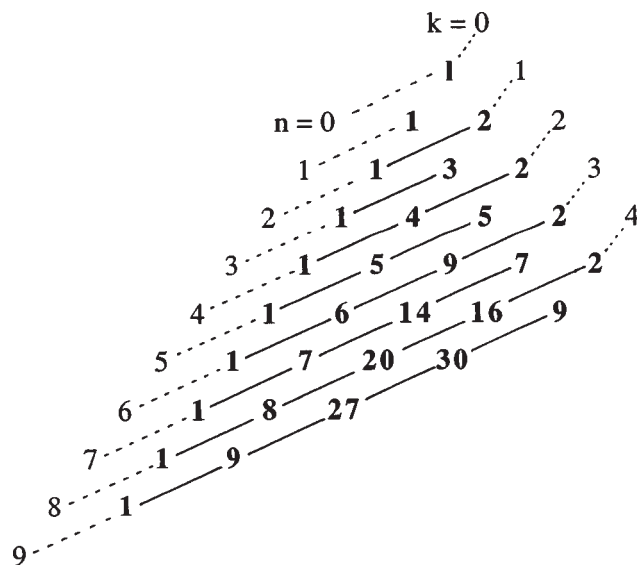$$L_N = L_{N-1} + L_{N-2}, \quad L_0 = 2, \, L_1 = 1 \quad \text{(Lucas)}. \tag{7}$$

Figure 5. Diagram showing the relation between the $p(G, k)$ numbers of a whole family of N^0 graphs ($N = 0, 1, 2, \ldots$) and the asymmetrical Pascal's triangle. Note that this APT is a mirror image of figure 2. The N^0 graph for $N = 0$ to 2 do not correspond to the conventionally defined cycle graphs, but obey the same recurrence relation as applied to the "real" cycle graphs.

Table 1
Lower members of Fibonacci (F_N) and Lucas (L_N) numbers.

N	0	1	2	3	4	5	6	7	8	9
F_N	1	1	2	3	5	8	13	21	34	55
L_N	2	1	3	4	7	11	18	29	47	76

Their smaller members are given in table 1. One of the relations between $\{F_N\}$ and $\{L_N\}$ is known as

$$L_N = F_N + F_{N-2}, \qquad (8)$$

which is derived from the inclusion–exclusion principle [8] (see figure 6). Here l is an edge arbitrarily chosen from G (or N^0 in this case), and $G - l$ is the subgraph of G obtained by deleting edge l from G. The subgraph $G \ominus l$ is derived by deleting l from G together with all the edges incident to l in G.

The recurrence relation of $p(G, k)$ for these graphs,

$$p(G, k) = p(G - l, k) + p(G \ominus l, k - 1), \qquad (9)$$

is shown in figure 6. The first term of rhs of equation (9) is the counting of l-exclusive choice from G, while the second term gives the counting of l-inclusive choice. Note that the argumet in the latter term is $k - 1$, since l has already been spared as a member of k edges.
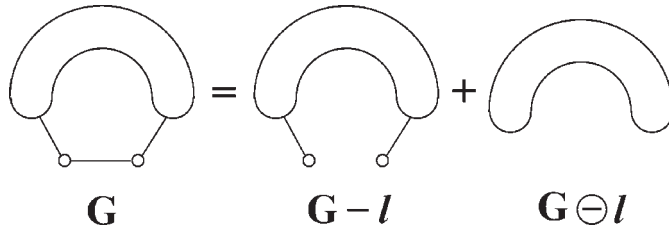
$$p(G, k) = p(G - l, k) + p(G \ominus l, k - 1)$$

Figure 6. Inclusion–exclusion principle as applied to the enumeration of $p(G, k)$ numbers for an arbitrary graph.

Important conclusion is that all the entries in APT of figure 2, or equation (2), have an exact one-to-one correspondence with the $p(N^0, k)$ numbers of cycle graphs $\{N^0\}$ ($N = 0, 1, \ldots$) and are derived from the relation (8) between the Fibonacci and Lucas numbers. This relation may symbolically be expressed as

$$\mathrm{PT} + \mathrm{PT}' \rightarrow \mathrm{APT}. \tag{10}$$

5. D-dimensional hydrogen atomic orbitals

Recently the present author has pointed out that the number of degeneracy of the atomic wavefunctions with angular momentum l in D-dimensional hydrogen atom is expressed as [10,12,13]
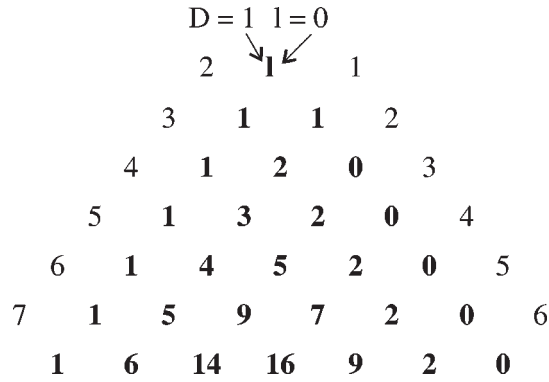
$$g(D, l) = {}_D H_l - {}_D H_{l-2} = \begin{cases} 1, & l = 0, \\ \frac{D+2l-2}{l}\binom{D+l-3}{l-1}, & l \neq 0, \end{cases} \tag{11}$$

where ${}_D H_l$ is the number of repeated combination of l objects from D different items, i.e.,

$$_D H_l = \binom{D+l-1}{l} \quad (D = 1, 2, \ldots, \ l = 0, 1, \ldots). \tag{12}$$

In fact, for $D = 3$ we have $g(D, 3) = 2l + 1$. It means that in our 3-dimensional world any atom has one s, three p, five d orbitals, etc., while in the hypothetical 4-dimensional world the number of degeneracy of angular momentum l is a squared number.

Equation (11) gives just the number of independent D-dimensional homogeneous harmonic polynomials of order l. The term $_D H_l$ appearing in equation (11) is the number of homogeneous products $x_i^p x_j^q x_k^r \cdots$ of order $l = p + q + r + \cdots$ chosen fom D variables, $x_i, x_j, \ldots, x_D$.

D = 1 1 = 0
    2   **1**   1
   3   **1**   **1**   2
  4   **1**   **2**   **0**   3
 5   **1**   **3**   **2**   **0**   4
6   **1**   **4**   **5**   **2**   **0**   5
7   **1**   **5**   **9**   **7**   **2**   **0**   6
1   **6**   **14**   **16**   **9**   **2**   **0**

$$g(D, l) = {}_D H_l - {}_D H_{l-2}$$

Figure 7. Asymmetrical Pascal's triangle obtained by the subtraction of two Pascal's triangles gives better expression for the number of degeneracy of the atomic wavefunctions of D-dimensional atom.

The harmonic polynomial, or the solution of the angular part of the atomic orbital wavefunctions, i.e., a polynomial $R_l(x_i, x_j, \ldots, x_D)$ of order l which satisfies the Laplacian equation

$$\Delta_D R_l = \sum_{k=1}^{D} \frac{\partial^2}{\partial x_k^2} R_l = 0 \tag{13}$$

in the Schrödinger equation for a hydrogen-like atom in D-dimensional world.

The number of equations corresponding to this condition is given by ${}_D H_{l-2}$. Then by subtracting this number from ${}_D H_l$ one obtains equation (11), or the number of degeneracy of D-dimensional hydrogen-like atomic orbitals with angular momentum l. Let us consider the whole family of ${}_D H_l$. By writing all the entries of equation (12) it is immediately found that ${}_D H_l$ also completely spans PT. In other words, there is one-to-one correspondence between the entries of PT and all the members of ${}_D H_l$.

Then the whole family of $g(D, l)$ can be found in the triangular array of $\mathrm{PT} - \mathrm{PT}''$ (figure 7), which is obtained by subtracting a PT from another PT which is shifted by two steps along the one of the slant edges. This fact can symbolically be written down as

$$\mathrm{PT} - \mathrm{PT}'' \rightarrow \mathrm{APT} + x, \tag{14}$$

where x stands for the slant edge, $1\,1\,0\,0\ldots$, of the right-hand roof of the triangle as shown in figure 7.

At first sight this roof seems to be odd. However, it turns out that this row gives the number of degeneracy of the angular part of the atomic orbital wavefunctions of one-dimensional hydrogen atom, namely, there are both one type of s and p orbitals in one-dimensional hydrogen atom.

By comparing two relations (10) and (14) one can conclude that the appearance of the same asymmetrical Pascal's triangle in these two cases might be accidental.
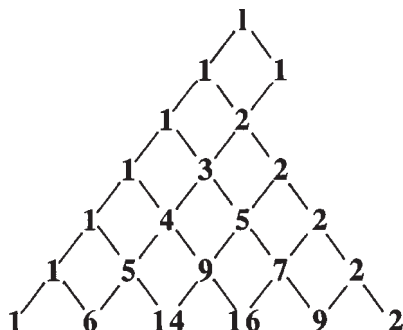
Figure 8. Triangular array of numbers giving the shortest steps from the summit and forming a pseudo-asymmetrical Pascal's triangle.

However, if figure 7 is modified into figure 8 by wiping out the zeros and drawing lines so as to connect nearest neighbors, each number in the triangle gives the number of possible shortest steps from the summit vertex. This is the hierarchical structure of all the family of the hydrogen-like atomic wavefunctions in multi-dimensional world [12].

In this connection there might be able to find other chemico-physical problems whose mathematical structures have some relevance to PT or APT.

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