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A GENERALISATION OF THE POLYA/DE BRUIJN ENUMERATION THEORY AND ITS APPLICATION TO "CHEMICAL COMBINATORICS"

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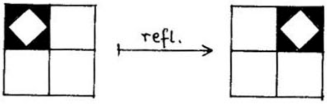
Besides the topic mentioned in the title, the main intention of this contribution is to call attention upon the interactions between mathematics and chemistry. Any combinorialist is probably aware of the fact that the phenomenon of isomerism, that is, the occurrence of different chemical compounds with identical composition gave rise to the notion of constitution, thus providing one of the roots of graph theory. Similarly, the problem of counting isomers initiated Polya's theory of enumeration under group action. Today such interaction is much better established between mathematics and other sciences such as physics, of course, but also engineering and economics. There exist well-defined borderlands like mathematical physics, system theory and operations research; even biomathematics has been created recently. So where is mathematical chemistry today? There was not much activity in this field for quite some time, due to twenty years of computer craze, where theoretical chemistry was commonly identified with numerical quantum chemistry. By now this long lasting computer age seems to come to an end. So, in recent years, growing attention is again being directed towards qualitative understanding of chemical phenomena. As a consequence, renewed interest in mathematical structures, to be employed in rigorous formulations of chemical concepts, can be observed.

Since the days of Cayley, an everlasting problem of mathematical chemistry has been the description of molecular structure. This is a "dynamical" problem because chemistry makes use of a hierarchy of levels of observation, which goes on growing due to the development of new experimental techniques. So the theory division had and has to follow, supplying corresponding levels of description. Roughly speaking, molecules are built up from fragments of comparatively few types. For these, the constituent atoms may be taken, but in organic chemistry (i.e. the chemistry of carbon compounds) a number of polyatomic fragments have been recognized as quasi-invariant building blocks of molecular structure. On the lowest level of description only the composition of molecules with respect to certain types of fragments is recorded. The next level specifies molecular constitution, that is, the bonding connectivity among the fragments. On this level, molecules are represented by graphs with coloured vertices, say, if we agree upon using colours to represent the various fragment types. On the next level, opening the door to what is called stereochemistry, molecules are recognized to live in 3-dimensional space. On this level the description records qualitative geometrical features, as e.g. by means of the popular rigid stick & ball models. Looking closer, most molecules are recognized to be flexible, and by high-speed experiments it is possible to distinguish among rapidly interconverting species which formerly collapsed into one average configuration. And chemistry goes on, but we will stop here and confine ourselves roughly to the level of stick & ball models. This is where Polya's enumeration theory has its most immediate applications in chemistry.

These applications refer to the notorious "isomer problem" which may be stated as follows: With respect to some specified fragmentation, two molecules are called <u>isomers</u>, if they have the same composition. The problem then is to describe all the isomers for any composition. In such a general setting this problem is much too hard. E.g. on the simple level of fragments being atoms and structure being bonding connectivity, the isomer problem would be to describe all the graphs with n vertices, say, of given colours and degrees. The only way to perform this is by means of some good computer program as e.g. developed by the Artificial Intelligence Group at Stanford in the 70's. Also, the corresponding enumeration problem is still unsolved. The situation becomes exponentially worse as stereochemical characteristics are included. So the only reasonable thing to do is to break down the isomer problem into a variety of easier problems by restriction to tractable subsets. Such subsets arise e.g. from some parent structure through substituting simple fragments, say hydrogen atoms, by other building blocks. Evidently, such structures are parametrized by mappings between finite sets. Let us adopt the following notation: We have a finite set $P = \{1,2,\ldots,i,\ldots\}$ of positions, where substitution may take place in the parent structure, and another finite set of types of substituents including the basic fragment that is present everywhere in the parent structure. The common name is ligands, hence we call this set $L = \{A,B,\ldots,X,\ldots\}$. Then any mapping $\varphi : P \rightarrow L$ represents a derivative structure if $\varphi(i)=X$ is taken to say that there is a fragment of type X in the i'th position. In lucky (and mathematically dull) cases, the correspondence between mappings and derivative structures is one-to-one. Often, however, it is many-to-one, that is, a given structure has several equivalent descriptions in terms of mappings. In most such cases, this equivalence is due to some symmetry of the parent structure. E.g., the familiar formulas of benzene derivatives are represented by mappings from the set $P = \{1,\ldots,6\}$ of ring carbon atoms into a set $L = \{H,X,Y,\ldots\}$ of ligand types. However, because of the hexagonal symmetry of the benzene ring, there are many duplicates: any formulas that are mutually interconvertible by rotations from the dihedral group D_6 provide equivalent descriptions of the same compound. So the final result is that the benzene derivatives with ligands in L are in one-to-one correspondence with the orbits in $L^P := \{\varphi : P \rightarrow L\}$ of the dihedral group D_6, where this group acts by acting on P, i.e. by permuting the positions of the ligands. Analogously, many families of (molecular and other) structures are parametrized by the orbits of a finite group G in a finite set L^P of mappings. With respect to applications in stereochemistry, on the level of stick & ball models, mappings are interpreted as distributions of model ligands over specified sites of a parent "skeleton" fixed in space. The group in action is the skeleton symmetry group or a subgroup thereof, which arises by intersection with the invariance group of the observation level in question.

There are now serveral possibilities, of increasing complexity, of how this group action looks like in detail. First and foremost, a symmetry operation acts on distributions by removing the ligands from their original positions to other sites, that is, by permuting the positions of ligands. Note that this site permutation does not depend on the ligands that are moved. If the ligand symmetry is sufficiently high as e.g. in the case of balls, this rearrangement will be the only effect. Formally, in such a case of <u>pure domain action</u>, a group G acts on the set of sites, P, by permutations π_g attributed to the $g \in G$, and $g \in G$ operates on mappings $\varphi : P \rightarrow L$ by taking to site $\pi_g(i)$ whatever ligand $X = \varphi(i)$ originally was at site i.

I



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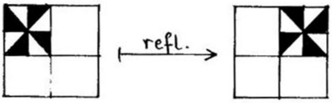
$$g : \begin{pmatrix} i \\ X \end{pmatrix} \mapsto \begin{pmatrix} \pi_g(i) \\ X \end{pmatrix} ,$$

$$g : \varphi \mapsto \varphi \circ \pi_g^{-1} .$$

If the ligands have some structure of their own, it may happen that a symmetry operation, besides moving the ligands, also changes their types. As the mildest increase in complication, this transformation of ligand types takes place independently of the positions. That is, we have <u>simultaneous actions on domain and range</u>: A group G acts on P as above, and moreover G acts on L by permutations λ_g, $g \in G$. Hence $g \in G$ operates on mappings $\varphi : P \rightarrow L$ by taking to site $\pi_g(i)$ any image $X = \varphi(i)$, while transforming it into $\lambda_g(X)$.

II



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$$g : \begin{pmatrix} i \\ X \end{pmatrix} \mapsto \begin{pmatrix} \pi_g(i) \\ \lambda_g(X) \end{pmatrix} ,$$

$$g : \varphi \mapsto \lambda_g \circ \varphi \circ \pi_g^{-1} .$$

Finally, and most awkwardly to deal with, the fate of a ligand may depend on its initial and final position. Then there is an individual action of G on L, $g \mapsto \lambda_g^{(i)}$, for any site $i \in P$, and the action on L^P is given by

$$\text{III} \qquad g: \begin{pmatrix} i \\ X \end{pmatrix} \mapsto \begin{pmatrix} \pi_g(i) \\ \lambda^{(i)}_g(X) \end{pmatrix} .$$

With the first of these actions we are on solid ground. This is the type considered by Polya in his classical paper (1937), where the associated restricted isomer problem is solved as follows. First we have to define composition, and we do this in almost the same manner as in chemistry, by writing H^2O instead of H_2O for the composition of the water molecule from two hydrogen and one oxygen atom. So we use the same symbols to denote ligand types as well as "indeterminates" assigned to them, and we record the composition of a mapping $\varphi : P \rightarrow L$ by means of the monomial

$$M(\varphi) := \prod_{i \in P} \varphi(i) = \prod_{X \in L} X^{m_\varphi(X)} \quad ; \quad m_\varphi(X) = \left| \varphi^{-1}(X) \right| ,$$

consisting of the ligands to the power of their frequency among the images of the various sites. We call this monomial the <u>gross formula</u> of φ. Clearly then, since the group G acts by site permutations exclusively, mappings in the same orbit have the same composition. So let M be any gross formula, that is, a monomial over L of degree $|P|$. Then

$$L^P{}_M := \{ \varphi \in L^P \mid M(\varphi) = M \}$$

is a G-subset of L^P, and its orbits are in one-to-one correspondence with the isomers of composition M. Their number is given by Polyas famous enumeration theorem.

Theorem (Polya): The number of G-orbits in $L^P{}_M$ coincides with the coefficient of M in the generating function

$$\left\langle \prod_{k\geq 1} \Big(\sum_{X\in L} X^k\Big)^{c_k(\pi_g)} \right\rangle_{g\in G} ,$$

where $c_k(\cdot)$ stands for he number of cyclic factors of length k, and the brackets denote averages.

The next item in the stock-in-trade of combinatorics books is a generalization of Polya's theory, due to de Bruijn, which was christened "Power Group Enumeration" by Harary and Palmer. Unfortunately, this is not what is required for the analogous treatment of type II actions. Chemists realized that, and they closed the books, concluding that for certain chemical enumeration problems solutions à la Polya were not in sight. We will first discuss what is wrong with de Bruijn's approach from the viewpoint of chemistry and then sketch the easy way out by dropping a seemingly canonical restriction. De Bruijn introduces a second group H that acts on L by permutations λ_h, so the direct product HxG acts on L^P by H acting on the range and G acting on the domain of mappings, i.e.

$$(h,g):\ \varphi \mapsto \lambda_h \circ \varphi \circ \pi_g^{-1} .$$

But now the mappings within an orbit no longer have the same composition. So de Bruijn introduces a coarser notion of composition that refers to the H-orbits in L instead of the single elements. Letting $\hat{X}$ denote the H-orbit in L that contains X, and using the same symbols as indeterminates as well, the composition of a mapping φ is now defined by the monomial

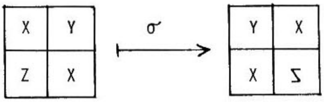
$$\hat{M}(\varphi) \ := \ \prod_{i\in P} \widehat{\varphi(i)} .$$

In this setting de Bruijn arrived at an analogue of Polya's theorem as follows.

Theorem (de Bruijn): The number of (HxG)-orbits in $L^P{}_M$ is given by the coefficient of M in the generating function

$$\Big\langle \prod_{k\geq 1} \Big(\sum_{\substack{X \in L \\ \text{fixed by } \lambda_h^k}} \hat{X}^k \Big)^{c_k(\pi_g)} \Big\rangle_{(h,g)\in H\times G} .$$

So now, which are the problems in making use of this result in the case of type II actions? First, the group is wrong. In de Bruijn's approach there are two groups which act jointly but independently on range and domain of mappings. We rather need a single group that simultaneously acts on both these sets. But this is no serious trouble since two easy steps take us home: specializing to H = G and next restricting the action of GxG to its diagonal subgroup. The second, more serious objection is that the classification, as provided by de Bruijn's notion of content, is too coarse. Let e.g. the group be the simplest reflection group, $G = \{e, \sigma\}$, and let $P = \{1,2,3,4\}$ denumerate the boxes in the square array below. For L let us take the letters of the alphabet together with their mirror images, if distinct, so $L = \{A, B, ᙠ, \ldots, Y, Z, \Sigma\}$. Mappings from P to L are visualized as arrangements of letters. $G = \{e, \sigma\}$ acts on L^P by σ reflecting any arrangement while e of course fixes them all.



Then e.g. the composition Z^4 includes five distinct monomials: Z^4, $Z^3\Sigma$, $Z^2\Sigma^2$, $Z\Sigma^3$, Σ^4. However, the mappings of gross formula $Z^2\Sigma^2$ constitute a proper G-set by themselves, as do those belonging to $Z^3\Sigma$ or $Z\Sigma^3$ and those associated with the other mirror image pair Z^4, Σ^4. So one should like to have these orbit numbers separately, not just their sum! Then, why attribute such crude "weights" to mappings? Because they are demanded by the so-called weighted version of Burnside's Lemma, which is customarily employed in the derivation of generating functions for orbit numbers.

Burnside's Lemma (weighted version): Let a group G act on a set S, and let $w: S \rightarrow \Omega$ be a "weight function" that is constant on the G-orbits in S. Let S_g denote the subset of fixed points of $g \in G$, and let $S \quad = w^{-1}(\omega)$ be the fibre sitting over $\omega \in \Omega$. Then

$$\left\langle \sum_{s \in S_g} w(s) \right\rangle_{g \in G} = \sum_{\omega \in \Omega} n(\omega)\omega ,$$

where $n(\omega)$ is the number of orbits in S_ω.

Applications of this result are restricted to weights that are constant over the orbits. The monomials $M(\varphi)$ have this property in the Polya case. In the de Bruijn case they don't, and looking for the closest admissable analogues, the $\hat{M}(\varphi)$ inevitably appear. With these two choices of the weight function, the average sums of fixed point weights are readily evaluated, resulting in the theorems cited before. It turns out, however, that the restriction to G-invariant weight functions is unnecessarily strong. Analogues of the weighted Burnside Lemma exist for a much larger class of weight functions. However, we will not discuss the most general version here but just the one we need at present.

Lemma (almost Burnside's): Let a group G act on a set S and on Ω, a set of weights, as well, and let $w : S \longrightarrow \Omega$ be a G-map, i.e. $w(gs) = gw(s)$ in obvious notation. Finally, let θ be any G-subset of Ω, and let $S_\theta = w^{-1}[\theta]$ denote the subset of elements in S with their weights in θ. Then

$$\left\langle \sum_{s \in S_g} w(s) \right\rangle_{g \in G} = \sum_{\omega \in \Omega} n(\omega)\omega ,$$

where $\sum_{\omega \in \theta} n(\omega)$ is the number of orbits in S_θ.

So, also in this quite more general situation, the coefficients of weights in the average sums of fixed point weights provide us with orbit numbers. Our result readily applies to type II actions as follows. Here we have $S = L^P$ with G acting simultaneously on P and on L. Ω is the set of monomials of degree $|P|$ over L, as before in the Polya case, and likewise the weight function is again $w : \varphi \mapsto M(\varphi)$. w is readily confirmed to be a G-map, which is quite obvious if mappings are identified with words over L taken as a strictly non-commutative alphabet, their weights being the corresponding monomials over L as a commutative alphabet, this time. The objects that now characterize composition are the G-orbits of monomials. We call them <u>generalized gross formulas</u>. These orbits are the natural substitutes of gross formulas in the Polya case, since the weights of mappings in an orbit range precisely over an orbit of monomials. Now a straightforward computation of the average sum of fixed point weights in the generalized Burnside Lemma yields the final result about the restricted isomer problem in the case of type II actions.

Let θ be a generalized content, that is, a G-orbit of monomials of degree $|P|$ over L. Then

$$L^P{}_\theta := \{\varphi \in L^P \mid M(\varphi) \in \theta\}$$

is a G-subset of L^P, and its orbits are in one-to-one correspondence with the isomers of composition θ. Referring to their enumeration we have

<u>Theorem (almost de Bruijn's):</u> The number of G-orbits in $L^P{}_\theta$ is obtained by summing over θ the coefficients of the monomials $M \in \theta$ in the generating function

$$\Big\langle \prod_{k\geq 1} \Big(\sum_{\substack{X\in L \\ \text{fixed by } \lambda_g^k}} X\lambda_g(X)\cdots\lambda_g^{k-1}(X) \Big)^{c_k(\pi_g)} \Big\rangle_{g\in G} .$$

As a concluding remark, the generating function above "produces" the complete series of orbit numbers for the various generalized contents. In case that one is rather interested in some single such numbers it is worthwile noting that the generalized compositions may be replaced by ordinary ones while simultaneously the group G is replaced by an appropriate stabilizer, as follows.

Proposition (reduction to Polya type enumeration): Let θ be an orbit of gross formulas and $M \in \theta$ be one of them. Denote by G_M its stabilizer. Then $L^P{}_M$ is a G_M-set, and there are equally many G-orbits in $L^P{}_\theta$ and G_M-orbits in $L^P{}_M$.

Restricted to $L^P{}_M$, the action of any stabilizer G_M is of type I, hence enumeration à la Polya is applicable.

Finally, the one-to-one correspondence above can be strengthened to the existence of common transversals, thus providing the basis of an efficient method to construct transversals of orbits. For details as well as references to the literature the present authors paper in Theoretica Chimica Acta 66, 91-110 (1984) should be consulted.

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