BASIC ALGEBRA IN INORGANIC CHEMISTRY

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ABSTRACT. This paper defines the basics of group theory and representation theory with a focus on domains that are applicable to foundational inorganic chemistry. Subgroups are introduced and Lagrange's theorem proved. Group actions and the relationship of groups and permutations are extended into representation theory. Representations are defined in the abstract and their applicable use in $\mathbb{R}^3$ as representing symmetries is recovered as a special case. Lastly, the relationship between all theoretical tenets and the chemistry in which they are used is discussed.

CONTENTS

1. INTRODUCTION

New advances in mathematics are often driven by the study of worldly phenomena. As such, when chemists realized that important consequences of molecular structure (as defined by the wave equation) are based in molecular symmetry, they needed a rigorous mathematical foundation on which to construct their theory. Moreover, since the wave equation is not solveable in terms of elementary functions, chemists have turned to alternate, more indirect methods of analyzing its properties. Arguably the most common of these is group theory, which is applied through the bridge of representation theory to describe the symmetry of various molecules, the symmetry being directly related to a number of chemical properties. This paper will lay out the basics of group theory and explain how some of its theorems have been applied to chemistry and to what end.

2. GROUP THEORY

Abstract algebra is the study of the structure of algebraic objects. One of the first examples we become familiar with is the real numbers, which are a continuum and an ordered field, thus satisfying many axioms that imply a rich theory. However, algebra also studies sets of objects that satisfy far fewer axioms.

Definition 2.1. A **group** $\langle G, \cdot \rangle$ is a set G along with a binary operation $\cdot$ on G that satisfies three group axioms: $\cdot$ is associative, there exists an identity element $e \in G$ satisfying $e \cdot g = g \cdot e = g$ for all $g \in G$, and, for all $g \in G$, there exists an $h \in G$ such that $g \cdot h = h \cdot g = e$.

A simple example of a group is $\langle \mathbb{Z}, + \rangle$, or the integers under addition. Addition combines any two integers into a third integer, adding is associative, 0 serves as an additive identity, and the inverse of any integer is its opposite ($-x$ corresponding to x).

Definition 2.2. Let A be a set, and let $[n]$ denote the set of all natural numbers from 1 to n, inclusive. If A and $[n]$ are in bijective correspondence, then we say that the **cardinality** of A is n, and denote this by $|A| = n$.

Definition 2.3. Let A be a set. If $|A| = n$ where $n \in \mathbb{N}$, then we say that A is **finite**. If $|A| \neq n$ for any $n \in \mathbb{N}$, then we say that A is **infinite**.

Since $\mathbb{Z}$ contains all of the natural numbers and more, $\mathbb{Z}$ is infinite. More rigorously, if we suppose for the sake of contradiction that there exists a bijective correspondence between $\mathbb{Z}$ and $[n]$ for any $[n]$, we can prove that the function is not bijective. Relating this back to group theory, since $\mathbb{Z}$ is infinite, we call a group such as $\langle \mathbb{Z}, + \rangle$ an **infinite group**.

Naturally, there also exist **finite groups**. One of the most well-studied classes of finite groups is the following.

Definition 2.4. For any $n \in \mathbb{N}$, let $\mathbb{Z}/n\mathbb{Z}$ denote the group defined by the set $\{0, 1, 2, \ldots, n\}$ under addition modulo n.

For example, the set $\mathbb{Z}/2\mathbb{Z} = \{0, 1, 2\}$ under addition modulo 2 is a finite group. Addition modulo 2 guarantees closure, associativity still holds, 0 is an identity, and inverses are as follows: $-0 = 0$, $-1 = 2$, and $-2 = 1$.

Now that we have defined groups, one of the first things we can do is ask about their structure. Indeed, we can study subsets of an arbitrary group G that have similar properties. The most important of the subsets of a group G is defined as follows.

Definition 2.5. A **subgroup** H of a group G is a nonempty subset of G that is closed under products (which are still formed with the original group operation) and inverses.

The first important property of subgroups that we shall prove is the following.

Remark 2.6. A subgroup is a group.

Justification. Let H be a subgroup of G. To prove that H is a group, it will suffice to show that H satisfies the three group axioms.

Axiom 1: Associativity of the elements in the subgroup follows directly from the associativity of the elements in the context of the original group.

Axiom 2: Let $g \in H$ be arbitrary. Then by closure under inverses, $g^{-1} \in H$. It by closure under products that $gg^{-1} = e \in H$, as desired.

Axiom 3: It follows by closure under inverses that there exist inverses in G for all $g \in G$. □

A simple example of a subgroup is that the **alternating group** A_n is a subgroup of the **symmetric group** S_n.

Definition 2.7. Consider the set $[n]$. The **symmetric group** (of order n) is the set of all bijections $f : [n] \to [n]$ under the operation of function composition. It is denoted by S_n.

In other words, the symmetric group is the set of all permutations of the numbers 1 through n. Now, every permutation of an amount of numbers can be written as the product of some number of **transpositions**, and it can be proven that no permutation can be written as both the product of an even number of transpositions *and* an odd number of transpositions. This fact allows for the following definition.

Definition 2.8. Consider the symmetric group of order n. The **alternating group** (or order n) is the subset of S_n consisting of all *even* permutations of order n under the operation of function composition. It is denoted by A_n.

These definitions allow us to prove the following proposition.

Proposition 2.9. *The alternating group A_n is a subgroup of S_n.*

Proof. To prove that A_n is a subgroup of S_n, it will suffice to show that A_n is closed under products and inverses. Let $\sigma, \sigma' \in A_n$ be two even permutations. Then they can be expressed as the product of an even number of transpositions. It follows since the sum of two even numbers is another even number that their product is the product of an even number of transpositions, itself. As to closure under inverses, since the inverse of the transposition $(x\ y)$ is the transposition $(y\ x)$, the inverse of any even permutation is equal to the product of the inverses of each underlying transposition, given in reverse order (e.g., the inverse of (1 2)(3 4) is (4 3)(2 1)), and thus the product of an even number of transpositions, itself. $\square$

As will be discussed in Section 5, subgroups are of critical importance not only in that they lead to many important results in group theory, but in that they come endowed with properties applicable to other fields. However, finding subgroups can be difficult — there are often many subsets of G to sort through.

Definition 2.10. Let G be a set. The **power set** (of G) is the set of all subsets of G. It is denoted by $\wp(G)$.

If G is an infinite group, the power set of G is also infinite (and, in fact, it can be proven that the power set of an infinite group is a of a higher order of infinity than that of the original group). If G is a finite group with $|G| = n$, it can be proven that $|\wp(G)| = 2^n$. Thus, it will be useful to eliminate some possibilities right off the bat. One of the most effective ways of narrowing our search is with Lagrange's theorem, which we shall now work up to.

Definition 2.11. Let H be a subgroup of G. We define each **right coset** (of H in G) to be the set of all products ha, where $a \in G$ is fixed and h ranges over the elements of H. It is denoted by Ha. Symbolically, we have that

$$Ha = \{ha \mid h \in H\}$$

We may analogously define the left coset of H in G, but without the loss of generality, we will work with right cosets (all subsequent proofs are naturally symmetric for left cosets).

A useful first property of cosets is the following.

Theorem 2.12. *If $a \in Hb$, then $Ha = Hb$.*

Proof. Let $x \in Ha$ be arbitrary. Then there exists $h \in H$ such that $x = ha$. Similarly, since $a \in Hb$, there exists $h' \in H$ such that $a = h'b$. Thus, we have that $x = h(h'b) = (hh')b$ by the associative law. But since H is a subgroup of G, $hh' \in H$. Therefore, $x \in Hb$, as desired. The proof is symmetric in the other direction. $\qquad\square$

With this result in hand, we are now ready to prove the following.

Theorem 2.13. *Let G be a group and let H be a fixed subgroup of G. Then the family of all the cosets Ha, as a ranges over G, is a partition of G.*

Proof. To prove that the collection of all cosets of H is a partition of G, it will suffice to show that any two cosets are either disjoint or equal, and every element of G is in some coset. We take this one constraint at a time.

Let Ha, Hb be arbitrary cosets of H in G. We divide into two cases (Ha, Hb are disjoint and Ha, Hb are not disjoint). If they are disjoint, we are done. On the other hand, if they are not disjoint, then there exists $x \in Ha \cap Hb$. Since $x \in Ha$, $x = h_1a$ for some $h_1 \in H$. Similarly, $x = h_2b$ for some $h_2 \in H$. It follows that $a = (h_1^{-1}h_2)b$. But since $h_1^{-1}h_2 \in H$ by the definition of a subgroup, the above fact implies that $Ha = Hb$, as desired.

Let $x \in G$ be arbitrary. Since $e \in H$ by the definition of a subgroup, $x = ex \in Hx$, as desired. $\qquad\square$

Additionally, we need the following.

Theorem 2.14. *Let G be a finite group, let H be be a fixed subgroup of G, and let $a \in G$ be arbitrary. If Ha is any coset of H, there is a one-to-one correspondence from H to Ha.*

Proof. Let $f : H \to Ha$ be defined by $f(h) = ha$ for all $h \in H$. To prove that f is bijective, it will suffice to show that it is injective and surjective. To begin, let $f(h_1) = f(h_2)$. Then $h_1a = h_2a$. But by the cancellation law, $h_1 = h_2$, as desired. Now let $x \in Ha$ be arbitrary. By the definition of Ha, $x = ha$ for some $h \in H$. Therefore, $f(h) = ha = x$, as desired. $\qquad\square$

We can now combine the last two results in an interesting manner — we now know that the collection of all cosets of a certain subgroup H partitions G into subsets all of equal cardinality. Thus, *the cardinality of G is a multiple of the cardinality of H.* Lagrange's theorem formalizes this notion.

Theorem 2.15 (Lagrange's Theorem)**.** *Let G be a finite group, and H any subgroup of G. The order of G is a multiple of the order of H.*

Proof. By Theorem 2.2, we may let the cosets of H divide G into n partitions. By Theorem 2.3, each of these n partitions has the same cardinality $|H|$. Therefore, since the elements in the group are divided into n partitions of size $|H|$, $|G| = n|H|$, as desired. $\qquad\square$

Although a simple result, Lagrange's theorem gives us a powerful tool in our quest to assert order on groups. One of the most immediate and most striking consequences of Lagrange's theorem is that it completely characterizes all groups of prime order.

Theorem 2.16. *Let G be a group. If G has a prime number p of elements, then G is a cyclic group. Furthermore, any element $a \neq e$ in G is a generator of G.*

Proof. Let a be an arbitrary non-neutral element of G. As we know, $\langle a \rangle$ is a subgroup of G. Thus, by Lagrange's theorem, $|\langle a \rangle| \mid |G|$. However, since $|G| = p$ is prime, either $|\langle a \rangle| = 1$ or $|\langle a \rangle| = p$. But since $a \neq e$, $|\langle a \rangle| \neq 1$. Therefore, $|\langle a \rangle| = p$, and we have that G is a cyclic group with generator a, as desired. $\square$

Similarly, Lagrange's theorem characterizes all cyclic subgroups of G, giving us valuable information about the possible orders of elements in G.

Theorem 2.17. *Let G be a finite group and $a \in G$. The order of a divides the order of G.*

Proof. Clearly, $|a| = |\langle a \rangle|$. But since $\langle a \rangle$ is a subgroup of G, Lagrange's theorem implies that $|\langle a \rangle| = |a| \mid |G|$, as desired. $\square$

3. Group Actions

Definition 3.1. A **group action** is a function

$$(\,\cdot\,) : G \times A \to A$$

satisfying two properties, namely that $g_1 \cdot (g_2 \cdot a) = (g_1 g_2) \cdot a$ for all $g_1, g_2 \in G$ and $a \in A$, and that $e \cdot a = a$ for all $a \in A$.

By the definition of the domain and codomain of $\cdot$, we can see that for an arbitrary $g \in G$, g maps every $a \in A$ to a unique $g \cdot a \in A$. Indeed, each $g \in G$ acts like a function on A. However, by property 1, $\cdot$ also makes the action of $g_1 g_2$ on a equivalent to applying g_2 first, and then g_1 to the resultant product $g_2 \cdot a$ (this is associativity). In other words, the $\cdot$ operation essentially doubles as relating an argument and a function to an output, *and* function composition. The second stipulation just guarantees that the identity element of G behaves like an identity function, so that when we "compose" an element $g \in G$ with e, the effect of g on A is unaltered, as it should be.

Since each $g \in G$ becomes an automorphism of A under the group action definition, a natural use of group actions is to describe permutations. For example, let $A = \{1, 2, 3\}$ and $S_2 = \{e, g\}$, where

$$g \cdot 1 = 1 \qquad\qquad g \cdot 2 = 3 \qquad\qquad g \cdot 3 = 2$$

and

	e	g
e	e	g
g	g	e

is the group multiplication table. It is trivial, albeit tedious, to show that the group action $\cdot$ satisfies properties 1-2 as defined, so the explicit proof will be omitted. Indeed, group actions allow us to rigorously abstract the group-like properties of permutation functions and apply all of the results of group theory to them.

4. Linear Representations

Representation theory was originally motivated by the desire to study groups and other algebraic objects by what they act on. Group actions formalize the notion of a group acting on a set, and representation theory takes the next step of formalizing the notion of a group acting on a vector space, a well-studied and well-defined mathematical object that can provide great reverse insight into algebraic structure.

Informally, a representation maps each element in a group to an automorphism of a vector space onto itself in an order-preserving manner, where group multiplication becomes function composition. Let's now build up to this formally.

Definition 4.1. Let V be an n-dimensional vector space over the complex numbers. We define the **general linear group of degree n** to be the set of invertible linear mappings from V to V. It is denoted by $GL_n(\mathbb{C})$. Symbolically, we have that

$$GL_n(\mathbb{C}) = \{f : V \to V \mid f \text{ is linear \& invertible}\}$$

It follows that there is a one-to-one correspondence between $GL_n(\mathbb{C})$ and the set of n-square invertible matrices. We are now ready to define a representation of a finite group.

Definition 4.2. Let G be a finite group. Then a **linear representation** (of G) is a homomorphism $\rho : G \to GL_n(\mathbb{C})$.

Note that since two representations may be essentially the same, but be encapsulated by entirely different matrices since in n-space, coordinate systems are relative.

Definition 4.3. Two representations ρ and ρ' are **similar** if there exists a linear transformation τ such that $\rho(s) = \tau \circ \rho'(s) \circ \tau^{-1}$ for all $s \in G$.

In the same way that we can use conjugation to convert between bases in linear algebra, conjugation allows us to convert between the bases of the matrices in the general linear group, matching up representations that are the same in different coordinate systems.

Now that we can equate similar representations across differing coordinate systems, we might ask what the simplest coordinate system is that we can use. This question motivates the following definition.

Definition 4.4. Let $(e_t)_{t \in G}$ be a standard basis indexed by the elements of G. Then the **regular representation** (of G) equates each $\rho(s)$ with the permutation matrix that sends $e_t \mapsto e_{st}$.

This representation will be very easy to work with, and we can equate it with many others through similarity.

In the same realm of simple representations, it is also worth mentioning the following.

Definition 4.5. The **trivial representation** is the representation $\rho : G \to GL_n(\mathbb{C})$ defined by $\rho(s) = e$ for all $s \in G$, where e is the identity function on $\mathbb{C}$.

As an example, consider the group $C_{2v} = \{e, C_2, \sigma_v, \sigma'_v\}$ with a group operation defined by

	e	C_2	σ_v	σ_v'
e	e	C_2	σ_v	σ_v'
C_2	C_2	e	σ_v'	σ_v
σ_v	σ_v	σ_v'	e	C_2
σ_v'	σ_v'	σ_v	C_2	e

One example of a representation of this group is the homomorphism $\rho : C_{2v} \to GL_3(\mathbb{C})$ defined by

$$\rho(e) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \rho(C_2) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\rho(\sigma_v) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \rho(\sigma_v') = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

It can be checked that the representation as defined is a homomorphism.

A curious thing to note is that in finite groups, every element has finite order. In other words, for any $s \in G$, $s^n = e$ for some $n \in \mathbb{N}$. This necessitates a constraint on the representation of an arbitrary finite group G.

Theorem 4.6. *If R_s is the n-square invertible matrix associated with $\rho(s)$, then $\det(R_s)$ is a root of unity.*

Proof. Since $s^n = e$, $R_s^n = E$. Thus, $|R_S|^n = 1$, so $|A| = \sqrt[n]{1}$. $\qquad\qquad \square$

5. Connections to Chemistry

Motivated by the need to understand the vibrational modes of molecules, which are heavily dependent on their symmetry, in the early twentieth century inorganic chemists took the at-the-time budding field of representation theory and applied it to their work. The connection is actually quite simple. Representation theory essentially abstracts the group-like character of automorphisms of a vector space, and a symmetry operation can be thought of as an automorphism of $\mathbb{R}^3$, specifically one that maps a certain set of points onto itself, permuting them linearly. All of these factors — automorphisms, linear transformations, and permutations — dramatically evoke representation theory, and indeed it has been a valuable tool for pulling information out of the algebraically unsolveable wave equation.

As chemists have refined their understanding of reaction kinetics over the years, they have gone from "two molecules must meet at the right speed and with the correct orientation in order to react" to "two orbitals must be within 10 electron volts of each other and have the same symmetry in order to form a molecular orbital." Thus, symmetry point groups, the foundation of molecular symmetry, directly govern which molecules can react, how they react, and to what extent, all without having to directly solve the wave equation for many many electrons and nuclei.
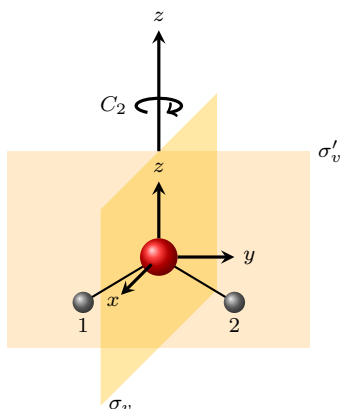
The group C_{2v} discussed above is an example of a symmetry point group. In fact, it is the symmetry point group that describes the H_2O molecule, pictured above. Indeed, each group element can be thought of a symmetry operation, with e keeping the molecule where it is, C_2 rotating the molecule by $\frac{360°}{2} = 180°$ about the z-axis, σ_v reflecting the molecule across the xz-plane, and σ'_v reflecting the molecule across the yz-plane. This property of the elements of C_{2v} is best captured by the given representation, which consists of linear automorphisms that directly describe each symmetry element: $\rho(\sigma_v)$, for example, is a matrix describing the reflection of a vector over the xz-plane, just like the symmetry operation in the picture above.

Besides mapping structure to properties, more advanced realms of group theory are also applicable to inorganic chemistry. For example, the now familiar domain of subgroups plays an important role in governing the properties of molecules with very complex point groups. For the linear molecule CO_2, for instance, the presence of an infinite rotation axis means that the group multiplication table corresponding to CO_2 is quite unwieldy and computationally intensive to do anything with. However, there is a simple finite subgroup of this infinite group (namely D_{2h}) that captures well enough the important vibrational modes of CO_2 in a much less computationally intensive manner. Similarly, Lagrange's theorem allows us to easily determine the possible subgroups of any molecule, and thus compare its vibrational modes with those of molecules corresponding solely to its subgroups.

REFERENCES

[1] Charles C. Pinter. A Book of Abstract Algebra. Dover. 2010.
[2] David S. Dummit and Richard M. Foote. Abstract Algebra. John Wiley and Sons. 2004.
[3] Jean-Paul Serre. Linear Representations of Finite Groups. Springer. 1971.

The image on page 8 is the author's rendering of a figure originally appearing in Miessler, Fischer, and Tarr's (2014) *Inorganic Chemistry* (Fifth edition).