Representation Theory and Physical Systems

Finny Kuruvilla

Math 126
December 16, 1998

A Brief History of Representation Theory in Physics and Chemistry

Representation theory lies at the core of several modern disciplines of science such as particle physics, molecular orbital theory, and quantum dynamics. It is hard to overstate the implications of group representations in these disciplines. The application of group and representation theory to the physical sciences loosely began in the 19th century as crystallographers were devising means to interpret diffraction patterns in order to infer chemical structure. Their efforts utilized concepts from group theory without access to the formalized results that mathematicians would soon develop. The first well-defined example of representation theory in physical systems was Hermann Weyl's monumental work entitled *Gruppentheorie und Quantenmechanik* published in 1928, formally bringing group representations to quantum mechanics to yield very elegant results.

After Weyl's groundbreaking work, heavy applications of group and representation theory were found in chemistry and spectroscopy during the 1920s and 1930s. Nuclear and particle physics found a central place for group representations in the 1930s and 1940s as did high-energy physics in the 1960s. A very beautiful application of group representations can be found in the work of Murray Gell-Mann who used the representations of SU(3) to predict the existence of the quark in 1961. (Its experimental existence would be found three years later at the Brookhaven National Laboratory.)

Classifying Molecular Structure

The most obvious way to utilize group theory in physical chemistry is simply as a molecular descriptor. Variations in molecular structure cause immense differences in reactivity and spectroscopy and thus it is important to be able to easily describe the conformation of any given molecule. These structures often have several symmetry elements. Group theory can easily satisfy the need to describe molecular structure since the symmetries of any object naturally form a group. There are two types of molecular group symmetries. A *point group* is a group of symmetries of an object where the elements of the group are restricted to rotations and reflections (elements which hold a point fixed). A *space group* is a group of object symmetries where the elements of the group include translations, glide reflections, rotations, and reflections.

It is clear that no finite molecule can have a translational symmetry so point groups are sufficient to classify ordinary molecules. (Crystals, however, which are treated as infinite repetitions of a particular unit cell can have translations or glide reflections in their symmetry.) Classifying a point group can be done by enumerating all the symmetry elements of the molecule although chemists have devised flowcharts to rapidly assign a point group to a given molecule (figure 1).

Adding new elements to character tables

When one thinks of group representations, while it is perhaps most common to think of the vector space as being $\mathbb{C}^n$, a representation can be over any vector space, including a vector space of functions. Examination of a typical character table from a physical chemistry text (figure 2) shows two additional columns of linear and quadratic functions where a given function corresponds to a particular irreducible representation.

Assigning these additional functions to the character table is perhaps best illustrated by example. Let us consider the C_{3v} character table. Fix a coordinate system and let the group elements act on that system, writing a matrix for each conjugacy class of the group. As can be seen in the C_{3v} case (figure 2), the matrices may sometimes be cast is block diagonal form and thus reduced further. With the irreducible forms shown, it is easily seen that the x and y coordinates are associated with the irreducible representation Eand the z coordinate the trivial representation, A_1. Hence the assignment of (x, y) and z to their corresponding irreducible representations in the original character table. By direct analogy, the other linear and quadratic functions may be used as a basis for some representation and thus "associated" with a particular irreducible representation. Associating functions with character tables will become useful for evaluating integrals, as will soon be shown.

Tensoring and Integration

Like any vector space, functional vector spaces can be tensored. These new spaces contain all products of the elements from the original spaces. It is a basic fact about representation theory that when vector spaces are tensored, characters multiply. Before implementing tensors in evaluating integrals, an important proposition is required.

Proposition. Consider the following integral over some domain D with point group symmetry G.

$$y = \int f \; dt$$

The value of the above integral, y, is zero unless f contains a component that acts a basis of the trivial representation of G.

Sketch of proof. In order to be nonzero, the integrand must be invariant under the elements of G. Now suppose that f has no component that can act as a basis of the trivial representation. Then G has some element u under which f is variant. Hence y must be zero.

By a simple extension to the above two ideas we obtain the following corollary:

Corollary. Consider the following integral over some domain D with point group G:

$$y = \int f_1 f_2 \cdots f_n \, dt$$

If the tensor product of the n functions does not contain the trivial representation, then the integral must evaluate to zero.

Some examples. Is it possible that some of the following integrals will be nonzero?

1. f = xy over an equilateral triangle centered at the origin. This domain has point group C_{3v} and from the character table (figure 2), xy may act as a basis for the irreducible representation E. Since E does not contain the trivial representation A_1, this integral must always be zero.
2. f = z^2 over a pentagon. Referring to the point group C_{5v}, z^2 is a basis for A_1, the trivial representation and thus may be nonzero.
3. f = (xy)z over a tetrahedron. The tetrahedron has point group T_d (see figure 3 for its character table). Tensoring our two functions yields the characters (9 0 1 1 1). This representation contains one copy of A_1 (since 1/24 * (9 + 3 + 6 + 6) = 1) and thus may be nonzero.
4. f = $(x^2 + y^2 + z^2)(yz)$ over a tetrahedron. Tensoring again in T_d gives the irreducible representation T_2 and thus must always be zero.

The Overlap integral and Molecular Orbitals

In quantum mechanics, one of the most basic integrals is a type of the following, where ψ is a wavefunction: (The integral is in fact a bilinear form over the vector space of quantum states, sometimes called a bra-ket because in Dirac notation it maps bra and ket vectors to complex scalars.)

This integral is termed the *overlap integral* and is at the core of molecular orbital construction. If

$$\langle \Psi_1 | \Psi_2 \rangle = \int \Psi_1 {}^* \Psi_2 \, dt$$

the overlap integral is zero, the atomic orbitals are nonbonding. Otherwise a pair of bonding and antibonding orbitals are formed. It can be easily seen how to link the two ideas of integrating with tensors and these basic quantum integrals.

Example. Construct the frontier molecular orbitals for water.

Considering the character table for water's point group, C_{2v}, (figure 2) and the geometry of water's orbitals (fgiure 4), we must first let the elements of C_{2v} act on the atomic orbitals of water. This gives us the following table of one-dimensional representations (and consequently characters).

	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
$\Gamma(p_x)$	1	-1	1	-1	→ B_1
$\Gamma(p_y)$	1	-1	-1	1	→ B_2
$\Gamma(p_z)$	1	1	1	1	→ A_1
$\Gamma(s_+)$	1	1	1	1	→ A_1
$\Gamma(s_-)$	1	-1	-1	1	→ B_2

From the arguments described above, when the p orbitals on oxygen are brought to the s orbitals of hydrogen, the overlap integral will only be nonzero if the product contains A_1 which only occurs iff orbitals of the same irreducible representation are bra-ketted (This is actually also a consequence of Schur's Lemma.) . Thus an A_1 on oxygen matches with an A_1 from the hydrogen 1s orbitals, and similarly for B_2. However B_1 on oxygen (its p_x orbital) is zero in all cases and thus remains nonbonding (see figure 4).

Spectroscopy and Selection Rules

The overlap integral is the ordinary "dot-product" of the bilinear forms in the space of ket vectors. There are much richer bilinear forms in this vector space that yield scalars whose values describe **spectral transition probabilities**.

$$\langle \Psi_1 | \mathrm{A} | \Psi_2 \rangle = \int \Psi_1 {}^* \mathrm{A} \Psi_2 \, dt$$

A is called the *transition moment operator* and can correspond to an operator to many descriptors such as electric or magnetic dipoles, multipoles, or polarizability tensors. ψ_1 corresponds to initial state while ψ_2 corresponds to the final state of the molecule.

If a given transition has nonzero bra-ket value, the transition is said to be *allowed*. Otherwise it is termed *forbidden.* With our tools from representation theory, all we need to do is tensor in the character of the representation for which A serves as a basis. If the trivial representation is a component of the triple-tensor, the transition is allowed, otherwise it is forbidden.

Example. Can water undergo an electric dipole transition from A_1 to B_1?

The electric dipole transition moment operator is simply x + y + z so we can break up the integral into three separate pieces: $<A_1 \mid x \mid B_1>$, $<A_1 \mid y \mid B_1>$, and $<A_1 \mid z \mid B_1>$. Water has symmetry C_{2v} and looking at the C_{2v} character table (see figure 2), we can read off the irreducible representations that correspond to x, y, and z which are B_1, B_2, and A_1, respectively. Our bra-kets then become $<A_1 \mid B_1 \mid B_1>$, $<A_1 \mid B_2 \mid B_1>$, and $<A_1 \mid A_1 \mid B_1>$. These integrands will have symmetry A_1, A_2, B_1, respectively (see figure 5 for tensor calculations). Only the first bra-ket can then be nonzero, since only it contains the trivial representation, which implies that water can undego an electric dipole transition, although only in the x-direction. (Experimental measurements confirm this prediction since all emitted light is polarized in the x-direction.)

Modal Analysis of the Buckminsterfullerenes

The buckminsterfullerene, or buckyball as it is sometimes called, represents an astounding structural form of carbon with important properties in physical chemistry as well as material science. Its molecular formula is C_{60} and its structure resembles that of a soccer ball (figure 6). Its identification hinged on its spectral properties, particularly infrared and Raman, two spectroscopies that explore the normal modes of the molecule. Calculating the number of potential modes, there are 60 vertices times 3 degrees of freedom per atom which allows for 180 degrees of freedom. Subtracting out 3 overall translational and 3 overall rotational degrees of freedom (which properly are not modes) yields 174 possible normal modes. The molecule has very beautiful symmetry which in fact corresponds to the alternating group on five letters, $A_{5,}$ adjoined to the parity operator. The order of the group is thus 120, though the group is not S_5. Group theory tells us that most of the 174 possible modes are in fact isoenergetic, leaving only 46 possible transitions.

Using the tools developed earlier, one can then ask the following question. Given the ground state of the molecule u and the transition moment operator Ω, the question reduces to: how many unique states v of the 46 possible modes is $<u \mid \Omega \mid v>$ nonzero?

In the buckminsterfullerene the ground state u is a basis for the trivial representation. Tensoring with u then becomes an identity operation so the question is reduced to asking how many of the 46 possible states v is $< \Omega \mid v>$ is nonzero. Ω in fact is associated with one particular irreducible representation, termed 3^-, so our task is to determine the multiplicity of states v that has irreducible representation 3^-. Using knowledge about our point group and its irreducible representations, one can apply the Frobenius reciprocity relation to show that the multiplicity of 3^- is 4 (see Sternberg for the calculation). This is in fact observed in practice (figure 7), an astounding feat accomplished with representation theory, illustrating only some of its penetrating elegance.

Bibliography:

Shlomo Sternberg. *Group Theory and Physics.* (1994)

F. Albert Cotton. *Chemical Applications of Group Theory*. (1990)