

Mathematics and the Buckyball

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1 Introduction

Ever since the discovery of the Buckyball C_{60} with 60 Carbon atoms bonded into a soccerball-shaped molecule and its cousins the other fullerenes, the versatile properties of the molecules have drawn intense interest from researchers across many different disciplines, including chemists, physicists and chemical engineers. One of the distinctive features of the Buckyball is its highly symmetric structure which is obviously mathematical. In fact, mathematics can help explain various properties of the Buckyball and, in general, any molecule, for problems such as:

1. How stable is the molecule?
2. How many distinct vibrational modes are there for the molecule?
3. Among all the vibrational modes, how many are observable by infrared or Raman spectroscopy? More precisely, why are there four visible lines in the infrared spectrum of the Buckyball and 10 lines in the Raman spectrum?

Chemists usually answer such questions by using computer packages and calculate the “selection rules” implicit in 3 by using “character tables”. The methods described here provide alternative techniques which are simpler and often give a more complete analysis. One of the principal current challenges is to provide a theoretical basis for the observed high temperature superconductivity of doped fullerenes. While there is, as yet, no consensus as to the nature of such an explanation, some of the mathematics described here promises to be relevant to several of the proposed models.

The mathematics for the Buckyball (and for molecules in general) combines techniques in several areas: topology (to describe the structure), group theory (to capture the symmetry), geometry (for 3-dimensional aspects) and graph theory (for relations and several key invariants). On one hand, mathematical invariants are related to various forces of equilibria in the molecule. On the other hand, such connections stimulate mathematics to move into new and interesting directions. Such fruitful interaction is unusual but not surprising since, after all, different disciplines merely reflect different sides of nature.

2 Topology and the fullerenes

Until quite recently, the structure of all known fullerenes consists of hexagons and pentagons. Among these, the number of hexagons varies from one type of fullerene to another but every fullerene has exactly twelve pentagons. This is not an accident. It is a consequence of a theorem of the great eighteenth century mathematician Leonhardt Euler. A famous formula of Euler, perhaps the first formula in topology, says the following: The surface of a polyhedron in three dimensional space is made up of (two dimensional) *faces*, (one dimensional) *edges*, and (zero dimensional) *vertices*. Let f denote the number of faces, e the number of edges, and v the number of vertices. Then Euler's formula says

$$f - e + v = 2.$$

For example, the surface of a cube has six (square) faces, twelve edges, and eight vertices and $6 - 12 + 8 = 2$. The regular icosahedron has twelve vertices and twenty (triangular) faces. Five edges emanate from each vertex, but each edge impinges on two vertices. So there are thirty edges ($5 \times 12/2$). Once again, $20 - 30 + 12 = 2$. Suppose we truncate the icosahedron at one of its vertices, as in the figure. This has the effect of replacing the vertex by a pentagonal face. We have added one face, deleted one vertex, and added five new edges and five new vertices. This clearly does not change the value of $f - e + v$, so it remains two. If we do this in a symmetric fashion at all the vertices, we obtain the buckyball. It has thirty two faces (twelve pentagons and twenty hexagons), ninety edges and sixty vertices, $32 - 90 + 60 = 2$.

(Picture of the Buckyball here).

Euler also derived a consequence of his formula if we make the additional assumption that exactly three edges emanate from each vertex.

Euler's theorem : For any polyhedron with three edges emanating from each vertex we have

$$\sum (6 - n)f_n = 12$$

where f_n denotes the number of n -gons.

This can be easily proved by observing the condition on the edges. Since each edge impinges on two vertices and three edges emanate from each vertex, we have $v = \frac{2}{3}e$. On the other hand, since each edge is on the boundary of two polygons, $e = \frac{1}{2} \sum n f_n$. Since $f = \sum f_n$ we have $2 = f - e + v = f - (1/3)e = \sum f_n - \frac{1}{6} \sum n f_n$, as desired.

For example, if all the polygons are to have four sides, the theorem says that there must be exactly six of them as in the cube. For fullerenes built entirely out of pentagons and hexagons, Euler's theorem places no restriction on the number of hexagons, and says that there are exactly twelve pentagons. For a beautiful discussion of the implementation of Euler's theorem in biological

forms, see Chapters 8 and 9 of the classic *On Growth and Form* by D'Arcy Thompson (first published in 1919)..

Many different fullerenes have been constructed on the computer and many have been produced in the laboratory. This poses the mathematical question of classifying all possibilities. For example, in the book *Convex Polytopes* by Branko Grünbaum published some twenty five years ago, it is proved that there is no fullerene with exactly one hexagon, but any other number of hexagons is permissible. Zero hexagons are possible (the dodecahedron, built entirely out of pentagons) and theoretical fullerenes exist with any number, two or more, of hexagons. Substantial and extensive results in the direction of classifying the mathematical possibilities have been obtained recently by Prof. Sah of the Mathematics Department at Stony Brook. For the rest of this paper we will concentrate on the buckyball, C_{60} .

In recent months there has been some evidence suggesting the existence of fullerenes with septagons as well as hexagons and pentagons. Of course, for each septagon we must add an additional pentagon beyond the basic twelve in order to conform to Euler's theorem.

3 The symmetry of the Buckyball

The symmetry of the Buckyball can be best described by rotations that move vertices to vertices, and edges to edges. If s is such a rotation then so is its inverse, s^{-1} . Additionally, if t is a second rotation, then st , the composition of s with t also is such a rotation. A collection of invertible transformations which is closed under compositions and inverses is known as a group. All such rotations form a group I , so called the icosahedral group. For two vertices u and v , there is a unique rotation that moves u to v and therefore I consists of 60 elements.

Although all the vertices of the buckyball are alike, in the sense that there is a symmetry carrying any one into any other, this is not true of the edges. For example, if we truncate the icosahedron close to the vertices, the edges of the pentagons will be shorter than the edges which are the left over portions of the original triangular edges. In one chemical model of the buckyball, the pentagonal edges are thought of as single bonds while the left over triangular edges are thought of as double bonds. While in more sophisticated models the fourth valence electron of each carbon atom is considered as delocalised, we shall adopt the convenient terminology of single and double bonds. So emanating from each vertex there are two single bonds, lying on a pentagon, and one double bond, lying on a hexagon. All pentagonal edges are single bonds, while every other edge on a hexagon is double. All double bonds of the buckyball are alike as are all the single bonds.

These bond structures give us some insight into the nature of the group I . For example, if we pick a double bond, b , there will be a unique double bond,

b' , opposite it, in the sense that b and b' lie on a plane bisecting the buckyball. If we draw the line joining the midpoints of b and b' , then a 180° rotation having this line as axis is a symmetry of the buckyball. There are thirty double bonds, and hence fifteen such pairs. Thus there are fifteen elements of “order two” (i.e. satisfying $r^2 = e$, where e denotes the identity element) in I . There are ten pairs of opposite hexagons. If we join the midpoints of these hexagons to form an axis, rotations through angle 120° and 240° about this axis are elements of I . Thus I contains twenty elements satisfying $t^3 = e$. There are six pairs of opposite pentagons, each non-trivial rotation about the axis joining the midpoints of such a pair is an element, p of I satisfying $p^5 = e$ and so there are twenty four such elements. Now $15 + 20 + 24 = 59$. Together with the identity element, e , we have accounted for all sixty elements of I .

(Figures to illustrate three types of rotations.)

The group I can be identified with the group A_5 , the group of even permutations of five objects, also called the alternating group on five letters (which will be further discussed in section 5.) This can be seen as follows: Let us go back to the plane passing through two opposite double bonds. Among all planes perpendicular to this plane and passing through the center of the buckyball, there will be two which also pass through pairs of double bonds, and these planes will be perpendicular to each other. In other words, we have a configuration of six double bonds consisting of three opposite pairs spanning three mutually perpendicular planes. The collection of thirty double bonds breaks up into five such configurations. These five configurations must be permuted amongst themselves by any element of I . A direct check, best visualized by actually performing rotations on a model, will show that only the identity element can fix all configurations. So we have identified I as a subgroup of the group, S_5 , of all permutations of five objects. But the only subgroup of S_5 containing sixty elements is the alternating group, A_5 .

For applications to spectroscopy, we must consider not only rotational symmetries of the buckyball but also allow reflections. The chemists call this larger group I_h . From the mathematical point of view, we can obtain this larger group by adjoining the inversion operator, P , where, in terms of a Cartesian coordinate system based at the center of the buckyball, $P(x, y, z) = (-x, -y, -z)$. The chemists and physicists call P the *parity* operator. Notice that $P^2 = e$ and that $Pg = gP$ for all elements, g , of I . The group I_h thus contains 120 elements. (But it is *not* isomorphic to the group S_5 .)

4 A brief history of spectroscopy.

The fact that metals glow when heated, and that the color is indicative of the temperature (“red hot”, “white hot”) has undoubtedly been known from the earliest period of metal working. The fact that a flame becomes intensely yellow when table salt is added to the burning substance, or that a sufficiently

hot fire becomes green in the presence of particles of copper has also doubtless been recognized since antiquity. At the beginning of the nineteenth century, dark lines were observed in the white light of the solar spectrum, at first by Wollaston and then in much greater detail by Fraunhofer who also examined the spectra of the fixed stars. He discovered that in some of them many dark lines appeared that were absent from the solar spectrum while dark lines that which occurred in the sun's spectrum sometimes did not appear in the spectrum of a star. This led the great astronomer Herschel to suggest that

it is no impossible suggestion that the deficient rays in the light of the sun and stars may be absorbed in passing through their own atmospheres.

Fraunhofer also observed that the bright yellow band present in the spectra of flames consisted of two close bright lines and that these lines seemed to coincide with two particular dark lines in the solar spectrum. The next half century of developments culminated in a general recognition of spectrum analysis as a method of physical and chemical research together with the key observation (due principally to Stokes and Kirchhoff) that a substance will tend to emit and absorb light at the same frequencies, i.e. that the emission lines and the absorption lines coincide. (Today we would modify this assertion to take into account the phenomenon of phosphorence as occurs in TV screens and other monitors.) Kirchhoff, who was distinguished as a mathematician as well as a physicist, based his arguments on intricate thermodynamical and mathematical considerations. It is interesting to quote from the article by Sir Arthur Schuster (a key player in the last third of the nineteenth century) in the 1911 edition of the Encyclopedia Britannica who writes

Though the experimental and theoretical developments were not necessarily dependent on each other, and by far the larger proportion of the subject which we now term "Spectroscopy" could stand irrespective of Gustav Kirchhoff's thermodynamical investigations, there is no doubt that the latter was, historically speaking, the immediate cause of the feeling of confidence with which the new branch of science was received, for nothing impresses the scientific world more strongly than just that little touch of mystery which attaches to a mathematical investigation which can only be understood by the few, and is taken on trust by the many, provided that the author is a man who commands general confidence.

In fact, the earlier name for the subject was "spectrum analysis"- analysis as in chemical analysis. Indeed, the principles of spectrum analysis, as formulated and applied by Bunsen and Kirchhoff (1859-1860) seized the imagination of the scientific world because they revealed a method of investigating the chemical nature of substances independently of their distances from the laboratory inasmuch as spectrum analysis could be applied to the sun and stellar bodies. In

addition, fame could be achieved by the use of spectrum analysis to discover new elements.

In 1882 Schuster formulated the extraordinary prescient suggestion that, in the future, the main function of the study of spectra would be to obtain information about the structure of atoms and molecules and the nature of the forces that bind them together. Starting with Balmer's formula for hydrogen atomic spectra it took about twenty five years of intensive work to come to the realization that order could be brought to the spectra of various substances by expressing the frequencies of the radiation as differences of various expressions called *terms*. (The Ritz combination principle.) Thus, in appropriate units, the frequencies of the spectral lines could be written as $\omega = E_m - E_n$. The description of the spectrum as differences of terms was known as term analysis, and it became a matter of importance to attach physical significance to the terms themselves rather than to the lines. This, of course, came about in the 1920's with the advent of quantum mechanics where the terms became identified with eigenvalues: In quantum mechanics the time evolution of the unperturbed atom or molecule is associated with a matrix, H , called the Hamiltonian, and the "stationary states" are its eigenvectors, i.e. those vectors satisfying $Hx = E_mx$, $Hy = E_ny$, and the terms themselves become identified with "energies".

In term analysis it soon became apparent that, while all line frequencies could be expressed as differences of terms, not all such differences give rise to observed lines. There are *selection rules* determining which differences of terms are actually observed. In quantum mechanics these selection rules are related to *transition probabilities* and take the following form: There is another matrix, A , related to the interaction of the atom or molecule with light by perturbation theory, such that the *amplitude* for the transition from state x to the state y (with the concurrent emission or absorption of light of frequency $E_m - E_n$) is given by the scalar product $\langle Ax, y \rangle$. The transition probabilities are the squares of the absolute values of the transition amplitudes, and hence the intensities of the spectral lines are proportional to $|\langle Ax, y \rangle|^2$. Thus a transition will be "forbidden" and the corresponding line will not be observed if

$$\langle Ax, y \rangle = 0. \tag{1}$$

So an explanation for why a certain transition is "forbidden", and the corresponding line is not observed, amounts to an explanation of why (??) holds. Invariably, the explanations of (??) in any given instance are of a group theoretical nature - that Ax and y transform differently under the symmetry group of the system, and this forces their scalar product to vanish. In more technical terms, (??) occurs as an application of a fundamental result in representation theory known as Schur's lemma, as we shall explain in the next section.

For example, in the case of ordinary emission and absorption spectra, the matrix A is associated with the electric dipole moment, and so transforms like an ordinary vector in three dimensional space describing the dipole. The infra

red spectrum of a molecule is associated to transitions between its vibrational states which are called k-phonon states in quantum mechanics. At ordinary temperatures the transitions will be between the “vacuum” or 0-phonon state, x and one phonon-states, y . The vacuum is completely symmetrical, and hence the transformation properties of Ax are the same as that of A , namely that of a vector in three dimensional space. The one phonon states always transform like the corresponding classical vibrating system. In the section after next we will see that a standard formula in the theory of group representations (the Frobenius reciprocity formula [?, ?]) tells us that in the case of the buckyball there are 46 distinct vibrational states, but only four of them transform in the same way as ordinary vectors in three space. So four lines should be visible in the infra red. In fact, it was the appearance of these four lines which was the signature for the positive identification of C_{60} .

In Raman spectroscopy light of a definite frequency impinges on the substance, and one measures the frequency shift in the scattered light. It is the electric quadrupole moment that accounts for the Raman effect, and hence for Raman experiments the matrix A must transform like a quadrupole moment. We will see that group theory predicts ten Raman lines for the buckyball. These lines have all recently been observed [?, ?, ?].

(Figures of the infrared spectrum and Raman spectrum.)

5 Group theory and selection rules

The idea of applying representation theory as the unifying theme for all quantum mechanical selection rules to determine observable spectral lines is first due to Wigner(1930). The theory of group representations was created by Frobenius and Schur at the turn of the century. A *representation* of a group, G , is simply a rule which assigns to each element, g , of G , a square matrix, $\rho(g)$ such that matrix multiplication is consistent with group multiplication.

Here are some examples of representations of groups:

A rotation, r_a , through angle a about the origin of the coordinate system in the Euclidean plane is represented by the matrix

$$\rho(a) = \begin{pmatrix} \cos a & -\sin a \\ \sin a & \cos a \end{pmatrix}.$$

The composition of two rotations (rotating through angle b followed by rotating through angle a is the same as rotating through angle $a+b$) makes the collection of all such rotations into a group. In symbols,

$$r_a r_b = r_{a+b}.$$

If we apply the rules of matrix multiplication we find

$$\begin{pmatrix} \cos a & -\sin a \\ \sin a & \cos a \end{pmatrix} \begin{pmatrix} \cos b & -\sin b \\ \sin b & \cos b \end{pmatrix} = \begin{pmatrix} \cos a \cos b - \sin a \sin b & -(\sin a \cos b + \sin b \cos a) \\ \sin a \cos b + \sin b \cos a & \cos a \cos b - \sin a \sin b \end{pmatrix}.$$

If we apply the trigonometric identities $\cos(a + b) = \cos a \cos b - \sin a \sin b$ and $\sin(a + b) = \sin a \cos b + \sin b \cos a$, we see that the matrix on the right is exactly the matrix $\rho(a + b)$ associated to rotation through angle $a + b$. This is an illustration of what we meant above by saying that the matrix multiplication is consistent with the group multiplication. The trigonometric identities that we all had trouble remembering in high school say that we have a representation of the group of rotations. We no longer need to remember these identities. All we need to remember are the rules of matrix multiplication! In the eighteenth century, the trigonometric identities were generalized to other kinds of functions and called “addition laws”. We now know that these early attempts were really precursors to the theory of group representations.

A rotation through angle a about the z - axis in three dimensional space is given by the matrix

$$\begin{pmatrix} \cos a & -\sin a & 0 \\ \sin a & \cos a & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

because multiplying a vector, $\mathbf{v}$, by this matrix does not move $\mathbf{v}$ at all if $\mathbf{v}$ lies on the z - axis, while if $\mathbf{v}$ lies in the xy plane the calculation is the same as the two dimensional case: multiplication by the above matrix keeps $\mathbf{v}$ in the plane and rotates it through angle a . Rotations about the x -axis and y -axis have similar simple expressions. In fact, there is nothing special about these axes: If r is a rotation about any axis, we can always find a (unique) matrix, M , so that multiplication by M implements this rotation. Indeed, the first column of M is the vector obtained by applying the rotation r to the unit vector, e_x , along the positive x - axis, the second column of M is obtained by applying r to the unit vector e_y and the third column of M is obtained by applying M to e_z .

If we now go back to our icosahedral group, we recall that every element of I (other than the identity) is a rotation about an appropriate axis. This means that we can associate a matrix, $\rho(a)$, (the one which implements the rotation) to every element, a , of I . (We associate the identity matrix to the identity element.) By its very definition, we have the “consistency condition”

$$\rho(a)\rho(b) = \rho(ab).$$

So we have a representation of I by 3×3 matrices. The row size (the same as the column size) of the matrix (three in this case) is called the *dimension* of the representation.

The reader might be surprised that the product of rotations about two distinct axes is a rotation about some third axis. But this is an illustration of another remarkable theorem of Euler’s: The composition of any number of rotations about varying axes passing through the origin in three dimensional space is always equal to a rotation about some axis (or is equal to the identity transformation).

Here is another example of a group representation. Consider the group, S_n , of all permutations of n objects. For applications to the buckyball, we will take $n = 5$. We like to think of the elements of S_5 as permuting the elements $\{u, w, x, y, z\}$ of some abstract five element set. (In section 3 we thought of each of these five elements as being a configuration of six double bonds of the buckyball.) Let us assign (distinct) standard basis elements in five dimensional space to each of these five elements. For example

$$u \leftrightarrow \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}, w \leftrightarrow \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, x \leftrightarrow \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, y \leftrightarrow \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, z \leftrightarrow \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

(This assignment is arbitrary, but we fix one once and for all.) Then let us associate to each permutation, a , the matrix, $\rho(a)$, whose columns are the result of applying the permutation a to the corresponding vectors. For example, if s denotes the cyclic permutation $u \rightarrow w \rightarrow x \rightarrow y \rightarrow z \rightarrow u$, the corresponding matrix is given by

$$\rho(s) = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix}.$$

In this way we have associated a five by five matrix to each of the 120 elements of S_5 . These 120 matrices multiply with one another according to the group law of S_5 . Again this is true by construction. So we have a five dimensional representation of S_5 , called the permutation representation. In general, we can construct the (n dimensional) permutation representation of S_n .

Using determinants, we can now give a succinct definition what we mean by even or odd for a permutation. It is easy to check that for any permutation, a , the determinant, $\det(\rho(a)) = 1$ or -1 , where ρ denotes the permutation representation. We say that a is *even* if $\det(\rho(a)) = 1$ and *odd* if $\det(\rho(a)) = -1$. Thus the group A_n , called the “alternating group” consists of those elements in S_n which satisfy $\det(\rho(a)) = 1$.

Sometimes a representation can be broken down into “blocks” of smaller representations. For example, consider the five dimensional permutation representation of S_5 described above. If $\mathbf{x}$ is a vector in this five dimensional space with coordinates $(x_1, x_2, x_3, x_4, x_5)$, and a is any element of S_5 the coordinates of $\rho(a)\mathbf{x}$ will be a permutation of the coordinates of $\mathbf{x}$. So if x has all its coordinates equal, $x_1 = x_2 = x_3 = x_4 = x_5$, the same will be true of $\rho(a)\mathbf{x}$, and indeed $\rho(a)\mathbf{x} = \mathbf{x}$. The set of all $\mathbf{x}$ satisfying this condition constitute a line, or one dimensional subspace, call it l , of our five dimensional space. Similarly, if

the coordinates of $\rho(a)\mathbf{x}$ satisfy $x_1 + x_2 + x_3 + x_4 + x_5 = 0$, so will the coordinates of $\rho(a)\mathbf{x}$. The set of all vectors satisfying $x_1 + x_2 + x_3 + x_4 + x_5 = 0$ can be parametrized by four out of the five coordinates, and hence constitute a four dimensional space. In terms of the geometry of five dimensions, this four dimensional space is the orthogonal complement, call it $l^\perp$, of l . We can now introduce a change of coordinate system in five dimensions which rotates l into the first coordinate axis. In terms of these new coordinates, the matrices $\rho(a)$ will all have been transformed (by a single change of coordinates) into matrices which have the block decomposition

$$\begin{pmatrix} 1 & 0 \\ 0 & \sigma(a) \end{pmatrix}.$$

where the $\sigma(a)$ are four by four matrices. We say that the permutation representation has been decomposed into a sum of the trivial representation (where every group element is represented by the number 1) and the four dimensional representation, σ . It turns out that this four dimensional representation can not be decomposed any further into smaller blocks. We say that it is irreducible.

More generally, if a representation of a group G contains within it a smaller representation in the sense described in the above example, it is called *reducible*. For the groups we are studying, this implies that its corresponding matrices, $\rho(g)$, can be “diagonalized” into smaller blocks of matrices by a single change of coordinates operating for all g in G . A representation which is not reducible is called *irreducible*. The irreducible representations of a group, G , constitute the elementary building blocks of the representation theory of G .

The first task in the study of the representation theory of a group is to determine all its irreducible representations. In 1901 Frobenius determined all the irreducible representations of all the groups A_n . For the case of $I = A_5$ there are five irreducible representations on Frobenius’ list. In addition to the trivial one dimensional representation common to all groups, there are two distinct three dimensional representations, one four dimensional representation, and one five dimensional representation. One of the three dimensional representations is the one constructed above coming from the geometrical action of I on three dimensional space. The four dimensional representation is just the representation, σ , of S_5 we constructed above by decomposing the permutation representation. The five dimensional representation also has an important physical significance: It turns out that the group, I , has a representation on the space of all possible quadrupole moments (of electric charges), that this space is six dimensional, and that it decomposes into two blocks consisting of the trivial representation and the irreducible five dimensional representation.

In the chemical literature these representations are labeled by various letters. We shall follow the custom of the physics literature and label the representations by their dimension, adding an additional identifying mark if there are two irreducible representations of the same dimension. So the irreducible representations of the icosahedral group I are labeled as **1**, **3**, **3'**, **4**, and **5**. Here the

labelling is chosen so that $\mathbf{3}$ corresponds to the defining action of the icosahedral group on geometrical three dimensional space. It follows from Schur's lemma, to be stated below, that in any irreducible representation of the group I_h , the parity operator, P is represented by either the identity matrix, Id or by its negative, $-Id$, and that the representation remains irreducible when restricted to the subgroup, I . So the representations of the group I_h are specified by attaching a $\pm$ sign to each irreducible representation of I . For example, the representations $\mathbf{3}^-$ corresponds to the usual action of I_h on geometrical three dimensional space since P was geometrically defined to be $-Id$. On the other hand, the representation $\mathbf{3}^+$ is known as the *axial vector* representation in the physics literature. It corresponds to the action of I_h on infinitesimal rotations (hence the name axial).

For two representations ρ and σ of a group G , an intertwining operator R is a matrix satisfying, for all a in G ,

$$R\rho(a) = \sigma(a)R. \quad (2)$$

We say ρ and σ are equivalent if there is an intertwining operator, R , which is invertible. Suppose that we have a representation, ρ , of G on the space of states of a quantum mechanical system, and the Hamiltonian operator, H , is an intertwining operator of ρ with itself. That is, $H\rho(a) = \rho(a)H$ for elements a of G . Let us draw the key consequence of this assumption: Suppose that x is a stationary state of H , so that $Hx = Ex$. Then $H\rho(a)x = \rho(a)Hx = \rho(a)Ex = E\rho(a)x$.

In other words, if x is an eigenstate of H with eigenvalue E , then $\rho(a)x$ is again an eigenstate of H with the same eigenvalue. Thus the collection of eigenstates of H with a given eigenvalue constitute a representation of G . It is a theorem that every representation of a finite group has a block decomposition into irreducible representations. This means that we can decompose the state x into a sum of eigenstates, each of which transforms according to some definite irreducible representation of G . We can choose a basis of states so that each eigenstate transforms according to some definite irreducible representation of G . Indeed, it is the practice to label the eigenstates in such a way that the label includes the irreducible representation to which it belongs.

Let us apply these ideas to the vacuum-to-one phonon transitions. For infrared spectroscopy of the buckyball we have seen that the Ax transforms as $\mathbf{3}^-$. That is, it belongs to some three dimensional space, V , of states, on which the representation of I_h is equivalent to $\mathbf{3}^-$. On the other hand, we may assume by the above discussion that the state y belongs to some space, W , which also transforms according to some irreducible representation. We will see in a moment that (??) holds unless the representation on W is also equivalent to $\mathbf{3}^-$. This is a consequence of one of the basic results in representation theory:

Schur's lemma. *Suppose that ρ and σ are irreducible representations of a group, G with an intertwining operator R . If ρ and σ are not equivalent then $R = 0$. If ρ and σ are equivalent, then either $R = 0$ or R is invertible.*

The proof of Schur's lemma is remarkably simple and can be found in any elementary text on representation theory. Let us apply it to quantum mechanics where we want to prove that the corresponding spectral line vanishes (i.e., (??) holds) under the assumption that Ax belongs to an irreducible representation space V , that y belongs to an irreducible space W and that the two representations are *not* equivalent. We will certainly have proved (??) if we prove that every vector in V is orthogonal to (has zero scalar product with) every vector in W . So let R denote the orthogonal projection of V onto W . We must show that $R = 0$. But R is an intertwining operator satisfying (??). Since we are assuming that the representations ρ and σ are not equivalent, the first part of Schur's lemma applies. That is all there is to it! In more elementary presentations of quantum chemistry this type of argument goes into the proof of the vanishing of "overlap integrals" for states of differing symmetry. But the power of the abstract statement of Schur's lemma lies in the vast number of its profound implications.

6 Counting the number of lines

Getting back to our buckyball spectrum, we see that the question of how many lines there are in the infra red now has a translation into a purely group theoretical question: In the block decomposition of the space of classical (one phonon) vibrational states into irreducibles, how many irreducibles are equivalent to $\mathbf{3}^-$?

This type of question is completely answered by a general formula discovered by Frobenius. In order to explain it, we need to introduce some notation: For any two representations ρ and σ of a group G acting on state spaces V and W , respectively, we let $\text{Hom}_G(V, W)$ denote the collection of all intertwining operators R satisfying (??). Clearly the sum of two matrices satisfying (??) satisfies (??) and if R satisfies (??) so does cR for any scalar, c . So the collection of R satisfying (??) forms a vector space. For example, if ρ and σ are both irreducible, then the first part of Schur's lemma asserts that $\text{Hom}_G(V, W) = \{0\}$, if ρ and σ are not equivalent. The second part of Schur's lemma implies that any two non-zero R satisfying (??) are proportional if ρ and σ are equivalent. Thus $\text{Hom}_G(V, W)$ is one dimensional if ρ and σ are equivalent.

Suppose we assume that ρ acting on the state space V is irreducible, but no longer assume that σ acting on W is irreducible. Let us break W up into irreducible blocks. Each irreducible block in this decomposition which is equivalent to ρ makes a one dimensional contribution to $\text{Hom}_G(V, W)$ while the blocks which are not equivalent to ρ make no contribution. Hence the dimension of $\text{Hom}_G(V, W)$ is the total number of blocks in the decomposition of W which are equivalent to V . (By the way, since $\text{Hom}_G(V, W)$ was defined directly without reference to any decomposition of W , we have just used Schur's lemma to *prove* that the number of blocks equivalent to V does not depend on exactly how we perform the decomposition.)

In terms of this notation, to show that the Buckyball has 4 visible infrared lines is the same as proving that the dimension of $\text{Hom}_{I_h}(\mathbf{3}^-, \text{Vib})$ is 4, where Vib denotes the space of vibrational states of the buckyball. To describe this space of vibrational states, it is convenient to consider a slightly larger space, the space of displacements of the molecule from equilibrium. Each atom can be (infinitesimally) displaced from its equilibrium position, and each atom can move independently in three dimensions. So the space of overall (infinitesimal) deviations of the molecule from equilibrium has dimension $60 \times 3 = 180$. Let us call this space Γ . The group I_h has a representation on Γ : an element g of I_h carries a vertex, X , of the buckyball into some other vertex $Y = gX$. At the same time, it will move a vector giving a displacement at X into a transformed displacement vector at Y .

Now there is a three dimensional space in Γ which consists of rigid (infinitesimal) translations of the molecule as a whole. This is a block in Γ which is equivalent to $\mathbf{3}^-$. There is another three dimensional block in Γ consisting of (infinitesimal) rigid rotations of the molecule as a whole. We have seen that this block is equivalent to $\mathbf{3}^+$. We wish to delete these six dimensions when talking about the vibrational states which are associated with distortions of the shape of the molecule. Therefore, the space Vib is 174 dimensional, and to prove that there are four infrared spectral lines, it is enough to prove that the dimension of $\text{Hom}_{I_h}(\mathbf{3}^-, \Gamma)$ is five.

This is, however, an immediate application of a formula of Frobenius which we now explain. Frobenius' formula has to do with the relation between representations of group, G , and the representations of a subgroup, H . Suppose we are given a representation, ρ , of the big group, G . We automatically get a representation of the subgroup H by considering the restricted $\rho(h)$ where h lies in H . We will denote the restricted representation by attaching a downward arrow, $\downarrow$, to the original representation.

Notice that even though the original representation of G is irreducible, the restricted representation need not be. Here is an example which is important for us: Take G to be I_h , and take H to be the subgroup fixing a vertex, X of the buckyball. So H consists of two elements, $H = \{e, r_X\}$, where r_X is reflection in a bisecting plane passing through X . The group H has only two irreducible representations, both one dimensional, the trivial representation, $\mathbf{1}_+$ and the "sign" representation, $\mathbf{1}_-$ which assigns the value -1 to r_X . Thus the three dimensional representation $\mathbf{3}^- \downarrow$ of H must decompose into a sum of these one dimensional representations. To see what this decomposition is, choose coordinates so that r_X is reflection in the y, z plane. Then the matrix representing r_X is

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

which shows that we have the block decomposition

$$\mathbf{3}^- \downarrow = \mathbf{1}_- \oplus \mathbf{1}_+ \oplus \mathbf{1}_+. \quad (3)$$

Suppose we start with a representation, (ϕ, U) of the subgroup H . There is a procedure called *induction* for constructing a representation of the big group, G , out of the given representation of the subgroup. When the groups G and H are understood from the context, we shall denote the induced representation of G by attaching an up arrow, $\uparrow$, to the original representation of H . The remarkable result of Frobenius is that the operations of induction and restriction are “adjoint” to one another in the following sense:

Frobenius reciprocity. *Let ρ be a representation of the group, G , and let ϕ be a representation of the subgroup, H , of G . Then $\text{Hom}_H(U, V \downarrow)$ is isomorphic to $\text{Hom}_G(U \uparrow, V)$. In particular, they have the same dimension. That is,*

$$\dim \text{Hom}_H(U, V \downarrow) = \dim \text{Hom}_G(V, U \uparrow). \quad (4)$$

Let us give some illustrations of this formula. Suppose we take H to be the subgroup having only the trivial representation. The induced representation in this case is just the natural action of G on the space of functions on G , known as the *regular* representation. For any representation, (ρ, V) of G , the left hand of (??) is just the number of one's that occur in the identity matrix of V , in other words it is just $\dim V$. Thus (??) implies

Maschke's theorem. *Every irreducible representation occurs in the decomposition of the regular representation with a multiplicity equal to its dimension.*

For example, let us take G to be the (rotational) icosahedral group, I . Then Maschke's theorem asserts that in the decomposition of the regular representation, the trivial representation, $\mathbf{1}$ occurs once, the representation $\mathbf{3}$ occurs three times as does $\mathbf{3}'$, the representation $\mathbf{4}$ occurs four times and $\mathbf{5}$ occurs five times. Thus the regular representation of I , which is sixty dimensional, decomposes into

$$1 + 3 + 3 + 4 + 5 = 16$$

irreducible representations. As a check, observe that

$$1^2 + 3^2 + 3^2 + 4^2 + 5^2 = 60.$$

Remember that the subgroup of I fixing any vertex, X , of the buckyball is just the trivial subgroup. In the space, Γ of displacements of the buckyball from equilibrium, the displacements of X constitute a three dimensional space on which the trivial group acts trivially. The induction procedure implies that, as a representation space of I , we may identify Γ with three copies of the regular representation. In other words, Γ decomposes into $3 \times 16 = 48$ irreducibles. Thus the space Vib of vibrational states decomposes into 46 irreducibles, since we have removed two copies of $\mathbf{3}$ when forming Vib . Now applying the arguments of the

preceding section shows that if F is a force matrix which is invariant under G , i.e. if F is in $\text{Hom}_I(Vib, Vib)$ then F can have (at most) 46 distinct eigenvalues.

Let us now turn to the full group I_h . The space, Γ , of displacements, is an induced representation, induced from the three dimensional representation of H with matrix of r_X as (??). In other words, Γ is the sum of three induced representations, one from $\mathbf{1}_-$, and two from $\mathbf{1}_+$. If we now apply (??) and (??) we see that

$$\dim \text{Hom}_{I_h}(\mathbf{3}^-, \mathbf{1}_- \uparrow) = 1$$

and

$$\dim \text{Hom}_{I_h}(\mathbf{3}^-, \mathbf{1}_+ \uparrow) = 2.$$

So

$$\dim \text{Hom}_{I_h}(\mathbf{3}^-, \Gamma) = 1 + 2 + 2 = 5$$

and therefore we complete the proof that there are four infrared spectral lines.

In fact, a straightforward application of (??) shows that we have the decompositions

$$\mathbf{1}_+ \uparrow = \mathbf{1}^+ \oplus 2 \times \mathbf{3}^- \oplus \mathbf{3}^+ \oplus 2 \times \mathbf{3}'^- \oplus \mathbf{3}'^+ \oplus 2 \times \mathbf{4}^+ \oplus 2 \times \mathbf{4}^- \oplus 3 \times \mathbf{5}^+ \oplus 2 \times \mathbf{5}^- \quad (5)$$

and

$$\mathbf{1}_- \uparrow = \mathbf{1}^- \oplus 2 \times \mathbf{3}^+ \oplus \mathbf{3}^- \oplus 2 \times \mathbf{3}'^+ \oplus \mathbf{3}'^- \oplus 2 \times \mathbf{4}^+ \oplus 2 \times \mathbf{4}^- \oplus 3 \times \mathbf{5}^- \oplus 2 \times \mathbf{5}^+. \quad (6)$$

We can use (??) and (??) to determine the number of lines in the Raman spectrum: Recall that in the Raman experiment, the operator, A , transforms like the electric quadrupole moment. The quadrupole moment is a tensor rather than a vector. In technical language, it is a symmetric tensor of degree two. What we need to know is that the space of quadrupole moments transforms, under I_h , like $\mathbf{1}^+ \oplus \mathbf{5}^+$. (The $\mathbf{5}^+$ corresponds to traceless tensors while the $\mathbf{1}^+$ corresponds to multiples of the identity. The reason for the $+$ is that the parity operator, P , has no effect on tensors of even degree.) Let us examine these two components separately. Notice that $\mathbf{1}^+$ does not occur at all on the right hand side of (??), and occurs once on the right hand side of (??). Hence we conclude from (??) and (??) that

$$\dim \text{Hom}_{I_h}(\mathbf{1}^+, Vib) = 2. \quad (7)$$

In other words there should be two Raman lines corresponding to the $\mathbf{1}^+$ representation of I_h . The $\mathbf{5}^+$ occurs twice on the right hand side of (??), and three times on the right hand side of (??). Hence we conclude from (??) and (??) that

$$\dim \text{Hom}_{I_h}(\mathbf{5}^+, Vib) = 2 + 3 + 3 = 8. \quad (8)$$

So there should be eight lines corresponding to $\mathbf{5}^+$. All ten lines have been observed. In fact the $\mathbf{1}^+$ lines can be distinguished, experimentally, from the $\mathbf{5}^+$ lines through the use of polarized light.

We should point out that decompositions such as (??) and (??) together with Schur's lemma offer a powerful tool for the location of the eigenvalues of invariant operators and not merely counting the number of distinct eigenvalues, which is the use we have made so far. For example, as we shall explain in the next section, the sixty dimensional space, $\mathbf{1}^+ \uparrow$, plays a central role in the electronic structure of the buckyball, and, hopefully, in understanding the high temperature superconductivity of doped buckyball crystals. So it will be important to analyze invariant operators, R , on this space, that is matrices, R , which lie in $\text{Hom}_{I_h}(\mathbf{1}^+ \uparrow, \mathbf{1}^+ \uparrow)$. Such a matrix has size 60 by 60. But Schur's lemma implies that there can not be any interaction between inequivalent components. In other words, R must have a block diagonal decomposition, each block corresponding to a summand in (5). Furthermore, each one of these blocks has a block decomposition into blocks of scalar matrices, where the number of blocks along each row and column is given by the *multiplicity* of the representation, while the size of the scalar matrices is given by the *dimension* of the representation. For example, the block corresponding to the second summand in (5) must have the form

$$\begin{pmatrix} AI_3 & BI_3 \\ CI_3 & DI_3 \end{pmatrix},$$

where A, B, C and D are scalars, while I_3 denotes the three dimensional identity matrix. There are two blocks on each row and column because of the coefficient 2. The size of each block is 3 by 3, because the dimension of the representation is three. Although this is a six by six matrix, computing its eigenvalues is the same as computing the eigenvalues of the two by two matrix

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix},$$

which involves only solving a quadratic equation. The I_3 tells us that each eigenvalue occurs with multiplicity three.

The largest multiplicity occurring on the right of (5) is 3. So, although R is a 60 by 60 matrix, in searching for the eigenvalues of R , the worst computation that we have to do is diagonalizing a three by three matrix, and this can be done analytically.

7 Graph theory and the spectrum of the Buckyball

The buckyball is an example of a graph. Here we are using the mathematical term "graph" to denote a collection of points, called vertices, with certain pairs

of points connected to one another by edges. Graph theory is yet another invention of Euler. He wrote the first paper on the subject in 1736. The term “graph” was introduced into mathematics in a paper entitled “Chemistry and Algebra” by the mathematician J. J. Sylvester in 1877. He in turn derived the term from “graphical notation” used by the great chemist F. A. Kekulé as early as 1854 for the two-dimensional projections of molecules. Since then, graph theory has developed into a subject of surprising variety and depth. Since graph theory deals with discrete objects, relations and their underlying properties, the insight and techniques have frequently been applied in varied areas such as algorithmic design, cognitive sciences, optimization, communications, physics and chemistry. Conversely, such applications often provide interesting problems and directions which enrich the theoretical developments. Current technology has been evolving and generating large discrete systems, massive amount of data and complex problems which require further understanding of discrete structures. To face such challenges, it is often essential to combine and utilize methods in many other areas of mathematics in order to develop a unified theme. Our study of the Buckyball is one such example.

One way of specifying a graph is to draw a picture with vertices and edges. Another is to use the *adjacency matrix* of a graph, which has rows and columns labeled by the vertices such that a one is at position (i, j) if the vertices i and j are joined by an edge, and a zero otherwise. For examples: The benzene ring has six vertices; let us label them as 1,2,3,4,5,6 connected cyclically: so 2 is joined to 1 and to 3, 3 is joined to 2 and to 4, etc., and 1 is joined to 6 and to 2. Its adjacency matrix is given by

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}.$$

In many applications of graph theory, the adjacency matrix plays an important role, but sometimes it goes under different names. For example, in organic chemistry, it is called the Hückel (Hamiltonian) matrix. In solid state physics and in statistical mechanics it is called the hopping matrix.

In the Hückel theory [?], one lists all the eigenvalues of the adjacency matrix (including repetitions) in decreasing order. Then one adds them, with multiplicity two (on account of electron spin) until one has added together n terms, where n is the number of vertices. Call this sum h . If $h > n$, the molecule is stable. For example, it is easy to check (and is immediate from group theory!) that the eigenvalues of the benzene matrix given above are 2,1,1,-1,-1,-2. So $2 + 2 + 1 + 1 + 1 + 1 = 8$, so $h = 8 > 6$. If we had three methane molecules, so that, for example, 1 and 2 are connected as are 3 and 4 and as are 5 and

6, then the adjacency matrix would consist of three blocks along the diagonal, each block being the two by two matrix

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

This two by two matrix has eigenvalues 1 and -1, and hence the eigenvalues of the corresponding six by six matrix are 1,1,1,-1,-1,-1, and its h is exactly n . In the Hückel theory, the h multiplies a negative quantity to get the energy. Larger h implies smaller energy. Thus the content of Hückel's theory says that the electrons can achieve lower energy by delocalizing themselves into the eigenstates of the benzene matrix, rather than forming alternating double and single bonds. So Hückel, in 1931, was able to give a mathematical model for the vision of the benzene ring that had appeared to Kekule in a dream some sixty years earlier, especially Kekule's vision (1872) of delocalisation of the alternating double bonds. Today, sixty years after Hückel, the idea of the resonating valence bond plays a leading role in some current theories of high temperature superconductivity.

In probability theory, knowledge of the eigenvalues of the adjacency matrix determines the rate of approach to equilibrium for the random walk on the graph. Much recent research has gone into relations between the geometry of the graph and the eigenvalues of the adjacency matrix, and these results are of importance in applications to communications engineering and to computer science.

Group theory can be used to evaluate of the eigenvalues of the adjacency matrix (and related matrices) when the graph admits enough symmetries, as for the buckyball. The adjacency matrix is invariant under the representation of the symmetry group of the graph. This implies that the matrix can be transformed to block diagonal form with block size at most three by three. But, in fact, group theory can be used to actually determine the block entries. The point is that the adjacency matrix can be built up out of group elements, and then the representation of the group determines the block entries. As an illustration, observe that the benzene adjacency matrix written above is the sum of two cyclic permutation matrices, and each of these has a definite value in every irreducible (one dimensional, in this case) representation (see [?, ?, ?]).

Applied to the buckyball, we are able to find the polynomial for the eigenvalues in closed form. In fact we obtain a closed form for a whole family of related matrices which depend on the relative weighting attached to the single and double bonds. For the case of the adjacency matrix of the buckyball, the eigenvalues together with the associated representations are listed in the box (also see [?, ?]). was obtained by Freedberg, Lee and Ren.) eigenvalues (counted with multiplicity) adds up to 46.15, hence $h = 92.30$. The ratio $92.3/60$ is even larger than the value $8/6$ for benzene.

The level immediately above the cutoff line, is a 5^- . The corresponding states are called LOMOs (Lowest Occupied Molecular Orbitals). The states

immediately below the cutoff at level thirty or 3^- . They are called LUMOs (Lowest Unoccupied Molecular Orbitals). These states, together with those lying in the next level down promise to play an important role in understanding the superconducting properties of doped C_{60} crystals.

(Begin box 2) The spectrum of the Buckyball

(end box 2)

To evaluate all the vibrational modes, the problem is somewhat complicated but the approach is very similar. There are several constants involved— the spring constants (for single bonds and double bonds) and the bending constants (for the next nearest neighbors, or even beyond). Instead of a 60×60 matrix, we need to consider a combination of several 180×180 matrices involving these constants (see ref.1 for technical details). By using group theory and the symmetry of the Buckyball, the 180×180 matrix can be decomposed into blocks of sizes at most 9×9 .

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References

- [1] F. R. K. Chung and Shlomo Sternberg, Laplacian and vibrational spectra of homogeneous graphs, *preprint*.
- [2] F.R.K.Chung, D.Rockmore, S.Sternberg, *preprint*.
- [3] C.A.Coulson, B. O’Leary, R.B. Mallon, *Hückel theory for Organic Chemists* Academic Press (1978)
- [4] R. F. Curl and R. E. Smalley, Fullerenes, scientific American, October (1991) 54-63.
- [5] M. S. Dresselhaus, G. Dresselhaus, P. C. Ekuland, Fullerenes, *preprint*.
- [6] S. J. Duclos, R. C. Haddon, S. H. Glarum, A. F. Hebard, and K. B. Lyons, Raman studies of alkali-metal doped A_xC_{60} films ($A = Na, K, Rb, Cs$; $x = 0, 3, 6$), *Science* **254** (1991) 1625.
- [7] R. Friedberg, T. D. Lee and H. C. Ren, Parity doublets and the pairing mechanism in C_{60} , Physics Review, B , 46, (1992) pp.14 150.

- [8] G. Frobenius, Über Gruppencharaktere, *Sitzungsber. Preuss. Akad. Wiss. Berlin* (1896) 985-1021 and Über die Primfaktoren der Gruppendeterminante, *Sitzungsber. Preuss. Akad. Wiss. Berlin* (1896) 1343-1382.
- [9] G. Frobenius, Über die Charaktere der alternierenden Gruppe, *Sitzungsberichte Preuss. Akad. Wiss.* (1901) 303-315
- [10] W. Krätschmer, Lowell D. Lamb, K. Fostiropoulos and Donald R. Huffman, Solid C_{60} : a new form of carbon, *Nature*, **347** (September 1990) 354-358.
- [11] Stuart Samuel, On the electronic structure of C_{60} , preprint.
- [12] S. Sternberg, *Group Theory in Physics*, Cambridge University Press (1992)
- [13] Kai-An Wang, Ping Zhou, Ying Wang, J. M. Holden, Song-lin Ren, G. T. Ni, P. C. Eklund, G. Dresselhaus and M. S. Dresselhaus, Raman scattering in M_xC_{60} films ($M = K, Rb, Cs; x = 0, 3, 6$), *Phys. Rev. B* (to appear).

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