Chapter 5: Chemistry, Quantum Mechanics, and Group Theory

The mid-twentieth-century account of theory reduction, like the deductive-nomological model of explanation, served the useful function of providing a simple model of an important kind of scientific reasoning expressed in a certain symbolic language, the theories of predicate logic. However, I have been arguing that philosophers of science were carried away by their enthusiasm for predicate logic as an instrument of philosophical analysis, as were philosophers of mathematics a generation earlier, an enthusiasm that limited their ability to address several important features of scientific and mathematical rationality, and indeed of predicate logic itself as a vehicle of that rationality. The case study that I investigate in this chapter, that of a widely-used methodology in chemistry applied to a particular problem, is designed to reveal a striking short-sightedness in the philosophical account of the use of symbols. The method 'reduces' a physical system (like a molecule) to its group of symmetries, thence to a collection of matrices, thence to sets of numbers which can be used to compute important features of the physical system.

1. Symbols, Icons, and Iconicity

My examination of how this analysis helps to solve problems in chemistry supports the following claims. (1) Other important formal idioms besides predicate logic organize science and mathematics, reducing spatial configuration and dynamic processes to numerical computation; they make possible analyses that are quite different from those offered by predicate logic. When different formal languages are used to analyze intelligible objects, they reveal different kinds of conditions of intelligibility. (2) The use of symbolic notation to investigate e. g. a chemical object typically makes use of iconic representations in tandem with the symbolic notation, and their conjunction is mediated and explained by natural language. (3) While symbolic notations may in

certain carefully defined situations be treated as uninterpreted, and manipulated in 'purely formal' ways, their rational deployment in the sciences as in mathematics requires that their interpretations be present and reinstated into the problem context, and these presences and reinstatements are often, though not always, indicated by means of icons. (4) Symbolic notations themselves have spatial and iconic dimensions that play important (and irreducible) roles in the knowledge they help to generate. We saw this in the chemical table and in the nucleotide sequences of genes, where not only horizontal but also vertical correspondences in the representations exhibited important features of the gene; horizontal correspondences were rather more iconic (representing spatial side-by-sideness or addition of component parts), and vertical correspondences were more esoteric. (5) A representation that is symbolic with respect to one kind of thing may become iconic with respect to another kind of thing depending on context. The use of numerals in chemical applications of group theory, for example, are symbolic with respect to molecules but have iconic features with respect to numbers; and if a computer programmer is inspecting them as part of a formal language (considered as an object of mathematical study) then they are in a different way even more iconic. Whether, or to what extent, a representation is iconic or symbolic cannot be read directly off the representation, but must take into account the discursive context, the context of use. To be effective in the reductive study of molecules by representation theory, those numerals for example must refer ambiguously to molecules in one sense and to numbers in another. Likewise, a hexagon must represent ambiguously a geometric figure, a molecule, a purified substance in the laboratory, a cyclic group, and a character table.

The tincture of iconicity that nuances every symbolic representation is important to my claim that there is no single correct symbolic representation of an intelligible thing. Icons, precisely because they are like the things they represent, are distortions, and distortions may take many forms; iconicity introduces style, and styles are manifold and changeable. Symbols, though they are relatively unlike the things they represent, must nonetheless share certain structural features with what they represent in order to count as representations at all, and just as there may

be more than one set of structural features essential to the thing (hence different symbolizations that capture them), there may also be more than one way to represent a given set of structural features. Consider the representation of the natural numbers by Roman and Arabic notation, and by the notation 0, S (0), SS (0), …, and so on. (I discuss this issue in Chapter 11.) Moreover, as we have seen, in general symbolic representations must be supplemented by icons and natural language to function as symbols.

Another way to make the point is to observe that symbols are always icons of idealized versions of themselves: the symbol (x) f (x) is also an icon of a certain well formed formula of predicate logic, considered as a mathematical thing. Gödel shows us that every well formed formula can also be represented (much more symbolically) by an integer whose prime decomposition encodes information about it, and that this representation yields important facts about the axiomatized systems of predicate logic, in particular, the results known as Gödel's two Incompleteness Theorems. In many areas of human endeavor, discourse precipitates new intelligible things (laws, university charters, Hamlet, the sonnet) to add to the furniture of the world. What is distinctive about mathematics is that things precipitated by its discourse (like the well formed formulas of predicate logic, considered as objects of study rather than just as modes of representation) are highly determinate, and come to stand in highly determinate relations with things that were already there, like the natural numbers, as happens in Gödel's proof. And they are moreover not exhausted or summarized by the notations that precipitated them; they typically turn out to have further features whose investigation requires other kinds of representations in order to succeed.

2. Representation Theory

Representation theory studies a group by mapping it into a group of invertible matrices; it is a kind of linearization of the group. (This technical term in mathematics unfortunately uses a

philosophical term central to this book, which appears on almost every page, but I think it will be clear from context when I am using the technical term.) Another way to formulate this definition is to say that a representation of a group G, which maps elements homomorphically from G into a group of n x n invertible matrices with entries in (for example, though it could be other fields) $\mathbf{R}$, sets up the action of G on the vector space $\mathbf{R^n}$ and so directly yields an $\mathbf{R}$G- module. (These terms are explained below.) Representation theory thus combines the results of group theory and linear algebra in a useful way. {1} The application of representation theory is an inherently reductive procedure, because it offers a means of studying highly infinitary and nonlinear mathematical entities (for example, all the automorphisms of the algebraic completion of the rationals that leave the rationals invariant), as well as complex physical entities like molecules, in terms of finite and linear entities, matrices, that also lend themselves well to computation. And since automorphism groups can be used to measure the symmetry not only of geometrical figures, but also of physical systems and algebraic systems, the applications of representation theory are many and various.

The reductive study of molecules in terms of symmetry groups is not a theory reduction in the sense of explaining molecular structure and behavior in terms of group theory by assuming that molecules are 'really' mathematical objects. (This is the odd thesis found in the cosmogony of Plato's *Timaeus*, where atoms are literally supposed to be composed of triangles.{2} It is instead reductive analysis: a problem involving molecules can be approached by first solving a problem about certain groups and matrices. In order for the problem reduction to be effective, some of the representations involved must in certain respects stand for molecules, in other respects for mathematical objects, and in yet other respects for macroscopic things in the laboratory. Moreover, it must be true that a molecule has a certain geometrical configuration in space which exhibits certain symmetries; a molecule has its configuration truly but approximately, since it vibrates and since its components are 'here, now' only in a highly qualified sense. And its components are a heterogeneous collection of atoms, themselves

energetic systems interacting in complex ways. Despite all these qualifications, geometric shape is an indispensable condition of intelligibility for chemical investigations of molecular structure.

Reductive analysis—what Peirce called creative abduction—is distinctive, because it tries to understand something in terms of what it is not: molecules in terms of groups of symmetry operations, groups in terms of matrices, matrices in terms of numbers (characters and determinants). Reality presents things that exist; and to exist is to be intelligible, to be possible for thought. However, intelligibility is not transparency, for the intelligibility of things is always problematic: things don't explain themselves. Things must be investigated to be understood, and investigation requires precisely articulated and organized representations. In the cases reviewed here, the representations have an algebraicity that allows them to be provisionally detached from their referents and to refer ambiguously, allowing unlike things to be thought together. Formal languages may precipitate further novel, intelligible things, with their own expressive limitations and their own problematicity. The instruments of reorganization may add something to the inventory of the universe, which, while helpful in solving problems, can also introduce new kinds of problems. Because algebraic notations refer ambiguously and also draw attention to themselves as they refer, they stand both for ways of organizing other things (and typically more than one kind of thing) and for themselves as intelligible things. As we shall see in the case study of this chapter, a hexagonal representation of a benzene molecule is an iconic representation of the shape of that molecule, but it is also the key to a series of symbolic representations in a highly refined strategy— the LCAO (linear combination of atomic orbitals) method—for making quantum mechanical calculations about the structure of that molecule more tractable, a method that exploits the constraints imposed by the symmetries of the system. Thus too predicate logic precipitates both the study of certain kinds of recursively constructed formulas in the theory of recursive functions, and also model theory, the study by logical means of other mathematical fields, reorganized when they are recast into the idiom of a theory in predicate logic. This duality of formal languages is what Gödel exploits in his great proofs. Whether the employment of a

representation is symbolic or iconic cannot be read off the representation: pictures have both symbolic and iconic uses depending on context, and so do obviously 'algebraic' representations.

3. Molecules, Symmetry, and Groups

Symmetry is measured by the number of automorphisms under which an object or system remains invariant. The bigger the automorphism group, the more symmetrical the thing is. For example, if we consider a molecule to be a certain figure in $\mathbf{R}^3$, the pertinent set of automorphisms is all the isometries of $\mathbf{R}^3$ (structure-preserving mappings of $\mathbf{R}^3$ to itself that in particular preserve distances); and the isometries under which that figure remains invariant form a group, which is called its symmetry group. Every physical system has a symmetry group G, and certain vector spaces associated with the system turn out to be $\mathbf{R}$G modules. (An $\mathbf{R}$G module is a vector space over $\mathbf{R}$ in which multiplication of elements of the group G by elements of $\mathbf{R}$ is defined, satisfying certain conditions; there is a close connection between $\mathbf{R}$G modules and representations of G over $\mathbf{R}$.) {3}

For example, the vibration of a molecule is governed by various differential equations, and the symmetry group of a molecule acts on the space of solutions of these equations. Another example concerns electronic internal energy: the kinds of energy levels and degeneracies that a molecule may have are determined by the symmetry of the molecule. Symmetry conditions alone will tell us what the qualitative features of a problem must be: how many energy states there are, and what interactions and transitions among them may occur under the action of a given field. The chemist *qua* mathematician (deploying group theory, representation theory, geometry, and analysis) can determine that transitions between certain quantized states (leading to absorption or emission of light) in the electronic or vibrational spectrum of a molecule are 'allowed' (and others are 'forbidden'), but to learn how great their intensity will be requires experiment and calculation aided by computer. A further example is molecular orbital theory, which assumes that

all atomic orbitals in a molecule extend over the entire molecule, so that the electrons occupying these orbitals may be delocalized over the entire molecule. Considerations of molecular symmetry properties are extremely useful in this theory and allow the chemist to draw many conclusions about bonding with few or highly simplified quantum computations. {4}

In the case study, I examine an instance of the latter kind of problem solving. It is the study of benzene, C_6H_6 (and a family of related carbocyclic molecules, C_4H_4, C_8H_8, $C_{10}H_{10}$, and so on) by means of a theory that competes with the valence bond theory: the molecular orbital theory, which analyzes molecular orbitals as linear combinations of atomic orbitals. I borrow my account from textbooks as well as from some of the original chemical articles (the interaction of the mathematics and empirical results is tidier in the former and messier in the latter) and show how different traditions of 'paper tools,' some mathematical and some chemical, are composed or superimposed on the same page. So that the meaning of the symbols and icons will be clearer, I will briefly explain some aspects of representation theory, and the real and complex analysis used by quantum mechanics.

As is well known, group theory was articulated in the work of Felix Klein in his inaugural address at Erlangen in 1872, and his research project that became known as the *Erlanger Programm*. It took its inspiration from the study of symmetries in geometry, and classified geometries in terms of those properties of figures that remain invariant under a particular group of transformations. Thus, Euclidean geometry is characterized by the group of rigid transformations (rotations and translations) of the plane, and projective geometry by the group of projective transformations. These infinite groups contain finite groups that can be associated with the symmetries of individual figures, like the square or equilateral triangle. {5}

Modern textbook expositions of group theory include very little in the way of iconic representations of the geometrical figures that gave rise to the theory in the first place. *A Survey of Modern Algebra* by Garrett Birkhoff and Saunders MacLane {6} makes use of a picture of a square, a regular hexagonal network, and a rectangle to introduce group concepts, but the chapter

on group theory in I. N. Herstein's *Topics in Algebra* {7} has no figures at all and even avoids geometrical examples in the problem sets. *Representations and Characters of Groups* by Gordon James and Martin Liebeck contains only one figure (a regular *n*-sided polygon, only schematically indicated) in the first 29 of its 30 chapters. Geometrical figures finally appear in the last chapter, which is devoted to the application of representation theory to chemistry! And indeed, *Chemical Applications of Group Theory* by F. Albert Cotton contains more geometrical figures than all the textbooks put together that I used as a student of mathematics at the University of Chicago forty years ago when Bourbaki held sway. But of course the geometry is re-organized because the geometrical figures have been reinstated in order to represent various symmetries and spatial configurations pertinent to molecules: what Euclid sought in his triangles, hexagons and tetrahedra was quite different from what these authors seek in theirs, though like Descartes (see Chapter 6) they must presuppose and use Euclid's results.

Only four types of symmetry elements and operations need to be considered in the study of molecular symmetry. A symmetry plane passes through a molecule; if when one drops a perpendicular line from each atom in the molecule to the plane, extends that line an equal distance in the other direction, and moves the atom to the other end of the line, an equivalent configuration results, that plane is a symmetry plane. The operation of reflection—which takes every (x, y, z) to $(x, y, -z)$ given an appropriate choice of coordinate system—is called σ, and the identity operation is designated E. Clearly, $\sigma^n = E$ when n is even and σ when n is odd. A regular tetrahedral molecule AB_4 possesses six planes of symmetry; a regular octahedral molecule AB_6 possesses nine.

If the mapping (x, y, z) to $(-x, -y, -z)$ (again with an appropriate choice of coordinates) takes the molecule into an equivalent configuration, then it has an inversion center and the operation is inversion, designated i. Once again, $i^n = E$ when n is even and i when n is odd. Note that octahedral AB_6 and planar AB_4 each have a center of inversion, but tetrahedral AB_4 does not. If when a molecule rotates about an axis by $2\pi/n$ degrees it moves into an equivalent

configuration, then the axis is called a proper axis and the operation of rotation a proper rotation: it is symbolized $C_n{}^m$, which means that the rotation $2\pi/n$ has been carried out m times. The molecule H_2O possesses a single twofold axis; a regular tetrahedral molecule AB_4 possesses three twofold axes and four threefold axes. Improper axes and rotations also exist: they are the result of effecting first a proper rotation and then a reflection in a plane perpendicular to the rotation axis. These operations are analogously designated $S_n{}^n$. It is clear that $C_n{}^n = E$ and $S_n{}^n = \sigma$ while $S_n{}^{2n} = E$. Tetrahedral AB_4 possesses three C_2 axes, as just mentioned, and each of these is simultaneously an S_4 axis. [Figure 5.1]. {8}

All symmetry operations on a given molecule return the molecule to an equivalent state; if we think of the product of two such operations as the effecting of first one and then the other, written right to left (so that YX = Z means first X is applied and then Y), then clearly a complete set of symmetry operations for a particular molecule can be thought of as a closed algebraic structure, and indeed as a group that acts on an n-dimensional vector space: an **R**G-module. There is a nomenclature for the kinds of symmetry groups that chemists encounter among the molecules they study. (The symmetry groups pertinent to the molecules of interest to chemists are for the most part finite groups, though some are infinite, like the group of proper rotations of a linear molecule, and the linear and planar space groups of crystals, or one-, two-, and three- dimensional polymers, or extended metallic structures.) The special groups corresponding to linear molecules are designated $C_{\infty v}$ and $D_{\infty v}$; those corresponding to molecules with multiple higher-order axes are designated T, T_h, T_d, O, O_h, I, and I_h. Groups corresponding to molecules with no proper or improper rotation axes are designated C_1, C_s, C_i, and those with only S_n (n even) axes S_{2n}. Finally, groups corresponding to molecules with a C_n axis that is not a simple consequence of an S_{2n} axis are designated C_{nh}, C_{nv}, C_n and D_{nh}, D_{nd} and D_n, depending on various conditions. For example, water (H_2O) belongs to the group C_{2v}; allene (C_3H_4) belongs to the group D_{2d}. {9}

4. Symmetry Groups, Representations, and Character Tables

As just noted, the convention has been established to employ five types of operations in describing the symmetry of a molecule: E, σ, i, C_n, S_n (along with various subscripts, superscripts, and primes, details not pertinent here). Each of these operations can be associated, for example, with a 3 x 3 matrix in a straightforward way. The identity operation

E may be expressed as $\begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}$ and the inversion operation i as $\begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix}$

while the matrix for the reflection operation σ depends on which Cartesian plane we choose as the plane of reflection. Appropriate 3 x 3 matrices for the rotations C_n and S_n can easily be constructed if we recall that the matrix for clockwise rotation around one axis through an angle θ can be expressed as

$\cos\theta \quad \sin\theta$

$-\sin\theta \quad \cos\theta$

and for counter-clockwise rotation as

$\cos\theta \quad -\sin\theta$

$\sin\theta \quad \cos\theta$

All of these matrices are invertible: their inverses are obtained by transposing rows and columns. Thus, a possible representation of the group C_{2v} (the point group of oxygen, H_2O) which contains the four operations E, C_2, σ_v and σ_v' will be the following group of matrices:

E: $\begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}$ C_2: $\begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix}$ σ_v: $\begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix}$ σ_v': $\begin{matrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}$

It is straightforward to check that the group multiplication table for the four operations maps in the right way to the multiplication of the matrices; and each operation and its inverse map in the right way to a matrix and its inverse. The representation we have just constructed takes each

element of the group C_{2v} to a certain 3 x 3 matrix, allowing us to interpret the action of C_{2v} on the vector space $\mathbf{R^3}$ in terms of matrix multiplication (of a 3 x 1 matrix by a 3 x 3 matrix), and constitutes $\mathbf{R}G$ as a module. {10}

But this representation is only one of an unlimited number of possible representations that use n x n matrices for some n, depending on how many dimensions we need to characterize the molecule in a given situation. In cases where we want to characterize the molecular orbital in terms of n atomic orbitals (or, in terms of certain kinds of linear combinations of atomic orbitals) the matrices may be very big. Of the many possible representations of a given symmetry group, those that are of fundamental importance, however, are called 'irreducible.' An irreducible representation is an $\mathbf{R}G$-module that is non-zero and has no $\mathbf{R}G$-submodules apart from {0} and itself; $\rho : G \rightarrow GL\ (n, \mathbf{R})$ (the n x n matrices with entries in $\mathbf{R}$) is irreducible if the corresponding $\mathbf{R}G$-module is irreducible. Any reducible representation (a set of n x n matrices) can be rewritten in terms of irreducible representations. The canonical representation will be a set of m x m matrices all block-factored along the diagonal in the same way, where corresponding blocks are irreducible representations of possibly varying size and with possible repetitions. Thus if for a given symmetry group there are four one dimensional irreducible representations and one two dimensional irreducible representation, any reducible n x n representation of that group can be mapped by a similarity transformation to the canonical representation, a set of 6 x 6 matrices with zeroes everywhere except for four appropriately chosen 1 x 1 matrices (just numbers) and one 2 x 2 matrix along the diagonals of each. The canonical representation is thus itself reducible, but exhibits the irreducible representations in what we might call iconic fashion. The role played by canonical forms in symbolic systems is often to exhibit structure in an especially perspicuous way; and this notion of perspicuity has little to do with physical vision. It has to do rather with the way in which complex things (here, reducible sets of matrices) may be analyzed in terms of simpler things (irreducible sets of matrices). Canonical forms exhibit the results of analysis; and this display may be called, in an abstract sense, iconic.

The trace of an n x n matrix (the function from the set of n x n matrices to $\mathbf{R}$ indicated by tr) is the sum of its diagonal entries. The function $\chi : G \rightarrow \mathbf{R}$, called the character of a representation $\rho : G \rightarrow GL\ (n, \mathbf{R})$, is defined in terms of the function tr. Independent of the choice of basis for the vector space, it is defined as the character of the corresponding $\mathbf{R}G$-module, $\chi\ (g) = \mathrm{tr}\ (g\rho)$ for all g in G; we then say that χ is an irreducible character of the group G if χ is the character of an irreducible $\mathbf{R}G$-module. Chemists construct 'character tables' that exhibit the characters of each symmetry operation of a given group (like C_{2v} above) at each irreducible representation, which can be used in light of the following useful facts. The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group (how many distinct elements it has), and so is the sum of the squares of the characters in any one irreducible representation of the group. The number of irreducible representations of a group is equal to the number of distinct classes in the group. Finally, if you think of the characters of two distinct irreducible representations as components of two vectors, those vectors are orthogonal. The canonicity of irreducible representations means that a great deal of important information can be read directly out of or into character tables.

Symmetry considerations and the theory of group representations immensely reduce the labor required for effective calculation of the properties of molecules, as we will see in the next section. A change in the geometry of a molecule results in significant physical alterations: things that did not interact before suddenly begin to interact, and these changes are reflected, or predicted, in the 'register' of the irreducible representations, which of course shift with the geometry. The anti-reductionist drift of this observation can be made even more strongly, as Robert Bishop does in his essay 'Patching Physics and Chemistry Together.' He writes, 'Molecular structure or shape plays a crucial causal role in chemistry. It dominates the interpretations of the calculations and experiments of chemists. More importantly, it has empirical and practical import.' Citing various examples where the causal import of the shape and in particular the chirality of molecules is paramount, he goes on to remind us that 'the 'true'

molecular Hamiltonian at the level of quantum mechanics—could we actually write it down—

would not exhibit any features corresponding to molecular structure… furthermore, the full

molecular Schrödinger equation would have too many symmetries.' Thus, the requirement of a

variety of modes of representation in applications of quantum mechanics to chemistry is neither a

superficial demand nor an accident of history: it expresses a fundamental differentiation (both

epistemological and ontological) between the two sciences. {11}

The textbook *Chemical Applications of Group Theory* comes equipped with 'Character

Tables for Chemically Important Symmetry Groups' twice: once as an appendix and once

reprinted as a handy booklet in the pocket of the cover. Most applications worked out in detail in

the book (with the exception of the treatment of crystals) involve a character table at some point.

Here is a simple example. Recall that the symmetry group for water is C_{2v}; it has four elements,

E, C_2, σ_v, and σ_v'. Each element is in a separate conjugacy class of the group, and since (as noted

above) the number of irreducible representations of a group is equal to the number of conjugacy

classes in the group, there are four irreducible representations for this group. Moreover, since (as

noted above) the sum of the squares of the dimensions of the irreducible representations of a

group is equal to the order of the group, these four irreducible representations must all be one-

dimensional. The character table for the group can be easily worked out and is:

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

The nomenclature in the leftmost column is a set of Mulliken symbols: one dimensional

representations are designated A or B, depending on whether they are symmetric or

antisymmetric with respect to rotation by $2\pi/n$ around the principal C_n axis; the subscripts 1 and 2

indicate that the representation is symmetric or antisymmetric with respect to a C_2 axis

perpendicular to the principal axis or to a vertical plane of symmetry. Two dimensional representations (there aren't any in this case) are designated E, with a further set of subscripts and superscripts to distinguish kinds of two dimensional representations; three dimensional representations are designated T with appropriate subscripts and superscripts, and so forth.

Characters are used to facilitate the reduction of a reducible representation, that is, they can be used to find, or circumvent the need to find, the similarity transformation which will reduce each matrix of a reducible representation to another belonging to the set of matrices in canonical form, with mostly zero entries and block-factored in the appropriate way along the diagonal. These tables are thus abridgments of an enormous amount of information from geometry, group theory, matrix algebra, and representation theory in relation to the field of the real (and sometimes complex) numbers.

5. The Benzene Ring and Carbocyclic Systems

I come now at last to the case study. The investigation of benzene and related carbocyclic molecules by means of LCAO-MO theory, where molecular orbitals are conjectured in terms of linear combinations of atomic orbitals, is treated in Chapter 7 of Cotton's *Chemical Applications of Group Theory*. The exposition is based on a series of chemical articles by Robert Mulliken, Robert Parr, F. Hund, Erich Hückel, and others beginning in the 1930s and continuing into the 1960s when the first edition of Cotton's textbook appeared. The leading competitor theory was valence bond theory, developed in the late 1920's by Walther Heitler and Fritz London, and then by John Slater and Linus Pauling. Valence bond theory actually provided the first quantum mechanical description of the benzene molecule, and in the 1930's fared better than the LCAO-MO explanation provided by E. Hückel, thanks mainly to the charismatic presentation offered by Pauling. But later the tide turned; valence bond theory was not easily extended to molecules larger than benzene, and LCAO-MO theory made important, speculative predictions that were

then verified. Apropos the benzene molecule, the LCAO-MO theory entails that the six p orbitals (perpendicular to the plane of the molecule) interact by lateral overlap to give six molecular orbitals, three bonding and three anti-bonding; taken together, they constitute the 'extended π bond.' According to Hund's rule and the Pauli exclusion principle, the six pertinent electrons will fill the three bonding orbitals, each of which is delocalized over all six carbon atoms.

The application of LCAO-MO theory to benzene is an especially nice example for my purposes, because it clearly exhibits the scientific importance and fruitfulness of the reduction under consideration while illustrating the theses I am trying to develop about symbolic and iconic representations. The representations used here are obviously highly symbolic; numbers, differential equations, and constructed orbitals are not 'like' and do not picture molecules. Yet these symbolic representations must be used in tandem with iconic representations (geometric figure, in this case a hexagon) which are essential to their use, given the causal importance of shape, and which require a context in natural language to explain the rational relation between icons and symbols. Moreover, the symbolic expressions themselves have an iconic dimension, in a sense that need not involve the visual-perceptual, as when canonical expressions exhibit the results of analysis. The use of molecular orbital theory, using the LCAO method, requires character tables; differential equations (wave equations) involving the Hamiltonian operator, the energy of the system and pertinent wave functions; geometrical forms augmented to represent molecules and their orbitals; and 'theoretical' energy level diagrams: the chemist strives to bring the theoretical computations into relation with tables of empirical results produced in lab.

To bring quantum mechanics to bear on chemistry, in order to solve certain especially puzzling problems, atoms and molecules must be thought of as functions that are solutions to certain differential equations. Quantum mechanics calls such functions 'orbitals' and much ink has been spilled over how orbitals are to be interpreted physically; in broad terms, they indicate where electrons may possibly be located given a certain energy state of an atom. A set of diagrams of increasingly energetic states of the hydrogen atom (one proton, one electron) from a

1931 article in a physics journal, shows the orbitals of the atom. [Figure 5.2] {12} These images

should be read as three dimensional clouds surrounding the nucleus of the atom; note that they

exhibit determinate symmetries, even though the 1966 textbook in which they is reproduced

warns in italics: 'the shapes of orbitals (electron cloud diagrams)… are *pictorial presentations* of

the mathematical solutions of the Schroedinger equation. *They do not represent reality;* the

shapes are not pictures of electric charges or matter. Also, in wave mechanics, the electron may

be regarded as neither particle nor wave. It is an indescribable entity whose properties are

(presently) best elucidated by the Schroedinger equation.' {13}

The textbook claims that the shape of the orbitals doesn't represent reality. The

arguments presented by Robert Bishop, cited briefly above, suggest that while 'shape' cannot be

properly attributed to orbitals it may be properly attributed to molecules; and this only shows that

the representations of chemistry must be given not only in terms of differential equations but also

in terms of geometry and (more broadly) topology. Important structural features of molecules,

which may be truly attributed to them, are lost when they are represented by differential

equations. Another difficulty also arises: the application of quantum mechanics to chemistry is

vexed because the differential equations, which are hard enough to solve in the case of the

simplest atom, hydrogen, become rapidly intractable as one moves up the chemical table, even

given recent advances in computer technology; and also as one considers the combination of

different kinds of atoms in a molecule, trying to determine what the molecular orbitals might be.

A good strategy for simplifying the computations involved is to consider the symmetries of a

molecule—taking into account its component atoms—as constraints on the solutions of such

problems, for these symmetries allow one to conclude expeditiously that certain integrals in the

calculations must be identically zero and exhibit other integrals in an especially perspicuous form.

Despite the fervid disclaimer in the 1966 textbook, orbitals apparently do belong to

configurations that are to a certain extent well depicted by geometrical figures and their

associated symmetry groups and irreducible representations, as well as by differential equations.

Indeed, if orbitals were really 'indescribable,' scientists would have a hard time investigating them. However, to be well described, they require a multiplicity of modes of representation working in tandem.

The central equation of quantum mechanics is the wave equation

$$H\Psi = E\Psi \qquad\qquad\qquad\qquad (Eq.\ 5.1)$$

which states that if the Hamiltonian operator H is applied to an eigenfunction Ψ, the result will be that same function multiplied by a constant called an eigenvalue, E. We can initially think of Ψ_i as an atomic orbital and the corresponding E_i as its energy. If several eigenfunctions give the same eigenvalue, the eigenvalue is called 'degenerate,' as when three $2p$ orbitals in an atom have equal energy; in this case, any linear combination of the initial set of eigenfunctions is a correct solution of the wave equation giving the same eigenvalue. If a symmetry operation (like E, C_2, σ_v, or σ_v' discussed above) is carried out on a system, clearly the Hamiltonian and the energy of the system must remain unchanged (since the system before is physically indistinguishable from the system after); thus the Hamiltonian operator commutes with any symmetry operation, as well as with any constant factor c.

Eigenfunctions are always constructed to be orthonormal, that is, orthogonal to each other and one 'unit' in length, so that the integral of the product of a pair of eigenfunctions is identically 0 if $\Psi_i \neq \Psi_j$ and 1 if $\Psi_i = \Psi_j$. The eigenfunctions of a molecule, linear combinations of the atomic orbitals, are bases for irreducible representations of the symmetry group to which the molecule belongs. In the case study at hand, the chemist takes the atomic orbitals of a molecule as a set of orthonormal functions, and seeks to make orthonormal linear combinations of them so that the combinations form bases for irreducible representations of the symmetry group of the molecule, corresponding to the molecular orbitals and so to the energy levels of the molecule. These 'symmetry adapted' linear combinations of atomic orbitals (SALCs) are acceptable formal solutions to the wave equation of the molecule, which must then however be cashed out in order to calculate the energies. Once we can write $\psi_k = \Sigma\ c_{ik}\ \varphi_i$ (denoting the kth

molecular orbital by a linear combination of atomic orbitals), this expression can be plugged into the wave equation written as $(H - E)\,\psi_k = 0$, and the left side integrated over all the spatial coordinates of the wave function. This results, however, in a rather daunting series of equations involving certain integrals called 'matrix elements' (described below) which are re-written as a system of homogeneous linear equations for which nontrivial solutions are sought. This process is sometimes streamlined by approximations such as the Hückel approximation, which makes certain simplifying assumptions about the integrals, matrix elements, in the wave equation. The Hückel approximation posits that all the $H_{ij} = \int \varphi_i\, H\varphi_j\, d\tau,$ which record the energies of interaction between pairs of atomic orbitals, as well as all the overlap integrals, $S_{ij} = \int \varphi_i\, \varphi_j\, d\tau$, which in a sense constitute the metric of the basis set, can be assumed to be 0 unless the ith and j^{th} orbitals are on adjacent atoms. ($H_{ii} = \int \varphi_i\, H\varphi_i\, d\tau$ gives the energy of the atomic orbital φ_i. H_{ii} is conventionally abbreviated α; H_{ij} is conventionally abbreviated β.) The Hückel Approximation, in its attempt to reduce complexity as much as possible, even assumes that the S_{ij} between nearest neighbors is zero. Because the Hückel Approximation sets so many integrals equal to zero, the difficulty of computation is greatly reduced. Symmetry considerations further simplify the computations.

In the case study at hand, the problem is to describe the internal structure of the planar, hexagonal molecule benzene (C_6H_6) in terms of the internal bonding of its atoms and in relation to empirical evidence about energy levels or states of the molecule; and this problem can be generalized to include the investigation of other carbocyclic molecules, C_nH_n. Despite a certain revival of Valence Bond theory in recent times, the present consensus is that in the case of benzene and related carbocyclic systems, molecular orbital theory provides greater insight into molecular structure than does the valence bond theory. Molecular orbital theory begins, as we have just noted, with the atomic orbital wave functions, and then uses the symmetry constraints imposed by the configuration of the molecule as a whole to determine how the latter combine to make the molecular orbital wave functions. Mathematically, the theory makes use of certain

projection operators to construct the requisite 'symmetry-adapted' linear combinations of atomic orbitals, each of which forms a basis for an irreducible representation of the symmetry group of the molecule, corresponding to a molecular orbital. In order to calculate the energies of the molecular orbitals, the chemist must solve the wave equation for that particular LCAO; the Hückel approximation, which as we just saw employs certain simplifying assumptions about integrals in the wave equation, is a useful device for simplifying that calculation. Each molecular orbital then corresponds to a line on an energy level diagram.

 In the analysis of benzene, the essential atomic orbitals are the six so-called $p\pi$ orbitals, perpendicular to the plane of the molecule at every vertex of the hexagon. All the essential symmetry properties of the LCAOs sought are determined by the operations of the uniaxial rotational subgroup C_6. [Figure 5.3] {14} When the set of six $p\pi$ orbitals—one on each carbon atom—is taken as the basis for a representation of the group C_6, this character table results {15} :

C_6	E	C_6	C_3	C_2	C_2^3	C_5^6	
A	1	1	1	1	1	1	
B	1	−1	1	−1	1	−1	
E_1	1	ε	$-\varepsilon*$	−1	$-\varepsilon$	$\varepsilon*$	$\Big\{$ $\Big\}$
	1	$\varepsilon*$	$-\varepsilon$	−1	$-\varepsilon*$	ε	
E_2	1	$-\varepsilon*$	$-\varepsilon$	1	$-\varepsilon*$	$-\varepsilon$	$\Big\{$ $\Big\}$
	1	$-\varepsilon$	$-\varepsilon*$	1	$-\varepsilon$	$-\varepsilon*$	
Γ_Φ	6	0	0	0	0	0	

$$\Gamma_\Phi = A + B + E_1 + E_2$$

The reducible representation Γ_φ is decomposed into the irreducible representations A, B, E_1 and E_2. (These are Mulliken symbols, briefly described above.) This decomposition becomes A_{2u}, B_{1g}, E_{1g} and E_{2u} in the group D_{6h} when the full symmetry of the benzene molecule is studied, but the advantage of working with the subgroup is that the computations are greatly simplified and the generality of the resulting rule is not impugned. The character table produces, by means of an application of the projection operator technique which in this case is especially straightforward, another array in which each irreducible representation is associated with a wave function that is the sum of the n $p\pi$ orbitals, each multiplied by the nth character entry in that row. {16}

$$A: \quad \Psi_1 = \Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 + \Phi_5 + \Phi_6$$

$$B: \quad \Psi_2 = \Phi_1 - \Phi_2 + \Phi_3 - \Phi_4 + \Phi_5 - \Phi_6$$

$$\Psi_3 = \Phi_1 + \varepsilon\Phi_2 - \varepsilon^*\Phi_3 - \Phi_4 - \varepsilon\Phi_5 + \varepsilon^*\Phi_6$$
$$E_1: \quad \{$$
$$\Psi_4 = \Phi_1 + \varepsilon^*\Phi_2 - \varepsilon\Phi_3 - \Phi_4 - \varepsilon^*\Phi_5 + \varepsilon\Phi_6$$

$$\Psi_5 = \Phi_1 - \varepsilon^*\Phi_2 - \varepsilon\Phi_3 + \Phi_4 - \varepsilon^*\Phi_5 - \varepsilon\Phi_6$$
$$E_2: \quad \{$$
$$\Psi_6 = \Phi_1 - \varepsilon\Phi_2 - \varepsilon^*\Phi_3 + \Phi_4 - \varepsilon\Phi_5 - \varepsilon^*\Phi_6$$

This array is then rewritten to get rid of imaginary coefficients and to normalize the molecular orbital wave functions to unity, which in turn produces the array on the left hand page of [Figure 5.4]. {17} Here we have a set of wave functions that we can regard as the molecular orbitals: they are linear combinations of the atomic orbitals, they are orthonormal (as planned), and they correspond to the six irreducible representations, and to the energy levels of the molecule. Their energies are calculated making use of the Hückel approximation, and the result

is as follows; we recall that H_{ii} is conventionally abbreviated α and H_{ij} is conventionally abbreviated β.

$E_B = \alpha - 2\beta$

$E_{E\ a} = E_{E\ b} = \alpha + \beta$

$E_{E\ a} = E_{E\ b} = \alpha - \beta$

$E_A = 1/6\ (6\alpha + 12\beta) = \alpha + 2\beta$

By convention, α is taken to be the zero of energy and β is taken to be the unit of energy. As we see on the right-hand page of Figure 5.4, these wave functions are correlated with a set of six hexagonal schemata that exhibits the molecular orbitals and their nodal planes; and an energy level diagram, which shows the six electrons located in the three bonding orbitals. Notice how the articulation of rows of numbers in the character table has been mapped onto the articulation of the lines of the energy level diagram (in a different sequence), via the array of the molecular orbital wave functions.

6. Measuring Delocalization Energy in the Benzene Molecule

The delocalization of electrons, or, the ability of electrons to spread out more in a molecule than in a single atom, drives down the energy of the system and so makes the molecule more stable. Valence bond theory notes that the experimentally measured energy of the system of a benzene molecule differs from the energy calculated for either of the two Kekulé structures, depicted as the middle pair in [Figure 5.5] {18}; this difference is called the 'resonance energy' and it is valence bond theory's way of measuring the stabilization of benzene. LCAO-MO theory instead assesses that stabilization by a 'delocalization energy.' One task for LCAO-MO theory is to verify that the delocalization energy it theoretically calculates for benzene accords with the results of experiment. In Cotton's textbook presentation, an empirical procedure for making this comparison is briefly sketched and the author notes 'the LCAO method is at least empirically

valid.' However, he also adds in a footnote, 'See Appendix III for some important qualifications concerning the evaluation of β.' Appendix III is entitled 'Some Remarks about the Resonance Integral,' and explains why 'the seemingly straightforward and obvious method for evaluating the integral β' is not so straightforward after all; examination of the scientific articles that lie behind this qualification confirm the point. {19}

In the suite of articles that address themselves to this project, we see that the process of bringing the theoretical model in line with empirical data does not simply serve to validate the theory; nor is it a suspect attempt to glue 'ad hoc hypotheses' onto LCAO-MO theory in order to reproduce the good correspondence between the valence bond model and empirical results. Rather, using LCAO-MO theory in tandem with the differential equations of quantum mechanics, chemists generate new hypotheses and extensive articulation of the model. That is, what counts as the LCAO-MO model of the benzene molecule is rather plastic, and the modifications it undergoes in order to accord with empirical data are substantive and add content to the theory.

An important paper published by Robert Mulliken in *The Journal of Chemical Physics,* 'LCAO Molecular Orbital Computation of Resonance Energies of Benzene and Butadiene, with General Analysis of Theoretical *Versus* Thermochemical Resonance Energies,' rehearses the earlier stages of the process of getting the model to answer to the data. {20} In 1938, M. Goeppart-Mayer and A. L. Sklar used the LCAO approximation to calculate the lower excited levels of benzene; 'using no other empirical data than the carbon-carbon distance and considering the six π-electrons alone, they obtained excitation energies which agreed fairly well with experiment.' {21} This result was, however, corrected a number of times over the course of a decade because of initially neglected terms and incorrect values for several integrals; in a later article by Parr, Craig and Ross {22} the theoretical predictions of valence bond theory seem to accord better with experiment. Apparently, however, the calculations of the energies of MO's using LCAO approximation were good enough to encourage Mulliken and Parr to use them to compute resonance (or rather, delocalization) energies.

The Mulliken and Parr article, 'LCAO Molecular Orbital Computation of Resonance Energies of Benzene and Butadiene, with General Analysis of Theoretical *versus* Thermochemical Resonance Energies,' begins with an equation. {23}

$$W_R = W_K - W_N$$

The authors observe that in valence bond theory, this means that the 'resonance energy' W_R of benzene is the difference between the energy W_K of a single Kekulé valence bond wave function ψ_K and the actual ground-state energy W_N. But in LCAO-MO theory, it means something different. They write, 'In the LCAO MO method, following Hückel, conjugation or resonance energy in olefinic or aromatic molecules may be conceived as the difference W_R between the energy W_K of a wave function in which the π_x electrons are assigned to two-center or 'localized' LCAO MO's (like those in ethylene) and the energy W_N of one in which they are assigned to the best n-center LCAO MO's obtained by solving a secular equation (n = number of atoms carrying π_x electrons).' {24} We recall that Cotton calls W_R 'delocalization energy.' Attaining good theoretical values for the terms in the master equation given above requires an analysis of all three, an analysis that is not a mere 'unpacking of what is already there,' but one that adds theoretical content made possible by the interaction of the modes of representation with each other and ultimately constraints imposed by experiment.

Section 2, 'The Normal State of Benzene,' addresses the term W_N, rewriting it as the sum of a core energy and a πx-electron energy:

$$W_N = W_{N,\text{core}} + W_{N\pi}.$$

The π_x-electron molecular orbitals are expressed as orthonormal linear combinations of $2p\pi_x$ atomic orbitals on the six carbon atoms:

$$\Phi_j = \Sigma_p \, C_{jp}\chi_p$$

The term $W_{N\pi}$ is expanded into a twelve term sum involving I_i, the energy of an electron in the MO φ_i in the field of the core, J_{ij} the 'coulomb integral' between the MO's φ_i and φ_j, and K_{ij} the 'exchange integral' between these MO's. The coefficients C_{jp} in the equation given above are

then found by minimizing the energy $W_{N\pi}$ with respect to them, subject to orthonormalization of the φ_j.

Section 3, 'The LCAO MO Kekulé Structure of Benzene,' addresses the term W_N in much the same way, arriving at a twelve term sum for $W_{K\pi}$ formally analogous to the one just described for $W_{N\pi}$. Section 4, 'Compression Energy Corrections and the Theoretical LCAO Resonance Energy of Benzene,' analyzes W_R in terms of the following equation, in which the constant bond length of 1.39 A for normal benzene is invoked.

$$W_R = W_{R1.39} - C_K$$

The term C_K denotes 'compression energy'; Mulliken, Rieke and Brown computed a reliable value for it. {25} The term $W_{R1.39}$ is called the 'gross vertical resonance energy,' an electronic change with no accompanying change in internuclear distances.

Section 5, 'Comparison of Thermochemical and Theoretical Resonance Energies of Benzene' explains an empirical value of W_R that can usefully be compared with the theoretical value, but section 6, 'Theoretical Analysis of Meaning of Thermochemical Resonance Energies, with Application to Benzene,' cautions that further correction terms must be included before the comparison is meaningful. These involve 'a perhaps very appreciable amount of what may be called higher order resonance energy, corresponding to numerous minor contributions of miscellaneous VB [valence bond] structures present in the actual wave function.' {26} In particular, the authors are concerned with 'second order hyperconjugation energy,' which they then elaborate upon, introducing further new terms, some of them correction terms, into the analysis of W_K.

Mulliken and Parr summarize the results of their efforts in the abstract of the paper: 'The decrease in π_x-electron energy for the change from a Kekulé to a proper benzene structure is computed purely theoretically by the method of antisymmetrized products of MO's (molecular orbitals), in LCAO approximation, using Slater $2p\pi_x$ AO's (atomic orbitals) of effective charge 3.18, and assuming a carbon-carbon distance of 1.39 A. The result (73.1 kcal / mole) is a

theoretical value for the gross (vertical) resonance energy of benzene taken for constant C—C distances of 1.39A. In order to make a comparison with the net or ordinary empirical resonance energy, several corrections to the latter are required. The principal one is for the 'compression energy' required to compress the single and stretch the double bonds of the Kekulé structure from normal single and double-bond distances to 1.39A. The others (not hitherto clearly recognized) involve hyperconjugation and related effects. The corrections are discussed and their magnitudes estimated, but a reliable value can be obtained only for the compression energy. Allowing for this alone, the computed net resonance energy is 36.5 kcal. This agrees, within the uncertainties due to the omitted correction terms, with the value (41.8 kcal) of the 'observed' resonance energy Δ based on thermochemical data.' {27}

What we see here is a rational process that cannot be characterized either as inductive justification (the model is supported by the empirical data) nor as deductive falsification (the model is falsified by the empirical data). Rather, it is not clear what counts as the best theoretical model for evaluating the resonance energy of benzene, especially since the model suggests a search for other things, unexpected by either Kekulé or the valence bond theorists: delocalization energy W_R that redefines what is meant by W_K and W_N, as well as 'compression energy' and 'hyperconjugation energy.' It is moreover not clear what counts as empirical evidence for resonance or delocalization energy. The article just discussed records a process of mutual adjustment, where empirical data serves as a somewhat plastic set of constraints on the model, and the model offers somewhat plastic means of articulating the components of the molecule's energy, which in turn suggest new ways of empirically detecting the molecule's energy. Here we see that the paper tools affect both theory construction and experimental practice, in a way that lies between representation and intervention. And, as in Klein's account of the role of Berzelian formulas as paper tools in the development of the theory of the binary constitution of organic substances and later in the articulation of the concept of substitution, the effectiveness of the

paper tools is not explained by appeal to theory alone or by appeal to empirical data. The paper

tools are a third something, a *tertium quid*, which shapes both theory and the collection of data.

In this case, LCAO-MO theory does not seem more reliable than valence bond theory,

though the authors suggest that the latter does not lead as clearly into the investigation of

hyperconjugation energy. Indeed, in the paper cited above and written 10 years earlier, Mulliken,

Rieke and Brown tell us that chemists earlier had conjectured that groups like CH_3 should have

the power to conjugate with other groups containing double or triple bonds, but all previous

discussion had been qualitative. However, as they demonstrate in this article, quantum

mechanical methods using the LCAO-MO method with numerical parameters derived from

empirical data, open up this conjecture to computation and experiment. {28}

Mulliken and Parr, 'unpacking' the terms of the equation $W_R = W_K - W_N$, exhibit a

process of analysis iconically, even though what is exhibited by means of spatial articulation term

by term is not visual but rather the highly abstract dissection of the energy of the benzene

molecule. The iconicity of the elaborate equation that emerges from this article might be

compared to Dante's spatial articulation of human vice and virtue in the *Commedia*. The

conceptual work of icons need not be confined to the domain of human perception.

LCAO-MO theory does, however, seem superior to valence bond theory in a different

context, when we examine a series of molecules in which benzene figures: planar, carbocyclic

molecules C_nH_n, where n is even. Cotton observes, 'According to valence bond theory, any such

system in which the number of carbon atoms is even would be expected to have resonance

stabilization, because of the existence of canonical forms,' of the following types depicted for the

first three members of the series: two squares for C_4H_4; two hexagons (the two Kekulé structures

for benzene, C_6H_6), and two octagons for C_8H_8. [Figure 5.5] However, LCAO-MO theory does

not make this prediction. The energy level diagrams generated by LCAO-MO theory for C_4H_4

and C_8H_8 exhibit, as Cotton tells us, 'the same general arrangement of levels [as for C_6H_6],

namely, a symmetrical distribution of a strongly bonding, non-degenerate A level and a strongly

antibonding, non-degenerate B level, with a set of E levels between them. It can be shown that such a pattern will always develop in an even-membered C_nH_n system…' But to attain a closed configuration, $4x + 2$ electrons are required to fill the lowest nondegenerate A level and then to fill completely the first x pairs of degenerate levels above it. Systems with $4n$ electrons, by contrast, are more stable with a set of alternating single and double bonds. Experiment shows that a planar, carbocyclic system C_4H_4 is too unstable to have any permanent existence; cyclobutadiene proves instead to possess a singlet electronic ground state that is a reactive rectangular molecule with two short double and two long single bonds. {29} And C_8H_8, cyclooctatetraene, is not planar, but more or less tub or boat form, and has no resonance stabilization of the kind predicted. {30} LCAO-MO theory offers a direct explanation of these facts, and moreover leads to the '$4n + 2$ Rule' just cited, which generalizes the result for benzene to other carbocyclic systems with $4n + 2$ electrons. {31} This is Hückel's Rule, one of the great theoretical achievements of LCAO-MO Theory.

Chapter 5 Notes

1 See, for example, G. James and M. Liebeck, *Representations and Characters of Groups* (Cambridge: Cambridge University Press, 1993), Ch. 3 and 4.

2 See my discussion in Sec. II of 'Plato and Leibniz against the Materialists,' *Journal of the History of Ideas* 57 / 2 (April 1996), 255-76.

3 James and Liebeck, *Representations and Characters of Groups*, Ch. 4, 5 and 30; see also K. Mainzer, *Symmetries of Nature: A Handbook for Philosophy of Nature and Science* (Berlin and New York: Walter de Gruyter, 1996), Ch. 2 and 4.

4 F. A. Cotton, *Chemical Applications of Group Theory*, Third Edition (New York: John Wiley and Sons, 1990), Part II (Applications).

5 Mainzer, *Symmetries of Nature,* op. cit., Ch. 2, sec. 2.31.

6 (New York: MacMillan, 1953).

7 (Waltham, Ma. and Toronto: Xerox College Publishing / Ginn and Company, 1964).

8 Cotton, *Chemical Applications of Group Theory*, Ch. 3. I would like to thank F. Albert Cotton for granting me permission to follow the exposition in his textbook very closely, here and in the next section. I could not have made my philosophical points without this borrowing. I would also like to thank Roald Hoffmann for extensive comments on this chapter, and for introducing me to Cotton's book via the link of Representation Theory, which is so important to Wiles' and Ribet's proof of Fermat's Last Theorem and also the key to Cotton's textbook.

9 Ibid., Ch. 3, sec. 3.11.

10 Ibid., Ch. 4, sec. 4.2.

11 R. C. Bishop, 'Patching Physics and Chemistry Together,' *Philosophy of Science*, Fall 2006 (details to come).

12 H. E. White, *Physical Review* 37 (1931), 1416.

13 F. Brescia, J. Arents, H. Meislich, A. Turk, *Fundamentals of Chemistry: A Modern Introduction*, 1966, 185-6.

14 Brescia et al., *Fundamentals of Chemistry*, 289.

15 Cotton, *Chemical Applications of Group Theory*, 144.

16 Ibid., 145.

17 Ibid., 146-147.

18 Ibid., 158.

19 Robin Hendry analyzes this debate in section 4 of his 'The Physicists, the Chemists, and the Pragmatics of Explanation,' forthcoming. He argues that John Clarke Slater, trained as a physicist, and Charles Coulson, trained as a chemist, approached the application of quantum mechanics to the study of molecular structure differently because they held different explanatory ideals. For the former, it was more important to get the fundamentals right in terms of physics; for the latter, it was more important to provide workable models of chemically interesting molecules. Like Bishop, quoted above, Hendry emphasizes the autonomy and explanatory success of chemical structure theory.

20 19 / 10 (Oct. 1951), 1271-1278.

21 Roothan and Parr, *Journal of Chemical Physics*, 17 (July 1949), 1001.

22 *Journal of Chemical Physics*, 18 / 12 (Dec. 1950), 1561-1563.

23 *Journal of Chemical Physics*, 19 / 10 (Oct. 1951), 1271-1278.

24 Ibid., 1271

25 'Hyperconjugation,'*Journal of the American Chemical Society,* 63, 41 (Jan. 1941), 41-56.

26 Mulliken and Parr, 'LCAO Molecular Orbital Computation of Resonance Energies of Benzene and Butadiene,' 1276.

27 Ibid., 1271.

28 Mulliken, Rieke and Brown, 'Hyperconjugation.

29 Reeves, Henery, Pettit, *Journal of the American Chemical Society*, 91 (1969), 5888-90; Dewar and Gleicher, *Journal of the American Chemical Society*, 87 (1965), 3255.

30 Person, Pimental, Pitzer, *Journal of the American Chemical Society*, 74 (1952), 3437.

31 Some chemists have objected that Cotton overstates the case, though he himself (and I) remain unconvinced, because full valence bond treatment of these molecules has improved in the recent past. See R. Hoffmann, S. Shaik, P. C. Hiberty, 'A Conversation on VB or MO Theory: A Never-Ending Rivalry?' in *Accounts of Chemical Research*, 36 /10 (Oct. 2003), 750-756.