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Theory and Intuition

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Theory and Intuition

by

E. A. McCullough, Jr.

SIXTY-FIFTH HONOR LECTURE DELIVERED AT THE UNIVERSITY

A basic objective of the Faculty Association of Utah State University, in the words of its constitution, is:

to encourage intellectual growth and development of its members by sponsoring and arranging for the publication of two annual faculty research lectures in the fields of (1) the biological and exact sciences, including engineering, called the Annual Faculty Honor Lecture in the Natural Sciences; and (2) the humanities and social sciences, including education and business administration, called the Annual Faculty Honor Lecture in the Humanities.

The administration of the University is sympathetic with these aims and shares, through the Scholarly Publications Committee, the costs of publishing and distributing these lectures.

Lecturers are chosen by a standing committee of the Faculty Association. Among the factors considered by the committee in choosing lecturers, are in the words of the constitution:

(1) creative activity in the field of the proposed lecture; (2) publication of research through recognized channels in the field of the proposed lecture; (3) outstanding teaching over an extended period of years; (4) personal influence in developing the character of the students.

E.A. McCullough, Jr., was selected by the committee to deliver the Annual Faculty Honor Lecture in the Sciences. On behalf of the members of the Association we are happy to present Professor McCullough's paper.

Committee on Faculty Honor Lecture

Theory and Intuition

by

E. A. McCullough, Jr.

**65th Faculty Honor Lecture
Utah State University
Logan, Utah**



Theory and Intuition

by

E. A. McCullough, Jr.*

Among the practitioners of science are people who are called *theorists*, and this lecture is concerned with the question, Just what is it that a theorist does?

If an experimentalist does experiments, then a theorist presumably does theories. What is a theory? My dictionary defines it as “. . . a system of assumptions, accepted principles, or rules of procedure devised to analyze, predict or otherwise explain the nature or behavior of a specified set of phenomena.”¹

Those who now understand perfectly what a theorist does may stop reading here because everything that follows will be superfluous. For those who are still somewhat in the dark, the rest of this lecture will attempt to explain, in rather more concrete terms, just what it means to be a theorist. Of course, I cannot presume to speak for all theorists; therefore, I am going to discuss only what it means to be a theorist within the context of my own specialty, theoretical chemistry.

Since I occasionally encounter people who seem to feel that “theoretical” is synonymous with “lacking any practical utility,” I also want to indicate why such is not the case, at least for theoretical chemistry. To put it another way, I hope to correct the misperception about theorists perhaps best expressed by my mother when she exclaimed, “You mean you get paid to do that?”

What does it mean to do theoretical chemistry? Let me begin by sketching very roughly what chemistry is. Science has been divided

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Scientific research is rarely an individual effort; it generally requires both help and money. It has been my privilege to collaborate with two very fine scientists and very fine people as well. They are Dr. Ludwik Adamowicz, a citizen of Poland, and Dr. Phillip A. Christiansen, now at Potsdam, New York. Financial assistance has been provided by the Utah State University Office of Research and the National Science Foundation.

into a number of subdisciplines: physics, chemistry, biology, etc. The boundaries between subdisciplines are somewhat arbitrary and often fuzzy, yet one can usually recognize the subdisciplines by the basic assumptions they employ and the phenomena they admit for consideration.

The principal axiom of chemistry is the atomic hypothesis: (1) most of the material contents of the universe are composed of very tiny entities called *atoms*; (2) each atom consists of a certain number of negatively charged *electrons* moving about a positively charged *nucleus*; and (3) although there are approximately one hundred fundamentally different kinds of atoms, they can combine with each other to form *molecules* in an enormous number of ways. The interpretation of natural phenomena in terms of atoms and molecules essentially defines the subdiscipline of *chemistry*.

To clarify what chemistry is, it may be helpful to consider some examples of what it isn't. At the one extreme, any phenomenon whose interpretation depends on knowing what an electron is, or on knowing what a nucleus is made of, isn't chemistry. All we need for chemistry are a few properties of electrons and nuclei.² Questions about *why* they have these properties are not chemical questions, not because they are uninteresting, but because they are unnecessary for chemistry. Instead, such questions belong in another subdiscipline, *physics*.

At the other extreme, consider biology. Biologists made considerable progress without ever having to invoke the assumption that living things were made of atoms. For example, the principles of genetics were worked out without this assumption. However, this example also illustrates the arbitrariness of dividing science into subdisciplines because we have since discovered an atomic interpretation of genetics in terms of the molecular structure of DNA. In fact, the atomic interpretation of biology has become so prevalent and fruitful that it has spawned a whole new subdiscipline, *biochemistry*.

Having more or less established the definitional boundaries of chemistry, we can proceed to theoretical chemistry. In defining theory, I wish to adopt the following abbreviated but much sharper version of the dictionary definition quoted earlier: A theory is a system of rules for predicting the behavior of a specified set of phenomena. If the specified phenomena belong to the subdiscipline of chemistry, we have a theory of chemistry. The choice of "predict" rather than

“explain” is very important. A rule that can explain but cannot predict is not really a theory in the scientific sense.

In many contexts, the term *rules* carries absolutist or dogmatic connotations, but such connotations are definitely not intended in scientific usage. Indeed, the one absolute in science is that there are no absolutes. The scientific “truth” of any theory is determined solely by the agreement between the predictions of the theory and experimental observations. This appeal to experimental evidence is precisely what distinguishes scientific truth from many other kinds of truth. Therefore, the term *rules* should be read as “instructions” or even as “recipe.”

The strength of any theory is measured by testing the scope and the precision of its predictions. The latter test means that ultimately we are seeking rules that predict the behavior of phenomena quantitatively. Mathematics is our most useful language for expressing quantitative statements precisely and concisely. Consequently, our strongest theories are expressed often most simply in mathematical terms. The converse isn’t necessarily true, of course. The mere fact that a theory can be expressed mathematically doesn’t make the theory strong. This fact is easy to forget in an era of computers. A computer certainly can be used to derive the predictions of any theory if the rules of the theory can be expressed in a suitable mathematical form. Once the rules have been programmed into the computer, the computer usually can derive the predictions much faster and more reliably than could any human. This use of computers is indispensable in many areas of theoretical research—theoretical chemistry, especially—but it does nothing to increase the validity of the theory. As the computer scientist Joseph Weizenbaum has remarked, “If astrology is nonsense, then computerized astrology is just as surely nonsense.”³

I now wish to address the question, What does it mean to be a theorist? If a theory is a set of rules for predicting the behavior of a specified set of phenomena, ostensibly the fundamental problem for theorists is to discover what are the rules. This is indeed the fundamental problem; but, surprisingly, it is not the task that occupies most theorists, and certainly not theoretical chemists. In fact, theoretical chemists never have to confront this problem, for the simple reason that the rules of chemistry are already known!

Astonishing as it may seem, this statement is absolutely correct, as far as we know. To have the rules of chemistry means to have the rules for the behavior of atoms and molecules, and we believe we have those rules. Furthermore, these same rules must be applicable to the behavior of any phenomenon that can be reduced to the behavior of atoms and molecules, which is almost everything from atoms on up. It certainly includes those phenomena comprising the subdisciplines of chemistry, biology, geology, and most of astronomy and physics as well.

Two questions come to mind immediately. First, do we have the rules for everything? The answer is no. For example, we have no theory that predicts all the properties of an electron. (There are many other examples.) Discovering the rules for these phenomena is the task a very small group of theorists have set for themselves. They are theoretical physicists working at the frontiers of fundamental physics. These pioneers are by and large regarded as the superstars by other theorists. In a very real sense, they create the world we live in.

The second question is, Why are there any other theorists? If we have the complete rules of chemistry, why do we need theoretical chemists? Indeed, why do we need any chemists at all? A complete theory of chemistry can predict the outcome of any chemical reaction. Of course, it may still be desirable to carry out selected chemical reactions in order to manufacture something useful, but that activity is the domain of *chemical engineering*. There is certainly no reason to carry out a chemical reaction in order to learn something new, for if we already have the rules, there is nothing new to be learned.

Although this view is actually held by some people, it is, at best, hopelessly simplistic. The reason is expressed very clearly by the theoretical physicist R. P. Feynman in his classic introductory physics text.⁴ We may, says Feynman, draw an analogy between the natural world and a game of chess. Scientific theories are then analogous to the rules of chess and working out the predictions of the theories corresponds to playing the game. But there is a very big difference between knowing the rules of chess and being able to play. So it is with chemistry. We know the rules, but we cannot play very well. Why? The theoretical physicist P.A.M. Dirac, who codiscovered the rules of chemistry, explained it this way:

The underlying physical laws necessary for the mathematical

theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.⁵

In other words, we don't understand what the rules are telling us.

Trying to understand what the rules are telling us is the principal task of the vast majority of theorists. I consider this task to be interesting, challenging, and important, and I would like to devote the rest of this lecture to describing how we go about it in the particular case of theoretical chemistry.

We first need to know, what are the rules of chemistry. Actually, there are two complementary sets of rules of roughly equal importance. Understanding what either set is telling us is sufficiently difficult that a theoretical chemist will often specialize in one set or the other.

The first set contains the rules for predicting the behavior of an individual molecule, given that it consists of so many electrons and nuclei with such and such properties (atoms are just special cases of molecules). These rules are known as *quantum mechanics*, and the application of them to chemistry is usually termed *quantum chemistry*.

It may not be readily apparent why we need any rules of chemistry other than quantum mechanics. The reason has to do with statistics. Almost any chemical phenomenon of interest will involve contributions from the individual behavior of enormous numbers of molecules, of the order of a billion-billion (10^{18}), at least. The behavior of any particular molecule at any particular time may vary over a wide range; but we don't really care, for most purposes, what each molecule is doing. Usually, we are only interested in the *average* behavior of all of them at once. The rules for inferring this average behavior from the spectrum of behavior of an individual molecule are called, appropriately enough, *statistical mechanics*.

Both quantum mechanics and statistical mechanics are relatively recent discoveries. Statistical mechanics dates from approximately the middle of the nineteenth century. Quantum mechanics is a child of the twentieth century but only barely. Born in 1900, it reached essentially full maturity as the theory of atoms and molecules between 1925 and 1929.

It is remarkable that the correct rules for predicting the average behavior of large numbers of molecules (statistical mechanics) were discovered before the correct rules for predicting the behavior of an individual molecule (quantum mechanics). How was that possible?

The answer is that prior to the discovery of quantum mechanics, theorists believed that they already had the correct rules for predicting the behavior of an individual molecule. These rules were *Newtonian mechanics*, which were laid down by Isaac Newton in 1687 and refined over the next two centuries into an elegant and all-powerful theory. In every case where these rules had been applied, they had worked perfectly; they correctly predicted the behavior of everything from billiard balls to planets. There was no reason to expect that they would not work just as well for molecules; but when the application to molecules was attempted, the predictions turned out to be wrong.

The first evidence that classical mechanics (as Newtonian mechanics is now called) was incorrect on the atomic scale was obtained by using statistical mechanics to predict the average behavior of a large number of molecules which individually obeyed classical mechanics. Initially, the predictions worked pretty well, which inspired confidence not only in statistical mechanics but also in the atomic hypothesis. Yes, incredible as it seems to a modern chemist, as late as 1900 there were still eminent chemists who argued that although atoms and molecules were useful mental models, they were not *real*. In fact statistical mechanics was largely responsible for demolishing this viewpoint by showing that literal acceptance of the atomic hypothesis allowed one to predict observable large scale properties of matter. Unfortunately, the developers of statistical mechanics⁶ didn't know when to quit. As they pushed their predictions further, the agreement between theory and experiment seemed to get worse. It gradually became apparent that the atomic hypothesis, classical mechanics, and statistical mechanics were mutually incompatible.

In 1900, Max Planck demonstrated that the trouble lay with classical mechanics,⁷ the last place a nineteenth-century physicist would have suspected. Planck's revolutionary discovery that the Newtonian rules simply didn't work for atoms and molecules marked the dawn of quantum mechanics. For the next three decades, theorists searched frantically for the new rules. It all came together between

1925 and 1929. A particularly crucial event for chemistry occurred in 1926. In that year, Erwin Schrödinger published a series of papers setting out the fundamental new rules for predicting the behavior of atoms and molecules.⁸ In essence, his rules can be reduced to the single statement

$$\hat{H}\Psi = \frac{ih}{2\pi} \frac{\partial \Psi}{\partial t}$$

which is called the *time-dependent Schrödinger equation*.

Before my physicist colleagues jump all over me, I should hasten to add that the Schrödinger equation cannot really predict *all* behavior of atoms and molecules,⁹ but it is certainly good enough for most chemical purposes. In particular, it can account for chemical bonding with a very high degree of accuracy.

As a theoretical chemist specializing in quantum mechanics, my job is trying to understand what the Schrödinger equation is telling us. You may find it difficult to believe that one fairly simple looking equation could tell us anything useful, much less contain all of chemistry. The apparent simplicity, however, is due to our having cast the equation into a particular mathematical form specially chosen to make it look simple. Before considering in detail the application of this equation to chemistry, we should pause to examine the new and strange worldview that quantum mechanics employs.

Whenever new rules of nature have been discovered, they have often required profound revisions in our way of looking at things. This is especially true with quantum mechanics. The revisions it requires might be divided into two classes: revisions of intuition and revisions of philosophy.

Revisions of intuition are necessary because the predictions of quantum mechanics often clash violently with our intuitive expectations about the behavior of things. This is clearly illustrated by the so-called wave-particle duality. At the fundamental level, classical physics recognized only two mutually exclusive categories of phenomena: waves and particles. For instance, an electron was a particle, whereas light was a wave. According to quantum mechanics, however, what we normally think of as a particle may sometimes act

like a wave and vice versa. Despite how bizarre and counterintuitive this seems to us, it is absolutely correct. Experiments exhibiting wave phenomena (interference, diffraction) are routinely performed with electrons, and a sensitive photocell can record the arrival of individual particles of light (photons). Since the predictions of quantum mechanics are in accord with experiment while our intuition is not, it is our intuition that must be revised. The problem with our intuition is that it is basically Newtonian because the rules of quantum mechanics reduce to the rules of Newtonian mechanics in the large-scale world of our everyday experience. We have no direct experience of the world of electrons, and when we extrapolate our Newtonian intuition to that level, it fails. We simply must accept revisions of our intuition if we hope to deal with the physical world.

Revisions of philosophy present quite a different problem. The *philosophical interpretation* of quantum mechanics still provokes fierce debate. In this lecture, I don't wish to embark on a discussion of the philosophy of quantum mechanics. Many excellent books have been written on the subject.¹⁰ I only wish to point out that our current, most widely accepted interpretation places stringent limitations on what we can possibly know about the world. In particular, the *most* we can know about any event is the probability, or chance, that it will happen. This limitation does not arise from incomplete information; the probability *is* the complete information. Obviously, this point of view represents a far cry from the deterministic certainty of Newtonian mechanics, and the philosophical implications are, to say the least, disquieting.

Some people find the implications so disquieting that they cannot accept them. This list has included some famous scientists—Albert Einstein, for one. Although admitting that quantum mechanics was eminently successful in predicting the probabilities of events, Einstein could never accept that probabilities were the most that could be known about nature. He believed that quantum mechanics was only the shadow of some more complete, as-yet-undiscovered theory.

Other people have gone in the opposite direction. Unable to accept an interpretation of quantum mechanics that asserts that natural events are inherently chancelike, they have been led to reject quantum mechanics altogether. I show part of an advertisement from a recent issue of *Scientific American*.¹¹

The Journal of Classical Physics

This new journal is intended for Scientists and knowledgeable laypersons who feel Quantum Wave Mechanics is non-predictive and ultimately counterproductive and that classical model development is preferred.

The assertion that quantum mechanics is “non-predictive” is simply wrong if the intended sense is “cannot predict the observable results of experiments.” The predictions may be strange and the philosophical implications unpalatable, but quantum mechanics works extremely well, and it has no competitors in this regard.

The Schrödinger equation supplies the machinery for making the predictions of quantum mechanics known to us. These predictions take the form of probabilities, the chance that an event of interest will occur. This probability information is contained in Ψ (Greek psi, pronounced “sigh”), which is called the *wavefunction*. For a molecule, Ψ could tell us the probability of finding the electrons arranged in a certain pattern about the nuclei at a certain time. Note that Ψ does not tell us that we *will* find the electrons arranged in that way, only the chance that we will. This information is sufficient, because given the probabilities of all possible arrangements of electrons and nuclei, we can calculate any measurable property of the molecule—the energy, for example. So Ψ is the answer, the output.

What is the input? What determines whether we get the wavefunction for methane or ethane? We supply that information in the form of \hat{H} , which is called the *hamiltonian operator*, a hamiltonian for short. Methane and ethane differ because the hamiltonians for the two molecules differ.

What is a hamiltonian? Unfortunately, there is no way to answer that question in a lecture like this. The best I can do is show one. This is the hamiltonian for the relatively simple molecule, diatomic hydrogen, H_2 .

$$\hat{H} = -\frac{1}{2M_H}(\nabla_a^2 + \nabla_b^2) - \frac{1}{2}(\nabla_1^2 + \nabla_2^2) -$$
$$\frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} + \frac{1}{r_{ab}}$$

Plug this hamiltonian into the Schrödinger equation, solve for Ψ , and

you have the complete story on H_2 , according to quantum mechanics.¹² The complexity of this hamiltonian illustrates that the apparent simplicity of the Schrödinger equation is deceptive. The equation is really far more complicated than it looks when written in the simple mathematical form presented earlier.

It is, in fact, so complicated that we are unable to solve it exactly in nearly every case. We can only solve it exactly for one molecule. We can't even solve it exactly for any atoms except hydrogen. It may seem rather pretentious to claim that an equation that can be solved exactly only for one atom and one molecule contains all chemistry. How can we be so certain it is correct?

There are several pieces of evidence. First, there are those few cases where we can obtain exact solutions. In these cases, the agreement with experiment is spectacular. For example, the Schrödinger equation predicts the wavelengths at which the hydrogen atom absorbs light to an accuracy of about one part in one hundred thousand. That a natural phenomenon could be described so precisely by a formal mathematical equation so surprised the mathematician Stanislaw M. Ulam that he questioned the physicist Enrico Fermi about it. Fermi replied, "It has no business being that good, you know Stan."¹³ We believe in the Schrödinger equation because we don't believe that this level of accuracy can be accidental. (Incidentally, classical mechanics gives hopelessly incorrect predictions for the hydrogen atom.)

A second reason for having faith in the Schrödinger equation is that even a rudimentary understanding of what it is telling us may lead to a sudden unification—one fundamental, beautifully simple interpretation of a whole set of previously incomprehensible phenomena. A classic chemical example of such a unification involved what Sherlock Holmes might have called *The Case of the Aromatic Sextet*.

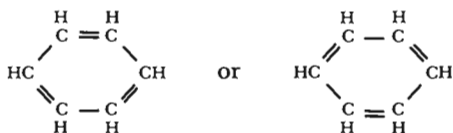
The *Aromatic Sextet* is not a musical group, but rather a term coined by chemists in prequantum-mechanics days. It refers to the unusual stability displayed by monocyclic polyenes with six pi electrons. In order to explain this phenomenon, I shall have to introduce just a bit of organic chemistry.

Chemists have long appreciated the unique ability of the carbon atom to form up to four covalent bonds. Well before the advent of

quantum mechanics, chemists also began to suspect that a covalent bond between two atoms involved a shared pair of electrons, one electron being donated by each atom. Thus, carbon must have four electrons readily available to form covalent bonds.

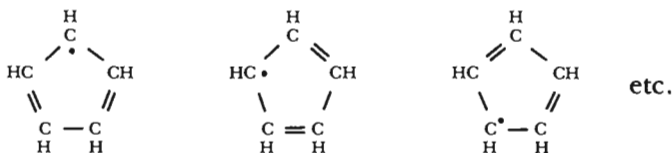
Suppose we take a carbon atom and bond it to a hydrogen atom, leaving the carbon with a residual bonding power of three. Then suppose we take a number of these carbon-hydrogen units and bond the carbons together to form a closed ring. The resulting molecule is called a *monocyclic polyene*.

Problems arise when we try to draw standard chemical bond diagrams for these molecules. Forming one bond between each carbon atom and its two adjacent neighbors still leaves one unpaired electron, a *pi* electron, on each carbon. The pi electron can be used to form additional bonds between carbons, but not in a unique way. For example, with the well-known six carbon monocyclic polyene, the benzene molecule, we find two apparently equivalent possibilities,

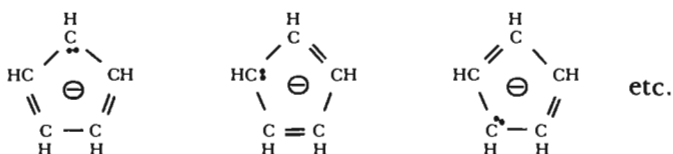


This bonding ambiguity suggests that benzene may be unusual, and it is. It is much more stable than chemists would have expected by analogy with nonring molecules of similar composition. A theory of the unusual stability of benzene was developed based on the bonding ambiguity. The equivalent diagrams were called *resonance structures*; and *resonance theory* postulated that the more of them you could draw, the more stable the compound would be, relatively speaking.

Resonance theory broke down when applied to the five carbon ring. This system has one electron that cannot be paired to form a bond. Such a molecule is called a radical, and the unpaired electron is usually indicated by a dot in the bond diagram. Since this electron could be located on any one of the five carbons, the cyclopentadienyl radical has five resonance structures.



Resonance theory then predicts unusual stability for this radical, which experimentally it doesn't seem to have. However, if we add an extra electron, forming the negatively charged cyclopentadienyl anion, we do get a system of unusual stability. This is puzzling, because the anion has the same number of resonance structures as the radical,



Furthermore, if we now remove both electrons, leaving a positively charged "hole" on one carbon, we again get five, because the hole could be on any one of the carbons. Yet this species, the positively charged cyclopentadienyl cation, is experimentally known to be very unstable.

Note that both the cyclopentadienyl anion and benzene have six pi electrons. The almost magical stability conferred by six pi electrons was the source of the term "aromatic sextet" (aromatic because the prototype, benzene, has a characteristic odor).

The mystery was solved by Erich Hückel in a series of papers he began publishing in 1931, only five years after Schrödinger. Hückel showed that a very crude application of the Schrödinger equation *predicted* that those monocyclic polyenes with six pi electrons would be relatively the most stable. Due to many oversimplifications, Hückel's treatment did not constitute even an approximate solution of the Schrödinger equation, in the sense to be discussed below. Nevertheless, he correctly showed that the pattern of stability displayed by the molecules is inherently contained in the Schrödinger equation. In fact, the pattern can be deduced almost entirely from *symmetry* considerations. Any symmetry of the molecular framework is preserved in the hamiltonian. This places mathematical restrictions on the form of the wavefunction, which ultimately appear in the behavior of the molecule. These restrictions can be discovered with the mathematical techniques of *group theory*. Group theory is the closest thing to getting something for nothing in quantum mechanics, for by using it we can learn something about the wavefunction without having to solve the

Schrödinger equation. Hückel's treatment took proper account of the symmetry, so it gave the correct pattern. Refined versions of his approach are being pursued today. The 1981 Nobel Prize in Chemistry was awarded for work that built directly on the foundation he established.

Hückel's work provided a qualitative understanding of what the Schrödinger equation could tell us for some fairly complicated molecules. At about the same time, others were attempting to understand what it could tell us quantitatively. They studied much simpler systems than Hückel, but systems still far too complicated to be solved exactly. Their approach was to develop and apply mathematically sound methods for finding *approximate* solutions of the Schrödinger equation.

There are many such methods, but they all share common features that distinguish them from the Hückel approach and its descendants. An approximate wavefunction of a certain form and level of approximation is selected, but then no further approximations are to be made. All subsequent computations are carried out as nearly exactly as possible to yield unambiguous numerical predictions. These methods are called *ab initio* methods. For some *ab initio* methods, it is possible to prove *convergence*, which means that within the chosen form, as the level of approximation is increased, the approximate wavefunction must approach, or converge to, the exact one. Such methods guarantee that we can obtain an answer of any desired accuracy simply by doing enough work. Unfortunately, for none of these methods is it possible to specify in advance what is "enough," and "enough" differs for different molecular properties. It also differs for different methods applied to the same molecule or the same method applied to different molecules. To top it off, experience has shown that unless we are clever, "enough" is invariably "too much" for most chemical problems.

The thing that prevents us from solving the Schrödinger equation exactly for atoms and molecules is *many electrons*, where "many" means "more than one." The hydrogen atom, with one electron, can be solved exactly. The helium atom and hydrogen molecule, both with two, are already insoluble. Thus, it was deemed imperative to obtain high-accuracy approximate solutions for these two systems if quantum mechanics was to be taken seriously as *the* theory of atoms and

molecules. Such solutions were indeed obtained very early. Quite sophisticated approximate wavefunctions were employed so that “enough” might be achieved at a fairly low level—since it all had to be done by hand. The calculations of E. A. Hylleraas on helium in 1929 and H. M. James and A. S. Coolidge on diatomic hydrogen in 1933 preceded the development of digital computers by more than a decade.

The work of James and Coolidge was especially important for chemistry because it demonstrated that quantum mechanics could describe a typical chemical bond with high accuracy. Subsequent calculations have carried their approach much further. The most recent comparison between theory and experiment indicates that quantum mechanics predicts the strength of the chemical bond in H_2 to an accuracy of at least five parts in one hundred thousand.¹⁴

Although two electrons are a distinct advancement over one, it still falls far short of all chemistry. Unfortunately, the special methods developed by James and Coolidge for two electrons have proved nearly impossible to generalize. The mathematical complications inherent in their choice of approximate wavefunction are just too great, even with computers. We need another way.

One possible way is to begin by asking, What makes the Schrödinger equation for several electrons insoluble? The answer is electron-electron interaction. Electrons are negatively charged; they repel one another. If electrons were noninteracting, an exact solution of the many-electron problem could be obtained by finding individual wavefunctions for the individual electrons instead of having to find one big wavefunction for all of them at once. A wavefunction for an individual electron is called an *orbital*. Although orbitals can never provide an exact solution for real interacting electrons, they might provide a decent approximation.

It is very simple to find orbitals if we completely ignore the electron-electron interaction. Unfortunately, that approximation is too crude; it gives very poor predictions. A better approximation is to account for as much of the interaction as possible. It isn't possible, of course, to incorporate *all* effects due to interaction into orbitals; that would be tantamount to an exact solution. It turns out that the most we can do is include the *average* effects. An approximation in which each orbital is allowed to adjust to the average repulsive interaction

produced by the electrons in all other orbitals is called a *self-consistent-field* or *SCF approximation*.

I say “an” approximation rather than “the” approximation because there are many SCF approximations. They differ in how much freedom is permitted for the orbitals to adjust. The simplest approximation is to retain as many features of orbitals for noninteracting electrons as possible. We may insist that the orbitals preserve *symmetry*, meaning, for example, that if a particular orbital for noninteracting electrons is spherical, it must remain spherical for interacting electrons. We may also insist on using only the absolute minimum number of orbitals. This is not one per electron but fewer because two noninteracting electrons may be described by the same orbital. A SCF approximation in which all these features of the noninteracting electron problem are imposed as restrictions is called a *restricted SCF approximation*. It provides the simplest description of a many-electron system that at the same time accounts for as much electron-electron interaction as possible.

It is not difficult to derive equations for restricted SCF orbitals, and these equations are much simpler than the many-electron Schrödinger equation. Even so, solving them is not easy, since each orbital depends on all the others through the average interaction. Although a surprising number of restricted SCF calculations on atoms were performed by hand, principally by D. R. Hartree and coworkers, the application of this approximation to molecules really had to await the introduction of computers. Much of the pioneering work in the development and computer implementation of methods for molecular SCF calculations was carried out by C. C. J. Roothaan and his collaborators in the 1950s and 1960s. Today restricted SCF calculations on molecules are as routine as any *ab initio* calculations are ever likely to become. They have even been performed on the guanine-cytosine base pair of DNA, a system with twenty-nine nuclei and one hundred thirty-six electrons.

How good is the restricted SCF approximation? Qualitatively, it is very good. It predicts the structure of the periodic table and the relative strengths of most chemical bonds very well. In fact, the explanation of these two subjects that we present to our students in freshman chemistry is based essentially on this approximation. Quantitatively, the *best* restricted SCF approximation is the one that puts

no limitations on the adjustment of the orbitals other than those already inherent in the definition of "restricted." Experience shows that "a best restricted" SCF calculation will typically yield better than ninety-eight percent of the total molecular energy for a small molecule. Now a quantitative approximation with less than two percent error would be eminently satisfactory in many applications. But it isn't necessarily good enough for chemistry.

To see why not, consider what we want to predict. We certainly want to be able to predict chemical bonding. How would that be done? Well, the most stable arrangements of any physical system are those of lowest *energy*. If the energy of two atoms is lowered by bringing them close together, they will tend to remain close together. That is what is meant by a bond. If, on the other hand, the energy is increased, they will tend to fly apart. So the formation of a chemical bond depends on the *difference* in energy between two atoms close together and two atoms far apart. The magnitude of the energy difference is precisely the *bond strength*.

As an example, take diatomic fluorine, F_2 . The best restricted SCF total energy of two separated fluorine atoms is -198.82 in convenient units called hartree, which need not concern us here. The energy of the two atoms at a typical bond distance is -198.77 in the same units. The energy has increased (become more positive or less negative) so the prediction is: no bond.

This prediction is somewhat embarrassing, for F_2 is a well-known molecule. Note that the two energies differ by only five in the fifth figure or -0.05 ; on that tiny difference hinges the prediction. But, if the restricted SCF approximation is only reliable to about two percent of the total energy, the numbers we are subtracting are probably only correct to about three figures at most. The residual error in the restricted SCF approximation has completely invalidated the prediction.

This is not an isolated example. In fact, we now know that the restricted SCF approximation is too simple an approximation to be quantitatively satisfactory for chemistry. Unfortunately, it is only conceptually simple. Computationally, it is already fairly difficult to apply, requiring extensive use of computers, etc. Doing better inevitably means doing even more work.

The most straightforward approach for doing better is what might be called the "brute force approach." It is possible to prove that

the restricted SCF approximation can be viewed as merely the first level of approximation in any one of a number of convergent approximate solution methods. The brute force approach says that if the first level isn't sufficient, proceed to the second level, or to the third, or however far it takes. Eventually, chemical bonding, or any other phenomenon for that matter, must fall out.

The trouble with the brute force approach is that it appears to be hopeless. Consider the F_2 example. If differences in the fifth figure of the total energy are the source of bonding, the level of approximation must be increased until both total energies are accurate to better than five figures. The fact that we cannot predict precisely what level that will be is a minor problem, which can be solved with experience. The major problem is that we are talking about at least one hundred times more accuracy than the restricted SCF approximation. One must be cautious in issuing pronouncements, but there seems to be no possibility in the foreseeable future of achieving this level of accuracy for any but the smallest molecules. Even if it could be achieved, it wouldn't suffice, for there are phenomena we want to predict that would require yet more accuracy. Two neon atoms don't form a normal chemical bond, but they do form a very weak *van der Waals* bond. To predict that at all, we would need something like two hundred times more accuracy still.

What do we really want? We don't want an exact solution of the Schrödinger equation; we want to predict chemical phenomena. To be sure, if we had an exact solution, we could make predictions, but we would settle for any level of approximation that gave the same predictions. Now it is clear that no approximation can reproduce *all* the predictions of the exact solution, but for some specific phenomenon it might be possible to devise a low level approximation that gave correct predictions. Unfortunately, even if it is possible, there are no straightforward mathematical techniques, no guaranteed methods, to guide us. We have to fall back on *intuition*.

Now falling back on intuition is admittedly a risky proposition. The unreliability of our intuition in the atomic realm has already been noted. Nevertheless, an intuitive approach seems to be the only way to make significant progress, and significant progress is already being made in just this way. Here is how intuition has been applied to the problem of chemical bonding.

The periodic table is periodic because different atoms may have similar properties. Fluorine and chlorine have different numbers of electrons (nine and seventeen respectively) but similar chemistry. Therefore, not all of the electrons can be equally important in chemical bonding. Of course, chemists have known this for a long time; the concept of a covalent bond as a shared electron pair ignores the other electrons. Chemists introduced the name *valence electrons* to denote those electrons that appear to play a major role in bonding. To translate these observations into quantum chemistry terms, it seems reasonable to assume that only the valence electrons need to be described accurately in order to predict bonding.

Again consider F_2 . The fluorine atom has one unpaired electron, so from the simplest viewpoint, F_2 is held together by a single electron pair covalent bond. The simplest step beyond restricted SCF then consists of increasing the level of approximation for just that pair. The treatment of all (sixteen) other electrons remains at a restricted SCF level. Now it can be shown that such treatment of the other electrons undoubtedly introduces large errors. But the assumption is that if these electrons are unimportant in bonding, whatever errors are committed in describing the behavior of these electrons will be the same whether the two fluorine atoms are close together or far apart. When the energy difference between the two arrangements of atoms is computed, these large errors should very nearly cancel out.

As a technical aside, let me indicate how the level of approximation for a pair of electrons can be increased. One very common method is to describe the pair by more than the minimum number of orbitals. To see how this works, suppose one electron is partially described by an orbital that gives a high probability of finding the electron say, in close to a nucleus. The other electron may at the same time be described by orbitals, some of which give a high probability of finding that electron far from the nucleus, hence far from the first electron. In this way, electron-electron interaction within a pair can be accounted for in detail, which is just a fancy way of saying that the two electrons can be kept apart better.

Now to return to F_2 and the crucial question: Can bonding be obtained with a low level approximation? The answer is yes.¹⁵ Improving the description of the bonding pair by just one orbital beyond restricted SCF leads to the prediction of a stable molecule. Quan-

tatively, however, the predicted bond strength is still pretty poor—less than half of the experimental value. To do better, it is necessary to realize that the fluorine atom really has five valence electrons. In addition to the unpaired electron, there are four others that behave similarly. Indeed, all five are described by equivalent orbitals in the restricted SCF approximation. Even though only one of them (the unpaired one) is primarily involved in bonding, bond formation may substantially alter the behavior of the other four; hence, errors in the description of this behavior may not cancel out. If the level of approximation is increased for these electrons as well, a bond strength within a few percent of experiment is obtained. Note that eight electrons are still being described only at the restricted SCF level. And note especially that the total energies are improved hardly at all; they are still accurate only to about three figures. To reiterate, the only way this approach can work is for the errors between the third and fifth figures to cancel in taking the difference in energy between two atoms far apart and two atoms close together. The actual calculations confirm our intuitive feeling that such cancellations can be built into a carefully chosen, low level approximation.

A more difficult example is diatomic nitrogen, N_2 . The nitrogen atom has three unpaired electrons, giving three electron pair bonds (a triple bond) in the molecule. The level of approximation for all six electrons must be increased in a mutually consistent way if the crucial cancellation of errors is to arise. One of the most thorough applications of this approach to diatomic nitrogen predicted about eighty-seven percent of the experimental bond strength.¹⁶ So the approach isn't perfect, but it does allow chemically relevant predictions to be made in a finite amount of time with a finite amount of money.

The substitution of intuition for brute force can be applied in the prediction of phenomena other than chemical bonding. A colleague and I recently attempted to calculate the energy required to remove the extra electron from the lithium hydride anion, LiH^- .¹⁷ Removing the extra electron gives the neutral lithium hydride molecule, LiH , so the removal energy is precisely the difference in total energy between anion and neutral. The extra electron can exist in several states, and for one state we computed an energy difference that was only about one one-hundred-thousandth of the total energy of either molecule. That is, the total energies only differed in the sixth figure; and at our

level of approximation, neither total energy could be expected to be accurate much beyond the second figure. Nevertheless, we were able to obtain a (I hope) reliable difference by a judicious choice of approximation, which insured maximum cancellation of error. How good is our prediction? I don't know. No one has done an experimental measurement of the removal energy yet.

This leads naturally into my last topic, which is, Why do we care what the Schrödinger equation is telling us? Is it mere intellectual curiosity? No, there are compelling practical reasons. We want to understand what the Schrödinger equation is telling us because that information is useful. We may need to understand the behavior of molecules in the upper atmosphere, interstellar space, or during an explosion, perhaps. Many exotic molecules that exist in these environments are hard to study in the laboratory because duplicating the extreme conditions of these environments is very difficult and expensive. If we could *predict* the behavior of these molecules, it would be far less time consuming and much less expensive as well.

There are other cases when theoretical calculations appear to provide not just an alternative method for obtaining the desired answer but the only method. For example, in order for two molecules to react with one another and form new molecules, they must be brought close together. Usually, there is an energy barrier or "hill" that must be surmounted before a reaction can occur. The late Henry Eyring showed that from a knowledge of the height of this barrier, the rate of reaction could be predicted. The rate of a reaction is very important information, especially if we hope to use the reaction for manufacturing purposes. Unfortunately, the top of an energy hill is not a stable arrangement of the atoms. Consequently, it is very hard to conceive of a direct experimental method for determining the barrier height. Of course, if we measured the rate, we might be able to work backward to get the barrier height, but the rate is what we want to predict. Fortunately, the Schrödinger equation can be used to predict the energy of an unstable arrangement of atoms just as well as a stable one. There seems to be no experimental alternative in this case.

Not all attempts to understand what the Schrödinger equation is telling us are motivated by such practical considerations. Many attempts are indeed made for the sole purpose of satisfying mere intellectual curiosity. The use of "mere" in this context has decidedly

negative connotations. In this era of economic hardship and shrinking research budgets, the value of such research may seem questionable. But attempting to understand what the Schrödinger equation is telling us is really a way of asking, What is the world like? We believe that the Schrödinger equation is the rule of behavior of an atom, and we believe that atoms are the basic building blocks of the world. Therefore, it seems to me that we ought to attempt to find out what the Schrödinger equation has to say for the same reason that we would seek the counsel of a wise and respected, but rather cryptic, philosopher, or religious leader, or poet. What is the world like? seems to be a fundamental human question. I'm no anthropologist, but I would guess that almost all cultures have belief systems that attempt to supply answers to that question. In our culture, science is one such belief system, and trying to understand what the Schrödinger equation is telling us is part of the ritual.

Nevertheless, the Schrödinger equation isn't dogma, not even for chemistry. If it ever fails to predict the behavior of chemical phenomena, it can and will be replaced. We don't believe this is likely to happen at any time in the near future, but it might, and some years from now another theoretical chemist may be presenting an honor lecture about understanding what the strange new rules of chemistry are telling us. If so, the introduction of the lecture is sure to contain a section harking back nostalgically to the good old days of 1982 when the rules of chemistry were as simple as

$$\hat{H}\Psi = \frac{i\hbar}{2\pi} \frac{\partial \Psi}{\partial t}$$

Notes

1. *The American Heritage Dictionary of the English Language*, ed. W. Morris (New York: Houghton Mifflin, 1969), p. 1335.
2. The necessary properties of most chemical purposes are mass, charge, spin, and magnetic moment, plus the fact that electrons and nuclei are very much smaller than typical atomic dimensions.
3. J. Weizenbaum, *Computer Power and Human Reason* (San Francisco: W. H. Freeman, 1976), p. 35.
4. R. P. Feynman, R. B. Leighton, and M. Sands, *Lectures on Physics* 1 (Reading, Mass.: Addison-Wesley, 1965), chapter 2.
5. P. A. M. Dirac, *Proceedings of the Royal Society* A123 (1929): 714.
6. The principal developers of statistical mechanics were L. Boltzmann and J. W. Gibbs, building on the earlier work of J. C. Maxwell.
7. Planck was not working directly on the statistical mechanics of molecules but on the closely related problem of black-body radiation.
8. Slightly earlier, Heisenberg had published a new theory of atoms and molecules that looked very different from Schrödinger's; however, Schrödinger quickly proved that the two theories are, in fact, equivalent.
9. The major problem with the Schrödinger equation is that it is not consistent with Einstein's principle of special relativity. Dirac's relativistic theory of an electron (c. 1928) indicated that relativistic effects could be approximately incorporated into the Schrödinger equation as correction terms. The corrections have a negligible effect on the chemistry of small atoms, but become progressively more important as the nuclear charge increases. Even Dirac's theory is not fully consistent with special relativity, and a fully consistent theory (quantum electrodynamics) was not developed until the late 1940s.
10. For a technical discussion see M. Jammer, *The Philosophy of Quantum Mechanics* (New York: John Wiley, 1974). For a nontechnical account written for nonscientists see G. Zukav, *The Dancing Wu Li Masters* (New York: William Morrow, 1979).
11. *Scientific American* (December 1981): 86.
12. Well, not quite the whole story. This hamiltonian omits the relativistic correction terms (see note 9).
13. S. M. Ulam, *Adventures of a Mathematician* (New York: Charles Scribner's Sons, 1976), p. 165.
14. K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules, Molecular Spectra and Molecular Structure*, vol. 4 (New York: Van Nostrand Reinhold, 1979), pp. 240-241.
15. G. Das and A. C. Wahl, *Journal of Chemical Physics* 56 (1972): 3532.

16. T. H. Dunning, Jr., D. C. Cartwright, W. J. Hunt, P. J. Hay, and F. W. Bobrowicz, *Journal of Chemical Physics* 64 (1976): 4755.
17. L. Adamowicz and E. A. McCullough, Jr., unpublished. A brief account of this work will appear shortly in the *Journal of Physical Chemistry*. See also E. A. McCullough, Jr., *Journal of Chemical Physics* 75 (1981): 1579.

