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Present State of Molecular Structure Calculations*

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We have come to the end of our conference. And so, as we gather for our banquet, it is right that we should thank the organizers of the conference, particularly Bob Parr and Joop de Heer. Perhaps a visitor from abroad may also take the opportunity, on behalf of all the other visitors as well as himself, of thanking our American hosts. Lastly—since this is the first conference of this kind at which so many wives and families have been present—an apology is now due to all our lady friends who, having patiently put up with our being separated from them during this last week, must now put up with our being together and talking yet more about our professional interests!

You have asked me to "wrap up" the conference. This suggests some sort of parcel. Now in England there is a limit to the length and depth of parcels permitted by the Post Office. As for the length of this particular parcel—I have calculated that if all the words spoken in these 30 hours of discussion were typed in a single row, it would just stretch from sea level to the top of Long's Peak. Fortunately it is not all going to be typed, though some of it is shortly to be published.[1] And as for its depth—that is what matters most and what I want to talk about. I do not propose to refer in detail to any particular papers, except incidentally or to quote what seems to me some significant *bon mot.* But I believe that it would be interesting to try to answer three questions, all of which must have been frequently in our minds during our meetings together. These questions are:

(1) What are the major successes of the last few years of molecular-structure calculations?

(2) What are our own major conclusions from the present conference?

(3) What are the lines along which it seems likely that future progress will be achieved, and what are the topics on which most time is likely to be spent?

You have asked me to give a personal opinion, and I will do so. But a personal opinion will not satisfy everyone, even though I shall try to be as fair and objective as I possibly can when dealing with controversial topics. Please forgive me, therefore, if you do not find yourself in complete agreement with all that I shall say.

(1) MAJOR SUCCESSES IN THE LAST FEW YEARS

It is important to remember how old quantum chemistry now is. It was in 1926 that Schrödinger introduced his wave mechanics; and within two years Heitler and London had made the first excursion into molecular-structure calculation with its aid. The subject is therefore just over 30 years old. It is not surprising that many of the plums have now been picked, and really interesting and novel fruit is harder to come by. For before our last conference of this kind—at Texas in 1956—it was fair to claim that the essential nature of the electron-pair bond was properly understood, and so were the reasons for approximate constancy of bond lengths and valence angles; and the difference between localized and delocalized bonding such as that shown by the σ electrons in a long-chain paraffin molecule or the π electrons in an aromatic system like naphthalene. We knew the reasons why resonating molecules were especially stable, and how this resonance affected their bond lengths. We understood the use—and limitations —of quantum numbers to describe the electron orbitals in a molecule, both in ground and excited states, and, even if we could not calculate them exactly, we could at least characterize many of the electronic transitions revealed in ultraviolet absorption spectra. It is from that background that we must now judge the successes of the last few years.

In this matter I should like to point to four situations where real progress seems to me to have been made. There are, of course, many other places where useful progress has been achieved. But I believe that these are the most substantial. With the exception of the last of the four, all these situations have been brought before us in papers at our present conference.

The first in our understanding of what we now call vibronic transitions. In most molecules vibrational and electronic effects may be almost completely separated, the coupling between the two being exceedingly small. This is sometimes referred to as the adiabatic approximation, in which, following the Born-Oppenheimer approach, the function of the electronic distribution is almost wholly to provide a potential field in which the atomic nuclei may execute their vibrations. But in certain molecules, particularly when there is a large degree of molecular symmetry, the vibrations of the nuclei, by destroying some of this symmetry, make possible weak electronic transitions which would be forbidden if, in the absence of vibration, the full molecular symmetry were preserved. Now electronic and vibrational motion must be considered together.

Closely related to this are the recent exciting appli-

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* This paper formed the "after-dinner speech" at the Conference Banquet on June 26, 1959. It seemed good, however, to print it in as nearly as possible the same style as it was given, since in that way the spirit of the conference could be recaptured more effectively than in a more formal document summarizing the proceedings of the conference. Indulgence is claimed for any resulting informalities in name and title!

[1] Revs. Modern Phys. (this issue).

cations of the Jahn-Teller theorem. This theorem, originally published in 1937, states that if a symmetrical nonlinear molecule has a state which is electronically degenerate, it will distort in such a way that the degeneracy is removed. The magnitude of the distortion is not provided by this discussion, nor is anything said about the type of vibrational motion which must ensue, particularly if the equilibrium distortions are not large. But recently a good deal of work has been done to estimate the distortion and to study the vibrations. The Renner effect in NH_2 studied by Longuet-Higgins and Pople, and the case of $C_6H_6^+$ studied by Moffitt and his collaborators, are excellent examples of the beautiful way in which theory can be used to elucidate what might otherwise have been a peculiarly complex situation.

The second major success of recent years has been in the electronic spectra of aromatic radicals, where electron-spin resonance effects have been interpreted with great accuracy. It is an odd fact, not yet properly understood, that there are certain situations involving an odd number of electrons (the excited states of ionized hydrocarbons such as naphthalene, anthracene), where the molecular-orbital approximation appears to work very well, even in a quite naive form; but there are others, such as the odd-numbered neutral radicals, where the valence-bond method is much better. It has, of course, been known for a long time that both methods converge to the same result, when taken to a sufficiently sophisticated level.

Another aspect of this situation is found in the recently discussed negative spin density. In a free radical such as allyl $H_2C-CH-CH_2$, in which there is one unpaired electron, it is found that the unpaired spin is most likely to be found on one or other of the two-end carbon atoms, in accordance with the simple resonance structures

$$H_2C=CH-\dot{C}H_2 \quad \text{and} \quad H_2\dot{C}-CH=CH_2.$$

But there is a small resultant spin of opposite sign on the central carbon atom, which may therefore be said to have a negative spin density. This—and other similar examples—represent a very interesting recent success.

The third line of progress is associated with the effect of a magnetic field. The chemical screening, as measured in nuclear magnetic resonance studies, has given us most important information about the distribution of charge in a polyatomic molecule. Not all the details of this theory have yet been adequately explored, but there can be little doubt that in this field substantial success has been achieved.

There is a fourth field that I must mention, even if it is not represented at our conference. I refer to the magnificent progress in the last four or five years in converting inorganic chemistry into a discipline with a pattern. Perhaps there have recently been too many conferences around the topic of complex ions, coordination compounds, and ligand-field theory. But I cannot avoid a certain feeling of regret that nothing has been said about these topics during this last week. It was almost inevitable that the wider scope of homologous series and the larger scale of molecular architecture should have made the basic understanding of organic chemistry easier than that of inorganic. But the gap is closing, and in that closure the theoretician is playing a notable part.

It may be argued that in giving this list of successes I am being optimistic. But I recall that in one of our sessions, when Dr. Boys was asked about the accuracy of certain conclusions, he said that if the question were asked after dinner he would be optimistic, but if before dinner, he would be pessimistic. Now this address of mine is an after-dinner speech, and I feel that I am not being unduly optimistic in claiming that although progress in the last five years has not been outstanding, it has been substantial, and has materially helped in the understanding of real chemical behavior. Naturally enough, there have also been disappointments, and I shall refer later to some places where we have had significant lack of success.

(2) MAJOR CONCLUSIONS FROM THIS PRESENT CONFERENCE

Let us now turn from the major developments of the last few years to the conclusions which have emerged from our discussions in the last week. There is one of these about which I feel very strongly, and because it is of such great importance for any future conferences on molecular structure, I make no apology for coming straight to it. It seems to me that the whole group of theoretical chemists is on the point of splitting into two parts. Anyone who attended all the sessions this week could be in little doubt but that the first and second halves were quite different—almost alien to each other. In its simplest form this difference was associated with the large-scale use of electronic computers, though, as I shall say later, I think there is a deeper aspect of it than just this. Now perhaps the time has come when we ought to separate ourselves into two or more groups, in much the same way that the one subject of chemistry divided itself in the course of time into organic, inorganic, physical, and analytical chemistry. It is the almost inevitable fate of a new subject, as it grows, to split.

I mention this situation now because on three different occasions during the last week we have heard someone use the phrase, "Oh, but you're not doing quantum chemistry." These occasions were: (1) about some of the heavy computational techniques used in calculating energy values for atomic helium and molecular hydrogen; (2) about some of the calculations of a highly empirical kind designed to estimate energy levels and charge distributions in heteronuclear aromatic molecules; (3) about the tabulation and interpretation of barriers to internal rotation in substituted ethane-type molecules, where Bright Wilson told us (quite wrongly, as I think!) that he wondered if he had the right Union Card! These three situations represent quite distinct aspects of what we used to call quantum chemistry. They differ considerably in their underlying assumptions. But if each of them is now rejected by the others as not being quantum chemistry, then the situation is indeed serious. For my own part, I am very far from laughing at it, and I want us to look at it as openly and dispassionately as possible. The questions that we are really asking concern the very nature of quantum chemistry; what relation it has to experiment, what function we expect it to fulfil, what kind of question we would like it to answer.

I believe that we are deeply divided on our own answers to these questions. It is an irony of fate that our divisions are a logical development of recommendations made at the 1956 Texas Conference, and they show very strikingly how easy it is to alter the balance in a growing subject. For in 1956 electronic computers were becoming developed commercially to the stage where it was feasible to program large computations. It was desirable that such computers should be made available to universities in several parts of the world. So that conference passed a recommendation urging that more such machines should be at the dispoal of university departments. This recommendation was widely quoted, and several groups (at Chicago, the Massachusetts Institute of Technology, Cambridge, and elsewhere) set out to exploit the new facilities by engaging in huge programs whereby a complete molecular wave function for a diatomic molecule (e.g., N_2 or CO) would be calculated, including all necessary integrals, in the space of a period measured in minutes, without any intervention by the operator of the machine. It is in no small measure due to the success of these programs that quantum chemistry is in its present predicament.

There are several comments that must be made about the two groups of quantum chemists. Thus there is an immense amount of great computational skill and acumen in the work of the first group. Further, there are certain problems where it appears at present that the only hope of settling a dispute is by computation, since the experimental measurements are too difficult. Examples of this sort of thing are the absorption of H^- as a function of wavelength—a matter of immense importance in the astrophysical study of solar radiation—and the symmetry and shape of the ground state of the methylene radical CH_2. The first of these problems was dealt with some years ago by Chandrasekhar; the second has been reported by Boys at this present conference. Obviously if work of this kind is to be effective, it must have high accuracy; and this inevitably involves much use of electronic computers. As a result it has seemed to many people that this group of chemists was so remote from the normal natural conventional concepts of chemistry, such as bonds, orbitals, and overlapping hybrids, as to carry the work itself out of the sphere of real quantum chemistry.

But this matter is not simple. For at the other extreme there are signs of great success in biology. In the action of certain drugs it seems that the charge on one particular nitrogen atom is of prime significance; in carcinogenic hydrocarbons it is the electrical properties of one (or perhaps two) parts of the molecule; in the oxidation-reduction reactions involved in metabolism it is the basic strength or the ionization potential or electron affinity. All these quantities can be calculated in what we hope is at least a consistent manner by using the grossest possible approximations, whose crudity appears nothing less than revolting to the "computors." Yet when the calculations are made, the resulting correlations are too good to be treated as simply accidental.

Where, in all this, does "real" quantum chemistry lie? To some extent this is a matter of terminology. But when we come to think about the possibilities of electronic computers, it seems to me that the work presented at our conference this week enables us to distinguish three levels of activity. I have discussed this matter carefully with several of the exponents of electronic computing, and although the precise boundaries between the three levels are not meant to be rigid, I find that most people agree very closely with my own division.

In the first place, if we are concerned with molecular or atomic systems containing 1–6 electrons, there now seems no reason why we should not get effectively exact solutions. For even now we can calculate certain of these energies as accurately as they can be measured. Bearing in mind the tremendous accuracy of all spectral measurements this must be counted as a very impressive result. As one of our members said, "The Pekeris 1078-term function for atomic helium is about as far as it is worthwhile going." And Kolos and Roothaan have now extended the famous James-Coolidge calculation on H_2 to include no less than 50 terms, so that this has now become almost the best determination of the dissociation energy of this or any other molecule. Then, in the second place, the speeding up of calculations, and the design of even faster machines, should enable us to extend the range of effectively exact solutions. I am inclined to think that perhaps the range 6–20 electrons belongs to this picture. But it must be remembered that an accuracy of this order of magnitude will be purchased very dearly. Even in the five-term James-Coolidge function—"the best compromise between accuracy and simplicity"—there is nothing easily visualized about the wave function, and it requires a further numerical integration on an electronic computer to derive from the full 13-term wave function either the electronic charge density or any other property of the molecule.

I see little chance—and even less desirability—of dealing in this accurate manner with systems containing more than 20 electrons. For I cannot help recalling Hartree's remark, that if we were to print the wave function values for the ground state of the iron atom with sufficiently small intervals in all the electronic coordinates, we should require a whole library to house the books in which they were printed; and that there are not enough atoms in the solar system to make the paper and ink necessary to do the same thing for the uranium atom. It looks as if somewhere around 20 electrons there is an upper limit to the size of a molecule for which accurate calculations are ever likely to become practicable. This range of 1–20 includes many interesting questions (e.g., the dissociation of F_2, the shapes of CH_2 and CH_3 in their ground and excited states, the reaction $H+H_2 \rightarrow H_2+H$ and much else), but there is a great deal that it leaves out! We are told that above the gateway to Plato's Academy there was written the sentence, "God is always doing Geometry." And certainly the mathematician Jacobi said, "God always arithmetizes." But if the range 1–20 electrons were all, we could ourselves add a further statement, "God is always computing." This is because we may hope that eventually all problems in this range will be solved accurately by computational techniques. Now surely, in this way of speaking, God *is* computing. But equally surely there is much more in chemistry than is covered by this range.

I believe that the distinction between those quantum chemists whose major interest lies in the field of 1–20 electrons, and consequently think in terms of full electronic computation, and those who do not think in these terms is so great that they deserve separate names. During this conference I have thought of them as group I (electronic computors) and group II (nonelectronic computors), though a friend has suggested as alternatives the *ab initio*-ists and the *a posteriori*-ists! I cannot help thinking that the gap between the two groups is so large that there is now little point in bringing them together. This is probably the last conference of the old kind. In future we should either have two distinct conferences, or else be prepared to plan parallel sessions for group I and group II enthusiasts.

I have spoken of the difference between group I and group II as if it were bound up with the use of electronic computers. But this is an oversimplification. I have already described group I by saying that their desire is for complete accuracy and in order to achieve this they are prepared to abandon all conventional chemical concepts and simple pictorial quality in their results. Against this the exponents of group II argue that chemistry is an experimental subject, whose results are built into a pattern around quite elementary concepts. The role of quantum chemistry is to understand these concepts and show what are the essential features in chemical behavior. These people are anxious to be told why, when one more vinyl group is added to a conjugated chain, the uv absorption usually shifts to the red; they are not concerned with calculating this shift to the nearest angstrom; all that they want is that it should be possible to calculate the shift sufficiently accurately that they can be sure that they really do possess the fundamental reason for the shift. Or, to take another example, they want to know why the HF bond is so strong, when the FF bond is so weak. They are content to let spectroscopists or physical chemists make the measurements; they expect from the quantum mechanician that he will explain *why* the difference exists. But any explanation *why* must be given in terms of concepts which are regarded as adequate or suitable. So the explanation must not be that the electronic computer shows that $D(H-F) \gg D(F-F)$, since this is not an explanation at all, but merely a confirmation of experiment. Any acceptable explanation must be in terms of repulsions between nonbonding electrons, dispersion forces between the atomic cores, hybridization and ionic character. It does not matter that in the last resort none of these concepts can be made rigorous. For chemistry itself operates at a particular level of depth. At that depth certain concepts have significance and—if the word may be allowed—reality. To go deeper than this is to be led to physics and elaborate calculation. To go less deep is to be in a field akin to biology. Once this is recognized it is not difficult to see that there is a perfectly sound basis for all three comments about "not doing quantum chemistry" that I reported earlier.

It would be a grave disaster if quantum chemistry were limited to either the "very deep" or the "shallow" level of concept and operation. And certainly it would be a serious loss if it did not maintain a close link with experiment and with conventional thought forms of chemistry. It is significant that in the last few years, group II people like Orgel and Jörgensen have made such excellent progress in ligand-field theory. For there the relation with experiment, both of shape of a complex and energy of electronic excitation, is immediate; yet theory adds to what experiment can provide, each supplementing the other.

There is always a danger—not entirely avoided this week—that group I people will forget that chemistry is associated with the real world. I recall an occasion shortly after the end of the last world war, when an exhibition of quantum chemistry was being opened in the Palais de la Découverte in Paris. There were lovely diagrams of the Kekulé and Dewar structures for benzene, and excellent numerical illustrations of the lowering in energy as more structures were allowed to resonate among themselves. But Linus Pauling, as he went round that exhibition and came to these diagrams, said, "Why don't you put a bottle of the stuff by the side of the diagrams?" It is, I believe, very important that we should recognize this interplay of theory and experiment. For that reason, if for no other, I was among those who were gratified when Professor Oosterhoff broke completely with tradition earlier today in our last session, and actually did an experiment before us!

I would like to carry this discussion of groups I and II a stage further. The concepts of classical chemistry were never completely precise, e.g., the notion of ionic character of a bond could never be unequivocally formulated. Thus, when we carry these concepts over into quantum chemistry we must be prepared to discover just the same mathematical unsatisfactoryness. Consider as an example, the representation of the wave function of a diatomic molecule A–B in terms of covalent, ionic, . . . functions. If we consider all states of ionization and excitation of both A and B, we shall have an overcomplete set of functions. This is anathema to group I, but it is the very lifeblood of group II, who seek for the simplest and most agreeable way of picking out from this overcomplete set a small group of three or four (usually not even mutually orthogonal!) which will be "good enough" for their purpose. Mathematically, of course, we could have dealt with the whole problem in terms of a single atomic nucleus+electrons, centered at either A or B. (Notice how many group I papers have recently been discussing single-center expansions!) But that would not be chemistry as group II understands it. Exactly analogous situations arise whenever, in an attempt to obtain a precise completeness in the set of basic functions, it is found necessary to include the continuum. It may be mathematically desirable to do this, but—in rather exaggerated language, which is not quite true—"who ever heard of a chemist who bothered about the continuum?"

This leads to a further difference between groups I and II. Many of the familiar concepts of chemistry are associated with the separation of the total groups of interactions between the various nuclei and their electrons into two sections. We may call these weak and strong interactions. Thus the idea of separate bonds in a polyatomic molecule rests upon the conviction that it is possible to choose certain orbitals (for one single bond) such that the interaction between them is strong, and yet the interaction between them and any other orbitals is weak. But this is at best a qualitative difference, depending on what we mean by strong and weak. Certainly we can never get 100% isolation of certain interactions from the rest; mathematically therefore, a bond is an impossible concept for group I. It is not surprising (see later) that it is practically never used by them. Yet the existence of bond properties is basic to all chemistry.

There are occasions where this separation into strong and weak interactions has been exceedingly effective. The great success of ligand-field theory (surely one of the most typical group II projects!) seems to be bound up with the fact that among the d electrons of a transition element, only one basic configuration (in the atomic sense) is needed. Ultimately, of course, many other configurations should be included, and we know that in some complexes an allowance should be made for the delocalization of some of these d electrons away from the central atom on to the ligands. But these may often be treated as perturbations.

It is not surprising that the orientations of these two groups of quantum chemists are so different that cross-fertilization has now become much less frequent than in earlier days.

WHAT HAVE WE FOUND OUT ABOUT ATOMS AND SMALL MOLECULES?

I have spent a long time on the difference between group I and group II because I believe the situation is critical. Many members of group I do not realize what has been happening to them; and members of both groups display an undesirable lack of sympathy for each other's work. But several other interesting conclusions have emerged this week, quite independent of any group I–group II division. Perhaps the simplest way of referring to some of these is in the form of a numbered list.

(1) It has at last become abundantly clear that until we can cope effectively with many-center integrals, there will be a holdup in polyatomic molecule calculations. As one of our conference said, "Ignorance of 4-center integrals has held up progress for 15 years"—a comment which made me want to hurry up with a manuscript that Michael Barnett and I have been writing on this subject for just about 10 years! But, alas, it is only too true that the techniques for effective evaluation of these integrals still elude us. These are what Mulliken and Roothaan recently called the "bottlenecks of molecular quantum mechanics."

(2) Great accuracy has been obtained with systems containing only 2–3 electrons. But with slightly more electrons (and often with the small number also) the errors are not always clear. It would be a great help if, when papers are being written, some guidance could be given about the likely size of the discrepancy between theory and experiment. Since some form of variational method is nearly always used to calculate the energy, it should be possible to say more about the limits of error than is usually said. For example, even with the prodigious calculations reported in this conference, as soon as the number of electrons exceeds about six, the D values for diatomic molecules are only about one-half of the true values, and the dipole moments are frequently 50% in error. This is a sobering conclusion, for very large amounts of time have gone into the values now being given to us.

(3) We need to introduce "split orbitals" (or should we call them open-shell configurations?) if we want to reproduce correct radial correlation of electrons in atoms or in molecules. It has been known for a long time that the best simple description of the ground state of helium is not $(1s)^2$, where both electrons are in the same orbital, but $(1s)(1s')$, where they are in different ones. We may think of the $1s$ orbital as being relatively close to the nucleus, and the $1s'$ orbital as

being more fully screened, and thus further away. This situation now appears to be quite general. It is certainly more important for inner shells than for outer ones, and does not seriously affect the energy (configuration interaction is far more important in lowering the energy). In cases where there is one or more unpaired electrons, the exchange terms between these electrons and the inner-shell electrons leads to Hartree-Fock equations which are different for the split orbitals, and so adds to the splitting. We could perhaps call this an exchange polarization. It is significant in calculations of spin density: the Li atom with one unpaired electron outside a split core of $(1s)^2$ type, and the O_2 molecule with two more electrons having α spin than β spin, are excellent examples.

(4) It is now perfectly clear that a single-configuration wave function must inevitably lead to a poor energy. This is because, among other defects, it completely neglects correlation energy. Indications are that among the electrons in the valence shells of atoms and molecules this correlation energy is roughly constant per pair of electrons. But if one electron of a pair is excited to an outer higher-energy orbit, the correlation energy from this pair is reduced. It is necessary, therefore, to calculate it for each case separately. The technique that has proved best appears to be that of including a large number of configurations in a molecular-orbital configuration interaction calculation. The configurations will now be chosen so as to simplify the mathematics. Consequently they will have little relation to some of the older concepts which previously dominated discussions of this kind. During this conference hardly anyone has talked much about hybridization or bond orbitals. It is as if almost any functions could be used, provided only that sufficient flexibility is assured by allowing a large enough number of linear terms. There is a tendency, as might have been expected, to use functions built up from atomic orbitals, and experience seems to suggest that self-consistent-field atomic orbitals are preferable to simple analytical ones, such as the much-used Slater orbitals. But a penalty is exacted from all those who use SCF atomic orbitals. Since these functions are normally provided in the form of a table of numerical values, the whole analysis must be carried through on a purely numerical basis, or else we must begin by finding some analytical expression which adequately represents the table of values. Thanks to the work of Löwdin and others, this is now reasonably practicable. On the other hand, when building up molecular orbitals by linear combination of atomic orbitals, it hardly seems worthwhile to find the best Roothaan-like combinations (frequently labeled as SCF molecular orbitals, though really it is only in a restricted sense that they are self-consistent). The advantage of the Roothaan functions is that many of the matrix components between the lowest energy configuration and higher configurations vanish. But if we are to include 10 or 20 or more configurations, this simplification is hardly worth the additional labor of first determining SCF coefficients.

(5) A further discovery of this conference concerns the status of Moffitt's ingenious method of "atoms in molecules." This method arose from the recognition that the binding energy in a molecule was only a small fraction of the energies of the component atoms, and should therefore be calculable by some form of perturbation theory. The first studies of Heitler, London, and Eisenschitz, 30 years ago, had led to a primitive form of interaction operator. But Moffitt very considerably extended the applicability of the idea so as to include both neutral and ionic states of the component atoms. Furthermore, several distinct states for each atom, both neutral and ionized, were to be included. Thus, to take a very simple example, in H_2 we could say that each hydrogen atom had certain probabilities of being in the $1s$, $2s$, $2p$, $\cdots$ state, and a certain probability of being in the form H^+, and certain other probabilities of being in the various two-electron states of H^-. It was because of this concentration on the individual atoms of the molecule that it received its title "atoms in molecules." It now appears that atoms in molecules are not really atoms in the isolated-atom sense, so that an expansion of the molecular wave function in terms of states of the isolated atoms does not converge very rapidly. Thus orbital exponents appear to differ fairly substantially, and hybridization is different in the different parts of the molecular wave function. As one of our conference said, "An atom isn't an atom when it gets into a molecule." This is a pity because it prevents us from using experimental atomic and ionic energies in the way that Moffitt had originally hoped. It also implies that the idea of a valence state is less satisfactory than we had formerly supposed. It is not true to say that in this last week we have killed the theory of atoms in molecules, but it is true to say that it has been very seriously wounded.

(6) One of the most vigorously pursued lines of research during the last few years has been the density matrix. It has frequently been pointed out that a conventional many-electron wave function tells us more than we need to know. All the necessary information required for the energy and for calculating the properties of molecules is embodied in the first- and second-order density matrices. These may, of course, be obtained from the wave function by a process of integration. But this is aesthetically unpleasing, and so attempts have been made, by Löwdin, McWeeny, and others, to work directly with these matrices. There is an instinctive feeling that matters such as electron-correlation should show up in the two-particle density matrix. But here we are confronted by a serious lack of success. We do know the conditions that must be satisfied by the many-electron wave function $\psi(1,2,\cdots n)$, but we still do not know the conditions

that must be satisfied by the density matrix

$$\Gamma(1,2;1',2')=\int\psi^*(1,2,3,\cdots n)\times(\psi(1',2',3,\cdots n)d\tau_3 d\tau_4\cdots d\tau_n.$$

Until these conditions have been elucidated, it is going to be very difficult to make much progress along these lines, although some considerable insight has been gained, particularly by McWeeny, by considering the contributions to the density matrix that arise from distinct and nearly separable groups of electrons.

Now clearly much else was reported during this week. But these are some of the major conclusions. It would be nice to be able to summarize in a simple fashion. I doubt if it is true, as one member claimed, that a "major break-through has occurred," but perhaps it is true, as Lee Allen said, that "a turning point has been reached this last summer," now that we have several computer programs actually running. (Incidentally, the successful development of autocoding and Fortrand and similar techniques reminds me that I shall feel that the computer firms will not have done their job properly until they have produced a computer that I can talk to, and which will listen to my voice, interpret my instructions, code itself, and then tell me the answer. This attractive prospect—I am assured—is by no means absurdly idealistic!) But to balance the optimism of the "turning point" let me add a quotation from Ruedenberg: "Diatomic molecules are peculiar because they only have two ends, and these ends are very close together."

(3) FUTURE PROGRESS

We must now turn to the third question: What are likely to be the directions of future work during the next few years? This is a most intriguing issue, but I believe that there have been several pointers this week, which do at least provide clues for the future. Here again it will be simplest to list some of these clues by number.

(1) The most important clue seems to me to be the recognition that the energy is not the only criterion of goodness of a wave function. In the past we have been preoccupied with energy. This was natural enough, for our wave equation is written in the form $H\psi=E\psi$, and the most powerful and widely used technique for getting approximate solutions to this equation requires us to concentrate almost exclusively on minimizing an energy function. Now we have already seen that there are great difficulties in getting even approximately exact energies, and it has not always been clear just how rough our associated wave functions are. The virial theorem has been used to improve wave functions, but it has been shown that since the introduction of almost any variational parameter allows us to satisfy this theorem, it is not of very great practical usefulness to us. Root-mean-square deviations, such as the evaluation of $\langle H^2\rangle-\langle H\rangle^2$, are difficult to calculate, and rather depressing in their results.

It may perhaps be the recognition that this preoccupation with energy was leading to sterility; or it may be due to the developments of many types of microwave experiment. But the fact is that attention is now becoming concentrated much more on the smaller terms in the Hamiltonian. These terms, usually neglected in earlier work, include spin-spin coupling, spin-orbit interaction, coupling of electron spin and nuclear spin, quadrupole moments, and the influences that result from the coupling of all these with an applied electric and magnetic field. The most well known of all these effects is the nuclear magnetic chemical screening, and there are now experimental measurements for particular molecules, which provide excellent tests for any proposed molecular wave function. It is well known that the ordinary diamagnetic susceptibility provides an estimate of $\langle r^2\rangle$. But there are now experimental measurements of many other functions of position, such as $\langle x^2\rangle$, $\langle x/r^3\rangle$, $\langle x^2-y^2)/r^3\rangle$. These measurements are interesting because they arise from small terms in the Hamiltonian. These small terms are not large enough to cause any serious modifications of the wave function or the energy (this is why they are associated with microwave measurements, where energy differences are minute). But they act as measuring rods, able to be placed within the electronic charge-cloud without affecting it. Further, different members of this series weight the charge cloud in different ways so that, for example, the mean value of r^2 will tend to weight the outer regions of the molecule, but the mean value of x/r^3 will weight those parts of the cloud near the particular origin being used (usually one of the nuclei). In this way we begin to see how it may be possible to test a given wave function for accuracy in one of several chosen respects, rather than, as at present, in just one aspect, its energy. Martin Karplus' survey at this conference is surely a pointer to much future work along similar lines.

(2) We shall be more concerned with excited states, and we must find better ways that at present for describing some of them. The primitive idea of one electron being promoted to a higher orbital needs to be supplemented by a discussion of the reorganization among the unexcited electrons. And sometimes it is impossible to describe an excitation in terms of a one-electron jump. The relation between valence-shell transitions and Rydberg-type transitions is crying out to be explored.

(3) We shall continue to talk about correlation energy, and its relation to the size and shape of a molecule. I myself hope that, as at this conference, we shall expose ourselves to those people—in this case the theoretical physicists—who have studied the electron theory of metals and of plasma, and shall train ourselves to adapt some of their techniques to our own purposes. For they have much to teach us. The uv

absorption of long conjugated carbon chains is just one example of this.

(4) I also think that we shall consider more fully the interactions between systems, This "omnibus" title covers several related types of problem. On the one hand it includes the repulsive interactions between nonbonded atoms in the same molecule (with its influence upon internal rotation, energy barriers, and the possible molecular deformations due to steric overcrowding); on the other hand, it must include inner-shell—outer-shell forces as discussed by Pitzer and McWeeny, and their influence on bond energies. In the final stage it will encompass chemical reactions. It is a sobering thought that we do not know enough about any single reaction to be able to make a realistic *ab initio* calculation of its rate. It is admittedly true that since reactions involve the breaking and rearranging of chemical bonds, we should try to make our knowledge of the nonreacting molecule as complete as we conveniently can before going on to consider reacting ones. But much of this knowledge has been available for several years. We ought to have been more concerned with this at our conference, and it ought not to have been possible for J. O. Hirschfelder to have to say, however jokingly, "I want to tell you all about intermolecular forces in two minutes." Here the situation can be summarized in three words: "Wanted, new concepts." But I foresee that in future conferences more will be said about this sort of thing.

(5) Finally there is the spreading of quantum chemistry into biology. Some reference has already been made to this. The indications here seem to be quite clear: that more and more use will be made of wave-mechanical ideas in this exciting field. It is already clear that the structure of a protein chain depends very intimately on bond distances and angles and the nature of the hydrogen bond. But work is being initiated, by John Griffith and others, on oxygen uptake by haemoglobin. Professor Pullman has given a preliminary survey to this present conference, which shows that many of the basic and acidic properties of the amino-acid residues may be accounted for in exceedingly simple terms. All this seems likely to continue, and to develop. The work itself, however, will almost inevitably be crude, and of the type that it is now fashionable to call semiempirical. Group I exponents will throw up their hands in horror at such attempts to estimate the electrostatic forces in an energy-rich phosphate bond; even group II members will mistrust the complete neglect of many terms and integrals which are known to be large. But in the establishment of correlations and primitive patterns of understanding it does not do to be too fussy. A rough track through the jungle precedes the construction of a metaled highway. And there is much experience possessed by professional biologists which could be linked with the deeper levels of interpretation associated with the quantum theory, to the enrichment of both. But let no one here make his claims too easily or too definitely. Biological systems are much more perverse than are laboratory chemical systems. In this field the prizes are immense—no less than the understanding and control of life itself. The future here may be far off. But, as was first said in rather different circumstances, "*Ce n'est que le premier pas qui coûte*"; and there are very few sensible people who would wish to deny that in this ultimate human enterprize there is to be no contribution from quantum chemistry.

This surely is the place to stop, where we have trained our eyes to seek the distant horizon. Yet perhaps, if we may bring them back to the regions covered by our last week's conference, three single sentences may be permitted. This has been a most interesting and significant conference, with many fruitful discussions "under the counter" or "behind the scenes." For some of us, in the words of a member of our conference, "More good is done round a coffee table than at a lecture bench"—which might conceivably be taken as an argument for a coffee break in the middle of each morning session. And, last of all, we shall probably all of us feel that we can agree with the doyen of quantum molecular physicists—Robert S. Mulliken—when he said, in what ought to go down to history as one of the most classic understatements of all time, "I believe the chemical bond is not so simple as some people seem to think."