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STATUS OF THE THEORY OF ELECTRONIC ORBITALS IN MOLECULES AND SOME OF ITS PROBLEMS†

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Theoretical investigations of the electronic orbitals of molecules have developed during recent years in three main directions: (I) quantitative molecular calculations by means of electronic computers, (II) semiquantitative and semiempirical calculations of various properties and parameters of molecules, and (III) the search for new methods of calculation. This last line of research is, of course, interlinked with the other two, and therefore we shall not devote a special section to it.

I. PROBLEM OF QUANTITATIVE MOLECULAR CALCUTIONS

With improvement in automatic computing technique the number of publications in which calculations are made on molecules without using any experimental data on their properties has rapidly increased. Only the numbers of electrons and the nuclear charges of the atoms forming the molecules are assumed to be known. The ultimate aim of such calculations is to find the energy and wave functions of various states of the molecules; by means of these data complete information can in principle be obtained on the properties of the molecules. Up to the present such calculations have been carried out mainly for diatomic molecules.

In solving the problem, however, one comes up against serious mathematical difficulties. For the most part the calculations are based on the method of molecular orbitals (MO), which are set up in the form of linear combinations of specified atomic orbitals (LCAO). The coefficients in these molecular one-electron functions are chosen to make the best possible allowance for the field of the remaining electrons (introduction of self-consistent field according to Roothaan[1]). From the molecular orbitals thus obtained, the complete antisymmetric wave function of the molecule is constructed. If we then confine ourselves to the mode of distribution of the electrons among the molecular spin-orbitals which represent the lowest energy (which corresponds to representing the complete wave function as a single determinant), the results are not very satisfactory, being strongly dependent on the atomic wave functions initially chosen. If, for example, Slater functions are used, the relative error in the total energy is small (of the order of 1%), but the absolute error often amounts to 20–30 eV. In conformity with this, values are obtained for the dissociation energy which are less than the experimental value by a factor of 2–3, and sometimes are even negative (with F_2 for example)[2,3]. Errors of the same order of magnitude are obtained in the dipole moments of molecules[2–5].

There are several reasons for such a great divergence from the experimental data. Firstly, Slater functions are too approximate, and simply do not reproduce the properties of the atoms sufficiently well. Therefore the result is markedly improved when Hartree–Fok atomic functions are used. Thus for the HF molecule calculations with these two types of function give errors in the total energy of ~29 eV[6] and ~15 eV[7] respectively (the value obtained for the dissociation energy by means of Hartree–Fok functions was 2.11 eV compared with the experimental 6.08 eV).

The error in the latter case is partly due to the fact that molecular orbitals constructed from Hartree–Fok atomic orbitals are still not the best one-electron molecular functions. However, the maximum decrease in energy which can be achieved by complete self-consistency in the molecular orbitals is probably not large. Thus according to Allen and Karo's estimate[2] also for the HF molecule, this decrease can probably amount to 2–3 eV. The remaining 12–13 eV difference from the experimental value is due to correlation effects, *i.e* to interaction between the electrons.

Three methods have been worked out in the theory of the atom for taking account of electron correlation: calculation of interaction between configurations, explicit introduction of interelectronic distances into the wave function, and the method of open shells.

The calculations show that the configurational interaction method is very laborious and not very effective. For example, the introduction of seven configurations into the wave function for the HF molecule lowers the total energy by only 0.02% (less than 1 eV)[7]. Such a small effect is disappointing. Moreover, in several cases the use of a limited number of configurations makes the calculated values of various properties of the molecules worse instead of better (see, for example, Ref. 8). Probably the form in which the complete wave function is sought is a configurational series which converges very slowly; this calls into question the effectiveness of such a method when applied to molecules. With increase in the number of basic functions the number of multiply excited configurations grows very rapidly amounting to thousands, which makes the method unsuitable even for the best modern computers.

The method of introducing interelectronic distances into the molecular wave function was tried out for the hydrogen molecule[9] as early as 1933. During recent years Kolos and Roothaan[10] have found the most exact wave functions and energy of the ground state of H_2 by this method; their wave function contains fifty variational parameters, and their value for the bonding energy (4.7467 eV) shows excellent agreement with the experimental value[11] (4.7466 ± ± 0.0007 eV).

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The open-shell method consists in introducing different orbitals for electrons having different spins. As a result, electrons of opposite spins are somewhat separated from one another spatially, which produces a decrease in energy. The method has been used for calculations on the hydrogen molecule and several other diatomic molecules[12-17], and also for benzene[18,19]. It gives some decrease in energy, but nevertheless no decisive improvement is achieved.

Introduction of interelectronic distances into the wave function and introduction of different orbitals for different spins must probably be regarded not as independent methods for calculating the correlation of the electrons but as ways of improving the convergence of the expansion in configurations[20]. For example, a combination of these methods in calculations on the He atom to a one-determinant approximation reduces the error from 1.1 to 0.05 eV (three variational parameters were introduced: two effective charges on the nucleus to allow for radial correlation and the parameter α in the correlation factor $g = 1 + \alpha r_{12}$)[20].

However, it is difficult to expect that a combination of these methods could be applied with equal simplicity and success to many-electron atoms or molecules. With increase in the number of electrons the number of non-linear variational parameters grows in proportion, and the number of terms in the correlation factor increases very rapidly. As the number of variational parameters required for the H_2 molecule approaches fifty, it is easy to imagine how great this number will be for, say, the fluorine molecule. Until recently, however, the correlation factor method had not been worked out at all for many-electron systems. It was not clear to what extent complicated electronic correlations play a part in atoms and molecules: whether only pair correlations are important, or ternary, quaternary, etc. as well, and how they should be allowed for. It was also not clear what excited configurations must be considered in the first place.

Recently this problem has been examined in detail in a series of papers by Sinanoğlu[21,22]. First solving the problem by a perturbation method, he found that, for atoms and molecules not containing conjugated bonds, the principal contribution to the correlation is made by the pair interactions of electrons located in the same orbital. This is because in these systems the orbitals are separated spatially from one another, as a result of which the probability of "collision" between electrons in different orbitals and having antiparallel spins is very small. The long-range part of the electron interaction potential is allowed for by the self-consistent field, and therefore the potential causing the correlation is short-range; its value at points where the electron of another orbital is predominantly located is practically zero.

The significance of the correlation of electrons in the same orbital was discussed as early as 1940 by Fok *et al.*[23] They pointed out the necessity for taking account of the pair correlation in bivalent atoms.

Sinanoğlu showed further[22] that ternary correlations play practically no part, and the only quaternary correlations of importance are those corresponding to two independent pair interactions ("collisions"). As a result he found that the complete wave function ψ of a many-electron atom or molecule without conjugated bonds, taking into account all correlations of any degree of complexity, can be represented with sufficient accuracy by the pair correlation functions u_{ij} in the form of a sum of two terms: a one-determinant function Φ_0 made up of Hartree–Fok orbitals, and a function χ (orthogonal to Φ_0) which represents the correlation; the function χ is expressed in terms of the u_{ij} as a finite sum of terms having definite coefficients:

$$\chi = \hat{A}\left\{\frac{1}{\sqrt{2}}\sum_{i>j}^{N}(1\,2\,3\ldots N)\frac{u_{ij}}{(ij)} + \sum_{i>j}^{N}\sum_{k>l}^{N}(1\,2\,3\ldots N)\frac{u_{ij}u_{kl}}{(ijkl)} + \right.$$
$$\left. + \frac{1}{2\sqrt{2}}\sum_{i>j}^{N}\sum_{k>l}^{N}\sum_{m>n}^{N}(1\,2\,3\ldots N)\frac{u_{ij}u_{kl}u_{mn}}{(ijklmn)} + \cdots\right\}, \quad (1)$$

where $\hat{A}$ is the antisymmetrisation operator (1, 2, 3, ..., N), and $(ijklmn)$ the product of the spin-orbitals. The number of pair correlation functions required for the calculation is determined by the spatial and spin symmetry of the system and is approximately equal to the number N of electrons: *i.e.* with large N it is considerably smaller than the total number of pair interactions $\frac{1}{2}N(N-1)$. The functions u_{ij} can be determined by minimisation of a functional, which is expressed in terms of Hartree–Fok molecular orbitals[24]. This can be done either by a direct variational method or by solving the corresponding equation. In essence the problem of finding u_{ij} is analogous to finding the correlation factor in calculations on the He atom or the H_2 molecule.

A test of these conclusions in the case of the Be atom and the LiH molecule gave excellent results[22]. The coefficients of configurations representing quaternary excitations, found by Watson[25] for Be by successive solution of the four-electron variational problem (taking into account 37 configurations), agreed well with the coefficients obtained simply by multiplying corresponding coefficients of configurations with binary excitation in conformity with Eqn. (1). The contribution (found by Sinanoğlu) of the correlation energy to the total energy of the Be atom was approximately only 1% smaller than that found by the variational method. Similar results were obtained also for the LiH molecule.

According to Sinanoğlu[22] the total energy of an atom or a molecule can be written in the form

$$E \simeq E_0 + E_1 + \sum_{i>j}^{N}\tilde{\varepsilon}_{ij}, \quad (2)$$

where E_0 is the orbital energy, E_1 the Hartree–Fok energy of self-consistency, and the last term represents the correlation energy, which is to a good approximation the sum of the effective correlation energies of individual electron pairs, although actually it includes not only pair but also more complex correlations.

This result confirms in particular descriptive models of the atom and the molecule in which a many-electron system is regarded as a set of electron pairs located in separate orbitals (or bonds) and interacting feebly among themselves. These results provide also in justification for the π-electron approximation, since they show that the correlation of σ and π electrons, which are located in different orbitals, is small. The correlation of π electrons among themselves in conjugated systems, however, will be given special consideration, since owing to delocalisation of the correlation potential (just as in metals) it will no longer be a short-range effect (see below). In these cases other methods must be used to estimate the correlation; perhaps methods developed in the theory of the solid state[26,27] will prove effective here. It is also significant that Sinanoğlu's method has made it possible for the first time to calculate rigorously intramolecular interactions of atoms not directly linked together, which is especially important for the theory of internal rotation.

Thus Sinanoğlu's investigations probably open the way to quantitative calculations on atoms and on molecules not containing conjugated bonds. As yet it is difficult to say how far the method will prove effective in practical application to many-electron molecules. It is now clear that successful calculation requires exact self-consistent one-electron molecular functions as zero approximation. So far such functions are known only for atoms. For diatomic molecules this problem can probably be solved by means of electronic computers, and, as can be seen from the literature, is included in the work plans of several computing centres. In the case of polyatomic molecules the problem of finding exact self-consistent orbitals is very complicated. Perhaps self-consistency must be confined here within the framework of Roothaan's LCAO method[1]. The calculation[22] on the LiH molecule mentioned above shows that with Roothaan's molecular orbitals Sinanoğlu's method also gives comparatively good results. Perhaps practical calculations of correlation energy will prove necessary only for a series of typical examples, on the basis of which an additive scheme can be constructed by means of Eqn. (2), which will allow the energies of any molecules not containing conjugated bonds to be calculated if the energies of the self-consistent molecular orbitals are known for them.

Apart from the fundamental problems of finding self-consistent molecular orbitals and allowing for electron correlation, quantitative calculations on polyatomic molecules involve a serious problem of computation, which is the calculation of many-centre integrals. Estimates by approximate formulae give unsatisfactory results[28,29]. Attempts are now being made, both in the USSR and in the USA, to find a method for the numerical calculation of many-centre integrals on electronic computers. Another way of overcoming this difficulty, proposed by Boys as early as 1950, consists in replacing hydrogenlike atomic functions by gaussian functions, with which all integrals are obtained without difficulty[30]. In practice, however, this method involves a loss of accuracy, for the expansion of hydrogenlike functions in gaussian functions converges only over a finite range of change in the variable.

In quantitative calculations on molecules (and also atoms) a further problem arises, that of the relativistic corrections[31]. With atoms the relativistic correction to the electron energy increases rapidly with increase in nuclear charge. Thus whereas for the C^{4+} ion it is 0.35 eV, for Al^{3+} the correction is already 11 eV. With neonlike ions[31] the relativistic correction already exceeds the correlation energy for $Z > 13$, and exceeds the total energy of coulombic repulsion of the electrons for $Z > 65$. It is significant that with large atoms the relativistic correction is extremely sensitive to small perturbations of the electron shell, due, for example, to correlation.

II. SEMIQUANTITATIVE CALCULATIONS

The possibilities of quantitative calculations on many-electron systems are limited, of course, by their unwieldiness. Improvement of methods of calculation and computer technique may perhaps allow exact calculations to be made for molecules containing up to twenty electrons, but such calculations will hardly ever be undertaken for heavier molecules. Coulson[32] has commented facetiously that merely to write down a table of values, with a sufficiently small interval, of the wave functions for the uranium atom will require so much paper and ink that all the atoms in the whole solar system will not suffice for their production. And if it is borne in mind that the majority of the molecules of greatest interest to chemistry contain more than twenty electrons (for benzene the number is 42), it becomes clear that, for chemistry as a whole, those quantitative calculations which can actually be carried out do not present a task of primary importance. For the experimenter it is far more important that theory should give qualitative, descriptive explanations of facts and generalisations which so often puzzle him, and which for the most part require for their explanation not cumbersome calculations but simple, aptly chosen models. An approximate approach, representing a qualitative solution of the problems, is especially necessary in the case of large molecules, in particular those which are biologically active.

In chemistry there are, of course, many individual problems, solution of which requires quantitative calculations; an example is the exact calculation on the CO molecule, since it is impossible experimentally to determine unambiguously its dissociation energy D, the value of which plays a fundamental part in thermochemistry. Hurley's calculation[33] by the method of "atoms in molecules" enabled a correct choice to be made (the highest of three experimental values, D = 11.24 eV, proved to be the true one). Knowledge of fairly exact wave function remains important also in explaining new facts, for sometimes it is impossible to decide whether the failure of an explanation is due to an incorrect model or to the approximate character of the wave function. Solution of most qualitative problems of the structure and properties of molecules requires molecular wave functions of intermediate precision. Exact functions for the solution of such questions would only be unnecessarily complicated. Simplified functions, which are convenient for practical calculations, can always be readily obtained from them.

We shall now consider the main applications and most important successes of semiquantitative and semiempirical calculations of the electronic orbitals of molecules.

1. Theory of Conjugated Systems

This branch of the theory of the electronic structure of molecules, the foundations of which were laid by Hückel[34], has been developed by many workers. Important contributions to the theory were made in papers by Coulson[35-38], Lennard-Jones[39,40], Mulliken[41-43], Longuet-Higgins[44], and others. During recent years a series of interesting calculations on conjugated systems has been undertaken by Koutecký and his collaborators[45-51]. Recently Ruedenberg has published a series of papers[52] in which he has examined systematically, from a unitary viewpoint, the whole theory of π electrons in molecules containing conjugated bonds, within the framework of the LCAO-MO method taking into account the non-orthogonality integrals and electron interaction. He has found several new and interesting relations for quantities analogous to "bond order", and in some sense has summed up a definite stage in the evolution of the π-electron theory of conjugated systems.

At the present time fundamentally new results in the theory of conjugated systems can be expected from taking into account non-adiabatic conditions (*i.e.* interaction between the motion of electrons and of nuclei) and especially electron correlation. Both problems can be examined most successfully by a method of secondary quantisation, which

has been well developed and successfully applied in quantum field theory and in the theory of the solid state[26,27].

As noted above, owing to the delocalisation of electrons in conjugated systems, their correlation is not localised in electron pairs, and the correlation of each electron with all the others is important here. As a result, the estimation of correlation effects involves considerable difficulties. In general, self-consistent molecular orbitals for conjugated systems are no longer a sufficiently good zero approximation. Correlation effects are no longer as small as in light atoms and in molecules not containing conjugated bonds.

Conjugated molecules, like other many-electron systems, have energy levels representing "collective" states, which are not represented in the one-electron approximation. In three-dimensional systems (metals, heavy atoms) these collective levels are separated from the "one-electron" states, when the number of electrons N is sufficiently large, by an energy gap which remains finite as $N \to \infty$.[26,27] In the case of conjugated chains, the unidimensional character of the latter results in the collective levels merging with the main band, formed by the one-electron states, as $N \to \infty$.[53]

With finite N the collective levels in the molecular chains may appear in the electronic spectra. However, calculations of these spectra by existing methods cannot be regarded as completely satisfactory. Many workers[54-68] have made such calculations within the framework of the LCAO-MO method. Since in this work the electron correlation has been either completely disregarded or allowed for approximately (by taking into account a small number of configurations), satisfactory results have not usually been obtained, either for the levels or for the oscillator strengths.

For the planar cyclic molecule $C_{18}H_{18}$, for example, calculation gives[69] the following positions of the levels (in cm^{-1}): $^1B_{2u}$ 13 230, $^1B_{1u}$ 16 800, and $^1E_{1u}$ 33 920, whereas the corresponding experimental values are 20 350, 21 345, and 27 060. Discrepancies are obtained not only in the absolute but also in the relative magnitude of the terms (the relative values are 1 : 1.30 : 2.60 and 1 : 1.05 : 1.35 as calculated and measured respectively). It is surprising that discrepancies are obtained here in spite of the semi-empirical character of the calculation, which was based on values for several parameters found from data on the electronic spectrum of benzene. For the oscillator strength f of the transition to the $^1E_{1u}$ level (collective state) in the $C_{18}H_{18}$ molecule, experiment gives 1.7, whereas the calculated value[69] is $f = 6.8$.

Another example is provided by the polyenes, for which it was long ago noted that calculation by the LCAO-MO method (like that based on the potential box model) gives too strong a dependence of the position of maximum absorption in the electronic spectrum on the length of the conjugated chain[70-73].

In order to improve calculations on conjugated systems, we must learn to allow considerably more exactly for the correlation of electrons. This may apparently be done in two ways, by applying methods of secondary quantisation and by introducing various simple models.

Recently Nikitin[74] has suggested a simple model for the potential interaction of electrons in conjugated cyclic systems. He introduced the angle $\varphi_1 - \varphi_2$ instead of the distance between electrons, and expanded the interaction potential in a Fourier series, in which he retained only the first two terms. The wave equation can then be solved exactly, and therefore with this model the electron correlation can be assessed exactly. Nikitin found a series of excited collective states, which in the absence of electron interaction merge with the one-electron states, as they should. Allowance for the electron correlation was found to diminish the contribution of their mutual repulsion to the excitation energy of the collective states. For the $C_{18}H_{18}$ molecule, in particular, the ratios of the terms given above proved to be 1 : 1.00 : 1.95, *i.e.* considerably closer to the experimental values. The oscillator strength for the transition to the $^1E_{1u}$ level in the same model is $f = 3.4$, which is also far closer to the true value. In view of the crude model used by Nikitin, these results must be regarded as extremely encouraging. However, the reason for the discrepancy in the absolute magnitude of the terms remains obscure.

Another very important line of advance in the theory of conjugated systems is to allow for the interaction of the motions of electrons and nuclei (non-adiabatic conditions). This interaction must be borne in mind in attempts to explain the above peculiarities of electronic spectra. Allowance for non-adiabatic conditions is in general necessary in cases in which the electronic excitation energy is comparable with the energy of a vibrational quantum. Such a situation occurs, for example, when an electronic term which is degenerate as a result of molecular symmetry is split on destruction of this symmetry by molecular vibrations. Then the adiabatic approximation for electrons and nuclei is not applicable. Electrons and nuclei should be treated as a single system, the wave function of which can be written in the superposition form:

$$\Psi = \sum_n \varphi_n(X)\,\psi_n(x, X), \qquad (3)$$

where $\psi_n(x,X)$ is the eigenfunction of the whole set of coordinates x of the electrons at specified values of the coordinates X of the nuclei, and $\varphi_n(X)$ is the wave function of the nuclei relating to the n-th electronic state. As a result of the interaction of electronic and nuclear motions, the equilibrium configuration of the nuclei differs from that in the absence of such interaction; in particular, the original symmetry is destroyed, and the degeneracy eliminated. This effect, which has been termed the dynamic Jahn–Teller effect[75-82], is encountered in cyclic systems, in ion-radicals, in complex compounds, and in several other cases.

The Jahn–Teller effect is closely linked with the hypothesis of the alternation of bond lengths in long conjugated chains[70-73,83]. The reason for this alternation is simply that it is energetically advantageous: with alternating long and short bonds the band of electronic energy levels is split into two equal parts, the lower (filled) band being somewhat depressed, which produces a gain in energy. The extent of the alternation is, of course, limited by the forced shortening of some and lengthening of other σ bonds. It is difficult to calculate the resulting effect exactly, and nothing final can yet be said concerning its magnitude. Until now the influence of alternation only on the electronic spectra and on the magnetic screening of protons in nuclear magnetic resonance has been considered.

Longuet-Higgins and Salem[83] used alternation to explain the spectral peculiarities of cyclic polyenes $C_{4n+2}H_{4n+2}$, in particular of $C_{18}H_{18}$. However, according to Gouterman[69], new, more precise data on the spectrum of the $C_{18}H_{18}$ molecule cannot be explained on this hypothesis: the vibrational

structure of the spectrum, which would be expected theoretically, is not observed, the term ratios (1 : 1.4 : 1.58) do not correspond to the experimental values (see above), and the smallest possible oscillator strength is $f = 4.5$; in order to obtain this value, however, it is necessary to assume maximum alternation of bond lengths (1.33 and 1.52), which is intrinsically unlikely and above all gives poor results for the magnetic screening of protons. The negative result in the case of the $C_{18}H_{18}$ molecule is not surprising, since according to Longuet-Higgins and Salem[83], alternation should occur when the number of links in the chain exceeds 30. Whether it does actually occur in such long chains will be shown by future investigations. At the present time it seems quite probable that several features of shorter conjugated systems are to a considerable extent due to electron correlation. Nevertheless, it is quite possible that interaction between electronic and nuclear motions also plays some (as yet not entirely clear) part.

In this connection we may note that, when the non-adiabatic nature of the system is taken into account, the wave function is substantially many-electron in character even in those cases in which terms representing interaction of the electrons have been omitted from the original Hamiltonian. Actually, as can be seen from Eqn. (3), the wave function ψ can be regarded as broken down into configurations, which allows for electron correlation. Such interaction of electrons through the motion of the nuclei is equivalent in the method of secondary quantisation to interaction of the electrons with virtual phonons. It would be very interesting to apply to the treatment of non-adiabatic conditions and electron correlation in conjugated systems the method developed by Bogolyubov[26,27] in connection with the theory of superconductivity. It may be hoped in this way to erect a many-electron theory of the optical, electrical, and magnetic properties of conjugated systems.

2. Dependence of the Energy of the Ground State of Molecules and Radicals on Their Structure

This problem is very important for chemistry, since it is linked with finding the way in which the energy of bond rupture depends on molecular structure. An extensive literature has been devoted to this question, but it cannot be said that sufficient clarity has been achieved or a method found for estimating bond energies even semiempirically.

For a long time it was accepted in chemistry that the difference in energy between isomeric molecules and so-called deviations from the additive scheme of organic chemistry were due to conjugation and hyperconjugation. As calculations improved, however, it became increasingly clear that an important role belongs here also to such factors as the type of hybridisation of the orbitals, the length and polarity of the bonds, etc.[84,85] Nevertheless, numerical calculations of these effects made no appreciable progress.

As noted above, calculations by the molecular orbital method have so far usually given unsatisfactory results for bond energies, whether or not the interaction of configurations was taken into account. Apart from a series of diatomic molecules and radicals, this method has been used for calculations on the molecules[86,87] H_2O, O_3, NH_3, CH_4, HCN, CO_2, SiH_4, Be_4, and HCHO, and the radicals[88-91] CH_3, CH_2, and NH_2 (summary table in Ref. 2). Owing to the complexity of the calculations and the different degrees of approximation in different papers, these calculations shed no light on the problem of the dependence of dissociation energy on molecular structure. On the other hand, similar calculations on electronic computers do not yet have such an aim.

One elegant method for approximate calculations on unconjugated molecules, which was worked out by Mamotenko[92] in the Karpov Institute of Physical Chemistry even before the Second World War, has unfortunately been undeservedly forgotten (and among non-Soviet scientists it is probably simply unknown). The basic idea of this method is to utilise the invariance of the determinantal wave function of the molecule with respect to linear transformations of the basic one-electron functions, and to choose as the latter those for which the mean energy of coulombic repulsion of the electrons would become a minimum and could to a first approximation be neglected. This method probably gives correct relative values for the energies of the initial molecules (for example hydrocarbons). Mamotenko obtained a value of 104 kcal (experimental 102 kcal) for the energy of rupture of the C–H bond in methane, and 48 kcal for the height of the barrier to internal rotation in ethylene.

In our opinion Mamotenko's method is worthy of thorough study and development. If allowance were made in it for interaction between configurations, the method could be extended to conjugated molecules.

One result of Mamotenko's calculations[92] has been to establish the strong dependence of the bond energy on the type of hybridisation. Thus, for example, the energy of the C–C bond diminishes by 18 kcal on passing from sp^2-hybridisation to sp^3-hybridisation when the bond length (1.30 Å) is unchanged, but by 39 kcal when the simultaneous lengthening of the bond to 1.52 Å is taken into account. This probably means that change in the type of hybridisation is the main cause of breakdown in additivity in organic chemistry, while conjugation plays a subordinate part here. Recently Dewar[93] reached the same conclusion. However, his arguments cannot be regarded as completely convincing, since they were based only on experimental data in which the effects of hybridisation and of conjugation (or hyperconjugation) operate at the same time, and it is impossible to separate them.

Mention must be made of a semiempirical method for calculating the energy of molecules, proposed by Moffitt[94] in 1951 and termed the "atoms in molecules" method. The main idea of the method is to make maximum use, in molecular calculations, of experimental data on various atomic parameters (ionisation potentials, electronic terms, etc.). Although several difficulties[95-98] arise here, it is possible that with further improvement this method will achieve success[33,99-102].

3. Geometry of Molecules

One of the traditional tasks of quantum chemistry is to explain and predict the shape and size of molecules. The theoretical prediction of the equilibrium configuration of atoms is especially important for electronically excited molecules and for labile intermediate structures (for example activated complexes, radicals, carbonium ions, etc.).

It is significant that the electron correlation varies comparatively little with change in valence angles and slight

changes in bond lengths. This follows directly from Sinanoğlu's results[22], since changes in valence angles do not involve breakdown of the bonding electron pairs which make the main contribution to the correlation. The change in correlation will then be slight, since it will depend solely on the pair correlation of "foreign" electrons and on quaternary and higher correlations. Probably these effects mainly govern the difference in energy between rotational isomers, since it is most likely that self-consistent orbitals for different isomers differ little. It is therefore not surprising that the one-electron treatment of the geometry of simple molecules proposed by Walsh[103] possesses great predictive power. Starting from a few postulates and knowing only the number of electrons in a molecule, Walsh was able to explain and predict the shape of triatomic and several other molecules both in the ground and in excited states. Walsh's method is very important for analysing the vibrational structure of electronic spectra. Recently his starting postulates were analysed by calculating molecules of the type HAH by the molecular-orbital method with different basic atomic functions[104]. This work showed that Slater functions reproduce Walsh diagrams quite well, but it was observed that his first postulate, that with a valence angle of 90° the s function of the A atom does not combine with other functions, is usually satisfied only very approximately.

In some cases, of course, the geometry of the molecules is governed by the Jahn–Teller effect. Relevant calculations have been carried out for a relatively small number of molecules and complexes[76-82,105-108], although this is one of the very important problems of quantum chemistry.

Until now, unfortunately, still fewer calculations have been made on the geometry of labile species. Here we can mention only calculations on the radicals mentioned above[88-91], CH_3, CH_2, and NH_2, and also the complexes[109-115] H_3, H_3^+, and H_4. Nevertheless, a theoretical examination of the configuration of unstable intermediate structures is extremely important for chemical kinetics. The present level of computing technique obviously does not make it possible to calculate the absolute value of the energy, but it will probably permit calculations on the basis of which conclusions can be drawn concerning the energetically most favourable configurations of molecules and complexes.

4. Excited States of Molecules. Probabilities of Optical Transitions

Interest has greatly increased recently in excited, especially triplet, states of molecules. This is because the latter play an important part in processses involving energy transfer in condensed media, in chemical reactions, in luminescence, and above all in quantum multipliers and generators. Here theory has developed mainly in the direction of determining the position of electronic levels, their dependence on internuclear distances, and the probabilities of transitions between them. To some extent these questions have already been touched on above.

Quantitative calculations of the energy of the excited levels of molecules as a whole depend on the state of computing methods in the theory of many-electron systems. Apart from a few of the simplest examples, calculations which have been made up to the present are semiquantitative in character. They are very useful for the classification of energy levels, and also for testing different methods of calculation. In several cases semiempirical approximate calculations enabled the qualitative dependence of absorption frequencies and band intensities on molecular structure to be found, and in this lies, of course, one of the most important contributions of quantum mechanics to molecular spectroscopy[54-68].

One of the most important problems of the theory of electronic orbitals of molecules consists in finding the dependence of excited levels on interatomic distances. The absence of such data imposes marked limitations on many investigations.

This problem was partly solved for simple polyatomic molecules by Walsh[103] — semiempirically, as stated above. For diatomic molecules Vanderslice and Mason proposed in a series of papers[116-118] a semiempirical method of finding the dependence of the energy of excited states on the internuclear distance. They used for this purpose Dirac's expression for the energy operator[119]

$$\hat{\mathbf{H}} = \Sigma J_{ij}\,\vec{S}_i\vec{S}_j\,, \qquad (4)$$

where J_{ij} is the exchange integral between the i-th and the j-th orbitals. With diatomic molecules the energy of the levels can be expressed by means of two exchange integrals (for $p\sigma$ and for $p\pi$ orbitals), values of which can be determined, depending on the internuclear distance, from any two known potential energy curves for the given molecule. This yields self-consistent results, agreeing well with available data‡, for a series of excited states of O–O, O–N, N–N, and several other molecules. At first sight, however, such success seems surprising, for Dirac's formula (4) takes no account of non-orthogonality integrals, and hence would appear to have no claim to be a quantitative description.

The question of the applicability of Dirac's vector model has been discussed recently by Mattheiss[120]. Instead of the usual atomic functions he used as bases semilocalised orbitals orthogonal to the orbitals of neighbouring atoms. Taking into account all ionic structures having one atomic orbital filled twice, as well as the ordinary covalent structures, he showed that Eqn. (4) is valid provided that the exchange integral J in it is replaced by the effective quantity

$$J_1' = J_1 + \frac{2M^2}{E - H_1}\,,$$

where J_1 is the exchange integral between neighbouring semilocalised orbitals ($J_1 > 0$), E the energy of the system, and H_1 the diagonal matrix element for the corresponding ionic state. The sign of J_1' may be either positive or negative.

The result obtained by Mattheiss is significant not only in connection with the work of Vanderslice and Mason, since formula (4) can be conveniently used also for other purposes, for example in calculations of spin–orbital interaction.

The probabilities of optical transitions (oscillator strengths) are extraordinarily sensitive to the choice of wave functions, and therefore the corresponding calculations are usually very approximate. This problem cannot be regarded as solved, either for molecules or even for atoms. In this connection a method of calculating oscillator strengths proposed by Vetchinkin[121] merits attention.

‡ For calculations of excited states of several diatomic molecules, see also Ref. 8.

The basic idea is to find optimum wave functions for calculating the given matrix element. For this purpose the wave function should satisfy several conditions, which can also be used to find the parameters which it contains. The energy calculated by means of these functions is, of course, somewhat higher than the minimum value reached with the given form of tentative function. The method was tested on the lithium atom and gave good results, not inferior to those calculated by the Hartree–Fok method. It is applicable with equal success to molecules. It is significant that a similar method can be suggested for calculation of matrix elements of other quantities, and also for finding values of ψ in the vicinity of the nucleus.

Apart from the problem of calculating oscillator strengths of "allowed" transitions, calculations of the probability of transitions between states of different symmetry are extremely important for electronic spectroscopy. These transitions occur because the vibrations of molecules somewhat disturb their symmetry; when this is taken into account, the corresponding matrix elements are non-zero (so-called vibronic transitions). Thus we have here the same problem of allowing for the interaction between electronic and vibrational motion as was discussed above. The Jahn–Teller effect and "forbidden" optical transitions in molecules are the principal manifestations of this interaction [122].

Theory gives fairly good results for the probabilities of "forbidden" transitions. Thus calculation gives 0.26 compared with an experimental value [123] of 0.1 for the oscillator strength of the transition $^1A_{1g} \rightarrow {}^1B_{1u}$ in benzene. The most probable cause of the discrepancy is the approximate character of the molecular orbital adopted. The effect of electron correlation on the probability of vibronic transitions has not been investigated.

Another important problem is the calculation of the probability of singlet–triplet transitions. Here it is most interesting to elucidate the role of paramagnetic impurities [124–126] and of complex formation [127].

5. Calculations of Weak Interactions

In comparison with the coulombic interaction of charges, many intramolecular interactions and interactions with external fields are characterised by very low energies (of the order of 10^{-4}–10^{-14} eV). These include spin–spin interaction of electrons and nuclei, spin–orbital interactions, interaction of magnetic moments of electrons and nuclei with external magnetic fields, interaction of quadrupole moments of nuclei with external electric fields, etc. The problems involved in calculating such interactions have become especially urgent in connection with the rapid development of microwave spectroscopy. The necessity for interpreting various data on electron and nuclear magnetic resonance, quadrupole resonance, and microwave spectroscopy made it essential to solve several new theoretical problems connected with the structure of molecules, radicals, and complex compounds. Furthermore, calculation of weak interactions makes it possible to assess the quality of approximate wave functions of molecules. This possibility is based on the fact that, with different weak interactions, the main contribution to the mean value is given by different regions of space. Thus, for example, the diamagnetic part of the susceptibility of molecules depends on $\langle r^2 \rangle$, the diamagnetic part of nuclear screening on $\langle r^{-1} \rangle$, spin–orbital interaction on $\langle r^{-3} \rangle$, hyperfine interaction of electron with nucleus on $\langle r^{-3} \sin^2 \Theta \rangle$ and $\langle r^{-3}(3\cos^2\Theta - 1) \rangle$, etc. In the case of the simplest molecules satisfactory results are obtained for these quantities [128–130], although they do differ from the true values by factors of 1.5–2.

More difficult calculations arise for the so-called paramagnetic parts of the suceptibility and nuclear screening, which occur in second-order perturbation theory. Calculation of these quantities by means of the formulae of the theory [131,132] requires knowledge of the eigenfunctions and eigenvalues of all excited states of the molecule. Since they are unknown, such a procedure is impossible in practice. Calculations based on formulae obtained by the variational method [133–135] require knowledge of the wave function of the ground state alone. Since, however, these quantities depend on the second derivatives of this function, calculations with approximate functions yield unsatisfactory results. Thus, for example, the Heitler–London function gives for the paramagnetic part of the susceptibility of the H_2 molecule 0.465×10^{-6}, whereas the experimental value [130] is 0.0846×10^{-6}. When a more versatile wave function is used, a value of 0.106×10^{-6} is obtained [130]. A very exact wave function is obviously required for complete agreement with experiment. Similar difficulties arise in calculating the paramagnetic part of nuclear screening. In both cases a method can be found for avoiding the main source of error — double differentiation with respect to the coordinates — if molecular functions are constructed from atomic functions in which (as was suggested by London [136]) account had already been taken of the precession of electrons in an external magnetic field. This procedure was originally used by Aleksandrov to calculate magnetic screening [137]. It is comparatively simple to obtain quite satisfactory results for the paramagnetic part of magnetic screening [137] and also the susceptibility [138].

Good agreement with experiment is also difficult to achieve for the value of the wave function in the vicinity of the nucleus $\psi(0)$, which is necessary for calculation of the "contact" term in the expression for the energy of spin–spin interaction of nuclei among themselves [139–140] and with electrons [141,142]. In the one-determinant approximation of the molecular orbital method $\psi(0)$ often vanishes; the experimental value can be approached by allowing for the interaction of configurations. Thus the calculation of $\psi(0)$ represents a fairly rare example of a considerable improvement in the calculated result produced by allowing for excited configurations [128,143]. Satisfactory results can be obtained for $\psi(0)$ also by the valence bond method [144].

Many interesting and important tasks arise in interpreting the hyperfine structure of electron paramagnetic resonance spectra. Here data are obtained for the distribution of electron spin density [145–149] which are extremely interesting from the point of view of the structure of radicals. In particular, it has been found that this quantity does not in general correlate with the effective charge.

Calculation of the electric field gradient q was one of the first applications of quantum mechanics to microwave spectroscopy [150]. Recent investigations have shown that the early conclusions concerning the relative part played by hybridisation and the ionic character of bonds in producing the electron field gradient in the vicinity of the nucleus [151] must be seriously revised. The main difference between calculated and experimental (obtained from quadrupole resonance) values of q has been shown to be due to the fact that simple Slater functions, with which these calculations are usually made, give a poor descrip-

tion of the electron distribution in a region of overlapping atomic orbitals[152]. The introduction of different effective charges for different spins ("open shells") and for different molecular orbitals ($2s$, $2p\sigma$, $2p\pi$) of the nitrogen molecule considerably improves the calculated results, good agreement with experiment being obtained for the quadrupole bonding constant[152].

In conclusion we may note an interesting new field of application of quantum mechanics which has been revealed in connection with the recently started investigations of triplet states of aromatic compounds by means of electron paramagnetic resonance[153]. Here in particular, the problem[153-155] of elucidating the role of electron correlation arises.

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We have dealt briefly with several lines of advance and problems in the calculation of electronic orbitals of molecules. Several other questions in this field, which we have not touched on, are no less urgent. Among these are, for example, the theory of the structure of complex compounds and electron-deficient compounds, ligand field theory, intermolecular interaction and the donor–acceptor bond, the theory of the hydrogen bond, etc. The theory of the electronic orbitals of molecules represents an important branch of quantum chemistry. Not only chemical sciences but also many branches of physics are concerned in developing this theory and perfecting the technique of calculations on many-electron systems.

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