QUANTUM-MECHANICAL METHODS AND THE ELECTRONIC SPECTRA AND STRUCTURE OF MOLECULES[1]

ROBERT S. MULLIKEN

Ryerson Physical Laboratory, The University of Chicago, Chicago, Illinois

Received July 10, 1947

This paper presents a review of the past and present state of development of the application of quantum mechanics to problems of molecular structure and spectra. Following this, various methods and problems are discussed with emphasis on the desirability of extensive development of semiempirical methods, using either the AO (atomic orbital) or the MO (molecular orbital) method of approximation. It is remarked that the MO method has special advantages when spectra as well as the structures of normal molecules are to be considered. In conclusion, two important needs are pointed out. One is the production of an authoritative compilation of quantitative data on the spectra of pure compounds. The other is a more general familiarity with and a more extensive application of existing possibilities for using quantum mechanics to understand molecular electronic energy levels and spectra.

I. THE PAST AND PRESENT

Dirac once stated that, in principle, the whole of chemistry is implicit in the laws of quantum mechanics. That theory, born in 1925–26, immediately showed itself fruitful for the understanding of the structures of atoms, molecules, and extranuclear matter in general. In particular, it gave the first real qualitative and roughly quantitative explanation of covalent chemical binding. A large proportion of the world's theoretical physicists rushed into quantum-mechanical explorations and computations in the hope that a quantitative understanding of atoms and molecules could now be realized. There was much successful slashing of virgin timber during the period 1927–34. The most striking success of theory was attained, perhaps, in the computations of Hylleraas on the helium atom and of James and Coolidge on the hydrogen molecule. Here quantum mechanics was shown capable of surpassing experiment in accuracy.

But except on the simplest systems the computations proved to be complicated and laborious without yielding more than approximate results. Frustrated and repelled, many of the theorists began to turn to other problems.

Meantime, interpretative spectroscopy went through a rapid period of fruitful development. Here a good general theoretical framework was speedily set up, and continuing detailed computations were less essential. First atomic, then diatomic, spectra became relatively well understood through the efforts mainly of physicists and chemical physicists. Finally the novelty wore off, and the physicists began to turn to other fields. Polyatomic spectra remained, but were complicated.

---

[1] This paper and the two following (5, 8) represent in part an elaboration, in part a condensation, of the paper presented at the Symposium on Color and the Electronic Structure of Complex Molecules which was held under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society at Northwestern University, Evanston and Chicago, Illinois, December 30 and 31, 1946.

World War II and the atomic bomb blasted away more of those still devoted to the fundamental and theoretical aspects of the structure and spectra of molecules, for these fields had little bearing on the immediate job of winning the war.

Indirectly through the development of radar, however, the war has given delayed stimulus to the new field of microwave spectroscopy, now expanding with explosive rapidity. This is bringing again a considerable number of physicists into intimate contact with problems of polyatomic spectra and structure.[2] There is also a trend toward a long-needed mingling of knowledge and interests among specialists in various regions of the spectrum and in other fields which yield information on the structure of molecules.

There remains a vast vacuum in the complementary field of the quantitative application of quantum mechanics to the detailed understanding of the electronic structure of molecules. The further development of this field holds manifold possibilities for the better understanding and prediction of molecular properties and molecular structure.

Looking back at the first flush of enthusiasm for the application of quantum-mechanical calculations to molecular problems, it appears that too much may have been expected from pure theory. Perhaps if less had been expected, more progress could have been made,—by seeking and using just the right combinations of theoretical formulas and experimental information. Even in those days, such semiempirical blends were used with conspicuous success by, among others, Slater, Van Vleck, Eyring, and Pauling in this country, Hückel in Germany, and Lennard-Jones and Penney in England. Essential to the successful concoction of these appears to be a combination of the viewpoints and methods of the chemist and the physicist. I believe that the time is ripe for a new emphasis on the use of semiempirical methods in the application of quantum mechanics to molecular problems.

II. METHODS AND PROBLEMS

Let us review in outline the quantum-mechanical methods that may be used in understanding molecules and their properties,—with particular reference to electronic spectra.

As an ideal goal, we might ask for the electronic eigenfunction and energy of every important molecule or class of molecules in its ground state and its important excited electronic states, as a function of all possible variations in the nuclear configuration,—thereby also including all isomers. We should also like to know how the eigenfunctions and energies vary under the influence of force fields, particularly those resulting from the approach of other molecules. From such information, desired behavior and properties could be deduced by relatively simple calculations.

A. Qualitative and quantitative methods: theory and experiment

The complete attainment of such a goal would surely take decades, if not generations. It has taken centuries to apply Newton's laws to practical situ-

---

[2] Written after attending the Symposium on Molecular Structure and Spectroscopy which was held at The Ohio State University, June, 1947.

ations, and we are not through yet. In the application of quantum mechanics we have only started. While working toward our ultimate goal, less complete information will be very useful at first. This can be obtained by applying quantum mechanics in a variety of ways differing in their relative quantitativeness and in their relative content of pure theory and of empirical data.

These applications in respect to the proportion of theory used may be divided roughly into four methods, all of which probably are worthy of much more extensive use than has yet been made of them:

(1) The qualitative method: judicious application of systematic qualitative and semiquantitative interpretations throughout the vast realm of inorganic and organic compounds in the solid, liquid, and vapor states.

(2) The semiempirical method: systematic theoretical computations of a relatively simple character, based on approximate wave functions of the molecular orbital or of the atomic orbital type, but making frequent use of empirical data as a substitute for, or even an improvement on, certain theoretical integrals. Empirical and semiempirical information likely to be useful for this purpose includes: frequencies, intensities, and other data from electronic spectra; excitation and ionization potentials, probabilities, and processes; dipole moments; thermal data; electronegativities derived from thermal data, dipole moments, and other sources; interatomic distances and bond angles from electron-diffraction, infrared, and microwave investigations; force constants and other information on bond properties from infrared and Raman spectra, including information on bond moments and polarizabilities as a function of internuclear distance, obtained from intensity measurements and other spectroscopic data.

(3) The approximate theoretical method: purely theoretical computations, using approximate molecular eigenfunctions of the molecular orbital or of the atomic orbital type.

(4) The accurate theoretical method: completely theoretical computations, using really accurate molecular eigenfunctions.

Computations of all types may be capable of very considerable extension with the use of the superpowerful computing machines now being developed.

B. The atomic orbital and molecular orbital approximation methods

Approximate theoretical methods for describing and computing electronic structures and spectra of molecules include, as is well known, the AO (atomic orbital) and the MO (molecular orbital) approximation methods. Here the word "orbital" is an abbreviation for "one-electron orbital eigenfunction." In simple molecules, each valence bond corresponds to a pair of electrons occupying a pair of linked AO's (AO method) or a single bonding MO (MO method). It is characteristic of the molecular problem that both of these methods, in different ways, are disappointingly far from exact in quantitative applications. More exact methods are available, but are far too complicated for application, at least for the present and probably for a long time to come, to any but very simple molecules.

The AO method fits well into the chemist's traditional conceptual framework of valence-bond structures. In its qualitative aspects, it is relatively simple for the ground states of molecules which can be described by a single definite set of chemical bonds, but loses this advantage in cases where "resonance" or "mesomerism" must be assumed.

The MO method is conceptually not as close to chemical valence ideas for ground states of molecules, but has certain other advantages. In particular, (*1*) the special and often arbitrary formulations used to describe the ground states of "resonating" molecules in the AO method disappear in the MO method, the MO description of such molecules being not different in kind or more complicated than for "normal" molecules; (*2*) the MO method usually is conceptually simpler and more transparent for the description of excited and ionized electronic states and electronic spectra than the AO method. Some of the most important cases where the MO method shows its characteristic advantages even for ground states are: molecules with polar bonds; molecules with double or triple bonds, including oxygen and all aromatic and conjugated molecules, molecules with trigonal conjugation as in BCl_3 or NO_3^-, molecules with cumulated double bonds, molecules with hyperconjugation, and so on; anomalous molecules like the boron hydrides; odd-electron molecules and radicals. The qualitative use (method 1 of Section II,A) of the MO method will be exemplified in the following paper on diborane and related molecules (5).

Since a large fraction of molecules showing color, or at least near-ultraviolet absorption, are molecules containing systems of double bonds, and in view of the general advantages of the MO method for excited electronic states, it is evident that this method should be particularly suited for understanding the electronic spectra of complex molecules. Moreover, as Hückel first showed, relatively simple yet significant semiempirical quantum-mechanical computations (method 2 of Section II,A) are feasible by an approximate form of the MO method.[3] These not only account remarkably well for the stability of aromatic and conjugated molecules, including free radicals, but also give a good account of the locations of their spectra. An apparent large discrepancy between the numerical value of the empirical parameter which fits the thermal data on resonance and conjugation energies, and the spectroscopic value of what theoretically ought to be the same parameter, is largely removed when a more refined treatment is used (7).

With the insertion only of an empirical correction factor (the need for which has been shown to diminish or disappear in cases where it has been feasible to use more accurate eigenfunctions), simple quantitative computations of the absolute absorption intensities of molecular spectra are likewise feasible. These can be used as an important aid in determining the nature of observed electronic spectra, or the geometrical configurations of the molecules to which they belong (6, 9, 10). The direction of polarization of the absorbed light can likewise be

---

[3] For a review see reference 4. At the present time Coulson and collaborators in England, among others, are carrying out important work in this direction. *Added in proof:* A valuable review on the MO method has just appeared (C. A. Coulson: Quarterly Reviews of the Chemical Society **1**, 144 (1947)); likewise, a valuable review on the use of the LCAO and the MO methods in interpreting electronic spectra (A. Maccoll: Quarterly Reviews of the Chemical Society **1**, 16 (1947)).

predicted theoretically, and can be observed in the case of molecules in crystals. Considerations of this sort have been used in the development of polaroid filters.

As above noted, qualitative and semiempirical quantitative applications of the MO method to problems of electronic structure and spectra have proved and should continue to prove fruitful. The AO method has also been applied in similar ways,[4] and its possibilities are worth exploring further; it may have special advantages for particular types of problems. Where possible, both methods should be used and the results compared.

Approximate computations of a more elaborate and more purely theoretical nature (method 3 of Section II,A) have also been carried out on the spectra of aromatic and dye molecules, particularly by the use of approximate wave functions of the MO and of the AO type, whose energies $\int \psi H \psi \, dv$ were determined (1, 2, 3,[5] 9[6]). Spectral frequencies and in some cases intensities were in this way computated quantitatively, and in rather good agreement with experiment. Except for the time-consuming nature of the computations by present means, this method shows considerable promise. Many of the integrals already computed in the work just mentioned could be taken over for use for other unsaturated molecules involving carbon or nitrogen atoms, thus bringing the effort required to moderate proportions. However, the results obtainable are limited by the roughness of the theoretical approximations used, and appear to be unreliable in the case of triplet states (7).

Hence the present writer is inclined to favor methods in which certain theoretically defined integrals are replaced by empirical parameters (method 2 of Section II,A). An illustration of the use of this method with MO approximate eigenfunctions will be given in the second paper following this one, which deals with the subject of twisting frequency and the barrier height for free rotation in ethylene (8).

III. THE FUTURE

In conclusion: There is at the present time a vast body of empirical data on the spectra of complex molecules. The data are, however, relatively unsystematic and poorly organized. Also, the rich possibilities (qualified by certain limitations) for their theoretical interpretation are not generally understood. This situation points to two important needs.

One is the production of an authoritative compilation of quantitative data on the spectra of pure compounds. In the case of absorption spectra, the need is for accurate maps of *absorption coefficient* against frequency, including systematic comparisons of a maximum variety of derivatives of important molecules. The charts of the American Petroleum Institute constitute an important step in

---

[4] *Cf.* Hückel (4), papers of Pauling and Wheland, and others.

[5] This interesting paper by Herzfeld and Sklar (3) on polymethine dyes contains also references to earlier papers.

[6] See Sklar (9) for review and references. It should be remarked here that the present writer does not fully subscribe to all of Sklar's methods and conclusions.

the direction of such a program. These maps should also be extended as rapidly as possible to include the very rich vacuum-ultraviolet region.

The second need is a more general knowledge and a more general application of the existing possibilities for understanding the various absorption peaks and emission spectra, in terms of the characteristic electronic energy levels of various groups or atoms and the changes in these by steric and other effects. The now largely empirical and often inaccurate attribution of particular peaks to particular molecular groups or situations can and should be replaced by an increase and diffusion of theoretical understanding of molecular electronic spectra, so that observation, diagnosis, and prediction can be smoothly and correctly coördinated. At the same time, other related optical properties, for example, refractivities and optical rotation, should be subjected to similar theoretical coördination, and the whole should be brought into line with a deeper understanding of the electronic structures and bond properties of molecules in their normal states.

REFERENCES

(1) Förster, T.: Z. physik. Chem. **47B,** 245 (1940) and earlier references.
(2) Goeppert-Mayer, M., and Sklar, A. L.: J. Chem. Phys. **6,** 645 (1938).
(3) Herzfeld, K. F., and Sklar, A. L.: Rev. Modern Phys. **14,** 294 (1942).
(4) Hückel, E.: Z. Elektrochem. **43,** 752, 827 (1937).
(5) Mulliken, R. S.: Chem. Rev. **41,** 207 (1947).
(6) Mulliken, R. S., and Rieke, C. A.: Phys. Soc. Rept. Progress Physics **8,** 231 (1941).
(7) Mulliken, R. S., and Rieke, C. A.: Rev. Modern Phys. **14,** 259 (1942) (abstract; it is hoped that full papers can be published soon).
(8) Mulliken, R. S., and Roothaan, C. C. J.: Chem. Rev. **41,** 219 (1947).
(9) Sklar, A. L.: Rev. Modern Phys. **14,** 232 (1942).
(10) Zechmeister, L.: Chem. Rev. **34,** 267 (1944); interesting applications to the carotenoid pigments are discussed.