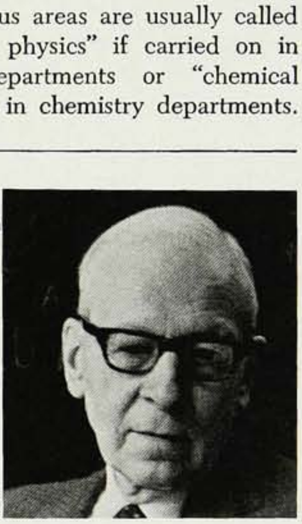
Spectroscopy, Quantum Chemistry and Molecular Physics

Where does the boundary between physics and chemistry lie? The development of molecular-structure models shows how ideas have passed freely between the two disciplines, with electromagnetic spectroscopy acting as the background continuum.

by Robert S. Mulliken

CERTAIN AREAS OF RESEARCH that used to be actively pursued by people called physicists in physics laboratories have now to a large extent, although not entirely, migrated to chemistry laboratories. Among the most prominent of the areas that have moved from physics toward chemistry are molecular spectroscopy, the theory of molecular structure and spectra and certain related areas, for example molecular mass spectroscopy. All these various areas are usually called "molecular physics" if carried on in physics departments or "chemical physics" if in chemistry departments. They are really just as much physics as they ever were; many modern chemists could perfectly well be classified as physicists.



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To see why this is so we must turn to the history of science, a field that, I have always believed, has been too much neglected in our institutions of learning and should be encouraged there. In spite of this belief, I paid little attention to this subject until circumstances recently pushed me into it; therefore my discussion may be sketchy or even inaccurate in parts.

Molecular structure

The customary point of view in chemistry, as developed during the 19th century and continued in this century, has been to think of a molecule as a composite of atoms held together by forces that to a large extent were a mystery until quantum mechanics came along. The work of Walter Heitler and Fritz London, both physicists, on the hydrogen molecule fitted well into this viewpoint. Their work was further developed by themselves and other physicists, notably John C. Slater and John H. Van Vleck. However, its greatest exploitation was by Linus Pauling, who as a chemist showed *in extenso* how what came to be known as the valence-bond theory could be used to explain various facts of chemistry, and in particular to explain chemical bonding although it was of little value for molecular electronic spectroscopy.[1]

At the same time a useful alternative approach was to think of the molecule as a unit with at least its outer layer regarded as belonging to the molecule as a whole and described by molecular orbitals (MO's). This approach was used by Felix Bloch for metals and was greatly advanced by my friend Friedrich Hund in his early application of quantum mechanics to diatomic molecules and to chemical bonding. The molecular-orbital approach, however, was foreign to chemical thinking although for physicists it was just as acceptable as Heitler's and London's approach, which I call the *atomic-orbital method* because it describes the structures of molecules in terms of orbitals of the separate atoms.[1] The molecular-orbital method, which Hund and I found rational for the explanation of molecular spectra, was then also developed in approximate semiempirical versions by Sir John Lennard-Jones, Eric Hückel, Charles Coulson, Christopher Longuet-Higgins, Michael Dewar, Robert Parr, John Pople and others. I have the impression that it was Dewar who rather forcibly brought it to the attention of American organic chemists by a salvo of a dozen or so papers in the *Journal of the American Chemical Society* that resembled a fireworks display with rockets that divide repeatedly.

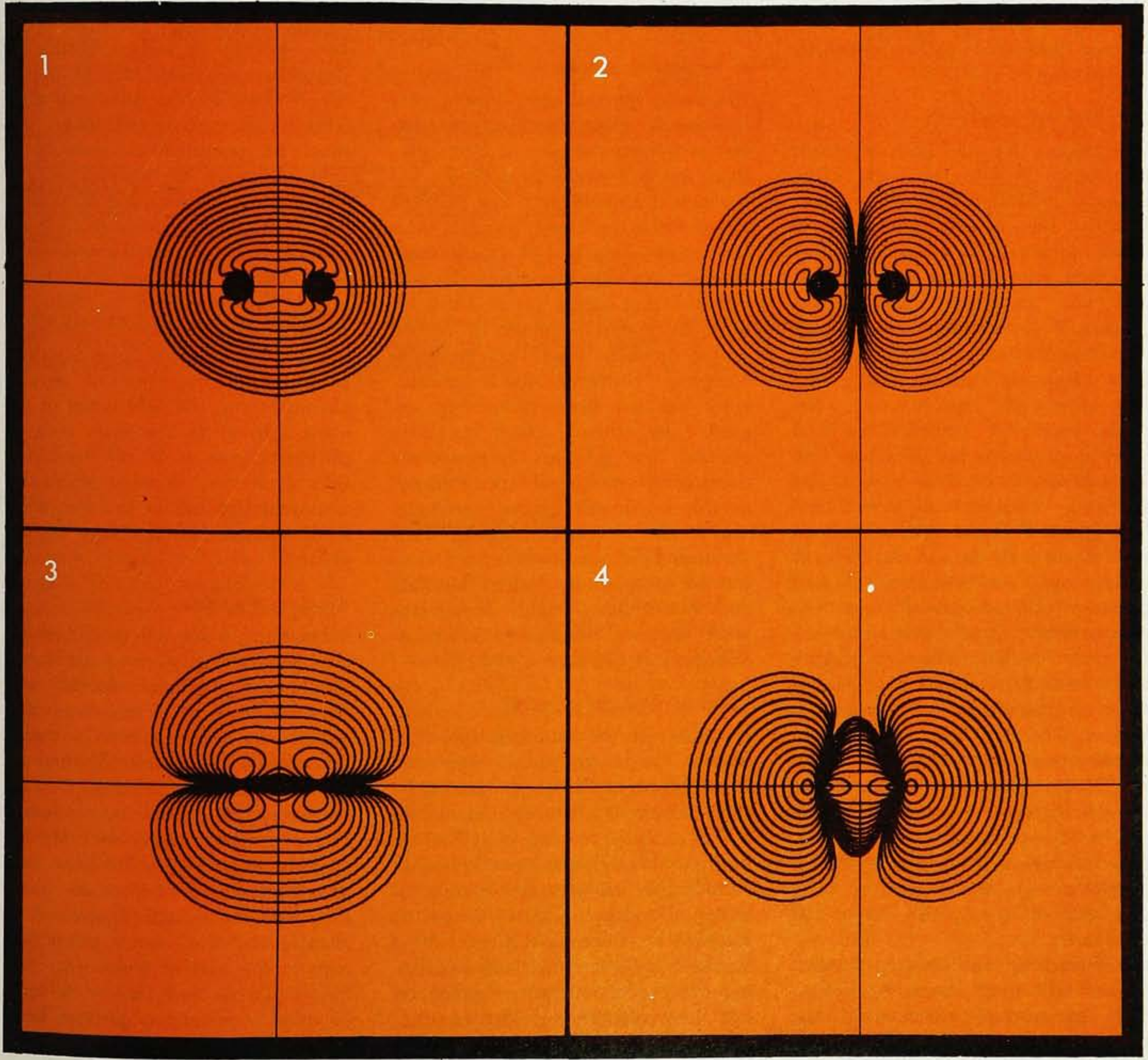
Spectroscopy . . .

When thinking over how our present understanding of the structure of atoms and molecules came about, I have become increasingly impressed by the role of spectroscopy (by this I mean *electromagnetic spectroscopy*). This role was evident already in the early days of quantum theory (1900–25), increasingly when quantum mechanics came along (from 1926 on), and still more in the new radiofrequency, microwave and molecular-beam-resonance spectroscopy of Isidore Rabi, Norman Ramsey, Polykarp Kusch, Willis Lamb, Charles Townes, Arthur Schawlow and their coworkers and others.[2]

In 1913 Niels Bohr published three papers on the constitution of atoms and molecules that arose out of his brief sojourn in Manchester with Ernest Rutherford in 1912. All that most of us remember of this early work is Bohr's theory of the hydrogen atom. His ideas on molecules, though qualitatively instructive, were not quantitatively useful. However, if we translate the "orbits" of the older quantum theory into the "orbitals" of quantum mechanics, Bohr's early discussion of molecular electronic structures has a correspondence to the later quantum-mechanical theories of chemical bonding in terms of localized molecular orbitals as first discussed by Hund (also a less close correspondence to Heitler–London types of theory).

In any event, Bohr's knowledge of the energy levels of the hydrogen atom, obtained from spectroscopy, was vital. Later his theory of the periodic system in terms of an Aufbauprinzip (literally, "synthesis principle"), the Bohr–Sommerfeld theory of atomic energy states, and the later development of the role of electron spin (George Uhlenbeck and Samuel Goudsmit, Al-

CONTOUR DIAGRAMS of the electron densities characteristic of the shell model of the oxygen molecule, as calculated by Arnold C. Wahl by an iterative self-consistent field method. These drawings were automatically made by the computer with an on-line plotter. The shells shown here are for (1) $2\sigma_g$ (2) $2\sigma_u$ (3) $1\pi_u$ (4) $3\sigma_g$ orbitals.



fred Landé, and Wolfgang Pauli) all had their original experimental basis to a large extent in atomic spectroscopy. Further, of course, the experiments of James Franck and Gustav Hertz on excitation and ionization by electron impact, molecular mass spectrometry, and the atomic-beam work of Otto Stern and Walther Gerlach, studies of the photoelectric effect and so on contributed mightily, but I feel that spectroscopy led the way. The state of affairs in 1922 was depicted in a delightful book by Paul Foote and Fred Mohler.[3]

The interplay between physics and chemistry, particularly conspicuous in areas of experiment and theory related to spectroscopy, has led to recognition of the borderline area generally called either "molecular physics" or "chemical physics" depending on whether one happens to be in a physics department or in a chemistry department.

. . . and astronomy

Spectroscopy has also been of special importance in astronomy and astrophysics. Information from the wavelengths, shapes and intensities of atomic (and in some cases molecular) spectrum lines of stars and galaxies, and also molecular spectra from planets, is our greatest single source of information about these distant objects. Recently radioastronomy, with long-wavelength spectroscopy, has made impressive contributions, and x-ray spectroscopy has joined in with observations made from rockets and satellites. I might well have added "astrophysics" to the title, as it is an area where both the old and the new spectroscopy are preëminent in the provision of experimental (or rather, *observational*) data. Instead of the two-part interplay between physics and chemistry, I might have undertaken to discuss the physics–astronomy–chemistry *triangle*. Here I may perhaps remind you that there exists a tripartite commission on spectroscopy of the three international unions of physics, chemistry and astronomy. Also I should mention the importance of spectroscopy in the study of plasmas and of the earth's upper atmosphere.

Tremendous contributions to astrophysics will result from the availability of orbiting astronomical observatories, which will allow us to study in detail the very extensive regions of the spectra of the sun and stars that are now blotted out by absorption in the earth's atmosphere, notably in the short-wavelength and vacuum ultraviolet and in the infrared. We already have some exciting information of this kind from the rocket spectra that, notably, Herbert Friedman and coworkers at the Naval Research Laboratory have been obtaining, and the stellar x-ray spectra obtained with rockets and satellites by Bruno Rossi, at Massachusetts Institute of Technology, and others. An important point here is that to interpret the new stellar spectra to be obtained with orbiting observatories, much more work needs to be done in laboratories on earth to extend our knowledge of atomic and simple molecular spectra—especially in the vacuum ultraviolet.

A neglected subject

In atomic spectroscopy, once a very fashionable subject among physicists but now neglected for a long time, there are still major gaps in our experimental knowledge. For example Bengt Edlén in Lund, Sweden, who has remained faithful to atomic spectroscopy, recently found that the pattern of higher-energy atomic levels for such an important atom as carbon differs radically from that generally accepted. However, atomic spectroscopy has not been *completely* neglected by others. There has been exciting new progress in previously unexplored aspects of spectroscopy, notably on doubly excited autoionizing levels of various atoms; synchrotron light was used as a source for this purpose by Robert Madden and K. Codling, highly monochromatic electron beams by George J. Schultz, J. Arol Simpson and others.

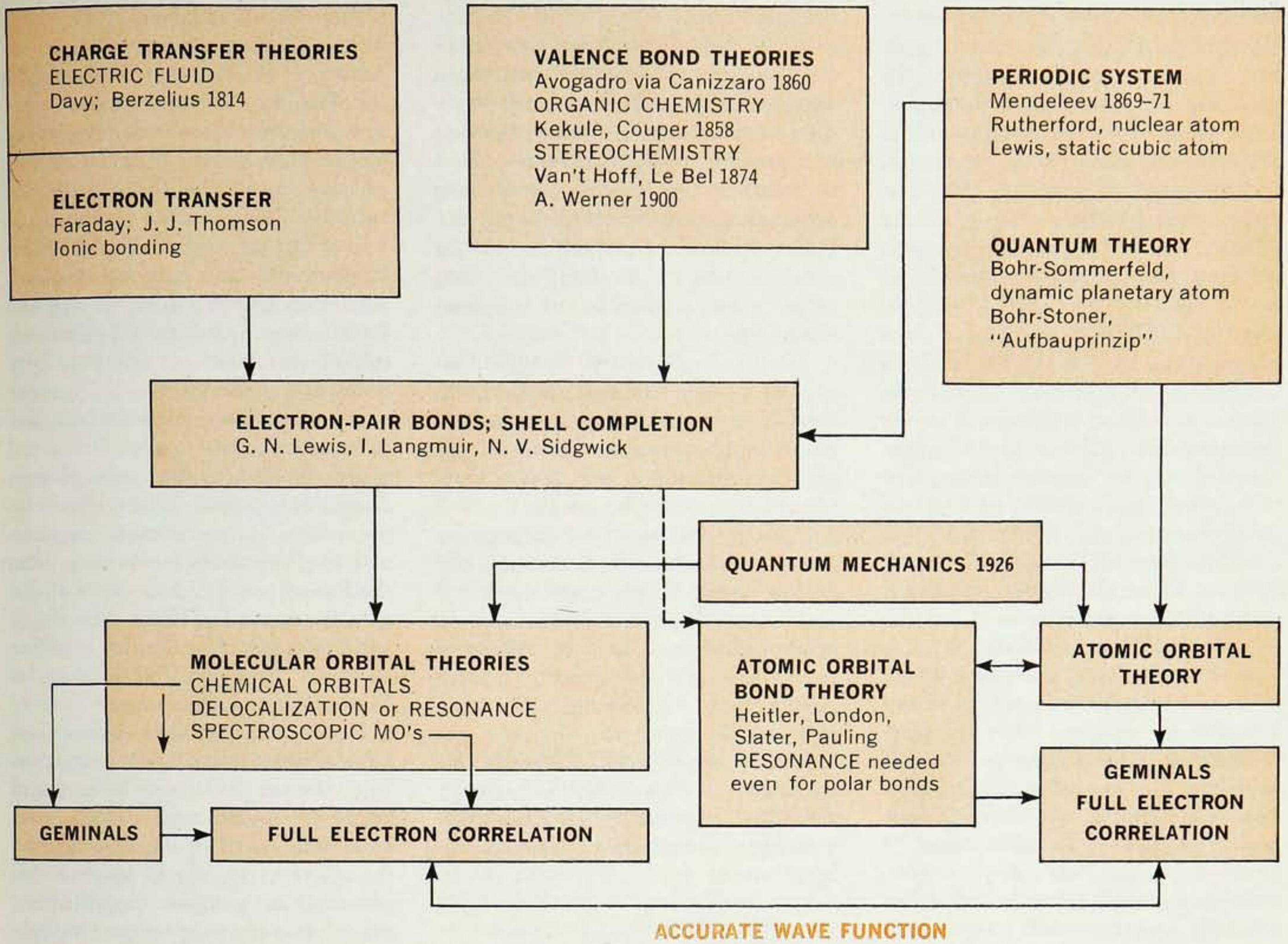
What is chemical physics?

But now let me return to chemical physics and quantum chemistry. Chemical physics has been defined by some people as anything that can be found in the *Journal of Chemical Physics*—although that journal now has considerable competition for some of its typical subject matter. When the *Journal of Chemical Physics* was founded in 1933, I had been publishing my papers on molecular spectra and their relations to molecular electronic structure, using a molecular-orbital description, mostly in *Physical Review*, with some in *Reviews of Modern Physics*. I was then conservative about the establishment of a new journal and was not one of its original sponsors. However, once it had been established, it appeared to be the most appropriate place for the publication of a series of articles I was then writing entitled "Electronic Structures of Molecules and Valence." And although Numbers I–IV of this series had been published in *Physical Review*, I shifted to the *Journal of Chemical Physics* for the rest of the series.

Harold Urey in his editorial in Vol. 1, No. 1 of the *Journal of Chemical Physics* in January 1933, wrote: "At present the boundary between the sciences of physics and chemistry has been completely bridged. Men who must be classified as physicists on the basis of training and/or relations to departments or institutes of physics are working on the traditional problems of chemistry; and others who must be regarded as chemists on similar grounds are working in fields which must be regarded as physics. These men, regardless of training and affiliations, have a broad knowledge of both sciences and their work is admired and respected by their coworkers in both sciences. The *methods of investigations* used are, to a large extent, not those of classical chemistry and the *field* is not of primary interest to the main body of physicists, nor is it the traditional field of physics. It seems proper that a journal devoted to this borderline field should be available to this group."

Amatory chemists

What, then, is the difference between chemistry and physics—or perhaps I should say, between chemists and physicists? I have sometimes suggested part of the answer by stating that chemists love molecules, and get to know them individually, in the same way that politicians love people. But what about physicists? My impression is that they are more concerned with fields of force and waves than with the individual personalities of molecules or of matter, except perhaps in the case of high-energy particles. To be sure, there are high-polymer physicists as well as high-polymer chemists, but still they differ



FLOW OF IDEAS leading to molecular- and atomic-orbital theories of electronic structure of molecules. These theories eventually lead to accurate wave functions (bottom of chart). The pivotal function of the electron-pair bond theory generally associated with G. N. Lewis is immediately apparent.

in their viewpoints and emphasis. Again, much of solid-state physics, although it is still in the hands of physicists, could be classified as chemical physics. In any event the chemical physicist or molecular physicist is clearly a borderline type of person who works at the boundary between the two disciplines.

To revert, perhaps it is only old fashioned chemists who love molecules. In beginning college chemistry in America today it appears to be typical to start with a large dose of theory before there is much acquaintance with molecules: theory before facts. The same tendency appears to be present in introductory physics. I think that direct confrontation with some of the properties of matter should come *first;* or at least, that concrete facts and examples should be given a generous amount of attention *along with* the related theory.

Takeover of ideas

It is very interesting to note how, over and over again, physicists have initiated ideas or started research of major importance that has then been taken over, to a large extent, by chemists. In 1918 F. J. Moore, an organic chemist at the Massachusetts Institute of Technology, wrote,[4] "Frequently chemistry has derived great advantages from the contributions of those who could bring to its problems the equipment and point of view of the trained physicist. Such a service was performed when Boyle and his associates delivered the science from the baleful mysticism and superstition in which alchemy had enveloped it, and again when Lavoisier dispelled the fog with which the vagaries of the phlogiston theory had surrounded the phenomena of combustion. In all these cases the men who ever seek phenomena had acquired undue influence and had given free rein to their phantasy, so that it was necessary that others who could weigh, measure, and define, should control their observations and connect the facts they had discovered by relationships capable of exact mathematical expression.

"The rise of modern physical chemistry marks a new movement of this kind which has exercised a dominant influence upon the science since the last decade of the nineteenth century. In one sense physical chemistry is not modern. At all periods since the time of Lavoisier certain eminent investigators have preferred to devote their attention to the borderland between the two sciences."

And so on. Thus Moore is saying

that there have been repeated sobering injections of physics into chemistry. As a familiar example, the very important idea that equal volumes of gas contain equal numbers of molecules came from Avogadro, long professor of physics in Turin, in 1811, while Ampère also advanced similar ideas. However, acceptance of Avogadro's proposal was delayed for nearly 50 years, until it was revived in 1860 as a result of a clear presentation by the Italian chemist Canizzaro in a little book he wrote in 1858. As Moore pointed out in the passage quoted above, major incursions of physics into chemistry that took place in the latter part of the 19th century gave rise to the term "physical chemistry," which then took its place alongside organic, inorganic, and analytical chemistry as one of the main branches of chemistry.

A fuller account than this one would show also the development by chemists of many important ideas and ways of thinking—for example, the ideas of acids and bases, oxidation and reduction, electronegativity, Werner's coördination theory, Kekulé's model of benzene, conjugation, steric effects, hydrogen bonding, chain reactions, thermal activation and kinetic phenomena. However, I shall not attempt here to cover this side of the complete story.

Tidal waves . . .

As we have seen, smaller waves have washed over from physics into chemistry ever since the early days of both, but physical chemistry perhaps represents the first big tidal wave. Although these smaller waves still kept on during the first quarter of this century, perhaps the next big waves came with the advent of quantum mechanics, which for the first time gave promise of good theoretical understanding of the true nature of chemical binding and the electronic structure of molecules. The situation is epitomized by Paul Dirac's well-known statement:[5] "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." The difficulties now look a little less formidable; perhaps Dirac did not foresee the coming development of digital electronic computers. In any event, quantum mechanics appeared, in principle at least, to reduce chemical theory to applications of a portion of physical theory. To a large extent the early stages of these applications initiated chemical physics. Perhaps chemical physics should be considered as a modern and even more physical variety of physical chemistry.

All this leads to the thought that physics has an unusual tendency to shed large portions of itself, or at least of its applications, as soon as the general principles are understood. Conspicuous examples are mechanical engineering and electrical engineering and now nuclear engineering. Of course even if physical chemistry and chemical physics are looked on as applied physics, they are still more in the research area; they are more science than engineering. However, it is worth noting that modern engineering development depends increasingly on new scientific research and that engineering education increasingly emphasizes training in basic science.

. . . and subwaves

Physical chemistry was, then, the first big tidal wave of physics to inundate chemistry. The even bigger wave of chemical physics consists of several distinct subwaves. The first of these must have become strongly felt in the period leading up to the founding of the *Journal of Chemical Physics* in 1933. Let us place them in the period 1926–38. I will distinguish the first *experimental* subwave and the first *theoretical* subwave as together making up the first chemical-physics wave. In the experimental subwave I will include several things I have already mentioned plus further study of molecular spectra in the optical region and the infrared, and also Raman spectra, with the great resultant enrichment of our knowledge of molecular energy levels. The work on diatomic optical spectra also gave information about nuclear spins and nuclear statistics. The main progress during this period in our knowledge of nuclear spins, magnetic moments and quadrupole moments came from the hyperfine-structure work of atomic spectroscopists. (There was also a small amount of molecular hyperfine structure work on the hydrides of bismuth and mercury.)

Nearly all this work was carried on in physics laboratories, except perhaps Raman and to a lesser extent infrared spectroscopy, which were soon adopted by the chemists—although not so much by chemical physicists as by organic chemists using these kinds of spectroscopy simply as analytical tools. In this period came the discovery of oxygen isotopes by William Giauque and Herrick Johnston, then Arthur King's and Raymond Birge's discovery of the carbon-13 isotope and Meiring Naudé's identification of nitrogen 15, all in 1929.

DID MICHELSON WRITE IT?

AN EXCERPT from the University of Chicago catalog for the year 1898–99. At that time Albert A. Michelson was head of the physics department, and it appears likely that he wrote the introduction to the physics section of the catalog, from which this passage was taken. Robert A. Millikan was an associate professor in the five-man department at that time.

"While it is never safe to affirm that the future of Physical Science has no marvels in store even more astonishing than those of the past, it seems probable that most of the grand underlying principles have been firmly established and that further advances are to be sought chiefly in the rigorous application of these principles to all the phenomena which come under our notice.

"It is here that the science of measurement shows its importance—where quantitative results are more to be desired than qualitative work. An eminent physicist has remarked that the future truths of Physical Science are to be looked for in the sixth place of decimals."

Three years later Urey, with Ferdinand Brickwedde and George Murphy, discovered deuterium. All these isotopes were found with the optical spectrum of an atom or molecule as a diagnostic tool, and all these people were chemical physicists.

Theory moves in

So much for the first experimental subwave. The first *theoretical* subwave, which initiated quantum chemistry, included the work of Heitler and London, Slater, Hubert James and Albert Coolidge, and other theoretical physicists who attempted a frontal assault on the theory of chemical bonding and molecular electronic structure. They made valuable qualitative progress (nearly quantitative only in the case of James and Coolidge's work on the hydrogen molecule, similar to that of Egil Hylleraas on the helium atom). They soon ran into integrals that were discouragingly difficult to evaluate, not to mention to compute. So theoretical physicists, frustrated and repelled, soon turned to areas other than atomic and molecular structure. Work on molecules and chemical bonding continued, but mostly by chemical physicists who were willing to put up with rough semiëmpirical approaches because of their interest in chemistry.

The second *experimental* chemical-physics subwave began with the successful molecular-beam magnetic-resonance work of Rabi and associates in 1938, a revolutionary development. This work always struck me as the first major demonstration of the romance of the next decimal place. Let me explain what I mean by referring to the dictum attributed to Albert Michelson about 1900, to the effect that everything important about physics was now known, and all that remained was to make measurements (for example, of the speed of light) to another decimal place. From that viewpoint, to make a measurement accurate to one more decimal place appears a singularly uninspiring prospect, and this may help to account for the very small number of people who went into physics in the early part of the 20th century.

But now in 1938 the work of Rabi gave the first major illustration that, with the help of quantum theory, each new decimal place shown to be accessible to experiment opens, more or less, a new experimental field. Following Rabi's work, there came a whole series of developments; microwave spectroscopy, nuclear magnetic resonance, electron paramagnetic resonance and its hyperfine structure, the Zeeman and Stark structures of NMR and EPR, quadrupole spectroscopy, and the work of Willis Lamb and R. Curtis Retherford. To a person who had been accustomed, as I had, to the one or two decimal places ordinarily obtainable for fine and hyperfine and Zeeman structures in optical spectroscopy, it was truly amazing to see the same quantities measured out to five, six, seven and eight decimal places. There was a harvest of new information in their work, both about nuclear features and about molecular fine-structure characteristics, of which the latter will eventually be of much interest in the detailed understanding of molecular electronic structure.

Masers and lasers

Hardly had this second experimental subwave left the hands of the physicists for those of the chemists than along came the third experimental subwave, the amazing development of masers and lasers, initiated largely by Charles Townes. Here Einstein's B coefficients for induced emission, after years of neglect of their remarkable implications, came into their own. And with the maser and laser came other fantastic developments that I shall not describe here, except to exclaim at how they have caused us to look, as never before, at the higher-order terms in the theory of the interaction of matter and light, which now for the first time have become accessible to experimental study. Masers and lasers were developed by physicists, but have already begun to pass, in part, into the hands of those chemists who are chemical physicists.

Some relatively new developments constitute yet another experimental subwave. They are concerned with the measurement of accurate and detailed energy spectra of electrons emitted from atoms and molecules ionized by various means. D. W. Turner uses the helium resonance line, with energy about 20 eV, to produce photoionization; V. Čermák employs Penning ionization (collisions with metastable excited atoms that carry more excitation energy than is needed to ionize the molecule to be examined). Edwin Lassettre measures energy-loss spectra of fast electrons scattered, with excitation or ionization, from molecules; scattering at small angles occurs with probabilities very close to those of optical-absorption intensities, and, at larger scattering angles, transitions that are forbidden in absorption become increasingly evident.

Computer chemistry

The second *theoretical* subwave picked up where the first quantum-chemistry wave, which had lost much of its force, left off. Tasks that were laid aside by theoretical physicists in the early 1930's because of mathematical and computational difficulty are now becoming gradually more feasible as a result largely of the computer revolution.

Approximate all-electron self-consistent-field molecular-orbital calculations are now possible not only for diatomic molecules but also for molecules as complex as ammonia, ethane, pyrrole, benzene, pyridine and pyrazine. Reference 1 contains a further description of this rapidly developing area of quantum chemistry. These calculations, of course, take up copious amounts of computer time.

Even more rapid progress could be made if funds were available to pay for more machine time. Sums that would be trivial compared with the expenditure on high-energy and space physics could, if devoted to quantum chemistry, make enormous advances in our knowledge of the solid, material world on which we live.

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The illustration of oxygen molecular orbitals is used with the permission of P. E. Cade, G. L. Malli and A. C. Wahl.

References

1. R. S. Mulliken, Science **157**, No. 3784, page 13 (1967). (Nobel Prize lecture, 1966.)
2. N. F. Ramsey, *Nuclear Moments,* Wiley, New York (1953); C. H. Townes, A. L. Schawlow, *Microwave Spectroscopy,* McGraw-Hill, New York (1955); N. F. Ramsey, *Molecular Beams,* Oxford (1956).
3. P. D. Foote, F. Mohler, *The Origin of Spectra,* Chemical Catalog Company, New York (1922).
4. F. J. Moore, *A History of Chemistry,* McGraw-Hill, New York (1918).
5. P. A. M. Dirac, Proc. Roy. Soc. **123A,** 714 (1929). □