QUANTUM CHEMISTRY and SOLID-STATE PHYSICS

By Luigi Z. Pollara and Arthur J. Freeman

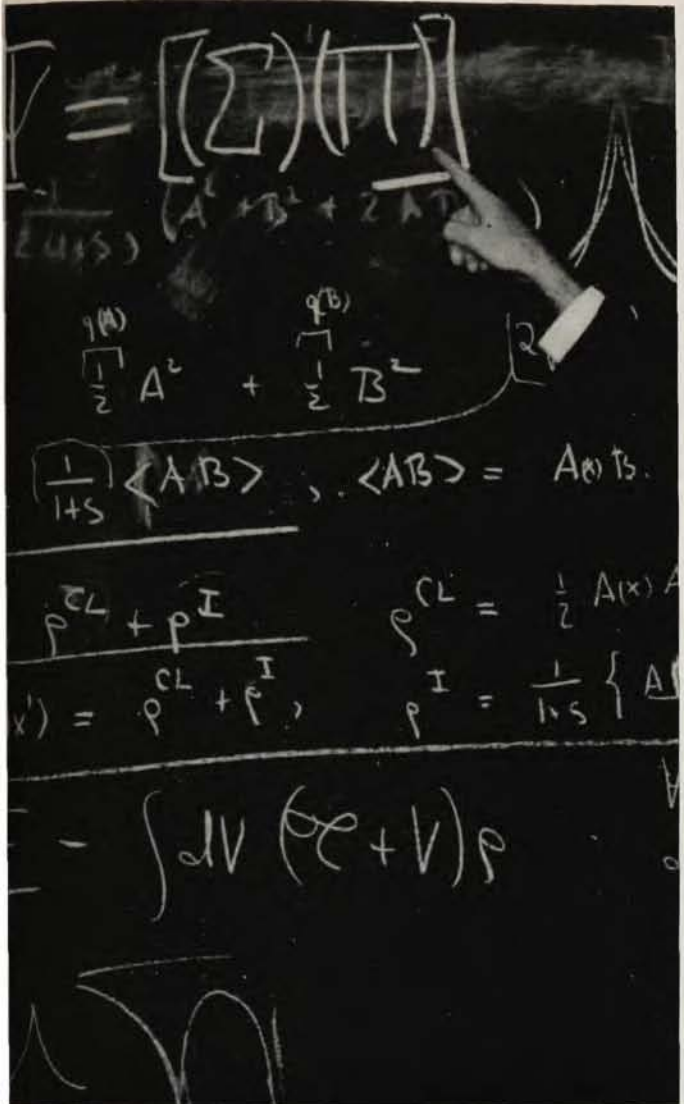
Summer Institutes are no longer rare, as their value in providing intensive training in today's rapidly developing fields of physics and chemistry has been well established. The announcement of the first such winter institute in the fall of 1960 was received with considerable interest and anticipation, particularly from those scientists either familiar with or aware of the three successful Summer Institutes previously given by Professor P. O. Löwdin and his Quantum Chemistry Group at the University of Uppsala (Sweden). The following is a report on the Winter Institute in Quantum Chemistry and Solid-State Physics, arranged by the new Quantum Theory Project of the University of Florida in collaboration with the University of Uppsala and supported by the National Science Foundation. The Institute consisted of two parts: an introductory course, held at the campus of the University of Florida during the last three weeks of December, 1960, and an advanced course given at Sanibel Island in the Gulf of Mexico during the first two weeks of January, 1961. The introductory course is described by Luigi Z. Pollara, head of the Department of Chemistry and Chemical Engineering at the Stevens Institute of Technology; the report on the advanced course was written by Arthur J. Freeman, a solid-state physicist at the Materials Research Laboratory, Ordnance Materials Research Office, Watertown, Mass.

The Introductory Course

It is difficult to imagine how National Science Foundation money could be better spent than to subsidize institutes, both winter and summer, such as the Winter Institute in Quantum Chemistry and Solid-State Physics held at the University of Florida, in Gainesville, with the cooperation of the University of Uppsala and under the direction of Per-Olov Löwdin.

In spite of the unusual term, covering the period from December 12, through the Christmas holidays, to December 30, fifty-one participants, representing many phases of the world of chemistry and physics, gathered on the opening date at an excellent banquet in Gainesville and, led by Professor Löwdin, drank a toast to Max Planck. The following day they plunged into a strenuous and exceedingly well-coordinated program dealing with the physical and mathematical bases of quantum chemistry. Starting from first principles, albeit on a high level, the so-called introductory course could be considered complete. It was instructive and in a sense amusing to hear men whose primary interest is organic chemistry discussing, throughout the day, Hermitian and anti-Hermitian operators, Hilbert space and expansion theorems, upper and lower bounds, and other concepts not generally characteristic of conversations among organic chemists.

There was amazement among the participants, culminating in expressions of admiration and gratitude, over the amount of planning that had gone into the individual lectures, the partitioning of the work, and the sequencing of ideas and concepts. In so large a field as quantum chemistry, it is no mean task to take a group with a heterogeneous background through the theory



of measurements in quantum-mechanical systems, the mathematics of quantum chemistry, and the theory of large molecules in only three weeks, but it can be done.

That others may benefit from the thought and effort that went into this planning, the time distribution in hours is indicated for the various formal lectures by Drs. Lundqvist (U. of Uppsala), Löwdin (U. of Uppsala and U. of Florida), Pauncz (Technion, Haifa), and de Heer (U. of Colorado). The detailed topics can be found in the report from the Winter Institute in Quantum Chemistry and Solid-State Physics (Quantum Theory Group, U. of Florida, Report #13, April 1, 1961).

The course started with a two-hour lecture by Löwdin on the historical development of quantum chemistry. In a series of eleven lectures, Lundqvist presented the basic concepts of quantum mechanics, measurements and their interpretation, the operational representation of observables, the uncertainty relations, and an introduction to spectral theory. Concurrently, Pauncz gave a vivid and delightful five-hour course on vectors and matrices. With clever use of his time, Pauncz terminated his presentation with the formulation of the eigenvalue problem in matrix notation.

In deference to the participants whose mathematical background was not sufficient to cope with the stiff pace set in the mathematical presentation, several hours were set aside each afternoon for questions and supervised problem solving. The participants thus prepared themselves daily for intelligent listening to the forthcoming lectures.

The general and large topic "Mathematics of Quantum Chemistry" was covered by Löwdin in a bloc of 27 lectures. In a free-wheeling but thorough manner, in fact laden with proof, he discussed Hermitian and normal operators and gave a complete discussion of the completeness concept and the expansion theorem. Upper and lower bounds of eigenvalues received considerable attention, as did the variational principle. Besides Slater determinants, the Hartree-Fock scheme, and the method of superposition of configurations, he discussed the partitioning technique for solving high-order secular equations.

Seven lectures by Pauncz, on projection operators and symmetry, more or less completed the mathematical background of the introductory course.

The stage was now set for some quantum chemistry and solid-state physics. With considerable style and economy, Pauncz lectured on the quantum chemistry of atoms and small molecules, including in his discussion a treatment of the MO-LCAO method and the Roothaan self-consistent field scheme. This series of six lectures was followed by ten lectures given by de Heer on the quantum chemistry of large molecules. Among other topics, de Heer sketched Pople's self-consistent field approximation. Twelve hours on the electronic structure of solids by Lundqvist completed the formal aspect of the course.

Mention should be included here of the efforts made for the comfort of the participants and for insuring the most constructive and pleasurable use of the limited time that was available for recreation.

The Advanced Course

PALM trees, warm sunshine, a subtropical isle famous for its shell banks and its beaches—this was the setting for the advanced part of the Winter Institute. New Year's Day, 1961, was moving day for the participants in the introductory part, marking not only the end of the first phase of the Institute but, symbolically and actively, bringing about a needed change and sense of reorientation for what was to follow. For those scientists (and their families) who were first joining the Institute for the advanced part,

the change in geography and climate was sudden and dazzling. Left behind were snowstorms and subzero temperatures—all part of one of the worst winters of the century—and this greatly added to the enthusiasm and eagerness of all concerned.

Formally, the structure of the advanced course was built upon a division into *basic lectures* and *advanced lectures,* making for a cross between a school and a scientific conference, with the resulting advantages of both. The basic lectures formed an extension of the work of the introductory part of the Institute and covered the quantum theory of many-particle systems from its fundamentals to current research efforts. The advanced lectures included surveys (and specialized lectures) of the developments in fields of high research interest. The basic lectures were given by the staff and the advanced lectures were given by invited speakers or by experts among the participants. The "students" were by no means passive; they were in fact exceptionally lively in discussing and questioning crucial points. In addition to these lectures there was a half-day symposium with papers contributed by the students. A rather novel part of the Institute went by the quaint title of "group activities". These were additional informal follow-up sessions, usually in the evening, which extended, or covered in greater detail, the content of the advanced lectures, and which permitted ample time for discussions in the context of the introductory course and the basic lectures. The group activities depended on the interest and stamina of the participants, oup photograph of the participants.

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cond row: R. Blinc, M. Brenman, R. uncz, B. V. Paranjape, G. Blyholder, M. Blinder, R. Gomer, N. Ullah, J. Heer, F. Rothwarf, D. Harris, H. H. elsen, L. Schaad, D. D. Ebbing, K. edenberg, R. G. Parr.

ird row: L. Goodman, P. Lykos, J. nderberg, P. G. Simpson, M. Green, M. Keefe, M. Geller, J. W. Eastman, C. M. nningham, V. H. Smith, A. J. Freeman, J. Carr, R. L. Flurry, M. M. Saffren, Szasz, R. Poshusta, O. J. Sovers, M. marc, W. C. Nieuwpoort, D. Smith, S. Handler, T. C. Collins, J. H. Henkel.

and, given the boundless eagerness and enthusiasm of the group, it was no surprise that these sessions were highly successful.

The isolation of Sanibel Island lent itself to the heavy scientific program, whereas its subtropical character and its ideal climate offered opportunities for outdoor relaxation not generally available in January. The unmarried participants stayed at the Hotel Casa Ybel, where the lectures were given, while most of the families stayed at neighboring motels. During the day there was usually some (although very little) time for swimming, shell collecting, or sunning on the superb beach; at night, fires on the beach were settings for informal discussions or beach parties.

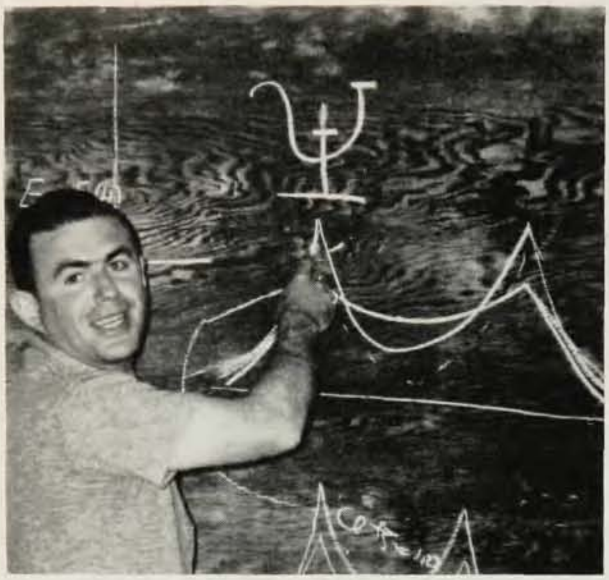
As part of the basic lectures, S. Lundqvist continued the course on modern perturbation theory and the diagram technique which started in the introductory part. R. Pauncz lectured on the solution of the spin-degeneracy problem by means of the projection-operator technique and the separation of space and spin. J. de Heer summarized the theory of chemical reactivity and gave a critical discussion of "reaction indices" for substitution in aromatic hydrocarbons as an example of what can be done quantum mechanically. The nonorthogonality problem and the method of symmetric and canonical orthogonalization were treated by Löwdin, the inverse of a cyclic overlap matrix was derived by Pauncz, the importance of overlap in magnetic theory of solids was stressed by J. Carr (Westinghouse), and certain optimum properties of the orthonormalized sets were pointed out by P. Lykos (Illinois Institute of Technology).

The solution of the Schrödinger equation by the partitioning technique was treated by Löwdin who showed the connection with various types of perturbation theory and stressed the importance of the continuous fractions and the bracketing theorem for the eigenvalues from both numerical and abstract points of view. By starting out from the expression for the reaction operator and including higher order interactions, he also showed a generalization of the Hartree-Brueckner self-consistent field approach to electronic systems. This leads to an exact SCF description which may be of importance in justifying the Hückel scheme for conjugated systems and the band theory for solids. Impurities and other localized perturbations were also treated by the partitioning method.

In the advanced lectures, the speakers sought first to build a firm foundation for their subject (by giving sufficient background material) and thus to make some of the more recent discoveries in their fields both an exciting and natural consequence of the earlier work. In this, they were for the most part successful, thanks to the generous amount of time allowed to their lectures, the informality of the surroundings, and the eagerness of the "students". A huge amount of technical information was presented and (apparently) absorbed on topics of great importance for solid-state physics and quantum chemistry.

F. Rothwarf, S. Lundqvist, E. Burstein.

E. Burstein (U. of Pennsylvania) lectured on microwave and optical properties of solids, but covered a much larger domain of physics by including a wide variety of phenomena involving the interaction of electromagnetic waves and solids. Aside from the more conventional treatment of the subject, including the effects of lattice vibrations (*and* anharmonic coupling of phonons) and plasma oscillations, he spoke of the very recent microwave measurements of the optical properties and the observations of tunneling in thin superconducting films, with their interesting analogies to semiconductors. The general concepts of effective mass and dielectric susceptibility were further discussed by G. Pratt (MIT) in connection with a justification of band theory based on modern perturbation theory and diagram techniques. As did several other speakers,



A. J. Freeman, author of the present report.

Pratt stressed the point that simple band theory is no longer adequate and that correlation has to be taken into account in the theoretical treatment of solids. The content of Pratt's exact electronic SCF theory seems to be identical with that of Löwdin's previously mentioned theory based on partitioning techniques.

In the theory of molecular spectra, H. H. Nielsen (Ohio State) lectured on the effect of resonance on vibrational and rotational energies, particularly for general polyatomic molecules of axial symmetry; the electronic spectra were covered in a group session with contributions from R. Parr (Carnegie Tech), P. Lykos, L. Goodman (Penn. State), N. Cohan (U. of Buenos Aires), and others. Parr also discussed the electronic structure of small molecules and the possibility of calculating accurate wave functions by means of the one-center method. Additional aspects of conjugated systems (which had been thoroughly treated in the introductory part) were presented by Parr, Lykos, and Pauncz. K. Ruedenberg (Iowa State) discussed in a novel way the detailed nature of the chemical bond on an atomic basis by dividing the cohesive energy into promotion energies of the free atoms, a quasi-classical energy, and an interference energy connected with the wave nature of electrons.

S. Lundqvist lectured on the theory of collective motion of systems and gave many aspects of the plasma model, the dielectric approach, the field-theory treatment, and the hydrodynamically based statistical model. Crystal-field and ligand-field theory, their success and inherent weaknesses, were covered by A. J. Freeman, whose discussion also dealt with the application of the unrestricted Hartree-Fock method to solid-state theory and how relaxation of these restrictions led to important consequences involving neutron magnetic form factors, hyperfine interactions, Knight shifts, effective fields (Mössbauer effects), and quadrupole polarizabilities.

In the theory of spin resonance, S. Blinder (Johns Hopkins) gave a simple but elegant derivation of the Fermi hyperfine Hamiltonian. H. Hameka (Johns Hopkins) treated magnetic susceptibilities and chemical shifts and pointed out the importance of gauge invariance for the theory and the difficulties in the present approach.

The correlation problem was treated from several points of view, and general aspects were given by various speakers. Pauncz described an application of the alternant molecular orbital method to the cyclic linear chain and to conjugated systems carried out by himself, de Heer, and Löwdin, and the latter treated the extension of the Hartree-Fock scheme obtainable by approximating the total wave function by a projection of a single determinant having different orbitals for different spins. Pratt (and later Löwdin) spoke about the theory of antiferromagnetism and pointed out that the present description is not invariant against time-reversal and that a revision is necessary. This stimulated much discussion of the problem centering about the incorrect description of the neutron magnetic scattering by a Néel determinant with fixed spins on two interpenetrating sublattices.

One of the most rewarding aspects of the Institute was the practical demonstration of the value of interacting disciplines. While both quantum-chemists and solid-staters approached each other with suspicion, the resulting fusion brought much light and little heat. Each left with a healthier and more meaningful understanding of the other's way of thinking. The torn and tattered, oft-used but rarely demonstrated cliché, the "unity of science", was dramatically illustrated by the lecture of Prof. Léon Brillouin (Columbia) in what may well have been the high point of the Institute. In discussing the "Similarities Between Long Proteins and Semiconductors", he showed how the discoveries of semiconductor physics could be used to understand many aspects of the conduction properties of biological molecules, including the possibility of having amplifying circuits in living systems.

One naturally tends to ask about the value of such an Institute. Although hard to measure, one can get at this in part by asking the participants. Judging from their responses and comments, one can say that the Institute successfully accomplished its aims. Perhaps the most enthusiastic response came from the experimentalists (who incidentally made up a large fraction of the group) who asserted that the Institute offered them a unique opportunity of getting theoretical training on a postdoctoral level without having to leave their laboratories for an extended period. Despite the intensity of the training, most felt that they had learned much and were grateful for the opportunity. For this they thanked the staff, Prof. Per-Olov Löwdin, Director, the Universities of Uppsala and Florida, and the National Science Foundation.