

The ‘Hyperbola of Quantum Chemistry’: the Changing Practice and Identity of a Scientific Discipline in the Early Years of Electronic Digital Computers, 1945–65

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Summary

In 1965, John A. Pople presented a paper entitled ‘Two-Dimensional Chart of Quantum Chemistry’ to illustrate the inverse relationship between the sophistication of computational methods and the size of molecules under study. This chart, later called the ‘hyperbola of quantum chemistry’, succinctly summarized the growing tension between the proponents of two different approaches to computation—the *ab initio* method and semiempirical method—in the early years of electronic digital computers. Examining the development of quantum chemistry after World War II, I focus on the role of computers in shaping disciplinary identity. The availability of high-speed computers in the early 1950s attracted much attention from quantum chemists, and their community took shape through a series of conferences and personal networking. However, this emerging community soon encountered the problem of communication between groups that differed in the degree of reliance they placed on computers. I show the complexity of interactions between computing technology and a scientific discipline, in terms of both forming and splitting the community of quantum chemistry.

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1. Introduction

The impact of computers on scientific disciplines after World War II has recently been a subject of great attention in the history of science and technology. The reason is obvious: computers have become indispensable components of laboratory equipment for solving complicated mathematical equations, making visual models and simulations, processing numerous empirical data, and operating a variety of instruments. This integration of computers into scientific practice has raised further intriguing questions, such as the changes in the organization of the experimental workplace and the role of the federal government in launching and boosting the information revolution. Computers are no longer simply the calculating machine:

they are the irreplaceable component of the 'Big Science' instrument in physics, the force for unifying different traditions in meteorology, and the source of shaping biomedical research as an information science, all in the context of a sociotechnical revolution comparable with the Industrial Revolution.¹

This paper examines the ways in which the development of computing technology affected quantum chemistry, intellectually and socially, in the two decades after 1945. Except for those fields directly related to military projects and weather forecasting, no other scientific discipline more eagerly explored and substantially benefited from the growing power of electronic digital computers in their early years than quantum chemistry. For quantum chemists, computers meant quintessentially tools for computing, that is, calculating numerically various integrals that were necessary for solving the Schrödinger equation. Quantum chemists sought to take advantage of high-speed computers, and organized meetings and conferences to exchange the information on how to improve computation. I argue that the development of quantum chemistry shows the subtle and complicated role of computers in shaping disciplinary identity. On the one hand, new possibilities opened up by electronic digital computers contributed to the formation of a community in quantum chemistry, but, on the other hand, this community soon encountered the problem of communication between groups that differed in the degree of reliance they placed on computers. This problem was closely intertwined with the epistemological question as to the legitimacy of two different approaches to computation: the *ab initio* method, which used no empirical data except fundamental constants, and the semi-empirical method, which simplified computational problems by neglecting some factors and using empirical parameters. Various answers to the epistemological question were contingent upon the status of computing technology as much as upon the personal commitments and interests of quantum chemists.

2. Quantum chemistry before World War II

The prospects facing quantum chemists on the eve of World War II were by no means bright. The intellectual breakthroughs that had excited chemists and physicists

¹ The following abbreviations are used in this paper. JSP: the John Clarke Slater Papers, American Philosophical Society; RMP: the Robert S. Mulliken Papers, the University of Chicago. The literature on the history of computers is now vast and growing. Paul E. Ceruzzi's *A History of Modern Computing* (Cambridge, MA: MIT Press, 1998) provides a good introduction to this subject and an updated list of historical studies. For the sociotechnical revolution and the role of the federal government in it, see Thomas P. Hughes, 'Funding a Revolution', in *Proceedings of the 1998 Conference on the History and Heritage of Science Information Systems*, ed. by Mary Ellen Bowden, Trudi Bellardo Hahn and Robert V. Williams (Medford, NJ: Information Today, 1999), pp. 8–13; National Research Council, Committee on Innovations in Computing and Communications, *Funding a Revolution: Government Support for Computing Research* (Washington, DC: National Academy Press, 1999). See also I. Bernard Cohen, 'The Computer: a Case Study of Support by Government, Especially the Military, of a New Science and Technology', in *Science, Technology and the Military*, ed. by E. Mendelsohn, M. R. Smith and P. Weingart (Boston, MA: Kluwer, 1988), pp. 119–54. Silvan S. Schweber and Matthias Wächter describe the impact of computers in science as a 'Hacking-type revolution', which sees the changes in more than one discipline and are linked with substantial social change: Silvan S. Schweber and Matthias Wächter, 'Complex Systems, Modeling and Simulation', *Studies in History and Philosophy of Modern Physics*, 31 (2000), 583–609. For the changes in the organization of the experimental workplace and the case of high-energy physics, see Peter Galison, 'Bubble Chambers and the Experimental Workplace', in *Observation, Experiment, and Hypothesis in Modern Physical Science*, ed. by Peter Achinstein and Owen Hannaway (Cambridge, MA: MIT Press, 1985), pp. 309–73; idem, *Image and Logic: A Material Culture of Microphysics* (Chicago, IL, University of Chicago Press, 1997). For the cases of meteorology and biology, see Frederik Nebeker, *Calculating the Weather: Meteorology in the 20th Century* (San Diego, CA: Academic Press, 1995); Timothy Lenoir, 'Shaping Biomedicine as an Information Science', in Bowden *et al.*, pp. 27–45.

around 1930—new interpretations of valence, theoretical calculations of molecular properties, and systematic analyses of band spectra—did not immediately lead to additional breakthroughs. Many pioneers left the field, including most notably two German scientists, Walter Heitler and Fritz London, whose paper on the hydrogen molecule in 1927 had marked the birth date of quantum chemistry. Indeed, their paper inspired further research in two ways. On the one hand, there were those who sought to improve Heitler and London's computational procedure for better agreement between theory and experiment. This effort culminated in Herbert M. James and Albert S. Coolidge's paper in 1933, which set the high standard of accuracy that could be reached by theoretical calculations. James and Coolidge, both Americans, left the field, however, realizing that a formidable amount of labour would be required to carry out computations with their desk calculator for most molecules other than hydrogen. The *ab initio* approach, which used no empirical data except fundamental constants such as the Planck constant and the electronic charge, prematurely entered a 'dark age'.² On the other hand, John C. Slater and Linus Pauling paved a way of extending Heitler and London's valence bond theory to polyatomic molecules without undertaking all the calculations. Working independently at the Massachusetts Institute of Technology (MIT) and California Institute of Technology, they developed the concept of hybridization with which they explained the directed property of valence in such molecules as water and methane.³ Pauling subsequently went after more complex molecules, dealing with the stability of aromatic and conjugated compounds. Pauling's version of the valence bond theory, or the 'theory of resonance', was an exemplar of the semiempirical approach, which simplified computational problems by neglecting some electronic interactions and replacing the difficult-to-calculate integrals with empirical parameters. The theory of resonance found wide applications to chemical problems ranging from reaction mechanism to acidity. In the late 1930s, however, Pauling shifted his main research interest to the structure and function of biological molecules that were too big to be handled even by the semiempirical approach.⁴ Similarly, this was a period of 'transitional years' for Slater, as he turned his attention to the energy bands of crystals.⁵

The situation was not much different for the pioneers of the molecular orbital theory, another conceptual framework of quantum chemistry. Robert S. Mulliken, for instance, felt a 'period of letdown', after publishing a series of fourteen papers

² Henry F. Schaeffer III, *Quantum Chemistry: The Development of Ab Initio Methods in Molecular Electronic Structure Theory* (Oxford: Clarendon Press, 1984), p. 4. For the importance of Heitler and London's 1927 paper, see Kostas Gavroglu and Ana I. Simões, 'The Americans, the Germans, and the Beginnings of Quantum Chemistry: the Confluence of Diverging Traditions', *Historical Studies in the Physical and Biological Sciences*, 25 (1994), 47–110.

³ Buhm Soon Park, 'The Contexts of Simultaneous Discovery: Slater, Pauling, and the Origins of Hybridisation', *Studies in History and Philosophy of Modern Physics*, 31 (2000), 451–74.

⁴ For Pauling's theory of resonance, see Buhm Soon Park, 'Chemical Translators: Pauling, Wheland, and their Strategies for Teaching the Theory of Resonance', *British Journal for the History of Science*, 32 (1999), 21–46; and Gavroglu and Simões (note 2). For Pauling's shift from quantum chemistry to molecular biology and immunochemistry, see Thomas Hager, *Force of Nature: The Life of Linus Pauling* (New York: Simon & Schuster, 1995), pp. 200–69; and Lily E. Kay, *Molecular Vision of Life: Caltech, The Rockefeller Foundation, and the Rise of the New Biology* (New York: Oxford University Press, 1933), pp. 143–93.

⁵ John C. Slater, *Solid-State and Molecular Theory: A Scientific Biography* (New York: John Wiley & Sons, 1975), pp. 163–208. For Slater's early work, see Silvan S. Schweber, 'The Young John Clarke Slater and the Development of Quantum Chemistry', *Historical Studies in the Physical and Biological Sciences*, 20 (1990), 339–406.

between 1932 and 1935 that had become the foundation of the molecular orbital theory.⁶ He then got into the routine work of producing and interpreting band spectra at the University of Chicago. Mulliken's work was semiempirical in the sense that he obtained the relative order of energy states from quantum mechanics but determined most energy levels from spectroscopic or thermochemical data. Unlike Mulliken, the German scientist Erich Hückel developed two methods by which to incorporate empirical information directly into the computational procedure of solving the Schrödinger equation. One method, based on the valence bond theory, was taken up by Pauling, who modified it into a more convenient form and popularized it among chemists as part of his theory of resonance. Hückel himself preferred the other method written in the language of the molecular orbital theory, but it was neglected for most of the prewar years.⁷ In Britain, there was an active research group led by Douglas R. Hartree, John E. Lennard-Jones, and Charles A. Coulson, all trained in the Cambridge tradition of mathematical physics. They sought to develop a workable yet rigorous computational scheme for atoms and molecules, but the difficulty of undertaking a large amount of calculations slowed the progress, particularly in the study of molecular properties. It is thus no wonder that Hartree and Lennard-Jones were deeply interested in constructing a model of the Differential Analyzer, an analogue computer developed around 1930 in America.⁸

To be sure, quantum chemistry had developed into a discipline by the late 1930s. Not only did quantum chemistry have a set of distinctive methods and concepts, but it became a teachable subject as its practitioners wrote textbooks.⁹ A new journal, the *Journal of Chemical Physics*, was also created as an important outlet of

⁶ Mulliken was not 'quite as enthusiastic as usual about the papers' written in the 1936–37, the 'period of letdown' for him: Robert S. Mulliken, *Life as a Scientist*, ed. by Bernard J. Ransil (Berlin: Springer, 1989), pp. 96–105. For Mulliken's early work in quantum chemistry, see Gavroglu and Simões (note 2); Buhm Soon Park, 'A Principle Written in Diagrams: the *Aufbau* Principle for Molecules and its Visual Representations, 1927–1932', in *Tools and Modes of Representation in the Laboratory Sciences*, ed. by Ursula Klein (Boston, MA: Kluwer, 2001), pp. 179–98.

⁷ Three kinds of explanation have been offered regarding the neglect of Hückel's molecular orbital theory before World War II. One considers the German institutional context in which neither physicists nor chemists saw Hückel's work as a legitimate subject in their communities. See H. Hartmann and H. C. Longuet-Higgins, 'Erich Hückel', *Biographical Memoirs of Fellows of the Royal Society*, 28 (1982), 153–62. Another notes that Hückel could not deal with the criticisms raised by W. G. Penney on the scientific basis of considering only π electrons while neglecting σ electrons in benzene: Shigeaki Kikuchi, 'A History of the Structural Theory of Benzene—the Aromatic Sextet Rule and Hückel's Rule', *Journal of Chemical Education*, 74 (1997), 194–201. A third seeks to find a reason in the successful popularization of Pauling's theory of resonance in the prewar years: Gavroglu and Simões (note 2); Andreas Karachalios, 'On the Making of Quantum Chemistry in Germany', *Studies in History and Philosophy of Modern Physics*, 31 (2000), 493–510; Stephen G. Brush, 'Dynamics of Theory Change in Chemistry: Part 2. Benzene and Molecular Orbitals, 1945–1980', *Studies in History and Philosophy of Science*, 30 (1999), 263–302. See also Jerome A. Berson, *Chemical Creativity: Ideas from the Work of Woodward, Hückel, Meerwein, and Others* (New York: Wiley-VCH, 1999), Chapter 3.

⁸ For British quantum chemists, see Ana Simões and Kostas Gavroglu, 'Quantum Chemistry *qua* Applied Mathematics. The Contributions of Charles Alfred Coulson (1910–1974)', *Historical Studies in the Physical and Biological Sciences*, 29 (1999), 363–406; idem, 'Quantum Chemistry in Great Britain: Developing a Mathematical Framework for Quantum Chemistry', *Studies in History and Philosophy of Modern Physics*, 31 (2000), 511–48. For the development of the Differential Analyzer, see Larry Owens, 'Vannevar Bush and the Differential Analyzer: the Text and Context of an Early Computer', *Technology and Culture*, 27 (1986), 63–95.

⁹ Arthur Haas, *Quantum Chemistry: A Short Introduction in Four Non-Mathematical Lectures*, trans. by L. W. Codd (London: Constable & Company, 1930); Linus Pauling and E. Bright Wilson, Jr, *Introduction to Quantum Mechanics with Applications to Chemistry* (New York: McGraw-Hill, 1935); Hans Hellmann, *Einführung in die Quantenchemie* (Leipzig: Franz Deuticke, 1937); Henry Eyring, John Walter and George E. Kimball, *Quantum Chemistry* (New York: John Wiley & Sons, 1944).

publications in quantum chemistry.¹⁰ For all these indications of disciplinary formation, however, it is notable that there were few statesmen for quantum chemistry, proclaiming 'I am a quantum chemist' or insisting 'we need quantum chemistry as an independent discipline'. In contrast to the founding fathers of physical chemistry—J. H. Van't Hoff, Svante Arrhenius, and Wilhelm Ostwald—about a half-century earlier, the pioneers of quantum chemistry seldom claimed their territory in the broad borderland of molecular spectroscopy, solid-state physics, chemical physics, and physical organic chemistry. They worked mostly in the physics or chemistry or mathematics department, with an exception of Lennard-Jones who took the Plummer Chair in Theoretical Chemistry established in 1932 at Cambridge University.¹¹ There were the practitioners of quantum chemistry, but a scientific community of their own—where they could discuss together the most urgent needs and set the future agenda—had yet to emerge.¹²

Quantum chemists partook in wartime research hardly as a group of serviceable specialty, and so there was no chance for them to get together and work for common goals. Like many other scientists, they saw their usual academic tasks disrupted, displaced, or reoriented. It is no wonder that military organizations on campus often determined what they could contribute. In the United States, for example, Mulliken saw his laboratory dismantled as the whole physical science division of the University of Chicago was reorganized around the Metallurgical Laboratory. Mulliken's graduate students and research associates were drafted, and he was assigned to a mission unrelated to his expertise. He was in charge of supervising the production and distribution of classified reports as Director of the Information Division. Mulliken's mind was thus detached from his daily work. 'During my time on the project', he said, 'I learned how to go home at the end of the day and forget the day's problems,

¹⁰ It should be borne in mind, however, that the *Journal of Chemical Physics* was not created as an official journal for quantum chemistry. Its creation was intertwined with a growing dissatisfaction with the *Journal of Physical Chemistry* under the editorship of Wilder D. Bancroft. For the role played by the Chemical Foundation, the American Institute of Physics, and the American Chemical Society in establishing a new journal, see John W. Servos, *Physical Chemistry from Ostwald to Pauling: The Making of a Science in America* (Princeton, NJ: Princeton University Press, 1990), pp. 315–21. In fact, the *Journal of Chemical Physics* covered far broader areas than the application of quantum mechanics to chemical problems, e.g. the spectroscopic study of atoms and molecules, the nature of solutions, the kinetics of reactions, and the statistical interpretation of thermodynamics. See Harold C. Urey, 'Editorial', *Journal of Chemical Physics*, 1 (1933), 1–2. Also, quantum chemists continued to publish their papers in local journals, such as Britain's *Proceedings of the Royal Society (London)*, Germany's *Zeitschrift für Physik*, and America's *Physical Review* and *Journal of the American Chemical Society*.

¹¹ For the origins of theoretical chemistry, of which quantum chemistry constituted a part, see Mary Jo Nye, *From Chemical Philosophy to Theoretical Chemistry: Dynamics of Matter and Dynamics of Disciplines, 1800–1950* (Berkeley, CA: University of California Press, 1993). Nye sees quantum chemistry as a 'field', rather than a 'subdiscipline' of chemistry: *ibid.*, conclusion, especially p. 273. During the prewar years, there were scientific meetings and sessions of larger conferences devoted to the subject of molecular structure and valence. See Simões and Gavroglu (note 8, 2000), pp. 520–4. However, while many welcomed the ongoing process of bridging the gap between physics and chemistry, it is difficult to find serious efforts to build a community in quantum chemistry *per se*.

¹² A similar situation has been found in materials science, which emerged as a new discipline in the 1960s: Bernadette Bensaude-Vincent, 'The Construction of a Discipline: Materials Science in the United States', *Historical Studies in the Physical and Biological Sciences*, 31 (2001), 223–48. Bensaude-Vincent notes that the practitioners of materials science did not immediately make a disciplinary community, and that their professional identity was defined by their educational backgrounds in physics, chemistry, metallurgy, mechanical engineering, or chemical engineering, rather than by their current field of research. To examine the growth of this 'fundamentally interdisciplinary academic science' (p. 224), she shifts her attention from traditional indicators of disciplinary formation—the development of an intellectual core, the establishment of new academic positions, the creation of journals and societies—to the role of federal funding and instrumental techniques.

and go to sleep promptly. This was a great change from previous times when my sleep had been interlaced with thinking about research problems.¹³ Slater had no control over the wartime change, too, despite his position as the head of the physics department. MIT physicists were diverted to various war projects, most notably to the Radiation Laboratory, while a number of outside physicists came in like an ‘invasion’. He himself was asked to explore the theory of the magnetron, of which he had little knowledge. Finding no appropriate role at MIT, he moved to Bell Laboratories in the autumn of 1941 and spent most of his time there until the end of the war.¹⁴ In a similar vein, E. Bright Wilson, a quantum chemist of Harvard University, recollected his wartime experience:

[I] was far removed from quantum mechanics. It did bring me into rather close contact with Jack Kirkwood and John von Neumann [in the Underwater Explosives Research Laboratory at Woods Hole], but we talked about explosions and not about wavefunctions. In fact, when I returned to Cambridge and science in 1945, I remember being asked to comment on a theoretical manuscript. The author was rather disgusted with my inability to understand his work and I was very much distressed myself with what four years had done to me.¹⁵

After the war quantum chemists returned to their laboratories only to find that the postwar reconstruction was not simply a restoration to the prewar status, for the social prestige and support had already gravitated toward the ‘twin poles of radar and the atomic bomb’.¹⁶ On campus, increasing demands for physicists specialized in electronics were only matched by aggressive efforts to recruit the nuclear physicists represented by the Los Alamos generation. New research institutes were established to entice prominent scientists and engineers, to make use of equipment from wartime organizations, and to secure federal funding. Under these circumstances, some quantum chemists—most notably Mulliken and Slater—sought to establish their own research institutes comparable in size and budget to those in nuclear science and electronics. Not surprisingly, their efforts did not materialize as they wished, and they were entangled with power struggles and infighting within

¹³ Mulliken (note 6), pp. 114–15. For the first and the last time in the sixty years of his professional career, Mulliken published no papers in the four years following 1943. See also Loren J. Butler, ‘Robert S. Mulliken and the politics of science and scientists, 1939–1946’, *Historical Studies in the Physical and Biological Sciences*, 25 (1994), 25–45 (pp. 37–38).

¹⁴ Slater (note 5), pp. 209–16.

¹⁵ E. Bright Wilson, ‘Some Personal Scientific Reminiscences’, *International Journal of Quantum Chemistry Symposium*, 14 (1980), 17–29 (p. 24).

¹⁶ For the emergence of radar and the atomic bomb as new cultural symbols in the postwar years, see Peter Galison, ‘Physics Between War and Peace’, in Mendelsohn *et al.* (note 1), pp. 47–85; Galison, *Image and Logic* (note 1, 1997), Chapter 4. Within two decades after the war, the rank of nuclear physicists in occupational status jumped from the fifteenth to the third, ahead of everyone except Supreme Court Justices and physicians, in the American mind. See Daniel J. Kevles, *The Physicists: The History of a Scientific Community in Modern America* (Cambridge, MA: Harvard University Press, 1971), p. 391. On the effects of World War II on postwar American physics, see also Paul Forman, ‘Behind Quantum Electronics: National Security as Basis for Physical Research in the United States, 1940–1960’, *Historical Studies in the Physical and Biological Sciences*, 18 (1987), 149–229; Daniel J. Kevles, ‘Cold War and Hot Physics: Science, Security, and the American State, 1945–56’, *Historical Studies in the Physical and Biological Sciences*, 20 (1990), 239–64; Roger L. Geiger, *Research and Relevant Knowledge: American Research Universities Since World War II* (New York: Oxford University Press, 1993); and Stuart W. Leslie, *The Cold War and American Science: The Military–Industrial–Academic Complex at MIT and Stanford* (New York: Columbia University Press, 1993).

their departments.¹⁷ However, quantum chemists were certainly among the beneficiaries of generous support for basic research by military agencies, although the scale of funding was considerably smaller than that in fields related to 'Big Science' projects. Most importantly, the invention of electronic digital computers during the war and their subsequent development in the postwar years brought the possibility of large-scale computation for quantum chemistry. Quantum chemists found the new tool.

3. Networking: conferences, information exchange, and a call for computers

In 1951, twenty-five physicists and chemists gathered at the Ram's Head Inn on Shelter Island, at the tip of Long Island, to discuss the present state of quantum-mechanical methods in valence theory. At the Saturday afternoon session, held in the local schoolhouse, the Englishman Charles A. Coulson sat at an eighth-grade desk, picked up an eighth-grade algebra book, and read in resonant tones, 'The world is incurably mathematical'. It was reported that on this all of the conferees agreed.¹⁸ Indeed, Coulson's reading not only epitomized the spirit of the conference, but heralded the changing practice in quantum chemistry: the revival of the *ab initio* approach, and the use of electronic digital computers.

The emphasis on computation made substantial effects, particularly because the Shelter Island Conference on Quantum Mechanical Methods in Valence Theory was a 'watershed' in building a network of quantum chemists around the world. This conference was neither the first nor the biggest postwar conference on this subject,¹⁹ but it certainly marked an important moment for building a community, similar to the quantum electrodynamics conference that had been held at the same place four years earlier.²⁰ In their small, closed, and elitist conference, quantum chemists discussed not only the current progress and problems of the field but also its future agenda and needs. Slater recalled that it 'really set the tone for the work going on during the next few years in the application of quantum theory to molecular structure'.²¹

The Shelter Island Conference was an outgrowth of concerns about the inadequacies of valence theory that had been expressed during the 1950 American Chemical

¹⁷ Buhm Soon Park, 'Against the Tide: Mulliken, Slater, and the Niche of Quantum Chemistry in the American Physics Community after World War II', *Journal of the Korean History of Science Society (Han'Guk Kwahak-Sa Hakhoe-Ji)*, 21 (1999), 239–70. See also Butler (note 13); Silvan S. Schweber, 'Big Science in Context: Cornell and MIT', in *Big Science: The Growth of Large-Scale Research*, ed. by Peter Galison and Bruce Hevly (Stanford, CA: Stanford University Press, 1992), 149–93.

¹⁸ Robert G. Parr and Bryce L. Crawford, Jr, 'Summary of Conference on Quantum-Mechanical Methods in Valence Theory', in *Conference on Quantum-Mechanical Methods in Valence Theory* (Washington, DC: US Department of Commerce, 1952), pp. 2–6 (p. 6). On the detailed account of the origins of the Shelter Island Conference, see Simões and Gavroglu (note 8, 1999), pp. 390–93.

¹⁹ The first gathering of those who were working on quantum mechanical applications to chemistry took place in Paris on 12–16 April 1948. See Simões and Gavroglu (note 8, 1999), pp. 387–90; Nye (note 11), pp. 258–59; Mulliken (note 6), pp. 125–27. For describing the Shelter Island Conference as a 'watershed', see Mulliken (note 6), p. 136.

²⁰ For the Shelter Island Conference of 1947 on quantum electrodynamics, see Silvan S. Schweber, 'Shelter Island, Pocono, and Oldstone: the Emergence of American Quantum Electrodynamics after World War II', *Osiris*, 2 (1986), 265–302; idem, *QED and the Men Who Made It: Dyson, Feynman, Schwinger, and Tomonaga* (Princeton, NJ: Princeton University Press, 1994), pp. 156–205. Despite the similarities between the two conferences, there were also some differences. The quantum electrodynamics conference was to be 'an American one', designed to 'demonstrate that theoretical physics in the United States had come into its own with the younger men who had been born and trained there'. In contrast, the quantum chemistry conference did not have such an intention, although Americans were a majority.

²¹ Slater (note 5), p. 241.



Figure 1. Participants at the Shelter Island Conference on Quantum Mechanical Methods in Valence Theory, held on 8–10 September 1951 (left to right): standing—Rüdenburg, Berlin, Barnett, Crawford, MacInnes, Margenau, Pitzer, Kimball, Ufford, Mulliken, Van Vleck, Löwdin, Lennard-Jones, Eyring, Slater, Coulson, Hirschfelder, Wheland, Shull, Sutton, Parr; seated—Mayer, Moffitt, Roothaan, Kotani. Source: Office of Naval Research, *Conference on Quantum Mechanical Methods in Valence Theory* (Washington, DC: Department of Commerce, 1952).

Society meeting. Some participants at that meeting had felt an acute need for ‘a reliable table of the difficult integrals which inevitably turn up in valence calculations’, and talked about having a conference to ‘find out which integrals would be most useful, and to avoid duplication of effort in computing them’.²² Sensing the desirability and timeliness of such a conference, Mulliken took the initiative to organize one with the sponsorship of the National Academy of Sciences and financial support from the Office of Naval Research. Great help came from D. A. MacInnes, Chairman of the NAS Committee on Scientific Conferences, who had in the past arranged several conferences of a similar type usually on Shelter Island.²³ Mulliken carefully drafted the list of fifteen scientists to be invited in consultation with Slater and Robert G. Parr of the Carnegie Institute of Technology. Besides themselves, the list included J. E. Lennard-Jones, D. R. Hartree, C. A. Coulson, M. Kotani, and P. O. Löwdin from abroad, and G. E. Kimball, S. Chandrasekhar, J. H. Van Vleck, J. O. Hirschfelder, H. Margenau, Clemens C. J. Roothaan, and J. E. Mayer from the United States.²⁴ Conspicuously missing from the list were such pioneers as Pauling, London, Heitler, and Hückel. This original list, though somewhat altered later (see Figure 1), reveals Mulliken’s intention of organizing a conference for

²² Parr and Crawford (note 18), p. 2.

²³ Robert S. Mulliken, ‘Proposal for Task Order Under Contract N6ori-20 to the Office of Naval Research from the University of Chicago, Department of Physics’, 7 December 1950, RMP, 64.9. For a list of the conferences held on Shelter Island from 1946 to 1951, see Schweber (note 20, 1994), p. 628.

²⁴ Mulliken (note 23).

currently active scientists.²⁵ The three-day schedule was drafted to focus on specific problems:

Sat. A.M. Valence theory: general (e.g. bond energies, hybridization, d orbitals, etc), and calculations by valence bond methods.

Sat. P.M. Valence theory: calculations by molecular orbital methods (semi-empirical; self-consistent-field; best MO).

Sun. A.M. Better wave functions and energies for atoms and molecules (variational methods, including configuration-interaction and r_{ij} methods).

Sun. P.M. Computational Methods for atomic and molecular energies (including analytic approximations, evaluation and tabulation, or approximation, of integrals).

Monday. Intermolecular forces (both cohesive and repulsive); and misc.²⁶

There was a consensus at the conference that the core problem of quantum-mechanical valence theory was the choice of starting wavefunctions. Much attention was thus focused on the question of how to transcend the primitive approximations usually starting from either the valence bond theory or the molecular orbital theory. Slater, Mulliken, and some other participants contributed to discussions on the ways to obtain a rapid convergence of successive approximations and the relative importance of correction terms added to conventional first approximations. There were also attempts to review the quantum-mechanical interpretation of chemical concepts, such as electron pairs, bond energies, bond orders, hybridization, and chemical reactivity. Lennard-Jones and Coulson were among those who sought to refine these concepts, by considering electron correlation and configuration interaction, factors that had often been previously neglected.²⁷

Along with efforts to improve approximation methods and to clarify chemical concepts, there were discussions on the practical problem of computing integrals, which had been 'bottlenecks' to solving the Schrödinger equation in the *ab initio* manner.²⁸ Those who adopted the semiempirical approach would circumvent this problem with two steps: first, they would reduce drastically the total number of integrals to evaluate by neglecting certain interactions in the molecule, and, second, they would either compute the integrals or replace them with empirical parameters. However, those who employed the *ab initio* approach would have to deal with three

²⁵ Linus Pauling and Fritz London were later invited, but they could not come. Pauling appeared not to be enthusiastic about the conference from the beginning. Although he might have been able to come because he was to be on the East Coast to attend the meeting of the American Chemical Society and the International Congress of Chemistry, which was held before and after the Shelter Island Conference, he declined. Pauling to Mulliken, 10 May 1951; Mulliken to Pauling, 21 June 1951; and Pauling to Mulliken, 30 July 1951, RMP, 64.9. By contrast, London appeared to be eager to attend the conference, expressing his regret over Mulliken's belated invitation: 'Your letter of August 13th inviting me to your Conference on Chemical Valency reached me here only today on my return from Oxford. It is too bad that I did not hear of your plans at an earlier date since my landing in New York happened to be just on the eve of the day when your group was supposed to take the well known train to Shelter Island, a place which is still much in my memory from similar gatherings I attended in the past.' However, London accepted Mulliken's explanation that in the past years he had not worked 'sufficiently in the field of valence theory to warrant [his] participation in the assembly of the 25 representatives of the quantum mechanics of Chemical Valency'. London to Mulliken, 7 September 1951, RMP, 64.9.

²⁶ Mulliken to Members of the Conference, 13 July 1951, RMP, 64.9.

²⁷ Parr and Crawford (note 18), pp. 4–5.

²⁸ On 'bottlenecks', see Clemens C. J. Roothaan, 'Evaluation of Molecular Integrals by Digital Computer', *Journal of Chemical Physics*, 28 (1958), 982–83; Robert S. Mulliken and Clemens C. J. Roothaan, 'Broken Bottlenecks and the Future of Molecular Quantum Mechanics', *Proceedings of the National Academy of Sciences*, 45 (1959), 394–98.

kinds of integral, regardless of the theory they chose: overlap, Coulomb, and exchange. Among them, the most difficult to evaluate were exchange integrals of the following type:

$$H_{12} = \iint [1s_a(1)1s_b(1)](e^2/r_{12})[1s_a(2)1s_b(2)] d\tau_1 d\tau_2$$

where $1s_a(1)$ referred to electron number 1 in a $1s$ atomic orbital on atom a , and so on, r_{12} was the distance between electrons 1 and 2, and e was the electronic charge. This integral was the integral that appeared in Heitler and London's treatment of the hydrogen molecule, and its evaluation required a separate paper by Yoshikatsu Sugiura in 1927. Yet it was only the very simplest example of a type. In general, the four $1s$ orbitals in this example were replaced by four atomic orbitals which were more complicated in form than $1s$ orbitals. The four orbitals might all be different, and might all correspond to different effective nuclear charges. Further, they might be located on three or four different centres instead of only on two. This general feature was the same for overlap integrals and Coulomb integrals. To make computation more complicated, the number of integrals of all kinds would increase enormously as the number of electrons in the molecule increased.

The computation of numerous and difficult integrals was not the kind of task that a single person could undertake: one definitely needed assistants to carry out computing jobs and a community to exchange the information with other scientists. The Shelter Island Conference provided a venue for quantum chemists from around the world to learn about each other's recent computations, computing methods, and computing tools. Masao Kotani (1906–98), a physicist of the University of Tokyo, later recollected: 'This conference gave me a very nice opportunity to get acquainted with many molecular scientists whom I had known only by names and papers'.²⁹ It was also an equally good opportunity for Western scientists to meet Kotani, who was known for his tables of two-centre integrals. The project of tabulating these integrals began in the mid-1930s. He carried out this project as one of the research programmes of the Committee for the Investigation of Catalytic Action, which had been newly established under the Japan Society for Promotion of Science. Two graduate students joined forces with him. They used mechanical desk calculators known as Tiger calculators and had a female assistant engaged in computation. More assistants were hired later to assist them. Kotani's group published two papers on the table of integrals before the war, and in 1951, they had just resumed working on integrals.³⁰ For Per-Olov Löwdin (1916–2000) of the University of Uppsala, Sweden, an invitation to the Shelter Island Conference meant a chance to mingle with leaders in quantum chemistry and a recognition of his recent work involving a large quantity of numerical computations of integrals. Löwdin's computational tool was the Swedish desk calculator 'FACIT-ESA-O', and, like Kotani, he was dependent

²⁹ Masao Kotani, 'Scientific Reminiscence—My Pilgrimage through Quantum Molecular Sciences', *International Journal of Quantum Chemistry: Quantum Chemistry Symposium*, 18 (1984), 11–20. For biographical information on Kotani, see also Kimio Ohno, 'Professor Masao Kotani', *ibid.*, pp. 1–9.

³⁰ Masao Kotani, A. Amemiya and T. Simose, 'Tables of Integrals Useful for Calculations of Molecular Energies', *Proceedings of the Physico-Mathematical Society of Japan*, 20 (extra number) (1938), 1–70; Masao Kotani and A. Amemiya, 'Tables of Integrals Useful for Calculations of Molecular Energies. II', *ibid.*, 22 (extra number) (1940), 1–28. After the war two more papers were published under the same title: Masao Kotani, E. Ishiguro, K. Hijikata, T. Nakamura and A. Amemiya, 'Tables of Integrals Useful for Calculations of Molecular Energies. III', *Journal of Physical Society of Japan*, 8 (1953), 463–71; and Masao Kotani, E. Ishiguro and K. Hijikata, 'Tables of Integrals Useful for Calculations of Molecular Energies. IV', *ibid.*, 9 (1954), 553–57. All of these papers were later put together as a book: Masao Kotani, A. Amemiya, E. Ishiguro and T. Kimura, *Table of Molecular Integrals* (Tokyo: Maruzen, 1955).

on 'trained computers', a group of four to six students to carry out the laborious computational work.³¹

'Human computers' equipped with mechanical desk calculators were the common tool in attacking the problem of integrals.³² Besides Kotani's and Löwdin's groups, it was reported that there were other groups compiling tables of two-centre integrals in a similar manner: notably those of Henry Eyring at Utah, Charles A. Coulson and Michael Barnett at King's College, London, and H. J. Kopineck at the Max Planck Institute, Göttingen. However, there were also those who tried to explore the use of other computing machines. In England, S. F. Boys was systematically computing two-, three-, and four-centre integrals using the EDSAC (Electronic Discrete Variable Automatic Computer) at Cambridge University, and in America, A. L. Sklar initiated a programme for evaluating two-centre integrals with the IBM punched-card machine at the Catholic University in Washington, DC. Mulliken's research group at the University of Chicago, the Laboratory of Molecular Structure and Spectra, pursued two ways: on the one hand, human computers led by Tracy Kinyon carried out innumerable computations of the integrals with such desk calculators as Marchants, Fridens, and Monroes; on the other, Clemens C. J. Roothaan and Klaus Ruedenberg sought to run computing programs on the IBM punched-card machine with the cooperation of Harrison Shull of Iowa State University. Some quantum chemists were looking for and trying alternatives to desk calculators.³³

The significant outcome of the Shelter Island Conference was not only the identification of research groups working on the integral problem but also the decision to exchange information among groups and to provide computed results for those who would need them in the near future. To this end, an informal 'integrals committee' centred at the University of Chicago was established as a 'clearing house for integral information'. The conference served as a wake-up call for quantum chemists who had concentrated on the semiempirical approach. Mulliken was definitely among them. He wrote in his autobiography: '[My conference] paper, about which I was somewhat enthusiastic when it was written, was essentially a semiempirical tour-de-force in which I had skillfully combined certain elements from LCAO-MO theory and valence-bond theory. At the time I was just on the verge of changing from an opinion favoring semiempirical to one favoring *ab initio* (purely theoretical) methods. Up to that time this had seemed too difficult for getting molecular wave functions and energies to be practical. The shift got under way following the Shelter Island conference in 1951.'³⁴

Quantum chemists had an occasion to meet again at the 1953 International

³¹ Löwdin acknowledged the assistance of four male students in the preface of his dissertation: Per-Olov Löwdin, *A Theoretical Investigation into Some Properties of Ionic Crystals* (Uppsala: Almqvist & Wiksells Boktryckeri Ab, 1948), p. vii. For his student computers, see also Löwdin to Slater, 12 January 1952, JSP, Löwdin #2. On Löwdin's career and viewpoints in quantum chemistry, see Buhm Soon Park, 'Computations and Interpretations: the Growth of Quantum Chemistry, 1927-1967' (unpublished doctoral thesis, Johns Hopkins University, 1999), Chapter 7.

³² Quantum chemistry was not the only field dependent on 'human computers'. In fact, projects in astronomy and aeronautics employed bigger teams of human computers who were mostly female workers. See Peggy A. Kidwell, 'American Scientists and Calculating Machines: From Novelty to Common Place', *Annals of the History of Computing*, 12 (1989), 31-40; idem, 'Harvard Astronomers and World War II—Disruption and Opportunity', in *Science at Harvard University*, ed. by C. A. Elliot and M. W. Rossiter (Bethlehem, PA: Lehigh University Press, 1992), 285-302; and Paul E. Ceruzzi, 'When Computers Were Human', *Annals of the History of Computing*, 13 (1991), 237-44.

³³ Parr and Crawford (note 18), pp. 5-6. See also Mulliken (note 6), pp. 117-39.

³⁴ Mulliken (note 6), p. 125.

Conference of Theoretical Physics in Tokyo and Kyoto. While playing a significant role in bringing this conference to Japan, Kotani organized a symposium on molecular physics in Nikko, a few days before the conference officially began.³⁵ In the Nikko symposium and the 'molecule' session of the conference, the quantum chemists reported on their current activities and discussed the issues that had been raised at the Shelter Island Conference.

By this time, Slater had much to talk about on the work of his research group—the Solid-State and Molecular Theory Group—at MIT. He was particularly proud of the recent work on the O₂ molecule by one of his graduate students, Alvin Meckler.³⁶ This work indeed reveals the steps, difficulties, and prospects of the *ab initio* approach. In the first place, the oxygen molecule was a careful choice by Slater. It was the simplest molecule showing ferromagnetism, a magnetic property more common in solids than molecules. This case was thus expected to throw light on how to bring ferromagnetism into an energy band theory of solid-state physics. In addition, Slater believed that it was possible to carry out the same analysis for oxygen as he had done in 1930 for hydrogen: that was to set up molecular orbitals as linear combinations of atomic orbitals (LCAOs), to obtain determinantal functions from these, to solve the resulting secular equations, and finally to get the energy levels of the various multiplet states of the molecule as functions of the internuclear separation. Using more than one determinantal function, each of which represented the 'electron configuration' (the way electrons were distributed), Slater's approach was basically what was later known as 'configuration interaction'. From the beginning, however, Slater and Meckler realized that the scale of the task was different. Instead of six determinantal functions as in the H₂ problem, with oxygen they had to deal with 495 determinantal functions. From them, they chose nine functions that had the same symmetry as the ground triplet state. It was then necessary to solve a secular equation of the ninth degree, rather than a quadratic one as with hydrogen. Beyond the enormously large number of integrals they had to compute, diagonalization of the matrix in the secular equation required computations of high accuracy and large amount. This was not the sort of computational work that could be done with desk calculators, perhaps not even with the IBM punched-card machines. Slater later described the situation:

When we began to count the number of exchange and other integrals that would have to be computed, it became obvious that it would be enormously large. Clearly a digital computer more powerful than the IBM machine that Pratt was using was needed. Meckler found that the MIT electrical engineers were developing a very advanced research computer, the Whirlwind I, to be used in testing ideas of computer design. Meckler made the acquaintance of

³⁵ The 1953 International Conference of Theoretical Physics was held under the auspices of the International Union of Pure and Applied Physics (IUPAP) and with support from UNESCO and the Rockefeller Foundation. Kotani had read a proposal for the conference at the Copenhagen General Assembly of the Physics Union two years earlier, representing the Japanese National Committee of Physics. Kotani had won the approval with the 'warm' support of Hendrik Kramers and other executive members of the Union. See Science Council of Japan, *Proceedings of the International Conference of Theoretical Physics* (Tokyo: Nippon Bunka Insatsusha Company, 1954), Foreword. On the Nikko symposium, see Science Council of Japan, *Symposium on Molecular Physics* (Tokyo: Maruzen, 1954), Preface.

³⁶ John C. Slater, 'Work on Molecular Theory in the Solid-State and Molecular Theory Group, MIT', in *Symposium on Molecular Physics* (Tokyo: Maruzen, 1954), pp. 1–4. Meckler's work was published in October 1953: Alvin Meckler, 'Electronic Energy Levels of Molecular Oxygen', *Journal of Chemical Physics*, 21 (1953), 1750–62.

the people working with this machine, and obtained permission to use it during nighttime hours, when they were not using it for their own research. This computer was years ahead of its time, and it made it possible for us to get into many aspects of our work before commercial computers were available.³⁷

Meckler undertook the computational work in cooperation with members of the Whirlwind Mathematics Group, who revealed and taught to him the technique of diagonalization.³⁸ Even with the Whirlwind computer, the difficulty of having to deal with a large number of exchange integrals still remained. To overcome this hurdle, Meckler adopted the idea that Boys had developed: instead of expanding the atomic orbitals in a series of exponential functions, $\exp(-ar)$, times powers of r and spherical harmonics of the angle, known as the STO (Slater-type orbital), he used Gaussian exponential functions, $\exp(-ar^2)$, which made computations of exchange integrals much easier. In addition to this work on the ground triplet state, Meckler did the same on the excited singlet state. The final results were impressive, quantitatively and qualitatively: the computed values of the binding energy, internuclear distance, and vibration frequency were in good agreement with experiment, off only by a few per cent; and his work showed that the triplet and singlet states converged at an infinite distance, the property that the energy band theory failed to explain for ferromagnetic materials.

Meckler's oxygen work was state of the art, employing the most recent computer technology and mathematical techniques: it deserved the compliment of 'a landmark in the theory of complicated diatomic molecules'.³⁹ For this reason, however, his work also illustrated how difficult it would be to make a further progress. Meckler alluded to this point in his paper:

In conclusion, may we again emphasize the fortunate situation with oxygen, that a fairly complete treatment of configuration interaction did not exceed human endurance and machine storage capacity. Except for oxygen and a few other very simple molecules, it is ridiculous to tabulate all the configurations arising from the atomic primitive set of orbitals, as has been done here. It is necessary to have an *a priori* measure by weight of the secular determinant, to be able to say that this configuration is important, this is not. Configuration interaction is imperative if orbital theory is to be used but it must be handled in a manner that does not surge to impracticability.⁴⁰

Slater was of the same opinion, and he actually reported to the participants of the Nikko symposium that his group was searching for manageable molecules to work on next with the minimum use of configurations or determinantal functions. Methane was a challenging candidate. There was no doubt about the rewards that the study of methane, the simplest molecule having tetrahedral bonds, would bring to the study of diamond, silicon, and germanium. However, the computational work was simply 'too formidable a task to undertake': there were 12,870 determinantal functions, and, from these, 104 had the symmetry required for the ground state, and it was thus necessary to solve a 104×104 secular equation. In this instance, the 104 configurations might be reduced to 22, assuming that each of four directed bonds

³⁷ Slater (note 5), p. 258.

³⁸ Meckler (note 36), p. 1760.

³⁹ Slater (note 5), p. 259.

⁴⁰ Meckler (note 36), p. 1760.

had only two electrons. This assumption appeared to be acceptable, considering the chemical evidence of the tetrahedral structure of methane. However, Slater cautioned: 'We can hardly accept this reduction of the configuration interaction problem, without testing its correctness by direct calculation. There have been altogether too many cases in the literature where *terms* were neglected on the basis of intuition, without calculation, and when later it was found that the neglected terms are really large.'⁴¹ Therefore, the MIT group decided to attack the problem of H₂O instead, for which there were only eighteen configurations, with the hope of understanding how much the electrons in the two different bonds might affect each other. Both technological and theoretical constraints were affecting quantum chemists. 'We feel', Slater said, 'quantum chemistry has still not advanced far enough so that we even know what are the best approximate methods to use for molecules, and can estimate their accuracy. We are trying by well-chosen examples to learn as much as we can about these methods.'⁴²

To be sure, Slater's MIT group was a step ahead of other groups in terms of its computing facilities. The prevalent tools for computing integrals were still human computers with desk calculators, as was reported at the Nikko symposium by Mulliken's Chicago group, Kotani's Tokyo group, Coulson's Oxford group, and Löwdin's Uppsala group. However, the tide was turning toward digital computers. The Chicago group made tables of Coulomb integrals with IBM punched-card machines, and stressed the use of digital computers for far more difficult integrals. At the same time, other concerns were raised about information exchange. As quantum chemists looked forward to using digital computers, the usefulness of tables of integrals was deemed to be not as great as it had appeared. Mulliken thus suggested that it might be better to develop a 'library of codes for an electronic digital computer, from which individual values of any given integral may be obtained when needed'.⁴³ Boys seconded Mulliken's suggestion, and Coulson reiterated the importance of information exchange: 'The need for co-operation on the widest possible scale, mooted at Shelter Island, is even more evident to-day.' There was also a need to exchange progress reports and consequently to standardize notations. It was thus agreed 'with enthusiasm that progress reports (including reports on pilot work) should be exchanged at fairly frequent intervals among all the principal centers, and sent to all actively interested', and that 'everyone should send suggestions for standardization to Mulliken at Chicago, at his earliest convenience'.⁴⁴

Two international conferences of 1955, one held in Stockholm and Uppsala and the other in Austin, Texas, kept the momentum and direction set in the previous meetings. The Swedish symposium reaffirmed the trend of 'going back to the basic principles'.⁴⁵ The latest news in quantum chemistry—Pauling being awarded the 1954 Nobel Prize, which rewarded his semiempirical study of the nature of the chemical bond—did not make participants complacent or satisfied. Rather, they strove to reach the same level of accuracy for complex atoms and molecules that had been achieved in the studies of the helium atom and hydrogen molecule in the early 1930s: 'If Heitler and London gave us the key to the qualitative understanding

⁴¹ Slater (note 36), pp. 3–4.

⁴² Ibid.

⁴³ 'Minutes of Informal Meetings on Molecular Integral Problems, First Session (at Kanaya Hotel, Nikko; Sept. 12, 1953)', in *Symposium on Molecular Physics* (Tokyo: Maruzen, 1954), pp. 109–18.

⁴⁴ Ibid.

⁴⁵ Inga Fischer-Hjalmar and Per-Olov Löwdin, 'Symposium on Quantum Theory of Molecules, Autoreferat', *Särtryck ur Svensk Kemisk Tidskrift*, 67 (1955), 361.

of the homopolar chemical bond, Hylleraas in his work on the helium atom and James and Coolidge in their work on the hydrogen molecule gave us a good reason for believing that, in principle, the many-electron Schrödinger equation in configuration space could provide us also with quantitative results of a sufficient accuracy.⁴⁶ It was at the Texas Conference that a call for using electronic digital computers was strongly made. The following recommendation was approved 'unanimously' at the end of the conference:

WHEREAS, the past contribution of high-speed electronic computers to the calculation of properties of molecules is impressive, and
 WHEREAS, these properties are of extreme importance to chemistry, physics, and biology, and
 WHEREAS, progress of this work is greatly hampered by the fact that, due to the great cost, high-speed computers are unavailable to most scientists in this field,
 THIS CONFERENCE recommends that governments, industries, foundations, and private philanthropists give special attention to the problem of providing more high-speed computing facilities for use in molecular problems.⁴⁷

This recommendation undoubtedly heralded the dawn of the computer era in quantum chemistry.⁴⁸

4. 'Broken bottlenecks'

The network of quantum chemists was certainly strengthened and expanded in the mid-1950s. Besides the conferences, they were able to make and maintain connections through correspondence, visiting, and working together. Löwdin is a good example. He spent his postdoctoral years working with Coulson, Mulliken, and Slater in their laboratories. His personal bond with Slater was particularly strong. Slater made some abortive attempts to lure him away from Sweden, and Löwdin called his Quantum Chemistry Group at the University of Uppsala a 'miniature' of Slater's Solid-State and Molecular Theory Group.⁴⁹ Similarly, H. Christopher Longuet-Higgins, a protégé of Coulson's, spent a year with Mulliken as a Research Associate, before he became Professor of Theoretical Physics at King's College, London. In 1954, he moved to Cambridge after his appointment as the Plummer Professor of Theoretical Chemistry as a successor of Lennard-Jones. Michael P. Barnett, another student of Coulson's, worked with Mulliken and later became a cornerstone of Slater's group.⁵⁰ While the University of Chicago and MIT emerged as favoured places for European scholars to conduct postdoctoral

⁴⁶ Ibid.

⁴⁷ University of Texas, *Molecular Quantum Mechanics Conference* (Austin, TX: University of Texas, 1956), p. 60.

⁴⁸ For example, see Michael P. Barnett, 'Present Status of Molecular Computation', *ibid.*, pp. 11–2.

⁴⁹ Löwdin was first appointed a Laborator (Associate Professor) of Quantum Chemistry at the University of Uppsala, and obtained a Chair in 1960. For the interaction between him and Slater, see Löwdin to Slater, 6 August 1953, JSP, Löwdin #4; Löwdin to Slater, 18 February 1955, and Slater's letter of recommendation, 11 February 1955, JSP, Löwdin #7; Löwdin to Slater, 21 September 1955, JSP, Löwdin #8. See also Per-Olov Löwdin, 'Quantum Sciences: Some Aspects on the American-Swedish Exchange in Quantum Sciences, Particularly the Uppsala-Florida Exchange Project', in *Partners in Progress: A Chapter in the American-Swedish Exchange of Knowledge*, ed. by A. Kastrup and N. W. Olsson (Swedish Council of America, 1977), pp. 255–76.

⁵⁰ Mulliken to The Academic Registrar of University of London, 13 March 1952, RMP, 28.19. For Barnett, see Coulson to Mulliken, 9 October 1951, RMP, 17.8, and Slater (note 5), p. 265.

research,⁵¹ there were also opportunities in Europe. Roothaan went to England for a year in 1955–56 on Fulbright and Guggenheim fellowships. Furthermore, Coulson embarked on the annual Summer School in Theoretical Chemistry at Oxford in 1955, attracting about sixty participants from many countries. Three years later, Löwdin started a similar annual meeting in Sweden, the Summer School of Quantum Chemistry.⁵²

The recommendation adopted at the 1955 Texas Conference was a common voice of this budding community: it clearly signified what the essential need was for the growth of quantum chemistry. Most notably, Löwdin's group was given an electronic digital computer of the type Alwac III-E in 1957, the first modern computer installed at the University of Uppsala. However, this case was rather exceptional. For several years other groups endeavoured to secure computing time on and off campus: for instance, the MIT group had to share the Whirlwind and later the IBM 704 and 709, until it could buy an IBM 709 as a used computer in 1961, and the Chicago group had to rely on outside computers, the Whirlwind at MIT and the UNIVAC (the Remington Rand 1103) at Wright-Patterson Air Force Base, Dayton, Ohio, until 1962 when Roothaan became the director of the University of Chicago Computation Center.⁵³

Despite the limited supply of electronic digital computers, the *ab initio* study of quantum chemistry took off in the mid-1950s. The work done by the Chicago group was particularly impressive. P. I. Merryman completed a program for the computation of exchange integrals on the Whirlwind computer, and Charles W. Scherr developed another program on the Remington Rand 1103 for all the two-centre integrals except the exchange ones. The experience gained from these two programs aided the completion of a powerful program, which featured automatic input and output for the computation of two-centre integrals. Roothaan explained:

The required input information consists of an identification tag for the type of integral, the quantum numbers and orbital exponents $\zeta = Z/n$ of the AOs [atomic orbitals], and the internuclear distance R ; this information is typed on a Flexowriter, producing simultaneously a punched type. This tape is fed to the computer together with the program type. After the computation is completed, the input information is printed out together with the integral value(s). Extensive tests have proven the integrals reliable to at least 7 significant figures. The total computing time for all the necessary integrals for a diatomic molecule of first row atoms is 37 or 100 minutes for the homopolar or heteropolar case, respectively, for each value of R .⁵⁴

While making progress on the problem of integrals, the Chicago group also led the accurate all-electron computation of the wavefunction of diatomic molecules,

⁵¹ For additional examples, see Coulson's correspondence with Slater, in which he described the strengths and weaknesses of postdoctoral applicants: Coulson to Slater, 25 April 1952, about A. B. Lidiard; Slater to Coulson, 4 November 1952, and Coulson to Slater, 20 November 1952, about S. L. Altmann; Coulson to Slater, 8 December 1952, and Slater to Coulson, 9 January 1953, about R. McWeeny; Coulson to Slater, 23 November 1954, about J. A. Hawgood. Source: JSP, C. A. Coulson #1.

⁵² S. L. Altmann and E. J. Bowen, 'Charles Alfred Coulson', *Biographical Memoirs of the Fellows of the Royal Society*, 20 (1974), 75–134; Löwdin (note 49), p. 260; and Per-Olov Löwdin, 'Invitation [to Summer School in Quantum Chemistry]', RMP, 66.14.

⁵³ Löwdin (note 49), p. 259; Slater (note 5), p. 265; Mulliken (note 6), pp. 156–59; and Clemens C. J. Roothaan, 'My Life as a Physicist: Memories and Perspectives', *International Journal of Quantum Chemistry: Quantum Chemistry Symposium*, 27 (1993), 1–11.

⁵⁴ Roothaan (note 28), p. 982.

on the basis of the approximation scheme developed by Roothaan. Roothaan's scheme adapted to molecular problems the procedure of the self-consistent Field (SCF) approximation, which had been widely used in atomic problems. The procedure was as follows: one electron was selected, and the potential field in which it moved was calculated by the average charge distribution of the other electrons, the Schrödinger equation for the electron was solved for this potential, and a newly obtained orbital was fed into the same procedure for the next electron. This procedure was repeated for all the electrons in the system, completing one cycle, and this cycle was repeated over and over again until it did not substantially change a set of orbitals, or until orbitals and consequently fields became self-consistent. A notable aspect of Roothaan's scheme was to express molecular orbitals as linear combinations of certain atomic orbitals, called a 'basis set', and to apply the self-consistency procedure to the combination coefficients, not to the atomic orbitals themselves.⁵⁵ This scheme provided convenience in handling molecular systems for quantum chemists. Roothaan's students, Scherr and Roop C. Sahni, calculated the energy state of nitrogen (N_2) and boron hydride (BH); Kotani and his co-workers treated the ground and low excited states of O_2 and Li_2 ; Harvey Kaplan of the MIT group made *ab initio* computations on the ammonia molecule (NH_3) with Roothaan's LCAO-SCF scheme.⁵⁶ A. Weiss, another student of Roothaan's, coded this scheme, which used the integrals as input data.

In the late 1950s a team of graduate students and postdoctoral researchers of the Chicago group made efforts to combine the molecular integrals program and the coded Roothaan scheme into one master program. Finally they wrote the program in machine language, after flying to and from the Air Force Base in Dayton for eighteen months. Perhaps this program was far more powerful than had been expected: the entire set of computations on N_2 , which had taken Scherr about a year with the help of two assistants, could now be repeated in 35 minutes; for first-row hydride molecules and radicals, such as HF and BH, the corresponding time was 10 minutes; for first-row heteropolar molecules (e.g. CO and LiF), 95 minutes. Proud and confident, Mulliken and Roothaan announced at the National Academy of Science that bottlenecks for performing any *ab initio* molecular computation were broken.⁵⁷

Indeed, the *ab initio* approach saw its renaissance in the 1950s. The number of papers was on the rise, more workers came in, bigger molecules were treated, more approximation methods were developed, and computed results became closer to experimental ones (see Table 1).

In connection with this, the use of electronic digital computers increased rapidly after 1955, according to a National Research Council survey (see Figure 2).⁵⁸ Of

⁵⁵ For a brief description of the self-consistent field procedure and Roothaan's scheme, see Peter W. Atkins, *Quanta*, 2nd edn (Oxford: Oxford University Press, 1991), pp. 326–28.

⁵⁶ Charles W. Scherr, 'An SCF LCAO MO Study of N_2 ', *Journal of Chemical Physics*, 23 (1955), 569–78; Roop C. Sahni, 'Electronic States of Molecules. I. Electronic Structure of BH', *Journal of Chemical Physics*, 25 (1956), 332–78; Masao Kotani, Yukio Mizuno and Kunihusa Kayama, 'Electronic Structure of Simple Homonuclear Diatomic Molecules. I. Oxygen Molecule', *Journal of the Physical Society of Japan*, 12 (1957), 707–36; and Harvey Kaplan, 'Study of the Electronic Ground State of the Ammonia Molecule', *Journal of Chemical Physics*, 26 (1957), 1704–13.

⁵⁷ Mulliken and Roothaan (note 28), pp. 394–98.

⁵⁸ National Research Council, *Chemistry: Opportunities and Needs* (Washington, DC: 1965), pp. 86–88. The same trend is found in the number of computer-related articles in *Chemical Abstracts* by year. A visible increase began around 1957: John D. Bolcer and Robert B. Herman, 'The Development of Computational Chemistry in the United States', *Reviews in Computational Chemistry*, 5 (1994), 1–63 (17–18).

Table 1. Molecules treated by the *ab initio* approach, 1928–60.

Years	Molecules treated ^a	Frequency
1928–30	He ₂ , Li ₂	2
1931–33	Be ₂ (2) ^b , BeH, H ₂ (2), He ₂ , He ₂ ⁺ , Li ₂ (3), LiH, H ₃ , H ₃ ⁺ , H ₂ O	14
1934–36	He ²⁺ , He ₂ ⁺ , HeH, Li ₂ , Li ₂ ⁺ , LiH, H ₃ ⁺ (2)	8
1937–39	H ₂	1
1940–42	CH ₄ (2)	2
1943–45	Li ₂	1
1946–48	H ₃ ⁺ , CH ₄	2
1949–51	He ₂ , Li ₂ , H ₃ , H ₄	4
1952–54	BH, BeH ⁺ , CH, CO, FH (5), H ₂ , He ₂ (2), Li ₂ (3), LiH, N ₂ , O ₂ , CH ₄ , NH ₄ ⁺ , C ₂ H ₄	21
1955–57	BH (3), FH(3), H ₂ (2), He ₂ (4), He ₂ ⁺ , HeH, HeH ⁺ (2), HeH ²⁺ (2), Li ₂ (2), LiH (3), N ₂ (3), NH, O ₂ , O ₂ ⁺ , H ₃ ⁺ , H ₂ O (5), O ₃ , CH ₃ , CH ₃ ⁺ , NH ₃ (4), H ₄ , CH ₄ (4), CH ₄ ⁺ , SiH ₄	49
1958–60	B ₂ , BF, BH, Be ₂ , BeH (2), BeH ⁺ , C ₂ , CH(6), CH ⁺ , CO (7), F ₂ (3), F ₂ ⁺ , FH (9), H ₂ (2), H ₂ ⁻ (3), He (5), He ₂ ⁺ , He ₂ ²⁺ , Li ₂ (4), LiF, LiH (12), LiH ⁺ , N ₂ (2), NH (5), NO (4), OH (7), OH ⁻ (2), CH ₂ , H ₃ (2), H ₂ O (2), CH ₃ ⁻ , NH ₃ , NH ₃ ⁺ , C ₂ H ₂ (2), HCHO (2), CH ₄ (6), CH ₄ ⁺ (3)	106

^a Source: W. G. Richards, T. E. H. Walker, and R. K. Hinkley, *A Bibliography of Ab Initio Molecular Wave Functions* (Oxford: Clarendon Press, 1971). The authors do not provide a comprehensive review of the calculations performed on the hydrogen molecule ion (H₂⁺), partly because it is a special case in which the Schrödinger equation can be solved exactly for fixed nuclei, and partly because its review would be a lengthy monograph in itself.

^b The numerals in parentheses indicate the numbers of papers studied on the molecule if more than one.

course quantum chemistry was not the only field in chemistry using computers: they also revolutionized X-ray crystallographic methods, and helped the investigation of problems in statistical mechanics by the Monte Carlo method. However, quantum chemistry was the leader in its use of computers. An estimated use of computing time for quantum chemistry in 1965 was 40,000 hours, the most among all fields of chemistry. As Roothaan said, it was ‘fortunate indeed that digital computers became available just at about the time of this renewed activity’.⁵⁹

There were ample reasons for Mulliken and Roothaan to depict a rosy future for quantum chemistry and to talk about the ‘colossal rewards’ that lay ahead from *ab initio* computations of the structure of matter. They predicted with confidence that these computations would lead toward a fundamental understanding of the rules of valence theory, the various properties of molecules, ions, and radicals, activated states in chemical reactions, the structure and stability of metals and other solids, and spectroscopically excited states. For some observable quantities, they argued, the results of theoretical computations were going to compete more and more strongly with experiment. For other quantities yet inaccessible or poorly accessible to experimental observation, as in the study of astrophysics and upper atmosphere phenomena, reliable theoretical computations would be essential.

⁵⁹ Roothaan (note 28), p. 982.

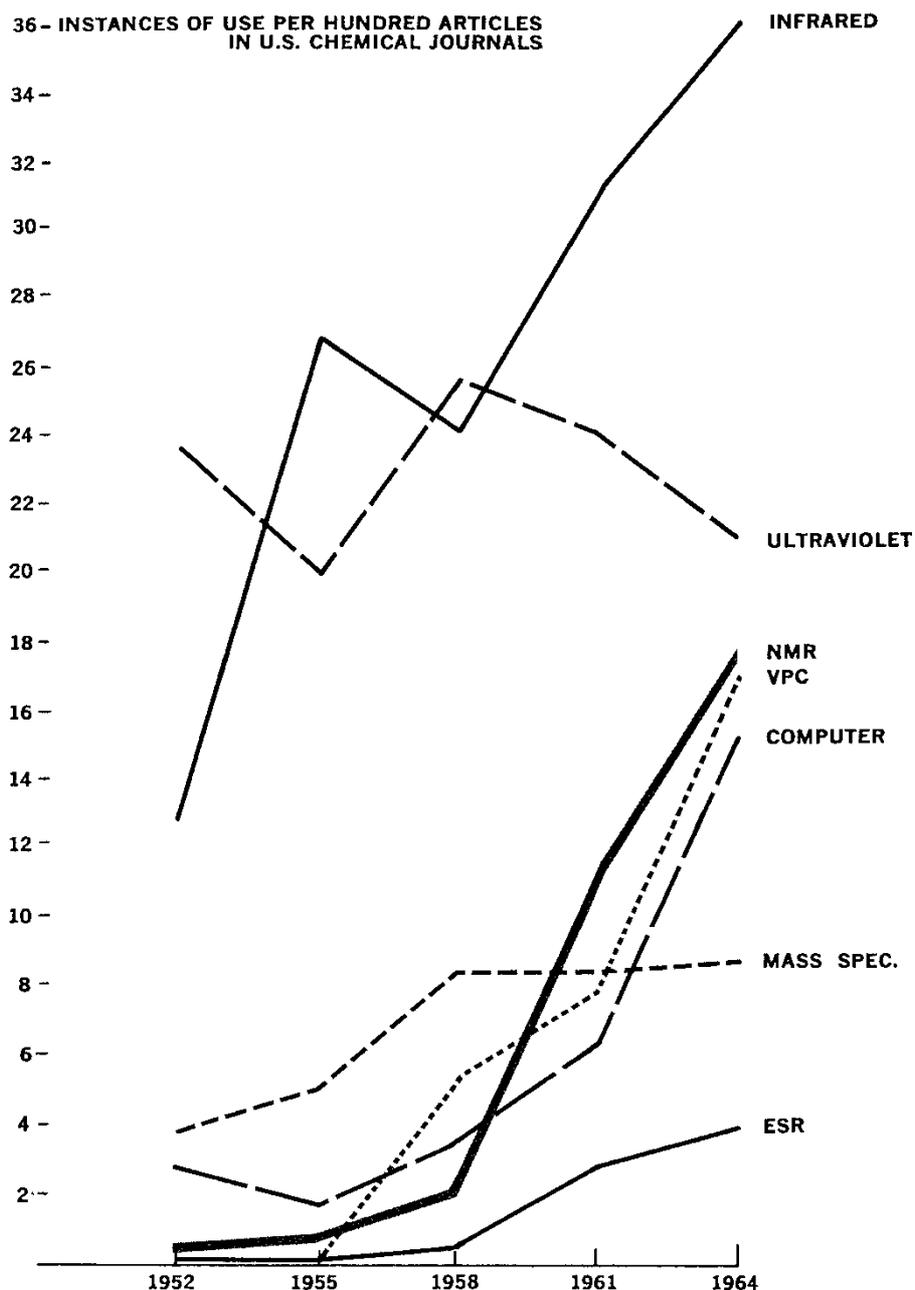


Figure 2. The use rate in chemical research in the United States for seven of the most commonly used types of instrument: infrared, ultraviolet, nuclear magnetic resonance (NMR), vapour-phase chromatographs (VPC), electronic digital computers, mass spectrometers, and electron spin resonance (ESR). The 'use rate' is defined as the number of instances of use cited per 100 papers in selected representative journals. Source: National Research Council, *Chemistry: Opportunities and Needs* (Washington, DC: National Research Council, 1965), p. 88.

Mulliken and Roothaan were optimistic about establishing a sound relationship between theory and experiment, or making 'new semiempirical generalizations which should be of great value in understanding and predicting the structure and behavior of large molecules and of solid and liquid aggregates'. They felt that quantum chemists were 'standing on the threshold of a new era'.⁶⁰

5. Tension: semiempirical versus *ab initio*

The 1950s witnessed the revival of the *ab initio* approach, the emergence of a community, and the arrival of digital computers as new computing tools. However, these changes did not allow an easy portrayal of the disciplinary identity of quantum chemistry. Was the community exclusively for *ab initio* workers? Did digital computers entirely replace desk calculators as main computing tools? Who would be the quantum chemist of the new era entering the 1960s? The clue to the answers to these questions lay in the status of the semiempirical study in quantum chemistry.

During the 1950s, the semiempirical approach underwent a significant change: Hückel's molecular orbital theory was refined and expanded, attracting much attention from chemists. As one chemist noted, the organic chemical literature dealing with this theory drastically increased: 'A mere handful of papers (approximately 20) in the thirties was followed by approximately 70 papers in the forties, whereas the decade of the fifties just completed has witnessed some 600 papers on this subject'.⁶¹ The rate of increase was impressive, but the number of papers was also considerable. It seems that the semiempirical approach of molecular orbital theory, let alone that of resonance theory, outnumbered the *ab initio* approach. This fact implies that quantum chemistry became a successful donor specialty for organic chemistry, but makes it more difficult to demarcate the line of its own territory.

The quantum chemistry conferences of the 1950s excluded neither the semiempirical approach nor the semiempirical theorists. Although the Shelter Island Conference did not have Pauling's presence, George W. Wheland, another tireless proponent of resonance theory, was there, and also Robert G. Parr, one of the creators of the PPP (Pariser-Parr-Pople) theory, which generalized the Hückel molecular orbital theory. For some participants, it was not easy to tell whether they subscribed to the *ab initio* approach or the semiempirical approach. A notable example was Coulson, who distinctively pursued both avenues. Not only did he develop mathematical techniques to compute three-centre integrals, he sought to elaborate the Hückel theory. He knew that the greatest merit of the semiempirical theory was to be found in its convenience as well as in its accuracy. For Coulson, there was 'no harm in [the semiempirical approach], provided that we recognize the limitations of such an enquiry'.⁶²

However, to find the limitations was controversial in itself. The apparent success of semiempirical study was often discounted as 'accidental or fortuitous', an outcome of neglecting important factors with no theoretical ground.⁶³ Löwdin dubbed the semiempirical and *ab initio* approaches as the 'easy' and 'hard' ways, and suggested

⁶⁰ Mulliken and Roothaan (note 28), p. 398.

⁶¹ Andrew Streitwieser, Jr, *Molecular Orbital Theory for Organic Chemists* (New York: John Wiley & Sons, 1961), Preface.

⁶² Charles A. Coulson, 'Quantum Theory, Theory of Molecular Structure and Valence', *Annual Review of Physical Chemistry*, 3 (1952), 1-18.

⁶³ For example, Masao Kotani, 'Introductory Talk', in *Proceedings of the International Conference of Theoretical Physics* (Tokyo: Nippon Bunka Insatsusha Company, 1954), pp. 593-98.

a review of the current semiempirical approach. He said, 'It would perhaps be good if, for some time, we could abandon the "optimistic" point of view that all complicated integrals are negligible and instead to investigate the *real* outcome of our theory—whether good or not. Instead of having plenty of excellent semi-empirical or semi-theoretical results, where the good agreement with experiments might be just fortuitous, it would certainly be better if we had a few *reliable* theoretical results, which could tell us about the eventual weakness of our present theory and give us some ideas about necessary improvements.'⁶⁴

A special meeting was arranged in 1958 during the last week of Löwdin's summer school to discuss the issue of the relationship between semiempirical and *ab initio* methods. Among the panellists were Pauling and Mulliken. George G. Hall of the University of London sketched the purpose and outcome of the meeting. He said, 'In the course of the past twenty five years the language of quantum mechanics has invaded almost every branch of chemistry. ... Many of the most useful ideas, however, are ones which do not belong to accurate quantum mechanics but arose first in certain approximate calculations and have since been developed by using them to explain experimental facts.'⁶⁵ Such concepts included resonance, hybridization, atomic and ionic radii, and electronegativity, all of which by then had become the chemist's common vocabulary. 'Unfortunately', Hall pointed out, 'it is becoming very clear that most of these ideas need careful re-examination both to establish their quantum mechanical status and to show how they can be refined or modified to explain the more extensive and more accurate experimental results now available.'

Hall observed that there was 'the growing tension between the so-called semiempirical methods and those based on *a priori* [*ab initio*] calculations',⁶⁶ and this tension was acutely felt, as the discussion moved to the future of quantum chemistry. For Mulliken, the calculation of good molecular wavefunctions should be considered the top of the research agenda. He argued:

As we make more and more calculations on different simple molecules, I believe we will be able to make better and better extrapolations from these which will assist in understanding the experimental data on a wider variety of molecules. In experimental chemistry we consider a large number of cases and try to understand by comparing them. In quantum mechanics it is better to take a few cases and make accurate calculations.⁶⁷

However, Mulliken's view was hardly prevalent. It was pointed out by Hall that, even if there were large improvements in computers and mathematical methods, there would still be difficulties in dealing with complex molecules that had three or more nuclei, more than fifteen electrons, and no high symmetry. Furthermore, Hall held that the prime concern of chemists was not only the numerical values of observables, but also 'less numerical concepts' such as bonds, electronegativities, and reactivities. In Hall's view, quantum chemists should work in the direction of developing useful semiempirical models, such as the resonance theory, which 'have little mathematical justification but yet serve as very useful models of the chemist's

⁶⁴ Per-Olov Löwdin, 'Recent Simplifications in the Molecular Orbital Theory of Calculating Energy Levels', *ibid.*, pp. 599–611.

⁶⁵ G. G. Hall, 'Chemistry and Quantum Chemistry', *Nature*, 183 (1959), 158–59.

⁶⁶ *Ibid.*

⁶⁷ Anders Fröman and Osvaldo Goschinski, 'Acta Vålådlensia Revisited: Per-Olov Löwdin in Scientific Discussion', in *Quantum Science Method and Structure: A Tribute to Per-Olov Löwdin*, ed. by Jean-Louis Calais *et al.* (New York: Plenum Press, 1976), 33–51 (p. 50).

concepts and experience'. They should also work to extrapolate from the simple to complex cases. Going a step further, F. A. Matsen of the University of Texas, who had organized the 1955 Texas Conference, reiterated the autonomy of chemistry:

There is a possibility that a core of ideas in chemistry or in physics may develop independently of quantum mechanics. [For] we believe that if a separate core should develop its connection with quantum mechanics could ultimately be established. The development of an alternate core could have two effects (1) it could enrich and enlarge our understanding, (2) it could impede the development of our understanding through the development of a language and attitude which must subsequently be modified. Pauling's remark that if chemists had got there first, they might have developed tetrahedral orbitals instead of *s*- and *p*-orbitals is perhaps not irrelevant here. Whichever the result the experimentalist must read his experiments and not be too disturbed by the *quantum chemical prophets* who are only too likely to say first, 'that's impossible' and later, 'we knew it all the time'.⁶⁸

No one argued more strongly for the semiempirical approach than Pauling. His view was well represented by a bold statement, 'Usually I am not very much interested in calculations because I know what the answers are going to be anyway.'⁶⁹ Indeed, Pauling's legendary knack for chemical data was the basis of his chemical intuition, which was both admired and criticized by others. He preferred, if possible, that he be led by his chemical intuition rather than by the drudgery of computations. To Pauling, the exact solution of the Schrödinger equation was but one of many ways of investigating nature; it was equally meaningful to make useful generalizations from approximate solutions of the Schrödinger equation, and solving numerous chemical problems with the semiempirical theory was more fruitful than discussing its quantum-mechanical legitimacy.⁷⁰

There are so many chemical problems, that are not well understood, that *I hope that the period of laying a sound framework of quantum chemistry will be approaching at least a temporary end*. I hope that some of the activity in this field will be directed to the finding of new generalizations. What are the properties of the hydrogen-bond for example? I think we might well be able to predict some properties. This is so important in biology that I should like to see more theoretical work of high order done on the hydrogen-bond.

The debate over the legitimate methodology in quantum chemistry came to the fore at the Conference on Molecular Quantum Mechanics in 1959. Held at the University of Colorado, Boulder, this conference was attended by more than one hundred scientists from around the world. It was the largest in size among the conferences of this kind in the 1950s. Parr served as Chairman, while Mulliken and Slater helped him as members of the steering committee.⁷¹ The concerns about the schism in the community were expressed often both in the formal presentations and informal coffee-table talks.

⁶⁸ For Hall's and Matsen's view, see *ibid.*, pp. 47–49. My emphasis.

⁶⁹ *Ibid.*, p. 41.

⁷⁰ *Ibid.*, p. 51. My emphasis.

⁷¹ Robert G. Parr, 'Papers from the Conference on Molecular Quantum Mechanics, Held at the University of Colorado, Boulder, Colorado, June 21–27, 1959: Introductory Note', *Reviews of Modern Physics*, 32 (1960), 169.

Bernard J. Ransil, for example, started his summary of the diatomic molecular programme at the Chicago group by alluding to the existence of the schism: 'The coming of age of the digital computer and its impact on the field of molecular structure has recently been variously characterized as "disastrous to theoretical chemistry" and as "means which will enable modern structural chemistry to become less of an art and more of a science".'⁷² The negative image of computers stemmed in large part from worries about whether the use of programmed computing machines might blunt a scientist's critical faculties and stunt the free play of his scientific imagination. The positive impact was reckoned with an expectation that digital computers would provide the means for critical calculations on which theoretical concepts might be justified, tested, or based. Ransil's tactic was to take neither side, instead pursuing 'a wide middle ground [that] exists where the digital computer, intelligently used as a research instrument, can quickly provide the theoretical chemist with accurate results to an illuminating but complex critical calculation.' He thus adopted a maxim that would guide him in both developing intuitions and undertaking computations: 'Go as far by calculation as is reasonably possible, guided by chemical and physical intuition and computer economics, without introducing empirical schemes or data.'⁷³

The after-dinner speech that Coulson gave at the banquet on the final evening captured the spirit of the Colorado Conference more effectively than any of the other formal presentations. Coulson first looked back on three decades of quantum chemistry: 'It is important to remember how old quantum chemistry now is. It was in 1926 that Schrödinger introduced his wave mechanics; and within two years Heitler and London made the first excursion into molecular-structure calculation with its aid. The subject is therefore just over 30 years old. It is not surprising that many of the plums have now been picked, and really interesting and novel fruit is harder to come by.'⁷⁴ No sooner had Coulson given these self-congratulatory remarks, adding some examples of major successes in the last few years, than he talked about the present state of the community. He made 'no apology for coming straight to it', since he believed it would have grave implications for any future conferences in the field.

It seems to me that *the whole group of theoretical chemists is on the point of splitting into two parts*. Anyone who attended all the sessions this week could be in little doubt but that the first and second halves were quite different—almost alien to each other. In its simplest form this difference was associated with the large-scale use of electronic computers, though, as I will say later, I think there is a deeper aspect of it than just this. Now perhaps the time has come when we ought to separate ourselves into two or more groups, in much the same way that the one subject of chemistry divided itself in the course of time into organic, inorganic, physical, and analytical chemistry. It is the almost inevitable fate of a new subject, as it grows, to split.⁷⁵

⁷² Bernard J. Ransil, 'Studies in Molecular Structure. I. Scope and Summary of the Diatomic Molecule Program', *Reviews of Modern Physics*, 32 (1960), 239–44.

⁷³ *Ibid.*, p. 239.

⁷⁴ Charles A. Coulson, 'Present State of Molecular Structure Calculations', *Reviews of Modern Physics*, 32 (1960), 170–77. See also Simões and Gavroglu (note 8, 1999); *idem*, 'Issues in the History of Theoretical and Quantum Chemistry, 1927–1960', in *Chemical Sciences in the 20th Century*, ed. by Carstein Reinhardt (Weinheim: Wiley-VCH, 2001), pp. 51–74 (pp. 72–74).

⁷⁵ Coulson (note 74), p. 171. My emphasis.

This situation of the growth and specialization of quantum chemistry posed the problem of communication within the discipline. During the conference week, Coulson occasionally came across someone using the phrase, 'Oh but you're not doing quantum chemistry'. It was heard in different places where heavy computational techniques were used in calculating energy values for the helium atom and hydrogen molecule; where calculations of a highly empirical kind were undertaken to estimate energy levels and charge distributions in heteronuclear aromatic molecules; and where there were discussions about the tabulation and interpretation of barriers to internal rotation in substituted ethane-type molecules. E. Bright Wilson of Harvard said jokingly that he wondered whether he had the right union card in one of these discussions. Coulson was, however, 'very far from laughing at it', because the above cases represented 'quite distinct aspects of what we used to call quantum chemistry'. The problems that quantum chemists faced were then about 'the very nature of quantum chemistry'; 'what relation it has to experiment, what function we expect it to fulfill, what kind of question we would like it to answer'.⁷⁶

At first glance, the question of disciplinary identity was bound up with the use of electronic computers. It was 'an irony of fate', Coulson said, that the present situation was a 'logical development' of recommendations adopted at the Texas Conference of 1955.⁷⁷ The speeding-up of calculations recently allowed quantum chemists to explore research areas where computation was the only hope of settling a dispute, such as the absorption of H^- and the ground-state structure of the methylene radical CH_2 , and led them to attack polyatomic molecules. Yet Coulson considered that at this moment there was 'an upper limit to the size of a molecule for which accurate calculations would likely become practicable'. That limit seemed to be somewhere around molecules having twenty electrons. Coulson depicted the practice of those working within the range of 1–20 electrons in a parody:

We are told that above the gateway to Plato's Academy there was written the sentence, 'God is always doing Geometry'. And certainly the mathematician Jacobi said, 'God always arithmetizes'. But if the range 1–20 electrons were all, we could ourselves add a further statement, 'God is always computing'. This is because we may hope that eventually all problems in this range will be solved accurately by computational techniques. Now surely, in this way of speaking, God *is* computing.⁷⁸

However, it was equally certain that there was much more in chemistry than was covered by this range. In fact, there were some signs of success in the study of biological molecules with the 'grossest possible approximations', the crudity of which might be 'nothing less than revolting to the "computers"'. Coulson made a distinction between two groups: 'Group I (electronic computers)', who had major interests in the field of 1–20 electrons and thought in terms of full electronic computation, and 'Group II (nonelectronic computers)', who did not think in these terms. It was also suggested, as alternatives, that these groups be called the *ab initio*-ists and the *a posteriori*-ists. The gap between the two groups was so large that there was little point in bringing them together. Coulson thus lamented: 'This is probably the last

⁷⁶ Ibid., pp. 171–72.

⁷⁷ Ibid.

⁷⁸ Ibid.

conference of the old kind. In future we should either have two distinct conferences, or else be prepared to plan parallel sessions for group I and group II enthusiasts.⁷⁹

Beyond the differences in methodology and interest, there were even further distinctions between group I and group II. In essence, they set different kinds of research goals, had different viewpoints on theory and experiment, and thus showed different levels of ontological commitment to traditional chemical concepts. As Coulson aptly pointed out, group I desired to reach complete accuracy, and, to this end, they were prepared to abandon all conventional chemical concepts and simple pictorial quality in their results. Against this, group II tended to argue that chemistry ought to be an experimental subject, whose results should be built into a pattern around quite elementary concepts. To them, the role of quantum chemistry was to understand these concepts and to show the essential features of chemical behaviour. As an example, Coulson took into consideration the study of conjugated systems: 'These people [of group II] are anxious to be told why, when one more vinyl group is added to a conjugated chain, the uv absorption usually shifts to the red; they are not concerned with calculating this shift to the nearest angstrom; all that they want is that it should be possible to calculate the shift sufficiently accurately that they can be sure that they really do possess the fundamental reason for the shift.'⁸⁰ Acceptable forms of explanation were different in the two groups. For group II, calculations without causal explanation were meaningless; all results ought to be given in conventional concepts, no matter how rigorously they were defined. To show this point more clearly, Coulson took another example from the study of chemical bonds:

they [group II] want to know why the HF bond is so strong, when the FF bond is so weak. They are content to let spectroscopists or physical chemists make the measurements; they expect from the quantum mechanician that he will explain *why* the difference exists. But any explanation *why* must be given in terms of concepts which are regarded as adequate or suitable. So the explanation must not be that the electronic computer shows that $D(\text{H-F})$ [the distance between H and F] $\gg D(\text{F-F})$ [the distance between F and F], since this is not an explanation at all, but merely a confirmation of experiment. Any acceptable explanation must be in terms of repulsions between nonbonding electrons, dispersion forces between atomic cores, hybridization and ionic character. It does not matter that in the last resort none of these concepts can be made rigorous.⁸¹

Coulson believed that chemistry would prosper in its position between physics and biology: 'To go deeper than this [level of depth in which chemistry has been located] is to be led to physics and elaborate calculation. To go less deep is to be in a field akin to biology.' He did not think that the same degree of rigour should be applied to different disciplines. Each discipline would operate at a particular level of depth, and at that depth, he believed, certain concepts would have 'significance and—if the word may be allowed—reality'. 'It would be a grave disaster', he thus said, 'if quantum chemistry was limited to either the "very deep" or the "shallow" level of concept and operation'.⁸² What he considered desirable and achievable was

⁷⁹ Ibid., pp. 172–73.

⁸⁰ Ibid., pp. 173–74.

⁸¹ Ibid., p. 174.

⁸² Ibid.

neither to narrow the gap between group I working on a very deep level and group II working on a shallow level nor to reduce entirely one group to the other, but only to restore adequate channels of communication between them. Quantum chemistry ought to maintain a close link with experiment and with conventional forms of thought in chemistry, while exploring the area of rigorous calculations with electronic digital computers.

6. 'Two-Dimensional Chart of Quantum Chemistry'

Coulson's concern about the schism within the community continued to echo around in the 1960s. Robert Parr, for instance, concluded his book *The Quantum Theory of Molecular Electronic Structure* (1963) with some thoughts on the future of quantum chemistry. 'Of course', he said, 'not everyone should strive to become a computer expert, but a surprising number of people are moving in that direction, and those who do not can profit by following the activities of those who do.' He continued:

For the practicing organic or inorganic chemist, physical chemist or spectroscopist, or for the biologist, each with his ever-increasing store of experimental knowledge about molecules and their behavior, the tools of molecular quantum mechanics ought to be increasingly useful. As quantum chemistry develops, purely theoretical calculations will become a standard method for accurate determination of properties of small molecules, and semiempirical methods will be tested and sharpened up, becoming less arbitrary and more accurate.⁸³

The range of applications of semiempirical methods was quite broad, but their validity was not always clear. For this reason, Parr insisted that the *ab initio* method be a source of improving semiempirical treatments.

The reality in the mid-1960s, however, was a further divergence between group I and group II quantum chemists, justifying Coulson's worrisome observation of 1959. Deeply concerned, John A. Pople took the opportunity to express again the need for maintaining a constructive relationship between the two groups. Pople, a protégé of Lennard-Jones, moved from the National Physics Laboratory, Teddington, England, to the Carnegie Institute of Technology in 1964.⁸⁴ The next year, he presented a paper 'Two-Dimensional Chart of Quantum Chemistry' (see Figure 3) at the International Symposium on Atomic and Molecular Quantum Theory held in Sanibel Island, Florida, where about 140 scientists from twenty different countries gathered to exchange new results and ideas. The symposium was dedicated to Robert S. Mulliken to honour his contributions in the field.⁸⁵ In this special occasion, Pople succinctly summarized the current trend in quantum chemistry by drawing a hyperbolic curve.

Here, each calculation of a molecular wavefunction was represented in two coordinates: the vertical coordinate corresponded to the sophistication of a computa-

⁸³ Robert G. Parr, *The Quantum Theory of Molecular Electronic Structure* (New York: W. A. Benjamin, 1963), p. 125.

⁸⁴ Pople's departure was reported in a London newspaper with the bold front-page headline, 'Another Brain Down the Drain'. Dermot Martin, 'John Pople and the Search for Chemical Truth', *Chemistry in Britain*, 28 (1992), 138–40.

⁸⁵ John A. Pople, 'Two-Dimensional Chart of Quantum Chemistry', *Journal of Chemical Physics*, 43 (1965), S229–S230. For the symposium dedicated to Mulliken, see Per-Olov Löwdin, 'Introduction', *Journal of Chemical Physics*, 43 (1965), S1.

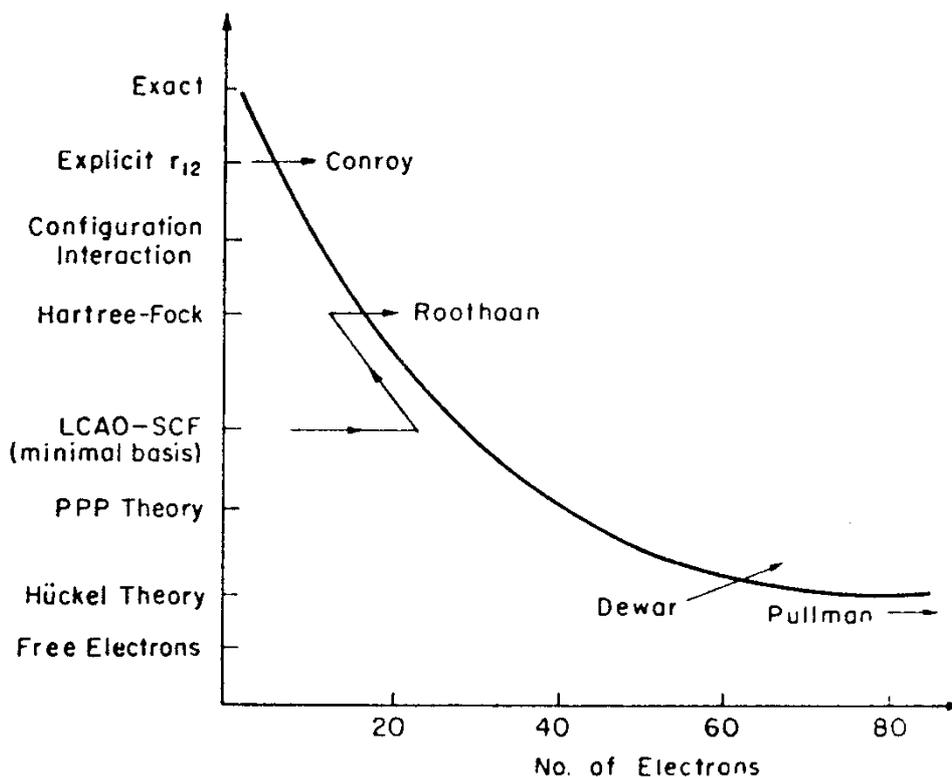


Figure 3. Pople's two-dimensional chart of quantum chemistry.

tional method, and the horizontal coordinate was a measure of the size of the molecule. Therefore, this curve illustrated the inverse relationship between the degree of computational sophistication and the number of electrons in a molecule. For example, Roothaan's LCAO-SCF method, which used a minimal basis set of Slater-type orbitals but made no approximations in the integrals, could deal with a molecule having about thirty electrons, that is, many diatomic molecules and some polyatomic molecules. One could improve the accuracy by using larger basis sets (approaching the Hartree-Fock method), or by taking into account more than single-determinant wavefunctions (configuration interaction). However, the improvement in these ways could only be made at the sacrifice of limiting the size of the molecule to much smaller ones. Exact solutions of the Schrödinger equation, which were at the top of the scale, were possible only for one-electron systems. Pople placed semiempirical methods, such as the Hückel theory and the PPP theory, below the level of the LCAO-SCF method with the minimal basis set. Semiempirical methods involved varying degrees of mathematical approximation—the justification of which was not always transparent—and frequently determined some parameters by appeal to experimental data. Nevertheless, semiempirical methods had undisputable merit in that they could deal with much bigger molecules.⁸⁶

To Pople, the schism within the community had much to do with the two different directions of progress pursued by quantum chemists. He said, 'I believe that much

⁸⁶ Pople (note 85), p. S229.

of the divergence between Group I and Group II quantum chemists arises because the former tend to progress vertically and the latter horizontally, so that the two move continually further apart.' Moving from bottom to top meant refining studies of a given molecule by improvements in technique, while moving left to right meant applying an established method to larger molecules. Instead of simple vertical or horizontal movements, Pople suggest that 'we should find ourselves approaching common ground in the center of the diagram to the benefit of the whole subject'. He was indeed convinced that 'such a movement would lead to its reunification'. To achieve this end, he encouraged group I to extend some of their simpler computational techniques to larger molecules, and he also asked group II to keep their methods continually under review by testing them against more precise calculations on smaller systems.

7. Conclusion

Pople's two-dimensional diagram, later called the 'hyperbola of quantum chemistry',⁸⁷ indeed signified the formation of specialized groups having distinct methodological commitments. One may argue that the inverse relationship between the computational sophistication and the complexity of the system has existed since the formative period of quantum chemistry in the 1930s. Yet it should be borne in mind that there was no visible community for quantum chemists at that time: there were individual quantum chemists, of course, no matter how they called themselves (theoretical physicists, theoretical chemists, chemical physicists, physical chemists, molecular physicists, or physical organic chemists), but it was only after World War II that their community or networks of research around the world began to take shape. The 1951 Shelter Island Conference was crucial in this respect. Twenty-five scientists who came to the conference by invitation formed a core group for subsequent meetings of a larger scale, and, more importantly, issues they set for further discussion became landmarks for the future development in quantum chemistry. The top of the agenda was the improvement in computation—computational techniques, the use of speedy computers, and the exchange of computed results. In the years between 1955 and 1965, electronic digital computers replaced previous computing tools, such as IBM punched-card machines and 'human computers' equipped with desk calculators, for *ab initio* calculations, and many quantum chemists came to be their own programmers. Yet desk calculators were still useful for most semiempirical methods, which saw broad applications in chemical research. The proponents of *ab initio* methods and those of semiempirical methods were thus different not only in their approach to solving the Schrödinger equation: they had different research interests and goals, different takes on the theory–experiment relationship, and different views on the role of computers. The tension between the two groups was almost inevitable.

⁸⁷ Martin Karplus, 'Three-Dimensional "Pople Diagram"', *Journal of Physical Chemistry*, 94 (1990), 5435–36. To be sure, not all methods fit into this diagram. As Karplus notes, density functional methods provide the accuracy and sophistication of Hartree–Fock-type calculations but can treat bigger molecules with the available computer time. He also suggests an important modification on Pople's diagram: by 1990, the linear scale in Pople's diagram, which covered the range from 1 to 100 electrons, has been replaced by a logarithmic scale that goes from 1 to 10⁶. This change implies that it has become possible to conduct *ab initio* calculations for reasonably complex molecules and their reactions with sufficient accuracy. A 'partial merging of groups I and II' is observed.

'Where ... does "real" quantum chemistry lie?', or so Coulson asked in 1959.⁸⁸ This question of disciplinary identity testifies to the substantial growth of the quantum-chemical community, on the one hand, and the emergence of specialized groups within it, on the other. To a great extent, both changes resulted from the increasing use of electronic digital computers in the 1950s. Computers were the source of both enriching and thereby splitting the discipline of quantum chemistry.

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⁸⁸ Coulson (note 74), p. 172.