

Nobel Centennial Essays

A Century of Chemical Dynamics Traced through the Nobel Prizes

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1998: Walter Kohn and John Pople

by J. Van Houten

Walter Kohn (1923–)

for his development of the density-functional theory

John Pople (1925–)

for his development of computational methods in quantum chemistry

This is the twelfth in a series of essays, written in commemoration of the centennial of the Nobel Prize, examining the history of chemical dynamics in the 20th century (1).^W Walter Kohn and John Pople developed computational methods that enabled improved energy calculations on molecules and other multi-atom systems in arbitrary configurations. Those methods yield information on equilibrium configurations, vibrational frequencies, dissociation energies, and naturally, chemical reactions. Kohn's work allows for studies on large systems (up to several hundred atoms) with moderate accuracy; Pople's work permits higher accuracy, but for somewhat smaller systems (up to 10–20 atoms). Chemists have taken advantage of those developments to perform calculations on systems during reactive encounters, thereby obtaining a better understanding of chemical dynamics and allowing for predictions regarding the course of chemical reactions based on the energies of various possible transition states.

During the first decades of the 20th century, the foundations of quantum mechanics were laid as scientists came to understand the electronic structure of atoms. This led to several Nobel Prizes—all in physics—to scientists whose names will be familiar to all college chemistry students: Planck (1918); Einstein (1921); Bohr (1922); Millikan (1923); de Broglie (1929); Heisenberg (1932); Schrödinger (1933); and J. J. Thomson (1906) for showing that the electron had particle properties, and his son, G. P. Thomson (1937) for utilizing wave properties of electrons (2). In his Nobel lecture John Pople recalled a well-known remark made in 1929 by Paul Dirac (who shared the 1933 physics Nobel Prize with Schrödinger): “The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved” (3). Pople called Dirac's statement “a cry both of triumph and of despair.”

Pople's interpretation of Dirac's words reflected the fact that it would take the rest of the 20th century to develop methods to solve those equations for anything but the simplest of molecules. Prior to 1998, only three Nobel Prizes had been awarded for theoretical descriptions of bonding in



Walter Kohn

John Pople

molecules: to Linus Pauling (1954) for elucidating the nature of the chemical bond, to Robert Mulliken (1966) for developing the molecular orbital theory named for him, and to Gerhard Herzberg (1971) for contributions to the knowledge of the electronic structure and geometry of molecules.^W However, Pauling's bonding theory was strictly qualitative, Herzberg's work was primarily spectroscopic, and accurate calculations for Mulliken's molecular orbitals were possible only for very simple molecules such as H₂. The 1981 Nobel Prize to Kenichi Fukui and Roald Hoffmann recognized theoretical descriptions of chemical reactivity based on the symmetry properties of frontier orbitals that were semi-quantitative at best (*Ig*). The work recognized by the 1998 Nobel Prize to Kohn and Pople made accurate theoretical calculations possible for large molecules and for reacting systems for the first time.

Pople's Development of Computational Methods of Quantum Chemistry

Pople began examining problems of electronic structure and bonding as a Ph.D. student with Sir John Lennard-Jones in Cambridge in 1948 (4). His dissertation topic dealt with the lone-pair electrons in water; it served as an initial step toward a theory of hydrogen bonding in water and for what he called “a preliminary, rather empirical study of the structure of liquid water.” After completing his Ph.D. in mathematics in 1951, Pople stayed on at Cambridge as a research fellow in Trinity College, and he “was able to relax a bit and formulate a more general philosophy for future research in chemistry. The general plan of developing mathematical mod-

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els for simulating a whole chemistry was formulated, at least in principle, some time late in 1952.” Since computational resources were extremely limited at that time, Pople attempted “to simplify existing theories enough to turn them into practical possibilities.” The work paralleled that of Pariser and Parr, and it led to what has become known as PPP theory.

Pople devoted much of his Nobel lecture to tracing the historical development of quantum mechanical computational methods for molecules (3). He noted that Heitler and London had performed an approximate calculation for the hydrogen molecule in 1929 that produced a bond energy that was only about 70% of the experimental value. However, he pointed out that “physicists were highly confident and most moved on to study the internal structure of the nucleus during the 1930s.” He went on to say, “In fact, their boldness was apparently justified, for no significant failure of the full Schrödinger-Dirac treatment has ever been demonstrated.”

Although physicists enjoyed success in their quantum mechanical descriptions of atoms, quantum chemists of the 1930s concluded that exact quantum mechanical solutions for molecules was hopeless. Thus they attempted to develop approximate methods to assist in qualitatively describing chemical phenomena and to provide some predictive capability. Pople pointed out that developing a theoretical model for a complex process using “an approximate but well-defined mathematical procedure of simulation” must involve five stages (3):

1. Selection of a target accuracy for the model.
2. Precise formulation of the approximate mathematical procedure, which should be both general and continuous.
3. Implementation of the mathematical formulas (i.e., computer programs) to permit application of those procedures in reasonable time and at reasonable cost.
4. Verification of the model against known chemical facts to determine whether the target accuracy has been achieved.
5. Application of the model to chemical problems for which the answer is unknown or in dispute.

Pople observed that this last, predictive, stage “is the one of most interest to the larger chemical community” (3).

Pople pointed out that “the foundations of the orbital theory of many-electron systems were laid [in the 1930s] by Hartree, Fock, and Slater” and that following World War II, Lennard-Jones and his group (which included Pople) “re-examined the Hartree-Fock equations with a view to transforming the [molecular] orbitals into localized or equivalent orbitals representing bonding and lone pairs” (3). He went on to say “However, the coupled three-dimensional differential equations appeared intractable and little progress was made towards their solution.” Pople noted that “A major advance occurred in 1951 with the publication...of the Roothaan equations” (5), which led to the development of the earliest versions of molecular orbital theory, known as linear combination of atomic orbital, self-consistent field (LCAO-SCF) theory. In 1954, Pople published a refinement,

known as Unrestricted Hartree-Fock (UHF), in which electrons of α -spin and β -spin are assigned to different molecular orbitals, with a Restricted Open Hartree-Fock (ROHF) option of double and single occupation (6).

Pople said: “During the 1950s integral evaluation was regarded as the main barrier to progress” (3). The use of Slater-type atomic orbitals as basis functions for LCAO-SCF theory allowed for analytical solutions for one- and two-electron integrals in the two-center case. “However,” he went on to say, “great difficulties were encountered for three- and four-center cases. It was common to describe this impasse as ‘the nightmare of integrals.’” The semiempirical approach to this dilemma was based on the zero-differential overlap approximation, which neglects products of different atomic orbitals in most integrals. Application of this approximation to conjugated organic π systems became known as Pariser-Parr-Pople theory (7). A decade later Pople and coworkers generalized this approach to treat all valence electrons, formulating the CNDO and INDO theories (8).

The alternative, *ab initio*, approach did not utilize approximation or empirical parameterization and was, thus, limited to very small molecules. Pople said, “Within the *ab initio* community, a truly major development was the introduction of gaussian-type basis functions” (3). In that approach the integrals of SCF theory could be evaluated analytically by factoring the radial parts into a form $P(x,y,z)\exp(-r^2)$. Although single gaussian functions were poor approximations of atomic orbitals, Pople said, “It was clear that prospects would improve if large numbers of basis functions could be handled.” With the introduction of computers into quantum chemistry in the 1950s, several research groups began developing *ab initio* programs using Slater and gaussian bases. Pople’s research group began *ab initio* work in 1968, quickly generating a new highly efficient integral algorithm that was capable of reproducing the results of earlier full Slater calculations for a series of small molecules (9). The computer code for their Hartree-Fock model, known as HF/STO-3G, was made available to the scientific community as GAUSSIAN70. The GAUSSIAN programs were later commercialized; Pople remained continuously involved in their development up to and including the version known as GAUSSIAN 92 (personal communication with Pople).

Pople admitted “Investigation of the minimal HF/STO-3G model quickly showed major failures” (3). For example, it failed to simulate distinctions between the σ and π bonds in acetylene. Additional refinements were required to provide accurate models for the pyramidal structure of NH_3 and the polarity of HCl, leading to the expansion of the basis set to include *d*-orbital functions to produce a Hartree-Fock model known as HF/6-31G*. That model was successful at differentiating between organic isomers and in modeling rotational potentials around C–O single bonds (10).

However, Pople pointed out: “The major fault implicit in all Hartree-Fock models is neglect of electron correlation between the motions of electrons of anti-parallel spin ($\alpha\beta$ correlation)” (3). To address this issue, the method was refined to include configuration interaction. Perturbation theory was

included in the 1970s based on a method introduced in the 1930s by Møller and Plesset, formulating models known as MP2, MP3 and MP4, where the numeral indicates the order of a polynomial equation for the energy of the system (11). However the applicability of this method was limited by the fact that computer time for the MP4 method, for example, scaled as the seventh power of the number of particles. During the next two decades further refinements were introduced. Near the end of his Nobel lecture discussion of the recent models, Pople asserts: “In recent years progress has been made in developing models which reproduce chemical energies to an accuracy approaching that achieved in good experimental work... The target of 1 kcal/mole is not far away for small molecules containing up to about fifty electrons” (3). In general, selection of a computational method involves some compromises between the selection of a basis set and the level of correlation.

Kohn’s Development of Density Functional Theory

The density functional theory (DFT) developed by Kohn provides an alternative to the *ab initio* approach discussed by Pople. In contrast to Pople, who has devoted much of his scientific career to theoretical descriptions of molecular structure and bonding, Walter Kohn had a wide ranging career as a physicist studying solid state applications to alloys, semiconductors, superconductivity, surface physics, and catalysis. Kohn originally developed DFT theory to describe the electronic structure of alloys; only later did chemists apply it to molecular systems.

The DFT approach does not attempt to tackle the complicated wave function in the Schrödinger equation for a large molecule, and it does not handle two-electron interactions explicitly. Instead, “Kohn showed in 1964 that the total energy for a system described by the laws of quantum mechanics can be theoretically calculated if the electrons’ spatial distribution (electron density) is known” (4). Kohn reported in his Nobel autobiography that DFT had its genesis in the fall of 1963 when he was on sabbatical in Paris at the Ecole Normale Supérieure (4). He said: “I read some of the metallurgical literature, in which the concept of the effective charge e^* of an atom in an alloy was prominent, which characterized in a rough way the transfer of charge between atomic cells. It was a local point of view in coordinate space, in contrast to the emphasis on delocalized waves in momentum space, such as Bloch-waves in an average periodic crystal, used for the rough description of substitutional alloys. At this point the question occurred to me whether, in general, an alloy is completely or only partially characterized by its electronic density distribution $n(r)$: In the back of my mind I knew that this was the case in the Thomas-Fermi approximation of interacting electron systems; also, from the ‘rigid band model’ of substitutional alloys of neighboring elements, I knew that there was a 1-to-1 correspondence between a weak perturbing potential $\delta v(r)$ and the corresponding small change $\delta n(r)$ of the density distribution. Finally it occurred to me that for a single particle there is an explicit elementary relation between the potential $v(r)$ and the density, $n(r)$, of

the ground state. Taken together, these provided strong support for the conjecture that the density $n(r)$ completely determines the external potential $v(r)$. This would imply that $n(r)$ which integrates to N , the total number of electrons, also determines the total Hamilton \mathcal{H} and hence *all* properties derivable from \mathcal{H} and N , e.g. the wavefunction of the 17th excited state, $\Psi^{17}(r_1, \dots, r_N)$! Could this be true? And how could it be decided? Could two different potentials, $v_1(r)$ and $v_2(r)$, with associated different ground states $\Psi_1(r_1, \dots, r_N)$ and $\Psi_2(r_1, \dots, r_N)$ give rise to the same density distribution? It turned out that a simple 3-line argument, using my beloved Rayleigh–Ritz variational principle, confirmed the conjecture. It seemed such a remarkable result that I did not trust myself.”

Kohn and Pierre Hohenberg, another American visitor in Paris, searched the literature to see if that simple result was already known. Finding that it was not, Kohn said: “In short order we had recast the Rayleigh–Ritz variational theorem for the ground state energy in terms of the density $n(r)$ instead of the many electron wave function Ψ , leading to what is now called the Hohenberg Kohn (HK) variational principle. We fleshed out this work with various approximations and published (12) it” (4). Upon his return to the U.S. at the conclusion of his sabbatical, Kohn and his postdoctoral student, Lu J. Sham, “derived from the HK variational principle what are now known as the Kohn-Sham (KS) equations, which have found extensive use by physicists and chemists, including members of my group (13). Since the 1970s I have also been working on the theory of surfaces, mostly electronic structure. The work with Lang in the early 1970s, using DFT, picked up and carried forward where J. Bardeen’s¹ thesis had left off in the 1930s” (14).

Kohn concluded his report on the development of DFT saying: “I have continued to work with postdoctoral fellows and students on DFT and other problems that I had put aside in previous years. Since the middle 1980s, I have also had increasing, fruitful interactions with theoretical chemists. I mention especially Robert Parr, the first major theoretical chemist to believe in the potential promise of DFT for chemistry who, together with his young co-workers, has made major contributions, both conceptual and computational” (4). When the 1998 Nobel Prize to was announced, Parr said of Kohn’s DFT: “There was obvious beauty in what he had done, and obvious applicability to chemistry” (15). Pople incorporated DFT into his methodologies in the 1990s.

Background of the Laureates

Both Kohn and Pople were born into middle-class European families during the period between the two World Wars, and both were affected by the events of World War II—Kohn most profoundly. Neither began his career as a chemist—Pople was originally a mathematician, and Kohn was (and still is) a physicist. Both spent time in Canada before settling in the U.S.; and their early careers almost intersected, at the Carnegie Institute of Technology (now Carnegie Mellon University) in Pittsburgh, where Pople arrived in 1961 just after Kohn had departed for a position

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at the University of California, San Diego after having spent eight years at Carnegie Tech.

Walter Kohn

Walter Kohn was born into a Jewish family in Vienna. His parents were part of the Viennese intellectual community and his father ran the family business selling art postcards. Kohn studied in a fine public high school in Vienna, the *Academische Gymnasium*, where his favorite subject was Latin. He reported that he “had no interest in, nor apparent talent for, mathematics which was routinely taught and gave me my only C in high school” (4). When Nazi Germany annexed Austria in 1938, everything changed for Kohn. The family business was confiscated, his sister fled to England, and he was expelled from his high school. The next year Kohn entered a Jewish school, the *Chajes Gymnasium*, where he had inspirational teachers in physics and mathematics. (Both those teachers and Kohn’s parents ultimately died as Holocaust victims.) After Kohn joined his sister as a refugee in England, he reported: “I had my mind set on becoming a farmer (I had seen too many unemployed intellectuals during the 1930s), and I started out on a training farm in Kent” (4). However, a bout with meningitis forced him to abandon his training, and he was enrolled in East Grinstead County School in Sussex where, he said, “after a period of uncertainty I decided to concentrate on mathematics, physics and chemistry.”

In 1940, as the German army swept through Europe and Britain anticipated an invasion, Kohn was interned along with other holders of “enemy alien passports”. He spent two months in various British camps, where his school sent him the books he needed and where, he said he, “also audited, with little comprehension, some lectures on mathematics and physics, offered by mature interned scientists” (4). In July 1940 he was shipped to a camp in Canada for German civilian internees and refugees. Kohn worked as a lumberjack in various Canadian camps while also continuing to receive inspiration in mathematics from interned teachers. He passed the entrance exams for McGill University and he said he was “looking forward to a career in physics, with a strong secondary interest in mathematics.” In January Kohn was “cleared by Scotland Yard of being a potential spy” so he was released from internment and taken in by the family of Professor Bruno Mendel in Toronto.

Kohn enrolled in the undergraduate program in mathematics and physics at the University of Toronto. His German nationality barred him from entry into the chemistry building at Toronto, where war research was being conducted at the time, so he was unable to take the required chemistry courses for his program. The dean arranged for Kohn and several other students to enter mathematics and physics as special students. In 1944, after his junior year, Kohn joined the Canadian Infantry Corps. While in the army he used his spare time to develop a theory on the precession of heavy symmetrical tops, resulting in one of his first scholarly publications (16). After one year in the service he received a wartime bachelor’s degree “on-active-service” although he had completed only two and one-half years of

the four-year program. Following his discharge he took a crash master’s program, including some of the senior courses he had missed, with a thesis consisting of his paper on tops and a paper on scaling of atomic orbitals. He received an M.A. in applied mathematics from the University of Toronto in 1946.

Kohn received a Lehman Fellowship to support his Ph.D. studies in physics at Harvard University. He said that having arrived at Harvard from the relative isolation of Toronto “I felt very insecure and set as my goal survival for at least one year” (4). He went on to say, “The department chair, J. H. van Vleck,² was very kind and referred to me as the Toronto-Kohn to distinguish me from another person who, I gathered, had caused some trouble.” Van Vleck tried to interest Kohn in working on the band-theory of solids, later known as the quantum defect method, but Kohn decided he did not want to do his Ph.D. thesis in solid state physics. Nevertheless, he continued: “In spite of my original disconnect with van Vleck, solid state physics soon became the center of my professional life and van Vleck and I became lifelong friends.”

Kohn became a Ph.D. student of Julian Schwinger,³ recalling that Schwinger “suggested that I try to develop a Green’s function variational method for *three*-body scattering problems,... while warning me ominously that he himself had tried and failed” (4). Kohn developed an alternative approach, later known as Kohn’s variational principle for scattering, which became his Ph.D. thesis. After completing his Ph.D in 1948, Kohn stayed on at Harvard for three years with “the choice of being a regular post-doctoral fellow or dividing my time equally between research and teaching. Wisely—as it turned out—I chose the latter.” Kohn and another post-doc, Sidney Borowitz, were “to assist Schwinger in his work on quantum electrodynamics and the emerging field theory of strong interactions between nucleons and mesons. In view of Schwinger’s deep physical insights and celebrated mathematical power, I soon felt almost completely useless. Borowitz and I did make some very minor contributions, while the greats, especially Schwinger and Feynman,³ seemed to be on their way to unplumbed, perhaps ultimate depths.”

Kohn spent the summer of 1949 working at Polaroid Laboratory in Cambridge, MA, just as the Polaroid camera was being developed. He was supposed to “bring some understanding to the mechanism by which charged particles falling on a photographic plate lead to a photographic image” and because he “needed to learn something about solid state physics”, he consulted van Vleck when he encountered things he didn’t understand (4). He went on to say: “It seems these meetings gave [van Vleck] the impression that I knew something about the subject” and that van Vleck, who was about to take a leave of absence, asked Kohn to teach a course in solid state physics “since you are familiar with [that subject].” Kohn, who was frustrated with his work on quantum field theory, and who saw that jobs were scarce, agreed, saying “I thought broadening my competence into a new, more practical, area might give me more opportunities.” He admitted, “Some of my students often understood much

more than I, they were charitable toward their teacher.”

When Kohn began seeking a permanent position he wished to return to Canada, where he was then a naturalized citizen. He said he “explored every Canadian university known to me. No opportunities presented themselves. Neither did the meager U.S. market for young theorists yield an academic offer” (4). An offer of a position at a new Westinghouse nuclear reactor laboratory near Pittsburgh was withdrawn because Kohn was not a U.S. citizen. However, during his visit to Pittsburgh, Kohn stayed with a Canadian friend who thought there might be an opening for a physicist at the Carnegie Institute of Technology: “It turned out that the department chair, Ed Creutz, was looking rather desperately for someone who could teach a course in solid state physics.... Within 48 hours I had a telegram offering me a job!”

After teaching a “compressed course in solid state physics” at Carnegie, Kohn took a leave to travel to Copenhagen on a U.S. National Research Council fellowship. Kohn said that he “had planned to revert to nuclear physics [in Copenhagen], in particular the structure of the deuteron. But in the meantime I had become a solid state physicist. Unfortunately no one in Copenhagen, including Niels Bohr, had even heard the expression ‘Solid State Physics’” (4). Nevertheless, when Kohn received an Ørsted fellowship that would allow him to remain at the Bohr Institute for a second year “a letter from Niels Bohr to my department chair at Carnegie quickly resulted in the extension of my leave of absence till the fall of 1952.” While in Europe, Kohn taught a summer school course at Les Houches, France, where, he said, “As an ‘expert’ in solid state physics, I offered a few lectures on that subject. Wolfgang Pauli,⁴ who visited, when he learned of my meager knowledge of solids, mostly metallic sodium, asked me, true to form, if I was a professor of physics or of sodium.”

Kohn returned to Carnegie Tech in 1952. With support from van Vleck he obtained a summer position with J. M. Luttinger at Bell Labs as an assistant of William Shockley.¹ He spent many summers working there on problems in solid state physics related to the transistor, saying that this work “gave me a perspective over this fascinating, rich field” and that there he would “grow up from amateur to professional” (4). In 1966 his work at Bell Labs “showed that superconductivity occurs even with purely repulsive interactions—contrary to conventional wisdom and possibly relevant to the much later discovery of high- T_c superconductors.”

Kohn moved to the University of California, San Diego in 1960, where he began working in earnest on DFT a few years later. In 1979 he accepted an appointment as the initial director of the NSF Institute of Theoretical Physics at the University of California, Santa Barbara, and he has remained in Santa Barbara to this day.

John Pople

John Pople was born and raised in Burnham-on-Sea, a small resort town on the west coast of England. His father owned a men’s clothing store, which had been the family

business for generations; his mother came from a farming family. Pople and his younger brother spent much of their time on farms as youths. However, Pople said that he suspected his mother wished she could have been a teacher and that “Both of my parents were ambitious for their children; from an early age I was told that I was expected to do more than continue to run a small business in this small town. Education was important and seen as a way of moving forward” (4). Due to the English class system Pople was not allowed to attend the excellent local preparatory school and, at the age of ten, he had to commute two miles by bicycle, 25 miles by train, and one mile on foot to a school in Bristol, the nearest big city.

Pople’s interest in mathematics developed early: “At the age of twelve, I developed an intense interest in mathematics. On exposure to algebra, I was fascinated by simultaneous equations and rapidly read ahead of the class to the end of the book. I found a discarded textbook on calculus in a wastebasket and read it from cover to cover” (4). He described a youthful research project “formulating the theory of permutations in response to a challenge about the number of possible batting orders of the eleven players in a cricket team. For a very short time, I thought this to be original work but was mortified to find $n!$ described in a textbook. I then attempted to extend $n!$ to fractional numbers by various interpolation schemes. Despite a lot of effort, this project was ultimately unsuccessful; I was angry with myself when I learned of Euler’s solution some years later. However, these early experiences were valuable in formulating an attitude of persistence in research.”

Pople continued working on mathematical problems, but, “All this mathematical activity was kept secret. My parents did not comprehend what I was doing and, in class, I often introduced deliberate errors in my exercises to avoid giving an impression of being too clever. My grades outside of mathematics and science were undistinguished so I usually ended up several places down in the monthly class order. This all changed suddenly three years later when the new senior mathematics teacher, R. C. Lyness, decided to challenge the class with an unusually difficult test. I succumbed to temptation and turned in a perfect paper, with multiple solutions to many of the problems. Shortly afterwards, my parents and I were summoned to a special conference with the headmaster at which it was decided that I should be prepared for a scholarship in mathematics at Cambridge University.... Most such awards were in the classics and I think that the mathematics and science staff were very anxious to compete. Ironically, during the last two years [in Bristol], I abandoned chemistry to concentrate on mathematics and physics” (4).

Pople entered Trinity College, Cambridge, in October 1943, at the height of World War II. He said he was one of “a small group of students in mathematics, science and medicine [who were not inducted in the military but who were, instead,] permitted to attend university before taking part in wartime research projects such as radar, nuclear explosives, code-breaking and the like” (4). When the war ended in 1945, Pople was forced to leave Cambridge to make room

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for returning servicemen. He took a job at the Bristol Aeroplane Company and, he said, he “had little idea of what my future career might be. My interest in pure mathematics began to wane; after toying with several ideas, I finally resolved to use my mathematical skills in some branch of science.”

Pople finally returned to Cambridge in 1947, when he began “taking courses in as many branches of theoretical science as I could manage [including] quantum mechanics (taught in part by Dirac)⁵, fluid dynamics, cosmology and statistical mechanics. Most of the class opted for research in fundamental areas of physics such as quantum electrodynamics which was an active field at the time. I felt that challenging the likes of Einstein⁶ and Dirac was overambitious and decided to seek a less crowded (and possibly easier) branch of science. I developed an interest in the theory of liquids, particularly as the statistical mechanics of this phase had received relatively little attention, compared with solids and gases.” Pople approached Sir John Lennard-Jones who, Pople said he, “had published important papers on a theory of liquids in 1937. He held the chair of theoretical chemistry at Cambridge and was lecturing on molecular orbital theory at the time. When I approached him, he told me that his interests were currently in electronic structure but he would very possibly return to liquid theory at some time” (4). Pople began working with Lennard-Jones, saying: “I began my career in theoretical chemistry at the beginning of July [1948]. I had almost no chemical background, having last taken a chemistry course at Bristol Grammar School at the age of fifteen.”

After receiving his Ph.D. in mathematics in 1951, Pople remained at Cambridge as a research fellow and mathematics lecturer until 1958. During that time, he interacted with a diverse array of former and future Nobel Laureates, and he also began his long-term collaboration with Robert Parr. In 1955 Pople developed an interest in NMR, which was then emerging as a powerful technique for studying molecular structures. He spent the summers of 1956 and 1957 working on the theoretical background of NMR at the National Research Council⁷ in Ottawa, Canada. That work led to a book on high resolution NMR (17).

Pople left Cambridge in 1958 because, “I had become dissatisfied with my mathematics teaching position at Cambridge. I had clearly changed from being a mathematician to a practicing scientist. Indeed I was increasingly embarrassed that I could no longer follow some of the more modern branches of mathematics, in which my undergraduate students were being examined. I therefore resolved to seek a job with greater scientific content” (4). He took a position as head of the new Basic Physics Division at the National Physics Laboratory near London, which involved administration and directing experimental work. However, he found administrative duties a considerable impediment to his scientific work, describing his time there as, “a rather fallow period.”

In the spring of 1961 Robert Parr, while attending an international conference in Oxford that Pople helped organize, urged him to go to the Carnegie Institute for a year; however, shortly after Pople arrived in Pittsburgh, Parr de-

parted for Johns Hopkins University. But his year in the U.S. convinced Pople to abandon his administrative post and to “seek an opportunity to devote as much time as possible to chemical research” (4). He realized that he “was approaching the age of forty, with a substantial publication record, but had not held any position in a chemistry department.” Finding opportunities in the U.K. and in the U.S., he decided to return to Pittsburgh in 1964 because, “the research environment for theoretical chemistry was clearly better in the U.S.”

Upon his return to Pittsburgh, Pople reported: “I resolved to get back to the fundamental problems of electronic structure that I had contemplated abstractly many years earlier. Prospects of really implementing model chemistries had improved because of the emerging development of high-speed computers. I was late in recognizing the role of computers... However, by 1964, it was clear that the development of an efficient computer code was one of the major tasks for a practical theoretician and I learned the trade with enthusiasm” (4). Pople’s research group had access to a computer in the nearby Mellon Institute. In 1967 Carnegie Tech and the Mellon Institute merged to form Carnegie Mellon University (CMU) and Pople remained on the faculty there until 1993, performing the research leading to the Nobel Prize. In 1981 Pople and his wife moved to the Chicago area to be near their adult daughter. However Pople continued to maintain his research group at CMU, “commuting frequently and communicating with [his] students by telephone and modem.” He obtained an adjunct appointment at Northwestern University in Evanston, IL, and he became a member of the faculty there in 1993.

An earlier essay noted that two of the 1986 Nobel Laureates recognized the importance of computational chemistry to the study of chemical dynamics (1i). Early in his Nobel lecture Dudley Herschbach said: “Ab initio electronic structure calculations have also begun to contribute significantly to the exploration of reaction dynamics, although (except for $H + H_2$) satisfying overall accuracy has yet to be achieved for potential energy surfaces” (18). Yuan Lee concluded his Nobel lecture with the observation that “because of recent improvements in the accuracy of theoretical predictions based on large-scale ab initio quantum-mechanical calculations, meaningful comparisons between theoretical and experimental findings have become possible” (19). The work of Walter Kohn and John Pople has provided the accuracy that Herschbach sought and, thus, the meaningful comparisons between theory and experiment that Lee described.

Notes

1. John Bardeen, William Shockley, and Walter Brattain shared the 1956 Nobel Prize in physics for their research on semiconductors and the invention of the transistor. Bardeen shared a second physics Nobel Prize with Leon Cooper and J. Robert Schrieffer in 1972 for developing the theory of superconductivity—known as BCS theory.

2. John H. van Vleck shared the 1977 physics Nobel Prize with Philip Anderson and Nevill Mott for their contributions to fundamental theoretical investigations of the electronic structure

of magnetic and disordered systems. Van Vleck's name is familiar to chemists for crystal field theory, which he developed as part of those investigations, and which later evolved into ligand field theory for transition metal coordination complexes.

3. Julian Schwinger, Richard Feynman, and S.-I. Tomonaga shared the 1965 physics Nobel Prize for their fundamental work in quantum electrodynamics.

4. Wolfgang Pauli received the 1945 physics Nobel Prize for developing the Pauli Exclusion Principle, which is familiar to all students of atomic electronic structure.

5. Paul Dirac shared the 1933 physics Nobel Prize with Erwin Schrödinger for developing the wave mechanical description of atomic structure.

6. Albert Einstein received the 1921 physics Nobel Prize for his description of the photoelectric effect.

7. Readers may recall that the Nobel Laureates with Canadian backgrounds were discussed previously—Henry Taube (1b), John Polanyi (1i), and Rudy Marcus (1j)—all also had worked at NRC, which was headed by yet-another future Nobel Laureate, Gerhard Herzberg.

Further Reading

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J. Van Houten is a member of the Department of Chemistry, Saint Michael's College, Colchester, VT 05439; jvanhouten@smcvt.edu.