NATIONAL ACADEMY OF SCIENCES

JOSEPH OAKLAND HIRSCHFELDER

1911—1990

A Biographical Memoir by

R. BYRON BIRD, CHARLES F. CURTISS, AND
PHILLIP R. CERTAIN

Biographical Memoir

Joseph O. Hirschfelder

JOSEPH OAKLAND HIRSCHFELDER

May 27, 1911–March 30, 1990

BY R. BYRON BIRD, CHARLES F. CURTISS, AND
PHILLIP R. CERTAIN

JOSEPH OAKLAND HIRSCHFELDER WAS one of the leading figures in theoretical chemistry during the period 1935-90. His sustained research program not only spanned five and one-half decades but a wide number of scientific areas as well: chemical kinetics, chemical applications of quantum mechanics, combustion, nuclear explosions, kinetic theory of gases, intermolecular forces, structure of liquids, and laser chemistry. He was elected to the National Academy of Sciences at the relatively early age of forty-two and he was chosen to be a fellow of the American Academy of Arts and Sciences at age forty-eight. At age sixty-five he received the National Medal of Science from President Gerald Ford "for his fundamental contributions to atomic and molecular quantum mechanics, the theory of the rates of chemical reactions, and the structure and properties of gases and liquids." Despite his exalted standing in the field of chemical physics, he was a very approachable and gregarious individual. He always insisted on being called "Joe," and he was always thus addressed by colleagues, students, secretaries, and janitors. It would seem unnatural for us to refer to him in any other way, even in this rather formal summary of his illustrious career.

The account below was prepared by three of his former graduate students and colleagues, based to a large extent on personal recollections. Additional information can be obtained from published sources[1-5] as well as from articles that contain a certain amount of autobiographical material.[6-10]

Joe was born in Baltimore, Maryland, on May 27, 1911, the son of Arthur Douglas and May Rosalie (Straus) Hirschfelder. Of his family and early childhood, Joe has written:[7]

> My paternal great grandparents emigrated from Germany to California in 1843. . . . Both my grandfather and father devoted their lives to medical research. Grandpa was the first child born in Oakland; he graduated in the first class at the University of California and became the first Professor of Clinical Medicine at Stanford. Dad entered the University of California at the age of 13. After receiving his MD, he joined the medical faculty of Johns Hopkins University, where he was the first doctor in the United States to use an electrocardiogram. . . . Later he became very much interested in the colloid chemistry associated with the physiological effects of drugs and accepted a Professorship in Pharmacology at the University of Minnesota.
>
> Thus, I was born in Baltimore and grew up in Minneapolis. When I was five years old, Dad built a chemistry lab for me in the basement of our home. When I was ten, he took me to an American Chemical Society Meeting in Los Angeles. And when I was 15, I helped Dad determine the distribution of colloidal particles in a Zsigmundy ultramicroscope—my contribution was to suggest a correction factor for the convection currents produced by passing street cars.

Joe was an undergraduate at the University of Minnesota from 1927 to 1929 and at Yale from 1929 to 1931. During this period he found he was not particularly suited to experimental sciences and decided to do theoretical work. He was attracted to Princeton since it was possible to take a double Ph.D. in theoretical physics and chemistry. His chief physics mentor was Eugene P. Wigner, and his chemistry supervisors were Henry Eyring[6] and Hugh S. Taylor.[7] After receiving his Ph.D. in 1936, he spent an additional year as a postdoctoral fellow with John von Neumann at the Institute for Advanced Study, during which time he also continued his work with Eyring and Taylor. Joe found Princeton a most exciting place, and he was a dedicated and diligent student; he worked on a variety of research problems including the polarizability of the hydrogen molecule and hydrogen-molecule ion (suggested to him by E. U. Condon); the separation of rotational coordinates from the N-particle Schrödinger equation (with Wigner); the energy of the H_3 molecule and the H_3 molecule ion (with Eyring and Rosen); the a priori calculation of the reaction rate between atomic and molecular hydrogen (with Eyring); a free-volume theory of liquids (with Eyring); and some applications of the virial theorem to the scaling of wave functions. Of the latter work Joe had this to say:[8]

> My discovery of the hypervirial theorem is curious: In 1932 when I was a graduate student, I doodled with derivatives of the Schrödinger equation and obtained a variety of seemingly useless relations which I carefully saved in my files. Then 28 years later, when I had to give a paper at a symposium in honor of Jack Kirkwood, I studied these doodles and found that I had discovered a generalization of the virial theorem!

In 1937 he went to the University of Wisconsin as a Wisconsin Alumni Research Foundation research associate; in 1940 he became an instructor in chemistry and physics, and in 1941 he was named an assistant professor in the Chemistry Department. During the five-year period between his arrival in Madison and his departure for activities related to the war, he continued his research on the applications of quantum mechanics to intermolecular forces and chemical kinetics, and he started a program devoted to intermolecular forces and properties of gases. It was during this period that he published his first paper with C. F. (Chuck)

Curtiss; Chuck did his senior thesis with Joe, and this was the beginning of many years of fruitful collaboration.

In 1942 Joe's academic career was interrupted by military research. For about two years he was with the National Defense Research Committee (NDRC) in Washington, D.C., where he worked as head of the Interior Ballistics Group on a wide variety of problems, such as the thermodynamics of propellent gases and the fluid dynamics and combustion in the barrels of guns, mortars, and rockets. In 1944-45 he was a group leader at the Los Alamos scientific laboratory. In 1945-46 he was head of theoretical physics at the Naval Ordinance Test Station at Inyokern, California, and in 1946 he served as the chief phenomenologist at the Bikini atomic bomb tests. These wartime experiences exposed Joe to a myriad of practical problems, which forced him to become a theoretician with a strong interest in experimental facts and phenomena. Thereby he was able to impart to his graduate students a genuine concern for being able to interpret theoretical results in a form useful to experimentalists and engineers.

During the atomic bomb project Joe worked with Hans Bethe and John Magee on the dynamics of nuclear explosions, including the formation of the fireball and the shock wave. He also studied range-energy relations for the penetration of high-energy protons, multiple Klein-Nishina scattering, and the prediction of fallout from nuclear blasts. During the next few years he chaired a five-member board of editors in preparing the 456-page book *The Effects of Atomic Weapons* (1950).

In 1946 he returned to Madison to become a full professor in the Department of Chemistry, a post he was to fill until his retirement. He started out by establishing the University of Wisconsin Naval Research Laboratory; he served as the director until 1959, when it was reorganized as the

University of Wisconsin Theoretical Chemistry Institute. He arranged to have a separate one-story, cinder-block building constructed on the UW campus several blocks west of the chemistry building. By 1950 he had between eight and ten students doing theoretical work, a somewhat smaller number doing experimental work, and five or six "computresses" (a group of young women with mathematics degrees, whom he had trained to be extremely responsible and accurate in making numerical computations using electromechanical desk calculators, tables of tabulated functions, graph paper, and French curves). No other professor in the Department of Chemistry had such a large entourage. Joe was among the first of the "entrepreneurial professors" on the campus; of course, financing such a large group and maintaining the building and equipment demanded of Joe enormous amounts of time and energy. In those days Joe's energies seemed unbounded as he supervised (very closely) his graduate students, organized meetings, attended committee meetings in Washington, presented papers at scholarly societies, and consulted for private industry and government agencies. Despite this whirlwind of activities he still had time to organize picnics, play tennis, and be very friendly and hospitable to students and colleagues. He seemed to be living life at about one and one-half times the speed of normal mortals.

Joe was one of the first theoretical chemists to engage in large-scale numerical computations. We have mentioned his computresses above, who enabled him and his graduate students to attack numerically a number of otherwise intractable problems. Joe was extremely insistent on accuracy in computing, and when he and his students published any kind of tabular results, he wanted to be 100 percent sure that tables of computed values could be trusted. He set very high standards in the field of chemical computations;

he often said that if you turn out one table of numbers that cannot be trusted, no one will trust any of your subsequent work and it will all be regarded as useless. He insisted that all students devise clever ways to check numerical results.

Joe had a very ambitious agenda for his laboratory, including both theoretical studies (equation of state for gases and liquids, transport property calculations, flames, shockwave phenomena, intermolecular forces) and experimental projects (flame velocities, critical phenomena, phase equilibria, interferometry). One of the main activities in the group was the development of theories of flames and combustion, an extremely difficult task involving the solution of the equations of change along with information on transport properties and chemical reaction rates. According to Professor Roger A. Strehlow of the University of Illinois, one publication from that period, "The Theory of Flame Propagation" (1949), had an enormous impact on subsequent flame structure studies. The work on flames also resulted in a key paper on the integration of stiff equations (1952), one of the earliest publications dealing with what is now called singular perturbation theory.

The UW Naval Research Laboratory was an exciting place to be a graduate student because of the tremendous stimulation provided by a very active professor, many other excellent students to interact with, and a constant stream of visitors; it was a wonderful experience to have the chance to meet such illustrious figures as Jack Linnett (from Oxford), Jan de Boer (from Amsterdam), Mel Green (from Princeton), Henry Eyring (from Utah), Ilya Prigogine (from Brussels), Jack Kirkwood (from Cal Tech), Al Matsen (from Texas), and many, many others. Joe's students were most fortunate to mature in such an inspiring environment. They were lucky to have a research adviser who knew personally all the key figures in his areas of interest. Joe's lectures on quantum mechanics and statistical mechanics were peppered with personal references to the people who had made the major contributions to these subjects. Students got a kick out of comments like: "Hans Bethe was telling me just the other day that . . ." or "Joe Mayer showed me a nifty way to derive this . . ." or "Johnny von Neumann suggested that . . ."

Joe was not regarded as a polished classroom lecturer and he did not always prepare his lectures carefully; however, what he lacked in preparation and organization was more than made up for by his buoyant and boyish enthusiasm and his clear perspective of the direction of movement of the field as a whole.

By 1950 he had decided that it was time to summarize some of the work done in his laboratory and combine this information with that from other research centers. In the summer of 1950 he invited several of his former students to collaborate with him in this adventure. The first draft of the book was done in 1950-51, and the second draft was prepared in 1951-52. The reviewing, editing, and proofreading took about a year and a half; Joe had the habit of making extensive changes in the page-proof stage of books and articles, with the result that the proofreading took longer than normal. In the spring of 1954 the treatise "The Molecular Theory of Gases and Liquids" was published. MTGL, as the book was soon nicknamed, appeared in a second corrected printing in 1964, and a Russian translation was published in 1961. In 1974 a list was published in *Current Contents* of the most cited books in physics and chemistry, and MTGL ranked fourth on the list. Forty-one years after its publication the book is still in print.

The MTGL book made it evident that further progress could not be made in the calculation of physical properties until more is known about intermolecular forces. Consequently, Joe began to concentrate his research efforts in that area. He became interested in the possibilities of making a priori calculations of the forces between molecules. He was a pioneer in this field before the technological development of computing facilities, which has now so greatly expanded the field. He investigated the use of hypervirial theorems, developed ideas on the use of the perturbation and variational theories to obtain upper and lower bounds, and perturbation theory as applied to almost degenerate states.

In the early 1960s, as the National Aeronautics and Space Administration took up President Kennedy's challenge to put a man on the moon, Joe was invited to submit a proposal to convert the UW Naval Research Laboratory into the Theoretical Chemistry Institute (TCI) to investigate the intermolecular forces and chemical dynamics. This allowed for tremendous expansion of both staff and facilities. It also allowed the creation of an experimental program in molecular beam reactive scattering, led by Richard B. Bernstein, closely allied to theoretical research. This was characteristic of Joe's approach to science: an interdisciplinary emphasis with theory tied closely to experiment. It was also during this period that he collaborated with P. O. Löwdin in the development of the concept of natural spin orbitals.

From 1963 to about 1970 TCI grew rapidly, with a large number of graduate students, postdoctoral fellows, and visiting scientists coming to Madison. In many ways the sheer magnitude of the effort firmly established theoretical chemistry as an essential component in all major chemistry departments.

After the Apollo program, funding shifted from NASA to the National Science Foundation. Gradually the support shifted from a block grant for TCI to grants for individual investigators. During the 1970s Joe began a longtime association with the University of California, Santa Barbara, where he interacted with chemists, physicists, and engineers. His research interests turned to the interaction of light with matter, and the nonlinear effects associated with intense lasers. On the occasion of his retirement in 1981, Joe wrote:[8]

> Intermolecular forces have been my principal interest for the last 44 years. Thus, after the publication of MTGL, I studied all kinds of intermolecular forces and their relativistic corrections and Born-Oppenheimer derivations. In order to calculate the interaction energies, I worked on variational and perturbation techniques applied to nondegenerate, degenerate, and almost-degenerate problems. However, I found that perturbation theory applied to practical electron exchange problems is a mathematical whirlpool so that I started to go around in circles and got sucked in, even deeper. Thus, I decided to make a big change in my research and study the dynamics of molecules with moving nuclei either in the presence or in the absence of external electromagnetic fields.

Joe said that after his retirement he wanted to continue doing research until he "lost his marbles."[10] From 1981 on, he kept interacting with colleagues and pursuing scholarly activities, splitting his time between Madison in the summer and Santa Barbara in the winter.

A good example of the vitality of Joe's intellect was his response to receiving radiation treatments for a tumor on his spine. Intrigued by how the radiation could destroy the tumor without damaging his spinal cord, he asked the medical physicists about the equations used to focus the radiation. The equations reminded him of those used in weather satellite tracking, and consequently Joe put the medical physicists in touch with a former postdoctoral associate, Robert Pyzalski, then working in meteorology. Pyzalski was able to be very helpful to the medical physicists, and indeed, meteorology lost him to medical physics, where his research could be devoted to helping mankind.

Joe's contributions were recognized by a number of important awards. He was elected to the National Academy of Sciences in 1953, the American Academy of Arts and Sciences in 1959, the Norwegian Royal Society in 1965, and the Royal Society of Chemistry of Great Britain in 1981. He received the Debye Award of the American Chemical Society in 1966, the Edgerton Gold Medal of the Combustion Institute in 1966, the National Medal of Science in 1976, and the Silver Medal of the American Society of Mechanical Engineers in 1981. He also received honorary degrees from Marquette University (1978) and the University of Southern California (1980).

In 1953 Joe married Elizabeth (Betty) Stafford Sokolnikoff, a much-admired textbook author and mathematics professor on the University of Wisconsin campus. Betty shared with Joe a love of travel and an intense interest in people. The two of them shared the hospitality of their home with hundreds of visitors from all over the United States and abroad. Betty followed closely the activities of Joe's students and their families; with her encyclopedic knowledge of the names and faces of theoretical chemists and physicists from all over the world, she was invaluable. She was his constant and devoted companion, and his exacting proofreader. They were a scintillating and fascinating couple.

Joe's scientific output included more than 250 scientific papers, several edited volumes, various chapters in handbooks, and the MTGL treatise. He directed the Ph.D. theses of thirty-nine students and collaborated with over 100 postdoctoral students and visiting professors. His scientific progeny is currently active in more than fifteen fields of science and engineering—attesting to his own extremely broad-ranging interests. Joe himself recognized no boundaries between scientific fields. If it was science, it was ipso facto interesting and worthy of study. To Joe, science was life itself, and he remained active scientifically until several weeks before his death on March 30, 1990.

Joe's strong feelings on science education are best reflected by his own words:[9]

> In industrial and government laboratories, interdisciplinary problems are solved by task forces composed of people having different skills and backgrounds. Frankly, I am very much concerned that the training which we give our students is so highly specialized that they are not prepared to tackle problems that are not closely connected with their theses. It is important that our students develop sufficient breadth that they can explain their ideas to people with different backgrounds. This is essential if they are to become useful members of an interdisciplinary task force.

As just one example of Joe's roving scientific mind, we cite his 1976 publication with Howard and Lightfoot (of the Chemical Engineering Department at the University of Wisconsin) on a hydrodynamic separation technique for optical isomers; this was prompted by his observation of the behavior of sea shells when he was hiking on the beach at Sanibel Island, Florida, during a quantum chemistry conference.[6]

He will long be thought of as one of the founding fathers of the field of theoretical chemistry. He will also be remembered because, when you'd run into him on the street or in the hall, he'd start out by saying, "Gee, am I ever having fun with our new theory of . . . ."

THE AUTHORS THANK Mrs. Elizabeth Hirschfelder for checking the manuscript and making some changes in the text.

NOTES

1. Biographical sketch. In *McGraw-Hill Modern Scientists and Engineers.* New York: McGraw-Hill (1980):65-67.

2. Joe retires. *Badger Chemist* 28:1 (1981). Additional information in 4:9 (1956), 5:3 (1957), 10:12 (1963), 13:4 (1966), and 16:3 (1969).

3. C. F. Curtiss, R. B. Bird, and P. R. Certain. *J. Phys. Chem.* 86:6A-8A (1982); on p. 8A there is an "academic genealogy" showing Joe's Ph.D.'s (his "academic children"), his "academic grandchildren," etc.

4. Obituary. *New York Times.* March 31, 1990, p. 11.

5. A. J. Ihde. *Chemistry as Viewed from Bascom's Hill.* Department of Chemistry, University of Wisconsin-Madison (1990):542.

6. J. O. Hirschfelder. Henry Eyring, 1901-1982. *Ann. Rev. Phys. Chem.* 34:10-16 (1983).

7. J. O. Hirschfelder. My adventures in theoretical chemistry. *Ann. Rev. Phys. Chem.* 34:1-29 (1983).

8. J. O. Hirschfelder. Some new directions in molecular quantum mechanics. *J. Phys. Chem.* 86:1045-52 (1982).

9. J. O. Hirschfelder. The scientific and technological miracle at Los Alamos. In *Reminiscences of Los Alamos, 1943-1955.* Edited by L. Badash, J. O. Hirschfelder, and H. P. Broida. Dordrecht, Netherlands: D. Riedel Publishing Company (1980):67-88.

10. Television interview with J. O. Hirschfelder by Channel 27 (WISC) in Madison, Wisconsin. June 1981.

SELECTED BIBLIOGRAPHY

1935

With E. Wigner. Separation of rotational coordinates from the Schrödinger equation for *N* particles. *Proc. Natl. Acad. Sci. USA* 21:113-19.

1936

With H. Eyring and N. Rosen. Calculation of the energy of the H_3 molecule and the H_3 molecule ion. *J. Chem. Phys.* 4:121-33.

1937

With D. Stevenson and H. Eyring. A theory of liquid structure. *J. Chem. Phys.* 5:896-912.

1939

With E. Wigner. Some quantum mechanical considerations in the theory of reactions involving an activation energy. *J. Chem. Phys.* 7:616-28.

1948

With R. B. Bird and E. L. Spotz. The transport properties of non-polar gases. *J. Chem. Phys.* 16:968-81.

1949

With C. F. Curtiss. Transport properties of multicomponent gas mixtures. *J. Chem. Phys.* 17:550-55.

With C. F. Curtiss. The theory of flame propagation. *J. Chem. Phys.* 17:1076-81.

1950

With others. The effects of atomic weapons. Los Alamos Scientific Laboratories, U.S. Government Printing Office.

With others. Lennard-Jones and Devonshire equation of state of compressed gases and liquids. *J. Chem. Phys.* 18:1484-1500.

1951

With R. J. Buehler. Bipolar expansion of coulombic potentials. *Phys. Rev.* 83:628-33 (Addenda 85:149).

1952

With C. F. Curtiss. Integration of stiff equations. *Proc. Natl. Acad. Sci. USA* 38:235-43.

1954

With C. F. Curtiss and R. B. Bird. *Molecular Theory of Gases and Liquids.* New York: Wiley; 2nd corrected printing (1964); Russian translation (1961).

1956

With J. S. Dahler. Long-range intermolecular forces. *J. Chem. Phys.* 25:986-1005.

1959

With P. O. Löwdin. Long-range interaction of two ls-hydrogen atoms expressed in terms of national spin-orbitals. *Mol. Phys.* 2:229-58.

1960

Classical and quantum mechanical hypervirial theorems. *J. Chem. Phys.* 33:1462-66.

1962

With C. A. Coulson. Hypervirial theorems applied to molecular quantum mechanics. *J. Chem. Phys.* 36:941-46.

1964

With W. B. Brown and S. T. Epstein. Recent developments in perturbation theory. *Adv. Quantum Chem.* 1:255-374.

1967

With W. J. Meath. Intermolecular forces. In *Advances in Chemical Physics, Vol. 12.* Edited by J. O. Hirschfelder. New York: Wiley-Interscience:3-106.

1970

With R. T. Pack. Adiabatic corrections to long-range Born-Oppenheimer interactomic potentials. *J. Chem. Phys.* 52:4198-4211.

With P. R. Certain and D. R. Dion. New partitioning perturbation theory. *J. Chem. Phys.* 52:5977-99.

1971

With L. A. Curtiss. Spontaneous ionization of a hydrogen atom in an electric field, I. *J. Chem. Phys.* 55:1395-1402.

Chemical dynamics. In *Advances in Chemical Physics,* vol. 21. Edited with D. Henderson. New York: Wiley:73-89.

1974

With P. R. Certain. Degenerate RS perturbation theory. *J. Chem. Phys.* 60:1118-37.

With C. J. Goebel and L. W. Bruch. Quantized vortices around wavefunction nodes. II. *J. Chem. Phys.* 61:5456-59.

1976

With D. W. Howard and E. N. Lightfoot. The hydrodynamic resolution of optical isomers. *AIChE Journal* 22:794-98.

1979

Similarity of Wigner's delay time to the virial theorem for scattering by a central field. *Phys. Rev. A* 19:2463.

1980

Reminiscences of Los Alamos, 1943-1945. Edited with L. Badash and H. P. Broida. Dordrecht, Netherlands: D. Riedel Publishing Company.

With K.-H. Yang. Generalization of classical Poisson brackets to include spin. *Phys. Rev. A* 22:1814-16.

1989

Where are laser-molecule interactions headed? In *Lasers, Molecules, and Methods.* Edited with R. E. Wyatt and R. D. Coalson. *Adv. in Chem. Phys.* vol. 73. New York: Wiley-Interscience:1-79.