FOUNDATIONS ADVANCES

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Robert Farrell Stewart (1936–2015)

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Robert (Bob) Farrell Stewart passed away on 16 September 2015. Born and raised in Seattle, Bob obtained his BA in Chemistry from Carleton College in Minnesota in 1958. It was there he met classmate Janet Trussell, who became his wife in 1959, and together they went to Pasadena where Bob obtained his PhD in Chemistry from Caltech in 1963. Bob's mentor there was Norman Davidson, and his thesis title *Polarized absorption spectra of purines and pyrimidines* reveals that although more widely known as a theoretician, Bob began his research career as an experimentalist.

From Pasadena Bob went to Seattle as a Postdoctoral Fellow of the US Public Health Service at the University of Washington. There he met Lyle Jensen and soon became interested in theoretical aspects of X-ray crystallography. Because of the very accurate X-ray data being collected in Jensen's laboratory, and the advent of full-matrix least squares, it was becoming apparent that the hydrogen-atom scattering factor then in use was inadequate, resulting in isotropic thermal parameters for hydrogen that were systematically low, and even negative. Bob saw that it would be more appropriate to use the scattering factor for a bonded hydrogen atom, derived from the wavefunction for molecular hydrogen. The report of this work, *Coherent X-Ray Scattering for the Hydrogen Atom in the Hydrogen Molecule*, has become one of the most widely cited papers in the crystallographic literature, and this bonded hydrogen-atom scattering factor is now universally adopted, having appeared in *International Tables for Crystallography* for several decades.

Bob and Jan Stewart, with their children Robert and Annamarie, made Pittsburgh their home in 1964. Bob was first at the Mellon Institute and then Carnegie Mellon University after its merger with Carnegie Institute of Technology in 1967. There he pursued his interest in the study of nuclear and electronic charge distributions in crystals – later known as 'charge-density studies'. His first paper on *Generalized X-Ray Scattering*

Factors appeared in 1969, and built on the earlier work of Barrie Dawson and Kaarle Kurki-Suonio. This was followed by a series of papers in *The Journal of Chemical Physics* that developed the use of generalized scattering factors to extract electron-density information as well as physical properties of molecules. Three papers – one of which remains unpublished – resulted from Bob's award of an Alfred P. Sloan Fellowship (1970–1972), which enabled him to further develop his ideas while visiting the late Ted Maslen in Perth, Western Australia, in 1971. In 1976, some time after his return from Perth, Bob published *Electron Population Analysis with Rigid Pseudoatoms*, which laid out the multipole model now widely applied in deriving the charge density in crystals from experimental X-ray and neutron diffraction data.

Less well known is Bob's role at the same time in the development of Gaussian basis sets, a collaboration with John Pople, who had moved to Carnegie Institute of Technology in 1964. The starting point was Bob's 1969 paper *Small Gaussian Expansions of Atomic Orbitals*, which acknowledged Pople for his encouragement, and which included this understatement: 'The major utility of these orbitals is for the evaluation of generalized scattering factors for x-ray diffraction studies . . . It should also be mentioned, however, that the Gaussian expansions reported here may be useful for *ab initio* calculations in quantum chemistry.' Pioneering applications of these STO-nG basis sets to molecular-orbital calculations were co-authored with Warren Hehre and John Pople between 1969 and 1970.

The decade of the 1970s was exceptionally productive for Bob. After his return from Perth he had lost interest in the single-exponential work and devoted an increasing effort to the solution of the equations for deriving radial functions of multipole expansions for diatomic molecules. With graduate students John Bentley and Joel Epstein, Bob published a substantial body of this work, investigating X-ray scattering (total and coherent), electron scattering, core deformation, vibrational averaging and vibrational force constants. The key publication from 1975, *Generalized X-ray Scattering Factors in Diatomic Molecules*, demonstrated not only that generalized scattering factors determined from finite multipole expansions about the nuclei necessarily satisfied certain expectation values of the diatomic molecular charge density, but outlined a mathematical procedure for their determination *via* least squares. The paper presented monopole, dipole and quadrupole scattering factors for the hydrogen pseudoatom in H_2, and concluded that these 'could be instrumental in a more accurate determination of the time-average proton positions in organic molecular crystals'. This preceded by several decades the use of transferable pseudoatoms from various databases, or iterative refinement of 'Hirshfeld atoms'.

Bob recognized very early that the pseudoatom parameters that describe a molecular electron-density distribution could also be used to derive other important chemical and physical properties. When I joined his group in 1980 Bob had already developed *VALRAY*, a very extensive system of computer programs for least-squares refinement against X-ray diffraction data to obtain pseudoatom parameters, and the code for mapping properties of molecules and crystals was in its infancy. Over the following three years we expanded and calibrated the code for computing the electrostatic potential, electric field, electron density and electric field gradient *via* several Fourier and direct-space strategies. This was later extended to include properties from Richard Bader's theory of Atoms in Molecules (AIM), notably through Bob's collaboration with Claus Flensburg in Copenhagen. For many years Bob used *VALRAY* as his primary research tool for careful calibration of experimental results against those obtained from *ab initio* theory.

A significant factor in Bob's considerable impact on modern charge-density analysis came through his presence at, and contributions to, several key international meetings. Many of us first got to know Bob in 1977 at the two-week-long Bat Sheva Seminar on Electron Density Mapping in Molecules and Crystals, organized by Leslie Leiserowitz, Joel Bernstein, Phillip Coppens, Fred Hirshfeld and others, held at the Weizmann Institute in Israel. The lecture notes from the meeting, published as a special issue of the *Israel Journal of Chemistry*, became a reference text for the field for many years. The following year Bob participated in a NATO Advanced Study Institute, organized by Pierre Becker in Arles, on Electron and Magnetization Densities in Molecules and Crystals; a comprehensive book of proceedings was published in 1980. Another NATO Advanced Study Institute, on The Application of Charge Density Research to Chemistry and Drug Design, was organized by George Jeffrey and Juan Piniella in Spain in 1990. The 1991 book of proceedings included an important chapter by Bob, *Electrostatic Properties of Molecules from Diffraction Data*, that included examples of the electrostatic potential, Laplacian and (3,−1) critical points of the electron density, based on rigid pseudoatom fits to experimental diffraction data measured by Bryan Craven's group at the University of Pittsburgh. Bob was also a regular speaker and active participant in the triennial Gordon Research Conferences on Electron Distribution and Chemical Bonding held at Plymouth State College between 1978 and 1995.

Bob's influence also grew through visits to research groups overseas. In addition to his time in Perth, Bob spent productive periods at the Universities of Groningen, hosted by Aafje Vos, and Copenhagen, hosted by Sine Larsen. His time in Groningen resulted in the important 1979 paper on *Mapping of Electrostatic Properties from Bragg Diffraction Data*, as well as *A Theoretical Study of Elastic X-ray Scattering*, jointly with Dirk Feil in 1980. Bob's first visit to Copenhagen was for half a year in 1991, and it coincided with his new focus on implementing aspects of Bader's AIM theory for experimental electron densities. This sabbatical in Copenhagen initiated a very fruitful and productive collaboration that continued with annual visits each summer for more than a decade. Bob took an active part in, and had a great impact on, the scientific life of Sine Larsen's group, including co-supervision of graduate students Claus Flensburg, Henning Osholm Sørensen and Anders Østergaard Madsen.

Bob stood out as a scientist of the old school, who only wanted to publish things that he felt were done in the 'right' way. But he often struggled with recognizing when good was good enough, and from the early 1980s he simply stopped publishing at the rate required to secure funding, often taking his name off papers because he wasn't wholly satisfied. In 1979 Bob wrote to me – a young graduate seeking to join him as a postdoctoral fellow – "I do not operate big time 'show-biz' research programs – with such endeavors most people sacrifice quality for quantity . . . A critical evaluation, as well as intellectual honesty, are the essential ingredients to scientific research. And I will hold the line on that as long as I can manage."

Bob was a very modest person, and his scientific rigour was essential to the development of electron-density research. He was a great scientist in a class of his own, and he has left an outstanding legacy of original work, much of it still underappreciated. He will be fondly remembered and missed by many, as the host of Friday afternoon 'seminars' at the Craig Street Inn, for his remarkable knowledge and love of Fourier transforms, American football and the theory and application of X-ray scattering, as a valued friend and mentor to many young scientists, and as an enthusiastic and stimulating colleague.