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Highlights of a Scientific Odyssey

Boyhood. I was born on August 3, 1943, in Jeffersonville, Indiana, to Thomas Harold Dunning (Sr.) and Beatrice Blanch Dunning (née Colvin). My parents were living in Jeffersonville because my father was working for DuPont, which manufactured explosives for the war effort at a plant in Louisville, Kentucky, just across the Ohio River from Jeffersonville. Shortly after my birth, my father volunteered for the military (Marines)—although he had a deferment because of the work he was doing—and my mother and I moved to Francisco, Indiana, to live with my maternal grandparents. I did not see my father again until after the war, but certainly did not lack for attention while living with my mother, her two younger sisters, and my grandparents. To this day, I still refer to my grandmother as “Mom,” which was what her daughters called her.

After the war, my parents decided to settle in Francisco, a small town (population 724) ∼30 miles north of Evansville. I remember Francisco with great fondness—it provided a “Tom Sawyer” type of lifestyle for a young boy. I can remember one of the rituals that my brother and our friends had was that as soon as school was over in mid-May, we would get up early in the morning, pack our fishing poles and gear on our bikes, grab something for lunch, and set out for one of the fishing holes in the surrounding farmland. We usually did not come home until dinner. As I think about it now, it amazes me that our mothers allowed us to do that; would we be so trusting today?

Even as a young child, I had an interest in science. My first love was astronomy. I marveled at the stars and planets that glowed so brightly at night. I was amazed that people who had lived millennia before us had looked at those same stars, plotted their paths in the sky, and even named them. However, chemistry sets were cheaper than telescopes, so one Christmas, my parents bought me a chemistry set. It only took a few experiments for me to realize how fascinating chemistry was: solutions would change from clear to brightly colored or would get hot (or cold) when two liquids were mixed together. Of course, the explosive nature of black powder, a simple mixture of charcoal, sulfur and potassium nitrate, has probably convinced more budding scientists to become chemists than any other single thing.

Another event convinced me of the power of chemistry. The Spring after I got my chemistry set, I decided to make a fertilizer for my mother’s indoor plants. The book that came with my chemistry set was the same book that was included in all of the sets, including the much larger one. So, I did not have all of the ingredients that I needed to make the fertilizer. Rather than leave anything out, I decided to substitute for the missing ingredients with compounds that had a similar name. With this simple act, I very efficiently killed all of my mother’s plants. The power of chemistry was undeniable.

One day, I finally got up enough nerve to knock on the door of the man who taught chemistry at our (very small!) high school (I think I was in the 7th grade) and asked him if he had any books on chemistry that he would recommend. He lent me what he had and I read them all. Now that I look back on it, he had very few chemistry books. Teachers, then as now, were not well-paid, but I suspect that, although he taught chemistry, he was not a chemist. Nonetheless, those books and my conversations with him were very stimulating.

A little later, after receiving a microscope for Christmas, I became interested in biology, especially the microscopic world—the number of microscopic creatures that lived in the pond behind our house not only delighted, but horrified me. I had not yet realized that we lived in a world that had come to equilibrium and that they posed no immediate danger (otherwise I would already be dead). In that day, the link between biology and chemistry was not as widely appreciated as it is today, so I stuck with chemistry, which was more quantitative.

During my junior high school years, my family bought a television set. The nearest TV stations were in Evansville and Princeton (about 7 miles west of Francisco). TV fare in the late 1950s was limited; however, I enjoyed the movies and educational programs. One of the educational programs was on nuclear physics. This was broadcast at 7:30 AM during my freshman year, and I got up every day to learn about the marvelous world of the ultrasmall—the electron and positron, the neutron, proton, meson, and many other particles with exotic names. The 1950s were a marvelous time for science, especially after the Soviets launched Sputnik and the country realized that its reputation in science and engineering was being challenged. Suddenly, my interest in science was “in fashion.”

In 1959, Chrysler closed its manufacturing plant in Evansville, where my father worked, and offered him a job in the new assembly plant being built in the suburbs of St. Louis, Missouri. This was a traumatic event. I had spent essentially all of my childhood living across the street from my maternal grandparents and a short 4-mile drive from my paternal grandfather. My maternal aunts and uncles lived just a few blocks away, many other paternal aunts and uncles lived nearby, and I had cousins galore. The impact was softened when all of my maternal uncles, who also worked at the plant in Evansville, decided to move en masse to work at the new Chrysler plant in St. Louis.

We moved to Manchester, Missouri, with my aunts, uncles and cousins moving nearby. I attended a newly built school, Parkway Junior/Senior High School, which was several miles from Manchester and drew students from many surrounding towns. I thoroughly enjoyed the new high school because it offered so many more courses to take. However, even at Parkway, I ran out of mathematics courses to take in my senior year, so I was assigned to a special class “of one” and learned set theory (calculus was not taught in high school then). Being of a rather practical bent, I never came to fully appreciate the beauty of set theory.

Another momentous event in high school was that I met Sandra Jane Holloway, who would become my wife and the mother of our three daughters: Angelique Decameron, Nicole Etienne, and Lara Adrienne.

Undergraduate Study at the University of Missouri−Rolla. After graduation from high school in 1961, I headed to college at the University of Missouri−Rolla (UMR), the UM’s science and engineering branch. At that time, it was called the Missouri School of Mines and Metallurgy, and on January 1, 2008, the name will be changed once again, to Missouri University of Science and Technology. UMR provided a top-notch undergraduate education in many fields of engineering, and the science departments were excellent, with many new, young faculty hires. My brother, Eric Dale, also attended UMR as did his daughter, Erica Dawn; both became engineers.

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When I went to UMR, I considered majoring in chemical engineering or nuclear engineering. However, once I got there I realized that my real interest lay in understanding the basis for the chemical phenomena that had so fascinated me in my youth. Three events came together that made my future direction very clear. The first was an organic chemistry course that I took as a sophomore. I was impressed at the professor's ability to explain the course of chemical reactions in terms of electrons and nuclei moving here and there. However, it seemed rather slick and I kept wondering if the beautiful explanations that he gave were, in fact, correct. That summer, I took a course in differential equations, which opened up an elegant new mathematical world for me. Finally, in my junior year, I took a course in quantum mechanics in the Physics Department. In that course, I learned about the differential equations that describe the structure and motion of atoms and molecules. The loop was now complete. I just did not realize how difficult it was to solve those equations for the organic molecules and reactions of interest to me.

In my senior year, I began doing some reading on the application of theory in organic chemistry (none of the faculty at UMR had expertise in this area, although they helped by providing references and books). During that year I read L. Pauling's *Nature of the Chemical Bond*, C. Coulson's *Valence*, Pauling and E. B. Wilson's *Introduction to Quantum Mechanics*, and Kenneth Wiberg's *Physical Organic Chemistry*. These are outstanding books from an historical perspective, containing many still valuable insights.

I was particularly impressed by the concepts and knowledge embedded in Professor Pauling's two books and decided to apply to CalTech for graduate school. I also applied to Harvard, MIT and the University of California at Berkeley. Harvard turned me down and I did not like the form letter that I got from MIT, but both CalTech and Berkeley made offers. After a personal letter from John Roberts at CalTech, I decided that CalTech was the place for me. So in the late summer of 1965, my wife, oldest daughter (Angelique) and I set off for Pasadena, California in a sporty 1961 Thunderbird that I had bought earlier that summer. I had worked that summer at Monsanto and would do so the following year; that, along with a fellowship from the Woodrow Wilson Foundation, provided a much welcome infusion of funds as I began my graduate career.

Graduate Study at the California Institute of Technology. CalTech is a very picturesque campus and, with its focus on science and engineering and the high quality of the faculty, an ideal environment for graduate education. Although the Los Angeles area was a sprawling megapolis, Pasadena, the home of CalTech, was a model suburban city with tree-lined streets, elegant homes, and a real downtown. Smog, of course, was a problem. When we arrived in Pasadena, it was very smoggy, and it was not until several days later that we realized that the San Gabriel Mountains loomed just to the north of the campus. On a clear day, one could even see the buildings housing the big telescopes on Mt. Wilson.

In 1965, there were two faculty members on the CalTech chemistry faculty who specialized in theoretical chemistry: B. Vincent McKoy and Russell M. Pitzer. That same year, William A. Goddard III joined the group as an Arthur Amos Noyes Fellow. These three, energetic young faculty members created an exciting and supportive environment for graduate studies in theoretical chemistry. The students who were drawn to these activities left me with a rich set of friends and colleagues: Joel Bowman, Dave Cartwright, Jeff Hay, Dave Huestis, Bill Hunt, Luis Kahn, Carl Melius, George Schatz, Don Truhlar, Al Wagner, Nick Winter, and many others.

After considering the research projects being offered by Profs. McKoy and Pitzer, the only ones who could formally accept students at that time, I decided to work with Vince McKoy on the excited states of unsaturated organic molecules; specifically, the ethylene molecule. This aligned well with my interest in theoretical organic chemistry and was one of the outstanding problems in this area: all calculations of the excitation energies of the singlet $\pi-\pi^*$ transition, referred to by Mulliken as the $N(\pi\pi)-V(\pi\pi^*)$ transition, were too large by several electron volts and could be brought into agreement with experiment only through empirical corrections. Vince suggested that we use an excitation operator approach; namely, the Tamm−Dancoff and random phase approximations (TDA, RPA). This approach has the advantage of yielding the excitation energy directly, rather than as a difference of two very large numbers. So I set about learning about excitation operator methods, which were derived using second quantization techniques, as well as the details of ab initio calculations on molecules.

While I was working on the ethylene problem, I became increasingly interested in the work of Bill Goddard. I slowly realized that what was later dubbed the generalized valence bond (GVB) method was the basis for a new understanding of the electronic structure of molecules. It was based on valence bond theory but, unlike that theory, was quantitative. In addition, because the orbitals in the GVB method had been optimized, much of the arbitrariness and awkwardness of the valence bond method were eliminated. For the next several years, Bill and his group struggled with the computational complications introduced by the nonorthogonal GVB orbitals. During this period, I was happy to sit on the sideline, watch, and learn.

My first calculations on ethylene used a minimum Slater basis set, with the integrals kindly provided by Russ Pitzer. The calculations predicted excitation energies of 10.2 eV (TDA) and 9.4 eV (RPA); the experimental value is 7.6 eV. Vince and I felt that we needed a more accurate ground state wave function for the ethylene molecule. Unfortunately, the computational cost of multicenter integrals over Slater orbitals was computationally prohibitive for basis sets larger than a minimum basis set. At about this time, Nick Winter and I visited Murray Geller at CalTech's Jet Propulsion Laboratory. He was one of the authors of a program called MOSES that used Gaussian functions to solve the Hartree−Fock equations. On the basis of Murray's enthusiasm, Nick and I began investigating the use of Gaussian orbitals in electronic structure calculations.

The results in the literature were promising but also somewhat disappointing; reasonable results were obtained, but the wave functions were still far from the HF limit. In 1965, S. Huzinaga had published a paper systematically optimizing Gaussian functions in atomic calculations. His results were much more encouraging, suggesting that comparable results could be obtained with a Gaussian/Slater ratio of 3:1. Because of the ease of doing integrals over Gaussian orbitals, this was a clear win. Of course, one still had to solve the matrix HF equations once the integrals were computed, and since the number of two electron integrals increased as N^4, where N is the number of basis functions, the iterative solution of the matrix Hartree−Fock calculations can become computationally expensive. This led to various attempts to "contract" the Gaussian basis sets, that is, group some of the functions together with fixed coefficients and treat the combination as a single function. Although there were contracted Gaussian basis sets in the literature, I decided to systematically explore the contraction of Huzinaga's sets using the water and nitrogen molecules as guides. I found that the rules for optimally contracting Huzinaga's set were rather simple and used these rules to develop basis sets for the first row atoms from boron to neon. I had not intended to publish these results: my goal, after all, had been to calculate a more accurate wave function for ethylene, but over the years, Fritz Schaefer kept complaining to me about the lack of a proper reference, so in 1970, I finally submitted a paper on this topic to the *Journal of Chemical Physics*. Over the years, this paper has accumulated over 4500 citations. Thanks, Fritz!

A brief summary of subsequent activities on the ethylene problem is in order at this point. As I was completing my work on basis sets, Bill Hunt (one of Bill Goddard's students), Bill Goddard, and I developed a new way to solve the matrix Hartree−Fock equations for open-shell systems. Once the new open-shell Hartree−Fock code was debugged, I immediately carried out calculations on the triple, T($\pi\pi$*), and singlet, V($\pi\pi$*), states of ethylene (it was straightforward in this case, even for the singlet state, because the open shell orbitals are orthogonal by symmetry). When I started running the calculations on the V($\pi\pi$*) state, I noticed that the expansion coefficients in the π* orbital were shifted onto the most diffuse 2pπ function, so I added an even more diffuse function, and the same thing happened again. Finally, after I had added three diffuse 2pπ functions, the coefficients settled into a normal distribution. The calculated excitation energy was just 7.42 eV, in excellent agreement with experiment. The average extent of the π* orbital above the molecular plane was 6.5 a_0, compared to 1.65 a_0 for the π* orbital in the T($\pi\pi$*) state. This is one of those instances that a fact, when discovered, often seems obvious in hindsight. The V state was always regarded as an "ionic" state and ionic states are diffuse. In addition, as we shall see later, ionic states are also strongly affected by the inclusion of electron correlation.

Postdoctoral Years. *Battelle Memorial Institute*. After my Ph.D. examination, I headed for Battelle Memorial Institute in Columbus, Ohio, where I had accepted a postdoctoral appointment with Russ Pitzer. At that time, Battelle was making a major investment in theoretical chemistry and had on its staff Professors C. William Kern, Isaiah (Shi) Shavitt, and Russ Pitzer (who had moved from CalTech to The Ohio State University). It had a very active seminar program, many distinguished visitors, and was one of the premier research centers in electronic structure theory.

At Battelle, I was involved in a number of projects, but I'll mention only three activities here. First, my work on basis sets continued at Battelle. In particular, I developed basis sets for the second row atoms, aluminum through argon. Shi then asked me about the utility of Gaussian functions for describing electron correlation. Dick Hosteny, another postdoctoral fellow, and I showed that contracted Gaussian functions were just as effective as Slater functions in configuration interaction (SDCI) calculations. When we showed these results to Shi, he immediately acknowledged that Gaussian functions may well be a real alternative to Slater functions for molecular calculations. We were elated.

My interest in the ($\pi\pi$*) states of organic molecules also continued. Dick Hosteny, Bob Gilman, and I, advised by Shi, carried out full π-electron CI calculations on *trans*-butadiene. By and large, the results agreed with our expectations based on the previous results for ethylene: the T($\pi\pi$*) state was very compact, whereas the V($\pi\pi$*) state was diffuse. However, much to our surprise, we found five compact states in addition to the ground state, N(^1A_g): ^3B_u (3.45 eV) and ^3A_g (5.04 eV) states and ^1A_g (6.77 eV), ^3B_u (8.08 eV), and ^5A_g (9.61 eV) states. Analyzing the wave functions, we found the wave functions for the first two excited states to be dominated by single excitations from the ground state, whereas for the last three excited states, the dominant configurations were double excitations from the ground state. If butadiene is considered to be formed from two coupled vinyl fragments, these are just the states that would be expected to arise from the two π-electron valence states of the two vinyl fragments, $N_A(\pi_A{}^2)N_B(\pi_B{}^2)$, $N_A(\pi_A{}^2)T_B(\pi_B\pi_B{}^*) \pm T_A(\pi_A\pi_A{}^*)N_B(\pi_B{}^2)$ and $T_A(\pi_A\pi_A{}^*)T_B(\pi_B\pi_B{}^*)$, where A and B refer to the two vinyl fragments. The NN configuration is the ground state, the NT ± TN configuration gives rise to the ^3B_u and ^3A_g states, and the TT configuration gives rise to the ^1A_g, ^3B_u, and ^5A_g states. Suddenly, the spectrum of excited state in unsaturated polyenes became much richer, a fact that Brian Kohler and others later verified in the laboratory.

During my year at Battelle, Russ Pitzer introduced me to Weldon Matthews and his student Bill White. Weldon and Bill were measuring the spectra of the CF molecule in the laboratory. After talking with them about their results, I decided to tackle the problem using Jurgen Hinze's new multiconfiguration SCF program. I used the GVB ideas that I learned from Bill Goddard to construct the wave functions for the various valence states of interest: the ground state ($X^2\Pi$) and $^4\Sigma^-$, $B^2\Delta$, and $^2\Sigma^\pm$ excited states. I constructed the wave functions assuming that all of the orbitals were orthogonal (strong orthogonality). The calculations included configurations that described each of the pairs coupled into a singlet [GVB(SO/PP)]; subsequent calculations included configurations to optimize the spin coupling [GVB(SO)]. Around this same time, Bill Hunt, Jeff Hay, and Bill Goddard developed a very efficient program for performing GVB(SO/PP) calculations.

While I was at Battelle, Bill Goddard offered me a postdoctoral fellowship as well as an instructor's appointment at CalTech. I jumped at the opportunity to get further involved in the development of the GVB method and return to CalTech in 1971. The next couple of years working with Bill Goddard, Bill Hunt, and Jeff Hay were very productive. The GVB(SO/PP) program written by Bill and Jeff was very powerful, and we carried out calculations on a broad range of molecules to better understand "what electrons were doing in molecules." As these calculations progressed, the efficacy of the GVB model for understanding the electronic structure of molecules was established. These ideas were summarized in an article written for *Accounts of Chemical Research*.

During my stay at CalTech, I enticed Charlie Bender, who had also been a postdoctoral fellow at Battelle, and Fritz Schaefer to carry out CI calculations on the ground and excited states of ethylene. Befitting the ionic nature of the V($\pi\pi$*) state, its spatial extent was found to be very sensitive to the inclusion of electron correlation. CI calculations decreased the average extent of the π* orbital in the V state by 20%, from 6.5 a_0 to ~5.2 a_0. The spatial extent of the N and T states were little affected by the inclusion of correlation effects. The CI calculations predicted a vertical excitation energy of 8.1 eV. The theoretical description of the ($\pi\pi$*) states of unsaturated organic molecules was becoming clear.

National Laboratory Years. Although I had planned on an academic career, I spent the next 28 years of my career, 1973−2001, as a research scientist and research manager in the national laboratories funded by the U.S. Department of Energy. The national laboratories provide excellent opportunities for young scientists: excellent resources, top-notch colleagues, and cutting-edge problems. Not quite curiosity-driven research, but close enough.

Los Alamos National Laboratory. In 1973, Barry Schneider, whom I met when he was a postdoctoral fellow with Howard Taylor at the University of Southern California, called and asked if I would be interested in a position in the Laser Theory Group at Los Alamos National Laboratory. Barry and Jim Cohen, another staff member, were interested in molecular systems with lasing potential and were looking for someone to complement their effort. It sounded like a great opportunity, and the computing resources at Los Alamos were unparalleled, so I accepted. Sandy and I, along with our two girls, Angelique and Nicole (who had been born in California), arrived in Los Alamos at the beginning of May 1973—to snow flurries. The next month, our third daughter, Lara, was born.

The Laser Theory Group was involved in modeling the lasers used to implode pellets of hydrogen gas (laser-induced fusion) and to separate uranium isotopes (laser isotope separation). Jeff Hay, a former student of Bill Goddard whom I recruited to Los Alamos, and I began an extended study of the rare gas monohalides (RgX), rare gas monoxides (RgO), and other exotic species, characterizing their potential as lasers. Lasing had just been observed in KrF, and the wavelength was in a region attractive for ultraviolet photochemistry. Jeff and I adapted the CI techniques that we had developed in our earlier studies and carried out a comprehensive series of calculations on these species, characterizing the ground and low-lying excited states of the molecules (the ground state was only very weakly bound) as well as the transitions between them. The calculations showed how the laser wavelength as well as its inherent intensity varied from rare gas to rare gas and halide to halide. These computational studies were an invaluable complement to the experimental studies of these species, which were very difficult to characterize in the laboratory.

While I was at Los Alamos, a national movement began to establish a computing center for computational chemistry. I brought this to the attention of the administration at Los Alamos, and they were very enthusiastic, asking me to participate in the planning activities. In the early 1970s, it was clear that theoretical chemistry was being constrained by the lack of computing resources available to academic chemists. In 1976, the first Cray 1s was delivered to Los Alamos, and it was up to 50 times faster than the other computers available at that time, but it was used by the weapons physics group at Los Alamos and not available to the broader scientific and engineering community.

In 1977, the National Resource for Computation in Chemistry was established at Lawrence Berkeley National Laboratory as a joint NSF-DOE facility. It was closed in 1981, just 4 years later. This was a great disappointment not only to Bill Lester, who had been appointed the NRCC director, and his staff, but also to those of us who had labored for several years to bring this resource, with all of its promise, into existence. The NRCC never had sufficient funding or computing resources to accomplish its mission. In addition, this was the time that chemists began buying minicomputers (primarily VAXes from Digital Equipment Corporation; this was sometimes referred to as the VAXination of chemistry), and the impetus for a national facility was fading. Clearly, timing is important, especially in computing-related fields.

After I moved from the Laser Theory Group to the Physical Chemistry—Chemical Physics Group at Los Alamos, I became interested in chemical reactions. Joe Martinez, who was one of the program managers in the Chemical Sciences Division at DOE, visited Los Alamos and described the new initiative that they were planning in combustion. The combustion of hydrocarbons is replete with chemical reactions that are poorly characterized experimentally, so this was an appealing new application for chemical theory. My work on chemical reactions took on a new emphasis.

Argonne National Laboratory. Shortly after I changed groups, Al Wagner, who had been a fellow graduate student at CalTech and was now on the staff at Argonne National Laboratory, called to tell me that Chris Wahl had left Argonne and wanted to know if I was interested in interviewing for Chris' position as head of the Theoretical Chemistry Group. Further, he noted that they were well-situated to participate in the new DOE initiative in combustion. Everyone at Los Alamos questioned the sanity of this move (it was so cold in Chicago), but it led to one of the most exciting and satisfying times in my career; however, it also led to the most depressing event in my life. After 20 years of marriage, Sandy decided she wanted to be on her own, and we were divorced.

At Argonne, Steve Walch, a postdoctoral fellow who came to work with me shortly before I left Los Alamos, and I then began calculations on the potential energy surfaces for a number of the reactions involved in the H_2-O_2 system. The results for the calculated barrier heights and reaction energies were encouraging, although they did not yet approach chemical accuracy. Nonetheless, the resulting information on the potential energy surfaces was of great interest to our colleagues in chemical kinetics and dynamics: Al Wagner used the data to calculate rate constants using transition state theory, and George Schatz and his students constructed global potential energy surfaces to study the detailed dynamics of the reactions. This collaboration between electronic structure theorists and theoretical chemical dynamicists became a hallmark of our research program at Argonne. This collaboration was further boosted when Larry Harding joined the group and Joel Bowman from Illinois Institute of Technology as well as George Schatz became regular visitors.

A little later on, I became interested in the reaction path Hamiltonian approach put forward by Bill Miller, Nick Handy, and John Adams. I felt that this was an approach that would provide the same kind of qualitative insights into reaction dynamics that GVB provided into molecular electronic structure. Working with Elfi Kraka and Rob Eades, we applied the reaction path Hamiltonian approach to two prototypical reactions: $Li + HF$ (a typical charge-transfer reaction) and $OH + H_2$ (a typical abstraction reaction). The results of these studies provided a wealth of qualitative insights into the dynamics of the chemical reactions. Unfortunately, I left for a new position at Pacific Northwest National Laboratory, and another set of chemistry problems, before I had an opportunity to fully explore this approach. However, Elfi continued working with reaction path (valley) methods with great success.

As the combustion initiative developed in DOE, Bill Kirchhoff, who joined DOE's Chemical Sciences Division after many years at the National Institute of Standards and Technology (NIST), became the program manager of the Chemical Physics program, the home of the combustion initiative. Bill was (and still is) a remarkable scientist. A molecular spectroscopist by background, he quickly became knowledgeable about the combustion program and, with Al Laufer, provided a guiding hand for 20 years. We were extremely fortunate to have Bill in that position because of his interest in science and his insistence on excellence. The success of this program was in no small part due to Bill's leadership.

As the work at Argonne progressed, I became increasingly frustrated with our inability to calculate accurate bond energies, reaction energetics, and reaction barrier heights. The calculated results were reasonable enough, but a clear path for systematically improving the accuracy of the calculated energies was not obvious. Focusing first on bond energies, I explored many avenues, but nothing that I did led to a major improvement in the calculated bond energies. Then, while visiting Argonne, Jan Amlöf and Peter Taylor stated that they were obtaining excellent results using a large set of Gaussian functions contracted to natural orbitals based on atomic CI calculations. Further, they found that the natural orbital occupation numbers grouped together in specific patterns. The results got better as they systematically increased the set of natural orbitals being used.

At that point, I decided that I did not understand the basis set dependence of electron correlation in atoms, much less molecules, so I set about systematically building up basis sets to accurately describe atomic correlation effects for an SDCI wave function. I took a simple tack: I started with a large *sp* basis set for an atom and progressively added *d* functions, optimizing the exponents of the *d* functions as I did so. Then, using a large *spd* set, I repeated the process for *f* functions and so on. There were two surprises. First, the energy lowering decreased approximately exponentially with increasing numbers of basis functions, and second, the energy lowering for the different angular momenta fell into groups. For example, the energy lowering for the first *f* function was approximately the same as that for the second *d* function, the energy lowering for the first *g* function was approximately the same as that for the second *f* function and the third *d* function. This led to the construction of "correlation-consistent" basis sets. We now had the means to construct basis sets that provided a finer and finer description of both the radial and angular spaces as the cardinal number of the basis set increased from double-ζ ($n = 2$), to triple-ζ ($n = 3$), to quadruple-ζ ($n = 4$), and so on. All of this was, of course, consistent with the results of Amlöf and Taylor. The paper on correlation-consistent basis sets for boron−neon was published in 1989 and now has over 7000 citations.

Throughout my career, I have been interested in computing technology because this was clearly key to improving our ability to describe the electronic structure of molecules. Fortunately, I was able to attract Ray Bair, another Goddard student, to Argonne, first as a postdoctoral fellow and then as a staff member. Ray is one of those rare individuals who has one foot in theoretical chemistry and one foot in computing technology. This was an extremely valuable talent as we explored new computing technologies for chemical computations. After a thorough assessment of the latest computing technologies, we decided to buy an FPS-164 Attached Processor for the Chemistry Division's VAX 11/780. Ray was instrumental in bringing this machine into production and in rewriting the quantum chemistry codes to make full use of its capabilities with contributions from Ron Shepard, who joined the group in this time period. The substantial speed-ups achieved over the VAX 11/780, nearly a factor of 10 on average, made the investment in rewriting the codes most worthwhile.

While I was at Argonne, I met Sylvia Ann Millhouse Perry, and we were married in 1982. With her two children, Kristin Millhouse Perry and Alan Tyler Perry, and my three children, our house became a very lively place. Shortly after we were married, Sylvia decided to attend the Jane Adams School of Social Work at the University of Illinois at Chicago. Although this required balancing graduate school with her role as a new wife and the mother in a blended family, she succeeded and obtained her Masters Degree in Social Work with honors in 1988.

Pacific Northwest National Laboratory. In 1988, Charlie Duke, who had left Xerox to become Deputy Director of Pacific Northwest National Laboratory, invited me to PNNL for a seminar. After my seminar, Bill Wiley, the PNNL director, told me that he had seen firsthand the enormous impact of molecular science on biology and felt that similar opportunities lay in other fields. He and Charlie had been laying the plans for a Molecular Science Research Center. He told me that he was interested in having me join the effort as head of the theory, modeling, and simulation effort. Shortly thereafter, I spoke with Bob Marianelli, who was the director of the DOE's Division of Chemical Sciences. He was very supportive of Bill Wiley's plans and also supported my move to PNNL. With that, I left the group at Argonne in Al Wagner's very capable hands and Sylvia, her two children, and I left for the state of Washington (my children, who were older, stayed in the Midwest).

Although the Molecular Science Research Center had the full support of Bill Wiley and Bob Marianelli and had selected an area of interest of critical importance to DOE (molecular science relevant to DOE's mission to clean up its sites), we had rough sailing. DOE's Office of Environmental Management, which, through a twist of fate, had been assigned to be the landlord of the new center, had little interest in the research that we were proposing to do. Fortunately, Bill Wiley recruited Mike Knotek, the head of the National Synchrotron Light Source at Brookhaven National Laboratory and formerly at Sandia National Laboratories, to replace Charlie Duke, who had returned to Xerox. Mike's assignment was to push the plans through the DOE system and create the MSRC. After 8 years, many false starts and stops, and a change in name to the Environmental Molecular Sciences Laboratory (EMSL), Mike and the rest of us prevailed. All along the way, Bill Wiley and Bob Marianelli never faltered in their support. It also helped that the scientific community stood by us. In review after review, they told the Office of Environmental Management that they needed the knowledge that EMSL would produce if they were to meet their cleanup goals in a timely fashion. Eventually, Ari Patrinos, the head of DOE's Office of Environmental and Biological Research became the landlord of EMSL, and we had another strong advocate for the research being done. To our great satisfaction, when the Office of Environmental Management started its environmental management science program, EMSL was the largest single recipient of funding.

During this period, I continued to push the development and use of the correlation-consistent basis sets. Before I left Argonne, Ricky Kendall, Robert Harrison, and I extended the sets to describe negative ions. At Argonne, I had also noted that as the cardinal number of the basis set increased, the calculated molecular properties often converged smoothly toward a well-defined limit. At PNNL, Kirk Peterson and I began a series of benchmark calculations to systemically explore the convergence and accuracy of the basis sets. This work demonstrated that the correlation-consistent sets led to smooth convergence toward an apparent complete basis set limit for a wide range of molecular properties. Dave Woon, who had joined the group earlier, extended the basis sets to the second row atoms (Al−Ar) and showed that properties for these species also converged smoothly. The coup de grace came when Dave Feller, in calculations of the binding energy of the H_2O dimer, found the same exponential convergence. Kirk, Dave Woon, and I had been calculating the binding energies of strongly bound molecules. The H_2O dimer is bound by only 5 kcal/mol. Clearly, the convergence of the calculations with the correlation-consistent sets was a very general phenomenon.

The development of the correlation-consistent basis sets led to an explosion of activities. Sotiris Xantheas and I studied the structure of waters clusters, $(H_2O)_n$; anion−water clusters, $H^-(H_2O)_n$ and $F^-(H_2O)_n$; the $H^- + (H_2O)_{1-2}$ reaction; the enthalpy of formation of HSO; the HSO−SOH isomerization energy, and the dissociation energy of NF and NCl. Kirk Peterson and I examined the $H + H_2$, $F + H_2$, and other reactions; the HF dimer; the bond energies in the CH_n and C_2H_n series; and the proton affinities of H_2O and NH_3 (with Sotiris and Dave Dixon). I also began studies of a number of weakly bound systems, including N_2−HF (with Dave Woon and Kirk Peterson), Ar−HF (with Tanja van Mourik), and Ar−HCl (with Dave Woon and Kirk Peterson) and very weakly bound molecules, the rare gas dimers (with Tanja van Mourik and Angela Wilson). Dave Woon and I also studied the $LiF(H_2O)_n$ system as a microsolvation model of an ionic solution with intriguing results. After three decades of "reasonably good" predictions of molecular properties, the results from these studies were almost unbelievable. Using the correlation consistent basis sets and coupled cluster models, we were now in the position of being able to calculate molecular properties nearly as accurately as they could be measured in the laboratory and, in some cases, more accurately.

During this period, it slowly dawned on us that we had finally achieved one of the major goals of quantum chemistry. By extrapolating the calculated results to the complete basis set limit ($n \rightarrow \infty$, where n is the cardinal number of the basis set), we were finally able to separate the error in the electronic structure method (the *intrinsic error*) from the error due to the use of an incomplete basis set (the basis set *convergence error*). We used a simple exponential function to extrapolate the results to the complete basis set; Jan Martin, Trygve Helgaker, and others proposed other, more theoretically motivated extrapolation functions. Kirk Peterson and I showed how the interplay between the convergence error and the intrinsic error gave rise to "Pauling points," points of fortuitous agreement with experiment, in the calculated dissociation energy of N_2. Many other examples of this phenomenon were found.

As part of the EMSL project, we committed to making a major advance in computational molecular science, an advance that would be essential to studying the large molecules of importance in environmental chemistry. This commitment was built on two foundations: acquisition of a major computing system for the EMSL—a massively parallel computing system—and the creation of a group devoted to developing the software needed to fully exploit this new computing capability. Ray Bair initiated this latter effort, but was later tapped to lead EMSL's Computing and Information Science Directorate. The High Performance Computational Chemistry group was then led by Martyn Guest and, finally, by Jeff Nichols. We were very fortunate to recruit Robert Harrison, whom I had brought to Argonne in 1988, to the effort as the chief chemistry architect. His combined knowledge of theoretical and computational chemistry, computer science, and applied mathematics is second to none and was key to the successful development of the new molecular modeling package, which was named NWCHEM. In this effort, he was very ably assisted by Ricky Kendall, Edo Apra, Dave Bernholdt, Michel Dupuis, T. P. Straatsma, Theresa Windus, Adrian Wong, and many others. Another key to this effort was the close collaboration of computational chemists, computer scientists, and applied mathematicians. In this regard, we were fortunate to attract Jarek Nieplocha (a computer scientist) and Rick Littlefield and George Fann (both applied mathematicians) to the project. Their participation allowed us to push the boundaries of what was possible in the development of NWCHEM. NWCHEM has allowed chemists to extend their studies to molecular systems that simply could not be addressed heretofore.

Office of Science, U.S. Department of Energy. The success of the computational effort in the EMSL project effort led to a call from the Office of the Undersecretary of Energy on Christmas Eve in 1998. They asked me to come to DOE Headquarters to help them extend this approach to other areas in DOE's Office of Science research portfolio. The Office of Science had been working on a new Scientific Simulation Initiative (SSI) for more than a year and was now ready to submit the formal request to Congress. So at the beginning of January 1999, I packed my bags and left for Washington, D.C. At DOE-HQ, I worked with Martha Krebs (Director of the Office of Science); Jim Decker (Deputy Director); Ed Oliver and Kimberly Rasar (both on leave from Oak Ridge National Laboratory); and Mike Knotek, who was now an assistant to Ernie Moniz, the Undersecretary of Energy. We finished the preparation of the paperwork and then, once the budget was submitted to Congress, began visiting Congressional offices.

The reception of the SSI was less than enthusiastic. Part of the problem was timing (timing again!). The President's Information Technology Advisory Committee (PITAC) had just released a report that stressed the critical importance of investments in software. The SSI had a very large hardware investment and only a modest software investment. At the same time, the Government Accounting Office issued a report chiding DOE for not making full use of the computers that it already had. Little wonder that Congress was not in a receptive mood.

The other part of the problem with the SSI was a failure to articulate the intent and merits of the initiative. The SSI had focused on two major challenges: the design of more efficient, less polluting engines and more accurate predictions of climate change. Many in Congress saw the first project as undue federal support for industry and the second as being outside DOE's mission area. Both of these assertions were incorrect. The proposed work on engine technologies was really an attempt to develop the basic computational modeling concepts, framework, and applications needed to describe a complex system that coupled chemical reactions, fluid flow, radiation transport, and dynamic mechanical devices: a truly computational "Grand Challenge." The Office of Science also had a long standing program in climate modeling, even through it did not have the visibility of the climate programs in other agencies, such as NASA. The net result was that Congress did not fund the SSI.

Despite this failure, my discussions with Congressional staff and staff in the Office of Management and Budget led me to believe that there were many who were sympathetic to the development of a major computing initiative in DOE. DOE is, in fact, one of the pioneers in scientific computing and is still responsible for a major part of the federal funding in this area. The following year, I worked closely with the leaders in computing at DOE's national laboratories, crafting a plan that avoided the pitfalls of the SSI and built on the strengths in computing and computer and computational science in the laboratories. On March 30, 2000, the Office of Science submitted this plan, entitled *Scientific Discovery through Advanced Computing*, to Congress. Jim Decker, Pat Dehmer, Ed Oliver, and I then began visiting Congressional Offices to explain this new program. Although we first encountered resistance (on the surface it appeared the same as the SSI), once we were able to describe the program in detail, they were supportive. Many months were spent visiting Congressional offices, holding information meetings, and related activities, but it paid off. Congress fully funded the program that fall.

Although SciDAC, as the program came to be called, has, as expected, had its ups and downs, the successes have clearly established the benefits of a focus on software and the multidisciplinary teams required to enable science and engineering applications to take full advantage of advanced computing hardware. SciDAC prepared the DOE community well for the push for new computing hardware that followed the start-up of the Earth Simulator in Japan. SciDAC is being emulated in the United Kingdom and elsewhere.

University Years. After my 2 years were completed at DOE-HQ, I decided I had spent enough years in the DOE laboratories and it was time to begin an academic career. I had always had a strong interest in teaching, beginning with the chemical physics course that I team-taught with Bill Goddard early in my career. In addition, the importance of computing was becoming increasingly recognized in academia.

University of North Carolina at Chapel Hill. After discussions with administrators and staff at MCNC (the non-profit organization that ran the North Carolina Supercomputing Center and the North Carolina Research and Education Network), administrators and faculty at the University of North Carolina, Duke University, North Carolina State University, and NSF officials, I decided to accept a position as head of NCSC and NCREN at MCNC and professor of chemistry at the University of North Carolina at Chapel Hill. I bounded into this job with renewed enthusiasm; this was an opportunity to bring the benefits of supercomputing to researchers and educators throughout the University of North Carolina system (16 universities) plus Duke and Wake Forest Universities.

Although I began some new initiatives in North Carolina, for example, the North Carolina Bioinformatics Grid, and enjoyed my interactions with my new colleagues (Tomas Baer, Roger Miller, Lee Pedersen, Weitao Yang, Bill Youngblood, Mark Johnson, John Killebrew, and others), my days in North Carolina were limited. The Fall after I arrived in North Carolina, the North Carolina General Assembly, in the throes of a fiscal meltdown and irritated at the recent wealth acquired by MCNC as a result of its sale of intellectual property to J. D. Uniphase, cut MCNC's budget for supercomputing from $7.2 million to $2.2 million. The Board of Directors stood by the Supercomputing Center the first year, making up the missing $5 million from MCNC's endowment fund, but when the General Assembly did not increase the funding the following year, it became clear that this path was not sustainable.

As a result, in the fall of 2002, just 18 months after I arrived in North Carolina, I accepted a position as a professor at the University of Tennessee at Knoxville, staff member at Oak Ridge National Laboratory, and Founding Director of the Joint Institute for Computational Sciences. One year later, the North Carolina Supercomputing Center, one of the first state supercomputing centers, closed its doors.

University of Tennessee at Knoxville and Oak Ridge National Laboratory. There was great excitement at the University of Tennessee (UT) and Oak Ridge National Laboratory (ORNL) when I arrived. UT along with Battelle Memorial Institute had recently been awarded the contract for managing Oak Ridge National Laboratory. One of the pledges that the state of Tennessee made when it sought this contract was to establish a number of joint institutes to foster collaboration between faculty at UT and staff at ORNL. One of those institutes was the Joint Institute for Computational Sciences (JICS).

Construction of a building to house JICS began just as I arrived in Tennessee. It was part of the new complex of buildings being constructed on the ORNL site. Another new facility was being built to house a 40 000 square foot computer room and associated offices for the Computing & Computational Sciences Directorate headed by Thomas Zacharia. ORNL had already recruited several staff from PNNL, including Robert Harrison and Jeff Nichols, so coming to Oak Ridge was almost like returning to PNNL.

As soon as I got to ORNL, I became involved in the effort to establish a leadership computing facility at Oak Ridge. In 2004, in response to the solicitation from DOE's Office of Science, we prepared a proposal for such a facility with Argonne National Laboratory as a major partner. Thomas was the PI and I was a co-PI on the proposal, along with several others, including Rick Stevens from Argonne National Laboratory. The competition was fierce, but Oak Ridge was selected for the award. One of the key features of our proposal was a balanced investment in hardware and software. The latter focused on the creation of computational end stations, a concept that had arisen in the report from the High-End Computing Revitalization Task Force. Computational end stations were to offer access to best-in-class scientific applications, along with access to world-class computational specialists: they are the computational equivalent of the experimental end stations associated with DOE's large user facilities. Unfortunately, despite the arguments for substantial investments in software, the investments are still heavily skewed toward hardware, although some of the shortfall is being addressed through the SciDAC program. It is still easier for agencies to make investments in hardware than in software.

Before I left North Carolina, Apostolos Kalemos, from Aristides Mavridis' group in Athens, came to work with me. Apostolos had substantial experience with multireference calculations on simple transition metal molecules, and I decided it was time to better understand the physics and chemistry of these important atoms. Years before at Argonne, Bea Botch, a graduate student with Jim Harrison at Michigan State University, and I had tackled the problem of describing the ground and low-lying states of the transition metal atoms. Our work had shed some light on the peculiar nature of the $4s3d^{n+1}$ and $3d^{n+2}$ states of these atoms, but we did not go beyond those limited studies.

The work on transition molecules continued when I moved to UT/ORNL and led to detailed studies on the ground and low-lying excited states of TiCH, VC and CrC. These calculations, along with the earlier studies from Mavridis' group, established that, with use of large basis sets and multireference configuration interaction methods, accurate results could be obtained for simple transition metal molecules. However, actually carrying out the calculations was both tedious and computationally expensive. It is a tribute to Apostolos' knowledge and perseverance that he was successful in these endeavors. He was also successful in developing simple valence bond descriptions of the various states of these molecules. Apostolos, Aristides, and I also studied the ground and low-lying excited states of CH_2 and SiH_2 and symmetry-breaking in BNB.

I finally had an opportunity to return to teaching at the University of Tennessee. The first year I taught a special topics course on quantum chemistry, and the second year, I taught the regular graduate quantum chemistry course. I found the existing textbooks in quantum chemistry to be unsatisfactory—

too oriented toward descriptions of techniques, not enough about the general principles that govern the electronic structure of molecules. I decided to prepare a set of notes for the classes, drawing from the material from my graduate student and postdoctoral days and the knowledge that I had accumulated over the succeeding years. Although preparation of the notes for the courses took considerable time and effort (and are still incomplete), it was exciting to be thinking through the concepts that I had learned in some 40 years of study and research and casting them in a form that would engage and instruct students.

University of Illinois at Urbana−Champaign. In April of 2004, I received a telephone call from Dick Alkire, a colleague from my days on the Chemical Sciences Roundtable, telling me that Dan Reed had stepped down as the director of the National Center for Supercomputing Applications at the University of Illinois at Urbana−Champaign and that he was chairing the search committee for his successor. He was seeking recommendations for possible candidates. I told him that I would think about individuals that I could recommend and get back to him. NCSA, which was established by NSF and the state of Illinois in 1986, is one of the nation's, indeed the world's, preeminent supercomputing centers with a distinguished history of innovations (Mosaic, Apache Web Server, Telnet, CM-2/CM-5 Connection Computers, computing clusters, etc.).

At the time, it was becoming clear that my vision for JICS did not align well with that of the management of Oak Ridge National Laboratory, despite the fact that I had clearly laid out my plans when I accepted the JICS directorship. However, Sylvia and I had just moved into our newly remodeled house in Knoxville, so I was inclined to stay at the University of Tennessee and continue to try to realize that vision. But Sylvia counseled me to forget about the house and to give full consideration to the opportunity in Illinois. After a few days I called Dick, and told him that I was interested in the position. I visited Illinois and found that the ideas of the search committee, the senior administration at the university, and NCSA management overlapped well with mine, and I accepted their offer with great enthusiasm.

NCSA, under the direction of Rob Pennington and Danny Powell, had laid out a very ambitious plan in their 2004 proposal to NSF. The proposal focused on two major themes: providing supercomputing resources to the nation's scientists and engineers (their traditional role as a supercomputing center), and building the comprehensive software systems required by existing and emerging communities to manage, integrate, and analyze their rapidly growing, diverse data sources and stores and computing resources. The latter software systems we later called *cyberenvironments*. In essence, cyberenvironments were intended make the national cyberinfrastructure as accessible to scientists and engineers as NCSA's Mosaic and succeeding web browsers had for the Internet. Clearly, NCSA management and staff were thinking ahead to the time when supercomputing would be needed by a much broader set of research communities who would need a more extensive infrastructure than traditional users did.

We are midway through our strategic plan—*NCSA 2010*—that includes these two elements as well as significant efforts in assessing the impact of innovative computing technologies for scientific and engineering applications, developing and applying advanced data visualization and analysis techniques, and in bringing computing and computational science into the classroom. At the current time, NCSA provides the largest computing system available in NSF's portfolio, *Abe* with a peak performance of nearly 90 teraflops. We are also developing prototype cyberenvironments for several science and engineering communities: earthquake engineering, environmental engineering, observational astronomy, and weather forecasting. The future looks bright.

When I moved to the University of Illinois, I decide to return to a chemistry problem that had fascinated me since the 1970s—hypervalent molecules. Jeremy Musher in 1969 defined hypervalent molecules as molecules of the elements of groups 15−18 in any valence state other than the lowest. PF_5, SF_4 and SF_6, and ClF_3 and ClF_5 are prototypical hypervalent molecules. In late 2006, Dave Woon joined my group at UIUC as an academic professional and we began a series of exploratory calculations on the SF_n ($n = 1-6$) molecules. We soon found that the situation was more complicated than portrayed in the literature. There were not just hypervalent molecules: there were hypervalent states in normal molecules. For example, the low-lying triplet state in SF_2 has one "hypervalent" bond and one "normal" bond. We have exploited GVB ideas to help explain these results with great success, but there are still many mysteries to be solved in understanding hypervalency.

The Future. What will the future be? At the current time, we are negotiating with NSF to place the nation's first *sustained* petascale computing system at UIUC/NCSA. This system, called *Blue Waters*, will be fielded in 2011 and will be a major step forward in computing. It is built on IBM's latest advances in processor, memory, and interconnect technologies and will provide a capability that exceeds that of *Abe* by more than 2 orders of magnitude. This project will keep me, Rob Pennington, and many others at NCSA busy for the next several years.

Dave Woon and I will continue our work on hypervalent molecules. Our work so far has shown that hypervalency is more complex than heretofore recognized and that it has a profound affect on the spectrum of states in molecules, but what impact does it have on the reactivity of molecules? I also plan to return to teaching at some point: I want to finish my lecture notes.

Whatever happens in the future, what will make the work exciting and enjoyable are the friends and colleagues with whom I will be working, especially my colleagues at NCSA (Randy Butler, Donna Cox, Eric Jakobsson, Jim Myers, John Towns, Michael Welge, Bob Wilhelmson, and Edee Wiziecki, as well as Danny Powell and Rob Pennington and many others), in the Department of Chemistry (Zan Luthey-Schulten, Nancy Makri, Todd Martinez, and many others), and at UIUC (Dick Alkire, Chip Zakoski, Marc Snir, and many, many others). That is the one constant in my career, and I cherish each and every one of them. They have taught me much of what I know, and they have always been there when I needed them. I only hope that I have also added to their lives.

In closing, as one of my favorite authors, Kurt Vonnegut, often says in his stories: "So it goes."

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