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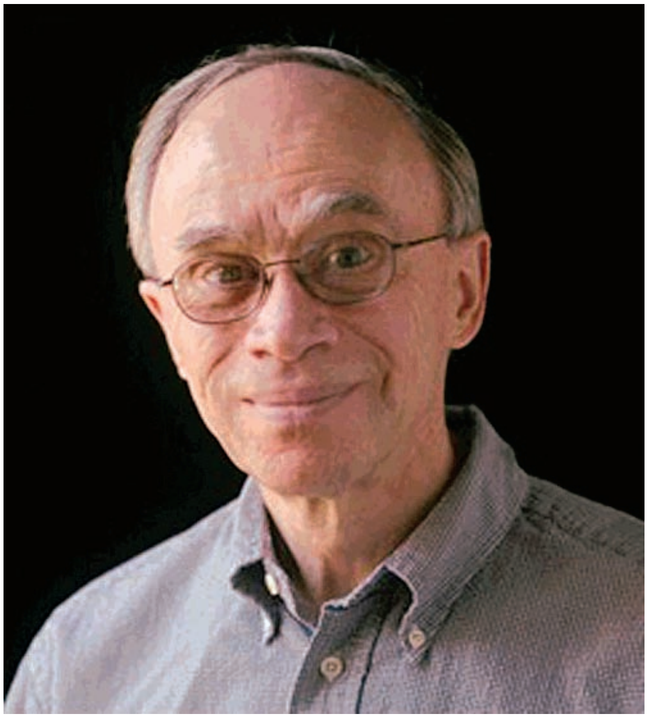

The Short Story of My Life and My Career in Quantum Propagation

At first I was surprised, maybe shocked would be a better way of describing it, and somewhat later delighted when Eric Bittner told me of his plans to organize this Festschrift. I did not anticipate that such an honor would fall in my direction. Thanks also to Editor George Schatz for agreeing to go along with this venture. In addition, I would like to thank the many contributing authors for their efforts. Let us start at the beginning.

My father grew up in Columbia, Mississippi, where my grandfather was the accountant for a logging operation. When my dad was 16, he decided that he had learned all that he needed from high school, so he went off to Georgia Tech, where he graduated with a degree in mechanical engineering. After a short stint in Milwaukee with an engine manufacturer, he joined a consulting engineering firm in Chicago. For many years, he was involved in the design of steam power plants, but gradually moved into commercial air conditioning. My mother was born in central Wisconsin, in a German emigrant community. My grandfather, a merchant, eventually moved the family to Chicago, where my mother finished high school. She then worked for a number of years for law firms in the Loop. My dad played saxophone at night in clubs on the North Side. My mom and dad met one evening when she happened upon a club where he was playing. After they were married, they lived in an apartment on the far North Side, a few blocks from Lake Michigan. That is the area where I was born and spent my first 3 years. However, because of the excellent reputation of its public schools, my parents bought a house in Oak Park, the first suburb encountered when traveling west from the Loop. With its many elegant homes dating from the 1880s to 1910s and streets shaded by towering oaks and elms, it was a wonderful place in which to grow up.

In the basement of our home, my dad had a well-equipped work shop, with many metal and wood working tools, most of which I learned to use before I graduated from Longfellow Elementary School. In addition, he had a well-equipped photography lab, where he developed film and made prints. This is where I began mixing chemicals to perform my first chemistry

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experiments. Some of what went on in this lab was not known to my parents (until years later)! With courageous friends, we experimented after school with pyrotechnics and explosives. We packed metal pipes with our gun powder formulations and exploded them near the railroad tracks. This was great fun! It amazes me that no one was injured during these experiments.

I attended Oak Park-River Forest High School, located just a few blocks from the site of Frank Lloyd Wright's home and studio and where many of his distinctive Prairie Style homes were built. In addition to the exceptional math and science courses, I especially enjoyed a course in metal working, where I learned to arc weld steel plates and to make aluminum castings. After getting off to a bad start and then repeating Algebra I in summer school, I did very well in my remaining 3 years of math courses. Just after graduating, I worked for a summer in a factory on the West Side of Chicago, loading and unloading trucks, and sometimes running a punch press.

In September 1957, I began daily commutes on the "L-train" from Oak Park to the South Side campus of the Illinois Institute of Technology. During my 4 years there, I enjoyed the science and math courses, which were rigorous and demanding. The organic chemistry lectures and labs were fun, especially organic lab, because of the smelly things that we synthesized. I had two outstanding teachers for my three physical chemistry courses, Peter Lykos and Audrey Companion, both theoretical chemists who had graduated from the Carnegie Institute of Technology. During the fall semester of Peter's course, one of those "life-changing" events occurred. For an experiment in p-chem lab, we had to write a program (in octal!) for a Univac computer to do a least-squares fit of the measured vapor pressure of a liquid versus $1/T$. This was the first time that undergraduates were required to learn how to program a computer in a university class! During my senior year, I did undergraduate research with Audrey, on the reflectance spectra of titanium oxides. I was very happy when our paper appeared in the *Journal of Physics and Chemistry of Solids*. At IIT, I had the opportunity to take an exceptional amount of quantum mechanics. In addition to a modern physics course and Audrey's quantum chemistry course, I took a year-long graduate physics course, which covered much of David Bohm's *Quantum Theory*. Little did I know at the time that some of Bohm's work would significantly influence my later research. During my final year at IIT, my choice of graduate schools was strongly influenced by Peter and Audrey.

I went off as a graduate student to Carnegie Mellon University (at the time it was the Carnegie Institute of Technology) specifically to join Bob Parr's group. Bob has always impressed me so much; not only is he a great scientist but he was also an inspiring teacher who gave memorable lectures. It was exciting to join his group, even though I felt that I did not know anything. John Pople was a visiting Professor that year, and I had the opportunity to take two courses from him. The year started off great, but in October I went into shock when I heard that Bob would be leaving for Johns Hopkins. With little hesitation, I decided to go to Baltimore with him; after all, at the time I had never been East of Pittsburgh. Upon arriving in Baltimore, I found an efficiency in an 1880s-era row house a few blocks from the Hopkins Homewood Campus. In addition to the Parr group, Klaus Ruedenberg came with his group from Iowa State. Three of his graduate students, Ken Miller, Ernie Mehler, and Dave Silver, had worked with Peter Lykos when they were chemistry undergraduates at IIT, so there were four of us from IIT studying theoretical chemistry at Hopkins. For my first project, Bob suggested working on "one-electron perturbations in self-consistent field theory", so I began learning what I needed about self-consistent field theory. After completing this study, I used the integral Hellmann–Feynman theorem to analyze the origin of the internal rotation barrier in ethane. Our final paper was a general analysis of integrated and integral Hellmann–Feynman theorems. At the start of my third year at Hopkins, I applied for a 2-year NSF Postdoctoral Fellowship and was delighted when I received this award. In August of 1965, it was off to England for a year.

My year in England was spent with Roy McWeeney at the University of Keele, in the Midlands. I worked on a hard project, the so-called *N*-representability problem, but not much progress was made by me (or anyone else at that time). It was now time to launch my career in dynamics. In August 1966, I joined the group of Martin Karplus, who had just moved to Harvard from Columbia. My office, in Prince House, was shared with Lee Pederson and Keiji Morokuma, with whom I enjoyed many informative discussions. My research that year involved the analysis of angular distributions and energy transfer for the hydrogen isotope reactions. I also spent considerable time studying books and papers on formal quantum scattering theory. In the spring of 1967, while strolling down one of the "infinite hallways" at MIT, I happened upon a showing of movies at the Science Teaching Center. These were among the first to illustrate quantum wave packet scattering from rectangular barriers and wells. I wondered if this approach could be extended to chemical reaction dynamics and that gave birth to the first research project that I worked on after arriving at UT. It was now August 1967, time to drive from Boston to Austin.

It is time to fill in a gap, concerning how I came to accept at faculty position at Texas. In the fall of 1965, when I was in England, I was surprised to receive a letter from Prof. W. A. Noyes, Jr. at the University of Texas. Albert had recently retired from the University of Rochester and came to Texas, in part to recruit physical chemists. He was interested in having me visit Austin, but we delayed this until the fall of 1966. The morning after my seminar, the Chairman made me a verbal job offer and I accepted shortly thereafter. While Albert was in the recruiting mode, the Department hired four Assistant Professors in physical chemistry, who had only one thing in common: our last names all started with "W". When I arrived at UT, the university had just installed a CDC6600, the fastest supercomputer available at any university. It is significant that UT is currently installing what will be the fastest supercomputer on earth, a 529 Teraflops Sun Microsystems facility with over 60 000 CPU cores.

Now, time to fill in a second gap, this time on the personal side. At the start of the Spring semester at Carnegie Tech, I met Linda, another graduate student. In May she took a job in Cincinnati, just as I was about to leave for Baltimore. However, she later accepted a job in Baltimore, where we were married. We have a daughter, Beth, born in Austin, who is very proud to be a native Texan.

As a new Assistant Professor, I wondered how long it would take to build up a research group, but this issue was quickly resolved. Just as I was settling into my office, I was visited by two students, both of whom were searching for a research advisor. After a couple of visits, I was delighted when both Jim Jackson and Ed McCullough, in effect, "created" my group. The first month at UT was a success! Jim began by computing resonance states in atomic collisions. I told Ed about the wave packet movies that I had seen earlier at MIT, and he began studying wave packet dynamics for the collinear $H + H_2$ reaction. Ed came up with an excellent computational method: discretize the Schrodinger equation on a large grid and use the

Crank−Nicolson algorithm for time propagation. For a series of time steps, Ed made density and flux maps and discovered "quantum whirlpools" in the collision complex. We were delighted when our paper was accepted in 1971 as a Communication in the *Journal of Chemical Physics*. Jim followed up on this with a time-dependent wave packet study of the planar $H + H_2$ reaction. Later, Aron Kupperman and his students Joel Bowman and Don Truhlar found vortices when they analyzed stationary-state wave functions for the collinear $H + H_2$ reaction.

After our first wave packet paper was published, John Weiner at Brown University pointed out their studies on Gaussian wave packet propagation using a technique that I was not aware of, the particle method. I became excited about this method and began investigating it during the summer of 1972. I spent almost all summer trying to get the method going for wave packet barrier scattering problems. The numerical methods proved to be unstable, so I reluctantly abandoned this approach. However, about 25 years later, I returned to "particle methods" with the determination to get them running. As we will see, the quantum trajectory method was born when particle methods started to work.

In addition to the time-dependent wave packet studies, in 1969 we started on time-independent studies of reactive scattering. From the late 1960s until the late 1970s, my group grew and included Paulette Middleton, Bob Walker, Susan Harms, Alan Elkowitz, Don Miller, Sue Latham, and Joe McNutt. Around 1970, we published the first of a series of studies using natural collision coordinates (NCC) that Rudy Marcus introduced in the late 1960s. One of these papers developed the Hamiltonian in NCC and introduced hindered asymmetric top states as a rotational basis set for three-dimensional reactive scattering problems. The theory and application of these functions was greatly extended in papers with Bob Walker, Paulette Middleton, Susan Harms, and Alan Elkowitz. Alan used the NCC-hindered asymmetric top basis-set approach to calculate total cross sections for the three-dimensional $H + H_2$ reaction. In late 1974, the manuscript presenting our results was accepted in the *Journal of Chemical Physics*. It was a pleasant surprise to find that our Communication and the one by Aron Kupperman and George Schatz would appear back-to-back in the journal.

In the meantime, Mike Redmon began our studies on the $F + H_2$ reaction using the best-available potential surface, "Muckerman 5". This reaction continued to attract our attention for the next 10 years. During this period, Yuan Lee and his group reported recoil velocity-scattering angle maps and there was evidence for resonances playing a role at some collision energies. Joe McNutt performed density and flux analyses for the collision complex for the three-dimensional reaction, and John Hutchinson carried out detailed classical trajectory studies. Don Miller developed basis sets that coupled electronic and nuclear angular momentum and Bob Walker (by then, a staff member at Los Alamos) and I carried out the first scattering studies, which incorporated electronic nonadiabatic effects. Unfortunately, the potential surfaces available at this time had deficiencies in the collision complex. Years later, an accurate potential surface was reported by H. J. Werner and co-workers in 1991 and accurate quantum reaction cross sections were reported by David Manolopoulos and co-workers during the period 1996−2000.

Starting with our calculations on the $F + H_2$ reaction, the role of resonances in reactive collisions became a research focus. During the late 1970s and early 1980s, Curt Shoemaker used formal scattering theory as a basis for computational studies of Feshbach resonances in model reactive systems. A few years later, Clay Marston used a semiclassical quantization scheme to predict resonance properties associated with periodic and quasiperiodic orbits in the FHH collision complex. During the early 1980s, I was fortunate to share a research grant with Eli Pollak at the Weizmann Institute and we focused on developing semiclassical models for resonances in the three-dimensional $H + H_2$ and $F + H_2$ reactions.

In the late 1960s I described a model, the RLM (rotating liner model), for reactions proceeding through a linear collision complex. When later extended (by other groups) to include bending modes, it evolved into the BCRLM (bending corrected rotating linear model). In collaboration with Gabriel Balint-Kurti, the BCRLM was used to compute cross sections for the three-dimensional $H + Cl_2$ reaction. Don Miller then extended this type of model to bent collision complexes and applied it to the $Li + HF \rightarrow LiF + H$ reaction.

Following pioneering initiatives by Don Truhlar, Don Kouri, Bill Miller, and others on the use of variational methods in quantum scattering theory, in the late 1980s we began using the Kohn, Schwinger, and Newton variational principles. T. G. Wei was involved in some of these studies, but the driving force was Ramu Ramachandran, one of whose studies led to a paper with the pedagogic title: "How Variational Methods in Scattering Theory Work". Xudong Wu and Mike D'Mello implemented a variational method for including the geometric phase in reactive scattering calculations.

A significant rebirth of our work on quantum reactive scattering arose through the productive collaboration between David Manolopoulos and Mike D'Mello. In 1988, David introduced an effective translational basis set for scattering calculations, the Lobatto shape functions. In collaboration with Mike, these functions were used in conjunction with the Kohn variational principle for extensive quantum scattering calculations on the three-dimensional $F + H_2$, $F + D_2$, $H + H_2$, and $H + D_2$ reactions. Our computed rovibrational state-resolved differential reaction cross sections for the latter reaction were in excellent agreement with crossed molecular beam results. Our manuscripts describing these comparisons led to articles in *Science* in 1994 and 1995. In the late 1990s, Ramu and I collaborated on studies of the $O(^3P) + HCl \rightarrow OH + Cl$ reaction, which ranged from the development of new potential energy surfaces, through classical and quantum scattering calculations, to the calculation of thermal rate constants.

Starting around 1980, laser−molecule interaction became another research theme in my group. This work began when Steve Leasure compared direct versus multiphoton excitation pathways in the HF molecule. Soon thereafter, we started using Floquet theory to deal with periodic perturbing fields. Claude Leforestier used this theory in conjunction with *R*-matrix theory to study molecular multiphoton dissociation. In a further study of laser-induced dissociation, we introduced an absorbing potential to damp the outgoing waves, possibly the first use of such a potential in quantum dynamics calculations. Kent Milfeld combined the Magnus approximation for the propagator with the Floquet theory and applied this method to the HF molecule. Man Mohan, visiting my group from the University of Delhi, in a project with Kent, used Floquet theory to describe laser-assisted reaction dynamics. Bob Brown used his extensive background in nonlinear dynamics in studies of molecular multiphoton dissociation. He showed that classical-phase space structures, resonance zones and Cantori, can act as bottlenecks for multiphoton absorption and can have significant effects upon wave packet localization, diffusion, and dissociation. The latter results appeared as a 1986 *Physical Review* Letter.

Johnny Chang used a very interesting approach, artificial intelligence (AI) tree-pruning techniques, to preselect paths for dynamical studies of multiphoton excitation. In the mid-1980s, Nimrod Moiseyev worked with Johnny on a method for computing highly excited eigenstates, the first step of which involved designing contracted basis sets with tree-pruning techniques. In some of our later studies dealing with laser−molecule interactions, Joe Yao, Tom Flosnick, and Chona Guiang investigated the use of Lanczos recursion to compute transition amplitudes in laser fields, the development of effective Hamiltonians for IR multiphoton absorption, and the design of laser fields to achieve wave packet localization in a molecule embedded in a solid matrix, respectively. The latter study, completed in 2000, was the last of our publications in this area of investigation.

Even though computational resources were steadily improving, in the early 1980s it was challenging, if not impossible, to "directly" diagonalize matrices with dimensions over about 1000. In 1982, Andre Nauts and I began exploring alternate approaches to the large matrix eigenproblem. Until an eventful day in 1983, it seemed as though we were stuck with this size of problem. Bob Silby from MIT was our visiting seminar speaker and I inquired if he knew of ways to go beyond the "10^3 bottleneck". He referred us to Volume 35 of *Solid-State Physics*, and after skimming several chapters, I realized that the Lanczos recursion algorithm provided just what we were seeking. Using only matrix−vector multiplication, Lanczos develops a sequence of tridiagonal matrices of increasing dimension, diagonalization of which yields approximations to the eigenvalues of the original large matrix. In addition, Andre and I realized that it was possible to simultaneously generate transition amplitudes between various pairs of states. Within about a week, we had a fast computer program that produced accurate eigenvalues and residues for matrices having dimensions of about 5000. Because the transition amplitudes are the residues at poles of the Green function, this method was termed the recursive residue generation method (RRGM). Before our first manuscript on RRGM, which appeared in *Physical Review Letters*, it is probably fair to say that the Lanczos algorithm was largely unknown to workers in quantum dynamics.

During the next several years, the RRGM was developed further, with co-workers including Jose Castillo, Israel Scheck, Jean-Philippe Brunet, and my UT colleague Rich Friesner. The work with Israel on a diagrammatic approach to the "chain parameters", namely, the diagonal and off-diagonal elements in the tridiagonal matrices, emphasized the roles played by linked and unlinked diagrams. Around 1990, Claude Leforestier, Rich Friesner, Jean-Philippe Brunet, and Joe Bentley used the RRGM to compute both IR absorption and stimulated emission pumping spectra. Also during this period, Csilla Duneczky used Lanczos to recursively develop individual S-matrix elements for scattering problems. In order to accelerate convergence of the algorithm for interior eigenvalues, it is advantageous to drive the recursion with the inverse of an energy shifted Hamiltonian, the Green function. Todd Minehardt implemented this approach during the period of 1995−1997. I am pleased that others, especially Tucker Carrington and Hua Guo, have greatly extended the Lanczos methodology, so that it is now very effective for huge matrix eigenproblems.

During the 1990s, we used the RRGM to study CH vibrational overtone relaxation in benzene and fluoroform. The benzene studies, in collaboration with Claude Leforestier and Christophe Iung, began in 1990, when I was a Visiting Professor at the University of Paris-Orsay. When we started, full 30-mode benzene appeared to be a formidable undertaking, so we began with reduced dimensionality models. Because the primitive vibrational basis sets were very large, we first used a contraction method to develop smaller basis sets. The RRGM was then used to compute stick spectra and survival probabilities for relaxation from CH($v = 2,3$). Within a few years, we completed time-dependent studies of CH overtone relaxation in 21-mode planar benzene. Todd Minehardt played a key role in later studies on the mechanism for energy redistribution from CH($v = 2$) in full 30-mode benzene.

While the benzene studies were going on, Andy Maynard investigated relaxation from the CH($v = 1,2$) overtones in nine-mode fluoroform. In other studies related to intramolecular dynamics, Sarah Schofield computed survival probabilities and wave packet localization lengths for many-dimensional systems composed of coupled anharmonic oscillators. Good agreement was found with predictions from statistical theories developed earlier.

In January 1998, I decided to take a fresh look at the particle methods that I had tried (with little success) back in the early 1970s. That spring, Courtney Lopreore was searching for a research group, and I was glad that she was courageous enough to work on "Bohmian mechanics". Over the coming months, we gradually improved the numerical methods but were unable to run long enough for good wave packet splitting in barrier scattering problems. However, in the fall, we implemented several changes that greatly improved the situation. One of these involved use of least-squares fitting procedures to evaluate spatial derivatives needed in the equations of motion for the trajectories. With these enhancements, we were immediately able to propagate for much-longer times. We now had the beginnings of the quantum trajectory method (QTM) and were delighted when our manuscript was accepted for publication in *Physical Review Letters*. The QTM was further developed over the next several years. Our work was greatly aided when we began to collaborate with Eric Bittner, at the University of Houston. Over the intervening years, Eric and his students have contributed greatly to the development and application of quantum trajectory methodologies. Also, in collaboration with Don Kouri and Dave Hoffmann, we explored the use of distributed approximating functionals (DAFS) for spatial derivative evaluation.

We then began to use the QTM for more-difficult problems. Kyungsun Na propagated an ensemble of quantum trajectories for dissociative systems with up to 15 bath modes coupled to the reaction coordinate. However, most of her work involved the use of quantum trajectories to analyze the mechanism for decoherence in a model system. While visiting Gerard Parlant at the University of Montpellier in 2000, we decided to apply the QTM to electronic nonadiabatic processes. Gerard derived the equations of motion and Courtney propagated ensembles of trajectories and analyzed the dynamics. In late 2001, we began to implement additional computational methods borrowed from classical fluid dynamics. Adaptive moving grid methods, including arbitrary Eulerian−Lagrangian (ALE) grids, offered new ways for us to both control and stabilize the trajectory dynamics. Corey Trahan and Keith Hughes worked on trajectory propagation with adaptive moving grids. In addition, Lucas Pettey developed a novel hybrid method that combines the best features of moving and fixed grids.

A significant development occurred when Corey Trahan suggested an alternative to using fitting methods to evaluate the spatial derivatives needed for trajectory propagation. He proposed integrating a system of differential equations for these derivatives along individual trajectories. I told him that there would probably be problems with such an approach and that he should continue working on other things. Fortunately, he ignored my advice and had the method, termed the derivative propagation method (DPM), working within a couple of days. Message for students: It is sometimes best to ignore the advice of your professors! Keith Hughes contributed greatly by extending and applying the DPM. In addition, we used the DPM to develop trajectory solutions for phase space distribution functions and Brad Rowland later analyzed the forces on trajectories for Wigner ensembles undergoing barrier scattering. In addition to propagating individual DPM trajectories, we continued to develop and apply methods involving the propagation of trajectory ensembles. Dima Babyuk extended the QTM to reactive scattering problems involving systems with hundreds of vibrational modes coupled to the reaction coordinate.

Recently, we have concentrated on a different approach to quantum trajectories. If the wave function is expressed in terms of the complex-valued action function (essentially, the phase of the wave function), then this function satisfies the complex-valued Hamilton−Jacobi equation. Chia-Chun Chou, Brad Rowland, and Julianne David are currently using complex-valued quantum trajectories to solve this equation. Much insight have arisen from these studies, and it appears that these methods may be effective for multidimensional barrier transmission problems.

Although the complex plane brings the main part of this story to an end, I would like to append some contributions that were not mentioned earlier. David Clark, T. G. Wei, and Clay Marston developed a semiclassical model for shock wave transport in molecular crystals. Jim Wright, Joerg Senekowitsch, T. G. Wei, and Chona Guiang were involved in developing potential surfaces. Joe Bentley and Chang-Ming Huang computated high-energy vibrational eigenstates for the planar acetylene molecule. Roman Nalewajski explored the collisional perturbation of regular and chaotic intramolecular dynamics. Amrendra Vijay developed a spectral filtering method based upon Hermite polynomials. In research orthogonal to quantum dynamics, Elizabeth Thomas, Eva Simmons, and Paul Patton developed a successful computational model for vertical signal processing in the cerebral cortex.

In conclusion, I give great credit to my graduate students and postdoctoral associates and to the visiting scientists who spent time with my group. Not only did they contribute many ideas and most of the results, it was fun to work with them, and all of this made it possible for me to have a great time doing “quantum propagation”.

Robert E. Wyatt