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Autobiographical Sketch of William Hughes Miller[†]

I was born in rural Mississippi (Kosciusko, earlier Red Bud Springs) on March 16, 1941, but within a few years my family moved to the "big city" (Jackson, pop. ~90 000 in the 1950s), where I grew up. The Millers and Hughes (my mother's family) had been in Mississippi for several generations; they were all of Scots-Irish origin (McAffee was another frequent name in the family tree), having come to America in the mid eighteenth century, settling originally in western North Carolina. Both of my parents (Weldon Howard Miller and Jewell Hughes Miller) finished high school, and my mother taught school for several years before she married. She finished first in her high school class (of ~20) and had a special affection for mathematics (though never having had anything beyond algebra and geometry). Most of my aunts and uncles remained small farmers, so I had many enjoyable summers with my country cousins, from whom I learned about milking cows (at 4 am!), riding horses, squirrel hunting, and so forth. Like many young boys, my main interest in early years was sports, and it was a great source of pride to have been the short-stop on the Little League baseball team that won the state championship (though I was devastated when we lost to Arkansas in a tri-state play-off also including Louisiana).

My first significant academic experience was in the fifth grade. My teacher, Miss Tessie Cork, was the terror of the school, a super-strict disciplinarian—in the days before corporal punishment was forbidden—but also an excellent teacher. I responded positively to the challenges she presented and decided that I liked learning, particularly mathematics but also history and English grammar. My math teacher in high school, Mr. John Ethridge, was also the tennis coach, and with his suggestion and encouragement, I took up tennis. (The competition in my predominantly rural state was not so great, and my partners and I won the state championship in mixed doubles and boys doubles, respectively, in my junior and senior years.) My Latin teacher for three years, Miss Annie Vernon Brent, was also an extremely dedicated teacher who made even learning Latin interesting. While in high school, I was attracted to the possibility of attending the US Military Academy at West Point (perhaps all that Robert E. Lee stuff got to me), even going so far as to obtain an appointment from my local Congressman. In the end, though, I decided that this might not be the wisest course.

The launch of Sputnik by the USSR in the fall of 1957 had an enormous impact on many people in my age group. (I have often thanked my Soviet, now Russian, colleagues for the positive effect this had on my life!) All of the sudden, there were extra math and science courses in the high schools, and it even became (almost) fashionable to be interested in them. General Motors instituted a set a national scholarships, and with one of these, I entered Georgia Tech as a Chemical Engineering major in 1959. (I had always liked math and I enjoyed the chemistry class that I had in high school, so this seemed like a reasonable synthesis of the two.) My freshman chemistry proffessor, Peter B. Sherry, gave an extremely stimulating Honors Chemistry course, talking mostly about molecular orbitals and the Schrödinger equation (even though I did not then know what a differential equation was) and very little about stoichiometry and solubility products. I immediately changed my major to Chemistry! Georgia Tech was a great environment for me; there were very few breadth requirements in those days, and I took all my electives in the Math Department. My senior year, I even taught one of the freshman calculus sections and found teaching extremely rewarding (much more so, I must say, than I did as a TA in freshman chemistry lab when I was a graduate student).

The chemistry faculty at Georgia Tech recommended that I go to Harvard for graduate school; their reasoning was not particularly deep ("... you′re going to have to compete with those guys when you get out, so you might as well start early, and on an equal footing ..."), but it was nevertheless very good advice. Dudley Herschbach had just returned to Harvard (from Berkeley) in 1963, the year I started graduate school, and with his charisma, I was captivated by the idea of studying chemical reactions at a completely molecular level. I was firmly committed to doing theoretical research and had wanted to work for Herschbach, but Dudley was (quite wisely) more interested at that time in recruiting able minds (and strong backs) to work in his molecular beam lab. He tried to talk me out of my theoretical proclivity ("... chemistry is primarily an experimental science ...") but to no avail. (Interestingly, Dudley has in recent years taken on some theoretical students, working on some very novel ways of solving the many electron Schrödinger equation.) Fortunately for me, E. Bright Wilson returned from a sabbatical during my first year, and in a departure from his earlier principles ("... graduate students should be trained experimentally ...") decided to take a few students to try some novel theoretical approaches. Perhaps this is because he was then, as Dudley is now, at a stage in his career where he had little left to prove and simply wanted to have some fun!

Bright Wilson was the absolutely perfect research director for me. He suggested some interesting beginning directions, but then pretty much left me alone so long as he felt I was not floundering. Even when I began to drift increasingly toward scattering theory and molecular collisions, not a field of his primary interest, he never tried to steer me away. He was a father figure in the highest sense. Also, there was also an incredibly stimulating group of fellow graduate students at Harvard in those days; Bill Reinhardt and Frank Weinhold were also in Wilson's group (Frank started working on aspects of density functional theory, Bill on relativistic effects in electronic structure, and I on lower bounds for eigenvalue problems), and Karl Freed was in Bill Klemperer's group. A few years ahead of us were Mike Zerner, Russell Pitzer, Roy Gordon, and Roald Hoffmann, and few years behind were David Chandler, Marshall Newton, Herschel Rabitz, Paul Brumer, and Bernie Shizgal, among others. During my graduate years, I had many friends in Herschbach's group, notably Walter Miller and Sanford Safron, and thus I absorbed much of the molecular beam folklore from them.

When I was home for Christmas during my third year as a grad student (1965), I ran into Margaret Ann Westbrook, a girl with whom I had gone to school through junior high and high school but who was much too sophisticated for me in those years (being Homecoming Queen, Miss Provine High School, etc.) Upon learning that she was not yet married, I set out to try to change that (e.g., I managed to get to the Sanibel

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Symposium in January 1966, and we had a rendezvous in Atlanta!), and we were then married in June, 1966. It still boggles the minds of our two daughters that this all came about in just six months! (I wish I had had a tape recorder when I told Bright Wilson of my plans, and he commenced on a very serious discourse on why it was probably not wise for graduate students to be married!)

After finishing my thesis, Margaret Ann and I set off for a most enjoyable postdoc year in Freiburg (hosted by Prof. Christoph Schlier). I was primarily involved in trying to work out a general approach for carrying out quantum reactive scattering calculations, a topic that I came back to again in the late 1980s, when postdoc John Zhang carried out some timely calculations using this approach (plus the S-matrix version of the Kohn variational principle) to address the question of whether resonances are observable in $H + H_2$ reactive scattering. But perhaps the most important consequence of this year in Germany was all the friends I made there, many of whom went on to academic careers, planting the seeds for a wonderful series of more than a dozen German postdocs who have come to Berkeley over the years to work with me. After Freiburg, it was back to Harvard for another postdoctoral year, in the Society of Fellows (I concur with the oft-stated view that being a postdoc is the greatest of all possible situations, except for the uncertainty of one’s future!), during which time I received a letter from Bruce Mahan (then department chair) offering an assistant professorship at Berkeley. Fritz Schaefer was also hired that year, and many years later, Fritz and I asked Bruce how it was that Berkeley hired two theorists the same year (something that departments would be very reluctant to do nowadays); Bruce responded something like "... we really did not give it a lot of thought, we just hired two of you, hoping that one might work out ..."!

My first encounter with semiclassical theory had been in a course of Dudley Herschbach’s, where he talked about Ford and Wheeler’s semiclassical treatment of elastic scattering [see *Theo. Chem. Accts. 103*, 236 (**2000**) for my perspective on the importance of this work]. I was convinced then that this was what one needed to do for inelastic and reactive scattering. I was also very much influenced by the fact that Martin Karplus, Don Bunker, and others had shown the practicality of carrying out numerical classical trajectory calculations to describe the dynamics of elementary bimolecular and unimolecular reactions. These thoughts gestated for several years, during which I tried to learn everything I could about the WKB approximation. It all came together during my first year at Berkeley, 1969−70, and led to a series of papers in the early 1970s on the “classical S-matrix”, i.e., a semiclassical approximation for the scattering amplitude for inelastic and reactive scattering that was based on the (numerically computed) classical trajectories of the process. It was patterned very much after the Ford and Wheeler treatment of elastic scattering, with things such as a “classical deflection function” for inelastic scattering, and so forth. Because this topic has always had a special place in my heart, it is been particularly satisfying that there is currently a revival of interest in using semiclassical theory (via the initial value representation) to provide a practical way of adding quantum mechanical effects to classical molecular dynamics simulations of complex molecular systems. For a review of this work, see a Feature Article I just recently wrote for the *Journal of Physical Chemistry*.

In the early 1970s, Phil Pechukas wrote some very illuminating papers on transition state theory (TST), emphasizing its fundamental dynamical assumption that there exists a “dividing surface” that no classical trajectory crosses more than once. (This dynamical view of TST was clear in Wigner’s original papers of the 1930s but was largely lost in the huge volume of work using Eyring’s thermodynamic interpretation, which is, of course, useful for other purposes.) Phil’s work sparked my interest in trying to find a fully quantum mechanical theory based on this dynamical assumption. There were many twists and turns in this work, starting with some papers in 1974 and 1975 on a formally exact quantum expression for the reaction rate and its semiclassical limit. I had interesting discussions with David Chandler on the topic in the following years, and in 1983, I wrote a paper (with Steve Schwartz and John Tromp) on quantum mechanical reactive flux correlation functions. Finally, in the early 1990s (with postdocs Tamar Seideman, Uwe Manthe, and others), we learned how to implement these ideas in an efficient way to calculate thermal rate constants $k(T)$, and microcanonical cumulative reaction probabilities $N(E)$. Though these fully rigorous quantum approaches were no longer TST, one could nevertheless see vestiges of it in both the results of such calculations and the methodology itself. [This work is also reviewed in a *J. Phys. Chem.* Feature Article, 1998.] As a byproduct of this work, the 1975 paper on the semiclassical limit of these formally exact rate expressions produced the “instanton” approximation (which involves a classical periodic orbit on the upside-down potential energy surface); the instanton was discovered independently (but later!) in the physics community and has seen a variety of applications. Also, in this 1975 paper was the definition of the cumulative reaction probability for a chemical reaction (the sum of the squares of the reactive S-matrix elements over all open channels of reactants and products), an expression also independently discovered (also later!) in physics as the “multichannel Landauer formula” for the transmission of electrons through various media.

There is one other scientific topic I would like to mention, namely the “reaction path Hamiltonian”. This work was largely motivated by many discussions with Fritz Schaefer about the progress quantum chemists had recently made in computing gradients (and even Hessian matrices) of potential energy surfaces, making it much more practical to search out and find stationary points on a potential surface and to follow the steepest descent path from a transition state down to reactants and products (Fukui’s “intrinsic reaction coordinate”). The idea was to build an approximate dynamical treatment based on this minimum energy path, and in many ways, it was simply an extension to general polyatomic systems of earlier work that Rudy Marcus had done on “natural collision coordinates”. This idea came to fruition when Nick Handy spent a sabbatical year at Berkeley, 1978−79, adding his familiarity with spectroscopic Hamiltonians. And though this work was in many ways less theoretically sophisticated than semiclassical theory, reactive flux correlation functions, and state-to-state reactive scattering, it has perhaps had a greater impact chemically because it is so simple to implement with available quantum chemistry packages, allowing one to find the (variationally best) transition state, include (approximately) the effects of reaction path curvature on tunneling corrections, etc., extending to reactions in general polyatomic systems these notions that Marcus had introduced earlier with his “natural collision coordinates”.

Acknowledgment. All of us know how much one’s accomplishments depend on the talent and dedication of their coworkers. Perhaps the most important benefit of having been at Berkeley throughout my career has been the outstanding quality

of graduate students and postdocs I have been privileged to work with. Their names are listed in the List of Colleagues, Research Groups, and Alumni, and it has been a tremendous pleasure to have seen so many of them back here for my 60th birthday. Though we spend our professional lives with our graduate students and postdocs, we live our REAL lives with our families, and in this regard, I have been truly blessed. Margaret Ann and I feel extremely proud (and lucky!) to have two such wonderful daughters: Alison was an undergraduate at Wesleyan University, finished her PhD in developmental psychology at Michigan last spring, and is now postdocing at Brown, while Emily graduated from Yale and will be receiving her MBA from Berkeley this spring (and will then be joining the real world!). They have been and continue to be a great source of joy. And there is one final essential member of the "family" who is well-known and much appreciated by all present and former members of my research group: Cheryn Gliebe, who has been my administrative assistant for many years. You all know that she is the person who makes things happen so efficiently around here, and most pleasantly so. We can never thank Cheryn enough for going the extra mile so many times to get the job done in first-class style.