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A Journey Through Chemical Dynamics

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Abstract

The charge with the invitation to write this autobiographical article was to describe what led me to a career in science and to choose the specific topics and scientific directions I have pursued. This is thus a very personal story and by no means a scientific review of the work that is mentioned. As will be clear, this journey was not an orderly, well-thought-out plan, but just "happened," one step after the other.

EARLY YEARS

Unlike authors of other autobiographical articles that I have read in this journal, I never had a chemistry set while growing up, or in fact any significant academic exposure. My parents grew up in rural Mississippi, my father not finishing high school; it was not really considered that important in small farming communities in the South in the early part of the twentieth century. My mother did finish high school, attending a boarding school in the area for her last two years; she taught school for several years afterward, until she was married (married women were not allowed to teach in public schools at that time, for you know what might happen with married women). She often said that mathematics was her favorite subject, especially Euclidian geometry, having to prove various theorems with only a compass and a straight edge. Of course, she never was introduced to "the calculus" (as it used to be called), or even trigonometry.

During World War II they moved to the "big city," Jackson (population ~90,000 during the 1950s), and that is where I grew up (born in 1941). My father's first job there was driving a milk truck, then working as a warehouse manager for a beer distributor, and finally they bought and operated a launderette; these were the years when most people did not have washing machines (much less dryers) in their homes and before coin-operated ones. (I can remember my father saving, "But we don't know anything about running a laundry," and my mother replying, "Yes, but we know how to work!") I spent my early teenage years at the clothes-folding table on weekends. The public schools I attended were certainly not the Bronx High School of Science but nevertheless provided good solid basic education. Many of the best, and most dedicated, teachers were "old-maid school teachers," i.e., women who never married. They were also extremely strict disciplinarians, something that I am sure would be illegal nowadays. My favorite subject was mathematics, although I also enjoyed history and English grammar (e.g., diagramming sentences); about the only things I really disliked were writing assignments in English class-and, of course, what is it that I have done most of my life but write papers! (It is much more interesting, though, to write when you have something you want to say and explain, rather than when given some artificial, assigned topic.)

However, like many small-town boys, one of my main interests was sports. Little League baseball arrived in Jackson when I was 9, so I had a full three years of it. (Our All-Star team of 1953 won the state championship.) I played football in elementary and junior high school, where I was linebacker (being too slow to be a running back) but broke my collarbone in practice when tackling our fullback (Billy Earl Earnhart), thus ending my career in this field (probably fortunately). In high school, the math teacher who I had for several years, Mr. Ethridge, was also the tennis coach, and he suggested I try tennis, and in my junior and senior years, my partners and I won the state mixed and boys' doubles state championships, respectively. You must realize that tennis was not a major high school sport in this part of the country, so the competition was not very stiff. I also played on the freshman tennis team in college, and when we had a match with the University of Miami, I realized that there was another level to this game of which I had not previously been aware (**Figure 1**).

By far the most important event during my high school years, however, was Sputnik in the fall of 1957, the beginning of my junior year. It is hard to imagine anything nowadays having the impact that it did (even the more tragic events of 9/11). The entire country immediately focused on science/engineering education. Special (voluntary) "early morning" science classes were introduced in my high school before regular school hours began, and there were many scholarship opportunities that sprang up spontaneously. For example, within a few months, General Motors (GM) established 100 scholarships (with at least one per state so that New York and California did not get them all—geographical affirmative action!), which were determined solely from SAT



Figure 1

The author, upon winning the Georgia Tech intramural tennis trophy, spring 1963.

scores (doubling the math and adding the English)—no letters of recommendation, no selection committees, etc.; they were probably administered by a single secretary. (After a few years, GM began giving funds directly to universities and let them make the selections.) I had been planning to go to Mississippi State, but upon receiving a GM scholarship, I chose Georgia Tech. Why? I had never visited there and knew no one who had attended. It was my math teacher/tennis coach who made the suggestion, and it sounded reasonable to me.

GEORGIA TECH

Although chosen without much information, Georgia Tech turned out to be ideal for me. It was (and is) a highly regarded science/engineering school at the undergraduate level (and now also at the graduate level) and attracted many of the best students from the Southeast, for not so many people chose to go to college so far from home in those days. There were thus many smart, competitive, nerdy engineering types, and I loved it! One had to select a major when applying, and I chose chemical engineering because I had a good chemistry course my senior year in high school, and chemical engineering sounded like a good combination of chemistry and mathematics. Chemical engineering in those days, however, was much focused on building

refineries (heat transfer, process control, etc.), which did not thrill me much, but I had a stimulating honors chemistry course my freshman year, given by Peter Sherry. He talked a great deal about the Schrödinger equation and how it described chemical phenomena, and although I did not know what a differential equation was at the time, it sounded like just what I wanted to learn about, so I changed my major to chemistry. [Carl Lineberger (1) has also noted the inspirational influence that Sherry had on him.]

In those days, there was not much concern about making engineering students well rounded, so there were few humanities requirements, and I took all my electives in upper-division math courses, many of which (real analysis, point set topology, etc.) were not directly useful later in theoretical chemistry but nevertheless did provide a good mathematical foundation. Another positive result of this was that during my senior year, I was invited to teach an approximately 25-student section of freshman calculus (1-h lecture, 5 days a week). I enjoyed it immensely (and was probably paid a pittance, but it seemed very generous to me). Much later, when I began to think about an academic career, it was this positive teaching experience that convinced me how much fun and rewarding it could be—much more so, I must say, than the freshman chemistry lab sections I dealt with as a graduate student.

I suppose I was a junior at Georgia Tech before I realized there was something like "graduate school," when one of the professors said, "Billy (as I was called then), you're going to have to think about where you want to go for graduate school." I said that I could not do that because my scholarship and savings had been used up for Georgia Tech, and when he said, "Oh no, they pay you to do this," I said, "You must be kidding!" Anyway, after learning the facts of life in this regard, the question was where to go. Claude Woods, who graduated from Georgia Tech two years before me, had gone to Harvard (doing microwave spectroscopy with E. Bright Wilson and later taking a faculty position at the University of Wisconsin), and some on the faculty at Georgia Tech thought they should "spread their good students around" to the various major research universities. Also, Wilse Robinson, an earlier Georgia Tech graduate, had recently been promoted to Professor at Caltech, so several faculty members recommended that I go there. However, by this time I did not want to go to another "institute of technology" but rather a "real university" and had also decided that I wanted to do theoretical research. I had done undergraduate research with Jerry Whitten, then a graduate student at Georgia Tech, who had discovered Frank Boys's papers about using Gaussian orbitals in electronic structure theory, and I thoroughly enjoyed it. The University of Wisconsin looked most appealing (one did not visit prospective graduate schools in those days but rather just studied the catalogs) because of the Theoretical Chemistry Institute led by Joe Hirschfelder. However, during the winter of 1962–1963, I read that it was -30°F in Madison, Wisconsin, and I could not imagine what that must be like. Finally, one of the old timers (a native Virginian) at Georgia Tech said that I should really just go to Harvard: "You're going to have to compete with those Yankee SOBs when you get out, so you might as well start early, on an equal footing!" Whether this was the argument that convinced me, I am not sure, but it turned out to be a good suggestion.

HARVARD

My time as a graduate student at Harvard of course greatly expanded my horizons, and many members of my graduate class have remained friends and colleagues for life (Frank Weinhold, Bill Reinhardt, Karl Freed, and others). Fortuitously for me, the fall of 1963 was also the time that Dudley Herschbach was recruited back to Harvard (from Berkeley, where he had started and been rapidly promoted to tenure); he arrived with an evangelical fervor for studying chemical reactions at the level of single collisions in crossed molecular beams, and I was captivated by

the challenge of developing the theoretical methods, models, etc., to deal with this new area of "chemical dynamics" at the molecular level. At this time, however, Herschbach was primarily focused on recruiting students for his molecular beam lab and not much interested in taking on anyone to do theory (quite a wise decision on his part, although ironic because he has done some quite interesting theoretical work with students in his later years). So in this regard my timing did not look good, for Roy Gordon and Martin Karplus—both of whom would have been excellent choices for me—were not yet on the faculty.

Luck intervened, however, as E. Bright Wilson, who had been on sabbatical in Europe when I began graduate school, returned with an interest in taking a few students to do theoretical research. Even though there had been, and were, some "professional" theorists in chemistry—e.g., Oscar Rice, Henry Eyring, Rudy Marcus, Joe Hirschfelder, Martin Karplus, and others—the prevailing view was that students should be trained experimentally, and if they wanted to go off and do theory later in life, that was their own business. But as Wilson put it, he had finally come to the point where he thought it was OK if a student knew more about Fourier transforms than about stopcock grease. Bill Reinhardt, Frank Weinhold, and I eagerly joined up. The topic Wilson suggested for me was developing ways to calculate lower bounds to eigenvalues (i.e., energy levels) to complement the standard variational method that provides an upper bound. This was a fun project, and I actually came up with a new lower-bound equation (2) with which I carried out a calculation for the helium atom; it was too cumbersome, however, for much more.

However, my attraction to the new area of chemical dynamics was still strong, and I spent much time with friends in Herschbach's group (Walter Miller and Sanford Safron from my class and many others who came with Herschbach from Berkeley) learning the folklore of molecular beam experiments. Also, Bill Reinhardt, Karl Freed, and others in my class were learning formal scattering theory in the graduate quantum mechanics course in physics given by Paul Martin. Throughout all of this, Wilson never expressed any hesitancy about my drifting in these directions away from his primary interests. He did keep an interest, however, often giving insightful comments and criticisms of notes I would write up. I remember him once saying, "Well, boys, all this Green's function business looks interesting, but can you explain it to me in terms of old-fashioned wave functions?" Of course, we could not initially, and by the time we could, we understood it all much better. So long as he felt we were engaged, he seemed willing to let us go in our own directions. He was the absolutely ideal research director for me.

SEMICLASSICAL THEORY

I was introduced to the 1959 papers of Ford & Wheeler (3, 4) in a graduate kinetics/dynamics course that Herschbach gave (in 1966, I believe). These papers showed how quantum effects in elastic scattering could all be described semiclassically, using the WKB approximation to obtain the phase shift of the radial Schrödinger equation for each partial wave (orbital angular momentum) and then performing the sum over partial waves via the stationary phase approximation. Although the elastic scattering of two atoms is not a very exciting "chemical process," it is the simplest atomic/molecular scattering problem and thus received a considerable amount of experimental and theoretical attention (5) in these early years of chemical dynamics, as a benchmark for more interesting collision processes.

This work made an enormous impression on me, for it seemed to be the natural way to treat collisions of "heavy" particles (i.e., atoms and molecules, which are "heavy" compared to electrons); it incorporated the correct classical mechanics of the process, with an approximate treatment of (all!) quantum effects due to interference and tunneling. I thought to myself, this is what we need to do for inelastic and reactive scattering, e.g., for the simplest prototypical atom-diatom collisions,

 $A + BC \rightarrow AB + C$. But it quickly became clear to me that I did not know how to do this, for one first needs the classical solution before one can construct a semiclassical approximation, and it was well known that the classical three-body problem could not be solved. So I spent several fruitless months playing around with perturbation theory and such and not getting anywhere. Then Don Bunker, one of the early persons carrying out numerical classical trajectory calculations to describe elementary chemical reactions (6), gave a physical chemistry seminar at Harvard talking about the $K + Br_2 \rightarrow KBr + Br$ reaction, I believe, one of the first A + BC reactions studied experimentally. This opened my eyes to the fact that the three-body (and *N*-body) problem was solvable classically, at least operationally, by numerically integrating the classical equations of motion step by step in time with some specified initial conditions. The challenge was then how to use these numerically generated classical trajectories as input to a semiclassical theory, but it was several more years before I figured out how to do this.

In the interim, I finished my PhD and spent a postdoctoral year in Freiburg, visiting Christoph Schlier's experimental molecular beam group. (Apart from my wife and I having an absolutely delightful year in Germany, a tangible benefit of this was that I got to know many young German scientists who later obtained faculty positions, producing PhD students, and over my career I have had 13 German postdocs, many of whom have had, or are having, extremely successful careers back in Germany.) During this time, I was mainly focused on working out the methodology (7) for doing rigorous quantum reactive scattering calculations (e.g., for $A + BC \rightarrow AB + C$). I did work out a general methodology for this, but it was much beyond my computational capabilities to carry out at the time; it was approximately 20 years later that I realized a practical and efficient way for implementing it.

After coming back for a year at Harvard (1968–1969) in the Society of Fellows (from which I had taken leave to spend the year in Freiburg), I accepted an offer to begin as Assistant Professor at the University of California, Berkeley, in the fall of 1969. Fritz Schaefer was also hired by Berkeley that year, and this began a long personal friendship and professional interaction. For example, I had learned about experimental work on Penning ionization from work by Arndt Niehaus in Freiburg and Bud Muschlitz at the University of Florida and had written a paper about its classical and semiclassical description (8). Talking with Fritz, it became clear that we could use his electronic structure approaches to calculate the relevant metastable potential energy curves and autoionization rates relevant to this process, and indeed one of my students carried out the first ab initio calculation for the simplest example (9), metastable helium colliding with a hydrogen atom, $He^*(1s2s^3S) + H \rightarrow He(1s^2) + H^+ + e^-$.

By this time, I had also finally worked out how to use numerically computed classical trajectories as input to a semiclassical theory for inelastic and reactive scattering. This was aided considerably by learning about Feynman path integrals from a 1969 paper of Phil Pechukas (10) (the first of several times I was stimulated by one of Phil's insightful papers). I never had a formal advanced (graduate-level) course in classical mechanics but had spent considerable time digesting relevant material from Goldstein's (11) book. It soon became clear, for example, how intimately related classical generating functions are to the unitary transformations of quantum mechanics, and by using this, one could express the semiclassical relation between classical and quantum mechanics most generally.

I called this topic the "classical *S*-matrix" (for reviews, see 12, 13) as it used classical trajectory information to approximate the scattering (*S*)-matrix (of probability amplitudes), the fundamental quantity of quantum scattering theory. After the first paper giving the basic formulation (14), a paper on inelastic scattering followed, illustrating how quantum effects of interference (coherence) are described semiclassically (15): It is essentially the same as in the classic "two-slit problem," where more than one classical path connects the initial and final states, and one adds the amplitudes

associated with each path, then forming the square modulus to obtain the transition probability. One also saw that this interference structure would produce classical "rainbow" effects (familiar from the Ford and Wheeler analysis of elastic scattering) in the final internal (e.g., vibrational and rotational) state distributions. Another paper (16) showed how this interference structure tended to average out (be quenched) if one averaged (or summed) over a number of initial (or final) states.

It was also shown (17) how "classically forbidden" processes could be described: These are transitions for which no classical trajectories connect the initial and final states, but by analytically continuing the trajectories along complex time paths, one can find trajectories that do. However, the classical action integral *S* (not to be confused with the *S*-matrix) along such trajectories is complex, so there is a factor $\exp[-2\text{Im}(S)/\hbar]$ in the probability for such transitions, making them exponentially small (and actually zero in the classical limit $\hbar \rightarrow 0$). This was recognized as a generalization of well-known barrier tunneling, the probability for which also has this form, and was thus referred to as "generalized tunneling." [Rick Heller (18) later called this "dynamic tunneling" and provided some insightful discussions and illustrations of it.]

Reactive scattering turned out to be more difficult to treat than (nonreactive) inelastic scattering because the classical trajectories are more complicated. My first attempt (19), with postdoc Charles Rankin, perplexed us for some while because the final vibrational state quantum number changed almost randomly with miniscule changes in initial conditions. We finally realized that this was because A + BC ($H + Cl_2$ in this case) were forming a collision complex that lived for some time before decomposing to products or back to reactants. (Our protocol had been to look only at final values of the collision as a function of initial conditions, and we never actually looked at the trajectories themselves; by finally opening the "black box" to look inside, we were able to understand what was going on!) This was the first example of what came to be known as "chattering trajectories" (a term I never particularly liked, but it caught on). In this paper, we treated this region by a statistical approximation, which was simple; it would have been prohibitive to have implemented the original classical *S*-matrix approach otherwise.

Finally, I note that during this time in the early 1970s, Rudy Marcus (20) was also pursuing similar directions (from a different approach), and he made some important contributions to the topic (e.g., on how selection rules come out naturally from the symmetry of the classical "quantum number functions"). Our work was quite close at certain times, and with other persons could have become acrimoniously competitive. However, Rudy was always generous and supportive of me, a beginning assistant professor (with him already a member of the National Academy of Science), and we have been good friends over these many years.

QUANTUM TRANSITION STATE THEORY

As noted above, interference effects are most prominent in quantum state–to–quantum state processes but tend to average out (be quenched, decohered, etc.) in more averaged quantities. The thermal rate constant, k(T), for a chemical reaction is such a quantity (thermally averaged over all initial quantum states and summed over all final ones), yet quantum effects (e.g., tunneling, zero point energy) can nevertheless sometimes still be significant. While I was beginning to think about these issues, an illuminating paper by Pechukas & McLafferty (21) appeared, analyzing classical transition state theory (TST) from a dynamical perspective (due to Wigner), namely that the "fundamental assumption" of TST is that no classical trajectory crosses the relevant dividing surface more than once. They used some clever geometrical arguments to show that this condition would in fact be satisfied up to some finite energy above the energy of the saddle point of the potential energy surface (PES) (the barrier height). For some finite energy above the barrier height, therefore, TST would be exact (in classical mechanics). Classical trajectory calculations (by some of my students) for the benchmark $H + H_2$ reaction showed (22) that TST was in fact essentially exact (classically) for energies up to ~0.2 eV above the saddle point and, furthermore, that it was only ~10% in error (too large) for the 3D version of the reaction for energies up to ~1 eV above the barrier. In this case, TST would give the rate accurately up to quite high temperatures (within classical mechanics).

The seed was thus planted that if one could implement the fundamental (dynamical) assumption of TST fully quantum mechanically, one would have an accurate treatment for chemical reaction rates up to quite high temperatures. This is a quest I have returned to several times, from different perspectives, over several decades. My first step (23) toward this goal was to start with a formally exact expression for the rate as a Boltzmann average of the quantum reactive scattering cross section (the equilibrium rate constant, which I refer to simply as the rate constant) and massage the expression to make it look as classical-like as possible, to which one could make the TST approximation (of no recrossing flux). The exact expression (before a TSTlike approximation) had the form of what we later called a "flux-side" time correlation function (24); evaluating it without approximation requires the full quantum time evolution, but only for short time. Years later, in fact, we learned some quite useful ways (25, 26) to carry out "exact" quantum rate calculations using these expressions based on flux correlation functions. This approach to a rigorous quantum TST, however, was not fully successful as there was no fully consistent and unique way to apply the "no recrossing trajectories" approximation quantum mechanically.

INSTANTONS

The formally exact rate expression noted above (in terms of a flux-side correlation function) involves a quantum mechanical trace of the Boltzmann operator, $\exp(-\beta \hat{H})$ (along with a flux operator and a projection operator). Several years earlier I had written several papers (27, 28) about a semiclassical approximation for the Boltzmann operator that was obtained by using the same type of semiclassical approximation that was used for the time evolution operator, $\exp(-i\hat{H}t/\hbar)$, in earlier classical *S*-matrix work: One simply made use of the well-known relation between these two operators, namely that the Boltzmann operator is the time evolution operator for the imaginary time $t = -i\hbar\beta$. Because the time evolution operator is given semiclassically as an exponential of the classical action (the time integral of the Lagrangian),

$$\exp\left\{\frac{i}{\hbar}\int_0^t dt' \left[\frac{m}{2}\left(\frac{dx(t')}{dt'}\right)^2 - V(x(t'))\right]\right\},\tag{1a}$$

along a classical trajectory (in real time t)

$$m\frac{d^2x(t)}{dt^2} = -V'(x(t)),$$
(1b)

the Boltzmann operator is the exponential of a real quantity (which looks like an integral of the Hamiltonian),

$$\exp\left\{\frac{-1}{\hbar}\int_{0}^{\hbar\beta}d\tau\left[\frac{m}{2}\left(\frac{dx(\tau)}{d\tau}\right)^{2}+V(x(\tau))\right]\right\},$$
(2a)

along a trajectory in imaginary time $t = -i\tau$ (where τ is real),

$$m\frac{d^2x(\tau)}{d\tau^2} = +V'(x(\tau)).$$
(2b)

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Equation 2b can also be interpreted as a trajectory in real time τ on the inverted potential $(V \rightarrow -V)$. Furthermore, when carrying out the evaluation (29) of the trace expression for the rate (using the stationary phase approximation, the fundamental semiclassical tool), it is a periodic trajectory for the Boltzmann operator that dominates the contribution, so one has the interesting result that the rate is determined by a periodic orbit on the inverted PES, which came to be called (by others) the instanton.

This imaginary time periodic orbit is the optimum tunneling path on a general multidimensional PES, showing the "corner-cutting" and other dynamical features seen from other approaches. This type of approximation has been used for a variety of applications involving tunneling phenomena. A recent and impressive example is work by Stuart Althorpe and colleagues (30) treating the tunneling splitting patterns in water clusters.

SEMICLASSICAL TRANSITION STATE THEORY

The instanton approach incorporates the TST approximation (of no recrossing trajectories) and is thus a semiclassical transition state theory (SC-TST). Before leaving this topic, however, I should mention another type of SC-TST that in some ways is more satisfactory than the instanton approximation.

In the early 1970s, various people (31) were developing trajectory-based methods for determining the "good" (i.e., conserved) classical action variables related to a minimum on a (multidimensional) PES; this involved generating the Poincaré surfaces of section swept out by the bounded classical trajectories. Having the classical Hamiltonian (the energy) in terms of the "good" action variables—which are the classical counterparts to the quantum mechanical quantum numbers thus allows one to determine semiclassical energy levels, a multidimensional generalization of the Bohr-Sommerfeld (WKB) result for 1D potential wells.

I was still focused on TST for reaction rates at this time and realized that "good" action variables should also exist about a saddle point on a PES, in complete analogy with those about a minimum. For the case of a totally harmonic saddle point (or minimum) for *F* degrees of freedom (DOFs), this is easy to see: One has the simple result that the energy (i.e., the classical Hamiltonian) is given in terms of the actions $\{n_k\}$ by

$$E(n_1, \dots, n_F) = V_0 + \sum_{k=1}^F \hbar \omega_k \left(n_k + \frac{1}{2} \right),$$
(3)

where V_0 is the energy of the saddle point (or minimum), and $\{\omega_k\}$ are the harmonic frequencies. [The classical actions are actually $(n_k + \frac{1}{2})\hbar$, but I do not distinguish between them and the quantum numbers themselves.] The essential difference between a minimum and a saddle point is that one of the frequencies at a saddle point (e.g., the *F*-th one) is imaginary, whereas they are all real for a minimum. For a minimum, one sets all the $\{n_k\}$ to integers, yielding the (vibrational) energy levels (if one did this for a saddle point, one would obtain complex energy levels, the Siegert eigenvalues), but for a saddle point, one uses energy conservation,

$$E(n_1,\ldots,n_F)=E,\tag{4}$$

to solve for the imaginary action n_F in terms of the (total) energy E and all the real actions $\{n_k\}$, k = 1, ..., F - 1,

$$\left(n_F + \frac{1}{2} \right) = \frac{-i}{\hbar |\omega_F|} \left[V_0 - E + \sum_{k=1}^{F-1} \hbar \omega_k \left(n_k + \frac{1}{2} \right) \right]$$

$$\equiv -i\pi \theta(E, n_1, \dots, n_{F-1}),$$

$$(5)$$

where the real quantity $\theta(E, n_1, \dots, n_{F-1})$ is a generalization of the 1D barrier penetration integral of WKB theory. The cumulative reaction probability N(E) is then given by

$$N(E) = \sum_{n_1=0} \cdots \sum_{n_{F-1}=0} [1 + e^{2\theta(E, n_1, \dots, n_{F-1})}]^{-1}$$
(6)

in terms of which the microcanonical and canonical rates are given by

$$k(E) = [2\pi\hbar\rho(E)]^{-1}N(E),$$
(7a)

$$k(T) = [2\pi\hbar Q_r(T)]^{-1} \int_{-\infty}^{\infty} dE e^{-\beta E} N(E),$$
(7b)

where $\rho(E)$ and $Q_r(T)$ are the density of reactant states (per unit energy) and reactant partition function, respectively.

In the paper where these ideas were initially presented (32), I noted that good action variables should also exist for a general saddle point, not just a harmonic one, although determining them would be a challenge since it was not possible in this case to run classical trajectories and have them map out Poincaré surfaces of section—because the trajectories would "run away" along the reaction coordinate (the mode with the imaginary frequency). For this reason, we explored the possibility of using an algebraic approach (Born's perturbation expansion of the Old Quantum Theory) (33), but this was not pursued.

A truly practical way for implementing the above approach was therefore not apparent until 1990, when I was visiting Cambridge and Nick Handy told me about his new software program SPECTRO (34), which computed (via electronic structure theory) the cubic and quartic anharmonic force constants about a minimum on a potential surface, and then vibrational eigenvalues using second-order perturbation theory, giving a Dunham-like expansion for the vibrational eigenvalues through quadratic order in the vibrational quantum numbers,

$$E(n_1,\ldots,n_F) = V_0 + \sum_{k=1}^F \hbar \omega_k \left(n_k + \frac{1}{2}\right) + \sum_{k,k'=1}^F x_{k,k'} \left(n_k + \frac{1}{2}\right) \left(n_{k'} + \frac{1}{2}\right).$$
(8)

The anharmonic constants x(k, k') are given by explicit expressions involving the cubic and quartic force constants and vibrational frequencies. Though Equation 8 gives the (quantum mechanical) vibrational energy levels in terms of the vibrational quantum numbers, one can also think of it as the classical Hamiltonian in terms of the "good" action variables, so it was immediately clear that one could use the above approach—even all the same formulae—also for a saddle point, simply noting that one frequency is imaginary (as are some of the anharmonic constants) (35). Equation 4 thus becomes a quadratic equation for the imaginary action (i.e., the generalized barrier penetration integral), with Equation 6, etc., still applying as written. Several applications were carried out with our students to illustrate the approach, with very good results. Having the energy through quadratic order in the quantum numbers turns out to be much better than one might expect from second-order vibrational perturbation theory (e.g., recall that the energy of a Morse potential is given exactly at this level, as is also the barrier penetration integral for an Eckart potential, both reasonable approximations for anharmonic PESs). Equation 8 also includes the couplings between all DOFs to this same order.

To finish this story, I note that John Barker and John Stanton (36), and their coworkers, have recently been using this approach (in conjunction with master equation models to include pressure effects on rate constants) with impressive results for various reactions involving small- to medium-size polyatomic molecules.

CLASSICAL ELECTRONIC DEGREES OF FREEDOM

In the latter part of the 1970s, I became interested in the possibility of developing a more dynamically consistent classical or semiclassical treatment for electronically nonadiabatic processes (i.e., those involving transitions between different Born-Oppenheimer PESs). Most treatments of such processes have treated the electronic DOFs via an expansion in (electronic) quantum states, with a classical description of the nuclear DOFs in terms of their coordinates and momenta, and the inconsistency inherent in describing different DOFs differently can sometimes fail to describe some aspects of their interaction correctly.

If the nuclear DOFs are to be treated classically, then we reasoned that a dynamically consistent approach required that electronic DOFs also be described classically. This did not mean treating electrons as classical particles, but rather introducing some collective electronic DOFs that modeled the two (or more) electronic states involved in the process of interest. The first approach of this type was work with postdoc Bill McCurdy, where we utilized the well-known equivalence of a two-state system with a spin-1/2 system (37). Because spin is an angular momentum, which we knew how to treat via classical action-angle variables, this led to the following classical electronic-nuclear Hamiltonian,

$$H(\mathbf{P}, \mathbf{R}, n, q) = \mathbf{P}^2 / 2\mu + nV_{11}(\mathbf{R})$$

$$+ (1 - n)V_{00}(\mathbf{R}) + 2\sqrt{(n + \frac{1}{2})(\frac{3}{2} - n)} \cos q V_{01}(\mathbf{R}),$$
(9)

where (**P**, **R**) are the nuclear momenta and coordinates, and (n, q) are the electronic action-angle variables. $V_{n,n'}(\mathbf{R})$ is the diabatic electronic Hamiltonian matrix (which is assumed to come from many-electron quantum chemistry), and there is an equivalent expression in terms of the adiabatic electronic representation. In other words, this approach makes no attempt at calculating the electronic PESs themselves but deals only with how they are used to treat the nuclear-electronic dynamics. Later work with postdoc Dieter Meyer generalized this to an arbitrary number (*N*) of electronic states (38),

$$H(\mathbf{P}, \mathbf{R}, \mathbf{n}, \mathbf{q}) = \mathbf{P}^2 / 2\mu + \sum_{k=1}^N n_k V_{kk}(\mathbf{R})$$
(10)
+
$$\sum_{k=k'=1}^N \sqrt{(n_k + \frac{1}{2})(n_{k'} + \frac{1}{2})} \cos(q_k - q_{k'}) V_{k,k'}(\mathbf{R}),$$

where there is now a pair of action-angle variables (n_k, q_k) for each electronic state k. (For N = 2, this reverts to Equation 9 by using conservation of $n_1 + n_2$ to eliminate one degree of freedom.) Other similar types of classical models were also explored for electronic DOFs, but it is Equation 10, in particular, that has had the most lasting interest.

Early applications of these "classical vibronic Hamiltonians" were at the fully classical level, i.e., computing trajectories from Hamilton's equations in all the classical DOFs (electronic and nuclear), using standard "quasi-classical" initial conditions, and binning the final action variables (i.e., quantum numbers). Also, when using the Hamiltonian of Equation 10, though initial conditions were specified in action-angle variables, the numerical trajectory calculations were carried out in the corresponding Cartesian electronic variables (because the equations of motion are simpler in terms of them),

$$x_k = \sqrt{2n_k + 1} \cos q_k, \quad p_k = -\sqrt{2n_k + 1} \sin q_k,$$
 (11a)

in terms of which the Hamiltonian becomes

$$H(\mathbf{P}, \mathbf{R}, \mathbf{p}, \mathbf{x}) = \mathbf{P}^2 / 2\mu + \sum_{k=1}^N \left(\frac{1}{2}p_k^2 + \frac{1}{2}x_k^2 - \frac{1}{2}\right) V_{kk}(\mathbf{R})$$
(11b)
+
$$\sum_{k < k'=1}^N (p_k p_{k'} + x_k x_{k'}) V_{k,k'}(\mathbf{R}).$$

Each electronic state thus appears like another vibrational degree of freedom and, within the quasi-classical model, is treated the same way. Reasonable results were obtained for a variety of applications, for example, giving a good description of resonance energy transfer between electronic and nuclear (vibrational and rotational) DOFs (39, 40).

Interest in these approaches revived in the 1990s when the goal was to implement them semiclassically, using various initial value representations of semiclassical theory (more on this later). A major contribution to this was work by Gerhard Stock and his PhD student Michael Thoss, at the Technical University of Munich. Stock had earlier been another of the excellent German postdocs to spend time with me (and Thoss did later); he had been intrigued by Dieter Meyer's work above, trying a variety of tweaks to find more accurate versions for treating pump-probe spectroscopy (41, 42). Back in Munich, Stock and Thoss used a different approach (a mapping procedure due to Schwinger) to obtain a vibronic Hamiltonian (43, 44) in terms of continuous DOFs. It turned out to be equivalent to Equation 11b, but most importantly, their derivation made it clear that this Hamiltonian is not an (approximate) model of the vibronic system, but rather an (exact) representation of it; i.e., if the Hamiltonian operator corresponding to it were used in the Schrödinger equation, the exact quantum dynamics would be obtained. (A proviso is that one considers the "polyad" of this Hamiltonian with one quantum of excitation in the N "electronic oscillators." It is easy to show that the sum of the electronic quanta is a constant of the motion; the N electronic states are thus the N states with one quantum of excitation in one of the oscillators.) Interest in this Meyer-Miller-Stock-Thoss (MMST) representation of a vibronic system was thus considerably heightened when it was realized that the only approximation is the semiclassical approximation.

REACTION PATH HAMILTONIAN

At the end of the 1970s I was beginning to think of what I might be able to do with dynamics for polyatomic molecules, something simple enough to be practical for general applications yet as quantitative as possible. The first challenge here is how to obtain the (Born-Oppenheimer) PES. By this time, it was feasible to carry out ab initio electronic structure calculations at a good level of accuracy for sizeable polyatomic molecules, but not the huge number of such calculations that would be necessary for the full (3N - 6)-dimensional space for an N atom system. Theorists had, however, recently developed ways to calculate the gradient (vector of first derivatives) of the PES with respect to nuclear coordinates and used this to find local minima and saddle points (transition states) on the PES quite efficiently. It was also possible (and feasible) to follow the minimum energy path (MEP) from a saddle point down to a minimum; the intrinsic reaction coordinate described by Fukui is the distance along the MEP. However, having the PES along the MEP in the full multidimensional space—although interesting for qualitative insight—was not enough to allow a dynamical treatment.

Nick Handy was at Berkeley on sabbatical at this time, and upon returning from the Sanibel Symposium, he described John Pople's talk about the development of efficient ways to calculate the matrix of second derivatives of the PES (the Hessian matrix). It thus immediately became apparent that one could obtain an approximate PES in the full dimensional space, namely a harmonic valley about the MEP, by calculating the Hessian along the MEP. The coordinates would thus be the distance along the MEP—the reaction coordinate—and local normal mode vibrational coordinates orthogonal to the MEP (obtained by diagonalizing the Hessian along the MEP). I thought of this as a generalization to the "natural collision co-ordinates" (45) that Rudy Marcus had earlier introduced for atom-diatom reactive scattering $(A + BC \rightarrow AB + C)$.

We worked out the form of the Hamiltonian (46) in these coordinates and saw that there were only three types of couplings between the various DOFs: The variation of the local normal mode vibrational frequencies along the reaction path coupled these modes to the reaction coordinate, as did a Coriolis-like coupling of one normal mode to another as they twisted about the reaction path, but the most important coupling resulted from the curvature of the reaction path into various normal mode directions. All these coupling terms were obtained from the MEP and Hessian along it, and one could discern many qualitative features of the dynamics (effects of reaction path curvature determining which were "promoting" or "accepting" modes, etc.) simply from seeing which coupling elements were largest. It was also possible to construct a variety of simple analytic approximations based on this "reaction path Hamiltonian," e.g., to calculate approximate tunneling corrections to TST rate constants (47).

My group, primarily in collaboration with Fritz Schaefer's—which had the ability to carry out the electronic structure calculations—made a variety of applications of this methodology to dynamics in several small polyatomic molecules. A number of these were motivated by experimental work in Brad Moore's group here at Berkeley. I enjoyed this work very much; it pulled me into projects that I would probably never have gotten involved with on my own, but when I did, I found them extremely interesting.

QUANTUM REACTIVE SCATTERING

Carrying out accurate quantum reactive scattering calculations for the simplest $A + BC \rightarrow AB + C$ chemical reactions, in full 3D space, had been the Holy Grail of chemical dynamics since the 1960s. As noted earlier, I presented one formulation for doing this while a postdoc in Freiburg but did not have the ability to implement it. George Schatz, as a graduate student with Aron Kuppermann, did carry out calculations for the benchmark $H + H_2$ reaction (using hyperspherical coordinates) in the mid-1970s (48, 49).

The essential complicating feature of reactive scattering (in contrast to inelastic, but nonreactive scattering) is that the natural (Jacobi) coordinates used in scattering calculations are the distance between the centers of mass of the two colliding molecules, plus the coordinates for the isolated molecules, but in a reactive scattering process, the coordinates of this type for the reactants are different from those of the products (being linear transformations of each other). For the simplest reactions, A + BC, the use of hyperspherical coordinates is one way to deal with this; although not the "natural" coordinates for reactants or products, they can span both regions and then be mapped onto the Jacobi coordinates for reactants and products in their respective regions. The methodology I had proposed (7) for dealing with this "coordinate problem" was to use an expansion of the wave function in functions of Jacobi coordinates of both reactants and products. This is essentially the same idea as the LCAO expansion of a molecular orbital, which uses basis functions in terms of coordinates that refer to different atomic nuclei. This was straightforward but involved nonlocal exchange interactions for the couplings between states of different arrangements.

In the late 1980s, interest in quantum reactive scattering revived owing to some experiments for the benchmark $H + H_2$ region that showed interesting, anomalous structure in an energy

region higher than previously accessible theoretically. Several groups took up the challenge to carry out calculations relevant to this.

While at a Sanibel Symposium, I was talking with Bill McCurdy about some of his work using complex scaling methods to describe resonance states, and in discussions the idea arose that it should be possible to use a basis set expansion for the translational functions in a coupled-channel expansion (rather than integrating coupled equations for them), with the appropriate incoming/ outgoing wave boundary conditions contained in basis functions themselves (50). This made my earlier formulation of the reactive scattering problem extremely straightforward: One simply had to compute matrix elements of the Hamiltonian between all the basis functions (including functions of different arrangements, i.e., in terms of different Jacobi coordinates) and then perform a standard linear algebra calculation to obtain the *S*-matrix.

John Zhang was then a postdoc with me and had considerable experience in reactive scattering as a graduate student with Don Kouri, so he quickly implemented this. Everything worked like a charm (being held up approximately a month by a most trivial programming bug that I will not go into here!), and he obtained the first fully converged reactive scattering cross sections relevant to these experiments (actually showing that the "interesting anomalous structure" in fact does not exist, or at least that it was not what was thought to be measured). John also applied this approach to several other A + BC reactions (D + H₂, F + H₂) (51–54).

This "S-matrix version of the Kohn variational method" is essentially the Rayleigh-Ritz variational method (the one used for calculating eigenvalues) with scattering boundary conditions. An interesting footnote to this work is that the Kohn variational method had largely been abandoned several decades earlier because of "Kohn anomalies," spurious singularities that appear in the energy dependence when it is applied with (real) standing wave boundary conditions. (These singularities become infinitely sharp in the limit of an infinite basis set, but one of course never reaches this limit.) It was thus somewhat of a surprise that such anomalies are completely absent, and the computations completely stable, when the variational method is applied with (complex) incoming/outgoing wave boundary conditions, i.e., directly for the S-matrix. There are other ways for carrying out reactive scattering calculations these days, but to me this is still the more general and straightforward way for doing so.

SEMICLASSICAL THEORY (AGAIN), THE INITIAL VALUE REPRESENTATION

As I approached my sixtieth year, I wondered what I might do in the last decade or so of my active career that would be interesting and also useful. With the focus on large, complex molecular systems, relevant to dynamics in molecular clusters, nanomaterials, biomolecular systems, etc., one could not help but be impressed with the ubiquity of classical molecular dynamics (MD) simulations of such processes. Classical MD is clearly sufficient in many (maybe even most) of these situations, but there are cases for which quantum mechanical aspects of the dynamics are important, and one would thus like to have the possibility of including quantum effects in such simulations. Since classical MD, i.e., classical trajectories, are the "input" to a semiclassical treatment, the question was whether this could be implemented for large molecular systems, those with hundreds (or even thousands) of DOFs. If so, then one knew from earlier work that it would provide a usefully accurate description of essentially all quantum effects in the dynamics.

There is really no fundamentally new semiclassical theory involved in this work; it is primarily a challenge to develop algorithmic approaches that enable its practical implementation for large molecular systems. The first problem to overcome was the nonlinear boundary value problem inherent in a "pure" semiclassical description, where one needs classical trajectories that connect specific initial and final states (e.g., position or momentum states, or specific quantum states characterized by action-angle variables); the "shooting" methods used in the 1970s would clearly not be feasible. The trick that dealt with this was a change of integration variables that replaces the nonlinear boundary value problem by a phase space integral over initial conditions (coordinates and momenta) of the trajectories. This initial value representation (IVR) (15, 17) was first devised to deal with "classical forbidden transitions," for which there were no (real-valued) solutions to the nonlinear boundary value problem, but it is key for dealing with large molecular systems because Monte Carlo methods can be used to evaluate the phase space integrals numerically (using much of the same methodology employed in classical MD simulations). I note that the IVR is not a "pure" semiclassical treatment (which would be to evaluate all the integrals by the stationary phase approximation—leading back to the nonlinear boundary value problem), but it is a more practical approach, especially for systems with many DOFs. It also has the practical advantage of integrating over "classical rainbow" structures that require a uniform asymptotic treatment, which is also quite difficult except for small molecular systems. The spirit of the IVR is thus to relinquish purity for practicality, a familiar approach in chemical theory.

My early semiclassical work noted the four possible choices one could use to express matrix elements to the time evolution operator: with the initial and final states being coordinate states, momentum states, or one a coordinate state and the other a momentum state (and maybe generalized coordinate and momentum states, e.g., action-angle variables). Soon after this, Rick Heller (55) noted that these four possibilities could be conveniently combined by using coherent states (i.e., Gaussian wave packets) that are hybrid states, intermediate between pure coordinate and pure momentum states. There also exist four analogous versions of the original IVR expressions, and motivated by Heller's work, Herman & Kluk (56) obtained an IVR expression based on coherent states that interpolates between these four versions of the IVR for the propagator. Following Herman & Kluk's work, Kenneth Kay (57–59) also made some useful and insightful contributions to the coherent state version of the IVR.

With the nonlinear boundary value problem replaced by a Monte Carlo integral over the phase space of initial conditions, the next challenge is dealing with the fact that the integrand is complex (i.e., has a phase, $\exp[iS/\hbar]$, where S is the classical action). If one fails to deal with this, and proceeds naively, the calculation will typically be enormously inefficient and thus impractical. One thus must develop algorithms that deal with this semiclassical version of the "sign problem," and a hierarchy of these has been developed, mostly focused on evaluating various time correlation functions. I refer to several reviews that describe these in detail and mention them here only briefly. First, the most primitive approach assumes that the two initial phase points (in the double phase space average involved in a time correlation function) are infinitesimally close to one another and approximates the integrand by linearizing all quantities in their difference (60, 61). This leads to the "classical Wigner" model, which, even though it cannot describe quantum coherence effects, can describe other quantum effects (e.g., barrier tunneling) quite well. It can be applied to essentially any problem for which a classical MD simulation is feasible. Second, the "forward-backward" IVR uses an idea suggested by some of Nancy Makri's (62) work, although it was implemented (63, 64) in a more rigorous way that has been shown in various applications to describe quantum coherence quite well. Finally, it has been demonstrated most recently that use of a time-dependent Metropolis sampling function in the Monte Carlo procedure (65) allows for an efficient evaluation of the double phase space average essentially exactly (i.e., only with numerical error) and reasonably efficiently (although still more difficult, of course, than a standard classical MD simulation).

A particularly interesting application of this semiclassical initial value representation (SC-IVR) methodology is to electronically nonadiabatic processes, where using the MMST representation of the electronic DOFs (cf. Equation 11b) makes it quite straightforward to provide a unified

treatment of the nuclear and electronic DOFs in nonadiabatic processes (66). It is interesting that the classical trajectories generated by the MMST Hamiltonian are Ehrenfest trajectories; i.e., the force experienced by the nuclei is the instantaneous average over all the electronic states, yet as "processed" semiclassically in the SC-IVR, the nuclear trajectories emerge (correctly) on one PES or another, not on an average PES. This is a quantum coherence effect and thus accurately treated by the "forward-backward" IVR algorithm, as has been demonstrated and discussed in detail (67).

At this stage, therefore, one has a hierarchy of algorithms for implementing SC-IVR methodology, from approaches that are almost as simple as standard classical MD but that are able to describe only some quantum effects to more complicated approaches that essentially provide a complete semiclassical description of all quantum effects.

FINAL OBSERVATIONS

As my late wife Margaret Ann, whom many of you knew, often remarked to me and to our two daughters, "timing is everything"—in life and love, and it also is in science. I consider myself truly fortunate to have lived through and participated in the formative years of theoretical chemical dynamics, to have gotten to know and count as friends so many bright and creative (and competitive!) persons. The current generation of theoretical chemists is even more impressive in many ways, tackling problems that were inconceivably complex 30–40 years ago, bringing to bear all the tools of molecular theory and computation to treat them. Theory is at long last universally considered an indispensable partner in dealing with the full range of molecular phenomena.

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