THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 105, NUMBER 12, MARCH 29, 2001

Tribute to William H. Miller[†]

Over a period of more than three decades, Bill Miller has made many profound and diverse contributions to theoretical physical chemistry of molecular motion. From semiclassical mechanics to reactive scattering, from chemical kinetics to path integrals, it is hard to think of any area of modern chemical dynamics that one does not immediately associate with Bill Miller. Bill has literally shaped the way theoretical dynamicists think. His enthusiasm and deep insight have set a model for students and colleagues and will continue to provide a source of inspiration for future generations of theoretical chemists.

Bill graduated first in his class from Georgia Tech and was accepted to Harvard's Ph.D. program. He joined E. Bright Wilson's group but went on to do his own work from the very beginning. Inspired by ongoing advances in molecular beam experiments, he began to work on various aspects of collision theory. During his Harvard years in Wilson's group and later as a Junior Fellow, Bill became convinced of the utility of semiclassical approximations for describing molecular dynamics and spent much effort in learning everything he could about the WKB approximation. Then, during his first year at Berkeley, this blossomed into what became known as "classical S-matrix theory". This very elegant work provided a comprehensive semiclassical interpretation of essentially every aspect of quantum phenomena observed in molecular collisions, from zero point motion to quantum interference and even tunneling. The two reviews that Bill wrote on the subject continue to serve as an excellent resource for researchers striving to master the skill of semiclassical algebra.

Following this early success, Bill's attention turned to the possibility of generating accurate results based on the full quantum dynamics encoded in the Schrödinger equation. From early attempts to compute the scattering matrix to the later triumph of a fully quantum mechanical simulation of the $H + H_2$ reaction in the late 1980s, Miller has convincingly demonstrated that it is possible to extract all relevant state-to-state or ensemble averaged features of elementary chemical processes reliably and accurately. That work has sparked many recent developments in this area which is currently targeting polyatomic processes with comparable accuracy.

Chemical reactions in polyatomic molecules involve multidimensional potential surfaces, and the latter are hard to visualize and even harder to represent numerically. Together with Nick Handy who was visiting Berkeley in the late 1970s, Bill found

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[†] Part of the special issue "William H. Miller Festschrift".

10.1021/jp0103981 CCC: $20.00

a way of capturing all essential features of polyatomic reactions in a fairly simple “reaction path Hamiltonian”, which has provided the starting point for such calculations for nearly two decades. Barrier crossing phenomena usually exhibit exponential kinetics, and finding the characteristic time constant—the reaction rate—is a central problem in reaction dynamics. Motivated by classical and quantum ideas on the reactive flux, Miller developed the “reactive flux correlation function” formalism, an elegant, fully quantum mechanical expression for the canonical rate constant of a reactive system. This theory continues to serve as the starting point in analytical and numerical calculations of reaction rates.

Aside from all these pioneering developments, Bill has shown how the path integral formulation of quantum mechanics, originally a subject comprehensible mainly to the physics community, can become useful in chemistry. Following his work, the use of the path integral to represent the Boltzmann density matrix in thermally averaged quantities is now routinely used by the theoretical chemistry community, and the use of stationary phase ideas to temper the “sign problem” in real time calculations have opened up new avenues and proven valuable in many different contexts. Bill also discovered the concept of tunneling via classical trajectories in imaginary time, a very instructive semiclassical picture that later became known as “instanton theory” in the physics community.

In the past few years, Bill has returned to semiclassical theory. Using the “initial value representation”, a transformation introduced in one of his early papers on this subject, Bill has made significant progress in developing practical methods for adding quantum effects to classical molecular dynamics simulations of the dynamics and spectroscopy of complex molecular systems.

Bill’s approach to science is rather unconventional. He seems to “see through” the algebra and often guess the result before doing the actual work (which he always carries to completion by himself, generating many volumes of the famous “Miller Notes”!). Bill’s deep, penetrating insight is well-known and respected, and his valuable advice is always sought and appreciated.

Besides laying all these cornerstones for chemical dynamics, Bill has been a mentor to an impressive list of graduate students and postdocs, whose names are given in this issue. Those who have profited from Bill’s guidance remember his insight and resourcefulness (yet another tool to try!), but also his kind, very gentle personality.

We thank our colleagues who contributed to this special issue honoring Bill’s 60th birthday and join all his friends in wishing him many enjoyable and productive years of research.

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