

William Hughes Miller

William H. Miller was born in Kosciusko, Mississippi, in 1941, and grew up in Jackson. He received a B.S. in Chemistry from Georgia Tech (1963) and a Ph.D. in Chemical Physics from Harvard (1967). During 1967-69 he was a Junior Fellow in Harvard's Society of Fellows, the first year of which was spent as a NATO postdoctoral fellow at the Physikalisches Institute of Freiburg University (Germany). He joined the chemistry department of the University of California, Berkeley, in 1969 and has been Professor since 1974, serving as Department Chairman from 1989 to 1993 and becoming the Kenneth S. Pitzer Distinguished Professor in 1999.

Professor Miller's research has dealt with essentially all aspects of molecular collision theory and chemical reaction dynamics. The more significant of his contributions include a comprehensive semiclassical scattering theory (the classical S-matrix) of inelastic and reactive scattering processes, the reaction path Hamiltonian for describing polyatomic reactions, the S-matrix Kohn variational method for state-to-state reactive scattering, and a rigorous quantum theory of chemical reaction rates (and its semiclassical limit, the "instanton" model) that generalizes transition state theory. Most recently his efforts have focused on developing the initial value representation (IVR) of semiclassical theory into a practical way of adding quantum effects to classical molecular dynamics simulations of chemical processes.

Professor Miller is a member of the International Academy of Quantum Molecular Sciences (1985), the National Academy of Sciences (1987), and the American Academy of Arts and Sciences (1993). His awards include the Annual Prize of the International Academy of Quantum Molecular Sciences (1974), the E. O. Lawrence Memorial Award (1985), the Irving Langmuir Award in Chemical Physics (1990), the American Chemical Society Award in Theoretical Chemistry (1994), the Hirschfelder Prize in Theoretical Chemistry (1996), the Ira Remsen Award (1997), the Spiers Medal of the Royal Society of Chemistry (1998), and the Peter Debye Award in Physical Chemistry (2003).

The Quantum Instanton Approximation for Thermal Rate Constants of Chemical Reactions

William H. Miller
Department of Chemistry
University of California
Berkeley, CA 94720 USA

A quantum mechanical theory for chemical reaction rates has recently been developed [*J. Chem. Phys.* **119**, 1329 (2003)] which is a generalization of the earlier semiclassical (SC) instanton approximation [*J. Chem. Phys.* **62**, 1899 (1975)]. This *quantum instanton* (QI) description has many of the qualitatively desirable features of the earlier SC model--e.g., the reaction rate is expressed wholly in terms of the Boltzmann operator of the system--but it corrects its major quantitative deficiencies by utilizing the *quantum* Boltzmann operator, $\exp(-H/kT)$, rather than its SC approximation. Since calculation of the quantum Boltzmann operator is feasible for quite complex molecular systems (by Monte Carlo path integral methods), having an accurate rate theory that involves only the Boltzmann operator could be quite useful. Application of the QI approximation to several one- and two-dimensional model problems illustrates its potential; e.g., it is able to describe thermal rate constants accurately (no more than ~10-20% error) from high to low temperatures deep into the tunneling regime, equally well for asymmetric as well as symmetric potentials. A recent application to the $H + CH_4 \rightarrow H_2 + CH_3$ reaction in its full (18d) cartesian space (using Monte Carlo path integral methods) illustrates how the approach can be implemented for reactions involving many degrees of freedom.



Using Semiclassical Theory to Include Quantum Effects in Classical Molecular Dynamics Simulations

William H. Miller
Department of Chemistry
University of California
Berkeley, CA 94720 USA

Semiclassical (SC) theory provides a good description of essentially all quantum effects (interference/coherence, tunneling, symmetry effects of identical particles, quantization of bounded motion, etc.) in molecular dynamics; this has been long appreciated and validated by many applications to small molecular systems [cf. *Adv. Chem. Phys.* **25**, 69-177 (1974)]. Since SC theory is built on the classical trajectories of the dynamical system, it should in principle be possible to use it also to add quantum effects to classical molecular dynamics simulations of *complex* molecular systems (i.e., those with many degrees of freedom), e.g., chemical reactions in solution, in clusters, in bio-molecular or any complex environment. The practical implementation of SC theory for systems with many degrees of freedom is based on various initial value representations (IVRs), which have recently undergone a re-birth of interest in this regard. This talk reviews the basic idea of the SC-IVR approach and describes a variety of recent applications that have been carried out using it. [For a recent overview, see *J. Phys. Chem. A* **105**, 2942-2955 (2001).]

