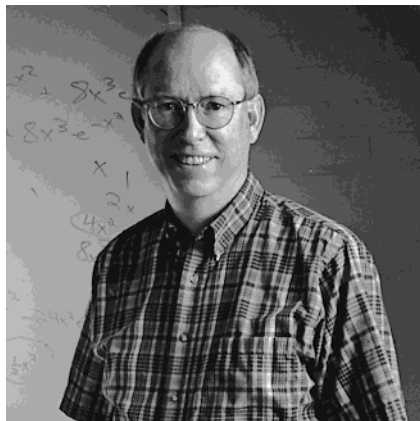


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Tribute to John C. Tully

It is a great pleasure, as well as a privilege, to introduce this special issue celebrating John Tully's scientific accomplishments with this short tribute. John's scientific career to date spans over 3 decades and in the process has traversed many of the frontiers of the theory of chemical reaction dynamics. His contributions, highlights of which we discuss below, range from the development of fundamental methodology to pioneering applications to chemical problems in the gas phase, the condensed phase, and, particularly, at the gas-surface interface. John Tully is among a small handful of his generation who are responsible for major transformations in the scope of theoretical chemistry during this time frame.

The first area in which John has made an enduring mark is the theory of nonadiabatic molecular dynamics. Nonadiabatic dynamics are ubiquitous in photochemistry as radiationless transitions, in carrier recombination at surfaces or in the solid state, in electron-transfer processes, and in many other areas. In a landmark paper in 1971, John, then a postdoc, developed a tractable extension of molecular dynamics that could describe such processes. John's "surface-hopping method" describes nonadiabatic dynamics in a picture in which motion propagates on a given potential energy surface almost all of the time with the exception of occasional jumps from one surface to another when a region of strong nonadiabatic coupling is encountered.

This method and its many descendents, including John's later generalization to "molecular dynamics with electronic transitions" (1990), have become the most widely used simulation methods for nonadiabatic dynamics involving many degrees of freedom. The impact of this type of dynamics through its

applications has also been substantial. Early simulations were often done with semiempirical potential energy surfaces, including the diatomics in molecules approach that John formulated in the early to mid 1970s. More recently, many groups have employed *ab initio* calculation of the potential surfaces and nonadiabatic couplings to predict branching ratios and to understand nonadiabatic reaction mechanisms. In this way, surface hopping has formed the underpinning for the modern understanding of photochemistry proceeding through "funnels" at conical intersections. It has been applied to prediction of not only electron transfer but also proton transfer reactions in the condensed phase. In addition, John has extensively explored the role of nonadiabatic processes in molecule-surface processes.

The second area to be transformed by John's research efforts is the theory of gas-surface reaction dynamics. Beginning in the mid-1970s, John and his postdocs and collaborators developed the key extensions of classical molecular dynamics necessary to make possible the atomistic simulation of fundamental gas-surface interactions, such as scattering, sticking, diffusion, and much more. These extensions include the use of generalized Langevin equation (GLE) methods to correctly mimic energy exchange between a small reaction region and the neighboring bulk, for example, at the bottom level of a slab model of a surface. John also employed the GLE in a very novel method to continuously redefine a surface reaction zone to follow a reacting or diffusing adsorbate over large distances across a surface. Separate developments addressed the problems of treating infrequent events at the gas-surface interface within

the confines of the short molecular dynamics time frame and the development of the realistic potentials necessary to mimic energy transfer, physisorption, and chemisorption.

While the development of this simulation capability is important in its own right, even more significant are the concepts concerning energy accommodation and exchange at the gas–surface interface that have arisen from John’s applications of these methods. How is energy transferred in gas–surface interactions? Why should scattering or sticking occur? How do these effects depend on the surface phonons and the incident conditions? What is the role of precursors? What are the mechanisms of laser-induced desorption? What is the role, if any, of nonadiabatic effects at metal surfaces? These are all questions that John’s simulation studies have addressed. The impact on modern surface science has been substantial because, although modern experimental techniques can provide the state-to-state information necessary to establish the reliability of simulations of this type (or even to develop the appropriate potentials if necessary), they provide no direct picture of what is happening in the gas–surface interaction itself. John’s simulations, often conducted in close collaboration with experimentalists, have been crucial in filling this gap.

There are numerous other significant scientific accomplishments, service duties above and beyond the call of duty, and well-deserved awards that we could comment on, but we shall try to follow John’s own example and let them speak for themselves. In his science, John sets an admirable standard of intellectual integrity that eschews hyperbole for directness and self-criticism and grandiosity for clarity and pedagogy. Scaling intellectual heights to achieve scientific success has never caused his feet to leave the ground. John, we are proud to mark your 60th birthday with this outstanding collection of papers. The enthusiasm that your community of students, postdocs, colleagues, and collaborators feels also surely speaks for itself with this issue. On behalf of everyone, we wish you all the best for the future as we congratulate you on your accomplishments to date.

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