Robert Wyatt's New Approach to Fundamental Problems in Quantum Chemistry

Perhaps the best caption for the moving pictures at right would be "Dance of the Probability Fluid." These are outtakes from the full computer movie (3.6M mov file). David Guzman of the TACC Scientific Visualization Group made the movie, using AVI software.

There are plenty of calculations behind the pretty pictures, also made at TACC, on the Longhorn and Lonestar Linux clusters, by Robert E. Wyatt, the W. T. Doherty Professor of Chemistry at The University of Texas at Austin. "Our codes are computationally intensive but also 'embarrassingly parallel,' so we can always use more processing power," Wyatt says, "and our use of the resources at TACC has helped us to show that our new methodology has many advantages over other methods of solving similar problems. The new computational methods, combined with the visualizations, give us new insights into physical and chemical processes."

The problem is to calculate the energetics of the dissociation of a metastable molecule. Wyatt (like others who do similar calculations) uses a model molecule composed of two fragments, A and B. Starting from the molecular state AB, what is the probability that, under any given conditions, AB will dissociate into the separated components A + B?

This may seem like a toy problem, but in real life many molecules demonstrate metastable behavior--a propensity to dissociate--and the work Wyatt is doing may ultimately have an impact on studies of the energetics of larger molecules. An important class of these is biomolecular, and Wyatt expects that his work may be particularly applicable to energy transfer problems in biological systems.

It can certainly have more immediate application for analysis of the many dynamical processes occurring over very short distances and in very short times in chemical physics. These include reactive scattering, photodissociation, and reactions seen in the new field of "femtochemistry." This field has been opened by the development of lasers with ultrashort pulses that help scientists trap and record intermediate reaction states with extremely short lifetimes--on the order of femtoseconds (one thousandth of a trillionth of a second).

Exact prediction of rapid chemical dynamics requires quantum approaches because of the small spatial scales of the events. The traditional computational approach to quantum chemical dynamics has involved the development of methods (algorithms) for solving the time-dependent Schrödinger equation, which describes how the wavefunction of a physical system (such as a dissociating molecule) evolves over time. Other approaches to this problem solve the equations on large-space fixed grids, but these methods are not straightforwardly extendable to systems with many atoms.

Quantum Trajectory Method

But there is another approach, which derives from the "quantum hydrodynamic" formulation of quantum mechanics. This viewpoint was first enunciated by Louis de Broglie and Erwin Madelung in 1926-27 and further developed by physicist David Bohm in 1952. There it sat until Wyatt and others began in the late 1990s to develop computational approaches based on the hydrodynamical formulation.

In 1999, Wyatt and his student Courtney Lopreore (now at the Salk Institute in La Jolla) developed a method they called the quantum trajectory method (QTM), which solves the equations of motion to find quantum trajectories for "fluid particles." The solution unfolds in the Lagrangian ("moving-with-the-flu-

id") reference frame, eliminating the need to solve the problem on a large grid or mesh. The development of this method stimulated many more investigations by dozens of theoretical chemists, and they quickly determined that the approach gives results that are as accurate as similar calculations based on direct solutions to the Schrödinger equation.

The "fluid" in this picture is the probability density discretized into small "particles." It is the dance of these particles, seen in Guzman's movie, that enables Wyatt to visualize the outcome: the number of particles escaping from the system at the lower right, for example, represents the overall probability of dissociation at a given energy. The tendency of the molecular system to remain intact is represented by the high-probability-density particles (colored red) that remain in the center of the picture; low-probability-density particles are colored blue.

For this particular movie, Wyatt and his student Corey J. Trahan (now at Texas Tech University) have added an additional twist to QTM. They are now able to solve for each particle trajectory independently, representing the (actual) interdependence of all trajectories by constraints on each trajectory's development. This improvement, which they call the derivative propagation method, dramatically reduces the computational time required and greatly facilitates the use of the method on massively parallel computational equipment. A major publication by Trahan and Wyatt appeared in the Journal of Chemical Physics in October 2003, detailing the method ("Evolution of classical and quantum phase-space distributions: A new trajectory approach for phase space hydrodynamics," J. Chem. Phys. 119, 7017-7029, 8 October 2003).

"The availability of the high-end systems at TACC for all of these studies was extremely important to our group," Wyatt says. "My work in the Institute for Computational and Engineering Sciences, the Institute for Theoretical Chemistry, and the Department of Chemistry and Biochemistry is inherently interdisciplinary, mixing fundamental chemistry, physics, and computational science. TACC's support of all these disciplines is an essential ingredient in pushing the frontiers forward. The movie in particular owes a great deal to the visualization skills of David Guzman and TACC's Scientific Visualization group. It gives us additional insights and serves as a wonderful pedagogical tool for interesting students in fundamental studies in chemical dynamics."