THE TWENTY-TWO MOST FREQUENTLY CITED APL PUBLICATIONS – IV

Issues 2, 3, and 4 of Volume 7 of the *Johns Hopkins APL Technical Digest* contain an introduction to and discussions of 20 of the 22 most frequently cited APL publications. The final article in the series will be published in the next issue.

MOLECULAR COLLISION THEORY

LAWRENCE W. HUNTER

L. W. Hunter, "On Infinite Order Sudden Approximations for Arbitrary Potential Energy," J. Chem. Phys. 62, 2855-2859 (1975).

It often comes as a surprise to people who work at APL that it has a long-standing, worldwide reputation in gas property calculations. These calculations are in a sense applications of molecular collision theory. The surprise is justified because the reputation has been built without fanfare and almost single-handedly, by Dr. Louis Monchick. I wrote to him in 1973 seeking an opportunity to pursue my interest in molecular collision theory. He sponsored me as a postdoctoral fellow for one year, during which time I wrote my paper on the "sudden approximation." The appointment also gave me an opportunity to develop an interest in some of APL's other activities in which I've been involved ever since

In order to predict the outcome of a molecular collision, it is necessary to solve an extraordinarily large set of coupled second-order differential equations of motion. There is one equation for each possible pair of internal energy states that can result from the collision. For a simple collision of an atom and a symmetrical diatomic molecule like nitrogen in which vibrations are neglected, reasonable accuracy requires over 300 equations at room temperature, while thousands are needed at higher temperatures. When vibrational energy transfer is allowed, the most complicated cases calculated so far are collisions of hydrogen with itself. Even today, the full numerical solution of the exact equations of motion is well beyond the reach of computers.

Thus, there has been considerable interest in approximate equations of motion. One approximation introduced before I entered the field was the "infinite order sudden" approximation, which neglects Coriolis effects and replaces the relative kinetic energy in all accessible final states by one average value. While the resulting description still consists of the same number of equations, other researchers had been able to uncouple them explicitly for a few simple cases. Unfortunately, in the

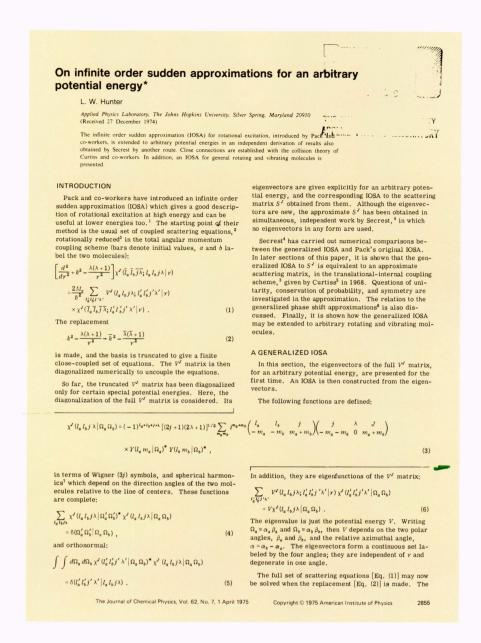
cases treated, the intermolecular force was drastically simplified. For realistic molecules, the force depends on all the orientation angles and atomic displacements, which vary as the molecules rotate and vibrate. As a result, the sudden equations become quite complicated. It was widely believed by people in the field that it would be impossible to uncouple these equations in general.

My contribution was to show that the general equations could, in fact, be uncoupled explicitly. My method applies to polyatomic molecules of any size. All possible rotational and vibrational degrees of freedom are allowed, and the intermolecular force is completely unrestricted. My results, still in use today, made it possible for the first time to carry out numerical calculations of rotational and vibrational energy transfer between realistic molecules. The numerical results proved to be quite accurate at high temperatures.

Uncoupling the equations of motion required the eigenvectors of an infinite order matrix. The only method available for finding the eigenvectors was pure trial and error. My success in guessing the answer eventually was due in part to experience with mathematical techniques (group representations) related to rotational symmetry. In addition, I learned a lot from three of the world's leading experts in molecular collision theory. L. Monchick provided valuable encouragement during my post-doctoral fellowship in APL's Milton S. Eisenhower Research Center. Previously, I had worked with R. F. Snider¹⁻³ at the University of British Columbia and with C. F. Curtiss⁴⁻⁶ at the University of Wisconsin Theoretical Chemical Institute.

Interest in molecular collision theory has kept pace with advances in experimental techniques for measuring collision cross sections of state-selected molecules. The results are of fundamental interest in the interpretation of spectroscopic line shapes⁷ and in the design of lasers

One of the applications I was able to pursue concerned calculating gas transport properties, including the thermal conductivity, species diffusivities, and viscosity. 8-10



The transport properties are obtained by summing molecular collision cross sections over internal states. A number of these sums could be evaluated by hand using techniques I applied to the sudden equations.

Many of the technologies of interest to APL are rooted ultimately in molecular motion. Combustion in airbreathing engines requires heat conduction and species diffusion. Radar tracking devices and heat-seeking guidance systems use microwave or infrared radiation that originates in molecular rotations and vibrations. However, anyone who begins a study of molecular motion with the goal of eventually understanding the technological applications can spend an entire career at the molecular level and never run out of challenges. It was one such challenge that led to the paper I published over 10 years ago.

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