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 postdoctoral fellowship in APL's Milton S. Eisenhower Research Center. Previously, I had worked with R. F. Snider[1-3] at the University of British Columbia and with C. F. Curtiss[4-6] 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 shapes[7] 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]

On infinite order sudden approximations for an arbitrary potential energy*

L. W. Hunter

Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland 20910
(Received 27 December 1974)

The infinite order sudden approximation (IOSA) for rotational excitation, introduced by Pack and co-workers, is extended to arbitrary potential energies in an independent derivation of results also obtained by Secrest by another route. Close connections are established with the collision theory of Curtiss and co-workers. In addition, an IOSA for general rotating and vibrating molecules is presented.

INTRODUCTION

Pack and co-workers have introduced an infinite order sudden approximation (IOSA) which gives a good description of rotational excitation at high energy and can be useful at lower energies too.[1] The starting point of their method is the usual set of coupled scattering equations,[2] rotationally reduced[3] in the total angular momentum coupling scheme (bars denote initial values, a and b label the two molecules):

$$\left[\frac{d^2}{dr^2}+k^2-\frac{\lambda(\lambda+1)}{r^2}\right]\chi^J(\bar{l}_a\bar{l}_b\bar{j}\bar{\lambda};l_a l_b j\lambda|r)$$
$$=\frac{2M_r}{\hbar^2}\sum_{l_a' l_b' j'\lambda'}V^J(l_a l_b j\lambda;l_a' l_b' j'\lambda'|r)$$
$$\times\chi^J(\bar{l}_a\bar{l}_b\bar{j}\bar{\lambda};l_a' l_b' j'\lambda'|r)\ . \qquad (1)$$

The replacement

$$k^2-\frac{\lambda(\lambda+1)}{r^2}\to\bar{k}^2-\frac{\bar{\lambda}(\bar{\lambda}+1)}{r^2} \qquad (2)$$

is made, and the basis is truncated to give a finite close-coupled set of equations. The V^J matrix is then diagonalized numerically to uncouple the equations.

So far, the truncated V^J matrix has been diagonalized only for certain special potential energies. Here, the diagonalization of the full V^J matrix is considered. Its eigenvectors are given explicitly for an arbitrary potential energy, and the corresponding IOSA to the scattering matrix S^J obtained from them. Although the eigenvectors are new, the approximate S^J has been obtained in simultaneous, independent work by Secrest,[4] in which no eigenvectors in any form are used.

Secrest[4] has carried out numerical comparisons between the generalized IOSA and Pack's original IOSA. In later sections of this paper, it is shown that the generalized IOSA to S^J is equivalent to an approximate scattering matrix, in the translational-internal coupling scheme,[3] given by Curtiss[5] in 1968. Questions of unitarity, conservation of probability, and symmetry are investigated in the approximation. The relation to the generalized phase shift approximations[6] is also discussed. Finally, it is shown how the generalized IOSA may be extended to arbitrary rotating and vibrating molecules.

A GENERALIZED IOSA

In this section, the eigenvectors of the full V^J matrix, for an arbitrary potential energy, are presented for the first time. An IOSA is then constructed from the eigenvectors.

The following functions are defined:

$$\chi^J(l_a l_b j\lambda|\Omega_a\Omega_b)=(-1)^{l_a+l_b+J+\lambda}[(2j+1)(2\lambda+1)]^{1/2}\sum_{m_a m_b}i^{m_a+m_b}\begin{pmatrix}l_a & l_b & j\\ -m_a & -m_b & m_a+m_b\end{pmatrix}\begin{pmatrix}j & \lambda & J\\ -m_a-m_b & 0 & m_a+m_b\end{pmatrix}$$
$$\times Y(l_a m_a|\Omega_a)^*\,Y(l_b m_b|\Omega_b)^*\ , \qquad (3)$$

in terms of Wigner ($3j$) symbols, and spherical harmonics[7] which depend on the direction angles of the two molecules relative to the line of centers. These functions are complete:

$$\sum_{l_a l_b j\lambda}\chi^J(l_a l_b j\lambda|\Omega_a'\Omega_b')^*\chi^J(l_a l_b j\lambda|\Omega_a\Omega_b)$$
$$=\delta(\Omega_a'\Omega_b'|\Omega_a\Omega_b)\ , \qquad (4)$$

and orthonormal:

$$\int\int d\Omega_a\,d\Omega_b\,\chi^J(l_a' l_b' j'\lambda'|\Omega_a\Omega_b)^*\chi^J(l_a l_b j\lambda|\Omega_a\Omega_b)$$
$$=\delta(l_a' l_b' j'\lambda'|l_a l_b j\lambda)\ . \qquad (5)$$

In addition, they are eigenfunctions of the V^J matrix:

$$\sum_{l_a' l_b' j'\lambda'}V^J(l_a l_b j\lambda;l_a' l_b' j'\lambda'|r)\,\chi^J(l_a' l_b' j'\lambda'|\Omega_a\Omega_b)$$
$$=V\chi^J(l_a l_b j\lambda|\Omega_a\Omega_b)\ . \qquad (6)$$

The eigenvalue is just the potential energy V. Writing $\Omega_a\equiv\alpha_a\beta_a$ and $\Omega_b\equiv\alpha_b\beta_b$, then V depends on the two polar angles, β_a and β_b, and the relative azimuthal angle, $\alpha=\alpha_b-\alpha_a$. The eigenvectors form a continuous set labeled by the four angles; they are independent of r and degenerate in one angle.

The full set of scattering equations [Eq. (1)] may now be solved when the replacement [Eq. (2)] is made. The

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 air-breathing 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.

REFERENCES

[1] L. W. Hunter and R. F. Snider, "Rotational Invariance and Molecular Collisions," *J. Chem. Phys.* **61**, 1151 (1974).
[2] L. W. Hunter and R. F. Snider, "On the Evaluation of Kinetic Theory Collision Integrals, II. Angular Momentum Coupling Schemes," *J. Chem. Phys.* **61**, 1160 (1974).
[3] L. W. Hunter and R. F. Snider, "Molecular Scattering Equations Derived from the Rotational Invariance of Wave Operators," *J. Chem. Phys.* **61**, 5250 (1974).
[4] L. W. Hunter and C. F. Curtiss, "Molecular Collisions. XVII. Formal Theory of Rotational and Vibrational Excitation in Collisions of Polyatomic Molecules," *J. Chem. Phys.* **58**, 3884 (1973).
[5] L. W. Hunter and C. F. Curtiss, "Molecular Collisions. XVIII. Restricted Distorted Wave Approximation to Rotational and Vibrational Excitation of Polyatomic Molecules," *J. Chem. Phys.* **58**, 3897 (1973).
[6] L. W. Hunter and C. F. Curtiss, "Molecular Collisions. XX. Generalized Phase Shift Approximation for Symmetric Top Molecules," *J. Chem. Phys.* **59**, 3889(1973).
[7] L. Monchick and L. W. Hunter, "Kinetic Theory of Spectral Line Shapes for Diatomic-Diatomic Molecular Collisions: Pressure Broadening and Dicke Narrowing," *J. Chem. Phys.* **85**, 713 (1986).
[8] L. W. Hunter, "Scalar Equations for the Transport Coefficients of a Dilute Gas in an Applied Field," *J. Chem. Phys.* **63**, 345 (1975).
[9] L. W. Hunter, "Exchange Symmetry and the Quantum Boltzmann Equations," *J. Chem. Phys.* **63**, 2010 (1975).
[10] L. Monchick and L. W. Hunter, "A Kinetic Theory of Quantum State Diffusion," *J. Chem. Phys.* **66**, 4141 (1977).