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THE NEED FOR IMPROVED NUMERICAL ALGORITHMS IN MOLECULAR SCATTERING*

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Many problems in theoretical chemistry require an understanding at the microscopic level of molecular scattering. That is, an understanding of what internal and external changes take place as two molecules approach one another, collide and then recede from one another. From this knowledge at the microscopic level one can then calculate many properties of macroscopic chemical systems which cannot be measured presently in the laboratory nor observed directly in our environment.

The applications of molecular scattering information are many and far-reaching. In laser physics this information is needed in the search for new chemical systems with better lasing properties and for performance improvement of existing ones. The discovery within the past ten years of a rich variety of molecules and molecular clouds in interstellar space has created a need in astrophysics for molecular scattering data. Many interstellar molecules cannot be made in earth-bound laboratories, leaving computation as the only method for the determination of their properties. The study of our own atmosphere involves many molecular scattering processes, including, for example, the formation and destruction of ions in the upper atmosphere and the creation of air pollutants. Many energy-related problems also require understanding of molecular scattering events. To understand combustion processes requires knowledge of the associated reactive scattering events and in nuclear reactors there are many inelastic and reactive collisions involved in the final disposition of the generated energy. This listing is just a brief mention of a few of the applications.

Quantum mechanical approaches to molecular scattering can be reduced to the solution of a system of second-order, ordinary differential equations of the form,

$$y''(r) + k^2 y(r) = V(r)y(r) \tag{1}$$

$$k^2 > 0 \tag{2}$$

$$y(0) = 0 \tag{3}$$

$$\lim_{r \to \infty} y(r) = \sin(kr+\eta) + \cos(kr+\eta)R \tag{4}$$

$$\eta = \text{constant} \ . \tag{5}$$

Here $V(r)$ is called the potential energy function or most often simply the potential. Another important class of equations have non-local potentials, i.e.,

$$y''(r) + k^2 y(r) = \int_0^\infty V(r,r')y(')dr' \ . \tag{6}$$

However, the discussion here will be limited to the local case. Eq. (1) will generally be a matrix equation with $V(r)$ a real, symmetric matrix and k^2 diagonal. In this case the sin and cos functions in Eq. (4) are to be regarded as diagonal matrices and R is real symmetric. The matrix R is the desired quantity. From it all micro- and macroscopic scattering information can be derived.

This problem is most commonly solved by starting with Eq. (3), assuming an arbitrary, non-singular matrix for $y'(0)$ and then numerically integrating outward to some large r such that $V(r) \approx 0$. the numerical solution then has the form

$$y(r) = \sin(kr+\eta)A + \cos(kr+\eta)B \tag{7}$$

and the desired solution is found by multiplying from the right by A^{-1}. That is

$$R = BA^{-1} \ . \tag{8}$$

The single equation problem illustrated in the figure below is representative of the nature of the problem. For small r where $V(r) > k^2$, the solution has exponential behavior. For large r where $V(r) << k^2$ the solution is oscillatory. Various methods have been devised to compute these functions, some of which try to take advantage of their known limiting behavior. A brief survey of these methods with representative references follows.

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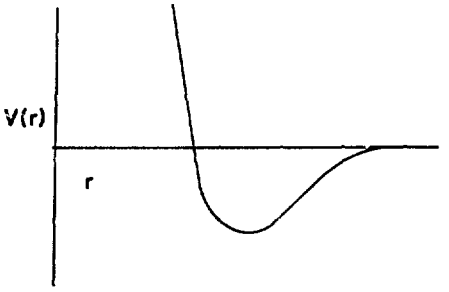

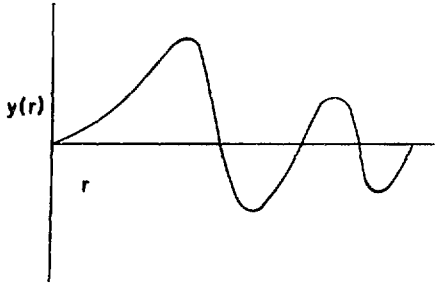

The Numerov[1] and de Vogelaere[2] algorithms are straight forward and have found wide application. The method of Gordon[3] which makes a piecewise linear approximation to V(r) is especially advantageous in the large r region. The variable phase method[4] represents y as a product of an oscillator y function and a modulating function which is smooth and slowly varying over a large part of the integrating range. Several methods[5,6] have also been developed for integrating the integral equations equivalent to Eq. (1). In addition a number of unconventional methods have recently been developed. These include the L^2 methods[7] (the solutions y are expanded in a basis of square integrable functions), the R-matrix propagator method[8] and an iterative method for finding a single column of the solution matrix y.[9] It is also possible to formulate the problem as a smaller system of linear, second-order partial differential equations and finite element methods for solving these have recently been proposed.[10]

Because of the matrix multiplication in Eq. (1), the computing time required for most of these methods increases as N^3 where N is the order of the matrix. The maximum cases solved to date typically involve N~100. The greatest need at the moment in molecular scattering, is for methods which allow a significant increase in N.

Other important needs for improved algorithms are 1) faster, more efficient programs, 2) error estimates with variable and automatic step size selection, and 3) programs which are generally reliable and easy to use.

With the exception of Gordon's method[3] computer programs for these methods are not generally available to or usable by people other than the developers. At the National Resource for Computation in Chemistry (NRCC), we are now attempting to bring together, test and make available the best of these programs. At this meeting, we hope to stimulate a broader dialogue on such problems between theoretical chemists and the community of numerical mathematicians.

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