Chemical Dynamics: Accurate Quantum Calculations at Last

An article of faith among physical scientists is that quantum mechanics is required for a rigorous description of the physical world at the level of atoms and molecules. But, much to their disappointment, chemists have up to now not been able to do accurate quantum calculations of even the least complicated reactions. This situation has changed in recent months, however, since two groups have announced their results for the hydrogen atom–hydrogen molecule exchange reaction: $H + H_2 \rightarrow H_2 + H$.

The calculations were published simultaneously by Aron Kuppermann and George Schatz of the California Institute of Technology, and by Robert Wyatt and Allan Elkowitz of the University of Texas, Austin. They came at a propitious moment and no doubt will provide a boost to one long-cherished dream of chemists: understanding in detail what takes place during a chemical reaction. The recent combination of molecular beam techniques for studying collisions and such new wrinkles as laser excitation of the products, the reactants, or both holds out the hope of obtaining the kind of information that can fruitfully be compared with theory in the near future. Such detailed understanding conceivably could lead to better chemical lasers, among other things.

In the meantime, the still formidable nature of the quantum calculations is such that it may not be practical to apply the same method to chemical systems that are much more complicated than triatomic systems of light atoms. Thus, the biggest contribution of the quantum results may be that they will serve as a benchmark against which various approximations that investigators will later apply to more complicated reactions can be tested.

Solution of the Schrödinger equation—the partial differential equation of quantum mechanics—for a chemical reaction begins with the separation of the electronic and nuclear motions. The usual justification for this procedure is that the electrons move so rapidly, as compared to the much heavier nuclei, that they can instantaneously adjust to changes in the positions of the nuclei. This is known as the Born-Oppenheimer approximation. In other words, a separate set of electronic wave functions exists for each set of nuclear coordinates. In turn, the effective potential energy field in which the positively charged nuclei move toward one another, as in a collision leading to a chemical reaction, is in part determined by these sets of electronic wave functions, which establish the distribution of negative electronic charge.

What the Caltech and Texas investigators did was to solve the Schrödinger equation for the nuclear motion in a system consisting of a colliding hydrogen atom and hydrogen molecule. The potential function they used had been calculated previously by Richard Porter (now at the State University of New York, Stony Brook) and Martin Karplus (now at Harvard University) when they were both at Columbia University. In three dimensions and at energies below that at which the hydrogen molecule dissociates, this potential, known as the Porter-Karplus surface, can be interpreted as constraining the reactant H and H_2 and the product H and H_2 to tubular regions of space. There is one tube for the reactants and one for each of the two possible product configurations, since the reactant hydrogen atom can react with either of the atoms in the molecule. The interatomic spacing within the hydrogen molecule determines the diameters of the tubes, while the coordinate along the axis of each tube corresponds to the distance between the atom and the molecule. The reaction occurs in the region where the three tubes meet.

Only Partial Agreement

Numerical integration of the Schrödinger equation in each of the tubes allowed the investigators to generate a complete set of independent solutions in each region. The investigators then formed linear combinations of these solutions, with the requirement that the resulting functions must join smoothly in the interaction region. Other conditions imposed included that the functions behave properly in the asymptotic regions far from the reaction zone and that they have the proper symmetry under exchange of identical particles (Pauli Principle). The calculations of the two groups of researchers diverged in their details, and some of their results agree to within about 15 percent, while others exhibit substantial disagreement. Why this is so is not understood at present.

The Caltech researchers were able to carry out their calculations over a wider range of collision energies than their Texas counterparts. As a result, they were able to observe a phenomenon akin to the resonances well known to high energy physicists. Predicted by the researchers on the basis of their earlier calculations of collisions restricted to one dimension (collinear collisions), these resonances either enhance or reduce the probability of a reaction occurring, depending on the quantum states of the reactants and products, and seem to correspond to a short-lived triatomic complex, according to Kuppermann.

The Caltech investigators also observed another quantum effect in their results—tunneling of a proton through the potential barrier separating the reactant hydrogen atom and molecule from the product atom and molecule. The effect of the tunneling phenomenon is to increase the reaction rate at low temperatures where there is insufficient thermal energy to permit particles to surmount the barrier. Tunneling of electrons in solids is widely observed, but, because of the heavier mass of the proton, tunneling by this particle is much less probable. Apparently it is still quite observable because the reaction rates calculated at 300°K were about three times those obtained by means of classical mechanics and about 18 times as great at 200°K.

These three-dimenstional quantum calculations represent a culmination of several years of development by a number of quantum chemists. As early as 1971, George Wolken, Jr., who is now at the Battelle Columbus Laboratories in Ohio, and Karplus reported on three-dimensional quantum calculations, but, in part because of the approximations they used and in part because they did not have access to enough computer time to do accurate calculations, their results were limited. In the main, however, the progression has been from classical mechanics to quantum mechanics in one dimension, then to two dimensions, and finally to the realistic case of three dimensions.

Aside from the pro forma dictum of science that the more known about a system or a process the better, researchers see a real value to accurate quantum calculations of this type. Macroscopic quantities, such as an experimentally determined rate constant for a chemical reaction, may be useful in helping engineers control a commercial process. But such quantities contain little or no information about what is actually happening on a molecular level in terms of the transfer of energy from one quantum state of a reactant to another quantum state of a product, because they represent an average of a large number of collisions, velocities, directions, and quantum states.

What chemists would most like to have are the above-mentioned state-to-state transition probabilities. With this knowledge, the way is open for chemists to "fine tune" reactions by controlling the transfer of energy on a molecular level. A chemical laser, for example, creates the population inversion in a gas needed for lasing by a chemical reaction, as, for example, when the product molecule is created in an excited vibrational or electronic state. One problem is how to produce the desired excited state efficiently, since the energy transferred follows a path that is dependent on the state from which it originates.

Unfortunately, such data have been beyond the reach of experimentalists, although there now appears to be hope in this regard. In recent years, chemists have been using molecular beam techniques and lasers to do increasingly detailed studies of chemical dynamics. Now they have begun combining molecular beam studies of reaction kinetics with the use of lasers to excite selectively certain quantum states in the reactant beams or in the products.

To cite one example, Richard Zare and his co-workers at Columbia University have used the fluorescence from laser-excited product molecules to determine the distribution of rotational and vibrational states in the products (*Science*, 30 August 1974, p. 739). More recently, Zare and Gary Pruett (now at the University of Pennsylvania) in their studies of the reaction $Ba + HF \rightarrow H + BaF$ have used a second laser to excite reactant hydrogen fluoride molecules into selected vibrational states. As a result they have been able to separate the vibrational distribution of the product barium fluoride caused by reaction with the hydrogen fluoride ground state from that caused by reaction with its first vibrational excited state. This information still is an average, but it is getting closer to what theorists calculate.

Thus, while no one would presume to predict a specific chemical system in which quantum chemical dynamics calculations could show the way to a better laser, information from such calculations might well suggest to researchers how or where they might go about looking for one. Even this sort of speculation remains "pie in the sky," however, until scientists can handle quantum calculations on more interesting systems than $H + H_2$.

A major problem standing in the way of calculations on such systems is the great amount of computer time required. In solving the Schrödinger equation for the reaction, scientists construct wave functions from a linear combination of certain already known functions, the basis functions. The accuracy of the results and the energy range over which they are valid depend on the nature and the number of basis functions used. But the amount of computer time required increases roughly as the cube of the number of basis functions. Kuppermann and Schatz at Caltech used about 100 such functions, and their calculations ran close to 1000 hours, while Wyatt and Elkowitz used about 50 basis functions of a different type, but they still needed over 300 hours. In a real sense, the breakthroughs of the two groups consisted of both the development of theoretical and numerical methods and the finding of sources to provide that much time on a computer.

In recent years, researchers have parlayed improvements in computational techniques and ever faster computers into a 500- to 1000-fold reduction in the time required to calculate molecular electronic wave functions. Some observers say that calculations of chemical reactions are in a relatively primitive state compared to that of the wave function calculations, and thus that comparable improvements in computation time might be expected. The fastest generally available computers are already about ten times as fast as those used in the hydrogen exchange reaction calculations. And on the computational front, John Light of the University of Chicago has been perfecting a different way of doing the calculations. Light expects that his method will require substantially less computer time than has been reported so far.

Benchmark for Comparisons

Such improvements, however, probably will still fall short of permitting accurate quantum calculations of reactions involving more than three relatively light atoms. Thus, theorists will likely have to resort to various approximation methods. In this regard, the accurate calculations are of prime importance, because it is only in comparison with these that scientists can judge the validity of the approximations. Moreover, investigators often do not need the full range of information that falls out of the complete calculations. Those features of the accurate calculations that need to be retained in the approximations in order to get the information wanted can, again, only be established in comparison with the former.

Approximation methods cover a continuous range from classical to quantum mechanical, although all of them use the potential surfaces calculated from quantum mechanics. One method that scientists are hopeful about is called the j_z conserving or centrifugal decoupling approximation. Developed independently by Russell Pack of the Los Alamos Scientific Laboratory in New Mexico and by Donald Kouri and Paul McGuire of the University of Houston, this method drastically reduces the computation time needed. In the accurate calculations, if there are N basis functions, there are then N coupled equations which are solved by matrix methods, thus giving rise to the terms "close coupling" or "coupled channel method."

The j_z conserving method reduces the coupling between the equations, so that the researcher has many small matrices rather than one large one. This reduces the computer time required by about the square root of N. The essence of the approximation is that for those reactions in which short-range forces predominate, the angular momentum about the z-axis of a properly chosen coordinate system can be considered to be constant. Wyatt and Elkowitz have applied this technique to the hydrogen exchange reaction, and are in the process of testing its validity.

A second category of approximations is called semiclassical. In these methods, Newton's laws are held to be valid, but certain quantum effects, such as those arising from interference of quantum mechanical wave functions, can be simulated. Because semiclassical calculations are sometimes less time-consuming than approximate quantum calculations, they may be the most useful in complex reactions. As one example, the quantum calculations done so far in three dimensions are valid only for the reactants and products in their electronic ground states. By allowing the spatial coordinates and time to become complex variables, theorists can simulate electronic transitions between quantum states using classical mechanics. Thomas George and his associates at the University of Rochester, for example, have obtained good agreement between classical and quantum calculations in some systems, but the calculations were restricted to the collinear collision case.

The close coupling quantum calculations still do not represent the ultimate quantum mechanical tour de force. The Porter-Karplus surface is a semiempirical one; that is, there is at least one adjustable parameter for chemists to fit by experiment. Kuppermann and his colleagues are now at work duplicating their calculations using a surface constructed entirely from first principles by Bowen Liu of the IBM Research Laboratory in San Jose, California. They are also getting ready to study the $H_2 + Cl$ reaction. Wyatt and Michael Redman at Texas will be attempting the $H_2 + F$ reaction. Both of these reactions are relevant to chemical lasers. And Wolken at Battelle, who now has Elkowitz as a postdoctoral student, is ready to get back in the game by calculating the $H + O_2$ reaction, which is the simplest flame.

—ARTHUR L. ROBINSON