Chemistry quantum by quantum

Quantum mechanics, the physical theory that describes the behavior of atoms and subatomic particles, is expected to play a major role in the description of the kinetics of chemical reactions. But this is so only if the basic quantum-mechanical equations for chemical reactions could be solved.

More than 50 years have passed since Erwin Schrödinger first wrote down the basic form of such equations, but only now, according to an announcement this week by the California Institute of Technology, has a solution been obtained for even the simplest chemical case, the reaction of a hydrogen atom with a hydrogen molecule. The work was done by Aron Kuppermann, professor of chemical physics, and graduate student George Schatz.

To solve the Schrödinger equation for the simplest atom is difficult enough. Textbooks tend to gloss over those for atoms with complicated electronic structure. Solution of the three-atom reaction required about 1,000 hours of time and many trillions of arithmetical operations on a large and fast computer, an aid not available to physical chemists until quite recently. Kuppermann spent a few years working out the mathematical techniques to guide the computer in solving the Schrödinger equation. Robert Wyatt and collaborators have been doing similar work at the University of Texas at Austin.

Kuppermann and Schatz report that they have shown "rigorously that the laws of quantum mechanics . . . can lead, when applied to chemical reactions, to a significantly different behavior from that predicted by classical mechanics." Instances of quantum-mechanical behavior include dynamic resonances, a phenomenon analogous to the resonances of particle physics, and quantum-mechanical tunneling, a phenomenon heretofore characteristic of low-temperature solid-state physics. The solution of the Schrödinger equation is considered of major importance in describing the dynamics of chemical reactions and predicting their rates, especially at low temperatures, where the deviance from classical mechanics is greatest.

The reaction for which the present solution is available is a very simple one in which a single hydrogen atom strikes a hydrogen molecule, detaching one of the atoms of the molecule and forming a new molecule, leaving the third atom single. The dynamical resonance shows up in the collision. Although a colliding hydrogen atom and a hydrogen molecule should repel each other, the calculation indicates that temporarily they stick together because of a redistribution of the energy of the collision among the three atoms. Resonances occur at discrete, quantized energy levels according to the prediction. They have never been seen experimentally, but now Kuppermann expects they soon will be. "Dynamical resonances could serve as sensitive probes of the forces at play during chemical reactions," he says. "The characteristics of these resonances are very sensitive to these forces."

Tunneling is expected to be very important in chemical reactions. It is one of the weird effects based on the wave-particle duality at the basis of Schrödinger's mechanics. Because it is a wave as well as a particle, an electron or an atom can make its way through an energy barrier that classical mechanics says it does not have enough energy to surmount. That is, it can go places and do things that classical mechanics would forbid it.

Tunneling tends to increase the rate of the hydrogen-hydrogen reaction. At room temperature the rate is three times what classical mechanics would predict; at 100 degrees C. below room temperature the factor is 18, and at temperatures near absolute zero tunneling allows the reaction to happen although classical mechanics forbids it entirely.

The lighter the atom, the more important is tunneling, and hydrogen is, of course, the lightest atom. Per-Olov Löwdin of the Universities of Florida and Uppsala suggests that hydrogen-atom tunneling may be important in biological processes such as aging. Tunneling between base pairs in nucleic acids could cause genetic errors that lead to deterioration of the processes that sustain life.

The approach taken in Kuppermann's and Schatz's investigations is analogous to what nuclear physicists use in studying nuclear collisions, and Kuppermann expects therefore a closer interaction between the two disciplines in the future. ☐

Will the universe expand forever?

Which is the way the world ends? Is it a bang or a whimper? T.S. Eliot opted for the whimper, but he did so largely on moral and theological grounds. Robert Frost couldn't decide between fire and ice.

It appears that on purely scientific grounds cosmologists can't completely decide either. Will the universe continue to expand forever, getting thinner and thinner and adiabatically colder until the game ends with a frozen whimper? Or will the expansion eventually stop, and a collapse ensue to a hot little ball in which saint and sinner alike will be barbecued? A "neighborhood meeting" was held in Cambridge, Mass., last week by the Smithsonian Astrophysical Observatory to discuss the question. No overwhelming consensus emerged, and none was really expected. In the opinion of George Field, the organizer of the meeting, the question may never be completely resolved.

The reason is that there are so many uncertainties and loose ends in the data, and so many assumptions to be made in drawing conclusions from them, that two equally competent observers can come up with virtually opposite conclusions from essentially the same data.

James E. Gunn of the California Institute of Technology and P.J.E. Peebles of Princeton University came to significantly different values of a crucial parameter in the argument, the ratio of the universe's actual matter density to the critical density required for closure. If the universe is dense enough, the mutual gravitational attraction of its parts will bring the expansion to a stop and reverse the motion. If the ratio of actual density to critical density (called omega) is one or greater, there is closure; if the ratio is much less than one, the universe is open.

Both Gunn and Peebles use essentially the motions of galaxies and clusters of galaxies to deduce gravitational effects and therefore density. Gunn comes up with an omega equal to 0.1; Peebles makes it 0.7. Given the uncertainties, this is a factor of about six difference. Not only is that large: Gunn's determination militates in favor of an open universe; Peebles's comes close to a closed one.

Field asked the two men how come they differed so widely. Gunn replied that the mass-to-luminosity ratio of galaxies was at stake. It is assumed that a galaxy's mass is related to its luminosity, and Gunn says his figure is 200 while Peebles used 400 or 500. Gunn also says he considers the luminosity density of the galaxies to be less than what Peebles thinks it is. Combining the two discrepancies gives the factor of six.

"That doesn't sound like my calculation," Peebles responds. "I didn't mention M/L or luminosity density." He believes the traditional figures applied to those concepts are unreliable, and he did his analysis, he insists, in a way that avoided recourse to them. Thus, the two men are even at cross purposes in discussing their differences.

There are a number of other tests both global and local that bear on omega or the deceleration parameter q_0, which is related to it. They include such things as counting distant objects in a given volume of space and comparing the number to that of nearer ones; using the apparent sizes of certain objects as yardsticks to measure the curvature of space; comparing present to primordial abundances of certain elements to get a handle on the density. All these are complicated measurements requiring difficult data reduction; more detail on the ways and means will be considered in subsequent articles along with the promise of future observing techniques.