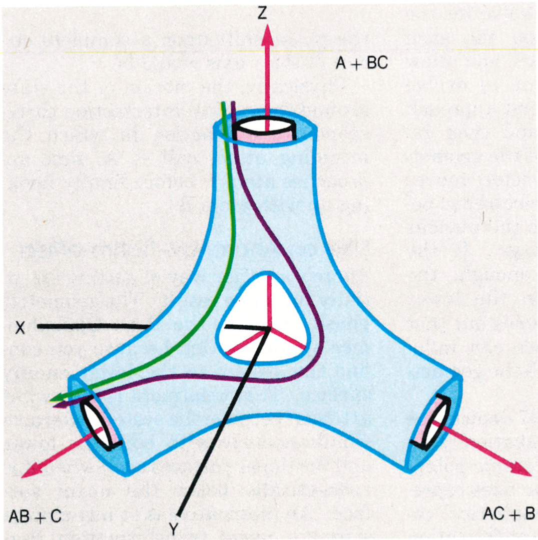
THE GEOMETRIC PHASE SHOWS UP IN CHEMICAL REACTIONS

One of the simplest chemical exchange reactions involves a system of three hydrogen atoms: $H + H_2 \rightarrow H_2 + H$. Surely, chemists have felt, one should be able to calculate the cross sections for this reaction from first principles. But the computations have not been easy. Only in the last six years or so have theorists, aided by efficient methodologies and access to supercomputers, been able to predict the cross sections in sufficient detail for comparison with experiments, which themselves have evolved in precision. The agreement has been good—well, almost. Small discrepancies, especially at higher total energies, stubbornly refused to yield to adjustments in either the calculations or the experiments. Now Yi-Shuen Mark Wu and Aron Kuppermann of Caltech have erased these pesky discrepancies by including a topological effect known as the geometric phase.[1] Michael Berry (University of Bristol) has called attention to the presence of this phase, which now bears his name, in a wide variety of physical systems.[2] (See Berry's article in PHYSICS TODAY, December 1990, page 34.)

The surprise is not the presence of a geometric phase but that it leads to observable effects in chemical reactions. Now chemists are likely to look for signs of the phase in similar systems, such as three alkali atoms. Kuppermann warns, "If you ignore the geometric phase, you do so at your own risk."



Potential energy surface for the reaction $H + H_2 \rightarrow H_2 + H$ in hyperspherical coordinates. The green path indicates the direct evolution of the system from one in which atom B is paired with atom C to one in which B is paired with A. Going on the purple path introduces a geometric phase shift.

Origin of the phase

Berry's phase arises as a system evolves in configuration space. Consider first an example in physical space. Hold your arm straight against your side and point your thumb in the forward direction. Do not rotate your thumb about your arm as you go through the following procedures: Lift your arm sideways until it is level with your shoulder. Then rotate your arm forward so that it sticks straight out in front of you. Finally, drop your arm back to your side. Notice that your thumb no longer juts forward but points in toward your side. While your arm has completed a trajectory and returned to its starting point, your thumb has rotated through an angle of 90° relative to its original direction. It has been globally, but not locally, changed.

To make the analogy with a physical system, your thumb is like the state vector of a system coupled to a slowly changing environment, your arm. If this system varies adiabatically, the state vector should come back on itself after a cyclic evolution in parameter space, but it might be multiplied by a phase factor. Part of the phase factor will be the dynamic phase that results from the time dependence of the Hamiltonian, and that phase would correspond to a rotation of the state vector locally about an axis perpendicular to the surface. (This kind of rotation is absent when the "state vector" is your thumb.) The other part of the phase factor is what Berry called a geometric phase, and it results, as you saw while cycling your arm, simply from the parallel transport of a state vector that does *not* rotate locally. The size of this phase depends on the path taken, and thus the geometric phase is sensitive to features of the topology. In particular, if there are obstructions in the landscape that prevent one from defining a phase universally, the geometric phase will be nontrivial.

Conical intersection

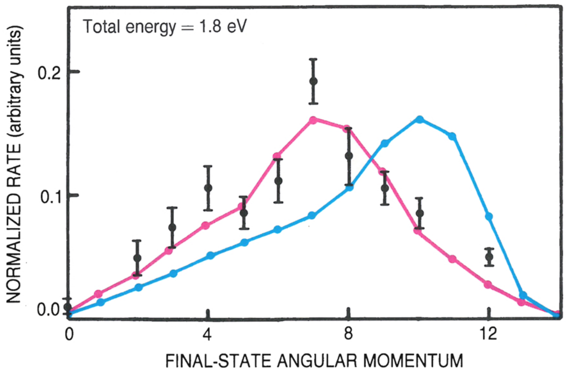
The simple system of three hydrogen atoms turns out to have one of those topological features that introduces a geometric phase. In particular, it has two electronic potential energy surfaces that come together at a "conical intersection." (The intersection is conical because the splitting of the energy surfaces is a linear function away from the intersection point.) The intersection is a point of degeneracy, and it corresponds physically to a configuration in which the three hydrogen atoms form an equilateral triangle. As the system moves away from this point, that is, as one hydrogen moves farther away from the other two, the system distorts, the degeneracy splits and the two electronic wavefunctions become distinct. This distortion is an example of the Jahn–Teller effect, originally identified for molecules in high symmetry states; it's interesting to see it affect a chemical reaction via the transition molecule H_3.

How does this conical intersection introduce a geometric phase? The standard treatment of the H_3 system is to apply the Born–Oppenheimer approximation, which separates the electronic and nuclear degrees of freedom. Then one can solve for the electronic wave function for each configuration of the nuclei, and allow the nuclear environment to evolve slowly as the reactants first approach one another, interact and then retreat. In the language of the geometric phase, the state vector moves adiabatically over the electronic potential energy surface as the nuclear coordinates slowly change. If the system energy is low enough, the state moves entirely on the lower energy surface. But it turns out that the upper energy surface can influence the reaction through the geometric phase.

The diagram on page 17 depicts the H_3 system evolving adiabatically on the lower of the two electronic potential energy surfaces. The axes represent symmetrized hyperspherical coordinates in nuclear configuration space. (A transformation of any point in this space can take one into a set of spatial coordinates describing the position of atom A relative to atom B, the position of the center of mass of the AB system relative to atom C, and the angle between those two vectors.) The green path indicates the direct evolution of the system from a state in which atoms B and C are paired to form the H_2 diatomic molecule to one in which atoms A and B are paired. The more indirect purple path goes around the y axis before reaching the final state.

Points on the y axis correspond to an equilateral-triangle configuration of the atoms (if the atoms are isotopically identical). That configuration in turn corresponds to the conical intersection of the energy surfaces. Thus, travel around the y axis introduces a geometric phase. (This diagram does not show the conical shape of the intersection explicitly.) The wavefunction corresponding to the purple path picks up a phase difference relative to the wavefunction associated with the green path, and the two can display interference effects. If the purple path were closed, the phase shift upon a complete circuit of the y axis would be π.

Physically, the motion of the state around the conical intersection corresponds to a reaction in which the incoming atom, call it A, first approaches atom C before finally hooking up with atom B.



Reaction rates for $D + H_2 \rightarrow DH + H$ versus the final-state rotational quantum number, with H_2 in the $(v = 1, j = 1)$ state. Data (black) fit the calculated curves better when they include the geometric phase (red) than when they do not (blue). (Adapted from ref. 8.)

Like an Aharonov–Bohm effect

There's another way of getting essentially the same result. The geometric phase arises in the Born–Oppenheimer approximation because you confine the system to the lower energy surface. That treatment is somewhat artificial because the system interacts simultaneously with both the lower and the upper surfaces even when it is energetically below the upper surface. An alternative is to introduce a singular gauge transformation that forces the electronic wavefunction to be single-valued everywhere. The effect of the gauge transformation is to add a vector potential to the Hamiltonian. That vector potential in turn gives rise to a fictitious magnetic field that acts like a flux tube at the origin. Then the problem looks like that in electromagnetism, in which Yakir Aharonov and David Bohm (both at the University of Bristol at the time) found that an electron will experience a phase shift as it encircles the flux tube.

Berry's phase has surfaced in a number of other systems.[3] Phase shifts are introduced into systems with spins coupled to a slowly varying magnetic field, and these have been seen in nuclear-magnetic-resonance interferometry. Optical measurements have detected phase shifts that enter as light changes direction or as its polarization vector changes orientation through a complete cycle. Spectroscopists have seen effects of the geometric phase in the spectra of trimers such as Na_3, where it causes the quantum number of pseudorotational angular momentum to be half-integral rather than the expected integral value. Berry's phase has also been used to describe some classical systems, such as the kinematics of deformable bodies.

The recognition that the geometric phase might be important in the H_3 system may have been foreshadowed by work that predates Berry's formulation. H. Christopher Longuet-Higgins (Cambridge University), together with colleagues, recognized in the late 1950s that the electronic wavefunction will acquire a phase shift in traversing a closed path that encircles a conical intersection.[4] The nuclear wavefunction must then have a compensating phase shift if the full wavefunction is to be single-valued. Alden Mead and Donald Truhlar (University of Minnesota) subsequently realized that this wavefunction change is a general molecular pheomenon that can be incorporated into a vector potential as in the Aharonov–Bohm effect.[5] They introduced the term, "the molecular Aharonov–Bohm effect." Mead and Truhlar outlined a treatment for a system with a conical intersection, but did not apply it to actual calculations.

Theory vs experiment

Experimental studies of the $H + H_2$ system are usually done on one of its isotopic analogs, such as $D + H_2 \rightarrow DH + H$, so that the reactants are labeled. Theoretical calculations of the total cross sections using several different approaches have meshed impressively with the data up through total energies of 1.6 eV. The minimum of the upper potential energy surface is 2.7 eV.

In the last few years, however, Richard Zare, David E. Adelman, Neil E. Shafer, Dahv A. V. Kliner, Hao Xu and Klaus-Dieter Rinnen of Stanford have taken the experiments into new territory.[6] They have done a series of experiments at higher energies than have been explored before, and they have studied the rates for reactions in which both the initial and final hydrogen molecules are in specific vibrational and rotational states, characterized by the quantum numbers v and j, respectively. In some of the reactions the initial hydrogen molecule was prepared in a single vibrational and rotational excited state with quantum numbers ($v = 1, j = 1$). One would expect the state-to-state cross sections to be particularly sensitive to any phase shifts in the reaction amplitudes.

In the Stanford experiments the initial deuterium atom is generated by photolysis of a deuterium iodide or deuterium bromide molecule, and the H_2 is prepared in a state-specific manner by Raman pumping. The experimenters detect the final HD state using a method known as 2 + 1 resonance-enhanced multiphoton ionization. In this technique, the molecule can be ionized only if it is in a specific state of both vibrational and rotational motion. Thus the Stanford group could find the (v,j) distribution of the product HD molecules.

The results of the Stanford experiments have been compared with theoretical calculations, which in recent years have been extended to these higher energies. The comparisons have revealed new disagreements.[7] In particular, with the initial molecule in the $v = 1$ state, plots of the rates of formation as a function of the angular momentum of the outgoing diatom peak at a lower value of j than do those of the calculations. These differences start showing up at a total energy of 1.8 eV and are significant at the highest total energy for which both calculations and measurements are available (2.3 eV).

Wu and Kuppermann decided to see if the discrepancies could be explained by the effect of the geometric phase. They started by doing calculations on the simpler system, $H + H_2 \rightarrow H_2 + H$. When they compared their results with the rotational state distributions measured by the Stanford group on the $D + H_2$ system, they found qualitative agreement.[1] Specifically, the values calculated with the geometric phase tended to peak, like the experimental data, at lower values of j. They also saw an effect in the total cross sections: When Wu and Kuppermann took the difference between the values calculated with and without the geometric phase, they found that the differences varied with energy in an oscillating manner suggestive of phase interferences. Indeed, one expects that the phase shift when the geometric phase is present will vary with energy differently than when the effect is not present.

More recently the Caltech theorists have completed the calculations for the $D + H_2$ system, so that their results can be compared directly with the experimental cross sections. They made these calculations for three different total energies and a range of initial and final vibrational states.[8] The correspondence with experiment is shown in the figure on page 18 for reactions in which the total energy is 1.8 eV, the initial diatomic molecule is in the ($v = j = 1$) state and the product molecule is in the ($v = 1, j$) final state. Kuppermann and Wu's calculations also indicate that the differential cross section is far more sensitive than is the total cross section to the inclusion of Berry's phase. —Barbara Goss Levi

References

1. Y.-S. M. Wu, A. Kuppermann, Chem. Phys. Lett. **201**, 178 (1993).
2. M. V. Berry, Proc. R. Soc. London, Ser. A **392**, 45 (1984).
3. J. W. Zwanziger, M. Koenig, A. Pines, Annu. Rev. Phys. Chem. **41**, 601 (1990).
4. H. C. Longuet-Higgins, U. Opik, M. H. L. Pryce, R. A. Sack, Proc. R. Soc. Lond., Ser. A **244**, 1 (1958). G. Herzberg, H. C. Longuet-Higgins, Discuss. Faraday Soc. **35**, 77 (1963).
5. C. A. Mead, D. G. Truhlar, J. Chem. Phys. **70**, 2284 (1979).
6. D. E. Adelman, N. E. Shafer, D. A. V. Kliner, R. N. Zare, J. Chem. Phys. **97**, 7323 (1992).
7. S. L. Mielke, R. S. Friedman, D. G. Truhlar, D. W. Schwenke, Chem. Phys. Lett. **188**, 359 (1992). D. Neuhauser, R. S. Judson, D. J. Kouri, D. E. Adelman, N. E. Shafer, D. A. V. Kliner, R. N. Zare, Science **257**, 519 (1992).
8. A. Kuppermann, Y.-S. M. Wu, Chem. Phys. Lett. (in press). ■

Tunnel Boring Begins at Superconducting Super Collider

SSC LABORATORY

The first of the Superconducting Super Collider's 60-foot-wide tunnel-access shafts opens down into a cavernous magnet-transfer area 236 feet below the sod of Ellis County, Texas. Some eight thousand 50-foot-long superconducting bending magnets will eventually be lowered down such access shafts, arrayed around the 54-mile-circumference underground SSC ring. Just after this picture was taken at the end of December, the first of the SSC's 250-ton "inchworm" tunnel borers was lowered down the shaft in segments to begin the actual boring of the 14-foot-high SSC tunnel.

Tunneling began in mid-January, starting at the "tunnel stub" visible at the far end of the cavern. Most of the boring will be through Austin chalk, but in this region the inchworm is boring through shale that necessitates a concrete tunnel liner. One of the virtues of the state-of-the-art inchworm is that it applies the concrete liner as it bores. The SCC schedule calls for tunnel boring to be completed by the end of 1996, but budget cuts proposed by President Clinton last month could stretch this out by several years.

—Bertram Schwarzschild