Javier Aoiz is a professor of chemical physics at the Universidad Complutense de Madrid in Spain. **Dick Zare** is a professor of chemistry at Stanford University in California.

Quantum interference in chemical reactions

F. Javier Aoiz and Richard N. Zare

Interference much like that observed in two-slit experiments can be seen in the outcomes of chemical processes in which multiple reaction mechanisms lead to the same final state.

Thomas Young conducted his celebrated double-slit experiment in 1801. Nowadays, quantum physicists pass not only light through screens with slits cut out but also electrons, neutrons, and even molecules as big as the soccer-ball-like fullerene C_{60}. In all cases we see the same kind of interference. Moreover, the interference is observed even if the particles are shot one at a time. However, if the apparatus is modified to register which slit each particle passes through, the interference is destroyed, as shown in figure 1a.

The double-slit experiment, as Richard Feynman observed in his famous *Feynman Lectures*, "has in it the heart of quantum mechanics. In reality, it contains the *only* mystery, . . . the basic peculiarities of all quantum mechanics." The question we and our colleagues have addressed is whether chemical reactions, studied one collision at a time, display a behavior analogous to that of the particles impinging on a pair of slits. The answer is a resounding yes. When more than one reaction trajectory leads to the same final outcome, interference appears as an oscillatory pattern in the angular distribution of the collision products.

Pass the deuterium

The specific process we considered is an exchange reaction in which a hydrogen atom impinges on a diatomic deuterium molecule and plucks off one of the deuteriums: $H + D_2(v = 0, j = 0 \text{ or } 1) \rightarrow HD(v', j') + D$. The symbols v and j denote vibrational and rotational quantum numbers, respectively, of the reagents; v' and j' refer to the products. We produced the H atoms by photolyzing hydrogen bromide molecules. By choosing specific laser wavelengths, we could control the velocity of the emitted H atom and hence the collision energy in the exchange reaction. The laser light needed to ionize the molecule determines the vibrational–rotational state of the HD product; the technique is called REMPI (resonance-enhanced multiphoton ionization). A position-sensitive detector records the HD angular distribution.

Figure 1b presents the $HD(v' = 1, j' = 1)$ angular distribution from an experiment with a collision energy of 1.97 eV. We have obtained similar results for different energies, for different vibrational–rotational states, and in reactions involving heavier atoms. The distribution is compared with the predictions of a full quantum calculation (black) and with those from a quasiclassical trajectory (QCT) calculation (red), a procedure that runs classical trajectories on an accurate potential energy surface and bins the results into different vibrational–rotational quantum states of the HD product. The experimental data and quantum calculation agree fairly well, but the QCT calculation does

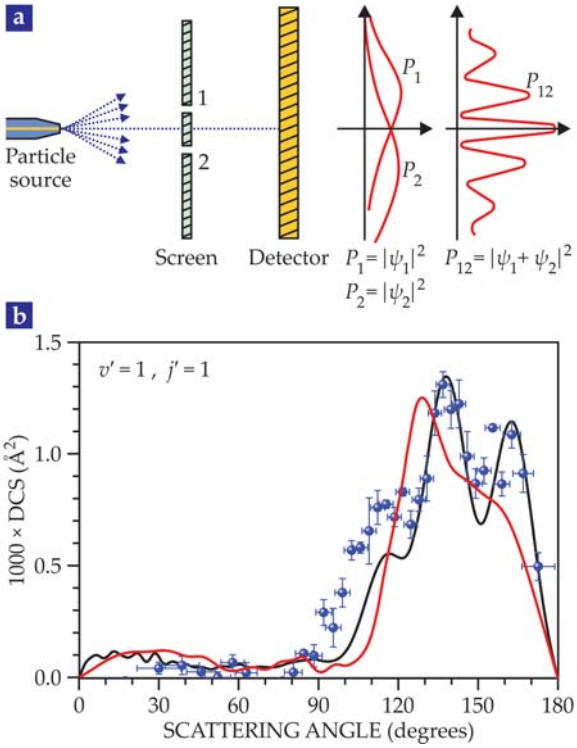

FIGURE 1. INTERFERENCE. When a quantum particle is shot through a single slit, **(a)** the probability that it is detected at a specified location is the absolute square of the quantum amplitude ψ. The probability distributions P_1 and P_2 show the results when, respectively, slit 1 or slit 2 is open. When both slits are open, the amplitudes are added first and then squared to give the probability P_{12}. (Adapted from *The Feynman Lectures on Physics*.) **(b)** Shown here is the angular distribution of hydrogen deuteride formed when H collides with D_2. Blue points are data, the black curve is a quantum mechanical simulation, and the red curve is a classical simulation. In all cases the HD produced had a specific, well-measured rotational–vibrational state. The oscillatory structure of the experimental results and quantum calculation is in stark contrast with the classical prediction. The differential cross section (DCS) is the particle physicists' measure of the probability distribution of the scattering angle.

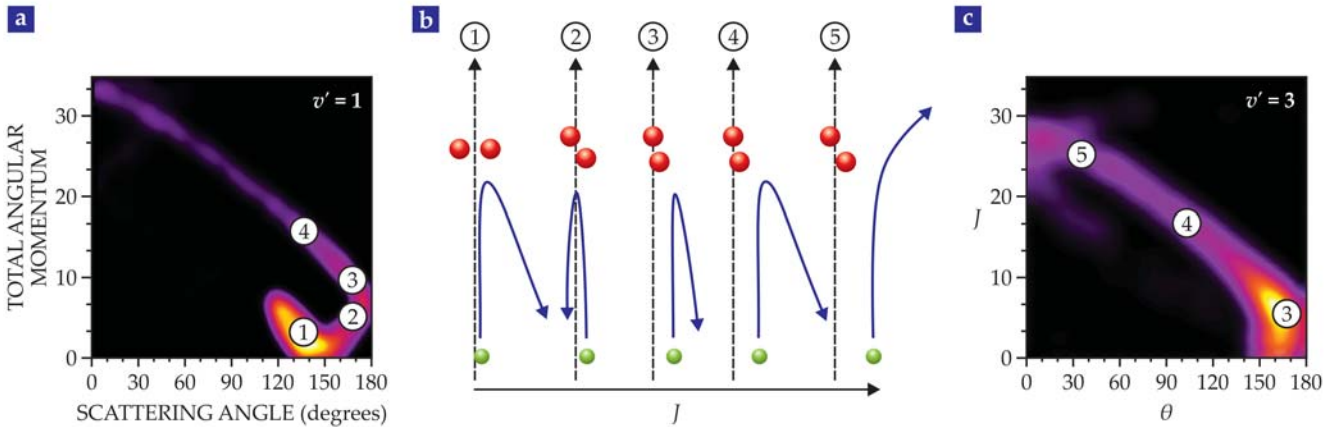

FIGURE 2. THE DEFLECTION FUNCTION. The joint distribution for scattering angle θ and total angular momentum J is expressed by the deflection function. **(a)** Shown here is the deflection function for the exchange reaction $H + D_2 \rightarrow HD + D$. The HD vibrational state is $v' = 1$, as in figure 1b. Probability increases as color changes from black-purple to yellow-white. **(b)** The numbered regions in panel a correspond to the same-numbered reaction pathways shown here. **(c)** Shown here is the deflection function when the HD vibrational state is $v' = 3$; again, numbers indicate reaction pathways shown in panel b.

a disappointing job and fails to capture the fingerlike pattern in the angular distribution. What is the origin of those oscillations? It certainly lies outside classical mechanics. Nonetheless, to understand the origin of the quantum phenomenon, we will turn to the classical world.

Different impact, same scattering

The crucial mathematical quantity we turn to is the classical deflection function, which maps the dependence of the scattering angle θ on the total angular momentum J. For many reactions, including the ones we studied, θ and J are strongly correlated. In joint distributions, such as those presented in figure 2, the correlations appear, roughly speaking, as a band that moves from low J (small impact parameters) and backward scattering angles close to 180° to high J and scattering angles in the forward region.

Close examination of the deflection function gives valuable information not only about the possible concurrent dynamical mechanisms that govern the reaction but also about the relative importance of those mechanisms. Figure 2a shows the function for the exchange reaction in which $D_2(v = 0, j = 0)$ goes to $HD(v' = 1, j' = 1)$. The several dynamical paths encoded in the deflection function are depicted in panel b. Panel c refers to $HD(v' = 3, j' = 1)$. In that case, high values of J are associated with forward scattering, and as J decreases, scattering tends toward increasingly backward angles, as described above. For the $v' = 1$ state of figure 2a, however, several mechanisms associated with different sets of J contribute to backward scattering, and sometimes different mechanisms lead to the *same* backward scattering. When that happens, the two reactions lead to interference in the real, quantum world.

For example, mechanism 1 of figure 2b, which makes the greatest contribution to the scattering intensity, leads to θ near 130° and occurs when the H collides almost side-on with the D_2. But mechanism 4, with its larger impact parameter and near head-on collision, also leads to θ near 130°. Scattering at 130° could be caused by reactions with $J \approx 3$ or $J \approx 15$ to 18. Similarly, reaction paths 2 and 3 lead to the same scattering angles. In a classical world, we could say from which J the scattering occurred, but as in the case of the double slit, the quantum world denies us that knowledge. For the $v' = 3$ case, mechanisms do not superpose; hence no interference is observed in the differential cross section (DCS).

Small mixing, big effect

Because quantum mechanics adds amplitudes first and then squares to get probabilities, a small amount of one mechanism mixed with a large amount of another leads to appreciable interference. For example, suppose mechanism 1 of figure 2b has 10 times the amplitude of mechanism 4 and that mechanism 1 alone leads to a DCS of 100 units. If the probabilities of the two processes add incoherently, then the DCS varies from $10^2 + 1$ to $10^2 - 1$; that is, the DCS varies from 101 to 99, which is a ±1% effect. However, if the two processes are coherent, the probability varies from $(10 + 1)^2$ to $(10 - 1)^2$—that is, from 121 to 81, which is a ±20% effect.

In a sense, the potential energy surface that is the basis for any dynamical calculation acts as an interferometer. The reaction paths on the surface are analogous to particle trajectories passing through slits cut into a screen. Interference is observed whenever two distinct reaction mechanisms lead to products scattered into the same angle at the same total energy and with the same internal states. The result is general: Oscillatory behavior in the DCS caused by interference is not limited to collisions between hydrogen atoms and hydrogen molecules, but it should occur in any scattering system in which the initial collision partners have a well-defined energy and the final scattering partners are observed in a state-selective manner, whether the collisions are reactive or inelastic. Classical scattering pictures are appealing and intuitive tools for describing chemical reactions, but there is no escaping that we live in a quantum world.

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Additional resources

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