Superpositions of Handed Wave Functions

Jeffrey A. Cina and Robert A. Harris

Chiral molecules, as well as achiral racemic mixtures, are everywhere. Yet it is well known that the wave functions representing the true stationary states of molecules that are observed to be handed should in fact be invariant under inversion, and therefore not exhibit chirality (*1, 2*). Such stationary states are rarely seen, and the quantum dynamics of the chiral states has never been observed. However, recent developments in ultrashort-pulse laser methods may enable the preparation and experimental investigation of a large class of states of chiral molecules that resemble the achiral stationary states in being linear combinations of left- and right-handed states (*3*). In addition, such experiments could provide an opportunity to observe the microscopic processes by which the "stationary" achiral states are degraded, and handed states stabilized, by interactions with the surrounding medium.

The quantum mechanical description of chiral molecules begins with a symmetric double-well potential (*1, 2*). That the two wells have equal depth is a reflection of parity conservation; the fact that, to a very good approximation, nature has no fundamental preference for either the left- or the right-handed isomer of a particular molecule. The left-handed isomer is represented by a wave function $\psi_L(x)$, localized in one well, while the wave function $\psi_R(x)$ for the right-handed isomer is localized in the other. The "chirality coordinate" x in these states is some complicated combination of the actual coordinates of the atomic nuclei. The stationary states referred to in the preceding paragraph are symmetric and antisymmetric linear combinations of left- and right-handed states; that is, specific superpositions of the chiral wave functions having the forms

$$\psi_\pm(x) = \frac{1}{\sqrt{2}}[\psi_L(x) \pm \psi_R(x)] \qquad (1)$$

Because the potential energy barrier between left- and right-handed wells is finite, the two states in Eq. 1 have energies differing by a small amount, $2\delta\hbar$. The chiral wave functions $\psi_L(x)$ and $\psi_R(x)$ should not be indefinitely stable. Via the quantum mechanical tunneling, a molecule that is initially left-handed should, in principle, convert back and forth to the right-handed form with a tunneling frequency that equals 2δ. The wave function at time t would be

$$\psi(x, t) = \psi_L(x)\cos\delta t + i\psi_R(x)\sin\delta t \qquad (2)$$

But, the tunneling frequency is tiny. It ranges from several megahertz for small molecules down to essentially zero for large ones. Because interactions of the molecule with its environment, even if that environment is highly rarefied, are unavoidably larger than δ, the time-dependent superpositions (Eq. 2) have never been seen in nature. In effect, the presence of a surrounding medium is believed to stabilize the handed states $\psi_L(x)$ and $\psi_R(x)$ (*4, 5*).

Even if states represented by Eqs. 1 or 2 had been prepared, everyday spectroscopic measurements of chirality would be insensitive to the fact that they represent superpositions of the left- and right-handed chiral wave functions. Such experiments typically measure the population difference between left and right, which is zero for $\psi_+(x)$ and $\psi_-(x)$ and the value $\cos 2\delta t$ for $\psi(x, t)$ at a specific time t, results that would not distinguish Eqs. 1 and 2 from appropriate physical mixtures of left- and right-handed molecules. Until recently, the question had apparently never been raised whether it is possible to prepare superpositions of chiral wave functions, which can be written in a general form

$$\psi(x) = c_L\psi_L(x) + c_R e^{i\varphi}\psi_R(x) \qquad (3)$$

a form which includes Eqs. 1 and 2 as special cases (*3, 6*). The question of what experiments would allow one to demonstrate that a state has the form of Eq. 3 was posed before but left unanswered (*2*).

We have put forward the suggestion that specific sequences of optical phase-controlled femtosecond light pulses could be used to both prepare and measure superpositions of chiral wave functions (*3, 7*). While phase-locking has long been put to use in forming sequences of multiple radio frequency pulses for magnetic resonance spectroscopy (*8*), as well as in nanosecond and picosecond optical spectroscopy (*9*), its emergence as a viable capacity in the femtosecond domain is relatively new (*7*). Our suggestion is to use one pair of phase-locked pulses to prepare the superposition of chiral wave functions and another to monitor the superposition in a special type of chiral mol-

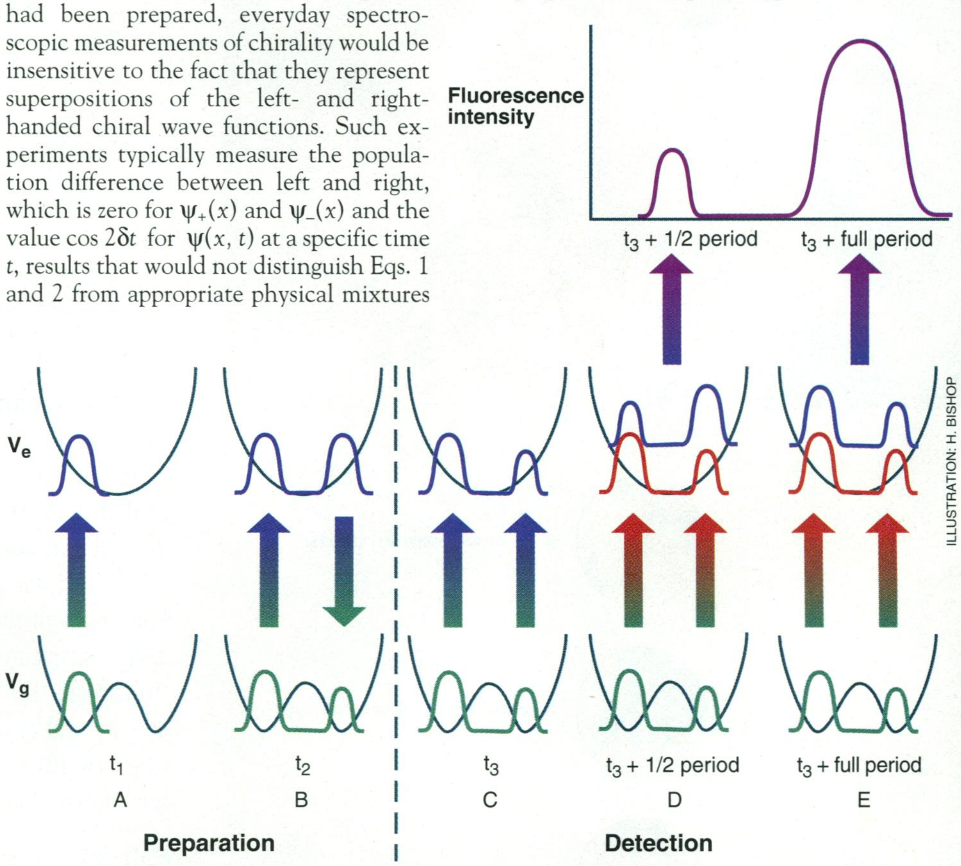

ILLUSTRATION: H. BISHOP

Preparation and detection of superpositions of handed molecules. (**A**) A left-handed molecule is copied onto the excited electronic-state potential by a pulse at t_1. (**B**) At t_2, one half-period later, the excited-state wave function is now right handed. A second pulse coherently adds part of that wave function to the original left-handed ground-state wave function. A superposition has been created. (**C**) At t_3, the first detection pulse creates a copy of the superposition onto the excited-state potential. (**D**) A second pulse is applied after one half-period. The overlap of blue and red wave functions is proportional to the fluorescence intensity shown in red above. (**E**) The second detection pulse occurs at a full period. The overlap is maximal.

J. A. Cina is in the Department of Chemistry and James Franck Institute, The University of Chicago, Chicago, IL 61637, USA. R. A. Harris is in the Department of Chemistry, University of California, Berkeley, CA 94720, USA.

ecule that is susceptible to the process of photoracemization.

Initially, the molecule is represented by the nuclear wave function $\psi_L(x)$ in the left-hand well of the electronic ground state (see figure). A short pulse of light creates a copy of $\psi_L(x)$ in the excited electronic state. We can actually carry out such a transfer of amplitude because the pulses are essentially instantaneous as far as the nuclei are concerned. The new wave function is a superposition of the original wave function, with a little removed, plus a copy on the excited-state potential curve. The superposition will change with time due to the presence of the excited-state wave function. In molecules prone to photoracemization, of which several examples have already been identified (*10*), there is a reduced or absent barrier in the excited electronic state. Suppose that the excited state potential well is harmonic, with angular frequency ω. Due to parity conservation, that well must be centered over the ground-state barrier, at $x = 0$. A wonderful thing happens to $\psi_L(x)$ in the excited-state potential. If we wait half a period, or π/ω, $\psi_L(x)$ turns into $\psi_R(x)$ by moving to the other side of the potential well without a change in shape. The ground-state wave function does not change because the elapsed time is negligible compared to the tunneling time scale δ^{-1}. Thus, we have a superposition of the form in Eq. 3, but with the glaring deficiency that $\psi_L(x)$ and $\psi_R(x)$ are in different electronic states.

That deficiency can be rectified by putting a copy of $\psi_R(x)$ back in the electronic ground state, using a second pulse that is phase-locked with the first. A second pulse, delayed by π/ω, results in a ground-state wave function of the form

$$\psi(x) = (1 - F^2)\,\psi_L(x) + F^2 e^{i\varphi}\psi_R(x) \qquad (4)$$

The constant F is a small parameter-determined field strength. The quantum mechanical phase φ is determined by the optical phase shift between the two pulses of the phase-locked pair. The wave function (Eq. 4) has the form of Eq. 3. Because there is a fixed optical phase shift between the light pulses, the preparatory pair of pulses sets up a superposition of chiral wave functions in the electronic ground state.

In order to detect the superposition of chiral wave functions we probe the molecule by exciting it electronically with a second pair of phase-locked pulses and monitoring the resulting fluorescence as a function of time delay between the two pulses of the detection pulse pair. The induced fluorescence would have an interference contribution that is directly proportional to the overlap of the original ground-state wave function with a copy of that wave function that was propagated in the excited-state potential for the interpulse delay. How this interference process makes the presence of the left-right superposition manifest is indicated in the figure.

The interference contribution to the fluorescence induced by the probe pulse-pair depends strongly on the delay time between the two subpulses of the probe pulse-pair. For delays much shorter than the time scale of nuclear motion, the propagated and unpropagated versions of the nuclear wave function are nearly identical, and hence overlap strongly. Such short delays give a large interference signal, and the large interference spike recurs for delays corresponding to full periods of excited-state motion. But those spikes would be observed even without having superposed a right-handed wave function with the original left-handed state. With the superposition state, however, a second series of interference peaks is predicted. These come at intrapulse delays that correspond to odd numbers of half-periods of motion in the excited electronic state, and arise because the left-handed portion of the wave function overlaps the right-handed portion of the original function, and vice versa, after evolving for half of a period on the excited-state potential curve.

There would be no interference spikes at all if the optical phases of the two probe subpulses were not locked, and the half-odd peaks would be absent if the wave function did not consist of a linear superposition of left and right. So, measuring the interference contribution to the fluorescence induced by the probe pulse-pair would provide a test of left-right superposition, which allows experimental differentiation between the state (Eq. 3) and a corresponding physical mixture of $|c_L|^2$ left-handed molecules and $|c_R|^2$ right-handed ones.

One pair of states that do not produce emission for half-period intrapulse delays is

$$\psi(x) = \frac{1}{\sqrt{2}}[\psi_L(x) \pm i\psi_R(x)] \qquad (5)$$

and these have an especially interesting property. Upon spatial inversion, the two states (Eq. 5) switch roles, so they are certainly chiral. Yet each one predicts equal population of left- and right-handed states. Besides failing to exhibit half-odd peaks that would betray their nature as superpositions of chiral wave functions, they would also fail to distinguish themselves from a racemic mixture in a conventional measurement of optical activity: Those measurements simply determine $|c_L|^2 - |c_R|^2$, which is zero for the states in Eq. 5. Equally interesting, the shapes of the two enantiamers look identical. In fact all wave functions where the coefficient of $\psi_L(x)$ differs from that of $\psi_R(x)$ by a phase have mirror images that are indistinguishable when ordinary optical properties are measured (*11*).

We have described the preparation and detection of superpositions of handed states under ideal circumstances. There will be some complicating factors, however. The excited state is not harmonic; the wave functions will spread as they propagate. Such spreading would tend to smear out the interference peaks.

Another feature of "nonideality" that is quite interesting in its own right is the process by which interactions with the surrounding medium, be it a condensed phase or a gas, degrade any superposition of handed states. That process could be observed directly by repeating the measurements described above for a range of delay times between excitation and detection. Preliminary calculations suggest that for handed molecules embedded in a low-temperature solid, a superposition state survives for tens to hundreds of femtoseconds, long enough for its degradation to be measured with currently available pulse durations. Thus, the proposed strategy affords a means of measuring the physical processes responsible for the interruption of tunneling (*4, 5*) separately from the tunneling process itself.

Finally, the idea that handed coherences may be constructed and their quantum interference verified expands our vision of chirality. Previously, our view of chirality, with the exception of atoms (*12*), had been governed by shapes. Here we have superposition states that are chiral in a sense that goes beyond the simple criterion of molecular shape.

References and Notes

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