A step toward a better understanding of molecular dynamics

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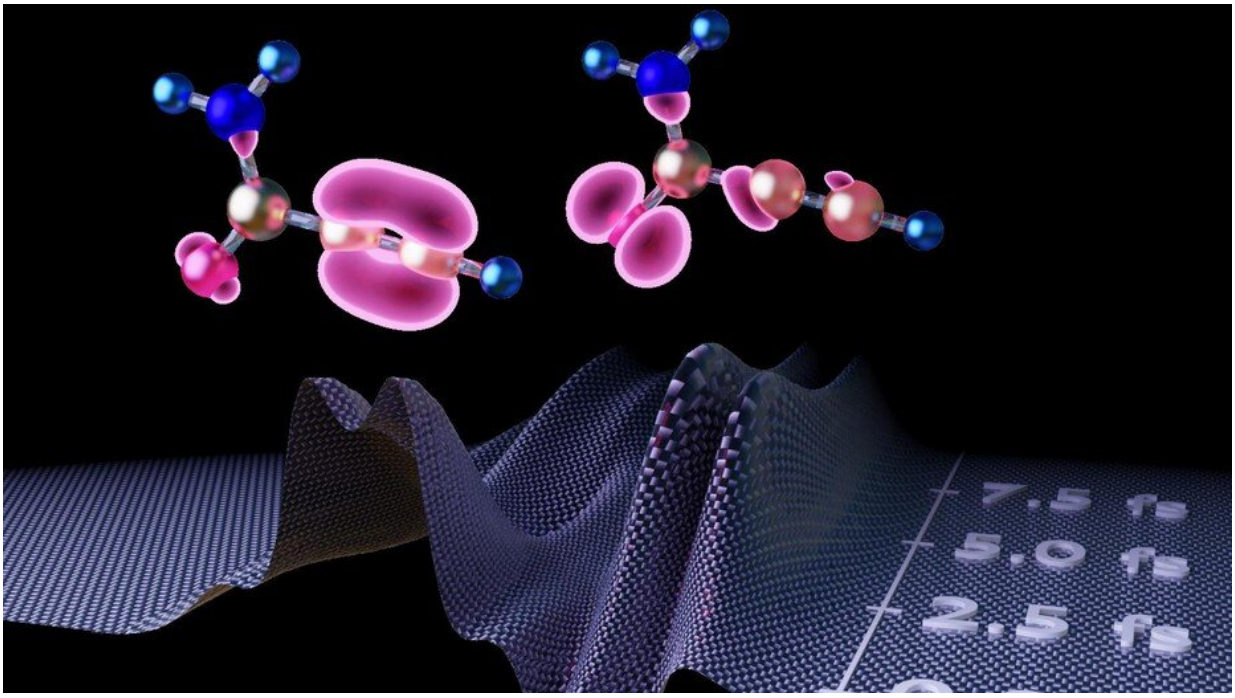

Credit: EPFL/LCPT

EPFL researchers, working at the boundary between classical and quantum physics, have developed a method for quickly spotting molecules with particularly interesting electron properties.

Laser technology is giving scientists an ever-closer look into molecular structures, and this sometimes leads to very interesting surprises. At

EPFL's Laboratory of Theoretical Physical Chemistry (LCPT), a research team studying the dynamics of polyatomic molecules—molecules made up of several atoms—came across one such surprise. They found that electrons in these molecules move quite differently from what would be expected in isolated atoms.

In isolated atoms, the oscillations of electron density are regular, but in most polyatomic molecules, the oscillations quickly become damped. This process is known as decoherence. However, in some molecules the oscillations last longer before decoherence sets in. The EPFL researchers developed a method which captures the physical mechanism behind decoherence, which consequently enables them to identify molecules with long-lasting coherences. Their method could prove interesting in the development of new electron-based technology or studying quantum effects in biomolecules. The findings were recently published in *Physical Review Letters*.

"Electron movement takes place extremely rapidly—on an attosecond scale—so it's very difficult to observe," says Nikolay Golubev, a post-doc at LCPT and the study's lead author. Furthermore, electron motion is strongly coupled to other processes in a molecule. This is why the research team incorporated additional piece of information into their study: the slower dynamics of the atomic nuclei and its influence on that of electrons. It was found that in most molecular structures the slow nuclear rearrangement damps the initially coherent oscillations of electrons and makes them disappear in a few femtoseconds.

A semiclassical approach

To determine whether this phenomenon is actually taking place, the researchers developed a theoretical technique for an accurate and efficient description of the dynamics of electrons and nuclei after the molecules are ionized by ultrashort laser pulses. They used what's

considered a semiclassical approach in that it combines quantum features, like the simultaneous existence of several states, and classical features, namely classical trajectories guiding the molecular wavefunctions. This method allows scientists to detect the decoherence process much faster, making it easier to analyze many molecules and therefore spot ones that could potentially have long-lasting coherences.

"Solving the Schrödinger equation for the quantum evolution of a polyatomic molecule's wavefunction exactly is impossible, even with the world's largest supercomputers," says Jiri Vanicek, head of the LCPT. "The semiclassical approach makes it possible to replace the untreatable quantum problem with a still difficult, but solvable, problem, and provides a simple interpretation in which the molecule can be viewed as a ball rolling on a high-dimensional landscape."

To illustrate their method, the researchers applied it to two compounds: propiolic acid, whose molecules present long lasting coherence, and propiolamide (a propiolic acid derivative), in which the decoherence is fast. The team hopes to soon be able to test their method on hundreds of other compounds as well.

Their discovery marks an important step towards a deeper understanding of molecular structures and dynamics, and stands to be a useful tool for observing long-lived electronic coherence in molecules. Backed with a better understanding of the decoherence process, scientists could one day be able to observe exactly how molecules act in biological tissue, for example, or create new kinds of electronic circuits.

More information: Nikolay V. Golubev et al. On-the-Fly ab initio Semiclassical Evaluation of Electronic Coherences in Polyatomic Molecules Reveals a Simple Mechanism of Decoherence, *Physical Review Letters* (2020). DOI: 10.1103/PhysRevLett.125.083001

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