Autoionization of molecular hydrogen: where do the Fano lineshapes go?

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Coherence between direct photoionization and autoionization paths results in *Fano profiles* [1], widely explored in atoms in the last 60 years. The advent of ultrafast laser technology made accessible time-resolved images of the delayed electron ejection in autoionization and the build-up of the Fano profile in time has been recently recorded for atoms in an experiment combining attosecond EUV pulses with near-IR femtosecond lasers [2]. The counterpart studies on molecules are scarcer due to the complexity added by nuclear motion, which takes place while the electron is being ejected from the autoionizing states. Consequently, Fano profiles are usually absent in measured cross sections for molecular photoionization and a reliable parametrization of its signatures, similar to that introduced by Fano in atoms [1] has not yet been achieved.

In the present work, we introduce a simple semiclassical model to describe the features appearing in the energy-differential cross sections for molecular autoionization. We use hydrogenic molecules as benchmark systems, for which accurate experimental and theoretical photoionization cross sections in the region of interest are available. Our approach is based on well-established models for Penning ionization [3], while also accounting for the presence of direct ionization, which interferes coherently with autoionization. We show that this interference is responsible for the pronounced structures observed at low nuclear kinetic energies and is well-described by the nuclear phase accumulated along two classical paths. The temporal build-up of these interferences is also found to be accurately represented within our model, in excellent agreement with the solution of the time-dependent Schrödinger equation. This time evolution is again shown to be dominated by nuclear dynamics: the electronic decay rate $\Gamma(R)$ determines the amplitude of the contribution at a given nuclear kinetic energy, but the timing is determined by how long the nuclear wavepacket takes to accelerate to the given energy as it slides down the potential curve. The observed interferences are thus found to be mainly governed by nuclear effects and fundamentally different from a Fano profile.

References:

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