Panta rhei - quantum dynamics of concerted electronic and nuclear fluxes in pericyclic reactions

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Traditional rules of organic chemistry suggest unidirectional fluxes of electrons during pericyclic reactions in the electronic ground states. These fluxes are illustrated by series of arrows from double to single bonds, or from single bonds, which are broken, to new bonds, which are formed during the reactions. To test these hypotheses and to discover quantitative details e.g., for the numbers of flowing electrons as well as the time scales and the synchronicity of electronic and nuclear fluxes, we design laser pulses which induce reactions from educts to products, and back. In order to analyze the quantum reaction dynamics, we define “surfaces of observers” between reactant and product configurations. The electronic and nuclear fluxes through corresponding surfaces are evaluated using the continuity equations and Gauss’ theorem which enable us to employ standard methods of quantum chemistry and dynamics, in the frame of the Born-Oppenheimer approximation (BOA). Applications range from small systems which allow non-BOA propagations of the representative wave function, for reference, to pericyclic reactions of small organic molecules such as semibullvalene or cyclooctatetraene, using models of reduced dimensionality. The results render the rules of organic chemistry as rather rough approximations to the real world, with significant deviations concerning e.g., the unidirectionality and the number of flowing electrons. The concerted electronic and nuclear fluxes are visualized by illuminating movies.