Molecular Science beyond the Born-Oppenheimer Paradigm

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In 1927 Born and Oppenheimer set a theoretical foundation of molecular structure based on the notion that electrons are far lighter and faster than nuclei, which naturally lead to the separation of nuclear and electronic motions, the Born-Oppenheimer (BO) approximation. Quantum chemistry (theory of electronic structure and potential energy surfaces (PES) for molecular structure and chemical reaction) and chemical dynamics on PES are thus constructed, which have been proven quite useful. With the advent of femto- and atto-second ultrafast laser technology, however, we are now in the era when even real-time dynamics of coupled electrons and nuclear motion can be observed. Hence we have been constructing a theoretical framework in such beyond-Born-Oppenheimer paradigm, which I term as "Theory of nonadiabatic electron wavepacket dynamics" or shortly "Time-Domain Quantum Chemistry".

This talk will cover:
1) Some topics from the Born-Oppenheimer approximation, including its validity range.
2) Some topics from nonadiabatic dynamics such as direct observation and control of quantum wavepackets due to nonadiabatic interactions.
3) Theory and some applications of the nonadiabatic electron wavepacket theory to chemical reactions mainly in excited states;

a) Chemistry beyond the notion of potential energy surface
b) Coupled proton electron-wavepacket transfer (CPEWT) as a universal mechanism of charge separation in organic and biological molecular systems such as that in photocatalytic reactions for water splitting and generation of oxygen molecules
e) Electron dynamics of direct- and auto-ionization from molecules.
f) Lorentz-force-like multidimensional effects of nonadiabatic interactions that can mechanically break the molecular optical symmetry.

General reference:
"Fundamental approaches to nonadiabaticity: Towards a chemical theory beyond the Born-Oppenheimer paradigm." Takehiro Yonehara, Kota Hanasaki, Kazuo Takatsuka, Chemical Reviews, **112**, 499-542 (2012).