Exploration of novel chemical reactions including non-adiabatic electron dynamics under laser fields.

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I. Objectives: The goal of the present study is to find a way to create and control electronic states for novel chemical reactions by applying laser fields and/or so-designed reaction fields. Inspired by the remarkable advances in the experimental measurements of ultrafast dynamics including electron dynamics in molecules [1,2], we develop a theory of nonadiabatic electron wavepacket dynamics as a tool to achieve the goal.

II. Degenerate electronic systems: Degenerate electronic systems are ubiquitous and play important roles in nature [3]. Chemical reactions driven by a dense manifold of degenerate electronic states proceed with a complicate electronic-state mixing by continuous nonadiabatic interactions. For instance, highly coherent electron dynamics causes a significant fluctuation of the charge distribution and a time-dependent variation of electronic polarization. In this way, such systems can provide a highly active chemical reaction field.

III. Boron cluster: Electronic wave functions of boron clusters away from the equilibrium geometries are very sensitive to the changes of molecular structure. The electronic characters of constituent boron atoms are well represented by the valence electron deficiency and small radii of valence orbitals, which allows for many applications in the experimental studies [4,5]. These properties yield high degrees of degeneracy of bonding character in the excited states of boron clusters, which emerges an active chemical reaction field that is dynamically modulated by persistent nonadiabatic transitions in the dense manifold.

IV. Contents of presentation: Toward laser control of chemical reaction, we apply the path-branching representation to describe the non-Born-Oppenheimer (NBO) electron dynamics. This approach makes it possible to treat nonadiabatic dynamics in optical fields that in turn induces additional nonadiabatic transitions [6-11]. Electronic wave packets evolve in time quantum mechanically along branching NBO paths. After showing its performance in a prediction scheme for an optimal laser pulse towards an aimed electronic state, we present and discuss the following illustrative examples; (a) a remarkable nonadiabatic charge transfer in (Na+Cl) [10], (b) activation of electronic states during complicated nonadiabatic dynamics (H_2@B_{12}) in structure isomerization dynamics, and (c) laser control of non-adiabatic bifurcation of reactive or non-reactive (energetically inelastic collision) dynamics of B_{12}+H_2 [12].

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