Incorporation of nuclear quantum effects to ab initio molecular dynamics approach

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We developed an AIMD code for excited-state reactions, which takes into account nonadiabatic transitions between adiabatic electronic states explicitly by the fewest switches algorithm [1]. The surface-hopping AIMD method has been applied to several dissociative recombination (DR) reactions, $HCNH^+ + e^-$ [2], $H_3O^+ + e^-$ [3], and $HD_2O^+ + e^-$ [4], as well as a photoisomerization reaction of azobenzene [5], to examine the tendency in the branching ratio of the products and to give insight to dynamical processes accompanying non-adiabatic transitions. Very recently, we also implemented the semiclassical tunneling method [6] to our AIMD code, and performed test calculations for the tunneling splitting in the umbrella inversion of ammonia and the intramolecular hydrogen transfer in malonaldehyde [7]. In the application to malonaldehyde, effects of multi-dimensionality were examined by assigning quantum zero-point energies only to significant vibrational modes and changing the amount of energy given to bath modes. In this talk, our extension of the AIMD approach to excited-state reactions and tunneling reactions is introduced and discussed.

References

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