Ab initio molecular dynamics of hypervelocity chemistry: Electronic structure and dynamics of O-NO_2 bond fragmentation

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Decomposition of high-energy molecules during a hypervelocity collision is accompanied by dramatic change in the system's electronic and nuclear configuration and thus presents a formidable challenge for ab initio molecular dynamics simulations. For example, to reproduce the O–NO_2 bond fragmentation in pentaerythritol tetranitrate (PETN), the electronic structure method employed to drive molecular dynamics must seamlessly describe the transition from the initial closed-shell configuration to a singlet diradical intermediate. We investigate the behavior of variational single-determinant methods in the region on the potential energy surface where the singlet diradical state becomes energetically favorable and discuss challenges for the corresponding molecular dynamics simulations.

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