Addressing the second derivative coupling in nonadiabatic molecular dynamics simulations

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Nonadiabatic molecular dynamics (NAMD) methods are now widely applied to model excited state processes, such as non-radiative decay via conical intersection. These techniques often employ the adiabatic representation of electronic states, resulting in singular first and second derivative coupling terms at such intersections. Despite these singularities, the second derivative coupling is often ignored without justification in NAMD simulations because it is expensive to compute. Here we present a justification for neglecting this term. We demonstrate that singularities in the second derivative coupling may be understood as artifacts of the adiabatic representation that arise when specific approximations are made to the molecular wave function. To eliminate these singularities we introduce a reformulation of the *ab initio* multiple spawning (AIMS) method for NAMD which we call diabatized Gaussians on adiabatic surfaces (DGAS). In DGAS, the total wave function is expanded in a basis comprising products of frozen Gaussian nuclear basis functions with locally diabatized electronic wave functions. The DGAS method effectively eliminates singularities in the second derivative coupling at conical intersections and also allows for the accurate description of long-range charge transfer events at trivial crossings between adiabatic states.