Explicit treatment of the time-dependent electromagnetic excitation in the nonadiabatic quantum dynamics in the adiabatic basis

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The shape of the excitation pulse has an effect on the subsequent nonadiabatic dynamics when the location of the initial wavepacket is close to the coupling region between different potential energy surfaces. Most computational studies make the sudden approximation, where the initial wavepacket after the (de-)excitation has the same shape as the ground state of the original surface. In this study, the excitation by the electromagnetic pulse is explicitly included in the Hamiltonian in the adiabatic representation. Since the nonadiabatic vector coupling makes the usual explicit split-operator algorithm unavailable, implicit integrators such as Crank-Nicolson method must be used instead [1]. We discuss and numerically show the conservation of the geometric properties by the implicit integrators and their symmetric composition to achieve an arbitrary even-order accuracy in the timestep [1] with a time-dependent potential. Furthermore, we study the effect of the exact shape of the excitation pulse on nonadiabatic dynamics to differentiate the regime where the excitation affects the subsequent dynamics and the sudden approximation is no longer valid.

[1] Seonghoon Choi, Jiří Vaníček, *The Journal of Chemical Physics*, **2019**, 150, 204112.