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Matching-pursuit/split-operator-Fourier-transform simulations of excited-state nonadiabatic quantum dynamics in pyrazine. VICTOR BATISTA, XIN CHEN, Yale University — A simple approach for numerically exact simulations of nonadiabatic quantum dynamics in multidimensional systems is introduced and applied to the description of the photoabsorption spectroscopy of pyrazine. The propagation scheme generalizes the recently developed matching-pursuit/split-operator-Fourier-transform (MP/SOFT) method [Y. Wu and V. S. Batista, J. Chem. Phys. 121, 1676 (2004)]. The time-evolution operator is applied, as defined by the Trotter expansion to second order accuracy, in dynamically adaptive coherent-state expansions. These representations are obtained by combining the matching-pursuit algorithm with a gradient-based optimization method. The accuracy and efficiency of the resulting computational approach are demonstrated in calculations of time-dependent survival amplitudes and photoabsorption cross sections, using a model Hamiltonian that allows for direct comparisons with benchmark calculations. Simulations in full-dimensional potential energy surfaces involve the propagation of a 24-dimensional wave packet to describe the S1 /S2 interconversion of pyrazine after after S0-S2 photoexcitation. The reported results show that the generalized MP/SOFT method is a practical and accurate approach to model nonadiabatic reaction dynamics in polyatomic systems.

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