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Direct dynamics using variational Gaussian wavepackets. Application to the intelligent control of benzene photochemistry[1] BENJAMIN LASORNE, MICHAEL J. BEARPARK, MICHAEL A. ROBB, Imperial College London, GRAHAM A. WORTH, University of Birmingham — The direct dynamics variational multi-configuration Gaussian wavepacket (DD-vMCG) method is based on the multi-configuration time-dependent Hartree (MCTDH) algorithm. It uses a time-dependent basis set of parameterised Gaussian functions, which are coupled so as to variationally provide the best possible representation of the wavepacket. This approach is designed to treat quantum effects in large molecules with on-the-fly calculation of the potential energy surface performed by an interfaced quantum chemistry program. Here, we apply this method to the study of the non-adiabatic photochemistry of benzene. Our aim is to rationalise how the way the wavepacket crosses the S_1/S_0 seam may modify the branching ratio Dewar benzene : benzvalene and enhance their production rather than non-radiative decay back to benzene. This study is intended to identify realistic non-radiative decay pathways that lead to alternative photochemical reactivity and to find corresponding targets that can be reached by optimal control experiments.

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