Calculations of Excited Electronic States by Converging on Saddle Points With Generalized Mode Following

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Calculations of excited electronic states can be carried out by finding saddle points on the surface that specifies the energy of the system as a function of the electronic degrees of freedom. This approach has several advantages over commonly used methods especially in the context of density functional calculations as collapse to the ground state is avoided and yet the orbitals are variationally adjusted for the excited state. A generalized mode following (GMF) method is presented for calculating excited states where an *n*-th order saddle point is found by negating the components of the gradient in the direction of the eigenvectors of the *n* lowest eigenvalues of the electronic Hessian [1]. The method is implemented using a generalized Davidson algorithm for finding the lowest few eigenvalues and eigenvectors, and direct optimization (DO) based on an exponential transformation for updating the orbitals [2] within a generalized gradient approximation of the energy functional. In calculations of potential energy curves for nuclear motion in the dihydrogen and ethylene molecules, the method is found to successfully track excited states through Coulson-Fischer points [3]. It is also found to converge more robustly than previous self-consistent field and direct optimization approaches in calculations of charge transfer excited states of nitrobenzene and N-phenylpyrrole, as well as an excited state of a large diplatinum and silver complex.

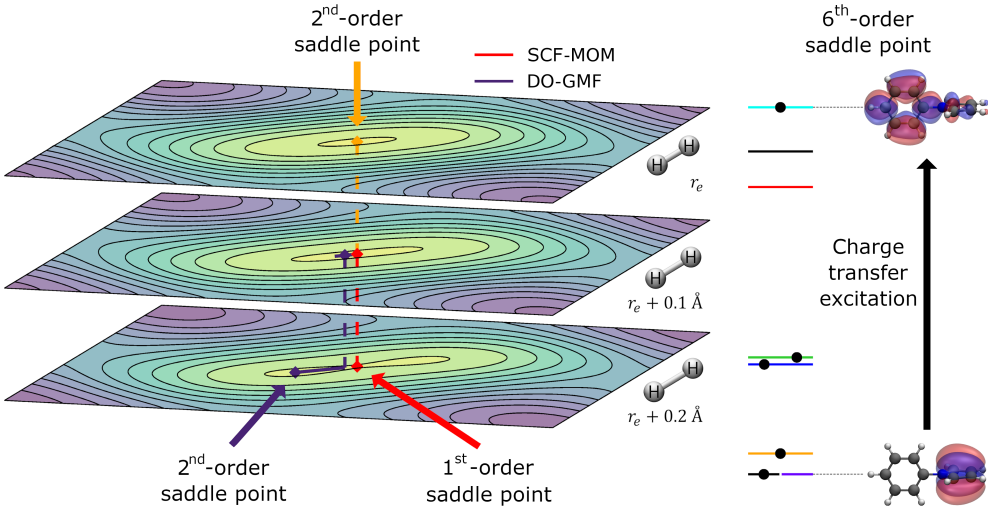

Figure 1: Left: Illustration of the convergence on a first order saddle point corresponding to HOMO-LUMO excitation of H_2 at three different interatomic distances. Right: Calculation of a charge transfer excitation in phenylpyrrole by converging on a 6-th order saddle point on the energy surface. (From ref. [1]).

References:
[1] Y. L. A. Schmerwitz, G. Levi and H. Jónsson, (submitted to *J. Chem. Theory Comput.* (2022).
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