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σ-SCF: A Direct Energy-targeting Method To Mean-field Excited States[1] HONGZHOU YE, MATTHEW WELBORN[2], NATHAN RICKE, TROY VAN VOORHIS, Department of Chemistry, Massachusetts Institute of Technology — The mean-field solutions of electronic excited states are much less accessible than ground state (e.g. Hartree-Fock) solutions. Energy-based optimization methods for excited states, like Δ-SCF, tend to fall into the lowest solution consistent with a given symmetry – a problem known as "variational collapse". In this work, we combine the ideas of direct energy-targeting and variance-based optimization in order to describe excited states at the mean-field level. The resulting method, σ-SCF, has several advantages. First, it allows one to target any desired excited state by specifying a single parameter: a guess of the energy of that state. It can therefore, in principle, find *all* excited states. Second, it avoids variational collapse by using a variance-based, unconstrained local minimization. As a consequence, all states – ground or excited – are treated on an equal footing. Third, it provides an alternate approach to locate Δ-SCF solutions that are otherwise hardly accessible by the usual non-aufbau configuration initial guess. We present results for this new method for small atoms (He, Be) and molecules (H_2, HF).

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[2]Current Affiliation: Department of Chemistry, California Institute of Technology

Hong-Zhou Ye
Massachusetts Inst of Tech-MIT

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