CHEAP AND RELIABLE OPTIMIZATION OF EXCITED STATE ORBITALS WITH THE SQUARE GRADIENT MINIMIZATION (SGM) APPROACH.

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Linear response (LR) protocols like time dependent density functional theory (TDDFT) or equation of motion coupled cluster (EOM-CC) are often used to compute energies of electronic excited states. While effective for valence excitations, LR methods are susceptible to catastrophic failure for problems like core excitations or charge-transfer states, where the optimal excited state orbitals differ considerably from the ground state reference. Orbital optimized (OO) methods are more effective for such problems, as they permit relaxation of excited state orbitals beyond linear response. Widespread usage of OO methods has however been hindered by their propensity to collapse to the ground state instead of the desired excited state. This is a direct consequence of excited states typically being unstable saddle points in orbital space.

We present a orbital optimization protocol that reliably converges to the closest stationary point to the initial guess, by minimizing the square of the energy gradient instead of explicitly attempting to extremize the energy. The computational cost of this square gradient minimization (SGM) method is only between 2-3 times the cost of ground state orbital optimization (per iteration). SGM+DFT therefore can be readily applied to large systems.

We subsequently demonstrate the utility of SGM by application to doubly excited states, core excitations and charge-transfer states. Specifically, we show that cheap DFT based OO approaches can predict energies of doubly excited states to significantly greater accuracy than expensive, LR coupled cluster approaches (that often have > 1 eV error). Similarly, we demonstrate that a DFT based protocol employing SGM predicts core excitation energies (at both the K and L edges) to < 0.5 eV RMS error (while TDDFT often has > 10 eV error). Finally, we demonstrate prediction of charge transfer excitation energies to low error with DFT/SGM – in stark contrast to standard TDDFT. Time permitting, we would also discuss use of SGM with methods like complete active space self-consistent field (CASSCF) to tackle strongly correlated excited states and model conical intersections.

References: Hait, D. and Head-Gordon M. J. Chem. Theory Comput., ASAP (2020); Hait, D. and Head-Gordon M. J. Phys. Chem. Lett. 11, 3, 775-786 (2020).