

Excited state orbital optimization with square gradient minimization and application to core-level spectroscopy

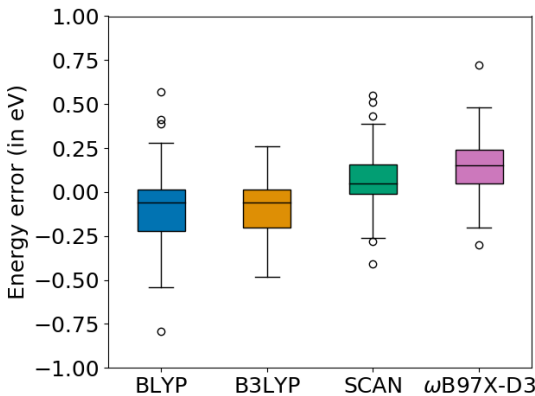
Diptarka Hait¹ and Martin Head-Gordon¹

Department of Chemistry, University of California, Berkeley, California 94720

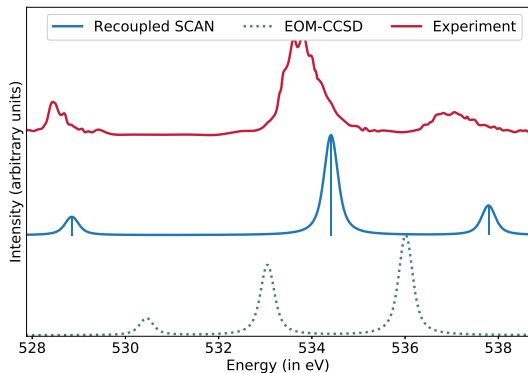
Linear response time dependent density functional theory (LR-TDDFT) is widely used to model electronic excited states. While often effective for valence excitations, TDDFT is susceptible to catastrophic failure for problems like core-level excitations or charge-transfer states, where the optimal excited state electron density differs considerably from the ground state reference. Orbital optimized (OO) methods like Δ SCF are more effective for such problems, as they permit relaxation of excited state orbitals beyond linear response. Widespread usage of OO approaches has however been hindered by their propensity to collapse to the ground state instead of the desired excited state. This “variational collapse” is a direct consequence of excited states typically being unstable saddle points of energy in orbital space (as opposed to local minima), which makes the performance of standard solvers like direct inversion of iterative subspace (DIIS) or geometric direct minimization (GDM) considerably less robust.

We present an orbital optimization protocol that reliably converges to excited states sans variational collapse. This is achieved by converting the energy (E) extremization problem to the minimization of $\Delta = \left| \vec{\nabla}_{\vec{\theta}} E \right|^2$ (i.e. the square of the E gradient vs $\vec{\theta}$, which parametrizes mixing between orbitals). All extrema of E are global minima of Δ , permitting this square gradient minimization (SGM) to reliably converge to the stationary point closest to the initial guess in orbital space¹. In addition, the computational cost of SGM is only 2-3 times the cost of ground state orbital optimization (per iteration). SGM/OO-DFT therefore can be readily applied to the large systems, offering a cheap and reliable path to access excited states. SGM can also be used with any other orbital-optimization based method, like complete active space self-consistent field (CASSCF).

We subsequently demonstrate the utility of SGM via application to core-level spectroscopy, using spin-pure OO-DFT methods like restricted open-shell Kohn-Sham (ROKS). ROKS/SGM predicts core excitation energies of closed-shell molecules with ≈ 0.3 eV RMS error vs experiment with several functionals^{2,3} (while TDDFT has > 10 eV error). This is comparable to the typical ~ 0.1 eV uncertainty in experimental values, indicating semiquantitative predictive power. Oscillator strengths are also reliably predicted, leading to computed spectra that can be directly compared against experiment without recourse to empirical shifts. Generalization to open-shell systems shows similarly good performance⁴, even for difficult systems like CO^+ where equation of motion coupled cluster singles and doubles (EOM-CCSD) qualitatively fails. This indicates that OO-DFT/SGM can be used to cheaply and reliably compute core-level spectra for states/species that arise in transient X-ray/XUV studies of chemical dynamics. This has led to several collaborative projects with experimental groups towards that objective, which will be briefly touched upon if space permits.



(a) Box plot of errors in lowest dipole allowed K-edge excitation for 40 small molecules.



(b) O K-edge of CO^+ .³ Recoupled SCAN is spin-pure OO-DFT for radicals⁴ (with the SCAN functional).

FIG. 1: OO-DFT prediction of core-level spectra.

¹D. Hait and M. Head-Gordon, *J. Chem. Theory Comput.* **16**, 1699 (2020).

²D. Hait and M. Head-Gordon, *J. Phys. Chem. Lett.* **11**, 775 (2020).

³D. Hait and M. Head-Gordon, *J. Phys. Chem. Lett.* **12**, 4517 (2021).

⁴D. Hait, E. A. Haugen, Z. Yang, K. J. Oosterbaan, S. R. Leone, and M. Head-Gordon, *J. Chem. Phys.* **153**, 134108 (2020).