

Multilevel Coupled Cluster methods for transient NEXAFS spectroscopy

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Coupled Cluster (CC) theory is among the most accurate methods for modelling molecular properties. Recently, we have implemented the core-valence separation (CVS) approximation [1]. In particular, we have combined this with a new implementation of CC3[2], resulting in unrivalled accuracy of core excitations.

Coupled Cluster theory has a high computational cost and steep scaling with system size. In order to overcome this problem, we have developed multilevel CC (MLCC) theory [3] where a smaller part of the molecule is treated with a high accuracy method and the rest more approximately. Local properties such as core excitations are ideally suited for such an approach [4]. Recently we demonstrated two orders of magnitude reduction in computational cost using the MLCC framework.

Recently, the first transient NEXAFS excited state measurements were performed at the Stanford Linear Accelerator Center (SLAC) by The Thymine Collaboration [5]. In the experiment, a new feature appeared after less than 100 fs time delay. In order to characterize this feature, the ground state geometry was optimized at the CCSD(T) level and the excited state geometries at the CCSD level. Excited state UV and X-ray spectra were simulated at the CCSD and CC3 level and show a remarkable agreement with experiment. The source of the new feature is determined to arise from population in the $n\pi^*$ state. Coupled Cluster dynamic calculations further corroborate this conclusion.

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References

- [1] S. Coriani and H. Koch, *J. Chem. Phys.* 2015, **143**, 181103
- [2] R.H. Myhre and H. Koch, *J. Chem. Phys.* 2016, **145**, 044111
- [3] R.H. Myhre, A. Sánchez de Merás and H. Koch, *J. Chem. Phys.* 2014, **141**, 224105
- [4] R.H. Myhre, S. Coriani and H. Koch, *J. Chem. Theory Comput.* 2016, **12**, 2633
- [5] The Thymine Collaboration: T. J. A. Wolf, R. H. Myhre, J. P. Cryan, S. Coriani, R. J. Squibb, A. Battistoni, N. Berrah, C. Bostedt, P. Bucksbaum, G. Coslovich, R. Feifel, K. J. Gaffney, J. Grilj, T. J. Martinez, S. Miyabe, S. P. Moeller, M. Mucke, A. Natan, R. Obaid, T. Osipov, O. Plekan, S. Wang, H. Koch* and M. Gühr