Warwick Centre for Predictive Modelling Seminar Series

Excited state calculations and theoretical spectroscopy of complex nanomaterials using Linear-Scaling Density Functional Theory

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Abstract: Linear-scaling approaches to density functional theory, particularly those employing efficient local orbital representations of the density matrix, have made great progress in the last two decades towards addressing the challenge of predicting ground state properties of large and complex systems. They have not, however, been routinely used for excited state properties, often because of the difficulty of representing unoccupied Kohn-Sham states using strictly localised orbitals. Recent work on in situ optimisation of Nonorthogonal Generalised Wannier Functions (NGWFs) to accurately represent unoccupied states [1] in large systems has made it possible to implement Linear-Response Time Dependent DFT methods (LR-TDDFT) [2] to study excitations. We have applied these methods to a variety of complex systems: pigment-protein systems including the Fenna-Matthew-Olson Complex [3]; simulated EEL spectra of defects in oxides; understanding the hierarchy of excited states in disordered molecular crystals; and tracing potential energy surfaces of photoexcited reactions [4]. Finally, while there exists a rather uncontrolled error in predictions from TDDFT based on the performance of the functional, many other factors such as sampling of configurations, solvatochromic shifts etc are possible to evaluate rigorously: the scope for introducing more rigorous approaches to predictive modelling for spectroscopy will be examined.

[1] L.E. Ratcliff et al, Phys Rev B 84 165131 (2011). [2] T.J. Zuehlsdorff et al, J. Chem. Phys 139, 064104 (2013). [3] D.J. Cole et al, J. Phys. Chem. Lett. 4, 4206 (2013). [4] J.-H. Li et al, Phys Chem Chem Phys 17, 12065 (2015).

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