Summer Internships 2023

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Exploring Electronic Structure Methods

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My research focuses on understanding the behaviour of and designing new methods to calculate the electronic structure of molecules. In particular understanding where and why existing methods fail tells us a lot about how to design new, better methods and algorithms. Below I list a number of possible research directions. These potential projects should be suitable for students with a good set of skills in theory and mathematics. I am also very happy to discuss potential projects not based on those listed here.

These summer projects should last about 8 weeks, and will involve working with and adding to a python software framework for manipulating and tracing multiple electronic states at different molecular geometries. Previous experience of python programming is essential, and a useful additional skill is experience with source code management (e.g. git) and collaborative software development (e.g. github or gitlab).

Describing Singlet Fission

Owing to its use in light-harvesting materials, there has been much recent interest in the *ab initio* study of singlet fission^{1;2}. Put simply, light excites an organic molecule into a low-lying excited singlet state, which relaxes into two coupled triplet states (coupled such that the result is still a singlet), which allow charge separation. If harnessed correctly, this is effectively a photovoltaic cell. Two problems generally arise when studying such molecules: i) they must be relatively large for the excited states to be sufficiently low in energy to be accessible with visible light. This makes computational simulation generally expensive; ii) for the excited state to relax to two triplets, it is generally thought that it must be an open-shell singlet. Such states cannot be correctly described by a single Slater determinant, so yet more costly multi-reference methods must be used.

In my group, we have been developing methods based on coupling non-orthogonal Slater determinants^{3;4}, and this approach is ideal to describing these open-shell singlet electronic states. This project will investigate the states of polyacene rings and their potential for describing singlet fission processes in molecules like the one below⁵



Understanding bond-breaking diabatically

A conventional view of a typical mechanism (e.g. an $S_N 2$ reaction) involves the simultaneous formation of one bond and breaking of another. In general there is a transition state during this process where there are two partial bonds. An alternative, unconventional view would be that this transition state is the superposition of two different Lewis-bonding configurations, those of the product and those of the reactant. Such states would be the 'diabatic states' where the electron configuration is not changed during the process. We are now able to find and track these states (if they indeed exist) during (e.g.) a Hartree–Fock calculation. The transition state may then be formed by a linear combination, using the Non-Orthogonal Configuration Interaction Method (NOCI)³. This project will look at some simple reactions and attempt to understand them via this 'diabatic' approach.

[5] L. E. A. Suarez, C. de Graaf, and S. Faraji, Phys. Chem. Chem. Phys. 23, 14164 (2021).

^[1] N. Monahan and X.-Y. Zhu, Ann. Rev. Phys. Chem. 66, 601 (2015).

^[2] N. J. Mayhall, J. Chem. Theory Comput. 12, 4263 (2016).

^[3] A. J. W. Thom and M. Head-Gordon, J. Chem. Phys. 131, 124113 (2009).

^[4] H. G. A. Burton, M. Gross, and A. J. W. Thom, J. Chem. Theory Comput. 14, 607 (2018).