

Department of Chemistry: Part III Projects 2017/18

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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. A familiarity with computer programming would be especially helpful. I am also happy to discuss potential projects not based on those listed here.

These projects are relatively flexible and so can be adapted for relatively short projects from 8 weeks, or extended to form the foundation of a PhD.

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 determinants⁵, 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.

The Photochemistry of Ethene

The ethene molecule has long been used as a fundamental model for the understanding of photoisomerization processes, and well-studied computationally through the potential energy surfaces of its ground and excited states, usually obtained through CASSCF or MRCI³, though recent attempts have been made to study it with density functional theory⁴. The Non-Orthogonal Configuration Method (NOCI)⁵ provides excited states directly from interacting different Hartree–Fock solutions, but does not in itself include dynamical correlation. One possible way to include dynamical correlation by including a modification of MP2 theory has recently been proposed⁶, and in combination with NOCI will allow a computationally cheap method where the potential energy surface can be quickly evaluated.

This project will use NOCI+MP2 to derive a the potential energy surface of the excited states of ethene and investigate its properties.

Understanding Strong Correlation

The Hubbard model is a relatively simple model of strong correlation, with lattice sites (corresponding to a single available orbital on an atom) which can be occupied by electrons, and which shows a rich range of behaviour in its electronic structure. The balance of onsite electron-electron repulsion, U , and kinetic energy, t , determines the nature of the system which moves from metallic for small U/t to insulating for large U/t . Recently, there has been an experimental realization of the Hubbard model with confined cold atoms⁷, and a number of studies showing a breakdown in single-reference correlation techniques at describing such systems⁸.

It is likely that symmetry-broken Hartree–Fock solutions will provide a better basis for correlation treatments. In this project we will investigate the various Hartree–Fock states of the Hubbard model for different U/t , applying correlation treatments to them to understand the origins of their breakdown.

High Accuracy Quantum Chemistry for Solids

Conventional wavefunction-based quantum chemistry techniques are becoming increasingly popular when applied to solid state systems owing to their systematic improvability which enables confidence in the results of calculations in areas where techniques like density functional approximations are known not to perform well. These techniques suffer from a poor scaling with system size however rendering only relatively small systems calculable at levels of theory with high accuracy. Coupled Cluster theory, known as the gold standard of Quantum Chemistry, has seldom been applied to solid state systems owing to the infeasibility of such calculations. Recently we have developed a stochastic approach to Coupled Cluster theory¹², which has proven to be able to tackle problems well out of reach of conventional coupled cluster approaches, and has so the potential to tackle problems in solids which are currently infeasible, including in the solid state. This project will investigate whether these calculations on the solid state can accurately represent strong correlation problems such as the Mott–Hubbard insulator transition.

Quantum Astrochemistry

How can we determine the chemical constituents of the stars and planets? Spectroscopy is the obvious answer, but surprisingly experimental data is not usually sufficient in all but the most common molecules. Such projects as ExoMol (www.exomol.com) attempt to draw together this experimental data, but still have limited success. Computational electronic structure techniques should be able to come to the rescue, but the generally available present-day methods do not have the power to predict to the subwavenumber accuracy required. With these highly accurate spectra, the prospect of identifying previously unknown species in exoplanets, space, or even in solar atmospheres becomes feasible. In recent years, members of the department have been developing Quantum Monte Carlo (QMC) techniques^{12;13} which can produce the required accuracy, through highly parallelizable codes. To predict vibrational spectra of a molecule, however, the potential energy surface of such molecules (as well as the dipole moments) is required in order to perform the quantum mechanical calculations on the nuclei in order to generate spectra. This project will apply the newly developed QMC methods to promising molecules suspected to be found in extraterrestrial environments such as C_2 and SiH (which are very challenging to determine experimentally) with the hope of identifying these molecules.

Understanding Spin and molecular magnets

The spin of the electron forms a crucial part of modern quantum chemistry, especially when considering transition metal complexes. However, the prediction of the spin state of a complex is often fraught with difficulties, and commonly used methods such as Density Functional Approximations often fail to describe spin states correctly. Even more complicated cases are when individual spins couple together, resulting in extremely challenging systems to calculate, usually requiring very expensive computational methods.

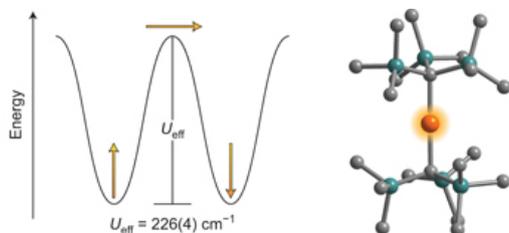


Figure 1: A mononuclear iron complex exhibiting molecular magnetism⁹.

Molecular magnets are one such example of where these spin states can be put to good use, and there has been recent interest in systems where a single transition metal nucleus' spin is able to support magnetic behaviour.⁹ This project will involve investigating whether Density Functional Approximations, coupled with techniques to locate solutions which are not normally found^{10;11} can be used to successfully describe these systems.

A Solution for Water?

Despite many decades of research, it is still not possible to compute accurately the phase diagram of water on the basis of *ab initio* calculations. The calculations of phase diagrams are computationally extremely challenging even on simple systems¹⁴ and require an accurate intermolecular potential. The current state of the art for such methods involves Quantum chemical calculations at the CCSD(T) level, or Diffusion Quantum Monte Carlo calculations, and it is unclear whether these are sufficiently accurate¹⁵. The stochastic methods in my group produce high-accuracy energies beyond those of CCSD(T) and this project will apply them to small water clusters to create the very best *ab initio* intermolecular potentials for water to enable it to be accurately modelled.

Do errors matter?

A number of very accurate methods in electronic structure for calculating energies produce estimates with error bars on them^{12;13}. Ideally one can run a calculation for longer to reduce the error bars to an insignificant level, but is this really necessary? An unanswered question is what to do in systems where the error bars are not insignificant. Given a molecular binding curve with associated random error bars, how would this affect a calculated vibration frequency of a molecule? Can we use make use of such noisy data to produce values with their own confidence intervals (error bars)? One approach to tackle this problem is to use a Bayesian approach to fitting, such as that of Gaussian Approximation Potentials¹⁶, which produce a probability distribution for an energy rather than a single fitted value. Very little investigation has gone into making use of this distribution rather than a single fitted curve as a basis for vibrational calculations. This project will explore these issues and hopefully posit some solutions to these problems.

Complex colours

The excited electronic states of molecules play an important role in many parts of chemistry, and as they are necessarily short-lived, they are difficult to study experimentally. Additionally theoretical methods for studying these states are also very limited, and often lack the accuracy to be predictive

(e.g. the colours of transition metal complexes are not in any way predictable). Recent research in my group has been investigating using Hartree–Fock Theory to investigate excited electronic states^{10;11}, but such methods are equally applicable to Density Functional Theory, where these excited electronic states have previously been ignored in the theory, as they are difficult to locate. This project will investigate the existence of these states and how they correspond to real excited states of molecules and assess their usability in small molecular systems.

Exploiting reconfigurable hardware

Modern high-performance computing systems are usually set up with large numbers of nodes, each with many CPU cores, each node being linked by very fast networks. Recently Graphics Processing Units (GPUs) have begun to be used within such supercomputers, where large amounts of data can be streamed and processed with relatively simple instructions very quickly. Alternative current developments in computer hardware work with hardware such as Field-Programmable Gate Arrays (FPGAs) which can be flashed with a custom circuit design to process streamed data in more complex ways than GPUs. Encoding these designs used to be the speciality of chip designers, but recent innovations have led to compilers which can translate conventional style programs into circuit designs for such FPGAs, allowing algorithms to be easily converted directly to hardware, with speedups measured in the hundreds when compared to CPUs. This project will investigate encoding Quantum Monte Carlo techniques (which are used for high-accuracy calculations of energies of materials) on FPGAs and the feasibility to rework these algorithms to take advantage of new computer architectures, and apply them to some challenging systems, such as solid-state hydrogen phase transitions.

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