Dr Alex Thom

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.

Exploring Density Space

While chemists are used to thinking of electrons in sets of molecular orbitals, the crucial parameter of interest in molecules is in fact the electronic density. Methods such as Hartree-Fock and Density Functional Theory perform searches in the space of possible densities to find the density with minimum energy which defines 'a solution'. In a simple system this can be envisaged as searching for the valleys in an undulating energy surface. Despite some recent methods to search for solutions on it[3], Little is known, however, about the nature of this energy surface — aside from that it has many peaks and troughs, and each trough is a potential electronic state. A conventional electronic structure calculation might start at a good guess somewhere on this surface and descend to find its local minimum which may not be the correct global minimum. This project will investigate the nature of this energy surface and its minima, seeking to understand what physical significance they have, and develop new methods to locate them.
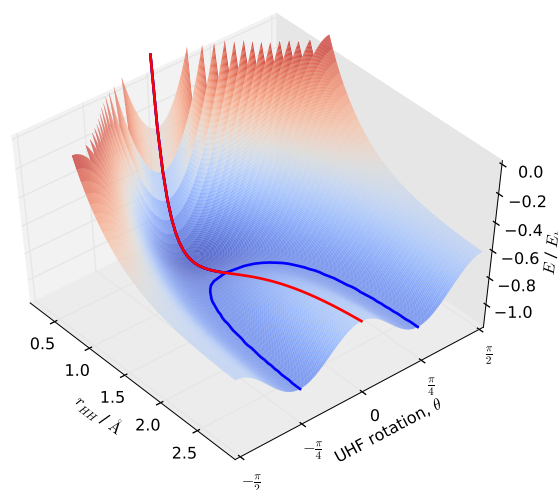

Figure 1: *The unrestricted Hartree-Fock energy surface of H_2. Blue lines indicate unrestricted solutions and red restricted solutions.*

Do errors matter?

A number of very accurate methods in electronic structure for calculating energies produce estimates with error bars on them[1,2]. 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)? This project will explore these issues and hopefully posit some solutions to these problems.

The Thermodynamics of a Computer Simulation

Computer simulations have long been used to investigate thermodynamic problems such as simulating phase changes, and calculations of this sort are now relatively routine (though still challenging). Often, however, difficult problems may be recast as a larger, but conceptually simpler problem. One such example of this is in Quantum Monte Carlo, where the energies of systems such as molecules are calculated from the evolution of 'particles' in imaginary time (each particle represents an instantaneous snapshot of the positions of all the electrons in such a system). The dynamics of these fictitious particle may be thought of in terms of processes such as diffusion and branching (where one particle splits into two), and by allowing these particles to evolve, the energy of the system is recovered. Having introduced fictitious particles, it is now possible for them to act as real particles would, and undergo such phenomena as phase transitions (e.g. condensation from a gas-like state to a liquid-like state), which can very much hinder the actual calculations which are to be performed. Very little is known about these phenomena, but a recent paper[4] has shown that they are observable, and indeed fundamental to the behaviour of these calculations. This project will investigate these phenomena in a method related to Quantum Monte Carlo, Stochastic Coupled Cluster Theory[1] to derive an understanding of this phase transition behaviour and its effect on the efficiency of such Quantum Monte Carlo methods.

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.
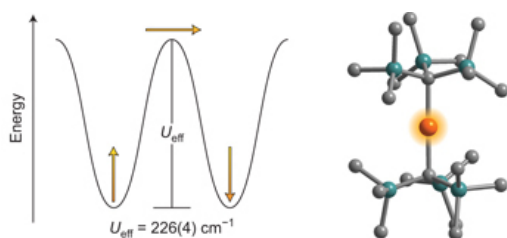
Molecular magnets are one such example of where these spin states can be put to good use, and there has been recent interest in systems where a single transition metal nucleus' spin is able to support magnetic behaviour.[5] This project will involve investigating whether Density Functional Approximations, coupled with techniques to locate solutions which are not normally found[3] can be used to successfully describe these systems.

Figure 2: *A mononuclear iron complex exhibiting molecular magnetism[5].*

Exploiting reconfigurable hardware

Modern high-performace 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 feasability to rework these algorithms to take advantage of new computer architectures.

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 infeasability of such calculations. Recently we have developed a stochastic approach to Coupled Cluster theory [1], 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. This project will extend the stochastic Coupled Cluster theory to investigate periodic systems and benchmark its effectiveness and scaling.

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[3] A. J. W. Thom and M. Head-Gordon, Phys. Rev. Lett. **101**, 193001 (Nov. 2008).
[4] J. J. Shepherd, L. R. Schwarz, R. E. Thomas, G. H. Booth, D. Frenkel, and A. Alavi(2012), arXiv:1209.4023.
[5] J. M. Zadrozny, D. J. Xiao, M. Atanasov, G. J. Long, F. Grandjean, F. Neese, and J. R. Long **5**, 577 (2013).