Project Ideas 2020/21

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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 (especially python) would be especially helpful. I am also very 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 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.

Quantum Chemistry on Quantum Computers

Quantum Computers can in principle solve extremely hard problems in significantly shorter times than conventional algorithms. Within the world of quantum chemistry, both Hartree–Fock[5] and Unitary Coupled Cluster Theory[6;7] have been used to do calculations on quantum computers, but these are limited in their application by the number of qubits available, which commonly corresponds to the number of orbitals which can be described, and the complexity of the quantum circuits.

This project will look at the possibility of using Stochastic Coupled Cluster Theory[8], and similar algorithms in conjuction with quantum hardware to increase the size of calculations possible.

Holomorphic Density Functional Theory

My group has recently extended the concept of holomorphic Hartree–Fock theory[4;9] to a holomorphic[10] Kohn-Sham formalism of Density Functional Theory. This approach allows tracing of solutions from Hartree–Fock to KS-DFT with many different functionals. This project will explore the many possibilities that this new theory brings, including how the DFT solutions behave with molecular geometry changes, and investigate whether they are a better approximation to the Full Configuration Interaction Solutions for theses systems.

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 MRCI[11], though recent attempts have been made to study it with density functional theory[12]. The Non-Orthogonal Configuration Interaction Method (NOCI)[3] 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 is to do so perturbatively. We have derived a NOCI-PT2[13] to include this dynamical correlation.

This project will use NOCI-PT2 to derive a potential energy surface of the ground and excited states of ethene and investigate their properties and look at dynamics on them.

Photochemistry in proteins

Full quantum chemical methods can provide extremely high accuracy energies for ground states along with good estimates of excitation energies of isolated small molecules. However, much photochemistry of interest involves such molecules interacting with a much larger environment, for example a chromophore in a protein scaffold. Unfortunately full quantum chemical methods scale prohibitatively quickly with system size, so cannot be simply applied to such systems, and the general approach is to describe the environment with a lower level of theory to the chromophore, retaining as much of the character of the environment and an accurate description of the molecule of interest.

My group has been developing new methods to study excited states via Non-Orthogonal Configuration Interaction[14], and this project will investigate whether they can be used effectively in a lower-level protein environment.

Understanding bond-breaking diabatically

A conventional view of a typical mechanism (e.g. an S_N2 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.

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 atoms[15], and a number of studies showing a breakdown in single-reference correlation techniques at describing such systems[16].

It is likely that symmetry-broken Hartree–Fock solutions will provide a better basis for corrlation treatements. 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.

Strong Correlation with Stochastic Coupled Cluster Theory

Conventional Coupled Cluster theory and its stochastic implementation[8] produce highly accurate energies for systems which are dominated by a single electronic configuration, but struggle or fail catastrophically in situations like bond-breadking where there are multiple competing configurations. We have recently extended the stochastic coupled cluster approach to include multiple reference determinants within an active space[17] and though this provides a promising starting point for a more general stochastic multireference approach, it is far from black-box for the user. More conventional multireference coupled cluster approaches generally involve a separate Active Space Configuration Interaction calculation to optimize an appropriate active space. This project will explore how an active space can be chosen automatically, and investigate whether a stochastic FCIQMC-like approach[18] can be used within the active space.

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[8], 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[8;18] 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 combine approaches based on Machine Learning and Gaussian Approximation Potentials[19] to the prediction of accurate spectra.

Effect of donor atoms and the crystal field on the single-molecule magnet behaviour of a cobalt and iron complexes: From Hartree-Fock to multi-reference method

Single-molecule magnets (SMMs) present the smallest possible unit for spin-based electronic devices revolutionising current and future technologies. Although, recent advances in SMMs have shown lanthanide-based complexes to be more promising, the cost and volatility of the rare-earth markets mean that a cheaper and more stable source of materials for SMM fabrication is needed. Independently, Sm and Nd are not popular for SMM while Co and Fe form part of the most interesting transition metal SMM reported. The magnetic properties of powerful classical intermetallics likes $SmCo_5$ and $Nd_2Fe_{14}B$ open a new research window for hybrid lanthanide-transition metal SMM design. However, understanding the intrinsic behaviour of each unit separately will form a prerequisite to useful investigation of their hybrids. Smaller systems made up of Co (Figure 2) and Fe could allow us to produce Kramers and non-Kramers ions with insight on the relationship between crystal field effect and minimisation of quantum tunnelling of magnetisation (QTM) in the ground state where breaking of M_s degeneracy and in turn QTM is formally forbidden without field (Figure 1).[20] The crux of the present study will therefore be to investigate factors necessary for the observation of single-molecule magnet behaviour in cobalt and iron complexes using techniques like HF, DFT and *ab initio*[21] multi-reference methods.

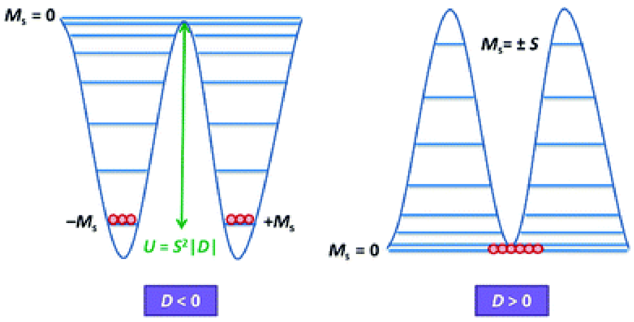

Figure 1: *Double-well energy diagram for negative (left) and positive (right) axial zero-field splitting parameter, D.*[22]

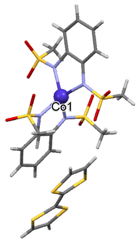

Figure 2: *A cobalt(II) complex of 1,2-bis(methanesulfonamido)benzene ligand with tetrathiafulvalenea(TTF) ligand as counterion.*[23]

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[3;24], 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 involve investigating the nature of metal-ligand charge transfer transitions and how accurately they can be predicted, comparing multiple DFT solutions with newly developed multireference approached based on multiple Hartree–Fock states (NOCI)[14;25].

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)[26] 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 conventionial 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, and apply them to some challenging systems, such as solid-state hydrogen phase transitions.

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