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Research Projects 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. 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.

Quantum Chemistry on Quantum Computers

Quantum computers make use of quantum superpositions of states to compactly represent information which would be exponentially large on a classical computer. Similarly, algorithms which have exponential complexity on a classical computer may be able to be cast into a polynomial complexity on a quantum computer. This has significant possibilities in Quantum Chemistry, where solving the Schrödinger Equation is formally exponentially scaling, and even approximate methods to calculate accurate energies quickly become unfeasible on a classical computer. Quantum computing is still, however, in its infancy, and at present we are in the era of Noisy Intermediate-Scale Quantum (NISQ) devices, which have very few quantum bits (qbits), and are very noisy, making even small calculations challenging, and so generally involve hybrid algorithms using both classical and quantum computers.

We have recently developed methods to perform Unitary Coupled Cluster, a popular method on today's quantum computers, classically using Monte Carlo[?], and this can be used to optimise similar calculations in quantum computers[?]. A promising alternative quantum algorithm for quantum chemistry, known as the Hardware Efficient Ansatz has recently been developed[?], where the explicit connection to a quantum chemical method is broken. This project will combine a classical Monte Carlo approach to solving electronic structure problems with this Ansatz to investigate its properties on larger systems, and how it may be improved.

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[?][?]. 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[?][?], 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 below[?].
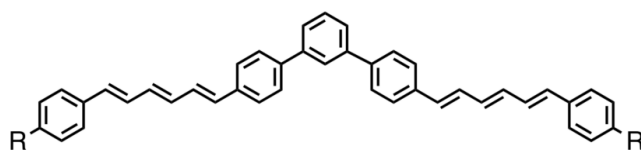
Exciting Solids and Compressed Atoms

Simulations of the solid state are challenging owing to the sheer numbers of atoms needed to reasonably reproduce a crystalline lattice. Techniques such as Periodic Boundary Conditions can alleviate this to an extent, though to perform calculations beyond the mean-field (e.g. Density Functional Theory) level requires large **k**-point lattices or equivalent supercells to reach convergence of correlated ground state energies. A yet more challenging problem is the accurate calculation of excitation energies in such systems, beyond the simple band-structure picture. In such situations the periodicity is generally broken by a localized excitation and so large supercells must be used.

The benchmarking of excited state electronic structure methods in such systems is very challenging owing to the general broadness of experimental excitation features. A particularly convenient test system is that of solid helium, which has an extremely large excitation energy and is expected to have a very localised electronic structure in both its ground and excited states. Existing calculations[?] can successfully replicate the increase in the excitation energy with increasing pressure as found in experiment[?], and loosely explained by closer neighbouring atoms exhibiting a stronger Pauli repulsion.

This project looks to investigate whether this pressure effects on the electronic excitations transfer to helium bubbles embedded in solids such as diamond, silicon and aluminium and resolve the disagreements between experimental measurements in such systems where at high pressures these excitations may no longer exist.

Modelling the Origin of Life (in collaboration with Prof. Archibald)

Since the discovery of the first exoplanet in 1992 over 5000 exoplanets have been found in the Universe. The spectroscopic detection of trace gases in their atmospheres enables us to ask one of the most fundamental questions in science: are we alone in the Universe or is there life in other planets? Atmospheric chemistry will play a central role in answering this question and in this project joint with Prof. Archibald's atmospheric chemistry modelling team and colleagues at the Initiative for Planetary Science and Life in the Universe this project will use a combination of kinetic modelling and *ab initio* calculations to investigate key reactions proposed as being important building blocks for life.

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[?], though recent attempts have been made to study it with density functional theory[?]. The Non-Orthogonal Configuration Interaction Method (NOCI)[?] 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 proposed[?], 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.

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

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[?] 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[?] 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[?] 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[?], 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[?,?] 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[?] to the prediction of accurate spectra.

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[?][?], 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)[?][?].