**Density Matrix Quantum Monte Carlo Simulation of Solids**

Molecules and solids are held together by chemical bonds made of highly quantum mechanical electrons that behave more like waves than particles. To understand even everyday materials quantitatively, and to predict the properties of new materials, we have to solve the many-electron Schrödinger equation. Unfortunately, this is easier said than done.

The Schrödinger equation for $N$ interacting electrons is a partial differential equation in $3N$ spatial variables. For systems of more than a few electrons, this is so intractable that approximations are required: the electron-electron interaction is replaced by a density-dependent effective potential or "mean field", allowing the $3N$-dimensional Schrödinger equation to be separated into $N$ three-dimensional equations, one for each electron.

Mean-field approaches such as density functional theory and Hartree-Fock theory have been enormously successful and underlie most of our quantitative understanding of condensed matter, but do not always work. In strongly-correlated solids, in particular, the mean-field approximation often fails and we are left with very limited options. This explains why, thirty years after they were first discovered, we still have little idea why high-temperature superconducting cuprates behave as they do. One of my main scientific interests is to help develop techniques to tackle the many-electron Schrödinger equation without mean-field approximations.

The technique with which I am most closely associated is the quantum Monte Carlo method, in which parallel computers are used to carry out huge numbers of idealised "experiments", averages of the results of which yields the results of real experiments almost exactly. In large systems, in particular, quantum Monte Carlo methods are far more accurate than any other available approach.

A few years ago, Ali Alavi and his group from Cambridge invented the full configuration interaction quantum Monte Carlo (FCIQMC) method [1,2], which has been enthusiastically received by quantum chemists. Density matrix quantum Monte Carlo (DMQMC) [3,4] is a new finite-temperature analogue of FCIQMC. Unlike FCIQMC, which is a ground-state method, DMQMC samples the $N$-electron density matrix at finite temperature and allows complete access to the quantum statistical physics of the system under study.

We are currently applying DMQMC to "warm dense matter" (WDM), which is in fact extremely hot ($kT$ is comparable to the Fermi energy) and no denser than ordinary matter. (Only astrophysicists could have chosen such a misleading name!) WDM can be found in laser fusion and shock-wave experiments, radiation damage cascades, solids illuminated by powerful lasers, and planetary cores. Electrons at WDM temperatures are created by the decay of plasmons in metallic nanospheres at room temperature and can catalyse chemical reactions such as water splitting that normally require much higher temperatures [5].

Our understanding of hot materials is very limited. Density functional theory can be applied to WDM in principle, but requires as input the exchange-correlation functional at high temperature, which is currently unknown. We have recently DMQMC to calculate this functional [6,7] and helped to resolve a serious disagreement between previous work by other groups using other methods [8,9].

This project will apply DMQMC to real warm dense materials. What happens to chemical bonds when electrons are suddenly heated? It is thought that they weaken and that the nuclear
repulsion pushes the atoms apart. If this cannot happen easily, as in a radiation damage cascade deep inside a solid, a "Coulomb explosion" may take place. DMQMC will allow phenomena such as this to be studied accurately and quantitatively for the first time.