Theoretical Chemistry on Supercomputing Facilities

Mark Vincent
Dept. of Chemistry, University of Manchester

Looking at past issues of CSAR Focus one can see that there are frequent references to computational chemistry on its pages. However, these tend to be references to a small part of what computational chemists do on supercomputers. In this article we will attempt to give an overview of what Computational Chemists are doing and why it is important to use state of the art computational facilities. I shall mainly concentrate on the work of the 'Theoretical and Computational Chemistry' group at The University of Manchester.

Dynamics – studying the movement of atoms.

One of the simplest chemical reactions is symbolically of the form

A + BC => AB +C

i.e. an atom reacting with a diatomic molecule giving a diatomic and an atom. Despite the simplicity of this reaction, complex dynamical processes are taking place. The vibrational and rotational states of the diatomic molecule (BC) have to be coupled to the translational motion of the atom A. For example, A can collide with BC head on or in a glancing blow (possibly leading to no reaction but energy transfer). To study such reactions requires an accurate scattering solution of the Schrodinger equation.

The other end of the size spectrum of molecules from a diatomic is a protein. The importance of understanding how proteins function so that drugs, pesticides or antibiotics can be developed that destroy the function of the enzyme, is important for human health and agriculture. To do this often requires knowledge of the dynamics of the protein. While it is true that the mode of operation of some enzymes can be relatively easily determined from their static X-ray structures, others catalyse reactions by changing from their ground state structure to a higher energy structure or by undergoing large amplitude motions. To determine if these large structural changes take place prior or during reactions in the protein requires the sampling of a huge part of the conformational space of the protein. One other form of dynamics is Car-Parrinello which we will mention later.
[Programs: CPMD, AMBER, NAMD, own codes]

Solids – The study of systems that are of large or infinite spatial extent.

As a large number of industrial catalysts are solids, the understanding of the way these function and the design of new catalysts is an important area of research. In addition, the study of the binding of pollutants and undesirable species to the surfaces of solids as a method of removing them from the environment is vital. Another area of interest is defects on the surface of solids, as these can be places that are highly reactive. The potentially large number of atoms involved in these studies requires massive computing resources. [Programs used: CRYSTAL, VASP, GULP, QM/MM]

Liquids – Models of solvation and the study of pure substances.

Many chemical reactions take place in the liquid phase with the reacting species being different from the solvent that constitutes the bulk of the liquid. However, sometimes the solvent actively participates in the reaction but is regenerated or released by the end chemical process and hence gives the superficial impression of just being a medium for the reaction. Modelling reactions with explicit classical or quantum mechanical water molecules present can give detailed insight into the processes taking place. Using water as a solvent at raised temperature and pressure (supercritical water) leads to a solvent medium with very different properties from normal water. One way of studying chemical reactivity in this form of water is by Car-Parrinello dynamics. The program used for these calculations (CPMD) runs very well on massively parallel machines but requires vast amounts of time. Other types of liquid of interest are liquid crystals, used commercially in display devices, which have the property of a fluid, but retain much more order of the molecules with respect to each other than a normal liquid. [Programs used: DL-POLY, CPMD and own codes]

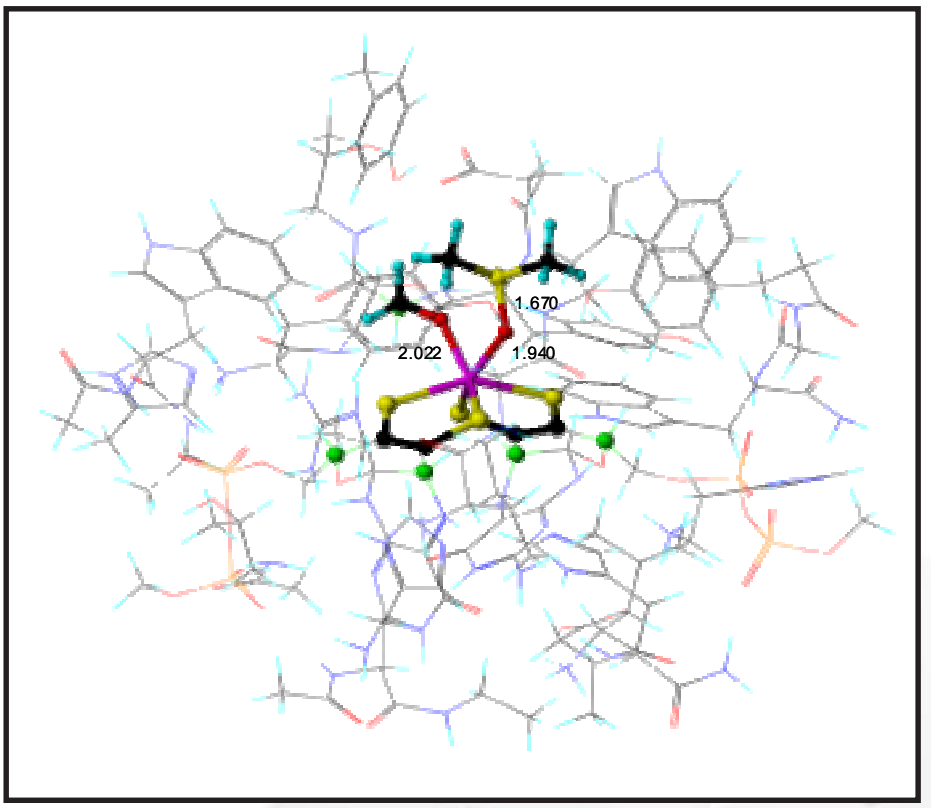

Figure 1: The active site of the enzyme DMSO reductase from the work of Dr Jonathan McNamara, Dr Matthias Mohr and Professor Ian Hillier using the crystal structure of L. J. Stewart et al, J. Mol. Biol., 2000, 299, 593.

Gas Phase – Isolated molecules or clusters of molecules.

Calculations performed on isolated molecules or clusters of molecules in the gas phase are free of complications due to periodic boundary conditions or solvents. A single molecule or a small cluster of molecules can be studied in detail and because they are small in size sophisticated theoretical approaches can be employed. However, these methods often require large amounts of memory and disk space. One use of the information from these studies is to obtain parameters for more approximate levels of theory (the so called semi-empirical theories). A genetic algorithm determines a set of parameters that can describe the electronic structure of a system whose size makes it prohibitive to study by more rigorous methods, but whose reactivity demands a quantum mechanical description. (It should be noted that the faster classical mechanics often cannot describe bond breaking and making processes.) The genetic algorithm code runs well on parallel machines, but requires large amounts of time.

We have also undertaken studies into the nature of the interaction between two fragments of molecule. In this we split the molecule into two parts and see how they interact. This provides information on the nature of the bonding between the fragments. While this does not necessarily require supercomputer facilities, due to the size of systems we have studied parallel computers are needed to yield results in a reasonable time frame. Other studies involved developing methods of obtaining wave functions that include electron correlation and looking at metal complexes that are potential molecular magnets (i.e magnets the size of a single molecule).
[Programs used: Gaussian, GAMESS-UK, CADPAC, locally written BOVB and Manchester University Semi-Empirical program (MUSE)].

This brief summary of theoretical chemical activity at The University of Manchester indicates that we study all of the common phases of matter and the chemistry taking part in them. A variety of computer codes are employed in our research, some of which are 'home grown'.

Acknowledgements

I am thankful for comments from Professor Ian Hiller, Professor Jonathan Connor, Dr Joe McDouall and Dr Andrew Masters.