Using computers to model chemical reactions, spectroscopic properties, molecular structures and many other things is an incredibly important aspect of modern chemistry. Indeed, with the increased availability of high-powered computers and easy to use software, computational chemistry is now as accessible as techniques such as NMR spectroscopy and is routinely used alongside experimental studies to gain a deeper insight into experimental observations. It is easy to see this by taking a quick look in the most prestigious chemistry journals (e.g. *J. Am. Chem. Soc.*), where many studies involve a combination of experimental and computational work using methods such as Density Functional Theory (DFT) or Molecular Mechanics (MM) approaches. One area where computational (in particular quantum-chemical) methods are particularly important is in mechanistic studies of chemical reactions and catalysis. It is very challenging to understand reaction mechanisms using experimental studies alone, but a combination of experiment and computational chemistry can allow us to gain a detailed understanding of mechanism that is of great use in a range of areas. For example, if we understand the mechanism of a homogeneous catalytic reaction it is possible to understand what factors might limit the catalyst turnover frequency and/or allow unwanted side reactions to occur. Armed with this knowledge it is possible to design new catalysts that are more active and/or more selective.

This project will focus on the development of approaches to overcome one of the major challenges with using quantum-chemical methods such as DFT to model reactions taking place in condensed phases (e.g. in solution). At the moment it is very common to perform mechanistic studies by modelling reaction intermediates and transition states in the gas-phase to build up a potential energy surface (PES) e.g. figure to the right. The PES can be related to the relative rates of different mechanistic possibilities and give information on regio- and potentially stereochemistry, side reactions and so on. However, in order to compare the results of gas-phase calculations with reactions taking place in condensed phases we need to apply a range of corrections (e.g. for solvation, entropy, potentially dispersive effects) that are not always that successful. This project will investigate the use of computational approaches to avoid the problems with these corrections. We will collaborate with experimental groups at York to investigate a range of systems of great current interest. These include organometallic chemistry (transition-metal-mediated electrophilic fluorination), organic/materials chemistry (liquid crystalline ionic liquids as reaction media), metalloenzymes (Mo-containing alkyn-functionalisation enzymes) and supramolecular chemistry (weak H-bonding in solution).

Extensive training will be provided in the use of computational chemistry software, how to work effectively in Linux and a range of methods for understanding electronic structure and mechanism in molecular chemistry. No prior experience of computational chemistry is required - a good imagination and chemical intuition tends to be more useful for mechanistic studies. By working closely with experimental groups you will gain insight into the challenges and opportunities of experimental mechanistic studies and how these are performed.

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**Project title:** Quantum-chemical modelling of reaction mechanisms in condensed phases  
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**Application Closing Date:** none  
**Interview Date:** to be arranged

**Funding Source:** student to secure own funding  
**Funding Types:** Self-funding  
**Funding scheme (if any):** none  
**Eligibility:** UK/EU/Overseas

For more information contact chemgrad@york.ac.uk or see our web page: http://www.york.ac.uk/chemistry/postgraduate  
The Department of Chemistry holds an Athena SWAN Gold Award and is committed to supporting equality and diversity for all staff and students.