Institution: University of York

Unit of Assessment: 9, Physics

Title of case study: Materials modelling using ab-initio electronic structure calculations

1. Summary of the impact (indicative maximum 100 words)

A computer program, CASTEP, has been developed to use quantum mechanics to calculate the structure and properties of materials. The code is distributed commercially via Accelrys Inc. with sales, for example, in the automotive, electronics and pharmaceutical industries in excess of £1m per year since 1998, accelerating to over £2.5m per year recently and total sales (late 2012) exceeding $30m. Commercial applications include designing new battery materials and electrodes to improve the performance of electric cars (Toyota), integrating organic electronic materials for light-weight flexible displays (Sony), and developing new catalysts for hydrogen-powered fuel cells (Johnson-Matthey).

2. Underpinning research (indicative maximum 500 words)

CASTEP is a robust and accurate, general-purpose materials modelling code built upon the Density Functional Theory (DFT) version of quantum mechanics. DFT was conceived in the 1960s, though the theoretical framework is still being actively developed, with important recent contributions by academic staff at York (Professor Rex Godby and Dr Matt Probert). The seminal CASTEP paper was published in 2002 [1] and Dr Probert and Dr Phil Hasnip from Physics, York are co-authors describing the development of the code.

CASTEP can be used to predict the properties of any material using the power of quantum mechanics, and also to support experimental studies of materials and processes by helping with the interpretation of experiments, offering a unique 'atom by atom' perspective. Sample published results using the code for commercially important developments have been reported in the open literature [2 – 3], but much industrial work is commercial-in-confidence.

The underlying research and development of CASTEP began in 1999 with a core team of UK academics - the CASTEP Developers Group (CDG) - and continues to date. Probert and Hasnip are founding members of the CDG. Probert joined the York Physics Department in 2000 and leads the York contribution, which is responsible for the calculation of the groundstate wavefunction, molecular dynamics and structure optimisation. Hasnip moved to York in 2005 and works for Probert as a PDRA. The first complete version of CASTEP was released in 2002, and there have been new releases annually since then, with each new release incorporating new science capabilities and calculation speed increases. The functionality developed at York is fundamental to every CASTEP-based study.

The CDG currently comprises six academics: Probert (York), Hasnip (York), Clark (Durham), Pickard (UCL), Refson (STFC), Yates (Oxford) and their associated research groups. Each member of the core team is responsible for writing and developing specific areas of functionality: Hasnip's primary area is the calculation of the groundstate wavefunction, and Probert's is molecular dynamics and structure optimisation.

In total, the York contribution to CASTEP amounts to more than 1/3 of the core of the code (both in terms of Probert and Hasnip having written more than 1/3 of the 'lines of code' and in terms of core functionality) providing key features that are needed by all users of the code. This core functionality includes finding the ground state energy and wavefunction of the system, and then using this to find the most stable arrangement of the atoms within the material. This is the essential first step in any CASTEP-based study. The core CASTEP functionality is summarised in ref [5]. The York contribution underpins the more advanced functionality, such as the calculation of the electronic band structure (using concepts developed at York), the phonon dispersion, and many experimentally important spectra such as Nuclear Magnetic Resonance (NMR), Electron Paramagnetic Resonance (EPR), Electron Energy Loss Spectoscopy (EELS), and Raman spectroscopy.

The York team have also developed new algorithms (along with rigorous theoretical proofs of correctness) that have been implemented to add extra functionality to CASTEP. Examples include

Langevin NPT molecular dynamics [6] and a real-space genetic algorithm for crystal structure prediction [7]. This functionality is used to simulate the finite temperature properties of the material (Langevin NPT) and in finding new catalyst structures using a genetic algorithm. Recently, Hasnip has developed a novel approach to electronic energy minimization which is faster and more robust, based upon mapping the charge density to an equivalent bosonic system (paper under peer-review).

Probert has supervised five postgraduate research students and two PDRAs since 2000 all of whom have contributed to the development of CASTEP, either as collaborators in the development of new functionality and/or as users of the code. Most of the functionality developed has been incorporated into the commercially available code, whilst the remainder is available for independent download as an add-on via the group website (http://www.cmt.york.ac.uk/cmd) or the CASTEP website (http://www.castep.org).

Through internal funding and by application to UK research council funding, three successive Beowulf computer clusters have been installed at York over the period 2002 – 12. These provided local high level computing facilities enabling testing of code relevant to the development of the CASTEP code, particularly the optimisation of parallelisation procedures.

Collaboration between the research groups of Godby and Probert and input from an EU network on theoretical spectroscopy co-ordinated by Godby has provided further impetus to CASTEP development. There have also been a number of developments by the CDG in supporting industrial and other users of the CASTEP code, such as the establishment of a community mailing list and forum, web sites, and a number of training workshops attended by York staff (most recently in Oxford (2013, 2009), Frankfurt (2012) and Delhi (2011)).

3. References to the research (indicative maximum of six references)

The following are key peer-reviewed references, that describe either the CASTEP code, or the fundamental theory that underlies it and its applications:

[1] M D Segall, P L D Lindan, M J Probert, C J Pickard, P J Hasnip, S J Clark, M C Payne *J Phys. Cond Matt* **14** (2002) 2717-43. “First principles simulation: ideas, illustrations and the CASTEP code”. DOI: 10.1088/0953-8984/14/11/301: [3397 citations]

[2] F. Von Wrochem, D. Gao, F. Scholz, H-G Nothofer, G. Nelles and J.M. Wessels, *Nature Nanotech* **5** (2010) 618. “Efficient electronic coupling and improved stability with dithiocarbamate-based molecular junctions” [Sony] DOI: 10.1038/nnano.2010.119 [32 citations]

[3] X. Wang *et al* Nature Materials **8** (2009) 76. ”A metal-free polymeric photocatalyst for hydrogen production from water under visible light” DOI: 10.1038/nmat2317 [568 citations]

[4] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, M. C. Payne *Zeitschrift für Kristallographie* **220** (2005) 567 “First principles methods using CASTEP” DOI: 10.1524/zkri.220.5.567.65075 [1450 citations]

[5] V.Milman, K. Refson, S.J. Clark, C.J. Pickard, J.R. Yates, S-P. Gao, P.J. Hasnip, M.I.J. Probert, A.Perlov and M.D. Segall, *J. Mol. Struc: THEOCHEM* (2010) “Electron and vibrational spectroscopies using DFT, plane waves and pseudopotentials: CASTEP implementation” DOI: 10.1016/j.theochem.2009.12.040 [24 citations]

[6] D. Quigley and M I J Probert *J. Chem. Phys.* **120** (2004) 11432 “Langevin dynamics in constant pressure extended systems” DOI: 10.1063/1.1755657 [27 citations]

[7] N L Abraham and M I J Probert, *Phys. Rev. B* **73** (2006) 224104 “: A periodic genetic algorithm with real-space representation for crystal structure and polymorph prediction” DOI: 10.1103/PhysRevB.73.224104; N L Abraham and M I J Probert, *Phys. Rev. B* **77** (2008) 134117 “Improved real-space genetic algorithm for crystal structure and polymorph prediction” DOI: 10.1103/PhysRevB.77.134117 [53+15 citations]

All citation data from Scopus, 14/11/2013

4. Details of the impact (indicative maximum 750 words)

The CASTEP material modelling software developed by York academic Dr Matt Probert and colleagues is a commercial software package to undertake density functional theory (DFT) quantum mechanical simulations. CASTEP is marketed by Accelrys Inc and used by over 830 different companies (including Boeing, Johnson Matthey, Dupont, Toyota, General Motors and

Unilever) and has generated over $30m sales since 2002. Accelrys is a leading scientific research and development software and service company, and is based in San Diego with European headquarters in Cambridge. It has an established position in the field of materials modelling and simulation currently based around the Materials Studio application, which includes CASTEP as a separately licensed component.

One customer is the Japanese car manufacturer Toyota, which has used the CASTEP code for a number of projects, which can be evidenced by a number of patent applications. They use CASTEP to predict the properties of any material using the power of quantum mechanics, and also to support experimental studies of materials and processes by helping with the interpretation of experiments, offering a unique 'atom by atom' perspective on what is happening. As an example, Toyota used CASTEP to develop new ceramic catalysts for exhaust gas purification [i]. The same car manufacturer has now used CASTEP to design improved lithium-hydride batteries for electric and hybrid vehicles [ii]. The development of efficient energy-storage batteries for electric and hybrid vehicles forms a major part of the international response to global warming and the move away from oil as an energy source. Many companies worldwide have used CASTEP to develop new battery materials over a number of years as part of this effort.

A different energy-based commercial application of CASTEP is the screening of potential fuel cell materials by Johnson Matthey [iii]. Fuel cells could play a key role in a future "hydrogen economy" replacing the internal combustion engine as the power source in vehicles. The key idea is to carry hydrogen as a fuel, and in the fuel cell to combine this with oxygen from the air, to generate energy (electricity) and have water as the only waste product. A related topic is the green generation of hydrogen to power these fuel cells, for which CASTEP has also been used (ref 4 above).

A different commercial application using CASTEP is work by Sony to develop light-weight flexible computer screen displays [iv] which was reported at an Accelrys User Group conference.

CASTEP is widely used within many materials-based industries - see http://accelrys.com/products/materials-studio/modules/CASTEP.html for a commercial overview. This can also be seen in the wide range of companies that cite CASTEP in their patent applications - over 100 patent applications by 2013 - of which over 50 have already been granted. These include companies such as Semiconducting Energy Lab Co, Canon, Fuji, Institut Francais du Pétrole, Toyota, etc. Of these, 75 have been filed since 2008.

The $30m sales figures are confirmed in a letter-of-support received in November 2012 from Accelrys. A commercial-in-confidence presentation to the CDG revealed a more detailed breakdown of the sales figures by sector (64% of sales to commercial organisations and 8% to Government organisations with the remainder purchased by academic users). Within the commercial organisations the largest customer group is the automotive industry, followed by the electronics industry. Ted Pawela, Senior Director of Materials Science Product Marketing wrote "*The quantum mechanics expertise and software provided to us by the CASTEP Developers Group enable us to provide more complete and valuable software solutions to our customers. Globally, we now have 830 unique customers who use this software, including such marquis companies as The Boeing Company, Johnson Matthey, Dupont, Toyota, General Motors, and Unilever. Sales revenue for the CASTEP software now exceeds $30,000,000. These statistics provide clear evidence of the importance of CASTEP to materials related product innovation, …."*

5. Sources to corroborate the impact (indicative maximum of 10 references)

A letter-of-support from Accelrys Inc confirms the commercial value of CASTEP to Accelrys (> $30m) and the range of industrial users that benefit from CASTEP.

Examples of CASTEP-based patent applications show two automotive uses of CASTEP: for developing new catalysts for vehicle exhausts, and new solid battery electrolytes:

[i] Patent EP1243329A1 "Ceramic body and ceramic catalyst body" (issued 2008);

[ii] Patent EP2555307 "Sulfide solid electrolyte material, battery and method for producing sulphide solid electrolyte material" (filed 2010)

An example of a CASTEP-based industrial research by Johnson-Matthey which shows the value of CASTEP in computationally screening potential fuel cell materials prior to experimental testing:

[iii] J. Gavartin, M. Sarwar et al, *ECS Transactions*, **25** (2009) 1335 "Exploring Fuel Cell Cathode Materials: A High Throughput Calculation Approach" [DOI: 10.1149/1.3210689].

An examples of a CASTEP-based presentations by industrial users which discusses the use of CASTEP by Sony in developing materials for new light-weight flexible computer screen displays: [iv] Accelrys European User Group 2011
http://accelrys.com/events/ugms/2011/europe/abstracts.html#fw