ECAM State of the Art Workshop 2: Electronic Structure
Date: September 12 - September 14, 2016, Cranage Hall, United Kingdom

Organisers: Mike Payne, (Cambridge University), Leon Petit (STFC Daresbury Laboratory)

1. Overview

The field of quantum mechanical calculations has grown enormously over the last 25 years and has become an indispensable tool in many diverse research areas. One illustration of this importance is that the publication rate of papers based on density functional theory (DFT) now exceeds 30 thousand papers per year and is still growing. This remarkable statistic can too easily mask the problems associated with DFT. The primary aim of this E-CAM State of the Art Workshop was to review the field of electronic structure calculations and identify emerging trends and potential new capabilities entering the field over the next five to ten years. An overview of the most relevant points presented by each speaker can be found on the following pages along with a brief summary of the discussion.

After years where large-scale applications were dominated by DFT, we are now seeing the broader adoption of post-DFT methodologies. These techniques offer higher accuracy than is possible with DFT and can address a wide range of problems where DFT has been shown to struggle. These advanced methods can, in some cases, reach absolute accuracy significantly higher than the apocryphal 'chemical accuracy' of 1 kcal/mol. Going beyond DFT, our description of electronic structure is no longer solely based on the electron density; instead it is increasingly expressed in terms of the electronic wave function, or Green's functions.

Typically, a choice of methods and implementations are available for tackling a new problem and this choice may present an additional hurdle to the use of electronic structure codes in new studies. One encouraging aspect of the meeting was the general consensus that accessibility to non-experts is a vital dimension in future method development; indeed, the success of DFT in addressing this issue is at the heart of its widespread use. Electronic structure theory is increasingly employed in a variety of situations beyond the academic research environment, which brings with it new requirements, including development of efficient means for treating extended time and length scales, an almost indispensable feature for industry.

One of the most important developments of the electronic structure field in the last few years has been the emergence of careful verification of solid-state codes within the so-called D-Codes project [1]. This is long overdue: chemists will correctly point out that verification and validation has been at the heart of their work for decades. The D-Codes project marks only the beginning. To date, the exercise has been limited to density functional theory codes, the majority of which being plane wave pseudopotential codes along with only a few all electron implementations. The success and usefulness of this first effort clearly highlights the importance of providing resources to follow the verification and validation

roadmap that Cotennier, and the community he has created, have already mapped out.

[1] K. Lejaeghere et al., Reproducibility in density functional theory calculations of solids, Science **351**, 2016. DOI: 10.1126/science.aad3000

2. Programme of the workshop

Day 1, 12th September

14:00—16:00	*registration*
16:00—16:45	Mike Payne, University of Cambridge
16:45—17:30	George Booth, King's College London *Are wavefunction methods a future of computational materials science?*
17:30—18:15	Alessandro de Vita, King's College London *Inference-accelerated molecular dynamics: can we predict first-principles forces?*

Day 2, 13th September

9:00—9:45	Mark van Shilfgaarde, King's College London *Green's function methods in electronic structure*
9:45—10:30	Leonardo Bernasconi, STFC *Electronic excitations and dynamics in the condensed phase*
10:30—11:00	*break*
11:00—11:45	Ivan Rungger, National Physical Laboratory *Beyond mean-field correlations for electron transport calculations*
11:45—12:30	Stefaan Cottenier, Ghent University *Verification and validation of DFT methods and codes: what's next?*
12:30—14:00	*lunch*
14:00—14:45	Julie Staunton, University of Warwick *Density functional theory and slowly varying fluctuations to describe magnetic and alloy phase diagrams*
14:45—15:30	Neil Drummond, Lancaster University *The CASINO quantum Monte Carlo program: current status and future directions*
15:30—16:00	*break*
16:00—16:45	David Rugg, Rolls-Royce *Electronic structure for improved predictive capability in structural materials - academic dream and/or industrial folly?*
16:45—17:30	Mark Casida, Université Grenoble-Alpes *Precision and accuracy in quantum (photo)chemistry*
17:30—18:15	*discussion of workshop report (1)*

Day, 3, 14th September 2016

9:00—9:45	Nicola Marzari, EPFL *The ADES model for computational materials science: Automation, Data, Environment, and Sharing*
9:45—10:30	James Kermode, University of Warwick

	Towards predictive multiscale materials modelling: uncertainty quantification for density functional theory
10:30—11:00	*break*
11:00—11:45	Andrea Ferreti, CNR–Istituto Nanoscienze *Bridging density-functional and many-body perturbation theory: orbital-density dependence in electronic-structure functionals*
11:45—12:30	*discussion of workshop report (2)*

3. List of participants

Last name	**First name**	**Affiliation**
Bernasconi	Leonardo	STFC RAL, UK
Booth	George	King's College London, UK
Casida	Mark	Université Grenoble-Alpes, FR
Castagna	Jony	STFC Daresbury Laboratory, UK
Cottenier	Stefaan	Ghent University, BE
De Vita	Alessandro	King's College London, UK
Drummond	Neil	University of Lancaster, UK
Engel	Edgar	University of Cambridge, UK
Fabris	Stefano	SISSA, Trieste, IT
Ferretti	Andrea	CNR-Institute of Nanoscience IT
Hasnip	Phil	University of York, United Kingdom
Jackson	Jerome	STFC Daresbury Laboratory, UK
Kermode	James	University of Warwick, UK
Lueders	Martin	STFC Daresbury Laboratory, UK
Marzari	Nicola	EPFL, CH
Migliorato	Max	University of Manchester, UK
Rugg,	David	Rolls-Royce PLC, UK
Rungger	Ivan	National Physical Laboratory, UK
Searle	Barry	STFC Daresbury Laboratory, UK
Staunton	Julie	University of Warwick, UK
Tomic	Stanko	University of Salford, UK
van Schilfgaarde	Mark	King's College London, UK
Weber	Cedric	King's College London, UK

4. Major outcomes

The organisers are particularly grateful for the speakers for carefully addressing their brief for the meeting by giving talks covering the broader issues related to their research areas and are equally grateful to all the participants for their contributions to the discussions.

Mike Payne introduced the meeting and provided an introduction to E-CAM, which is the recently launched Horizon 2020 Centre of Excellence (CoE) associated with the CECAM network. He then reiterated the aims of the meeting namely to review current status and emerging trends in the electronic structure field. In the following we note only the most important and relevant points made by each speaker.

George Booth provided a review of progress in wave function based methods, both the classic explicitly correlated wave function methods of theoretical chemistry, such as Configuration Interaction (CI), and the rapidly developing Full Configuration Interaction Quantum Monte Carlo (FCIQMC) method. The approach has to confront the exponential scaling of the CI wave function but succeeds because the majority of the weight of this wave function is in a relatively small number of determinants. This method has been shown to be accurate well beyond the classical "required level" of theoretical chemistry of 1 kcal/mol.

Alessandro de Vita talked about methods to intelligently extract interatomic force data from ab initio calculations. Machine learning techniques were presented in the context of molecular dynamics simulations of crack propagation, where force field parameters were obtained on-the-fly from DFT calculations, but only when geometries are encountered that had not previously been calculated, with a significant reduction in computational cost. Examples were provided where this method fails, but equally other examples were provided where forces were accurately predicted - reducing the number MD steps where ab initio calculations were required by an order of magnitude.

Mark van Schilfgaarde described Green's function based approaches to electronic structure, specifically the quasiparticle self-consistent GW method (QSGW). GW originates in many-body theory and gives an accurate description of optical properties, considerably superior to DFT. Traditionally the GW method has been applied perturbatively on top of DFT. QSGW is a self-consistent, non-perturbative scheme, which shows considerable improvements over earlier methods. Possibilities of combining QSGW with methods for treating strong correlation (DMFT), which is missing from the theory, were discussed.

Leonardo Bernasconi discussed calculations of excited states – for a long time a taboo subject for DFT which is strictly a ground state theory. However, with the introduction of time dependent DFT (TD-DFT) and time dependent Hartree Fock (TD-HF) there are now methods which can work very well for a range of excited state problems. In particular, TD-B3LYP, which mixes DFT and HF, gives good results both for Wannier-Mott excitons and Frenkel excitons but does not work well for charge transfer excitations. The next challenge is excited state dynamics where state crossings present a major challenge to theory, this is important for instance in describing fluorophores in dye-sensitised solar cells.

Ivan Rungger talked about realistic calculations of electron-transport beyond the standard Landauer-Buttiker model thus including beyond mean-field correlations. This was based on a multiscale approach: standard electronic structure methods, such as the Smeagol TD-DFT transport code, were combined with the Anderson impurity model, which describes correlation. There are significant technical challenges with this approach but it will be an important tool to model electrical spin manipulation in electroactive molecules.

Stefaan Cottenier provided an overview of the D-Codes project – covering both the scientific and sociological successes of the work. He correctly stated that the physicists had been left a long way behind the theoretical chemists in the area of verification and validation (V&V) and that we had only just started to put this right. The work to date has, in fact, only addressed the issue of verification of codes – proving that they yield consistent result. The question of validation -- is the answer correct? -- has yet to be addressed. A roadmap for future V&V, which now just requires a moderate investment of resources to pursue, was presented.

Julie Staunton presented a theory of magnetic materials based on a statistical mechanics treatment of spin fluctuations. Building upon the local moment picture of magnetism, a formal theory of the free energy, as a function of temperature and field, is provided by the disordered local moment (DLM) theory. The applications of this theory to metamagnetic FeRh and to spin-fluctuations in MnO were presented as well as discussion of rare-earth intermetallics and the a-g martensitic transformation in steel. Developments of the method, involving the non-local coherent potential approximation, were exposed.

Neil Drummond convinced us of the accessibility of Quantum Monte Carlo (QMC) calculations by setting up and running an entire QMC calculation during his talk! Various technical developments such as optimised Jastrow factors and backflow corrections have enhanced the method and can be packaged with relative ease. Even though a great deal of attention has been paid in ensuring the use of QMC codes is easy and intuitive, making it possible for non-experts to use multideterminant trial wavefunctions remains challenging.

David Rugg, as Senior Research Fellow in charge of materials research at Rolls Royce, provided an industrial perspective. The role and importance of university-based collaborations in their research programme was pointed out in a wide range of different materials science areas. The complexity and potential cost implications of the materials challenges facing a company like Rolls Royce are both daunting and humbling. It was pointed out that understanding and/or rationalising materials behaviour is what they really require – not only parameter free, atomic scale simulation of an event.

Mark Casida provided a historical perspective of the rise of theoretical chemistry from its breakthrough era in the 1970s and the development of Hartree-Fock and post Hartree-Fock methods. In this context he talked generally about accuracy and precision in quantum chemistry and more specifically about TD-DFT for photochemical applications. He also discussed technical issues, such as scaling, and emerging methods such as “dressed TD-DFT”, where double excitations are included in the theory, and over what timescale adoption of such methods can be expected.

Nicola Mazari described technical work to address the issue of predictive accuracy in DFT and realistic complexity. He discussed the rapidly growing field of materials informatics by describing the development and application of the AiiDA tool, which aims to address the issues of automation, provenance (of

calculations), reproducibility of calculations as well as providing the ability to generate workflows and protocols for complex derived properties and then use these in high-throughput applications. A case study was provided by the finding of new 2-dimensional materials out of the set of all known layered 3-dimensional systems.

James Kermode described the 'Python-isation' of Fortran codes, which can be semi-automated and thus applied to any electronic structure code. Controlling calculations using python brings many advantages of modularity and interoperability and allows a much more flexible use of DFT technology. He described his work on uncertainty propagation in electronic structure methods based on Baysian analysis. By examining the effect of errors in the exchange functional used in DFT, a measure of the absolute error in calculated properties could be obtained.

Andrea Ferreti discussed the use of Koopman's compliant functionals as a method of bridging between DFT and Many Body Perturbation Theory (MBPT). The Koopman's compliant approach re-introduces the derivative discontinuity present in the exact, but unknown, Kohn-Sham functional which is lacking in the usual approximations. This leads to the concept of orbital dependent density functionals, which do not have unitary invariance, but which allow accurate prediction of spectroscopic properties.

5. Community Needs

In the first discussion session the organisers asked those not giving presentations, for their thoughts about the status and prospects for the field of electronic structure and then the discussion was open to all participants. The following summarizes the resulting debate:

Density functional theory is now a mature technology that is increasingly finding application in industrial settings. Industrial use demands accuracy and precision, which are now being addressed by validation and verification exercises such as the D-Codes project. A recurring theme of the meeting was the importance of having well specified error bars, and clear definitions of the applicability of the different methods. These specifications are prerequisites for use of electronic structure codes outside of the academic environment and by users who are not necessarily familiar with the underlying theoretical basis. Significant progress towards these goals is being made in the software engineering of different electronic structure packages and this has been shown to provide not only a robust framework for conducting DFT-level calculations but also makes advanced methods as as approachable as possible. While these developments suggest a "black-box" mentality, the importance of physical insight was expressed, particularly in an industrial setting where modelling is often used to support interpretation of experimental findings. While new methods for very high accuracy prediction of ground-state and optical properties were discussed, it is clear that dynamics, multiscale modelling and finite temperature remain challenging topics, each being addressed by different efforts. To expand the applicability of existing DFT and post-DFT theories, advanced techniques from computer science are already being applied and can be expected to play an ever

increasing role, these include not only the use of massively parallel, hybrid CPU/GPU hardware but also efficient strategies based on machine learning.

6. Funding and resources

Members of our community are under increasing pressure from funding agencies to do industrially relevant research. This brings with it the requirement for industrial standards of quality control, namely error quantification. In this context, consistent investment is required in order to dedicate development resources to verification and validation. At present there is widespread uncertainty as to how such work should be financed, because, unlike feature addition, this work is, with notable exceptions such as the UK's CCP projects, not normally funded through research grants.

7. Developments for society and industry?

Developments in electronic structure theory have wide reaching technological implications. The workshop featured mostly, but not exclusively, physicists and methods from solid state theory; developments in these particular areas lead to societal benefits by improving the understanding of materials, and their properties, and in the discovery of new materials for applications. Specific classes of materials directly addressed at the workshop include, but are not limited to, photovoltaic materials, catalysts, fracture resistant alloys for aerospace applications and magnetocalorics.

Enabling the use of current state-of-the-art techniques of electronic structure theory in industry promises to allow many more problems to be addressed than can be examined by academic research groups alone and means that research efforts are focused on problems of direct commercial relevance. This will allow cheaper and more effective product development in a wide range of industries. Detailed reviews of the economic impact of electronic structure and molecular modelling have recently been provided [2,3].

[2] https://gerhardgoldbeck.files.wordpress.com/2014/01/the-economic-impact-of-modelling.pdf
[3] https://gerhardgoldbeck.files.wordpress.com/2014/02/psik-industry-interactions-report1.pdf