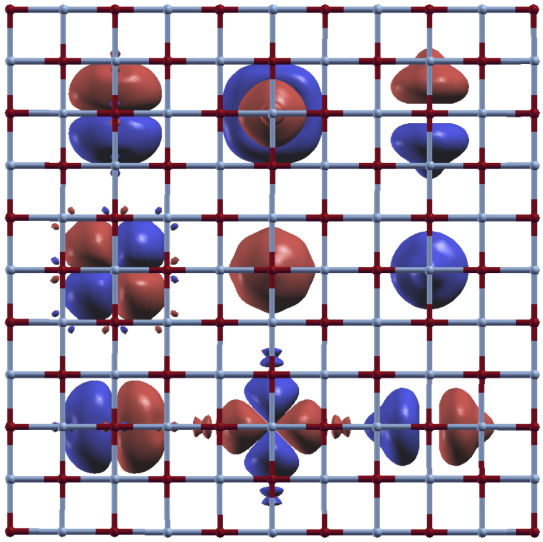
Workshop Report:
Efficient localised orbitals for large systems, strong correlations and excitations

Cavendish Laboratory, University of Cambridge

July 2nd to July 5th, 2012



A Workshop of the CECAM JC Maxwell node

Supported by CECAM, Psi-k and the ESF

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Abstract and Summary

In parallel with continuing progress in linear-scaling methods relying on optimised, localised orbitals, recent developments have established the potential for efficient use of such functions in diverse areas including quantum transport, correlated systems and electronic excitations. This workshop brought together expertise in these topics to clarify the state of the art in optimisation and localisation procedures, and to focus efforts in the development of optimised local orbitals for advanced electronic structure methods.

Scientific content of the Workshop

The workshop was generously supported by the CECAM JC Maxwell node, CECAM Headquarters, and the Psi-k network through the European Science Foundation. It attracted 47 world-class participants, both EU and non-EU. Over six half-day sessions, the workshop hosted 26 excellent talks and a small poster session, to which honorary prizes were awarded. The workshop timetable provided generous time for discussion, intended to encourage the participation of younger scientists. Invited speakers were asked to give 30 minute talks, followed by 15 minutes for discussion. Contributed talks lasted 20 minutes, followed by 10 for discussion. The coffee, lunch and pre-dinner periods also provided ample opportunity for discussion and these sessions proved to be very lively in character. It is our hope that cross-disciplinary communication during these sessions has fostered further interaction between groups computing optimised local orbitals for diverse purposes.

Motivation

This event continued the occasional series of CECAM workshops previously held in Lyons with the co-sponsorship of Psi-k:

- Local orbital methods for large scale atomistic simulations, July 1998;
- Local orbitals and linear-scaling ab initio calculations, September 2001;
- Linear-scaling ab initio calculations: applications and future directions, September 2007.

The emphasis of these previous workshops was the use of local orbitals within linear-scaling methods for large-scale density-functional theory (DFT) calculations. The interest in developing such methods from the early 1990s led to new efforts in the optimisation of basis sets consisting of (pseudo) atomic orbitals within the condensed matter community, which had adopted the pseudopotential plane-wave methodology as its standard. A particularly fruitful outcome of the previous workshops was the interaction between the condensed matter physics and quantum chemistry communities. These basis sets are now being heavily exploited in transport calculations and there is currently interest in using them to develop more efficient methods for many-body perturbation theory within the GW approximation.

Alongside the development of more accurate atomic-type basis sets, work has also been carried out on the development of linear-scaling methods that employ a set of local orbitals optimised in situ to the unique chemical environment of each atom. These optimised orbitals have recently been shown to provide consistency in the definition of the projectors used in DFT+U calculations, for example, and methods have also been developed to refine optimised orbitals to describe bound but unoccupied (conduction band or virtual) states in addition to the occupied (valence band or real) states required for the self-consistent determination of the ground state.

The aim of this CECAM workshop was to widen the scope of local orbitals in methods for treating strongly-correlated systems (e.g. DFT+U and dynamical mean field theory) and excitations (e.g. time-dependent DFT and many-body perturbation theory). The workshop brought together 47 scientists, from around the world, with experience of optimising local orbitals, primarily from the community developing linear-scaling DFT methods, with those seeking to exploit local orbitals to expand the scope and scale of electronic structure methods that go "beyond DFT". By promoting much greater interaction between these somewhat disconnected groups, progress in the development of these new methods will be accelerated to the benefit of both groups of participants: those with experience of optimising local orbitals will be introduced to new areas of application for their work; those seeking to develop new methods will benefit from that experience. This workshop was particularly timely given the recent resurgence of interest in local orbitals.

State of the art

The generation of localised orbitals is a matter which has concerned many branches of electronic structure theory over the past two decades and the last few years, in particular, have been ones of intense progress. An efficient orbital representation is typically one in which the operators of interest can be expressed with adequate accuracy, small matrix rank and, where possible, predictable matrix sparsity. Systematic improvability is a further desirable attribute. Differing criteria have been employed to optimise these orbitals, used to represent non-interacting quasiparticles, e.g., Kohn-Sham states, many-body quasiparticles, or their product states, depending on the context.

In linear-scaling implementations of Kohn-Sham density functional theory [1-8], together with its extensions to excited state phenomena [9-11], one is often concerned with finding orbitals that are strictly localised, so that the Hamiltonian matrix is sparse, and which afford a sparse representation of the single particle density-matrix for insulators and finite-temperature metals. These orbitals may be refined *in situ* on a fixed underlying basis, for example to minimise the total energy, or they may be initially optimised in a pre-processing step and fixed thereafter.

In methods for strongly-correlated systems, such as DFT+DMFT, DFT+U and DFT+SIC, in their numerous incarnations, one often must define spaces to which many-body corrections or exact conditions on the exchange correlation functional, beyond LDA-based approximations, are applied. These spaces may or may not encapsulate the effects of orbital hybridisation or the competing tendencies of localisation and delocalisation near a metal-insulator transition. Numerous orbital optimisation criteria are in use to this field [12-20], such as maximisation of measures of orbital localisation, maximisation of the Coulomb repulsion or minimisation of its anisotropy, minimisation of the total energy, recovery of many-body expectation values or minimisation of energy dependence.

In many-body perturbation theory GW calculations for the evaluation of quasiparticle properties, local orbitals allow for a reduction of the computational load. This, in turn, facilitates the implementation of self-consistency schemes which have proved to be important for molecular systems and molecular transport problems [21,22]. The possibility of representing orbitals in terms of localised Wannier-like functions has also been used to reduce the computational load of GW calculations performed with schemes and codes

based on plane-waves basis sets [23]. In contrast with plane-waves basis sets, local orbitals also allow for feasible all-electron GW calculations.

Localised orbitals may furthermore form highly efficient bases for extracting tight-binding models from the *ab initio* calculations. In particular, Wannier functions have been shown to provide excellent representations for Fermi surface properties [24], orbital magnetoelectric coupling [25], electron-phonon interactions [26], van der Waals effects [27], magnetically induced lattice distortions [28], spin-wave excitation spectra [29] and many-body quasiparticles [30].

Optimisation algorithms are a matter for technical investigation and optimisation in and of themselves [31-33], often carrying over from one criterion to the next, and sessions of this workshop placed some focus on these. As an example, the complications resulting from orbital non-orthogonality, advantageous as it may admit increased localisation and matrix sparsity, or constraints on the orbitals they represent, have attracted careful attention over the years [34-38].

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Executive summary

Outcomes of key presentations

An exciting aspect of this event was that many speakers, while highlighting ground-breaking achievements in their own sub-fields, placed strong emphasis on aspects of their work which resonated with the cross-disciplinary theme of the workshop. In this way, delegates typically remained very engaged with the talks and discussions on topics in electronic structure theory rather different to their own specific areas of expertise.

The opening talk, given by Volker Blum (Fritz Haber Institute, Berlin, Germany), exemplified this aspect very nicely and generated lots of interest. Dr Blum spoke on numeric atom-centred basis sets for all-electron *ab initio* simulations, that is the generation of a hierarchical basis set library for all elements of the periodic table, for both DFT and many-body calculations. The presentation covered large and relativistic systems, not limited to the periodic or non-periodic cases, issues of parallelisation and scaleability, GPU and Exascale computing hardware and a diverse range of spectroscopic properties. A principal outcome was the broad utility and reliability of a hierarchical classification of numeric atomic basis sets. A related talk was given by Xinguo Ren (Fritz Haber Institute, Berlin, Germany), in which he described the use of such basis orbitals for theories beyond density functional theory, including exact-exchange, non-local correlations and the Møller-Plesset perturbation theory. The talk offered a very positive outlook on the applicability of accurate localised orbitals, by means of resolution of the identity techniques, to many-body theories of electronic structure.

Arash Mostofi (Imperial College London) spoke about two novel applications of optimised non-orthogonal orbitals in the context of linear-scaling DFT, a DFT+U implementation using self-consistently determined projectors and a method for computing dispersion interactions using the properties of Wannier functions. A notable conclusion of this presentation was the importance of properly treating the tensor index positions associated with nonorthogonal functions, and the rapidly growing range of advanced functionality available in current linear-scaling DFT codes, sometimes even overtaking conventional cubic-scaling methods in this regard.

Another fine exemplar of the advanced status of linear-scaling methods was the presentation given by David Bowler (University College London), who described a broad range of functionality including constrained DFT,

EXX, a real-time implementation of time-dependent DFT, spin-polarisation and the van der Waals interaction. The interesting question of the relative merits of spatial and numerical truncation of the density matrix was raised, which is sure to receive further attention in the future, and very positive results were discussed on the convergence behaviour of the constrained DFT functionality, and stable propagation in TDDFT.

Continuing in the vein of advanced electronic structure methods within linear-scaling density functional theory were the presentations of Chris-Kriton Skylaris (University of Southampton), Nicholas Hine (Imperial College London), Jacek Dziedzic (University of Southampton) and Gilberto Teobaldi (University of Liverpool). Dr Hine gave a very accessible introduction to the Projector Augmented Wave technique and went on to describe its far from trivial combination with the linear-scaling DFT formalism, in which the Kohn-Sham eigenstates do not explicitly appear, and agreement with all-electron results. Dr Skylaris presented methodology and results for calculating bio-molecular interactions in very large systems, in particular free energies of hydration and protein-ligand binding. A key outcome of Dr Dziedzic's talk was the possibility of implementing Hartree-Fock exchange, and hence hybrid functionals, with linear-scaling cost using localised basis functions. Dr Teobaldi presented an implementation of a very novel projector self-consistent constrained DFT technique within linear-scaling DFT, with a view to studying electro-chemical processes.

The Dynamical Mean-Field Theory, and in particular its combination with density-functional theory (DFT+DMFT), is a sophisticated many-body method which is currently enjoying much interest and in which localised orbitals are exploited to great effect. The two talks given on DFT+DMFT at this workshop, by Silke Biermann (École Polytechnique, Paris, France) and Cédric Weber (University of Cambridge), were a very welcome addition, epitomising the advantages of a high-accuracy localised description in many strongly-correlated materials. Dr Biermann gave a very accessible introduction to the method and described current developments ongoing in the field. Great focus was placed, in particular, on the role and nature of localised orbitals in the construction of the Hubbard Hamiltonian and its parameters. Dr Weber described a new implementation of the DFT+DMFT method in the context of linear-scaling density-functional theory, a technically impressive development that opens up many avenues for application, but also which combines very elegantly two fields where the concept of orbital locality is central. As well as applications to well known metal-oxides,

Dr Weber focused on the application of DFT+DMFT to the heme kernel of the human haemoglobin molecule, which he showed exhibits some fascinating many-body physics not readily accessible using simpler methods.

A novel feature of this workshop was its "Perspective" talks, during which three delegates of particular experience in the field of local orbital optimisation were invited to offer a more personal view on the subject. These proved to be a great success both in terms of scientific content and insight, and very enjoyable. The first, delivered by Nicola Marzari (École Polytechnique Fédérale de Lausanne), was focused on the concept of locality in electronic structure and the resurgence of interest in this topic due to its relevance to practical calculations, particularly in connection with the Berry phase theory of polarisation and magnetisation in solids. Prof Marzari went on to discuss the use of localised orbitals in the context of corrections to approximate density functionals such as constrained DFT, DFT+U and generalised self-interaction corrections which restore the piecewise linearity of the energy functional with respect to orbital occupancy. The second, given by Emilio Artacho (CIC nanoGUNE Consolider, Spain, and University of Cambridge, U.K.) was a very informative historical perspective on the field of local orbital development. Prof. Artacho not only gave prominence to the context of developments in the field of linear-scaling DFT, but also to quantum chemical, strongly correlated and tight-binding methods, and he shed light on past and present work on the case of nonorthogonal orbitals. This talk was very instructive for younger delegates and hugely enjoyable for all. The third and final perspective was offered by Martin Head-Gordon (Univeristy of California, Berkeley), who discussed sophisticated new wave-function based quantum chemical techniques under development in his group, in which localised orbitals are used extensively to reduce the complexity of many-body calculations. The topics of gauge invariance and variationality were discussed in detail, echoing themes which cropped up frequently during the workshop. Prof. Head-Gordon's talk was extremely interesting and impressive in its scope, not least as it clearly illustrated that there is a great deal to be gained by exchanges (and correlations) between the quantum chemical and materials physics communities.

Report on selected discussions

An interesting question of crucial importance for the optimisation and use of local orbitals in electronic structure calculations, be they for ground-state

or excited-state properties, is the accurate representation of genuinely delocalised or partly delocalised electrons. Such extended states occur not only in highly excited systems such as Rydberg atoms, but can also be important in the linear-response excitation regime and in the ground-state description of interfaces, layered heterostructures, carbon nanostructures and nanoclusters. A description in terms of strictly localised orbitals may sometimes omit these states entirely, or yield a very poor description of their energy levels. A number of solutions in terms of the local orbital framework were discussed in detail, which may well lead new developments, among them the use of more extended truncation regions only for these states, or the augmentation of local orbital basis sets with small numbers of extended basis functions, for example plane-waves.

The topic of convergence was discussed frequently during the workshop. This has two facets, namely the convergence behaviour of different algorithms when applied to a given system, and the convergence of a given algorithm with respect to the run-time parameters that control its accuracy. This matter was debated intensively and particularly in the context of methods for correcting conventional approximate density functionals using localised orbitals, for example the constrained DFT and DFT+U methods. Specifically, the parameters required to properly converge a given DFT calculation may not necessarily suffice when one moves to such corrective methods. The relative merits of different charge analysis schemes for defining constrained DFT, and their impact on convergence behaviour, were analysed in detail. A positive outcome of this discussion was the realisation that corrective schemes defined in terms of localised Wannier functions for the Kohn-Sham eigenstates do not explicitly place any additional requirements on the localisation of the orbitals, either in real space or reciprocal space. This is a promising avenue for further implementation of, and collaboration on developing, Wannier-based methods.

A fascinating topic of immediate importance to linear-scaling methods using local orbitals is the truncation of the density kernel matrix. The last number of years has seen intense activity in the area of implementing post-DFT techniques in linear-scaling codes. Some of these techniques are designed explicitly for the study of excited states, and some use unoccupied states to improve the description of correlation in the ground-state. For both, however, it is not yet clear under what circumstances, if any, the density kernel, Green's function, or polarisation tensors may be truncated, either spatially or numerically, while retaining a controllable accuracy. This matter

was discussed extensively in discussions during the workshop and new developments introduced at the workshop may allow for numerical experiments to be carried out to study this question. In particular, new implementations both of real-time propagation TDDFT in linear-scaling codes, and many-body perturbation theory implemented in the product basis of local orbitals provide ideal laboratories for the study of matrix truncation in the dynamical regime.

A topic of interest discussed during the workshop, particularly in the session on strong electronic correlation, was the selection of appropriate orbitals, or population measures, for defining schemes to correct the approximate density functional theory ground-state for localised Coulomb interactions and self-interaction errors. These methods include constrained DFT, DFT+U and DFT+DMFT, and a number of possible approaches to population analyses were discussed, including but not limited to the Becke weight scheme, maximally localised Wannier functions, nonorthogonal generalised Wannier functions, and symmetry-adapted Wannier functions. Schemes based on the use of Wannier functions admit a further self-consistency to be located by updating the Wannier functions either during DFT energy minimisation or afterwards, and then iterating. In the DFT+DMFT context, also, the matter of self-consistency over the charge density, and the possibility to combine this with Wannier orbital self-consistency, were discussed. An outcome of these debates was the acknowledgement that different criteria for optimising population analyses may be favourable for different methods, for example in DFT+DMFT one may prefer to have projection onto a well-defined energy window and well-defined angular momenta, while for constrained DFT one may wish to combine different properties, say well-defined angular momenta together with an extremised total-energy. These lively discussions were very fruitful and reflect ongoing intensive developments in this particular area.

A final example of a matter deliberated in detail during the workshop is the broken unitary invariance exhibited by a number of very sophisticated methods for treating the poor description of electronic correlation effects often yielded by approximate density functionals. Such methods were exemplified in the energy minimising self-interaction corrected TDDFT method presented by Dirk Hofmann (University of Bayreuth) and the some of the coupled-cluster quantum chemistry methods presented by Martin Head-Gordon (Univeristy of California, Berkeley). These methods retain a variational principle, crucially, so that the energy can be extremised additionally with respect to the choice of gauge. These fascinating techniques are at-

tracting much attention at present, and there is much scope for fundamental research in this area which may prove to be focused by these discussions.

Recommendations

There were a number of aspects of this workshop which proved very conducive to a collegiate atmosphere and to promoting discussions between delegates. The workshop's lectures took place at the Physics Department of the University of Cambridge, and the coffee breaks and lunches were provided in finger buffet style in a foyer area close to the lecture theatre. The posters were placed around the foyer where delegates mingled at lunchtime. These aspects ensured that the delegates did not disperse between lectures. It also generated a welcoming atmosphere for the younger delegates to approach the speakers with questions, and also to receive plenty of feedback on their posters.

One third of the time allotted to each speaker, both invited and contributed, was allocated to questions and discussion. We strongly recommend this guideline for future workshops as it was found that the session chairpersons had no difficulty at all in maintaining the discussion for this length of time, in fact it was often lively throughout. This time period also allowed for considered and detailed answers from the speakers, and a relaxed and friendly atmosphere during the discussion period of each talk.

A somewhat novel aspect of this workshop was its three invited "Perspective" talks, two of which took place in an after-dinner context. This entailed some extra work in ensuring that adequate audio-visual equipment was available for talks in the rooms where dinner was served, and also no discussion period following these talks, but they were extremely enjoyable for the delegates. It furthermore gave the speakers the opportunity to offer a more personal overview of their topic in a relaxed environment. These three very memorable talks were some of the highlights of the workshop, and the organisers are sure to repeat this exercise in their upcoming workshops.

Conclusions

The principal objective of this workshop was to bring together researchers who use and develop local orbital electronic structure methods to share their expertise in a spirit of collaboration, be they in diverse areas such as total-energy and force methodology, strong electronic correlations, Berry phase

techniques, electronic transport or computational spectroscopy. Many of these researchers confront the same types of problems in local orbital development, and approach them in different ways, but may not frequently meet each other at more topic-specific conferences. In bringing these researchers together, we hope that this workshop has initiated the development of a new sense of community among researchers on local orbital methods.

The workshop was an unmitigated success in meeting its principal objectives, and it may, in time, prove to have been a landmark meeting in the history of local orbital development, coming as it did during a stage of rapid expansion and renaissance in the development of local orbital methods, particularly in the areas of strong correlation, self-interaction corrections and many-body perturbation theory. The atmosphere during the workshop was very collegiate and friendly, even during the most heated discussions on technical matters. A number of delegates remarked that they had been hitherto unaware that such a great deal of work was ongoing in fields different to their own, on problems that they themselves confront in their research. It is expected that a number of collaborative efforts has been initiated during this workshop, and a number of professional friendships made, and we hope that this workshop has been the first of many for a new community of researchers on local orbital optimisation methods.

Meeting programme

Day 1 - Monday 2nd July 2012

- 11.00 **Resistration: Small Lecture Theatre landing**
- 12.00 Lunch. 12:50 Welcome address by Mike Payne
- **Session 1: Orbital optimisation and linear-scaling methods I**
- 13.00 Volker Blum
  Numeric atom-centered basis sets for all-electron ab initio simulations: The FHI-aims code, surfaces, and biomolecular structure
- 13.45 Arash A. Mostofi
  Strong correlations and dispersion interactions with non-orthogonal local orbitals
- 14.30 Coffee break
- 15.00 David R. Bowler
  Recent Developments in the Linear Scaling DFT code CONQUEST: Constrained DFT, TDDFT and Basis Sets
- 15.45 Stephan Mohr
  Improving the scaling of the BigDFT electronic structure code
- 16.30 Nicholas Hine
  Linear Scaling DFT with in-situ-optimised Local Orbitals using the Projector Augmented Wave Formalism
- 19.30 Dinner at Trinity Hall College
- 21.00 **Perspective: Nicola Marzari**
  The importance of being local

Day 2 - Tuesday 3rd July 2012

- **Session 2: Transport and Topology**
- 09.15 Kalman Varga
  Multidomain decomposition approach to electronic structure calculations
- 10.00 Coffee break
- 10.30 Ivo Souza
  Applications of spinor Wannier functions to ferromagnetic metals and topological insulators
- 11.15 Ivan Rungger
  Large scale electron transport simulations
- 12.00 Lunch
- **Session 3: Strong correlation and self-interaction**
- 13.00 Silke Biermann
  Dynamical Mean-Field Theory and extensions: first principles calculations for correlated materials
- 13.45 Cedric Weber
  Dynamical mean-field theory applied to linear scaling density functional theory
- 14.30 Coffee break
- 15.00 Feliciano Giustino
  GW quasiparticle calculations using the self-consistent Sternheimer equation: progress and outlook
- 15.45 Gilberto Teobaldi
  Projector self-consistent constrained DFT
- 19.30 Dinner at St. Catherine's College
- 21.00 **Perspective: Emilio Artacho**
  Twenty years of local orbitals and linear scaling

Day 3 - Wednesday 4th July 2012

- **Session 4: Application of localised orbital methods**
- 09.00 Davide Tiana
  Describing the chemical interaction using the electron charge density. Are real space techniques complementary to Wannier functions?
- 09.30 Lydia Ansari
  A metal (tin) nanowire transistor
- 10.00 Coffee break
- 10.30 Chris-Kriton Skylaris
  Biomolecular interactions from linear-scaling ab initio quantum mechanical calculations with thousands of atoms
- 11.15 Wei Ku
  Symmetry-respecting Wannier functions and their applications to strongly correlated condensed matter systems
- 12.00 Lunch
- **Session 5: Beyond DFT with localised orbitals**
- 13.00 Weitao Yang
  Non-orthogonal localized molecular orbitals for linear-scaling calculations of electronic ground and excited states
- 13.45 Jacek Dziedzic
  Linear-scaling Hartree-Fock exchange in ONETEP
- 14.30 Coffee break
- 15.00 Claude Ederer
  Combining First Principles Electronic Structure Calculations with Many-Body Algorithms and Model Hamiltonians
- 15.45 Dirk Hofmann
  Energy minimizing self-interaction correction in TDDFT: curing long-standing problems
- 16.15 – 17.30 **Poster session**
- 19.30 Dinner at Trinity Hall College

Day 4 - Thursday 5th July 2012

- **Session 6: Orbital optimisation and linear-scaling methods II**
- 09.15 Xinguo Ren
  Beyond LDA and GGAs using numeric atom-centered basis functions
- 10.00 Coffee break
- 10.30 Jean-Luc Fattebert
  O(N) algorithm for grid-based DFT computations on massively parallel computers
- 11.15 **Perspective: Martin Head-Gordon**
  Localized orbitals and strong spin correlations – progress and problems
- 12.00 Lunch available

Abstracts: Invited "Perspective" talks

Twenty years of local orbitals and linear scaling

Emilio Artacho
CIC nanoGUNE Consolider, Spain,
and University of Cambridge, U.K.

The present workshop can be seen as part of a line of CECAM workshops on local orbitals and linear scaling that started in the mid nineties and have been quite consistently irregular, both in time and in emphasis, but always healthy and vibrant, reflecting the state of and activity in the field. The two concepts, local orbitals and linear scaling, married from the very beginning, since the key to linear-scaling computation was always "talk local" (except the Hartree bit for which one has to be smooth). Atomic orbitals appeared from the start as one of the options, and with them came the chemists [1]. The very first proposals of linear scaling (as we understand it now [2]) sprang in 1992, and atomic orbitals were immediately called upon in the form of tight-binding Hamiltonians, on which every possible concoction was tried. I will try to connect those concepts with non-orthogonal bases and with strong correlations (the other two prominent ones in the workshop) within a historical perspective, which I will try to get as biased as possible.

1. This is of course a physicist perspective. As it happened, chemists got into linear-scaling from the start, if not first.

2. As for graphene, there is of course a prehistory to this, full of recursion methods and Green's functions.

Localized orbitals and strong spin correlations – progress and problems

Martin Head-Gordon
University of California, Berkeley, U.S.A.

Wave function based methods in quantum chemistry describe electron correlations through high-rank amplitude tensors either through configuration interaction, coupled cluster theory, or perturbation theory. The greater the degree of entanglement, the higher the order of the tensor necessary to describe the wave function. Localized orbitals provide a way of reducing the complexity, either through cutoffs, or, making models that truncate high rank tensors using locality arguments. I shall discuss some of our efforts to make such models, both within coupled cluster theory, and valence bond theory. Applications will illustrate both successes and challenges.

The importance of being local

Nicola Marzari
École Polytechnique Fédérale de Lausanne, Switzerland

Ideas about locality and localized orbitals in the electronic-structure of solids and molecules have had a central conceptual importance in quantum mechanics - from the early ideas of Wannier, Kohn, and des Cloizeaux, to the development of e.g. the localization criteria of Foster-Boys, Edminston-Ruedenberg, and Royston-Vasey. Later years have seen a resurgence of interest in the field, thanks to the relevance of localized orbitals to practical electronic-structure calculations, and their formal link to the Berry phase theory of polarization and magnetization in solids. I will provide a brief overview of these developments, together with more recent ideas related to the issue of accuracy in calculations based on density-functional theory, and the interplay between localization, piecewise linearity, and self-interaction.

Abstracts: Invited talks

Dynamical Mean-Field Theory and extensions: first principles calculations for correlated materials

Silke Biermann
École Polytechnique, Paris, France

We will give a short introduction to electronic structure calculations for correlated materials, using dynamical mean field (DMFT) methods. In particular, we will describe the combined density functional dynamical mean field scheme "LDA+DMFT", with illustrations on transition metal oxides and iron pnictides. Then, we will further comment on current developments in the field, namely the calculation of the local Coulomb interactions ("Hubbard U"), and the consequences of its dynamical (partially screened) nature. Emphasis will be put on the role of localized orbitals in the construction of the Hamiltonian and its solution.

Numeric atom-centered basis sets for all-electron ab initio simulations: The FHI-aims code, surfaces, and biomolecular structure

Volker Blum
Fritz-Haber-Institut der MPG, Berlin, Germany

In the context of the FHI-aims code (Fritz Haber Institute ab initio molecular simulations), we have developed accurate numeric atom-centered basis sets for efficient all-electron simulations of molecules and solids. For density functionals (LDA, GGA and hybrid functionals), this framework allows to perform production calculations with essentially converged accuracy (meV per atom level if required). Scalability on state of the art computational platforms (BlueGene/P, Cray, large Intel/Infiniband clusters) is a priority. We describe the basics of the code, a scalable eigensolver development "ELPA", as well as applications towards structure searches in the space of peptides (short proteins) of up to 20 amino acids, and surface structure and stability of large-scale commensurate graphene-like phases grown on SiC.

Work performed with Matthias Scheffler, Xinguo Ren, Patrick Rinke, Lydia Nemec, Mariana Rossi, Franziska Schubert, Carsten Baldauf (all Fritz Haber Institute of the Max Planck Society), Rainer Johanni (Garching Computing Center of the Max Planck Society), the ELPA consortium (http://elpa.rzg.mpg.de), and many collaborators in the FHI-aims project (http://aims.fhi-berlin.mpg.de). Work on ELPA was supported by German Ministry for Education and Research (BMBF) under grant number 01IH08007E.

Recent Developments in the Linear Scaling DFT code CONQUEST: Constrained DFT, TDDFT and Basis Sets

David R. Bowler
London Centre for Nanotechnology, UCL, UK
Tsuyoshi Miyazaki
NIMS, Tsukuba, Japan

Linear scaling or O(N) electronic structure codes have been under development for around fifteen years[1]. After an initial explosion of interest, the practical difficulties of implementation and efficiency have led to a slow down in development and applications. In this talk I will present details of recent developments in the massively parallel CONQUEST linear scaling DFT code, and make some comments on the linear scaling field in general.

The CONQUEST code[2] is one of the leading O(N) codes, and has demonstrated not only excellent scaling to over two million atoms and many thousands of cores[3] but also practical applications to nanostructures on semiconductor surfaces[4], and recently to biological systems. I will describe the details of the CONQUEST code, including recent developments in basis functions and parallelisation. I will also discuss recent improvements including constrained DFT[5], exact exchange and TDDFT, all of which have been implemented with linear scaling.

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Combining First Principles Electronic Structure Calculations with Many-Body Algorithms and Model Hamiltonians

Claude Ederer
Materials Theory, ETH Zurich, Switzerland

The construction of effective electronic Hamiltonians that describe the "essential" degrees of freedom in complex transition metal oxides is very desirable to obtain a clear picture of the physical mechanisms leading to the diverse phase diagrams and order phenomena that are often observed in such compounds [1]. In addition, since the standard approximations to density functional theory (DFT) often fail to correctly describe the electronic properties of such "correlated" materials, the construction of realistic tight-binding-like Hamiltonians can be used as starting point for a more sophisticated treatment of electron-electron interaction using numerical many-body techniques such as e.g. dynamical mean-field theory (DMFT).

In this talk I will discuss the use of maximally localized Wannier functions [2] for the construction of effective low-energy Hamiltonians of complex transition metal oxides. In particular I will focus on two specific examples: i) the construction of effective two-band models for the prototypical material LaMnO3 [3], and ii) the interesting case of the p-electron magnet and Mott insulator rubidium superoxide, RbO2 [4].

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O(N) algorithm for grid-based DFT computations on massively parallel computers

Jean-Luc Fattebert
Lawrence Livermore National Laboratory, USA
Daniel Osei-Kuffuor
Lawrence Livermore National Laboratory, USA

To reduce the cost of Density Functional Theory calculations of a molecular system made of N atoms, one can represent the electronic structure by a set of truncated localized functions instead of the traditional extended eigenfunctions. These functions are very similar to the Maximally Localized Wannier Functions associated to the occupied states of the system. This approximation leads to a much reduced number of degrees of freedom for large systems (N¿ 500 atoms), while preserving a sufficient accuracy [1]. Discretizing these localized functions by finite differences on a regular uniform mesh, we use a very scalable parallel implementation based on spatial domain decomposition. However, a global coupling exists between these localized functions, which requires the calculation of selected elements of the inverse of a sparse overlap matrix. On large parallel computers with over 1,000 cpus, the main computational issue becomes how to efficiently calculate the needed matrix elements of the inverse, using data distributed all over the machine. We propose a new scalable parallel algorithm, which uses specific characteristics of the overlap matrix and its inverse, to reduce the global calculation to a set of calculations that each involves only a subset of the processors, independently of the global problem size.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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GW quasiparticle calculations using the self-consistent Sternheimer equation: progress and outlook

Feliciano Giustino
University of Oxford, Oxford, United Kingdom

During the past two decades the GW method has had a number of successes and witnessed significant growth within the computational electronic structure community. Besides its well-established predictive capability in the calculation of quasiparticle bandgaps, the GW method is appealing since it performs consistently well across widely different materials and does not require the use of adjustable parameters. The main bottleneck of the GW method is that it scales as the fourth power of the system size, and is therefore limited to small systems containing at most 50-100 atoms. In order to circumvent this difficulty we introduced an alternative approach to GW calculations based on the self-consistent Sternheimer equation [1]. In this method the screened Coulomb interaction is evaluated by solving self-consistent linear-response equations as in density-functional perturbation theory, and the Green's function is obtained by directly solving inhomogeneous linear systems. In this talk I will present the Sternheimer-GW method and review our recent progress on realizing two full-scale implementations of this method, one using a planewaves basis, and one using a local orbital basis [2]. Careful comparison between dielectric matrices calculated with planewaves or local orbitals shows that localised basis sets can achieve accuracy comparable to planewaves calculations through a systematic optimisation of the basis [3]. I will also discuss some key advantages of our local orbital approach, such as the use of only two-centre integrals and the theoretical scaling of order O(N3).

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Linear Scaling DFT with in-situ-optimised Local Orbitals using the Projector Augmented Wave Formalism

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Linear-Scaling approaches to Density Functional Theory with local orbitals are now quite well-established: Most existing approaches, however, use only norm-conserving pseudopotentials. This limits the accuracy that can be obtained at feasible computational cost in many applications, eg to those containing transition elements and oxygen.

The Projector Augmented Wave method [1] combines the accuracy of ell-electron methods with the speed and flexibility of the pseudopotential formalism, but it has only previously been used with plane-wave and grid-based codes.

The local orbital approach used in the the ONETEP [2] LS-DFT code has strong connections to plane-wave methods via the underlying psinc basis. Applying the PAW transformation to the density matrix allows us to bypass the use of eigenstates, enabling a Linear-Scaling implementation of PAW with in-situ optimisation of local orbitals.

I will demonstrate equivalence of the results to those obtained from accurate all-electron methods and from other PAW implementations, and discuss application to nanocrystals, including a study of pressure-induced phase transformations in nanomaterials.

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Symmetry-respecting Wannier functions and their applications to strongly correlated condensed matter systems

Wei Ku
Brookhaven National Laboratory, New York, U.S.A.

This talk will cover briefly our method of constructing symmetry-respecting Wannier functions [1] and their applications in studying strongly correlated materials [2-7]. The talk will then introduce recently developed electronic structure methods these Wannier functions enable, including the band structure unfolding method [8-10], and computation of one-particle spectral function of materials with disordered impurities (vacancy, substitution, or intercalation) [11-13].

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Strong correlations and dispersion interactions with non-orthogonal local orbitals

Arash A. Mostofi
Imperial College London

In this talk I will focus on two strands of work. First, I will describe the underlying methodology behind a linear-scaling implementation of DFT+U within the ONETEP code[1]. A unique feature is that the Hubbard projectors can be non-orthogonal and are determined self consistently during the optimisation procedure, rather than being chosen arbitrarily a priori[2]. I will show some results for a prototypical dilute magnetic semiconductor (Ga,Mn)As in the very dilute (0.1%) doping limit. Second, I will describe a very simple approach based on orthogonal Wannier functions for including dispersion interactions in DFT non-self-consistently[3,4] and explain the problems associated with applying it within a framework of non orthogonal generalised Wannier functions (NGWFs), such as those used in most linear-scaling DFT codes. Finally, time-permitting, I will briefly discuss and show recent results of our implementation of a van der Waals DFT density functional[5] based on the approach of Soler[6].

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Beyond LDA and GGAs using numeric atom-centered basis functions

Xinguo Ren
Fritz Haber Institute of the Max Planck Society

Numeric atom-centered orbitals (NAOs) have been established as an efficient basis-set choice for ground-state LDA/GGA calculations. In this talk I will describe a practical procedure, based on the resolution-of-identity technique, that allows us to do efficient "beyond LDA/GGA" calculations using NAOs [1]. A number of such functionalities, whereby exact-exchange and/or non-local correlations are involved, have been implemented in the FHI-aims code [2], including hybrid-density functionals, Moller-Plesset perturbation theory, the random-phase approximation, and the GW method. Illustrating examples will be shown to demonstrate the current capability of our NAO-based implementations. In addition, I will also present our recent methodology developments, focusing on renormalized 2nd-order perturbation theory (r2PT) for electron correlation energies [3]. Various benchmark results for r2PT will be presented.

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Large scale electron transport simulations

Ivan Rungger
School of Physics and CRANN, Trinity College Dublin, Ireland

We present recent developments of the ab initio electron transport code SMEAGOL [1], which is based on the non-equilibrium Green's function (NEGF) method, and obtains the DFT Hamiltonian from the electronic structure code SIESTA [2]. On the one hand the efficiency of the code was improved, firstly for the calculation of the leads' self-energies [3], which allows the use of large electrodes, as well as for the evaluation of the scatterer's Green's function, which is based on the recursive Green's function method. The code scales linearly with system length for quasi one-dimensional systems. New functionalities include the computation of energy barriers under current flow and constrained DFT.

We show different applications where the new developments are used. We study the long-range transport and scattering properties of adatoms and step-edges on semi-conducting and metallic surfaces. The theoretical surface band structure is directly compared to STM experiments via Fourier transform of the scattered surface states [4]. We then evaluate changes in energy barrier height driven by current-induced forces in Al-nanowires and for adatoms on carbon nanotubes [5]. We finally calculate the conductance through water confined between an Au STM tip and the sample, and compare to STM experiments in ambient conditions. Electron transport for liquid water is evaluated over a representative number of configurations [6] extracted from force-field based classical molecular dynamics simulations performed using the NAMD program.

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Biomolecular interactions from linear-scaling ab initio quantum mechanical calculations with thousands of atoms

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The ability to represent accurately interactions between biomolecular assemblies at the atomic level is required for computational simulations in important areas such as drug optimisation and enzyme catalysis. Usually such simulations are performed by empirical classical force fields or with hybrid quantum/classical (QM/MM) approaches. Linear or reduced scaling ab initio electronic structure approaches based on localised orbitals offer a new and exciting possibility for obtaining biomolecular interactions as they allow the entire biomolecular system to be treated at the quantum level of theory. However, to be useful for such applications, the energy needs to be converged tightly enough to allow differences of less than 1 kcal/mol to be calculated (chemical accuracy) and the basis set should be of near-complete quality. I will show how these goals can be achieved with the ONETEP linear-scaling program [1], with the in situ optimization on Nonothogonal Generalised Wannier functions (NGWFs) [2] expressed in a psinc basis set [3]. This approach naturally overcomes the transferability issues of empirical force fields as well as the arbitrariness of QM/MM interfaces but appropriate schemes for configurational sampling [4] need to be developed as well as schemes for treating the solvent [5]. Towards these goals, I will present examples of calculations of hydration free energies and protein-ligand free energies of binding obtained by DFT calculations on entire proteins with thousands of atoms.

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Applications of spinor Wannier functions to ferromagnetic metals and topological insulators

Ivo Souza
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In this talk I will discuss the use of Wannier functions (WFs) to study spin-orbit physics. The first example concerns ferromagnetic metals, where the combination of broken time reversal and spin-orbit gives rise to a spontaneous Hall conductivity in zero magnetic field, as well as a spontaneous orbital magnetization. Both quantities can be expressed as Brillouin zone integrals of the Berry curvature and related k-space quantities. I will describe how a mapping of the ab initio Bloch bands onto disentangled WFs allows to compute efficiently and accurately such quantities via a generalized Slater-Koster interpolation scheme ("Wannier interpolation")[1,2]. As second application, I will discuss the magnetoelectric response in 3D topological insulators. The evaluation of this response requires a smooth gauge for the valence Bloch states across the Brillouin zone, which can be achieved by constructing localized WFs for the valence bands[3].

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Multidomain decomposition approach to electronic structure calculations

Kalman Varga
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To extend the applicability of the density functional theory (DFT) based simulations for larger systems, we have introduced a multidomain decomposition method to solve the Kohn-Sham equations. In the multidomain decomposition approach, one divides the system into smaller overlapping subdomains. The Kohn-Sham equations can be solved independently in each subdomain. Using the subdomain eigenfunctions as basis states one obtains a structured sparse block matrix representation of the Hamiltonian. This block structure allows both matrix inversion and matrix multiplication to be performed very efficiently extending the range of DFT calculations to larger systems. We have also extended this approach for time-dependent [2] and electron transport problems [3]. The approach has been applied for calculation of properties of various problems including field emission [4], hydrogen desorption [5] and time-dependent electron transport [6].

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Dynamical mean-field theory applied to linear scaling density functional theory

Cedric Weber
University of Cambridge, U.K.

Phenomena that are connected to quantum mechanics, such as magnetism, transport, and the effect of impurity atoms and disorder, and their relation to material design and energy needs are important for almost every branch of the industry. Density functional theory (DFT) was successful at making accurate predictions for many materials, in particular compounds which have a metallic behaviour. DFT combines high accuracy and moderate computational cost, but the computational effort of performing calculations with conventional DFT approaches is still non negligible and scales with the cube of the number of atoms. A recent optimised implementation of DFT was however shown to scale linearly with the number of atoms (ONETEP), and opened the route to large scale DFT calculations.

Nonetheless, one bottleneck of DFT and ONETEP, is that it fails at describing well some of the compounds where strong correlations are present, in particular because the computational scheme has to capture both the band-like character of the uncorrelated part of the compound and the Mott-like features emerging from the local strongly correlated centres. A recent progress has been made in this direction by the dynamical mean-field theory (DMFT), that allows to describe the two limits (metal and insulator) in a remarkable precise way when combined with DFT.

The ONETEP+DMFT implementation will be shortly discussed, and its applications illustrated by two examples: i) the interplay of Mott and Anderson localization within disordered Vanadium dioxide and ii) a typical biological molecular system, iron porphyrin, which plays an important biological function in human haemoglobin.

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Non-orthogonal localized molecular orbitals for linear-scaling calculations of electronic ground and excited states

Weitao Yang
Duke University, Durham, NC, U.S.A.

Non-orthogonal localized molecular orbitals (NOLMO) is the most localized representation of electrons. We here explored NOLMO for linear scaling calculations of ground and excited states. For ground states, we developed a minimum principle which has been used for carrying out linear-scaling calculations with NOLMO. Comparing with results based on orthogonal localized orbitals, the method based on NOLMO is shown to give significantly more accurate results. For excited states, we developd a reformulation of TDDFT equations in terms of NOLMO. Its novel use here leads to a set of time propagation equations which can be solved with linear-scaling effort. We have tested the method for several large molecular systems within the self-consistent charge density-functional tight-binding method (SCC-DFTB) and demonstrated its accuracy. This opens up pathways for TDDFT applications to large bio- and nanosystems.

Abstracts: Contributed talks

A metal (tin) nanowire transistor

Lida Ansari
Tyndall National Institute, Cork, Ireland

Energy bandgaps are observed to increase with decreasing diameter due to quantum confinement in quasi-one-dimensional semiconductor nanostructures or nanowires. A similar effect is observed in semimetal nanowires for sufficiently small wire diameters: a bandgap is induced, and the semimetal nanowire becomes a semiconductor. We demonstrate that on the length scale on which the semimetal?semiconductor transition occurs, enables the use of bandgap engineering to form a fieldeffect transistor near atomic dimensions and eliminates the need for doping in the transistors source, channel, or drain. By removing the requirement to supply free carriers by introducing dopant impurities, quantum confinement allows for a materials engineering to overcome the primary obstacle to fabricating sub-5 nm transistors, enabling aggressive scaling to near atomic limits.

Linear-scaling Hartree-Fock exchange in ONETEP

Jacek Dziedzic
University of Southampton, School of Chemistry
Quintin Hill, Chris-Kriton Skylaris
University of Southampton, School of Chemistry

Local and semilocal functionals have long been known to underestimate band gaps and to incorrectly describe the energetics of small molecules, among other deficiencies [1]. The hybrid functional approach, where Hartree-Fock exchange is included into the exchange-correlation functional provides a more accurate description of geometries and of several properties, such as bond energies and band gaps, particularly for metal oxides [2].

We present an approach for evaluating Hartree-Fock exchange energy with a computational cost that scales linearly with the number of atoms. We show in detail how the localisation of the basis functions makes this possible and what conditions are necessary for making the approach consistent. We describe the implementation of this approach in the linear-scaling DFT code ONETEP [3], which can perform such calculations with near-complete basis set accuracy. We validate the method and implementation against energies computed with conventional, cubic-scaling DFT codes.

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Energy minimizing self-interaction correction in TDDFT: curing long-standing problems

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Stephan Kümmel
University of Bayreuth, Bayreuth, Germany

The self-interaction error of commonly used density functionals leads to a number of well-known problems in (time-dependent) density functional theory. A particularly pronounced and practically important one is the serious overestimation of charge transfer (CT) in extended molecular systems. We present a solution scheme for the self-interaction problem within the time-dependent Kohn-Sham framework [1]. It is based on Perdew-Zunger self-interaction correction [2] and employs the Generalized Optimized Effective Potential approach [3] where unitary optimiziation of the functional is guaranteed via explicitly energy minimizing transformations [4].

Calculations for standard test systems reveal that excitations of different character are well described by this approach [1]. In particular, we investigate static and dynamic charge transfer. Our self-interaction-free approach reliably predicts CT excitations and exhibits integer electron jumps, whereas (semi)local functionals in the same situations underestimate CT excitation energies and lead to (unphysical) fractional electron transfers.

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Improving the scaling of the BigDFT electronic structure code

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Daubechies wavelets are the only known basis set which is orthogonal and has compact support. These properties together with its adaptivity and algebraic localization in Fourier space make then an ideal basis set for electronic structure calculations. I shall explain how we exploit the features of this basis set in the BigDFT electronic structure code. I shall next discuss the limitations of the standard cubic version of the BigDFT code which come both from the cubic term arising from the orthogonality constraints and from the long range nature of the electrostatic interactions. This long range poses big challenges for the solution on large parallel machines since it requires a large amount of communication. Next, I shall outline the basic principles of the linear scaling version of BigDFT which is under development. We have developed an approach which essentially overcomes the notorious ill-conditioning problems arising form the use of localization regions in linear scaling methods.

Projector self-consistent constrained DFT

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In the pursuit of a more sustainable energy-economy, great efforts are currently being made to develop improved, industrially viable photocatalytic, photovoltaics, electrochemical energy conversion (fuel cells) and storage (batteries) devices. Atomic-scale understanding of the different materials and interfaces constituting such devices is crucial for the development of novel solutions. This, in turn, requires the possibility of accessing the atomic-scale parameters governing the thermodynamics and kinetics of charge (energy) transfer processes at the device interfaces.

Recently, very encouraging results have appeared regarding the potential of constrained Density Functional Theory (cDFT) for the study of charge (energy) transfer and chemical reactivity [1]. Here we present the implementation of cDFT in the ONETEP program [2], based on the existing framework of tensorial invariance and self-consistency for non-orthogonal projectors [3,4]. The linear-scaling (LS) nature of the cDFT implementation and its compatibility with the LS-DFT+U functionality in ONETEP [5] open up for cDFT(+U) simulation of systems up to a few thousands of atoms on academically available hardware. This should make the method useful for the study of the extended photo- and electrochemical interfaces present in photocatalysts, solar cells, fuel cells, and batteries.

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Describing the chemical interaction using the electron charge density. Are real space techniques complementary to Wannier functions? (Talk cancelled)

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Quantum chemistry is a successful theory, able to predict global properties of molecular species, such as binding energies, molecular geometries, spectra very accurately. However, its main results, the wave function of the molecule and its associated energy, are difficult to correlate to such cornerstone chemical concepts as individual atoms, functional groups as well the bonds and interactions among them. To build a connection between quantum results and chemical concepts, there have been proposed many different a posteriori analyses of these results that extract chemical information. This is particularly true in solid state calculations. Indeed, the use of Bloch orbitals yields a delocalised picture of the chemical interactions over the whole crystal. Thus, the recovering of the chemical bond using the classic" Lewis description[1] can be tasking. An alternative representation to Bloch functions in the study of crystalline solids is represented by Wannier functions (WFs)[2]. Providing a local, atomic orbital description of the chemical interactions, WFs can be considered the generalisation to periodic systems of the concept of molecular orbitals used by chemists to study bonding in molecules and clusters[3]. Another type of approach can be the description of chemical interactions based on the electron charge density. Developed in nineties, the quantum theory of atoms in molecules (QTAM), the domain averaged Fermi hole analysis (DAFH) and the electron localised function (ELF) have proved to be powerful tools in the study of the chemical interactions. During my talk, a general review of QTAM, DAFH and ELF will be provide examining the ?complementarity or the overlapping of such techniques with WFs.

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Abstracts: Contributed posters

Pressure-induced structural transformations in nanomaterials

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Semiconductor nanomaterials, including nanocrystals, nanorods and tetrapods, display a number of peculiar and tunable properties that distinguish them from their bulk counterparts and make them versatile materials for use as e.g. tunable photovoltaic devices and nanoscale stress sensors. Of particular interest is their response to applied pressure, as they transform from one crystalline or amorphous structure to another. Accurate simulations are important for understanding finite size effects in the atomistic mechanisms of phase transformations (difficult to observe clearly in macroscopic experiments), for the opportunity to uncover novel metastable phases stabilised in finite systems, and for potentially innovative applications of nanomaterials to energy applications. Ab initio methods are essential to accurately describe the bond breaking/making in phase transformations and the realistic description of surfaces (often covered by complex surfactants). However, the computational cost limits both the length- and time-scales attainable. In this project we combine ONETEP [1] and an electronic enthalpy method [2] to apply pressure to finite systems without explicit description of the pressure transmitting medium. To model with quantum mechanical precision nanomaterials (including their surfaces) composed of transition metals such as CdS, CdSe and ZnO currently favoured by technological applications, Bloechl's projector augmented wave formalism (PAW) is used [3].

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Performance of local orbital basis sets in the self-consistent Sternheimer method for dielectric matrices of extended systems

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Miguel A. Perez-Osorio, Pablo Ordejon and Feliciano Giustino

We investigate the performance of the numerical pseudo-atomic basis of the SIESTA package for the calculation of dielectric matrices of extended systems. The dielectric matrix is calculated with the self-consistent Sternheimer method, which does not need an explicit sum over conduction states. To asses the quality of the basis sets we compare results to standard planewave calculations using the same computational parameters. We show results of the frequency-dependent dielectric function for the semiconductors diamond, silicon and germanium, thus covering a range of materials with more insulating to more metallic character. The dielectric constants obtained with our method are in very good agreement with the reference planewaves calculations. We find that when including polarization orbitals only a few additional zetas are required for obtaining converged results.

Thermodynamics of surfaces and dopants in rutile-like VO_2

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Vanadium oxide (VO_2) is a thermochromic material with potential applications in smart windows coatings and in sensor devices. We present here a density functional theory investigation of the surface properties and the stability of dopants for the high-temperature metallic phase, which has a tetragonal, rutile-like structure. We find that the (110) surface is the most stable one with a surface energy of only 0.29 J/m2. The (011) surface also appears in the equilibrium Wulff morphology. For the most stable surface, we investigate the stability of different degrees of oxidation/reduction as a function of temperature and oxygen chemical potential, and we find that under most conditions, the (110) surface will be fully oxidised. We also discuss here the solubility of dopants in the bulk structure. We find that Ti and Ge are the most soluble in VO_2 among all the tetravalent cations considered in this study. We also discuss the solubility of tungsten (W) cations assuming different charge compensation mechanisms.

O(N) DFT calculations using Daubechies wavelets in the BigDFT code

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The fact that wavelets exhibit at the same time orthogonality and compact support makes them an ideal candidate basis set for O(N) calculations where one has to deal with localized quantities. We are currently implementing a new approach to O(N) DFT using Daubechies wavelets as an underlying basis set. The KS orbitals are expressed via an intermediate basis set which we call trace minimizing basis (TMB) and which adapts itself to its chemical environment. Therefore we can achieve excellent accuracy using only a very small number of these basis functions. In particular we can calculate energies and forces with an accuracy comparable to that of a reference standard DFT code with cubic scaling. In addition the underlying wavelet basis enables us to calculate the derivatives of our basis functions analytically, which opens new perspectives in many applications.

List of delegates

Organisers

1. David O'Regan, École Polytechnique Fédérale de Lausanne, Switzerland.
2. Simon Dubois, University of Cambridge, United Kingdom.
3. Peter Haynes, Imperial College London, United Kingdom.
4. Paolo Umari, Università degli Studi di Padova, Italy.

Invited speakers

5. Artacho Emilio, CIC nanoGUNE Consolider, Spain, and University of Cambridge, U.K.
6. Silke Bierman, École Polytechnique, Paris, France.
7. Volker Blum, Fritz Haber Institute, Berlin, Germany.
8. David Bowler, University College London, United Kingdom.
9. Claude Ederer, ETH Zurich, Switzerland.
10. Jean-Luc Fattebert, Lawrence Livermore National Laboratory, California, U.S.A.
11. Feliciano Giustino, University of Oxford, United Kingdom
12. Martin Head-Gordon, University of California, Berkeley, U.S.A.
13. Nicholas Hine, Imperial College London, United Kingdom.
14. Wei Ku, Brookhaven National Laboratory, New York, U.S.A.
15. Nicola Marzari, École Polytechnique Fédérale de Lausanne, Switzerland.
16. Arash Mostofi, Imperial College London, United Kingdom.

17. Mike Payne, University of Cambridge, United Kingdom.
18. Xinguo Ren, Fritz Haber Institute, Berlin, Germany.
19. Ivan Rungger, Trinity College Dublin, Ireland.
20. Chris-Kriton Skylaris, University of Southampton, United Kingdom
21. Ivo Souza, DIPC, University of the Basque Country.
22. Kalman Varga, Vanderbilt University, Tennessee, U.S.A.
23. Cédric Weber, University of Cambridge, United Kingdom.
24. Weitao Yang, Duke University, North Carolina, U.S.A.

Workshop delegates

25. Lampros Andrinopoulos, Imperial College London, United Kingdom.
26. Lida Ansari, Tyndall National Institute, Ireland.
27. Paul Boulanger, CEA-Grenoble, France.
28. Jun Cheng, University of Cambridge, United Kingdom.
29. Peter Cherry, University of Southampton, United Kingdom.
30. Danny Cole, University of Cambridge, United Kingdom.
31. Fabiano Corsetti, Imperial College London, United Kingdom.
32. Niccolo Corsini, Imperial College London, United Kingdom.
33. Jacek Dziedzic, University of Southampton, United Kingdom.
34. Dirk Hofmann, University of Bayreuth, Germany.
35. Hannes Huebener, Imperial College London, United Kingdom.
36. Greg Lever, University of Cambridge, United Kingdom.
37. Tom Mellan, University College London, United Kingdom.

38. Stephan Mohr, Basel Universität, Switzerland.
39. Daniel Opalka, University of Cambridge, United Kingdom.
40. Laura Ratcliff, CEA-Grenoble, France.
41. Alvaro Ruiz-Serrano, University of Southampton, United Kingdom.
42. Priyanka Seth, University of Cambridge, United Kingdom.
43. James Spenser, Imperial College London, United Kingdom.
44. Gilberto Teobaldi, University of Liverpool, United Kingdom.
45. Davide Tiana, University of Bath, United Kingdom.
46. Karl Wilkinson, University of Southampton, United Kingdom.
47. Tim Zuehlsdorff, Imperial College London, United Kingdom.