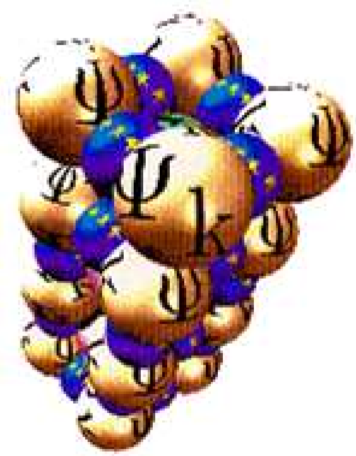
Ψ_k Newsletter

AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

Number 113 October 2012



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1 Editorial

In this Psi-k Newsletter we have two reports on recent workshops, a number of abstracts of recent papers and a scientific highlight article. The latter is by Michel Freyss (Cadarache, France) and collaborators on "First-principles DFT+U study of radiation damage in $\mathbf{UO_2}$: f electron correlations and the local energy minima issue".

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2 Psi-k Activities

”Towards Atomistic Materials Design”

2.1 Reports on Workshops supported by Psi-k

2.1.1 Report on Workshop ”Atomic structure of nanosystems from first-principles simulations and microscopy experiments” (AS-SIMEX 2012)

Helsinki, Finland - Stockholm, Sweden

May 15-17, 2012

Supported by Psi-k Network, NanoTP COST action MP0901, Aalto University, and Tampere University of Technology, Finland.

Organizers:
Dr. Arkady Krasheninnikov (Aalto University and University of Helsinki, Finland)
Prof. Adam Foster (Aalto University and Tampere University of Technology, Finland)
Prof. Risto Nieminen (Aalto University, Finland)
Dr. Teemu Hynninen (Aalto University and Tampere University of Technology, Finland)

`http://tfy.tkk.fi/boat/`

The workshop ”Atomic structure of nanosystems from first-principles simulations and microscopy experiments” took place on a ship going from Helsinki to Stockholm and back on May 15-17, 2012 . The workshop was attended by 47 participants (including the organizers) from all over the world. The financial support from the Psi-K network with additional support from the COST Action MP0901 NanoTP, the National Graduate School in Materials Physics and Academy of Finland made it possible to invite a considerable number of world-renowned experts in the computational materials science and nanoscience and, at the same time, minimize the accommodation expenses for students and young researchers. The workshop was motivated by the recent progress in the transmission electron microscopy (TEM) and scanning probing methods (SPM), which made it possible to not only unravel the atomic structure of various systems with a resolution of better than 0.1 nm, but also carry out elemental analysis and determine the types of particular atoms in the sample. Moreover, based on spectroscopic in-situ techniques (for example, electron energy loss spectroscopy, EELS), the charge state and the bonding configuration of individual atoms and point defects in the material can be identified. The unequivocal interpretation of the experimental data can considerably benefit from the juxtaposition of the data to the results of first-principles calculations. The accuracy of the measurement is now so high that in addition to the information on the atomic configuration (that is atom positions), the detailed information on the spatial distribution of the electron density and on the electron structure of the system is required. First principles simulations, and specifically density-functional theory (DFT) approaches, have provided lots of insight into the electronic structure and properties of various solids. Besides, using DFT and time-dependent DFT molecular dynamics, one can simulate production of defects under electron irradiation and their time evolution. Taking these into account, the main idea behind this workshop was to bring together the TEM experts and computational materials scientists to discuss the progress in TEM analysis and visualization of the atomic structure of nanosystems and how DFT simulations can help in the interpretation of the images. The workshop was focused on carbon systems, but also other materials were discussed. Particular attention was given to irradiation effects in various nanoscale materials, including carbon nanomaterials, such as graphene (the 2010 Nobel Prize in Physics was awarded for studies on graphene). Considerable attention has also been given to the recent progress in computational methods. The lectures given by the experts working on TEM experiments were combined with those presented by the developers of the relevant simulation methods. The latest and most important results in the field were discussed by the speakers and during the poster session. In addition to the already published results, a considerable amount of new unpublished data was presented. A combination of complementary topics (theory/experiment, theoretical method development/applications etc.) resulted in interesting and productive scientific discussion which should have a strong impact on the development of the field and could eventually give rise to new collaborations. Due to a considerable number of students and young postdocs from EU countries who participated in the workshop(about 50% of the attendees), the event was also important in the context of training of young researchers. Overall, based on the response we received from the participants, the workshop was a success. With regard to the objectives of the COST Action MP0901 NanoTP the workshop was definitely beneficial, as it strengthened the collaboration between the groups and stimulated interesting scientific discussions and new scientific projects.

The list of invited speakers included:

Florian Banhart (U. Strasbourg, France)
Peter Bøggild (TU Denmark)
Hua Jiang (Aalto University, Finland)
Ute Kaiser (U. Ulm, Germany)
Jani Kotakoski (U. Helsinki, Finland)
Steven Louie (U. California, Berkeley, USA)
Jannik Meyer (U. Vienna, Austria)
Kazu Suenaga (AIST, Japan)
Eli Sutter (Brookhaven National Laboratory, USA)
David Tomanek (Michigan State University, USA)
Jamie Warner (U. Oxford, Great Britain)

Programme

Tuesday 9, May 15th

12:40 Alexander Schwarz, "Magnetic Exchange Force Microscopy and Spectroscopy"

13:20 Tim Oliver Wehling, "Transition metal adatoms on surfaces: Effects of local Coulomb interactions"

14:00 Toni Ivas, "Self-Assembly and Two-Dimensional Spontaneous Resolution of Cyano-Functionalized [7]Helicenes on Cu(111)"

14:20 Coffee at posters

15:00 Thomas Michely, "Towards graphene hybrid materials"

15:40 Pavel Jelinek, "Scanning Probe Microscopy: theory meets experiment"

16:20 Peter Liljeroth, "Quantitative nc-AFM imaging of the atomic scale contrast in epitaxial graphene on Ir(111)"

16:40 Discussions

18:00 Stephen Pennycook, "Aberration-Corrected STEM and First-Principles Theory: Unraveling the Atomic Origin of Materials' Properties"

18:40 Jani Kotakoski, "Knock-on Damage in Graphene Under an Electron Beam - Role of Lattice Vibrations and Bond Rotations"

19:20 Ingmar Swart, "Direct observation of the Linear Combination of Molecular Orbitals model in real space by combined scanning tunneling microscopy and atomic force microscopy"

19:40 Samuel Paul Jarvis, "Identifying passivated dynamic force microscopy tips on H:Si(100)"

Wednesday, May 16th

14:00 Werner Hofer, "Theory of scanning tunneling microscopy: studying dynamic processes"

14:40 Friedrich Esch, "Dynamics of truly monodisperse clusters under the STM"

15:20 Peter Spijker, "Insights from the modeling of AFM measurements at the calcitewater interface"

15:40 Coffee at posters

16:20 Boris I. Yakobson, "From nanotubes to grahEnes, graphAnes, and other elemental layers"

17:00 Dmitri Golberg, "In situ transmission electron microscopy reveals defects vs. properties of nanomaterials"

17:40 Toma Susi, "Atomic-scale description of electron beam damage in nitrogen-doped graphene and carbon nanotubes"

18:20 Jeppe V. Lauritsen, "Atomically resolved STM imaging of molecular adsorption on MoS2 nanocatalysts"

19:00 Filippo Federici Canova, "Atomic scale dynamics of frictional processes"

19:20 Hannu-Pekka Komsa, "Defects in electron irradiated transition metal dichalcogenides"

19:40 Pekka Koskinen, "Twisting Graphene Nanoribbons into Carbon Nanotubes"

Thusday, May 17th

9:00 Andrey Chuvilin, "Inclusion of radiation damage dynamics in HRTEM image simulations"

9:40 Jose Ignacio Martinez, "Improvement of STM Resolution with H-sensitized Tips 36"

10:00 Carla Bittencourt, "Electronic states of a thin graphite by NEXAFS-TXM: Mapping polarization dependence of the carbon K-edge"

10:20 Marek Kolmer, "Electronic properties of dangling-bond nanostructures formed on hydrogen passivated Ge(001) surface by STM tip-induced hydrogen desorption"

10:40 Domenique Weiner Graphene on Rh(111): combined DFT, STM and NCAFM studies

11:00 Coffee at posters

11:30 Franz J. Giessibl, "Revealing the Angular Symmetry of Chemical Bonds by Atomic Force Microscopy"

12:10 Julian Stirling, "Inherent coupling of lateral and normal forces in qPlus AFM"

12:30 Jakub S. Prauzner-Bechcicki, "Chemically functionalized metal oxide surface: self-assembly of terephthalic acid on rutile TiO2(110)"

12:50 Anatoliy Slobodskyy, "Cutting SSRM on CIGS solar cells"

List of participants

1	Martinez	Jose-Ignacio	Spain
2	Cruz-Irisson	Miguel	Mexico
3	Spijker	Peter	Switzerland
4	Susi	Toma	Finland
5	Stirling	Julian	UK
6	Komsa	Hannu-Pekka	Finland
7	Kolmer	Marek	Poland
8	Prauzner-Bechcicki	Jakub	Poland
9	Lehtinen	Ossi	Finland
10	Swart	Ingmar	Netherlands
11	Jarvis	Samuel-Paul	UK
12	Federici-Canova	Filippo	Finland
13	Åhlgren	Elina-Harriet	Finland
14	Liljeroth	Peter	Finland
15	Koskinen	Pekka	Finland
16	Emelyanova	Svetlana	Finland
17	Ojanperä	Ari	Finland
18	Puska	Martti	Finland
19	Ruzibaev	Avaz	Finland
20	Drost	Robert	Finland
21	Weiner	Domenique	Germany
22	Ivas	Toni	Switzerland
23	Slobodskyy	Anatoliy	Germany

24	Järvinen	Päivi	Finland
25	Cucolo	Anna-Maria	Italy
26	Bouamama	Khellil	Algeria
27	Hämäläinen	Sampsa	Finland
28	Chembeleeva	Margarita	Russia
29	Oja	Riku	Finland
30	Hashemi	Javad	Finland
31	Bittencourt	Carla	Belgium
32	Giessibl	Franz	Germany
33	Schwarz	Alexander	Germany
34	Esch	Friedrich	Germany
35	Lauritsen	Jeppe	Denmark
36	Hofer	Werner	UK
37	Jelinek	Pavel	Czech Republic
38	Yakobson	Boris	USA
39	Kotakoski	Jani	Austria
40	Golberg	Dmitri	Japan
41	Chuvilin	Andrey	Spain
42	Michely	Thomas	Germany
43	Wehling	Tim	Germany
44	Pennycook	Stephen	USA
45	Hynninen	Teemu	Finland
46	Foster	Adam	Finland
47	Krasheninnikov	Arkady	Finland

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

Cavendish Laboratory, University of Cambridge, U.K.

July 2nd to July 5th, 2012

A Workshop of the CECAM JC Maxwell node, supported by CECAM and the Psi-k network through the European Science Foundation.

David D. O'Regan,
École Polytechnique Fédérale de Lausanne, Switzerland.
Simon M.-M. Dubois,
University of Cambridge, U.K.
Paolo Umari,
Università degli Studi di Padova, Italy.
Peter D. Haynes,
Imperial College London, U.K.

http://www.cecam.org/workshop-739.html

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 attracting 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

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.

3 Abstracts

Non-unitary triplet pairing in the centrosymmetric superconductor $\mathrm{LaNiGa_2}$

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Abstract

Muon spin rotation and relaxation experiments on the centrosymmetric intermetallic supercon- ductor $\mathrm{LaNiGa_2}$ are reported. The appearance of spontaneous magnetic fields coincides with the onset of superconductivity, implying that the superconducting state breaks time reversal symme- try, similarly to non-centrosymmetric $\mathrm{LaNiC_2}$. Only four triplet states are compatible with this observation, all of which are non-unitary triplets. This suggests that $\mathrm{LaNiGa_2}$ is the centrosym- metric analogue of $\mathrm{LaNiC_2}$. We argue that these materials are representatives of a new family of paramagnetic non-unitary superconductors.

Phys. Rev. Lett. 109, 097001 (2012)
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Ab initio description of quasiparticle band structures and optical near-edge absorption of transparent conducting oxides

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Abstract

Many-body perturbation theory is applied to compute the quasiparticle electronic structures and the optical-absorption spectra (including excitonic effects) for several transparent conducting oxides. We discuss HSE+G_0W_0 results for band structures, fundamental band gaps, and effective electron masses of MgO, ZnO, CdO, SnO_2, SnO, In_2O_3, and SiO_2. The Bethe-Salpeter equation is solved to account for excitonic effects in the calculation of the frequency-dependent absorption coefficients. We show that the HSE+G_0W_0 approach and the solution of the Bethe-Salpeter equation are very well-suited to describe the electronic structure and the optical properties of various transparent conducting oxides in good agreement with experiment.

(Journal of Materials Research **27**, 2180 (2012))
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Thermal conductivity of diamond nanowires from first principles

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Abstract

Using *ab initio* calculations we have investigated the thermal conductivity (κ) of diamond nanowires, unveiling unusual features unique to this system. In sharp contrast with Si, $\kappa(T)$ of diamond nanowires as thick as 400 nm still increase monotonically with temperature up to 300 K, and room-temperature size effects are stronger than for Si. A marked dependence of κ on the crystallographic orientation is predicted, which is apparent even at room temperature. [001] growth direction always possesses the largest κ in diamond nanowires. The predicted features point to a potential use of diamond nanowires for the precise control of thermal flow in nanoscale devices.

(Physical Review B, **85**, 195436 (2012))
`http://dx.doi.org/10.1103/PhysRevB.85.195436`
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Elastic anomalies and long/short-range ordering effects: A first-principles investigation of the $\mathrm{Ag}_c\mathrm{Pd}_{1-c}$ solid solution

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Abstract

We investigate the elastic properties of the binary alloy Ag-Pd. The lattice constant of this system shows significant deviations from the linear behaviour anticipated by the semi-empirical Vegard's rule. This effect was formerly studied by assuming total substitutional disorder, and described by the coherent potential approximation (CPA).

Theoretical phase diagram investigations have however suggested three ordered phases at low temperatures, and we extend our first-principles investigation to include such scenarios through the adoption of an extended unit cell representation and a recently developed multi-sublattice generalisation of the original CPA. This allows us to explore equilibrium lattice constant and bulk modulus within a unified approach even in the presence of partial long-range order. We obtain significant variations of the bulk modulus in comparison to the totally disordered picture, and again very rich deviations from more intuitive predictions of a simple linear behaviour. We follow former suggestions to analyse the different regimes in connection with topological transitions of the Fermi surface, examined through Bloch spectral function calculations.

(Physical Review B **86**, 094106 (2012))
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Magnetic structure of hexagonal $YMnO_3$ and $LuMnO_3$ from a microscopic point of view

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Abstract

The aim of this work is to establish a basic microscopic picture, which stands behind complex magnetic properties of hexagonal manganites. For these purposes, we consider two characteristic compounds: $YMnO_3$ and $LuMnO_3$, which form different magnetic structures in the ground state ($P\underline{6}_3c\underline{m}$ and $P\underline{6}_3\underline{c}m$, respectively). First, we construct an electronic low-energy model for the Mn $3d$ bands of $YMnO_3$ and $LuMnO_3$, and derive parameters of this model from the first-principles calculations. From the solution of this model, we conclude that, despite strong frustration effects in the hexagonal lattice, the relativistic spin-orbit interaction lifts the degeneracy of the magnetic ground state. Furthermore, the experimentally observed magnetic structures are successfully reproduced by the low-energy model. Then, we analyze this result in terms of interatomic magnetic interactions, which were computed using different types of approximations (starting from the model Hamiltonian as well as directly from the first-principles electronic structure calculations in the local-spin-density approximation). We argue that the main reason why $YMnO_3$ and $LuMnO_3$ tend to form different magnetic structures is related to the behavior of the single-ion anisotropy, which reflects the directional dependence of the lattice distortion: namely, the expansion and contraction of the Mn-trimers, which take place in $YMnO_3$ and $LuMnO_3$, respectively. On the other hand, the magnetic coupling between the planes is controlled by the next-nearest-neighbor interactions, which are less sensitive to the direction of the trimerization. In the $P\underline{6}_3c\underline{m}$ structure of $YMnO_3$, the Dzyaloshinskii-Moriya interactions lead to the spin canting out of the hexagonal plane, which is additive to the effect of the single-ion anisotropy. Finally, using the Berry-phase formalism, we evaluate the magnetic-state dependence of the ferroelectric polarization, and discuss potential applications of the latter in magnetoelectric switching phenomena.

(Phys. Rev. B. **86**, 054407 (2012))
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Theoretical Analysis of Electronic and Magnetic Properties of NaV_2O_4: Crucial Role of the Orbital Degrees of Freedom

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Abstract

Using realistic low-energy model with parameters derived from the first-principles electronic structure calculation, we address the origin of the quasi-one-dimensional behavior in orthorhombic NaV_2O_4, consisting of the double chains of edge-sharing VO_6 octahedra. We argue that the geometrical aspect alone does not explain the experimentally observed anisotropy of electronic and magnetic properties of NaV_2O_4. Instead, we attribute the unique behavior of NaV_2O_4 to one particular type of the orbital ordering, which respects the orthorhombic $Pnma$ symmetry. This orbital ordering acts to divide all t_{2g} states into two types: the 'localized' ones, which are antysymmetric with respect to the mirror reflection $y \to -y$, and the symmetric 'delocalized' ones. Thus, NaV_2O_4 can be classified as the double exchange system. The directional orientation of symmetric orbitals, which form the metallic band, appears to be sufficient to explain both quasi-one-dimensional character of interatomic magnetic interactions and the anisotropy of electrical resistivity.

(Phys. Rev. B. **86**, 104409 (2012))
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Low-Energy Models for Correlated Materials: Bandwidth Renormalization from Coulombic Screening

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Abstract

We provide a prescription for constructing Hamiltonians representing the low-energy physics of correlated electron materials with dynamically screened Coulomb interactions. The key feature is a renormalization of the hopping and hybridization parameters by the processes that lead to the dynamical screening. The renormalization is shown to be non-negligible for various classes of correlated electron materials. The bandwidth reduction effect is necessary for connecting models to materials behavior and for making quantitative predictions for low-energy properties of solids.

(Phys. Rev. Lett. **109**, 126408 (2012))
http://arxiv.org/abs/1204.4900

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Strain effects and band parameters in MgO, ZnO, and CdO

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Abstract

We have derived consistent sets of band parameters (band gaps, crystal-field splittings, effective masses, Luttinger, and E_P parameters) and strain deformation potentials for MgO, ZnO, and CdO in the wurtzite phase. To overcome the limitations of density-functional theory in the local-density and generalized gradient approximations we employ a hybrid functional as well as exact-exchange-based quasiparticle energy calculations in the G_0W_0 approach. We demonstrate that the band and strain parameters derived in this fashion are in very good agreement with the available experimental data and provide predictions for all parameters that have not been determined experimentally so far.

(Appl. Phys. Lett., accepted (2012))
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Density-functional Theory for f-electron Systems: the α-γ Phase Transition in Cerium

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Abstract

The iso-structural α-γ phase transition in cerium is analyzed using density-functional theory with different exchange-correlation functionals, in particular the PBE0 hybrid functional and the exact exchange plus correlation in the random-phase approximation ((EX+cRPA)@PBE0) approach. We show that the Hartree-Fock exchange part of the hybrid functional actuates two distinct solutions at zero temperature that can be associated with the α and γ phases of cerium. However, despite the relatively good structural and magnetic properties, PBE0 predicts the γ phase to be the stable phase at ambient pressure and zero temperature, in contradiction with low temperature experiments. EX+cRPA reverses the energetic ordering, which emphasizes the importance of correlation for rare-earth systems.

(Phys. Rev. Lett., in print (2012))

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A Benchmark of GW Methods for Azabenzenes: Is the GW Approximation Good Enough?

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Abstract

Many-body perturbation theory in the GW approximation is a useful method for describing electronic properties associated with charged excitations. A hierarchy of GW methods exists, starting from non-self-consistent G_0W_0, through partial self-consistency in the eigenvalues (ev-scGW) and in the Green's function (scGW_0), to fully self-consistent GW (scGW). Here, we assess the performance of these methods for benzene, pyridine, and the diazines. The quasiparticle spectra are compared to photoemission spectroscopy (PES) experiments with respect to all measured particle removal energies and the ordering of the frontier orbitals. We find that the accuracy of the calculated spectra does not match the expectations based on their level of self-consistency. In particular, for certain starting points G_0W_0 and scGW_0 provide spectra in better agreement with the PES than scGW.

(Submitted to Phys. Rev. B (2012))
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4 SCIENTIFIC HIGHLIGHT OF THE MONTH

First-principles DFT+U study of radiation damage in UO_2: f electron correlations and the local energy minima issue

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Abstract

The present highlight reviews recent advances in first-principles modelling of radiation damage in UO_2. It focuses on the influence of strong correlations and the problem of metastable states that occur with some approximations that localize electrons, in particular the density functional theory (DFT)+U approximation. It gives an illustration that DFT+U calculations quantitatively describe atomic transport phenomena in strongly-correlated uranium dioxide, provided that one circumvents the DFT+U local energy minima issue that affects f-electron systems. The occupation matrix control (OMC) scheme is one of the techniques developed to tackle the metastable state issue. We demonstrate here its efficiency on perfect and defective UO_2 through the study of oxygen diffusion. We use OMC to calculate UO_2 bulk properties, defect formation energies, migration energy barriers, and we show that in order to avoid the metastable states and systematically reach the ground state of uranium dioxide with DFT+U, the monitoring of occupation matrices of the correlated orbitals on which the Hubbard term is applied is crucial. The presence of metastable states can induce significant differences in the calculated total energies, which explains the origin of the discrepancies in the results obtained by various authors on crystalline and defect-containing UO_2. Also, for the bulk fluorite structure of UO_2, we show that the widely used Dudarev approach of the DFT+U systematically yields the first metastable state when no control is done on the orbital occupancies. As for oxygen diffusion, the calculated migration energy relating to the interstitialcy mechanism compares very favourably to experimental data. Also, vacancy migration and Frenkel pair formation energies are shown to agree well with existing data.

1 Introduction

Uranium dioxide is the standard nuclear fuel used in pressurized water reactors and has been extensively studied during the last decades, both experimentally [1–8] and computationally [9–23]. In order to better understand the behaviour of this material under irradiation and in particular to gain some insight into point defect formation and migration, its accurate description by first-principles methods is necessary. Such a description, however, remains challenging. Previous first-principles calculations [9–11] based on the density functional theory [24, 25] in the local density approximation (LDA) and in the generalized gradient approximation (GGA) failed to capture the strong correlations between the $5f$ electrons of uranium entirely. Within these two approximations, uranium dioxide is found to be a ferromagnetic metallic compound while it is actually an antiferromagnetic Mott-Hubbard insulator below 30 K. It is only with the development of approximations such as hybrid functionals for exchange and correlation [18, 26, 27], self-interaction correction (SIC) [16, 28] or approximations based on the addition of a Hubbard term to the Hamiltonian, such as DFT+U [29–31] and DFT+DMFT [32, 33], that the strong correlations between the $5f$ electrons of UO_2 could be better described.

Furthermore, the increase in available computing power enabled the study of large UO_2 supercells and with it the investigation of the formation and migration energies of point defects [15, 19, 22, 23, 34–36] and of the incorporation of fission products [37–41], mainly xenon, iodine, strontium, barium, zirconium, molybdenum and caesium, and of helium [42, 43]. These studies are of prime importance to better understand the behaviour of UO_2 under irradiation. Resulting migration energies can be used as input data in higher scale models (classical molecular dynamics, kinetic Monte Carlo simulations, rate theory...) and should therefore be calculated with high accuracy. Up to now, the large UO_2 supercells that are required to perform these calculations, containing around one hundred atoms, can only be studied using the DFT+U method because calculations using hybrid functionals or DFT+DMFT are still computationally prohibitive.

Unfortunately, significant discrepancies were observed in the formation and migration energies of point defects calculated at the DFT+U level and published in recent years, although the same method, the projector augmented-wave (PAW) method, and very similar calculation parameters were used. By a study of perfect UO_2 crystal [17], we were able to show that these discrepancies stemmed from the use of the DFT+U approximation. This formalism localizes the $5f$ electrons and creates numerous local energy minima (or metastable states), which makes it difficult to find the ground state of the system (see Sect. 2). Unlike the LDA or GGA approximations, the DFT+U formalism creates an orbital anisotropy that increases the number of metastable states, and consequently, the final state reached by the self-consistent algorithm and its associated total energy may be different depending on the starting point of the calculation (initial lattice parameter, initial uranium magnetic moments, etc). The DFT+U method is based on the Hartree Fock (HF) approximation. The latter has been known to exhibit such multiple solutions for a long time [44, 45]. This increased number of energy minima has also been observed in UO_2 within other approximations that localize electrons, such as hybrid functionals [36], as well as in other $4f$ and $5f$-compounds such as γ-Ce [46, 47], PrO_2 [48], PuO_2 [49] and rare earth nitrides [50]. The DFT+U study on cerium by Amadon *et al.* [47] in particular showed that the density matrix in the correlated subspace had to be monitored carefully, especially to study magnetism. Moreover, the work of Jomard *et al.* [49] on plutonium oxides PuO_2 and Pu_2O_3 provided a practical procedure which consists in comparing the energies of all energy minima and therefore allowed to unequivocally determine the ground state.

With a 96-atom UO_2 unit cell as typically used for the study point defects and impurities, the difference in the total energy between the ground state and metastable states can reach up to 3 eV. The existence of these metastable states therefore strongly affects the calculated formation energies of point defects and, as a consequence, any result derived from these formation energies:

concentration of defects, solubility of fission products, etc. It is therefore important to ensure that the ground state of the system has indeed been reached.

In this review, we report a detailled study of the ground state and metastable states of uranium dioxide obtained with DFT+U and investigate the influence of the metastable states on the structural and electronic properties of the material. We present the theoretical background for the DFT+U formalism and the orbital anisotropy it implies for the $5f$ orbitals. We show that if one wishes to reach the ground state systematically, the most effective method is to switch off all wave-function symmetries and to precondition the electronic occupancies of the $5f$ orbitals, i.e., to impose initial $5f$ electron occupation matrices and monitor them during the calculations. This so-called occupation matrix control scheme (OMC) is an alternative to more recent schemes developped to avoid metastable states in f-compounds: the U-ramping scheme [51] and the quasi-annealing scheme (QA) [52]. Using the DFT+U method with the OMC scheme, we have studied the stability of the Jahn-Teller (JT) distortion in UO_2 and calculated oxygen and uranium point-defect formation energies in both the fluorite and the Jahn-Teller distorted structures. Our results are compared with those from the literature and we discuss the discrepancies observed. Finally, the DFT+U results on the migration mechanisms and energies of oxygen ions in UO_2 are reported.

2 The DFT+U method and the local minima issue

2.1 The DFT+U method

Given the failure of standard density functional theory approximations (namely, the local density approximation LDA and the generalized gradient approximation GGA) to describe correctly uranium dioxide, we used the DFT+U approximation (*i.e.* the LDA+U or the GGA+U approximation) that improves the treatment of the correlations between the uranium $5f$ electrons. The DFT+U energy functional introduces a correction to the standard DFT energy functional given by

$$E^{\mathrm{DFT+U}} = E^{\mathrm{DFT}} + E_{\mathrm{Hub}} - E_{\mathrm{dc}}. \tag{1}$$

The first term E^{DFT} is the standard DFT (LDA or GGA) contribution to the energy. The second term E_{Hub} is the corrective electron-electron interaction term to account for the enhanced electron correlations and it takes a similar form as the U term of Hubbard model [53] in the static mean field approximation. E_{dc} is the double-counting correction. E_{Hub} and E_{dc} depend on the occupation matrices of the correlated orbitals.

There are various formulations of the DFT+U functionals. Although they can all be written in the form given in equation (1), they differ with the choice of

- the DFT exchange-correlation functional (LDA or GGA).
- the formulation of the Hubbard term E_{Hub} and the values of the U and J parameters contained in E_{Hub}.

- the double-counting term E_{dc}.
- the Kohn-Sham orbital projection method used to calculate the electron occupancies. However, with equal U and J values and with the same double-counting term, two electron occupancy calculations using two different projection methods will give similar results [54].

The Hubbard term

We used the two currently available approaches to describe the Coulomb interaction Hubbard term E_{Hub}. They were respectively introduced by Liechtenstein *et al.* [30] and Dudarev *et al.* [31]. The Hubbard interaction term is expressed in the following rotationally invariant form:

$$\begin{aligned} E_{\text{Hub}}[n^I_{mm'}] &= \frac{1}{2}\sum_{\{m\},\sigma,I}\{\langle m,m''|V_{ee}|m',m'''\rangle n^{I\sigma}_{mm'}n^{I-\sigma}_{m''m'''} \\ &\quad +(\langle m,m''|V_{ee}|m',m'''\rangle - \langle m,m''|V_{ee}|m''',m'\rangle)n^{I\sigma}_{mm'}n^{I\sigma}_{m''m'''}\}, \end{aligned} \tag{2}$$

where $n^{I\sigma}_{mm'}$ is the occupation matrix on site I (see Sect. 2.1.1). E_{Hub} can be expressed as a function of the direct Coulomb U and exchange J interactions:

$$U = \frac{1}{(2l+1)^2}\sum_{m,m'}\langle m,m'|V_{ee}|m,m'\rangle \tag{3}$$

and

$$J = \frac{1}{2l(2l+1)}\sum_{m\neq m',m'}\langle m,m'|V_{ee}|m',m\rangle \tag{4}$$

The Dudarev approach is a simplified form of the Liechtenstein approach. It uses the difference $(U-J)$, contrary to the Liechtenstein approach in which the U and J terms come into play separately.

The double-counting term

The third term in Eq. (1), the double-counting term E_{dc}, is not specific to the DFT+U formalism but is required in all methods that add a correlation term to the standard DFT functional. The double-counting term is aimed at substracting the LDA or GGA exchange-correlation contribution already counted in E^{DFT}. There are several expressions for the double-counting term. In the so-called around mean field (AMF) approach, introduced by Czyżyk and Sawatzky [55], E_{dc} takes the following form:

$$E^{\text{AMF}}_{\text{dc}} = UN_{\uparrow}N_{\downarrow} + \frac{1}{2}\frac{2l}{2l+1}(U-J)\sum_{\sigma}N^2_{\sigma}, \tag{5}$$

where N is the total number of electrons, N_σ is the total number of electrons with spin σ ($\uparrow$ or $\downarrow$) and l is the quantum orbital number of the orbitals on which the DFT+U correction is applied.

In the fully localized limit approach (FLL), introduced by Anisimov *et al.* [56], the double-counting term is expressed as:

$$E_{\mathrm{dc}}^{\mathrm{FLL}} = \frac{1}{2}UN(N-1) - \frac{1}{2}J\sum_{\sigma}\left(N_{\sigma}^{2} - N_{\sigma}\right). \tag{6}$$

The main difference between the AMF and FLL double-counting terms is that the AMF tends to favor low spin configurations of the system whereas the FFL tends to favor high spin configurations [54]. In UO$_2$, the AMF and FLL approaches, however, yield the same results, i.e. a high spin configuration with a magnetic moment of $\pm 2\mu_{\mathrm{B}}$ on uranium cations.

2.1.1 Occupation matrices

Occupation matrices describe the electron occupancies of the correlated orbitals and play an important role in the DFT+U formalism (see Eq. (2)). An occupation matrix is defined as:

$$n_{m,m'}^{\sigma} = \sum_{n,\mathbf{k}} f_{n,\mathbf{k}}^{\sigma}\langle\psi_{n,\mathbf{k}}^{\sigma}|P_{m,m'}|\psi_{n,\mathbf{k}}^{\sigma}\rangle, \tag{7}$$

in which $\psi_{n,\mathbf{k}}^{\sigma}$ is a valence wave function corresponding to the state (n,$\mathbf{k}$) of spin σ and $f_{n,\mathbf{k}}^{\sigma}$ is the corresponding occupation number. $P_{m,m'}$ are projection operators on the localized orbitals. As an example, an occupation matrix for correlated $5f$ orbitals with spin up ($\uparrow$) takes the form:

$$n_{m,m'}^{\uparrow} = \begin{pmatrix} n_{-3,-3}^{\uparrow} & n_{-3,-2}^{\uparrow} & \cdots & \cdots & n_{-3,+3}^{\uparrow} \\ n_{-2,-3}^{\uparrow} & n_{-2,-2}^{\uparrow} & \ddots & & \vdots \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ \vdots & & \ddots & n_{+2,+2}^{\uparrow} & n_{+2,+3}^{\uparrow} \\ n_{+3,-3}^{\uparrow} & \cdots & \cdots & n_{+3,+2}^{\uparrow} & n_{+3,+3}^{\uparrow} \end{pmatrix} \tag{8}$$

There is no unique way to define occupation matrices of localized atomic states [57]. In the present review, the occupation matrices were calculated in the basis of real spherical harmonics. The DFT+U formalism is rotationally invariant [30], which implies that it is always possible to find a basis in which the occupation matrix is diagonal.

2.2 The occurence of metastable states

In the DFT+U approximation, the strongly correlated electrons are localized on specific orbitals, contrary to standard DFT approximations which, in the case of UO$_2$, fill the orbitals with fractional electron occupancies. For this reason, with LDA and GGA, UO$_2$ is found metallic instead of insulator as it should be. The counterpart for this localization of the f electrons is the existence of various ways of filling the correlated orbitals, from which only one electron configuration corresponds to the ground state of the system. This leads to the existence of multiple local energy minima (or metastable states) in which calculations can get trapped because of the difficulty to go from one electron configuration to another. It is thus necessary to make sure that the ground state of the system is reached in all DFT+U calculations. In the case of

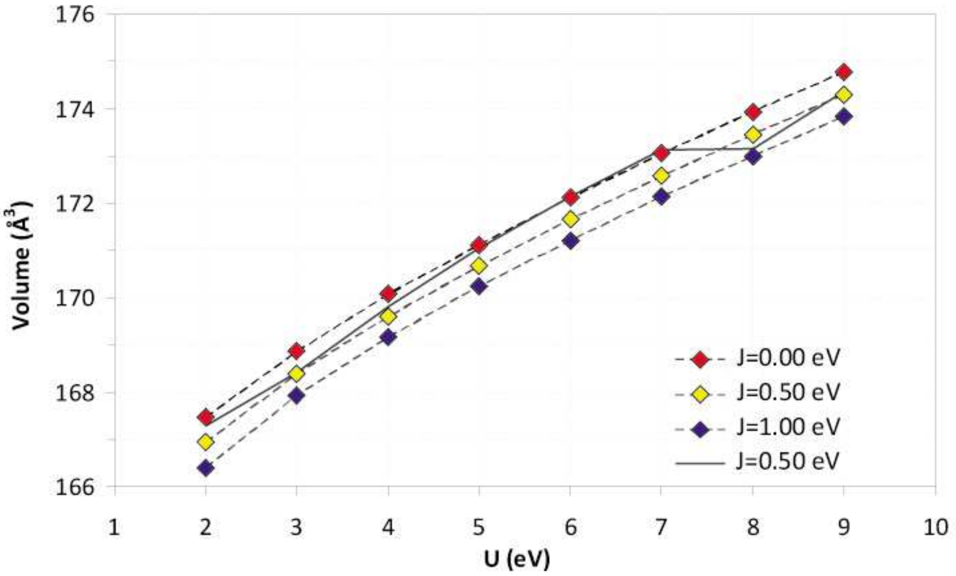


Figure 1: Variation of the 12-atom UO_2 supercell volume as a function of the U and J parameters of Liechtenstein DFT+U. The black line corresponds to the calculations from an arbitrary input wave function, in which the monitoring of the occupation matrices has not been performed.

bulk UO_2, the occurence of the metastable states is linked to the various possibilities for the two $5f$ electrons to occupy the seven $5f$ orbitals of the U^{4+} ions.

As can be easily experienced with DFT+U calculations even on the bulk UO_2 crystal, a DFT+U calculation starting from an arbitrary input wave function does not automatically converge to the lowest energy state. For instance, the convergence toward metastable states can be seen Fig. 1 which shows the variation of the UO_2 volume as a function of the U-parameter of the DFT+U method. The curve corresponding to the calculations from an arbitrary input wave function is rather erratic whereas the curves corresponding to the ground state of the crystal are perfectly smooth. Such a blunt illustration of the occurrence of metastable states can also be seen in Fig. 3 of the article by Jomard *et al.* for PuO_2 [49].

An efficient method to reach the ground state electronic configuration consists in testing several initial electron occupancies as a starting point of the calculation and determining the final occupancies that correspond to the lowest energy state. Such a scheme was used for the DFT+U study of several other correlated $4f$ and $5f$ compounds, such as cerium [46, 47], rare-earth nitrides [50] or plutonium oxides [49]. We have applied this method to UO_2. We defined initial input f electron occupation matrices and we imposed them during the calculation of the DFT+U potential. We thus preconditioned the calculation of the potential which was then applied as a correction to the standard DFT potential. Occupation matrices are imposed during the first 10 to 30 electronic steps, depending on the complexity of the system. After these initial constrained steps, the calculation is left to converge self-consistently on its own.

In order to determine the ground state occupancy of bulk UO_2, we imposed as a first step initial diagonal occupation matrices. There are $C_2^7 = 21$ different ways of filling the seven $5f$ levels with

Table 1: UO_2 states reached as a function of the initially imposed diagonal occupation matrices (defined by m_i and m_j) not taking into account the symmetries of the crystal and with Liechtenstein DFT+U. Δ is the UO_2 band gap. The lowest energy is fixed to zero.

i	j	Initial Matrix	$E - E_{\mathrm{min}}$ (eV / U_2O_4)	Δ (eV)
-3	-2	[1100000]	1.67	0.8
-3	-1	[1010000]	0.15	1.9
-3	0	[1001000]	0.01	2.5
-3	1	[1000100]	0.03	2.3
-3	2	[1000010]	0.07	2.5
-3	3	[1000001]	0.03	2.3
-2	-1	[0110000]	1.67	0.8
-2	0	[0101000]	1.72	0.9
-2	1	[0100100]	1.67	0.8
-2	2	[0100010]	2.68	0.2
-2	3	[0100001]	1.67	0.8
-1	0	[0011000]	0.00	2.4
-1	1	[0010100]	0.78	1.6
-1	2	[0010010]	0.07	2.5
-1	3	[0010001]	0.03	2.3
0	1	[0001100]	0.00	2.4
0	2	[0001010]	0.16	2.0
0	3	[0001001]	0.01	2.5
1	2	[0000110]	0.07	2.5
1	3	[0000101]	0.15	1.9
2	3	[0000011]	0.07	2.5

two electrons. Since there are several degenerate f levels, some of the electronic configurations are identical by symmetry. However, in order to check the consistency and the accuracy of the procedure, we did not take into account the f-level degeneracies and we studied all 21 electronic configurations. The imposed occupation matrices can be defined by the two quantum numbers m_i and m_j corresponding to the filled orbitals. As an example, the diagonal occupation matrix corresponding to occupied m_{-2} and m_3 orbitals will be noted [0100001].

Table 1 gives the energies of the UO_2 states reached as a function of the diagonal occupation matrices initially imposed, not taking into account the symmetries of the crystal. A study by Larson *et al.* [50] and our systematic study of UO_2 [17] indeed showed that keeping the crystal symmetries would hamper even more the convergence to the ground state. As a static mean field approximation, DFT+U (or Hartree Fock) indeed stabilizes symmetry-broken solutions [58]. Of course, lifting the symmetry results in a higher computational cost but is compensated by the accuracy of the result.

We see from Table 1 that ten states are reached depending on the starting electron occupation configuration. The calculations with the initial occupation matrices [0001100] and [0011000] lead to the ground state of the UO_2 crystal. Several of the other final states are just few tenth of meV / UO_2 above the ground state but they can display electronic properties different from the ground state, as shown by the band gap values. When the symmetries of the crystal are kept, metallic states can even be obtained. Structural properties also exhibit slight differences, as will be shown in Sect. 3. The final $5f$ orbital occupation matrices obtained for the ground state of UO_2 (with the collinear $1\mathbf{k}$ antiferromagnetic order - see Sect. 3), using the Liechtenstein DFT+U and without symmetries, are reported below.

Spin ↑ component:

$$\begin{pmatrix}
0.61126 & 0.00000 & 0.44840 & -0.00058 & 0.00000 & -0.00039 & 0.00001 \\
0.00000 & 0.11832 & 0.00000 & 0.00000 & -0.00001 & 0.00000 & 0.00000 \\
0.44840 & 0.00000 & 0.37479 & -0.00004 & 0.00000 & -0.00060 & 0.00001 \\
-0.00058 & 0.00000 & -0.00004 & 0.64060 & 0.00008 & -0.44102 & -0.00002 \\
0.00000 & -0.00001 & 0.00000 & 0.00008 & 0.02762 & -0.00006 & -0.00442 \\
-0.00039 & 0.00000 & -0.00060 & -0.44102 & -0.00006 & 0.35045 & 0.00002 \\
0.00001 & 0.00000 & 0.00001 & -0.00002 & -0.00442 & 0.00002 & 0.03100
\end{pmatrix}$$

Spin ↓ component:

$$\begin{pmatrix}
0.03167 & 0.00000 & 0.00366 & 0.00000 & 0.00000 & 0.00000 & 0.00000 \\
0.00000 & 0.09432 & 0.00000 & 0.00000 & 0.00000 & 0.00000 & 0.00000 \\
0.00366 & 0.00000 & 0.02519 & 0.00000 & 0.00000 & 0.00000 & 0.00000 \\
0.00000 & 0.00000 & 0.00000 & 0.02927 & 0.00000 & 0.00080 & 0.00000 \\
0.00000 & 0.00000 & 0.00000 & 0.00000 & 0.02472 & 0.00000 & -0.00349 \\
0.00000 & 0.00000 & 0.00000 & 0.00080 & 0.00000 & 0.02226 & 0.00000 \\
0.00000 & 0.00000 & 0.00000 & 0.00000 & -0.00349 & 0.00000 & 0.02832
\end{pmatrix}$$

Note that the ground state occupation matrices have been determined by testing not only diagonal occupation matrices, but also numerous non diagonal ones. These matrices will be the input occupation matrices for all subsequent calculations of UO_2 supercells and will precondition the DFT+U calculations in order to avoid the convergence toward a metastable state. They were used for all calculations reported below on UO_2 bulk properties, as well as point defect formation and migration. This scheme was also used in the study of thermodynamic properties of UO_2 [59].

2.3 Methods developed to avoid metastable states

In order to perform accurate DFT+U calculations and make sure that the calculations converge to the ground state of the system, an *ad hoc* procedure has to be applied to avoid the convergence of the calculations to a local energy minima. Up to now, three procedures have been developed, including the one (OMC) used in the previous section and which we recall:

• The occupation matrix control scheme (OMC) [17]: It requires a systematic search of the ground state electronic configuration (in the form of the occupation matrices of the correlated orbitals) for the bulk perfect crystal. This ground state occupation matrix has to be imposed at the beginning of subsequent calculations (for the first 10 to 30 electronic iterations) in order to precondition the convergence of the calculation toward the ground state. This procedure proved efficient for perfect bulk systems and systems with point defects or fission gases. The convergence to the ground state is also better ensured by switching off symmetries in order to lift degeneracies.

• The U-ramping scheme [51]: The Coulomb U parameter of the DFT+U method is slowly increased from 0 (standard DFT calculation) to its desired value, typically by steps of 0.1 eV. Results on the incorporation of rare gases in UO_2 [60] show that the U-ramping method is efficient on defective systems. The ground state of perfect bulk UO_2 could, however, not be reached using this method.

• The quasi-annealing scheme (QA) [52]: A fictitious fluctuation of the external potential is introduced, which is gradually suppressed in order to explore the potential surface. The results for the UO_2 perfect crystal are similar to the ones obtained with the occupation matrix scheme [61] (see below). For point defects or fission gas behaviour in UO_2, no comparison has been possible so far because of the different exchange-correlation functionals used (LDA+U vs. GGA+U).

A comparison was performed between the OMC and QA methods for a DFT+U calculation of the absolute total energy of the UO_2 crystal. The results are reported in Table 2 and show a small 10 meV / UO_2 difference between the OMC and the QA calculations. This discrepancy is not likely due to metastable states, but rather to a minor difference in calculation parameters. The 180 meV difference with the calculation using an arbitrary input wave function is, on the contrary, clearly due to the convergence to a metastable state. Up to now, only the QA approach has been proved as successful as the OMC scheme in reaching the ground state of bulk UO_2.

Table 2: Absolute DFT+U energy (eV/UO_2) of the UO_2 crystal calculated with the OMC scheme, the QA scheme and from an arbitrary input wave function, using otherwise the same calculation parameters [61].

	OMC	QA	arbitrary
Total energy (eV/U_4O_8)	-117.136	-117.095	-116.959

The main advantage of the OMC scheme is that when the ground state occupancy is known, one can perform calculations of supercells containing point defects or impurities without any increase of computational time. It is often argued that the OMC scheme requires numerous calculations in defective systems in order to find the ground state. This is not true if one can assume that the ground state occupation matrices of the perfect crystal can be used for the defective structure. Far from the defect, occupation matrices are not modified and are identical to those of the ground state. Close to the defect, on the contrary, the ground state occupation matrices will be quickly reoptimized into more complex electronic occupancies. In the end, the OMC scheme on defective supercell only requires one or a few calculations, depending whether near the defect cations with various oxidation states and different occupation matrices must be imposed (see Sect. 4.1). This is not the case with the U-ramping and QA methods in which the U parameter has to be slowly increased and the fluctuation of the external potential slowly removed, respectively. The OMC scheme is straightforwardly available in the ABINIT [62] code and was implemented by our group in the VASP code.

2.4 Calculation parameters

All calculations reported here were carried out within the PAW formalism [63] for the calculation of the Kohn-Sham wave functions, as implemented in the VASP [64, 65] and ABINIT [62, 66] codes. For the exchange and correlation energy, we used the GGA functional as parametrized by Perdew, Burke, and Ernzerhof (PBE) [67]. The U and J values of the DFT+U approximation were set to 4.50 eV and 0.54 eV, respectively, as determined by Yamazaki and Kotani from the analysis of X-ray photoemission spectra [68, 69]. These values were kept constant in all calculations, whatever the defect considered. It is indeed *a priori* unnecessary to change these values once they have been defined for a given material: on the one hand, the U and J values in UO_2 mainly depend on the hybridization of uranium $5f$ and oxygen $2p$ orbitals, which is not significantly modified with the presence of a point defect in the material. Even if uranium ions around a point defect change their oxidation states (see Sect. 4.1), only a slight change in their local interaction U can be expected. For simplicity, we neglect these differences. On the other hand, U and J describe the Coulomb interaction between electrons that are located on the same atomic site, hence referred to as intra-atomic interactions. Given that the $5f$ electrons are strongly localized, it is unlikely that the presence of a defect would significantly change the very nature of these interactions.

For bulk calculations with a 12-atom UO_2 conventional cell, a 600 eV cut-off energy for the plane-wave basis set was used and a 6x6x6 Monkhorst-Pack for the sampling of the irreducible part of the Brillouin zone. For the 96-atom supercells, the cut-off energy was slightly reduced to 500 eV and a 2x2x2 Monkhorst-Pack was used. We add or remove oxygen or uranium atoms from this supercell to create either interstitial or vacancy point defects. The oxygen interstitial and vacancy induce a supercell volume variation of 0.3 % and 0.02 %, respectively. We can therefore consider that the supercell size is large enough to accommodate these defects. In all defect calculations, we used the collinear $1\mathbf{k}$ antiferromagnetic order as an approximation of the paramagnetic order of the UO_2 fluorite phase above 30 K. Moreover, we used a Gaussian smearing for fractional occupancies with a smearing width of 0.1 eV.

To determine the migration barriers, we used the CI-NEB (climbing-image nudged elastic band) method [70] as implemented in the VASP package. Since the determination of saddle points is efficient with only a small number of intermediate images along the reaction path, we used five images for the calculations of the minimum energy path.

In all calculations, spin-orbit coupling (SOC) was neglected. The inclusion of SOC causes drastic modifications in the occupation matrices of uranium atoms since it induces the filling of nondiagonal spin components that give rise to the orbital magnetic moment. Moreover, taking SOC into account significantly increases the number of metastable states since additional occupation matrices are to be considered, as a consequence of which a new systematic search for the ground state would have to be carried out. This, however, remains to be done to see the effect of SOC on defect formation and migration energies.

3 DFT+U results on bulk properties of UO_2

Above its Néel temperature of 30 K, UO_2 is paramagnetic and crystallizes in the fluorite structure (CaF_2): the uranium U^{4+} ions form a face-centred cubic sublattice while oxygen O^{2-} ions occupy the tetrahedral sites. Below 30 K, UO_2 is antiferromagnetic (AFM) and exhibits a static Jahn-Teller distortion of the oxygen sublattice [4, 71–74].

In fluorite UO_2, whose space group is $Fm\bar{3}m$, the point group of uranium is O_h and the crystalline field splits the seven $5f$ orbitals of the uranium atom into two threefold-degenerate levels (T_{1u} and T_{2u}) and one nondegenerate level (A_{2u}). As regards the antiferromagnetism in UO_2, experiments [3, 73, 75] and recent first-principles calculations [76] show that UO_2 has a non-collinear 3**k** antiferromagnetic order. However, due to the high computational cost, neither the non-collinear antiferromagnetism nor paramagnetism can be taken into account in point-defect calculations and we consider a collinear 1**k** antiferromagnetic order (also often referred to as the AFM1 or AFM(001) order), in which the spins of uranium atoms change sign along the Oz axis. This approximate 1**k** AFM order changes the point group of uranium from O_h to D_{4h}. In this case, the crystalline field splits the $5f$ orbitals into two twofold-degenerate levels (2 x E_u) and three nondegenerate levels (A_{2u}, B_{1u}, and B_{2u}).

The structural parameters and elastic constants are calculated for both the fluorite phase and the Jahn-Teller distorted phase, with a special attention to the magnetic ordering. In all cases, we imposed the appropriate occupation matrix at the beginning of the calculations to make sure that the lowest energy state is reached and that the results correspond to the ground state properties of the crystal in the structure considered.

3.1 The UO_2 fluorite phase

The structural parameters, bulk modulus and elastic constants of UO_2 in the fluorite phase are reported in Table 3.

Table 3: Lattice parameters (a, b, c), elastic constants (C_{11}, C_{12} et C_{44}) and bulk modulus (B) of UO_2 in the fluorite phase, calculated using Liechtenstein DFT+U.

	DFT+U	Experiments [77, 78]
Point group	D_{4h}	O_h
(a, b, c) (Å)	5.57; 5.57; 5.49	5.47
C_{11} (GPa)	346	389
C_{12} (GPa)	118	119
C_{44} (GPa)	58	60
B (GPa)	194	207

DFT+U structural parameters and elastic constants are in very good agreement with experimental values, despite the approximation on the magnetic ordering. The 1**k** antiferromagnetic order, however, causes a slight compression of the lattice along the z axis, which modifies the point group symmetry of uranium atoms. The T_{2u} levels of the O_h symmetry are split into an occupied E_u level and an empty B_{2u} level in the D_{4h} symmetry. Since the doubly degenerate level E_u $[x(y^2 - z^2)$ and $y(z^2 - x^2)]$ is oriented along the z axis, the compression occurs in this direction. We have also observed that in the first metastable state, the lattice is not compressed but expanded. With the Dudarev DFT+U, it is the other way around. The determination of the c/a ratio therefore constitutes a simple test to check if the ground state has been reached. Table 4 summarizes these results as a function of the DFT+U approaches used.

Table 4: c/a ratio of the UO_2 unit cell as a function of the state obtained and the DFT+U approximation used.

	Liechtenstein	Dudarev
Ground state	Compression $c/a = 0,99$	Dilatation $c/a = 1,01$
1^{st} metastable state	Dilatation $c/a = 1,01$	Compression $c/a = 0,99$

It should also be stressed that when occupation matrices are controlled, i.e. when the ground state is reached, the two DFT+U approaches yield similar electronic states: occupation matrices are identical, only the cell parameters differ (see Table 4). This is consistent with the fact that the Dudarev approach is a simplified version of the Liechtenstein approach. When occupation matrices are not controlled, however, calculations with the Dudarev approach do not reach the ground state. Instead, they reach the first metastable state, located 25 meV/UO_2 above the ground state.

3.2 The Jahn-Teller distortion

As mentioned before, below 30 K the oxygen sublattice displays a static Jahn-Teller distortion (JT) and the magnetic order is a non-collinear 3**k** AFM order [74]. The oxygen cage is distorted with an estimated displacement of oxygen atoms of 0.014 Å in the <111> directions, changing the space group from Fm$\bar{3}$m to Pa$\bar{3}$ [74].

As a first step, the stability of the JT distortion was studied with an approximated 1**k** AFM order and compared to the fluorite structure with the same magnetic structure. Second, the relative stability of the 1**k** and 3**k** AFM orders were compared in the JT distorted phase (see Sect. 3.3).

In the study of the JT distorted structure, the oxygen atoms are located initially in the experimentally determined positions (space group: Pa$\bar{3}$). The lattice structure is then optimized and the total energy compared to that of the UO_2 ground state in the fluorite structure with a 1**k** AFM order. Our results indicate that the JT distortion stabilizes the lattice by 52 meV/UO_2, which is significant. Several calculations were done for the JT phase with various initial occupation matrices. All calculations converged to the same final state, emphasizing that when symmetries are broken, as induced by the oxygen atomic displacements, the DFT+U calculations reach the ground state more easily.

Despite the numerous studies of the AFM order in the JT phase, there are few experimental data on the structural parameters of this phase. The elastic constants at 0 K can be determined by extrapolation of data from the 1967 study by Brandt and Walker [79]. In Table 5, we report the calculated and experimental lattice parameters, elastic constants and bulk modulus of UO_2 in the JT distorted phase.

Table 5: Lattice parameters (a, b, c), elastic constants (C_{11}, C_{12} and C_{44}) and bulk modulus (B) of uranium dioxide in the Jahn-Teller distorted phase with a 1**k**-antiferromagnetic order, calculated with the Dudarev DFT+U and compared to experiments.

	DFT+U	Experiments
(a, b, c) (Å)	5.054	–
C_{11} (GPa)	358	400
C_{12} (GPa)	109	126
C_{44} (GPa)	65	59
B (GPa)	192	217

The DFT+U values are in good agreement with the experimental data. The elastic constants of the JT phase are not very different from those in the fluorite phase. More significant is the result that the crystal lattice with the JT distortion remains cubic, which is not the case in the fluorite phase obtained using DFT+U (see Table 3). The oxygen sublattice distortion that we obtain corresponds to 0.09 Å displacements essentially in the $\langle 100 \rangle$ direction, which are, however, much too large compared to the ones reported from experiments (0.014 Å displacements in the $\langle 111 \rangle$ direction) [80]. The fact that the directions are different may be explained by our approximation of a collinear 1**k** AFM magnetic order instead of the 3**k** order.

In the JT 1**k** phase, the occupation matrices of all uranium atoms are identical and they only differ by the sign of some matrix elements. Those occupation matrices are noted $\mathrm{OM_{JT}}$ and will be subsequently used as initial occupation matrices for calculations with supercells containing point defects. Those results also show that in the perfect bulk crystal, the electron occupations of the uranium atoms are directly linked to the oxygen positions due to the fact that the oxygen atoms govern the crystal field applied to the uranium atoms. This crystal field modifies in return the point group symmetry at the uranium site, hence the $5f$ orbital degeneracies. In the 1**k** fluorite structure, the symmetry point group is $\mathrm{D_{4h}}$ and the crystal field imposes a particular form for the occupation matrices. When the oxygen cage is distorted, the point group symmetry becomes $\mathrm{C_{3i}}$ and the occupation matrices have a different form.

3.3 Non-collinear magnetic order

In order to check that the DFT+U can also describe correctly the magnetic ground state of UO_2, we have compared the stability of the collinear 1**k** AFM order with the experimentally observed low-temperature 3**k** AFM order [4, 80, 81]. The calculations were performed in the Jahn-Teller distorted phase, which is the one co-existing with the 3**k** AFM order. The calculations were performed in a 12-atom supercell, containing four inequivalent uranium sites, i.e. the smallest supercell enabling one to reproduce the 3**k** AFM order.

The results show that the **3k** AFM order has approximately the same total energy as the **1k** AFM order, with an energy difference of only 0.6 meV/UO_2. The **3k** AFM order, however, is not obtained as the most stable one, contrary to experimental evidence. The inclusion of the spin-orbit coupling in the calculation may change this trend but its inclusion, in combination with the OMC scheme, remains challenging (see Sect. 2.4). The spin-orbit coupling was taken into account in the studies of the AFM order of UO_2 by Laskowski *et al.* [76] and Gryaznov *et al.* [21]. Laskowski *et al.* used an all-electron first-principles method and also found that the **1k**-configuration is more stable than the **3k** one (by around 10 meV/UO_2). On the contrary, Gryaznov *et al.* found the **3k** AFM structure to be more stable than the **1k**-AFM order by 95 meV/UO_2. From the distortion of the cubic lattice ($c/a < 1$) obtained by Gryaznov *et al.*, however, it is clear that the calculations of the **1k**-AFM order did not reach the ground state (see Table 4) and thus the relative energies calculated between the magnetic phases are biased.

In our DFT+U calculations with the non-collinear **3k** order, the cell is perfectly cubic (a=b=c), contrary to what was obtained with the collinear **1k** order in the fluorite phase. Moreover, we find that the non-collinear **3k** order is associated with a distortion of the oxygen sublattice with oxygen displacements of 0.09 Å in the $\langle 111 \rangle$ direction. Even if the direction of the distortion is in agreement with the experimental data [82], the magnitude of the displacements is still significantly larger than the experimental estimation of 0.014 Å. Our results, however, are in agreement with the first-principles studies by Laskowski *et al.* and Gryaznov *et al.* who found a distortion of the oxygen sublattice of 0.16 Å and 0.09 Å, respectively.

4 Oxygen point defect formation energies in UO_2

Until recently, point-defect formation energies in uranium dioxide UO_2 were a matter of debate due to the significant discrepancies between the various studies published in the literature. The authors of the previous papers [14,15,19,22,83] on point defects in UO_2 all used the same PAW method implemented in the same code (VASP), the same Dudarev DFT+U approximation and very similar calculation parameters: the cut-off energies for the plane wave basis only differ by a few tens of eV and the values of U and J are identical. Despite these similarities, significant discrepancies not consistent with the accuracy expected from DFT were observed between the various studies, as can be seen in Table 6. The differences in the formation energies can reach 2.0 eV for uranium Frenkel pairs (consisting of a vacancy and an interstitial, non-interacting) and up to 2.7 eV for the Schottky defect (consisting of an oxygen vacancy and two uranium vacancies).

The oxygen point defect and Schottky defect formation energies are calculated as follows:

Interstitial $\mathrm{I_o}$: $E^{\mathrm{F}}_{\mathrm{I_o}} = E^{\mathrm{N+1}}_{\mathrm{I_o}} - E^{\mathrm{N}}_{\mathrm{UO_2}} - \frac{1}{2}E_{\mathrm{O_2}}$,

Vacancy $\mathrm{V_o}$: $E^{\mathrm{F}}_{\mathrm{V_o}} = E^{\mathrm{N-1}}_{\mathrm{V_o}} - E^{\mathrm{N}}_{\mathrm{UO_2}} + \frac{1}{2}E_{\mathrm{O_2}}$,

Schottky defect S : $E^{\mathrm{F}}_{\mathrm{S^i}} = E^{\mathrm{N-1}}_{\mathrm{V_U}} + 2 \times E^{\mathrm{N-1}}_{\mathrm{V_O}} - 3 \times \frac{N-1}{N} \times E^{\mathrm{N}}_{\mathrm{UO_2}}$,

Oxygen Frenkel pair $\mathrm{FP_o}$: $E^{\mathrm{F}}_{\mathrm{FP_o}} = E^{\mathrm{N-1}}_{\mathrm{V_o}} + E^{\mathrm{N+1}}_{\mathrm{I_o}}$,

where N is the number of atoms in the defect-free supercell, here $N = 96$. $E^{\mathrm{N}}_{\mathrm{UO_2}}$ is the total energy of the defect-free supercell, $E^{\mathrm{N+1}}_{\mathrm{I_o}}$ and $E^{\mathrm{N-1}}_{\mathrm{V_o}}$ the energies of the supercell containing an

Table 6: Formation energies (eV) of point defects in uranium dioxide calculated using DFT+U. The reference states used for the uranium and oxygen atoms are also indicated.

Author	References		I_o	I_u	V_o	V_u	FP_o	FP_u	S
	Uranium	Oxygen							
Iwasawa [14]	U_α (DFT+U)	$O_{2(g)}$	$-0,4$	$4,7$	$4,5$	$8,4$	$4,1$	$13,1$	$--$
Gupta [15]	–	$O_{2(g)}$	$-1,6$	$8,2$	$5,6$	$6,0$	$4,0$	$14,2$	$7,2$
Nerikar [19]	U_α	$O_{2(g)}$	$-1,3$	$6,1$	$5,3$	$9,0$	$4,0$	$15,1$	$7,6$
Yu [22]	U_α (DFT+U)	$O_{2(g)}$	$-2,4$	$2,5$	$5,1$	$4,5$	$2,6$	$7,0$	$3,6$
Tiwary [83]	–	–	$--$	$--$	$--$	$--$	$3,9$	$10,1$	$7,4$

interstitial and a vacancy, respectively. $\frac{1}{2}E_{O_2}$ is the energy by atom of the di-oxygen molecule in its triplet state, taken as the reference. The uranium point defect energies are calculated using the equivalent expressions for uranium. The point defect calculations are performed keeping the supercells neutral, but allowing for local charge redistribution inside the supercell in order to balance the presence of the defects.

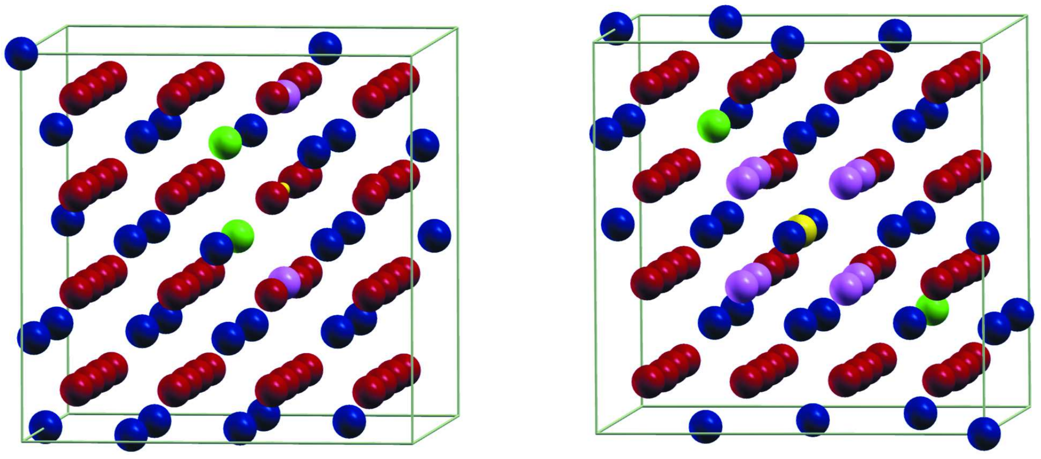
For extrinsic point defects (vacancies and interstitials), formation energies are not always calculated using the same reference energy. This impacts the formation energies and may be the cause of some discrepancies. For intrinsic point defects (Frenkel pairs and Schottky defects), however, reference energies do not come into play. As a result, any discrepancy in the formation energies of such defects, as reported in Table 6, is likely due to the occurrence of metastable states.

4.1 Formation energies of oxygen point defects in the fluorite and the JT structures of UO_2

For point defect calculations, we first imposed on each uranium atom the electronic occupancies obtained for the perfect fluorite structure, as is usually done when modelling perfect UO_2. In doing so, however, the system did not relax into the lowest energy state but was trapped in a state in which the U^{4+} oxidation state of all uranium ions was preserved. To reach the lowest energy state, it was required to impose the presence of U^{5+} or U^{3+} cations in the supercell, depending on the defect modelled. Note that several charge states were considered for uranium atoms and that U^{5+} (respectively U^{3+}) ions were found to yield the lowest total energies when an oxygen interstitial (respectively vacancy) was incorporated into the system.

In both the fluorite and Jahn-Teller distorted phases, we observed two U^{5+} or two U^{3+} cations in presence of an oxygen interstitial or of an oxygen vacancy, respectively. In the case of the oxygen interstitial, we performed several additional calculations to determine the most stable location of U^{5+} cations and found it to be the second coordination sphere of the extra interstitial oxygen atom. The optimal separation distance between the two U^{5+} cations is d = 9.64 Å in the presence of the oxygen interstitial. The magnetic moments of these two cations changed from $\pm 2\mu_B$ to $\pm 1\mu_B$, suggesting the loss of one electron. By contrast, in the presence of an oxygen vacancy, the U^{3+} cations are found to be in the first coordination sphere of the missing oxygen

Figure 2: Optimized final configuration of the defective supercell containing an oxygen vacancy (left) and interstitial (right). The point defects are in yellow. Also represented (in green) are the most favourable positions for U^{3+} (left) and U^{5+} (right) cations created by charge compensation reasons. Pink spheres represent oxygen atoms that were significantly displaced from their fluorite positions.



atom (see Fig. (2)).

Table 7: Formation energies (eV) of oxygen point defects (interstitial, vacancy and Frenkel pair) in uranium dioxide calculated using DFT+U, in the fluorite and the JT structure of UO_2.

	$E^{\mathrm{F}}_{\mathrm{Io}}$ (eV)	$E^{\mathrm{F}}_{\mathrm{Vo}}$ (eV)	$E^{\mathrm{F}}_{\mathrm{FPo}}$ (eV)
Fluorite (with $\mathrm{OM_F}$)	-0.05	5.30	5.25
Jahn-Teller (with $\mathrm{OM_{JT}}$)	0.47	6.01	6.48

Table 7 reports the formation energies of the oxygen interstitial, vacancy and Frenkel pair in both the fluorite and the JT distorted structures. For the oxygen interstitial, it can be seen that the formation energy is almost zero in the fluorite phase and 0.47 eV in the JT phase. Both these energies are small and the question of the sign of the oxygen interstitial formation energy is still a matter of debate. It seems consistent, however, to find a positive formation energy for the Jahn-Teller distorted UO_{2+x} phase given that this hyperstoichiometric phase is not stable at 0 K [84]. As for the fluorite structure, the near zero value seems surprisingly high given that UO_2 is known to oxidize easily. The DFT+U approximation, however, is not likely the cause for such a high formation energy. It is rather because of the GGA-PBE functional that fails to accurately describe the O atom and the O_2 molecule, resulting in a calculated O_2 dissociation energy that is off by 30%, 20% of which is due to the PBE functional. If we correct our value to exactly reproduce the experimental dissociation energy, the formation energy becomes -0.7 eV for the oxygen interstitial.

In both the fluorite and the Jahn-Teller distorted structures, oxygen interstitials induce a decrease of the distance between neighbouring uranium atoms, resulting in a local decrease in the cell parameters. This is in agreement with experimental observations that the cell parameters decrease with the addition of oxygen in the material [85].

For the oxygen vacancy, the formation energies are similar in the fluorite structure (5.30 eV) and the Jahn-Teller distorted structure (6.01 eV). As regards the atomic displacements of the defect nearest neighbours, we found that the oxygen vacancy only triggers slight modifications in the bonding distances (less than 0.05 Å). As a consequence, the cell parameters remain unchanged with and without the defect.

For both oxygen interstitials and vacancies, the above results seem to show that the crystal field in UO_2 has only a moderate influence on the formation energies.

The Frenkel pair formation energy determined from neutron scattering experiments is estimated at 4.5 ± 0.5 eV, [86] which also compares well with our value of 5.25 eV calculated in the fluorite phase. Note that these energy values constitute a marked improvement over what standard DFT calculations have provided us with in the past.

DFT+U thus enables us to better apprehend the formation of point defects in UO_2 and its association with OMC scheme enables not only to circumvent the issue of metastable states but also provide us a simple procedure to treat the change of valence of the cations induced by the presence of point defects.

5 Oxygen migration energies in UO_2

The migration paths of oxygen defects were calculated using the Climbing-Image Nudged Elastic Band method (CI-NEB) [70]. This method enables one to determine the minimum energy path of an atom between two equilibrium positions in the chosen migration direction by calculating the forces acting on the migrating atom. The relaxation of the positions of the remaining atoms of the system is also taken into account. In our calculation, the forces were computed using the DFT+U framework associated with the OMC scheme, as described before. The total energy of the system is calculated for various intermediary migration steps and the migration energy is defined as the energy barrier (or saddle point) along the migration path. In this study, we considered the migration of vacancy and interstitial atoms with the migration mechanisms as follows:

- Two vacancy mechanisms, in which an oxygen atom moves to a nearest neighbour oxygen vacancy, along the <100> or the <110> direction.
- An interstitial mechanism, in which an interstitial atom in an octahedral site moves to the next nearest octahedral interstitial site.
- An indirect interstitial mechanism (interstitialcy mechanism), in which an atom in an octahedral site replaces an oxygen atom on a lattice site, which in turn moves to an octahedral interstitial site (see Fig. 3).

In order to be able to compare our results to experimental activation energies of diffusion, the calculations have been performed in the fluorite phase of UO_2. An important problem to consider for the migration calculations is the existence at 0 K of the Jahn-Teller UO_2 phase, more stable and less symmetric than the fluorite phase. This has important consequences in the CI-NEB calculations. When an atom migrates through the lattice, it breaks all symmetries

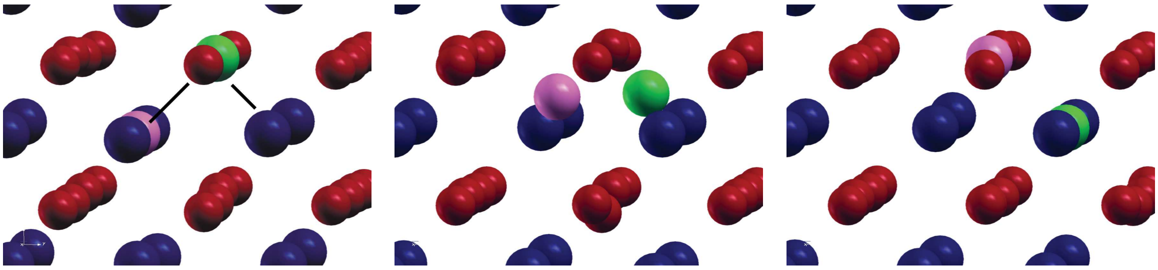


Figure 3: Minimum energy path of the interstitialcy (indirect) mechanism for oxygen self-diffusion in UO_2, calculated using DFT + U. The initial interstitial oxygen atom is in pink. The displaced oxygen lattice atom is in green.

along its trajectory. When symmetries are broken in a DFT+U calculation of UO_2 , the ground state is easier to reach but the fluorite structure tends to change back toward the Jahn-Teller distorted phase (see Sect. 3.2 and Ref. [35]). It results in a low total energy for the nonsymmetric saddle point compared to the symmetric initial and final (fluorite) configurations of the CI-NEB calculation. This constitutes a possible source of error in the determination of the migration barrier. To overcome this difficulty, it is necessary to calculate the total energy of the initial and final configurations in a very specific way, namely by performing a complete relaxation of the second and second-to-last intermediate images.

Figures 4 and 5 present the total energy curves obtained for oxygen self-diffusion via interstitial and vacancy mechanisms, respectively. It is important to emphasize that in these curves the total energy difference between an image and its symmetrical image is very small. Such a result was not *a priori* guaranteed given the large number of metastable states in the system. It emphasizes once again that the careful control of the electronic occupancies constitutes an efficient means of obtaining reliable DFT + U energies.

The <110> vacancy mechanism differs from the four other mechanisms in the sense that the associated migration path is not linear as initially envisaged. The oxygen atom first migrates toward nearby uranium atoms before moving into the oxygen vacancy. This deviation from the initial linear path is due to the Coulomb repulsion between surrounding oxygen atoms located in the same plane.

In Table 8 we report the formation and migration energies obtained from DFT+U calculations, as well as the activation energy for oxygen diffusion. The activation energy is defined according to the experimental approach detailled in Ref. [87] as the sum of the oxygen interstitial formation and migration energies. It should be stressed that the formation energy of the oxygen interstitial that we calculated in Sect. 4.1, i.e. -0.7 eV, must be corrected in order to calculate the activation energy. Indeed, this formation energy is defined as the energy required to add an oxygen atom in perfect UO_2, along with the creation of two U^{5+} cations for charge compensation. The point defect model [87] used to calculate the activation energy, however, requires the U^{5+} cations to be far from the oxygen interstitial, thus non interacting. It is therefore necessary to add to our -0.7 eV value the binding energy of two holes with the oxygen interstitial, which was evaluated to be 0.4 eV using charged supercell calculations. The oxygen interstitial formation energy with unbound U^{5+} is therefore -0.3 eV, as shown in Table 8.

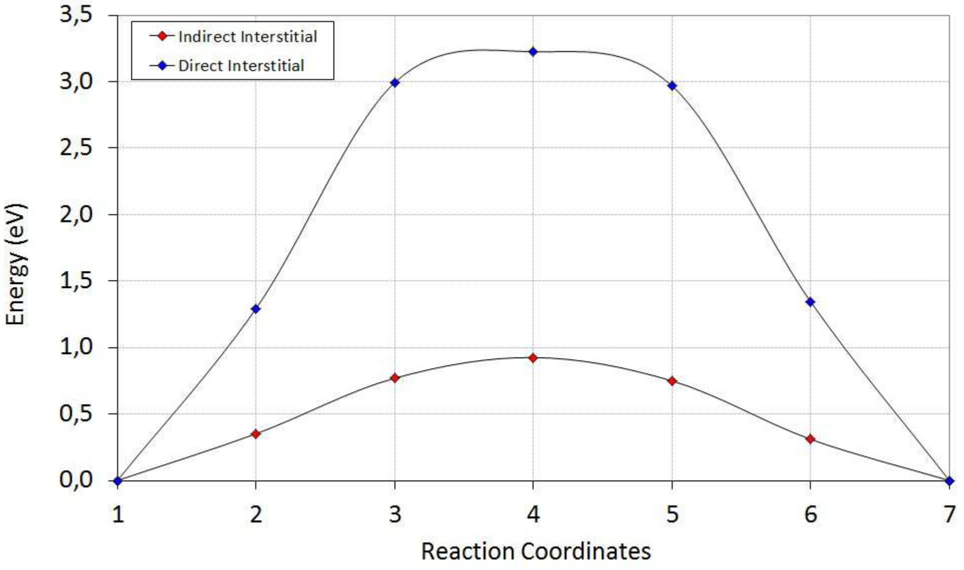


Figure 4: Total energy curve for oxygen self-diffusion in UO_2 via interstitial mechanisms (direct and indirect), calculated within the DFT + U approximation.

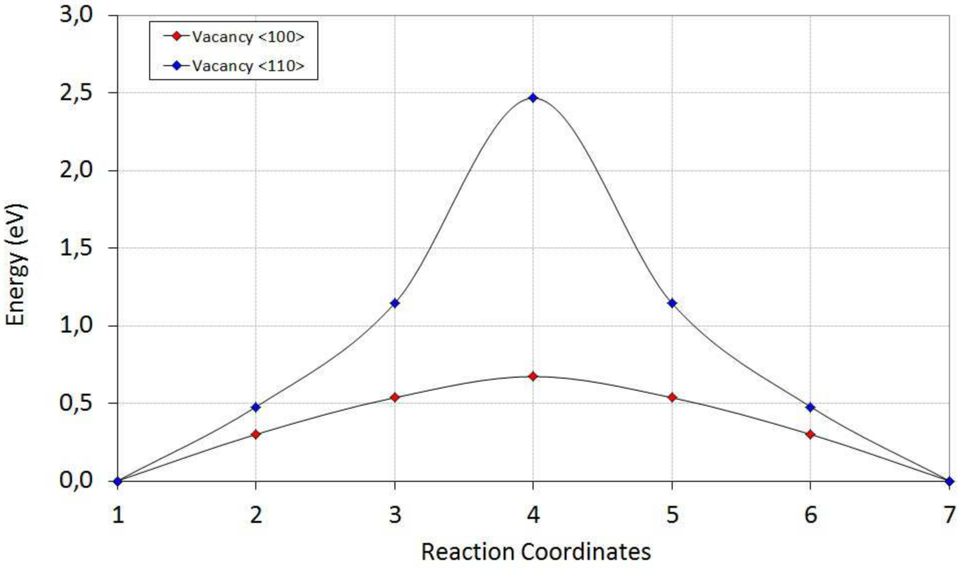


Figure 5: Total energy curve for oxygen self-diffusion in UO_2 via vacancy mechanisms (along the <100> and the <110> directions), calculated within the DFT + U approximation.

Table 8: Oxygen interstitial and vacancy formation and migration energies (in eV) calculated using the Liechtenstein DFT+U. For the oxygen interstitial mechanism, the activation energy can be compared with the experimental value.

	Formation energies (eV)	Migration energies (eV)	Activation energies (eV)
Direct	-0.30	3.22	2.92
Interstitialcy	-0.30	0.93	0.63
Vacancy <100>	5.30	0.67	/
Vacancy <110>	5.30	2.47	/

We see from Table 8 that the lowest migration energies are obtained for the interstitialcy and the vacancy <100> mechanisms, with migration energies of 0.93 and 0.67 eV, respectively. Standard DFT calculations already predicted these two mechanisms to be the most favorable [88] but quantitatively the migration energies are, however, significantly different. In particular, the migration energy for the vacancy <100> mechanism is twice lower with DFT+U (0.67 eV) than it is with standard DFT (1.2 eV). It can be also noted that the DFT+U values for the migration energies reported in Table 8 differ significantly from the ones calculated in Ref. [89] with the same DFT+U approach. In the latter study, the authors report a large negative (unphysical) value for the migration barrier associated with the oxygen interstitialcy mechanism. The main source of deviation from our results is probably that they did not control the $5f$ electronic occupancies in order to overcome the difficulties related to the presence of metastable states: the saddle-point calculation, which is less symmetric and therefore reaches the ground state more easily, has converged to a low energy state, while the initial symmetric configuration reached a higher energy metastable state.

From Table 8 we also see that the calculated DFT+U activation energies for the direct and interstitialcy mechanisms are 2.92 and 0.63 eV, respectively. The activation energy relative to the interstitialcy mechanism compares very favorably with the activation energy found experimentally [87] for oxygen diffusion (0.75 ± 0.08 eV) indicating that the interstitialcy mechanism is indeed the most probable migration mechanism, as found in other fluorite systems. The experimental work consisted in combinining tracer diffusion coefficient and electrical conductivity measurements carried out at different oxygen potentials and temperatures on UO_2 samples that contained different impurity levels. These experiments point to an oxygen migration being due to isolated oxygen interstitials over a wide range of oxygen potential. It also sheds some light on the discrepancies observed in oxygen diffusion coefficients reported previously. It is the combination of such experimental work and accurate first-principles DFT+U calculations that can provide a means of identifying the details of the migration mechanism in UO_2. Finally, our calculations can also be compared to vacancy migration values suggested from diffusion coefficient measurements in UO_{2-x} . Kim and Olander's work [90] provides us with a value of 0.5 ± 0.1 eV compared to the theoretical value of 0.67 eV.

6 Conclusion

We report here an encouraging correspondence between experimentally determined oxygen point defect formation and migration energies and those calculated from first-principles using the DFT+U approximation. We focus on the local energy minima issue that significantly affects DFT+U calculations (but also hybrid functionals calculations) for f-compounds. Calculation results were compared against a comprehensive range of experimental data involving interstitial and vacancy migration energies, and Frenkel pair formation energies. This study strongly points out that DFT+U calculations associated with electronic occupancy control, quantitatively describe oxygen transport phenomena in uranium dioxide. We also show that the fluorite structure is not the most stable phase at 0 K, as seen experimentally. The most stable phase is a Jahn-Teller distorted structure that exhibits a distortion of the oxygen cage with oxygen displacements along the <111> direction, in agreement with experiments. In the specific case of

UO_2, the existence of the Jahn-Teller distortion facilitates the search of the lowest energy states due to the symmetry breaking it induces.

These results open up the prospect of using first-principles DFT+U calculations as part of a predictive approach to determining transport properties in other actinide oxides. We are now further focusing on fission product diffusion, in particular xenon and krypton. In line with recent studies [23, 41, 91], different charge states for the defects will also be taken into account.

The future challenges for the modelling of radiation damage in UO_2 will consist in using the DFT+DMFT method (DFT+dynamical mean field theory) [32] and using recent non-local correlation functionals for van der Waals interaction. In particular, the DFT+DMFT method not only allows a better treatment of the $5f$ electron correlations, but also largely removes the problem of the local energy minima [92]. It would also enable the modelling of the paramagnetism of UO_2 above the Néel temperature. The non-local correlation functionals, such as VdW-DF (van der Waals density functional) [93, 94], will improve the description of rare gas fission products in nuclear materials.

7 Acknowledgements

This work was funded by the MATAV Nuclear Ceramics Basic Research Program. It was partly supported by the European Commission through the FP7 F-BRIDGE project (Contract No. 211690). Calculations were performed using French HPC resources available at TGCC and CINES under the allocation made by GENCI (Grand Equipement National de Calcul Intensif). David A. Andersson, Christopher R. Stanek, Blas P. Uberuaga (Los Alamos National Laboratory, USA), F. Bottin, M. Torrent, F. Jollet and Jean-Paul Crocombette (CEA) are gratefully acknowledged for discussions and collaborations on related studies.

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