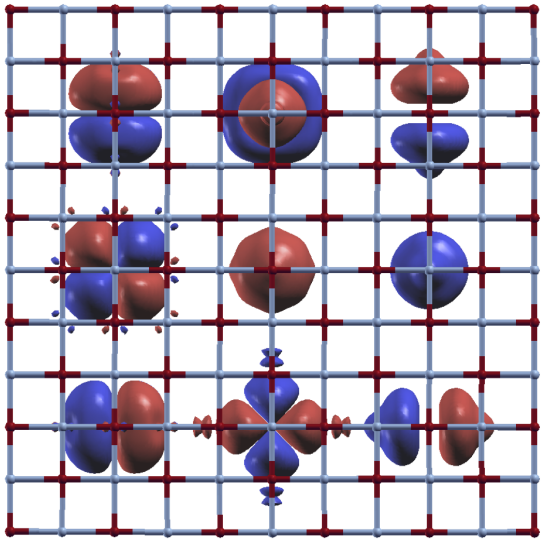
Efficient localised orbitals for large systems, strong correlations and excitations

Cavendish Laboratory, University of Cambridge

July 2nd to July 5th, 2012



A Workshop of the CECAM JC Maxwell node

Supported by CECAM, Psi-k and the ESF

Centre Européen de Calcul Atomique et Moléculaire

Organisers

- David D. O'Regan
  Laboratory of Theory and Simulation of Materials (THEOS),
  École Polytechnique Fédérale de Lausanne,
  Station 12, 1015 Lausanne, Switzerland.
  david.oregan@epfl.ch

- Simon M.-M. Dubois
  Cavendish Laboratory, University of Cambridge,
  J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom.
  smmfnd2@cam.ac.uk

- Peter D. Haynes
  The Thomas Young Centre, Imperial College London,
  London SW7 2AZ, United Kingdom.
  p.haynes@imperial.ac.uk

- Paolo Umari
  Dipartimento di Fisica "Galileo Galilei",
  Universit degli Studi di Padova, via Marzolo 8, Padova, Italy.
  pumari@sissa.it

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 aims to bring 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.

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, 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 mostly 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.

Scientific content of the Workshop

The workshop was generously supported by the CECAM JC Maxwell node, CECAM Headquarters, the European Science Foundation and the Psi-k network. It attracted 47 world-class, both EU and non-EU. Over six half-day sessions, the workshop hosted 26 excellent talks and a small poster session for junior delegates, to which honorary prizes were awarded. The workshop timetable provided generous time for discussion, intended to encourage the participation of younger scientists. Invited speakers are asked to give 30 minute talks, followed by 15 minutes for discussion. Contributed talks last 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 the great cross-disciplinary communication observed during these sessions will foster further interaction between groups treating 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 the 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 that 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 already 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.

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 products 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 locating orbitals which 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 permits to implement self-consistency schemes which 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 allow for all-electrons GW calculations.

Localised orbitals may furthermore form a 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 quasi-particles [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 will place 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].

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 any 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 Moller-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 variationally 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 overtaking conventional cubic-scaling methods. 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 Nicholas Hine (Imperial College London), Chris-Kriton Skylaris (University of Southampton), 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 novel projector self-consistent constrained DFT technique within linear-scaling DFT, with a view to studying electro-chemical processes.

Organiser's assessment and impact of the event

Report on selected discussions

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. 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.

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. An outcome of this discussion was the acknowledgement that different criteria for optimising population analyses may be favourable for different methods. 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 sophisticated methods for treating the poor description of electronic correlation effects often yielded by approximate density functionals. 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 were very helpful to producing 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 junior delegate's posters were placed around the foyer where delegates mingled at

lunchtime. All of these aspects ensured that the delegates did not disperse between lectures. It also generated a welcoming and non-intimidating atmosphere for the younger delegates to approach the speakers with questions, and also to receive plenty of feed-back on their posters.

One third of the time allotted to each speaker, both invited and non-invited, 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.

Assessment summary

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 from 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 area-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.

List of delegates

1. Dubois, Simon (smmfnd2@cam.ac.uk)
   University of Cambridge, United Kingdom.

2. Haynes, Peter (p.haynes@imperial.ac.uk)
   Imperial College London, United Kingdom.

3. O'Regan, David (david.oregan@epfl.ch)
   EPFL, Lausanne, Switzerland.

4. Umari, Paolo (pumari@sissa.it)
   Universit degli Studi di Padova, Italy.

5. Artacho, Emilio (ea245@cam.ac.uk)
   CIC nanoGUNE Consolider, Spain, and University of Cambridge, U.K.

6. Bierman, Silke (silke.bierman@cpht.polytechnique.fr)
   École Polytechnique, Paris, France.

7. Blum, Volker
   Fritz Haber Institute, Berlin, Germany.

8. Bowler, David (david.bowler@ucl.ac.uk)
   University College London, United Kingdom.

9. Ederer, Claude (claude.ederer@mat.ethz.ch)
   ETH Zurich, Switzerland.

10. Fattebert, Jean-Luc (fattebert1@llnl.gov)
    Lawrence Livermore National Laboratory, California, U.S.A.

11. Giustino, Feliciano (feliciano.giustino@materials.ox.ac.uk)
    University of Oxford, United Kingdom

12. Head-Gordon, Martin (mhg@cchem.berkeley.edu)
    University of California, Berkeley, U.S.A.

13. Hine, Nicholas (nicholas.hine@imperial.ac.uk)
    Imperial College London, United Kingdom.

14. Ku, Wei (weiku@bnl.gov)
    Brookhaven National Laboratory, New York, U.S.A.

15. Marzari, Nicola (nicola.marzari@epfl.ch)
EPFL, Lausanne, Switzerland.

16. Mostofi, Arash (a.mostofi@imperial.ac.uk)
Imperial College London, United Kingdom.

17. Payne, Mike (mcp1@cam.ac.uk)
University of Cambridge, United Kingdom.

18. Ren, Xinguo (xinguo@fhi-berlin.mpg.de)
Fritz Haber Institute, Berlin, Germany.

19. Rungger, Ivan (runggeri@tcd.ie)
Trinity College Dublin, Ireland.

20. Skylaris, Chris-Kriton (c.skylaris@soton.ac.uk)
University of Southampton, United Kingdom

21. Souza, Ivo (ivo_souza@ehu.es)
DIPC, University of the Basque Country.

22. Varga, Kalman (kalman.varga@vanderbilt.edu)
Vanderbilt University, Tennessee, U.S.A.

23. Weber, Cédric (cw489@cam.ac.uk)
University of Cambridge, United Kingdom.

24. Yang, Weitao (weitao.yang@duke.edu)
Duke University, North Carolina, U.S.A.

25. Andrinopoulos, Lampros (l.andrinopoulos09@imperial.ac.uk)
Imperial College London, United Kingdom.

26. Ansari, Lida (lida.ansari@tyndall.ie)
Tyndall National Institute, Ireland.

27. Boulanger, Paul (paul.boulanger@cea.fr)
CEA-Grenoble, France.

28. Cheng, Jun (jc590@cam.ac.uk)
University of Cambridge, United Kingdom.

29. Cherry, Peter (pjc1g11@soton.ac.uk)
University of Southampton, United Kingdom.

30. Cole, Danny (djc56@cam.ac.uk)
University of Cambridge, United Kingdom.

31. Corsetti, Fabiano (fabiano.corsetti08@imperial.ac.uk)
Imperial College London, United Kingdom.

32. Corsini, Niccolo (niccolocorsini@hotmail.com)
Imperial College London, United Kingdom.

33. Dziedzic, Jacek (j.dziedzic@soton.ac.uk)
University of Southampton, United Kingdom.

34. Hofmann, Dirk (dirk.hofmann@uni-bayreuth.de)
University of Bayreuth, Germany.

35. Huebener, Hannes (hannes.huebener@materials.ox.ac.uk)
Imperial College London, United Kingdom.

36. Lever, Greg (gl319@cam.ac.uk)
University of Cambridge, United Kingdom.

37. Mellan, Tom (t.mellan@ucl.ac.uk)
University College London, United Kingdom.

38. Mohr, Stephan (stephan.mohr@unibas.ch)
Basel Universität, Switzerland.

39. Opalka, Daniel (do293@cam.ac.uk)
University of Cambridge, United Kingdom.

40. Ratcliff, Laura (laura.ratcliff@cea.fr)
CEA-Grenoble, France.

41. Ruiz-Serrano, Alvaro (a.ruiz-serrano@soton.ac.uk)
University of Southampton, United Kingdom.

42. Seth, Priyanka (ps479@cam.ac.uk)
University of Cambridge, United Kingdom.

43. Spenser, James (j.spencer@imperial.ac.uk)
Imperial College London, United Kingdom.

44. Teobaldi, Gilberto (g.teobaldi@liverpool.ac.uk)
University of Liverpool, United Kingdom.

45. Tiana, Davide (d.tiana@bath.ac.uk)
University of Bath, United Kingdom.

46. Wilkinson, Karl (k.wilkinson@soton.ac.uk)
University of Southampton, United Kingdom.

47. Zuehlsdorff, Tim
Imperial College London, United Kingdom.

Meeting programme

The workshop timetable provides generous time for discussion, intended to encourage the participation of younger scientists. Invited speakers are asked to give 30 minute talks, followed by 15 minutes for discussion. Contributed talks last 20 minutes, followed by 10 for discussion. We have invited three leading members of the electronic structure community to give "Perspective" talks, to give an overview of key aspects of methods using local orbitals. **See http://www.cecam.org/workshop-0-739.html for abstracts.**

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 Bierman
  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

Posters

- Niccolo Corsini, Peter D. Haynes, Carla Molteni, and Nicholas D. M. Hine
  Pressure-induced structural transformations in nanomaterials
- Hannes Huebener, Miguel A. Perez-Osorio, Pablo Ordejon, and Feliciano Giustino
  Performance of local orbital basis sets in the self-consistent Sternheimer method for dielectric matrices of extended systems
- Thomas Mellan, Anna L.Gould, and Ricardo Grau-Crespo
  Thermodynamics of surfaces and dopants in rutile-like VO_2
- Laura Ratcliff, Paul Boulanger, Stephan Mohr, Luigi Genovese, Stefan Goedecker
  O(N) DFT calculations using Daubechies wavelets in the BigDFT code

References

[1] V. I. Anisimov, J. Zaanen and O. K. Andersen, Phys. Rev. B, **44**, 943 (1991).

[2] S. Goedecker, Rev. Mod. Phys. 71, 1085 (1999).

[3] C. K. Skylaris, A. A. Mostofi, P. D. Haynes, O. Dieguez, and M. C. Payne, Phys. Rev. B 66, 035119 (2002).

[4] N. D. M. Hine, P. D. Haynes, A. A. Mostofi, K. Skylaris, and M. C. Payne, Comput. Phys. Commun. 180, 1041 (2009).

[5] D. R. Bowler, T. Miyazaki, and M. J. Gillan, Journal of Physics: Condensed Matter 14 (11), 2781 (2002).

[6] T. Ozaki, Phys. Rev. B 67, 155108 (2003).

[7] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejón and D. Sanchez-Portal, J. Phys.: Condens. Matter 14, 2745 (2002).

[8] J. Kim, F. Mauri, and G. Galli, Phys. Rev. B 52 (3), 1640 (1995).

[9] J.-L. Fattebert and F. Gygi, Phys. Rev. B 73, 115124 (2006).

[10] A. M. N. Niklasson and M. Challacombe, Phys. Rev. Lett. 92, 193001 (2004).

[11] G. Cui, W. Fang and W. Yang, Phys. Chem. Chem. Phys., 2010, 12, 416421.

[12] X. Blase and P. Ordejón, Phys. Rev. B 69, 085111 (2004).

[13] F. Lechermann, A. Georges, A. Poteryaev, S. Biermann, M. Posternak, A. Yamasaki, and O. K. Andersen, Phys. Rev. B 74 (12), 125120 (2006).

[14] B. Amadon, F. Lechermann, A. Georges, F. Jollet, T. O. Wehling and A. I. Lichtenstein, Phys. Rev. B 77, 205112 (2008).

[15] M. J. Han, T. Ozaki, and J. Yu, Phys. Rev. B 73 (4), 045110 (2006).

[16] M. Stengel and N. A. Spaldin, Phys. Rev. B 77, 155106 (2008).

[17] D. D. ORegan, M. C. Payne, and A. A. Mostofi, Phys. Rev. B 83, 245124 (2011).

[18] C.-C. Lee, H. C. Hsueh, and W. Ku, Phys. Rev. B 82, 081106(R) (2010).

[19] T. Miyake and F. Aryasetiawan, Phys. Rev. B 77 (8), 085122 (2008).

[20] O. K. Andersen and T. Saha-Dasgupta, Phys. Rev. B 62, R16219R16222 (2000).

[21] O. Eriksson, J. M. Wills, M. Colarieti-Tosti, S. Lebégue, and A. Grechnev, Int. J. Quantum Chem. 105 (2) (2005).

[22] K. S. Thygesen and A. Rubio, J. Chem. Phys. 126, 091101 (2007); K. S. Thygesen, and A. Rubio Phys. Rev. B 77, 115333 (2008); C. Rostgaard, K. W. Jacobsen, and K. S. Thygesen, Phys. Rev. B 81, 085103 (2010).

[23] X. Blase, C. Attaccalite, and V. Olevano, Phys. Rev. B 83, 115103 (2011).

[24] P Umari, Geoffrey Stenuit and Stefano Baroni, Phys. Rev. B 79, 201104 (2009); P. Umari, X. Qian, N. Marzari, G. Stenuit, L. Giacomazzi, S. Baroni Phys. Stat. Sol. b 248, 527 (2011).

[25] X. Wang, D. Vanderbilt, J. R. Yates and I. Souza, Phys. Rev. B 76, 195109 (2007).

[26] S. Coh, D. Vanderbilt, A. Malashevich, I. Souza Phys. Rev. B 83, 085108 (2011).

[27] F. Giustino, M. L. Cohen and S. G. Louie, Phys. Rev. B 76, 165108 (2007).

[28] P. L. Silvestrelli, Phys. Rev. Lett. 100, 053002 (2008).

[29] R. Kováčik and C. Ederer, Phys. Rev. B 81, 245108 (2010).

[30] E. Sasioglu, A. Schindlmayr, C. Friedrich, F. Freimuth, S. Bleugel Phys. Rev. B 81, 054434 (2010).

[31] D. R. Hamann and D. Vanderbilt, Phys. Rev. B 79, 045109 (2009).

[32] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).

[33] I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B 65, 035109 (2001).

[34] X. F. Qian, J. Li, L. Qi, C. Z. Wang, T. L. Chan, Y. X. Yao, K. M. Ho, and S. Yip, Phys. Rev. B 78, 245112 (2008).

[35] E. Artacho and L. Miláns del Bosch, Phys. Rev. A 43 (11), 5770 (1991).

[36] C. A. White, P. Maslen, M. S. Lee, and M. Head-Gordon, Chemical Physics Letters 276 (1-2), 133 (1997).

[37] K. S. Thygesen, Phys. Rev. B 73, 035309 (2006).

[38] D. D. ORegan, Mike C. Payne, and Arash A. Mostofi, Phys. Rev. B 83, 245124 (2011).

[39] A. Edelman, T. A. Arias, and S. T. Smith, SIAM J. Matrix Anal. Appl. 20 (2), 303 (1998).