Workshop on Precision Quantification in DFT

23-24 May 2019 – Louvain-la-Neuve, Belgium

Organizing committee

S. Cottenier, K. Lejaeghere, G.-M. Rignanese, M. Verstraete

Scientific committee

S. Cottenier, X. Gonze, F. Jollet, K. Lejaeghere, G.-M. Rignanese, M. Torrent, M. Verstraete

Logistic support

V. Gandibleux

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Program *(last minute changes are possible, see website for the final version)*

Wednesday 22nd May 2019

19.00	Social dinner

Thursday 23th May 2019

Status of the Delta project *(15 minutes each - no questions)* - Discussion leader: Xavier Gonze

9.00	The Delta paper :how has it been used, and what do we learn from that?	Stefaan Cottenier
9.15	The Delta test revisited	Kurt Lejaeghere
9.30	Assessing DFT reproducibility with a systematic benchmark: chemical variety	Martin Callsen
9.45	Assessing DFT Reproducibility with a Systematic Benchmark: Experimental Variety	Thomas Ruh
10.00	Discussion	

10.30	Coffee

Pseudopotential development *(15 minutes each - no questions)* - Discussion leader: Stefan Goedecker

11.00	Extended norm-conserving pseudopotentials	Don Hamann
11.15	Accessment of accuracy and efficiency of paw datasets in materials simulations	Natalie Holzwarth
11.30	The PseudoDojo project	Matteo Gantomassi
11.45	The JTH PAW data table	Francois Jollet
12.00	Pseudopotentials for high-throughput DFT calculations	Kevin Garrity
12.15	Discussion	

12.45	Lunch

Workflow and data management *(15 minutes each - no questions)* - Discussion leader: Gian-Marco Rignanese

14.00	Making scientific data accessible: the NOMAD Laboratory	Claudia Draxl
14.15	An operating system and a dissemination platform for computational science	Nicola Marzari
14.30	Workflow and data management with ASE	Jens J. Mortensen
14.45	Libxc - a library of exchange and correlation functionals	Miguel Marquez
15.00	Automated uncertainty analysis and quantification for highprecision DFT calculations	Jörg Neugebauer
15.15	Discussion	

15.45	Coffee

Beyond total energies *(15 minutes each - no questions) -* Discussion leader: Matthieu Verstraete

16.15	Benchmarking Electronic Structure Beyond Structural Properties of Solids	Volker Blum
16.30	Precision and efficiency in solid-state pseudopotential calculations	Nicola Marzari
16.45	Reproducibility in response calculations of solids	Gian-Marco Rignanese
17.00	Discussion	

Friday 24th May 2019

Accuracy assessment *(15 minutes each - no questions)* - Discussion leader: Martin Friak

9.00	Accuracy of electronic structure calculations	Peter Blaha
9.15	How to estimate the prediction uncertainty of computational chemistry methods ?	Pascal Pernot
9.30	Benchmarking DFT and beyond-DFT methods for thermodynamics and electronic properties	Geoffroy Hautier
9.45	Error quantication for density-functional theory calculations of surface energy and work function	Sam De Waele
10.00	Discussion	
10.30	Coffee	

Pushing numerical convergence *(15 minutes each - no questions)* - Discussion leader: Rudolf Zeller

11.00	Towards ultimate precision in density-functional theory	Andris Gulans
11.15	Precision Quantification of Phonons and Vibrational Free Energies	Keith Refson
11.30	Highly accurate atomization reference energies for pseudpotential benchmarking	Stefan Goedecker
11.45	Numerical analysis for density functional theory	Antoine Levitt
12.05	Discussion	
12.30	Lunch	

Beyond DFT *(15 minutes each - no questions) -* Discussion leader: Jiri Klimes

14.00	GW100 benchmarking GW for molecules	Michiel Van Setten
14.15	Main-group test set for materials science and engineering with user-friendly graphical tools for error analysis: systematic benchmark ofthe numerical and intrinsic errors in state-of-the-art electronic-structure approximations	Igor Ying Zhang
~~14.30~~	Minimax Isometry Method	~~Merzuk Kaltak~~
14.30	Discussion	

Participants whishing to do so, can put a poster on display throughout the entire duration of the workshop.

the Delta paper :
how has it been used, and what do we learn from that?

S.Cottenier [1,2]

[1] Department of Electrical Energy, Metals, Mechanical Constructions and Systems, Ghent University, Belgium
[2] Center for Molecular Modeling (CMM), Ghent University, Belgium

Three years ago, the DFT code developer's community published a self-assessment of the precision of 40 different methods and codes [1]. In this presentation, we examine how this paper has been used: who cites it, and for which reasons? Does this fulfill the initial purpose? And what can we learn from this for future precision studies?

References

[1] K. Lejaeghere et al., Science 351 (2016) aad3000

The Delta test revisited

K. Lejaeghere[1]

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The Delta test was designed to perform a systematic assessment of precision across density-functional theory codes. It evaluates their agreement based predicted equations of state for the elemental crystals, using the so-called Δ criterion [1]. Thanks to the efforts of a broad collaboration of code developers and expert users, a large data set was established, confirming the excellent precision of recent electronic-structure packages and potentials [2].

In this presentation, I will revisit the results of the original Delta tests, extended with data provided after its publication and available on the Delta project website [3]. It will be shown that different error measures can be used to analyse the results. A direct comparison of equation of state parameters is also possible, but should be done with care, as the sensitivity of the equation of state parameters can be unexpectedly large without actually affecting Δ much [4].

References

[1] K. Lejaeghere, V. Van Speybroeck, G. Van Oost and S. Cottenier, Crit. Rev. Solid State **39**, 1-24 (2014).

[2] K. Lejaeghere *et al.*, Science **351**, aad3000 (2016).

[3] https://molmod.ugent.be/deltacodesdft

[4] K. Lejaeghere, "The uncertainty pyramid for electronic-structure methods" in Uncertainty Quantification in Multiscale Materials Modeling (Eds. Y. Wang and D. McDowell), Elsevier (2019), accepted.

ASSESSING DFT REPRODUCIBILITY WITH A SYSTEMATIC BENCHMARK: CHEMICAL VARIETY

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Recently the precision of 40 numerical methods has been assessed for a test set of 71 elemental crystals [1]. Despite already being a large project by itself, this was only the first step on a long way towards finally answering the ubiquitous question of reproducibility and precision of DFT. One step on the roadmap of the "Delta 2.0" project is extending the benchmark set by diatomic materials in order to assess the quality of predictions for a wide range of chemically more diverse environments.

In order to scan chemical diversity in a systematic way, we examined for every element X (where X runs from Hydrogen to Curium) six different cubic oxides with stoichiometries that are chosen in such a way that the formal oxidation state of element X varies from +1 to +6. This presentation will showcase some first insights gained from the extended test set. In particular the focus will be on the transferability of conclusions from the initial 71-element delta test set and the sensitivity of the extended test set.

References

[1] K. Lejaeghere, *et al.,* Science **351,** 6280 (2016).

Assessing DFT Reproducibility with a Systematic Benchmark: Experimental Variety

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Recently, the precision of 40 different Density Functional Theory (DFT) approaches for periodic solids was assessed in an extensive study (the "Delta Project") using a test set of 71 elemental crystals [1]. To further investigate the question of reproducibility and precision of DFT codes additional benchmark crystals are necessary to capture the vast diversity of real solids and materials.

One step toward a more diverse test set is the addition of "real" experimentally known structures for every element (up to Americium). The cases have been selected in a way that they represent different prototypes of chemical bonding (covalent, ionic, metallic). In order to find such cases the Inorganic Crystal Structure Database (ICSD) [2] was searched for possible candidates. The electronic difference densities of roughly 1450 cases were calculated using WIEN2k [3] which were then used to classify the main bonding type and choose additional test cases.

This presentation will describe the process of making the final selection, summarize the test cases that have been chosen, and address some issues regarding "gaps", where no experimentally known examples could be found.

References

[1] K. Lejaeghere, et al., Science 351, 6280 (2016).

[2] https://icsd.fiz-karlsruhe.de

[3] http://www.wien2k.at

EXTENDED NORM-CONSERRVING PSEUDOPOTENTIIALS

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The principles of generalized norm conservation [1] and systematic convergence optimization [2] have been combined to generate pseudopotentials of accuracy and efficiency competitive with augmented potentials.[3] These ONCVPSPs, consisting of a local potential and a diagonal non-local operator, can be based on valence plus shallow-core state or valence plus scattering-state all-electron wave functions for each angular momentum ℓ. This approach has been extended to allow deeper core levels to become active to enable simulations of materials at extreme temperatures and pressures. The original algorithms developed to construct ONCVPSPs have been modified and are now robust for as many as 5 non-local projectors per ℓ. Significantly higher plane-wave cutoffs are of course necessary. The new approach can also be used to extend accuracy to high-lying conduction bands by adding more scattering states to standard potentials. Dirac all-electron wave functions are used to construct ONCVPSPs simulating fully-relativistic calculations.

These extended norm-conserving potentials perform comparably to the standard variety in ambient-conditions benchmark tests. For extreme-condition testing, a confined-single-atom model was developed which compared well for pressure vs. volume and temperature with close-packed solid calculations up to Ts of ~5 Ha. This was then used to compare all-electron and pseudo confined atoms up to ~100 Ha and densities ~10 times ambient. Finally, close-contact forces needed for high-T AIMD simulations were tested, and found to remain accurate with a great deal of non-local projector overlap. Such AIMD simulations and comparisons of computed equations of state to experiment have yet to be performed.

References

[1] . D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[2] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev. B **41**, 1227 (1990).

[3] D. R. Hamann Phys. Rev. B **88**, 085117 (2013); **95**, 239906 (2017).

ACCESSMENT OF ACCURACY AND EFFICIENCY OF PAW DATASETS IN MATERIALS SIMULATIONS

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The community of computational condensed matter researchers have benefited enormously from the work of the developers who maintain high quality public domain software for density functional electronic structure calculations. For example, we use the ABINIT[1] and the QUANTUM ESPRESSO[2] packages interchangeably for structural and energy simulations with the help of atomic datasets generated by our ATOMPAW[3] code. For purposes of asscessment, it is possible to use the same datasets with both ABINIT and QUANTUM ESPRESSO. We find that in the limit of highly converged calculations, it is possible to achieve very close numerical results. However, the approach toward convergence appears to be quite different in the two codes. This is particularly true for density functional perturbation theory calculations used for example in calculating lattice vibrations.

References

[1] X. Gonze, F. Jollet, F. A. Araujo, *et at.* Computer Physics Communications **205**, 106 (2016).

[2] P. Giannozzi, O. Andreussi, T. Brumme, *et at.* Journal of Physics: Condensed Matter **29**, 465901 (2017).

[3] N. A. W. Holzwarth, A. R. Tackett, G. E. Matthews, Computer Physics Communications **135 329 (2001).**

The PseudoDojo project

M. Giantomassi[1], M. J. van Setten[1], E. Bousquet[2], M. J. Verstraete[2], D. R. Hamann[3], X. Gonze[1], and G.-M. Rignanese[1]

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The PseudoDojo [1, 2] is an open-source python project for developing and systematically testing pseudopotentials. At present it contains four different batteries of tests executed with ABINIT and AbiPy (presence of ghost-states, delta-factor [3], GBRV benchmark [4], phonons with DFPT). The tests are performed as a function of the energy cutoff and the results are used to provide hints for the energy cutoff for actual production calculations. The pseudopotential files are available on the PseudoDojo web-interface in the ABINIT psp8 format, in the UPF2 format used by QE and in the PSML format [5] shared by SIESTA and ABINIT. The input files, the results produced by the pseudopotential generator, and the results of the tests are presented via jupyter notebooks as static HTML pages. Finally, each pseudopotential is linked to a JSON file with a full record of the different tests performed to validate the pseudopotential.

References

[1] M. J. van Setten *et al.*, Comput. Phys. Commun. **226**, 39-54 (2018)

[2] D. R. Hamann, Phys. Rev. B **88**, 085117 (2013)

[3] K. Lejaeghere *et al.*, Science **351**, 1415 (2016)

[4] K. F. Garrity *et al.*, Comp. Mater. Sci. **81**, 446 (2014)

[5] A. Garcia *et al.*, Comput. Phys. Commun. **227**, 51 (2018)

The JTH PAW data table

F. Jollet[1] and M. Torrent[1] and N. Holzwarth[2]

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[2] Department of Physics, Wake Forest University, Winston-Salem, NC 27109 USA

In this talk, we shall present the way the JTH PAW data table has evolved since its first publication [1], We shall detail the different improvements that have been carried out, especially the way it is tested. In peculiar, we shall show that it is necessary to have a large All Electron data base to validate the PAW data, more extended than the Δ factor one. We shall discuss the XML common format and some numerical problems we had to solve.

References

[1] F. Jollet, M. Torrent, and N. Holzwarth. Generation of projector augmented-wave atomic data: a 71 element validated table in the XML format. *Comp. Phys. Comm.*, 185:1246–1254, 2014.

Pseudopotentials for high-throughput DFT calculations

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High-throughput density functional theory (DFT) calculations require a comprehensive set of pseudopotentials or PAWs that are 1) accurate in any realistic material, 2) computationally efficient, and 3) systematically tested. Here, we present the GBRV pseudopotential library[1], optimized for such high-throughput calculations. We present our initial design criteria, testing procedure, and validation. Since the initial publication of our library, there has been been significant progress in the field of pseudopotential design and testing. In light of these works, we discuss changes in the GBRV library over time, updated testing sets and results, and possible future directions for pseudopotential development.

References

[1] K.F. Garrity *et. al.*, Comput. Mater. Sci. **81** 446 (2014)

Making scientific data accessible: the NOMAD Laboratory

C. Draxl[1]

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[2] Fritz Haber Institute of the Max Planck Society, Berlin

Knowledge and understanding of materials is based on their characterization by a variety of measured and/or computed properties. This includes structural features, mechanical and thermal behavior, electronic and magnetic properties, the response to light, and more. For the computational side, the NOMAD Laboratory (Novel Materials Discovery) Centre of Excellence (https://nomad-coe.eu) has created a data infrastructure to collect, share, and keep data available for at least ten years. The variety of data uploaded to the NOMAD Repository (https://nomad-repository.eu) allows for in-depth explorations and discoveries.

The NOMAD Encyclopedia (https://encyclopedia.nomad-coe.eu) is a graphical user interface that allows for making millions of calculations accessible and tangible. The NOMAD Analytics Toolkit (https://analytics-toolkit.nomad-coe.eu) provides a collection of examples and tools to demonstrate how materials data can be turned into knowledge. This platform hosts "interactive codes" in terms of data-science notebooks that present the application of data-analytics models. They concern topics like crystal-structure prediction, property prediction, error estimates, classification of materials, and more.

Prerequisite for all this is a FAIR [1,2,3] data infrastructure, where normalized data in unified, formats and reliable metadata [4] are key.
I will demonstrate NOMAD's capabilities, and discuss our current efforts to extend the data archive by experimental data. An issue, in this context, is understanding errors in both experiment and theory; related to this, assigning error bars and trust levels to high-throughput screening results, as obtained by density-functional theory. For the latter, I will discuss our recent efforts to learn fully converged results of complex materials from errors of calculations of simple materials [5].
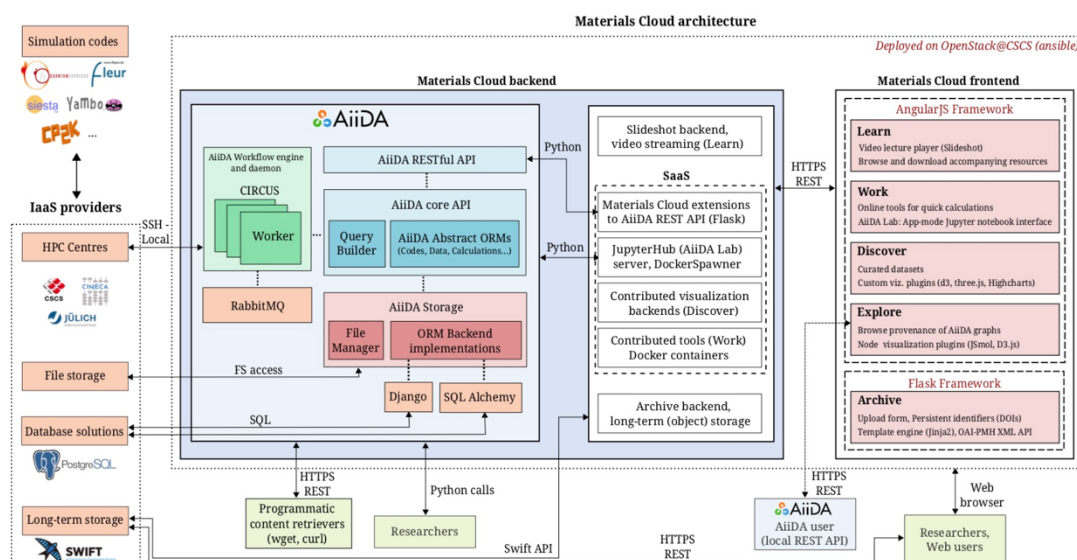
References

[1] M. D. Wilkinson et al., Sci. Data 3, 160018 (2016).

[2] C. Draxl and M. Scheffler, MRS Bulletin 43, 676 (2018).

[3] C. Draxl and M. Scheffler, J. Phys. Mater. (2019); DOI: https://iopscience.iop.org/article/10.1088/2515-7639/ab13bb

[4] L. M. Ghiringhelli, C. Carbogno, S. Levchenko, F. Mohamed, G. Hus, M. Lüder, M. Oliveira and M. Scheffler, npj Comput. Mater. 3, 46 (2017).

[5] C. Carbogno, et al., in preparation.

An operating system and a dissemination platform for computational science

G. Pizzi, S. Huber, M. Uhrin, S. Zoupanos, L. Talirz, S. Kumbhar, E. Passaro, A. Yakutovich, and N. Marzari[1]

[1] Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), EPFL, Lausanne, Switzerland

I will briefly describe the vision and implementation behind AiiDA [1], an informatics platform for computational science built around the four pillars of Automation, Data, Environment, and Sharing, and aiming to enable reliable, persistent, and searchable high-throughput calculations of complex properties, and of the Materials Cloud [2], a dissemination platform to archive and explore raw and curated data sets, while also provinding user services and educational tools [3].

References

[1] G. Pizzi, A. Cepellotti, R. Sabatini, N. Marzari, and B. Kozinsky, AiiDA: automated interactive infrastructure and database for computational science, Comp. Mat. Sci. 111, 218-230 (2016). http://aiida.net

[2] http://materialscloud.org

[3] G. Pizzi, Open-Science Platform for Computational Materials Science: AiiDA and the Materials Cloud. https://link.springer.com/referenceworkentry/10.1007/978-3-319-42913-7_64-1

Workflow and data management with ASE

Jens Jørgen Mortensen[1]

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The Atomic Simulation Environment (ASE) [1] is a Python library containing tools for working with atoms. We will show how to use ASE for storing the results of "precision quantification" calculations in databases and how to work with the data. We will also go through an example showing how to use ASE for doing the actual calculations.

References

[1] A. H. Larsen, J. J. Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dulak, J. Friis, M. N. Groves, B. Hammer, C. Hargus, E. D. Hermes, P. C. Jennings, P. B. Jensen, K. Kaasbjerg, J. Kermode, J. R. Kitchin, E. L. Kolsbjerg, J. Kubal, S. Lysgaard, J. B. Maronsson, T. Maxson, T. Olsen, L. Pastewka, A. Peterson, C. Rostgaard, J. Schitz, O. Schtt, M. Strange, K. Thygesen, T. Vegge, L. Vilhelmsen, M. Walter, Z. Zeng, and K. W. Jacobsen, J. Phys.: Condens. Matter **29** 273002 (2017)

Libxc – a library of exchange and correlation functionals

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LIBXC [1, 2] is a library of exchange-correlation functionals for density-functional theory. We are concerned with semi-local functionals (or the semi-local part of hybrid functionals), namely local-density approximations, generalized-gradient approximations, and meta-generalized-gradient approximations.

Currently we include more than 400 functionals for the exchange, correlation, and the kinetic energy, spanning more than 50 years of research. Moreover, LIBXC is by now included in more than 20 codes, not only from the atomic, molecular, and solid-state physics, but also from the quantum chemistry community.

References

[1] "Recent developments in LIBXC - a comprehensive library of functionals for density functional theory", S. Lehtola, C. Steigemann, M.J.T. Oliveira, and M.A.L. Marques, Software X **7**, 1-5 (2018)

[2] "Libxc: a library of exchange and correlation functionals for density functional theory", M.A.L. Marques, M.J.T. Oliveira, and T. Burnus, Comput. Phys. Commun. **183**, 2272-2281 (2012)

Automated uncertainty analysis and quantification for high-precision DFT calculations

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Methodological as well as computational progress in ab initio based atomistic simulations have substantially improved the predictive power in materials design over the last few years. A key aspect in achieving this high predictive power was to ensure that the large number of controllable parameters, which we have in state-of-the-art density functional theory calculations, guarantee a sufficiently high convergence. For finite temperature calculations, this commonly amounts to a convergence of better than 1 meV/atom in parameters such as supercell size, k-points, mesh sizes, energy cutoff etc. Doing this manually is from a scientific perspective routine work and thus not very appealing but expensive in labor and requires often months to train researchers adequately.

To automatize the complex uncertainty analysis and control we study and develop algorithms, which take the precision in the derived quantity as a convergence goal and automatically determine the convergence parameter to achieve it. The algorithms are implemented and tested using pyiron [1] (http://pyiron.org) – an integrated development environment (IDE) for computational material science. This tool provides an efficient and user-friendly environment for rapid prototype development and implementation of complex simulation protocols. Our investigations revealed that many of the commonly used rules of the thumb for choosing convergence parameters become invalid for high precision calculations.

References

[1] J. Janssen, S. Surendralal, Y. Lysogorskiy, M. Todorova, T. Hickel, R. Drautz, J. Neugebauer, Comp. Mater. Sci. **163**, 24 (2019).

Benchmarking Electronic Structure Beyond Structural Properties of Solids

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The "Delta" benchmark between different electronic structure codes (https://molmod.ugent.be/deltacodesdft) served as a milestone for code verification in the computational materials science community, offering a comprehensive means to assess the relative precision of different implementations for basic structural properties of solids, across the periodic table. However, practical use cases demand a host of other observables, either in individual simulations or in high-throughput scenarios, and comprehensive sets of benchmarks are often unavailable in such cases. Energy band structures are such a case, complicated by the fact that different energy ranges must be captured and that a wide variety of different approaches to relativistic band-structure corrections exists in the literature. We conducted and provide a systematic set of band structure benchmarks [1] for 103 compounds including elements up to Bi (Z=83). The benchmark set covers scalar-relativistic case (DFT-PBE), where in principle all implementations should agree closely, as well as for different levels of spin-orbit coupling and for hybrid density functionals (HSE06). We use the all-electron codes FHI-aims and Wien2k as high-precision reference approaches. Within the FHI-aims code, a number of higher-level approaches to electronic structure are also available, lending themselves to future benchmark efforts both for molecules and solids; we comment particularly on benchmarking potential for GW and the Bethe-Salpeter Equation for neutral excitations.

References

[1] W. P. Huhn and V. Blum, Phys. Rev. Materials **1**, 033803 (2017).

Precision and efficiency in solid-state pseudopotential calculations

G. Prandini, A. Marrazzo, I.E. Castelli, N. Mounet, and N. Marzari[1]

[1] Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), EPFL, Lausanne, Switzerland

Despite the enormous success and popularity of density-functional theory, systematic verification and validation studies are just starting to appear [1]. Here, we propose a protocol to test publicly available pseudopotential libraries, based on several independent criteria including verification against all-electron equations of state and plane-wave convergence tests for phonon frequencies, band structure, cohesive energy and pressure. Adopting these criteria we obtain curated pseudopotential libraries (named SSSP or standard solid-state pseudopotential libraries), that we target for high-throughput materials screening ("SSSP efficiency") and high-precision materials modelling ("SSSP precision").

References

[1] K. Lejaeghere *et al.*, *Science* **351** (6280), 1415 (2016). http://molmod.ugent.be/deltacodesdft

[2] G. Prandini, A. Marrazzo, I. E. Castelli, N. Mounet and N. Marzari, npj Computational Materials **4**, 72 (2018). http://materialscloud.org/sssp

Reproducibility in response calculations of solids

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Recently efforts have been devoted to evaluating the response properties (elastic tensors, phonon band structures, dielectric tensors, piezoelectric tensors) for a large number of compounds [1-8] which have been made accessible online [9-11]. These results have been obtained with different codes (VASP, QUANTUM ESPRESSO, and ABINIT) and different methods (finite differences and density functional perturbation theory). Similar to the effort that was undertaken for assessing the reproducibility of density functional theory calculations [8], there is a need to evaluate the reproducibility of response calculations of solids.

In this talk, we will share some ideas on this topic. We will also discuss the possible standardization that may result from the effort to be undertaken.

References

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Accuracy of electronic structure calculations

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The accuracy of electronic structure calculations depends on two factors: First of all on the specific approximation used for the unknown exchange-correlation functional within Kohn-Sham (KS) density functional theory. There are many different approximations like the local density approximation, numerous generalized gradient approximations (GGA), meta-GGAs, hybrid functionals, DFT+U or van der Waals functionals. All of them have their merits and are quite successful for certain applications, but none of them has reached « chemical accuracy » (0.4 eV/atom) for all possible systems or properties. Typically, accurate functionals for solids are less accurate for molecules, functionals yielding good geometry (bond distances) may not give good energetics (cohesive energy) and vice versa. The use of different functionals for different systems/properties leaves the truly « ab initio » way of electronic structure calculations. In Ref. [1] we have compared a large number of different functionals and accessed their accuracy. Recently we extended these studies to various van der Waals functionals [2]. In general, the best functionals yield MARE of about 0.5 % for lattice parameters and 4 % for binding energies for strongly bound systems, while the errors for weakly bound systems, even when using dedicated van der Waals functionals, are 2 and 4 times larger, respectively. Perdew et al. [3] showed recently, that our « standard » PBE-GGA makes a wrong structure prediction for about 20-30% of all investigated systems, while the SCAN meta-GGA improves a lot for main group compounds, but the reliability for transition metal compounds is unfortunately still limited.

The second factor concerns the solution of the KS equations by a particular method implemented in a specific computer code. Roughly speaking, fast but less precise plane-wave pseudopotential methods compete with slower but in general more reliable all-electron codes like WIEN2k [4]. It is worth noting that using a particular code does not guarantee precise results, as all codes have various options to increase precision or, alternatively speed-up the calculations. This ranges from using different pseudopotentials to various series truncations, numerical grids or additional basis functions.

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How to estimate the prediction uncertainty
of computational chemistry methods ?

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Prediction uncertainty is a very interesting performance estimator, filling the needs of the end user to choose an appropriate method [1]. Its estimation involves generally a statistical treatment of error samples on references databases, through error statistics or model calibration. Both approaches present difficulties because one is dealing mostly with systematic model errors rather than random errors.

• Standard error statistics, such as the mean unsigned errror, cannot be used to infer prediction uncertainty, notably because error distributions are not necessarily normal, even after linear scaling [2]. We propose to replace them by probabilistic indicators, such as Q_{95}, the 95 % percentile of the distribution of unsigned errors. If the errors distribution is normal, Q_{95} provides the enlarged uncertainty u_{95} recommended, for instance, in the thermochemistry literature [3].

• A major problem with error statistics is their non-transferability to other observables. The BEEF family of density functional approximations attempts to solve this problem by encoding the prediction uncertainty into its parameters posterior distribution via an *ad hoc* Bayesian calibration method [4]. We have shown that the BEEF approach is statistically unsatisfactory [5]. More elaborate calibration strategies, based on stochastic embedding models [6], might be worth to explore.

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Benchmarking DFT and beyond-DFT methods for thermodynamics and electronic properties

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From a tool of understanding and rationalization, ab initio techniques have clearly become a tool for predictive materials design. However, these techniques rely on approximations that are sometimes difficult to a priori evaluate. Rules of thumbs exist and the expert will be able to qualitatively assess the performance of a method for a specific property. However, statistically sound and unbiased benchmarks are required if true predictive materials design is to be performed.

I will use examples of benchmarks studies especially focusing on thermodynamic quantities such as formation energies or electronic properties such as band gap.[1,2] I will highlight the importance of having a clear assessment of the error bar of a property for a given technique but also stress general challenges in terms of size, curation and chemical diversity of the experimental data or automatic convergence of the computations.

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Error quantification for density-functional theory calculations of surface energy and work function

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Density-functional theory (DFT) predictions of materials properties are becoming ever more widespread. With increased use comes the demand for estimates of the accuracy of DFT results. In view of the importance of reliable surface properties, this presentation discusses the calculation of surface energies and work functions for a large and diverse test set of crystalline solids. This set consists of all elementary metals and metalloids up to bismuth, except for the lanthanides. They are compared to experimental values by means of a linear regression. This results in an estimate for the uncertainty on the DFT value and enables the separate determination of a predictable and stochastic uncertainty contribution. Two of the most prevalent functionals, the local density approximation (LDA) and the Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation (GGA-PBE), are evaluated and compared. It is found that both LDA and GGA-PBE yield accurate work functions with error bars below 0.3 eV, which is comparable to the experimental precision. LDA also provides satisfactory estimates for the surface energy with error bars smaller than 10%, but GGA-PBE significantly underestimates the surface energy for materials with an important correlation energy contribution.

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Towards ultimate precision in density-functional theory

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A large part of studies in modern solid-state physics and materials science relies on density-functional theory (DFT). It is implemented in diverse codes, and many of them rely on pseudopotentials, compact basis sets or other features. Their purpose is to improve computational performance, but it comes at the price of reduced precision. Therefore, it is important to be able to verify and systematically improve such approaches, which, in turn, requires indisputable reference data. We address ultimate precision in DFT by employing the full-potential linearized augmented plane waves + local-orbitals (LAPW+LO) method implemented in `exciting` [1]. We calculate total energies of atoms and 55 molecules of the G2-1 set using LAPW+LO and unrelated numerical approach that is based on the multi-resolution analysis [2]. The results obtained with these two methods agree within ~ 1 μHa/atom, which demonstrates that LAPW+LO attains the complete-basis limit within this error margin [3]. For periodic systems, there are no such reference tools for crosschecking the LAPW+LO method. We therefore use the duality of the LAPW+LO basis and variable atomic-sphere sizes to show that the ~ 1 μHa/atom precision is attained also for solids.

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Precision Quantification of Phonons and Vibrational Free Energies

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Computing phonon frequencies and vibrational free energies within a DFT/lattice dynamics framework presents considerable additional computational challenges above those encountered in ground-state calculations. Accurate free energy calculations are essential to establish polymorph stability of molecular crystals where the internal energies differ by meV [1]. These crystals are characterised by very low-frequency (THz) intramolecular modes which give the largest entropic contribution to the vibrational free energy.

Phonon frequencies are the result of near-complete cancellation of large terms in the dynamical matrix, and the difference is exquisitely sensitive to computational grids, basis-set size, SCF residual, Brillouin-Zone sampling and more. Furthermore the use of electron-density-dependent dispersion corrections to DFT introduces additional convergence issues.

We will present a study of convergence challenges aimed at determining the precision limits of free energies for organic molecular polymorphs. Using the CASTEP plane-wave DFT code[2] we have calculated phonons for several systems, including desloratadine, coronene and naphthalene, and established a variatey of criteria necessary to approach convergence.

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Highly accurate atomization reference energies for pseudpotential benchmarking

Stefan Goedecker

Pseudopotential calculations aim at reproducing all-electron calculations within a chosen exchange correlation functional with errors that are less than the errors arising from the exchange correlation functional itself. Since exchange correlation functionals are approaching the much sought after chemical accuracy of 1 kcal/mol, pseudopotentials should not give rise to errors that are not much larger than this value (The Journal of chemical physics 138, 104109 (2013)). To assess the accuracy of pseudopotential calculations highly accurate all-electron reference values are needed. Obtaining in all electron calculations guaranteed errors lower than the chemical accuracy is impossible with standard atom centered basis sets. Using a novel multi-wavelet basis set we were however able to calculate the atomization energies of some 250 molecules with an accuracy of 0.001 kcal/mol. (The Journal of Physical Chemistry Letters 8, 1449-1457 (2017)). These reference values allow for the first time to check in a reliable way the accuracy of pseudopotentials for atomization energies. It will be shown that pseudopotentials that perform well in the Delta test do not necessarily also give low errors in atomization energies.

Numerical analysis for density functional theory

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The quantification of precision of DFT computation has been a major subject of interest in recent years. This is complicated by the large number of approximations and numerical parameters needed for a given computation. This has also been a source of inquiry in the applied mathematics community, where a number of approaches (a priori and a posteriori error analysis, uncertainty quantification) enable the computation of error bars, inside a given model (e.g. Born-Oppenheimer DFT with PBE and a given pseudopotential). I will describe recent work aimed at making this a reality for DFT computations, focusing in particular on the understanding of errors in Brillouin zone sampling, and the computation of a posteriori error estimators for the discretization error of plane-wave DFT.

GW100 benchmarking *GW* for molecules

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The GW100 set is a benchmark set of the ionization potentials and electron affinities of 100 molecules computed using the *GW* method using different independent *GW* codes and different *GW* methodologies [1]. The quasiparticle energies of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are calculated for the GW100 set at the G0W0@PBE level. The use of different codes allows for a quantitative comparison of the type of basis set (plane wave or local orbital) and handling of unoccupied states, the treatment of core and valence electrons (all electron or pseudopotentials), the treatment of the frequency dependence of the self-energy (full frequency or more approximate plasmon-pole models), and the algorithm for solving the quasi-particle equation.

The current data includes reference data at CCSD(T) level [2] and 7 different flavors of *GW* self-consistency [3]. In the mean while 8 different codes ran GW100 resulting in over 23 data sets.

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Main-group test set for materials science and engineering with user-friendly graphical tools for error analysis: systematic benchmark ofthe numerical and intrinsic errors in state-of-the-art electronic-structure approximations

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Understanding the applicability and limitations of electronic-structure methods needs careful and efficient comparison with accurate reference data. Knowledge of the quality and errors of electronic-structure calculations is crucial to advanced method development, high-throughput computations and data analyses. In this paper, we present a main-group test set for computational materials science and engineering (MSE) [1], that provides accurate and easily accessible crystal properties for a hierarchy of exchange-correlation approximations, ranging from the well-established mean-field approximations to the state-of-the-art methods of many-body perturbation theory. We consider cohesive energy, lattice constant and bulk modulus of a set of materials that representatives for the first- and second-row elements and their binaries with cubic crystal structures and various bonding characters. A strong effort is made to achieve high numerical accuracy for cohesive properties as calculated using the local-density approximation (LDA), several generalized gradient approximations (GGAs), meta-GGAs

and hybrids in all-electron resolution, and the second-order Møller–Plesset perturbation theory (MP2) and the random-phase approximation (RPA) both with frozen-core approximation based on all-electron Hartree–Fock, PBE and/or PBE0 references [2, 3]. This results in over 10 000 calculations, which record a comprehensive convergence test with respect to numerical parameters for a wide range of electronic-structure methods within the numerical atom-centered orbital framework. As an indispensable part of the MSE test set, a web site is established http://mse.fhi-berlin.mpg.de. This not only allows for easy access to all reference data but also provides user-friendly graphical tools for post-processing error analysis.

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Minimax Isometry Method

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A compressive sensing approach for the Matsubara summation of many-body perturbation theory is presented. By constructing low-dimensional, almost isometric subspaces of the Hilbert space we obtain optimum imaginary time and frequency grids that allow for extreme data compression of fermionic and bosonic functions in a wide temperature regime. The method is applied to a low-scaling algorithm[1] of the random phase[2] and GW approximation[3, 4] of the grand potential for insulating and metallic compounds.

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