CFCAM discussion meeting proposal: Pseudopotentials and PAW atomic data: beyond a "black art"?

I. ORGANIZERS

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II. FORMAT

1 day and half workshop; January 28-29th 2014 in Paris; 20 participants

III. SCIENTIFIC BACKGROUND

Many physical and chemical properties of solids are determined by the structure and dynamics of the valence electrons. This is true in particular for the formation of chemical bonds, but also for the magnetic behavior and for low-energy excitations. In contrast, the core electrons only affect indirectly these properties. Based on these observations, Density Functional Theory (DFT) electronic structure calculations often assume that the complicated interaction between valence electrons and the ions (formed by the atom nuclei and the core electrons) can be replaced by an effective potential called pseudopotential. The core states are thus eliminated and the valence electrons are described by nodeless pseudo-wavefunctions. This is particularly useful when a planewave basis-set is used to describe the electronic wavefunctions (since it allows one to limit the basis-set size).

Norm-conserving (NC) pseudopotentials enforce the condition that, inside of a cutoff radius, the norm of each pseudo-wavefunction be identical to its corresponding all-electron wavefunction [1, 2]. Ultrasoft pseudopotentials relax the norm-conserving constraint to further reduce the basis-set size [3]. Another related technique is the Projector Augmented Wave (PAW) formalism [4].

Since it is almost impossible to produce nodeless orbitals with only a single spherical potential, the pseudopotential usually consists of several components, one for each angular momentum present in the valence space. In the PAW formalism, it also required to provide a series of atomic quantities (the partial wave and projector basis sets).

In the last thirty years, many efforts have been made for years to generate such pseudopotentials (and the require atomic data), improving their accuracy and their transferability to many systems. However, the large diversity of approaches, added to the well-known difficulty to generate efficient and transferable pseudopotentials, makes the generation of atomic datasets tedious. Moreover, one sometimes needs special sets for very specific problems. Indeed, when one wants to study for instance materials under high pressure, it is necessary to have very small augmentation regions and semi-core electrons in the valence, and therefore, to generate non-standard atomic data. To do this, one is willing to compare the different approaches to choose the most suited to the studied case. This is the same for *GW* calculations, for which it is sometimes needed to increase the size of the partial wave basis.

Most of the codes are provided with a more or less complete atomic data table (see for instance Refs. [4–9]). As well known, the success and popularity of DFT codes using plane-wave basis sets (VASP, QUANTUM-ESPRESSO, CASTEP, GPAW, ABINIT) depends on the availability of high-quality atomic data. This quality can only be tested with respect to all electron (AE) calculations, which constitute in principle a reference. Recent initiatives have emerged on this topic [10–14] to measure the agreement between pseudopotential and AE calculations.

However, first results seem to show that the differences obtained different AE code (WIEN2k and ELK for instance) are of the same order of magnitude as the differences between pseudopotential results and AE results. This obviously raises the question of the validation of the AE codes among them (or maybe the use by non-expert users...) and of the accuracy that can be reached with pseudopotentials.

IV. MOTIVATION AND OBJECTIVES

We therefore believe that there is a need for a CFCAM workshop, with 3 objectives:

1. to discuss about the way to generate atomic data
   - Which schemes are the best or the better suited to one element ?
   - What are the criteria to choose a pseudisation scheme or pseudisation energies, or matching radii?
   - How to share the know-how on the generation of atomic data to go beyond the idea it is merely a "black art"?
2. to gather all the existing attempts to validate atomic data on AE calculations
   We could move towards an open-source repository. Any one could propose a new dataset for a given element. This pseudo would have to pass a series of tests to be validated (among which comparison with all-electron calculations). There would actually be two important figures to provide for a given atomic dataset: not only its accuracy but also its smoothness. Based on the results of these tests (for which, there would be different levels... no need to test deeply a pseudo with bad logarithmic derivatives for instance), the future user would be able to choose more easily (knowing the accuracy of the pseudo and the required cut-off to reach a low, normal, and high accuracy). For this, we need a data base of AE calculations. The results in [10], [11], [12], [14] are already a good starting point, but a validation with different AE codes is probably needed. It would be nice to have the corresponding input and output files, which include more information. This is particularly true for comparison between different AE codes, but also for the subsequent calculations with the plane-wave code (e.g. the k-point sampling).
3. to define a common format for the atomic data files
   Alternatively, the atomic data generators could produce the different existing formats (the repository would contain the input files for the generator as well). For PAW atomic data, several codes are already able to read a common format using XML specifications (https://wiki.fysik.dtu.dk/gpaw/setups/pawxml.html). For NC pseudopotentials, some formats can already be used by several codes.

V. TENTATIVE LIST OF PARTICIPANTS

- P. Bloechl
- S. Cottenier
- A. Dal Corso
- C. Draxl
- K. Garrity
- P. Giannozzi
- X. Gonze
- D.R. Hamann

- N. Holzwarth
- F. Jollet
- G. Kresse
- E. Kucukbenli
- K. Lejaeghere
- N. Marzari
- J. J. Mortensen
- M. Oliveira
- G.-M. Rignanese
- S. Sharma
- M. Stankovski
- M. Torrent
- D. Vanderbilt

VI. FINANCIAL SUPPORT

We are asking for 2keuros per half day i.e. a total amount of 6 keuros.
We intend to support:
4 overseas travels: 4x 600 =2400 euros
10 european travels: 10x200= 2000 euros
3 meals per participants: 20 x 3 x25= 1500 euros
administrative costs: 100 euros.

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