Enclosure 1b. Category 1 Application form – English version

APPLICATIONS ARE PREFERABLY DRAWN UP IN ENGLISH. AN ENGLISH TRANSLATION HAS TO BE ENCLOSED WITH APPLICATIONS SUBMITTED IN DUTCH.

The application form is available in English on the website https://www.vscentrum.be/en/access-and-infrastructure/project-access-tier1

Title of the application:

Insight into the stacking of 2D COFs from *ab initio* and force-field calculations

Name and first name of the applicant:

Vandenbrande Steven

Institution:

Ghent University

Research group / department:

Center for Molecular Modeling

Title / position:

PhD Student (FWO Fellow)

e-mail address:

Steven.Vandenbrande@UGent.be

Total computing time that is needed, in node days:

2 200 node days

Total disk storage that is applied for (in GiB):

65GiB

1. Title of the research project (with IWETO or FRIS link if available) within the framework of which computing time is applied for:

The FWO grant of S.V. is entitled “Development of force fields to design tailor made organosilica materials”.

2. Describe your research project in short. Explicitly mention the scientific questions that you are planning to address and the overall scientific goals of the project. (max. 1 A4 in Arial 12):

Covalent Organic Frameworks (COFs) are porous crystalline materials where organic linker molecules (for example phenyl groups) are stitched together by connectors (typically consisting of oxygen and boron atoms) into an ordered framework. Promising applications of these COFs include, amongst others, their use as support materials for highly functional heterogeneous catalysis and gas storage and separation.

Topologically, we can distinguish two- and three-dimensional COFs. Similar to graphite, two-dimensional (2D) COFs are composed of layers or sheets that are bounded without any covalent bonds between the layers and a few of these 2D COFs (COF-1, COF-5, COF-6, COF-8, COF-10) will be studied in this project. The precise stacking configuration (distance between the layers, arrangement of neighboring layers, …) is governed by a subtle interplay of electrostatic, exchange-repulsion, polarization and dispersion interactions between the layers. Elucidating the role of different building blocks of the COFs mentioned above in the relative stability of various possible stacking arrangements is the main scientific goal of this computational study.

Because mean-field theories, such as the popular Density Functional Theory (DFT) method, are in practice not able to capture the very important dynamic electron correlation for these systems, several dispersion correction schemes (D3, Tkatchenko-Scheffler, MBD, dDsC) for DFT functionals will be investigated. A comparison of these schemes has not been performed before for these types of systems. The comparison that will therefore be done in this study is interesting because it allows to study the influence of how short-range dispersion is treated, the importance of many-body effects on dispersion and the density-dependence of dispersion coefficients. Because all these mentioned dispersion correction schemes are implemented in the newest version of VASP, this will be the software used to perform all DFT calculations for this project. Also our recently developed force-field model for non-covalent interactions (MEDFF) will be validated and optionally improved based on the results obtained from dispersion-corrected DFT calculations. Note that because force-field calculations are several orders of magnitude faster than *ab initio* calculations, the force-field calculations can easily be

performed on the TIER-2 infrastructure and are not part of this TIER-1 proposal.

By combining results from the two approaches, ab initio and force-field calculations, we will gain insight in how and why different stacking structures of COFs appear. Finally a comparison with experimental results from XRD measurements will be made.

3. Provide an abstract (10 lines) for scientific communication on the website in layman's terms. See also item 12 of this application form.

Covalent Organic Frameworks (COFs) are an interesting new class of crystals because they contain very small holes or nanopores. They can be pictured as miniature sponges, where the miniature pores can be used for instance to store gas molecules inside the COF. This intriguing property renders these crystals candidates for new technologies, for instance to store CO2 molecules captured from exhaust gases.

This study will investigate two-dimensional COFs, a subclass of crystals where layers of the material are stacked closely on top of each other. Because the stacking arrangement can have a strong influence on the properties of the COFs, we will study the interactions between the layers using newly developed quantum mechanical methods.

4. Financing institution or channel, financing the research project in full or in part (FWO, BOF, IWT, EU, ...): Please attach the confirmation letter as enclosure (see instructions in enclosure 3 "EasyChair proposals submission procedure").

FWO PhD Fellowship, 11U1914N and 11U1916N, confirmation letters attached.

5. Name and email address of the promoter(s) of the research project:

Toon Verstraelen (Toon.Verstraelen@UGent.be)
Veronique Van Speybroeck (Veronique.VanSpeybroeck@UGent.be)

6. Persons mandated by the Applicant to compute on the Tier-1 within the framework of the present project: Please provide for every person:
    - name and first name
    - institution
    - research group / department
    - title / position

- experience of using HPC resources in the past (Tier-0/Tier-1/Tier-2 infrastructure in Belgium and abroad)

- Vandenbrande Steven (vsc40685)
  Ghent University
  Center for Molecular Modeling
  PhD Student (FWO Fellow)
  Experience with installing, testing and using software on UGent Tier2 infrastructure

- Verstraelen Toon (vsc40019)
  Ghent University
  Center for Molecular Modeling
  Professor
  Experience with installing, testing and using software on UGent Tier1 and Tier2 infrastructure and SHARCNET (Compute Canada National HPC)

- Van Speybroeck Veronique (vsc40021)
  Ghent University
  Center for Molecular Modeling
  Professor
  Experience with using software on UGent Tier1 and Tier2 infrastructure

7. Explain why this project needs to run on a Tier-1 system, why the machine you have requested is suitable for the project and how the use of the system will enable the science proposed (max. ½ A4 in Arial 12).

To study the stacking of 2D COFs, systems containing several layers of the material need to be simulated. As an example we mention a COF-10 unit cell (dimensions 32Å x 32Å x 7Å) with 2 layers containing 264 atoms. For this system size, typical for the proposed study, we can benefit optimally from the available computational resources on the TIER-1 infrastructure. The stacking will be studied by scanning the potential energy surface along several (up to 20) interlayer distances, a task we will refer to later on as **SCAN**. The **SCAN** procedure needs to be performed for different stacking configurations (inclined, serrated, zig-zag, armchair) and different shifting distances between the layers. Performing these calculations for several 2D COFs leads to a high total workload justifying our demand for the computational resources on TIER1.

Another type of calculation are the optimization and normal mode analysis of monolayers (**OPT/NMA**). These results are necessary to obtain the parameters of the MEDFF force fields that will be constructed and used in the next part of the research project. Obviously the number of **OPT/NMA**

calculations to be performed is rather small, but as reaching the optimimal structure can take a lot of steps, this again adds a substantial computational effort to the project.

8. Justify the number of node days requested. This should include information such as: number and nature of computing tasks, software used, and the sequence in which they will be performed.

   Indicate for each typical computing task the required resources:

   - wall clock time (note that 3 days is the maximal wall clock time for any job; checkpointing should be used for longer run times)
   - memory (maximum 64 GiB/node)
   - number of nodes
   - number of CPU cores
   - disk space (estimated volume in GiB and the total number of files); make a clear distinction between usage of Tier-2 DATA/HOME partitions and the Tier-1 SCRATCH partition
   - number of tasks, and an indication of how many such tasks would be submitted concurrently.

   This information should take the form of a table (an example is provided as Table 2 in the appendix). Provide additional descriptions of the computing tasks and comments as needed. Resource estimates should be preferably based on the results of actual calculations on Tier-1 (via, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, …). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results and explain how you have calculated/rescaled the wall clock times, number of cores, etc.

   (max. 1 A4 Arial 12).

All calculations will be performed using VASP. The bulk effort of the project consists of **SCAN** tasks. A **SCAN** will be performed for 5 different COFs, each in 4 stacking configurations for 20 shifting distances. This leads to a total of 400 **SCAN** tasks and the time for one such task is accurately estimated from a scaling test performed for COF-10 (see §9). Note that in the scaling test one single-point calculation takes slightly more than 2 hours on 2 nodes, but 20 single-point calculations (one for each interlayer distance) are required for each **SCAN** task. Note that WAVECAR files containing wave function data can be discarded, reducing the need for storage volume.

The **OPT/NMA** tasks will also be performed for 5 different COFs and additionally for 5 different dispersion correction schemes, leading to a total of 25 **OPT/NMA** tasks. The total time of each optimization is hard to assess a priori, as it depends on the initial structures that are used as input. Both optimization and normal mode analysis calculations can be checkpointed, so there is no problem with the wall time limit when such **OPT/NMA** tasks take more than 3 days to run to completion.

	Node day calculation				
Computational task	# of such tasks	Wall clock time (days) per task	# Tier-1 nodes per task	# node days per task	# CPU cores per task
SCAN	400 = 5 x 4 x 20	2	2	= 1600	32
OPT/NMA	25 = 5 x 5	12	2	= 600	32

Storage volume estimate				
Computational task	Memory usage (GiB) / node per task	OpenMP / MPI / hybrid / vSMP	Tier-2 DATA/HOME volume (GiB) + number of files	Tier-1 SCRATCH volume (GiB) + number of files
SCAN	2	MPI	40GiB = 400 x 100MiB	40GiB = 400 x 10MiB
OPT/NMA	30	MPI	25GiB = 25 x1 000MiB	25GiB = 25 x1 000MiB

9. Describe the software required to perform the computing task(s). Please clearly provide the following per item in this regard:

- a reference to the software's web page
- the software license system (open source, GPL, etc.)
- if there is no free academic use of the software, state which license makes the installation and the use valid on the Tier-1 by the Applicant (+ add a copy of the signed license)
- if need be, which license server will be used (name + IP address)
- whether the software is already available on the Tier-1 (see https://www.vscentrum.be/cluster-doc/software/tier1-muk) and, if this is not the case, compilation and installation instructions (possibly with reference to existing Tier-2 installation)

Provide the results of scaling tests that were conducted with this software, preferably on Tier-1 (using, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, …). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results.

Provide both a table and scaling plot such as table 1 and plot 1 in the appendix (max. 2 A4 in Arial 12).

Used software:

VASP 5.4.1

- http://www.vasp.at
- License: attached at the end of the document
- The software is already available on the TIER1 infrastructure.

A scaling test for VASP has been performed on TIER-1 by Kurt Lejaeghere, a researcher with expertise with the VASP program on TIER-1. The results in Table 1 are obtained for a single-point calculation of the 1x1x2 supercell of COF-10, one of the systems that will be studied in this project and the same data are represented graphically in Illustration 1. Clearly the scaling over 2 nodes is nearly perfect and certainly acceptable

up to 4 nodes. Given the large number of tasks required, running many tasks concurrently on 2 nodes seems a proper strategy. For even larger systems than COF-10, parallelization over more than 2 nodes can be considered.

# nodes	# cores	absolute timing (s)	speedup	# cores x timing
1	16	16 472	1.00	263 560
2	32	8 505	1.94	272 147
4	64	4 957	3.32	317 251
8	128	3 605	4.57	461 490
16	256	2 046	8.05	523 843

Table 1: Multi-node scaling for a single-point calculation on COF-10

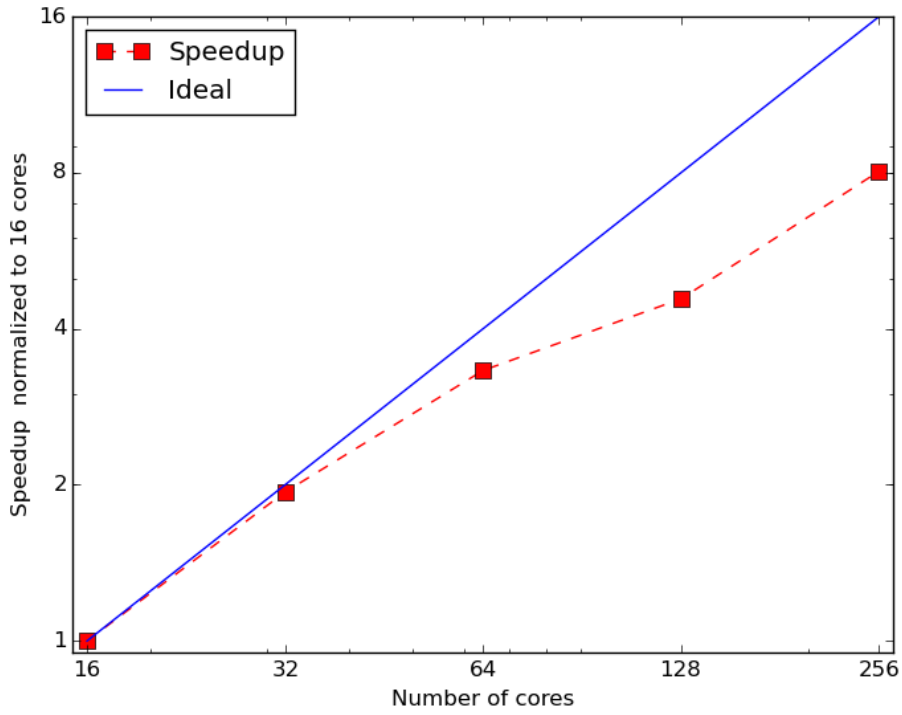

Illustration 1: Multi-node scaling for a single-point calculation on COF-10

10. Describe how you will manage the resources requested in the period during which the task is to be performed. What usage pattern do you anticipate (similar usage on monthly basis, bursts, …)?

Both **SCAN** and **OPT/NMA** calculations will be spread out evenly over the duration of the project.

11. List the granted computing time allocations to the promoter(s) of this research project, on the Flemish Tier-1 system, as well as other Tier-1 and Tier-0 systems. Also, describe the scientific output obtained within the framework of computing time that was granted during the past two years on the Flemish Tier-1 or on other Tier-1 or Tier-0 supercomputers. DOI links are sufficient.

Quantum contributions to the polarizability . Node days: 1568

Dynamical kinetic study of zeolite-catalyzed reactions. Node days: 4371

Structural transformations during dehydroxylation reactions of UiO-66 type metal-organic frameworks; an extension with normal mode analysis. Node days: 2726

Structural transformations during dehydroxylation reactions of UiO-66 type metal-organic frameworks. Node days: 4720

Modeling aldol condensations in metal-organic frameworks with hybrid functional calculations. Node days: 2304

Unraveling reaction pathways on UiO-66 type systems with metadynamics. Node days: 4432

The electronic and magnetic structure of breathing metal-organic frameworks. Node days: 4725

Molecular dynamics study of pentene in H-ZSM-5: towards a better estimate of adsorption enthalpies. Node days: 1824

Dynamical kinetic study of zeolite catalyzed reactions. Node days: 4371

Exploring the kinetics and selectivity of butene cracking using molecular dynamics simulations. Node days: 4864

Characterizing adsorption properties of C4-C6 alkenes on H-ZSM-5 using molecular dynamics simulations. Node days: 4260

Unraveling dehydroxylation pathways on UiO-66 type systems with metadynamics. Node days: 3304

Dynamical first principle benchmark studies on alkene methylation in H-ZSM-5. Node days: 1400

Investigating the phases of MIL-53-type materials. Node days: 4644

Investigating active sites in hydroxylated and dehydroxylated UiO-66 for catalysis of Oppenauer-type oxidation. Node days: 2110

Shape tuning of CdSe nanostructures by ab initio determination of the anisotropic growth mechanism. Node days: 4752

Ab initio molecular dynamics study on the role of water in the reaction mechanism during methanol conversion in H-SAPO-34. Node days: 4880

Articles:

http://dx.doi.org/10.1039/C4RA16800C

http://dx.doi.org/10.1039/C4CE01672F

http://dx.doi.org/10.1002/chem.201500473

http://dx.doi.org/10.1016/j.jcat.2015.01.013

http://dx.doi.org/10.1002/cctc.201402146

http://dx.doi.org/10.1021/cs400706e

http://dx.doi.org/10.1039/c4mh00127c

http://dx.doi.org/10.1039/C3CP54132K

http://dx.doi.org/10.1021/acs.jpcc.5b06809

http://dx.doi.org/10.1016/j.jcat.2015.08.015

12. Are the applicants of this application bound by a confidentiality agreement? If so, the title and the abstract of this application will not be published on the website of the FWO / Flemish Supercomputer Center.

No

SOFTWARE LICENSE AGREEMENT FOR THE USE OF VASP5.2 BY ACADEMIC INSTITUTIONS

The Universität Wien, Austria (UW in the following) and
Ghent University, Belgium (UG in the following) [1]
conclude the following agreement:

(1) The UG acquires a non-exclusive academic license for the use of the software-package VASP (Vienna ab-initio simulationprogram) for ab-initio local-density-functional total-energy and molecular-dynamics calculations, versions VASP5.2 and VASP4.6, by the research group Functional Nanomaterials (FUNNANO)[2]. Under this licence the use of the software is restricted to a maximum of six researchers or students, all belonging to this research group and to the same organisatorial unit and working at the same location. The licence does not cover the use of VASP by external collaborators working at other institutions.

(2) The license covers access to the source-code, the program documentation and to the data-base for ultrasoft pseudopotentials and PAW-potentials. UW reserves the exclusive property of the software. It declines any liability for the software and any responsibility for the results of calculations produced with the program. The license does not cover any maintenance service for the software or support for its implementation.

(3) The license is not transferable to another research group of UG without the written agreement of UW. UW reserves the right to refuse authorization of such a transfer. A transfer to a research group not belonging to UG is excluded.

(4)The UG guarantees that the software or parts thereof shall not be made accessible to third parties without the explicit written consent of UW. Access to the code and to the data-base shall be made available through an account of the UW. The UG guarantees that the password for this account will be known only to one contact-person and shall not be communicated to temporary co-workers or guests. All installations of the source code, the executable or the data-base must be copy-protected and accessible only to the authorized users.

[1] Please insert here the name of the institution concluding this agreement with UW. This institution must be a legal person and the agreement must be signed by an authorized representative of this institution. Define the acronym (replacing .....) under which this institution is referred to in the text of the agreement.

[2] Please insert here the name and affiliation research group for which the license is acquired

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(5) If VASP is used as the basis of further methodological or software-development, UG agrees to make these additions available to UW. UW will also be entitled to include these additions in further releases of VASP.

(6) In future publications of work performed using VASP, the use of the software shall be properly acknowledged, e.g. in the form
"The calculations have been performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut für Materialphysik of the Universität Wien [1-3]."
[1] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
If the PAW-version is used, reference will be made to
[2] G. Kresse and D. Joubert, Phys. Rev. **59**, 1758 (1999).
If special features implemented in VASP will have been used, reference should be made to the relevant publications as listed on the VASP home-page.

(7) The UG accepts to pay to UW a licence fee Euro 4.000,- (fourthousand Euro). The licence fee is strongly discounted and applies only to academic institutions with undergraduate teaching.

(8) The licensee will use VASP exclusively for non-profit research. If VASP is used in contractual research in cooperation with or for industry or for military institutions, the financial conditions will have to be re-negotiated.

(9) UW declares that it has the full power and authority to grant the rights granted in this agreement without the consent of any other person, and that the license and use of the software by the licensee will not in any way constitute an infringement or other violation of any copyright, proprietory right or any other rights of any third party.

(10) Any disputes arising from the license agreement are subject to the laws of the Republic of Austria.

(11) The terms of this agreement shall prevail any terms or conditions of the licensee.

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For the Universität Wien:

Jürgen Hafner
Fakultät für Physik, Universität Wien
Sensengasse 8/12, A-1090 Wien, Austria

Date

For the UG

Name (in print): Michel Waroquier
Institution: Faculty of Sciences, Ghent University

Address: Technologiepark 903, BE-9052 Zwijnaarde, Belgium

Date: 26 January 2010

For the research group entitled to use VASP5.2:

Name (in print): Veronique Van Speybroeck (FUNNANO)

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new
horizons

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02 550 15 88

date
1 June 2016

concern **Employment Certificate**

TO WHOM IT MAY CONCERN

The undersigned, Head of Section Personnel of the Research Foundation – Flanders (FWO), Foundation of Public Utility, institution identity code 0880.212.840, Egmontstraat 5, 1000 Brussels, Belgium, testifies that mister Steven Vandenbrande, born in Leuven (BE) on 09 July 1988, was the beneficiary of a full-time PhD Fellowship from 1 October 2013 till 30 September 2015 from the above mentioned institution.

During this period he was affiliated with Prof. Van Speybroeck and Prof. Verstraelen and conducted his research at the Universiteit Gent.

He devoted all his time to scientific research as specified by the by-laws of the FWO, stipulating that an employee has the obligation to spend all his time on scientific research excluding all other occupations with the exception of limited tasks on request of his university.

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Stephan Duray

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Stephan Duray

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