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:

Defect engineering in UiO-66: How linker defects affect the electronic structure.

Name and first name of the applicant:

De Vos Arthur

Institution:

Ghent University

Research group / department:

Center for Molecular Modeling

Title / position:

PhD Student

e-mail address:

arthur.devos@ugent.be

Total computing time that is needed, in node days:

4116

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

6468 GiB

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

IAP Functional Supramolecular Systems (FS2)

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):

Metal-organic frameworks (MOFs) are hybrid materials that combine both organic and inorganic building blocks. Their porous structure is ideal for a number of applications such as gas storage and catalysis. In recent days also their electronic properties yield interesting applications such as photovoltaic, photocatalysis and integration in electrochemical devices.

However, when looking from a computational point of view, these MOFs are usually treated as perfect crystal. Defects are often not considered yet they can be used, to functionalize the MOFs in a way enhanced properties are achieved. For example, it has already been argued that defects play a crucial role in catalysis acting as active sites and doubling the reaction rate of the hydrogen evolution reaction (HER) [1]. These properties are, to a large extent, influenced by the electronic properties of the induced active defect sites and how they alter the band gap edges and introduce possible band gap states.

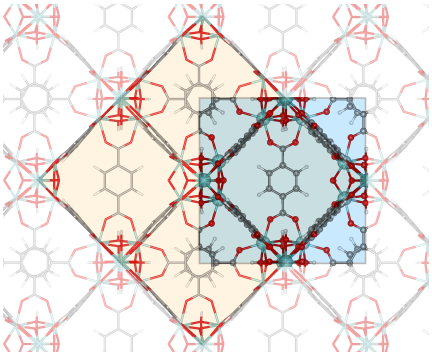

Fig. 1. Cross section of the UiO-66 where two missing linkers are created in the 4 brick unit cell. One of these missing linkers is enclosed in the transparent blue square.

In this research project missing linker defects will be created in a highly stable and well-studied MOF for photocatalytic applications. A systematic study of how missing linker defects affect the electronic structure has, to the best of or knowledge, not yet been preformed. It has however already been reported how 1 ,2 or 3 missing linkers can be create, in a 4 brick unit cell of UiO-66. This can be done in 1, 8 or 32 symmetry-inequivalent ways, respectively [2].

Furthermore these defect structures are potentially interesting to post-functionalize the UiO-66 inorganic brick, as the extra active site, induced by a missing linker, is a potential functionalization site. Therefore the ab initio data of the defect structures and their electronic structures can be

reused to investigate the electronic and catalytic properties of functionalizations on these different defect sites.

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

Metal-Organic Frameworks (MOFs) are hybrid materials that combine both organic and inorganic building blocks. Their electronic properties are strongly dependent on structural effects, which allow tuning for a wide range of applications. One example is the widely investigated UiO-66. In its synthesized form, the material contains missing linkers, so we aim to study their influenced on the electronic structure. Periodic density functional theory calculations will be performed to elucidate the equilibrium structure and density of sate of these materials.

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").

BELSPO

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

Prof. Dr. ir. 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)

   De Vos Arthur
   Ghent University
   EA 17, Center for Molecular Modeling
   ir. / PhD student
   vsc41228
   Experience with Tier 1 and Tier2 infrastructure of UGent

   Van Speybroeck Veronique
   Ghent University

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Prof. Dr. ir. / Professor
vsc40021
Experience with Tier1 and Tier2 infrastructure of UGent

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).

The amount of computing power goes beyond what can comfortably be done (within a reasonable timeframe) on a TIER2 cluster. Considering the optimization at least 462 calculations (42 materials x 11 optimizations) with 3 nodes/task are required. Density of states calculations (42x) on optimized material will be performed for which hybrid calculation on 2 nodes will be used. Moreover, the queuing times for such jobs can easily take several days. Because UiO-66 is a highly studied material with very interesting properties and publications appear everyday, waiting for several weeks on such calculations and such a hot topic is impossible.

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).

Calculation flow (see also Table 2 in the appendix):

1) Structure optimization:
   To obtain the optimal missing linker defect structures a 4 step process (full relaxation, equation of state, equilibrium volume relaxation and single point) is followed. Up three missing linkers are created in the 4 brick unit cell of UiO-66. These structure have respectively 456, 420 and 402 atoms. The number of structures created in this way is 1 for the defect free, 1 for 1 missing linker defect, 8 for 2 missing linker defect and 32 for 3 missing linkers giving a total of 32 structures.

   I. Full relaxation
      In the first step the defect structures are created out of the defect free optimized structure and are completely relaxed (atomic position, cell shape and volume). For this task 3 nodes (48 cores) are necessary and a walltime of 3 days. See also

Fig. 2 in the appendix where 3 nodes appears to be a good compromise between speedup and computational resources. The optimized structure from this step will be used as a starting guess to calculate the equation of state.

II. Equation of state
The equation of state will be calculating by optimizing the structure of step I for 9 fixed volume points (-4%-4%) around its optimized volume [3]. For each of these points 3 nodes (48 cores) are used and a walltime of 3 days.

III. Equilibrium volume relaxation
From the equation of state the equilibrium volume will be calculated by fitting a Rose-Vinet curve. For this volume, the atomic positions and shape will be optimized keeping the volume fixed. Because the starting structure is already close to the equilibrium structure the walltime will be set to one day on 3 nodes (48 cores).

IV. Single point on the optimized equilibrium volume
A final a single point calculation is done on the optimized structure to obtain a reliable energy.

2) Analysis
After the optimization is done a post-analysis is performed. It has to be said that the required memory in Table 2 in the appendix will never be necessary all at once because large intermediate files will be removed as soon as parts of the analysis are finished. Therefore the necessary memory at a single moment will never exceed 3 TB

I. Density of states
On all 42 defect structures, density of states calculations will be performed. As these calculations need higher settings they need an increased amount of memory resources (see Table 2). Therefore the memory of 1 node is insufficient and for these short calculations (1 day) 2 nodes are necessary in hybrid mode (using 8 out of 16 cores per node).

II. Partial charge analyses:
Because photocatalysis is a very interesting application of the UiO-66 and its applicability is determined by the band gap edges, a further investigation is necessary. We will therefore calculate for the 42 defect structures the partial charge density that is assigned to the band gap edges. These consist of 2 calculations that can be calculated from the converged WAVECAR of the density of states (1 node and 0.25 days). Also band gap states could arise in the material caused by the introduced missing linker defect. In order to be able to clarify these states, their partial charges of will also be calculated (2 calculations, 1 node, 0.25 days)

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).

VASP/5.4.1-intel-2016a-mt-vaspsol-20150914

-http://www.vasp.at

-License: see at the end of the file

-The software is already available on the TIER1 infrastructure

Extensive scaling tests have previously been performed using the VASP software package [4,5]. Optimal scaling can be obtained by combining intranode MPI parallelization and internode k-point parellization. This k-point parallelization divides the job into near-serial subprocesses over points on a discrete grid. However for our system only one k-point is used for the major part of the jobs (all except the density of state and partial charge density calculations) and therefore k-point parallelization is not possible.

We performed additional tests on the TIER1 infrastructure for a defect structure with three missing linkers (see Table 1 and Fig 2 in the appendix). These tests consist of single point calculation and a cutoff of 700 eV. These settings will be used for the UiO-66 missing linker defect structures. From these tests (see Fig 2 in appendix) we conclude that a

good compromise between speedup and the consumed computational cost can be achieved by running the job on 3 nodes.

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, …)?

The calculations are intended to be performed on a continuous basis over the allowed project time, however as the applicant is absent from 7th July till the 6th of August we ask to delay the project time to the beginning of August.

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.

During the previous TIER1-projects and the pilot usage, several aspects of nanoporous materials have been investigated:

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 the UiO-66 type metal-organic framework. Node days: 4720.

Modeling aldo 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 selective of butane 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

Accurate pK a calculations of pH - sensitive dye molecules. Node days: 5280.

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.2015http://dx.doi.org/10.10

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.

    yes / ~~no~~

[1] *Electronic origins of photocatalytic activity in d0 metal organic frameworks, Maxim A. Nasalevich et al. DOI: 10.1038/srep23676*

[2] *Free Energy of Ligand Removal in the Metal-Organic Framework UiO-66. Jessica K. Bristow et al. DOI: 10.1021/acs.jpcc.6b01659*

[3] *Mechanical properties from periodic plane wave QM codes: the challenge of the flexible nanoporous MIL-47(V) framework*, Danny E.P. Vanpoucke et al. DOI: 10.1021/acs.jpcc.5b06809

[4] *http://www.hector.ac.uk/cse/distributedcse/reports/vaspo1/vaspo1_kpoint.pdf*

[5] *http://www.hector.ac.uk/cse/distributedcse/reports/vaspo2/vaspo2.pdf*

Should you have any questions or encounter any difficulties during the electronic submission of an Application, please contact by e-mail:
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For the other institutions: caroline.volckaert@FWO.be

Appendix: Example tables and plots

# nodes	# cores	absolute timing (s)	speedup	# cores x timing
1	16	9232.36	1.000	147717.76
2	32	5327.61	1.747	170483.52
4	64	3803.73	2.479	243438.72
8	128	2253.77	4.258	288482.56
16	256	1734.12	5.681	443934.72

Table. 1. Computational and time for the scaling test. The reported time is for one ionic step. The number of ionic step can vary that is needed for a full optimization but is always below 3 days.

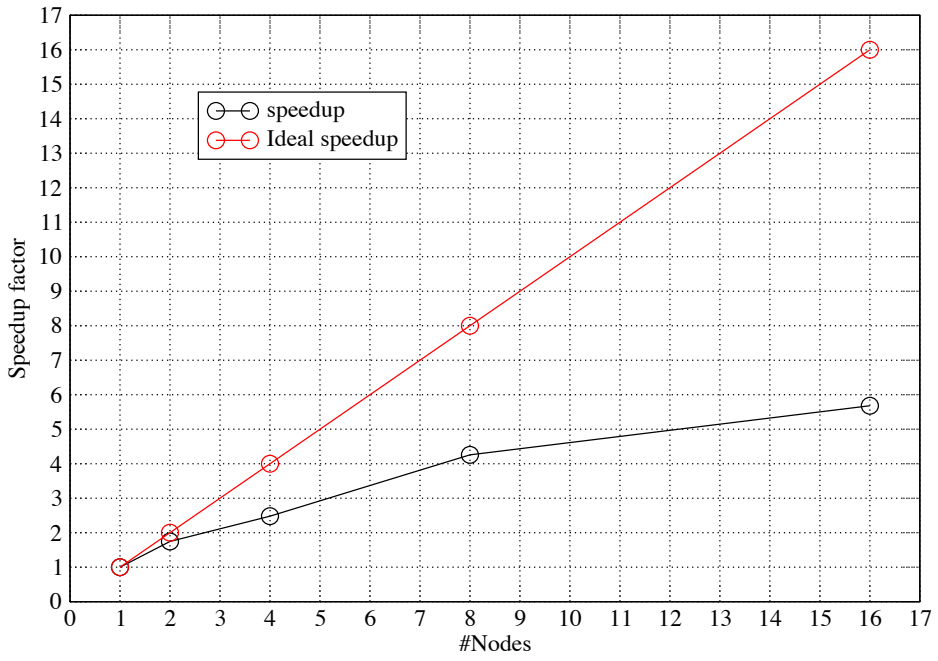

Fig. 2. Speedup results for a typical defect configuration where the number of nodes is varied.

	Node day calculation							Storage volume estimate	
Computational task	# of such tasks	Wall clock time (days) per task	# Tier-1 nodes per task	# node days per task	# CPU cores per 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
Geometry optimization I: Full relaxation	42x1	3	3	9	48	25	MPI	0.2 GiB + 18 files	1 GiB + 19 files
Geometry optimization II: Equation of state	42x9	3	3	9	48	25	MPI	0.2 GiB + 18 files	1 GiB + 19 files
Geometry optimization III: Equilibrium volume	42x1	1	3	3	48	35	MPI	0.2 GiB + 18 files	1 GiB + 19 files
Geometry Optimization IV: Single point of equilibrium volume	42x1	1	1	1	16	35	MPI	0.2 GiB + 18 files	1 GiB + 19 files
Analysis I: Density of state (DOS)	42x1	2	2	1	16	45	MPI	8 GiB + 19 files	30 GiB+20 files
Analysis II: Partial charge	42x4	0.25	1	0.25	16	60	MPI	8 GiB +19 files	30 GiB+20 files
Total	/	/	/	4116				1461.6 GiB	6468 GiB

Table. 2. Work plan and computational resources to complete the tasks.

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Ghent University, Belgium (UG in the following) [1]
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(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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"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.

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(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.

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

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For the Universität Wien:

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Date

For the UG

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Date: 26 January 2010

For the research group entitled to use VASP5.2:

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