# Enclosure 1b. Category 1 Application form – English version

**Title of the application**: The electronic and magnetic structure of Breathing Metal-Organic Frameworks.

**Name and first name of the applicant**: Vanpoucke Danny Eric Paul

**Institution**: Ghent University

**Research group / department**: Center for Molecular Modeling / Department of Applied Physics

**Title / position**: Dr. Dr. / Postdoctoral researcher

**e-mail address**: Danny.Vanpoucke@UGent.be

**Total computing time that is needed, in node days**: 4725

**Total disk storage that is applied for**: 245Gb

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

First principle chemical kinetics in nanoporous materials (KINPOR)
( BOF project: DEF/09/ERC/403 )

2. **Short description of the research project within the framework of which computing time is applied for (max. 1 A4 in Arial 12):**

Metal-Organic Frameworks (MOFs) are a new and important class of porous materials with a wide range of possible industrial applications. Due to their large pore volume, they present materials with enormous "surface-area to volume" ratio, making them of great interest for catalysis, gas-storage, and also sensing applications.

In case of the latter type of applications, the sensing aspect often results in a modification of the electronic and/or magnetic structure of the host material.

In this project, we will investigate the stability of different magnetic configurations of MIL-47/53 type MOFs, to assess the viability of these frameworks as magnetic sensors. The main focus will go the MIL-47/53 type MOFs with experimentally known magnetic transition(s). Although, such transitions are known, no *ab-initio* quantum mechanical studies of these aspects have yet been performed for the MOFs studied in this project. Because the MOFs of interest are also part of the class breathing MOFs, the relation between the magnetic configuration (more specifically the intra-and inter-chain coupling terms) and the large-pore/narrow-pore geometry are of interest (application as pressure sensor).

By investigating the variation of the magnetic stability as function of the metal-centre in the MOF (e.g. Sc-Ti-V-Cr) it becomes possible to predict/propose suitable metal centres for specific sensing applications.

3. **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).**

BOF project: DEF/09/ERC/403

4. **Promoter of the research project:**

Prof. Dr. ir. V. Van Speybroeck

5. **Persons mandated by the Applicant to compute on the TIER1 within the framework of the present project: Please provide for every person:**

**name and first name:** Van Speybroeck Veronique
**institution:** Ghent University
**research group / department:** Center for Molecular Modeling / Department of Applied Physics
**title / position:** Prof. Dr. ir. / professor
**experience with TIER1/TIER2 infrastructure in Belgium and abroad**

- Pilot user of the Ghent STEVIN TIER2 infrastructure

**name and first name:** Vanpoucke Danny Eric Paul
**institution:** Ghent University
**research group / department:** Center for Molecular Modeling / Department of Applied Physics
**title / position:** Dr. Dr. / Postdoctoral researcher
**experience with TIER1/TIER2 infrastructure in Belgium and abroad**

- Local cluster of the CMS group (University of Twente, The Netherlands)
- Huygens Supercomputer (SARA computing Center, The Netherlands)
- Ghent STEVIN TIER2 infrastructure (pilot user)
- Ghent MUK TIER1 infrastructure (pilot user + project granted for 8300 node days)

6. **Description of the computing task, justification for the computing time, disk storage and memory that are applied for, and description of the software tools required (max. 3 A4 in Arial 12). Please clearly provide the following in this regard:**
   - **the number of nodes/cores that are applied for per computing task, with a subdivision of the computing time in sub-tasks indicating the sequence of the sub-tasks**
   - **whether these tasks use diversification (OpenMP, MPI, hybrid OpenMP/MPI …)**
   - **the estimated memory use of a computing task (maximum 64GiB/node)**
   - **whether a vSMP system will be used**
   - **the requirements for disk storage (estimated volume in GiB and the total number of files), more specifically for:**
     - **required input files (data set, parameter files, etc.)**
     - **SCRATCH volume used during the performing of the computing tasks**
     - **result files**

Within this research project, the magnetic configuration of MOFs will be investigated using *ab-initio* DFT methods. For this we will make use of the **VASP program**. Our goal is to investigate MOFs with a MIL-47/53 topology containing different metal-oxide chains (selected *3d*-block metals) [we will refer to these as systems]. Each of these **7 systems** will lead to multiple magnetic configurations (on average 5 inequivalent configurations, leading to a **total of 35 configurations**), which allows the calculation of inter-and intra-chain coupling terms. The in depth systematic study of these configurations follows a standard scheme of calculations:

1) **Geometric optimization** : Using an fit to an equation of state, requiring 10-15 fixedd volume relaxations.[1]
2) **Phonon-calculation** to (a) test the quality of the optimized structure, and (b) provide an estimate of thermal contributions to the energy.
3) Post-processing calculations:
    a. **Density of states**
    b. **Band structure**

| Esitimate of the average resources required for a single magnetic configuration: | | | | |
|---|---|---|---|---|
| Task | cores per node* **Nodes** | #runs | Storage (Gb) | Total calculation time (node days) |
| Geometry optimization | 16* **12** | 13 | 20 | 95 |
| Phonon-Calculation | 16* **12** | 1 | 5 | 38 |
| Density of States | 16* **11** | 1 | 2 | 0.5 |
| Band structure | 16* **32** | 1 | 2 | 1.5 |
| **Total for 1 configuration:** | | | **29** | **135** |
| **Total for the entire project (~35 configurations):** | | | **245*** | **4725** |

**1** * after removal of deprecated files of the relaxation.

*The estimates presented in the table above are based on previous investigations of MIL-47(V) system on the TIER1 infrastructure (cf. point 10 III)*.

The values in the table indicate two important aspects of the calculations required in this investigation: (1) Most of the resources are required for the generation of accurate ground-state configurations, (2) due to the presence of **k-point parallelism** in the most recent versions of the VASP program, it is possible to make efficient use of **multi-node parallelisation** (http://www.hector.ac.uk/cse/distributedcse/reports/vasp01/vasp01_kpoint.pdf). For this reason we will use **12 full nodes** for relaxations and phononcalculations, where 12 irreducible k-points are present, while 11 and 32 nodes will be employed for the density of state and band-structure calculations with 41 and 160 irreducible k-points respectively. The systems will require **10-20 GB of memory per node** for the calculations, placing them perfectly in the range of memory available on the TIER 1 nodes. The storage capacity would vary during the calculations (need to retain wave-function coefficients and charge-densities to speed up the structural optimization) with a maximum of about 30 GB for a single magnetic configuration. Upon completion of the entire set of calculations for a single configuration, this amount will be reduced to about **7 GB storage per magnetic configuration**. The number of files of the entire project is limited <15000 files.

The VASP program that will be used in this project makes use of **hybrid openMP/MPI parallelisation** to distribute the calculation over different cores and nodes. Previous experience with Power5 and Power6 machines (Huygens supercomputer at SARA, The Netherlands) learns that vSMP is not suitable for the VASP program.

[1] *Accuracy of structure optimizations, phonons and elasticity of metal-organic frameworks*. An Ghysels, Danny E. P. Vanpoucke, Kurt Lejaeghere, and Veronique Van Speybroeck (in preparation)

7. **Please indicate why the TIER1 is the appropriate machine to perform the computing task (max. 1/2 A4 in Arial 12):**

The required CPU-time for this project is very hard to almost impossible to acquire on existing TIER2 facilities within a reasonable timeframe (The queuing times for such large jobs (12 nodes or more) can easily go up to one week, and this project requires over 100 of this type of calculations) In addition, the presence of MPI parallelism on the TIER1 machine, and K-point parallelisation of the VASP program, makes this infrastructure ideally suited. At the Ghent university, only the gengar (which is currently being decommissioned), gulpin and delcatty clusters are suited for such calculation, and the former two are known to be up to a factor two less efficient than the muk-cluster (TIER1).

8. **Summary of the software required to perform the computing task, and possible installation and compilation instructions (max. 2 A4 in Arial 12). Please clearly provide the following per item in this regard:**
   - **a reference to the software's web page**
   - **the software licence system (open source, GPL, etc.)**
   - **if there is no free academic use of the software, state which licence makes the installation and the use valid on the TIER1 by the Applicant (+ add a copy of the signed licence)**
   - **if need be, which licence server will be used (name + IP address)**
   - **whether the software is already available on the TIER1 (see https://vscentrum.be/nl/tier1-rekenen) and, if this is not the case, compilation and installation instructions (possibly with reference to existing TIER2 installation)**

**Software:**

a) VASP 5.3.3 +DFT D3
   i. http://www.vasp.at/
   ii. Licence: cf. Appendix
   iii. Software is available for users (linked to the licence in appendix)

b) Intel compilers, FFTW, blas, (sca)lapack
   i. Part of the basic installation of the infrastructure

9. **Period during which the task is to be performed:**

The calculations are intended to be performed in the timeslot: June 2014-December 2014.

10. **Describe the results that were obtained within the framework of computing time that was attributed during the past two years on the TIER1 or on other TIER1 or TIER0 supercomputers (max. 2 A4 in Arial 12):**

During the previous project and the pilot period, several aspects of MIL-47/53 type MOFs have been investigated:

I.) Accurate ab-initio calculation of the thermal, electronic and mechanical properties of MOFs

For high quality atomic scale results in solid state physics, quantum mechanical calculations within the density functional (DFT) approximations present the current state of the art. In this work we have studied how the properties of a MOF vary under different numerical settings (real-space and reciprocal space integration grids, the presence of symmetry...). It shows that dense integration grids are required to reduce egg-box effects to manageable levels. In addition, Pulay stresses are shown to artificially push breathing MOFs into a narrow pore configuration. [1] **{~700 node days}**

II.) Functionalized MOFs

In this work, the influence of functional groups on the geometric and electronic structure of MOFs is investigated. It shows the functional group introduces a gap-state and a rotation of the linker molecule. Using the calculated charges of the functionalized MOF frameworks, a force-field is constructed to calculate Henry-coefficients for $CO_2$ adsorption in these frameworks. [3] **{~1000 node days}**

III.) Electronic structure of MOFs

This work was a preliminary test (3 magnetic configurations, 1 system) for the current project. It shows clear differences in behaviour are observable for MOFs with different magnetic configurations. [2] **{~400 node days}**

IV.) Breathing MOFs

In this work, breathing curves for different MIL47-like MOFs were constructed. Clear stability trends as function of the metal cluster are observed. Further processing of the obtained data is still required. **{~8000 node days}**

[1] *Accuracy of structure optimizations, phonons and elasticity of metal-organic frameworks*. An Ghysels, Danny E. P. Vanpoucke, Kurt Lejaeghere, and Veronique Van Speybroeck (in preparation)

[2] *The ab-initio electronic structure of Metal-Organic Frameworks: The case of MIL-47(V).* Danny E.P. Vanpoucke and Veronique Van Speybroeck (in preparation)
[3] *The Role of Functional groups in Metal-Organic frameworks.* Danny E.P. Vanpoucke, Toon Verstraelen, and Veronique Van Speybroeck (in preparation)

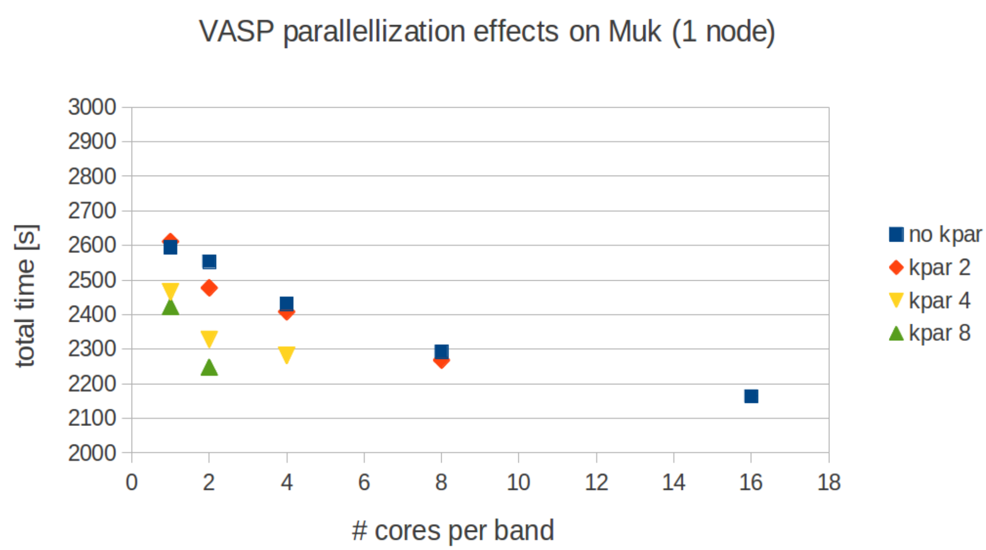
# VASP on Muk: performance

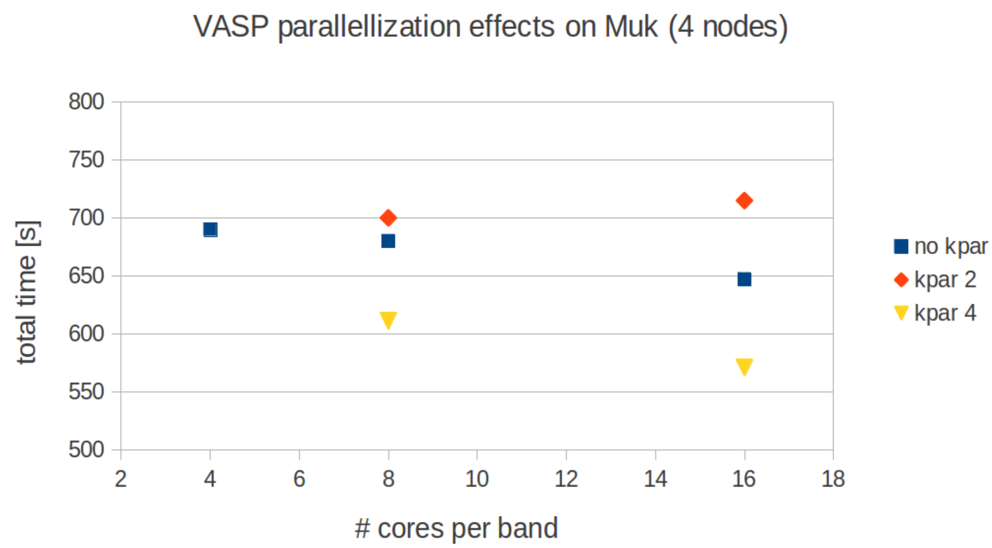
The new VSC Tier1 machine, Muk, consists of:

- 528 computing nodes, with two 8-core Intel E5-2670 (Sandy Bridge) processors each (2.60 GHz clock frequency)
- 64 GB RAM and a 500 GB local 7.2k RPM disk per node
- 400 TB local scratch (DDN SFA10k with 580 of 1 TB 7.2k RPM (data) and 20 of 15k RPM disks (metadata)), accessible through a GPFS-shared file system
- a Mellanox Connect-X FDR Infiniband network
- 4 login nodes, each identical to a computing node

Test problem: Pt induced nanowie on Ge (100) with 320 electronic bands and 8 irreducible k-points in a 3-step geometry optimization (LDA, 345 eV cut-off)

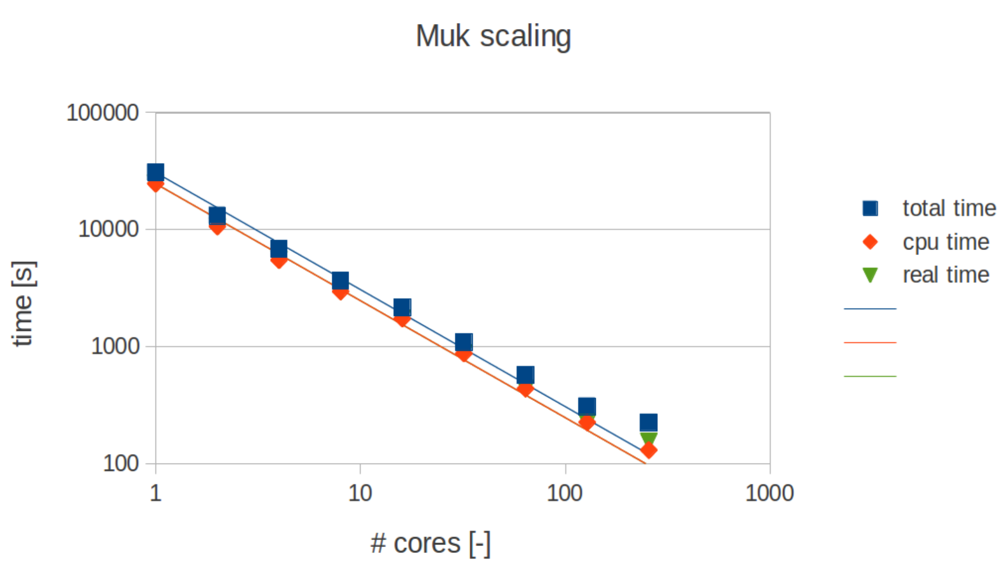
## 1 Optimal settings for VASP

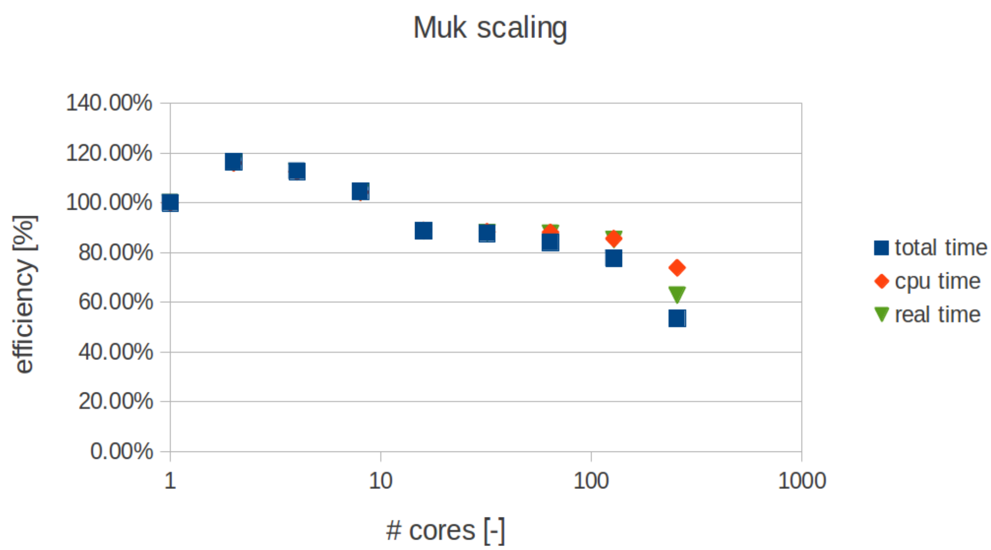





The total duration of a computational run decreases as the number of cores per band (within a node) increases. The optimal setting for NPAR is hence equal to the number of nodes. K-point parallellization is very efficient, but for multinode calculations, it is best to use it only when more than 2 k-points are computed simultaneously. The optimal setting for KPAR is hence equal to the number of k-points, or as large as possible (if this number is larger than 2).

## 2 Muk scaling






Muk displays an almost ideal scaling behaviour up to 100 cores. For even more cores, the cpu time keeps scaling reasonably well, but other issues, such as data transfer, consume increasingly more time.

## 3 Limitations

Preliminary tests with VASP have been performed using cells with up to 1728 atoms (CuZr supercells). 1000-atom structures can still be computed on 512 cores (32 full nodes), but for the 1728-atom cells, it is already necessary to revert to hybrid-mode calculations (partial use of the node), in particular 512 cores or 128 partially filled nodes.

# 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.

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

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

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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DIRECTIE ONDERZOEKSAANGELEGENHEDEN

Afdeling Onderzoekscoördinatie

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- 05/394789
- 05/394790
- 05/394791
- 05/394792

Aan: Prof. Veronique Van Speybroeck
**Vakgroep Toegepaste Fysica**
Proeftuinstraat 86
9000 Gent

| uw kenmerk | ons kenmerk | datum |
|---|---|---|
| | DOZA/IL/DDC/TE/DL/203b-2009 | 31/08/2009 |
| **contactpersoon** | **e-mail** | **tel. en fax** |
| Terry Ediers | BOF@UGent.be | T +32 9 264 30 90<br>F +32 9 264 35 83 |

**Betreft** : ERC Starting Grants – Toekenning BOF onderzoeksmiddelen

01000148830003
Prjdef: I/00057 Doctyp: Contract

Waarde collega,

Het Bestuurscollege van 20 oktober 2008 heeft zich akkoord verklaard met het principe om voortaan een 4-jarig BOF-onderzoeksproject toe te kennen aan de laureaten van een ERC Starting Grant die hun ERC-onderzoeksactiviteiten willen ontplooien aan de UGent.

De betreffende onderzoeksmiddelen worden u als houder van een ERC Starting Grant door de voorzitter van de Onderzoeksraad[1] toegekend. Het project zal gefinancierd worden voor een bedrag van € 193.000.
Hiervan is € 160.000 voor personeelsmiddelen (4 jaar doctoraatsbursaal)
€ 33.000 voor werkingsmiddelen

Deze middelen staan beschikbaar op WBS-element I/00057/02, met ingang van 1 oktober 2009, voor een totale periode van 5 jaar (duur ERC Grant). Deze periode is niet verlengbaar. Aan deze middelen wordt het codenummer 05Z40309 toegekend. Gelieve dit nummer in al uw briefwisseling te vermelden.

Om de doctoraatsbursaal aan te werven, dient het gebruikelijke formulier "Voorstel tot aanwerving contractueel ATP, WP en doctoraatsbursalen" bezorgd te worden aan de directie Personeel en Organisatie (document terug te vinden op https://www.ugent.be/nl/werken/aanwerving/formulieren/wp/). In bijlage kan u reeds een 'Voorstel tot Aanwerving' terugvinden met in vet de reeds gekende gegevens voor u ingevuld.

Een eventuele meerkost voortvloeiend uit een door u voorgestelde afwijking van de toegekende personeelskenmerken (doctoraatsbursaal) zal leiden tot een compensatie ten laste van de toegekende werkingsmiddelen en/of een vermindering van de periode van aanstelling.

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[1] Bevoegheid verleend bij beslissing van het Bestuurscollege van 20 oktober 2008