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Deliverable D2.3 QE and SIESTA workflows for advanced materials parameters (Task 2.2.3-5): Part 1



# D2.3

# QE and SIESTA workflows for advanced materials parameters (Task 2.2.3-5): Part 1

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# **1 Executive Summary**

At the core of the INTERSECT [1] project is the Interoperable Material to Device (IM2D) simulation box for the on-demand calculation of materials properties. The syntactic infrastructure for such capability is provided by AiiDA [2] through the availability of optimized workflows.

In this document, that updates and complements the content of deliverable D2.2 (M13), we present the AiiDA workflows for materials properties implemented as part of INTERSECT with particular focus on the features designated to provide more advanced materials properties. AiiDA infrastructure manages the data pipeline and process workflows; Quantum ESPRESSO (QE) [3] and SIESTA [4] are the Density Functional Theory (DFT) engines used for the actual calculation of the materials properties. The list of implemented materials on demand includes: total energy, energy band structure, energy band gap, effective mass, dielectric function, (charged) defect formation energy [5], and NEB [6]. Other advanced properties will be implemented and discussed in Deliverable D2.7 due at M37.

Within the INTERSECT project, the implemented materials on demand are made available to the GINESTRA<sup>™</sup> code [7], through aiida-ginestra plugin (see also D2.1 and D2.4) to upscale the device-oriented GINESTRA<sup>™</sup> code to advanced materials properties (materials-to-device and device-to-materials interoperable pathways).

#### **2 Introduction**

The AiiDA infrastructure is designed to automate the computation of materials properties from first-principles calculations through the use of highly-optimized workflows. In the context of the INTERSECT project, the AiiDA workflows are exploited towards establishing a control centre for computation as well as for exchange of information – for both, input and output quantities – between the quantum mechanical simulation tools (QE and SIESTA) and the GINESTRA<sup>TM</sup> software for atomistic and continuum modeling of electronic devices.

Algorithms for the AiiDA workflows have been designed to fit the needs of the INTERSECT project, as for example in the choice of the physical parameters required for the simulation of the properties of the electronic device (DoA, ANNEX1). The implemented workflows include computation of structural and electronic properties, such as band gap, effective mass, dielectric constant, etc. (see also deliverable D1.1). The present deliverable complements the description started in D2.2 of the implementation of specific workflows for advanced on-demand properties (e.g., structural import data and relaxation, band structure calculation, determination of defect formation energy, computation of dielectric constants, and more).

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#### **2.1 About this document**

This document represents the deliverable D2.3 of the INTERSECT project and it is prepared under the Task 2.2. "Simulation hub: Automated workflows for materials' data on demand of Work Package 2 – Interconnection and Interoperability Implementations. The content of this document is intended to complement D2.2 where the general structure of AiiDA workflows has been discussed. Within the present deliverable, specific workflows for advanced on-demand properties will be described.

#### **3 AiiDA workflows**

## 3.1 AiiDA in a nutshell

AiiDA is a Python infrastructure designed for optimal use of high-performance computing by means of an automated framework for high-throughput computational workflows. Its software architecture is conceived with the dual goal of providing maximum efficiency in the management of workflows as well as full control and retrieval of the input/output data provenance. The schematic overview of AiiDA is displayed in Figure 1.



Figure 1. Schematic overview of AiiDa v1.0 [8]. AiiDA is hosted at https://github.com/aiidateam/aiida-core

Calculations and workflows are implemented in the custom language provided by AiiDA's core API and run by the AiiDA engine. All the information needed to enable reproducibility of the results is automatically recorded in the provenance graph. The content of the provenance graphs is stored in a file repository on the local file system, including a relational database. The mapping between the database and the Python API is performed by an Object Relational Mapper (ORM). Besides the

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workflow language, the ORM also provides the tools to interact with the nodes of the provenance graph and inspect their content. The QueryBuilder is the tool that allows efficient traversal of the provenance graph to select (sets of) nodes of interest.

The end-users communicate with AiiDA through either a command line interface called VERDI [9], or via Python shell (scripts). The REST API can be used to query the provenance graph through HTTP calls. AiiDA itself can communicate with computing resources either locally or over SSH to run calculations on those resources and comes with built-in support for most well-known and used job schedulers.

AiiDA is conceived to be a domain-agnostic infrastructure, capable of delivering the same benefits to any type of complex task in the whole spectrum of computational science. Within this logic, a flexible plugin system has been designed to provide users with the possibility to extend core functionalities in order to match the needs for a specific computational task. By means of the plugin system, it is possible for example to add custom data types, to interface external simulation codes with specific input generators and parsers, and to implement custom workflows. Plugins can be implemented and installed completely independently of the AiiDA core code. An online registry of plugins exists, where users can upload their plugin packages for community use.

In order to introduce the possibility of interruptible workflows, AiiDA implements the so-called **workchains**, a process class that allows users to specify units of work (like the processing of data or the submission of subprocesses) as steps (see D2.2). In this way, the AiiDA engine controls the execution of workflows between steps, preventing any possibility for the next step in the chain to start before all subprocesses of the previous steps have finished. Most importantly, if the engine is stopped by any event, no progress is lost because, upon restarting, the engine will continue the workflow execution from the last persisted step (or the engine will keep waiting for running subprocesses, if any).

The existence of workchains encourages to write modular workflows. Lower-level workchains are dedicated to specific code-dependent tasks, e.g., error handling, restarting or automatic tuning of parameters. Higher-level workchains implement additional functionalities, hence providing fully automated turn-key solutions that separate scientific know-how from code-specific technical aspects of the simulation at hand. Finally, being implemented in Python, workchains allow users to exploit the full power of this programming language, as well as direct access to the content of the provenance graph. This is used in the implementation of powerful error-handling mechanisms that can deal with failures of calculations run as part of the workflow.

The various AiiDA functionalities required within the INTERSECT project are implemented across several software packages that will be introduced next. In the following we describe two packages,

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namely aiida-quantumespresso and aiida-siesta, which interface AiiDA with the Quantum ESPRESSO and SIESTA codes, respectively.

## 3.2 Aiida-quantumespresso package

The availability of automatic workflows for the calculation and handling of physical quantities for the data-on-demand aspects of the INTERSECT project is of general and pivotal importance for the realization of a multi-physics, multi-code infrastructure of the type envisaged with the IM2D simulation box. With the development and use of a specific plugin (repository at https://github.com/aiidateam/aiida-quantumespresso), AiiDA offers the possibility to access and automatically control the execution of complex quantum mechanical calculations performed with the QE suite [3]. A number of workflows specific to this software have been implemented to allow highly-accurate calculations of materials properties from first principles. In general terms, the AiiDA workflows/workchains cover the whole process from the retrieval of the initial structure of the system under investigation to, e.g., the determination of the ground state, band structure, and all the needed steps in order to access the final physical quantity of interest, as shown in Figure 2 for the case of relaxation of diamond crystalline structure.





Details of the several workflows implemented as part of the aiida-quantumespresso package will be presented in Section 4 of the present deliverable.

# 3.3 Aiida-siesta package

A plugin (repository at <u>https://github.com/siesta-project/aiida\_siesta\_plugin</u>) is available also for the SIESTA electronic structure software [4], which, at variance with QE, uses a basis set of atomic orbitals. Nevertheless, the internals of the code are wrapped by the plugin, which handles largely the same

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basic AiiDA objects as the QE plugin (e.g. for structures, k-points, forces, etc). Workchains specific to SIESTA are available for computing, in a highly-automated and restartable fashion, a number of materials properties, as detailed in Section 4 of the present deliverable.

## 3.4 Aiida-POST

Aiida-POST is a plugin that extends the functionalities of the AiiDA's web interface that conforms to the Representational State Transfer (REST) architecture. The REST API allows for querying the database through a web service, exposing the underlying database where AiiDA is running, for their node properties and relationships. AiiDA-POST was developed to fulfil the specific needs of the INTERSECT project and it is <u>https://gitlab.cc-asp.fraunhofer.de/intersect/ext to aiida</u>. AiiDA-POST acts like a bridge to convey information to and from AiiDA through HTML communication. It deals with the submission of workflows, retrieval and query of data, material structure import, status checking of ongoing calculations, and more. All of that can be done locally or remotely through HTTP calls.

#### 3.5 AiiDA-Defects

AiiDA-defects, a plugin of the AiiDA platform, is a python package designed to automate calculations of defect formation energy (DFE) from first principles. The original implementation has been done for integration with QE, as a DFT engine. However, since the AiiDA-Siesta package can often use the same AiiDA objects as QE and employ the existing implementation, most solutions already developed for QE can be straightforwardly used for the SIESTA extension. AiiDA-defects consists of several modules allowing the creation, exploration, and manipulation of pristine and defective cell/supercell structures and containing AiiDA workflows to automatically calculate defect formation energies according to different correction schemes (see Sec. 4.8). The alpha version of the AiiDA-Defects plugin is available on GitHub (repository at <a href="https://gitlab.cc-asp.fraunhofer.de/intersect/aiida-defects">https://gitlab.cc-asp.fraunhofer.de/intersect/aiida-defects</a>), it has been tested as well as used for production; an improved beta version is currently being developed.

# 4 Advanced properties on-demand

An important concept that makes possible the goals of the INTERSECT project is *the automation of advanced simulations*. In particular, it allows the calculation of the properties when they are required without requiring a large overhead. In this section, we list the properties for which we developed AiiDA workflows for their calculation on-demand. Many of those properties require from the user uniquely the selection of the material and the code, when there is more than one DFT code with the same capability (QE, SIESTA).

Most of the DFT codes, however, require many inputs even for the simplest calculations. In order to simplify the procedure and make the IM2D more user friendly, we developed various protocols to automatically define non-essential inputs. Non-expert users can override most of the inputs, while expert users can access and handle them when needed. This will be discussed in detail in D2.5 in

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terms of the semantic upscale of the IM2D infrastructure. Other workflows such as DFE and NEB, however, are very specialized and - in this initial implemented version - require further inputs from the users.

# 4.1 COD structures importer

The first step to calculate the properties of a given material is to provide its atomistic structure. We implemented a plugin to auxilate the user in this process: an importer from the Crystallography Open Database (COD) [11] (see also D4.2 and D4.6).

The COD is a popular and open-access database for organic, inorganic, metal-organics compounds, and minerals. It allows the contributions of published and unpublished crystal structures by registered users and counts with more than 300.000 entries [12]. To query and retrieve structures in the COD databases, an importer plugin was developed with the following entry in the aiida package:

## aiida-core/aiida/tools/dbimporters/plugins/cod.py

A query can be performed by simply providing the chemical formula, e.g., *NaCl*. The COD database responds informing a list of structures that match the query. These structures are then stored in the AiiDA database and become readily available to have their properties calculated on-demand. The COD is therefore, one of the main sources of material structures in the Intersect scope.

# 4.1 Ground-state atomistic structure (relaxation)

The ground-state structure is obtained via the relaxation of the atomic structure, through total-energy-and-force minimization procedure. A workchain for this property was implemented in the *aiida-quantumespresso* package:

#### aiida\_quantumespresso/workflows/pw/relax (PwRelaxWorkChain)

It handles the atom position and unit cell volume relaxation. Also, it provides error checking, such as sanity checks for the volume change between iterations, restart capabilities, and the option for a final self-consistent-field calculation (SCF). By employing this workchain in a database with over 30.000 materials, a success rate for automatic relaxation over 70% is obtained.

In turn, the relaxation workchain is based on the basic workchain for Quantum ESPRESSO PW calculations:

# aiida\_quantumespresso/workflows/pw/base (PwBaseWorkChain)

It handles the basic restart and error handling of the PwCalculation class, in case of failure due to recoverable problems. This workchain also allows us to pass a family of atomic pseudopotential rather than input them individually for each chemical element. Also, the k-point mesh, used for the Brillouin

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Zone sampling, can be automatically generated by providing just the required spacing between k-points in the reciprocal space. In practice, every other workchains for Quantum ESPRESSO are constructed, directly or indirectly, upon the *PwBaseWorkChain*.

Similarly, we have also a base workchain for calculations with Siesta:

#### aiida-siesta/workflows/base (SiestaBaseWorkChain)

In the case of SIESTA, the base workchain can be directly used to perform the relaxation of a structure, by simply passing the appropriate option among the input parameters. If relaxation does not converge in a single SIESTA run, the workchain restarts automatically.

# 4.2 Total energy

The total energy of the system is calculated in the final SCF calculation after the structure relaxation. Therefore, it is one of the outputs of the relaxation workchain. The SIESTA plugin always includes the total-energy among its output-values dictionary, which is also returned by workflows.

# 4.3 Electronic band structure

The band structure of the materials are calculated with the *PwBandStructureWorkChain*:

# aiida\_quantumespresso/workflows/pw/band\_structure (PwBandStructureWorkChain)

This workchain firstly determines the calculation inputs based on the specified protocol. Then it employs the relaxation workchain. It then determines the symmetry of the crystal structure and generates a standardized high-symmetry path through the Brillouin zone using the SeeKPath analyzer available in AiiDA. Finally, it computes the band structure, which is stored as node objects in the AiiDA database. An example of automated band structure calculation for Si bulk is shown in Figure 3.

In SIESTA, the electronic band-structure is computed by the *BandgapWorkChain*, which is an extension of the *SiestaBaseWorkChain* that introduces some logic to automatically obtain the bands as part of the workflow to determine the metallic or insulating nature of the material and, possibly, the band gap (see also D2.1).



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**Figure 3**. Band structure on a standard high-symmetry path for bulk Si, computed with the PwBandStructureWorkChain.

# 4.4 Band gap

The band gap is determined through the analysis of the band structure. Therefore, the band-gap workchains are based on the, e.g., *PwBandStructureWorkChain*. This property can be calculated with either Quantum ESPRESSO and/or SIESTA:

# aiida\_post/workflows/bandgap (PwBandGapWorkChain)

#### aiida-siesta/workflows/bandgap (BandgapWorkChain)

That is because the workchains to calculate the band structure for Quantum ESPRESSO and SIESTA produce the same AiiDA object. In this way, the band gap can be calculated with the same underlying code. The success rate is similar to that of the relaxation workchain.

#### 4.5 Effective mass

The effective mass is also extracted from the analysis of the band structure. Therefore, the calculation of this property is also based on the *PwBandStructureWorkChain*. We perform a quadratic fitting of the band structure near the top/bottom of the valence/conduction bands, typically at the centre of the Brillouin zone. From the band curvature, the effective mass for electrons or holes is inferred (Figure 4). It was implemented as an extra calculation in the bandgap workchain:

aiida\_post/workflows/bandgap (get\_effective\_mass)



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*Figure 4.* Example of the fitting procedure to determine the curvature of parabolic dispersion of the band structure near the center of the Brillouin zone.

Since, as discussed above, SIESTA and QE generate the same AiiDA band-structure object, SIESTA can reuse the function implemented for the fitting to obtain the effective mass.

# 4.6 Dielectric constant

The dielectric constant accounts for the amount of electric potential energy that can be stored in a given volume of the material in the form of induced polarization due to an external field. It can be easily calculated through Density Functional Perturbation Theory (DFPT) with the PHonon code of the QE suite [13]. The workflow was implemented in the *aiida-defects* package (see below), as it is an input for other workchains in that package.

# aiida\_defects/formation\_energy/formation\_energy\_qe (get\_permittivity)

The PHonon code calculates the static dielectric tensor, and the dielectric constant is obtained by averaging the diagonal terms of the tensor. In the test case for NaCl (GGA-PBE calculation) the dielectric constant was obtained to be 5.66, in agreement with the experimental results. The present implementation supports advanced solutions for correction of the electronic structure (e.g. DFT+U), beyond standard DFT accuracy. For instance, in the case of crystalline GeSe the value of the dielectric constant is 18.0 for GGA-PBE and 15.0 for corrected PBE+U calculation, in closer agreement with the experimental value 15.3 [14].

In the case of SIESTA, the electronic contribution to the static dielectric constant can be computed, via the Kramers-Kronig (KK) relations, from the frequency-dependent imaginary part of the dielectric constant, which is directly related to the optical absorption, and computable using the standard perturbation-theory expressions involving transition energies and the matrix elements of the

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momentum operator. A simple workflow that performs the computation of the optical absorption and then performs the KK post-processing step is implemented in the *OpticalWorkchain*.

# 4.7 Density of states

The *PdosWorkChain* was implemented to calculate the total and partial density of states (DOS). The outline of this workchain is as follows:

- SCF (pw.x), to generate the initial wavefunction
- NSCF (pw.x), to generate eigenvalues with a denser k-point mesh
- Total DOS (dos.x), to generate total densities of states
- Partial DOS (projwfc.x), to generate partial densities of states by projecting wave functions onto atomic orbitals

The *PdosWorkChain* is implemented in the *aiida-quantumespresso* package:

#### aiida\_quantumespresso/workflows/pdos/base (PdosWorkChain)

An example of the automatic calculation of the total and partial DOS (pDOS) for a Mott metal-oxide, namely iron sulfide, is shown in Figure 5 as a function of the Hubbard U correction.



*Figure 5.* Automatic calculation of total and partial DOS of Mott insulation in iron sulfides in the test suite of the PDOS plugin.

Using SIESTA, the total DOS can be obtained in a straightforward manner from the file containing the eigenvalues, which is always produced when using a diagonalization-based solver. The pDOS can be computed in a direct way, without the projections used in QE, since the underlying basis set consists of pseudo-atomic orbitals (PAOs). Both sets of results (DOS and pDOS) can be computed with the *DOSWorkchain*, which leverages the base workchain to optionally relax the structure and to re-sample the electronic structure with a denser set of k-points.

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It should be pointed out, however, that a further step of interface specification is needed to make these DOS workflows fully integrated in the IM2D and accessible to  $GINESTRA^{TM}$ . At the simplest level, workflows could provide the total DOS at the Fermi level, either intrinsic or specified from the  $GINESTRA^{TM}$  side. A further step is to provide a total-DOS curve within a specific energy range. The most detailed pDOS information would require a specification of exactly which PAOs (or projections in the case of QE) should be involved. The refinement of the interface requires the formal definition of more terms in the gluing ontology.

#### 4.8 Defect formation energy

Defects often form and strongly affect the structural, electronic, elastic and optical properties of crystalline and amorphous materials [15]. The long-term stability and performance of several semiconductor devices is governed by the creation/annihilation and transport of defects and impurities [5,16]. The defect formation energy is a key property to describe the defects formation in materials, as it allows to determine the most favourable defects, i.e., the most likely to form, in a given system and under selected environmental and thermodynamic conditions [16].

The defect formation energy and, more generally, the thermodynamics of defects in solids are advanced properties, that cannot be straightforwardly extracted by the output of standard DFT calculations. Rather, this requires a more refined theoretical framework and the definition of a multistep post-processing procedure, which we implemented in a set of workflows that constitutes the aiida-defect plugin.

#### 4.8.1 Theoretical framework

The point defects in solids include either the removal of an atom from a lattice site, the replacement with another atom, or its embedding in an interstitial site. The formation of point defects and/or of free electron and/or hole carriers constitute a defect reaction [17], whose enthalpy at fixed pressure and fixed temperature is commonly referred to as the DFE. In thermodynamic equilibrium, the concentration of a defect is proportional to  $e^{-E^f/k_BT}$ , where  $k_B$  is the Boltzmann's constant, T is the temperature and  $E^f$  is the formation energy of the defect. Thus, the knowledge of DFE is key to having a detailed description of non-ideal materials and investigating materials as they actually enter in real systems, e.g. synaptic devices. The formation energy of a defect X in the charge state q is defined as [5]

$$E^{f}[X^{q}] = E_{tot}[X^{q}] - E_{tot}[bulk] - \sum_{i} n_{i}\mu_{i} + q[E_{F} + E_{v} + \Delta V_{corr}].$$
(1)

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 $E_{tot}[X^q]$  is the total energy derived from a supercell calculation – usually performed at the DFT level – of the system containing the defect X relaxed in the charge state q, and  $E_{tot}[bulk]$  is the total energy for the pristine crystal (host, generally bulk) using an equivalent supercell. The integer  $n_i$  indicates the number of atoms of type *i* (host or impurity atoms) that have been added to  $(n_i > 0)$  or removed from  $(n_i < 0)$  the supercell to form the defect, and the  $\mu_i$  are the corresponding chemical potentials, representing the energy of the reservoirs with which atoms are being exchanged.  $E_F$  is the Fermi energy, referenced to the valence band maximum in the host,  $E_v$ , and represents the energy of the reservoir for electrons and/or holes. The last term in Eq. (1),  $E_{corr} = q\Delta V_{corr}$ , is a correction term to

align the reference potential in the defective supercell with that in the host system. This accounts for finite-size corrections within the supercell approach, such as electrostatic and/or elastic interactions between supercell replicas, or finite k-point sampling, as in the case of shallow defects. Eq.1 provides the fundamental expression for the stability of the charged defects and the charge transition states, as a function of the Fermi level.

## Chemical potential

The chemical potential  $\mu_{\alpha}$  of a species or compound  $\alpha$  represents the energy of the reservoir with which the species or compound is exchanged and relates with the thermodynamic stability of a material, its component elemental species and competing phases. The range of elemental chemical potentials gives indications on phase stability as a function of the growth condition, and it is crucial to predict the nature and concentration of defects present in the sample [18]. The assumption that a selected material is thermodynamically stable [19] leads to a set of conditions on the elemental chemical potentials, from which the stability range (if it exists) can be extracted. These conditions have been formalized in a computational procedure [18], which provides the chemical potentials starting from total energy calculations of elemental or parent systems. This procedure has been implemented in the form of an automated algorithm included in the aiida-defect package.

#### Fermi energy

The Fermi energy,  $E_{F'}$  represents the chemical potential of the electrons and the analysis of the variation of the defect formation energy as a function of  $E_F$  gives information on the nature of the dominant charge carriers [20]. Moreover, since equilibrium defects and carriers concentrations – at a given temperature T – depend on  $E_{F'}$  a value of the Fermi energy referred to as the self-consistent  $E_F$  can be obtained self-consistently from the charge neutrality condition imposed at equilibrium [17]. More specifically, in a solid-state insulator/semiconductor composed of one or more atomic species, in thermodynamic equilibrium with the environment, both electron and hole carriers can be present

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through thermal activation across the band gap  $E_{g}$ . The relative carrier concentrations read, respectively,

$$n_{0} = \int_{E_{g}}^{\infty} f_{e}(E)\rho(E)dE; \ p = \int_{-\infty}^{0} \left[1 - f_{e}(E)\right]\rho(E)dE, \ (2)$$

and where  $\rho(E)$  is the density of states per unit volume, while  $f_e(E)$  is the Fermi-Dirac distribution function. From quantum statistical mechanical considerations follows that the concentration of a defect X in the charge state q can be written as [15,17]:

$$C_{X^{q}} = N_{X}g_{X^{q}}exp\left(-\frac{E^{f}}{k_{B}T}\right), (3)$$

where  $N_{\chi}$  is the density of crystal sites where each defect can form, and  $g_{\chi^q}$  is the degeneracy of the defects' charge states. Ultimately, the condition of charge neutrality can be expressed as

$$n_0 - \sum_{X} \sum_{q} q C_{X^q} = p_0.$$
 (4)

Since each term in Eq. (4) is a function of the Fermi energy, the self-consistent  $E_F$  can be obtained by solving self-consistently Eqs. (1-4) at a given *T*. All these quantities can be thus obtained starting from quantities extracted from DFT simulations. The entire procedure is also implemented within the aiida-defect package.

#### Finite-size supercells and electrostatic corrections

In solid-state physics, defects are usually modeled in a supercell subject to periodic boundary conditions. The use of supercells, however, implies that the isolated defect is replaced by a periodic array of defects, often containing unrealistically large defect concentrations and resulting in artificial interactions between the defects that cannot be neglected [5]. The most common numerical schemes [5,21] insert *a posteriori* a correction term  $E_{corr}$  term the definition of DFT, see Eq. (1). Among the several schemes proposed in the litterature (e.g., Makov and Payne [22], Lany and Zunger [23]) here, we focused on the approach originally developed by Freysoldt, Neugebauer, and Van de Walle [24], further extended by Komsa and Pasquarello [25], now implemented in the AiiDA-defects plugin.

The approach by Freysoldt, Neugebauer, and Van de Walle (FNV) [24] is based on the splitting of the creation of charged defects into three steps. First, the charge q is introduced for a single defect by adding or removing electrons from the defect state, while all other electrons are frozen, generating an

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unscreened charge density  $\rho_c$ . Second, the electrons are allowed to screen the introduced charge, giving rise to a change in the electrostatic potential of the charged defect with respect to the neutral defect  $V_{q/0}(r) = V_{defect, q}(r) - V_{defect, 0}(r)$ . Third, the artificial periodicity and a compensating homogeneous background charge  $-q/\Omega$  ( $\Omega$  being the volume of the supercell) are imposed. The FNV correction is, then, expressed as

$$E_{corr}^{FNV} = E_{lat} - q\Delta V_{q/0} \qquad (5)$$

where  $E_{lat}$  is the macroscopically screened lattice energy of a model defect charge distribution  $\rho_c$ (with neutralizing jellium background  $-q/\Omega$ ) given by the difference between the electrostatic energies of the isolated (system described in the first step) and periodic defect charge distributions (system described in the third step). Different charge models give different lattice energies: for a point-charge model,  $E_{lat}$  would correspond to the first term in  $E_{corr}^{MP}$  [21]. The potential alignment term (last term in Eq. (5)) is obtained by comparing the potential from the model charge to the difference neutral) potential (charged VS in the DFT calculation:  $\Delta V_{q/0}(r) = \left(V_q^{DFT} - V_0^{DFT}\right)|_{far} - V^{model}|_{far}$ [24]. The FNV scheme applies to supercells and defect charge distributions of any shape and yields corrected defect formation energies that are largely independent of the adopted charge model, provided the defect charge is localized within the simulation cell. Komsa and Pasquarello (KP) [25] introduced a generalization of the FNV correction scheme conceived to be suitable for systems with one or more interfaces. The scheme combines classical electrostatics and electronic-structure calculation by extracting from the latter the dielectric profile and the electrostatic potential. Spurious electrostatic interactions are therefore removed while retaining the dielectric and quantum-mechanical features of the considered system.

#### 4.8.2 Description of the AiiDA-Defects plugin

The AiiDA-Defects plugin of the AiiDA platform is a python package designed to automate calculations of defective systems with QE through AiiDA. It consists of several modules allowing the creation, exploration and manipulation of pristine (host) and defective supercell structures starting from the conventional/unit cell of a selected material through AiiDA (*aiida\_defects/tools*) and containing AiiDA workflows to calculate defect formation energies according to FNV-KP correction schemes (*FormationEnergyWorkchainQE*) automatically. The latter includes workflows for the automated calculation of the DFT ground-state electronic structure, electrostatic potential and charge densities (*aiida\_defects/pp*), the macroscopic bulk dielectric constant (*formation\_energy\_qe(get\_permittivity*)) and the component elemental chemical potentials (*formation\_energy/chemical\_potential*), which can be used independently from the other modules of the package.

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The AiiDA-Siesta package, with a previous step of generating the appropriate electrostatic potential information using the same AiiDA objects as QE, can reuse the existing implementation to compute the formation energy of charged defects. This is in fact a very powerful trend in the AiiDA ecosystem: workflows are being increasingly abstracted so that they work basically unchanged for various underlying codes. In addition, it is foreseen that individual pieces of a workflow might be handed over to the code most suited to them. In this particular example, Siesta could relax structures and QE compute the dielectric constant.

# Modules for defect creation and structure manipulation (*aiida\_defects/tools*)

Starting from a given host structure, which can be a unit/conventional cell or a supercell, the *defects.py* and *structure\_manipulation.py* modules allow the automatic creation of any desired supercell pristine (host) and/or defective structure containing vacancies, substitutional defects (and/or antisites) or clusters of defects obtained by the combination of several vacancies and/or substitutional defects. Two (related) supercells – one host and one defective – can be compared inferring the positions and types of any defects present and the distance between a selected defect and the other atoms' sites computed. These modules employ the capabilities of *pymatgen* [26].

# Workflows to obtain required ground-state DFT quantities

Workflows based on the basic workchain for QE PW calculations *PwBaseWorkChain* are implemented in the *formation\_energy\_qe.py* module. It can be decided either to perform automatic self-consistent field or relax simulations to obtain the DFT ground-state total energy – ingredient in the calculation of the defect formation energy (Sec. 4.8.1) – for the host supercell structure, and the defective supercell structure both in its neutral and charged state (with given charge *q*), or to specify the AiiDA node corresponding to such calculations if already performed. The DFT total energy is then properly used in the calculation of the defect formation energy (Sec. 4.8.1). Workflows based on the workchain for QE PP calculations *PpWorkChain* are implemented in the *pp/pp.py* module to automatically obtain the DFT electrostatic potential and ground state charge densities for the mentioned systems. Such quantities are then used in the calculation of the FNV-KP correction scheme (Sec. 4.8.1). The dielectric constant that enters in the formula of V<sup>model</sup> is calculated as described in Sec 4.6.

# Workflows to calculate the chemical potentials

The *ChemicalPotentialWorkchain* and the *FermiLevelWorkchain* workchains included in *formation\_energy/chemical\_potential* implement the approaches described in Sec. 4.8.1 to automatically determine the Fermi energy and the ranges of the elemental chemical potentials of the

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species composing the material under study. The density of states  $\rho(E)$  that enters in Eq.2 is obtained from following the *PdosWorkChain* described in Sec 4.7.

# Workflows to compute the desired corrections to the defect formation energy

Workflows in *formation\_energy/potential\_alignment* implement the Makov and Payne, and the Lany and Zunger correction schemes for the defect formation energies described in the previous Section. While the KP correction scheme, or Gaussian counter-charge method, and the scheme by FNV, are implemented workflows formation\_energy/corrections, in in in particular the GaussianCounterChargeWorkchain, PotentialAlignmentWorkchain, the and the ModelPotentialWorkchain workchains. In the improved version of AiiDA-Defects under development, the correction of choice will be the KP-FNV Gaussian counter-charge approach as it provides a rather general framework for calculating energy corrections for defects in supercells for bulk materials or including up to two interfaces.

To test the capabilities of this advanced set of workflow, we calculated the formation energy of point defects in crystalline GeSe, which is one of the materials of interest for the realization of memristors and selectors, studied in WP3 (pilot 1). The provenance graph for the evaluation of the formation energy of a Ge vacancy by means of the AiiDA-defects plugin is reported in Figure 6.



*Figure 6.* Provenance graph for the calculation of the formation energy of a Ge vacancy in crystalline GeSe through the AiiDA-Defects plugin.

Figure 7 summarizes preliminary results obtained with the AiiDA-Defects approach, in case of a Ge vacancy ( $V_{Ge}^{q}$ ), with charge state *q* ranging from -3 to 0, in crystalline GeSe (structure in the Figure).

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The plot shows the different stable charged states as a function of the Fermi energy and the corresponding charge state transition (bold dot). Charged defects (q=-1 and q=-2) are more stable than neutral one (q=0) and the highest charged state (q=-3) for any possible value of the  $E_F$  from  $E_F=0$  eV (VBT) to  $E_g\sim 1$  eV (CBM). The complete set of results about point defects in GeSe will be collected for publication in a scientific journal.



**Figure 7**. Formation energy of neutral and charged (charge states: q=-1, -2, -3) Ge vacancies in a 3x2x1 supercell of crystalline GeSe as a function of the Fermi energy calculated through the AiiDA-Defects plugin.

## 4.9 Barrier energies for diffusion of defects (NEB workflow)

The diffusion of a defect can be seen as composed of individual events, in each of which the defect moves from one site in the crystal to another. In statistical-mechanical terms, the probability of an event depends on its activation energy, in this case the height of the energy barrier along the path from the initial to the final state. This is an example of a more general class of problems (including catalysis, ion conductivity and other chemical reactions) in which conformational changes can be described by a path along the *Potential Energy Surface* (PES) of the system. The optimal or *Minimum Energy Path* (MEP) passes through a saddle point (the "transition state") in going from the initial or reactants basin to the final or product basin. Various algorithms for transition-state search have been developed over the years. When the initial and final states are well-defined, one of the methods of choice is the Nudged Elastic Band (NEB) algorithm, which uses a string of images of the system in configuration space to represent a path. The images are figuratively linked by springs along the local tangents to the path, and react also to the projection of the forces derived from the PES in the

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perpendicular direction. An initially guessed path is then converged towards the MEP, and the transition state approximated by the position(s) of the highest-energy image(s). See Fig. 8, and refs [6,27-28] for more details about the basic algorithm and some refinements added over the years.

$$\mathbf{F}_i^{\text{NEB}} = \mathbf{F}_i^{\perp} + \mathbf{F}_i^{S\parallel},$$



*Figure 8.* Sketch of the potential energy surface with initial and optimized transition paths joining two stability basins. In the inset, the various components of the forces involved in path optimization with the NEB algorithm.

Given the initial and final states, and a few operational parameters (e.g., number of images, values of the spring constant(s), tolerances for convergence) the NEB algorithm produces directly the energy barrier, which can be used as a parameter in a coarser-grained simulation (for example, one based on the Kinetic Monte Carlo method).

Since there are many kinds of possible defects in a crystal, and a number of diffusion mechanisms for each of them, the complexity of a barrier-energy workflow comes mainly from the *specification* of the physical processes taking place (i.e, vacancy exchange, interstitial diffusion, pair exchange) and of the details about the sites involved. Hence, the most appropriate structure for the workflow is a layered one, with the specification at the outer layers, and the NEB workhorse at the core. The design of the outer layer will take into account an *ontology* of defects and diffusion processes, which is within the scope of WP1.

In more detail:

# (Specification layer):

• Starting from a "pristine structure", insert an original defect (interstitial, vacancy, etc), to generate a "defected structure" (so far unrelaxed).

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• Using the "defected structure", consider the process(es) taking place, and sketch a path (e.g., for an atom exchange, which path might atom A take, with atom B using another route for steric reasons). This is where some degree of physical intuition enters.

The input(s) for this stage (and so for the whole workflow) could formally be just the pristine (host) structure and the kind of defect considered. A very high-level and complete workflow takes care to determine the possible site(s) for the defect, and the possible diffusion mechanisms, and analyze the barriers for each. Given the variety of processes that can be involved in diffusion, automating such a task in a turn-key workflow is extremely challenging, and in practice the inputs are the following:

- A textual annotation for the kind of process involved.
- The initial and final points of the diffusion event considered.

The implemented workflow has support for a few representative kinds of processes: vacancy exchange, atom exchange, and interstitial diffusion. Each of these need specific heuristics for the generation of the starting path.

The outputs of this stage are the initial and final structures, and possibly a set of intermediate points in the path.

# (Preparation and execution of the NEB procedure):

- The next stage optionally relaxes the endpoints, and generates a set of starting images for the NEB. Here the options are the number of images, and the interpolation method (i.e., the starting path from the initial to the final state). The preferred one is the IDPP (image-dependent pair potential) scheme [28], implemented in the ASE package (https://wiki.fysik.dtu.dk/ase/), which aims at interpolating distances among atoms rather than the coordinates themselves. End-point relaxation is formally an option but almost universally needed. The end results are the relaxed end points and the set of images.
- The results of the previous stage are directly piped into the current NEB workhorse already implemented in SIESTA using the internal scripting capabilities afforded by the embedded Lua interpreter. The options here are the basis set and quality parameters (k-points, cutoffs, etc), tolerances for the NEB algorithm, spring constant, etc. Default values for these parameters are provided by appropriate protocols.

The workflow, as described, is the result of a recent refactoring of a previous version (in a private *aiida-barrier* package) driven by the needs of actual research within INTERSECT, such as the definition of the specific user cases. In order to favor the semantic upscale, we are identifying - in collaboration with other partners (FRA, EPFL and AMAT) - a unified set of definitions (based on ontology) and of

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input parameters that will allow us to define the appropriate common data structures and a cleaner logic. This will also be also beneficial for the optimization of the turn-key workflow.

The development of the overall NEB workflow required the solution of technical issues interlinked with specific details of the internal operation of SIESTA. For example, the treatment of vacancy-exchange events benefits from the introduction of extra variational freedom at the vacant site(s), which is achieved in SIESTA by the use of "ghost atoms" that carry extra basis orbitals but do not contribute to the dynamical effects. The handling of these extraneous atoms unduly complicated the logic of the older workflow. The refactored workflow is leaner and more easily extensible to new physical processes, apart from being more suitable for the integration into the IM2D.

The alpha version of the new workflow is available in the *intersect* branch of the *aiida-siesta* code repository, and is undergoing testing to confirm that it can match the results and degree of control of the older workflow for the existing use cases. For this, apart from the "turn-key" interface appropriate for IM2D, extra "expert" input options are being progressively turned on. The documentation is also being updated. In addition, it is planned to add more robust support for experimental features of the older workflow, in particular a variable-cell NEB algorithm that can be used to study phase transitions. This is now easier since the basic data structure used by the new workflow to represent the NEB images is a list of structures (i.e. a *TrajectoryData* object in AiiDA), rather than just arrays of coordinates. Eventually, a new *aiida-barrier* package, encoding the heuristics for different physical processes, and an ontology-based specification, can be offered.

#### **5.** Conclusion and perspectives

In this deliverable, we reported on the developments towards calculating material properties on-demand using state-of-the-art DFT methods. Since the deliverable D2.2, we have increased the list of properties made available by automatic workflows. In particular, we achieved the calculation of projected density of states, effective mass, dielectric constant, defect formation energy, and estimation of the barrier energy for defect diffusion. Our designs aimed at a balance between efficiency and accuracy of the material complex property calculations. We have achieved a high level of automation. Properties such as the band gap, total energy, effective mass, etc., can be calculated without requiring any input from the user. At the same time, many of the workchains expose their advanced inputs, giving a chance for the various *personas* (D1.1) to modify them at will. Future work will continue improving the robustness of these workflows through testing and feedback from the users, and complete on-going developments for novel properties.

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## ACRONYMS

- **API** Application Programming Interface
- CIF Crystallographic Information File
- **CBM** Conduction Band Minimum
- COD Crystallography Open Database
- **DFE** Defect Formation Energy
- **DFT** Density Functional Theory
- **DOS** Density of States
- FNV Freysoldt, Neugebauer, and Van de Walle
- KK Kramers-Kronig
- KP Komsa, Pasquarello
- **IDPP** Image-Dependent Pair Potential
- IM2D Interoperable Materials-To-Device
- MEP Minimum Energy Path
- **ORM** Object Relational Mapper
- pDOS Partial Density of States
- **PES** Potential Energy Surface
- QE Quantum Espresso
- **REST** Representational State Transfer
- SCF Self- Consistent Field
- VBT Valence Band Top