MONAMI Report Summary

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Final Report Summary - MONAMI (Modeling of Nano-scaled Advanced Materials Intelligently)

The consortium has been focused on a collaborative effort of developing novel techniques and paradigms concerning theoretical modelling of nano-scale advanced materials. The objectives were to identify novel methodologies and appropriate approximations to successfully undertake simulations of the materials which will be useful in future to our society. An important aspect here is the ability to carry out this development all the way from idea and concept to working computer softwares. In addition to this technical development, we have focused on establishing knowledge concerning an emerging class of materials; nano-scaled materials with potential for tailored properties and novel functionality. Training of younger scientists is a natural aspect of this ambition and is a strategically relevant outcome of our efforts. It is envisaged that the collaboration initiated by the established consortium will promote an intensified collaboration between European and Indian research laboratories and universities for a longer time-period. In terms of detailed scientific activities, the consortium has focused on nano-magnetism, correlated electronic structure of complex materials, molecular material functionalised with contacting to solid state surfaces and non-equilibrium phenomena of materials. A large body of published results have emerged out of this effort.

Project context and objectives:

The context of the project lies in theoretical investigations of physical properties of nanomaterials to compare them with their bulk counterpart using computer modelling and simulation tools, which are accurate enough to understand and design novel materials. The physical properties of nanomaterials that have been investigated are electronic, magnetic, optical and mechanical. At the fundamental level, the properties of materials, including nanomaterials, are governed by the laws of quantum mechanics and present day ab-initio electronic structure calculations based on density functional theory and very accurate quantum chemical methods are ideal tools for the investigation of electronic, magnetic and optical properties of nanomaterials. However, the analysis and prediction of many material properties require a combination of quantum mechanical tools and atomistic simulations designed for larger length scales, using effective models. Hence, practical and alternative approaches have been to view materials through windows of different length scales and develop modelling in three broad domains viz. microscopic, mesoscopic and macroscopic regimes covering the length scales 0.1 - 1 nm, 1 - 100 nm and larger than 100 nm respectively. The MONAMI project has been successful in this regard, e.g. by the construction of an atomistic spin-dynamics simulation tool which allows for the study of magnetisation dynamics down to the sub-pico-second time scale at length scales up to 100 nm. Overall, the community engaged in theoretical simulations of materials has realised the importance of bridging different length scales from macroscopic to mesoscopic to microscopic, by using the so-called multiscaling methods. MONAMI has as mentioned been active in this field and generated several methodologies and softwares that realise this goal. This applies to the mentioned spin-dynamics efforts, but equally important progress has been made in the field of quantum-transport as well as correlated electronic structures.

One of the concepts that have played a major role in the conceptual as well as computational developments covering all the length scales of interest in a number of areas of chemistry, physics and materials science is the concept of single-particle
density, which serves as the basic variable in the so-called density functional theory (DFT). On the microscopic length scale, it is the electron density that has played a major role in providing a deeper understanding of chemical binding in atoms, molecules and solids. In the intermediate mesoscopic length scale, an appropriate picture of the equilibrium and dynamical processes has been obtained through the single particle number density of the constituent atoms or molecules. A wide class of problems involving nanomaterials, interfacial science and soft condensed matter has been addressed using the density based formalism as well as atomistic simulation in this regime.

The proposed consortium has focused on a collaborative effort of developing novel techniques and paradigms concerning theoretical modelling of nano-scale advanced materials. The objectives were to identify novel methodologies and appropriate approximations to successfully undertake simulations of the materials which will be useful in future to our society. An important aspect was the ability to carry out this development all the way from idea and concept to working computer softwares, and this was successfully achieved in several sub-projects. In addition to this technical development the MONAMI project focused on establishing knowledge concerning an emerging class of materials; nano-scaled materials with potential for tailored properties and novel functionality. Training of younger scientists formed a natural aspect of this ambition, and is a strategically relevant outcome of the research efforts. Finally, it is envisaged that the collaboration initiated by the established consortium will promote an intensified collaboration between European and Indian research laboratories and universities.

Project results:

The main scientific and technological results can be found in the different work packages (WPs) that the project was organised under. In the first of these WPs, focus was on ab-initio calculation of physical properties of nanostructured materials. For these ab-initio investigations a bottom up approach was adopted, where we began from something very small like a molecule, or a small nanoparticle, or a quantum dot modelled as a collection of few interacting electrons in a suitable confining potential resembling the shape of the quantum dots. For such systems, we employed very accurate quantum chemical methods which not only provides information about the ground state of these systems but also about their excited state properties. In order to investigate the properties of large molecular structures, nanotubes or nanosystems having hundreds of atoms where quantum chemical methods are not feasible, we employed DFT in the framework of all-electron as well as pseudopotential methods. Equilibrium geometries, and vibrational spectra, were computed using standard plane-wave (PW) basis sets and supercells. For the low-energy bands, localised Wannier functions (WFs) were used to projected out a minimal basis of Nth-order muffin-tin orbitals (NMTOs). These single-particle orbitals, in the form of their tight-binding (TB) Hamiltonian and Coulomb-interactions, have become the basis for the simulation of nanosystems with thousands of atoms and also for nanosystems with strong electronic correlations. For some of the materials of interest in this WP, electronic structure theory based on DFT using conventional energy functionals (local density approximation and generalised gradient approximation) were found to be insufficient. It also became clear that an approach based only on model Hamiltonians also has drawbacks in that many of the parameters of these models are hard to estimate and that kinematic effects (band formation) often are described inaccurately. It therefore became very important to combine the best features of conventional electronic structure theory and many-body physics, and we were successful in integrating both these features via dynamical mean field theory (DMFT). Several publications were reported in peer reviewed journals on this topic.

The area of molecular magnetism, which began as a scientific curiosity in the later part of the last century, has now matured into a vigorous field of research. While the initial interest in the field was in discovering molecular materials with bulk magnetisation new paradigms have emerged in the last fifteen years. The current thrust revolves around discovering new single molecule magnets (SMMs), photomagnets, spin crossover systems and all organic magnets. The overall purpose of the sub-project on molecular magnetism was to provide theoretical models for magnetism of high nuclearity transition metal complexes and low-dimensional magnetic systems by combining conventional spin Hamiltonian techniques with modern density functional theory into novel approaches, which are capable to treat ground and excited states of molecular magnets. Several scientific papers have been the outcome of this effort, that were published in peer reviewed journals.
The field of spintronics received renewed interest when pioneering work by Ohno and co-workers showed that a small concentration of Mn in GaAs rendered the system ferromagnetic with transition temperatures of almost 100 K. A doped semiconducting system that exhibits ferromagnetism at room temperature is ideal for spintronics applications as it provides a ready source of spin polarised electrons. In this respect, transition metal doped semiconducting and oxide nanoparticles offer an attractive option due to the size dependence of the properties. However, the details of the electronic structure of transition metal doped semiconducting and oxide nanoparticles is unknown, and were the focus of this project. Hence, an investigation based on dynamical mean field theory, with a so called exact diagonalisation (ED) solver, was undertaken. The ED solver was developed within the MONAMI project. The study showed the crucial importance of electron correlations beyond that of conventional theory (LDA and GGA), in particular when comparing experimental and theoretical electron spectroscopical data.

The progress in experimental control has enabled a remarkable progress in the study of quantum transport. The aim of the MONAMI team was therefore to theoretically study electronic transport through systems in the nanometre size regime. The transport properties of such systems need to be understood on the basis of their atomic structure. It is of great relevance to establish the connection between the microscopic characteristics of an electronic system, e.g. the atomic configuration and the electronic structure and transport properties, e.g. the electrical current and conductance. This notion has generated a large effort in recent years to calculate the quantum transport properties from first principles. Owing to the complexity of the problem, such studies are strongly dependent on the existence of reliable numerical treatments and requires an efficient method to treat quantum transmittance in real systems. Within the project we developed a generalised quantum chemical technology for electron transport in single molecules and nanostructures. This modelling was based on scattering theory formulated in the context of non-equilibrium Greens functions.

In recent years, the study of metal nano-clusters has been a subject of immense interest from the experimental as well as theoretical points of view. Among the important properties of nanoparticles, the response properties have received special attention. They are crucial not only for understanding many of the other physical-chemical properties but also for interpreting various experimental results. To address these issues, we developed a reliable method for accurate calculation of the response and optical properties of nanomaterials, both in the static and dynamic (frequency-dependent) regime, using density functional theory. Of crucial importance in this density functional theory based calculation, was to have a reliable description of the exchange-correlation (XC) energy density functional, particularly for the excited states. We therefore derived such functionals, and employed them in a developed density functional perturbation method to reliably compute the linear and non-linear response properties.

With its Dirac like electron spectrum, graphene promises much by way of electronic applications. Graphene nanostructures have very interesting electronic properties arising particularly from the edge states. It is known that certain types of edges such as zigzag edges of graphene are magnetic in that the edge atoms posses a magnetic moment, while other edges such as the arm chair edges are nonmagnetic. The magnetism at these edges can likely be exploited for spintronic applications. We have undertaken several detailed investigation of how the edge magnetism is affected by:

a) shape and geometry of the nanostructure;
b) doping and
c) disorder.

Several papers have been published by the MONAMI team, on this topic. This study provided a fundamental understanding of how correlations, Dirac dispersion and size effects combine to give interesting phenomenon, e.g in magnetism, and is hopefully useful for the design of graphene based devices.

DFT calculations are usually performed with a PW basis set (such as LAPW, PAW, or using pseudopotentials) because this combines ease of programming with high numerical accuracy and robustness. It does, however, limit the use to three-
dimensional (3D) crystals, or forces one to repeat the system of interest periodically in three dimensions, i.e. to use supercells. This is computationally cumbersome and unintelligible, in essence because atoms are almost round and their effective one-electron potential almost spherical. The cut-off of a PW set is determined by the electron with the highest angular momentum, so that the resolution, e.g. in the vacuum outside a 3D-atom is forced to be as high as in the atom. Truly minimal basis sets of localised orbitals are, on the other hand, intelligible. Chemical binding and electronic structure is understood in terms of sp2 bonds etc. and not PWs. Truly minimal basis sets of localised orbitals may also be used in real space (as opposed to k-space) for methods in which the computational effort increases merely linearly with the size (N) of the system, so-called order-N methods. Truly minimal basis sets of localized Nth-order muffin-tin orbitals (NMTOs) are complete for one-electron potentials expressible as super-positions of spherically symmetric potential wells, which may overlap, but not further than to the centre of the nearest neighbour. The overlapping muffin-tin approximation (OMTA) is a huge improvement over the muffin-tin approximation (MTA) used originally in the LAPW method, and it is a substantial improvement over the atomic-spheres approximation (ASA) used in the LMTO method. In the OMTA, the NMTO method is very fast and intelligible because it generates the basis set directly in real space, by inversion of matrices in local partial-wave representation (structure matrices), i.e. without projection from all the Bloch-functions in a supercell as done in standard Wannier-function schemes. So NMTOs lend themselves to real-space calculation, and the development along these research directions have been a key enterprise within MONAMI. Hence, in a collaboration between the Stuttgart and Twente nodes, an efficient NMTO method has been developed, parts of which is ready for production work with materials specific interest.

The confinement of electrons in nanostructured materials often lead to strong Coulomb interactions and, hence, strong electronic correlations. As a consequence prominent effects such as the Coulomb blockade or the Kondo resonance emerge. In the case of spintronics materials such as half-metallic ferromagnets, Mn-doped GaAs and Mn/Fe-based molecular magnets as well as in transition metal oxide heterostructures already the natural confinement within the transition metal 3D orbitals gives rise to essential many-body effects. For realistic modelling of such systems, it is absolutely necessary to include the electronic correlations. We have treated this issue using DMFT both with the above mentioned NMTO technique, but also in a self-consistent mode in an all-electron full-potential method. Several papers have been published on this topic by the Uppsala node and the Wien node.

In the second WP of MONAMI, atomistic simulations were used to study various properties of nano-structured systems. Specifically, these included confined solids and liquids, growth, self-assembly and organisation of nano particles by various methods and magnetic properties of nano structured solids. A variety of tools which simulate the behaviour of materials over length scales spanning nano meters to microns have been used. In all cases, we relied on inputs, whether in terms of potentials, parameters or the nature of approximations used, from more microscopic or ab-inito calculations. These inputs were then used for solving more coarse grained dynamical evolution equations. The main aim of this WP was to determine the cooperative behaviour of materials at the nano-scale which do not depend directly on electronic degrees of freedom.

Solids and liquids under confinement often behave very differently from bulk solids. In solids, confinement may introduce or suppress fluctuations depending on the nature and strength of the confining potential. These fluctuations can induce structural changes in the solid. Since the nature of confinement may be tailored using external means, these phenomena offer ways to influence the structure and properties of nano-structured solids. These may be exploited in the design of devices like actuators, sensors or switches. Similarly, fluids in confined spaces are important in the context of nanostructured materials and microfluidics. The equilibrium and dynamical properties of soft matter confined at interfaces and within nano-pores are also of immense importance. Several projects concerned with the development of tools for studying such confined liquids and solids were under focus of the MONAMI team, and several papers were published on this topic. This concerned e.g. the growth and self-assembly of nanoparticles. In order to be able to make use of various electrical, optical or rheological properties of nanoparticles, they need to be grown from solution and assembled into arrays. We have therefore studied the various factors which govern these processes using microscopic and coarse grained simulations and theory. Furthermore, directed self-assembly of nanoparticles and colloids have immense importance for applications as chemical and biological sensors, novel materials and fabrication of nano- and micro fluidic devices. Modification of nanoparticles by attachment of polymer chains can...
in principle allow altering and control of the geometry and interaction of materials in the nanometer scale that can in turn result in unique binding properties or self-assembly. We developed several novel method to simulate self-assembly of such systems.

With the increasing interest in advanced magnetic materials for data storage and processing there is an increasing need for a detailed atomistic description of magnetic materials, and especially their dynamical properties. This may be witnessed in the recent developments in experimental techniques for studying magnetisation dynamics on short time scales and with findings on ultrafast magnetisation dynamics. The commonly used approach for studying magnetisation dynamics, micromagnetism, provides a framework for understanding magnetisation dynamics on length scales of micrometers and has with increasing computational power become a field of large technological importance. However, here the magnetism is treated only as a continuum vector field on a length scale of micrometers. This limits the applicability and accuracy of the approach making it inadequate for describing various modern experiments on magnetisation dynamics. It is therefore desirable with an atomistic approach based on the quantum description of solids, which properly displays the connection between the electronic structure of the material and the magnetisation dynamics. Such a method was developed within MONAMI, and is a simulation tool that is available to the general public. The developed method is called UppASD, and can currently use billion of spins in the simulation box, a considerably larger amount than any other method can use. The UppASD method has been used to investigate the dynamical properties of several nano-magnetic systems, which have led to several papers published in peer reviewed journals.

Another WP concerned building bridges between the different length scales through the relevant density variables in two major ways:

(i) in a sequential approach, where different properties are calculated within the shorter length scale, which are then used either in simulation or a theoretical modelling in the next higher length scale; and
(ii) in a combined or simultaneous approach, where the two adjacent length scales are treated in a coupled manner.

Our ambition was to extend the applicability range of quantum mechanical electronic-structure simulations to cover chemical and physical phenomena and properties at the scale of nanoparticles and bulk material. While linear scaling technology now is applicable in the range up to 10 000 atoms, we were in particular concerned with quantum modelling of general magnetic and electric properties, covering the full wave length region, as well as involving linear as well as non-linear interactions. In addition, we focussed on the type of force, reaction, or spectrum that can be associated with a nanostructured materials.

Conventional solids are either atomic or molecular solids. In recent years, clusters have attracted a lot of attention and are often called 'artificial atoms'. They have size-dependent properties and hence if they are used as the building blocks, there can emerge a new class of materials which can have very interesting and tunable properties. These new cluster assembled materials (CAM) can be extended systems forming a solid of clusters or may be a finite super cluster of the building block clusters. These often have novel properties. There are a number of parameters that we have within MONAMI identified that can be adjusted to tune the properties of the CAM. Examples are: the number of metal atoms in each cluster, the nature of these atoms, composition and arrangement of atoms in the clusters, such as bimetallic alloy type or multiple shell type clusters etc. The main tools used in these investigations is based on density functional theory, where the density represents the particles comprising the clusters and CAM.

The electron density as a basic variable in DFT can determine the interaction potentials needed for the calculation of interaction used in MD simulations. However, a DFT calculation at each time-step is computationally a very expensive method. The continuous electron density of molecules can however be coarse-grained to generate moments around each atomic centres leading to atomic charges and dipoles which can be used to obtain intermolecular interaction that can in turn be used as potential for MD simulations. However, for such atomistic MD simulations, it is important to have proper polarisable force fields which in fact offer significant advantages over fixed-charge potentials. To accommodate for this we have derived a self-
consistent scheme for molecular assembly which is used to determine the charges and dipoles in atomic sites of each molecule. These quantities are used to determine the interaction potential between the molecules and is now included in an efficient and improved simulation tool developed within MONAMI. Several publications have been made on this topic by the MONAMI team. In addition, we have developed coarse grain simulation techniques for meso-scale phenomena. One particularly useful feature of these coarse-graining models is the capability to integrate out the fast motion of the atoms, leaving a set of beads from which the low-resolution (coarse-grained) model is constructed. Beads interact with each other via an appropriate potential. The developed coarse grain model is constructed from effective coarse-grained pair potentials, extracted from the atomic-level pair correlation functions. The latter are obtained from atomistic simulations, so that the important structure information in an atomistic simulation is propagated into the corresponding coarse grain model.

Finally, first-principles electronic structure methods can typically handle tens to hundreds of atoms. However, 1000 atoms still only represents a length scale of 2 nm, while transport measurements typically probe a number of length scales which are larger than this. To be able to study transport properties without introducing free parameters, we developed a first-principles method of studying transport at longer length scales. A wave-function-matching (WFM) code based upon tight-binding muffin-tin-orbitals (TB-MTO) has been developed in Twente and is now routinely used to study scattering regions containing O(104) atoms explicitly and to generate parameters as input to phenomenological theories.

Potential impact:

Dissemination has taken place primarily via publications of scientific peer reviewed papers, text books covering the MONAMI topics, presentations at scientific conferences, and the arrangement of workshops. The MONAMI webpage also offers dissemination channels. In addition, MONAMI has been active in bridging the gaps between academia and industry, and as a result of this action, a Swedish based company, Sandvik Tools AB, have decided to place one of their employees with the Uppsala node of MONAMI. This person uses tools developed within MONAMI to undertake simulations / investigations of advanced materials for commercial use. The person doing this work is Dr Cecilia Årshammar, and she represents an ideal example both of the impact of transfer of know-how from academia to industry, as well as the effects of the gender action plan of MONAMI. As a result of this plan, several female scientists have been employed as PhD students and postdocs in the MONAMI project. An important strength of the network is also the transfer of knowledge through soft wares, which implicitly implies training of thousands of European and Indian end users outside the network. This involves continuous updating, maintaining and documenting the world-leading software packages like: Dalton, DIRAC, ERGO, Cascade, RSPt, and UppASD. The MONAMI project has also been active in seeking collaborations to other EU networks, e.g. MOLPROP and NANOQUANT.

An important impact of MONAMI is the training of young scientists. This training was mainly aimed at young researchers with knowledge in computational methods based on many levels of theory. This was accomplished though streamlined course curricula, including summer and winter school attendance. The following questions were primarily addressed:

- the applicability of the computational methods;
- their theoretical background and reliability;
- the hierarchical combination of the methods to tackle complex problems;
- the ability to address method development in materials science;
- the ability to use advanced computer facilities;
- insight in the development of advanced scientific computer programs;
- the building of skills to use advanced visualization, graphical interfaces and web portals.

Project website: [http://www.iacs.res.in/monami/Home.html](http://www.iacs.res.in/monami/Home.html)

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