

## Subproject C3.13

# Subsystem Quantum Chemistry for Nanostructures

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### Introduction and Summary

The CFN young scientist group of Christoph Jacob (subproject C3.13) was established in March 2010. Therefore, this report only concerns the first ten months of this subproject. This time mainly served as a start-up period. A first Ph.D. student (Andrew Atkins) started his work in October 2010. Another Ph.D student and a postdoctoral researcher are expected to join in the first half of 2011. Scientifically, a number of projects have been started that can be anticipated to lead to first results within the remaining time of the current CFN funding period.

The main goal of subproject C3.13 is the development of quantum-chemical methods for the treatment of both molecular nanostructures and nanostructures on surfaces. Such systems commonly comprise hundreds to ten-thousands of atoms and are thus very large from the perspective of quantum chemistry. Yet, the special properties of nano-sized systems usually preclude a classical description and require an explicit quantum-mechanical treatment of the atomistic details. Even with density-functional theory (DFT), which is the only quantum-chemical method that can possibly be applied to systems of this size, only simplified model systems can be handled. However, it is currently impossible to extend such a treatment to more realistic (and thus larger) systems. Furthermore, if the accuracy of DFT is not sufficient, there is no possibility to systematically improve the theoretical description because applying more accurate wave-function theory (WFT) based methods is not feasible.

Subsystem methods, in which the total system is divided into smaller subsystems, offer a way out of this dilemma. Each of the smaller subsystems can then be treated separately in the environment of the other subsystems. Such a subsystem approach offers a number of advantages. First, subsystem methods are in general more efficient than a conventional quantum-chemical treatment of the full system. Since the computational effort needed for the calculation of one subsystem is usually independent of the size of the full system, one obtains methods that naturally scale linearly with the system size. Second, from a chemist's point of view a partitioning into subsystems provides a more natural way for the interpretation of the results since it offers a picture in terms of the chemical building blocks. Finally, subsystem approaches provide the possibility to focus on interesting parts of the system, yielding embedding methods. Since the subsystems are treated individually, it is easily possible to employ a more accurate treatment only for one or a few selected subsystems of interest, making it possible to systematically improve upon a DFT treatment by using WFT.

One realization of such a subsystem approach is the frozen-density embedding (FDE) scheme within DFT, initially proposed by Wesolowski and Warshel [1,2]. This DFT-in-DFT embedding scheme has until now mainly been applied to weakly interacting subsystems, for instance for studying solvent effects on molecular properties. The reason for this limitation is the need to use approximations for the kinetic-energy component of the embedding potential in this scheme. However, a subsystem description of molecular nano-structures and of nanostructures on surfaces requires the possibility to treat covalent bonds between subsystems. Therefore, one important goal of the research in subproject C3.13 is the extension of the FDE scheme to such situations.

Second, the FDE scheme can be extended to WFT-in-DFT embedding [3]. Within such a scheme it is possible to selectively improve the description of selected subsystems. The implementation of such WFT-in-DFT embedding methods as well as the development of improved schemes that do not rely on approximations for the kinetic-energy is currently ongoing. A third topic of the CFN young scientist group is the application of embedding and subsystem methods to the calculation of spectroscopic properties as well as for interpreting calculated spectra. In this area, the current work

focuses on electronically excited states (in particular X-ray absorption spectroscopy) and on vibrational spectroscopy. Finally, within subsystem approaches accurate quantum-chemical methods are still required for treating the individual subsystems. An area where the currently available computational methods face serious problems is transition metal chemistry. In many cases, DFT with the currently available exchange-correlation functionals fails for transition metal compounds, while the application of wave-function based methods is often not feasible, in particular for clusters containing multiple transition metal centers. Therefore, work towards both efficient and accurate quantum-chemical methods for transition metal chemistry is currently in progress.

In the ten months since March 2010, subproject C3.13 has already led to three publications in *J. Chem. Phys.*, *J. Phys. Chem. A*, and *J. Phys. Chem. B*. These mainly follow up on previous work at ETH Zurich, which is, however, also relevant to the ongoing and planned research within the CFN young scientist group. In addition, four publications have been submitted or will be submitted in January 2011, including one single-author publication on work conducted solely in Karlsruhe.

### 1. Development of subsystem DFT methods applicable to covalent bonds

The FDE scheme relies on the use of approximations for the kinetic-energy component  $v_T$  of the embedding potential. With approximations derived from generalized-gradient approximation (GGA) kinetic-energy density functionals, weak interactions between subsystems such as hydrogen bonds can be described rather accurately. However, these approximations break down for bonds with a covalent character. Thus, to be able to directly apply the FDE scheme to subsystems connected by covalent bonds, improved approximations to  $v_T$  are needed.

As a first step toward this goal, we implemented a method for the numerical calculation of accurate reference potentials for  $v_T$  by reconstructing the Kohn-Sham potential corresponding to a given density, based on the algorithm by Wu and Yang [4]. Using this implementation, in Ref. [C3.13:1] we presented accurate embedding potentials for a selected set of model systems, in which the subsystems are connected by hydrogen bonds of various strength (water dimer and F–H–F–), a coordination bond (ammonia borane), and a prototypical covalent bond (ethane). These accurate potentials have been analyzed and compared to those obtained from popular kinetic-energy density functionals. This reveals several important shortcomings of the present functionals and provides important directions for the development of improved approximations. Work along these lines is currently in progress.

An alternative approach to developing subsystem DFT methods that can be applied to covalent bonds is to circumvent the problems arising from the deficiencies of the available kinetic-energy functionals and instead treat the covalent bonds between the subsystems by introducing “capping groups” [5]. This leads to an extension of the FDE scheme employing a more general partitioning of the electron density, dubbed 3-FDE. Initially, a pilot implementation of this scheme and its application to proteins have been presented. However, the 3-FDE scheme requires the iterative determination of the “cap potentials”, i.e., the Kohn-Sham potential in the region of the introduced caps. This step is currently rather time-consuming. Therefore, in collaboration with the group of Lucas Visscher at VU University Amsterdam, we are working on an improved 3-FDE implementation that makes use of the algorithm applied in Ref. [C3.13:1]. To initialize this project, Karin Kiewisch from Amsterdam visited our group at the CFN for one week in september 2010. In addition, work towards applying the 3-FDE scheme to nanostructures, which requires other ways of defining the subsystems and other capping groups than for proteins, is also in progress.

This work will be particularly relevant for extending the FDE scheme to solids and surfaces, one of the main goals of subproject C3.13. Such an extension will require an adequate description of the bonds within the solid (ionic, covalent, or metallic) by both using improved kinetic-energy functionals and more general density partitionings.

One area of applications for such subsystem methods for surfaces arises from a collaboration with the group of Ljiljana Fruk (subproject A5.7), who are interested in bonding energies of different ligands on gold, silver, and copper nanoparticles. To tackle this question, we now started calculations of small model systems. However, once subsystem-DFT and WFT-in-DFT embedding methods (see below) can be applied to study molecules on surfaces, this will allow for the treatment of more realistic system and make the application of more accurate theoretical methods possible.

## 2. Development of wave-function theory (WFT) in DFT embedding methods

An second topic within subproject C3.13 is the extension of the FDE scheme to WFT-in-DFT embedding. Starting point for this work is the implementation of a simplified scheme, in which the embedding potential is obtained from a previous DFT-in-DFT calculation [6]. This scheme has been shown to be very useful for the calculation of local excitation energies in cases where (time-dependent) DFT is able to provide an accurate ground-state density, but fails for the excited state. An extensive review article on embedding methods for calculating such local excitation energies is currently in preparation.

However, if DFT already fails for the ground state (e.g., for transition metal compounds, see below), more elaborate schemes in which the embedding potential is updated iteratively are required. Our existing implementation has now been extended to include such schemes. In addition, it has been generalized to support different program packages for the WFT calculations. To this end, we make use of a scripting framework developed over the past years [7]. Most of this work is performed in collaboration with Andre Gomes (University of Lille), who visited our group for one week in september 2010.

All of the available WFT-in-DFT embedding schemes still rely on an approximate kinetic-energy functional and thus suffer from the limitations of the available functionals discussed in the previous section. However, in a WFT-in-DFT calculation the high-level WFT calculation is commonly the step that requires most computer time. Compared to this, a DFT calculation on the full system (or a significant part of it) becomes feasible. Starting from such a DFT calculation on the full system, it is then possible to calculate an accurate embedding potential. This can be achieved using the computational methods and the implementation introduced in Ref. [C3.13:1].

Unfortunately, it turns out that the embedding potentials obtained in this way are not suitable for WFT-in-DFT calculations. The reason for this is that if the orbitals are represented in a finite basis set, the required reconstruction of the Kohn-Sham potential is an ill-defined problem that has many solutions. This is actually a long-standing problem in DFT that also shows up when evaluating orbital-dependent functionals using the optimized effective potential (OEP) method. The algorithm by Yang and coworkers employed in Ref. [C3.13:1] addresses this problem by introducing a constraint that requires the reconstructed potential to be as smooth as possible. However, this is not the “correct” potential. In addition, the final potential obtained from this algorithm sensitively depends on the choice of several numerical parameters. Recently, we have solved this important problem by employing a more physical constraint, which leads to a numerically stable algorithm yielding high-quality embedding potentials suitable for WFT-in-DFT embedding. The corresponding publication will be submitted in January 2011.

### 3. Embedding and subsystem methods for theoretical spectroscopy

Embedding and subsystem methods are particularly suited for studying spectroscopic properties of complex molecular systems. Many spectroscopy properties are related to only a specific part of the total system. In this case, embedding methods allow one to focus on the important subsystem for an efficient calculation of the spectroscopic properties of interest. This can be exploited for studying solvent effects on electronic excitation energies [8] or NMR chemical shifts [9], as well as for calculating local excitation energies of impurities in solids with WFT-in-DFT embedding [7].

One spectroscopic technique that is very local is X-ray absorption spectroscopy (XAS), which measures the excitation of a core electron to an unoccupied valence states. The energy of this excitation is specific to a certain element, so that XAS mainly probes the local environment of the corresponding atoms [10]. Within the CFN, the young scientist group of Daniel Schaadt (subprojects A2.7 and A4.5) uses XAS for characterizing copper-doped GaN substrates. Therefore, one goal of our future research is the development of embedding methods for the accurate calculation of XAS spectra, that should ideally also be able to yield accurate results over a wide energy range, and that should be applicable both for molecules in solution and by embedding small clusters in a periodic structure also for solids. As a first step towards this goal, in the first month of his Ph.D. project, Andrew Atkins, has started investigating the performance of existing (time-dependent) DFT methods for the calculation of XAS spectra. For this investigation, high-resolution spectra of iron complexes measured by Matthias Bauer in the group of Prof. Grunwaldt (Institute for Chemical Technology and Polymer Chemistry, KIT) provide accurate reference data.

Not all spectroscopic properties are local. Often, spectra can be understood in terms of an interaction of many subsystems. This is for instance the case for collective electronic excitations in nanostructures, that can be analyzed as coupled local excitations. Similarly, vibrational spectra of extended molecular systems consisting of many similar units such as (bio-)polymers, are determined by the interaction between local vibrations of these units. However, when performing full quantum-chemical calculations this simple picture is lost and instead a very complicated, delocalized picture is obtained.

For vibrational spectra, this can be addressed by using a localization of normal modes [11], that makes it possible to reconstruct a subsystem picture from the full calculations. Following up on earlier work at ETH Zurich, this analysis tool has been applied to study the Raman optical activity spectra of different conformations of synthetic polymers (in collaboration with the group of Benoit Champagne in Namur, Belgium) [C3.13:2], as well as for understanding the amide III vibrations in polypeptides [C3.13:3]. In addition, there is ongoing work concerning the vibrational spectroscopy of polypeptides and proteins. A publication investigating Raman optical activity signatures of protein  $\beta$ -turns has recently been submitted. All these projects have been conducted in collaboration with the group of Markus Reiher at ETH Zurich. In Karlsruhe, a collaboration with the group of Oliver Hampe (INT) has been initiated, who measure infrared spectra of polypeptides in the gas phase. By comparing these measured spectra to those calculated for different conformers, it is possible to determine the gas-phase structures. On the other hand, gas-phase spectra provide an ideal reference for benchmarking the accuracy of theoretical calculations, since no solvent effects alter the spectra.

The localization of normal modes only reconstructs a subsystem picture from a full calculation. To avoid this expensive calculation for large systems, it would be advantageous to apply a subsystem description from the beginning. A method that has gained increased popularity in the past years for the calculation of polypeptide and protein vibrational spectra, the so-called "Prague model" [12], calculates the Hessian matrix as well as property tensor derivatives for small fragments and

assembles the results, neglecting any interaction not contained within the smaller fragments. A paper benchmarking this model against full calculations is currently in preparation. The results indicate that the error caused by neglecting the interaction between the subsystems is often very large, leading to qualitatively wrong spectra. Therefore, it seems necessary to embed each fragment in the environment of the other fragments, for instance by extending the 3-FDE scheme (see above) to vibrational spectroscopy.

#### 4. Improved DFT methods for transition metal chemistry

Transition metal compounds (such as clusters on surfaces, complexes used in homogenous catalysis, or active centers in metalloproteins) are currently one of the largest challenges for theoretical chemistry. In addition to containing a large number of atoms, an adequate inclusion of non-dynamic electron correlation is of utmost importance. In wave-function based ab initio calculations, this requires large active spaces, which pushes the available methods to their limit, in particular for molecules containing several metal centers. Therefore, DFT is currently the only viable option for routine calculations on such molecules.

For such open-shell systems, the conventional DFT is generalized to spin-DFT and the spin density is (in addition to the total electron density) the fundamental quantity, on which the exchange-correlation energy depends. For this exchange-correlation energy, an approximate functional, depending both on the electron density and on the spin density, has to be used. However, the currently available functionals exhibit serious deficiencies. First, energy differences between spin states are strongly dependent on the exchange-correlation functional that is used. Second, a so-called “broken-symmetry” treatment is often needed, which often yields reliable energies, but results in unphysical spin densities. Third, even in cases where a “broken-symmetry”-treatment is not required, the spin densities obtained with different exchange-correlation functionals differ significantly [13]. But for the prediction of magnetic properties of transition metal clusters, a reliable calculation of both the energies of different spin states and of their spin densities (which, for instance, determine magnetic hyperfine couplings) is required.

Starting from the spin-density as central quantity in spin-DFT, we are currently working on understanding some of the failures of the available functionals. In a benchmark study, we carefully investigated their failure for predicting the spin-densities in iron-nitrosyl complexes by comparing to accurate complete-active space (CASSCF) calculations and by analyzing the origin of the differences between different functionals [14]. In addition, a review of the foundations of spin-DFT is in preparation.

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