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## Frozen-Density Embedding

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# Summary

The frozen-density embedding (FDE) scheme within density-functional theory (DFT) provides a very powerful tool for the quantum chemical treatment of large systems. It is based on a partitioning of the electron density into the density of an active subsystem and a frozen environment. In the calculation of the density of the active subsystem, the effect of the frozen environment is represented by an effective embedding potential, that contains the electrostatic potential of the environment, an exchange-correlation component and a kinetic-energy component. In contrast to most other embedding schemes used in theoretical chemistry, the FDE scheme provides a formulation that is in principle exact.

This thesis deals with various aspects of the FDE scheme. An introduction of the methods of theoretical chemistry, in particular of DFT, and of the FDE scheme is given in Part I of this thesis.

Part II of this thesis provides theoretical extensions and improvements of the FDE scheme. In Chapter 4 it is shown how the FDE scheme can be applied to the calculation of nuclear-magnetic resonance (NMR) shieldings. Since the description of magnetic properties within DFT requires the use of the current density as a basic variable—in addition to the electron density—this makes a generalization of the FDE formalism necessary. By starting from nonrelativistic current DFT and by partitioning not only the electron density, but also the current density, such a generalized FDE formalism is given. It is shown that this introduces a formal dependence of the nonadditive kinetic-energy functional, which appears in the effective embedding potential, on the current densities in the subsystems.

If the usual approximations are introduced and the current dependence of the exchange-correlation potential of the nonadditive kinetic-energy functional are neglected, one arrives at a formulation in which the currents in the two subsystems that are induced by an external magnetic field are not coupled, and the NMR shielding can be calculated as a sum of contributions calculated for the individual subsystem. Since the NMR shielding only depends on the induced current in the vicinity of the NMR active nucleus, the contribution arising from the induced current in the subsystem containing this nucleus is dominant and the contribution due to the induced current in the other subsystem can usually be neglected. Altogether, this extension of the FDE scheme provides a simple and efficient scheme for calculating NMR shieldings

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in large systems.

Even though the FDE scheme is in principle exact, a kinetic-energy component  $v_T$  appears in the embedding potential that is given by the functional derivative of the nonadditive kinetic-energy functional. To calculate  $v_T$ , an approximate kinetic-energy functional is needed and the applicability of the FDE scheme is limited by the accuracy of the available approximate functionals. Chapter 5 is devoted to improving the available approximations for the kinetic-energy component  $v_T$  of the embedding potential.

One strategy for developing approximate functionals is to investigate physical limits that are known exactly. In the present case, the form of  $v_T$  is investigated in the exact long-distance limit, i.e., in the limit of an infinite separation of the two subsystems. It can be shown that with the available approximate kinetic-energy functionals a wrong form of  $v_T$  is obtained in the regions of the frozen subsystem. The kinetic-energy component should cancel the electrostatic and exchange-correlation components, but the available approximate kinetic-energy functionals are not able to compensate the large nuclear attraction.

For two test systems, a  $\text{H}_2\text{O}\cdots\text{Li}^+$  complex and an organic dye molecule surrounded by 30 water molecules, it is shown that this wrong behaviour of  $v_T$  leads to too low-lying virtual orbitals, that can lead to serious problems by causing convergence problems and by introducing spurious excitations in calculations of response properties. Based on the knowledge of the exact form of  $v_T$  in the long-distance limit, a correction can be proposed that enforces the correct form in this limit and removes the observed problems.

In Part III of this thesis (Chapters 6 and 7) an implementation of the FDE scheme is described. This implementation uses a very flexible setup, in which the total system is composed from an arbitrary number of fragments. For each frozen fragment, it can be chosen whether its density is kept completely frozen or if it is updated in freeze-and-thaw cycles. This allows a number of different setups. By employing a number of frozen fragments it is possible to use an approximate environment density, that is obtained as a sum of the densities of isolated molecules. On the other hand, it is also possible to relax the densities of all fragments in freeze-and-thaw cycles, which provides an efficient alternative to conventional DFT calculations. In addition, intermediate setups can be employed, in which the densities of a few frozen fragments are relaxed. This makes it possible to describe the polarization of the environment with respect to the nonfrozen subsystem.

The implementation employs an efficient numerical integration scheme with an integration grid that is mainly centered on the nonfrozen subsystem, and makes use of linear scaling techniques for the evaluation of the electrostatic potential and the electron density of the frozen subsystems. For large environments, the size of the in-

tegration grid does not increase and, therefore, the required computer time is almost constant when the size of the environment increases. This makes it possible to treat very large environments, for instance in studies of solvent effects, and the efficient implementation described here has already been used in a number of applications.

Part IV of this thesis includes two applications of the FDE scheme. In Chapter 8, the accuracy of FDE is investigated for weakly interacting  $\text{CO}_2 \cdots X$  ( $X = \text{He, Ne, Ar, Kr, Xe, Hg}$ ) van der Waals complexes. By comparing the results of fully converged freeze-and-thaw FDE calculations in which the densities of both subsystems are optimized to conventional supermolecular DFT calculations, it is possible to investigate possible problems in the approximate functionals used for the kinetic-energy component of the embedding potential. It is found that while the agreement is very good if no basis functions centered on the frozen system are included, problems arise when these basis functions are included. This is attributed to the problems in the available approximate kinetic-energy functionals that are investigated in Chapter 5.

As a second result, Chapter 8 shows how the FDE scheme can be used to apply different approximations to the exchange-correlation potential in different regions. In the case of the investigated  $\text{CO}_2 \cdots X$  complexes, no common exchange-correlation approximation leads to a good agreement of the induced dipole moment calculated in a supermolecular DFT calculation with the experimental data. The induced dipole moment is mainly due to the polarization of the rare gas atom due to the quadrupole moment of the  $\text{CO}_2$  molecule. It turns out that no approximation is able to describe both the polarizability of the rare gas atom and the quadrupole moment of  $\text{CO}_2$  correctly. While a conventional GGA functional such as PW91 yields an accurate quadrupole moment for  $\text{CO}_2$ , it overestimates—because of its wrong asymptotic behaviour—the polarizability of the rare gas atom. On the other hand, the asymptotically correct SAOP potential results in polarizabilities that agree very well with experiment, but it yields an inaccurate quadrupole moment for  $\text{CO}_2$ . The FDE scheme provides a way to circumvent these problems by combining the PW91 functional for  $\text{CO}_2$  with SAOP for the rare gas atom. This combination leads to induced dipole moments that are in good agreement with experiment.

An important field of application of the FDE scheme is the description of solvent effects on molecular properties. A realistic description of such solvent effects requires the inclusion of a large number of solvent molecules to account for the large solvent environment as well as calculations for a large number of solvent structures to account for the dynamics of the solvent. Therefore, an efficient method such as FDE is required for the calculation of the molecular properties.

In Chapter 9, a comparison of FDE with another solvent model, the discrete reaction field (DRF) model, a QM/MM scheme employing a polarizable force field, is given. The performance of FDE and DRF is compared for dipole and quadrupole

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moments, excitation energies, and polarizabilities. These tests have been performed for a water molecules surrounded by a solvent shell of 127 water molecules, and only one representative structure has been used.

It is found that the two solvent models agree well for the ground-state properties (dipole and quadrupole moments). This shows that the electron density and the occupied orbitals calculated with FDE and DRF are very similar. However, there are significant differences for the response properties (excitation energies and polarizabilities). The analysis shows that this is due to two main reasons. First, the description of the virtual orbitals differs between the two solvent models. In FDE, the kinetic-energy component of the embedding potential provides a more accurate description of the effects of Pauli repulsion than the purely electrostatic model employed in DRF. Second, DRF includes the response of the environment, whereas this term is missing in FDE. While it is found that this environment response can be neglected in the case of excitation energies, it becomes important when calculating polarizabilities.

Several projects are already ongoing that build upon the results included in this thesis. The extension of FDE to the calculation of NMR shieldings is currently being applied to the calculation of the solvent shifts of the nitrogen shielding of acetonitrile in different solvents.<sup>a</sup> Furthermore, the extension of FDE to other magnetic properties, such as spin–spin couplings is underway.

A very promising extension of FDE is the application of its embedding potential to couple wave-function based *ab initio* methods to DFT. Currently, we are working on the application of such an *ab initio*-in-DFT embedding scheme to calculate electronic excitation energies of molecules in solution.<sup>b</sup>

One of the main challenges remains the extension of the applicability of FDE to systems in which there are covalent bonds between the active subsystem and the environment. This will require the development of improved approximate kinetic-energy functionals. One promising approach might be the application of the ideas that were used in Chapter 5 to derive the exact long-distance limit in a self-consistent scheme for the calculation of the exact embedding potential.<sup>c</sup>

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<sup>a</sup>R. E. Bulo, Ch. R. Jacob, and L. Visscher, “NMR Solvent Shifts of Acetonitrile from Frozen-Density Embedding Calculations”, to be submitted (2007).

<sup>b</sup>A. Severo Pereira Gomes, Ch. R. Jacob, and L. Visscher, in preparation (2007).

<sup>c</sup>Ch. R. Jacob and L. Visscher, in preparation (2007).