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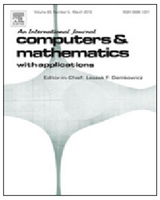

# Multi-domain muffin tin finite element density functional calculations for small molecules

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ABSTRACT

In this contribution a multi domain finite element density functional code for molecules is presented. The method makes use of higher order elements to enforce the continuity of the orbitals between the spherical domains and the interstitial domain. The salient computational details of the algorithm are described in some detail. Results of calculations for the orbital energies of methane, ethane, water, ammonia and benzene are given and compared with those obtained using GPAW.

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## 1. Introduction

When calculating the properties of molecules using the Hartree–Fock [1] or density functional theory [2] methods, the combination of Coulomb potentials due to the nuclei provides a challenge with respect to choosing a basis set that approximates the true orbitals everywhere.

Gaussian orbital methods have been the mainstay of computational chemistry for more than 40 years [3]. They are computationally convenient because the required matrix elements can be obtained from relatively simple formulae. However, Gaussian orbitals give an inadequate description of the orbitals close to the nuclei and likewise their long-range behaviour is incorrect. Slater orbitals, used for example by the Amsterdam Density Functional (ADF) program [4], are by definition well suited for the description of orbitals close to any of the nuclei but the numerical evaluation of the required matrix elements is computationally demanding. For periodic solids, muffin-tin type calculations using LAPW [5] and related methods are a very powerful tool. Muffin-tin type calculations have already been performed 50 years ago for molecules using the Multiple Scattering X $\alpha$ calculations pioneered by Slater and Johnson [6–8].

Since the mid 1980s, the method of finite elements [9,10] has been applied in molecular and solid state physics to systems of increasing complexity [11–21]. In parallel the numerical implementation of the method of finite elements method has seen many advances including h–p fem, hanging nodes [22] and adaptive refinement [23].

In the present contribution results of a multi domain muffin-tin type density functional calculation for a few light molecules will be presented. The motivation for using the method of finite elements is to provide an alternative way to calculate the properties of molecules and to serve as a comparison to other methods such as the projector augmented wave method [24] as implemented in GPAW [25–27].

In the GPAW method, the density-functional equations can be discretized in three ways: (i) Finite-difference (FD): uniform real-space grids, (ii) Plane waves (PW): expansion in plane waves and (iii) Linear combination of atomic orbitals (LCAO): expansion in atom-centred basis functions. This study uses the FD approach which can treat both free and periodic boundary conditions. The uniform real-space grid in the FD approach provides a simple discretization for the Kohn–Sham

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and Poisson equations. Physical quantities such as wavefunctions, densities, and potentials are given by the values at the grid points, while the derivatives in this approach are calculated using finite differences of accuracy $O(h^6)$ [26].

In Section 2, an overview of the multi-domain finite element approach and a brief introduction to density functional theory are presented. In Section 3, the computational details are presented. Section 4 presents the results obtained for the hydrogen atom as test case and orbital energies for the molecules methane ($CH_4$), ethane ($C_2H_6$), water ($H_2O$), ammonia ($NH_3$) and benzene ($C_6H_6$). Finally, we draw our conclusions and give an outlook for further work in Section 5.

## 2. Method

### 2.1. Molecular Hamiltonian

We consider a molecule governed by the many body Hamiltonian

$$H = -\sum_{i=1}^{N} \nabla_i^2 + \sum_{i>j=1}^{N} \frac{2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N}\sum_{j=1}^{M} 2\frac{Z_j}{|\mathbf{r}_i - \mathbf{R}_j|} + \sum_{i>j=1}^{M} 2\frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}, \tag{1}$$

with $M$ nuclei of charge $Z_i$ at $\mathbf{R}_i$ considered stationary and $N$ electrons at $\mathbf{r}_i$. The unit of length is $1\ a_{\mathrm{Bohr}} = 52.92$ pm, while the unit of energy is 1 Rydberg $= 13.6057$ eV. The Hamiltonian does not depend on the electronic spins and all orbitals are doubly occupied by electrons with opposite spins, leading to the restriction, that $N$ must be even. The full $N$-body problem cannot be solved exactly, hence an approximation is required. In this contribution, we use the density functional theory (DFT) approach within the local density approximation (LDA).

### 2.2. Density functional approach

The formalism for the spin compensated density functional approach [2] is given below. Practical DFT calculation was made possible by mapping the fully interacting ground state Hamiltonian in Eq. (1) to the non-interacting auxiliary system [28]. Both systems have the same ground state density defined by

$$\rho(\mathbf{r}) = 2\sum_{i=1}^{\frac{N}{2}} |\psi_i(\mathbf{r})|^2 \tag{2}$$

and the optimal choice of orbitals satisfies

$$[-\nabla^2 + v_{\mathrm{eff}}]\psi_i = \epsilon_i \psi_i, \tag{3}$$

where

$$v_{\mathrm{eff}}(\mathbf{r}) = v(\mathbf{r}) + 2\int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + v_{xc}(\mathbf{r})$$

with the external potential $v(\mathbf{r})$, in this case due to the nuclei, the exchange–correlation potential $v_{xc}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r})}$ and the orbital energies $\epsilon_i$. Here the exchange–correlation energy $E_{\mathrm{xc}}$ is approximated by a functional of the density $\rho$.

### 2.3. The Muffin-Tin finite element approach

We consider a molecule defined by the nuclear positions and nuclear charges $\mathbf{R}_i$ and $Z_i$ inside a sphere $\Omega$ of radius $r_{\max}$ centred on the origin. The outer boundary is chosen as a sphere for computational convenience when implementing the boundary condition for solving the Poisson equation. The sphere is subdivided into $M$ spherical domains $\Omega_i$, $i = 1, \ldots, M$ around the nuclei with radii $r_{\mathrm{mt}i}$ and the remaining interstitial domain $\Omega_0$ as shown in Fig. 1. In the interstitial domain $\Omega_0$ Cartesian coordinates will be used and thus we have

$$[-\nabla^2 + v_{\mathrm{eff}}]\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad \text{for } \mathbf{r} \in \Omega_0, \tag{4}$$

while in $\Omega_i$, in terms of an expansion in real valued spherical harmonics $R_{lm}$, i.e.

$$\psi_i(\mathbf{r}) = \sum_{l \le l_{\max}} f_{ijlm}(r_j) R_{lm}(\hat{\mathbf{r}}_j) \quad \text{for } \mathbf{r} \in \Omega_j \ \ \mathbf{r}_j = \mathbf{r} - \mathbf{R}_j, \tag{5}$$

a coupled system of radial differential equations results:

$$\left[-\frac{1}{r_j^2}\frac{\partial}{\partial r_j} r_j^2 \frac{\partial}{\partial r_j} + \frac{l(l+1)}{r_j^2}\right] f_{ijlm}(r_j) + \sum_{l'm'} \langle lm\,|v_{\mathrm{eff}}|l'm'\rangle_j(r_j) f_{ijl'm'}(r_j) = \epsilon_i f_{ijlm}(r_j) \quad l, l' \le l_{\max}, \tag{6}$$

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