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REGULAR ARTICLE

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DFT ×TB — a unified quantum-mechanical hybrid method

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Abstract A unified quantum mechanical hybrid method on the basis of density functional theory (DFT) is presented. The method is based on an LCAO-Kohn-Sham ansatz. While a part is treated with standard DFT, for the remaining system non-orthogonal tight-binding (TB) approximations are made for potential and basis functions. This means that it is possible to have covalent bonds in between the DFT and TB parts. The charge fluctuation within the system is controlled by the self-consistent charge technique. Theory, implementation, and first example molecules are presented in this article, and further development is discussed.

1 Introduction

Progress in the development of quantum theoretical methods, in particular in density-functional theory (DFT), and in computer technology in the past decades allow accurate computation of molecules, clusters, and solids up to several 100 atoms. In spite of many fast modern computational methods, there is always demand to go to larger systems, to run longer molecular dynamics (MD) trajectories, or to compute more structures. Therefore, much effort has been made to establish computational tools to treat systems of increasing complexity accurately.

Often one is only interested in a relatively small part of a system, which one would like to describe at high accuracy. The surrounding is not of particular interest in those calculations but, however, influences the region of interest considerably and hence cannot be neglected in the computation. Several strategies have been proposed in the past to deal with this issue.

The most popular schemes that treat parts of a system at different accuracies directly separate the whole system geometrically into core region and environment. This direct separation usually allows the application of the whole spectrum of atomistic methods, including post-Hartree–Fock ab initio theory, DFT, semi-empirical methods, and classical molecular mechanics (MM). According to the choice of atomistic methodology, these techniques are often called QM/MM [1–4] (the core region is computed using a quantum-mechanical (QM) method, while the environment and the interaction of the core and environment are treated classically) or QM/QM′ [5] (both regions are treated quantum mechanically at different levels of accuracy, e.g. QM = DFT, QM′ = semi-empirical). Also, the successive increase in accuracy in placing computational regions in a multilayer with increasing accuracy around the core has been suggested in the ONIOM approach [6].

A very simple treatment is to use basis sets of different quality in the different parts of the molecule, e.g. if the simulation of a certain spectroscopic quanitity is requested only for a part of the molecule, or for one type of atoms. This gives, sometimes, a very reasonable approach especially for the computation of NMR parameters (see, e.g. Ref. [7]). On the other hand, often an artificial charge transfer is introduced between parts of the system due to the different quality of description of the chemical potential. In particular, this artifact is omnipresent in all-electron computations, and hence nowadays hybrid schemes involving the geometrical separation of the system are preferred in most applications.

These methods work very well for many applications. For example, those related to the description of molecules in a solvent. If pure covalent bonds need to be cut at a reasonably large distance of the core region and saturation of resulting dangling bonds is straight forward, these methods can also be applied successfully. However, as soon as covalent bonds need to be cut two significant problems arise: (1) the quantum mechanical computation is running in this case with artificial boundary conditions, which are determined by the

Dedicated to Professor Karl Jug on the occasion of his 65th birthday.

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choice of bond saturation, e.g. by link atoms [8] or capping pseudopotentials [9], and (2) the proper choice of the model, including the saturation of the molecule, leads to significant manual work effort. A good test for the reliability of the results is then to test if the quantity of interest converges with the increase in the core region. For a review on these types of hybrid methods, see, e. g., Ref. [10].

The aim of this work is to establish a unified quantum mechanical, DFT-based, QM/QM' high-level/low-level method, which

- has a unified Hamiltonian and hence avoids the introduction of artificial boundary conditions into the quantum system,
- is not restricted to a purely geometrical separation of the system,
- includes only Kohn-Sham (KS) theory with additional approximations to the Hamiltonian and to the basis functions,
- reduces the computational effort of KS-DFT computations significantly,
- is reliable, and
- manually easy to use.

In this approach, the low-level method is the density-functional based tight-binding (DFTB, hereafter TB) method, which has been applied for a large series of systems with remarkable success [11], and is up to several orders of magnitude faster than standard DFT. We assign the atoms of the method into two groups, which do not necessarily belong to geometrical regions: A DFT part, denoted with (D) in the following, and a TB part, which we will denote with (T). This new method will be called in the remainder DFT×TB to refer to its origins (DFT and (DF)TB), and to emphasize the unification of the two methods by the × symbol.

2 Theory

2.1 Notations and conventions

In the following, we denote basis functions, in this case atomic orbitals (AOs) ϕ, with Latin indices i, k. Molecular orbitals ψ have Greek indices α, β. Atomic indices are capital Latin letters I, K. In this convention, orbital indices and atomic indices are always related to each other, and basis function $\phi_i = |i\rangle$ is located at the atomic centre I at $\underline{R}_I$. If a sum is running over all basis functions i which belong to atom I, we will write $\sum_{i\epsilon\{I\}}$. For auxiliary functions, Greek letters μ, ν are chosen as indices. The index of the DFT part is D, and of the TB part T. This index is given in parenthesis on the upper right to quantities which depend on either part only. In analogy to the atomic sums, $\sum_{i\epsilon\{D\}}$ runs over all elements i which are members of the D region. For matrix-related quantities, a double index is given, denoting the corresponding matrix block. With this convention, the overlap matrix of the system reads as

$$\underline{\underline{S}} = \begin{pmatrix} \underline{\underline{S}}^{(DD)} & \underline{\underline{S}}^{(DT)} \\ \underline{\underline{S}}^{(TD)} & \underline{\underline{S}}^{(TT)} \end{pmatrix}. \tag{1}$$

As the overlap and Kohn-Sham matrices are symmetric, only one of the off-diagonal blocks (DT) and (TD) has to be evaluated. The same convention is used for quantities which are related to atoms, e.g. $V^{(I)}$ or $\varrho^{(I)}$. If a sum is running over all elements of a part, we write, e.g. for atomic potential contributions, $\sum_{I\epsilon\{D\}} V^{(I)}(\underline{r})$.

2.2 DFT×TB within the LCAO-DFT framework

The theory of the DFT×TB method is based on DFT within a local orbital framework. To keep the theory and implementation of the method as simple as possible, we write the molecular orbitals ψ_α as a Linear Combination of Atomic Orbitals (LCAO) ansatz

$$\begin{aligned} \psi_\alpha &= \sum_{k=1}^{N} C_{k\alpha}\phi_k \\ &= \sum_{k\epsilon\{D\}} C_{k\alpha}\phi_k^{(D)} + \sum_{k\epsilon\{T\}} C_{k\alpha}\phi_k^{(T)} \\ &= \sum_{k=1}^{N} C_{k\alpha} \mid k \rangle . \end{aligned} \tag{2}$$

Here, N is the total number of atomic orbitals (AOs) of the system, N_D is the number of AOs in the DFT part, and N_T is the number of AOs in the TB part. It is important to note that we are using 'natural' atomic orbitals, i.e. those which are solutions of a DFT calculation of the spherical atom, using the same computational details as for the molecule which shall be treated in DFT×TB. These atomic orbitals can be expressed in terms of any suitable basis functions, which could be numerical, Slater-type, or, as done in this implementation, Gaussian-type orbitals (GTOs).

The LCAO ansatz is split into two contributions: one arises from the AOs of the DFT part, the other from the AOs of the TB part. In the TB part, a minimal set of atomic orbitals is chosen. However, these orbitals are constructed using a much larger basis set and hence well adapted to the computational method (exchange-correlation functional and 'underlying' basis functions) of the system. For the DFT part, the basis set χ is unitarily transformed to an atomic basis set ϕ:

$$\phi_i = \mid i \rangle = \sum_k C_{ik}^{\text{atom}} \chi_{ik}. \tag{3}$$

The number of AOs per atom is determined by the requested accuracy, and in the following we will use the full set of AOs, which covers the same space as the original basis functions.

The Kohn-Sham orbitals are obtained by solving the Secular equations

$$\sum_k C_{i\alpha} \left(F_{ik} - \varepsilon_\alpha S_{ik}\right) = 0. \tag{4}$$

The overlap S_{ik} and Kohn-Sham F_{ik} matrices are given as in standard LCAO–DFT:

$$S_{\mathrm{ik}} = \left\langle \phi_i \mid \phi_k \right\rangle = \left\langle i \mid k \right\rangle \tag{5}$$

$$\begin{aligned} F_{ik} &= \left\langle \phi_i \mid \hat{T} + V_{\mathrm{eff}}(\underline{r}) \mid \phi_k \right\rangle \\ &= \left\langle i \mid \hat{T} + V_{\mathrm{eff}}(\underline{r}) \mid k \right\rangle, \end{aligned} \tag{6}$$

where the effective potential

$$V_{\mathrm{eff}}(\underline{r}) = V_{\mathrm{ext}}(\underline{r}) + V_H(\underline{r}) + V_{xc}(\underline{r}) \tag{7}$$

is a sum of external potential, Hartree potential and exchange-correlation potential.

2.3 The effective potential in DFT×TB

The first term of the effective potential, the external potential, is a sum of atom-dependent (and, if applicable, additional external contributions to the Hamiltonian) contributions

$$V_{\mathrm{ext}}(\underline{r}) = \sum_{I=1}^{N_{\mathrm{atom}}} -\frac{Z_I}{\left|\underline{R}_I - \underline{r}\right|}. \tag{8}$$

The other two contributions, Hartree and exchange-correlation potential, depend on the electronic density

$$V_H(\underline{r}) = \int \frac{\varrho(\underline{r}')}{\left|\underline{r} - \underline{r}'\right|}\, \mathrm{d}^3 r' \tag{9}$$

$$V_{xc}(\underline{r}) = V_{xc}\left[\varrho(\underline{r})\right]. \tag{10}$$

The full molecular potential can always be written in a series of atomic contributions $V^{(I)}$

$$V_{\mathrm{eff}}(\underline{r}) = \sum_I V^{(I)}(\underline{r}) = \sum_{I\epsilon\{D\}} V^{(I)}(\underline{r}) + \sum_{I\epsilon\{T\}} V^{(I)}(\underline{r}). \tag{11}$$

This series can, as the atomic orbitals, be separated into a sum of contributions of the DFT part and of a sum of TB potential contributions.

The external potential is already given in a series of atomic contributions. Also, the electron density, and hence the Hartree potential, can be written in atomic series

$$\varrho(\underline{r}) = \sum_I \varrho^{(I)}(\underline{r}). \tag{12}$$

In the same way, the exchange correlation potential can be written in a series of atomic contributions, which can in practice be achieved by special projection operations [12]:

$$V^{(I)}(\underline{r}) = V_{\mathrm{ext}}^{(I)}(\underline{r}) + V_H^{(I)}(\underline{r}) + V_{xc}^{(I)}(\underline{r}). \tag{13}$$

2.4 Computation of matrix elements in DFT×TB

Within the representation of the potential in atomic contributions, we introduce the self-consistent charge (SCC) tight-binding approximations in the TB part of the system. In the zero-order approximation [13–15], several potential contributions to the Kohn-Sham matrix are neglected, and a tight-binding-like expression with strict two-centre character replaces the Kohn-Sham matrix elements of Eq. 6 in the tight-binding section:

$$F_{ik}^{(TT)} = \begin{cases} \left\langle i \mid \hat{T} + V^{(I)} + V^{(K)} \mid k \right\rangle & \text{for } I \neq K \\ \varepsilon_k = \left\langle k \mid \hat{T} + V^{(K(k))} \mid k \right\rangle & \text{for } I = K \\ 0 & \text{otherwise.} \end{cases} \tag{14}$$

Hence, only potential contributions of the centres the basis functions are located at are considered. The two-centre approximation is justified by screening arguments: The electrons screen the contributions of the three-centre integrals and hence they become small and can be neglected within this approximation. This approximation to DFT is also known as the DFTB method and has been applied with great success for a large series of molecules, clusters, solids, surfaces, and liquids. However, for high accuracy, in particular for systems with moderate charge transfer, the DFTB approximation can be improved by consideration of the unscreened charges within a self-consistent charge (SCC) scheme: Following Elstner et al. [16], this second-order Coulomb contribution to the Kohn-Sham matrix is given by

$$F_{\mathrm{Coulomb}\,ik}^{(TT)} = \frac{1}{2} S^{(TT)} \sum_{\xi=1}^{N_{\mathrm{shell}}} \left(\gamma_{i\xi} + \gamma_{k\xi}\right) q_\xi, \tag{15}$$

where q_ξ represents the orbital charge [16]. The SCC parameter matrix $\underline{\underline{\gamma}}$ is computed using the hardness information of the free atoms. Details on the evaluation of $\underline{\underline{\gamma}}$ can be found in Ref. [16].

The Kohn-Sham matrix element of the TB part of the molecule is then given by

$$F_{ik}^{(TT)} = F_{0\,ik}^{(TT)} + F_{\mathrm{Coulomb}\,ik}^{(TT)}. \tag{16}$$

These SCC–DFTB corrections are now applied to the DFT×TB computation. Besides the beneficial effect of increased accuracy, these corrections are essential for this method to equilibrate the chemical potential and to avoid spurious charge transfer between DFT and TB parts. The four blocks of the Kohn-Sham matrix are given below:

$$\begin{aligned} F_{ik}^{(DD)} &= \left\langle i \mid \hat{T} + V_{\mathrm{eff}}^{(D)}(\underline{r}) \mid k \right\rangle \\ &\quad + \frac{1}{2} S_{ik}^{(DD)} \sum_{\xi\epsilon\{T\}} \left(\gamma_{i\xi} + \gamma_{k\xi}\right) q_\xi \end{aligned} \tag{17}$$

$$\begin{aligned} F_{ik}^{(DT)} &= \left\langle i \mid \hat{T} + V_{\mathrm{eff}}^{(D)}(\underline{r}) + V^{(K)}(\underline{r}) \mid k \right\rangle \\ &\quad + \frac{1}{2} S_{ik}^{(DT)} \sum_{\xi\epsilon\{T\}} \left(\gamma_{i\xi} + \gamma_{k\xi}\right) q_\xi \end{aligned} \tag{18}$$

$$\begin{aligned} F_{ik}^{(TT)} &= \left\langle i \mid \hat{T} + V^{(I)}(\underline{r}) + V^{(K)}(\underline{r}) \mid k \right\rangle \\ &\quad + \frac{1}{2} S_{ik}^{(TT)} \sum_{\xi\epsilon\{D,T\}} \left(\gamma_{i\xi} + \gamma_{k\xi}\right) q_\xi. \end{aligned} \tag{19}$$

In Eq. 17, the full potential of the DFT part is considered in the matrix elements. The polarisation of the TB part enters the DFT part through the SCC–DFTB second-order approximation, and hence the sum in the last term is running only over the indices of the TB part. In Eq. 18, the potential contributions contain the full potential of the DFT part, and the atomic potential of the TB part. Hence, the SCC correction needs to be applied again only for those contributions arising from the TB part of the system. Finally, Eq. 19 contains only matrix elements of the TB part of the molecule, and is a pure two-centre expression. Therefore, the SCC correction needs to be applied to the whole system, and the sum in the right-hand part of the equation runs over all contributions of the system.

As in standard DFT and SCC–DFTB, these equations are solved iteratively until convergence is reached. During the SCF–SCC procedure, the atomic potentials of the TB part remain constant, while the effective potential of the DFT part is updated in the SCF procedure. At the same time, the charges of the system are updated. Convergence is reached when both $V_{\text{ext}}^{(D)}$ and q_ξ satisfy the convergence criterion.

2.5 Computation of total energy and properties

At this point, the Kohn-Sham orbitals and orbital energies are known and it is possible to compute properties as done in a standard LCAO-DFT computation. The total energy of a DFT computation is given by

$$E_{\text{tot}} = \sum_\alpha n_\alpha \left\langle \psi_\alpha \mid \hat{T} \mid \psi_\alpha \right\rangle + \frac{1}{2}\int V_H(\underline{r})\varrho(\underline{r})\, \mathrm{d}^3 r + \int V_{\text{ext}}(\underline{r})\varrho(\underline{r})\, \mathrm{d}^3 r + E_{xc}\left[\varrho(\underline{r})\right] + E_{\text{nuc}} \tag{20}$$

All quantities can be computed in a straightforward way from the molecular orbitals. However, direct implementation of Eq. 20 is not efficient, as the computation of the exchange correlation energy involves a numerical integration over the whole system, and adequate approximations are necessary for this expression.

2.6 Generation of atomic parameters

The DFT×TB hybrid method involves three types of atomic parameters, which can all be computed in a straightforward way within the density-functional theory. These parameters are (1) the basis functions, i.e. atomic orbitals ϕ_i, (2) the atomic potentials $V^{(I)}$, and (3) the orbital hardness values of the atoms.

These parameters are obtained in a spherical atomic computation for each element which is contained in the system. To consider the embedding of the atom within a molecular framework, basis functions and potential contributions are somewhat contracted. Such a contraction is achieved by an additional spherical harmonic potential $(r/r_0)^2$, which has been suggested for the first time by Eschrig to improve DFT band structure calculations in the solid state [17]. This approximation has been used in all DFTB and SCC–DFTB computations so far, and a value of $r_0 = 2r_c$, r_c being the covalent radius of the atom, has been proven to be a very reasonable approximation for all elements of the periodic table. On the other hand, the atomic reference energies ε_k of Eq. 14 need to be obtained by free spherical atom computations to ensure the correct dissociation limit. For the SCC corrections, the atomic orbital hardness

$$\eta_k = \frac{\partial^2 E}{\partial n_k^2} = \frac{\partial \varepsilon_k}{\partial n_k} \tag{21}$$

has to be computed. For these computations, we use the orbitally resolved hardness implementation as proposed in Ref. [18,19] for free spherical atoms.

3 Implementation

The basic theory of DFT×TB has been discussed in the previous section. To a large extent, DFT×TB theory is independent of the details of a DFT implementation, in particular the choice of basis functions, the representation of electron density, and the way of computing potential contributions within the LCAO framework.

We implemented the method into the deMon LCGTO program [20]. This code makes particular choices on the numerical and analytical description of these quantities, which allow a relatively uncomplicated practical implementation, which will be discussed in this section.

3.1 Representation of basis functions, electronic density, and potential contributions

For DFT computations, deMon uses contracted Gaussian-type orbitals (cGTOs) χ. The integral block of the program is designed in such way that most of the integrations are performed on whole contractions, and not on the primitive Gaussian functions. Therefore, it is computationally rather inexpensive to use a basis of atomic orbitals, which usually involve long contractions of GTOs. These AO basis sets contain the same set of Gaussian primitives, but with different contraction coefficients. As they are AOs, represented as specially contracted GTOs, they satisfy orthonormality. In the DFT×TB implementation in deMon, the transformation of Eq. 3 is applied [21]. Depending on user choice, it is possible to remove high-energy AOs from the basis, but if this is not done the basis is absolutely equivalent to the original cGTO basis. The result, the AO basis, is set up internally in the form of cGTOs, and used for the DFT×TB computation.

In deMon, the electronic density $\varrho(\underline{r})$ is represented in an auxiliary basis of Hermite Gaussian functions $a_\mu(\underline{r})$

$$\varrho(\underline{r}) = \sum_\mu^{n_{\text{aux}}} x_\mu a_\mu(\underline{r}), = \sum_\mu^{n_{\text{aux}}} x_\mu \mid \mu \,\rangle\,, \tag{22}$$

where x_μ denote the charge-density coefficients. The charge-density coefficients are computed by the following procedure from the density matrix (for details, see Ref. [22,23]):

The electron repulsion integral matrix (ERI matrix) has the dimension of $n_{\text{aux}} + 1$ and is defined by

$$G_{\mu\nu} = \left\langle \mu \, || \, \nu \right\rangle \quad \text{for} \quad \mu, \nu \leq n_{\text{aux}} \tag{23}$$

$$G_{\mu\nu} = \left\langle \mu \right\rangle \quad \text{if} \quad \mu = n_{\text{aux}} + 1, \nu \leq n_{\text{aux}} \tag{24}$$

$$G_{\mu\nu} = \left\langle \nu \right\rangle \quad \text{if} \quad \nu = n_{\text{aux}} + 1, \mu \leq n_{\text{aux}} \tag{25}$$

$$G_{\mu\nu} = 0 \quad \text{for} \quad \mu, \nu = n_{\text{aux}} + 1. \tag{26}$$

The Coulomb vector J is defined as

$$J_\mu = \sum_{ik} P_{ik} \left\langle ik \, || \, \mu \right\rangle , \tag{27}$$

for all n_{aux} auxiliary basis functions. Its last element is the number of electrons, or the integrated charge of the molecule.

$$J_{n_{\text{aux}}+1} = N = \int \varrho(\underline{r}) \, \mathrm{d}^3 r. \tag{28}$$

Similarly, the last element of the charge density coefficients is the Lagrange multiplier, which gives the unassigned charge during the charge density fitting procedure:

$$x_{n_{\text{aux}}+1} = \lambda_J . \tag{29}$$

The new set of charge density coefficients and the value of the λ_J are obtained by

$$\underline{x} = \underline{\underline{G}}^{-1} \cdot \underline{J}. \tag{30}$$

In the representation using the fitted density also, the auxiliary basis functions are atom-centred and each contribution of the electronic density can be attributed to an atom, or to either the DFT or the TB part. Representation of the electron density in an auxiliary basis allows the efficient computation of the Hartree integrals avoiding costly four-centre terms:

$$\left\langle i \mid V_H(\underline{r}) \mid k \right\rangle = \sum_\mu x_\mu \left\langle ik \, || \, \mu \right\rangle + \lambda_J \left\langle i \mid j \right\rangle . \tag{31}$$

The Lagrange parameter λ_J ensures the conservation of the number of electrons during the fitting of the charge-density coefficients. In the deMon implementation, a special projection allows also the computation of the exchange-correlation integrals in a similar way

$$\left\langle i \mid V_{xc}(\underline{r}) \mid k \right\rangle = \sum_\mu z_\mu \left\langle ik \, || \, \mu \right\rangle . \tag{32}$$

For further details of the charge-density and exchange-correlation fitting technique implemented in deMon, we refer the reader to the work of Köster et al. in Ref. [22]. With the expressions given above, we can attribute each potential contribution to an atom, and finally perform the TB approximations.

3.2 Implementation of matrix elements in DFT×TB

We apply now the TB approximations to the matrix elements. The overlap matrix can be defined as a full matrix

$$S_{ij} = \left\langle i \mid j \right\rangle \tag{33}$$

The blocks of the Kohn-Sham matrix

$$\underline{\underline{F}} = \begin{pmatrix} \underline{\underline{F}}^{(DD)} & \underline{\underline{F}}^{(DT)} \\ \underline{\underline{F}}^{(TD)} & \underline{\underline{F}}^{(TT)} \end{pmatrix} \tag{34}$$

are computed by applying Eqs. 31, and 32 in Eqs. 17, 18, and 19. This way, we obtain for the DFT block of the Kohn-Sham matrix

$$\begin{aligned} F_{ik}^{(DD)} = & \left\langle i \mid \hat{T} + V_{\text{eff}}^{(D)}(\underline{r}) \mid k \right\rangle \\ & + \frac{1}{2} S_{ik}^{(DD)} \sum_{\xi \epsilon \{T\}} \left(\gamma_{i\xi} + \gamma_{k\xi} \right) q_\xi \end{aligned} \tag{35}$$

$$\begin{aligned} \left\langle i \mid V_{\text{eff}}^{(D)}(\underline{r}) \mid k \right\rangle = & \left\langle i \mid \sum_{I \epsilon \{D\}} - \frac{Z_I}{\left| \underline{r} - \underline{R}_I \right|} \mid k \right\rangle \\ & + \sum_{\mu \epsilon \{D\}} \left(x_\mu + z_\mu \right) \left\langle ik \, || \, \mu \right\rangle \\ & + \lambda_J \left\langle i \mid k \right\rangle . \end{aligned} \tag{36}$$

For the off-diagonal DFT×TB block, the final expression of the Kohn-Sham matrix is given by

$$\begin{aligned} F_{ik}^{(DT)} = & \left\langle i \mid \hat{T} + V_{\text{eff}}^{(D)}(\underline{r}) + V^{(K)}(\underline{r}) \mid k \right\rangle \\ & + \frac{1}{2} S_{ik}^{(DT)} \sum_{\xi \epsilon \{T\}} \left(\gamma_{i\xi} + \gamma_{k\xi} \right) q_\xi \end{aligned} \tag{37}$$

$$\begin{aligned} \left\langle i \mid V_{\text{eff}}^{(D)}(\underline{r}) \mid k \right\rangle = & \left\langle i \mid \sum_{I \epsilon \{D\}} - \frac{Z_I}{\left| \underline{r} - \underline{R}_I \right|} \mid k \right\rangle \\ & + \sum_{\mu \epsilon \{D\}} \left(x_\mu + z_\mu \right) \left\langle ik \, || \, \mu \right\rangle \\ & + \lambda_J \left\langle i \mid k \right\rangle \end{aligned} \tag{38}$$

$$\begin{aligned} \left\langle i \mid V^{(K)}(\underline{r}) \mid k \right\rangle = & \left\langle i \mid - \frac{Z_K}{\left| \underline{r} - \underline{R}_K \right|} \mid k \right\rangle \\ & + \sum_{\mu \epsilon \{K\}} \left(x_\mu + z_\mu \right) \left\langle ik \, || \, \mu \right\rangle . \end{aligned} \tag{39}$$

Finally, the elements of the TB block are computed as

$$\begin{aligned} F_{ik}^{(TT)} = & \left\langle i \mid \hat{T} + V^{(I)}(\underline{r}) + V^{(K)} \mid k \right\rangle \\ & + \frac{1}{2} S_{ik}^{(TT)} \sum_{\xi \epsilon \{D,T\}} \left(\gamma_{i\xi} + \gamma_{k\xi} \right) q_\xi \end{aligned} \tag{40}$$

$$\begin{aligned} & \left\langle i \mid V^{(I)} + V^{(K)} \mid k \right\rangle \\ & \quad = \left\langle i \mid - \frac{Z_I}{\left| \underline{r} - \underline{R}_I \right|} - \frac{Z_K}{\left| \underline{r} - \underline{R}_K \right|} \mid k \right\rangle \\ & \quad + \sum_{\mu \epsilon \{I,K\}} \left(x_\mu + z_\mu \right) \left\langle ik \, || \, \mu \right\rangle . \end{aligned} \tag{41}$$

3.3 Update of charge-density coefficients and orbital charges

With the formulas given in the previous subsection, all integrals can be computed in a straightforward way. The expansion coefficients during the SCF–SCC procedure remain to be determined. While the LCAO coefficients $C_{k\alpha}$ of Eq. 2 are obtained easily by solving the secular equations, the calculation of charges, charge-density coefficients, and exchange-correlation coefficients is a more challenging task.

The DFT×TB charges are computed using the Mulliken approximation for each set of orbitals with the same n and l quantum numbers

$$q_\xi = n_\xi^0 - \sum_{l \epsilon \{\xi\} k} n_k P_{lk} S_{lk}. \tag{42}$$

As the potential in the TB part is a sum of constant atomic potential contributions, the charge-density and exchange-correlation coefficients $\underline{x}^{(T)}$ and $\underline{z}^{(T)}$ do not change during the SCF and can be taken directly from the atomic computation, which is running for each atom type during the initialization process of the deMon program. The update of these coefficients has to be done only for the DFT part ($\underline{x}^{(D)}$ and $\underline{z}^{(D)}$). Hence, we need to redefine the Coulomb fitting procedure of Eqs. 26 to 30. As we are restricting the update of charge-density coefficients to the DFT part of the problem, only a subspace of the ERI matrix and the Coulomb vector has to be considered: In the construction of the ERI matrix in Eq. 26, the auxiliary orbital limit n_{aux} needs to be replaced by the number of auxiliary basis functions of the DFT part $n_{\text{aux}}^{(D)}$. The same holds for the number of elements of $\underline{J}$. With this modification, a time-determining step, the inversion of the ERI matrix, is reduced considerably. Then, also the density matrix P_{ik} is projected to the DFT part, $P_{ik}^{(DD)}$, and $\underline{J}^{(D)}$ can be computed with a much shorter summation in Eq. 27.

The projection of the density matrix to the DFT part is done in the following procedure: First, the Mulliken matrix

$$\underline{\underline{M}} = \underline{\underline{P}} \cdot \underline{\underline{S}} \tag{43}$$

is computed. The (DD) block of $\underline{\underline{M}}$ contains all features of the Mulliken matrix of the subsystem described by DFT. In particular, the charge of the DFT system is given by the sum of its diagonal elements

$$N^{(D)} = \sum_{i \varepsilon \{D\}} M_{ii}^{(DD)} \tag{44}$$

With this matrix, we can reversely define the (DD) block of the density matrix

$$\underline{\underline{M}}^{(DD)} = \underline{\underline{P}}^{(DD)} \cdot \underline{\underline{S}}^{(DD)} \tag{45}$$

and obtain

$$\begin{aligned} \underline{\underline{P}}^{(DD)} &= \underline{\underline{M}}^{(DD)} \cdot \left(\underline{\underline{S}}^{(DD)}\right)^{-1} \\ &= \underline{\underline{P}}^{(DD)} \cdot \underline{\underline{S}}^{(DD)} \cdot \left(\underline{\underline{S}}^{(DD)}\right)^{-1} \end{aligned} \tag{46}$$

With these equations, all quantities necessary for the iterative solution of the DFT×TB Kohn-Sham equations are known. The DFT×TB equations have to converge simultaneously for charge-density coefficients and relative charges. Both quantities influence each other, and have to be modified exactly in the same way during the SCF.

3.4 Computation of total energy

According to the DFT implementation in deMon, the total energy can be written in the form

$$\begin{aligned} E_{\text{tot}} = {} & \sum_{ik} P_{ik} F_{ik} + \sum_{ik} \sum_{\mu} P_{ik} \left\langle\, ik \mid\mid \mu \,\right\rangle x_\mu \\ & - \frac{1}{2} \sum_{\mu\nu} x_\mu x_\nu \left\langle\, \mu \mid\mid \nu \,\right\rangle + E_{xc}\left[\varrho\right] + E_{\text{nuc}} \end{aligned} \tag{47}$$

Also here, the separation of the system into DFT and TB parts leads to considerable simplification of this expression: While the first part is computationally inexpensive and straightforward, the computation of long sums of integrals should be avoided, and the numerical integration of the exchange correlation energy should be restricted to the DFT part.

With these simplifications, Eq. 47 can be written in the form

$$E_{\text{tot}} = \sum_{ik} P_{ik} F_{ik} + E^{(D)} + E^{(T)} + E^{(D-T)} + E_{\text{SCC}} + E_{\text{nuc}} \tag{48}$$

with the following contributions: The double counting contributions of the DFT part are given by

$$\begin{aligned} E^{(D)} = {} & \sum_{i \epsilon \{D\} k \epsilon \{D\}} \sum_{\mu \epsilon \{D\}} P_{ik}^{(DD)} \left\langle\, ik \mid\mid \mu \,\right\rangle x_\mu \\ & - \frac{1}{2} \sum_{\mu \epsilon \{D\} \nu \epsilon \{D\}} x_\mu x_\nu \left\langle\, \mu \mid\mid \nu \,\right\rangle + E_{xc}\left[\varrho^{(D)}\right]. \end{aligned} \tag{49}$$

For the TB block, the two-centre approximations are taken into account, and the energy contribution is written as a sum of atomic contributions

$$\begin{aligned} E^{(T)} = {} & \sum_{I \epsilon \{T\} \geq K \epsilon \{T\}} \sum_{i \epsilon \{I\} k \epsilon \{K\}} \sum_{\mu \epsilon \{I,K\}} P_{ik}^{(TT)} \left\langle\, ik \mid\mid \mu \,\right\rangle \left(x_\mu + z_\mu\right) \\ & - \frac{1}{2} \sum_{\mu \epsilon \{I\} \nu \epsilon \{K\}} x_\mu x_\nu \left\langle\, \mu \mid\mid \nu \,\right\rangle. \end{aligned} \tag{50}$$

The double counting contributions of the interaction of the two parts is computed with the consistently applied TB approximations

$$\begin{aligned} E^{(D-T)} = {} & \sum_{K \epsilon \{T\}} \sum_{i \epsilon \{D\} k \epsilon \{K\}} \sum_{\mu \epsilon \{D,K\}} P_{ik}^{(DT)} \left\langle\, ik \mid\mid \mu \,\right\rangle \left(x_\mu + z_\mu\right) \\ & - \frac{1}{2} \sum_{\mu \epsilon \{D\} \nu \epsilon \{K\}} x_\mu x_\nu \left\langle\, \mu \mid\mid \nu \,\right\rangle. \end{aligned} \tag{51}$$

Finally, the SCC Coulomb correction energy is applied to the contributions of the TB part, and to its interaction with the DFT part:

$$E_{\text{SCC}} = \frac{1}{2} \sum_{\xi \epsilon \{D,T\}} \sum_{\zeta \epsilon \{T\}} \gamma_{\xi\zeta} q_\xi \, q_\zeta. \tag{52}$$

Table 1 Benchmark computations. The system is given in the first column, followed by the methodology, the number of atoms treated with DFT N_{DFT}, the number of TB atoms N_{TB}, the number of dimension of the G matrix N_{ERI}, the dimension of the (DD) block of the density matrix $N_P^{(DD)}$, the dimension of the full density matrix N_P and the charges of the DFT and TB parts of the system Q_D and Q_T

System	method	N_{DFT}	N_{TB}	N_{ERI}	$N_P^{(DD)}$	N_P	Q_D	Q_T
He_2	DFT	2	0	8	2	2	0.0000	0.0000
	DFTB	0	2	0	0	2	0.0000	0.0000
	DFT×TB	1	1	4	1	2	0.0000	0.0000
H_2	DFT	2	0	8	2	2	0.0000	0.0000
	DFTB	0	2	0	0	2	0.0000	0.0000
	DFT×TB	1	1	4	1	2	0.0008	−0.0008
C_2H_6	DFT	8	0	92	16	16	0.0000	0.0000
	DFTB	0	8	0	0	16	0.0000	0.0000
	DFT×TB	4	4	46	8	16	0.1687	−0.1687
C_2H_4	DFT	6	0	84	14	14	0.0000	0.0000
	DFTB	0	6	0	0	14	0.0000	0.0000
	DFT×TB	3	3	42	7	14	0.1626	−0.1626
C_2H_2	DFT	4	0	76	12	12	0.0000	0.0000
	DFTB	0	4	0	0	12	0.0000	0.0000
	DFT×TB	2	2	38	6	12	0.0417	−0.0417

4 Benchmark calculations

In the first implementation, for technical reasons we restrict the DFT part to use the same basis set as the DFTB part, i.e. a minimal basis set of atomic orbitals, which have been obtained by atomic computations using the PBE functional [24], and a DZVP basis with A2 auxiliaries [25]. The confinement radius of the additional harmonic potential to construct basis functions and potential is chosen to be 3 r_c. In Table 1, the Mulliken charges, the dimension of the electron repulsion matrix, and density matrix blocks are given. As minimal basis sets are used, the size of the DFT part will increase in later practical computations. The first example is a Helium dimer at a distance of 1.2 Å. This example is chosen to see if an artificial charge transfer can occur if the subsystems have no covalent or ionic interaction. As Table 1 shows no atomic charges for the two atoms, DFT and TB parts behave equally for this system. The second example is H_2, at SCC-DFTB[16] bond length of 0.74 Å. In all following examples, the geometry has been fully optimised within SCC-DFTB as implemented in deMon. We observe that also the breaking of a covalent bond is described correctly within DFT×TB. In the next examples, we break the single, double, and triple bonds between the two carbons of ethane, ethene, and ethyne. The system is separated in such a way that one half is treated with DFT, and the other half with TB. Again, we do not observe considerable charge transfer in between the two parts of the molecule. However, we observe a trend that a small charge is always floating to the TB part.

5 Discussion and Conclusions

With this preliminary implementation, it is impossible to provide a complete perspective of the performance of DFT×TB. However, first conclusions can be drawn on the basis of the first results.

Computational Performance: The method is clearly faster than LCGTO–DFT. The speedup depends on size and partition of the system and is determined by the following facts:

1. The number of necessary integral computations is strongly reduced. While the kinetic energy integrals are identical, already the three-centre sum of the external potential is reduced for the TB part, for which all three-centre contributions are neglected. Even more impact has the neglect of three centre terms for the Hartree- and exchange-correlation integrals.
2. The numerical grid is restricted to the DFT region. Hence, the number of grid points is determined only by the DFT part.
3. The charge-density fitting procedure is restricted to the DD part. This implies that (1) only charge-density coefficients of the DFT part need to be computed, (2) a much smaller ERI matrix (G) needs to be inverted, and (3) the integration runs only over a much shorter sum over the DD block of the density matrix (see Eq. 27).
4. All linear algebra operations of the G matrix are reduced to the size of the DFT part.
5. All linear algebra operations of the SCF procedure are reduced as the TB part runs always with a minimal basis.

Depending on the ratio of full system to the DFT part, the speedup may be several orders of magnitude from our experience with standard DFTB computations. However, TB and DFT have the same scaling of computer time with respect to the number of basis functions when it comes to matrix algebra, which is time determining for large matrices. Efficient implementations of DFTB, as for example in the present experimental version of deMon [20], show that molecular dynamics simulations of systems containing 1000 heavy atoms can easily be treated on a standard PC workstation with 1 GByte of memory in acceptable performance, and we can expect a comparable run time with DFT×TB.

Accuracy The accuracy of the approach cannot be discussed here in final. As the SCC parameters in the γ matrix of Eq. 15 determine the difference of chemical potential between the different parts, their accurate computation is crucial for the whole method. Additionally, the choice of the contraction coefficients of the basis set, and the underlying Gaussian basis, have considerable impact on the results. A more detailed evaluation of the influences of these numerical parameters is in progress.

Transferability We gave the theory above applicable for general Kohn-Sham DFT. A generalisation to hybrid functionals is not obvious. The implementation is strongly simplified if DFT takes advantage of a fitted charge density or a fitted potential, as the TB information is easier to be handled in this way. However, also the implementation using a four-centre integration technique for the Coulomb potential is possible.

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