Computationally efficient implementation of hybrid functionals in SIESTA

M. H. Hakala and A. S. Foster

Aalto University

SCIENCE +
TECHNOLOGY

RESEARCH REPORT

Aalto University publication series
SCIENCE + TECHNOLOGY 19/2013

Computationally efficient implementation of hybrid functionals in SIESTA

M. H. Hakala and A. S. Foster

Aalto University
School of Science
Department of Applied Physics
COMP/SIN

Aalto University publication series
SCIENCE + TECHNOLOGY 19/2013

ISBN 978-952-60-5268-7 (pdf)
ISSN-L 1799-4896
ISSN 1799-4896 (printed)
ISSN 1799-490X (pdf)
http://urn.fi/URN:ISBN:978-952-60-5268-7

Unigrafia Oy
Helsinki 2013

Finland

Aalto University

Abstract

Aalto University, P.O. Box 11000, FI-00076 Aalto www.aalto.fi

Author
M. H. Hakala and A. S. Foster

Name of the publication
Computationally efficient implementation of hybrid functionals in SIESTA

Publisher School of Science

Unit Department of Applied Physics

Series Aalto University publication series SCIENCE + TECHNOLOGY 19/2013

Field of research Computational Physics

Abstract

In this work we have implemented hybrid functionals into the SIESTA code, with the main goal to implement a fast general solver within the SIESTA framework that performs efficiently and scales linearly with increasing system size. We describe the implementation of the solver and apply it to study the properties of five insulating materials; NaCl, CaF2, CeO2, TiO2 and HfO2. We show that a systematic improvement in the basic description of the properties of these materials over standard Density Functional approaches can be obtained at a reasonable additional computational cost.

Keywords density-functional theory, exchange

ISBN (printed) **ISBN (pdf)** 978-952-60-5268-7

ISSN-L 1799-4896 **ISSN (printed)** 1799-4896 **ISSN (pdf)** 1799-490X

Location of publisher Helsinki **Location of printing** Helsinki **Year** 2013

Pages 22 **urn** http://urn.fi/URN:ISBN:978-952-60-5268-7

Computationally efficient implementation of hybrid functionals in SIESTA

M. H. Hakala[1] and A. S. Foster[1]

[1]*Department of Applied Physics, Aalto University,*
P.O. Box 11000, FI-00076 Aalto, Finland

(Dated: August 3, 2013)

Abstract

In this work we have implemented hybrid functionals into the SIESTA code, with the main goal to implement a fast general solver within the SIESTA framework that performs efficiently and scales linearly with increasing system size. We describe the implementation of the solver and apply it to study the properties of five insulating materials; NaCl, CaF_2, CeO_2, TiO_2 and HfO_2. We show that a systematic improvement in the basic description of the properties of these materials over standard Density Functional approaches can be obtained at a reasonable additional computational cost.

I. INTRODUCTION

Since its development[1], Density Functional Theory (DFT) has increasingly come to dominate in computational solid-state physics, providing an accurate framework for interpreting and predicting materials properties. However, the standard Local Density Approximation (LDA)[2] and the Generalized Gradient Approximation (GGA)[3,4] have proved to be flawed in more complex systems. For example, the locality of the correlation in LDA and GGA functionals means that non-local van der Waals interactions are treated incorrectly[5] and must be explicitly added[5–12]. Similarly, the lack of derivative discontinuities and the spurious self interaction in standard LDA and GGA functionals means that band gaps are, in general, underestimated. Including even a small fraction of exact exchange using a "hybrid" functional, including non-local contributions, partly corrects for this[13–15], and also provides more accurate geometries and energies for many molecules[16–19], and bulk structures including improved band gaps[20–28]. Such hybrid functionals also give a better description of charge localization[29] and magnetic coupling[30].

The SIESTA methodology and implementation[31–33] has become one of the most widely used DFT-based codes in solid-state physics. Implementing a linear combination of strictly confined numerical atomic orbitals, the enforcement of spatial locality allows the construction of the Hamilonian to be linear-scaling. By varying the degree of confinement it is possible to trade precision for computational speed. When combined with methods that enforce the solution of the Kohn-Sham to yield localized Wannier functions, it is therefore possible to achieve linear-scaling in both computational cost and memory. Recently, efforts have focused on adding more functionality to the code[33], while maintaining its overall efficiency. In an effort to also offer the capability of hybrid functionals in SIESTA, we have added both screened and unscreened versions of Hartree-Fock solver into the code, allowing us to run calculations with a greatly improved treatment of electron exchange. Our implementation includes a general input structure for the contribution of Hartree-Fock exchange, so that the user can choose the functional most relevant to the science and system size e.g. PBE0[34], B3LYP[35]. Large calculations can be facilitated by the use of the screened hybrid functionals, such as HSE[16] and HSE06[36]. To validate the solver we have calculated several semiconducting/insulating bulk materials and compared the electronic properties calculated by standard GGA and hybrid functionals.

II. THEORY

The hybrid approach to the generation of more accurate functionals was originally introduced by Becke in 1993[37]. This approach relies on the adiabatic connection method[38] wherein a fraction of the local or semi-local exchange within a standard functional is replaced by a proportion of non-local Hartree-Fock exchange:

$$E_X^{HF} = -\frac{1}{2}\sum_{k,l}\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_k^*(\mathbf{r}_1)\psi_l^*(\mathbf{r}_2)(\frac{1}{r_{12}})\psi_k(\mathbf{r}_2)\psi_l(\mathbf{r}_1). \tag{1}$$

For large-scale calculations, the previous equation rapidly becomes a computational bottleneck due to the scaling with the number of basis functions and prefactor for evaluating each term. Screened hybrid functionals, on the other hand, are able to incorporate Hartree-Fock exchange into bulk materials with significantly lower computational requirements. In addition, screened hybrid functionals lack certain undesirable features experienced with the full Hartree-Fock exchange. Without the screening the exchange hole has a tail contribution that is not cancelled out by the local correlation in these functionals. The use of screening reduces the long-range tail of the exchange yielding a better description for the total exchange-correlation hole. Furthermore, for some materials full Hartree-Fock exchange overestimates the optical gap. As the screening lowers the amount of exchange, a better description of the optical gap for these materials is also gained. An in-depth discussion on the properties of the orbital dependent functionals is provided in Ref.[14].

With screened functionals the Hartree-Fock integral kernel of 1/r is split into short-range (SR) and long-range (LR) parts and only the short-range part is included in the functional. In principle this division is arbitrary, but the error function below has the benefit of being easily implemented:

$$\frac{1}{r_{12}} = \underbrace{\frac{\mathrm{erfc}(\omega r_{12})}{r_{12}}}_{SR} + \underbrace{\frac{erf(\omega r_{12})}{r_{12}}}_{LR}. \tag{2}$$

The parameter ω is a screening parameter and a positive real number. For given functionals this is a fixed parameter obtained usually via fitting. We are using value $\omega = 0.15\,Bohr^{-1}$ in our calculations, and we are effectively using the HSE06 functional[16,36], given by:

$$E_{XC}^{HSE06} = 0.75E_X^{PBE-SR} + 0.25E_X^{HF-SR} + E_X^{PBE-LR} + E_C^{PBE}. \tag{3}$$

Here also the exchange part of the GGA functional (in this case we use PBE[39]) is screened. This means that the exchange hole of the functional is screened with:

$$J^{\omega PBE,SR}(\rho,s,y) = J^{PBE}(\rho,s,y) \times \text{erfc}(\frac{\omega y}{k_F}). \tag{4}$$

Finally, though not in scope of this paper, we note that certain other functionals can be constructed by taking the LC part of exchange into account. These are for instance non-local van der Waals density functionals vdW-DF-09[40] and LCS-VV09[41].

III. METHODS

A. The SIESTA method

SIESTA[31,32] is a real space linear combination of atomic orbitals basis code, implementing DFT within the generalized gradient approximation. Core electrons are represented by norm-conserving Troullier-Martins pseudopotentials. It uses strictly confined numerical orbitals with flexibility with respect to the cutoff radii, number of split-zeta basis functions, and number of polarization orbitals used in the calculations. In SIESTA, usually only a small number of basis functions per atom are required and these orbitals are of finite spatial extent, leading to a sparse Hamiltonian and overlap matrix. Thus SIESTA is relatively fast and makes calculations of hundreds or even thousands of atoms feasible by trading numerical precision for computational speed. Furthermore, because of the localized basis set, there is little extra cost associated with the presence of vacuum in the system and non-periodic boundary conditions are possible. Hence, SIESTA represents an especially efficient choice for systems such as surfaces.

In the standard SIESTA methodology, the two-centre Hamiltonian matrix elements are calculated using a 1-D FFT convolution of the numerical orbitals on a radial grid. The remaining terms, such as the Hartree and exchange-correlation energies, are evaluated using an auxiliary basis set. Here the electron density is constructed on a uniform Cartesian mesh where there are non-zero orbital contributions. The Hartree potential can then be computed either by a Fast Fourier Transform (FFT) or via hierarchical multigrid methods if formal linear-scaling or open boundary conditions are required. Because a standard calculation only requires a single forward and backward FFT per SCF cycle, the deviation of this algorithm from linear-scaling has negligible consequence for the total computational time within a calculation. The use of the same approach to the solution of the Poisson equation could be employed in the calculation of Hartree-Fock exchange integrals. However, because each integral has to be performed separately due to the non-local nature of the potential, the scaling of the Poisson solver becomes an important consideration for a linear-scaling methodology. Hence, it is important that the use of global FFTs be avoided for the calculation of the Hartree-Fock exchange terms.

B. Fock matrix calculation

For practical calculations, the Fock matrix is represented via basis functions $\phi_\lambda(\mathbf{r})$; an atomic orbital basis in our case. This leads to the following expressions for that define the Hartree-Fock energy:

$$\begin{aligned} E_X^{HF} &= -\frac{1}{2}\sum_{\mu,\nu} P_{\mu\nu} K_{\mu,\nu} && (5) \\ K_{\mu\nu} &= \sum_{\lambda,\sigma} P_{\lambda\sigma}(\mu\nu|\lambda\sigma) && (6) \\ (\mu\nu|\lambda\sigma) &= \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_\mu(\mathbf{r}_1)\phi_\lambda(\mathbf{r}_1) g(\mathbf{r}_{12}) \phi_\nu(\mathbf{r}_2)\phi_\sigma(\mathbf{r}_2), && (7) \end{aligned}$$

where K is the Fock matrix and the integral in Eq. 7 are named as electron repulsion integrals (ERI's). The interaction potential $g(\mathbf{r}_{12})$ in these equations is commonly the standard Coulombic 1/r. However, this can also be divided into a short-range (SR) and long-range (LR) parts as mentioned previously.

1. ERI calculation

The evaluation of the electron repulsion integrals (ERIs) is the key to the efficient implementation of Hartree-Fock exchange. This problem has been extensively addressed in the context of Gaussian basis functions[42,43] including for the case of periodic solids as implemented in the CRYSTAL program[44]. Because of the proliferation of basis function types within the solid-state density functional theory there has been increasing recent interest as to how to perform these integrals for more general functions, including planewaves. Two studies have already considered the case of numerical atomic orbitals[45,46] as general approach.

In the present work we take an alternative approach to try to achieve efficient calculation of the ERIs for numerical atomic orbitals. Rather than attempting to perform the expensive numerical integration required for a general radial function on a grid, we introduce a second auxiliary fitting basis set to express the PAOs in terms of analytic functions. Given the efficient algorithms that have already been developed for Gaussian basis functions, we chose to expand the PAOs as a linear-combination of such functions. The electron repulsion integrals can then be computed using RYS quadrature[47].

For accuracy and convergence it is essential to minimize the mismatch error especially at the cutoff radius of the orbitals. For computational expediency, we fit the tail part of the SIESTA orbital with a single Gaussian and only use more contractions closer to the atomic center. This reduces the number of contractions for most of the integrals. Furthermore, to speed up calculations we consider the 8-fold permutational symmetry, where the following integrals are equal and thus only one instance needs to be calculated:

$$(\mu\nu|\lambda\sigma) = (\mu\nu|\sigma\lambda) = (\nu\mu|\lambda\sigma) = (\nu\mu|\sigma\lambda) = (\lambda\sigma|\mu\nu) = (\sigma\lambda|\mu\nu) = (\lambda\sigma|\nu\mu) = (\sigma\lambda|\nu\mu). \quad (8)$$

For the forces we have modified this algorithm to include also gradients of the integrals. All the gradients are done analytically within the RYS quadrature. With Gaussians and RYS quadrature it is rather easy to split the 1/r Coulombic kernel into SR and LR parts with the error function as described in Eq. 2. Thus the same algorithm can be used with all three kernels and in our implementation we provide interface for all of them.

2. *Direct integral screening*

Efficient screening of integrals is a key component in making the calculations fast. Here user provided tolerance controls which integrals are neglected. We have found that the value of 10^{-6} Ry is generally good value for the tolerance, but this should be tuned for each system separately. Especially with screened SR-kernels, prescreening can reduce the number of calculated integrals by several orders of magnitude. We are using two types of direct screening within our implementation. The Schwarz inequality gives an upper bound to the ERI with respect to distance of the individual shell pairs:

$$|(\mu\nu|\lambda\sigma)|^2 \leq |(\mu\nu|\mu\nu)||(\lambda\sigma|\lambda\sigma)|. \tag{9}$$

Multipole type screening, referred to as 1DS in Ref.[48], gives an approximation to the SR-ERI with respect to the distance of the two charge distributions:

$$(\mu\nu|\lambda\sigma)_{SR} \approx \sum_{l=0}^{L}\sum_{j=0}^{L'} q_l^{\mu\nu}(\mathbf{P}) q_j^{\lambda\sigma}(\mathbf{Q}) \frac{\tilde{C}_{l+j}(\mathbf{R_{PQ}})}{\mathbf{R}_{PQ}^{(l+j)}}. \tag{10}$$

Here q are multipole terms, $\tilde{C}$ the multipole coefficients and $\mathbf{R}_{PQ}$ the distance between centers of charge distributions P and Q.

3. DM based integral screening

To further screen integrals in order to gain speed-up one can take the density matrix (DM) elements into consideration. This can be combined into both Schwarz and 1DS screening methods. For semiconducting and insulating systems the density matrix has been shown[49,50] to decay exponentially as $\lim_{|\mathbf{r}_1-\mathbf{r}_2|\to\infty} \rho(\mathbf{r}_1, \mathbf{r}_2) \propto \exp(-\sqrt{E_{gap}}|\mathbf{r}_1 - \mathbf{r}_2|)$, where E_{gap} the energy difference between the highest occupied and lowest unoccupied band or molecular orbital. Taking this into account when studying this type of material, the two previously mentioned screening techniques can be further enhanced as:

$$P_{max} \times E_{schwarz,1DS} \leq E_{tolerance}, \tag{11}$$

where

$$P_{max} = max\{|P_{\mu\lambda}|, |P_{\mu\sigma}|, |P_{\nu\lambda}|, |P_{\nu\sigma}|\}. \tag{12}$$

As during the SCF iterations, the density matrix changes, it would be desirable to have a fixed DM for screening to keep the procedure stable. For this we are using a PBE generated DM. PBE is generally known to underestimate the gap. Thus, it yields a slower decaying DM compared to hybrids. As PBE generally gives a good estimate for DM this is good and conservative approach to include DM based screening.

For SIESTA one must note the fact that in SIESTA the density matrix has the sparsity pattern of Hamiltonian. Here only terms with overlapping (direct and via pseudopotential) basis functions are considered. As exchange is non-local property, may this sparsity pattern lead to difficulties in the convergence or in the worst case scenario to poorer accuracy. With semiconducting and insulating materials, where the charge is more localized, this in general does not have a significant role. Furthermore with HSE functional the exchange operator is screened again alleviating the undesirable affects of density matrix sparsity pattern. Still, one must pay extra care in choosing and testing proper basis functions for given materials when exchange is involved.

4. Storage and load balancing

As nowadays the clusters and supercomputers are more available the emphasis has been in parallel efficiency. One significant issue is the load balancing. We are dividing the orbital pairs into a groups called bins and then balance those over the nodes. For the first calculation the bins are divided evenly over the nodes giving rather good initial balancing. If the integrals are calculated on the fly, the dividing is dynamically balanced. This way the exchange calculation scales linearly with respect to the number of CPU's even for a modest size systems and over a huge amount of CPU's.

In practical calculations, if possible, it is most efficient to store the integrals. Nowadays in the supercomputers there are usually hundreds of gigabytes of memory available and also parallel/shared disk systems making the IO relatively fast. We provide options to store the integrals either to the memory or to the disk. We only store the significant integrals and using mentioned screening techniques is essential to reduce the required storage. With the memory we are storing the whole sparse K matrix at every node. This is not ideal, but removes the tedious communication of single integrals between nodes during the integral evaluation. With this approach we make the most intensive part of the calculation "embarrassingly parallel". One approach to reduce the memory consumption is to use hybrid parallelization of OpenMP/MPI. Thus, for example, on a quad-core processor there is no need to store matrices four times, but instead just once.

If the memory is an issue there is also a way to use parallel IO to store the compressed bins into the disk system. We implemented the approach where every node is a reader/writer. In a supercomputer with a parallel filesystem this is the most efficient approach. Also in addition to parallel calculations we provide a way to distribute the bins over a grid/distributed system.

This distributed computing can be used to store the integrals to disk, then later merged together to perform a SCF cycle without the expensive integral evaluation.

5. *Fitting SIESTA orbitals*

When benchmarking calculations, we have observed that the quality of the fitted orbitals sometimes play significant role in the convergence. In addition confining the orbitals may have a minor effect to the accuracy, but provide a significant speedup. Also the accuracy of the density matrix and good initial geometry are essential if the convergence becomes an issue. For the latter two, one can always increase the accuracy by k-point sampling and grid cutoff, and for the geometry a PBE relaxed system is a good starting point.

The origin of the problems with respect to basis set in SIESTA is twofold. First, there is the mismatch error. SIESTA uses numerical orbitals (for the radial part) that go sharply to zero at the specified cutoff radius. These cannot be fitted accurately with a small number (1-4) of Gaussian contractions. Instead, we fit these orbitals first with a few Gaussians and choose the amount that catches the qualitative behaviour of the given radial function. Then we take the numerical values from the fitting function and feed those values back to SIESTA. Thus we completely remove the mismatch error below the cutoff. This treatment does not change the radial part of the basis functions significantly and does not affect the results between the original and fitted basis.

The second issue is the smooth decay of the K matrix elements. The sparsity pattern of SIESTA is determined by the cutoff radius of each orbital. It would be desirable that for very small overlap, the K matrix elements would also be vanishing. Indeed if the fitting would be strictly zero after the cutoff radius for the auxiliary basis this would be the case. But as the Gaussians decay exponentially it is possible that the tail parts of the auxiliary basis functions are yielding too large K matrix values. This effect is small and gives only minimal contribution to the total energy, but it may cause some numerical stability issues. To overcome this problem we increase the cutoff radius for those orbitals where the mismatch error is large around the cutoff radius. Thus as the Gaussians decay exponentially a small increase in the cutoff radius makes the fitting error vanish. The price to pay is that now the sparsity pattern increases making the whole calculation more expensive.

Finally it should be noted that tuning the basis set becomes even more important when using hybrid functionals in SIESTA. In addition to the convergence issues, one can get clear speedup from more localized basis functions. Naturally the more localized the basis functions are, the greater is the effect of screening making calculation of the integrals much faster.

IV. RESULTS

A. Setup

In order to test the capabilities of our hybrid implementation in SIESTA, we have chosen to calculate five different bulk materials with different electronic properties. These systems were CaF_2, CeO_2, NaCl, TiO_2 (rutile and anatase phases) and HfO_2 (monoclinic, tetragonal and cubic phases). This set of systems ranges from narrow to wide gap insulators, and includes a variety of lattice structures and valence character.

In the calculations core electrons are represented by PBE generated norm-conserving pseudopotentials using standard Troullier-Martins parametrization. We note that a few studies show minor differences arising when using non-fitted pseudopotentials with exact exchange functionals[51,52], but in general those differences are rather small. In addition we are not using exact exchange, but only a fraction of screened exchange making the choice of PBE pseudopotentials reasonable. The basis set for the combined systems was optimized for PBE to provide fast and yet relatively accurate results for ground state properties. The used basis set was double ζ with polarization for Na($3s^1$), Cl($3p^5$), Hf($6s^2$), O($2p^4$), Ca($4s^2$), Ce($6s^2$), Ti($4s^2$,$3d^2$) and double ζ for Cl ($3s^2$), Hf($5d^2$), O($2s^2$), Ce($5s^2$, $5p^6$, $4f^2$), F($2s^2$,$2p^5$) and single ζ for Ce($5d^0$). All systems were calculated with a k-point mesh of $7 \times 7 \times 7$, a mesh cutoff of 250 Ry and an energy shift of 5 meV. This was sufficient to converge the lattice structures to a high accuracy.

In order to test the accuracy of our results and the hybrid implementation in SIESTA we repeated the calculations using the VASP code[53,54]. It uses a plane wave basis and the projector augmented wave method[55–57] to treat the valence and core states, respectively. The calculations were fully converged using an energy cutoff of 400 eV and a Γ-point centered $4 \times 4 \times 4$ grid to sample the Brillouin zone. As a final benchmark, we also repeated our calculations using the PBESol functional[58] implemented in SIESTA.

	Lattice constant (Å)						Band gap (eV)					
System	PBE^a	PBE^b	HSE^a	HSE^b	PBEsol^a	Exp.	PBE^a	PBE^b	HSE^a	HSE^b	PBEsol^a	Exp.
CaF_2	5.60	5.51, 5.50[59]	5.59	5.47	5.56	5.45[60]	6.7	7.4, 8.0[59]	8.8	9.4	6.6	12.1[61]
CeO_2	5.43	5.46, 5.43[62]	5.36	5.40	5.36	5.41[63,64]	5.9	6.6	6.2	7.6		6.0[65]
NaCl	5.69	5.70	5.67	5.66	5.60	5.63[66]	5.0	5.0	6.2	6.2	5.0	9.0[67]
TiO_2 anatase	a=3.90	3.81	3.89	3.78	3.85	3.78[68]	1.7	2.4	3.3	3.9		3.2[69]
	c=9.78	9.68	9.75	9.57	9.74	9.51[68]						
TiO_2 rutile	a=4.70	4.64, 4.65[70]	4.69	4.59	4.65	4.59[71]	1.5	1.8, 1.7[72]	3.1	3.1	1.5	3.0[73]
	c=3.03	2.97, 2.97[70]	3.02	2.96	2.99	2.96[71]						
HfO_2 cubic	a=5.14	5.08, 5.07[74]	5.13	5.04	5.15	5.08[75]	3.3	3.8, 3.8[74]	5.3	5.2		
HfO_2 tetragonal	a=5.12	5.08, 5.06[74]	5.11	5.04	5.13	5.15[76]	4.1	4.7, 4.6[74]	6.0	6.2		
	c=5.24	5.24, 5.18[74]	5.21	5.16	5.23	5.29[76]						
HfO_2 monoclinic	a=5.16	5.13[74]	5.19		5.13	5.12[77]	3.6	4.1[74]	5.1			5.7[78]
	b=5.23	5.19[74]	5.28		5.30	5.17[77]						
	c=5.38	5.31[74]	5.33		5.27	5.30[77]						
	β=98.8^o	98.8^o[74]	98.8^o		98.5^o	99.2^o[77]						

TABLE I: Lattice constant and band gap values for all calculated systems using SIESTA^a and VASP^b. Unreferenced values are calculated in this work. Note that the CeO_2 gap is calculated ignoring the $4f$ states in the gap, as is the usual convention.

For all of the systems we have calculated lattice constant parameters and approximated the fundamental gap via the difference between the highest occupied and lowest unoccupied band energies. In all our hybrid calculations we used the HSE06[36] with screening parameter $\omega = 0.15\, Bohr^{-1}$.

B. Geometry and electronic structure

In Table I we compare the calculated lattice parameters and band gaps for PBE, PBESol and HSE06 functionals with experimental values. In general, as expected for a GGA functional, PBE itself already gives good agreement with experimental lattice structures for these systems, and PBESol slightly improves the agreement in nearly all cases. HSE06 provides at least as good agreement, if not better, but the differences are not significant for any of the systems studied. HSE06 also maintains the hierarchy of phases for TiO_2 and HfO_2 seen for with PBE, with rutile and monoclinic phases predicted as the most stable respectively.

When we compare the band gaps in Table I and Density of States in Fig. I between different systems, we clearly see significant differences. As discussed earlier, the exchange and correlation approximations used in the PBE functional means that it underestimates the experimental band gap in every case (and this is effectively unchanged in PBESol), by up to around half in the case of TiO_2, CaF_2 and NaCl. The HSE06 functional and the inclusion of part of exact exchange corrects this for all systems, although the correction is certainly not complete. For TiO_2, in both phases, the band gap is now in very good agreement with experiment, and for HfO_2 the HSE06 gap is much closer to experiment, but for the wider gap materials, the HSE06 gap is still a significant underestimation, reflecting the fact that the treatment of exchange is still an approximation[26].

For CeO_2, the difference in band gap between PBE and HSE06 is quite small as PBE already gives a reasonable value, in agreement with previous studies[79]. However, the $4f$-states in the gap, critical in studies of ceria oxidation, are demonstrated to be much closer to the conduction band in HSE06 (see Fig. 1), and this is important when studying defects in ceria and related charge localization[80,81].

FIG. 1: (Color online) Density of the states for TiO_2 in the anatase and rutile phases, CeO_2, CaF_2, NaCl and HfO_2 in the monoclinic phase. In the graphs the upper curve is HSE06 and lower PBE. The energies are in eV and the Fermi energy is shifted to zero.

C. Scaling

Although the overall scaling of the SIESTA code is certainly a limiting factor in any calculations, it is important to note that for hybrid calculations most of time is spent in the Fock solver. This scales linearly, making hybrid calculations very efficient for massively parallel architectures. In order to demonstrate its capabilities for massively parallel calculations, we take as test systems bulk CaF_2, containing a with 97 and 291 atoms.

The basis set is the same as in previous sections, but, in order to test the system at very high accuracy, we have used an integral cutoff of 10^{-6}, a mesh corresponding to energy cutoff of 400 Ry and 5×5 k-point mesh sampling.

First, comparing the basic wall clock time of a run on 8 processors, we see that our hybrid functional is 4.85 times slower than the same system run with PBE. This number can change compared to used basis, system parameters and system properties and should only be considered as a qualitative number specific to this system. However, it does show that hybrid calculations can be run at computational cost little higher than conventional DFT within SIESTA.

In order to study the parallel scaling, we compare the properties of SR-HFX solver vs. the PBE solver. The scaling calculations were done using a distributed cluster with Infiniband interconnects and with SIESTA version 2.0.2. Fig. 2 shows that the SR-HFX solver scales almost ideally up to 128 processors, while the PBE solver does not scale that well after 16 processors. Though hybrid solver outperforms PBE, it is important to note that the overall scaling of SIESTA code is not improved, and full linear scaling can only be achieved by more fundamental changes in the load distribution in future versions of SIESTA.

FIG. 2: Comparison of the implemented SR-HF solver and PBE with number of CPU's. For the 97 atom system the calculations started from 4 CPU's and thus corresponding speedups refer to this value. Similarly for 291 atom the initial setup was 32 CPU's and higher speedups refer to this value.

V. SUMMARY

We have implemented a general solver for performing hybrid functional calculations into the SIESTA code. The implementation provides access to improved functionals such as HSE06, PBE0 and B3LYP, at reasonable cost above conventional DFT calculations. By the use of screening and appropriate basis optimization it is possible to run hybrid calculations at less than five time the cost of a GGA calculation. In general, extra care is needed when setting up the basis sets in comparison to standard SIESTA calculations, but otherwise the method is reliable and the results are reproducible. We have validated the implementation by calculating the geometry and electronic structure of a variety of bulk insulating materials. Our results are in good agreement with previous studies, and demonstrate the improvement offered by hybrid functionals in accurate description of electronic structure. In combination with future developments in parallel performance of the SIESTA code in general, this will aid the maintenance of SIESTA's position as one of the leading methods for solid state studies.

Acknowledgments

We thank professor Julian Gale for assistance with SIESTA code and getting the project started. We wish to thank Daniel Grimwood for the aid in the initial coding work. We also wish to thank Daniel Sanchez-Portal for useful discussions. We acknowledge support from the Academy of Finland and ESF FANAS programme, and computer resources from the CSC, Finland and iVEC/NCI, Australia.

---

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964).

[2] W. Kohn and L. Sham, Phys. Rev. **140**, 1133 (1965).

[3] D. C. Langreth and J. P. Perdew, Phys. Rev. B **21**, 5469 (1980).

[4] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).

[5] H. Rydberg, M. Dion, N. Jacobson, E. Schroder, P. Hyldgaard, S. Simak, D. Langreth, and B. Lundqvist, Physical Review Letters **91**, 126402 (2003).

[6] Dion, M., Rydberg, H., Schröder, E., L. h, D. C., Lundqvist, and B. I., Phys. Rev. Lett. **92**, 246401 (2004).

[7] K. Johnston, J. Kleis, B. I. Lundqvist, and R. M. Nieminen, Physical Review B (Condensed Matter and Materials Physics) **77**, 121404 (pages 4) (2008).

[8] A. Gulans, R. M. Nieminen, and M. J. Puska, Phys. Rev. B **79**, 201105 (2009).

[9] O. H. Pakarinen, J. M. Mativetsky, A. Gulans, M. J. Puska, A. S. Foster, and P. Grutter, Phys. Rev. B **80**, 085401 (2009).

[10] O. A. Vydrov and T. Van Voorhis, The Journal of Chemical Physics **130**, 104105+ (2009).

[11] O. A. Vydrov and T. Van Voorhis, Physical Review Letters **103** (2009), ISSN 0031-9007.

[12] P. Lazić, M. Alaei, N. Atodiresei, V. Caciuc, R. Brako, and S. Blügel, Physical Review B **81**, 045401 (2010).

[13] W. K. and. M. C. Holthausen, *A Chemist's Guide to density functional theory* (Wiley, 2001).

[14] S. Kuemmel and L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).

[15] G. Kresse, M. Shishkin, M. Marsman, and J. Paier, J Phys-Condens Mat **20**, 064203 (2008).

[16] J. Heyd, G. E. Scuseria, and M. Ernzerhof, The Journal of Chemical Physics **118**, 8207 (2003).

[17] J. Heyd and G. E. Scuseria, The Journal of Chemical Physics **120**, 7274 (2004).

[18] J. Heyd and G. E. Scuseria, The Journal of Chemical Physics **121**, 1187 (2004).

[19] F. Furche and J. Perdew, J Chem Phys **124**, 044103 (2006).

[20] J. Heyd, J. Peralta, G. Scuseria, and R. Martin, J Chem Phys **123**, 174101 (2005).

[21] J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber, and J. G. Angyan, J Chem Phys **124**, 154709 (2006).

[22] J. D. Silva, M. Ganduglia-Pirovano, and J. Sauer, Physical Review B (2007).

[23] I. C. Gerber, J. G. Ángyán, M. Marsman, and G. Kresse, The Journal of Chemical Physics **127**, 054101+ (2007).

[24] A. Alkauskas, P. Broqvist, F. Devynck, and A. Pasquarello, Physical Review Letters **101**, 4 (2008).

[25] D. I. Bilc, R. Orlando, R. Shaltaf, G.-M. Rignanese, J. Íñiguez, and P. Ghosez, Physical Review B **77**, 13 (2008).

[26] M. Marsman, J. Paier, A. Stroppa, and G. Kresse, J Phys-Condens Mat **20**, 064201 (2008).

[27] J. Wróbel, K. J. Kurzydłowski, and J. Piechota, Physical Review B **80**, 155124 (2009).

[28] L. F. J. Piper, A. DeMasi, S. W. Cho, K. E. Smith, F. Fuchs, F. Bechstedt, C. Koerber, A. Klein, D. J. Payne, and R. G. Egdell, Applied Physics Letters **94**, 022105 (2009).

[29] C. D. Valentin, G. Pacchioni, and A. Selloni, Physical Review Letters **97**, 166803 (2006).

[30] P. Rivero, I. Moreira, G. E. Scuseria, and F. Illas, Physical Review B **79** (2009), ISSN 1098-0121.

[31] J. Junquera, O. Paz, D. Sánchez-Portal, and E. Artacho, Phys. Rev. B **64**, 235111 (2001).

[32] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).

[33] E. Artacho, E. Anglada, O. Dieguez, J. D. Gale, A. Garcia, J. Junquera, R. M. Martin, P. Ordejon, J. M. Pruneda, D. Sanchez-Portal, et al., J Phys-Condens Mat **20**, 064208 (2008).

[34] C. Adamo and V. Barone, The Journal of Chemical Physics **110**, 6158 (1999).

[35] A. Becke, J. Chem. Phys. **98**, 5648 (1993).

[36] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, The Journal of Chemical Physics **125**, 224106 (2006).

[37] A. Becke, J. Chem. Phys. **98**, 1372 (1993).

[38] J. Harris, Phys. Rev. A **29**, 1648 (1984).

[39] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[40] O. A. Vydrov and T. Van Voorhis, The Journal of Chemical Physics **130**, 104105+ (2009).

[41] O. A. Vydrov and T. Van Voorhis, Physical Review Letters **103** (2009), ISSN 0031-9007, URL `http://dx.doi.org/10.1103/PhysRevLett.103.063004`.

[42] M. H.-G. Peter M. W. Gill and J. A. Pople, J. Phys. Chem. **94**, 5564 (1990).

[43] S. Obara and A. Saika, J. Chem. Phys. **84**, 3963 (1986).

[44] Pisani, C., Dovesi, R., Roetti, and C., *Hartree-Fock Ab Initio Treatment of Cryslalline Systems* (Lecture Notes in Chemistry 48 and Springer, 1988).

[45] M. Toyoda and T. Ozaki, Computer Physics Communications **181**, 1455 (2010), ISSN 0010-4655, URL `http://www.sciencedirect.com/science/article/pii/S0010465510001141`.

[46] H. Shang, Z. Li, and J. Yang, The Journal of Physical Chemistry A **114**, 1039 (2010).

[47] R. Lindh and U. R. and. B. Liu, J. Chem. Phys. **95**, 5889 (1991).

[48] A. F. Izmaylof, G. E. Scuseria, and M. J. Frisch, J. Chem. Phys. **125**, 104103 (2006).

[49] W. Kohn, Int. J. Quantum. Chem. **56**, 229 (1995).

[50] S. Goedecker, Rev. Mod. Phys. **71**, 1085 (1999).

[51] A. Höck and E. Engel, Phys. Rev. A **58**, 3578 (1998).

[52] M. Moukara, M. Stadele, J. A. Majewski, P. Vogl, and A. Gorling, Journal of Physics: Condensed Matter **12**, 6783 (2000).

[53] Kresse, G., Furthmüller, and J., Comp. Mat. Sci. **6**, 15 (1996).

[54] Kresse, G., Furthmüller, and J., Phys. Rev. B **54**, 11169 (1996).

[55] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[56] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[57] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[58] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. **100**, 136406 (2008).

[59] A. Foster, T. Trevethan, and A. Shluger, Physical Review B (2009), URL `http://link.aps.org/doi/10.1103/PhysRevB.80.115421`.

[60] M. Wakaki, K. Kudo, and T. Shibuya, *Physical Properties and Data of Optical Materials (Optical Science and Engineering)* (CRC, 2007), ISBN 0824727614.

[61] V. E. Borisenko, *Physics, Chemistry and Application of Nanostructures: Reviews and Short Notes to Nanomeeting 2003 Minsk, Belarus 20-23 May 2003* (World Scientific Publishing Company, 2003), ISBN 9812383816.

[62] M. B. Watkins, A. S. Foster, and A. L. Shluger, J. Phys. Chem. C **111**, 15337 (2007).

[63] L. Gerward and J. S. Olsen, Powder Diffr. **8**, 127 (1993).

[64] L. Gerward, J. S. Olsen, L. Petit, G. Vaitheeswaran, V. Kanchana, and A. Svane, J. Alloys Compd. **400**, 56 (2005).

[65] E. Wuilloud, B. Delley, W. D. Schneider, and Y. Baer, Phys. Rev. Lett. **53**, 202 (1984), URL `http://dx.doi.org/10.1103/PhysRevLett.53.202`.

[66] C. Kittel, *Introduction to Solid State Physics* (Wiley, 1995), ISBN 0471111813.

[67] A. K. Cheetham and P. Day, *Solid State Chemistry: Volume 2: Compounds (Oxford Science Publications) (Vol 2)* (Oxford University Press, USA, 1992), ISBN 0198551665.

[68] M. Horn, C. F. Schwerdtfeger, and E. P. Meagher, Zeitschrift fur Kristallographie **136**, 273 (1972).

[69] S. Kowalczyk, Solid State Communications **23**, 161 (1977), ISSN 00381098, URL `http://dx.doi.org/10.1016/0038-1098(77)90101-6`.

[70] G. H. Enevoldsen, H. Pinto, A. S. Foster, M. C. Christensen, A. Kühnle, M. Reichling, W.Hofer, J. V. Lauritsen, and F. Besenbacher, Phys. Rev. B **78**, 045416 (pages 19) (2008).

[71] R. Wyckoff, *Crystal Structures* (Interscience and New York, 1963).

[72] H. P. Pinto, G. H. Enevoldsen, F. Besenbacher, J. V. Lauritsen, and A. S. Foster, Nanotechnology **20**, 264020 (2009).

[73] L. Kavan, M. Gratzel, S. Gilbert, C. Klemenz, and H. Scheel, J Am Chem Soc **118**, 6716 (1996).

[74] A. S. Foster, F. L. Gejo, A. L. Shluger, and R. M. Nieminen, Phys. Rev. B **65**, 174117 (2002).

[75] J. Wang, H. P. Li, and R. Stevens, J. Mater. Sci. **27**, 5397 (1992).

[76] D. W. Stacy, J. K. Johnstone, and D. R. Wilder, J. Am. Cer. Soc. **55**, 482 (1972).

[77] D. M. Adams, S. Leonard, D. R. Russel, and R. J. Cernik, J. Phys. Chem. Solids **52**, 1181 (1991).

[78] M. Balog, M. Schieber, M. Michiman, and S. Patai, Thin Solid Films **41**, 247 (1977).

[79] J. L. F. Da Silva, M. V. Ganduglia-Pirovano, J. Sauer, and G. Kresse, Physical Review B **75** (2007), ISSN 1098-0121.

[80] M. V. Ganduglia-Pirovano, J. L. F. D. Silva, and J. Sauer, Phys. Rev. Lett. **102**, 026101 (2009).

[81] C. Zhang, A. Michaelides, D. A. King, and S. J. Jenkins, Physical Review B **79**, 075433 (2009).

Aalto-ST 19/2013

ISBN 978-952-60-5268-7 (pdf)
ISSN-L 1799-4896
ISSN 1799-4896
ISSN 1799-490X (pdf)

Aalto University
School of Science
Department of Applied Physics
www.aalto.fi

BUSINESS +
ECONOMY

ART +
DESIGN +
ARCHITECTURE

SCIENCE +
TECHNOLOGY

CROSSOVER

DOCTORAL
DISSERTATIONS