Abstract. First-principle calculations are performed within Density Functional Theory to determine the accuracy of numerical atomic orbital basis sets used for studies of highly-doped silicon nanowires. Boron, phosphorous, gallium and arsenic atoms are used as dopants. Structural and electronic properties are studied and the performance of optimised basis sets is benchmarked. A good compromise between efficiency and accuracy is offered by optimised double zeta polarised basis sets. The transferability of numerical atomic orbitals for studies of silicon nanowires is tested by applying in nanowires with different orientations.

1. Introduction
One-dimensional semiconductor nanostructures, particularly silicon nanowires (SiNWs), have attracted extensive research efforts over the past decade [1]. In recent device applications SiNWs cover a wide range of areas such as transistors for light emitting diodes (LEDs), ballistic field-effect transistors (FETs) and sensitive nanosensors. SiNW solar cells are expected to increase absorption of light, thereby, yielding higher efficiencies at lower cost. One can change the electronic and optical properties through doping of the SiNWs [2, 3] as demonstrated by evidence on tuneable control of their conductivity and photoluminescence [4, 5]. Therefore a detailed understanding of the structural and electronic properties of doped SiNWs is important. In particular, there is a growing need to address large-scale device simulations from first principles and a good compromise between efficiency and accuracy is sought [6]. To this end, atomic orbitals offer tractable basis sets but a systematic approach to improve their predicting capabilities is needed prior to applying them in practice [7, 8].

Here, our aim is to discuss quantitative estimates in SiNWs derived from Density Functional Theory (DFT) implementations using numerical atomic orbitals (NAOs) [9]. We employ Density Functional Theory to investigate the electronic structure of [110]-oriented hydrogenated SiNWs with diameters 1.15nm and highly-doped with boron, phosphorous, arsenic and gallium. These nanostructures are particularly relevant for the recent proposal of junctionless transistors [10] where doping concentrations as high as $10^{21}$ are required. We report on the convergence of different contractions of primitive and optimised NAOs by studying the structural and electronic properties of SiNWs with an uneven distribution of dopants.
2. Methodology

We perform DFT calculations within a generalized gradient approximation (GGA) to the exchange and correlation functional. Norm-conserving fully relativistic pseudopotentials and numerical atomic basis functions are generated by the software package ADPACK [13]. The systematic convergence of the quality of the basis sets is performed by increasing the number of primitive orbitals describing the valence electrons and by adding higher angular momentum functions (d-polarisation). A Monkhorst-Pack k-point sampling on a 15x1x1 grid in the Brillouin zone along the nanowire axis direction is used. The SiNW is put in a supercell with more than 24 Å vacuum spacings in the lateral directions to avoid any interactions between the neighbouring image nanowires. The SiNWs and the unit cell lattices are fully relaxed. Structural optimisation calculations are performed until the absolute value of force acting on each atom is 0.01eV/Å.

Substitutional doping of hydrogen passivated SiNWs is achieved by exchanging two silicon atoms in the supercell with B, P, Ga and As atoms. This yields a doping concentration of 4.34 % . We have taken two different configurations of each doped SiNW by placing dopants at uneven sites and have assigned them as configuration 1 and configuration 2. Figure 1 shows the example of B-doped geometry optimised nanowires.

3. Results and Discussions

The calculated total energy for the various NAO basis sets reduces with increasing the basis size and/or applying orbital optimisation as can been seen in Figure 2. By increasing the contraction and adding d-orbital polarisation functions, the total energy per atom converges to less than 0.01eV per atom. This is a minimum requirement regarding the basis set sufficiency of NAOs and it is demonstrated here for the extended system of SiNWs. The respective convergent values for the NAO basis sets are 2.04eV, 1.89eV, 1.63eV and 2.46eV for SiNWs doped with B, P, As and Ga, respectively. The optimisation of orbitals overall yields significant improvement and it becomes less important as the number of contractions increases as may be expected unless explicitly indicated, there is no difference between both the configurations of each system. A simple inspection of Figure 2 may suggest that optimised orbitals do not yield significant improvements when multiple-ζ basis sets are used. This may hold well for the structural properties. But a previous comparison with plane wave benchmark calculations in hydrogenated and hydroxylated
SiNWs [14] has indicated that electronic structure features and transport properties derived thereafter greatly improve by orbital optimisation. This is demonstrated in Figure 2 by comparing the band structures between primitive and optimised double-ζ polarised NAO for the first few valence and conduction sub-bands. The sensitivity to orbital optimisation is lesser for the valence electronic states.

Figure 2: Variation of the total energy per atom in [110]-oriented silicon nanowires for different numerical atomic basis and dopant atoms, that is, (a) boron doped (Si_{46}B_{2}H_{32}), (b) phosphorous doped (Si_{46}P_{2}H_{32}), (c) gallium doped (Si_{46}Ga_{2}H_{32}) and (d) arsenic doped (Si_{46}As_{2}H_{32}). All values are referenced to the calculation using the s4p4d1 NAOs.
Figure 3: Comparison of the first few valence and conduction (sub-)bands of (a) gallium doped (Si$_{46}$Ga$_2$H$_{32}$) and (b) arsenic doped silicon nanowire (Si$_{46}$As$_2$H$_{32}$) calculated using primitive (red solid lines) and optimized double-zeta polarized NAOs (black solid lines).

Finally, the transferability of optimised orbitals is explored by two types of control calculations. First, we consider phosphorus doped SiNWs with three different orientations [100], [110] and [111]. We
then exchange the NAOs as obtained from the various systems and compare their electronic structure. For example, we took the contracted orbitals obtained after orbital optimisation in [110]-oriented P-doped SiNW as inputs for calculations with [100]- and [111]-oriented P-doped SiNWs. For a fixed orientation, the total energies obtained after geometry relaxation are equal for the various NAO basis sets independent on the wire orientation used for the orbital optimisation. This procedure also yields almost identical band structures. The result of our comparison for the [100] orientation is shown in Figure 4. This procedure can prove very efficient in larger nanowires (or indeed other systems) where orbitals can be optimised in a small controlled environment and then transferred to the bigger system.

Figure 4: Transferability comparison of optimised numerical atomic orbitals. The band structure of a [100]-oriented P-doped is shown as calculated using orbitals obtained either from optimisation within the same structure (magenta solid lines) or from optimisation performed on [110]-oriented nanowires (blue dashed lines).

Concluding remarks
In summary, we evaluated the implementation of numerical atomic basis sets by studying the total energy and electronic bands of silicon nanowires with hydrogen surface terminations and doped with B, P, As and Ga atoms. It has been shown that there is systematic improvement with respect to the contraction scheme. Whilst total energies may converge with increasing basis size, optimised NAOs offer a better option to study the electronic properties of SiNWs with fixed basis size. In particular, the optimised double-zeta polarized basis set offers a reasonable approximation. It was also shown that there is some transferability of optimised NAOs which can be used to address nanowire calculations in more complex (larger) environments. These results complement studies that put on a firm basis the use of NAOs as an efficient method, alternative to plane waves, to calculate the properties of silicon nanowires.

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