Supplementary information for
Core Electron Binding Energies in Solids from Periodic
All-Electron Δ-Self-Consistent-Field Calculations

J. Matthias Kahk,†,§ Georg S. Michelitsch,‡ Reinhard J. Maurer,‡,‖ Karsten Reuter,‡
and Johannes Lischner*,¶ (2021)

† Department of Materials, Imperial College London, South Kensington, London SW7 2AZ,
United Kingdom

‡ Chair for Theoretical Chemistry, Technische Universität München, Lichtenbergstr. 4,
D-85747 Garching, Germany

¶ Department of Physics and Department of Materials, and the Thomas Young Centre for
Theory and Simulation of Materials, Imperial College London, London SW7 2AZ, United
Kingdom

§ Institute of Physics, University of Tartu, W. Ostwaldi 1, 50411 Tartu, Estonia

‖ Department of Chemistry, University of Warwick, Gibbet Hill Rd, Coventry, CV4 7AL,
United Kingdom

E-mail: j.lischner@imperial.ac.uk
### Table of Contents

Core hole localization in $2\times2\times1$ supercell of magnesium .......................................................... 3  
Experimental core electron binding energies ....................................................................................... 4  
High frequency (optical) dielectric constants .................................................................................... 7  
Extrapolation of calculated core electron binding energies ................................................................. 8  
k-point grids, finite size corrections, and numerical results ................................................................. 15  
Relaxed structures ................................................................................................................................... 20  
Total energies of positively charged supercells: effect of spin .......................................................... 23  
Basis sets ................................................................................................................................................. 24  
Sample control.in files ......................................................................................................................... 43
Core hole localization in $2 \times 2 \times 1$ supercell of magnesium

An isosurface plot of the vacant core eigenstate (Mg 1s core hole in a $2 \times 2 \times 1$ supercell of magnesium) is shown in Figure S1. The empty core orbital is found to be localized at one of the magnesium atoms and its wavefunction has almost perfect spherical symmetry.

Fig. S1. A localized core hole in a $2 \times 2 \times 1$ supercell of magnesium. An isosurface of the probability density of the empty core eigenstate (isovalue $= 1 \times 10^{-6}$) in the converged calculation of $E_{N-1,\alpha}$ is shown in blue. The positions of the Mg atoms are shown in gray.

We have also examined the electronic structure of the core hole final state using Mulliken analysis (Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833-1840.) The results are given in Table S1. The per-atom charge analysis indicates that the magnesium atom with a core hole carries a positive charge that is somewhat less than unity, and the rest of the positive charge is distributed among the remaining Mg atoms. A closer look at the populations of the different angular momentum channels indicates that in fact, the occupancy of basis functions of p-symmetry is higher for the atom with a core hole. This is indicative of screening of the core hole by the sea of conduction electrons. The per-atom spin analysis indicates that almost the entire spin of the total system is carried by the atom with a core hole, and the spin polarization arises from s states. This is consistent with the removal of one electron from a localized s-orbital. We note that the precise values of the Mulliken populations are dependent on the chosen basis set: they provide a reasonable qualitative description of the electronic structure of the core hole state, but they cannot be interpreted as a quantitative measure of the extent of screening.
Table 1. Mulliken analysis of the electronic structure of a Mg $2\times2\times1$ supercell with a localized Mg 1s core hole

<table>
<thead>
<tr>
<th>Atom</th>
<th>Electrons</th>
<th>Per-atom charge analysis</th>
<th></th>
<th>Per-atom spin analysis</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>$s (l = 0)$</td>
<td>$p (l = 1)$</td>
<td>$d (l = 2)$</td>
<td>Total</td>
</tr>
<tr>
<td>1</td>
<td>11.28</td>
<td>0.72</td>
<td>3.69</td>
<td>7.09</td>
<td>0.45</td>
</tr>
<tr>
<td>2</td>
<td>11.96</td>
<td>0.04</td>
<td>4.77</td>
<td>6.78</td>
<td>0.37</td>
</tr>
<tr>
<td>3</td>
<td>11.98</td>
<td>0.02</td>
<td>4.79</td>
<td>6.78</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>11.96</td>
<td>0.04</td>
<td>4.77</td>
<td>6.78</td>
<td>0.37</td>
</tr>
<tr>
<td>5</td>
<td>11.98</td>
<td>0.02</td>
<td>4.79</td>
<td>6.78</td>
<td>0.37</td>
</tr>
<tr>
<td>6</td>
<td>11.96</td>
<td>0.04</td>
<td>4.77</td>
<td>6.78</td>
<td>0.37</td>
</tr>
<tr>
<td>7</td>
<td>11.98</td>
<td>0.02</td>
<td>4.79</td>
<td>6.78</td>
<td>0.37</td>
</tr>
<tr>
<td>8</td>
<td>11.91</td>
<td>0.09</td>
<td>4.75</td>
<td>6.81</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Experimental core electron binding energies

For metals and graphite, the binding energies are given relative to the Fermi level. For insulators, values referenced to the valence band maximum are reported.

**Li 1s in lithium metal**


Average: 54.85 eV

**Be 1s in beryllium metal**


* recommended reference value based on three different measurements

Average: 111.85 eV

**Na 1s in sodium metal**


Citrin, P. H. *Phys. Rev. B* 1973, 8, 5545. 1071.76 eV

Average: 1071.75 eV
### Na 2p in sodium metal

<table>
<thead>
<tr>
<th>Author</th>
<th>Journal</th>
<th>Year</th>
<th>Page</th>
<th>Value (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrin, P. H.</td>
<td>Phys. Rev. B</td>
<td>1973</td>
<td>8, 5545</td>
<td>30.52</td>
</tr>
</tbody>
</table>

**Average:** 30.51 eV

### Mg 1s in magnesium metal

<table>
<thead>
<tr>
<th>Author</th>
<th>Journal</th>
<th>Year</th>
<th>Page</th>
<th>Value (eV)</th>
</tr>
</thead>
</table>

**Average:** 1303.24 eV

### Mg 2p in magnesium metal

<table>
<thead>
<tr>
<th>Author</th>
<th>Journal</th>
<th>Year</th>
<th>Page</th>
<th>Value (eV)</th>
</tr>
</thead>
</table>

* recommended reference value based on three different measurements

**Average:** 49.79 eV

### C 1s in graphite

<table>
<thead>
<tr>
<th>Author</th>
<th>Journal</th>
<th>Year</th>
<th>Page</th>
<th>Value (eV)</th>
</tr>
</thead>
</table>

**Average:** 284.41 eV

### Be 1s in BeO

<table>
<thead>
<tr>
<th>Author</th>
<th>Journal</th>
<th>Year</th>
<th>Page</th>
<th>Value (eV)</th>
</tr>
</thead>
</table>

**Average:** 110.00 eV
<table>
<thead>
<tr>
<th>Element</th>
<th>Reference</th>
<th>Energy (eV)</th>
<th>Average (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 1s in hex-BN</td>
<td>Hamrin, K. et al. <em>Phys. Scr.</em> 1970, 1, 277-280.</td>
<td>188.4 eV</td>
<td>188.3 eV</td>
</tr>
<tr>
<td>C 1s in β-SiC</td>
<td>Bermudez, V. M. <em>J. Appl. Phys.</em> 1988, 63, 4951-4959.</td>
<td>281.9 eV</td>
<td>281.9 eV</td>
</tr>
</tbody>
</table>
Si 2p in silicon

Average: **99.03 eV**

High frequency (optical) dielectric constants

<table>
<thead>
<tr>
<th>Material</th>
<th>Reference</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>* averaged over in-plane and out-of-plane directions.</td>
<td></td>
</tr>
</tbody>
</table>
Extrapolation of calculated core electron binding energies

Li 1s in lithium metal

Be 1s in beryllium metal
Na 1s in sodium metal

![Na 1s in sodium metal graph](image)

Na 2p in sodium metal

![Na 2p in sodium metal graph](image)
Mg 1s in magnesium metal

Mg 2p in magnesium metal
C 1s in graphite

Be 1s in BeO
O 1s in BeO

B 1s in hex-BN
N 1s in hex-BN

C 1s in diamond
Si 2p in $\beta$-SiC

C 1s in $\beta$-SiC
Si 2p in silicon

Finite size corrections are only given (and applied) for insulators. “MP corr. BE” stands for the calculated binding energy with the Makov-Payne correction using the experimental (optical) dielectric constant. “MP (fit $\varepsilon$) corr. BE” stands for the calculated binding energy with the Makov-Payne correction using a fitted dielectric constant that makes the binding energy independent of supercell size for the largest supercells.

Li 1s in lithium metal

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>$\Delta$SCF (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$\times$1$\times$1</td>
<td>1</td>
<td>30$\times$30$\times$30</td>
<td>55.08</td>
</tr>
<tr>
<td>2$\times$2$\times$2</td>
<td>8</td>
<td>15$\times$15$\times$15</td>
<td>54.57</td>
</tr>
<tr>
<td>3$\times$3$\times$3</td>
<td>27</td>
<td>10$\times$10$\times$10</td>
<td>54.88</td>
</tr>
<tr>
<td>4$\times$4$\times$4</td>
<td>64</td>
<td>8$\times$8$\times$8</td>
<td>54.88</td>
</tr>
<tr>
<td>5$\times$5$\times$5</td>
<td>125</td>
<td>6$\times$6$\times$6</td>
<td>54.87</td>
</tr>
</tbody>
</table>

Extrapolated value: 54.88
### Be 1s in beryllium metal

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>ΔSCF (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>2</td>
<td>48×48×32</td>
<td>110.24</td>
</tr>
<tr>
<td>2×2×1</td>
<td>8</td>
<td>24×24×32</td>
<td>111.07</td>
</tr>
<tr>
<td>3×3×2</td>
<td>36</td>
<td>16×16×16</td>
<td>111.66</td>
</tr>
<tr>
<td>4×4×3</td>
<td>96</td>
<td>12×12×11</td>
<td>111.80</td>
</tr>
<tr>
<td>5×5×3</td>
<td>150</td>
<td>10×10×11</td>
<td>111.89</td>
</tr>
<tr>
<td>6×6×4</td>
<td>288</td>
<td>8×8×8</td>
<td>111.87</td>
</tr>
</tbody>
</table>

Extrapolated value: 111.88

### Na 1s in sodium metal

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>ΔSCF (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>1</td>
<td>30×30×30</td>
<td>1071.37</td>
</tr>
<tr>
<td>2×2×2</td>
<td>8</td>
<td>15×15×15</td>
<td>1071.55</td>
</tr>
<tr>
<td>3×3×3</td>
<td>27</td>
<td>10×10×10</td>
<td>1071.56</td>
</tr>
<tr>
<td>4×4×4</td>
<td>64</td>
<td>8×8×8</td>
<td>1071.58</td>
</tr>
<tr>
<td>5×5×5</td>
<td>125</td>
<td>6×6×6</td>
<td>1071.57</td>
</tr>
</tbody>
</table>

Extrapolated value: 1071.56

### Na 2p in sodium metal

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>ΔSCF (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>1</td>
<td>30×30×30</td>
<td>31.48</td>
</tr>
<tr>
<td>2×2×2</td>
<td>8</td>
<td>15×15×15</td>
<td>30.63</td>
</tr>
<tr>
<td>3×3×3</td>
<td>27</td>
<td>10×10×10</td>
<td>30.64</td>
</tr>
<tr>
<td>4×4×4</td>
<td>64</td>
<td>8×8×8</td>
<td>30.65</td>
</tr>
<tr>
<td>5×5×5</td>
<td>125</td>
<td>6×6×6</td>
<td>30.65</td>
</tr>
</tbody>
</table>

Extrapolated value: 30.65
### Mg 1s in magnesium metal

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>ΔSCF (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>2</td>
<td>48×48×32</td>
<td>1302.85</td>
</tr>
<tr>
<td>2×2×1</td>
<td>8</td>
<td>24×24×32</td>
<td>1303.11</td>
</tr>
<tr>
<td>3×3×2</td>
<td>36</td>
<td>16×16×16</td>
<td>1303.22</td>
</tr>
<tr>
<td>4×4×3</td>
<td>96</td>
<td>12×12×11</td>
<td>1303.24</td>
</tr>
<tr>
<td>5×5×3</td>
<td>150</td>
<td>10×10×11</td>
<td>1303.25</td>
</tr>
<tr>
<td>6×6×4</td>
<td>288</td>
<td>8×8×8</td>
<td>1303.25</td>
</tr>
</tbody>
</table>

Extrapolated value: 1303.25

### Mg 2p in magnesium metal

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>ΔSCF (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>2</td>
<td>48×48×32</td>
<td>50.16</td>
</tr>
<tr>
<td>2×2×1</td>
<td>8</td>
<td>24×24×32</td>
<td>49.52</td>
</tr>
<tr>
<td>3×3×2</td>
<td>36</td>
<td>16×16×16</td>
<td>49.63</td>
</tr>
<tr>
<td>4×4×3</td>
<td>96</td>
<td>12×12×11</td>
<td>49.69</td>
</tr>
<tr>
<td>5×5×3</td>
<td>150</td>
<td>10×10×11</td>
<td>49.68</td>
</tr>
<tr>
<td>6×6×4</td>
<td>288</td>
<td>8×8×8</td>
<td>49.70</td>
</tr>
</tbody>
</table>

Extrapolated value: 49.69

### C 1s in graphite

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>ΔSCF (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>4</td>
<td>36×36×12</td>
<td>283.26</td>
</tr>
<tr>
<td>2×2×2</td>
<td>32</td>
<td>18×18×6</td>
<td>283.92</td>
</tr>
<tr>
<td>3×3×3</td>
<td>108</td>
<td>12×12×4</td>
<td>284.09</td>
</tr>
<tr>
<td>4×4×4</td>
<td>256</td>
<td>9×9×3</td>
<td>284.18</td>
</tr>
<tr>
<td>2×2×1</td>
<td>16</td>
<td>18×18×12</td>
<td>283.24</td>
</tr>
<tr>
<td>4×4×2</td>
<td>128</td>
<td>9×9×6</td>
<td>283.95</td>
</tr>
<tr>
<td>6×6×3</td>
<td>432</td>
<td>6×6×4</td>
<td>284.11</td>
</tr>
</tbody>
</table>

Extrapolated value: 284.44
### Be 1s in BeO

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>$q^2\alpha/2L$ (eV)</th>
<th>$\Delta$SCF (eV)</th>
<th>MP corr. BE (eV)</th>
<th>MP (fit $\epsilon$) corr. BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>4</td>
<td>30×30×18</td>
<td>4.85</td>
<td>108.07</td>
<td>109.74</td>
<td>109.92</td>
</tr>
<tr>
<td>2×2×1</td>
<td>16</td>
<td>15×15×18</td>
<td>3.99</td>
<td>109.06</td>
<td>110.43</td>
<td>110.58</td>
</tr>
<tr>
<td>3×3×2</td>
<td>72</td>
<td>10×10×9</td>
<td>2.62</td>
<td>109.77</td>
<td>110.67</td>
<td>110.77</td>
</tr>
<tr>
<td>4×4×3</td>
<td>196</td>
<td>8×8×6</td>
<td>1.81</td>
<td>110.07</td>
<td>110.69</td>
<td>110.76</td>
</tr>
<tr>
<td>5×5×3</td>
<td>300</td>
<td>6×6×6</td>
<td>1.61</td>
<td>110.16</td>
<td>110.71</td>
<td>110.77</td>
</tr>
<tr>
<td>6×6×3</td>
<td>432</td>
<td>5×5×6</td>
<td>1.42</td>
<td>110.23</td>
<td>110.72</td>
<td>110.77</td>
</tr>
</tbody>
</table>

Extrapolated values: 110.79 110.77 110.77

Experimental dielectric constant = 2.9, fitted dielectric constant = 2.62

### O 1s in BeO

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>$q^2\alpha/2L$ (eV)</th>
<th>$\Delta$SCF (eV)</th>
<th>MP corr. BE (eV)</th>
<th>MP (fit $\epsilon$) corr. BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>4</td>
<td>30×30×18</td>
<td>4.85</td>
<td>526.34</td>
<td>528.02</td>
<td>528.16</td>
</tr>
<tr>
<td>2×2×1</td>
<td>16</td>
<td>15×15×18</td>
<td>3.99</td>
<td>527.16</td>
<td>528.53</td>
<td>528.65</td>
</tr>
<tr>
<td>3×3×2</td>
<td>72</td>
<td>10×10×9</td>
<td>2.62</td>
<td>527.85</td>
<td>528.76</td>
<td>528.83</td>
</tr>
<tr>
<td>4×4×3</td>
<td>196</td>
<td>8×8×6</td>
<td>1.81</td>
<td>528.15</td>
<td>528.77</td>
<td>528.82</td>
</tr>
<tr>
<td>5×5×3</td>
<td>300</td>
<td>6×6×6</td>
<td>1.61</td>
<td>528.23</td>
<td>528.78</td>
<td>528.83</td>
</tr>
<tr>
<td>6×6×3</td>
<td>432</td>
<td>5×5×6</td>
<td>1.42</td>
<td>528.31</td>
<td>528.79</td>
<td>528.84</td>
</tr>
</tbody>
</table>

Extrapolated values: 528.86 528.83 528.83

Experimental dielectric constant = 2.9, fitted dielectric constant = 2.67

### B 1s in hex-BN

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>$q^2\alpha/2L$ (eV)</th>
<th>$\Delta$SCF (eV)</th>
<th>MP corr. BE (eV)</th>
<th>MP (fit $\epsilon$) corr. BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2×2×1</td>
<td>16</td>
<td>15×15×12</td>
<td>3.50</td>
<td>187.81</td>
<td>188.56</td>
<td>188.44</td>
</tr>
<tr>
<td>4×4×2</td>
<td>128</td>
<td>8×8×6</td>
<td>1.83</td>
<td>188.10</td>
<td>188.49</td>
<td>188.43</td>
</tr>
<tr>
<td>6×6×3</td>
<td>432</td>
<td>5×5×4</td>
<td>1.23</td>
<td>188.22</td>
<td>188.49</td>
<td>188.45</td>
</tr>
</tbody>
</table>

Extrapolated values: 188.42 188.44 188.44

Experimental dielectric constant = 4.67, fitted dielectric constant = 5.49
### N 1s in hex-BN

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>$q^2\alpha/2L$ (eV)</th>
<th>$\Delta$SCF (eV)</th>
<th>MP corr. BE (eV)</th>
<th>MP (fit $\varepsilon$) corr. BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2×2×1</td>
<td>16</td>
<td>15×15×12</td>
<td>3.50</td>
<td>395.54</td>
<td>396.28</td>
<td>396.42</td>
</tr>
<tr>
<td>4×4×2</td>
<td>128</td>
<td>8×8×6</td>
<td>1.83</td>
<td>395.96</td>
<td>396.35</td>
<td>396.42</td>
</tr>
<tr>
<td>6×6×3</td>
<td>432</td>
<td>5×5×4</td>
<td>1.23</td>
<td>396.11</td>
<td>396.37</td>
<td>396.42</td>
</tr>
</tbody>
</table>

Extrapolated values: 396.39, 396.42, 396.42

Experimental dielectric constant = 4.67, fitted dielectric constant = 3.95

### C 1s in diamond

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>$q^2\alpha/2L$ (eV)</th>
<th>$\Delta$SCF (eV)</th>
<th>MP corr. BE (eV)</th>
<th>MP (fit $\varepsilon$) corr. BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>2</td>
<td>12×12×12</td>
<td>6.44</td>
<td>280.93</td>
<td>282.06</td>
<td>282.66</td>
</tr>
<tr>
<td>2×2×2</td>
<td>16</td>
<td>6×6×6</td>
<td>4.29</td>
<td>283.11</td>
<td>283.86</td>
<td>284.27</td>
</tr>
<tr>
<td>3×3×3</td>
<td>54</td>
<td>4×4×4</td>
<td>3.00</td>
<td>283.66</td>
<td>284.19</td>
<td>284.47</td>
</tr>
<tr>
<td>4×4×4</td>
<td>128</td>
<td>3×3×3</td>
<td>2.29</td>
<td>283.81</td>
<td>284.21</td>
<td>284.43</td>
</tr>
<tr>
<td>5×5×5</td>
<td>250</td>
<td>6×6×6</td>
<td>1.86</td>
<td>283.97</td>
<td>284.30</td>
<td>284.47</td>
</tr>
<tr>
<td>6×6×6</td>
<td>432</td>
<td>6×6×6</td>
<td>1.54</td>
<td>284.05</td>
<td>284.32</td>
<td>284.46</td>
</tr>
</tbody>
</table>

Extrapolated values: 284.43, 284.45, 284.46

Experimental dielectric constant = 5.7, fitted dielectric constant = 3.7

### Si 2p in β-SiC

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>$q^2\alpha/2L$ (eV)</th>
<th>$\Delta$SCF (eV)</th>
<th>MP corr. BE (eV)</th>
<th>MP (fit $\varepsilon$) corr. BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>2</td>
<td>48×48×48</td>
<td>6.03</td>
<td>98.42</td>
<td>99.35</td>
<td>99.71</td>
</tr>
<tr>
<td>2×2×2</td>
<td>16</td>
<td>24×24×24</td>
<td>3.60</td>
<td>98.50</td>
<td>99.06</td>
<td>99.27</td>
</tr>
<tr>
<td>3×3×3</td>
<td>54</td>
<td>16×16×16</td>
<td>2.49</td>
<td>98.76</td>
<td>99.14</td>
<td>99.29</td>
</tr>
<tr>
<td>4×4×4</td>
<td>128</td>
<td>12×12×12</td>
<td>1.91</td>
<td>98.88</td>
<td>99.17</td>
<td>99.28</td>
</tr>
<tr>
<td>5×5×5</td>
<td>250</td>
<td>10×10×10</td>
<td>1.51</td>
<td>98.95</td>
<td>99.18</td>
<td>99.27</td>
</tr>
</tbody>
</table>

Extrapolated values: 99.24, 99.27, 99.28

Experimental dielectric constant = 6.52, fitted dielectric constant = 4.7
### C 1s in β-SiC

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>$q^2\alpha/2L$ (eV)</th>
<th>$\Delta$SCF (eV)</th>
<th>MP corr. BE (eV)</th>
<th>MP (fit $\varepsilon$) corr. BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>2</td>
<td>48×48×48</td>
<td>6.03</td>
<td>279.68</td>
<td>280.61</td>
<td>280.81</td>
</tr>
<tr>
<td>2×2×2</td>
<td>16</td>
<td>24×24×24</td>
<td>3.60</td>
<td>280.82</td>
<td>281.38</td>
<td>281.50</td>
</tr>
<tr>
<td>3×3×3</td>
<td>54</td>
<td>16×16×16</td>
<td>2.49</td>
<td>281.04</td>
<td>281.42</td>
<td>281.51</td>
</tr>
<tr>
<td>4×4×4</td>
<td>128</td>
<td>12×12×12</td>
<td>1.91</td>
<td>281.15</td>
<td>281.44</td>
<td>281.51</td>
</tr>
<tr>
<td>5×5×5</td>
<td>250</td>
<td>10×10×10</td>
<td>1.51</td>
<td>281.22</td>
<td>281.45</td>
<td>281.50</td>
</tr>
</tbody>
</table>

Extrapolated values: 281.48 281.50 281.51

Experimental dielectric constant = 6.52, fitted dielectric constant = 5.33

### Si 2p in silicon

<table>
<thead>
<tr>
<th>Supercell</th>
<th>Atoms</th>
<th>k-grid</th>
<th>$q^2\alpha/2L$ (eV)</th>
<th>$\Delta$SCF (eV)</th>
<th>MP corr. BE (eV)</th>
<th>MP (fit $\varepsilon$) corr. BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×1×1</td>
<td>2</td>
<td>36×36×36</td>
<td>5.28</td>
<td>97.45</td>
<td>97.90</td>
<td>98.46</td>
</tr>
<tr>
<td>2×2×2</td>
<td>16</td>
<td>18×18×18</td>
<td>2.94</td>
<td>98.63</td>
<td>98.88</td>
<td>99.19</td>
</tr>
<tr>
<td>3×3×3</td>
<td>54</td>
<td>12×12×12</td>
<td>2.00</td>
<td>98.80</td>
<td>98.97</td>
<td>99.19</td>
</tr>
<tr>
<td>4×4×4</td>
<td>128</td>
<td>9×9×9</td>
<td>1.51</td>
<td>98.89</td>
<td>99.02</td>
<td>99.18</td>
</tr>
<tr>
<td>5×5×5</td>
<td>250</td>
<td>7×7×7</td>
<td>1.21</td>
<td>98.96</td>
<td>99.07</td>
<td>99.20</td>
</tr>
</tbody>
</table>

Extrapolated values: 99.17 99.18 99.19

Experimental dielectric constant = 11.7, fitted dielectric constant = 5.22

### Relaxed structures

All structures were relaxed in FHI-aims using the DFT with the exchange-correlation functional SCAN and the default “tight” basis sets and integration grids. Variable-cell relaxation with fixed angles between the unit cell vectors were performed, until all forces were below 0.005 eV/Å. In some cases, numerical stability issues were observed during structural relaxation (mismatch of real and predicted energy gain between successive relaxation steps). Numerical stability issues with the SCAN functional have been previously noted, e.g. Bartok et al. *J. Chem. Phys.* 2019, 150, 161101. To overcome this issue, the numerical grids were tightened as follows: the “radial multiplier” was increased by a factor of two, one additional localized angular grid division was uncommented, and the outermost angular grid was increased to match the uncommented value. The relaxed structures are given below, in the FHI-aims geometry.in format. All quantities are given in units of Ångström.
**k-point grids used in geometry relaxation**

Lithium metal: 12×12×12

Beryllium metal: 18×18×12

Sodium metal: 12×12×12

Magnesium metal: 18×18×12

Graphite: 18×18×9

BeO: 18×18×12

hex-BN: 18×18×8

Diamond: 18×18×18

β-SiC: 18×18×18

Silicon: 18×18×18

### Lithium metal

<table>
<thead>
<tr>
<th>lattice_vector</th>
<th>3.48166314</th>
<th>-0.00000000</th>
<th>0.00000000</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice_vector</td>
<td>0.00000000</td>
<td>3.48166513</td>
<td>0.00000000</td>
</tr>
<tr>
<td>lattice_vector</td>
<td>-0.00000000</td>
<td>0.00000000</td>
<td>3.48166512</td>
</tr>
<tr>
<td>atom</td>
<td>-0.00000000</td>
<td>0.00000000</td>
<td>0.00000000</td>
</tr>
<tr>
<td>atom</td>
<td>1.74083158</td>
<td>1.74083256</td>
<td>1.74083256</td>
</tr>
</tbody>
</table>

### Beryllium metal

<table>
<thead>
<tr>
<th>lattice_vector</th>
<th>2.26150031</th>
<th>0.00827131</th>
<th>0.00000000</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice_vector</td>
<td>-1.12335037</td>
<td>1.96244733</td>
<td>0.00000000</td>
</tr>
<tr>
<td>lattice_vector</td>
<td>0.00000000</td>
<td>0.00000000</td>
<td>3.57104216</td>
</tr>
<tr>
<td>atom</td>
<td>0.00188679</td>
<td>1.31275315</td>
<td>2.67828164</td>
</tr>
<tr>
<td>atom</td>
<td>1.13626315</td>
<td>0.65796560</td>
<td>0.89276052</td>
</tr>
</tbody>
</table>

### Sodium metal

<table>
<thead>
<tr>
<th>lattice_vector</th>
<th>4.19260705</th>
<th>-0.00000000</th>
<th>0.00000000</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice_vector</td>
<td>-0.00000000</td>
<td>4.19260951</td>
<td>0.00000000</td>
</tr>
<tr>
<td>lattice_vector</td>
<td>0.00000000</td>
<td>0.00000000</td>
<td>4.19260949</td>
</tr>
<tr>
<td>atom</td>
<td>0.00000002</td>
<td>0.00000002</td>
<td>0.00000002</td>
</tr>
<tr>
<td>atom</td>
<td>2.09630350</td>
<td>2.09630473</td>
<td>2.09630472</td>
</tr>
</tbody>
</table>
### Magnesium metal

<table>
<thead>
<tr>
<th>lattice_vector</th>
<th>3.16084026</th>
<th>0.01677186</th>
<th>0.00000000</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice_vector</td>
<td>-1.56577757</td>
<td>2.74565180</td>
<td>0.00000000</td>
</tr>
<tr>
<td>lattice_vector</td>
<td>0.00000000</td>
<td>0.00000000</td>
<td>5.16338856</td>
</tr>
<tr>
<td>atom</td>
<td>0.00607990</td>
<td>1.83830438</td>
<td>1.29063688</td>
</tr>
<tr>
<td>atom</td>
<td>1.58898278</td>
<td>0.92411917</td>
<td>3.87275156</td>
</tr>
</tbody>
</table>

### Graphite

<table>
<thead>
<tr>
<th>lattice_vector</th>
<th>1.22503480</th>
<th>2.12182291</th>
<th>0.00000000</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice_vector</td>
<td>1.22503516</td>
<td>-2.12182275</td>
<td>0.00000000</td>
</tr>
<tr>
<td>lattice_vector</td>
<td>-0.00000000</td>
<td>-0.00000000</td>
<td>-6.90943766</td>
</tr>
<tr>
<td>atom</td>
<td>0.00000051</td>
<td>0.00228806</td>
<td>-5.18207532</td>
</tr>
<tr>
<td>atom</td>
<td>-0.00000058</td>
<td>-0.00228823</td>
<td>-1.72736234</td>
</tr>
<tr>
<td>atom</td>
<td>1.22503564</td>
<td>-0.70503486</td>
<td>-5.18207532</td>
</tr>
<tr>
<td>atom</td>
<td>1.22503436</td>
<td>0.70503513</td>
<td>-1.72736233</td>
</tr>
</tbody>
</table>

### BeO

<table>
<thead>
<tr>
<th>lattice_vector</th>
<th>1.34620893</th>
<th>2.32221793</th>
<th>-0.00000000</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice_vector</td>
<td>1.34620938</td>
<td>-2.32221782</td>
<td>0.00000000</td>
</tr>
<tr>
<td>lattice_vector</td>
<td>-0.00000000</td>
<td>-0.00000000</td>
<td>-4.36284836</td>
</tr>
<tr>
<td>atom</td>
<td>1.34620922</td>
<td>-0.77673125</td>
<td>0.00114554</td>
</tr>
<tr>
<td>atom</td>
<td>1.34620905</td>
<td>0.77673129</td>
<td>-2.18027864</td>
</tr>
<tr>
<td>atom</td>
<td>1.34620923</td>
<td>-0.77302324</td>
<td>-2.71221950</td>
</tr>
<tr>
<td>atom</td>
<td>1.34620904</td>
<td>0.77302328</td>
<td>-0.53079533</td>
</tr>
</tbody>
</table>

### hex-BN

<table>
<thead>
<tr>
<th>lattice_vector</th>
<th>2.49434294</th>
<th>0.00322099</th>
<th>0.00000000</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice_vector</td>
<td>-1.24441379</td>
<td>2.16179992</td>
<td>-0.00000000</td>
</tr>
<tr>
<td>lattice_vector</td>
<td>-0.00000000</td>
<td>0.00000000</td>
<td>6.75674636</td>
</tr>
<tr>
<td>atom</td>
<td>0.03056985</td>
<td>-0.01400160</td>
<td>3.37837068</td>
</tr>
<tr>
<td>atom</td>
<td>-0.02873139</td>
<td>1.45627531</td>
<td>0.00000250</td>
</tr>
<tr>
<td>atom</td>
<td>-0.03128564</td>
<td>0.01468785</td>
<td>0.00000250</td>
</tr>
<tr>
<td>atom</td>
<td>0.03312410</td>
<td>1.42758586</td>
<td>3.37837068</td>
</tr>
</tbody>
</table>
Diamond

\[
\begin{array}{cccc}
\text{lattice\_vector} & 2.50282191 & -0.00738214 & -0.00521996 \\
\text{lattice\_vector} & 1.24494967 & 2.17114328 & -0.00524220 \\
\text{lattice\_vector} & 1.24565517 & 0.71917935 & 2.04918084 \\
\text{atom} & 0.62435420 & 0.36039068 & 0.25500547 C \\
\text{atom} & 4.36907272 & 2.52254984 & 1.78371314 C
\end{array}
\]

\(\beta\)-SiC

\[
\begin{array}{cccc}
\text{lattice\_vector} & 2.17088417 & 2.17088417 & -0.00607491 \\
\text{lattice\_vector} & -0.00607102 & 2.17089000 & 2.17089000 \\
\text{lattice\_vector} & 2.17088420 & -0.00607489 & 2.17088420 \\
\text{atom} & -0.00056996 & -0.00057059 & -0.00057060 Si \\
\text{atom} & 1.08449429 & 1.08449541 & 1.08449543 C
\end{array}
\]

Silicon

\[
\begin{array}{cccc}
\text{lattice\_vector} & -0.00000000 & 2.71693088 & 2.71693088 \\
\text{lattice\_vector} & 2.71693342 & -0.00000000 & 2.71693342 \\
\text{lattice\_vector} & 2.71693596 & 2.71693596 & 0.00000000 \\
\text{atom} & -0.00000007 & -0.00000012 & 0.00000019 Si \\
\text{atom} & 1.35846741 & 1.35846684 & 1.35846588 Si
\end{array}
\]

Total energies of positively charged supercells: effect of spin

<table>
<thead>
<tr>
<th>Supercell</th>
<th>(E_{\text{tot}}) (no spin)</th>
<th>(E_{\text{tot}}) ((N_{\text{up}}-N_{\text{down}}=1))</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\times1\times1</td>
<td>-4331.66</td>
<td>-4331.86</td>
<td>-0.20</td>
</tr>
<tr>
<td>2\times2\times1</td>
<td>-17356.00</td>
<td>-17356.00</td>
<td>0.00</td>
</tr>
<tr>
<td>3\times3\times1</td>
<td>-39062.17</td>
<td>-39062.16</td>
<td>0.01</td>
</tr>
<tr>
<td>4\times4\times2</td>
<td>-138904.32</td>
<td>-138904.33</td>
<td>-0.01</td>
</tr>
<tr>
<td>5\times5\times2</td>
<td>-217041.96</td>
<td>-217041.96</td>
<td>0.00</td>
</tr>
<tr>
<td>6\times6\times2</td>
<td>-312543.51</td>
<td>-312543.51</td>
<td>0.00</td>
</tr>
<tr>
<td>6\times6\times3</td>
<td>-468818.76</td>
<td>-468818.76</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Supercell</th>
<th>(E_{\text{tot}}) (no spin)</th>
<th>(E_{\text{tot}}) ((N_{\text{up}}-N_{\text{down}}=1))</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2\times2\times2</td>
<td>-3275.81</td>
<td>-3275.78</td>
<td>0.03</td>
</tr>
<tr>
<td>3\times3\times3</td>
<td>-11068.96</td>
<td>-11068.95</td>
<td>0.01</td>
</tr>
<tr>
<td>4\times4\times4</td>
<td>-26244.79</td>
<td>-26244.79</td>
<td>0.00</td>
</tr>
<tr>
<td>5\times5\times5</td>
<td>-51264.33</td>
<td>-51264.33</td>
<td>0.00</td>
</tr>
<tr>
<td>6\times6\times6</td>
<td>-51264.33</td>
<td>-51264.33</td>
<td>0.00</td>
</tr>
</tbody>
</table>

* all energies are given in eV. For lithium, the spin-polarized calculation for the 1\times1\times1 supercell did not converge, so this datapoint is omitted.
Basis sets

In FHI-aims, both the integration grid and the basis functions need to be defined for each type of atom in each calculation. In this work, four types of settings were used for different atoms, as described below.

- For the atom with a core hole, the “special” basis sets given below were used. This are based on the “tight” default settings, with additional core basis functions to allow the remaining core electrons to relax in the presence of the core hole.

- For the nearest neighbours of the atom with a core hole, the “tight” default settings were used.

- For the second nearest neighbours of the atom with a core hole, the “intermediate” default settings were used.

- For all other atoms, the “light” default settings were used.


- The same basis sets were always used for evaluating $E_{N-1,\text{ch}}$ and $E_{N-1,\text{ground}}$. 
Lithium

# "Core" basis functions and numerical settings for Li atom.
# Based on "tight" defaults (V. Blum, 2009).

species Li_core
# global species definitions
nucleus 3
mass 6.941
#
l_hartree 6
#
cut_pot 4.5 1.8 1.0
basis_dep_cutoff 1e-4
#
radial_base 29 7.0
radial_multiplier 2
angular_grids specified
   division 0.4484 110
   division 0.5659 194
   division 0.6315 302
   division 0.6662 434
   division 0.8186 590
   division 0.9037 770
   division 6.2760 974
   outer_grid 974
   outer_grid 434

# Definition of "minimal" basis
#
valence basis states
   valence 2 s 1.
# ion occupancy
   ion_occ 1 s 2.

# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
#
# Constructed for dimers: 1.80 A, 2.25 A, 2.75 A, 3.50 A, 4.50 A
# "First tier" - improvements: -189.23 meV to -6.35 meV
hydro 2 p 1.6
hydro 2 s 2
hydro 3 d 2.6

# "Second tier" - improvements: -4.69 meV to -0.41 meV
hydro 3 p 4.6
hydro 2 p 1.8
hydro 3 s 6.2
hydro 4 d 4.7
hydro 4 f 4.1

# "Third tier" - improvements: -0.20 meV to -0.15 meV
# hydro 4 d 0.95
# hydro 3 p 6.2
# hydro 3 s 1.7

# Additional basis functions for atom with a core hole
hydro 1 s 4.0
hydro 1 s 6.0
hydro 2 s 5.0
Beryllium

# "Core" basis functions and numerical settings for Be atom.
# Based on "tight" defaults (V. Blum, 2009).
#
# Definition of "minimal" basis
#
# valence basis states
valence 2 s 1.999
valence 2 p 0.001
# ion occupancy
ion_occ 2 s 1.

# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
#
# Constructed for dimers: 1.75 A, 2.0 A, 2.375 A, 3.00 A, 4.00 A
#
# "First tier" - improvements: -677.26 meV to -34.75 meV
  ionic 2 p auto
  hydro 3 s 2.9
  hydro 3 d 3.5

# "Second tier" - improvements: -16.34 meV to -1.26 meV
  hydro 3 p 3.1
  hydro 4 d 4.7
  hydro 3 p 2.4
  hydro 4 f 7.6
  hydro 2 s 2.9

# "Third tier" - improvements: -0.27 meV to -0.05 meV
#  hydro 2 p 8.2
#  hydro 5 g 10.8
#  hydro 4 f 7
#  hydro 3 s 2.3
#  hydro 4 d 3.8

# Additional basis functions for atom with a core hole
  hydro 1 s 5.0
  hydro 1 s 7.0
  hydro 2 s 6.0
Boron

# "Core" basis functions and numerical settings for B atom.
# Based on "tight" defaults (V. Blum, 2009).

species        B_core
#  global species definitions
nucleus             5.0
mass                10.811
#
l_hartree           6
#
cut_pot             4.0 2.0 1.0
basis_dep_cutoff    1e-4
#
radial_base         32 7.0
radial_multiplier   2
angular_grids       specified
  division 0.3742  110
  division 0.5197  194
  division 0.5753  302
  division 0.7664  434
#
  division 0.8392  770
#
  division 1.6522  974
#  outer_grid  974
outer_grid  434

# Definition of "minimal" basis
#
# valence basis states
valence      2  s   2.
valence      2  p   1.0
#  ion occupancy
ion_occ      2  s   1.

# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
#
# Constructed for dimers: 1.25 A, 1.625 A, 2.5 A, 3.5 A
#
# "First tier" - improvements: -710.52 meV to -92.39 meV
  hydro 2 p 1.4
  hydro 3 d 4.8
  hydro 2 s 4
# "Second tier" - improvements: -33.88 meV to -2.20 meV
  hydro 4 f 7.8
  hydro 3 p 4.2
  hydro 3 s 3.3
  hydro 5 g 11.2
  hydro 3 d 5.4
# "Third tier" - improvements: -1.28 meV to -0.36 meV
  hydro 2 p 4.7
  hydro 2 s 8.4
  hydro 4 d 5.8
# "Fourth tier" - improvements: -0.25 meV to -0.12 meV
  hydro 3 p 2.2
  hydro 3 s 3
  hydro 4 f 9.8
  hydro 5 g 12.8
  hydro 4 d 10
# Further functions
  hydro 4 f 14
  hydro 3 p 12.4

# Additional basis functions for atom with a core hole
  hydro 1 s 9.0
  hydro 1 s 7.0
  hydro 1 s 3.0
  hydro 2 s 5.0
  hydro 2 p 6.0
Carbon

"Core" basis functions and numerical settings for C atom.
Based on "tight" defaults (V. Blum, 2009).

species       C_core

#     global species definitions
nucleus               6.0
mass                  12.0107
#

l_hartree           6
#

cut_pot             4.0 2.0 1.0
basis_dep_cutoff    1e-4
#
radial_base        34 7.0
radial_multiplier  2
angular_grids specified
  division   0.2187   50
  division   0.4416  110
  division   0.6335  194
  division   0.7727  302
  division   0.8772  434
  division   0.9334  590
  division   0.9924  770
  division  1.0230  974
  division  1.5020 1202
  outer_grid  974
  outer_grid  434

#     valence basis states
valence      2  s   2.
valence      2  p   2.0
#     ion occupancy
ion_occ      2  s   1.
ion_occ      2  p   1.

#     Definition of "minimal" basis
#

#     Suggested additional basis functions. For production calculations,
#     uncomment them one after another (the most important basis functions are
#     listed first).
# Constructed for dimers: 1.0 Å, 1.25 Å, 1.5 Å, 2.0 Å, 3.0 Å
#
# ####################################################################
# "First tier" - improvements: -1214.57 meV to -155.61 meV
  # hydro 2 p 1.7
  # hydro 3 d 6
  # hydro 2 s 4.9
# "Second tier" - improvements: -67.75 meV to -5.23 meV
  # hydro 4 f 9.8
  # hydro 3 p 5.2
  # hydro 3 s 4.3
  # hydro 5 g 14.4
  # hydro 3 d 6.2
# "Third tier" - improvements: -2.43 meV to -0.60 meV
  # hydro 2 p 5.6
  # hydro 2 s 1.4
  # hydro 3 d 4.9
  # hydro 4 f 11.2
# "Fourth tier" - improvements: -0.39 meV to -0.18 meV
#  # hydro 2 p 2.1
#  # hydro 5 g 16.4
#  # hydro 4 d 13.2
#  # hydro 3 s 13.6
#  # hydro 4 f 17.6
# Further basis functions - improvements: -0.08 meV and below
#  # hydro 3 s 2
#  # hydro 3 p 6
#  # hydro 4 d 20
#
# Additional basis functions for atom with a core hole
  # hydro 1 s 10.0
  # hydro 1 s 8.0
  # hydro 1 s 4.0
  # hydro 2 s 6.0
Nitrogen

# "Core" basis functions and numerical settings for N atom.
# Based on "tight" defaults (V. Blum, 2009).
#
#species N_core
#     global species definitions
nucleus 7
mass 14.0067
#
l_hartree 6
#
cut_pot 4.0 2.0 1.0
basis_dep_cutoff 1e-4
#
radiial_base 35 7.0
radial_multiplier 2
angular_grids specified
    division 0.1841 50
    division 0.3514 110
    division 0.5126 194
    division 0.6292 302
    division 0.6939 434
#    division 0.7396 590
#    division 0.7632 770
#    division 0.8122 974
#    division 1.1604 1202
#    outer_grid 974
outer_grid 434

# Definition of "minimal" basis
#
#valence basis states
valence 2 s 2.
valence 2 p 3.
# ion occupancy
ion_occ 2 s 1.
ion_occ 2 p 2.

# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
# Constructed for dimers: 1.0 A, 1.1 A, 1.5 A, 2.0 A, 3.0 A
#
# ##############################################################################
# "First tier" - improvements: -1193.42 meV to -220.60 meV
#    hydro 2 p 1.8
#    hydro 3 d 6.8
#    hydro 3 s 5.8
# "Second tier" - improvements: -80.21 meV to -6.86 meV
#    hydro 4 f 10.8
#    hydro 3 p 5.8
#    hydro 1 s 0.8
#    hydro 5 g 16
#    hydro 3 d 4.9
# "Third tier" - improvements: -4.29 meV to -0.53 meV
#    hydro 3 s 16
#    ionic 2 p auto
#    hydro 3 d 6.6
#    hydro 4 f 11.6
# "Fourth tier" - improvements: -0.75 meV to -0.25 meV
#    hydro 2 p 4.5
#    hydro 2 s 2.4
#    hydro 5 g 14.4
#    hydro 4 d 14.4
#    hydro 4 f 16.8
# Further basis functions - -0.21 meV and below
#    hydro 3 p 14.8
#    hydro 3 s 4.4
#    hydro 3 d 19.6
#    hydro 5 g 12.8
#
# Additional basis functions for atom with a core hole
#    hydro 1 s 11.0
#    hydro 1 s 9.0
#    hydro 1 s 5.0
#    hydro 2 s 8.0
#    hydro 2 s 10.0
#    hydro 2 p 6.5
#    hydro 3 s 6.2
#    hydro 3 p 6.2
Oxygen

# "Core" basis functions and numerical settings for O atom.
# Based on "tight" defaults (V. Blum, 2009).
#
# >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>

species O_core

#     global species definitions
nucleus 8
mass 15.9994
#
1_hartree 6
#
cut_pot 4.0 2.0 1.0
basis_dep_cutoff 1e-4
#
radial_base 36 7.0
radial_multiplier 2
angular_grids specified
division 0.1817 50
division 0.3417 110
division 0.4949 194
division 0.6251 302
division 0.8014 434
# division 0.8507 590
# division 0.8762 770
# division 0.9023 974
# division 1.2339 1202
# outer_grid 974
outer_grid 434

# Definition of "minimal" basis
#
# >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>

#     valence basis states
valence 2 s 2.
valence 2 p 4.
#
# ion occupancy
ion_occ 2 s 1.
ion_occ 2 p 3.

# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
# Constructed for dimers: 1.0 Å, 1.208 Å, 1.5 Å, 2.0 Å, 3.0 Å
#
# "First tier" - improvements: -699.05 meV to -159.38 meV
#     hydro 2 p 1.8
#     hydro 3 d 7.6
#     hydro 3 s 6.4
#
# "Second tier" - improvements: -49.91 meV to -5.39 meV
#     hydro 4 f 11.6
#     hydro 3 p 6.2
#     hydro 3 d 5.6
#     hydro 5 g 17.6
#     hydro 1 s 0.75
#
# "Third tier" - improvements: -2.83 meV to -0.50 meV
#     ionic 2 p auto
#     hydro 4 f 10.8
#     hydro 4 d 4.7
#     hydro 2 s 6.8
#
# "Fourth tier" - improvements: -0.40 meV to -0.12 meV
#     hydro 3 p 5
#     hydro 3 s 3.3
#     hydro 5 g 15.6
#     hydro 4 f 17.6
#     hydro 4 d 14
#
# Further basis functions - -0.08 meV and below
#     hydro 3 s 2.1
#     hydro 4 d 11.6
#     hydro 3 p 16
#     hydro 2 s 17.2
#
#
# Additional basis functions for atom with a core hole
#     hydro 1 s 12.0
#     hydro 1 s 10.0
#     hydro 1 s 6.0
#     hydro 2 s 10.0
#     hydro 2 p 8.0
#     hydro 2 p 6.0
#     hydro 3 d 8.0
Sodium

species Na_core
# global species definitions
nucleus 11
mass 22.98976928
#
1_hartree 6
#
cut_pot 4.5 2.0 1.0
basis_dep_cutoff 1e-4
#
radial_base 40 7.0
radial_multiplier 2
angular_grids specified
division 0.5925 110
division 0.7843 194
division 1.0201 302
division 1.1879 434
# division 1.3799 590
# division 1.4503 770
# division 7.0005 974
# outer_grid 974
outer_grid 434

# Definition of "minimal" basis
#
valence basis states
valence 3 s 1.
valence 2 p 6.
# ion occupancy
ion_occ 2 s 2.
ion_occ 2 p 6.

# Suggested additional basis functions. For production calculations,
# uncomment them one after another (the most important basis functions are
# listed first).
#
# Constructed for dimers: 2.0 A, 2.5 A, 3.0 A, 3.75 A, 4.5 A
# First tier - improvements: -60.09 meV to -10.02 meV
  hydro 2 p 1.2
  hydro 3 s 1.8
  hydro 3 d 3.8

# Second tier - improvements: -2.94 meV to -1.27 meV
  hydro 4 p 3.1
  hydro 3 s 10
  hydro 4 f 6.2
  hydro 4 d 1.3

# Third tier - improvements: -0.83 meV to -0.07 meV
  hydro 3 d 7.8
  hydro 3 p 2.3
  hydro 5 g 9.6
  hydro 4 p 0.85
  hydro 5 f 1.8
  hydro 2 s 0.6

# Further basis functions that fell out of the optimization - noise level...
  hydro 5 g 0.1
  hydro 4 d 3.4
  hydro 4 s 0.1

# Additional basis functions for atom with a core hole

  hydro 1 s 15.0
  hydro 1 s 13.0
  hydro 1 s  9.0
  hydro 2 s 13.5
  hydro 2 s 11.5
  hydro 2 p 10.5
  hydro 2 p  8.5
  hydro 3 d  7.0
  hydro 3 p  8.0
Magnesium

# "Core" basis functions and numerical settings for Mg atom.
# Based on "tight" defaults (V. Blum, 2009).

species        Mg_core
#     global species definitions
nucleus             12
mass                24.3050
#
  l_hartree           6
#
  cut_pot             5.0          2.0  1.0
  basis_dep_cutoff   1e-4
#
  radial_base        40 7.0
  radial_multiplier  2
  angular_grids      specified
    division  0.5421   50
    division  0.8500   110
    division  1.0736   194
    division  1.1879   302
    division  1.2806   434
    division  1.4147   590
    division  1.4867   770
    division  1.6422  974
    division  2.6134 1202
  outer_grid         974
  outer_grid         434

#     Definition of "minimal" basis
#
#     valence basis states
#     ion occupancy

valence      3  p   0.001
valence      3  s   1.999

ion_occ      2  s   2.
ion_occ      2  p   6.

#     Suggested additional basis functions. For production calculations,
#     uncomment them one after another (the most important basis functions are
#     listed first).
# Constructed for dimers: 2.125 Å, 2.375 Å, 2.875 Å, 3.375 Å, 4.5 Å
#
# "First tier" - improvements: -230.76 meV to -21.94 meV
   hydro 2 p 1.5
   ionic 3 d auto
   hydro 3 s 2.4
#
# "Second tier" - improvements: -5.43 meV to -1.64 meV
   hydro 4 f 4.3
   hydro 2 p 3.4
   hydro 4 s 11.2
   hydro 3 d 6.2
#
# "Third tier" - improvements: -0.92 meV to -0.22 meV
#   hydro 2 s 0.6
#   hydro 3 p 4.8
#   hydro 4 f 7.4
#   hydro 5 g 6.6
#   hydro 2 p 1.6
#   hydro 3 d 1.8
#
# "Fourth tier" - improvements: -0.09 meV to -0.05 meV
#   hydro 4 p 0.45
#   hydro 5 g 10.4
#   hydro 2 s 12.4
#   hydro 4 d 1.7
#
# Additional basis functions for atom with a core hole
hydro 1 s 16.0
hydro 1 s 14.0
hydro 1 s 10.0
hydro 2 s 14.5
hydro 2 s 12.5
hydro 2 p 11.5
hydro 2 p 9.5
hydro 3 d 8.0
hydro 3 p 9.0
Silicon

# "Core" basis functions and numerical settings for Si atom.
# Based on "tight" defaults (V. Blum, 2009).
#
# species        Si_core
#    global species definitions
nucleus             14.
mass                28.0855
#
    l_hartree       6
#
    cut_pot              4.0  2.0  1.0
    basis_dep_cutoff    1e-4
#
    radial_base       42  7.0
    radial_multiplier  2
    angular_grids       specified
    division 0.4121   50
    division 0.7665   110
    division 1.0603   194
    division 1.2846   302
    division 1.4125   434
    division 1.4810   590
    division 1.5529   770
    division 1.6284   974
    division 2.6016  1202
    outer_grid         974
    outer_grid       434

# Definition of "minimal" basis
#
# valence basis states
# valence          3 s  2.
# valence          3 p  2.
# ion occupancy
# ion_occ          3 s  1.
# ion_occ          3 p  1.
# Constructed for dimers: 1.75 Å, 2.0 Å, 2.25 Å, 2.75 Å, 3.75 Å

# "First tier" - improvements: -571.96 meV to -37.03 meV
hydro 3 d 4.2
hydro 2 p 1.4
hydro 4 f 6.2
ionic 3 s auto

# "Second tier" - improvements: -16.76 meV to -3.03 meV
hydro 3 d 9
hydro 5 g 9.4
hydro 4 p 4
hydro 1 s 0.65

# "Third tier" - improvements: -3.89 meV to -0.60 meV
ionic 3 d auto
hydro 3 s 2.6
hydro 4 f 8.4
hydro 3 d 3.4
hydro 3 p 7.8

# "Fourth tier" - improvements: -0.33 meV to -0.11 meV
# hydro 2 p 1.6
# hydro 5 g 10.8
# hydro 5 f 11.2
# hydro 3 d 1
# hydro 4 s 4.5

# Further basis functions that fell out of the optimization - noise
# level... < -0.08 meV
# hydro 4 d 6.6
# hydro 5 g 16.4
# hydro 4 d 9

# Additional basis functions for atom with a core hole
hydro 2 p 15.0
hydro 2 p 12.0
hydro 2 p 5.0
hydro 2 s 14.0
hydro 1 s 16.0
hydro 1 s 9.0
Sample control.in files

Below, the contents of the control.in files, excluding the species definitions, for the calculation of the C 1s core electron binding energy in a 3×3×3 supercell of β-SiC are given. In particular:

- The charge_1 control.in file is used to calculate the total energy of the ground state of the N-1 electron system

- The init_part_1 and init_part_2 control.in files are used in successive runs to localize a core orbital onto a particular atom, and next, to create a localized core hole. In these runs, the nuclear charge of the “target” atom for localizing a core hole is increased by 0.1 e. In init_part_1, restart files are written. In init_part_2, restart files are read in and written out.

- The hole_run control.in file is used to calculate the total energy of the core hole state. In hole_run, restart files are read in.

- The point_charge_in_a_box control.in file is used to calculate the total energy of a system with just a point charge in a periodic box, with a uniform compensating background. This value is used for applying the Makov-Payne correction. In practice, the point charge is artificially created by inserting a hydrogen atom with the electron removed (except for a tiny fraction of an electron as the present version of FHI-aims does not permit calculations with an electron count of exactly zero.)

charge_1 control.in

xc                      dfauto scan
spin                    collinear
default_initial_moment  0.0
relativistic            zora scalar 1e-12

k_grid                  16 16 16
preconditioner         kerker off
override_illconditioning .true.

charge                   1.0
init_part_1 control.in

xc           dfauto scan
spin          collinear
default_initial_moment 0.0
relativistic   zora scalar 1e-12

k_grid       16 16 16
restart_write_only   restart_file
restart_save_iterations 20
KS_method       serial

preconditioner   kerker off

override_illconditioning .true.

charge          0.1

init_part_2 control.in

xc           dfauto scan
spin          collinear
default_initial_moment 0.0
relativistic   zora scalar 1e-12

k_grid       16 16 16
restart   restart_file
KS_method       serial

preconditioner   kerker off

override_illconditioning .true.

charge          1.1
force_occupation_projector 28 1 0.0 28 54
sc_iter_limit 1
### hole_run control.in

<table>
<thead>
<tr>
<th>Option</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>xc</td>
<td>dfauto scan</td>
</tr>
<tr>
<td>spin</td>
<td>collinear</td>
</tr>
<tr>
<td>default_initial_moment</td>
<td>0.0</td>
</tr>
<tr>
<td>relativistic</td>
<td>zora scalar 1e-12</td>
</tr>
<tr>
<td>k_grid</td>
<td>16 16 16</td>
</tr>
<tr>
<td>restart_read_only</td>
<td>restart_file</td>
</tr>
<tr>
<td>KS_method</td>
<td>serial</td>
</tr>
<tr>
<td>preconditioner</td>
<td>kerker off</td>
</tr>
<tr>
<td>override_illconditioning</td>
<td>.true.</td>
</tr>
<tr>
<td>charge</td>
<td>1.0</td>
</tr>
<tr>
<td>force_occupation_projector</td>
<td>28 1 0.0 28 54</td>
</tr>
<tr>
<td>output</td>
<td>mulliken</td>
</tr>
</tbody>
</table>

### point_charge_in_a_box control.in

<table>
<thead>
<tr>
<th>Option</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>xc</td>
<td>dfauto scan</td>
</tr>
<tr>
<td>spin</td>
<td>none</td>
</tr>
<tr>
<td>relativistic</td>
<td>none</td>
</tr>
<tr>
<td>KS_method</td>
<td>serial</td>
</tr>
<tr>
<td>charge</td>
<td>0.9999999999</td>
</tr>
<tr>
<td>k_grid</td>
<td>1 1 1</td>
</tr>
</tbody>
</table>