The PAW and US-PP database

Georg KRESSE

Institut für Materialphysik and Center for Computational Materials Science
Universität Wien, Sensengasse 8, A-1090 Wien, Austria
Overview

- ultra-soft versus PAW potentials
- LDA and GGA
- the PAW potentials
- tests
- the energy zero
the general rule is to use PAW potentials wherever possible

- less parameters involved in the construction of PAW potentials
  - improved accuracy for:
    - magnetic materials
    - alkali and alkali earth elements, early 3d elements to left of periodic table
    - lathanides and actinides
  - generation of datasets is fairly simple (certainly easier than for US-PP)
  - general construction scheme is similar for US-PP and PAW potentials

- most of the PAW potentials were generated 5 years after the US-PP
  a different philosophy
an accurate treatment of these elements in ionic compounds is very important: oxides e.g. perovskites

strongly ionised and small core radii around 2.0 a.u. (1 Å) are desirable

e.g. Ca: one would like to treat 3s, 3p, 4s states as valence states it is very difficult to represent 3s and 4s states equally well in any pseudopotential description (mutual orthogonality)

in PAW, this is no problem at all, and the energy cutoffs remain modest (for Ca 200 eV)
Pseudopotentials tend to fail in spin-polarised calculations

- non linear core corrections were included in the US-PP’s!
- pseudo-wavefunction for a norm-conserving pseudopotentials
  - all electron
  - pseudo
  the peak in the d-wavefunction is shifted outward to make the PP softer
- similar compromises are made in our US-pseudopotentials (aug. charge)
- as a result, the valence-core overlap is artificially reduced and the spin enhancement factor $\xi(r)$ is overestimated

$$\xi(r) = \frac{m(r)}{n_{\text{valence}}(r) + n_{\text{core}}(r)}$$
PAW versus US-PP potentials

- the PAW potentials are generally of similar hardness across the periodic table
- most of the PAW potentials were optimised to work at a cutoff of 250-300 eV
- PAW potentials are usually slightly harder than US-PP
- for compounds where often species with very different covalent radii are mixed, the PAW potentials are clearly superior
- for one component systems the US-PP might be slightly faster (at the price of a somewhat reduced precision)
- for the US-PP the radial cutoff were chose according to the covalent radius (periodic table)
- the US-PP become progressively softer when you move down in the periodic table
The US-PP potentials

they come in two different flavours, LDA and GGA

- all LDA potentials apply the exchange correlation form according to Ceperly and Alder as parameterized by Perdew and Zunger
  they are located in the files `pot/potcar.date.tar` at the file-server

- for the LDA part, the GGA potentials use the same parametrisation, and apply the generalised gradient corrections PW91
  download location: `pot_GGA/potcar.date.tar`

- **spin polarized PW91 calculations**, set `VOSKOWN=1` in the INCAR file

  “VASP bug”: different methods to interpolate between non spin polarised and fully spin polarized local density functionals exist
  for the PW91 functional the interpolations should be done according to Vosko Wilk and Nusair
specific XC-functionals can be selected by setting the GGA flag in the INCAR; the default is determined by the POTCAR file.

Possible options are

\[
GGA = PW|PB|LM|91|PE|RP
\]

with the following meaning:

- PB Perdew-Becke
- PW Perdew-Wang 86
- LM Langreth-Mehl-Hu
- 91 Perdew-Wang 91
- PE Perdew-Burke-Ernzerhof PBE (VASP.4.5)
- RP revised Perdew-Burke-Ernzerhof rPBE (VASP.4.5)
The PAW potentials

three different flavours, one LDA (CA) and two GGA’s (PW91 and PBE)

- download location of LDA potentials: paw/potcar.date.tar
- download location of PW91 potentials: paw_GGA/potcar.date.tar
- download location of PBE potentials: paw_PBE/potcar.date.tar

- I recommend to use either the LDA or the PBE potentials

  the PBE implementation follows strictly the PBE prescription, whereas the PW91 description is not that strict
  (for the LDA part, the parametrisation of Perdew and Zunger is used, instead of Perdews Pade approximation)

  for the PBE potentials, you do not need to specify VOSKOWN=1 in the INCAR file, since this is the default
Information in the POTCAR file

PAW Al 17Apr2000
3.00000000000000000
parameters from PSCTR are:
   VRHFIN =Al: s2p1
   LEXCH = CA
   EATOM = 53.7936 eV,  3.9537 Ry
   TITEL = PAW Al 17Apr2000
   LULTRA = F use ultrasoft PP ?
   IUNSCR = 1 unscreen: 0-lin 1-nonlin 2-no
   RPACOR = 1.500 partial core radius
   POMASS = 26.982; ZVAL = 3.000 mass and valenz
   RCORE = 1.900 outmost cutoff radius
   RWIGS = 2.650; RWIGS = 1.402 wigner-seitz r (au A)
   ENMAX = 240.957; ENMIN = 180.718 eV
ICORE = 2  local potential
LCOR = T  correct aug charges
LPAW = T  paw PP
EAUG = 291.052
DEXC = -.032
RMAX = 2.970  core radius for proj-oper
RAUG = 1.300  factor for augmentation sphere
RDEP = 1.966  core radius for depl-charge
QCUT = -4.208; QGAM = 8.417  optimization parameters

Description

<table>
<thead>
<tr>
<th>l</th>
<th>E</th>
<th>TYP</th>
<th>RCUT</th>
<th>TYP</th>
<th>RCUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.000</td>
<td>23</td>
<td>1.900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.000</td>
<td>23</td>
<td>1.900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>.000</td>
<td>23</td>
<td>1.900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.000</td>
<td>23</td>
<td>1.900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>.000</td>
<td>7</td>
<td>1.900</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
PAW Al 17Apr2000 1st line: type element date_of_generation
3.00000000000000 2nd line: valency
VRHFIN =Al: s2p1 comment in the V_RHFIN file (atomic configuration)
LEXCH = CA exchange correlation type (comp. GGA flag)
EATOM = 53.7936 energy of isolated pseudoatom
TITEL = redundant with 1st line
LULTRA = F is this an US PP
RWIGS = 2.650 radius at which logar. derivative was tested during gener.
ENMAX = 240.957 required energy cutoff
ENMIN = 180.718 absolut lower limit for energy cutoff
LPAW = T is this a PAW PP
EAUG = 291.052 energy cutoff for augmentation charge
RDEP = 1.966 radius of PAW sphere
RAUG = 1.3 soft augmentation charges are nonzero at RDEP/RAUG
**Standard PAW potentials and Energy Cutoffs**

<table>
<thead>
<tr>
<th></th>
<th>B_h 700</th>
<th>C_h 700</th>
<th>N_h 700</th>
<th>O_h 700</th>
<th>F_h 700</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>318</td>
<td>400</td>
<td>N</td>
<td>400</td>
<td>F</td>
</tr>
<tr>
<td>B_s</td>
<td>250</td>
<td>273</td>
<td>N_s</td>
<td>250</td>
<td>F_s</td>
</tr>
<tr>
<td>Al</td>
<td>240</td>
<td>245</td>
<td>P</td>
<td>270</td>
<td>Cl</td>
</tr>
<tr>
<td>Al_h</td>
<td>295</td>
<td>380</td>
<td>P_h</td>
<td>390</td>
<td>Cl_h</td>
</tr>
<tr>
<td>Ga</td>
<td>134</td>
<td>173</td>
<td>As</td>
<td>208</td>
<td>Br</td>
</tr>
<tr>
<td>Ga_d</td>
<td>282</td>
<td>287</td>
<td>Se</td>
<td>211</td>
<td></td>
</tr>
<tr>
<td>Ga_h</td>
<td>404</td>
<td>410</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>95</td>
<td>103</td>
<td>Sb</td>
<td>172</td>
<td></td>
</tr>
<tr>
<td>In_d</td>
<td>239</td>
<td>241</td>
<td>Te</td>
<td>174</td>
<td>I</td>
</tr>
<tr>
<td>Tl</td>
<td>90</td>
<td>98</td>
<td>Bi</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>Tl_d</td>
<td>237</td>
<td>237</td>
<td>Bi_d</td>
<td>242</td>
<td></td>
</tr>
</tbody>
</table>

G. Kresse, The PAW and US-PP Database
Standard PAW potentials, guideline to the table

- The best compromises are marked red.
- Potentials $X_d$ treat the semi core d electrons as valence.
- Potentials marked with $X_h$ use very small core radii, and are only required under extreme circumstances:
  - Strong compression
  - Very short bonds
  - The $Al_h$–$Cl_h$, $Ga_h$ $Ge_h$ are useful in combination with the standard 1st row potentials.
1st row pseudopotentials

<table>
<thead>
<tr>
<th></th>
<th>B(_h)</th>
<th>C(_h)</th>
<th>N(_h)</th>
<th>O(_h)</th>
<th>F(_h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>318</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
</tr>
<tr>
<td>B(_s)</td>
<td>250</td>
<td>C(_s)</td>
<td>N(_s)</td>
<td>O(_s)</td>
<td>F(_s)</td>
</tr>
</tbody>
</table>

- B–F are the standard PAW potentials
even dimers are described very reliably (CO, N\(_2\), ..., 1% error)

- B\(_h\)–F\(_h\) are only required for exceptional “reference” calculations
  for instance to establish DFT reference results

- the soft potentials (B\(_s\)–F\(_s\)) are sufficient, when short bonds do not occur
  if there are no bonds between 1st row elements, you can use them

O\(_s\) is sufficiently accurate for most oxides (Al\(_2\)O\(_3\), V\(_x\)O\(_y\), Fe\(_x\)O\(_y\))

C\(_s\) is often sufficiently reliable for organic molecules, if some accuracy tradeoffs are
allowed (good enough for single and double bonds)
<table>
<thead>
<tr>
<th></th>
<th>PAW</th>
<th>hard</th>
<th>AE</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1.447</td>
<td>1.446(^a)</td>
<td></td>
</tr>
<tr>
<td>Li₂</td>
<td>5.120</td>
<td>5.120(^a)</td>
<td></td>
</tr>
<tr>
<td>Be₂</td>
<td>4.520</td>
<td>4.521(^a)</td>
<td></td>
</tr>
<tr>
<td>Na₂</td>
<td>5.663</td>
<td>5.67(^a)</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>2.141</td>
<td>2.128</td>
<td>2.129(^a)</td>
</tr>
<tr>
<td>N₂</td>
<td>2.076</td>
<td>2.068</td>
<td>2.068(^a)</td>
</tr>
<tr>
<td>F₂</td>
<td>2.633</td>
<td>2.621</td>
<td>2.615(^a)</td>
</tr>
<tr>
<td>P₂</td>
<td>3.570</td>
<td>3.572(^a)</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>1.839</td>
<td>1.835</td>
<td>1.833(^a)</td>
</tr>
<tr>
<td>α(H₂O)(°)</td>
<td>105.3</td>
<td>104.8</td>
<td>105.0(^a)</td>
</tr>
<tr>
<td>BF₃</td>
<td>2.476</td>
<td>2.470</td>
<td>2.464(^b)</td>
</tr>
<tr>
<td>SiF₄</td>
<td>2.953</td>
<td>2.948</td>
<td>2.949(^b)</td>
</tr>
</tbody>
</table>

- results for the bond length of several molecules obtained with the PAW and AE approaches
- using standard PAW potentials (and hard PAW potentials)
- well converged relaxed core AE calculations yield identical results


### Standard PAW potentials and Energy Cutoffs

<table>
<thead>
<tr>
<th>Element</th>
<th>B_h</th>
<th>C_h</th>
<th>N_h</th>
<th>O_h</th>
<th>F_h</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>700</td>
<td>700</td>
<td>700</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>B_s</td>
<td>318</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Al</td>
<td>240</td>
<td>245</td>
<td>270</td>
<td>280</td>
<td>280</td>
</tr>
<tr>
<td>Al_h</td>
<td>295</td>
<td>380</td>
<td>390</td>
<td>402</td>
<td>409</td>
</tr>
<tr>
<td>Ga</td>
<td>134</td>
<td>173</td>
<td>208</td>
<td>211</td>
<td>216</td>
</tr>
<tr>
<td>Ga_d</td>
<td>282</td>
<td>287</td>
<td>390</td>
<td>402</td>
<td>409</td>
</tr>
<tr>
<td>Ga_h</td>
<td>404</td>
<td>410</td>
<td>410</td>
<td>410</td>
<td>410</td>
</tr>
<tr>
<td>In</td>
<td>95</td>
<td>103</td>
<td>172</td>
<td>174</td>
<td>175</td>
</tr>
<tr>
<td>In_d</td>
<td>239</td>
<td>241</td>
<td>241</td>
<td>241</td>
<td>241</td>
</tr>
<tr>
<td>Tl</td>
<td>90</td>
<td>98</td>
<td>105</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td>Tl_d</td>
<td>237</td>
<td>237</td>
<td>237</td>
<td>237</td>
<td>237</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>700</td>
<td>700</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>B_s</td>
<td>250</td>
<td>273</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Al</td>
<td>240</td>
<td>245</td>
<td>270</td>
<td>280</td>
</tr>
<tr>
<td>Al_h</td>
<td>295</td>
<td>380</td>
<td>390</td>
<td>402</td>
</tr>
<tr>
<td>Ga</td>
<td>134</td>
<td>173</td>
<td>208</td>
<td>211</td>
</tr>
<tr>
<td>Ga_d</td>
<td>282</td>
<td>287</td>
<td>390</td>
<td>402</td>
</tr>
<tr>
<td>Ga_h</td>
<td>404</td>
<td>410</td>
<td>410</td>
<td>410</td>
</tr>
<tr>
<td>In</td>
<td>95</td>
<td>103</td>
<td>172</td>
<td>174</td>
</tr>
<tr>
<td>In_d</td>
<td>239</td>
<td>241</td>
<td>241</td>
<td>241</td>
</tr>
<tr>
<td>Tl</td>
<td>90</td>
<td>98</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td>Tl_d</td>
<td>237</td>
<td>237</td>
<td>237</td>
<td>237</td>
</tr>
</tbody>
</table>
• potentials with X_d treat the semi core d electrons as valence
  (3d for Ga and Ge, 4d for In and Sn, etc.)
  – for high accuracy, it is generally advisable to treat the semi-core states as
    valence (hence the corresponding potentials are marked red)
  – but in many cases, even with the frozen semi-core d-states good results are
    obtained
    these potentials reduce the number of valence electrons (NBANDS) often
    drastically
  – please make tests (it depends on how accurate results you need)

• the hard potentials for Al_h–Cl_h, Ga_h, Ge_h, should be used for added accuracy
  in oxides, when combined with the standard O potential
  these potentials are rarely required (in zeolites the changes are almost negligible
  when you change from Si to Si_h)
### Standard PAW potentials for “simple” metals

<table>
<thead>
<tr>
<th>Element</th>
<th>H</th>
<th>H_h</th>
<th>Li</th>
<th>Li_sv</th>
<th>Be</th>
<th>Be_sv</th>
<th>Na</th>
<th>Na_pv</th>
<th>Mg</th>
<th>Mg_pv</th>
<th>Na_sv</th>
<th>K_pv</th>
<th>K_sv</th>
<th>Ca_pv</th>
<th>Ca_sv</th>
<th>Rb_pv</th>
<th>Sr_sv</th>
<th>Rb_sv</th>
<th>Cs_sv</th>
<th>Ba_sv</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250</td>
<td>700</td>
<td>140</td>
<td>271</td>
<td>300</td>
<td>308</td>
<td>81</td>
<td>300</td>
<td>210</td>
<td>265</td>
<td>700</td>
<td>150</td>
<td>259</td>
<td>150</td>
<td>290</td>
<td>121</td>
<td>226</td>
<td>220</td>
<td>220</td>
<td>187</td>
</tr>
</tbody>
</table>
Contrary to the common believe,

these elements are exceedingly difficult to pseudize

- in particular in combination with strongly electronegative elements (F) errors can be larger then usual

- the present versions are very precise, and should offer a highly reliable description (phonon calculations for alkali-halides by Martijn Marsman)

for X\_pv pseudopotentials the semi core p states are treated as valence (2p in Na and Mg, 3p in K and Ca etc.)

for X\_sv pseudopotentials, the semi core s states are treated as valence (1s in Li and Be, 2s in Na etc.)

at least relaxing the semi core p states is required, since in strongly ionic environments these elements loose all their “valence” electrons, and the semi-core states relax substantially
**Semi core states**

there are limits to how many semi-core states can be treated as valence

e.g. 3s and 4s in Ca:

the node in the 4s state must be accounted for in some manner

- semi-core state that lie 2 Ry below the valence states can be treated easily as valence (cutoffs $\approx$ 200 eV)

- states at 3 Ry are more difficult (cutoffs $\approx$ 300 eV)

- $> 3$ Ry very difficult, and the potentials become relatively hard (400 eV)
### Transition metal pseudopotentials

<p>| | | | | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc_sv</td>
<td>Ti</td>
<td>178</td>
<td>V</td>
<td>192</td>
<td>Cr</td>
<td>227</td>
<td>Mn</td>
<td>269</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti_pv</td>
<td>222</td>
<td>V_pv</td>
<td>263</td>
<td>Cr_pv</td>
<td>265</td>
<td>Mn_pv</td>
<td>269</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y_sv</td>
<td>Zr_sv</td>
<td>229</td>
<td>Nb_pv</td>
<td>207</td>
<td>Mo</td>
<td>224</td>
<td>Tc</td>
<td>228</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hf</td>
<td>220</td>
<td>Ta</td>
<td>223</td>
<td>W</td>
<td>223</td>
<td>Re</td>
<td>226</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hf_pv</td>
<td>220</td>
<td>Ta_pv</td>
<td>223</td>
<td>W_pv</td>
<td>223</td>
<td>Re_pv</td>
<td>226</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>267</td>
<td>Co</td>
<td>267</td>
<td>Ni</td>
<td>269</td>
<td>Cu</td>
<td>273</td>
<td>Zn</td>
<td>276</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_pv</td>
<td>293</td>
<td>Ni_pv</td>
<td>367</td>
<td>Cu_pv</td>
<td>368</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>213</td>
<td>Rh</td>
<td>228</td>
<td>Pd</td>
<td>250</td>
<td>Ag</td>
<td>249</td>
<td>Cd</td>
<td>274</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru_pv</td>
<td>230</td>
<td>Rh_pv</td>
<td>271</td>
<td>Pd_pv</td>
<td>350</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os</td>
<td>228</td>
<td>Ir</td>
<td>210</td>
<td>Pt</td>
<td>230</td>
<td>Au</td>
<td>229</td>
<td>Hg</td>
<td>233</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os_pv</td>
<td>228</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

G. Kresse, The PAW and US-PP Database
**Transition metal PAW potentials, guideline to the table**

- for X\_pv pseudopotentials, the semi core p states are treated as valence
- for X\_sv pseudopotentials, the semi core s states are treated as valence
- X\_pv potentials are required for early transition metals, but one can freeze the semi-core p states for late transition metals (in particular noble metals)
- when to switch from X\_pv potentials to the X potentials depends on the required accuracy and the row
  - for the 3d elements, even the Ti, V and Cr potentials give reasonable results
  - 4d elements are most problematic, and I advice to use the X\_pv potentials up to Tc\_pv
  - 5d elements: 5p states are rather strongly localised (below 3 Ry), since the 4f shell becomes filled
  one can use the standard potentials starting from Hf, but I recommend to perform test calculations from the data base
Actenides and Lathanides

- it is no trouble to generate PAW potentials for these elements, and we have already a rather extensive database

**is standard DFT applicable to these strongly correlated elements?**

- yes: if the f electrons are itinerant (band like)
- no: if the f electrons are strongly localised (strong correlation effects, SIC)

similar problems do occur in some transition metal oxides (NiO, V₂O₃, V₂O₄, Fe₂O₃, FeO etc.)
Pseudopotential that treat the f-electrons as valence

<table>
<thead>
<tr>
<th>Ce</th>
<th>300</th>
<th>Pr</th>
<th>252</th>
<th>Nd</th>
<th>253</th>
<th>Pm</th>
<th>258</th>
<th>Sm</th>
<th>255</th>
<th>Eu</th>
<th>249</th>
<th>Gd</th>
<th>256</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tm</td>
<td>257</td>
<td>Yb</td>
<td>291</td>
<td>Lu</td>
<td>255</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>La</th>
<th>219</th>
<th>Ac</th>
<th>169</th>
<th>Th</th>
<th>247</th>
<th>Pa</th>
<th>252</th>
<th>U</th>
<th>252</th>
<th>Np</th>
<th>254</th>
<th>Pu</th>
<th>254</th>
</tr>
</thead>
<tbody>
<tr>
<td>L_{a,s}</td>
<td>136</td>
<td>Ac_{s}</td>
<td>119</td>
<td>Th_{s}</td>
<td>169</td>
<td>Pa_{s}</td>
<td>193</td>
<td>U_{s}</td>
<td>209</td>
<td>Np_{s}</td>
<td>210</td>
<td>Pu_{s}</td>
<td>211</td>
</tr>
</tbody>
</table>

- in all cases, the lower semi-core p shell is treated as valence
- for the standard potentials, even the semi-core s states are treated as valence (count the number of electrons)
- the standard versions are recommended (oxides and sulfides)
- except for inter-metallic compounds, where the soft versions might be sufficiently accurate
- the actenides and La PAW have been tested, but the other lanthanide PAW potentials are largely untested
f-electrons in the core

standard model for localised f-electrons
the f-electrons are not treated explicitly, but are kept frozen in the core

<p>| | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>3</td>
<td>181</td>
<td>Pr</td>
<td>3</td>
<td>181</td>
<td>Nd</td>
<td>3</td>
<td>182</td>
</tr>
<tr>
<td>Tb</td>
<td>3</td>
<td>155</td>
<td>Dy</td>
<td>3</td>
<td>155</td>
<td>Ho</td>
<td>3</td>
<td>154</td>
</tr>
</tbody>
</table>

- X_3 implies that the potential has been created for valency 3
  X_2 implies that the potential has been created for valency 2

- the formal valency, in the POTCAR file is larger, since the semi-core p states are also included when counting the valence electrons
  in fact, in all cases, the lower semi-core p shell is treated as valence
US-PP

- generally similar naming conventions as for PAW potentials
- generally less accurate, in particular 1st row and 2nd row standard US-PP are less precise, since they have been generated with slightly larger core radii
- no US-PP for lanthanides and actinides are available
- the “simple metal” US-PP are of much worse quality
The energy zero

• in VASP all energies are referred to the reference state for which the potential was generated!
  this is in most cases not the real groundstate of the atom

• to determined the energy of the grounstate of the atom place the atom in a larger non cubic box to break initial symmetry (i.e. 11 Å × 10 Å × 9 Å)
  use the Γ point only

  INCAR:
  ISPIN = 2  ! spin polarized
  ISMEAR = 0 ; SIGMA = 0.2 ! for small sigma conv. for TM is diff.
  MAGMOM = 2  ! initial magnetic moment

  one should use the energy value energy without entropy of the OUTCAR file
  since this coverges most rapidly to the correct energy for sigma→0

• \[ E_{\text{coh}} = E_{\text{metal/molecule}} - nE_{\text{atom}} \]
Generation of potentials upon user request

- requests for new US or NC-PP will not be processed in any case !!!!

- requests for new PAW potentials, are only processed under special circumstances
  - the precise reason for the request must be specified
    - if the PAW potential is buggy, I will try to generate a new one
  - potentials for special circumstances (high compression, very short bonds) will be generated only
    * if I am included as a coauthor of the article
    * if the generation is possible in reasonable time span
    * in any case, expect that it will take 1-2 months until such requests are processed!! (PP generation is a very distracting and timeconsuming work)

- the pseudopotential generation package is not available !!!!