The PAW and US-PP database

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Overview

- ultra-soft versus PAW potentials
- LDA and GGA
- the PAW potentials
- tests
- the energy zero

US-PP or PAW potentials

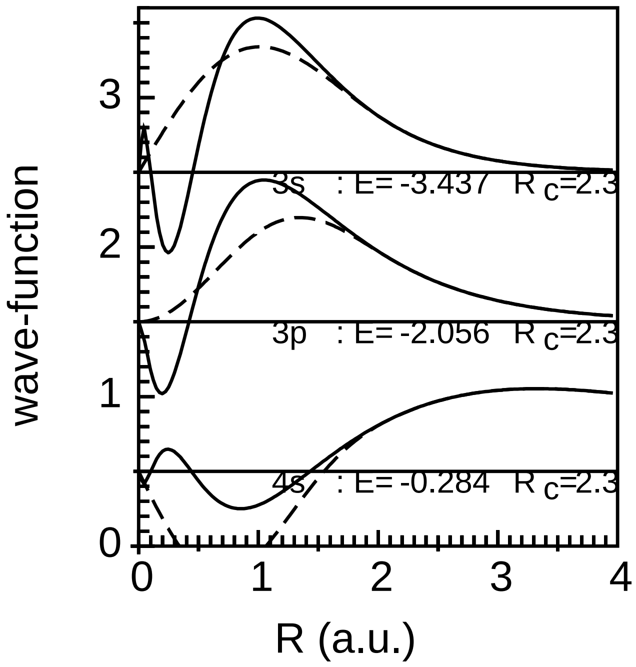
the general rule is to use PAW potentials wherever possible

- 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

Alkali and alkali earth metals

- 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

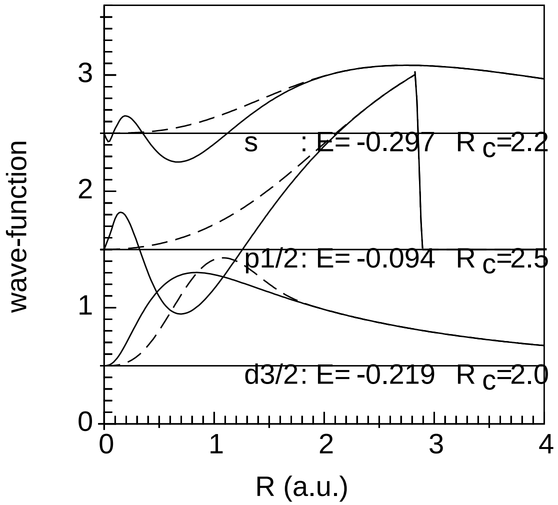


it is very difficult to represent 3s and 4s states equally well in any pseudopotential description (mutual orthogonality)

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 artifically reduced and the spin enhancement factor $\xi(r)$ is overestimated

$$\xi(r) = \frac{m(r)}{n_{\mathrm{valence}}(r)+n_{\mathrm{core}}(r)}$$

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 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

- 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)

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

  J.P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).

  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

The GGA tag in the INCAR file

specific XC-functionals can be selected by setting the GGA flag in the INCAR; the default is determiend 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
3.0000000000000000
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
  l     E      TYP  RCUT    TYP  RCUT
  0   .000     23  1.900
  0   .000     23  1.900
  1   .000     23  1.900
  1  1.000     23  1.900
  2   .000      7  1.900
```

PAW Al 17Apr2000	1st line: type element date_of_generation
3.0000000000000	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

B_h	700	C_h	700	N_h	700	O_h	700	F_h	700
B	318	C	400	N	400	O	400	F	400
B_s	250	C_s	273	N_s	250	O_s	250	F_s	250
Al	240	Si	245	P	270	S	280	Cl	280
Al_h	295	Si_h	380	P_h	390	S_h	402	Cl_h	409
Ga	134	Ge	173	As	208	Se	211	Br	216
Ga_d	282	Ge_d	287						
Ga_h	404	Ge_h	410						
In	95	Sn	103	Sb	172	Te	174	I	175
In_d	239	Sn_d	241						
Tl	90	Pb	98	Bi	105				
Tl_d	237	Pb_d	237	Bi_d	242				

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 usefull in combination with the standard 1st row potentials

1st row pseudpotentials

B_h	700	C_h	700	N_h	700	O_h	700	F_h	700
B	318	C	400	N	400	O	400	F	400
B_s	250	C_s	273	N_s	250	O_s	250	F_s	250

- 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_2O_3, V_xO_y, Fe_xO_y)

  C_s is often sufficiently reliable for organic molecules, if some accuracy tradeoffs are allowed (good enough for single and double bonds)

	PAW	hard	AE
H_2	1.447		1.446[a]
Li_2	5.120		5.120[a]
Be_2	4.520		4.521[a]
Na_2	5.663		5.67 [a]
CO	2.141	2.128	2.129[a]
N_2	2.076	2.068	2.068[a]
F_2	2.633	2.621	2.615[a]
P_2	3.570		3.572[a]
H_2O	1.839	1.835	1.833[a]
$\alpha(H_2O)(^\circ)$	105.3	104.8	105.0[a]
BF_3	2.476	2.470	2.464[b]
SiF_4	2.953	2.948	2.949[b]

[a] NUMOL, R.M. Dickson, A.D. Becke, J. Chem. Phys. **99**, 3898 (1993).

[b] GAUSSIAN94, S. Goedecker, et al., Phys. Rev. B **54**, 1703 (1996).

- 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

B_h	700	C_h	700	N_h	700	O_h	700	F_h	700
B	318	C	400	N	400	O	400	F	400
B_s	250	C_s	273	N_s	250	O_s	250	F_s	250
Al	240	Si	245	P	270	S	280	Cl	280
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Remaining rows

- 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 rarelly required (in zeolites the changes are almost negligible when you change from Si to Si_h)

Standard PAW potentials for “simple” metals

H	250		
H_h	700		
Li	140	Be	300
Li_sv	271	Be_sv	308
Na	81	Mg	210
Na_pv	300	Mg_pv	265
Na_sv	700		
K_pv	150	Ca_pv	150
K_sv	259	Ca_sv	290
Rb_pv	121	Sr_sv	226
Rb_sv	220		
Cs_sv	220	Ba_sv	187

Simple metal PAW potentials, guideline to the table

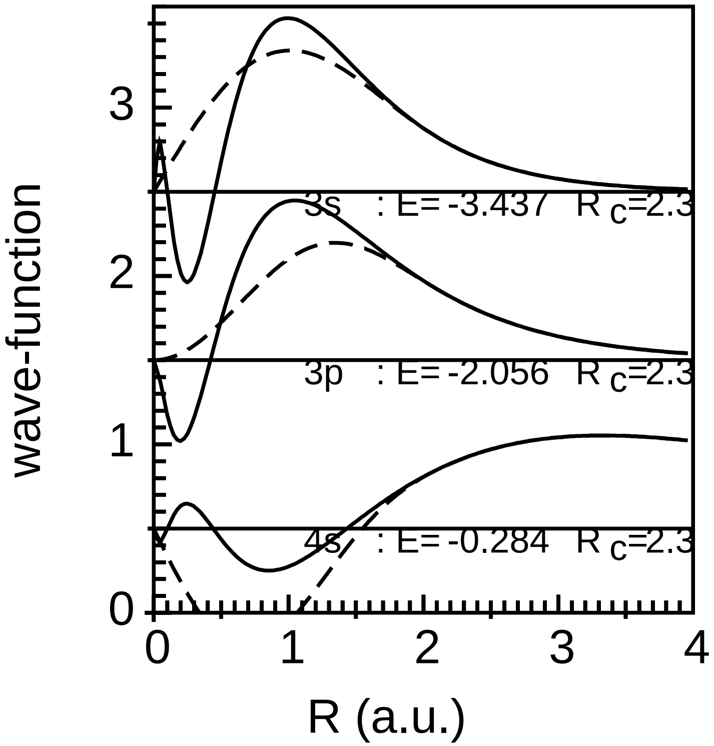
- Contrary to the common believe,

  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:

mutual orthogonality

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

		Ti	178	V	192	Cr	227	Mn	269
Sc_sv	222	Ti_pv	222	V_pv	263	Cr_pv	265	Mn_pv	269
						Mo	224	Tc	228
Y_sv	211	Zr_sv	229	Nb_pv	207	Mo_pv	224	Tc_pv	228
		Hf	220	Ta	223	W	223	Re	226
		Hf_pv	220	Ta_pv	223	W_pv	223	Re_pv	226
Fe	267	Co	267	Ni	269	Cu	273	Zn	276
Fe_pv	293			Ni_pv	367	Cu_pv	368		
Ru	213	Rh	228	Pd	250	Ag	249	Cd	274
Ru_pv	230	Rh_pv	271	Pd_pv	350				
Os	228	Ir	210	Pt	230	Au	229	Hg	233
Os_pv	228								

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, V_2O_3, V_2O_4, Fe_2O_3, FeO etc.)

Pseudopotential that treat the f-electrons as valence

Ce	300	Pr	252	Nd	253	Pm	258	Sm	255	Eu	249	Gd	256
								Tm	257	Yb	291	Lu	255
La	219	Ac	169	Th	247	Pa	252	U	252	Np	254	Pu	254
La_s	136	Ac_s	119	Th_s	169	Pa_s	193	U_s	209	Np_s	210	Pu_s	211

- 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 lathanide 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

Ce_3	181	Pr_3	181	Nd_3	182	Pm_3	183	Sm_3	184			Gd_3	154
								Sm_2	183	Eu_2	99		

Tb_3	155	Dy_3	155	Ho_3	154	Er_3	155	Tm_3	154	Yb_2	112	Lu_3	155
						Er_2	119						

- 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 2row standard US-PP are less precise, since they have been generated with slightly larger core radii
- no US-PP for lathanides and actenides are available
- the “simple metal” US-PP are of much worse quality

The energy zero

- in VASP all energies are referred to the 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 !!!