Accuracy and Validation of Results

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Overview

- **How is the precision controlled in VASP**

  – the plane wave energy cutoff

  – technical errors

  – the critical parameters `ENAUG, ENCUT, LREAL, ROPT`

  – the "super-flag" `PREC`

- **Related issues**

  – k-point sampling

  – slab thickness

Energy cutoff

- controls the completeness of the basis set

  at each k-point only the plane waves that fulfil

  $$\frac{\hbar^2}{2m_e}|\mathbf{G}+\mathbf{k}|^2 < E_{\text{cutoff}}$$

  are included

  different number of plane waves at each k-point

- E_{cutoff} is controlled by `ENCUT` in the INCAR file

  the number of plane wave for each k-point is written to the OUTCAR file:

  ```
  k-point  1 :  0.25000.25000.2500  plane waves:   1546
  k-point  2 :  -.25000.25000.2500  plane waves:   1557
  ```

- defaults for `ENCUT` are supplied in the pseudopotential files (POTCAR)

  usually the maximum `ENMAX` is chose as energy cutoff

Convergence correction

- VASP applies an automatic convergence correction based on the kinetic energy of wave-functions in the atomic limit

  ```
  energy of atom 1      EATOM=-1393.0707
  kinetic energy error for atom= 0.0229
  ```

- works well in the atomic limit, and for free electron metals

  corrects for 80 % of the total error

- for d-elements and bulk calculations, corrections are only partial

- due to correction, the energy might increase when the cutoff is increased
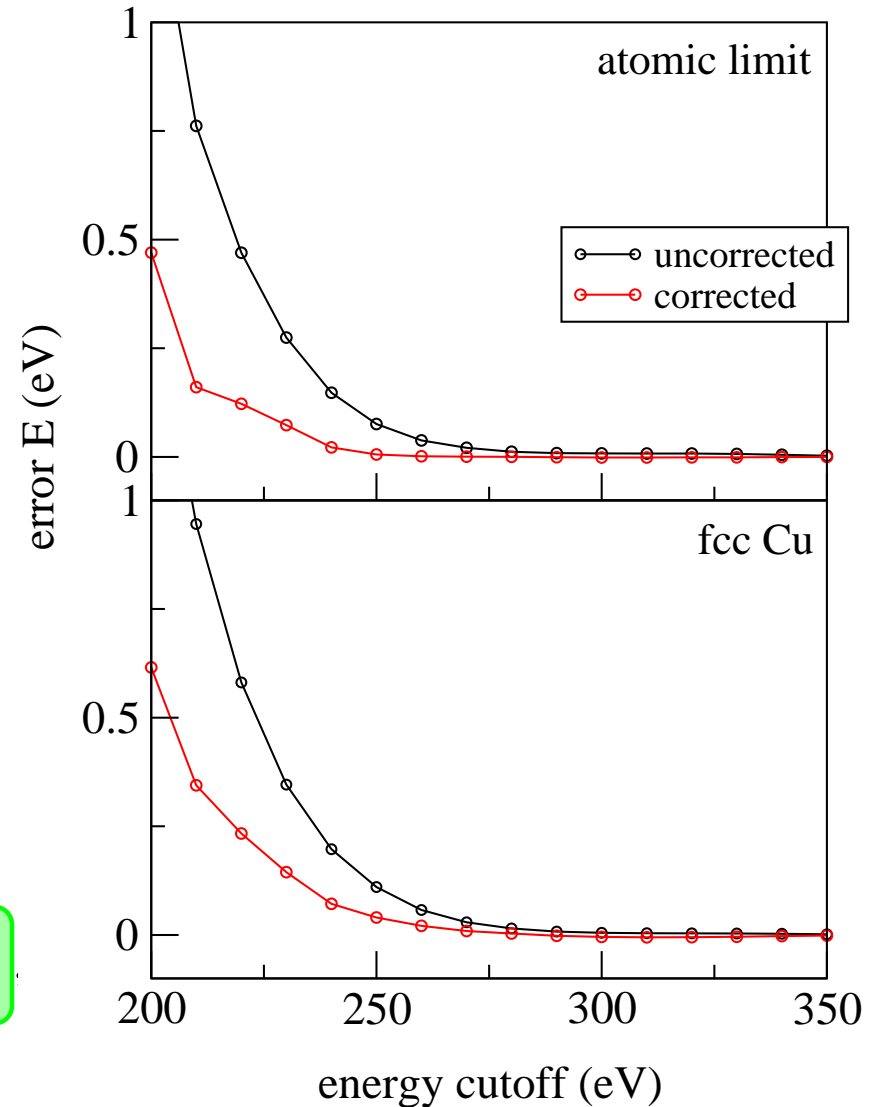
Can you rely on the default cutoff ?

it depends

- ENCUT is a very reasonable compromise between accuracy and speed

- you can rely on ENCUT, as long as the

  cell-shape and the volume remain unchanged

  – frozen phonon calculations

  – surface and slab calculations

  – adsorption of molecules on surfaces

- otherwise you might need to be rather careful

  the basis set changes   discontinuously   when the cell-shape is changed, since new

  plane waves are included when they satisfy the cutoff criterion

  $$\frac{-\hbar^2}{2m_e}|\mathbf{G}+\mathbf{k}|^2 < E_{\text{cutoff}}$$

k-points and cutoff

energy versus volume for fcc Cu

- by using more k-points or a higher energy cutoff, the energy surface becomes smoother
  at 270 eV and using 8x8x8 k-points, the energy veries smoothly

- in general, elastic constants are most prone to such errors
 if you sample the energy surface on a coarse scale, problems are less severe (recommended distortions 1 %)

Legend:
- 240 eV, 2x2x2
- 270 eV, 2x2x2
- 240 eV, 8x8x8
- 270 eV, 8x8x8

Axes: E (eV) vs volume V (A^3)
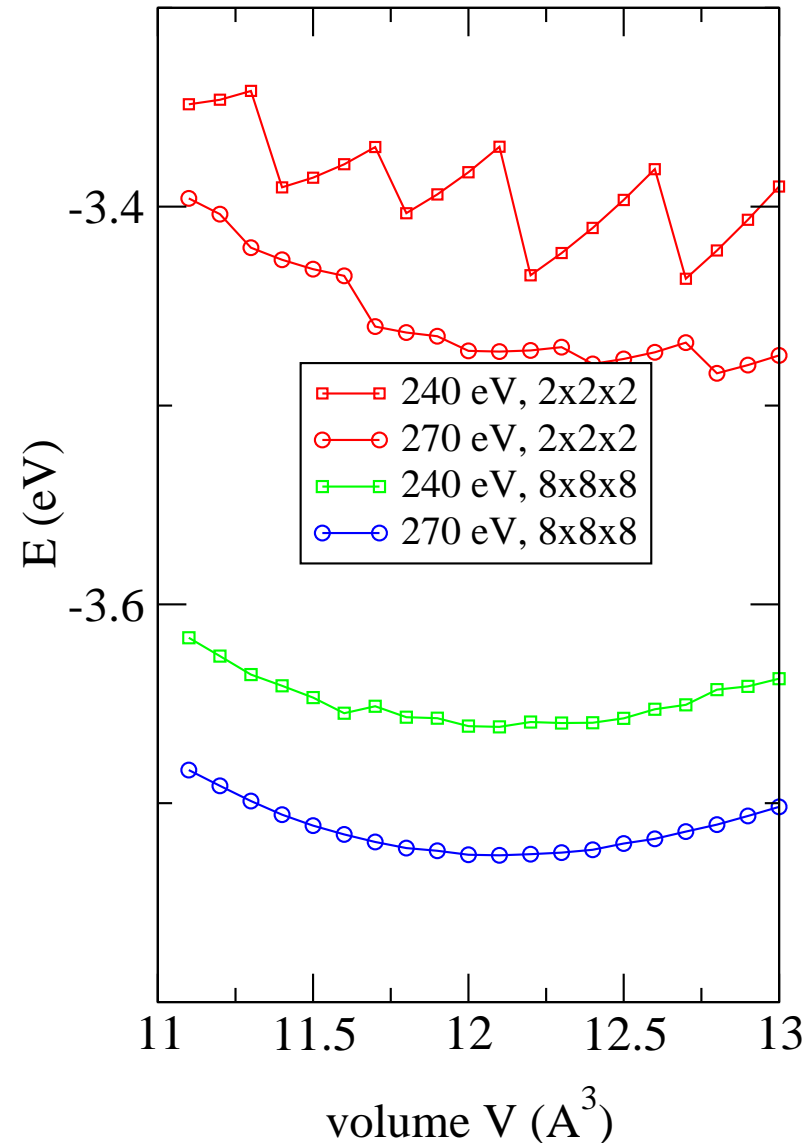
Fixed basis-sets instead of fixed cutoff

- possible by restarting with `ISTART=2` but such calculations clearly yield much too small volumes even at 270 eV (5 % error)

- effectively the cutoff decreases when the volume is increased (since the reciprocal lattice vectors become shorter)

- fixed basis set calculations are **obviously a very bad idea**
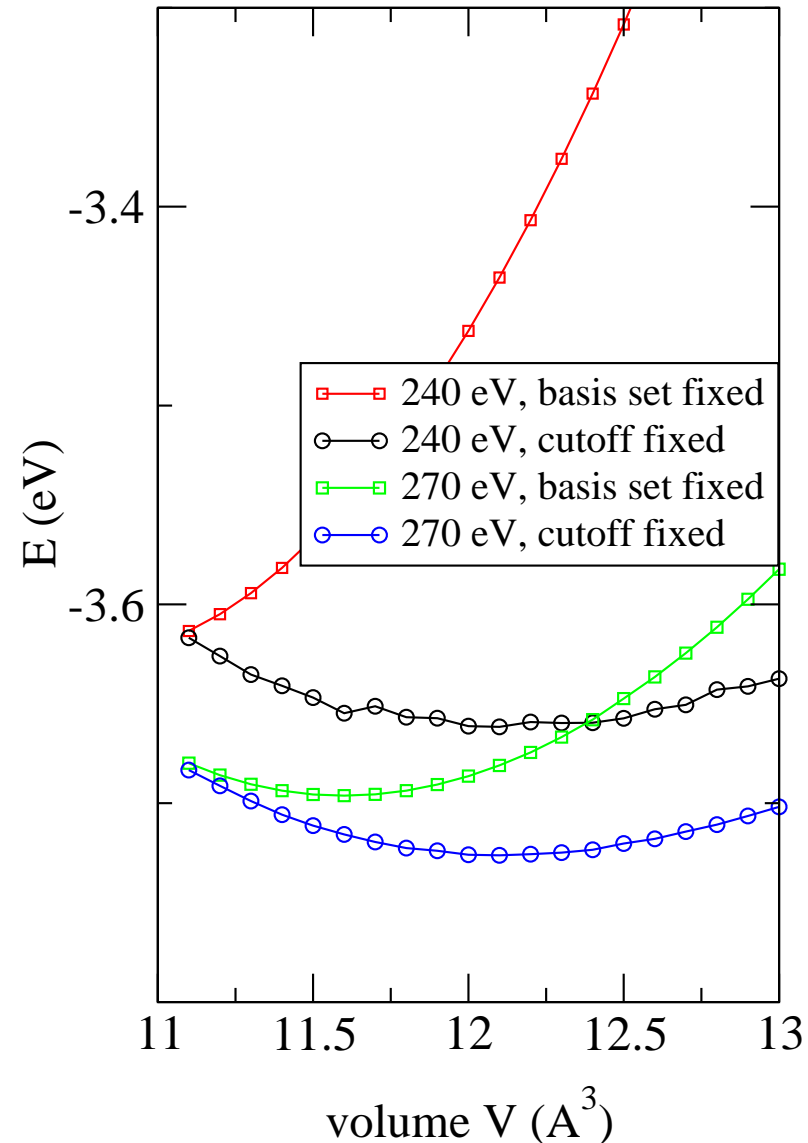
Fixed basis-set calculations
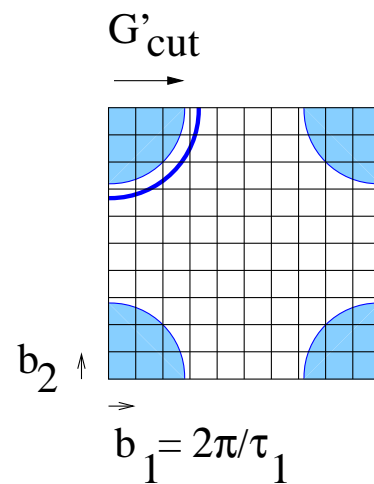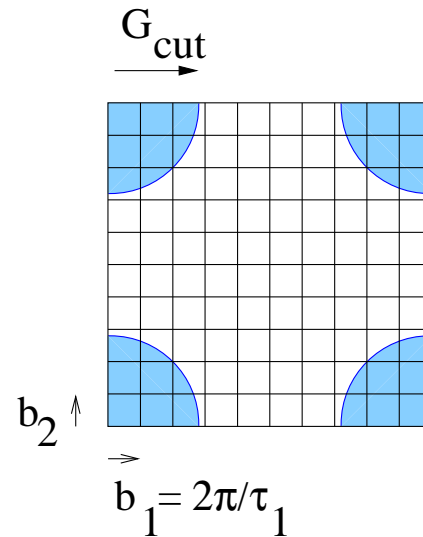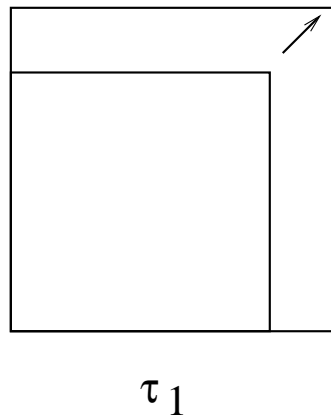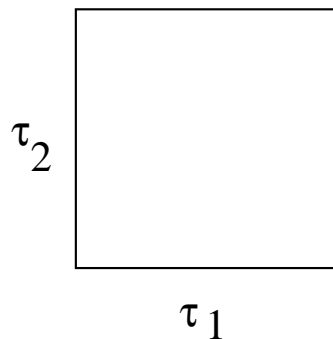
- the cutoff decreases by a factor τ_1/τ'_1 when the lattice is expanded from $\tau_1 \to \tau'_1$

- for the expanded lattice the basis set corresponds effectively to a lower cut-off G'_{cut} and therefore a lower quality,
  $\Rightarrow$ the energy is overestimated at larger volumes
  $\Rightarrow$ the volume is underestimated for fixed basis-set calculations

Stress tensor

- the stress tensor is implicitly calcu-
  lated at a fixed basis set
  upon cell-shape or volume relaxation
  one obtains too small volumes
  (2-5 % errors at the default cutoff)

- cutoff must be increased by 20-30%,
  when cell relaxations are performed

- calculations at the equilibrium lattice
  parameter of fcc Cu:
  270 eV: p=-50 kBar (contract)
  350 eV: a few kBar (correct result)

default cutoff
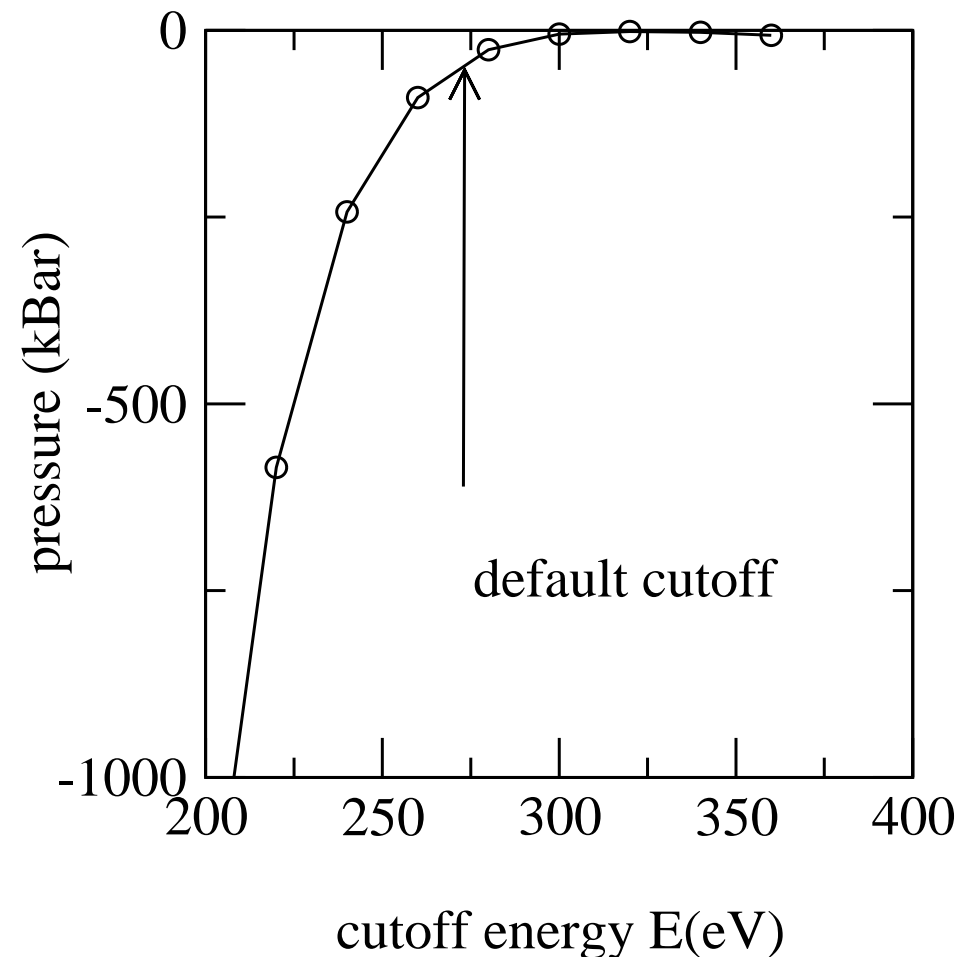
Cell-shape relaxations

- increase the cutoff by 30 %

  and restart the calculations, after the first ionic relaxation has succeeded
  the basis set is then adopted to the new geometry

- quick and dirty (if you need to save computer time)

  the error in the stress tensor is rather uniform, and it can be supplied in the INCAR
  file

  – calculate the stress tensor at a larger energy cutoff

  – calculate the stress tensor at the desired low energy cutoff

  – supply the difference of the average of the diagonal elements of the stress tensor
    (pressure) in the INCAR file (should be a negative value)

  ```
  PSTRESS = p(low cutoff)-p(high cutoff)
  ```

The most common mistakes

- **energy differences from calculations with different energy cutoffs**

  Pt slab calculations with 3x3x4 atoms at the default cutoff 230 eV
  add CO molecule and calculate adsorption energy (CO default 400 eV)

  errors will be propotional to the number of Pt atoms and around 200 meV

- **energy differences from calculations with different KPOINTS**

Validating results

- **cutoff and aliasing errors:**

  - increase the cutoff

  - or try to perform `PREC=Accurate` calculations

  - possibly switch of the real space optimisation

Related errors:

- increase the number of k-points

- increase the slab thickness

- for defects increase the size of the supercell to remove artificial interactions

TEST, TEST, TEST ....

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 $\boxed{\text{LDA}}$ or the $\boxed{\text{PBE}}$ 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
  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

3.000000000000   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 pseudopotentials

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

- 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

[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).

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
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Ga_d	282	Ge_d	287						
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In_d	239	Sn_d	241						
Tl	90	Pb	98	Bi	105				
Tl_d	237	Pb_d	237	Bi_d	242				

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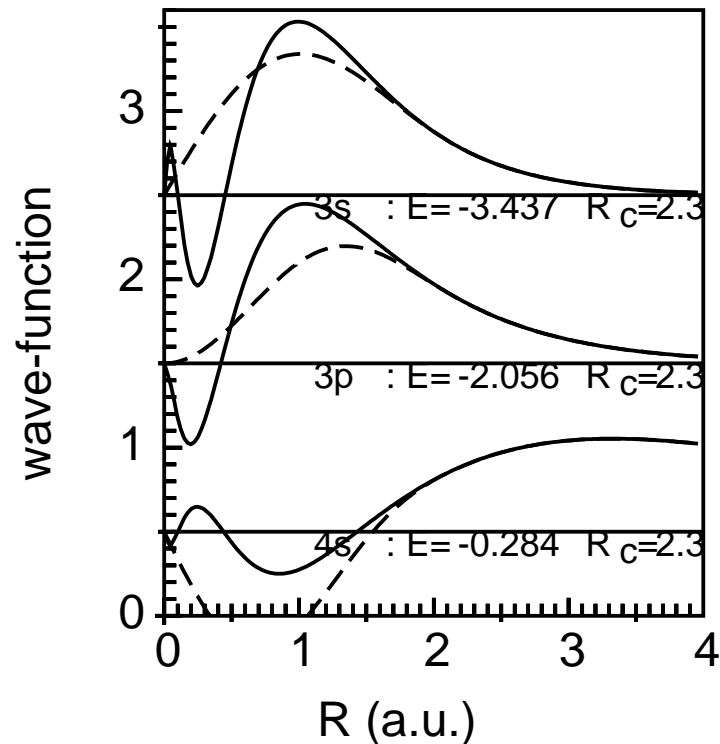
there are limits to how many semi-core states can be treated as valence

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.)

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

On site Coulomb repulsion

- L(S)DA fails to describe systems with localized (strongly correlated) d and f electrons $\rightarrow$ wrong one-electron energies

- Strong intra-atomic interaction is introduced in a (screened) Hartree-Fock like manner $\rightarrow$ replacing L(S)DA on site

$$E_{\text{HF}} = \frac{1}{2} \sum_{\{\gamma\}} (U_{\gamma_1 \gamma_3 \gamma_2 \gamma_4} - U_{\gamma_1 \gamma_3 \gamma_4 \gamma_2}) \hat{n}_{\gamma_1 \gamma_2} \hat{n}_{\gamma_3 \gamma_4}$$

determined by the PAW on site occupancies

$$\hat{n}_{\gamma_1 \gamma_2} = \langle \Psi^{s_2} \mid m_2 \rangle \langle m_1 \mid \Psi^{s_1} \rangle$$

and the (unscreened) on site electron-electron interaction

$$U_{\gamma_1 \gamma_3 \gamma_2 \gamma_4} = \langle m_1 m_3 \mid \frac{1}{|\mathbf{r} - \mathbf{r}'|} \mid m_2 m_4 \rangle \delta_{s_1 s_2} \delta_{s_3 s_4}$$

($|m\rangle$ are the spherical harmonics)

- $U_{\gamma_1 \gamma_3 \gamma_2 \gamma_4}$ given by Slater's integrals F^0, F^2, F^4, and F^6 (f-electrons)

- Calculation of Slater's integrals from atomic wave functions leads to a large overestimation because in solids the Coulomb interaction is screened (especially F^0).

- In practice treated as fitting parameters, i.e., adjusted to reach agreement with experiment: equilibrium volume, magnetic moment, band gap, structure.

- Normally specified in terms of effective on site Coulomb- and exchange parameters, U and J.

  For $3d$-electrons: $U = F^0$, $J = \frac{1}{14}(F^2 + F^4)$, and $\frac{F^4}{F^2} = 0.65$

- U and J sometimes extracted from constrained-LSDA calculations.

Total energy and double counting

Total energy

$$E_{\text{tot}}(n, \hat{n}) = E_{\text{DFT}}(n) + E_{\text{HF}}(\hat{n}) - E_{\text{dc}}(\hat{n})$$

Double counting

LSDA+U $\qquad E_{\text{dc}}(\hat{n}) = \frac{U}{2}\hat{n}_{\text{tot}}(\hat{n}_{\text{tot}} - 1) - \frac{J}{2}\sum_{\sigma}\hat{n}_{\text{tot}}^{\sigma}(\hat{n}_{\text{tot}}^{\sigma} - 1)$
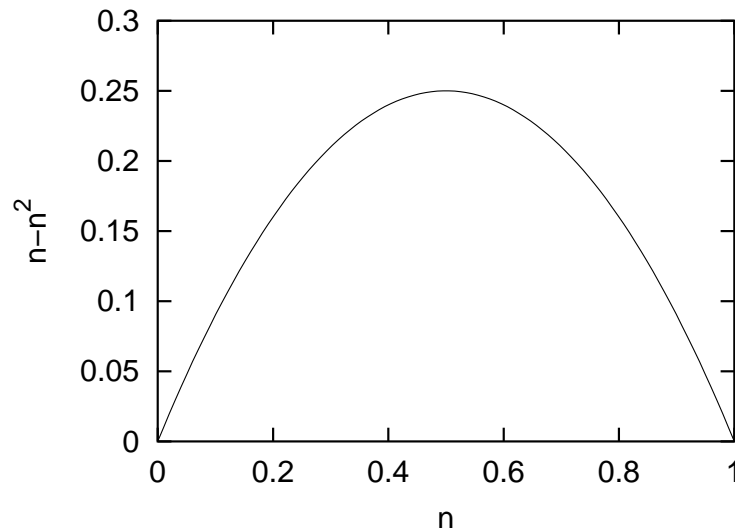
LDA+U $\qquad E_{\text{dc}}(\hat{n}) = \frac{U}{2}\hat{n}_{\text{tot}}(\hat{n}_{\text{tot}} - 1) - \frac{J}{4}\hat{n}_{\text{tot}}(\hat{n}_{\text{tot}} - 2)$

Hartree-Fock Hamiltonian can be simply added to the AE part of the PAW Hamiltonian

- Orbital dependent potential that enforces Hund's first and second rule

  - maximal spin multiplicity

  - highest possible azimuthal quantum number L_z
    (when SOI included)

Dudarev's approach to LSDA+U

$$E_{\text{LSDA+U}} = E_{\text{LSDA}} + \frac{(U-J)}{2} \sum_\sigma \left[\left(\sum_{m_1} n^\sigma_{m_1,m_1} \right) - \left(\sum_{m_1,m_2} \hat{n}^\sigma_{m_1,m_2} \hat{n}^\sigma_{m_2,m_1} \right) \right]$$

- Penalty function that forces idempotency of the onsite occupancy matrix,
  $\hat{n}^\sigma = \hat{n}^\sigma \hat{n}^\sigma$

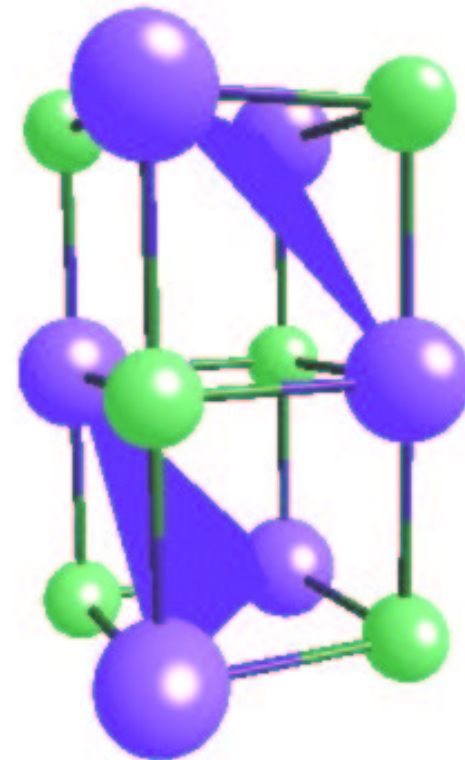- real matrices are only idempotent, if their eigenvalues are either 1 or 0 (fully occupied or unoccupied)

$$E_{\text{LSDA+U}} = E_{\text{LSDA}}(\{\varepsilon_i\}) + \frac{(U-J)}{2} \sum_{\sigma,m_1,m_2} \hat{n}^\sigma_{m_1,m_2} \hat{n}^\sigma_{m_2,m_1}$$
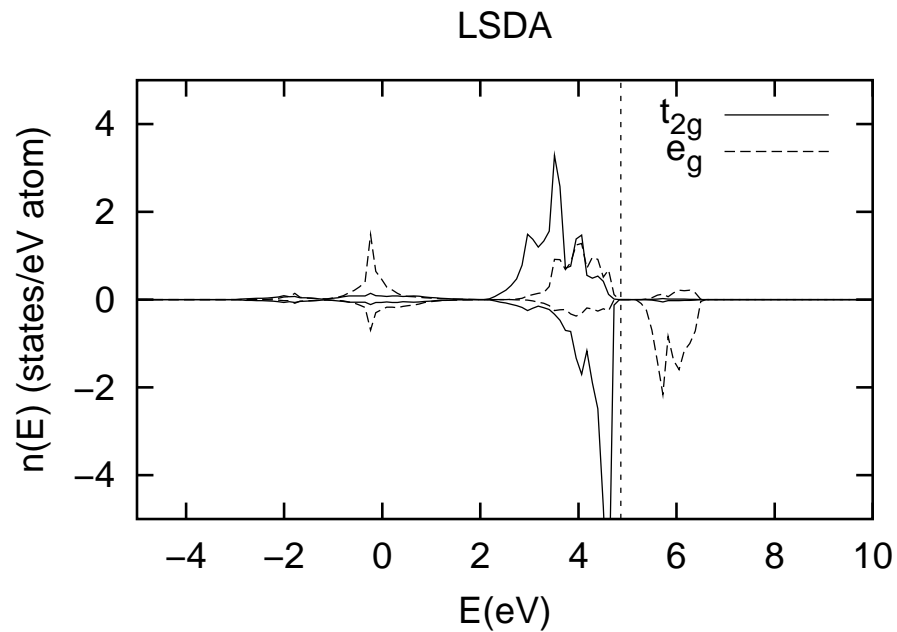
An example: NiO, a Mott-Hubbard insulator

- Rocksalt structure

- AFM ordering of Ni (111) planes

- Ni 3d electrons in octahedral crystal field
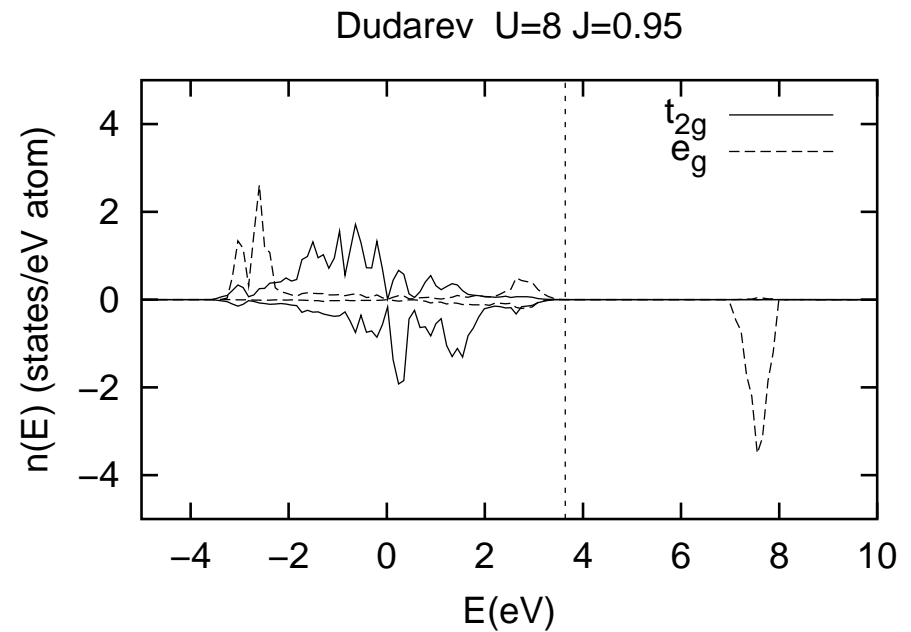
  t_{2g} $(3d_{xy}, 3d_{xz}, 3d_{yz})$

  e_g $(3d_{x^2-y^2}, 3d_{z^2})$

LSDA

Dudarev U=8 J=0.95

$|m_{\mathrm{Ni}}|$ = 1.15 μ_{B}

E_{gap} = 0.44 eV

$|m_{\mathrm{Ni}}|$ = 1.71 μ_{B}

E_{gap} = 3.38 eV

Experiment

$|m_{\mathrm{Ni}}|$ = 1.64 - 1.70 μ_{B} E_{gap} = 4.0 - 4.3 eV

Hands on Session IV

Martijn MARSMAN

Institut für Materialphysik and Center for Computational Material Science

Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria

Overview

- fcc Ni, an elementary ferromagnetic metal

- NiO, antiferromagnetic coupling

- LSDA+U (Dudarev's approach)

- SOI: freestanding fcc Fe and Ni (100) monolayers

- Constraining magnetic moments

- What to do about convergence problems?

fcc Ni

```
fcc:
 -10.93
  0.5 0.5 0.0
  0.0 0.5 0.5
  0.5 0.0 0.5
    1
Cartesian
0 0 0


k-points
0
Gamma
 11 11 11
   0  0  0
```

POSCAR

- Volume set to 10.93 Å

- fcc primitive cell

KPOINTS

- 11×11×11 Γ-centered Monkhorst-Pack grid

POTCAR

`makepaw_GGA Ni`

(a PAW-GGA PW91 potential)

```
SYSTEM  = Ni fcc bulk
ISTART  = 0
ISPIN   = 2
MAGMOM  = 1.0
ISMEAR  = -5
VOSKOWN = 1
LORBIT  = 11
```

Or copy the files from:

`~vw/4_1_Ni`

- Spin polarized calculation (collinear)

- Initial magnetic moment: $1 \ \mu_{\mathrm{B}}$

- Interpolation of the correlation part of the exchange-correlation functional according to:
  S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

- k-mesh integration:
  tetrahedron method with Blöchl's corrections

- Orbital resolved DOS
  and calculation of local magnetic moment

The magnetic moment

In OSZICAR (total magnetic moment):

```
         N       E                     dE              d eps        ncg      rms           rms(c)
DAV:     1     0.139935173959E+02    0.13994E+02    -0.35801E+03   2338   0.828E+02
DAV:     2    -0.623612680591E+01   -0.20230E+02    -0.19281E+02   2282   0.123E+02
DAV:     3    -0.643764005251E+01   -0.20151E+00    -0.19906E+00   2536   0.140E+01
DAV:     4    -0.643786482872E+01   -0.22478E-03    -0.22442E-03   2344   0.459E-01
DAV:     5    -0.643786514671E+01   -0.31798E-06    -0.31687E-06   1832   0.173E-02    0.793E+00
...
DAV:     9    -0.545953126374E+01    0.48409E-02    -0.96206E-03   2946   0.839E-01    0.847E-02
DAV:    10    -0.545946513577E+01    0.66128E-04    -0.77007E-05   1364   0.126E-01
    1 F= -.54594651E+01 E0= -.54594651E+01  d E =0.000000E+00  mag=      0.5781
```
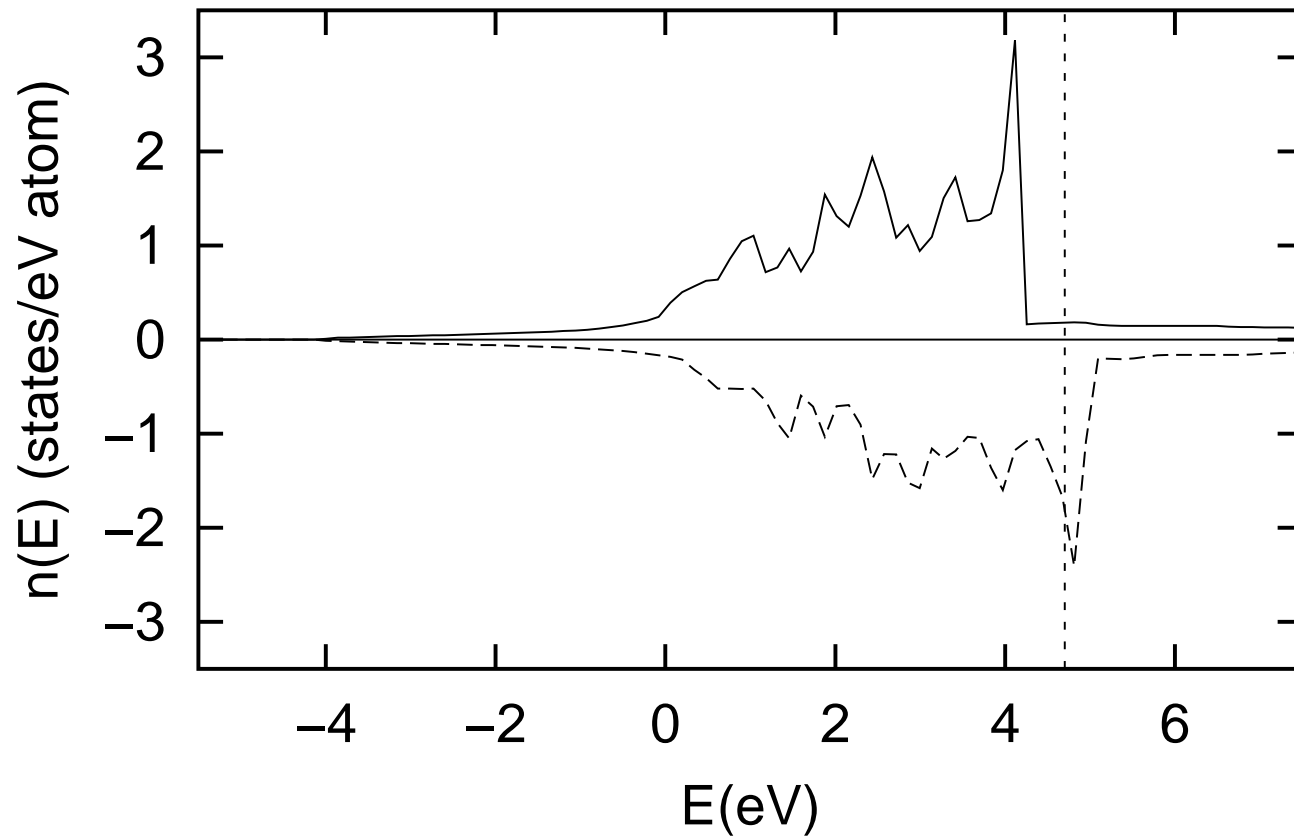
in OUTCAR (integration of magnetic moment in the PAW sphere):

```
 magnetization (x)

# of ion     s       p       d      tot
------------------------------------------
   1      -0.007  -0.026   0.625   0.591
```

fcc Ni

Exchange splitting ≈ 0.5 eV

Proper initialization of magnetic moment

- Too small initial moment will/may lead to a nonmagnetic solution
 (the previous example with `MAGMOM = 0.0`)

```
...
DAV:   9     -0.540773198300E+01     0.31931E-03   -0.39421E-04   2091   0.339E-01     0.300E-02
DAV:  10     -0.540780668590E+01    -0.74703E-04   -0.46454E-05   1059   0.106E-01
   1 F= -.54078067E+01 E0= -.54078067E+01  d E =0.000000E+00  mag=      0.0020
```

- Badly initialized calculations take longer to converge

- Coexistence of low- and high spin solutions

NiO

- Rocksalt structure

- AFM ordering of Ni (111) planes
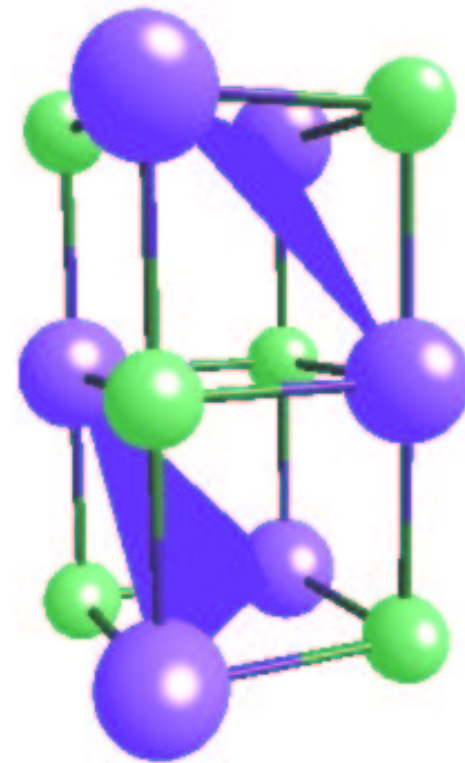
```
NiO AFM
 4.17
 1.0 0.5 0.5
 0.5 1.0 0.5
 0.5 0.5 1.0
 2 2
Cartesian
 0.0 0.0 0.0
 1.0 1.0 1.0
 0.5 0.5 0.5
 1.5 1.5 1.5

k-points
0
Gamma
  4   4   4
   0   0   0
```

POSCAR

- AFM coupling:
  4 atoms in the basis (instead of 2)

KPOINTS

- $4 \times 4 \times 4$ Γ-centered
  Monkhorst-Pack grid

POTCAR

`makepaw Ni O_s`

(PAW-LDA potentials)

```
SYSTEM    = NiO

ISPIN     = 2
MAGMOM    = 2.0 -2.0 2*0

ENMAX     = 250
EDIFF     = 1E-3

ISMEAR    = -5

AMIX      = 0.2
BMIX      = 0.00001
AMIX_MAG  = 0.8
BMIX_MAG  = 0.00001

LORBIT    = 11
```

INCAR

- Initial magnetic moment:
  $\pm 2\,\mu_{\mathrm{B}}$ (Ni), $0\,\mu_{\mathrm{B}}$ (O)

- AMIX=0.2 and AMIX_MAG=0.8 (default)
  BMIX and BMIX_MAG practically zero,
  i.e. linear mixing

Or copy the files from:

`~vw/4_2_NiO`

The magnetic moment

In OSZICAR (total magnetic moment = **0!**):

```
         N       E                   dE           d eps      ncg      rms          rms(c)
...
DAV:  13     -0.267936242334E+02    0.12794E-03   -0.12638E-04   552   0.298E-01   0.169E-02
DAV:  14     -0.267936352231E+02   -0.10990E-04   -0.21775E-05   520   0.107E-01
   1 F= -.26793635E+02 E0= -.26793635E+02  d E =0.000000E+00  mag=      0.0000
```
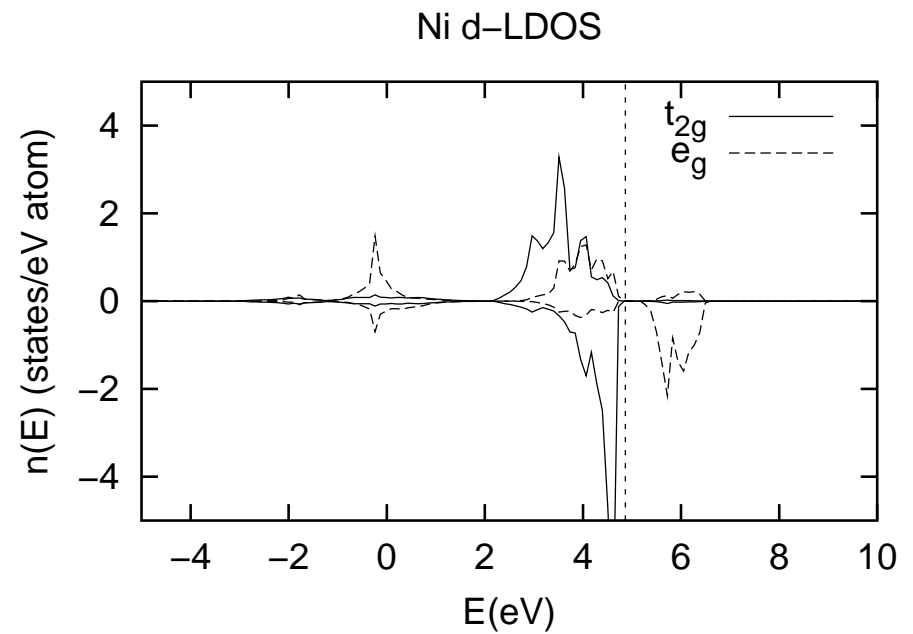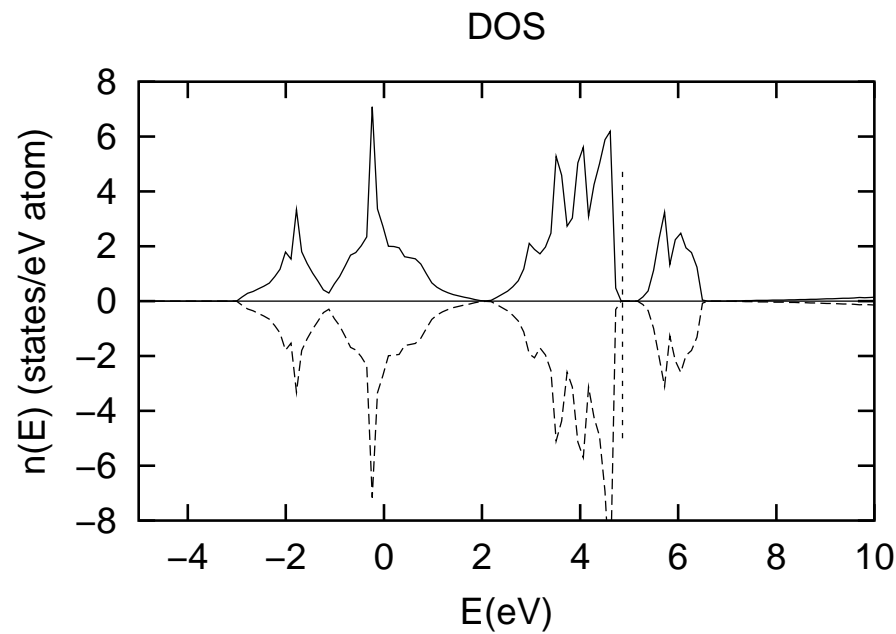
in OUTCAR (integration of magnetic moment in the PAW sphere):

```
 magnetization (x)

# of ion     s       p       d      tot
------------------------------------------
   1      -0.012  -0.014   1.245   1.219
   2       0.012   0.014  -1.242  -1.216
   3       0.000  -0.001   0.000  -0.001
   4       0.000  -0.001   0.000  -0.001
--------------------------------------------------
tot       0.000  -0.003   0.003   0.000
```

Total DOS, and LDOS Ni d-orbitals

DOS

Ni d–LDOS

$|m_{\mathrm{Ni}}| = 1.21\ \mu_{\mathrm{B}}$ (exp. $1.70\ \mu_{\mathrm{B}}$) $E_{\mathrm{gap}} = 0.44$ eV (exp. 4.0 eV)

LSDA+U; Dudarev's approach

```
...
LDAU       = .TRUE.
LDAUTYPE  = 2
LDAUL     = 2 -1
LDAUU     = 8 00  0.00
LDAUJ     = 0.95  0.00
LDAUPRINT = 2
```

Or copy the files from:

` ~vw/4_3_NiO_LSDA+U`

addition to INCAR of NiO calc.

- Switch on L(S)DA+U

- Select Dudarev's approach
  (LSDA+U Type 2)

- L quantum number for which on site interaction is added
  (-1 = no on site interaction)

- U parameter

- J parameter

- Print occupation matrices in OUTCAR

L,U, and J must be specified for all atomic types!

On site occupancies (see OUTCAR)

```
atom =   1  type =  1  l = 2

 onsite density matrix

...

...

 occupancies and eigenvectors

o = 0.1696 v =   0.0000   0.0000   0.0000   0.0000   0.0000   0.0013  -0.0006  -0.9999  -0.0007  -0.0104
o = 0.1696 v =   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000  -0.0011  -0.0104   0.0011   0.9999
o = 0.9770 v =   0.0000   0.0000   0.0000   0.0000   0.0000   0.7787  -0.1766   0.0015  -0.6020   0.0005
o = 0.9770 v =   0.0000   0.0000   0.0000   0.0000   0.0000   0.2456  -0.7972   0.0005   0.5516  -0.0015
o = 0.9770 v =   0.0000   0.0000   0.0000   0.0000   0.0000   0.5774   0.5774   0.0000   0.5774   0.0000
o = 0.9803 v =  -0.0193   0.7166   0.0001  -0.6972  -0.0039   0.0000   0.0000   0.0000   0.0000   0.0000
o = 0.9803 v =   0.8163  -0.3914  -0.0039  -0.4249  -0.0001   0.0000   0.0000   0.0000   0.0000   0.0000
o = 0.9803 v =   0.5774   0.5774   0.0000   0.5774   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000
o = 1.0248 v =  -0.0032   0.0016  -1.0000   0.0016   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000
o = 1.0248 v =   0.0000   0.0027   0.0000  -0.0027   1.0000   0.0000   0.0000   0.0000   0.0000   0.0000
```

$$d_{xy}^{\uparrow} \quad d_{yz}^{\uparrow} \quad d_{z^2-r^2}^{\uparrow} \quad d_{xz}^{\uparrow} \quad d_{x^2-y^2}^{\uparrow} \quad d_{xy}^{\downarrow} \quad d_{yz}^{\downarrow} \quad d_{z^2-r^2}^{\downarrow} \quad d_{xz}^{\downarrow} \quad d_{x^2-y^2}^{\downarrow}$$

when `U=0` and `J=0` (i.e. just LSDA) the on site occupancies are as follows:

```
o = 0.3462 v =  0.0000  0.0000  0.0000  0.0000  0.0000 -0.0048  0.0028  0.9951  0.0020 -0.0986
o = 0.3462 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.0005  0.0039 -0.0986 -0.0044 -0.9951
o = 0.9491 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.5774  0.5774  0.0000  0.5774  0.0000
o = 0.9495 v =  0.0000  0.0000  0.0000  0.0000  0.0000 -0.0588  0.7347 -0.0004 -0.6759  0.0059
o = 0.9495 v =  0.0000  0.0000  0.0000  0.0000  0.0000  0.8144 -0.3563  0.0059 -0.4581  0.0004
o = 0.9527 v =  0.0477 -0.0256  0.9974 -0.0221 -0.0420  0.0000  0.0000  0.0000  0.0000  0.0000
o = 0.9527 v =  0.0020  0.0403  0.0420 -0.0423  0.9974  0.0000  0.0000  0.0000  0.0000  0.0000
o = 0.9598 v =  0.5774  0.5774  0.0000  0.5774  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
o = 0.9599 v = -0.1186  0.7577  0.0085 -0.6391 -0.0579  0.0000  0.0000  0.0000  0.0000  0.0000
o = 0.9599 v =  0.8064 -0.3005 -0.0579 -0.5059 -0.0085  0.0000  0.0000  0.0000  0.0000  0.0000
```

$$d_{xy}^{\uparrow} \quad d_{yz}^{\uparrow} \quad d_{z^2-r^2}^{\uparrow} \quad d_{xz}^{\uparrow} \quad d_{x^2-y^2}^{\uparrow} \quad d_{xy}^{\downarrow} \quad d_{yz}^{\downarrow} \quad d_{z^2-r^2}^{\downarrow} \quad d_{xz}^{\downarrow} \quad d_{x^2-y^2}^{\downarrow}$$

The Ni d-LDOS and local magnetic moment

LSDA

Dudarev U=8 J=0.95
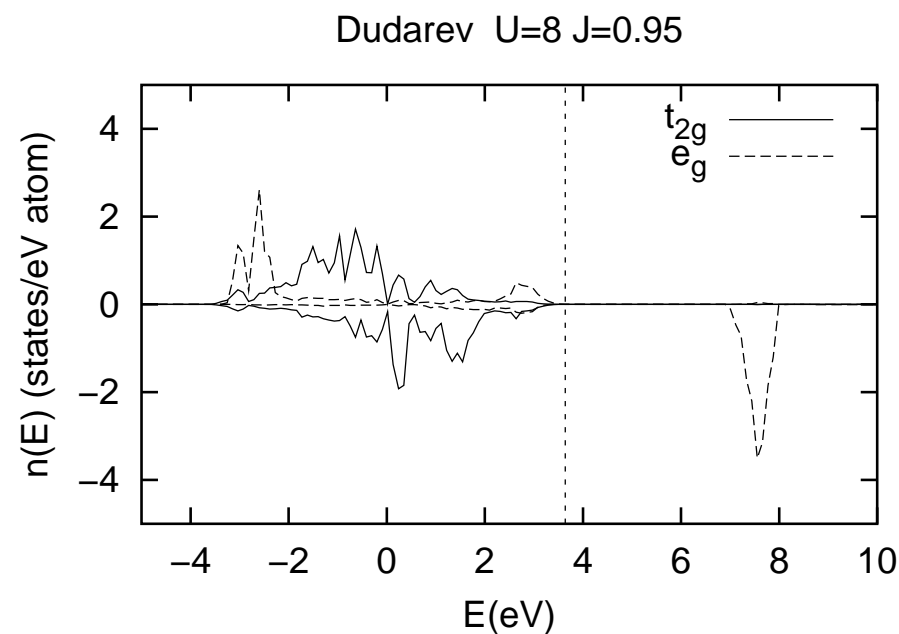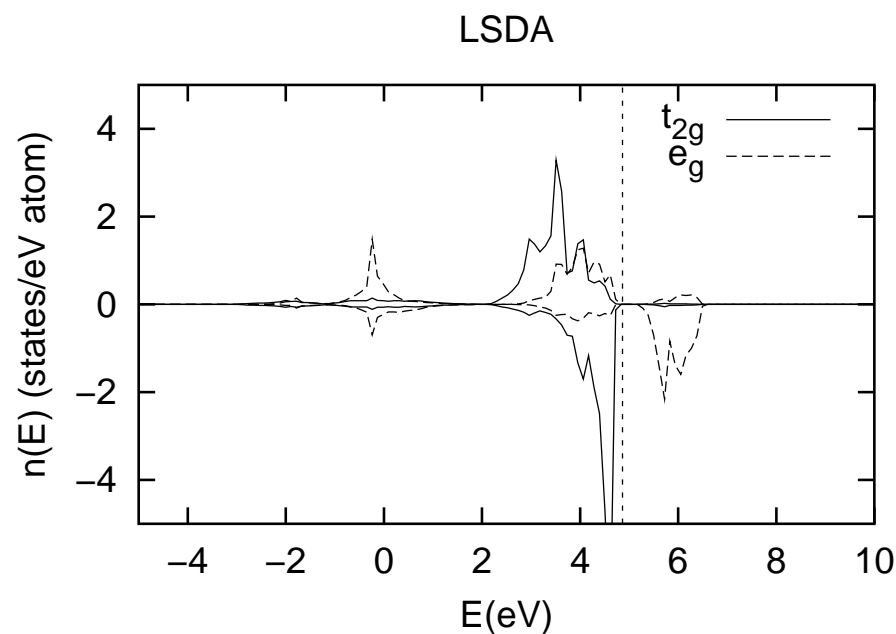
```
        magnetization (x)

# of ion    s        p        d        tot
-----------------------------------------------
    1     -0.003   -0.006    1.721    1.711
    2      0.003    0.006   -1.719   -1.710
    3      0.000   -0.001    0.000   -0.001
    4      0.000   -0.001    0.000   -0.001
-----------------------------------------------
tot        0.000   -0.002    0.002    0.000
```

Total Energy

On site occupancy matrix is NOT idempotent $\rightarrow$

Total energy contains penalty contribution!

```
...
DAV:  15    -0.229633055256E+02   -0.11057E-03   -0.50020E-05   520   0.104E-01   0.118E-02
DAV:  16    -0.229633263321E+02   -0.20806E-04   -0.16650E-05   520   0.492E-02
   1 F= -.22963326E+02 E0= -.22963326E+02  d E =0.000000E+00  mag=      0.0000
```

The total energy for $(U - J) > 0$ is in that case always higher than for $(U - J) = 0$ (just LSDA, see below):

```
...
DAV:  13    -0.267936242334E+02    0.12794E-03   -0.12638E-04   552   0.298E-01   0.169E-02
DAV:  14    -0.267936352231E+02   -0.10990E-04   -0.21775E-05   520   0.107E-01
   1 F= -.26793635E+02 E0= -.26793635E+02  d E =0.000000E+00  mag=      0.0000
```

Comparing the total energies from calculations with different $(U - J)$ is meaningless!