Standards and Reference Energies

Contents

1 The *MedeA* Standard 500

MedeA uses a standard for Precision VASP calculations, automatically applying the directive `PREC = Accurate` and a plane wave cutoff of 500 eV (900 eV for hard potentials where the PAW potential definition in the `POTCAR` file has *ENMAX* $>$ 450 eV). The *MedeA VASP GUI* option `Standard 500` is recommended when an overall precise plane cutoff and setting is required. Using a standard cutoff of 500 eV within a project facilitates the comparison of data from compounds containing different elements like, *e.g.*, in the calculation of heat of formations or defect energies.

VASP **parameters covered by** Precision `Standard 500` **:**

- VASP precision is set to accurate
- Planewave cutoff energy is set to 500 eV (900 eV for hard PAW potentials which have *ENMAX* $>$ 450 eV)

VASP **parameters recommended to be set in addition, to comply with** `Standard 500` **:**

- Reciprocal space projection
- Convergence criterion for SCF cycle: 10^{-7} eV
- Convergence criterion for geometry optimization: 0.001 eV/Å
- Conjugate gradient algorithm for geometry optimization

For crystalline structures:

- K-spacing of 0.2 Å^{-1}, shift origin to Γ
- For non-local exchange based functionals (e.g. hybrid functionals): k-spacing of 0.5 Å^{-1}, shift origin to Γ, and set X, Y, and Z axis components of the k-mesh factors to 2
- K-space integration using the tetrahedron method including Blöchl corrections

For molecular structures:

- Box ensuring a minimum of about 8 Å empty space between the molecule and its nearest-images over the periodic boundary condition
- Γ-point only
- K-space integration using Fermi smearing with a 0 eV smearing width

DOCUMENTATION

2 Reference Energies for the Calculation of the Heat of Formation

The computation of the electronic contribution to heats of formation for compounds requires reference energies for all constituent elements in their standard state. Below is a list of model structures for all elements in their standard state, which is applied for calculating the energy of formation as a property from the *MedeA VASP 6 GUI*. For a few cases, where, *e.g.*, van der Waals interactions have to be included, the standard state structures are replaced by other structures that are correctly covered by standard DFT functionals. Correction energies are then used to obtain the energy of the standard state structures.

In structure optimization calculations for the reference systems, in general a non-magnetic Hamiltonian is used, however, spin-polarization is required for O_2, Cr (antiferromagnetic), γ-Mn (antiferromagnetic), Fe, Co, Ni, and lanthanides heavier than Ce for potentials including *f* electrons as valence states.

For solids, all cell parameters and internal degrees of freedom need to be relaxed. For atoms and molecules a fixed box of 10 $\mathring{\mathrm{A}}$ in each dimension is used (for S_8 molecules a cubic box of 15 $\mathring{\mathrm{A}}$), for molecules the atomic positions need to be relaxed.

For computing energies of formation, the application of the *Standard 500* setting as outlined above is recommended to obtain a suitable accuracy.

Table1: Summary of models and technical details for the calculations of reference energies of the elements

Elements	Structure	Correction, techn. details
H	H_2 molecule	
He	He atom	
Li	bcc	
Be	α-Be, hcp	
B	α-B, R-3m	
C	diamond, Fd-3m	-1.897 kJ/mol, because graphite is the low temperature phase
N	N_2 molecule	
O	O_2 molecule	spin-polarized, because molecule exists in triplet state
F	F_2 molecule	
N	Ne atom	
Na	bcc	
Mg	hcp	
Al	fcc	
Si	Fd-3m	
P	Cmca, black phosphorus	
S	S_8 molecule	-13.04875 kJ/mol, condensation
Cl	Cl_2 molecule	
Ar	Ar atom	
K	bcc	
Ca	α-Ca, fcc	
Sc	α-Sc, hcp	
Ti	α-Ti, hcp	
V	bcc	
Cr	α-Cr, bcc, antiferromagnetic	spin-polarized
Mn	γ-Mn P4/mmm, antiferromagnetic	-4.348 kJ/mol = α-Mn, spin-polarized
Fe	α-Fe, bcc	spin-polarized
Co	β-Co, hcp	spin-polarized
Ni	fcc	spin-polarized
Cu	fcc	
Zn	hcp	
Ga	α-Ga, Cmca	

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Elements	Structure	Correction, techn. details
Ge	Fd-3m	
As	R-3m	grey metallic
Se	P3121	grey metallic
Br	Br_2 molecule	-22.85 kJ/mol, condensation
Kr	Kr atom	
Rb	bcc	
Sr	α-Sr, fcc	
Y	hcp	
Zr	α-Zr, hcp	
Nb	bcc	
Mo	bcc	
Tc	hcp	
Ru	hcp	
Rh	fcc	
Pd	fcc	
Ag	fcc	
Cd	hcp	
In	I4/mmm	
Sn	α-Sn, Fd-3m	transition temperature of 286 K to β-Sn, I41/amd
Sb	R-3m	
Te	P3121	
I	Cmca	
Xe	Xe atom	
Cs	bcc	
Ba	bcc	
La	α-La, dhcp	
Ce	γ-Ce, fcc	
Pr	dhcp	
Nd	dhcp	
Pm	dhcp	
Sm	R-3m	
Eu	bcc	
Gd	hcp	
Tb	hcp	
Dy	hcp	
Ho	hcp	
Er	hcp	
Tm	hcp	
Yb	fcc	
Lu	hcp	
Hf	hcp	
Ta	α-Ta, bcc	
W	α-W, bcc	
Re	hcp	
Os	hcp	
Ir	fcc	
Pt	fcc	
Au	fcc	
Hg	R-3m	2.3 kJ/mol melting (JANAF)
Tl	α-Tl, hcp	
Pb	fcc	
Bi	R-3m	
Po	Pm-3m	

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Table 1 – continued from previous page

Elements	Structure	Correction, techn. details
At	no structure	
Rn	Rn atom	
Fr	no structure	
Ra	bcc	
Ac	fcc	
Th	α-Th, fcc	
Pa	I4/mmm	
U	α-U, Cmcm	
Np	Pnma	
Pu	α-Pu, P121/m1	
Am	dhcp	
Cm	dhcp	