VASP Workshop

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Outline

- Density functional theory
- Vienna Ab-initio Simulation Package (VASP)
- Setting up a VASP calculation
  - Tutorial 1: Structure optimization
  - Tutorial 2: Electronic structure
- Parallelization schemes
- Post-processing tips

Density functional theory

$$H[n]\phi_i(r) = \epsilon_i \phi_i(r)$$

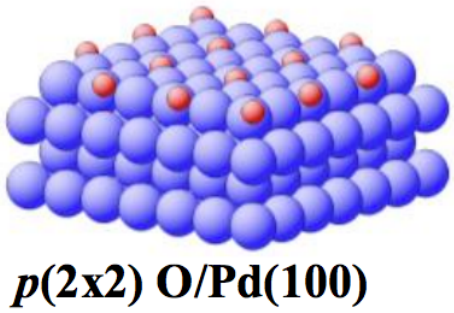
$$\left(\frac{-1}{2}\nabla^2 + \int_\Omega \frac{n(r)}{|r-r'|} dr' + V_{xc}(r) + V_{ext}(r) \right) \phi_i(r) = \epsilon_i \phi_i(r)$$

Kinetic energy

Electron-electron

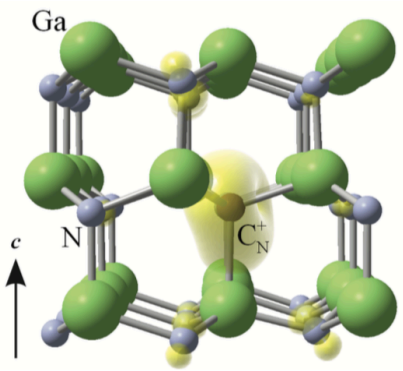
Exchange-correlation potential

Electron-ion potential

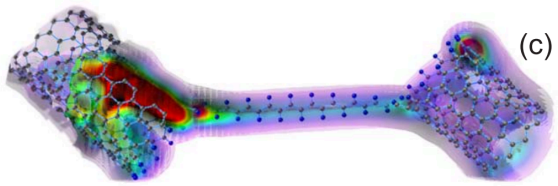


p(2x2) O/Pd(100)

Surf. Sci. 541, 101 (2003)



Phys. Rev. B 89, 035204 (2014)



Phys. Rev. B 76, 205322 (2007)

Approximations of V_{XC}

- Different approaches to the exchange-correlation potential are implemented
  - LDA: Local density approximation
  - **GGA: Generalized gradient approximation**
  - **Hybrids, such as HSE**
  - Meta-GGAs
  - VdW-functionals: Grimme D2 and D3, Tkatchenko-Scheffler, vdW-DF
  - …
- But also more advanced methods
  - GW
  - ACFDT in RPA (adiabatic connection fluctuation dissipation theorem in the random phase approximation)
  - MP2 (2^{nd} order Møller-Plesset)

Vienna Ab-initio Simulation Package (VASP)

- Density Functional Theory (DFT)
- Uses a plane-wave basis
  - Number of plane waves is determined by a cutoff energy → controls accuracy of basis and can be systematically increased
- Uses periodic boundary conditions
  - Simulating lower-dimensional systems requires adding vacuum
- Uses PAW pseudopotentials
  - Projected-augmented Wave pseudopotentials
  - Not all-electron: Core electrons are “frozen” and replaced by a pseudopotential

What quantities can VASP calculate

- **Total energies, forces & relaxed structures**
- **Band structures**
- DOS and projected DOS (density of states)
- Magnetic properties
- Response to electric fields or ionic displacement (dielectric constants, Berry phase, phonons (Gamma only), elastic constants,…)
- Optical properties (absorption spectra, dielectric function,...)

Setting up a VASP calculation

VASP requires 4 input files to run a calculation

1. POSCAR
2. POTCAR
3. KPOINTS
4. INCAR

For further details refer to VASP manual

http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html

https://cms.mpi.univie.ac.at/wiki/index.php/The_VASP_Manual

POSCAR

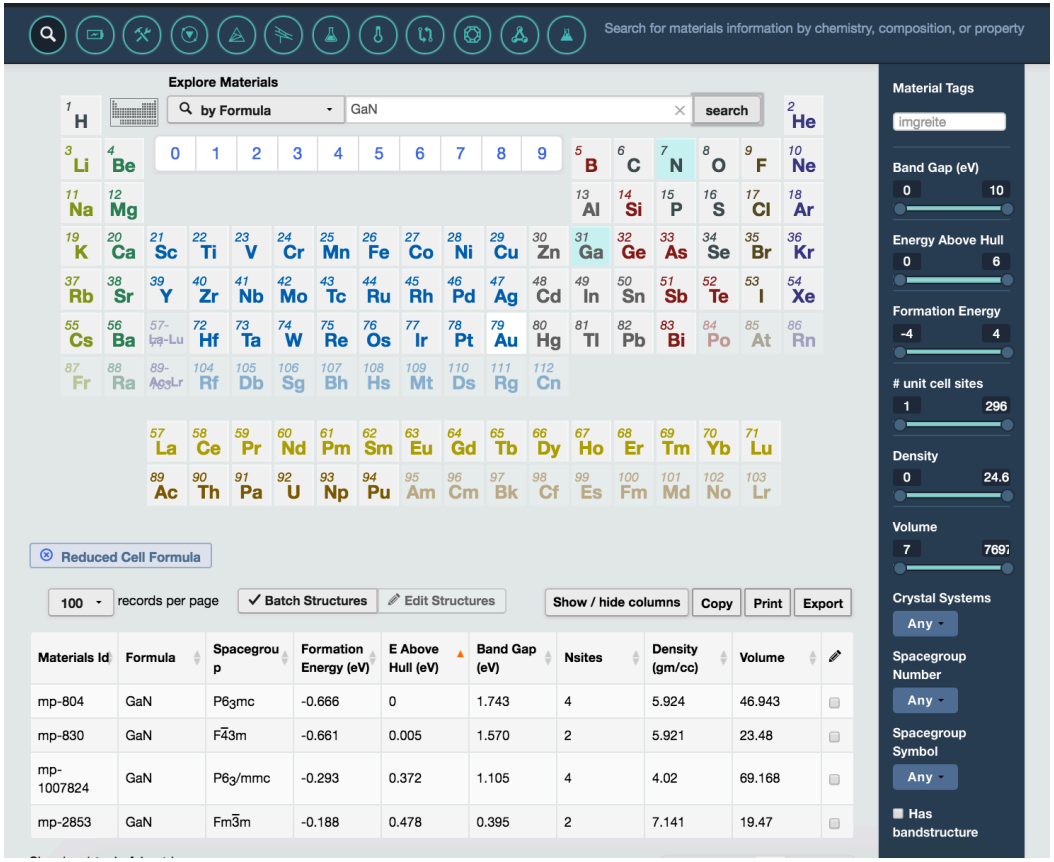
Define the structure of your material, i.e Bravais lattice and basis.

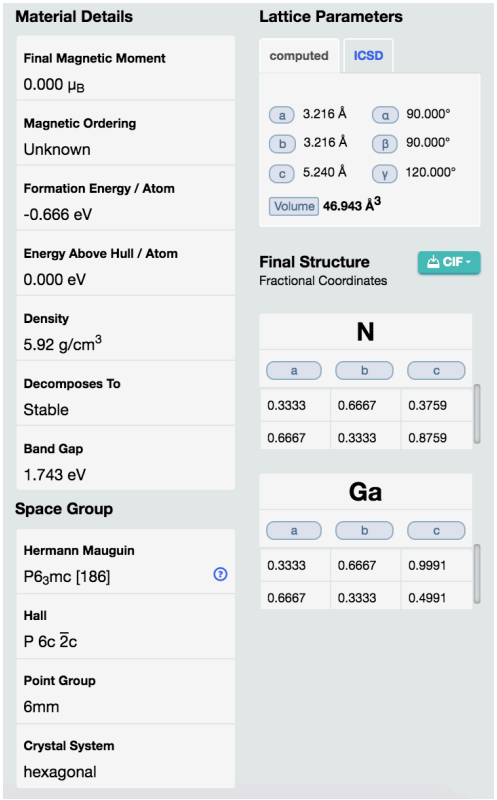
```
GaN wurtzite
3.189
0.50246  -0.87029  0.00000
0.50246   0.87029  0.00000
0.00000   0.00000  1.63140
Ga    N
2     2
Direct
0.33333  0.66667  0.00000
0.66667  0.33333  0.50000
0.33333  0.66667  0.37648
0.66667  0.33333  0.87648
```

```
#Header
#Lattice constant

#Lattice vectors

#Elements
#No. Atoms per element
#Coordinate system

#Coordinates
```

Visualize structures with VESTA - http://jp-minerals.org/vesta/en/

POSCARs & the Materials Project





www.materialsproject.org

Structures are obtained from the Inorganic Crystal Structure Database (ICSD)

POTCAR

- Contains the PAW potentials for all elements defined in the POSCAR.

- POTCAR data sets start with a description of:
  - Element name and atomic mass
  - Number of valence electrons
  - Default energy cutoff
  - Parameter used to generate the PAW dataset

N POTCAR

PAW_PBE N 08Apr2002
5.00000000000000
parameters from PSCTR are:
VRHFIN =N: s2p3
LEXCH = PE
EATOM = 264.5486 eV, 19.4438 Ry

TITEL = PAW_PBE N 08Apr2002
LULTRA = F use ultrasoft PP ?
IUNSCR = 1 unscreen: 0-lin 1-nonlin 2-no
RPACOR = 1.200 partial core radius
POMASS = 14.001; **ZVAL = 5.000** mass and valenz
RCORE = 1.500 outmost cutoff radius
RWIGS = 1.400; RWIGS = 0.741 wigner-seitz radius (au A)
ENMAX = 400.000; ENMIN = 300.000 eV

#Header
#No. of valence electrons
#valence orbitals
#Recommended plane wave cutoff energies

KPOINTS

- Define the points VASP uses to sample the first Brillouin zone in reciprocal space.

```
Automatic generation - MP scheme
0
Monkhorst-Pack
8 8 6
0 0 0
```

- Define the path of k-points along which band structures are calculated.

INCAR

The INCAR file contains all of the input parameters that control the calculation.

Define settings to specify:

1. Type of calculation; eg. self-consistent field (SCF), structure optimization, density of states, band structure, dielectric properties, etc.

2. Inputs regarding precision, required level of convergence, choice of numerical algorithms.

For all INCAR tags ref:
http://cms.mpi.univie.ac.at/wiki/index.php/Category:INCAR

Example 1: GaN Structure optimization

1. Define initial POSCAR and KPOINT grid
2. Create POTCAR for GaN

   cat Ga/POTCAR N/POTCAR >> POTCAR
3. Define optimization parameters in INCAR

```
SYSTEM = GaN
LWAVE= .True.
LREAL = .FALSE.
# Parameters
ISMEAR = 0
SIGMA = 0.05
ENCUT = 400
PREC = Accurate

#Cell Optimisation
EDIFFG = -0.005
EDIFF  = 1E-5
ISIF   = 3
IBRION = 2
```

Example 1: Structure optimization output

Total energy following structure optimization is output at end of *OSZICAR* file

```
N      E                     dE             d eps       ncg     rms         ort
SDA:  1   -0.115016930235E+03   0.25406E+01    0.00000E+00   512   0.176E+02 0.000E+00
CGA:  2   -0.117416954127E+03  -0.24000E+01   -0.24655E+01   512   0.118E+01-0.225E+00
CGA:  3   -0.117803679652E+03  -0.38673E+00   -0.38703E+00   512   0.302E+00-0.392E-02
CGA:  4   -0.117912013796E+03  -0.10833E+00   -0.10837E+00   512   0.510E-01-0.358E-03
CGA:  5   -0.117924142175E+03  -0.12128E-01   -0.12125E-01   512   0.219E-01-0.233E-04
CGA:  6   -0.117931700856E+03  -0.75587E-02   -0.75631E-02   512   0.753E-02-0.634E-04
CGA:  7   -0.117935095864E+03  -0.33950E-02   -0.33988E-02   512   0.175E-02-0.190E-04
CGA:  8   -0.117935693145E+03  -0.59728E-03   -0.59788E-03   512   0.662E-03-0.117E-04
CGA:  9   -0.117935831345E+03  -0.13820E-03   -0.13836E-03   512   0.135E-03 0.209E-05
CGA:  10   -0.117935876522E+03   -0.45178E-04   -0.45331E-04   512   0.283E-04-0.352E-05
  3 F= -.11793588E+03 E0= -.11793588E+03  d E =-.109175E+00  mag=     0.0000
```

Final optimized structure is output to *CONTCAR*

Example 2: GGA band structure workflow

1. Use optimized structure to run a self-consistent field (SCF) calculation. Set NSW = 0 (1 step scf)

   cp CONTCAR POSCAR

2. Define INCAR for non-SCF calculation using CHGCAR from Step 1.

```
SYSTEM = GaN
ICHARG = 11          #use charge density from file; do not update
LWAVE= .True.
LREAL = .FALSE.

# Parameters
ISMEAR = 0
SIGMA = 0.05
ENCUT = 400
PREC = Accurate

#Cell Optimisation
EDIFF  = 1E-5
```

Example 2: GGA band structure workflow

3. Setup path of KPOINTS for band structure calculation and submit simulation.

```
Kpoint path GaN
15  ! 15 intersections
Line-mode
Reciprocal
 0.000 0.000 0.0 ! Gamma
 0.500 0.000 0.0 ! M

 0.500 0.000 0.0 !M
 0.666 0.333 0.0 !K

 0.666 0.333 0.0 !K
 0.000 0.000 0.0 !G

 0.000 0.000 0.0 !G
 0.000 0.000 0.5 !A
```

```
#Number of kpoints to interpolate between
#Instruct VASP to interpolate between pairs of kpoints
#kpoint coordinate system
```

Example 2: EIGENVAL format

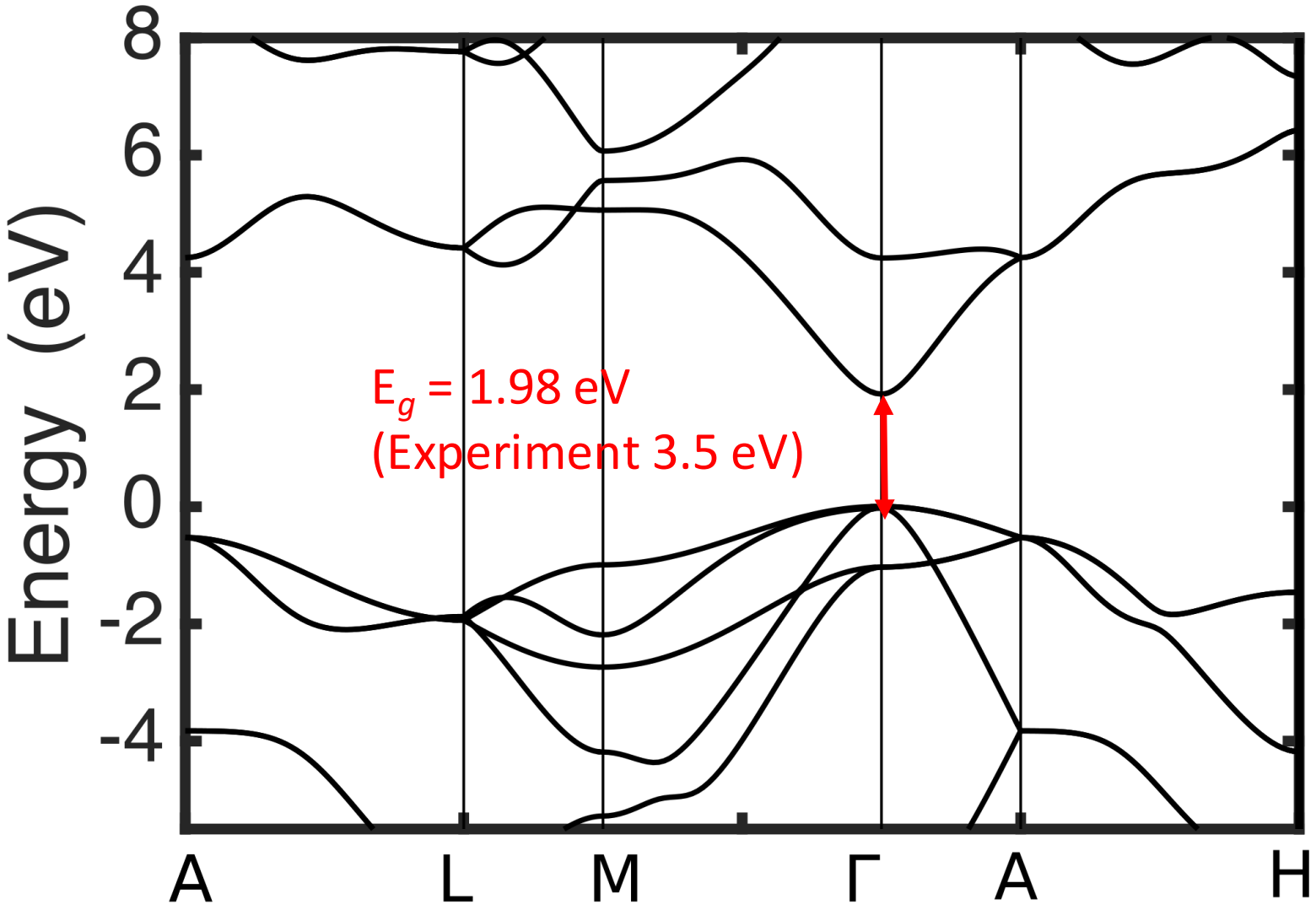
```
4   4   1   1
 0.1156815E+02  0.3204707E-09  0.3204707E-09  0.5202551E-09  0.5000000E-15
 1.000000000000000E-004
 CAR
GaN
 10  30   10

 0.0000000E+00  0.0000000E+00  0.0000000E+00  0.6944444E-02
  1     -15.783947
  2     -13.319151
  3      -5.637542
  4       0.760612
  5       0.760922
  6       1.852311
  7       1.868450
  8       1.868791
  9       5.343214
 10       7.858293
```

#number of bands
#number of kpoints

#kpoint coordinates
#Band index & eigenenergy

Same information can be found in OUTCAR and vasprun.xml

GaN GGA band structure



Example 3: HSE band structure

1. GGA calculation first to get a good starting wave function.
2. HSE self-consistent calculation restarting from GGA WAVECAR.

```
SYSTEM = GaN
ISTART = 1
LWAVE= .True.
LREAL = .FALSE.
PREC =Accurate

# Parameters
ISMEAR = 0
SIGMA = 0.05
ENCUT = 400

#SCF
EDIFF  = 1E-5

#Hybrid functional HSE flags
LHFCALC = .TRUE.      #do a hybrid calculation
AEXX = 0.25           #use 25% exact exchange
HFSCREEN = 0.2        #default HSE06 screening length (in Å-1)
PRECFOCK = Fast       #precision to use for the FFT grids for Hartree-Fock. Other options are Normal and
                        Accurate. Fast is sufficient to do relaxations and most other calculations
ALGO= All             #the scf algorithm to use. 3 options for hybrids: All, Normal, and Damped
```

Example 3: HSE band structure

- Non-selfconsistent calculations not possible: need wave functions
- Method
  1. Converge wave function, with HSE and a standard k-point grid
  2. Copy contents of IBZKPT file to the KPOINTS file
     cp IBZKPT KPOINTS
  3. Edit the KPOINTS file and add the points for the band structure at the end, using 0 as weight
  4. INCAR:
     - set NELMIN to at least 5 (zero weight k-points do not enter the convergence criterion).
     - Set ALGO= Normal (correct ordering unoccupied bands)
  5. Plot the EIGENVAL file, omitting the non-zero weight k-points (as these are not part of the band structure)
- For computational efficiency (to avoid memory problems): split the band structure calculations in segments, run separately, and merge before plotting

Example 3: HSE band structure KPOINTS

KPOINT path
21
Reciprocal lattice

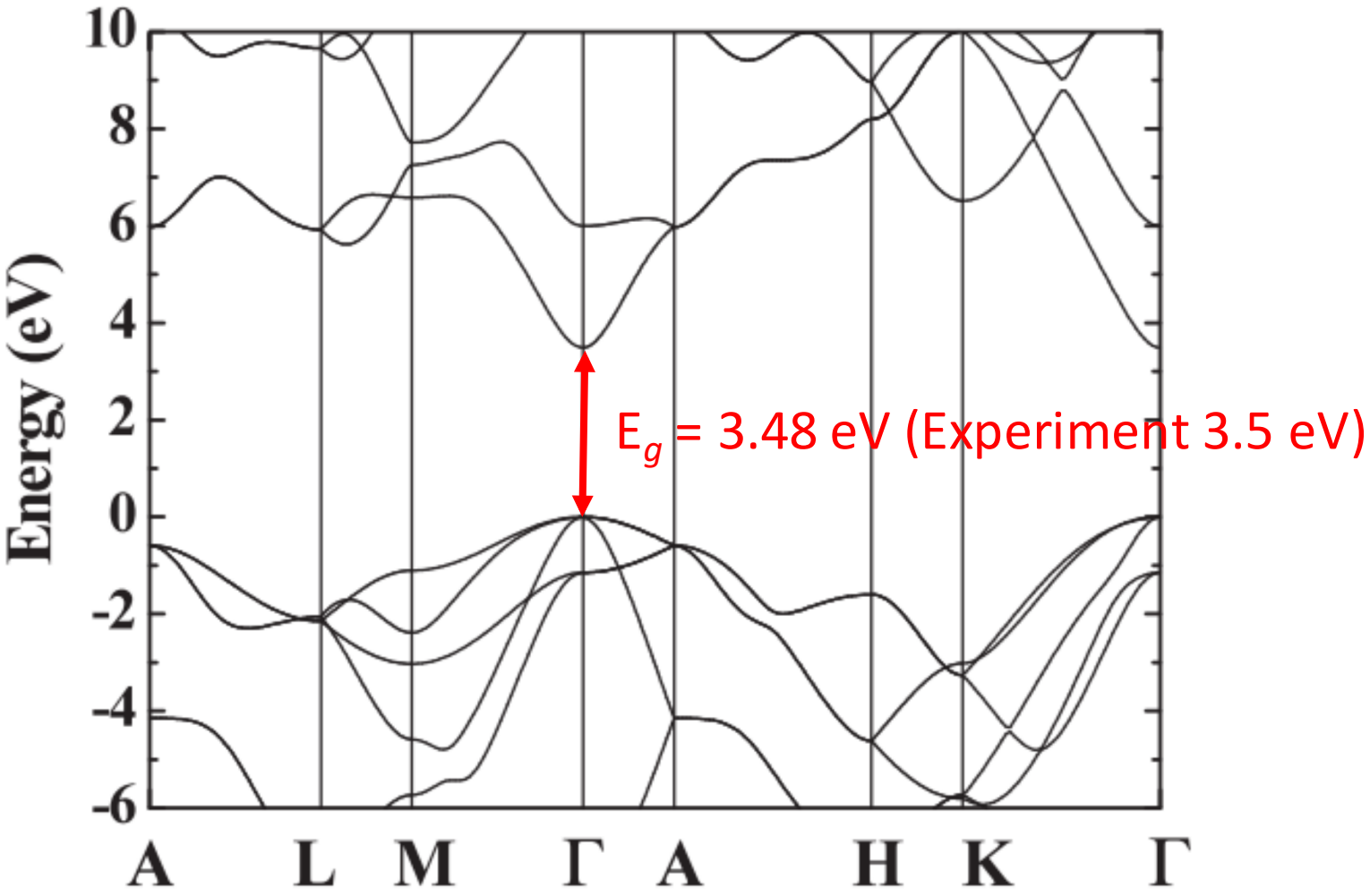
0.12500000000000	0.12500000000000	0.12500000000000	2
0.37500000000000	0.12500000000000	0.12500000000000	6
-0.37500000000000	0.12500000000000	0.12500000000000	6
-0.12500000000000	0.12500000000000	0.12500000000000	6
0.37500000000000	0.37500000000000	0.12500000000000	6
-0.37500000000000	0.37500000000000	0.12500000000000	12
-0.12500000000000	0.37500000000000	0.12500000000000	12
-0.37500000000000	-0.37500000000000	0.12500000000000	6
0.37500000000000	0.37500000000000	0.37500000000000	2
-0.37500000000000	0.37500000000000	0.37500000000000	6
0.00000000000000	**0.00000000000000**	**0.00000000000000**	**0**
0.05000000000000	**0.00000000000000**	**0.00000000000000**	**0**
0.10000000000000	**0.00000000000000**	**0.00000000000000**	**0**
0.15000000000000	**0.00000000000000**	**0.00000000000000**	**0**
0.20000000000000	**0.00000000000000**	**0.00000000000000**	**0**
0.25000000000000	**0.00000000000000**	**0.00000000000000**	**0**
0.30000000000000	**0.00000000000000**	**0.00000000000000**	**0**
0.35000000000000	**0.00000000000000**	**0.00000000000000**	**0**
0.40000000000000	**0.00000000000000**	**0.00000000000000**	**0**
0.45000000000000	**0.00000000000000**	**0.00000000000000**	**0**
0.50000000000000	**0.00000000000000**	**0.00000000000000**	**0**

#total number of kpoints

#kpoints from IBZKPT

#kpoint path from zone-center to M for band structure

GaN HSE band structure



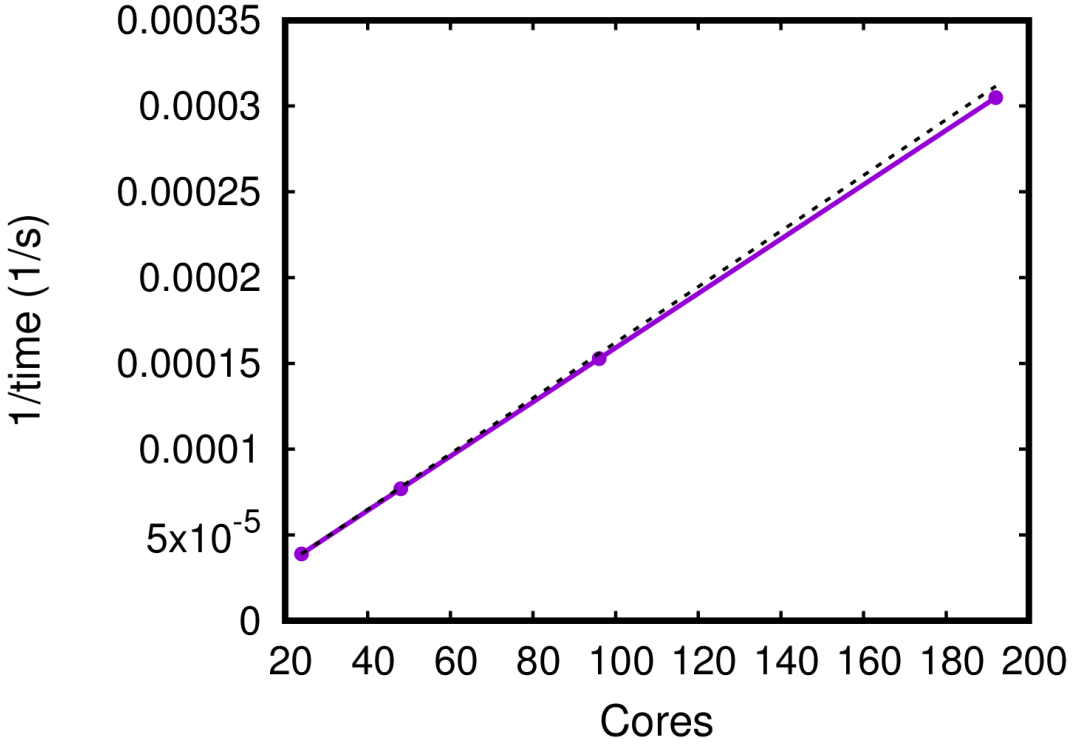
Running VASP jobs efficiently

- VASP is a highly parallelized code capable of running simulations on large structures.

- Three different variables for parallelization in VASP:
  - KPAR
  - NPAR
  - NCORE

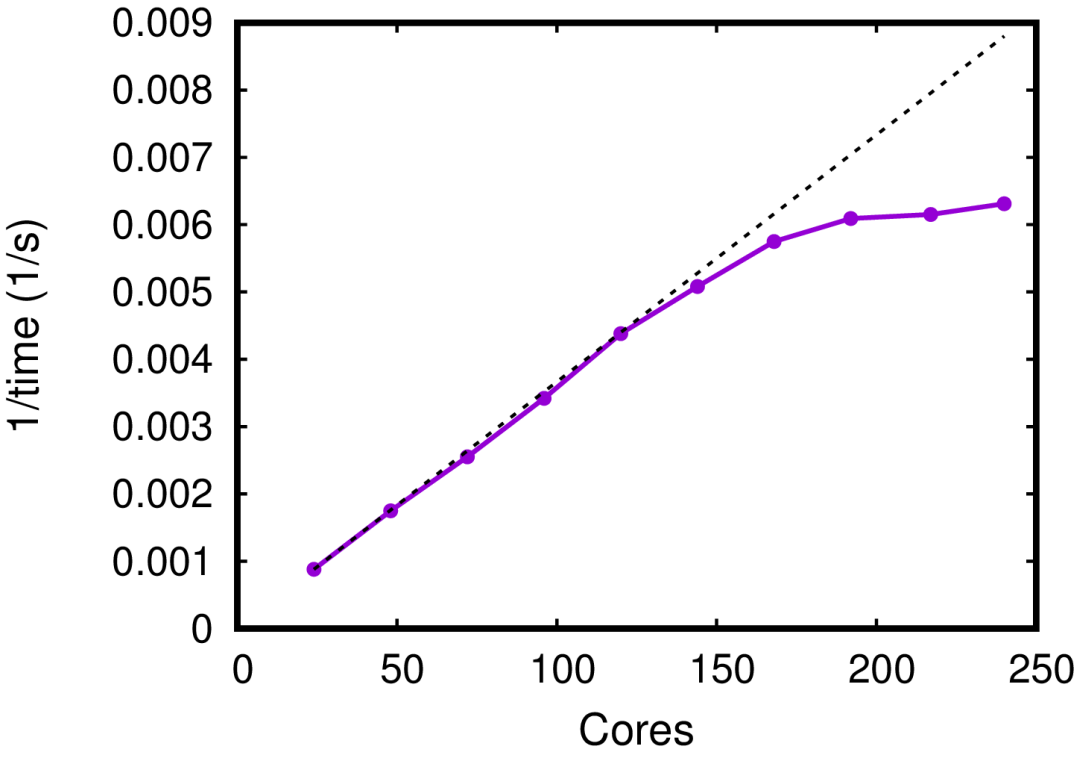
KPAR

- **Most efficient method** to parallelize
- Only able to parallelize over k-points in IBZKPT file! **NOT** those listed in the HF routine of VASP (if using hybrids)
- Set KPAR to number that divides the number of k-points in IBZKPT file
- VASP does not check if the number is actually efficient (or usable)
- Remainder of cores will be used for NPAR



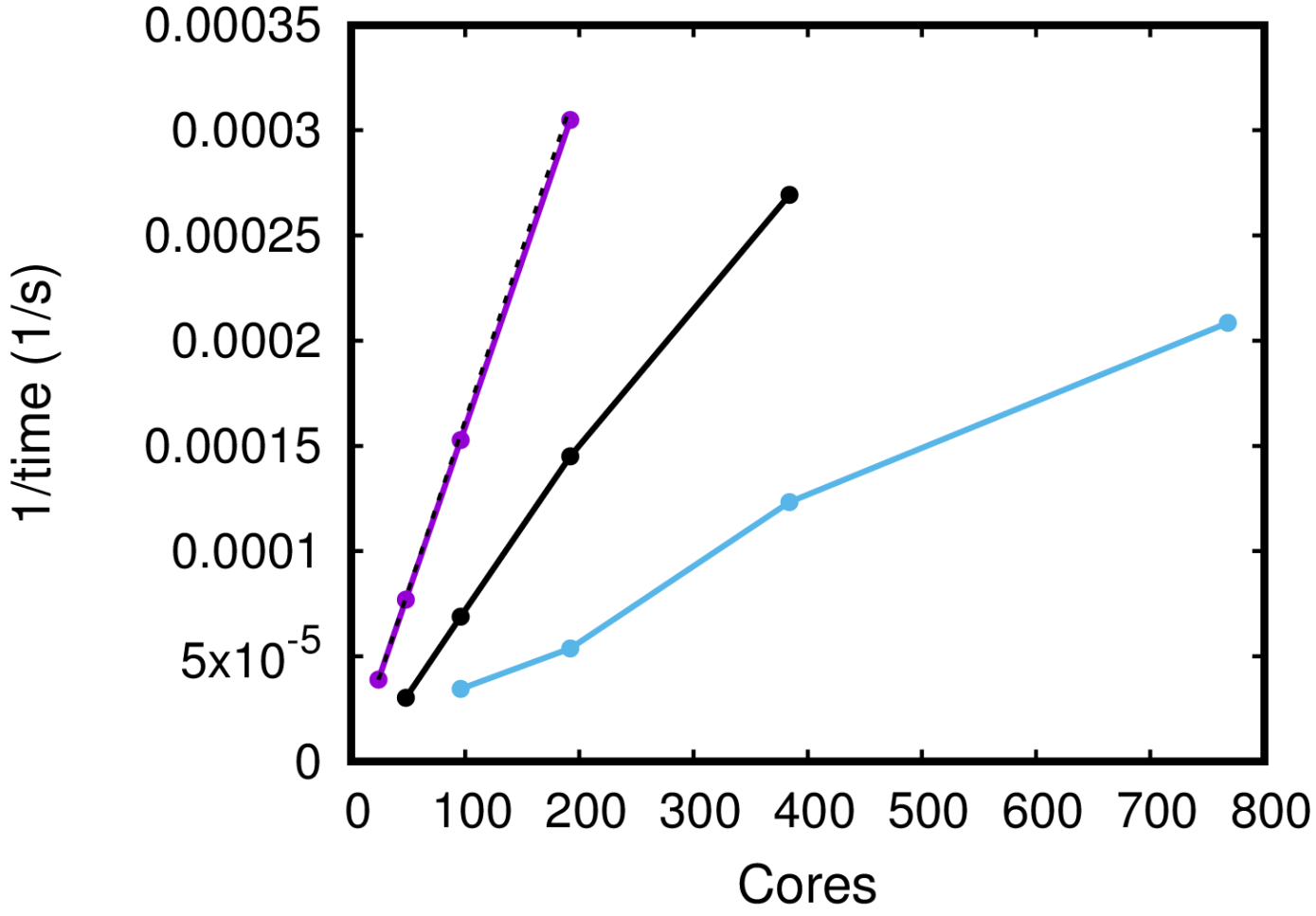
NPAR

- Parallelization over bands. Default in VASP
- GGA: NPAR = SQRT(NBANDS)
- HSE: NPAR should divide the number of bands (NBANDS), if not, VASP will adjust the number of bands up (not efficient, waste of cpu time)
- Maximum parallelization: NPAR = NBANDS, but **NOT** efficient
- Best to only use 1 or 2 nodes; HSE: NPAR=NBANDS/4



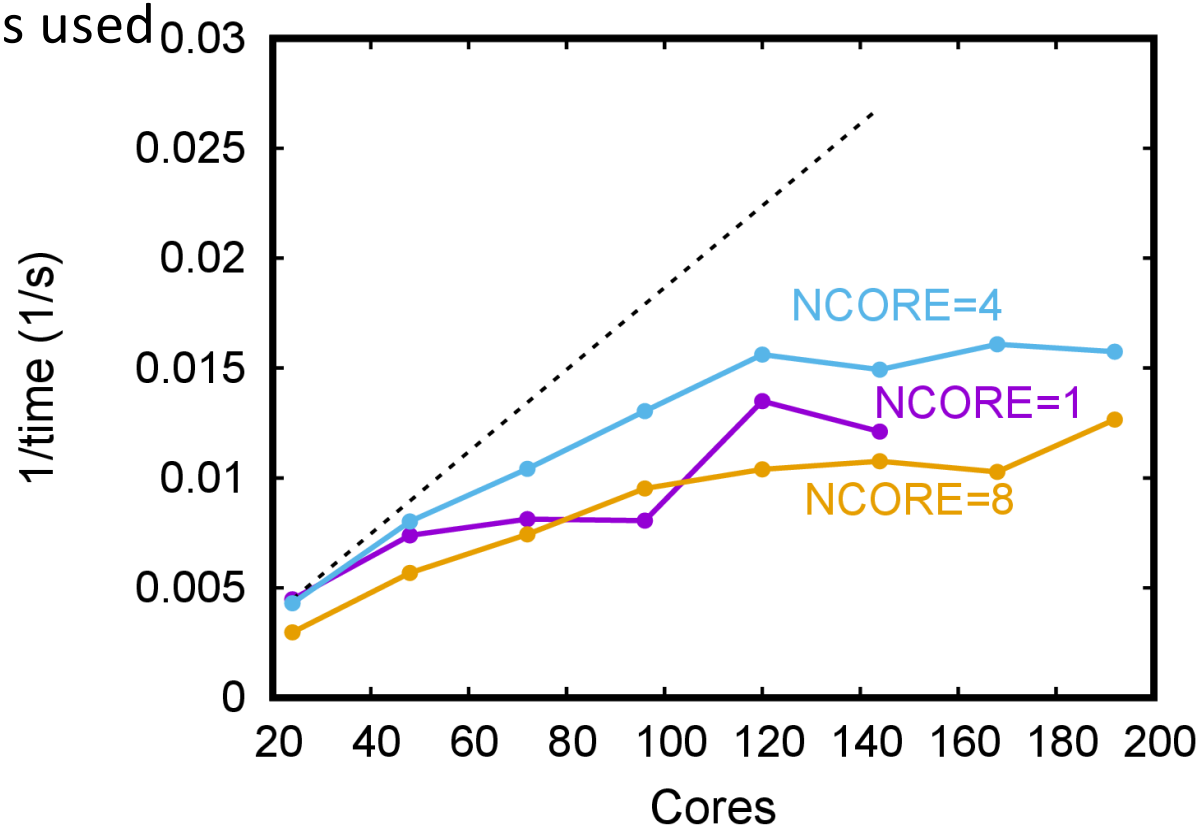
NPAR vs. KPAR

KPAR (near) linear scaling! NPAR always less efficient



NCORE

- Number of cores “sharing work on individual orbital”
- Intended for GGA, HSE is experimental
- HSE: Worst efficiency of the three methods
- NCORE=#cores/NPAR
- NCORE=1 is not the same as not setting it!
- If NPAR is present: NPAR is used



Summary of VASP parallelization

- If possible: use KPAR
  - Only k-points in IBZKPT
- Next best option: NPAR
  - GGA: SQRT(NBANDS)
  - HSE: Should divide NBANDS
  - Rule of thumb:
    - 1 or 2 nodes: ok
    - HSE: NBANDS/4: max number of NPAR

Post processing tips

- Any package that allows you to read in text files and plot 2D or 3D data, e.g., Gnuplot, Python, MATLAB.
- Output (repeated) in several files: OUTCAR, vasprun.xml, OSZICAR, EIGENVAL
- Several recent Python packages that parse VASP output files, and that can be used to setup and control the calculations

pymatgen

www.pymatgen.org

https://wiki.fysik.dtu.dk/ase/

Questions?