VASP: Accurate force calculations and VASP datasets

Georg KRESSE

Institut für Materialphysik and Center for Computational Materials Science

Universität Wien, Sensengasse 8, A-1090 Wien, Austria
Overview

- PAW foundations
  - simple introduction
    underlying basic ideas
  - relevance to VASP calculations
- How to control VASP precision
  - errors introduced by various approximations
  - flags to control them
- the PAW potentials distributed with VASP
exact potential (interstitial region)  pseudopotential

Al  effective Al atom  PAW Al atom
3p  2p  3p
3s  1s  3s

2p and 1s are nodeless !!!!

nodal structure is retained

2p and 1s are nodeless !!!!
PAW: basic idea

- **transformation:**
  \[
  |\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_{lm\epsilon} \text{spheres} (|\phi_{lm\epsilon}\rangle - |\tilde{\phi}_{lm\epsilon}\rangle) \langle \tilde{p}_{lm\epsilon} |\tilde{\Psi}_n\rangle
  \]

- the one-center expansion coefficients can be determined by multiplying the pseudo-wavefunction with the projector function at this site
  \[
  C_{lm\epsilon}^1 = \langle \tilde{p}_{lm\epsilon} |\tilde{\Psi}_n\rangle
  \]

- inside each sphere the wavefunctions can be recalculated by multiplication of these coefficients with the appropriate basis functions (partial waves)
  \[
  |\tilde{\Psi}_n\rangle^{\text{sphere}} = (\approx) \sum_{lm\epsilon} C_{lm\epsilon}^1 |\tilde{\phi}_{lm\epsilon}\rangle
  \]
  \[
  |\Psi_n\rangle^{\text{sphere}} = (\approx) \sum_{lm\epsilon} C_{lm\epsilon}^1 |\phi_{lm\epsilon}\rangle
  \]

- the pseudo wavefunction is expanded in a plane wave basis set
  \[
  \langle r |\tilde{\Psi}_n\rangle = \sum_G C_{n,G} e^{iGr}
  \]
Projector augmented wave method


- wave function (and energy) are decomposed into three terms:

\[ |\Psi_n\rangle = |\tilde{\Psi}_n\rangle - \sum_{\text{atoms}} |\tilde{\phi}_{lm\varepsilon}\rangle c_{lm\varepsilon} + \sum_{\text{atoms}} |\phi_{lm\varepsilon}\rangle c_{lm\varepsilon} \]

no mixed terms between different spheres and plane waves ⇒ efficient

- pseudo wavefunction expanded in plane waves:

\[ \langle r | \tilde{\Psi} \rangle = \sum_G C_G e^{iGr} \]

- one-center expansion coefficients:

\[ C_{lm\varepsilon} = \langle \tilde{p}_{lm\varepsilon} | \tilde{\Psi} \rangle \]
• the pseudo-wavefunctions do not have the same norm as the AE wavefunctions inside the spheres

• to deal with long range electrostatic interactions between spheres a soft compensation charge $\hat{n}$ is introd. (similar to FLAPW)

$\text{Hartree energy becomes: } E_H = \tilde{E} - \tilde{E}^1 + E^1$

$E_H[\tilde{n} + \hat{n}] - \sum_{\text{sites}} E_H[\tilde{n}^1 + \hat{n}^1] + \sum_{\text{sites}} E_H[n^1 + \hat{n}^1]$

$\hat{n}^1$ pseudo-charge at one site $\hat{n}^1$ compensation charge at site
How to control VASP calculations

**INCAR file**

- the plane wave energy cutoff
- technical issues (precision) of the calculations
- how to determine ground state and to which accuracy
- how to relax and required precision

**example file:**

```plaintext
ENCUT = 200  required energy cutoff
PREC = Accurate controls FFT grid
LREAL = .FALSE. real space projection technique
EDIFF = 1E-6 required precision in eV
ALGO = Fast how to get to the groundstate
IBRION = 5 dynamic properties from finite differences
```
Energy cutoff

- controls the completeness of the basis set
  at each k-point only the plane waves that fulfill
  \[ \frac{\hbar^2}{2m_e} |\mathbf{G} + \mathbf{k}|^2 < E_{\text{cutoff}} \]
  are included, where \( \mathbf{G} \) is a reciprocal lattice vector (waves commensurate with cell)
  different number of plane waves at each k-point

- \( E_{\text{cutoff}} \) 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 wavefunctions in the atomic limit.
  energy of atom 1 $E_{ATOM} = -1393.0707$
  kinetic energy error for atom = 0.0229

- It works well in the atomic limit, and for free electron metals.
  It corrects for 80% of the total error.

- For d-elements and bulk calculations, corrections are only partial.

- Due to the correction, the energy might increase when the cutoff is increased.
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

\[
\frac{\hbar^2}{2m_e} |G + k|^2 < E_{\text{cutoff}}
\]
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 varies 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 %)
Number of plane wave fixed instead of fixed cutoff

- 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
- The stress tensor is implicitly calculated 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)
Cell-shape relaxations: bottom line

- usually required for phonon calculations, and less “time-consuming” than manual search of the optimal cell-shape
- 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
- after cell shape relaxation
  - freeze the lattice parameters
  - and relax again using the usual smaller energy cutoff
    usually forces are small, but for phonon calculations practically zero forces are required
Technical errors and how to control them

- for phonons very accurate forces are required
- it’s good to know more about the internal of plane wave codes, than usually
- “internals”
  - FFT grids
  - double grid technique
  - fast evaluation of non local part of Hamiltonian
Technical errors related to the truncated FFT mesh

Real space

\[ x_1 = \frac{n_1}{N} \tau_1 \]

Reciprocal space

\[ g_1 = \frac{n_1}{N} \frac{2\pi}{\tau_1} \]

FFT
Technical errors related to the truncated FFT mesh

**Real Space**

- $\tau_1 = \frac{n_1}{N} \tau_1$

**FFT**

**Reciprocal Space**

- $g_1 = \frac{n_1 2\pi}{\tau_1}$

- $G_{\text{cut}}$
Technical errors related to the truncated FFT mesh

real space

FFT

reciprocal space

\[ x_1 = \frac{n_1}{N} \tau_1 \]

\[ g_1 = \frac{n_1 2\pi}{\tau_1} \]
Technical errors related to the truncated FFT mesh

\[ x_1 = \frac{n_1}{N} \tau_1 \]

\[ g_1 = \frac{n_1}{N} \frac{2\pi}{\tau_1} \]
Evaluation of the charge density, folding theorem

\[ G_{\text{cut}} \]

\[ \Psi_G \]

\[ 2G_{\text{cut}} \]

\[ \rho_G \]

\[ \Psi_r \]

\[ \times \]

\[ \rho_r \]

\[ \text{FFT} \]
Evaluation of the local part of the Hamiltonian $H\psi$

\[ H \psi = 2G_{\text{cut}} \]
\[ \frac{4\pi \varepsilon^2}{G^2} \]
\[ \Psi_G \]
\[ V_G \]
\[ V_r \]
\[ \psi_r \]
\[ \rho_G \]
\[ G_{\text{cut}} \]
\[ \text{add} \]
\[ \text{FFT} \]
\[ R_{\text{cut}} \]
\[ (\text{residual vector}) \]
The FFT grid

- the folding theorem implies that the charge density contains components up to $2 \times G_{\text{cut}}$ where
  \[ \frac{\hbar^2}{2m_e} |G_{\text{cut}}|^2 = E_{\text{cut}} \]

- the Hartree potential contains Fourier components up to $2 \times G_{\text{cut}}$ as well

- the residual vector $H\psi$ contains Fourier components up to $3 \times G_{\text{cut}}$

To avoid any errors, the Fourier grid must contain all wave-vectors up to $2 \times G_{\text{cut}}$

This is true for both, the evaluation of the charge-density and the residual vector

- if this is not the case, components in the charge density are wrapped around from the other side of the box: “wrap around errors”

The proper terminus technicus is aliasing errors

High frequency components are aliased to low frequency components (similar to AD converters, where you perform oversampling to avoid such errors)
What sort of errors does aliasing cause

- None in the forces, even translational symmetry is conserved
- The energies are slightly shifted by aliasing errors of the order of 1-2 meV/atom
- Aliasing errors are of course rather dependent on the cell/supercell, and they change when the supercell changes
- Supercells might not have exactly a multiple of the energy of a primitive cell

G. Kresse, VASP: Accurate force calculations and VASP datasets.
The catch: Exchange correlation energy

\[ \frac{4\pi e^2}{G^2} \]

\[ \rho_G \quad \text{FFT} \]

\[ V_G \]

\[ \rho_r \]

\[ V_{xc}(\rho_r) \]

\[ V_r \]

\[ 2G_{cut} \]

Hartree potential

Discretisation errors are introduced, destroying the translational symmetry.

Large error for GGA.
What sort of errors does this cause

- the translational invariance is destroyed

  if all atoms are shifted by an arbitrary vector $\vec{\tau}$ the energy should remain exactly identical
  LDA, and more so GGA, destroys the translational symmetry
  equivalently, the sum of all ionic forces should be zero

\[ \sum_{i=1}^{N_{\text{atoms}}} \vec{F}_i = 0 \]

offers a convenient way to check for such errors

- symmetry inequivalent atoms are no longer strictly symmetry equivalent

  VASP however symmetrizes the charge and the forces explicitly
  to quantify this sort of errors, you need to switch off symmetry (ISYM=0)

  0.001 eV/A per atom
The PAW compensation charge on regular grid

- the pseudo-wavefunctions do not have the same norm as the AE wavefunctions inside the spheres
- to deal with long range electrostatic interactions between spheres, a “soft” compensation charge $\hat{n}$ is introd. (similar to FLAPW)

![Diagram showing compensation charge](image)

- these localized compensation charges can be rather hard and are not well represented on the plane wave grid

$\Rightarrow$ dual grid technique
Representation of the compensation charge: Dual grid technique

data transfer occurs only in reciprocal space, grids are not necessarily “aligned”
evaluation of the potentials (XC) is also done on the fine grid, which often saves
you in GGA
### PREC, ENCUT and FFT grids

<table>
<thead>
<tr>
<th>PREC</th>
<th>ENCUT</th>
<th>NGX</th>
<th>NGxF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>( \text{max}(\text{ENMAX}) )</td>
<td>( \frac{3}{2} \ G_{\text{cut}} )</td>
<td>2 NGx</td>
</tr>
<tr>
<td>Accurate</td>
<td>( \text{max}(\text{ENMAX}) )</td>
<td>( 2 \ G_{\text{cut}} )</td>
<td>2 NGx</td>
</tr>
</tbody>
</table>

**Old**

| Low    | \( \text{max}(\text{ENMIN}) \) | \( \frac{3}{2} \ G_{\text{cut}} \) | \( 3 \ G_{\text{aug}} \) |
| Med    | \( \text{max}(\text{ENMAX}) \) | \( \frac{3}{2} \ G_{\text{cut}} \) | \( 4 \ G_{\text{aug}} \) |
| High   | \( \text{max}(\text{ENMAX}) \times 1.3 \) | \( 2 \ G_{\text{cut}} \) | \( \frac{16}{3} \ G_{\text{aug}} \) |

\[
\frac{\hbar^2}{2m_e} |G_{\text{cut}}|^2 = \text{ENCUT}
\]

\( \text{max}(\text{ENMAX}/\text{ENMIN}) \) corresponds to the maximum \( \text{ENMAX}/\text{ENMIN} \) found in POTCAR
PREC= Normal and Accurate

- for Accurate wrap around errors are avoided, whereas for Normal 3/4 of the required grid dimensions are used. Normal is an excellent compromise but not recommended for phonon calculations.

- the energy cutoff ENCUT should be set manually in any case. This makes the calculations more concise and better controlled. For stress calculations and cell shape deformations, one needs to increase ENCUT from the default value.

- the grids for the compensations charges have exactly twice the dimension than those of the coarser grids. (Hartree and XC potentials are also evaluated on those grids.)

PREC= Normal offers a very high accuracy at modest computational costs.
Non local part of the potentials

- in the PAW and PP methods, the following expressions occurs

\[
\sum_{lme,l'm'e'}^{\text{spheres}} \langle \tilde{p}_{lme} | D_{lme,l'm'e'} \langle \tilde{p}_{l'm'e'} | \Psi \rangle
\]

most time consuming part

- the expression can be evaluated in real space or reciprocal space

\[
C_{lme}^1 = \langle \tilde{p}_{lme} | \Psi \rangle = \\
\sum_{G} \tilde{p}_{lme}(k + G) C_{G + kn} = \sum_{r} \tilde{p}_{lme}(r) \Psi(r)
\]

- in reciprocal space \(N_{\text{planewaves}} \times N_{\text{spheres}} \times N_{lme}\) operations are required
  \(H|\Psi\rangle\) scales quadratically with the number of ions

- in real space \(N_{\text{points}} \times N_{\text{spheres}} \times N_{lme}\) operations are required, since \(\tilde{p}_{lme}(r)\) is localized around ions \(\Rightarrow H|\Psi\rangle\) scales linearly with the number of ions

G. Kresse, VASP: Accurate force calculations and VASP datasets.
LREAL flag

- **LREAL = .FALSE.** reciprocal space: slower but more accurate
  - strongly recommended for phonon calculations (if you can afford it)

- **LREAL = Auto** real space: much much faster, but less accurate
  - the absolute energies are also slightly modified, and hence calculations with and without real space evaluation should not be compared
  - real space evaluation causes some noise in the forces
  - \( \Rightarrow \) lower precision in particular for phonon calculations
**Summary**

**INCAR file for phonon calculations:**

- **ENCUT = XXX** required energy cutoff
- **PREC = Accurate** avoid wrap around errors
- **LREAL = .FALSE.** reciprocal space projection technique
- **EDIFF = 1E-6** high accuracy required
- **ALGO = Fast** fast determination of ground state
- **IBRION = 5** finite differences

- **for large systems LREAL = .FALSE.** can be exceedingly expensive and you might try **LREAL = Auto**
  
  but in this case you must perform careful tests

- **PREC = Accurate** is usually a good idea
in a large supercell a single atom is displaced, from forces \( \Rightarrow \) force constants

- Advantage: Simple
- Disadvantage:
  - Large supercells required
  - Exceedingly high precision on forces required:

\[
\Delta f = f_{\text{max}} \left( \sqrt{\left( \frac{f}{f_{\text{max}}} \right)^2 + e} - \frac{f}{f_{\text{max}}} \right)
\]

\( e \) ... fractional error in forces

attainable precision using VASP: \( e \approx 10^{-4} \)

\[
f/f_{\text{max}} \approx 1/10 \text{ and } e \approx 10^{-2}
\]

\( \Rightarrow \) errors in low frequency phonons of the order of 40%
Phonons are difficult, hence test, test, test ...

- Start with small supercell containing around 8-16 atoms

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>bcc</td>
<td>2x2x2 supercell with 2 atoms in each cubic cell</td>
</tr>
<tr>
<td>graphite</td>
<td>2x2 in basal plane, height 1</td>
</tr>
<tr>
<td>diamond</td>
<td>8 atom cubic cell</td>
</tr>
<tr>
<td>fcc</td>
<td>difficult, 4 atoms</td>
</tr>
</tbody>
</table>

- ENCUT = XXX  required energy cutoff
  PREC = Accurate  avoid wrap around errors
  LREAL = .FALSE.  reciprocal space projection technique
  EDIFF = 1E-6    high accuracy required
  ALGO = Fast     fast determination of ground state

- test with respect to k-points
  try to use k-point grids that are dividable by the number of desired replications
Large system

- replicate your system in each direction
- when the system is replicated in direction $x$, the k-point grid can be reduced in the corresponding direction by a factor $x$
- Otherwise leave the INCAR file unchanged, except for possibly switching on real space technique
  \[ \text{LREAL} = \text{Auto} \]
  \text{real space projection technique}

savings can be so substantial, you might not have another option

- compare phonon frequencies at high symmetry points $\Gamma$, (X, K) with previous calculations

  \text{perfect agreement MUST be obtained at these points}
Pitfall: k-point sampling problem

initial KPOINTS file for small cell
0  # automatic k-point determination
Monkhorst Pack grid
6 6 6
0 0 0

- even grid generation parameters do not include the Γ points (if Monkhorst is selected), whereas odd grids do
- when the cell is doubled in each direction, the value 6 must be reduced to 3, in order to get identical k-points
  but now the Γ point will be included by VASP!

Solution: proper KPOINTS file for large cell
0  # automatic k-point determination
Monkhorst Pack grid (or Gamma)
3 3 3
0.5 0.5 0.5  # manual shift by 1/2 1/2 1/2 away from Gamma
**Pitfall: smearing methods and tetrahedron method**

- avoid to use Blöchls tetrahedron method with quadratic corrections it is not variational in the occupancies, and therefore forces are not a derivative of energy (up to 10% errors for metals)

- Metals:
  
  ISMEAR = 1 ; SIGMA = 0.1

  or (default)

  ISMEAR = 2 ; SIGMA = 0.2

- insulators

  ISMEAR = 0 ; SIGMA = 0.05

  using ISMEAR = 2 ; SIGMA = 0.1 for insulators can cause unphysical occupancies larger than 1 (10 % errors in insulators)
three different flavors, one LDA (CA) and two GGA’s (PW91) and new PBE

- I recommend to use either the LDA or the PBE potentials
- all LDA potentials apply the exchange correlation form according to Ceperly and Alder as parameterized by Perdew and Zunger
- the PBE implementation conforms strictly to the PBE prescription,
- in VASP the PW91 implementation is sloppy
  for the LDA part, the parameterization of Perdew and Zunger is used, instead of Perdew’s Pade approximation
  “VASP bug”: different methods to interpolate between non spin polarized and fully spin polarized local density functionals exist
  for the PW91 functional the interpolations should be done according to Vosko Wilk and Nusair

  VOSKOWN = 1
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
...
  POMASS = 26.982; ZVAL = 3.000 mass and valenz
...
  ENMAX = 240.957; ENMIN = 180.718 eV
  ICORE = 2 local potential
  EAUG = 291.052
...
Description
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</table>
How good are the PAW potentials

- we performed systematic Gaussian and VASP calculations using quadruple-zeta and quintuple-zeta basis sets (Gaussian) and hard potentials (VASP)

- average difference between Gaussian and VASP is 0.5 kcal (20 meV) for the formation energy of molecules (w.r.t. isolated atoms)
  
  \[ n \text{X} + m \text{Y} \rightarrow \text{X}_n \text{Y}_m \]

  maximum difference is 2 kcal (80 meV) for CO\(_2\)

  the average DFT error is 8 kcal (much larger than the technical errors)

- using the standard potentials the precision of VASP is comparable to Gaussian calculations using double zeta+polarisation basis sets, but without any basis set superposition error problems
### Standard PAW potentials and Energy Cutoffs

<table>
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G. Kresse, VASP: Accurate force calculations and VASP datasets.
1st row pseudopotentials

<table>
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<td>F</td>
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<tr>
<td>F_s</td>
<td>250</td>
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</tbody>
</table>

- B–F are the standard PAW potentials
even dimers are described very reliably (CO, N₂, -..., 1% error)

- **hard potentials** 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 (Al₂O₃, VₓOᵧ, FeₓOᵧ, but not SiO₂)

  C_s is often sufficiently reliable for organic molecules, graphite and diamond, if some accuracy tradeoffs are allowed (good enough for single and double bonds)
## Standard PAW potentials and Energy Cutoffs

<table>
<thead>
<tr>
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<th>C</th>
<th>N</th>
<th>O</th>
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potentials with \texttt{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
  \textbf{please make tests} (it depends on how accurate results you need)

the hard potentials for \texttt{Al.h–Cl.h, Ga.h, Ge.h} can be used for added accuracy in oxides, when combined with the standard O potential

\textbf{BUT:} recently I found some peculiarities and problems with these potentials
\texttt{Al.h} still does not work, new \texttt{Si.h} is obviously reliable
### Standard PAW potentials for “simple” metals

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</table>
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 important, since in strongly ionic environments these elements loose all their “valence” electrons, and the semi-core states relax substantially
### Transition metal pseudopotentials

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G. Kresse, VASP: Accurate force calculations and VASP datasets.
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 localized (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.
Vibrational properties of carbon nanotubes

Very large $6 \times 6 \times 2$ supercell is required to obtain a reasonable dispersion for the acoustic modes


nanotubes are created by rolling up graphite

G. Kresse, VASP: ACCURATE FORCE CALCULATIONS AND VASP DATASETS.
Ab initio results for phonon modes in G-band

phonon frequencies of $(n,0)$ zigzag and $(n,n)$ armchair tubes and in the G-band calculated by ab initio density functional theory (symbols) and zone folding (lines, using force constants calculated by same density functional approach)

phonons are characterized by their symmetry and the direction of vibration $L$ (longitudinal) parallel to tube axis, $T$ (transferal) normal to tube axis

lower axis and upper axis show the diameter and the index for zigzag tubes $(n,0)$, respectively


Phonon softening by a Peierls like mechanism

- displacing the atoms in the nanotube according to the $A(L)$ mode opens a band gap in otherwise metallic tubes

First principles band structure in the vicinity of $k_F$ for the (12,0) zigzag nanotube in a) the equilibrium positions, b) for a distortion compatible with the $A(T)$ mode, and c) for a distortion compatible with an $A(L)$ mode below each band-structure diagram, the phase $\phi$ of the eigenstates $a_i$ (corresponding to the band with energy $\epsilon_i$) are shown for states in the vicinity of $k_F$. 

G. Kresse, VASP: Accurate force calculations and VASP datasets.
Low frequency modes

\[ \Delta f = f_{\text{max}} \left( \sqrt{\left( \frac{f}{f_{\text{max}}} \right)^2 + e} - \frac{f}{f_{\text{max}}} \right) \]

\[ e \approx 10^{-4}, \ f_{\text{max}} = 2000, \ f = 20, \ \Delta f = 10 \]
Conclusions and Outlook

- Phonon calculations require careful tests and very high accuracy. "Difficult" even using integrated packages. Understanding the underlying ab initio program is important.

Future: Linear response in VASP

- Second derivatives with respect to ions (alpha stage)
- Dielectric tensors (RPA and LDA) (alpha stage)
- Born effective charges (alpha stage)
- Optical properties by summation over states (RPA)
  - Frequency depended dielectric functions (beta stage)
- IR intensities (partially working)
- Raman intensities (planned)