VASP: Accurate force calculations and VASP datasets

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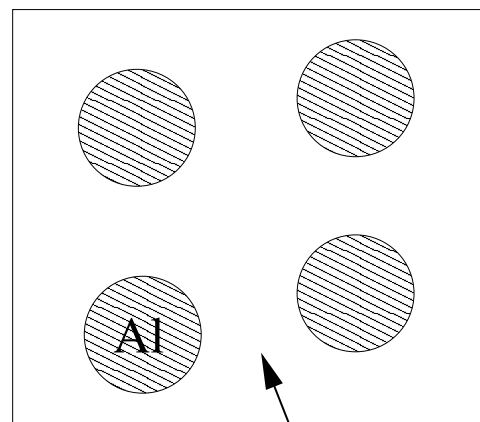
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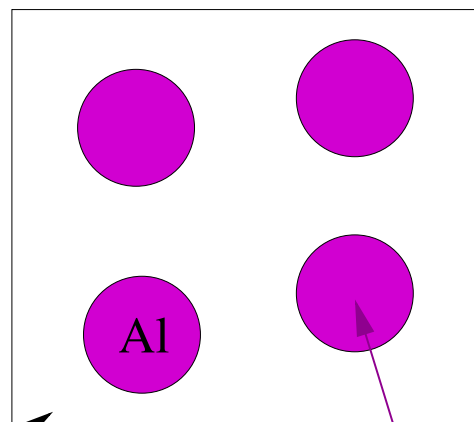
Overview

- **PAW foundations**

  - simple introduction
    underlying basic ideas

  - relevance to VASP calculations

- **How to control VASP precision**

  - errors introduced by various approximations

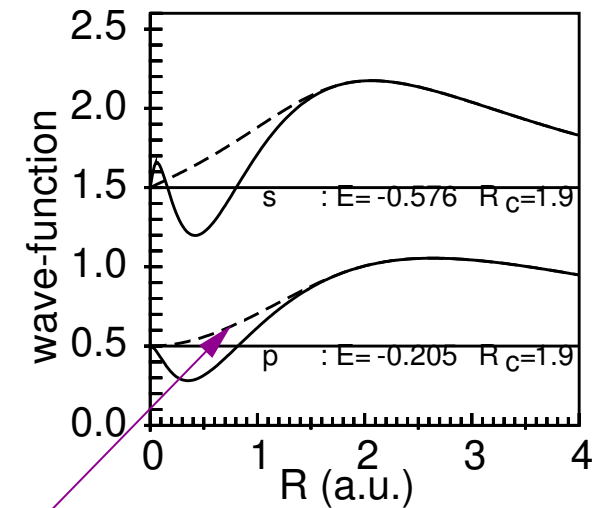 - flags to control them

- **the PAW potentials distributed with VASP**

Pseudopotentials

exact potential (interstitial region)   pseudopotential

Al		effectiv Al atom	PAW Al atom
3p		2p	3p
3s	→	1s	3s
~~2p~~			
~~2s~~		2p and 1s are	nodal structure
~~1s~~		nodeless !!!!	is retained

PAW: basic idea

- <u>transformation:</u> $$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_{lm\varepsilon}^{\text{spheres}}(|\phi_{lm\varepsilon}\rangle - |\tilde{\phi}_{lm\varepsilon}\rangle)\langle\tilde{p}_{lm\varepsilon}|\tilde{\Psi}_n\rangle$$

- the one-center expansion coefficients can be determined by multiplying the pseudo-wavefunction with the projector function at this site

$$C^1_{lm\varepsilon} = \langle\tilde{p}_{lm\varepsilon}|\tilde{\Psi}_n\rangle$$

- inside each sphere the wavefunctions can be recalculated by multiplication of these coefficients with the appropriate basis functions (partial waves)

$$|\tilde{\Psi}_n\rangle^{\text{sphere}} = (\approx) \sum_{lm\varepsilon} C^1_{lm\varepsilon}|\tilde{\phi}_{lm\varepsilon}\rangle$$

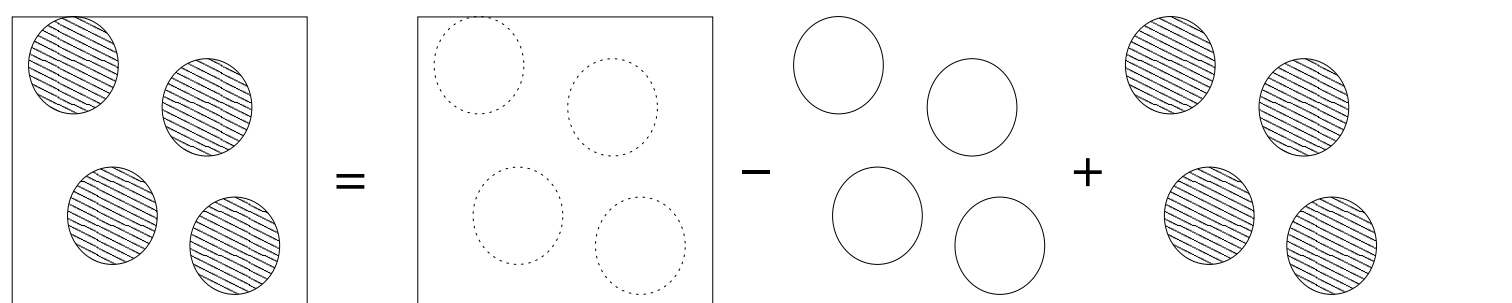$$|\Psi_n\rangle^{\text{sphere}} = (\approx) \sum_{lm\varepsilon} C^1_{lm\varepsilon}|\phi_{lm\varepsilon}\rangle$$

- the pseudo wavefunction is expanded in a plane wave basis set

$$\langle\mathbf{r}|\tilde{\Psi}_n\rangle = \sum_{\mathbf{G}} C_{n,\mathbf{G}}e^{i\mathbf{G}\mathbf{r}}$$

Projector augmented wave method

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

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

|			
exact	pseudo (node less) plane waves	pseudo−onsite radial grids	exact onsite radial grids

no mixed terms between different spheres and plane waves $\Rightarrow$ efficient

- pseudo wavefunction expanded in plane waves: $\langle \mathbf{r}|\tilde{\Psi}\rangle = \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}$

- one-center expansion coefficients: $C^1_{lm\varepsilon} = \langle \tilde{p}_{lm\varepsilon}|\tilde{\Psi}\rangle$

Hartree energy

- 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)

AE = pseudo + compens. - pseudo+comp. onsite + AE-onsite
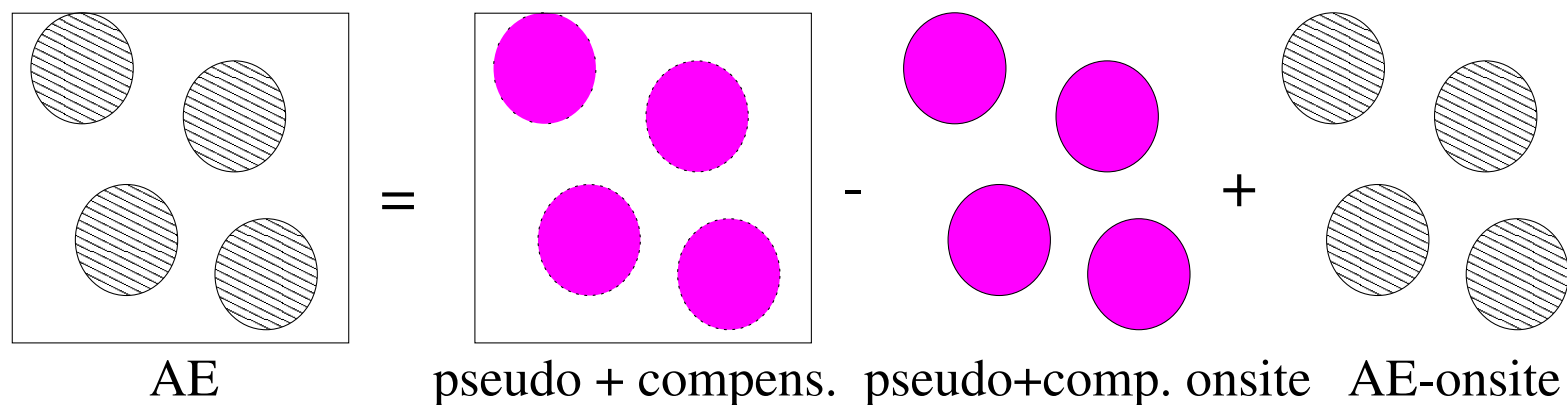
- Hartree energy becomes: $E_H = \tilde{E} - \tilde{E}^1 + E^1$

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

$\tilde{n}^1$ 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:

  `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_{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      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 the correction, the energy might inc
  when the cutoff is increased
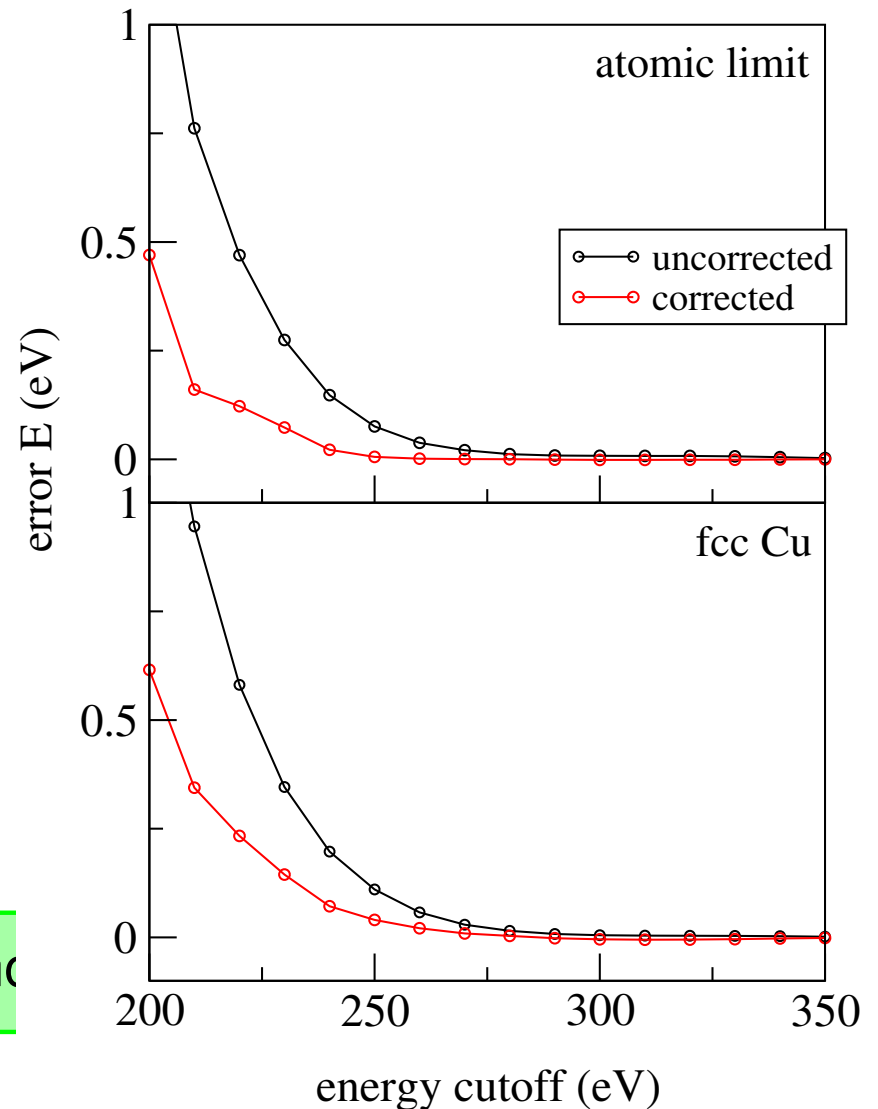
Can you rely on the default cutoff ?

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 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 %)
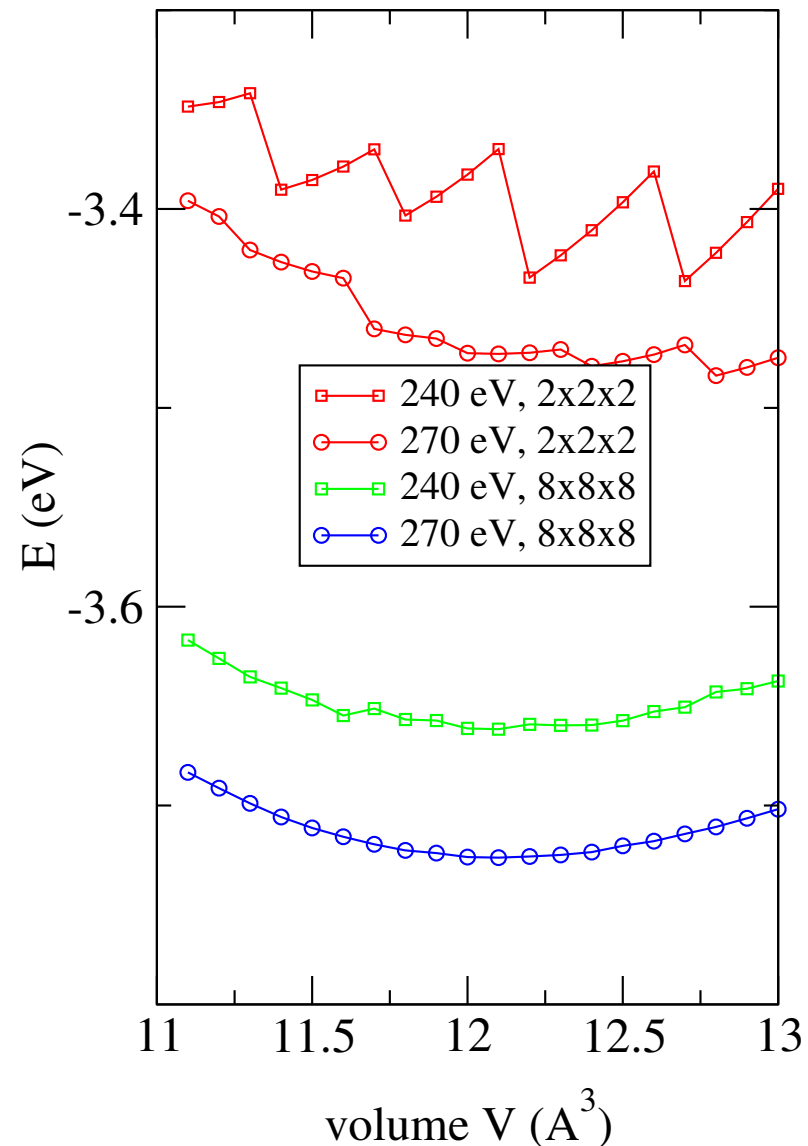
Number of plane wave fixed instead of fixed cutoff

- 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**
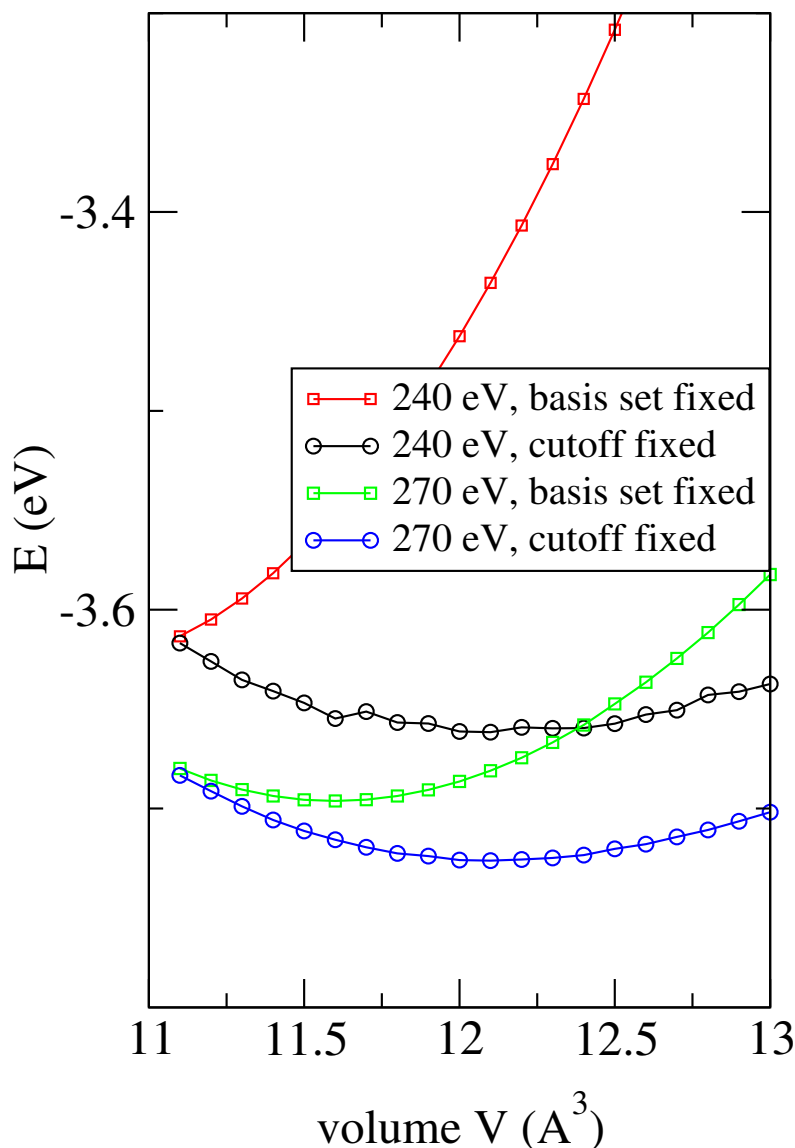
Stress tensor and cell-shape relaxation

- 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)
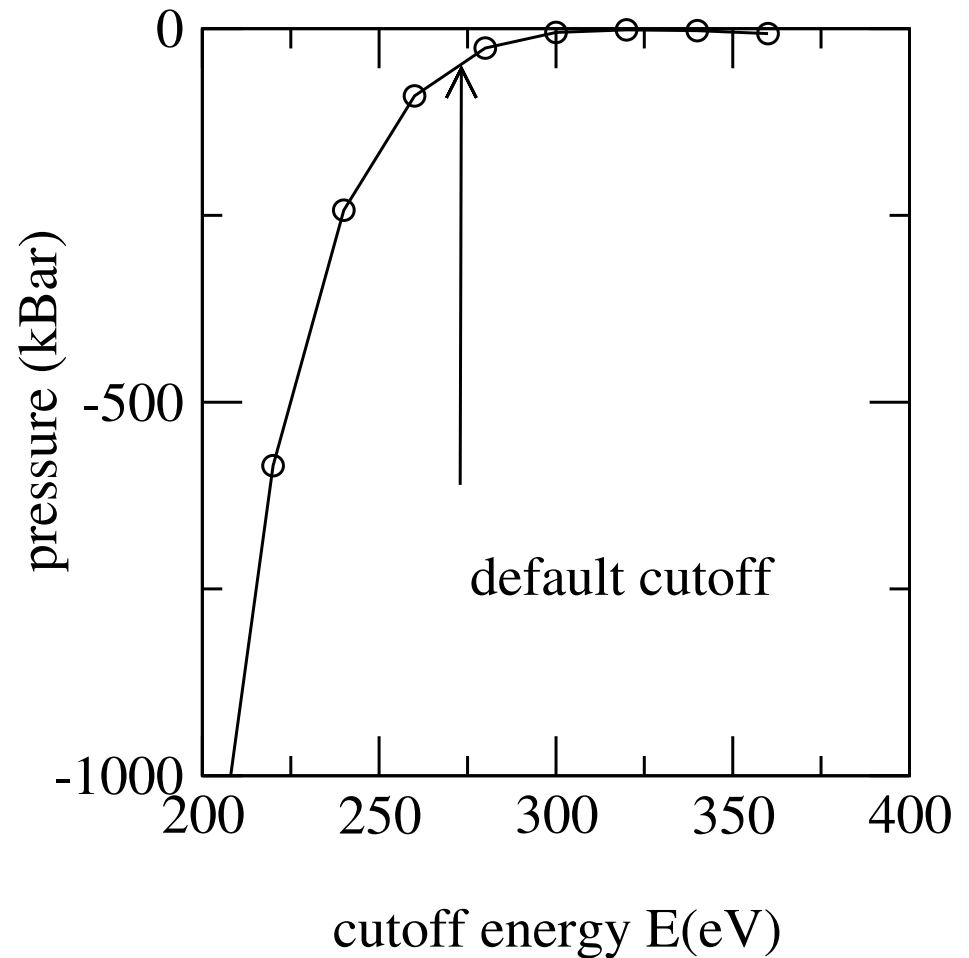
Cell-shape relaxations: bottom line

- 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
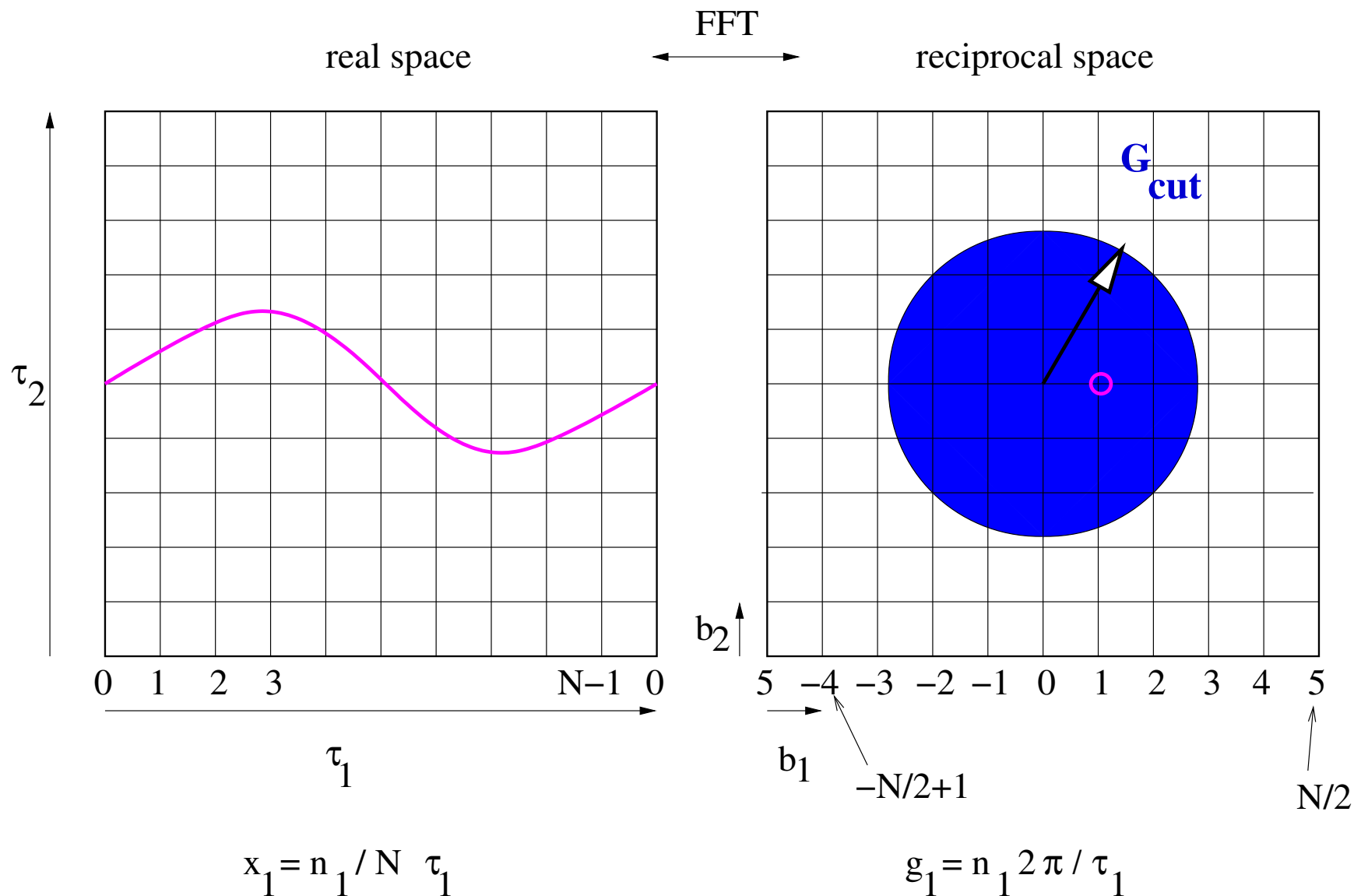
Technical errors related to the truncated FFT mesh

Technical errors related to the truncated FFT mesh

FFT

real space   reciprocal space

G_{cut}

τ_2

b_2

0 1 2 3   N−1 0   5 −4 −3 −2 −1 0 1 2 3 4 5

b_1

−N/2+1   N/2

τ_1

$$x_1 = n_1 / N \; \tau_1$$

$$g_1 = n_1 \, 2\pi / \tau_1$$

Technical errors related to the truncated FFT mesh

FFT

real space · reciprocal space

$x_1 = n_1 / N \; \tau_1$

$g_1 = n_1 \, 2\pi / \tau_1$

G_{cut}

τ_2

τ_1

b_2

b_1

$-N/2+1$

$N/2$

0 1 2 3 N−1 0

5 −4 −3 −2 −1 0 1 2 3 4 5
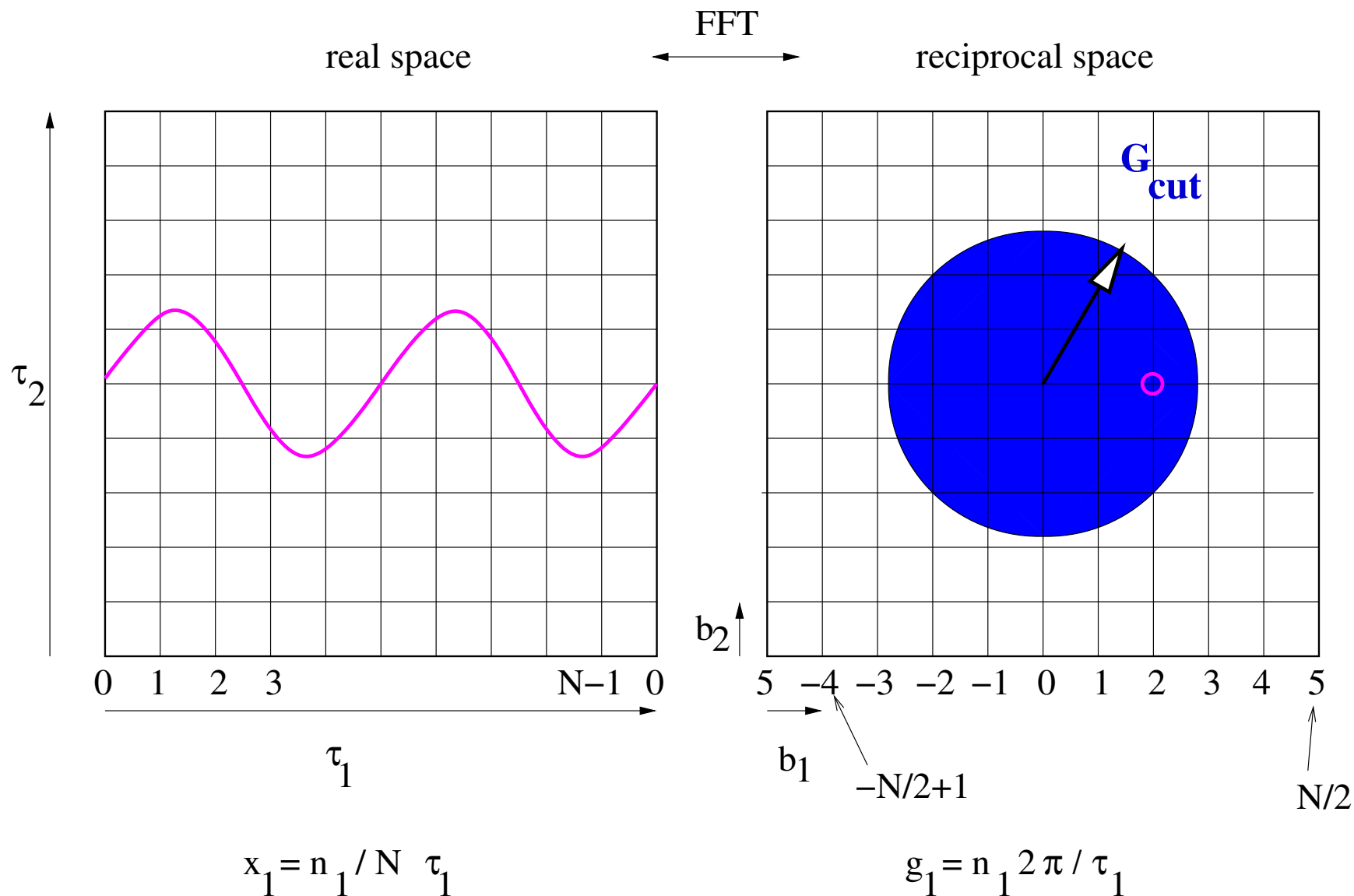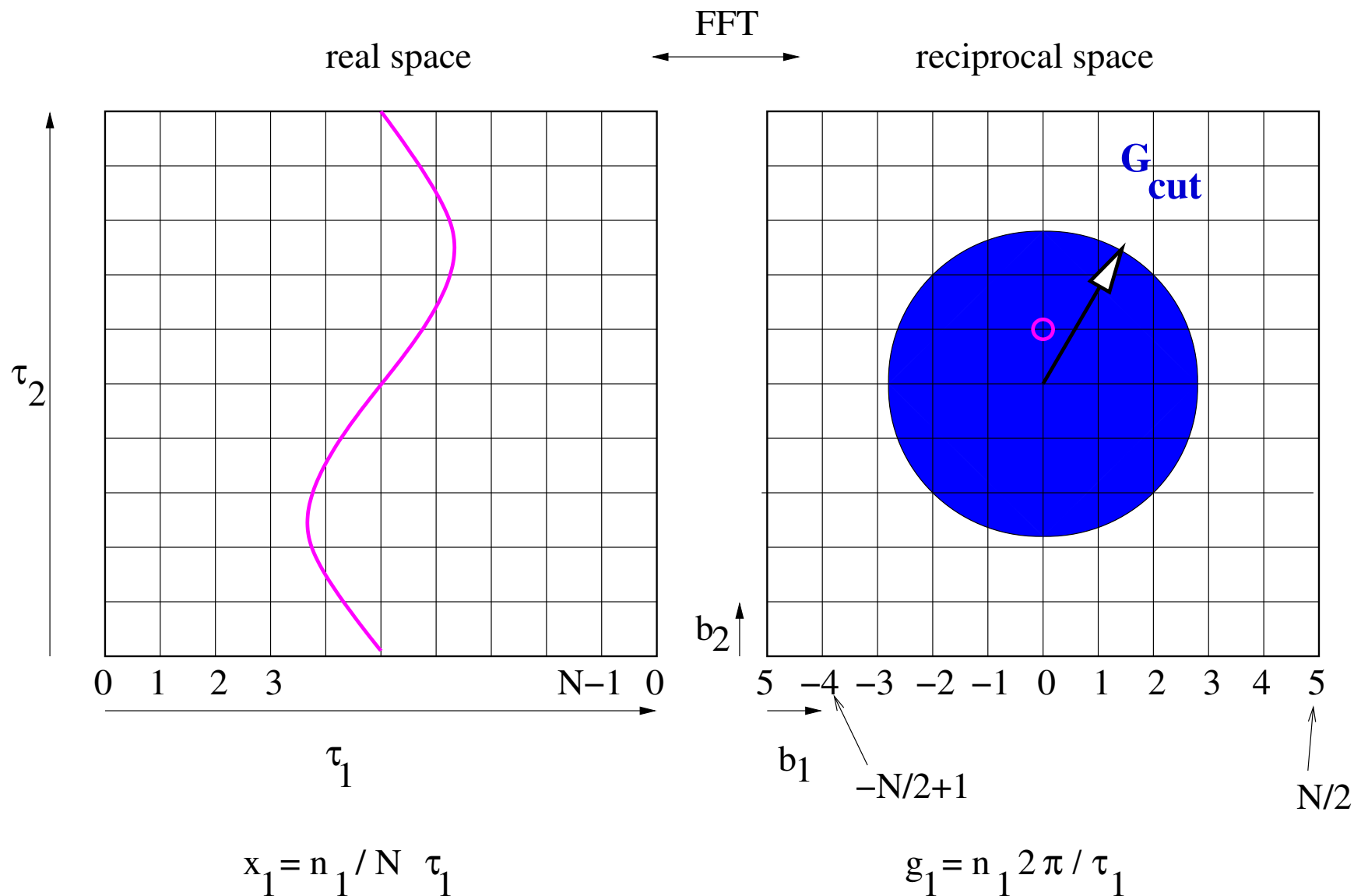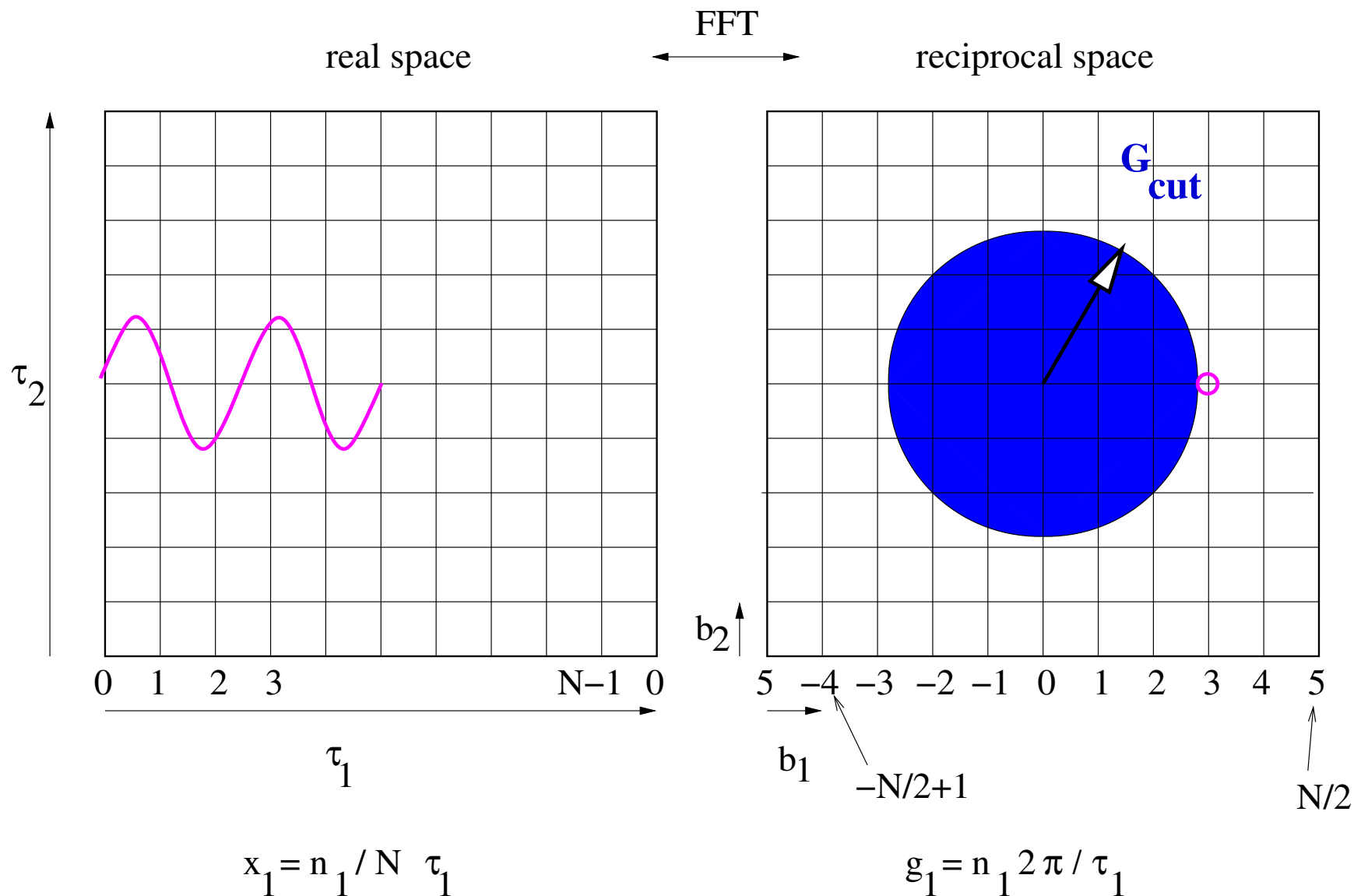
Evaluation of the charge density, folding theorem
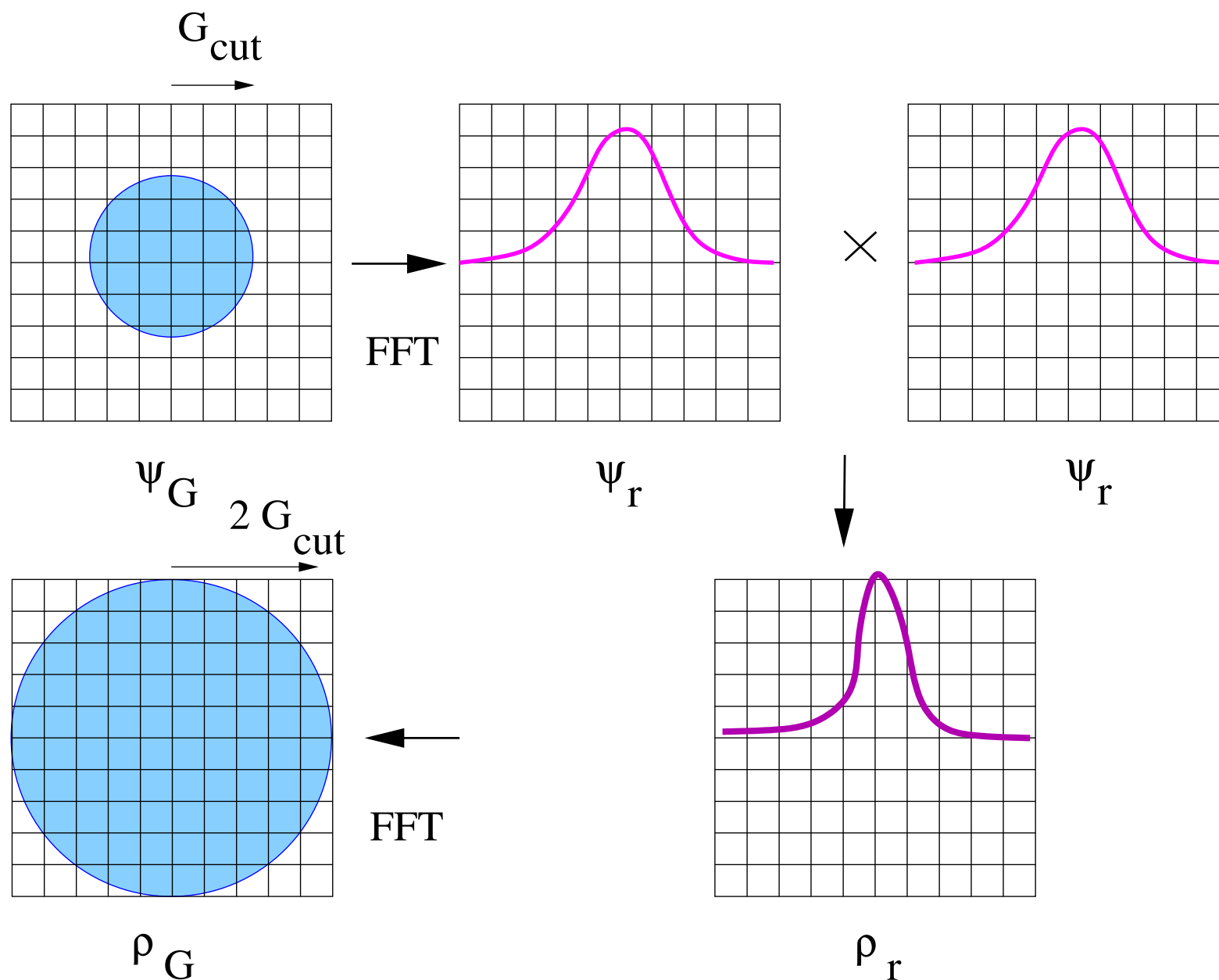
Evaluation of the local part of the Hamiltonian $\mathbf{H}\psi$

$2G_{cut}$

ρ_G

$\frac{4\pi e^2}{G^2}$

V_G

FFT

V_r

$\times$

ψ_r

G_{cut}

ψ_G

add

R_G

$3G_{cut}$

FFT
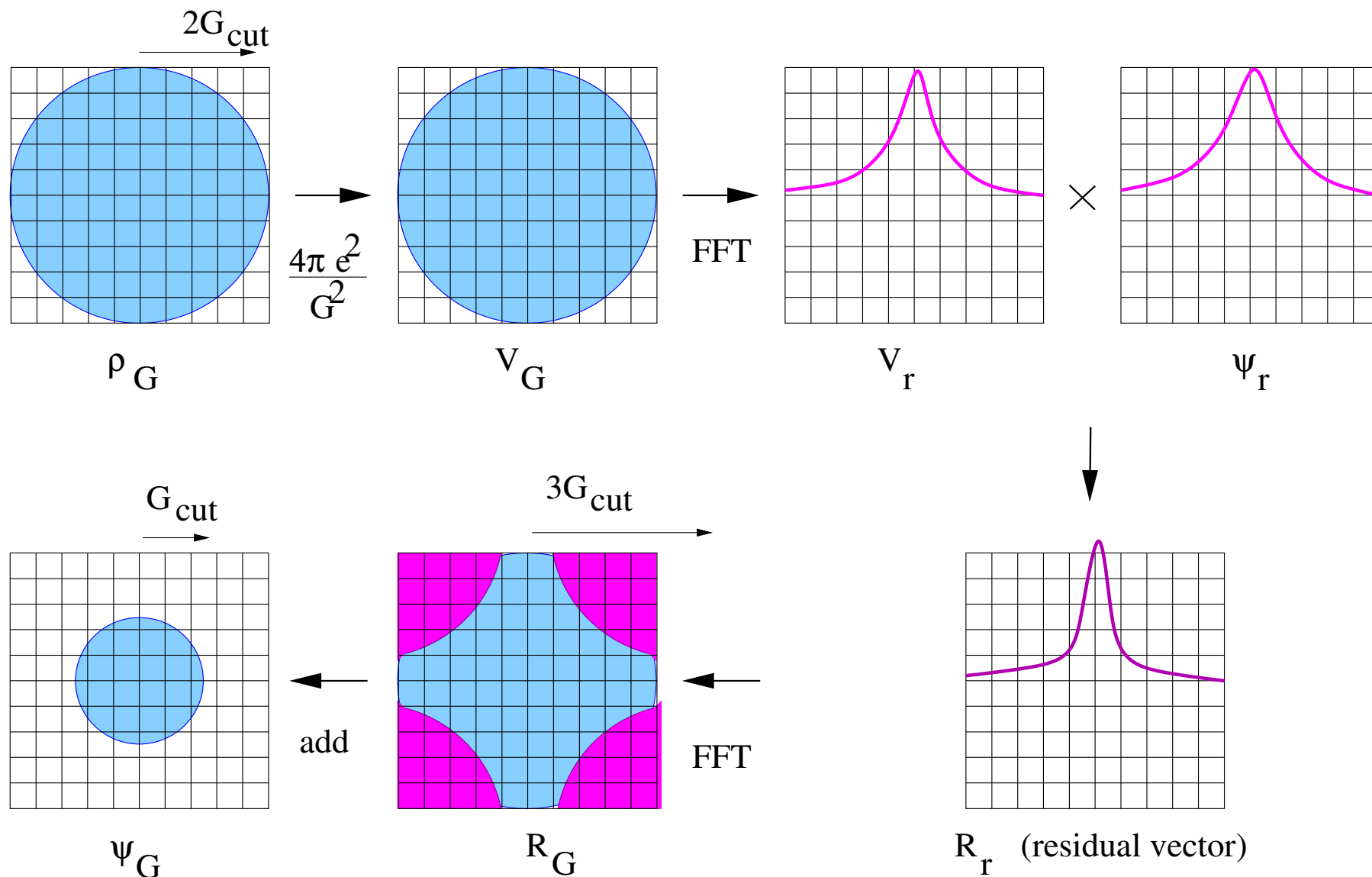
R_r (residual vector)

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 $\mathbf{H}\psi$ 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

The catch: Exchange correlation energy

$2G_{cut}$

ρ_G

Hartree potential

V_G

$\dfrac{4\pi e^2}{G^2}$

FFT

V_r

FFT

ρ_r

xc potential

$V_{xc}(\rho_r)$

discretisation errors
are introduced, distroying
the translational symmetry

large error for GGA
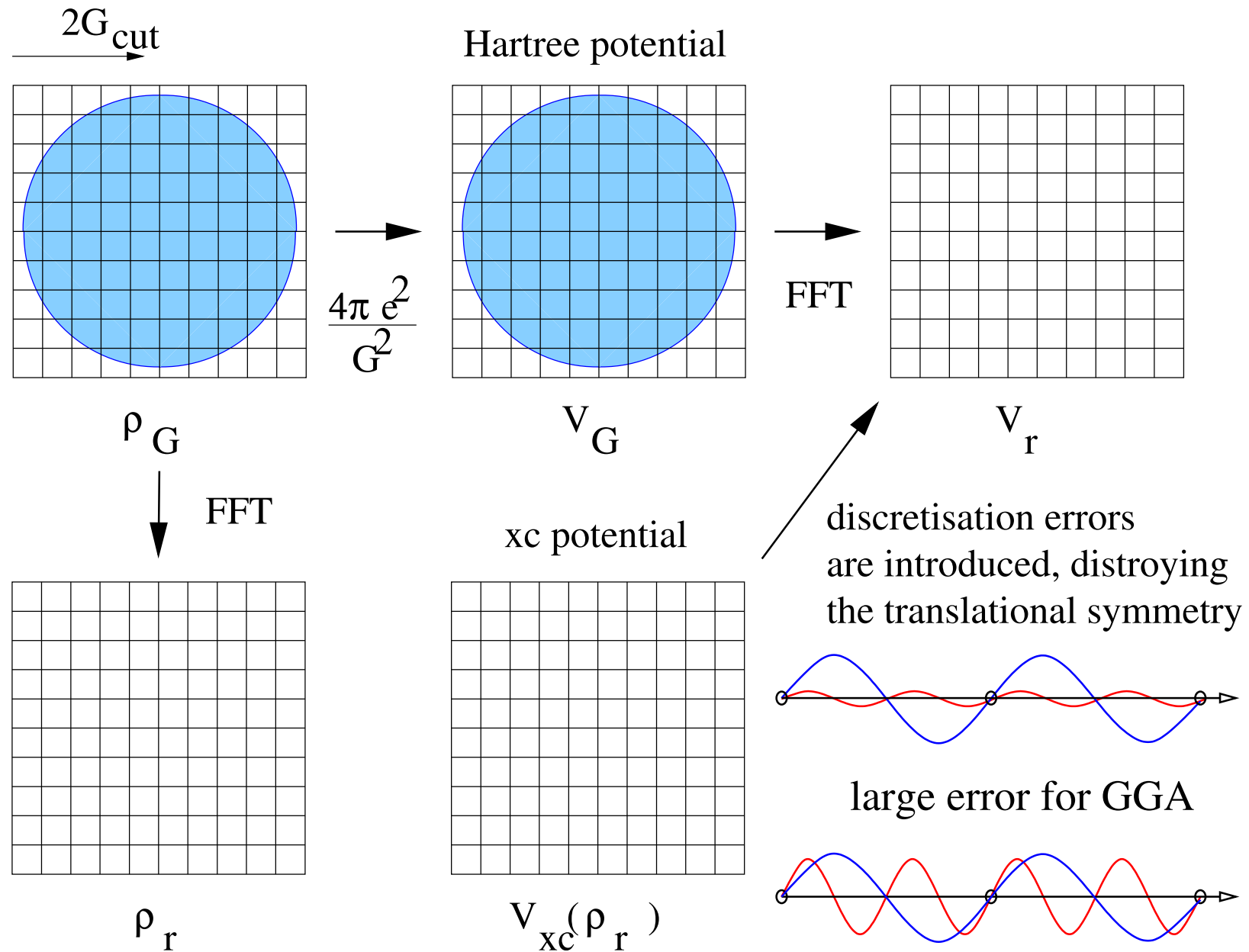
What sort of errors does this cause

- **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)

AE | pseudo + compens. pseudo+comp. onsite AE-onsite
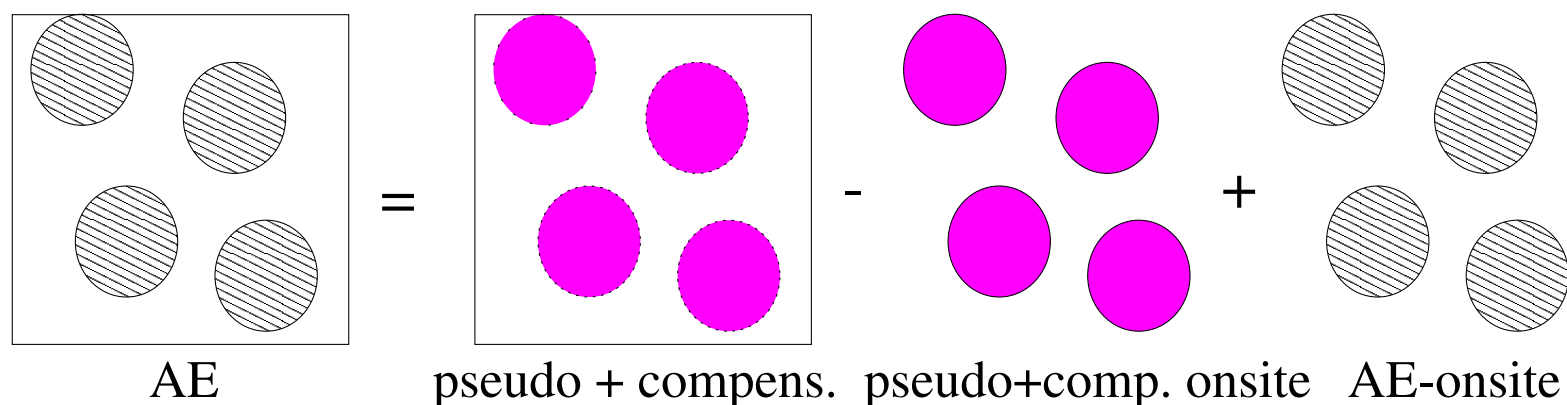
- these localized compensation charges can be rather hard and are not well represented on the plane wave grid

$\Rightarrow$ dual grid technique

Representation of the compensation charge: Dual grid technique

real space

FFT

reciprocal space

τ_2

τ_1

0 1 2 3   N−1 0

b_2

b_1

coarse grid points
low energy
cutoff

additional fine
grid points

high energy
cutoff
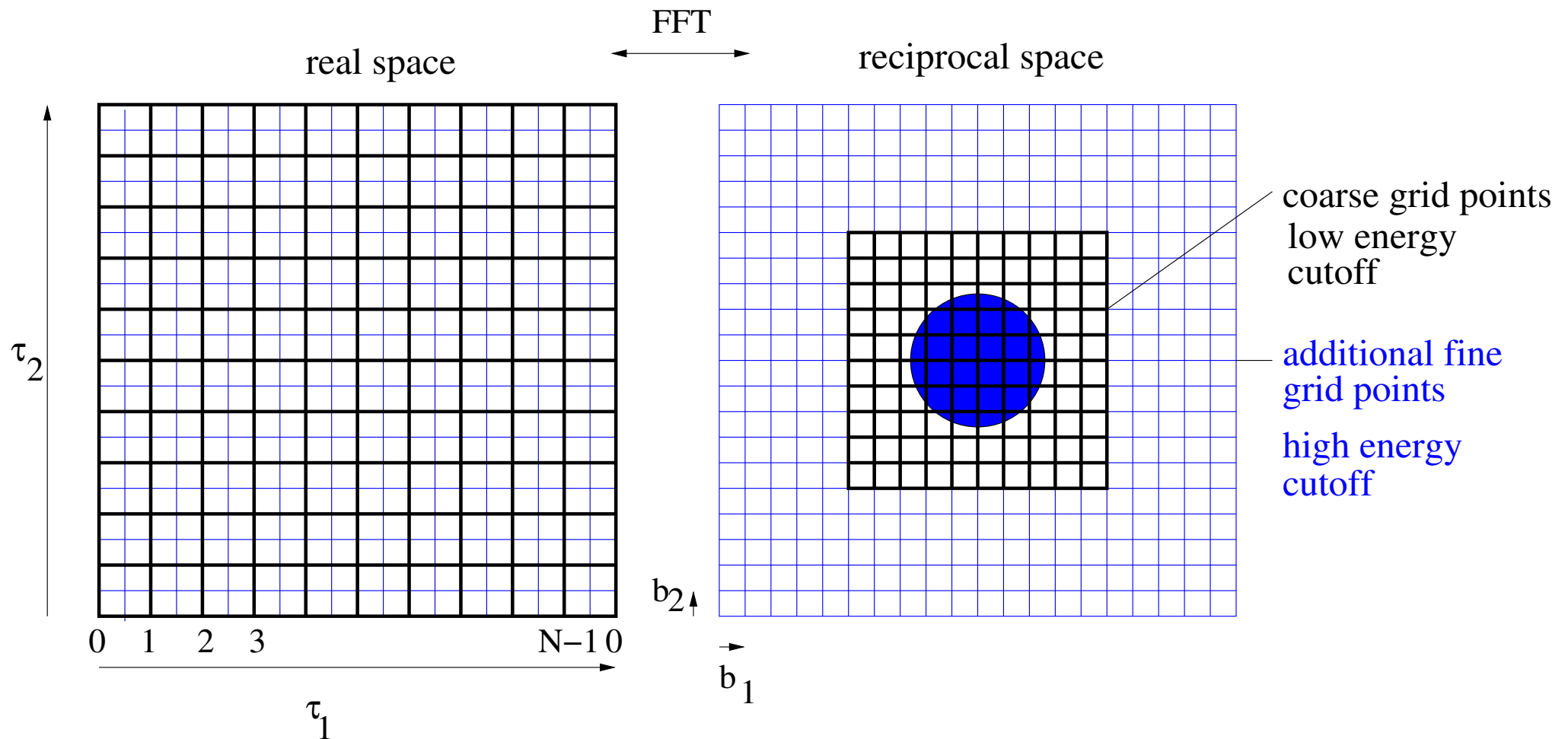
data transfer occurs only in reciprocal space, grids are not necessarily "aligned"
evaluation of the potentials (XC) is also done on the fine grid, which often saves
you in GGA

PREC, ENCUT *and FFT grids*

PREC	ENCUT	NGX	NGXF
Normal	max(ENMAX)	$3/2\ G_{\text{cut}}$	2 NGX
Accurate	max(ENMAX)	$2\ G_{\text{cut}}$	2 NGX
old			
Low	max(ENMIN)	$3/2\ G_{\text{cut}}$	$3\ G_{\text{aug}}$
Med	max(ENMAX)	$3/2\ G_{\text{cut}}$	$4\ G_{\text{aug}}$
High	max(ENMAX)*1.3	$2\ G_{\text{cut}}$	$16/3\ G_{\text{aug}}$

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

max(ENMAX/ENMIN) corresponds to the maximum ENMAX/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

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

$$\sum_{lm\varepsilon,l'm'\varepsilon'}^{\text{spheres}} |\tilde{p}_{lm\varepsilon}\rangle D_{lm\varepsilon,l'm'\varepsilon'} \langle \tilde{p}_{l'm'\varepsilon'}|\Psi\rangle$$

most time consuming part

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

$$C^1_{lm\varepsilon} = \langle \tilde{p}_{lm\varepsilon}|\Psi\rangle =$$

$$\sum_{\mathbf{G}} \tilde{p}_{lm\varepsilon}(\mathbf{k}+\mathbf{G}) C_{\mathbf{G}+\mathbf{k}n} = \sum_{\mathbf{r}} \tilde{p}_{lm\varepsilon}(\mathbf{r}) \Psi(\mathbf{r})$$

10 p
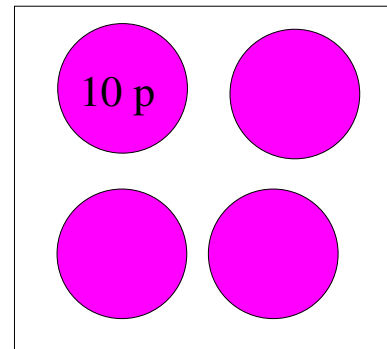
- in reciprocal space $N_{\text{planewaves}} \times N_{\text{spheres}} \times N_{\text{lm}\varepsilon}$ operations are required
  $\mathbf{H}|\Psi\rangle$ scales quadratically with the number of ions

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

Reciprocal / Real space

`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

Phonons from finite differences

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:

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

e ... fractional error in forces
attainable precision using VASP: $e \approx 10^{-4}$

$f/f_{max} \approx 1/10$ and $e \approx 10^{-2}$

$\Rightarrow$ errors in low frequency phonons of the order of 40%
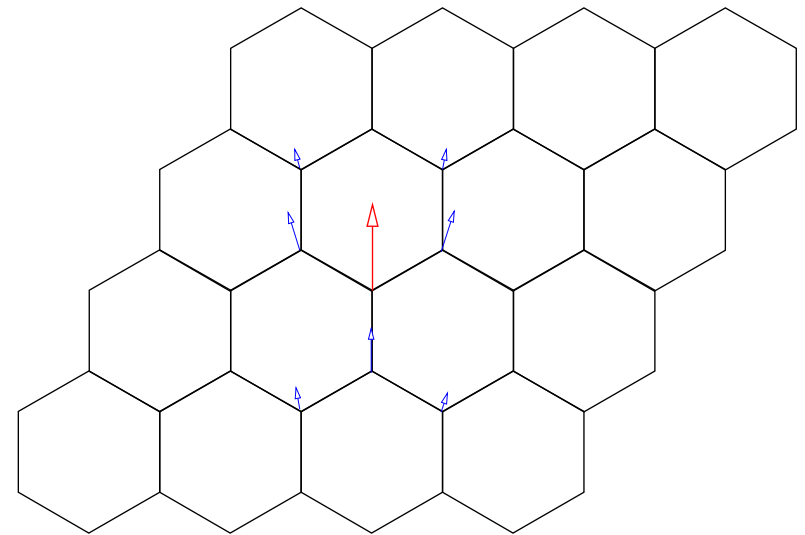
> *Phonons are difficult, hence test, test, test ...*

- **Start with small supercell containing around 8-16 atoms**

bcc	2x2x2 supercell with 2 atoms in each cubic cell
graphite	2x2 in basal plane, height 1
diamond	8 atom cubic cell
fcc	difficult, 4 atoms

- `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

  `LREAL = Auto`   real space projection technique

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

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

  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)

The PAW potentials

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 Perdews 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
```

```
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
```

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 X + m Y $\Rightarrow$ X$_n$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

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				

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)

- 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 (Al_2O_3, V_xO_y, Fe_xO_y, but not SiO_2)

  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

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				

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 can be used for added accuracy in oxides, when combined with the standard O potential

  BUT: recently I found some pecularities and problems with these potentials

  Al_h still does not work, new Si_h is obviously reliable

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 important, since in strongly ionic environments these elements loose all their "valence" electrons, and the semi-core states relax substantially

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 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
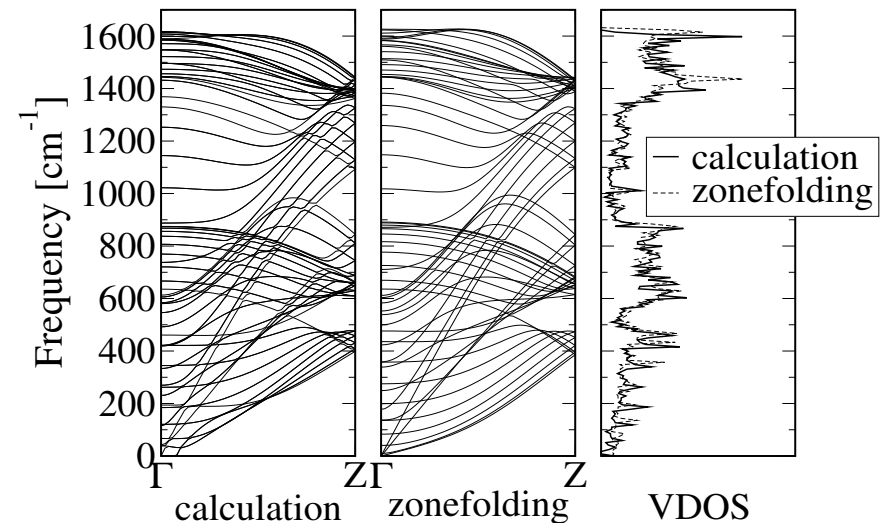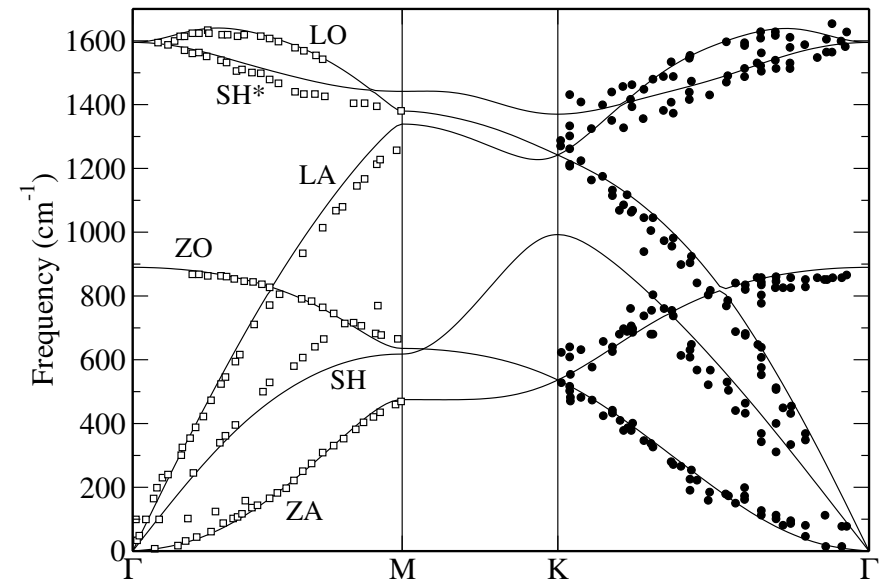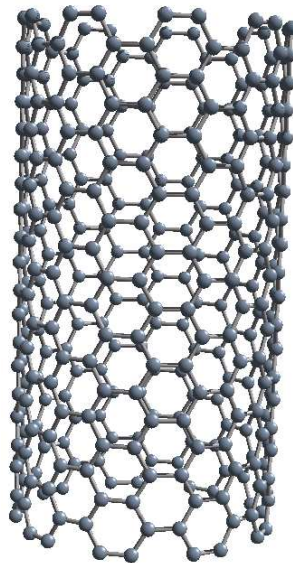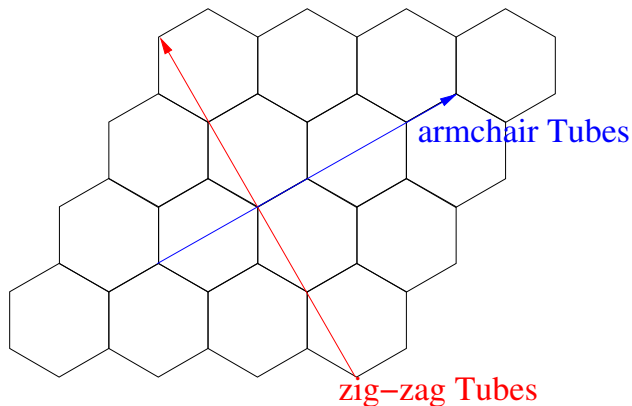
Vibrational properties of carbon nanotubes

Very large $6 \times 6 \times 2$ supercell is required to obtain a reasonable dispersion for the acoustic modes
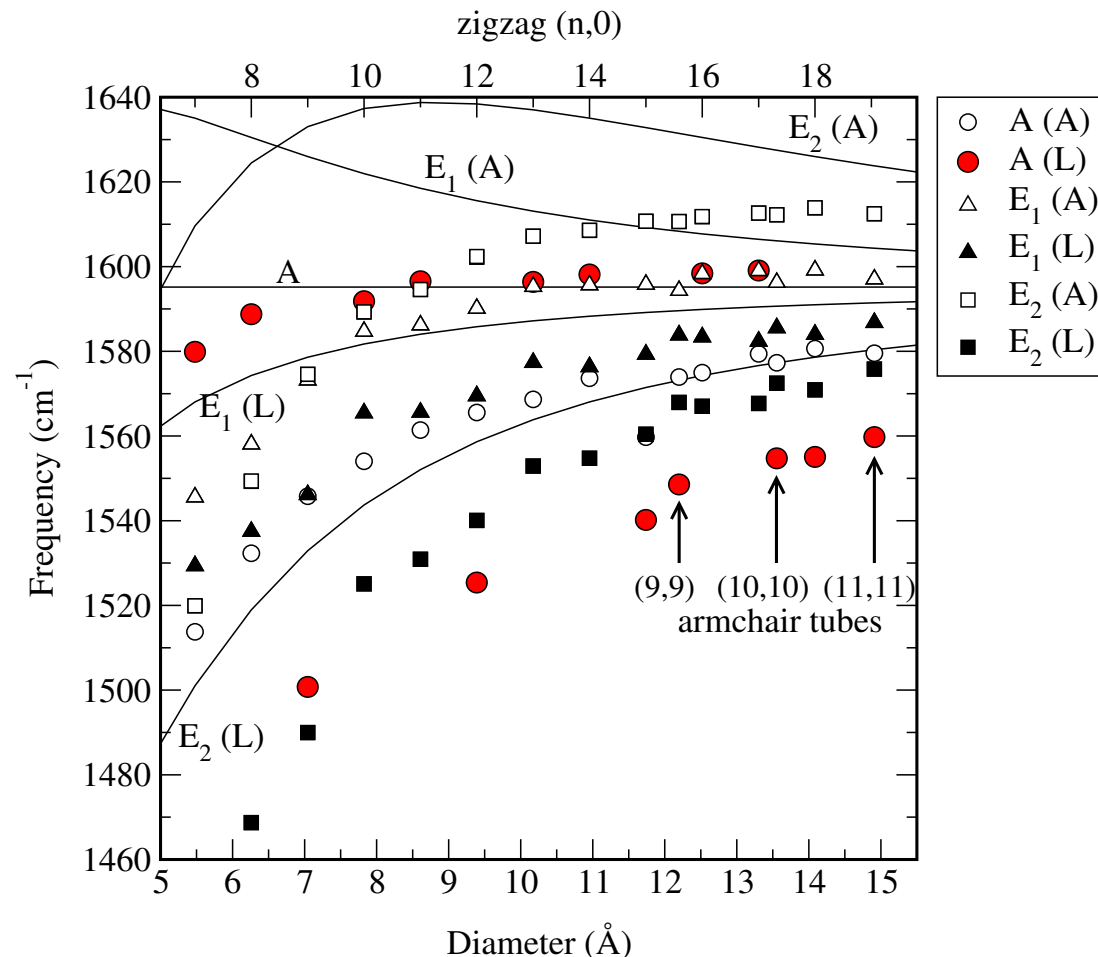
G. Kresse, J. Furthmüller, and J. Hafner, Europhys. Lett. **32**, 729 (1995).

O. Dubay and G. Kresse, Phys. Rev. B **67**, 035401-1-13 (2003).

nanotubes are created by rolling up graphite

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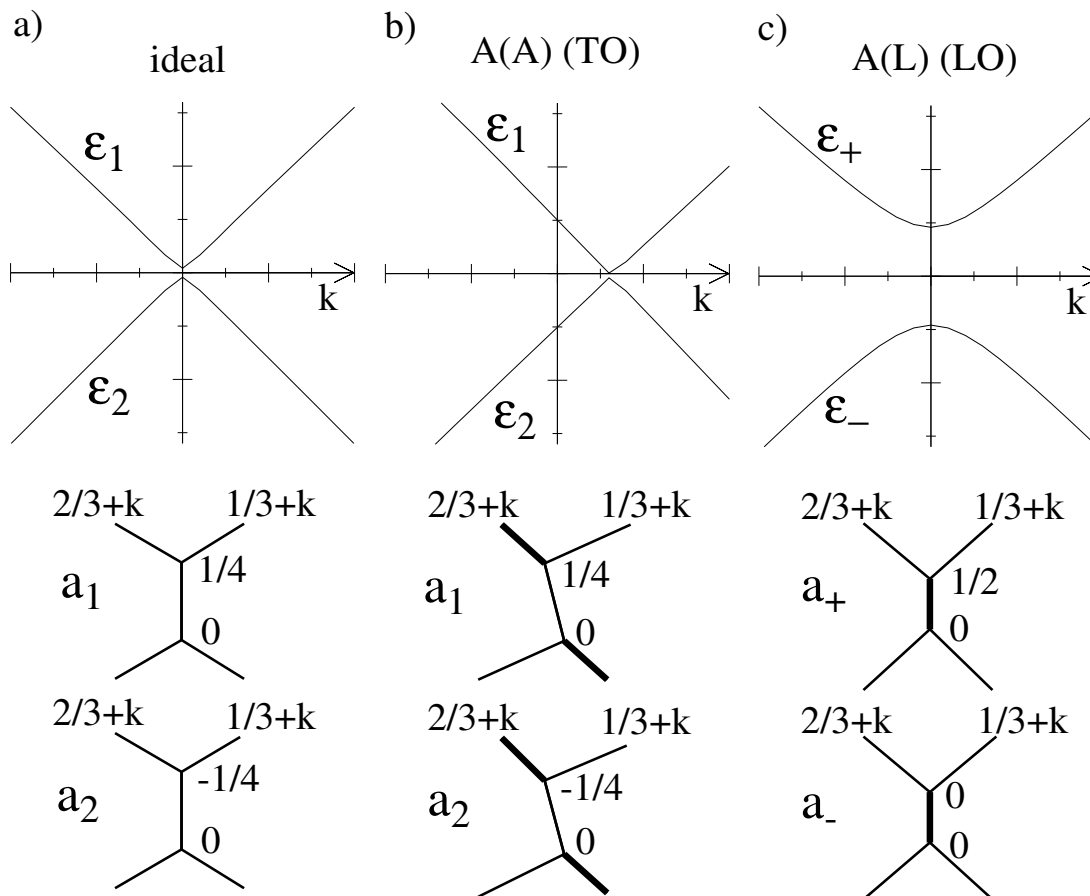
lower axis and upper axis show the diameter and the index for zigzag tubes $(n,0)$, respectively

O. Dubay, G. Kresse, and H. Kuzmany, Phys. Rev. Lett. **88**, 235506 (2002).
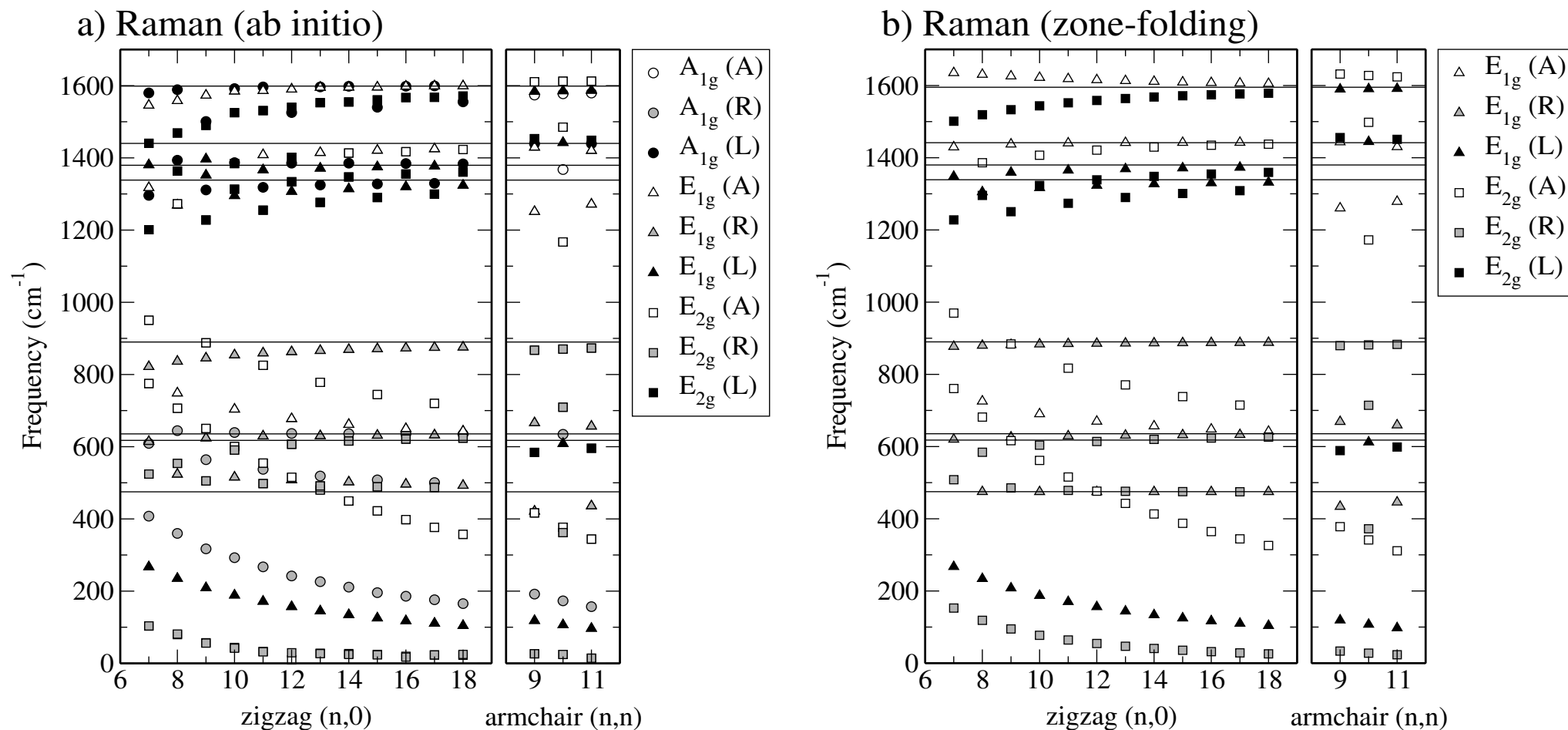
O. Dubay and G. Kresse, Phys. Rev. B **67**, 035401-1-13 (2003).

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

a) ideal

b) A(A) (TO)

c) A(L) (LO)

ε_1 ε_2

ε_1 ε_2

ε_+ ε_-

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 ϕ of the eigenstates a_i (corresponding to the band with energy ε_i) are shown for states in the vicinity of k_F

Low frequency modes

a) Raman (ab initio)

b) Raman (zone-folding)

$$\Delta f = f_{\text{max}} \left(\sqrt{\left(\frac{f}{f_{\text{max}}} \right)^2 + e} - \frac{f}{f_{\text{max}}} \right), \quad e \approx 10^{-4}, \ f_{\text{max}} = 2000, \ f = 20, \ \Delta f = 10$$

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)