CENTER FOR
MOLECULAR MODELING

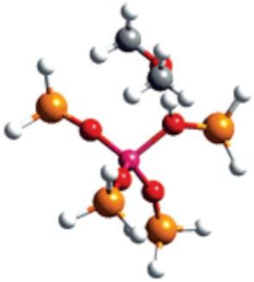
CMM Computer Tutorials

Dr. Kurt Lejaeghere

A quick introduction to VASP

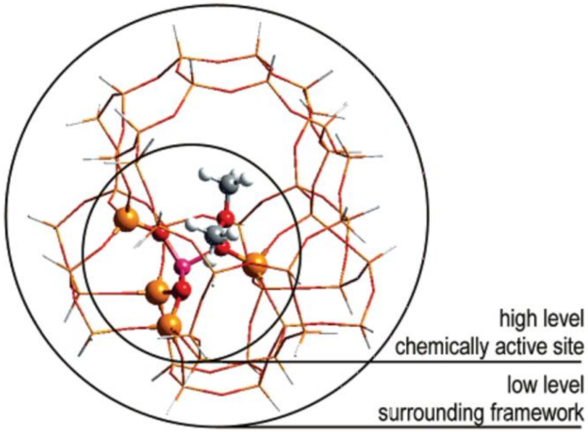
clusters vs periodic models: taking into account topology

small cluster



older publications: neglect of topology

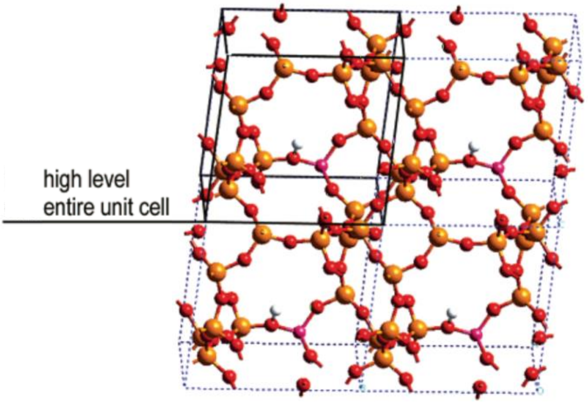
extended cluster



limited account of structure + fix outer hydrogens

computationally attractive

periodic model



porous structure fully taken into account

computationally expensive

D. Lesthaeghe et al., Ind. Eng. Chem. Res. **46**, 8832 (2007)

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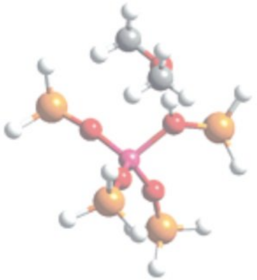

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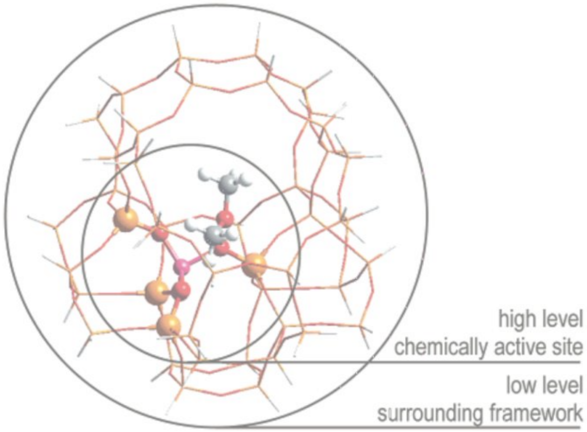

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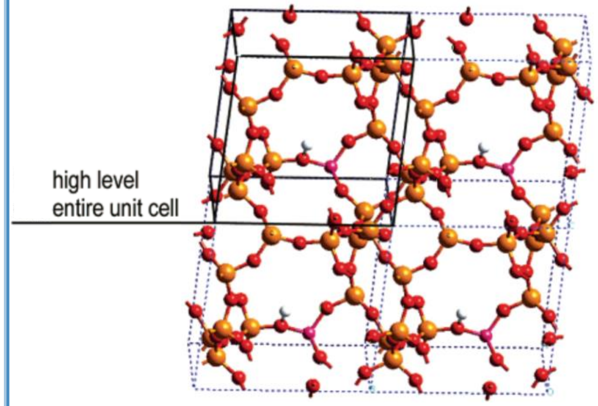

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CONTENT OVERVIEW

- crystallography
- plane wave basis sets
  - basis sets: general idea
  - working in reciprocal space
- the projected-augmented wave method
- using the VASP software

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CRYSTALLOGRAPHY

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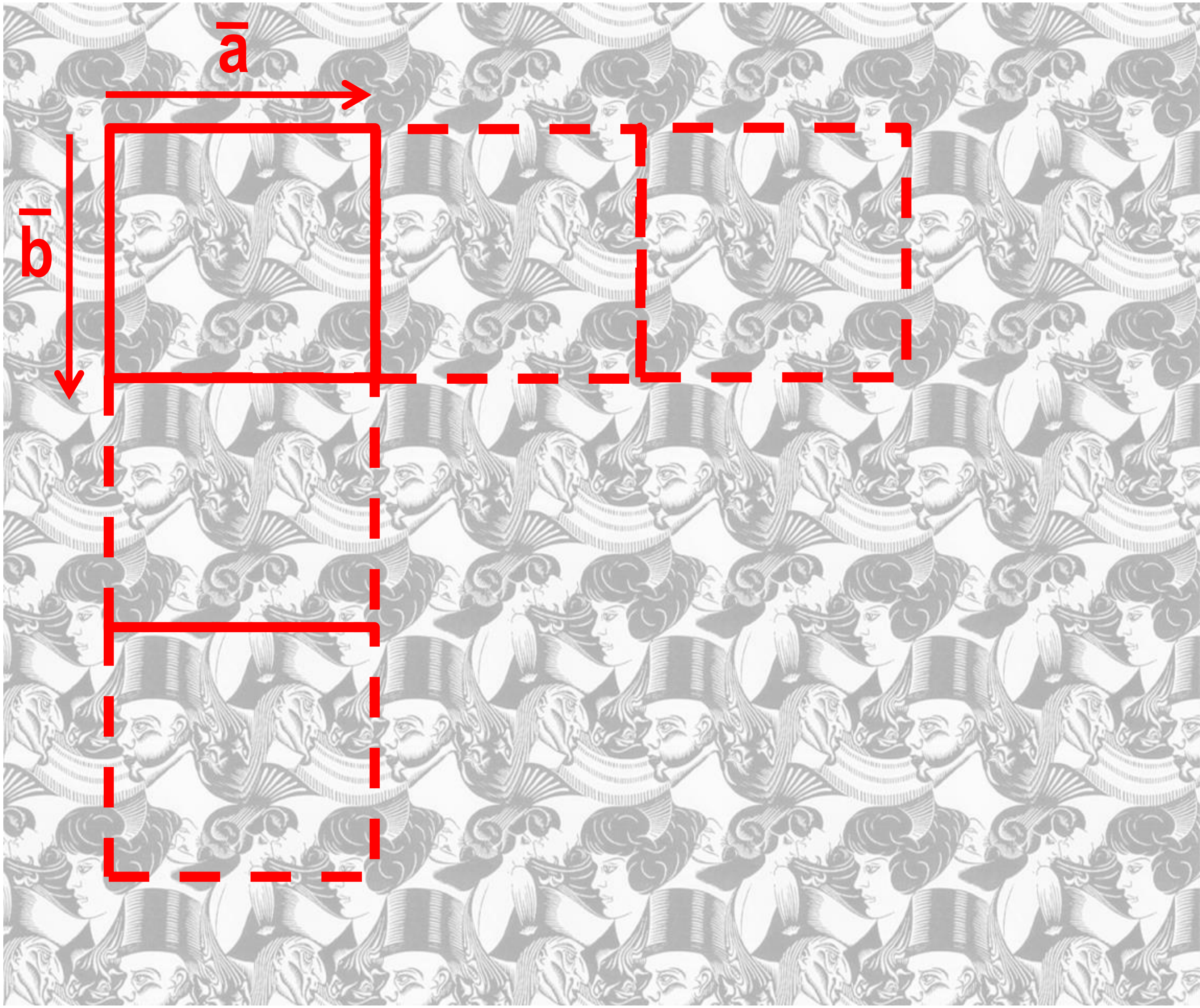
crystal structure
periodic repetition of a unit cell

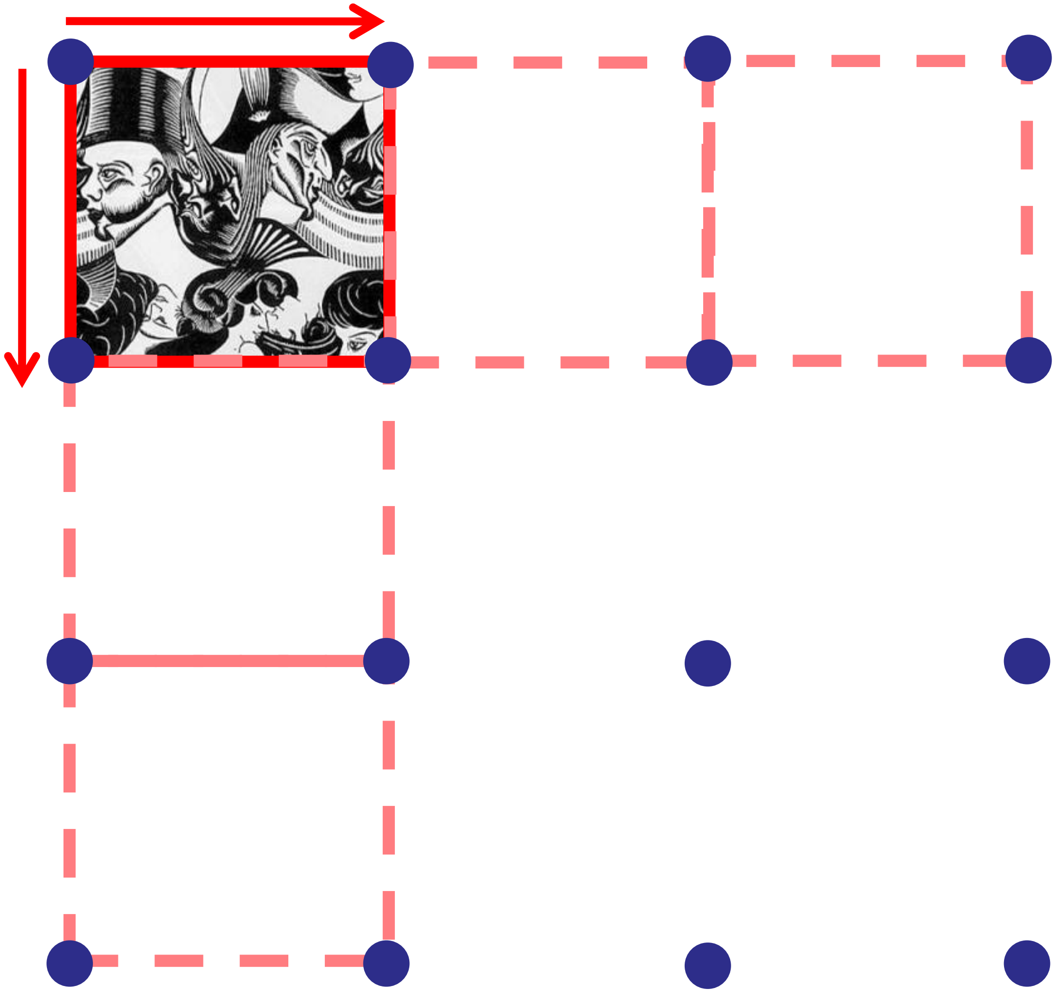
unit cell
repeatable part of the lattice
shape from lattice vectors
not unique

lattice vectors
real-space basis
not necessarily orthonormal
generates translation symmetry



CRYSTALLOGRAPHY

crystal structure = Bravais lattice + motif



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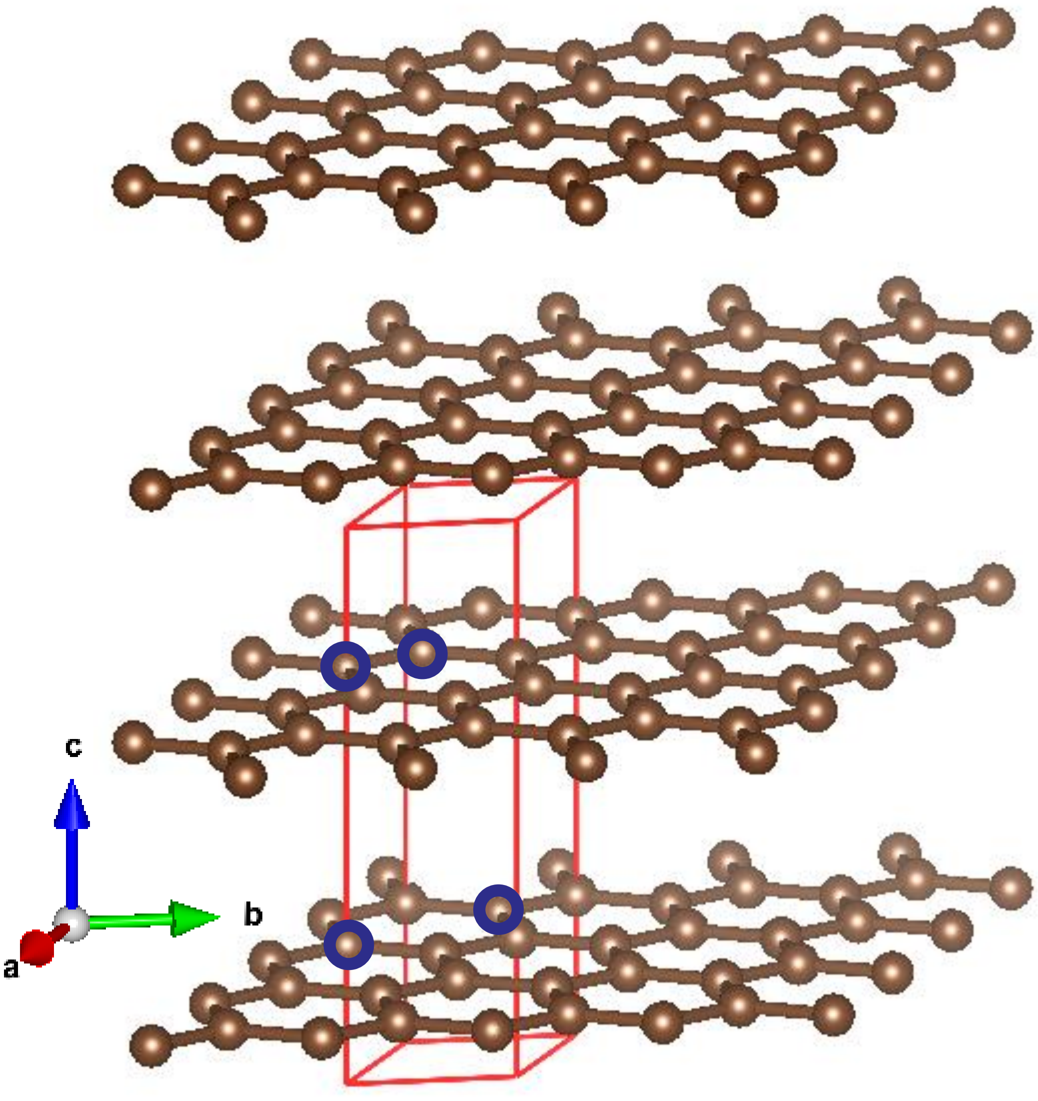

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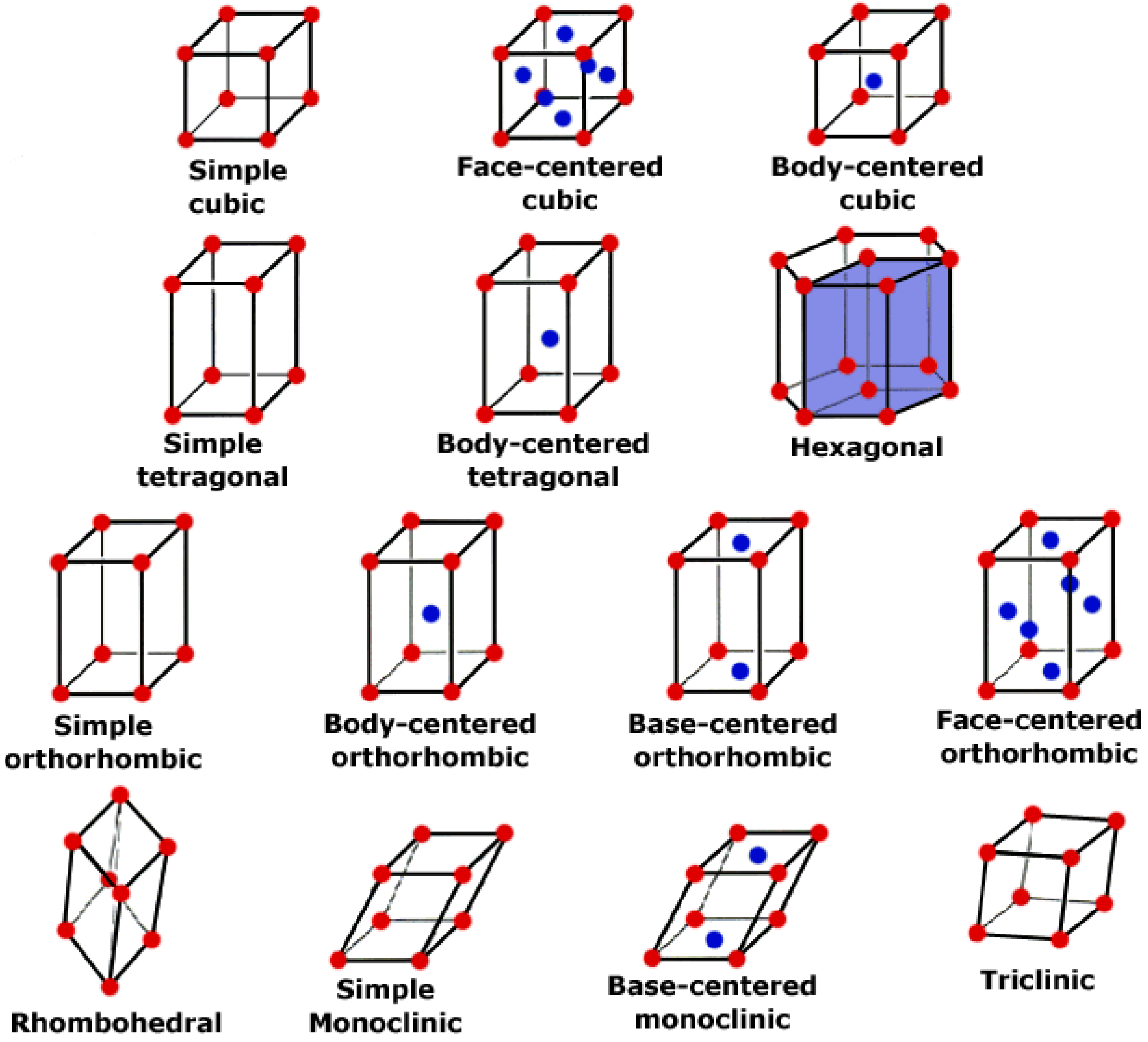

CONTENT OVERVIEW

- crystallography
- plane wave basis sets
  - basis sets: general idea
  - working in reciprocal space
- the projected-augmented wave method
- using the VASP software

BASIS SET : GENERAL IDEA

DFT constructs the density from single-particle orbitals. We need a way to express these orbitals. In many practical methods, this is done by expressing them in a basis

$$\Psi_m = \sum_{i=1}^{\infty} c_i^m \phi_i$$

The space of single-particle functions Ψ_m has infinite dimension, there are therefore an infinite number of basis functions ϕ_i needed. In practice, this infinite sum will be truncated once good accuracy is achieved.

BASIS SET : GENERAL IDEA

in practice:

$$\left[-\frac{1}{2}\nabla^2 + \sum_{\alpha=1}^{M}\left(-\frac{Z_\alpha}{|\bar{r}-\bar{R}_\alpha|}\right) + \int \frac{\rho(\bar{r}')}{|\bar{r}-\bar{r}'|} + v_{xc}(\bar{r})\right]\varphi_k(\bar{r}) = \epsilon_k \varphi_k(\bar{r})$$

how to solve this equation for a given functional?

projection on a complete basis set $|\xi_m\rangle$:

$$\langle \xi_m | \hat{H}_{KS} | \varphi_k \rangle = \epsilon_k \langle \xi_m | \varphi_k \rangle \ \forall m$$

$$\sum_{n=1}^{\infty} \langle \xi_m | \hat{H}_{KS} | \xi_n \rangle \langle \xi_n | \varphi_k \rangle = \epsilon_k \sum_{n=1}^{\infty} \langle \xi_m | \xi_n \rangle \langle \xi_n | \varphi_k \rangle \ \forall k', k$$

$$HC = ESC$$

i.e. solving a matrix-form generalized eigenvalue equation
for the expansion coefficients and energy eigenvalues

BASIS SET : GENERAL IDEA

in practice:

$$\left[-\frac{1}{2}\nabla^2 + \sum_{\alpha=1}^{M}\left(-\frac{Z_\alpha}{|\bar{r}-\bar{R}_\alpha|}\right) + \int \boxed{\frac{\rho(\bar{r}')}{|\bar{r}-\bar{r}'|}} + \boxed{v_{xc}(\bar{r})}\right]\varphi_k(\bar{r}) = \epsilon_k\varphi_k(\bar{r})$$

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$$\sum_{n=1}^{\infty}\langle\xi_m|\hat{H}_{KS}|\xi_n\rangle\langle\xi_n|\varphi_k\rangle = \epsilon_k\sum_{n=1}^{\infty}\langle\xi_m|\xi_n\rangle\langle\xi_n|\varphi_k\rangle \ \forall k', k$$

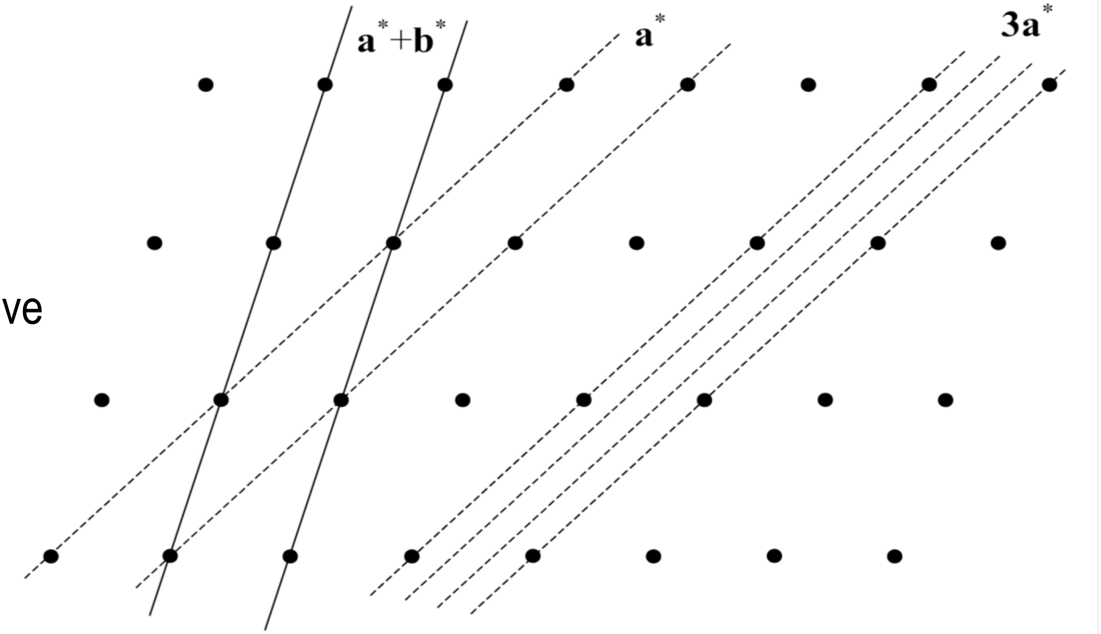
$$HC = ESC$$

i.e. solving a matrix-form generalized eigenvalue equation recursively

$$\varphi_k^{(0)} \Rightarrow \hat{H}_{KS}^{(0)} \Rightarrow \varphi_k^{(1)} \Rightarrow \cdots$$

PLANE WAVE BASIS SETS (PW)

reciprocal lattice



All reciprocal-space vectors that lead to a plane wave

$$f(\vec{r}) = A\, e^{i\vec{K}\cdot\vec{r}}$$

that is commensurate with the Bravais lattice in real space (= if the plane wave has a particular value α in the point $\vec{r}_0$, then it has the same value α in all points $\vec{r}_0 + \underbrace{\ell\,\vec{a} + m\,\vec{b} + n\,\vec{c}}_{\vec{T}}$), form together the **reciprocal lattice** of that Bravais lattice.

$$e^{i\vec{K}\cdot\vec{r}_0} = e^{i\vec{K}\cdot\left(\vec{r}_0+\vec{T}\right)} \;\Rightarrow\; e^{i\vec{K}\cdot\vec{T}} = 1$$

$$\vec{a}^* = 2\pi\frac{\vec{b}\times\vec{c}}{\vec{a}\cdot(\vec{b}\times\vec{c})}\;;\; \vec{b}^* = 2\pi\frac{\vec{c}\times\vec{a}}{\vec{a}\cdot(\vec{b}\times\vec{c})}\;;\; \vec{c}^* = 2\pi\frac{\vec{a}\times\vec{b}}{\vec{a}\cdot(\vec{b}\times\vec{c})}$$

$$\vec{K} = \ell'\vec{a}^* + m'\vec{b}^* + n'\vec{c}^*$$

PLANE WAVE BASIS SETS (PW)

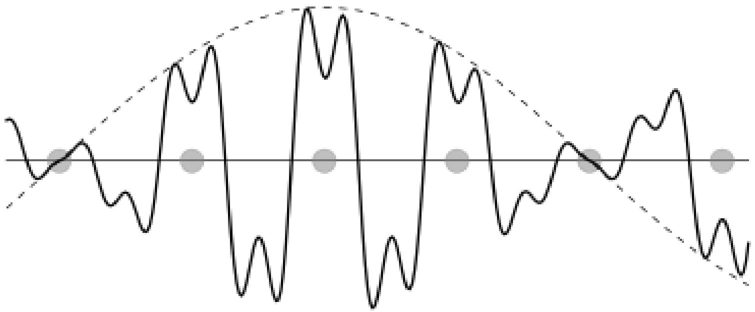
Bloch’s theorem

Bloch's theorem
eigenfunctions of infinitely periodic Hamiltonians can be labelled by a continuous quantum number *k* in the first Brillouin zone, each of which takes the form

$$\varphi_{\bar{k}n}(\bar{r}) = u_{\bar{k}n}(\bar{r})\,\mathrm{e}^{i\bar{k}\cdot\bar{r}}$$

where $u_{\bar{k}n}(\bar{r})$ follows the periodicity of the lattice, so

$$\varphi_{\bar{k}n}(\bar{r}) = \sum_{\vec{K}} u_{\bar{k}n,\bar{G}}\,\mathrm{e}^{i(\bar{k}+\vec{K})\cdot\bar{r}}$$



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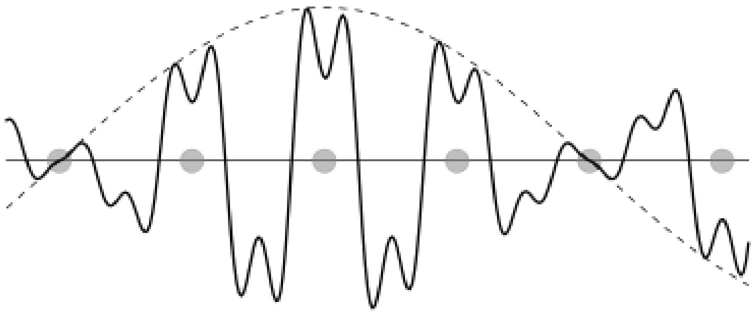
an expansion of the Kohn-Sham eigenfunctions into a plane-wave basis naturally arises!



PLANE WAVE BASIS SETS (PW)

truncating the basis set

$$\varphi_{\bar{k}n}(\bar{r}) = \sum_{\vec{K}} u_{\bar{k}n,\vec{K}}\, \mathrm{e}^{i(\bar{k}+\vec{K})\cdot\bar{r}}$$

it is impossible to use an infinite-size basis set

⇨ limit the calculation to a finite number of plane waves, using a maximum wave number as truncation criterion

$$|\bar{k}+\vec{K}| \leq K_{cut}$$

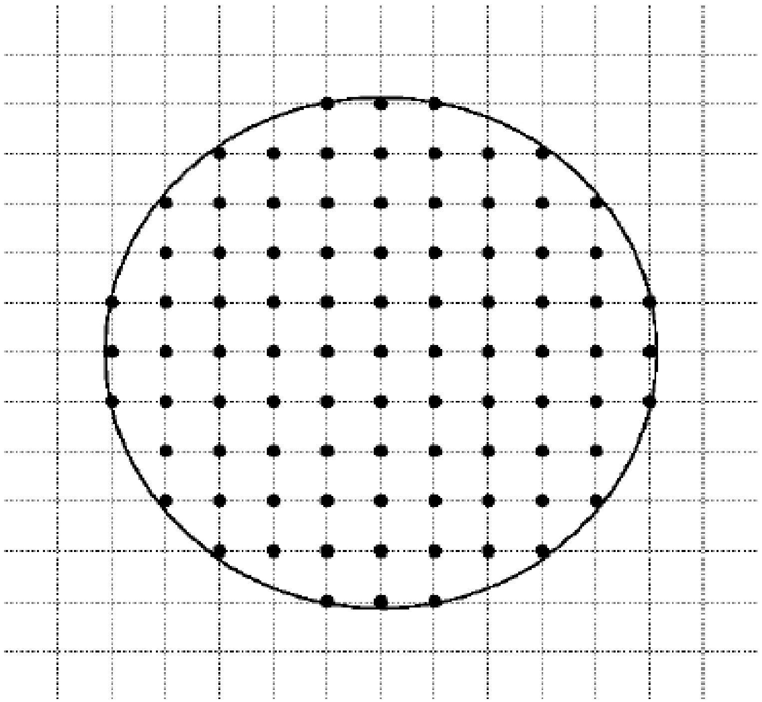
⇨ alternative views:

- only plane waves with an energy below $E_{cut} = \frac{1}{2}K_{cut}^2$
- maximum spatial resolution of $\lambda_{min} = \frac{2\pi}{K_{cut}}$

PLANE WAVE BASIS SETS (PW)

truncating the basis set

Schematic representation of the plane waves that are taken into the basis set :



$$\frac{1}{2}(\mathbf{K})^2 \leq E_{max}$$

$$n_1^2 + n_2^2 + n_3^2 \leq \frac{E_{max} L^2}{(2\pi)^2}$$

The basis set size depends only on the **volume of the box** and the **cut-off**

For a given E_{max}, you need more plane waves to describe a larger cell (smaller reciprocal lattice vector)

The larger you take E_{max}, the larger your basis, the more accurate your calculation, and the more expensive your calculation.

PLANE WAVE BASIS SETS (PW)

Brillouin zone sampling

$$\varphi_{\bar{k}n}(\bar{r}) = \sum_{\vec{K}} u_{\bar{k}n,\vec{K}}\ \mathrm{e}^{i(\bar{k}+\vec{K})\cdot\bar{r}}$$

it is impossible to determine solutions for an infinite number of quantum numbers *k* within the first Brillouin zone

⇨ observable quantities arise as integrations over *k*

⇨ sample the continuous quantum number *k* at discrete points

most common sampling method:

Monkhorst-Pack meshes = uniformly spaced grid around the Γ point

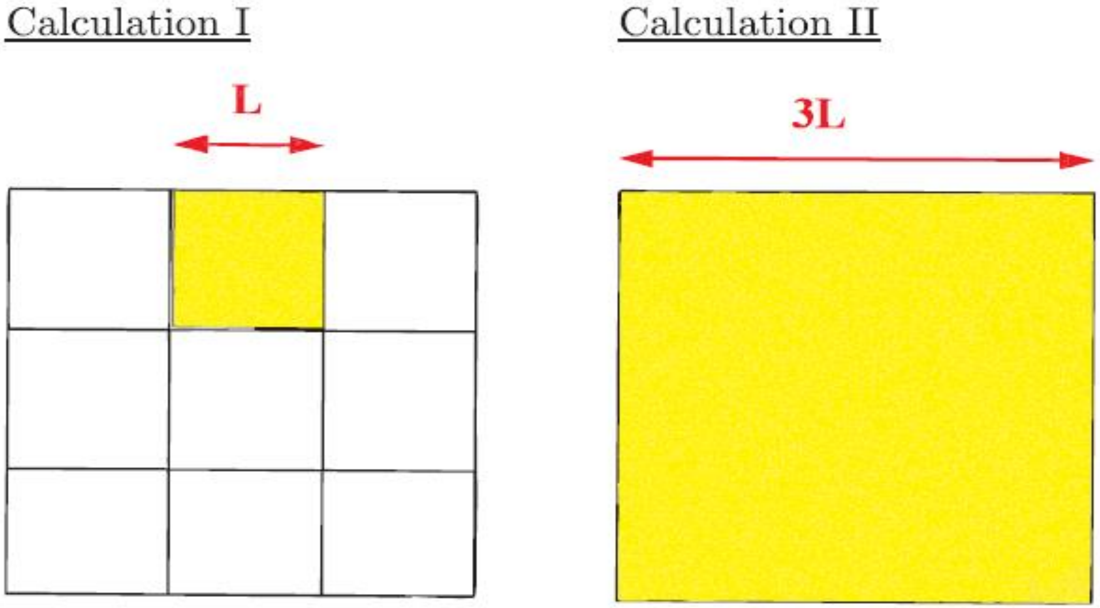
H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976)

PLANE WAVE BASIS SETS (PW)

Brillouin zone sampling

Γ-sampling may be accurate enough if large simulation cells are used.

Illustration with two-dimensional example



Calculation I

Calculation II

Simulation cells in real space

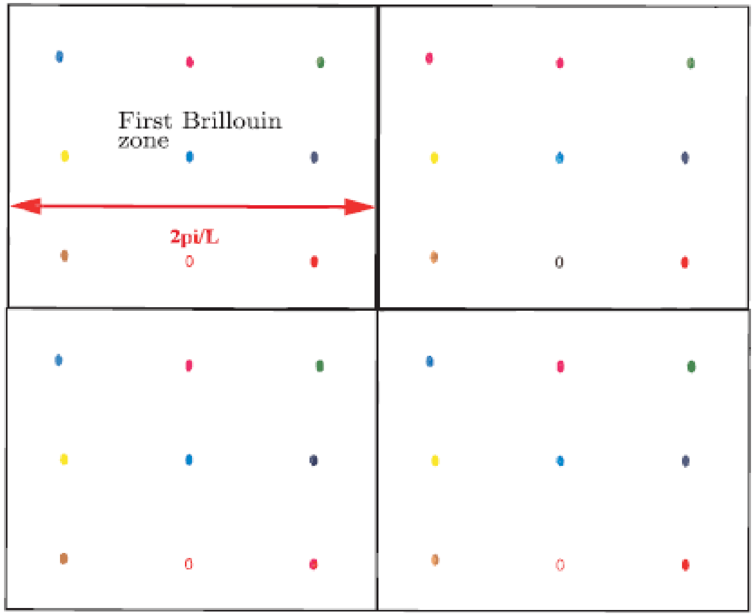
Calculation I:
a two dimensional cubic simulation cell LxL with Brillouin zone sampling points (0,0), (2/3,0), (-2/3,0), (-2/3,0), (-2/3,0), (0,2/3), (2/3,2/3), (-2/3,2/3), (2/3,-2/3), (-2/3,-2/3).

Calculation II:
a two dimensional cubic simulation cell 3Lx3L in a Γ-point calculation.

PLANE WAVE BASIS SETS (PW)

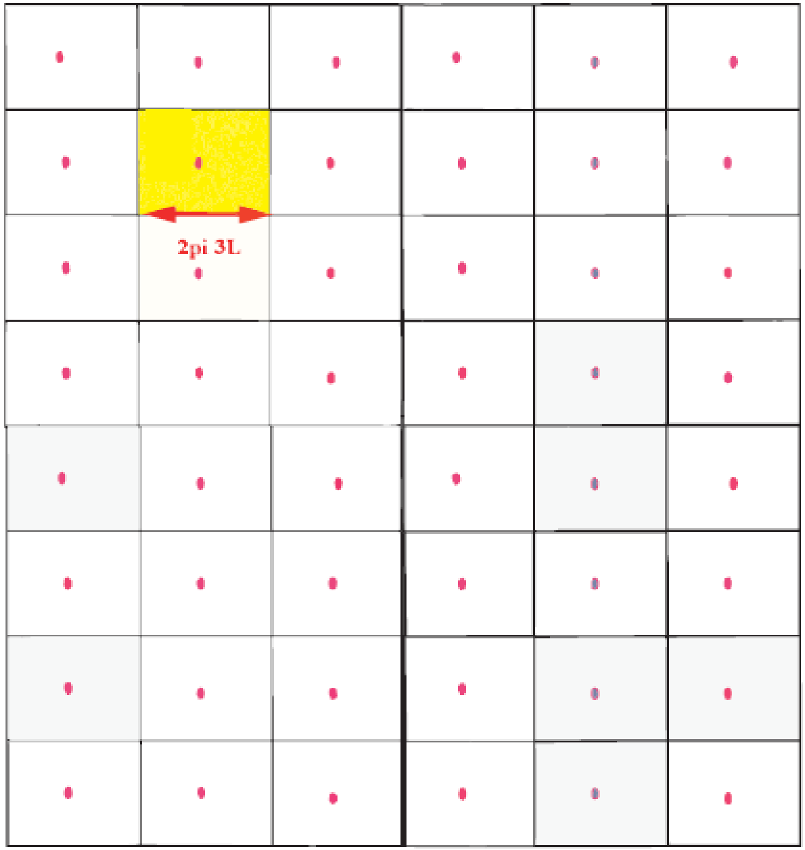
Brillouin zone sampling

Brillouin zones for both calculations
Same plane waves are used in both calculations but in Calculation II, the atoms have more freedom within the larger real-space cell.



Calculation I

$$\psi_{ik}(\mathbf{r}) = \sum_{\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K}).\mathbf{r}} \psi_i(\mathbf{K}+\mathbf{k})$$



Calculation II

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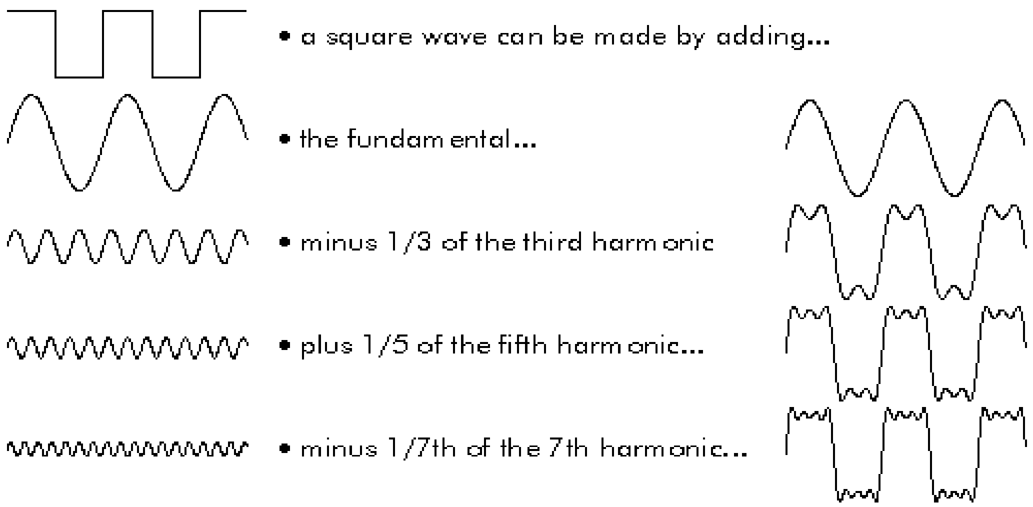
PLANE WAVE BASIS SETS (PW)

Basis set size

What makes a plane wave basis set to be large?



The steeper the feature you want to describe, the more basis functions (plane waves) are needed (Gibbs phenomenon).

PLANE WAVE BASIS SETS (PW)

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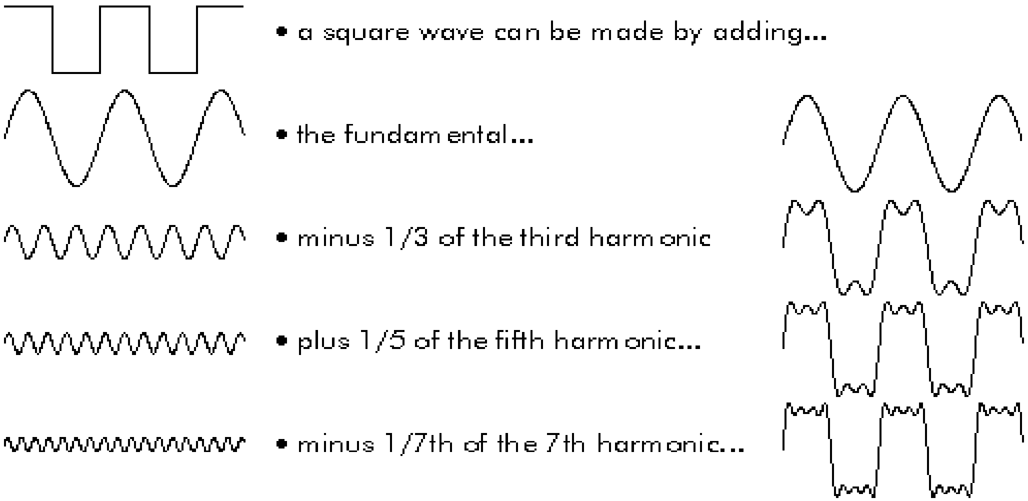


- a square wave can be made by adding...
- the fundamental...
- minus 1/3 of the third harmonic
- plus 1/5 of the fifth harmonic...
- minus 1/7th of the 7th harmonic...

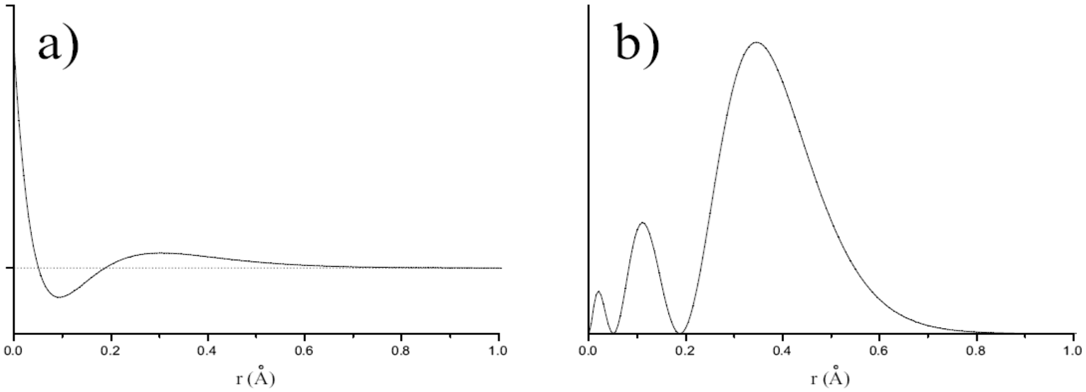


Figure 2.1: *Radial part of wave function (a) and radial probability distribution (b) of a 3s electron in Ca (Y-axis has arbitrary units).*

The steeper the feature you want to describe, the more basis functions (plane waves) are needed (Gibbs phenomenon).

Back-of-the-envelop estimate for
Ca-3s: 10^8 plane waves.
Diagonalize 10^8x10^8 matrices...?

The steepest features appear near
to the nuclei:
→ use basis functions that have such
steep features built in

PLANE WAVE BASIS SETS (PW)

Frozen core approximation

Not all electrons are the same ... :

Core electrons

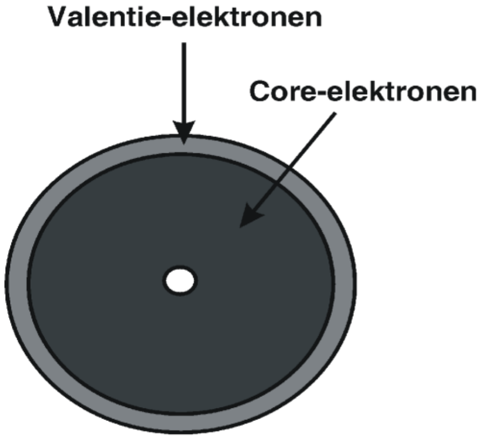
- Deeply bound
- Localized around core region
- Are subject to the attractive Coulomb potential with respect to the positive nucleus and interaction mainly with other core electrons
- Orbitals do not change substantially when placed in various molecular environments

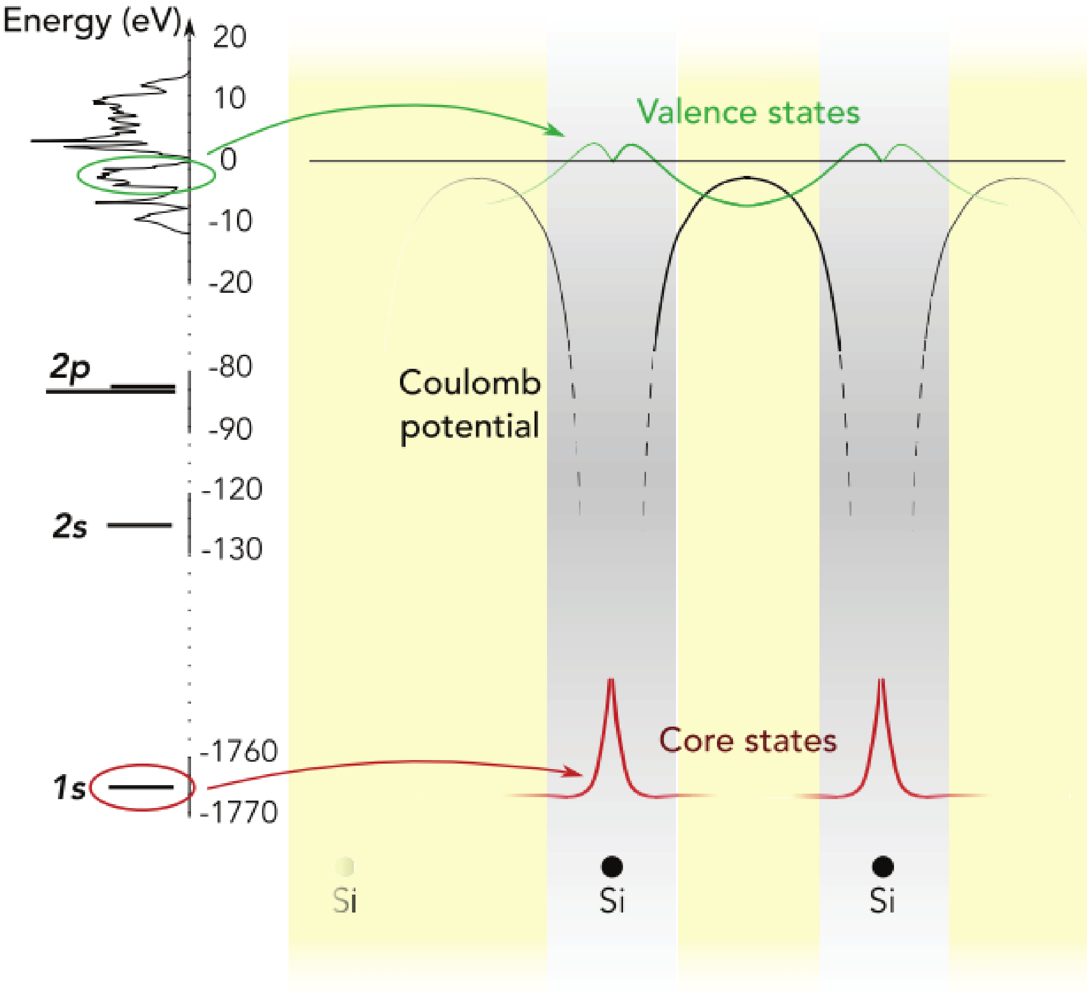
Valence electrons

- Single particle energies are situated near the Fermi-level
- Charge density is concentrated in region further from the nucleus
- The valence electrons feel a screened Coulomb potential due to the other core electrons
- Valence wavefunctions are subject to strong oscillations in core region, as they are orthonormal to the core wavefunctions
- These valence wavefunctions undergo drastic changes depending on the molecular environment in which they are placed

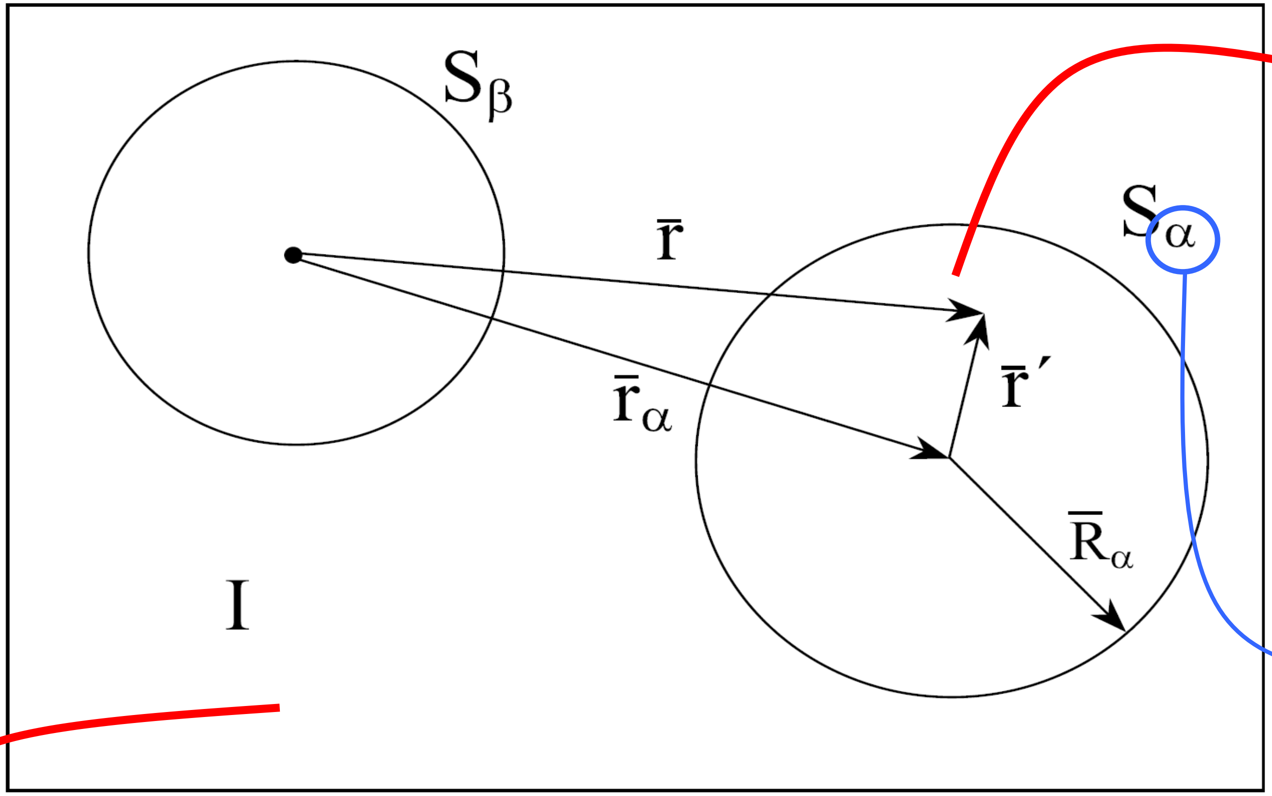
PLANE WAVE BASIS SETS (PW)

Frozen core approximation





VOLUME PARTITIONING



‘near’ a nucleus:

- electrons behave almost as in a free atom (steep changes, many plane waves would be needed)
- most efficient to use atom-like basis functions here

Identifies which sphere/atom

far away from the nucleus:

- electron density is much smoother (‘almost constant’ = free electron)
- much fewer plane waves needed

→ Partition space into a region of atom-like behaviour and a region of free-electron-like behaviour.

THE PAW METHOD

What does it want to achieve ?

→ rewrite a single-particle Kohn-Sham orbital as a sum of three contributions, each of which can conveniently be expressed in a basis.

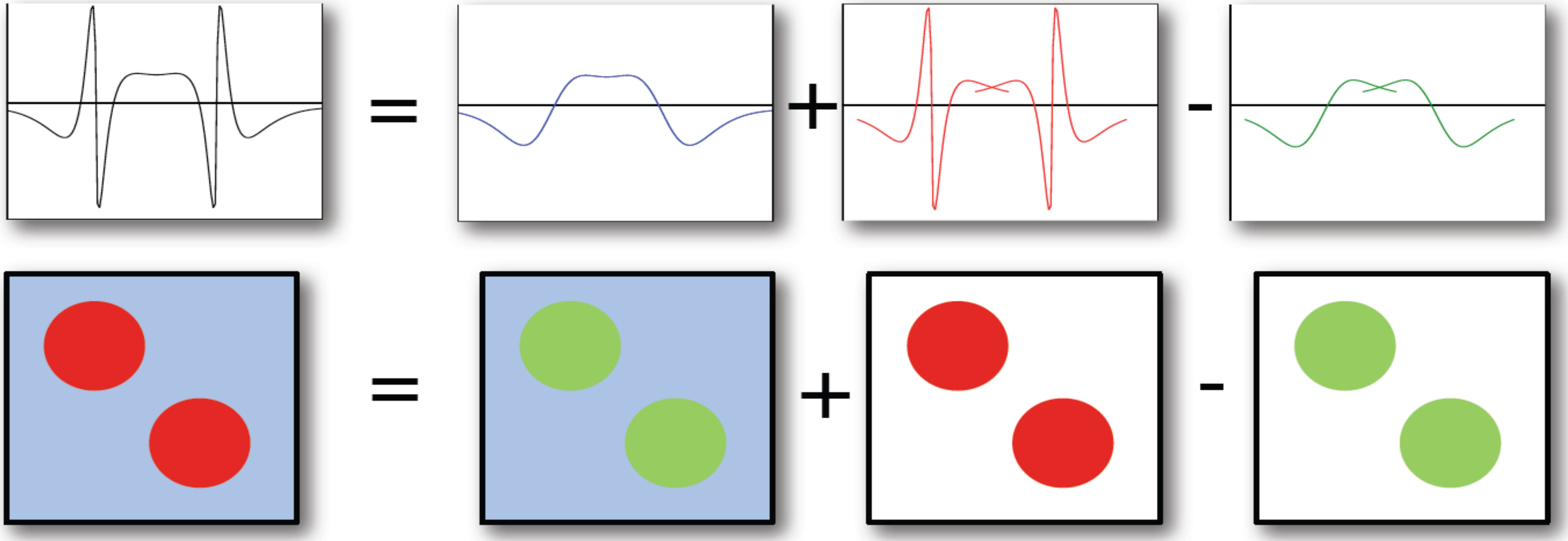
$$\psi_n(\vec{r}) = \tilde{\psi}_n(\vec{r}) + \sum_a \psi_n^a(\vec{r}) - \sum_a \tilde{\psi}_n^a(\vec{r})$$

all-electron (Kohn-Sham) wave function	pseudo wave function	all-electron 1-center wave function	pseudo 1-center wave function
defined everywhere	defined everywhere	defined inside spheres	defined inside spheres
steep inside spheres smooth outside spheres	smooth everwhere	steep inside spheres	smooth inside spheres
(no suitable basis, that's the problem…)	expressed in plane wave basis	expressed in partial wave basis	expressed in pseudo partial wave basis

(slide by P. Blöchl)

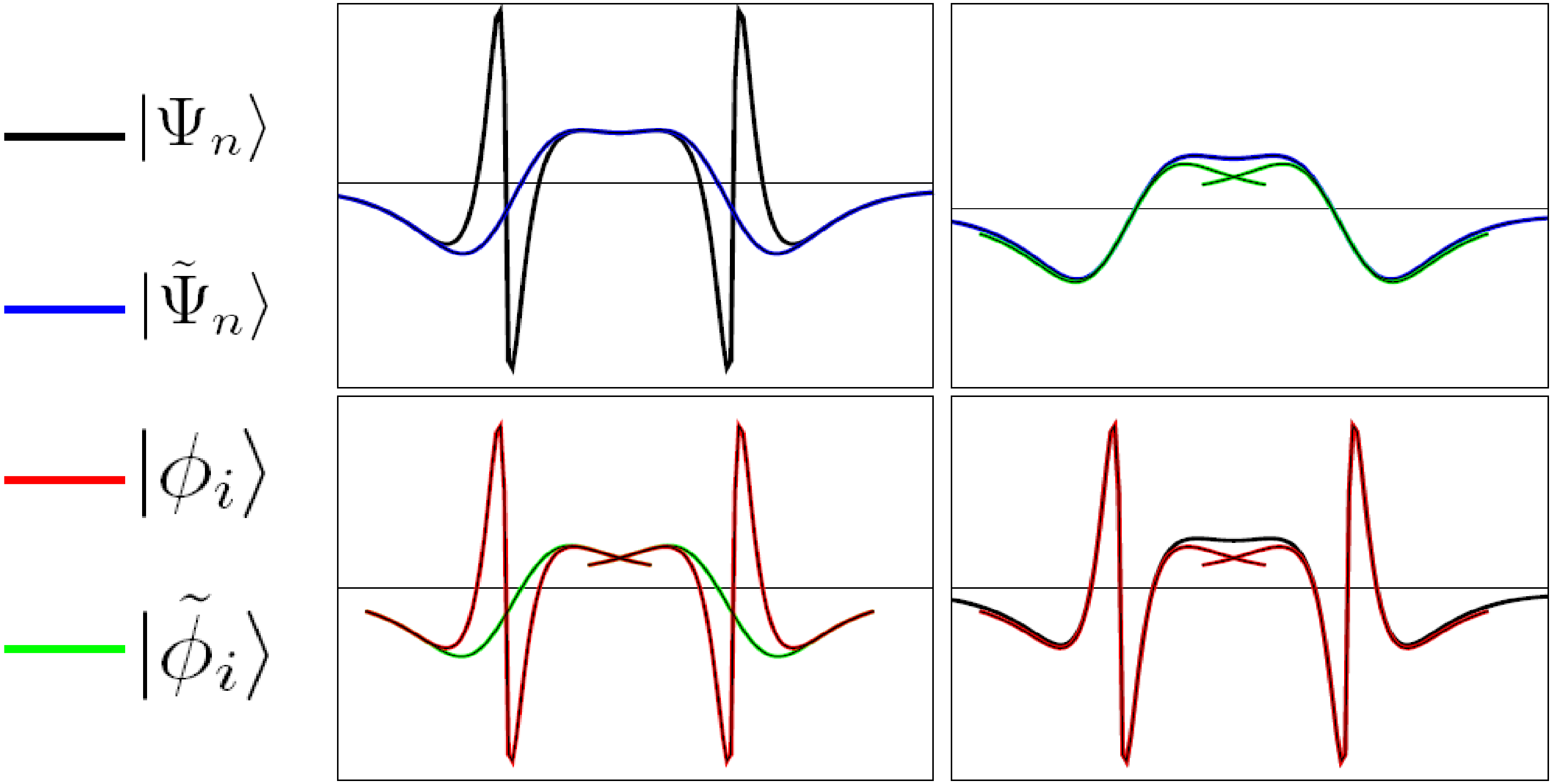
PAW augmentation

$$\underbrace{|\psi\rangle}_{\text{all-electron}} = \overbrace{|\tilde{\psi}\rangle}^{\text{pseudo}} + \overbrace{\underbrace{|\psi^1\rangle}_{\text{1-center, all-el.}}}^{\sum_\alpha |\phi_\alpha\rangle\langle\tilde{p}_\alpha|\tilde{\psi}\rangle} - \overbrace{\underbrace{|\tilde{\psi}^1\rangle}_{\sum_\alpha |\tilde{\phi}_\alpha\rangle\langle\tilde{p}_\alpha|\tilde{\psi}\rangle}}^{\text{1-center, pseudo}}$$



THE PAW METHOD

$$|\Psi\rangle = |\tilde{\Psi}\rangle + \sum_i \Big(|\phi_i\rangle - |\tilde{\phi}_i\rangle\Big)\langle\tilde{p}_i|\tilde{\Psi}\rangle = |\tilde{\Psi}\rangle + \sum_R \Big(|\Psi_R^1\rangle - |\tilde{\Psi}_R^1\rangle\Big)$$



p-σ orbital of a Cl$_2$ molecule

THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) = \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

By making a choice for each of the three numbered objects,
the rewriting we are aiming for can be unambiguously defined.

a = sum over atoms in the unit cell (or ‘augmentation spheres’)
i = sum over basis functions

THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) = \boxed{\tilde{\psi}_n(\vec{r})} + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

pseudo wave function

- outside the spheres:
  - identical to the all-electron wave function (which we don't know yet)
  - surely smooth, as the all-electron wave function is smooth there

- inside the spheres:
  - different from the all-electron wave function
  - smooth

→ How the pseudo wave function will look like,
will be fully determined by the three choices we'll make.

THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) = \tilde{\psi}_n(\vec{r}) + \underbrace{\sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle}_{\text{difference between all-electron and pseudo wave functions}}$$

alternative way to express this difference:

$$\psi_n(\vec{r}) = \underbrace{\left(1 + \sum_a \mathcal{T}^a \right)}_{\mathcal{T}} \tilde{\psi}_n(\vec{r})$$

THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) = \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

make a choice for the all-electron partial waves

- outside the spheres:
  - it will not matter how they look like, continue the behaviour they had inside the spheres

- inside the spheres:
  - anything that can serve as efficient basis functions for the steep part of the all-electron wave function
  - often taken as solutions of the free-atom Schrödinger equation

THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) = \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

You can use the (as yet unspecified) transformation operators to produce smooth pseudo-versions of the all-electron partial waves:

$$\phi_i^a(\vec{r}) = (1 + \mathcal{T}^a)\, \tilde{\phi}_i^a(\vec{r})$$

Alternatively, by making a choice for these pseudo partial waves, the transformation operators are defined:

$$\mathcal{T}^a \tilde{\phi}_i^a = \phi_i^a - \tilde{\phi}_i^a$$

Therefore…

THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

make a choice for the pseudo partial waves

- outside the spheres:
    - choose them to be identical to the all-electron partial waves

- inside the spheres:
    - choose them such that they can serve as a basis for the pseudo wave function inside the sphere:

$$\tilde{\psi}_n(\vec{r}) \;=\; \sum_i C_{ni}^a \, \tilde{\phi}_i^a(\vec{r}) \qquad \vec{r} \in \text{sphere `a'}$$

THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) = \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

(omitting the proof/derivation here) the expansion coefficients are determined by applying appropriate projectors to the pseudo wave function. There is quite some freedom to **choose** these element-specific **projectors**.
The choice made determines how smooth the pseudo wave function will be.

$$\tilde{\psi}_n(\vec{r}) = \sum_i C_{ni}^a \phi_i^a(\vec{r}) \qquad \vec{r} \in \text{sphere `a'}$$

THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) \;=\; \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

By defining

$$\sum_i \langle \tilde{p}_i^a \left| \tilde{\psi}_n \right\rangle \phi_i^a(\vec{r}) \;=\; \psi_n^a(\vec{r})$$

the all-electron 1-center functions (steep, inside sphere, expressed in a partial wave basis)

and

$$\sum_i \langle \tilde{p}_i^a \left| \tilde{\psi}_n \right\rangle \tilde{\phi}_i^a(\vec{r}) \;=\; \tilde{\psi}_n^a(\vec{r})$$

the pseudo 1-center functions (smooth, inside sphere, expressed in a pseudo partial wave basis)

we find that the Ansatz leads to the desired expression:

THE PAW METHOD

How does it achieve this ?

→ PAW Ansatz :

$$\psi_n(\vec{r}) = \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

$$\Downarrow$$

$$\psi_n(\vec{r}) = \tilde{\psi}_n(\vec{r}) + \sum_a \psi_n^a(\vec{r}) - \sum_a \tilde{\psi}_n^a(\vec{r})$$

THE PAW METHOD

Practical procedure :

After having made the required choices :

$$\psi_n(\vec{r}) \quad = \quad \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

you know the transformation operator and can replace ψ_n in the Kohn-Sham equations by $\mathcal{T}\tilde{\psi}_n$. This leads to a transformed KS-equation, with $\tilde{\psi}_n$ as the unknown. Solve it for $\tilde{\psi}_n$, after which you can finally fill out all items in the right-hand side of the above expression.

THE PAW METHOD

Important issue :

$$\psi_n(\vec{r}) = \tilde{\psi}_n(\vec{r}) + \sum_a \sum_i \left(\underbrace{\phi_i^a(\vec{r})}_{1} - \underbrace{\tilde{\phi}_i^a(\vec{r})}_{2} \right) \left\langle \underbrace{\tilde{p}_i^a}_{3} \middle| \tilde{\psi}_n \right\rangle$$

The choice of the element-dependent projector functions (the “P” in PAW) determines how smooth the pseudo wave function will be, and hence how small the plane wave basis (and the speed of the calculation) will be.

Generating suitable projectors is partly a kind of art, comparable to the art of generating good pseudopotentials.

Well-tested tabulations of projector functions are either a proprietary part of code (e.g. for VASP), or are freely available for use across codes (e.g. http://users.wfu.edu/natalie/papers/pwpaw/newperiodictable/).

An extensive discussion on PAW generation can be found at http://arxiv.org/pdf/1309.7274.pdf .

CONTENT OVERVIEW

- crystallography
- plane wave basis sets
  - basis sets: general idea
  - working in reciprocal space
- the projected-augmented wave method
- using the VASP software

what about VASP?

- originally developed at the University of Vienna by Georg Kresse and Jürgen Furthmüller
- originally a plane-wave pseudopotential code targeting MD applications
- now one of the major PAW codes for solid-state research
- proprietary software: source files and PAW potentials may not be distributed; only licensed users

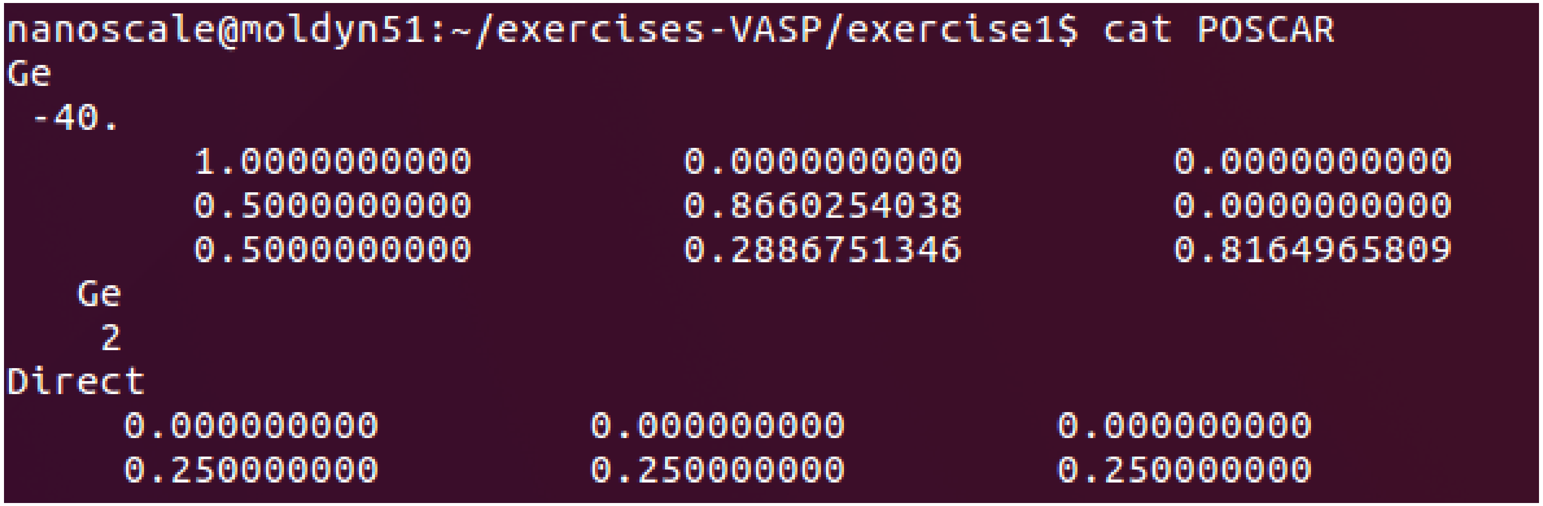
this tutorial: VASP 5.2.2 on CMM's moldyn machines
your thesis: VASP 5.4.4 on UGent HPC
!! be careful: PAW potentials have changed format as from VASP 5.2.12

4 compulsory input files:

POSCAR:	geometry of the unit cell position of the atoms
KPOINTS:	Brillouin zone sampling
INCAR:	all other kinds of settings (cut-off energy, number of steps, …)
POTCAR:	PAW potential (proprietary!) strictly considered functional-dependent, but mostly PBE used

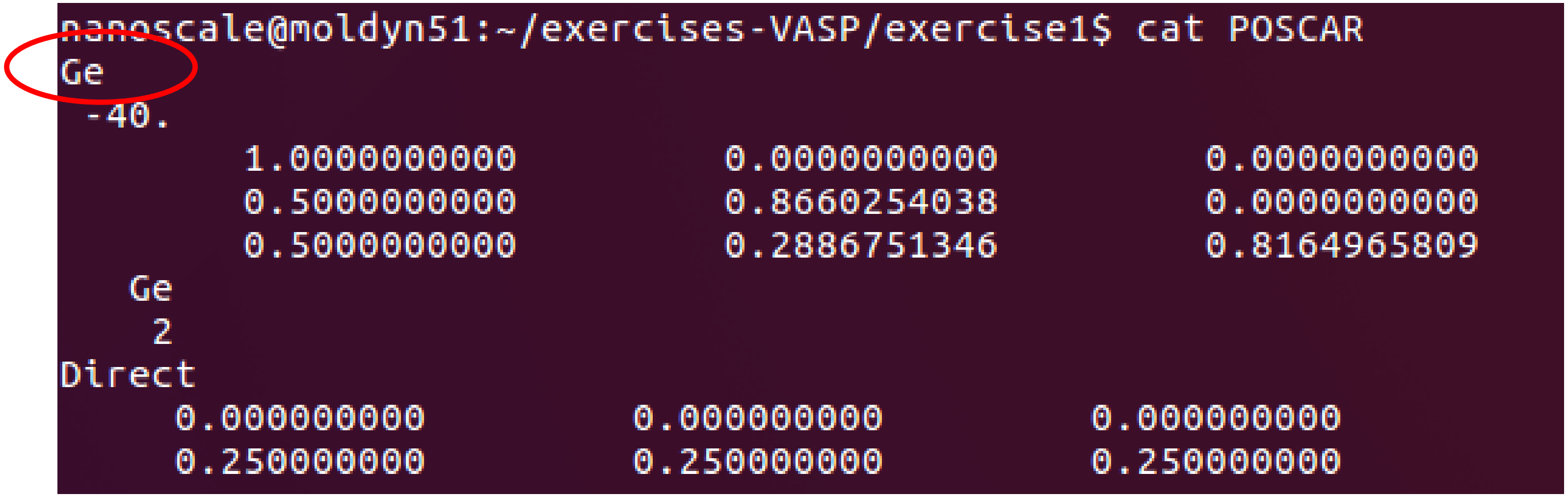
CAUTION! input files always have the same name, so perform different calculations in different directories

POSCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat POSCAR
Ge
 -40.
        1.0000000000         0.0000000000         0.0000000000
        0.5000000000         0.8660254038         0.0000000000
        0.5000000000         0.2886751346         0.8164965809
   Ge
    2
Direct
     0.000000000         0.000000000         0.000000000
     0.250000000         0.250000000         0.250000000
```

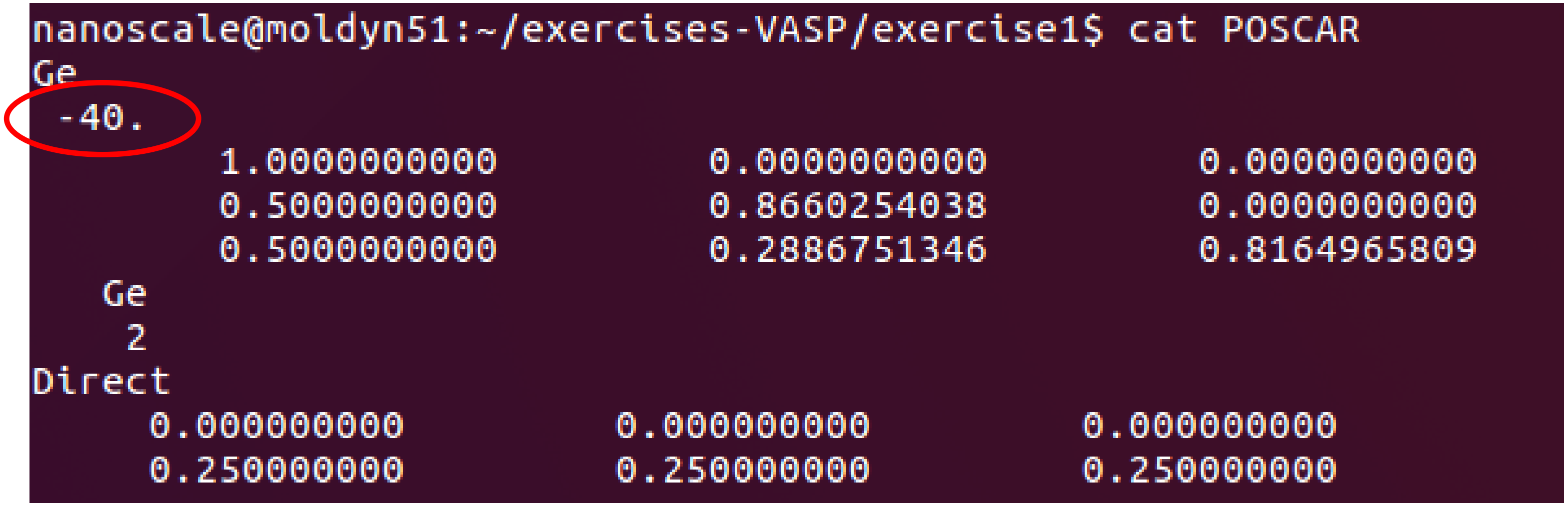
POSCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat POSCAR
Ge
 -40.
        1.0000000000         0.0000000000         0.0000000000
        0.5000000000         0.8660254038         0.0000000000
        0.5000000000         0.2886751346         0.8164965809
   Ge
    2
Direct
     0.000000000         0.000000000         0.000000000
     0.250000000         0.250000000         0.250000000
```

title (free format)

POSCAR:

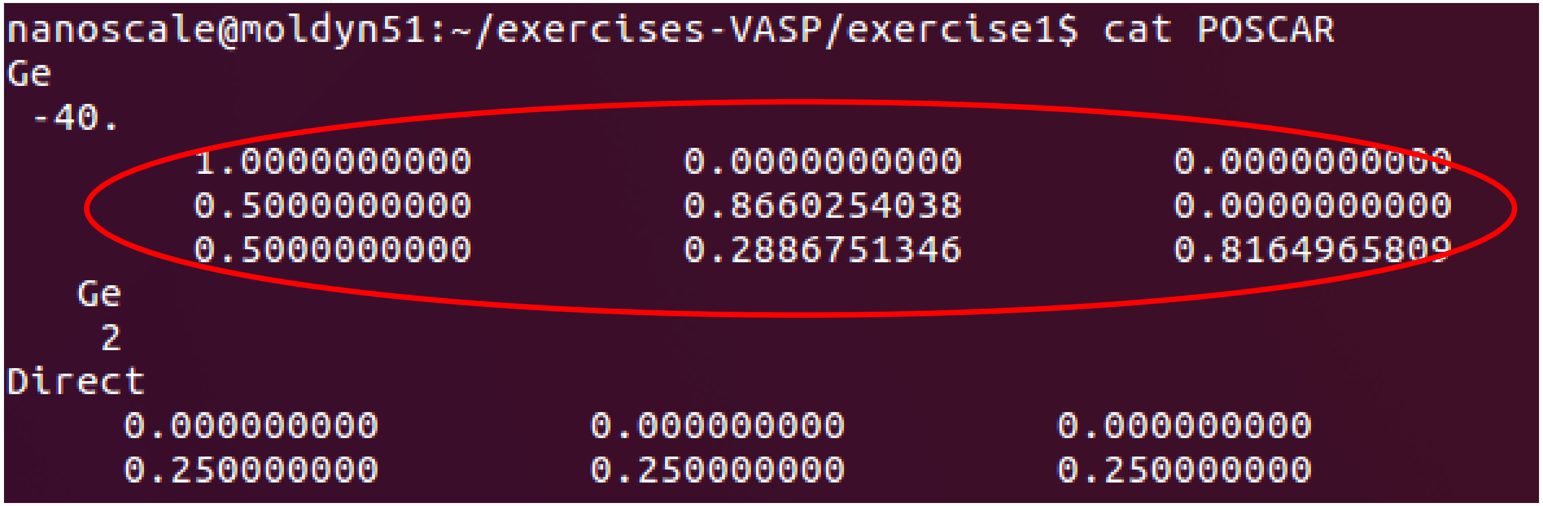


```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat POSCAR
Ge
 -40.
        1.0000000000         0.0000000000         0.0000000000
        0.5000000000         0.8660254038         0.0000000000
        0.5000000000         0.2886751346         0.8164965809
   Ge
    2
Direct
     0.000000000         0.000000000         0.000000000
     0.250000000         0.250000000         0.250000000
```

title (free format)

scaling factor (positive) or volume (negative)

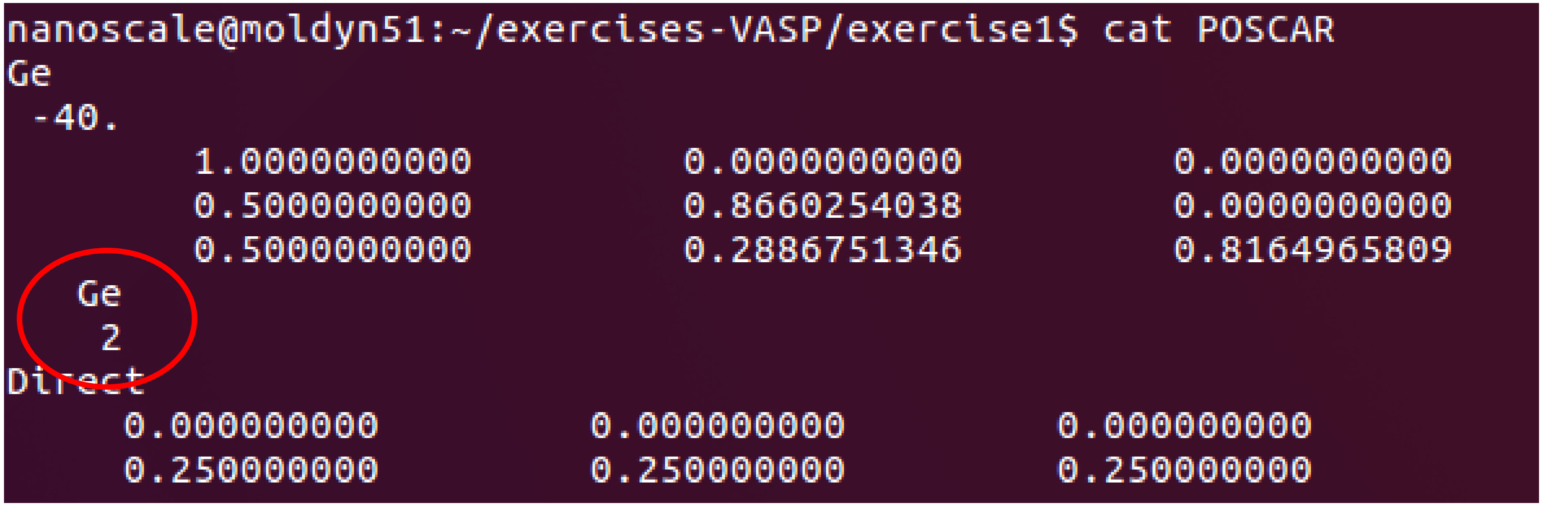
POSCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat POSCAR
Ge
 -40.
        1.0000000000         0.0000000000         0.0000000000
        0.5000000000         0.8660254038         0.0000000000
        0.5000000000         0.2886751346         0.8164965809
   Ge
    2
Direct
     0.000000000         0.000000000         0.000000000
     0.250000000         0.250000000         0.250000000
```

title (free format)
scaling factor (positive) or volume (negative)
unit cell vectors (read horizontally)

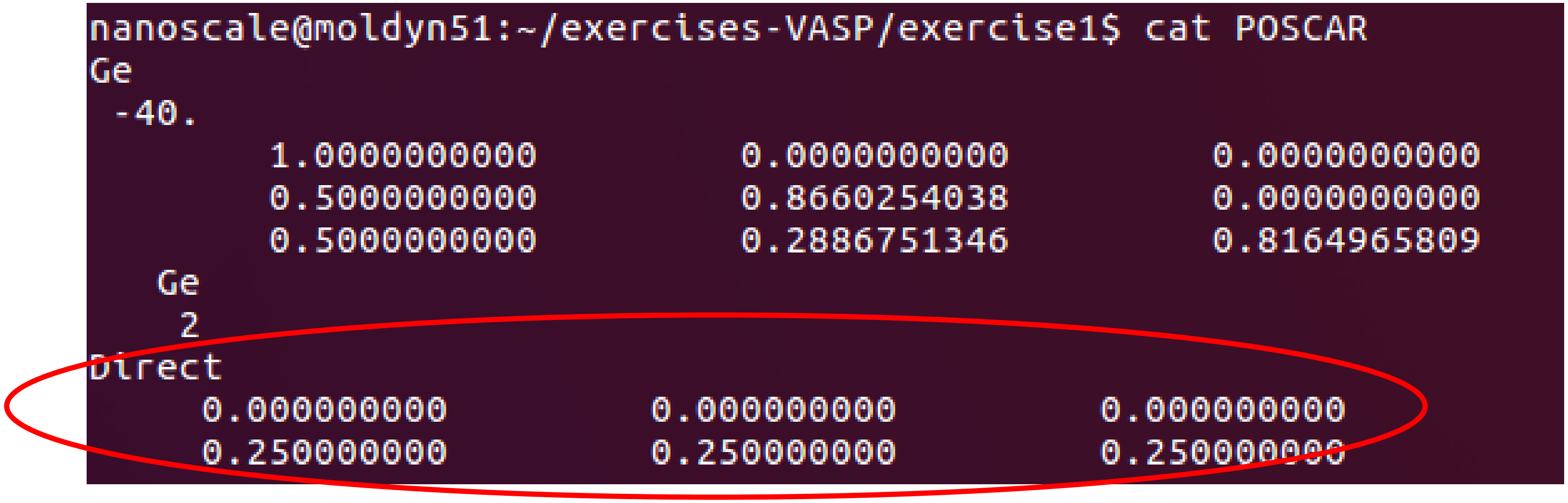
POSCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat POSCAR
Ge
 -40.
        1.0000000000         0.0000000000         0.0000000000
        0.5000000000         0.8660254038         0.0000000000
        0.5000000000         0.2886751346         0.8164965809
   Ge
    2
Direct
     0.000000000         0.000000000         0.000000000
     0.250000000         0.250000000         0.250000000
```

title (free format)
scaling factor (positive) or volume (negative)
unit cell vectors (read horizontally)
atom types and number of atoms for each (separated by spaces)

POSCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat POSCAR
Ge
 -40.
        1.0000000000         0.0000000000         0.0000000000
        0.5000000000         0.8660254038         0.0000000000
        0.5000000000         0.2886751346         0.8164965809
   Ge
    2
Direct
     0.000000000         0.000000000         0.000000000
     0.250000000         0.250000000         0.250000000
```

title (free format)

scaling factor (positive) or volume (negative)

unit cell vectors (read horizontally)

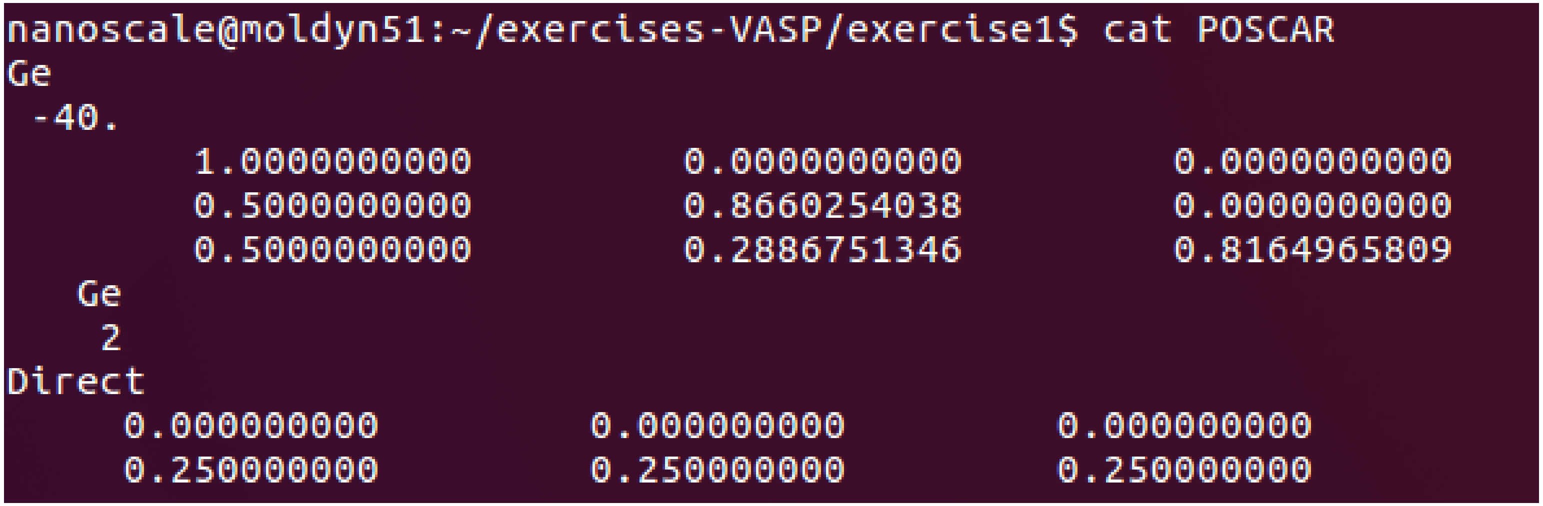
atom types and number of atoms for each (separated by spaces)

atomic coordinates with respect to the unit cell vectors (Direct)

or with respect to Cartesian coordinates (Cartesian)

→ same order as atom types!

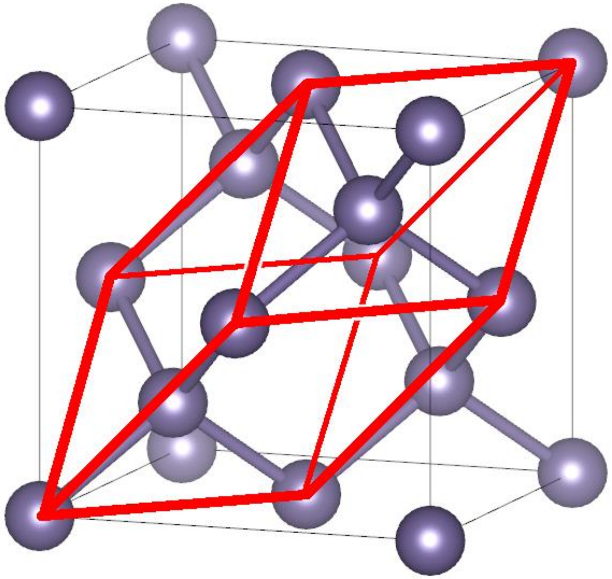
POSCAR:



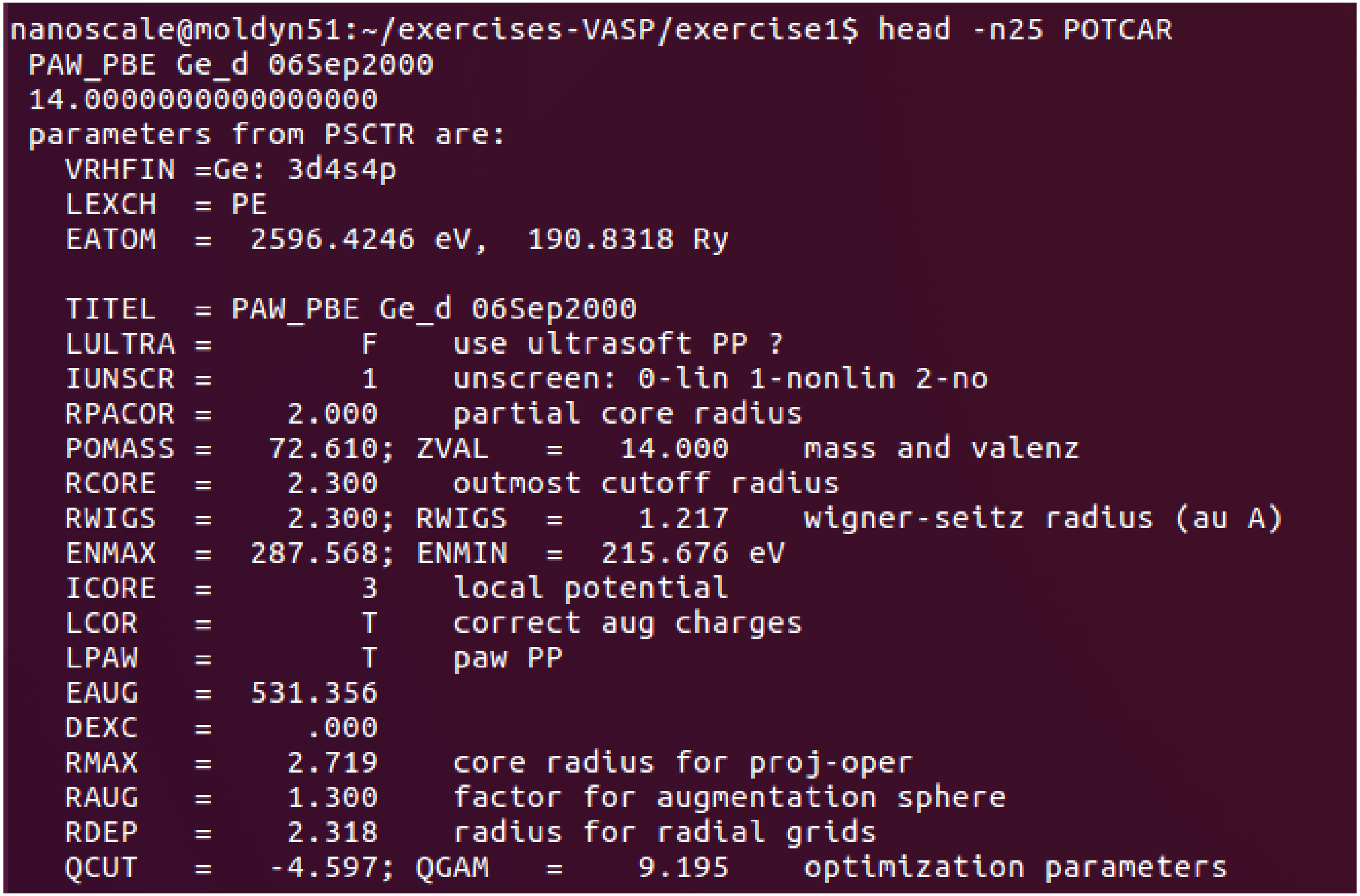
```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat POSCAR
Ge
 -40.
        1.0000000000         0.0000000000         0.0000000000
        0.5000000000         0.8660254038         0.0000000000
        0.5000000000         0.2886751346         0.8164965809
   Ge
    2
Direct
     0.000000000         0.000000000         0.000000000
     0.250000000         0.250000000         0.250000000
```

volume of 40 Å^3
i.e. conventional unit cell parameter of $40^{1/3}$ Å = 3.420 Å
i.e. primitive unit cell parameter of $40^{1/3} * \sqrt{2} / 2$ Å = 2.418 Å

2 germanium atoms per (primitive) unit cell

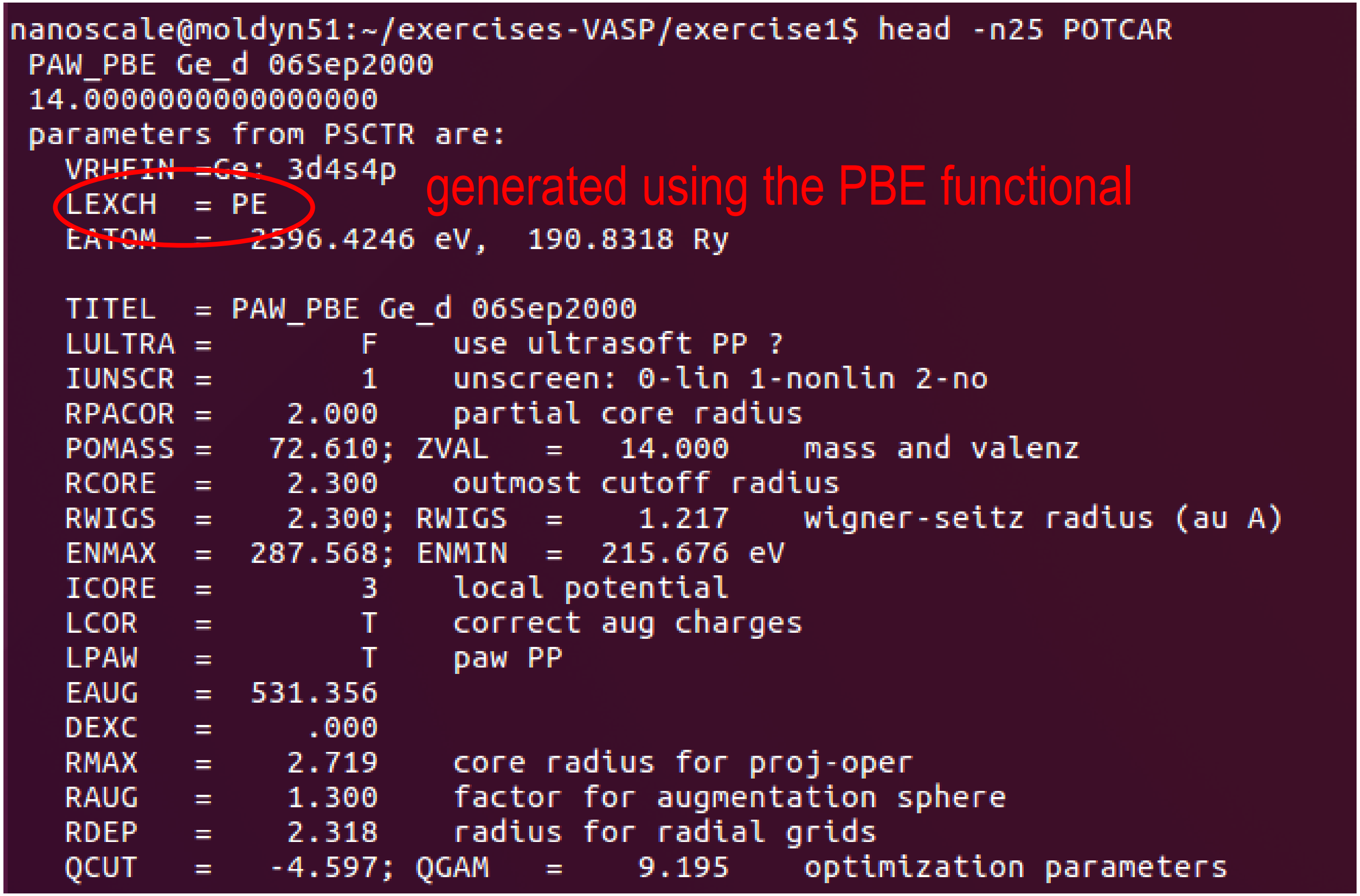


POTCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ head -n25 POTCAR
 PAW_PBE Ge_d 06Sep2000
 14.0000000000000000
 parameters from PSCTR are:
   VRHFIN =Ge: 3d4s4p
   LEXCH  = PE
   EATOM  =  2596.4246 eV,  190.8318 Ry

   TITEL  = PAW_PBE Ge_d 06Sep2000
   LULTRA =        F    use ultrasoft PP ?
   IUNSCR =        1    unscreen: 0-lin 1-nonlin 2-no
   RPACOR =    2.000    partial core radius
   POMASS =   72.610; ZVAL   =   14.000    mass and valenz
   RCORE  =    2.300    outmost cutoff radius
   RWIGS  =    2.300; RWIGS  =    1.217    wigner-seitz radius (au A)
   ENMAX  =  287.568; ENMIN  =  215.676 eV
   ICORE  =        3    local potential
   LCOR   =        T    correct aug charges
   LPAW   =        T    paw PP
   EAUG   =  531.356
   DEXC   =     .000
   RMAX   =    2.719    core radius for proj-oper
   RAUG   =    1.300    factor for augmentation sphere
   RDEP   =    2.318    radius for radial grids
   QCUT   =   -4.597; QGAM   =    9.195    optimization parameters
```

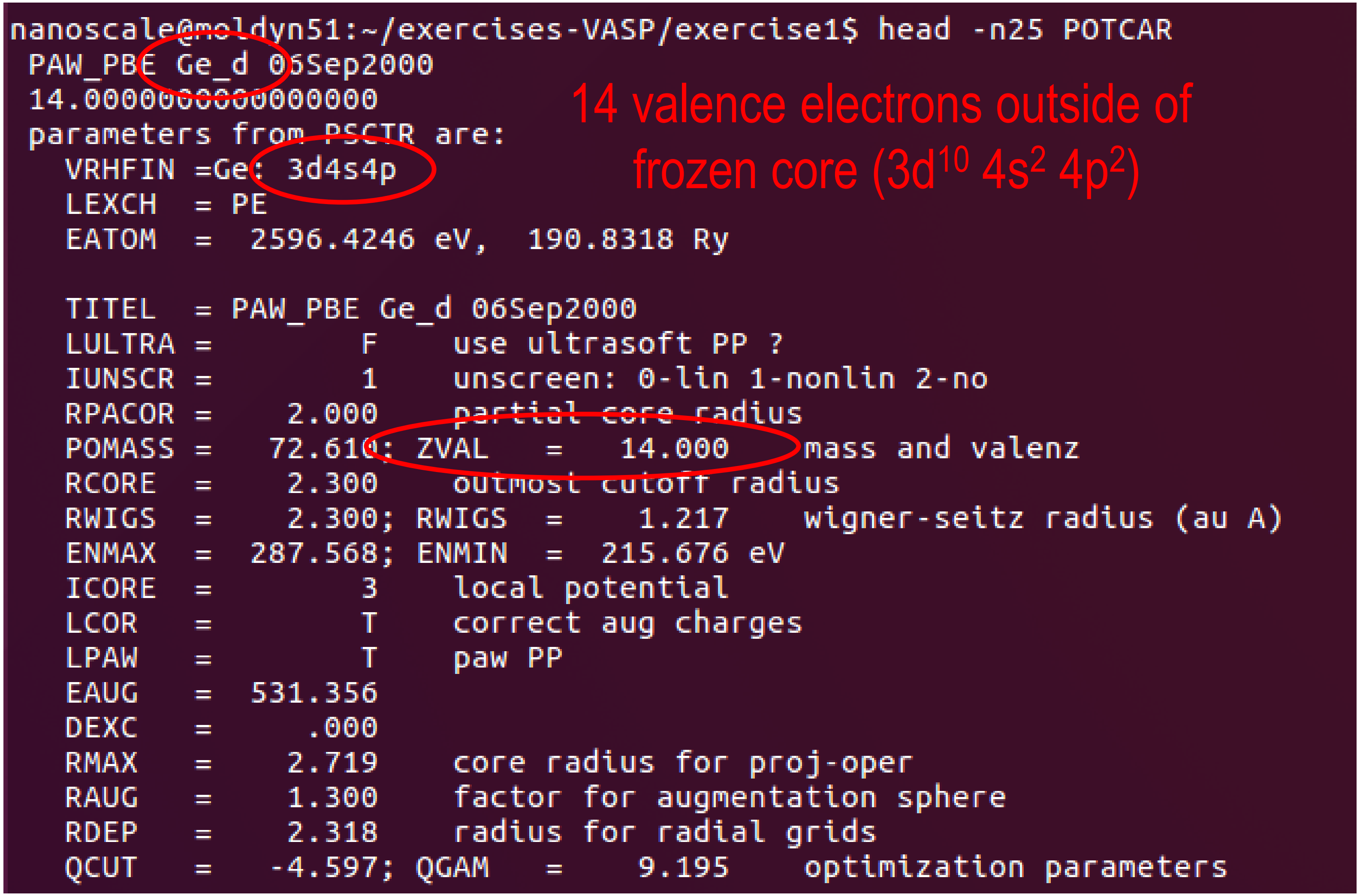
POTCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ head -n25 POTCAR
 PAW_PBE Ge_d 06Sep2000
 14.0000000000000000
 parameters from PSCTR are:
   VRHFIN =Ge: 3d4s4p
   LEXCH  = PE
   EATOM  =  2396.4246 eV,  190.8318 Ry

   TITEL  = PAW_PBE Ge_d 06Sep2000
   LULTRA =        F    use ultrasoft PP ?
   IUNSCR =        1    unscreen: 0-lin 1-nonlin 2-no
   RPACOR =    2.000    partial core radius
   POMASS =   72.610; ZVAL   =   14.000    mass and valenz
   RCORE  =    2.300    outmost cutoff radius
   RWIGS  =    2.300; RWIGS  =    1.217    wigner-seitz radius (au A)
   ENMAX  =  287.568; ENMIN  =  215.676 eV
   ICORE  =        3    local potential
   LCOR   =        T    correct aug charges
   LPAW   =        T    paw PP
   EAUG   =  531.356
   DEXC   =     .000
   RMAX   =    2.719    core radius for proj-oper
   RAUG   =    1.300    factor for augmentation sphere
   RDEP   =    2.318    radius for radial grids
   QCUT   =   -4.597; QGAM   =    9.195    optimization parameters
```

generated using the PBE functional

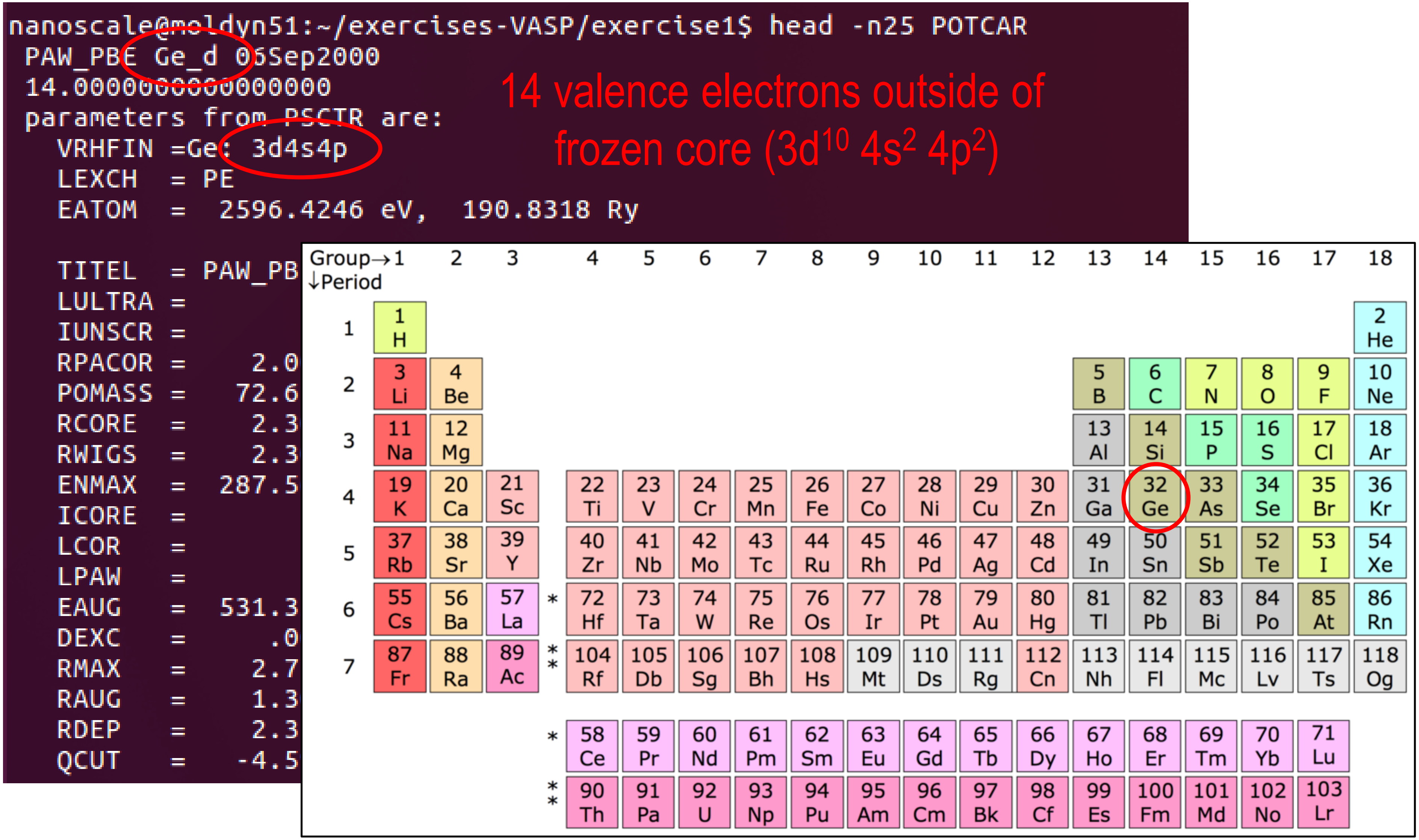
POTCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ head -n25 POTCAR
 PAW_PBE Ge_d 06Sep2000
 14.0000000000000000
 parameters from PSCTR are:
   VRHFIN =Ge: 3d4s4p
   LEXCH  = PE
   EATOM  =  2596.4246 eV,  190.8318 Ry

   TITEL  = PAW_PBE Ge_d 06Sep2000
   LULTRA =        F    use ultrasoft PP ?
   IUNSCR =        1    unscreen: 0-lin 1-nonlin 2-no
   RPACOR =    2.000    partial core radius
   POMASS =   72.610; ZVAL   =   14.000    mass and valenz
   RCORE  =    2.300    outmost cutoff radius
   RWIGS  =    2.300; RWIGS  =    1.217    wigner-seitz radius (au A)
   ENMAX  =  287.568; ENMIN  =  215.676 eV
   ICORE  =        3    local potential
   LCOR   =        T    correct aug charges
   LPAW   =        T    paw PP
   EAUG   =  531.356
   DEXC   =     .000
   RMAX   =    2.719    core radius for proj-oper
   RAUG   =    1.300    factor for augmentation sphere
   RDEP   =    2.318    radius for radial grids
   QCUT   =   -4.597; QGAM   =    9.195    optimization parameters
```

14 valence electrons outside of frozen core ($3d^{10}$ $4s^2$ $4p^2$)

POTCAR:

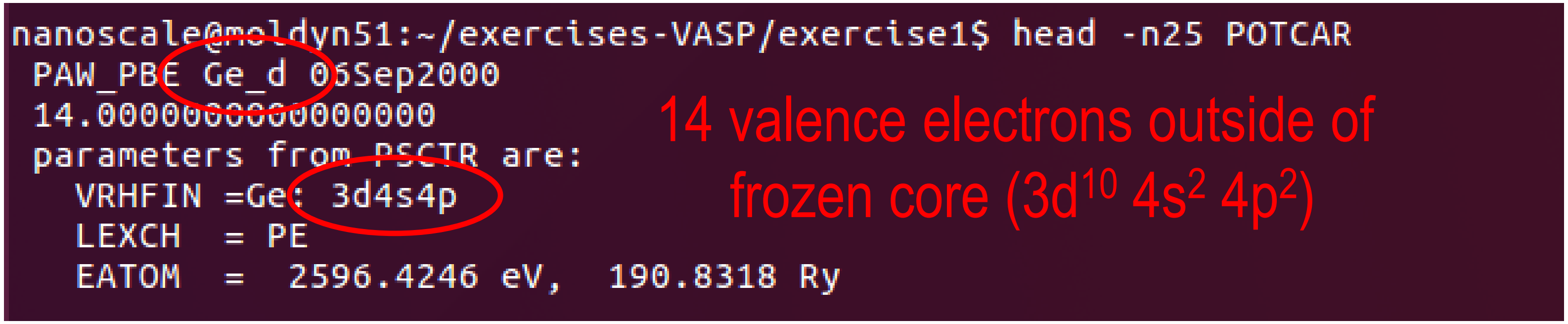


```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ head -n25 POTCAR
 PAW_PBE Ge_d 06Sep2000
 14.0000000000000000
 parameters from PSCTR are:
   VRHFIN =Ge: 3d4s4p
   LEXCH  = PE
   EATOM  =  2596.4246 eV,  190.8318 Ry

   TITEL  = PAW_PB
   LULTRA =
   IUNSCR =
   RPACOR =    2.0
   POMASS =   72.6
   RCORE  =    2.3
   RWIGS  =    2.3
   ENMAX  =  287.5
   ICORE  =
   LCOR   =
   LPAW   =
   EAUG   =  531.3
   DEXC   =     .0
   RMAX   =    2.7
   RAUG   =    1.3
   RDEP   =    2.3
   QCUT   =   -4.5
```

14 valence electrons outside of frozen core ($3d^{10}$ $4s^2$ $4p^2$)

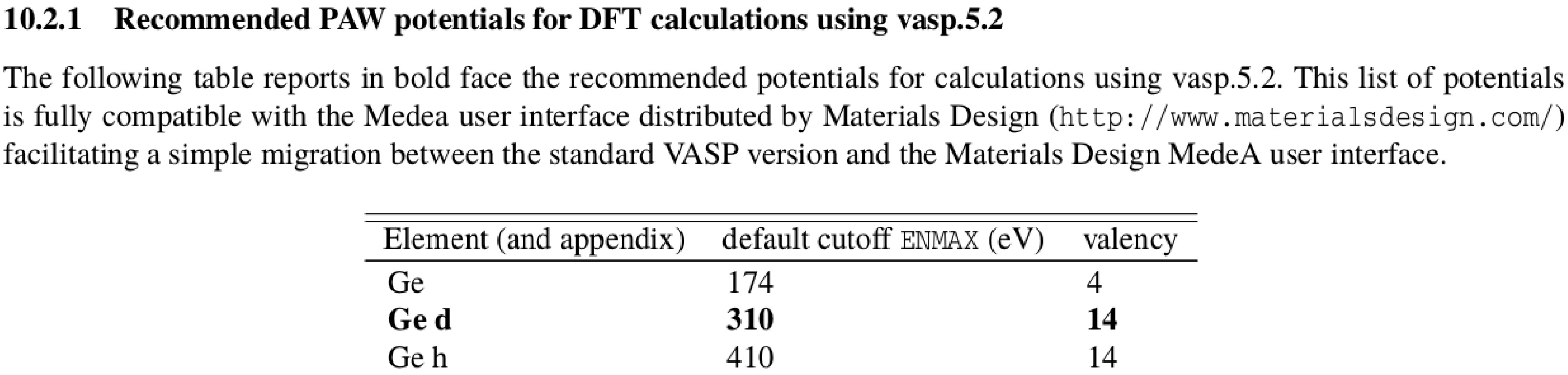
Group→ ↓Period	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
				*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
				**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

POTCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ head -n25 POTCAR
 PAW_PBE Ge_d 06Sep2000
 14.0000000000000000
 parameters from PSCTR are:
   VRHFIN =Ge: 3d4s4p
   LEXCH  = PE
   EATOM  =  2596.4246 eV,  190.8318 Ry
```

14 valence electrons outside of frozen core ($3d^{10}$ $4s^2$ $4p^2$)



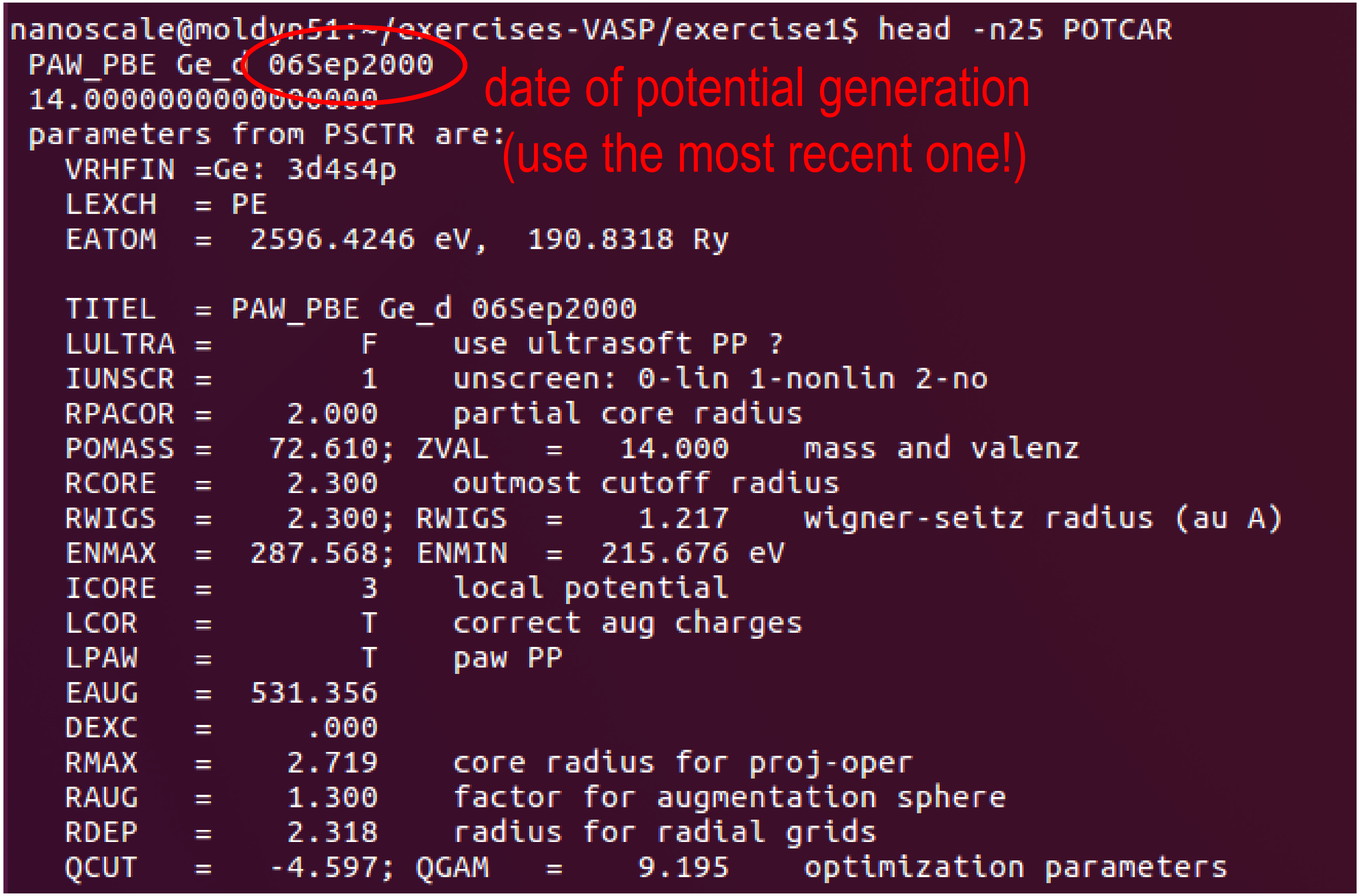
10.2.1 Recommended PAW potentials for DFT calculations using vasp.5.2

The following table reports in bold face the recommended potentials for calculations using vasp.5.2. This list of potentials is fully compatible with the Medea user interface distributed by Materials Design (`http://www.materialsdesign.com/`) facilitating a simple migration between the standard VASP version and the Materials Design MedeA user interface.

Element (and appendix)	default cutoff `ENMAX` (eV)	valency
Ge	174	4
Ge d	**310**	**14**
Ge h	410	14

check the VASP manual!

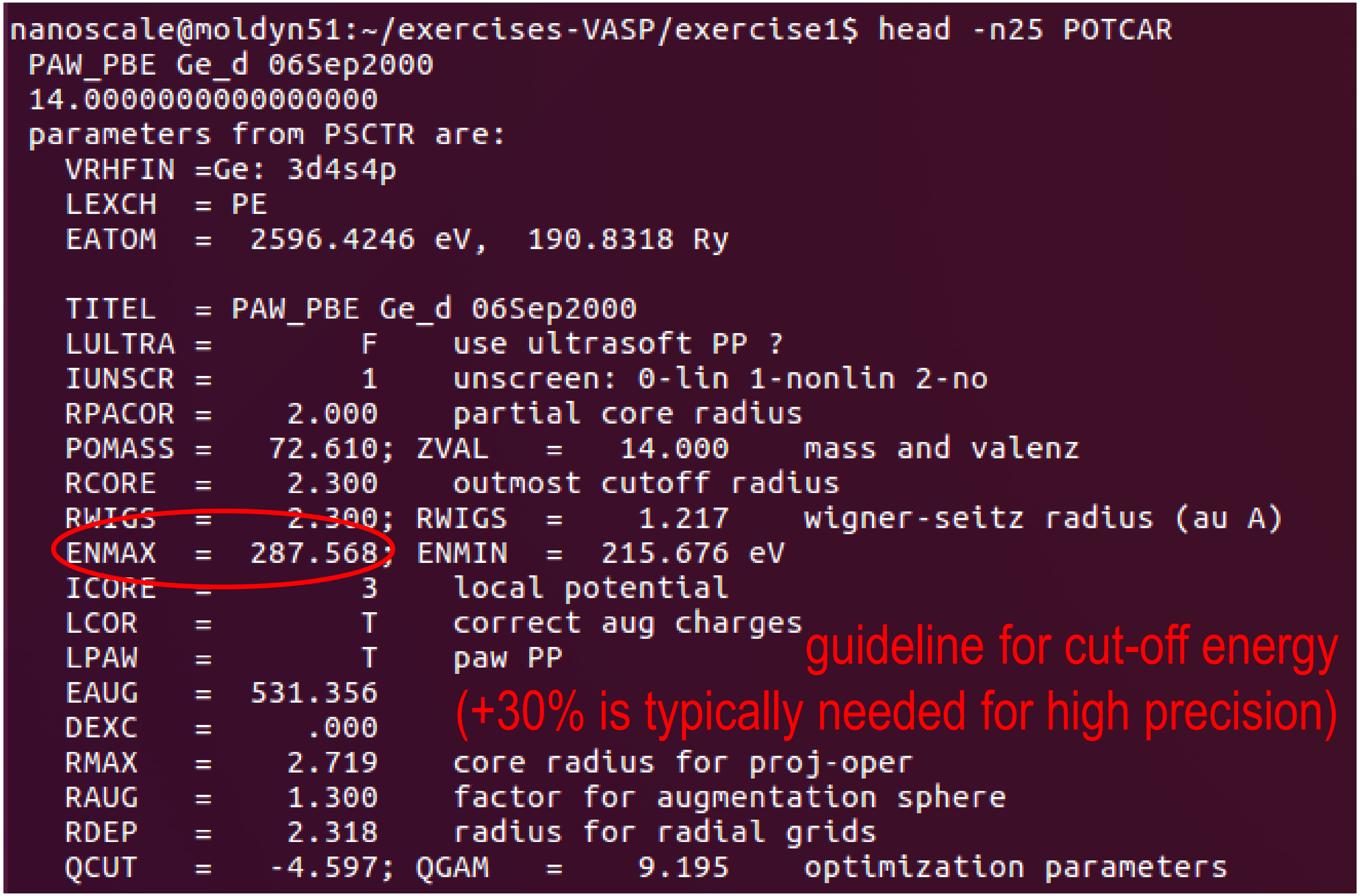
POTCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ head -n25 POTCAR
 PAW_PBE Ge_d 06Sep2000
 14.0000000000000000
 parameters from PSCTR are:
   VRHFIN =Ge: 3d4s4p
   LEXCH  = PE
   EATOM  =  2596.4246 eV,  190.8318 Ry

   TITEL  = PAW_PBE Ge_d 06Sep2000
   LULTRA =        F    use ultrasoft PP ?
   IUNSCR =        1    unscreen: 0-lin 1-nonlin 2-no
   RPACOR =    2.000    partial core radius
   POMASS =   72.610; ZVAL   =   14.000    mass and valenz
   RCORE  =    2.300    outmost cutoff radius
   RWIGS  =    2.300; RWIGS  =    1.217    wigner-seitz radius (au A)
   ENMAX  =  287.568; ENMIN  =  215.676 eV
   ICORE  =        3    local potential
   LCOR   =        T    correct aug charges
   LPAW   =        T    paw PP
   EAUG   =  531.356
   DEXC   =     .000
   RMAX   =    2.719    core radius for proj-oper
   RAUG   =    1.300    factor for augmentation sphere
   RDEP   =    2.318    radius for radial grids
   QCUT   =   -4.597; QGAM   =    9.195    optimization parameters
```

date of potential generation
(use the most recent one!)

POTCAR:

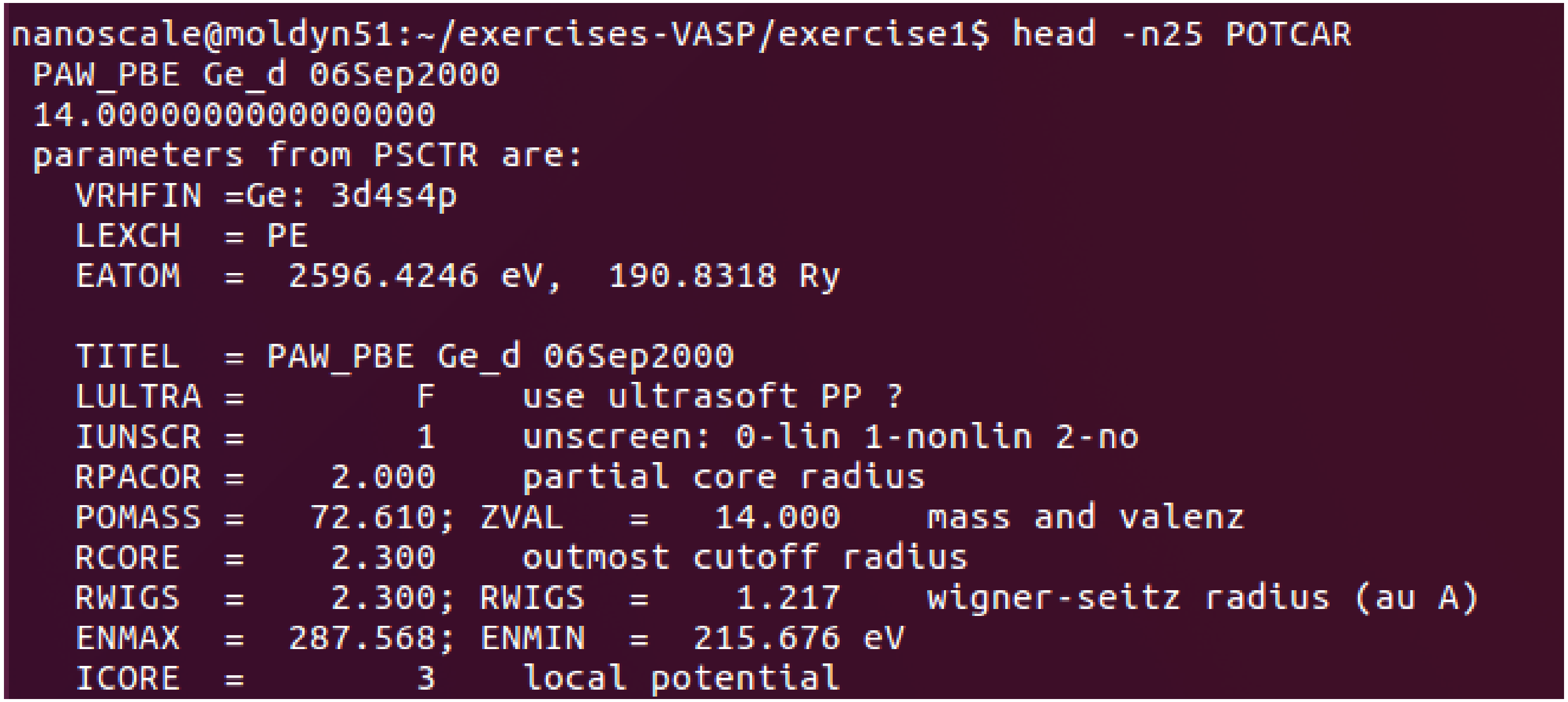


```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ head -n25 POTCAR
 PAW_PBE Ge_d 06Sep2000
 14.0000000000000000
 parameters from PSCTR are:
   VRHFIN =Ge: 3d4s4p
   LEXCH  = PE
   EATOM  =  2596.4246 eV,  190.8318 Ry

   TITEL  = PAW_PBE Ge_d 06Sep2000
   LULTRA =        F    use ultrasoft PP ?
   IUNSCR =        1    unscreen: 0-lin 1-nonlin 2-no
   RPACOR =    2.000    partial core radius
   POMASS =   72.610; ZVAL   =   14.000    mass and valenz
   RCORE  =    2.300    outmost cutoff radius
   RWIGS  =    2.300; RWIGS  =    1.217    wigner-seitz radius (au A)
   ENMAX  =  287.568; ENMIN  =  215.676 eV
   ICORE  =        3    local potential
   LCOR   =        T    correct aug charges
   LPAW   =        T    paw PP
   EAUG   =  531.356
   DEXC   =     .000
   RMAX   =    2.719    core radius for proj-oper
   RAUG   =    1.300    factor for augmentation sphere
   RDEP   =    2.318    radius for radial grids
   QCUT   =   -4.597; QGAM   =    9.195    optimization parameters
```

guideline for cut-off energy

(+30% is typically needed for high precision)

POTCAR:



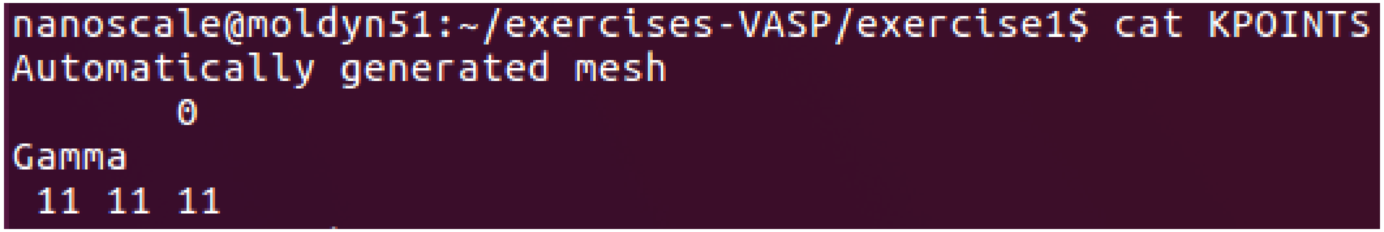
```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ head -n25 POTCAR
 PAW_PBE Ge_d 06Sep2000
 14.0000000000000000
 parameters from PSCTR are:
   VRHFIN =Ge: 3d4s4p
   LEXCH  = PE
   EATOM  =  2596.4246 eV,  190.8318 Ry

   TITEL  = PAW_PBE Ge_d 06Sep2000
   LULTRA =        F    use ultrasoft PP ?
   IUNSCR =        1    unscreen: 0-lin 1-nonlin 2-no
   RPACOR =    2.000    partial core radius
   POMASS =   72.610; ZVAL   =   14.000    mass and valenz
   RCORE  =    2.300    outmost cutoff radius
   RWIGS  =    2.300; RWIGS  =    1.217    wigner-seitz radius (au A)
   ENMAX  =  287.568; ENMIN  =  215.676 eV
   ICORE  =        3    local potential
```

multi-atom POTCAR? `cat POTCAR1 POTCAR2 … > POTCAR`

in the same order as in the POSCAR!

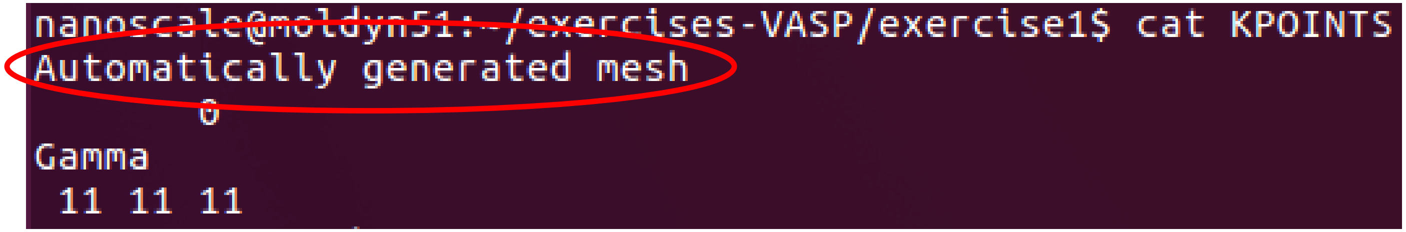
CAUTION! the POTCAR overwrites atom type information in the POSCAR

KPOINTS:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat KPOINTS
Automatically generated mesh
       0
Gamma
 11 11 11
```

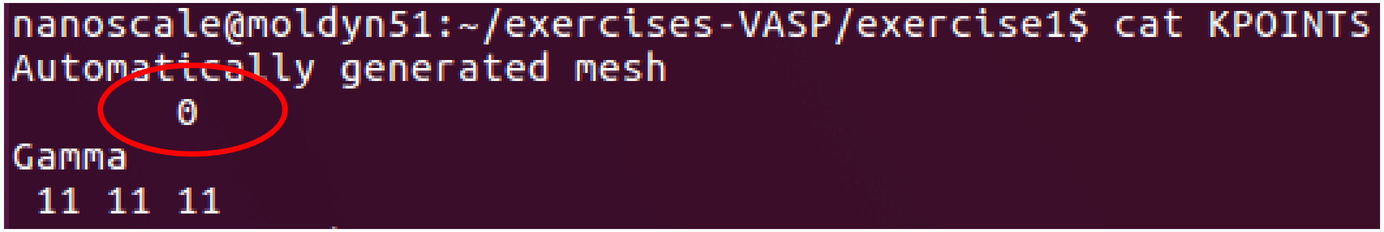
KPOINTS:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat KPOINTS
Automatically generated mesh
       0
Gamma
 11  11  11
```

title (free format)

KPOINTS:

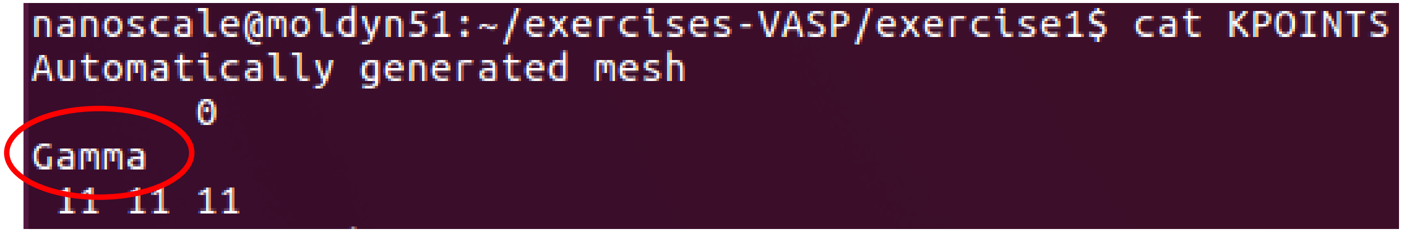


```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat KPOINTS
Automatically generated mesh
       0
Gamma
 11  11  11
```

title (free format)

number of k-points (manual mode) or 0 (automatic k-point mesh)

KPOINTS:



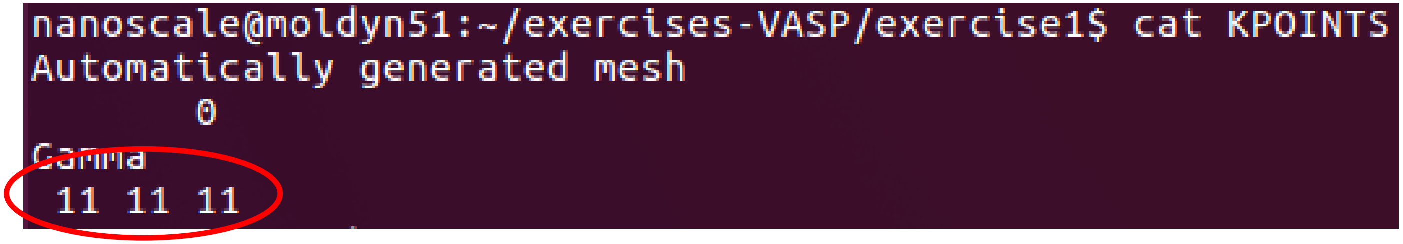
```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat KPOINTS
Automatically generated mesh
       0
Gamma
 11 11 11
```

title (free format)

number of k-points (manual mode) or 0 (automatic k-point mesh)

k-mesh type: Γ- (`Gamma`) or non- Γ-centred (`Monkhorst-Pack`)

KPOINTS:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat KPOINTS
Automatically generated mesh
       0
Gamma
 11  11  11
```

title (free format)

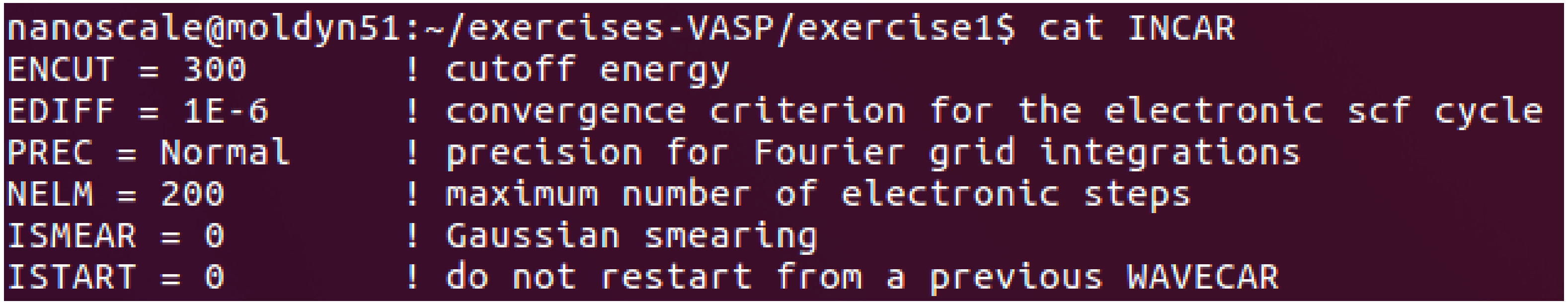
number of k-points (manual mode) or 0 (automatic k-point mesh)

k-mesh type: Γ- (`Gamma`) or non- Γ-centred (`Monkhorst-Pack`)

number of k-points in each reciprocal lattice direction

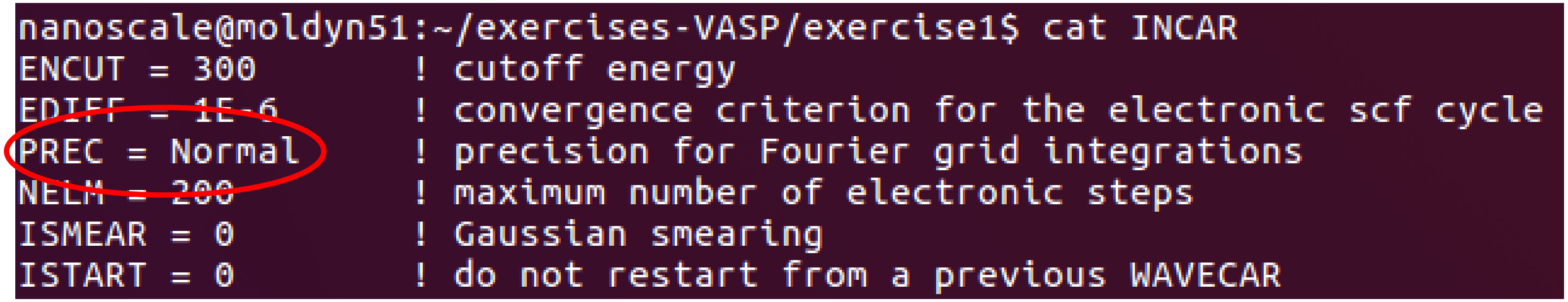
note: in practice, fewer k-points calculated due to symmetric equivalency (so-called irreducible Brillouin zone, see output file IBZKPT)

INCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat INCAR
ENCUT = 300       ! cutoff energy
EDIFF = 1E-6      ! convergence criterion for the electronic scf cycle
PREC = Normal     ! precision for Fourier grid integrations
NELM = 200        ! maximum number of electronic steps
ISMEAR = 0        ! Gaussian smearing
ISTART = 0        ! do not restart from a previous WAVECAR
```

INCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat INCAR
ENCUT = 300          ! cutoff energy
EDIFF = 1E-6         ! convergence criterion for the electronic scf cycle
PREC = Normal        ! precision for Fourier grid integrations
NELM = 200           ! maximum number of electronic steps
ISMEAR = 0           ! Gaussian smearing
ISTART = 0           ! do not restart from a previous WAVECAR
```

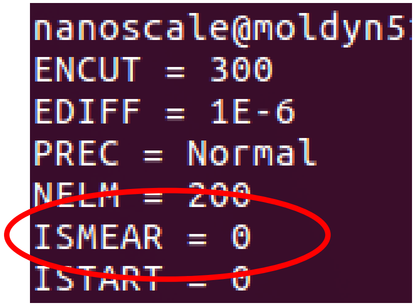
$$\left[-\frac{1}{2}\nabla^2+\sum_{\alpha=1}^{M}\left(-\frac{Z_\alpha}{|\bar{r}-\bar{R}_\alpha|}\right)+\int\frac{\rho(\bar{r}')}{|\bar{r}-\bar{r}'|}+v_{xc}(\bar{r})\right]\varphi_k(\bar{r})=\epsilon_k\varphi_k(\bar{r})$$

solving the Kohn-Sham equation is often easier in reciprocal space

⇩

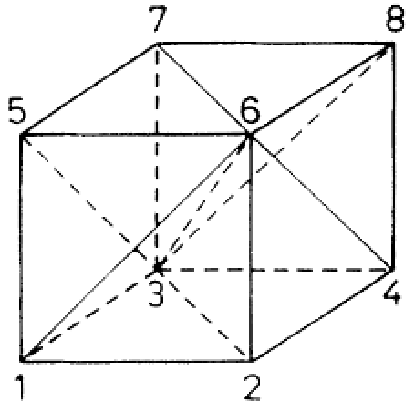
Fast Fourier Transform from real-space grid to reciprocal space
(dense grid is better, see e.g. Nyquist theorem → use `Accurate` in your thesis)

INCAR:

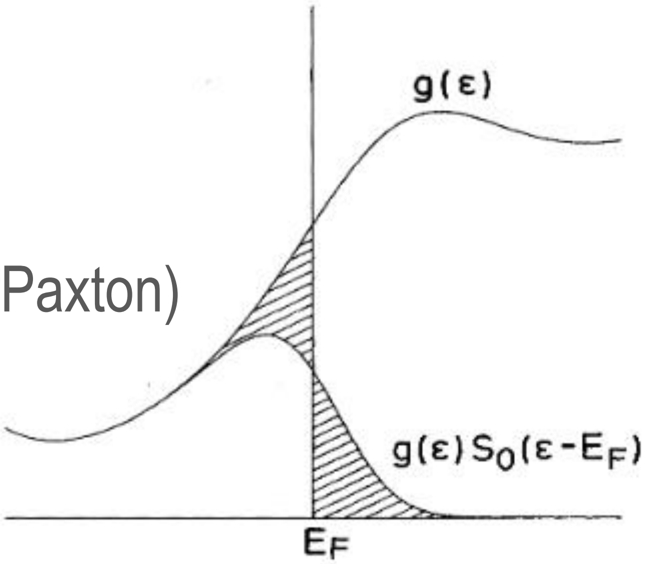


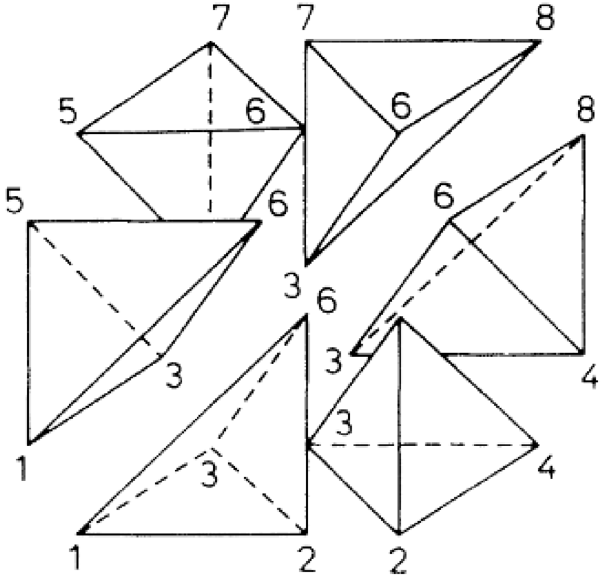
```
nanoscale@moldyn5
ENCUT = 300
EDIFF = 1E-6
PREC = Normal
NELM = 200
ISMEAR = 0
ISTART = 0
```

smearing is a technique to spread electrons over unoccupied levels to improve convergence



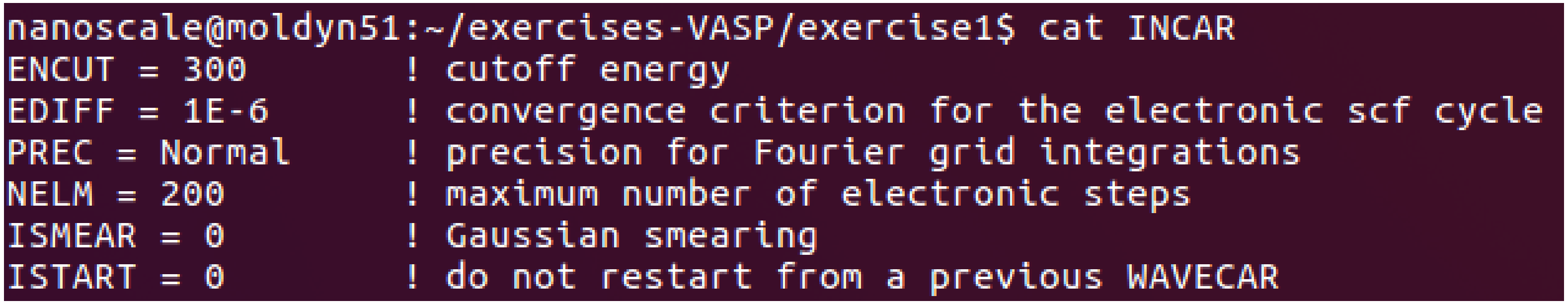
ISMEAR 0 (Gaussian)
when band gap
ISMEAR 1 (Methfessel-Paxton)
for metals





ISMEAR -5 (tetrahedron method)
accurate but not suitable for relaxation of metals (wrong forces)

INCAR:



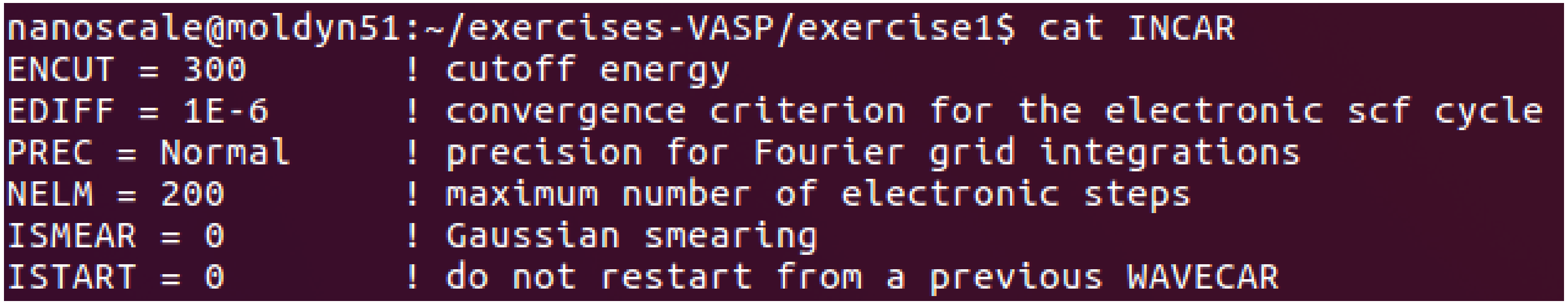
```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat INCAR
ENCUT = 300       ! cutoff energy
EDIFF = 1E-6      ! convergence criterion for the electronic scf cycle
PREC = Normal     ! precision for Fourier grid integrations
NELM = 200        ! maximum number of electronic steps
ISMEAR = 0        ! Gaussian smearing
ISTART = 0        ! do not restart from a previous WAVECAR
```

in this tutorial, all calculations are on 1 CPU

for your thesis, use more CPUs on the HPC with appropriate parallelization!
NCORE = # cores / node (semilocal functionals) or 1 (hybrid functionals, GW, …)
KPAR = # nodes (semilocal functionals) or as high as possible (hybrid xc, GW, …)

CAUTION! higher parallelization leads to higher RAM memory

INCAR:



```
nanoscale@moldyn51:~/exercises-VASP/exercise1$ cat INCAR
ENCUT = 300         ! cutoff energy
EDIFF = 1E-6        ! convergence criterion for the electronic scf cycle
PREC = Normal       ! precision for Fourier grid integrations
NELM = 200          ! maximum number of electronic steps
ISMEAR = 0          ! Gaussian smearing
ISTART = 0          ! do not restart from a previous WAVECAR
```

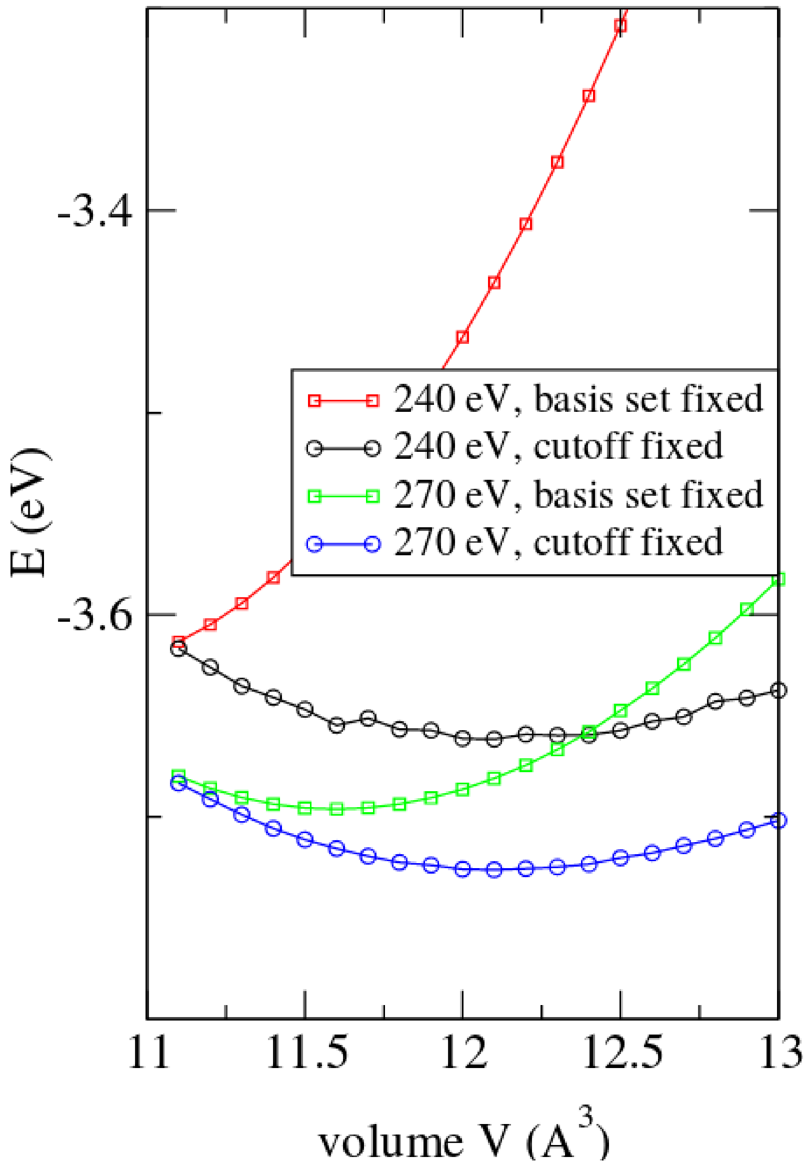
many more keywords possible: have a look at the VASP manual!

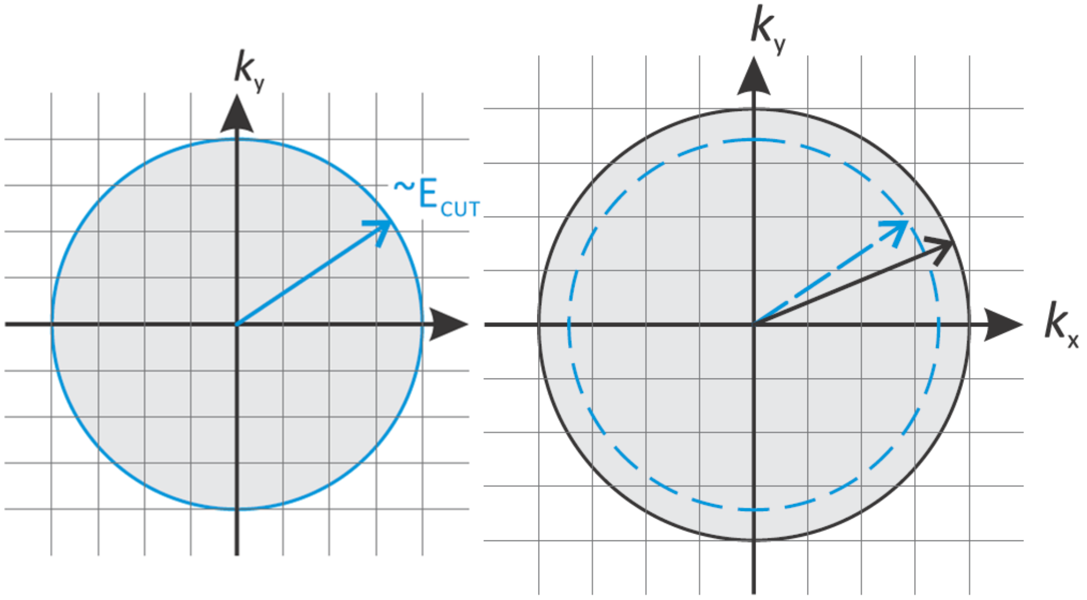
many output files:

OUTCAR:	all information on the electronic and ionic convergence cycles
vasprun.xml:	similar to OUTCAR, but in xml format
OSZICAR:	summary of the electronic and ionic convergence
CONTCAR:	geometry after relaxation
IBZKPT:	k-points in the irreducible Brillouin zone
EIGENVAL:	electronic energy levels and occupation for each k-point
WAVECAR:	wavefunction expansion coefficients → for restart purposes
CHG(CAR):	charge density → for analysis and restart purposes

… dedicated output files for different types of calculations

Pulay effect





E_{CUT} determines sphere in reciprocal space

sphere expands as if E_{CUT} becomes larger

Shrink in real space

Birch-Murnaghan equation of state

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right]^3 B_0' + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right]^2\left[6-4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\}$$