Density-Functional Theory for Practitioners - Tutorial 3

Orlando Silveira Júnior, Adolfo Otero Fumega and Ondřej Krejčí,
(Developed by Patrick Rinke and Milica Todorović)

Aalto University
School of Science
Department of Applied Physics

Aalto University
School of Science

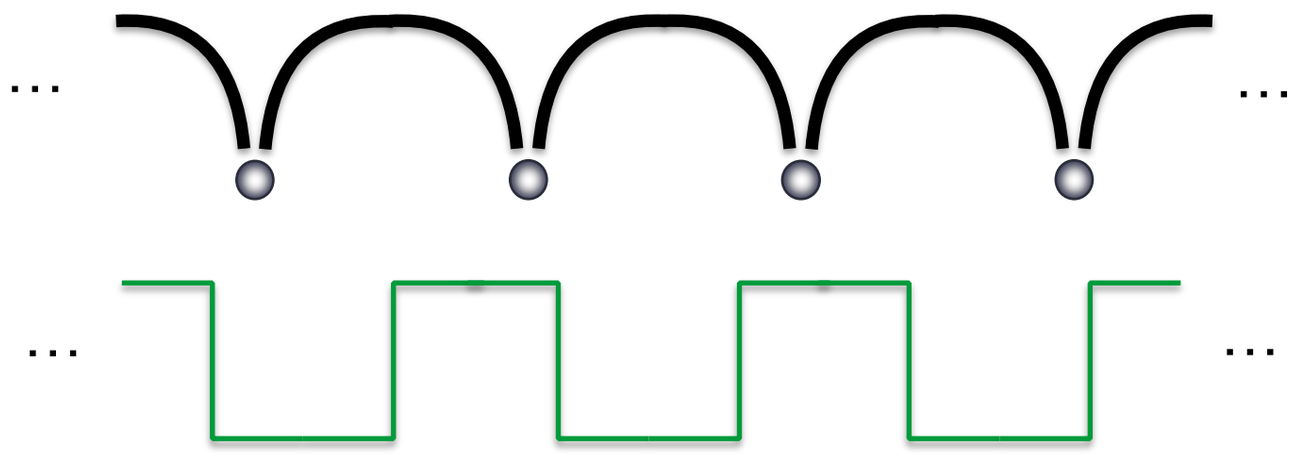
House Keeping – Bloch Theorem

periodic potential:
(translational symmetry)

$$U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$$

R is one of our lattice vectors:

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$



Then you can find solution Schrödinger equation with that potential in this form:

Still 1 e⁻ wavefunction

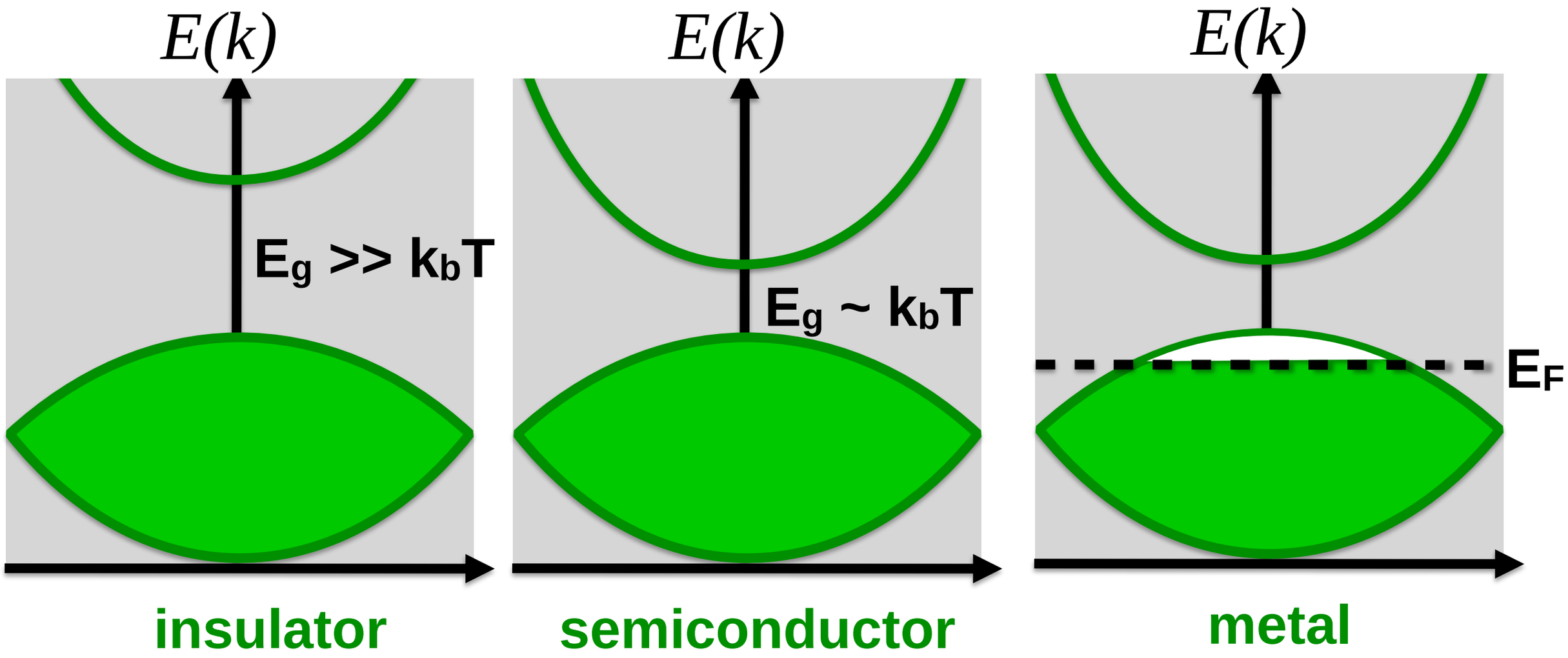
$$\psi(\mathbf{r}) = e^{i\mathbf{kr}}u(\mathbf{r})$$

Phase factor

$$u(\mathbf{r}+\mathbf{R}) = u(\mathbf{r})$$

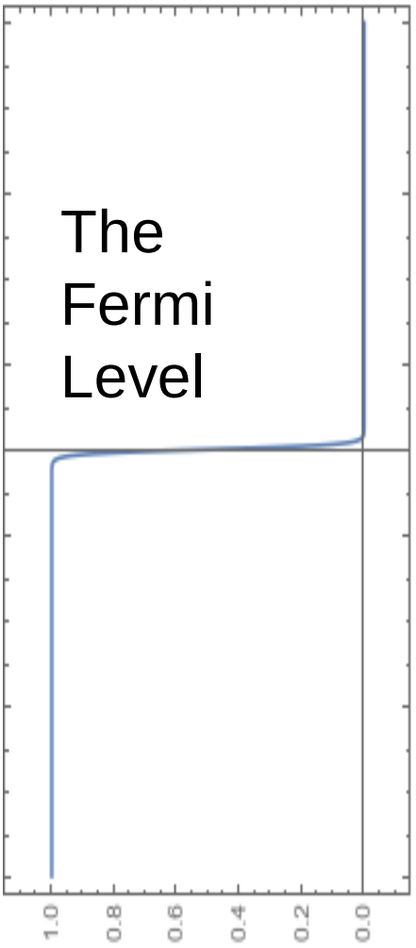
Periodically repeating part

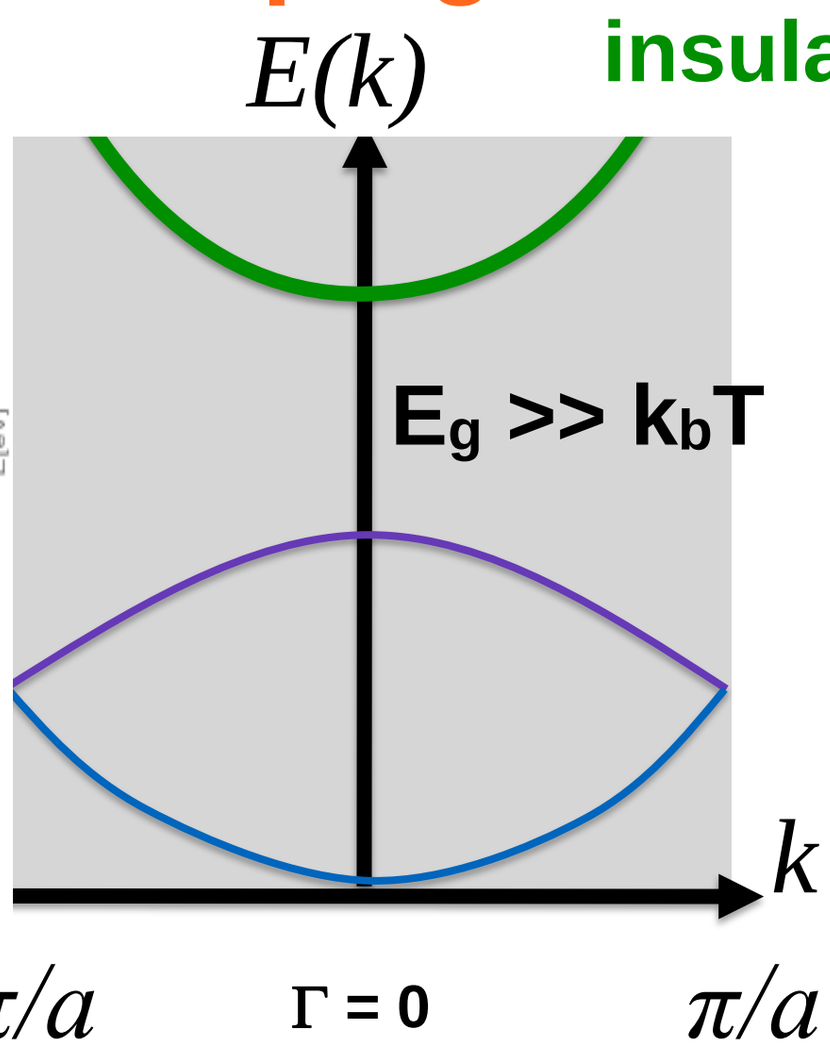
House Keeping – Band structure confusion

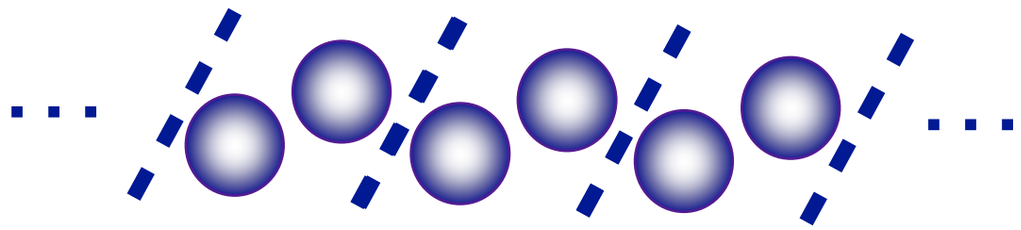


The Fermi energy marks the energy of the highest occupied state.

House Keeping – 1D chain of “2He atoms”

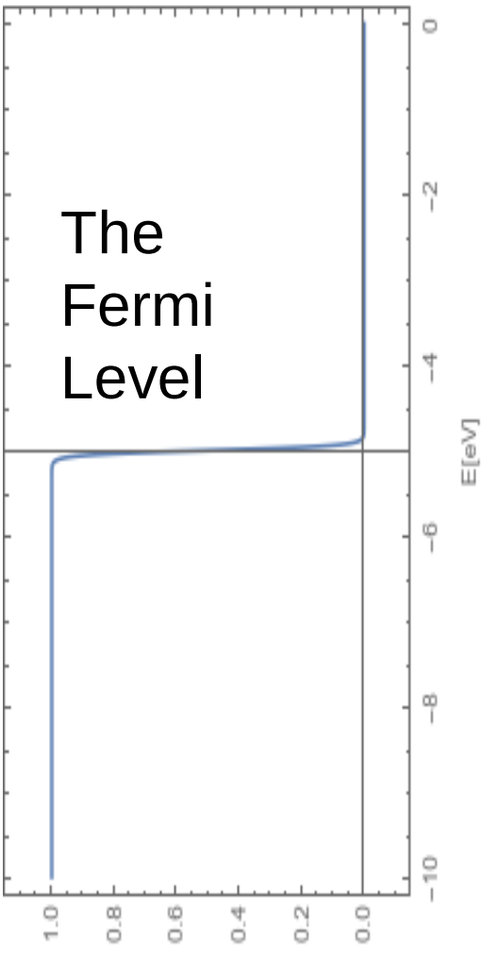




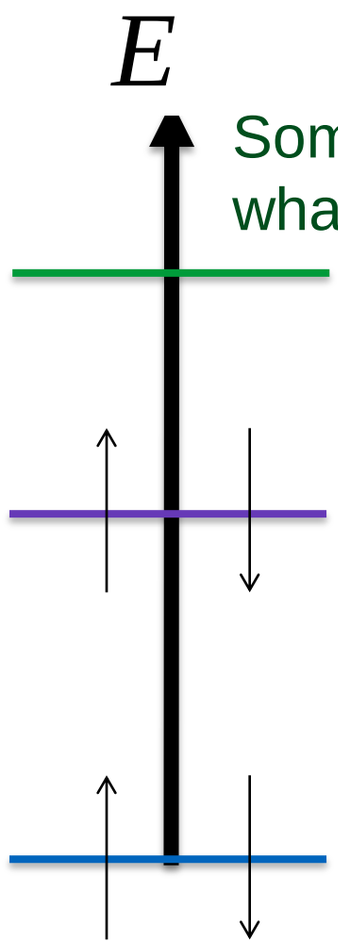


The Fermi energy marks the energy of the highest occupied state.

House Keeping – Back to molecule “2He atoms”

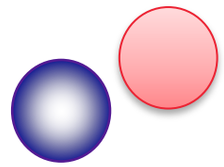


Occupancy

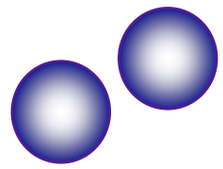


Phase of the 1s orbital

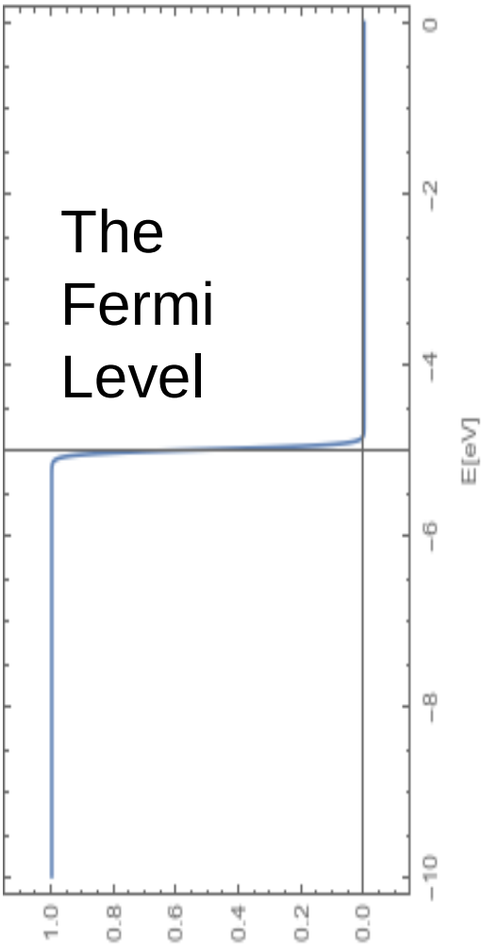
antibonding

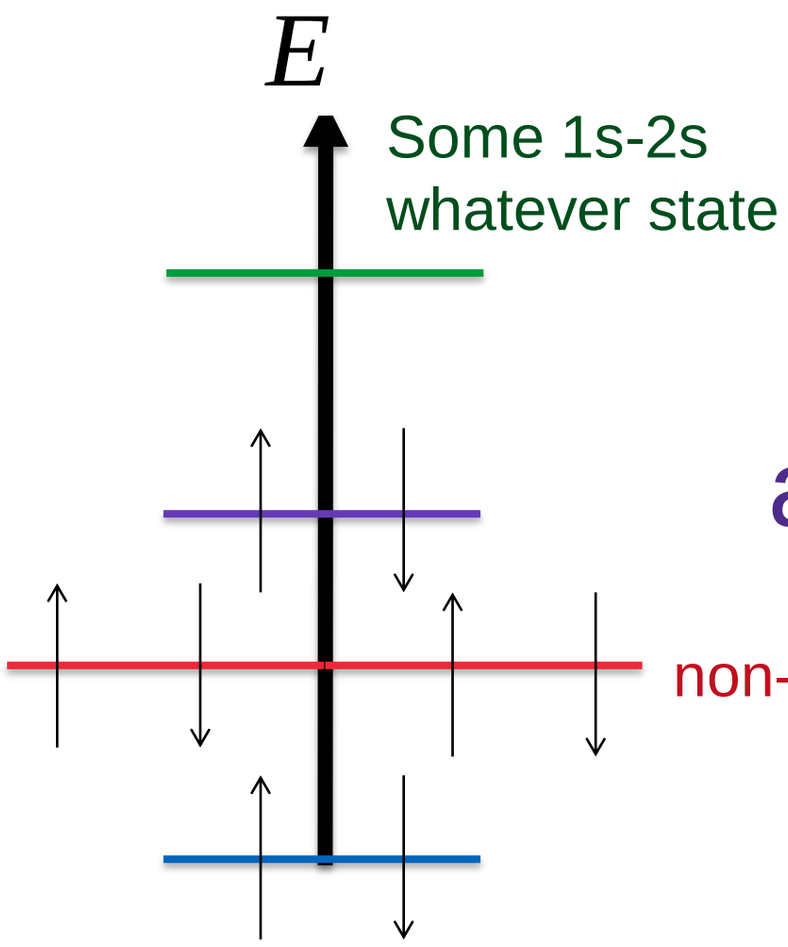


bonding

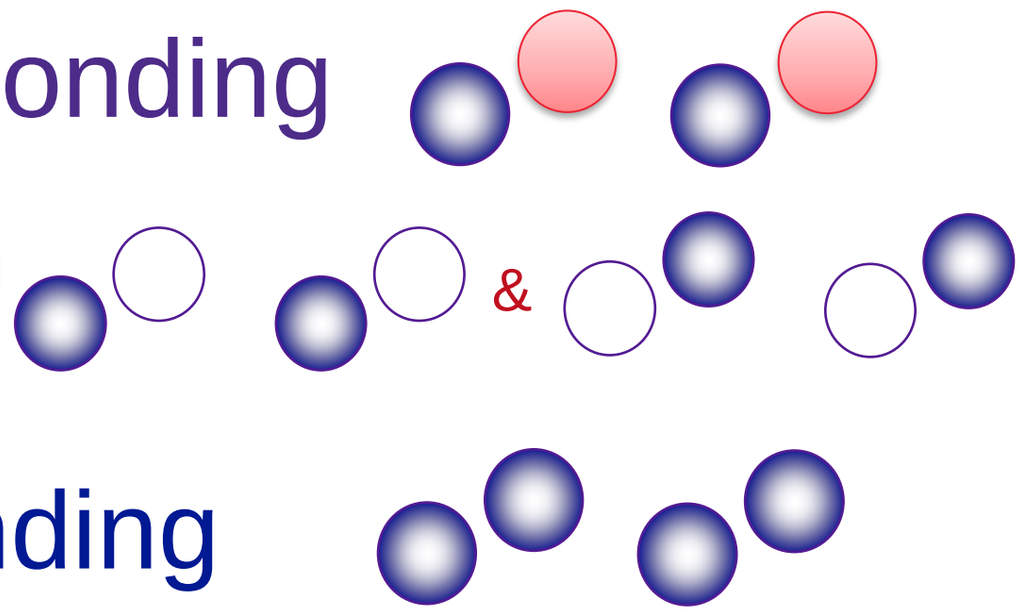


House Keeping – Back to molecule “4He atoms”

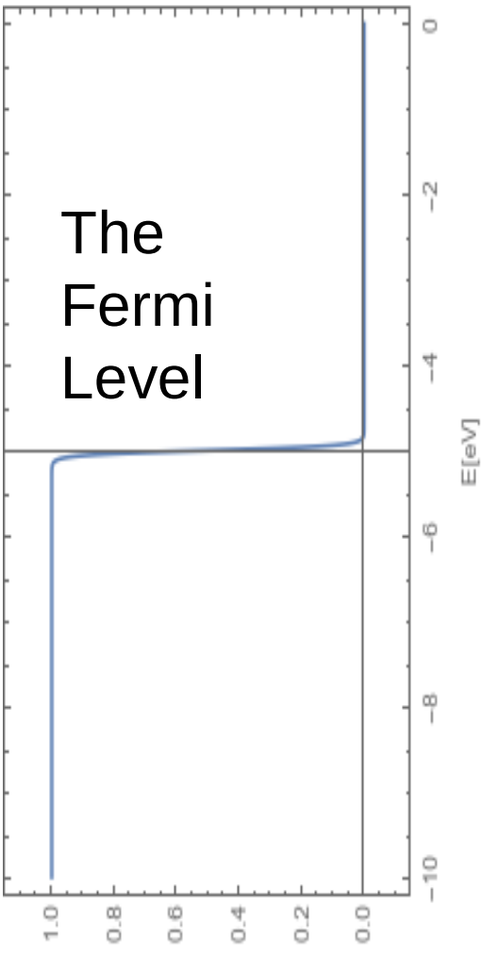




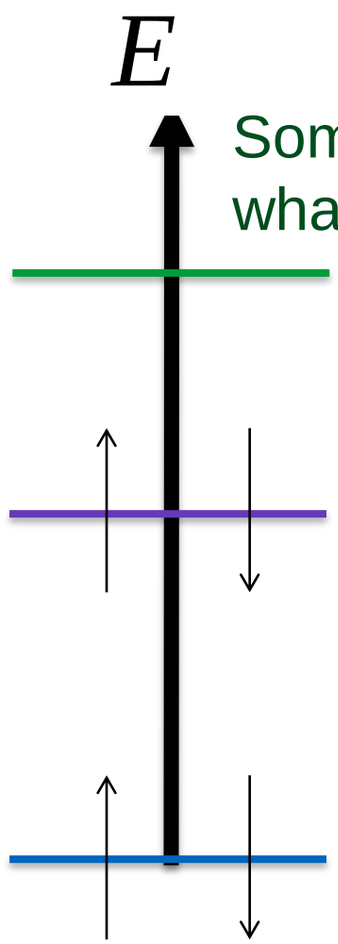
Phase of the 1s orbital



House Keeping – Back to molecule “2He atoms”

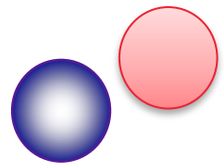


Occupancy

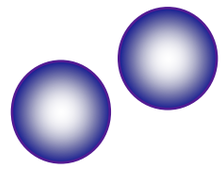


Phase of the 1s orbital

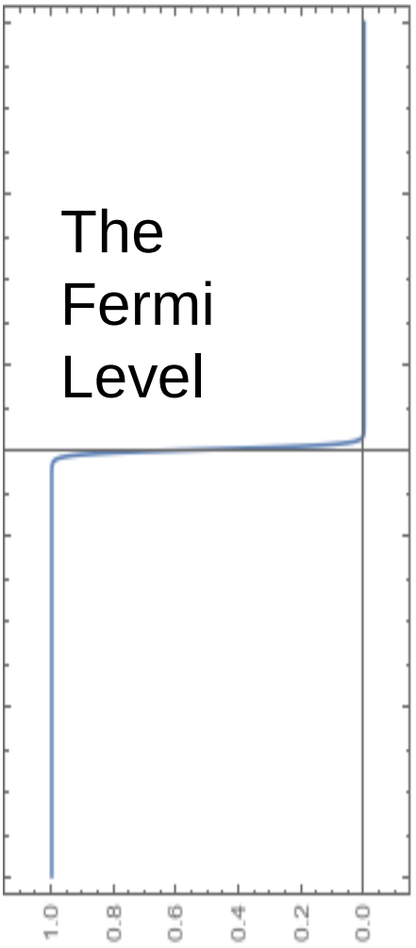
antibonding

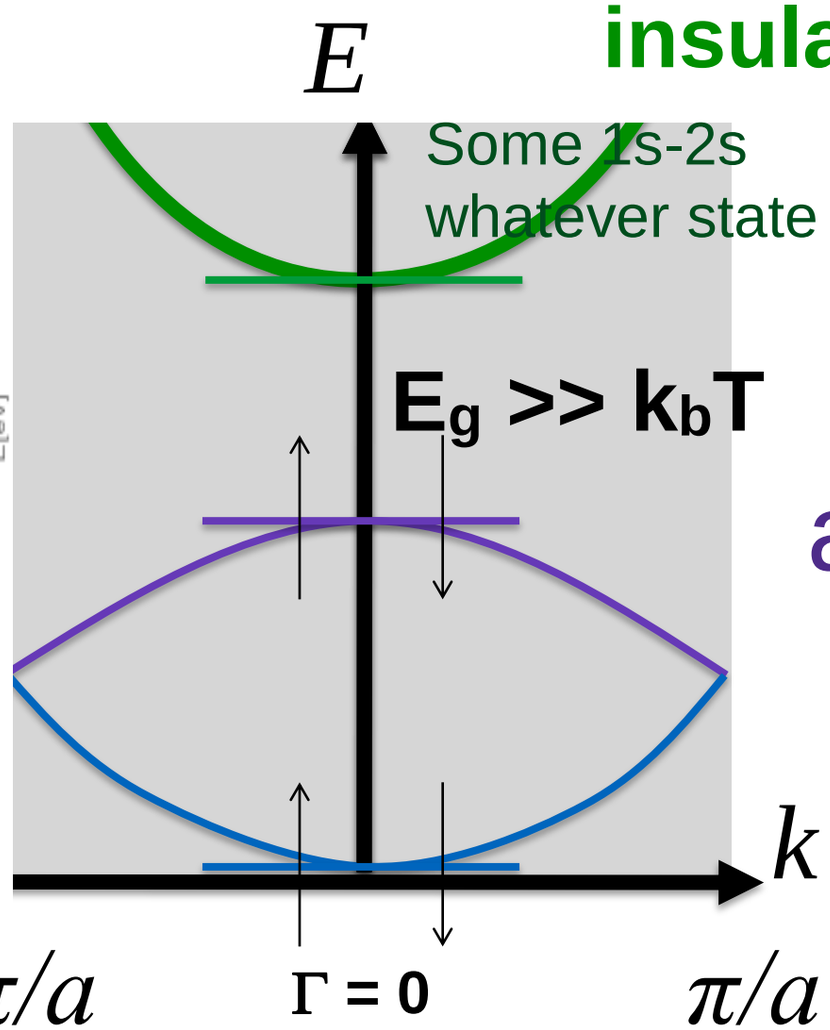


bonding



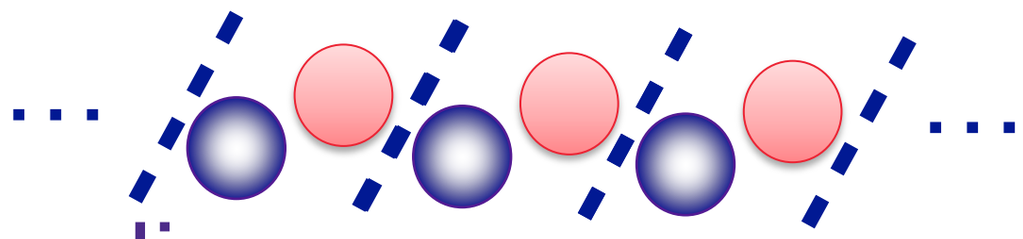
House Keeping – 1D chain of “2He atoms”





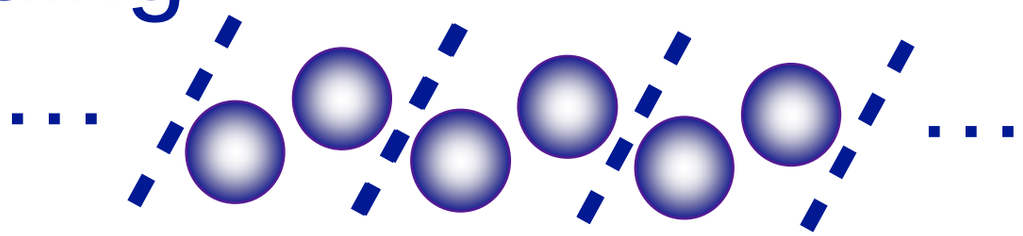
insulator

Phase of the 1s orbital



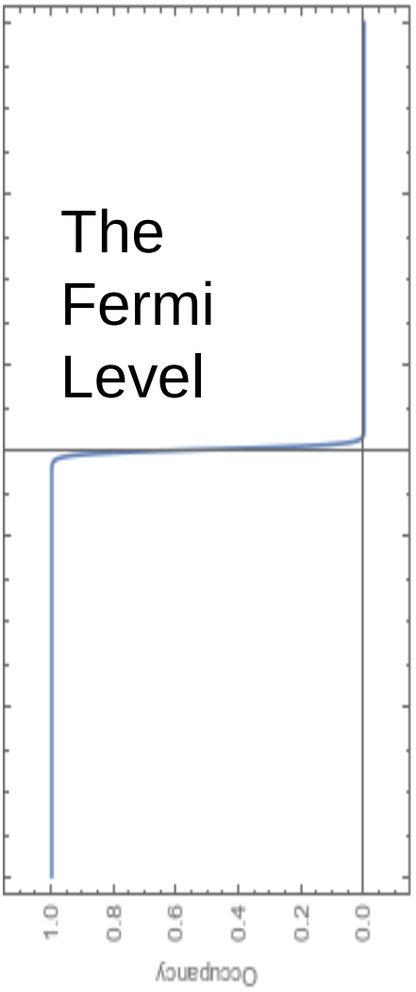
antibonding

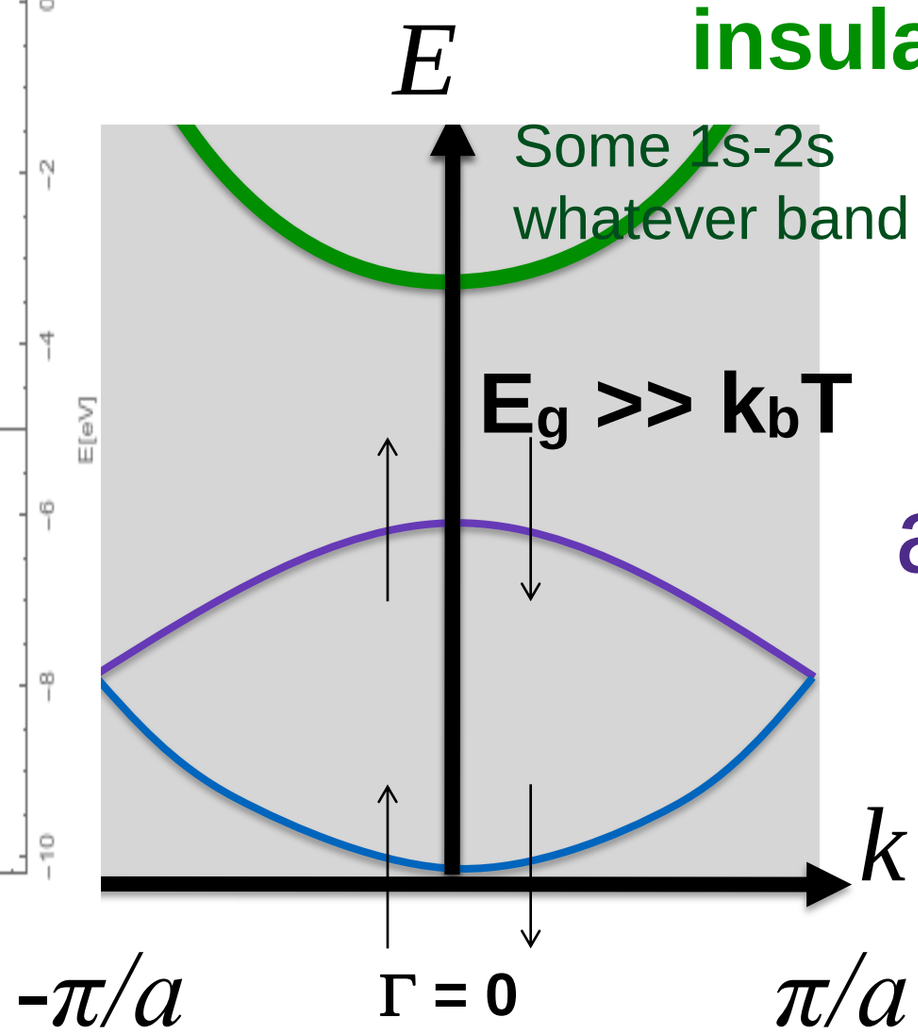
bonding



Only 2 atoms in the unit cells – 4 e^-

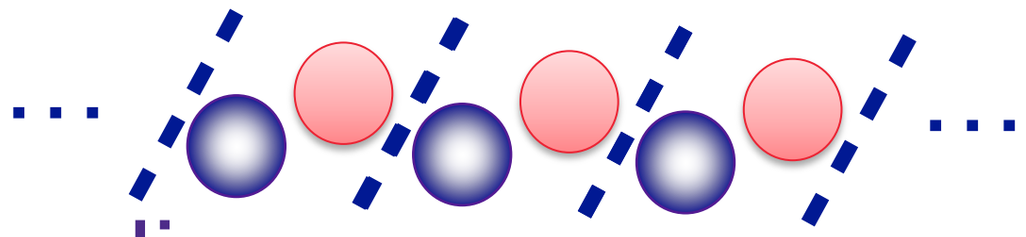
House Keeping – 1D chain of “2He atoms”





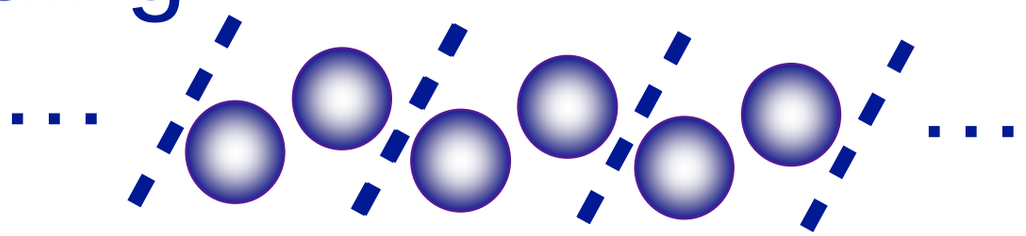
insulator

Phase of the 1s orbital



antibonding

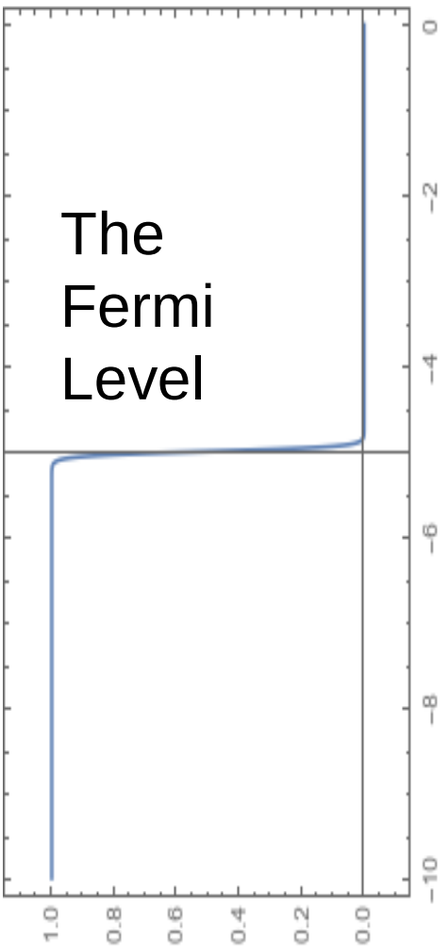
bonding

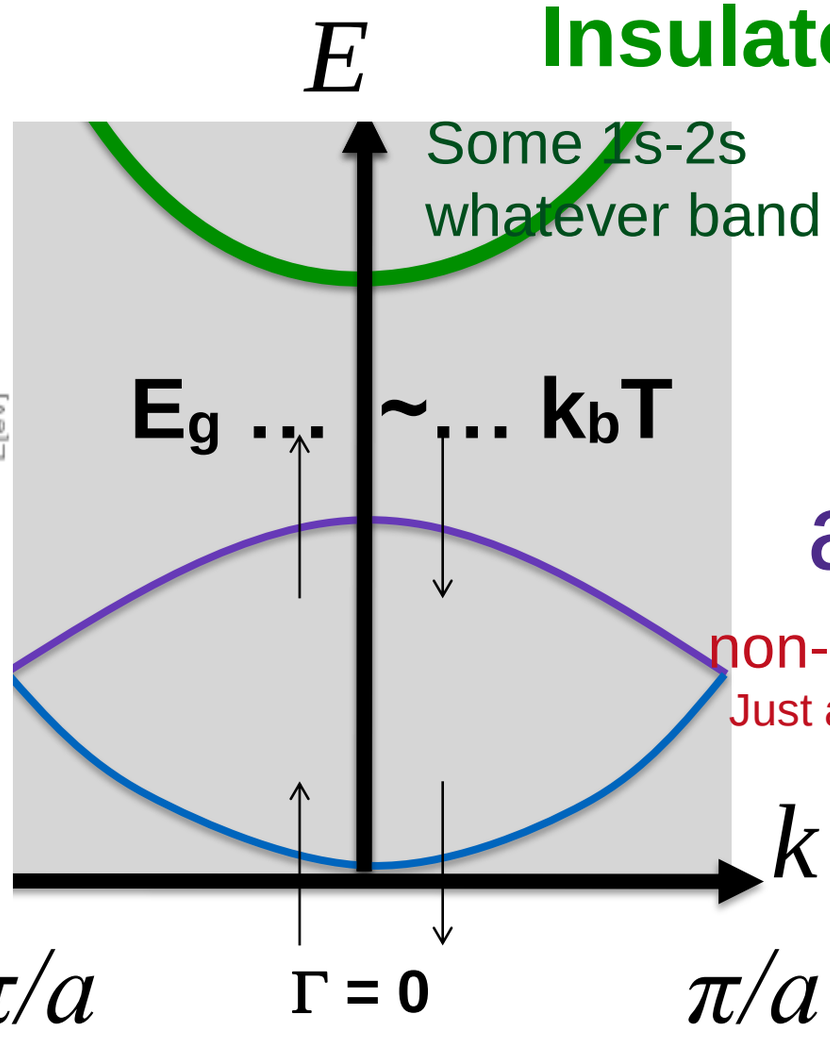


Only 2 atoms in the unit cells – 4 e^-

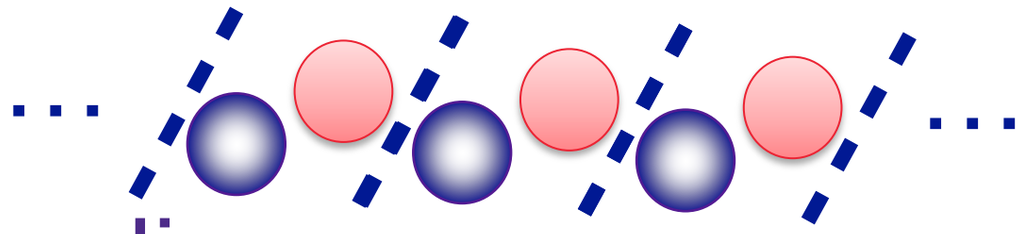
House Keeping – 1D chain of “2He atoms”

Insulator vs. Semiconductor





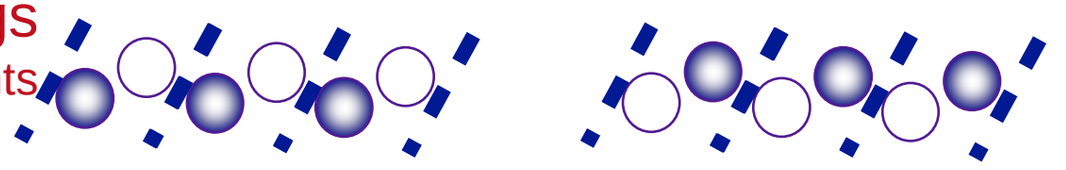
Phase of the 1s orbital



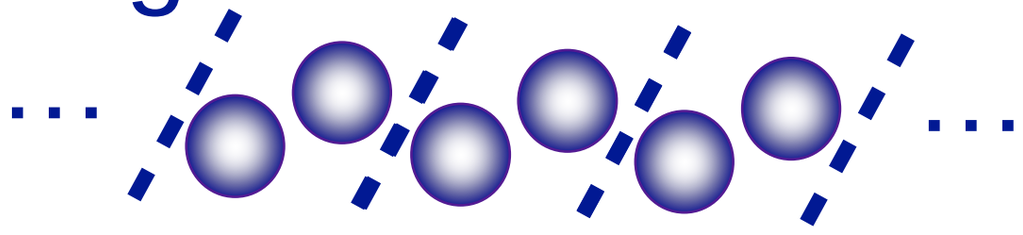
antibonding

non-bondings

Just at 2 **k**-points



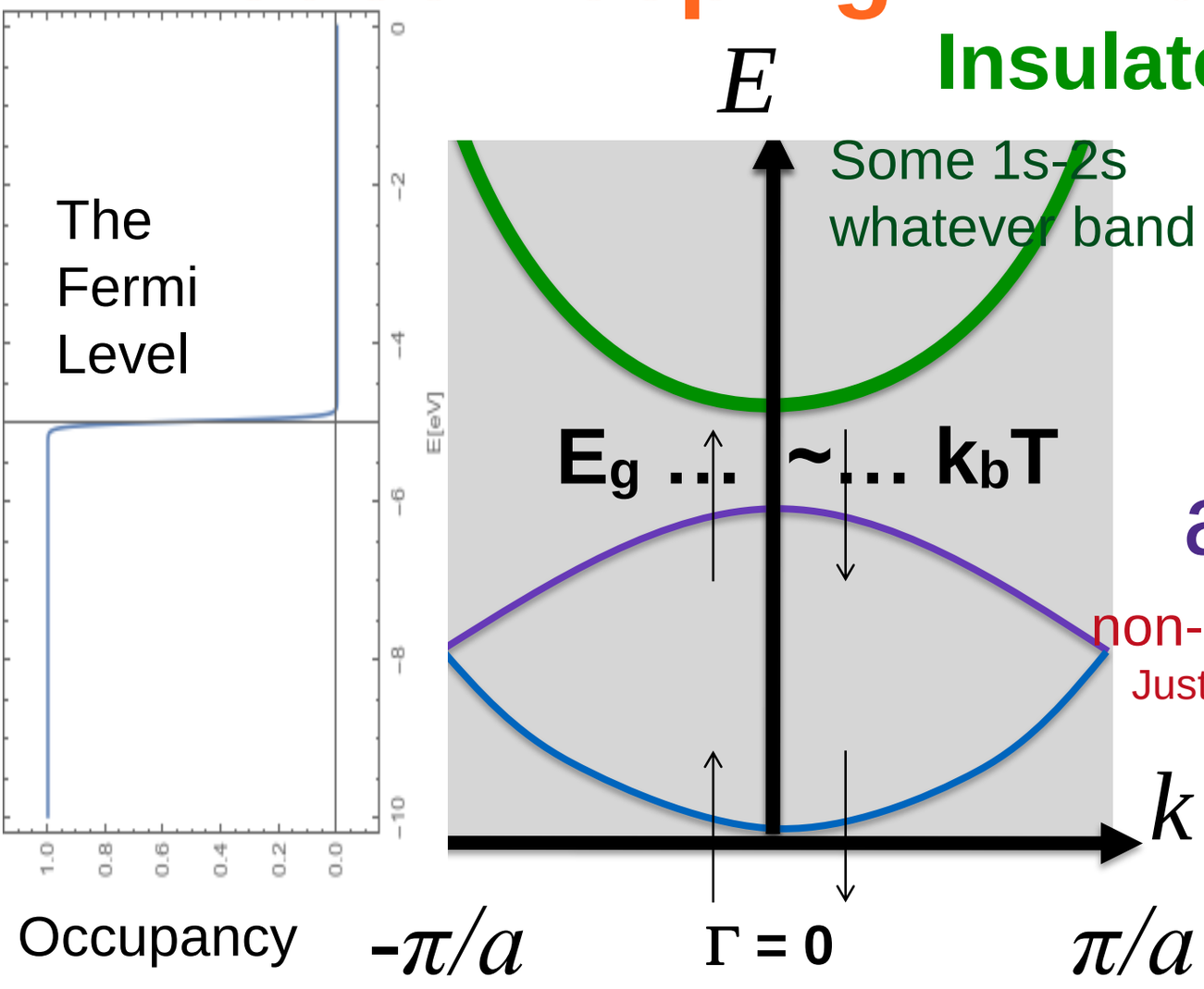
bonding



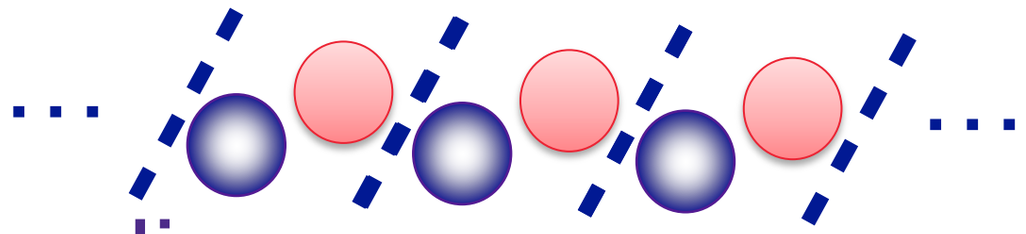
Insulator vs. semiconductor is only divided by the size of gap

House Keeping – 1D chain of “2He atoms”

Insulator vs. Semiconductor



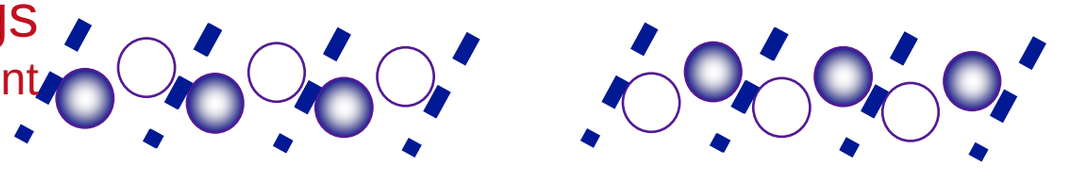
Phase of the 1s orbital



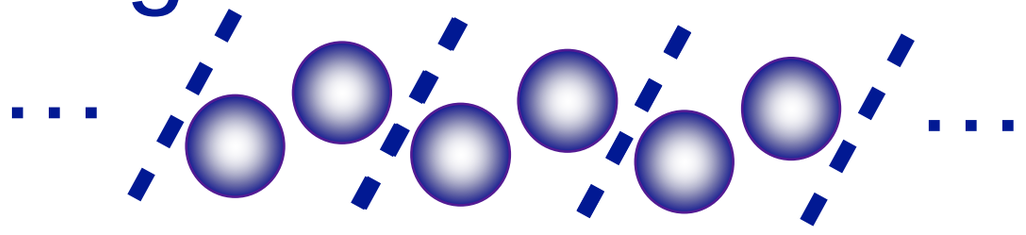
antibonding

non-bondings

Just at 1 **k**-point



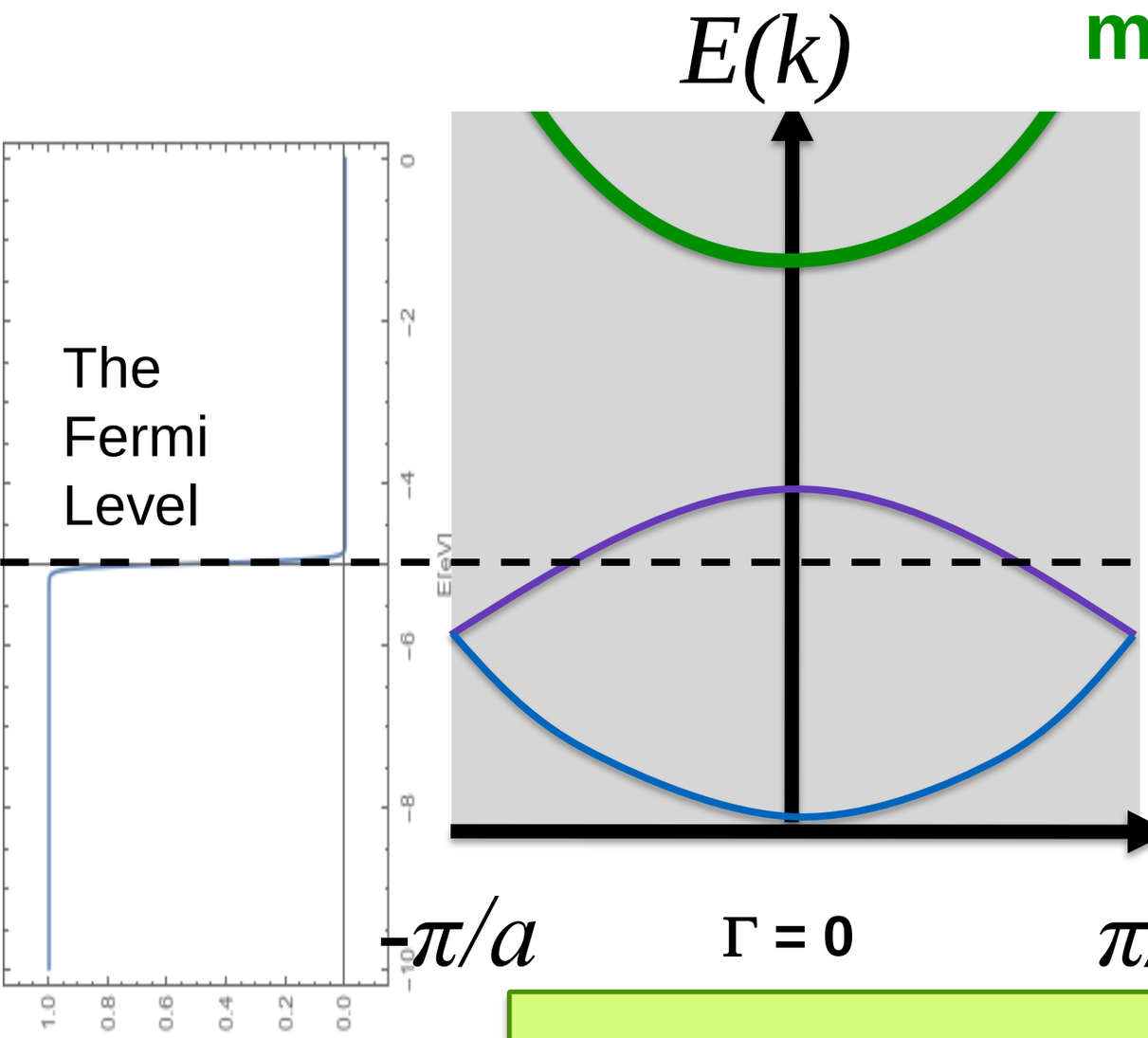
bonding



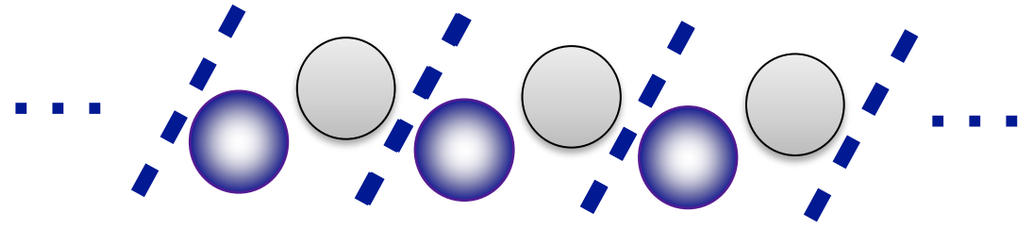
Insulator vs. semiconductor is only divided by the size of gap

House Keeping – 1D chain of “He-H atoms”

metal



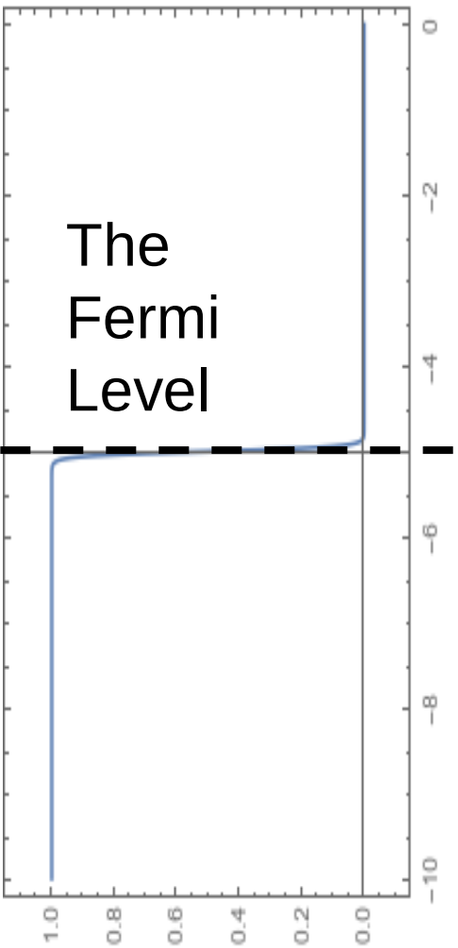
E_g = 0 !!!



The Fermi energy marks the energy of the highest occupied state.

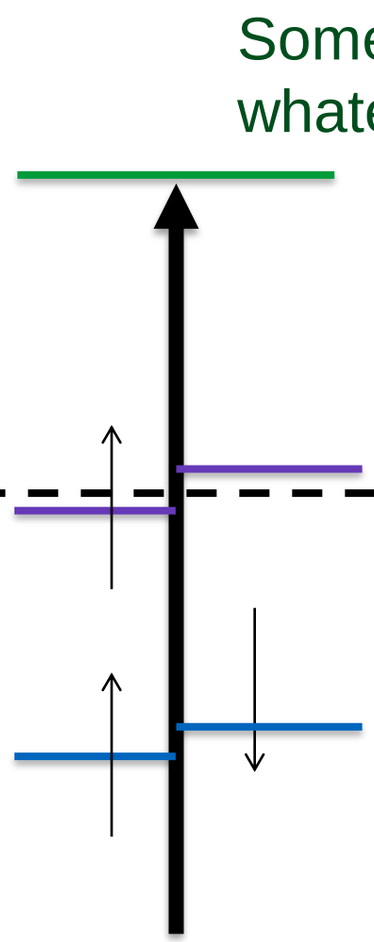
House Keeping – Back to molecule “He-H atoms”

metal



The Fermi Level

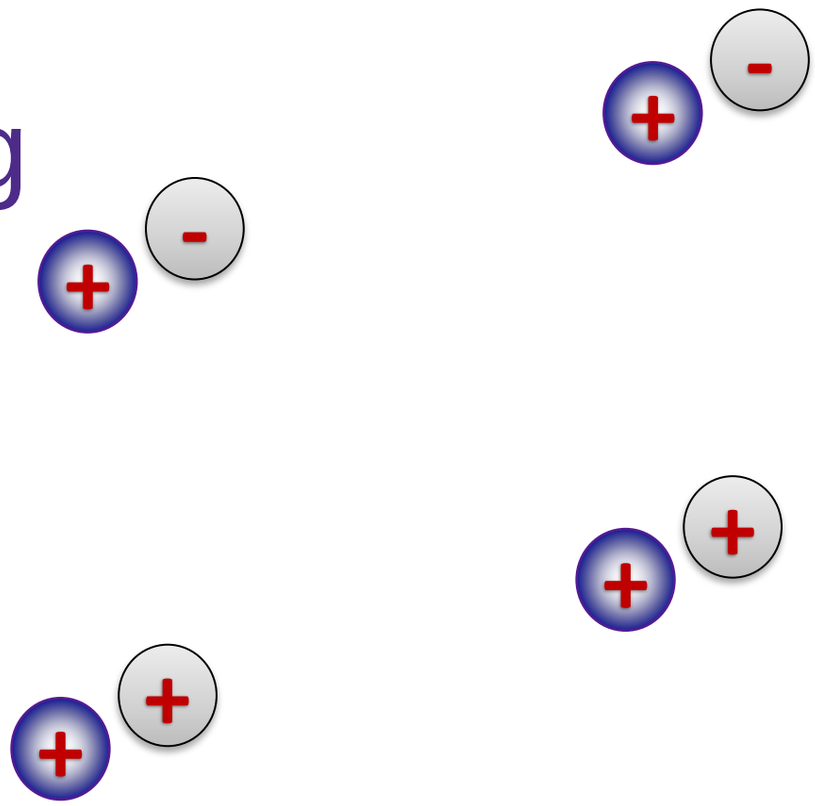
Occupancy



Some 1s-2s whatever state

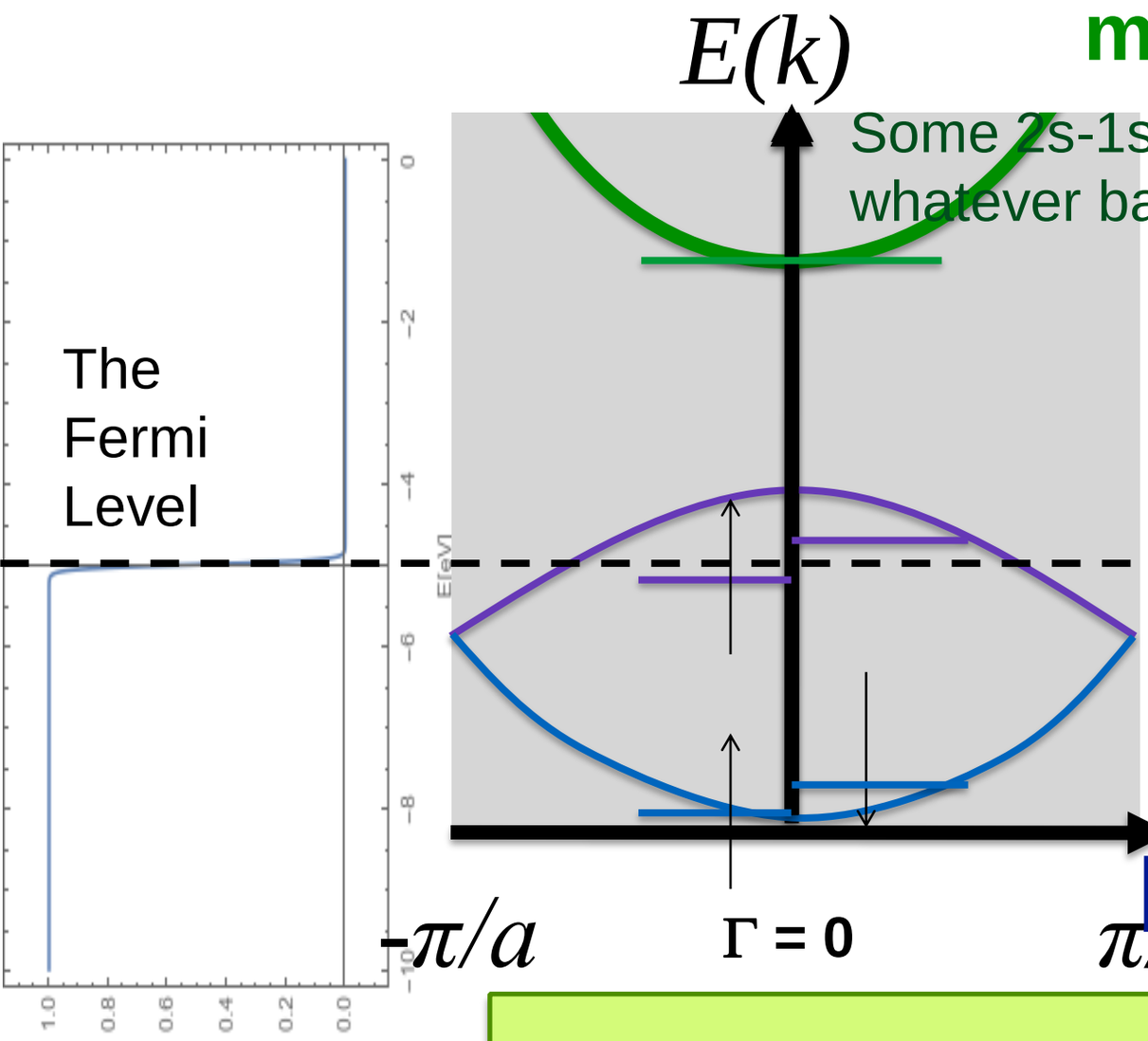
antibonding

bonding



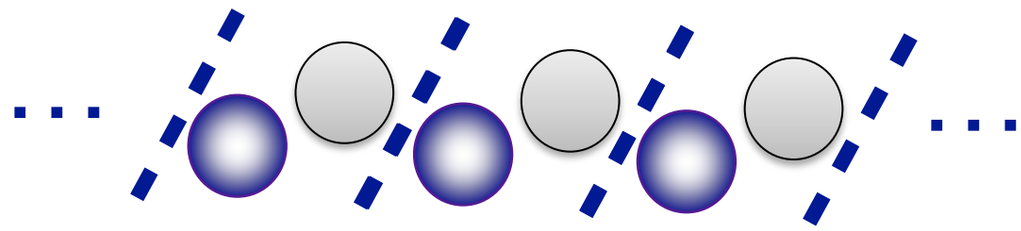
House Keeping – 1D chain of “He-H atoms”

metal



antibonding

E_g = 0 !!!



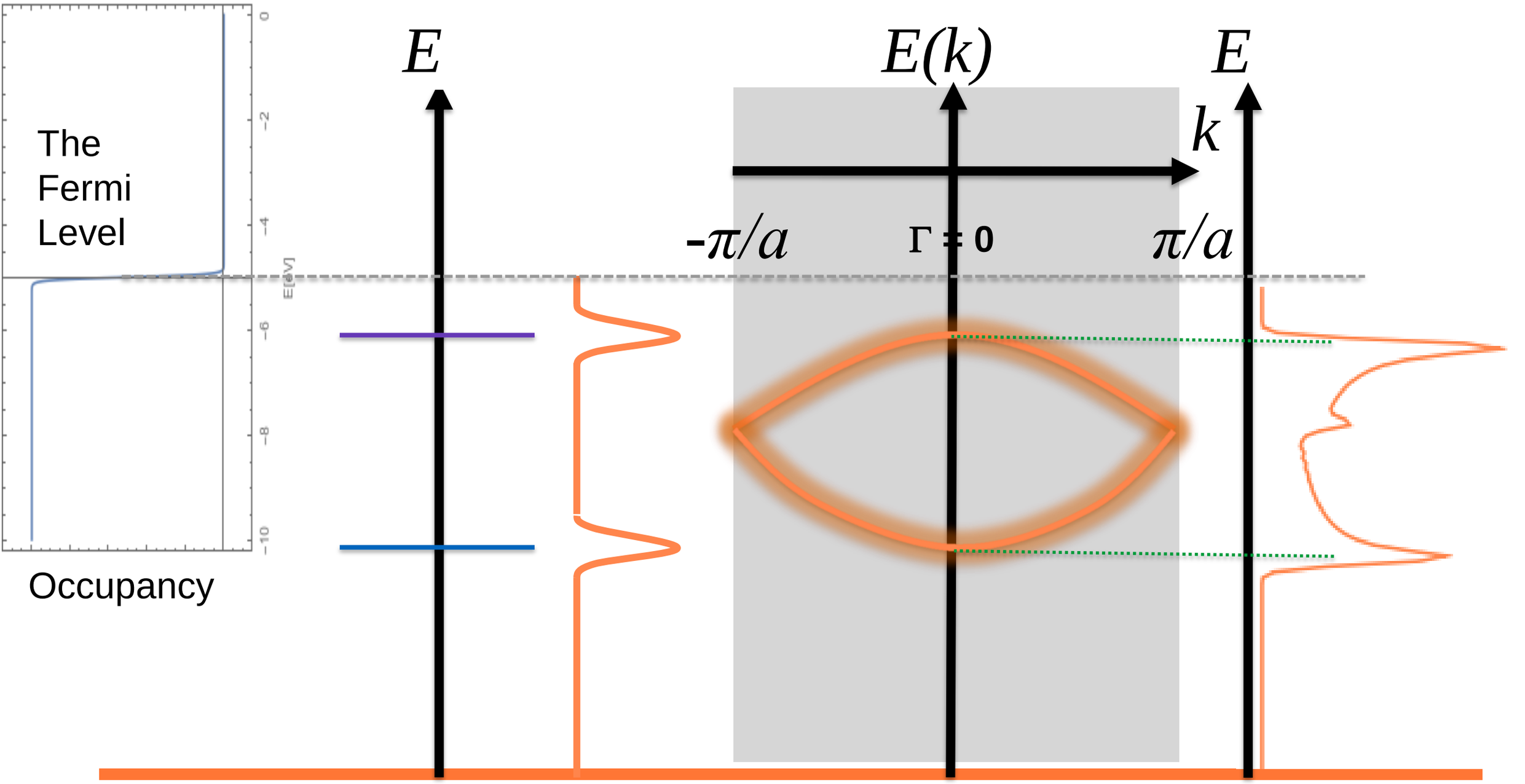
bonding

No gap – electron can anytime be excited into the conduction part of the band

House Keeping – Measurables: occ. states spectroscopy

gas molecule "He_2 ": No momentum

1D "He_2" solid: Momentum resolved × momentum integrating

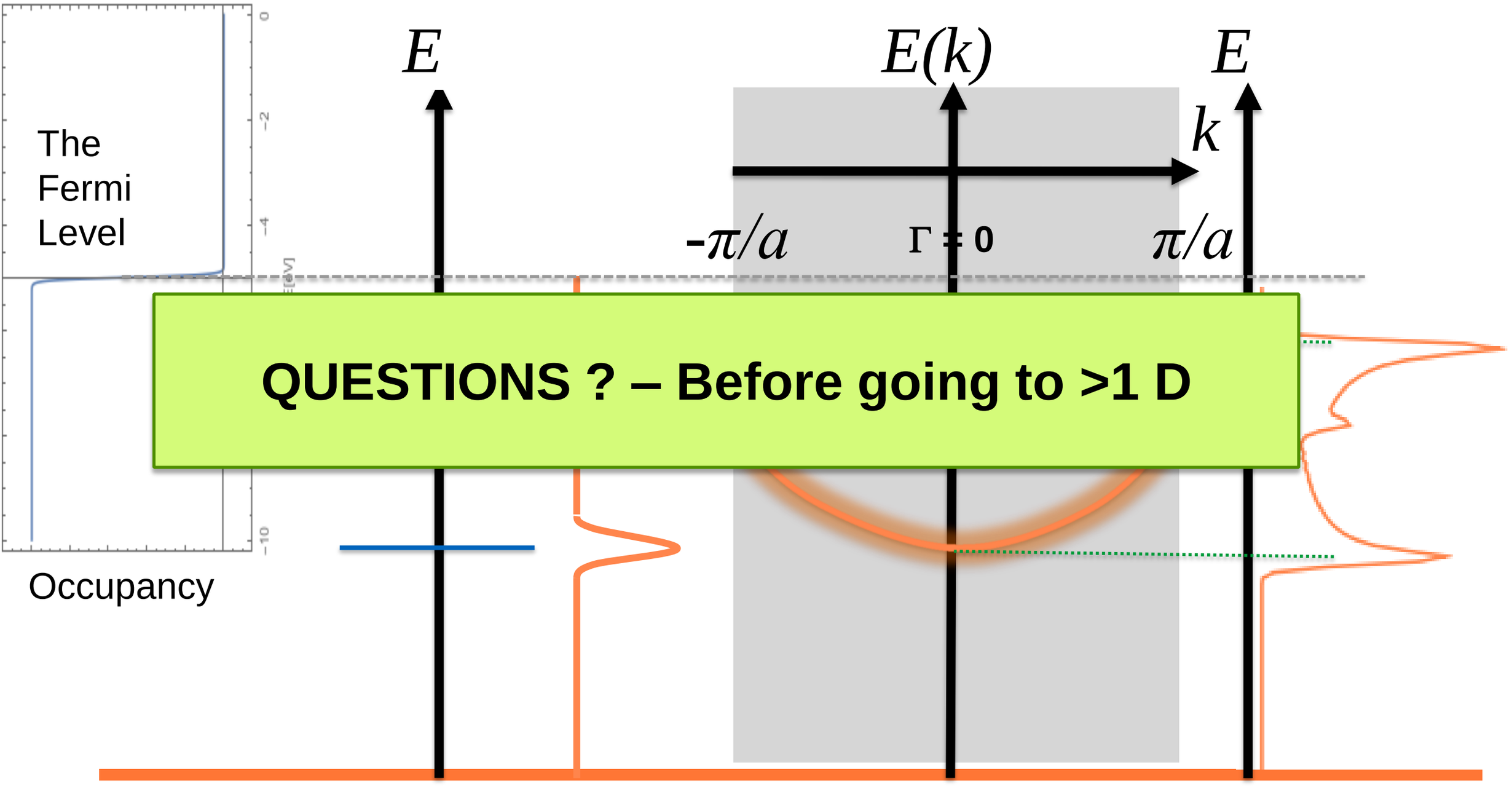


Aalto University
School of Science

House Keeping – Measurables: occ. states spectroscopy

gas molecule "He_2 ": No momentum

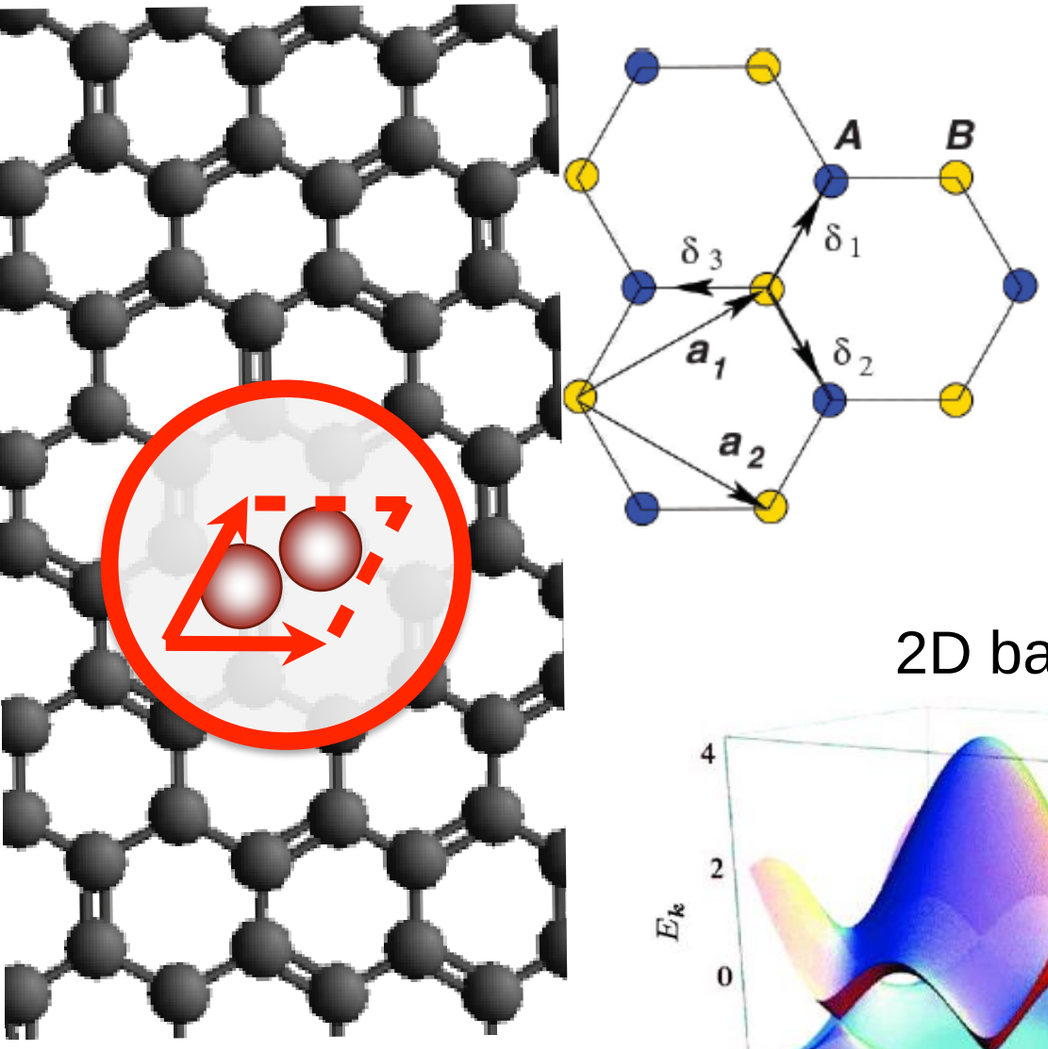
1D "He_2" solid: Momentum resolved × momentum integrating



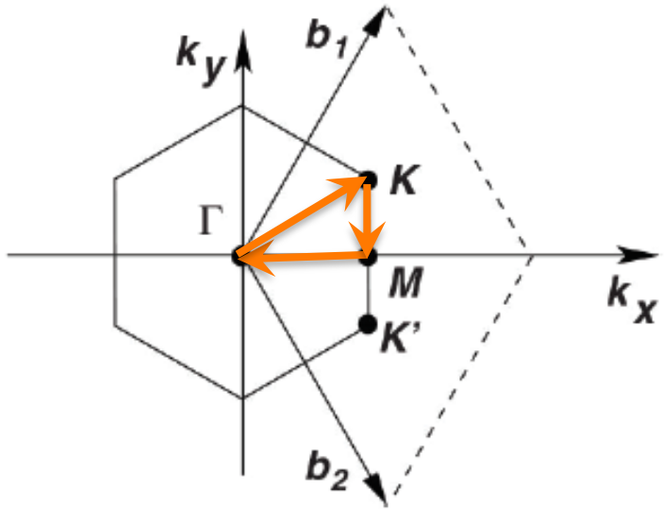
QUESTIONS ? – Before going to >1 D

House Keeping – 2D band structure

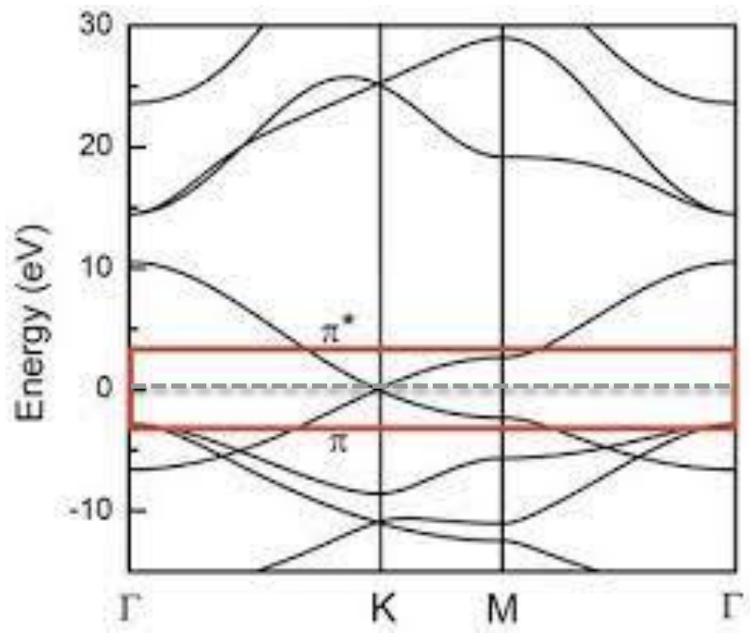
Graphene
Real space lattice:



1st Brillouin zone

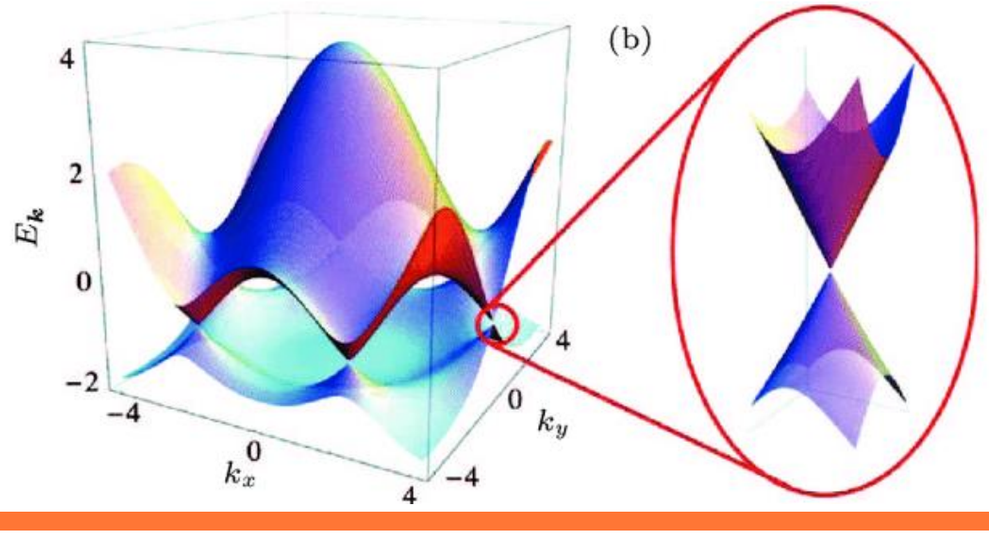


1D projection:



The Fermi Level

2D band structure:

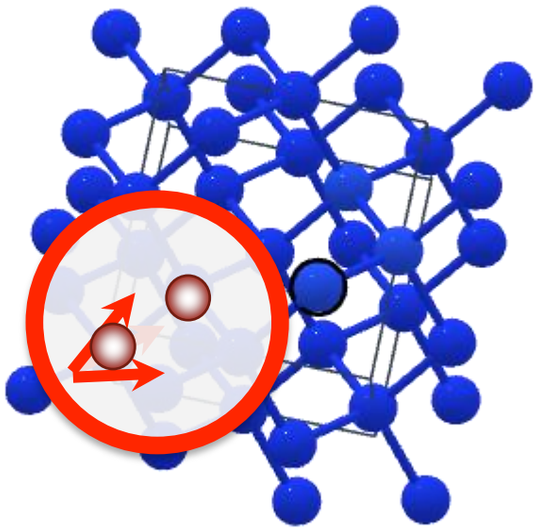


Aalto University
School of Science

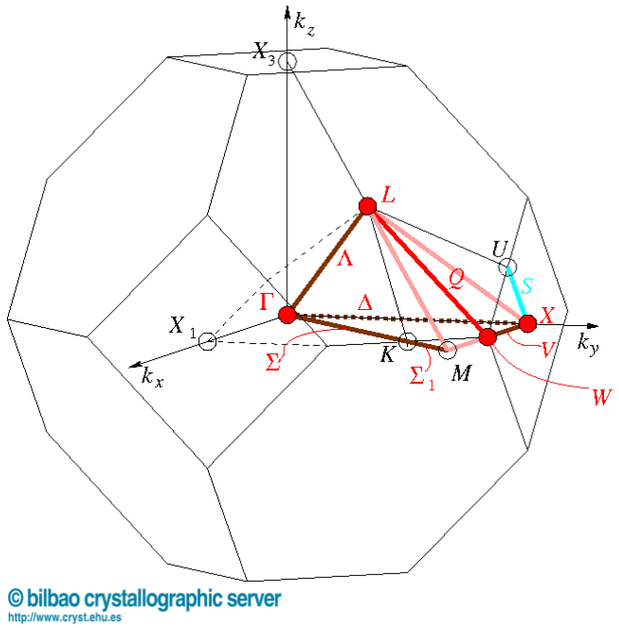
2D band structure - Zhao, Jing *et al.* Chinese Physics B. 22. 057701, (2013)
1D projection - https://www.phys.uni-sofia.bg/~vpopov/elbsphdsgrf.htm

House Keeping – 3D band structure

Silicon
Real space lattice:

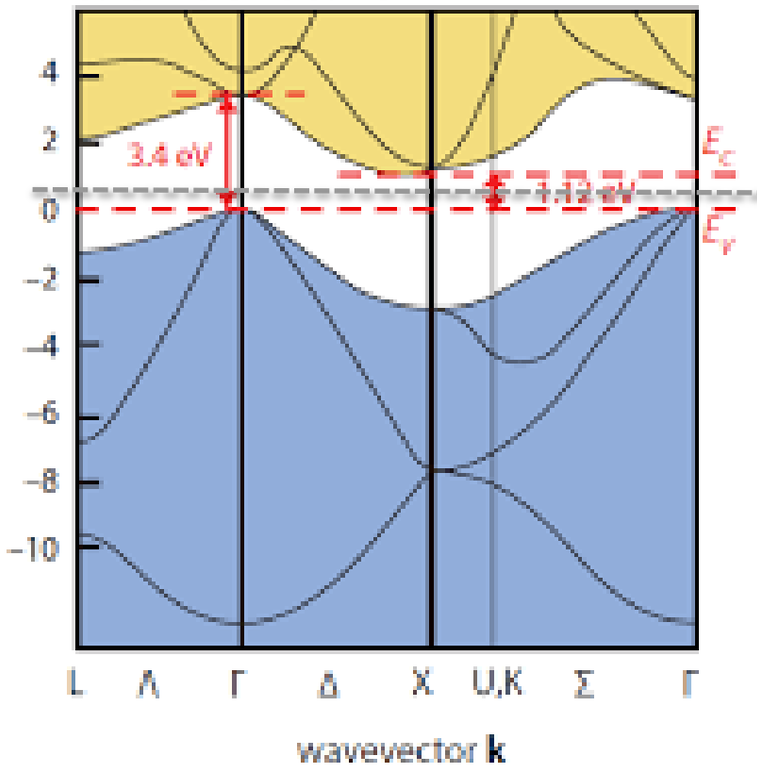


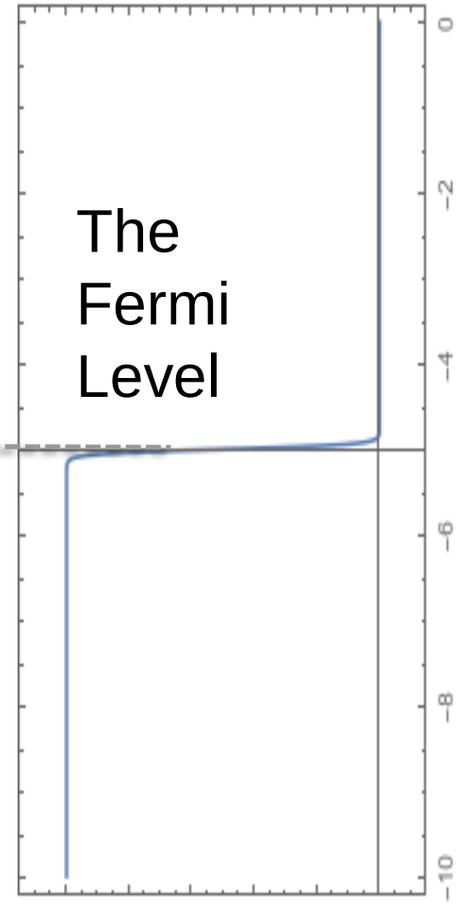
1st Brillouin zone



1D path
Along 3D band structure
**no real standardization*

E vs. top of the valence band





Occupancy

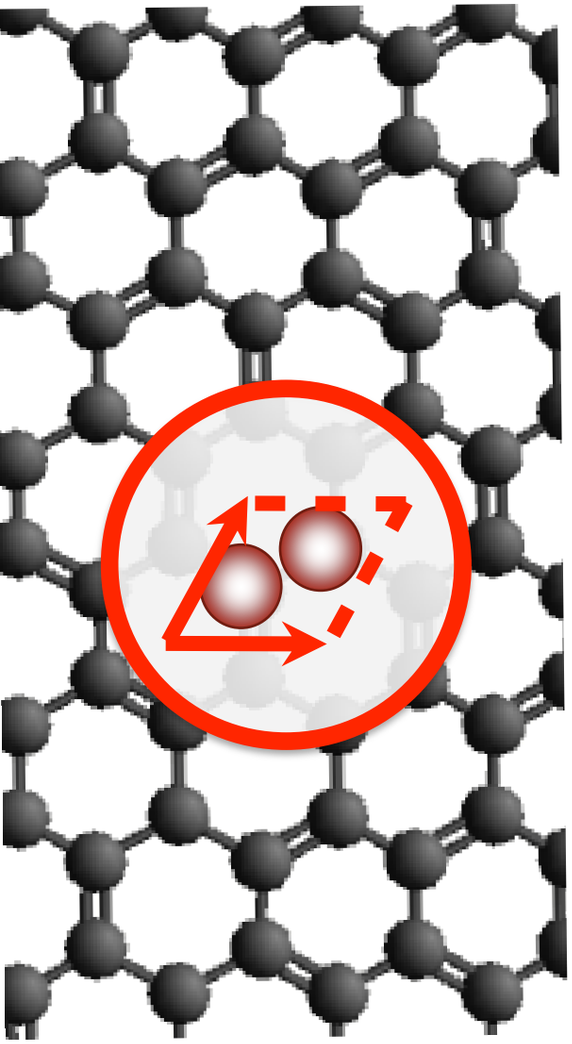
https://www.cryst.ehu.es/cryst/get_kvec.html - add there *Fd-3m* = 227

Aalto University
School of Science

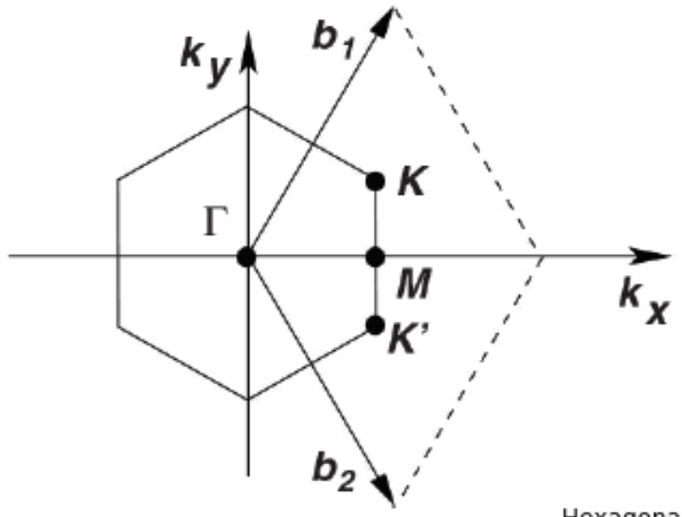
Real-space lattice: https://materialsproject.org/materials/mp-149
1D band projection: https://myengineerings.com/crystalline-silicon/

House Keeping – 2D crystal calculations

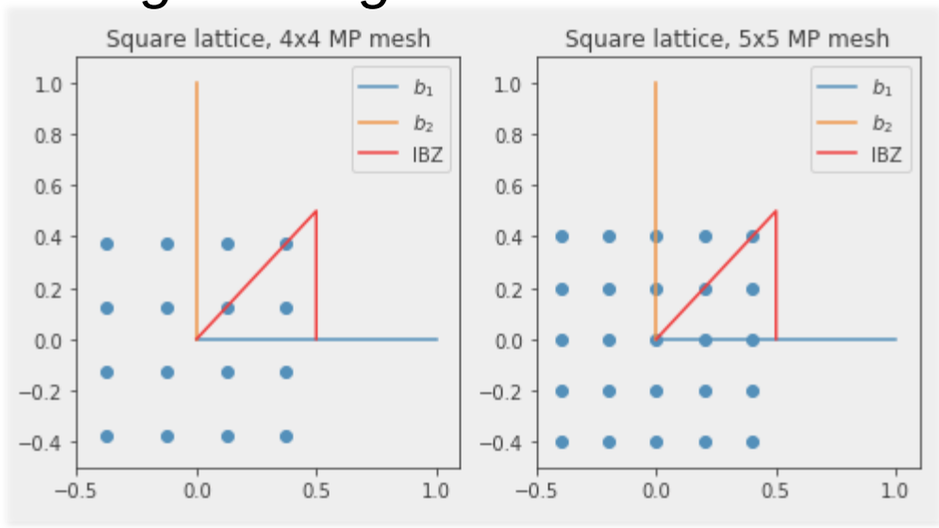
Graphene
Real space lattice:

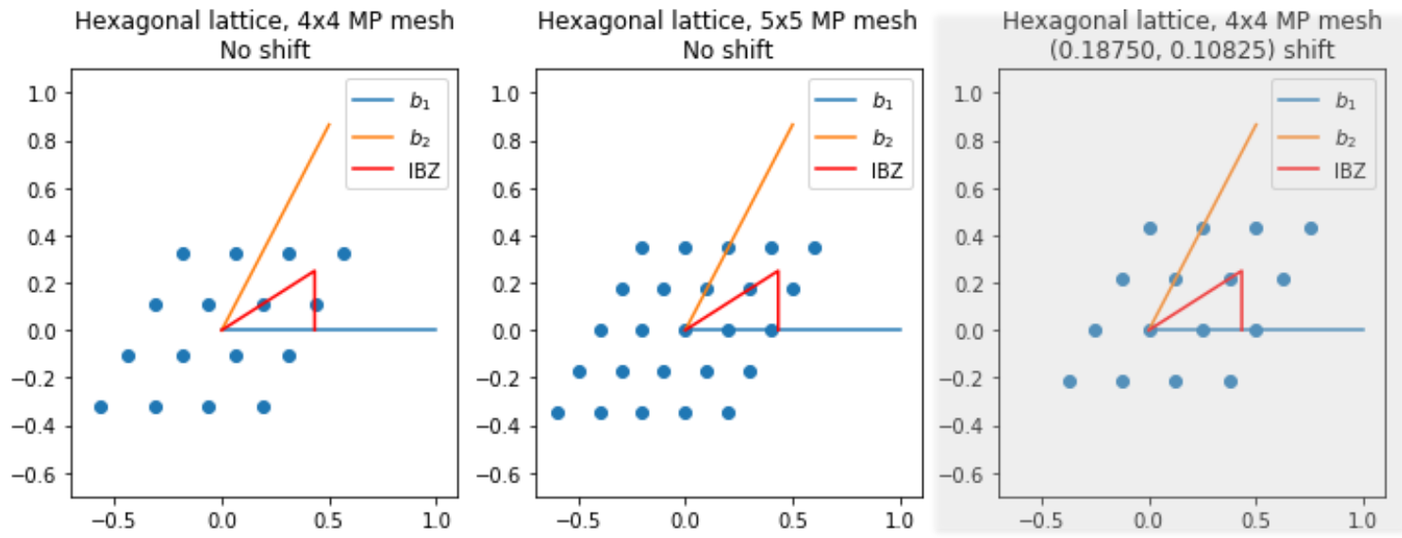


1st Brillouin zone



1st BZ:
Has to be represented on a GRID!!!
Discreet grid – e.g Monkhorst-Pack mesh





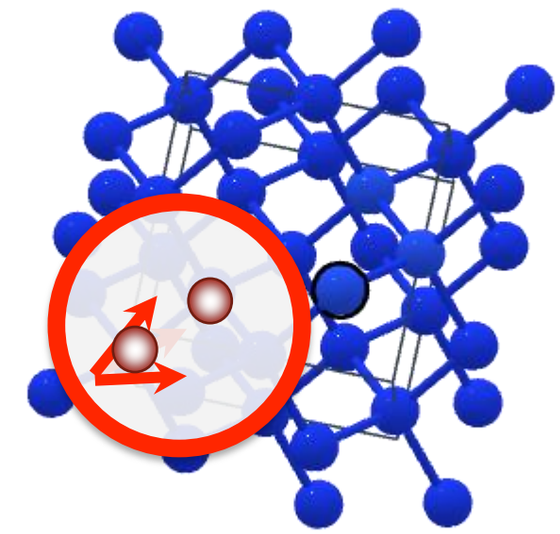
You only need to specify the density allong axis.

Aalto University
School of Science

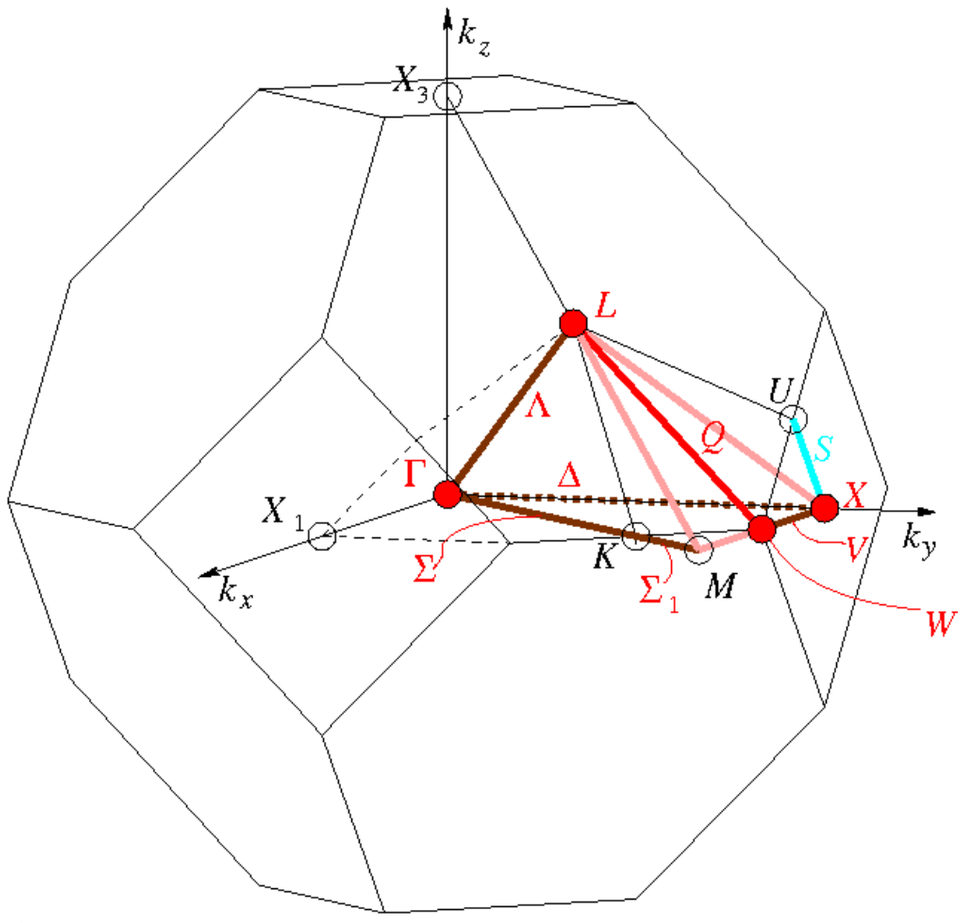
MP mesh: https://sites.psu.edu/dftap/2019/02/01/shifting-of-kpoints-in-hexagonal-lattices/

House Keeping – 3D crystal calculations

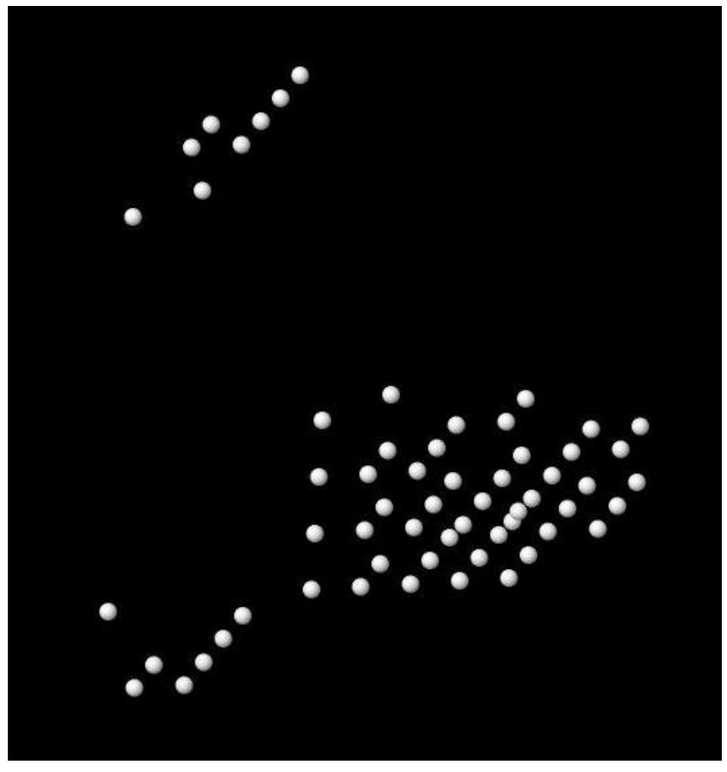
Silicon
Real space lattice:



1st Brillouin zone



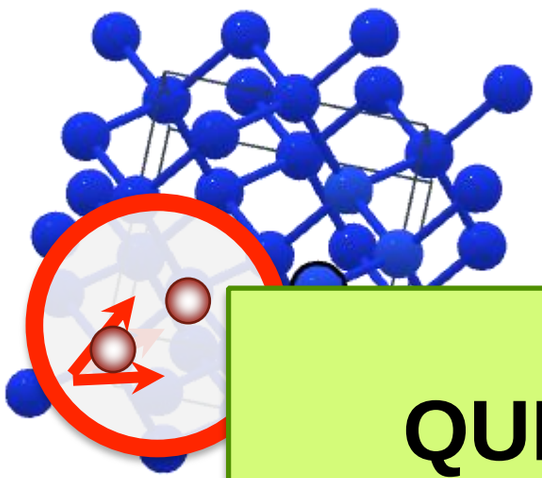
1st BZ:
Has to be represented on a GRID!!!
1 type of 3D representation:



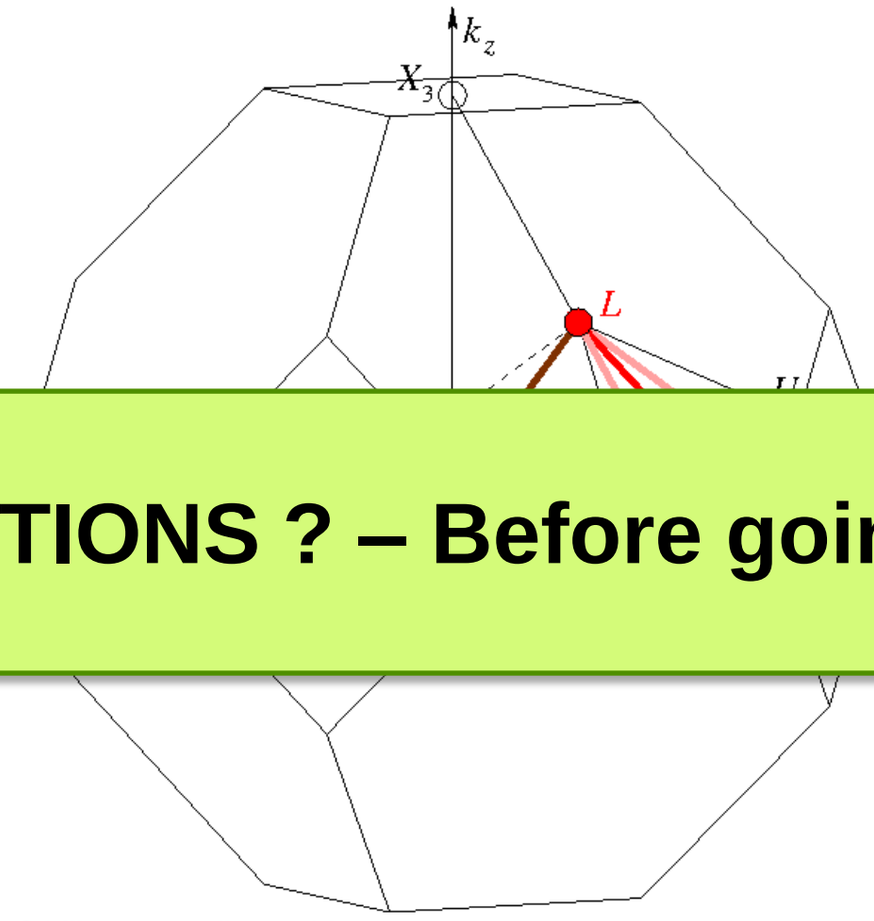
You only need to specify the density allong axis.

House Keeping – 3D crystal calculations

Silicon
Real space lattice:

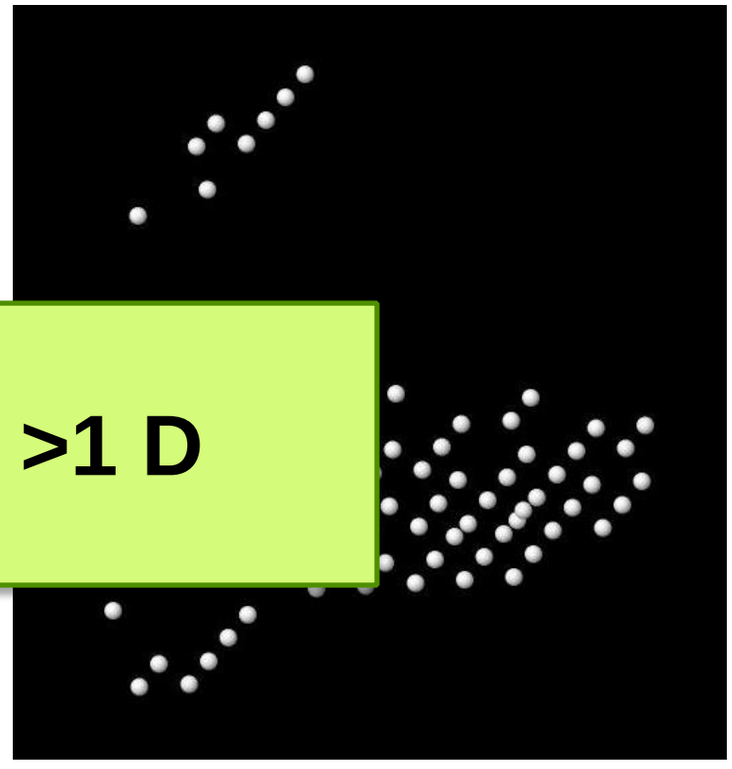


1st Brillouin zone



© bilbao crystallographic server
http://www.cryst.ehu.es

1st BZ:
Has to be represented on a GRID!!!
1 type of 3D representation:

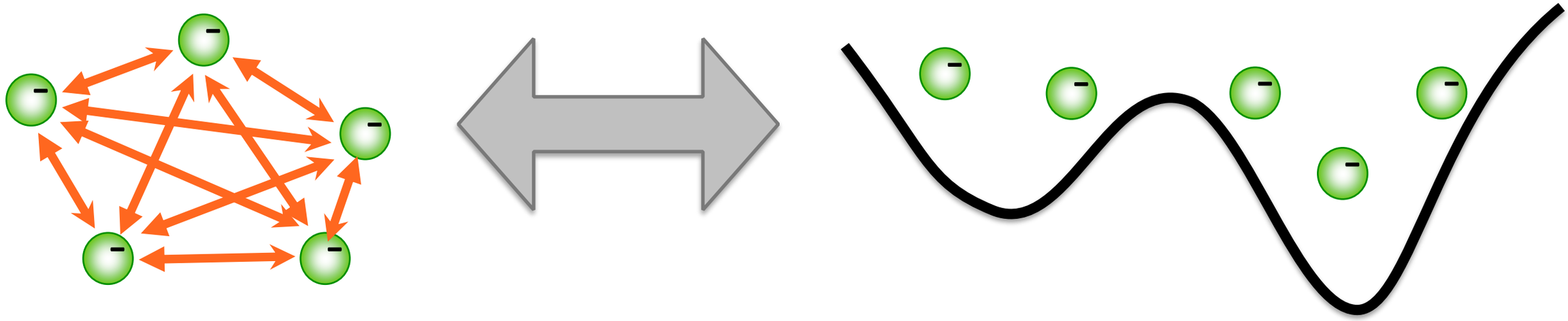


QUESTIONS ? – Before going to >1 D

You only need to specify the density allong axis.

Last week at the same time

$$v_{\mathrm{ext}}(\mathbf{r}) \Leftrightarrow n_0(\mathbf{r}) = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2$$



Kohn-Sham DFT:

- **interacting system can be mapped onto fictitious non-interacting system.**
- **this makes DFT tractable.**

W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

Kohn-Sham (KS) equations

Now we can solve coupled equations:

$$v_{\mathrm{aux}}[n](\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{Hartree}}[n](\mathbf{r}) + v_{\mathrm{xc}}[n](\mathbf{r})$$

KS potential

KS orbitals/wave functions

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{\mathrm{aux}}[n](\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

KS eigenvalues

$$n(\mathbf{r}) = \sum_i^{N_e} |\phi_i(\mathbf{r})|^2$$

W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

Basis functions

Let’s expand Kohn-Sham states in a basis.

$$\phi_j(\mathbf{r}) = \sum_i c_{ij}\varphi_i(\mathbf{r})$$

Many basis choices:

- **plane waves or real space**
  - **linear augmented plane waves (LAPW)**
  - **projector augmented plane waves (PAW)**
- **local orbitals (LCAO)**
  - **Gaussian orbitals**
  - **numeric atom centered orbitals (NAOs)**

Basis functions in FHI-aims

In FHI-aims: flexible basis function choice

$$\varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} Y_{lm}(\Omega)$$

radial function

spherical harmonic

solution of a radial Schrödinger equation:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{\text{cut}}(r) \right] u_i(r) = \epsilon_i u_i(r)$$

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Basis functions in FHI-aims

- **free atom like:** $v_i(r) = v^{\mathrm{DFT}}_{\text{free atom}}(r)$
- **Hydrogen like:** $v_i(r) = Z/r$
- **free ions, harm. osc. (Gaussians), ...**

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{\mathrm{cut}}(r)\right] u_i(r) = \epsilon_i u_i(r)$$

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Basis functions in FHI-aims

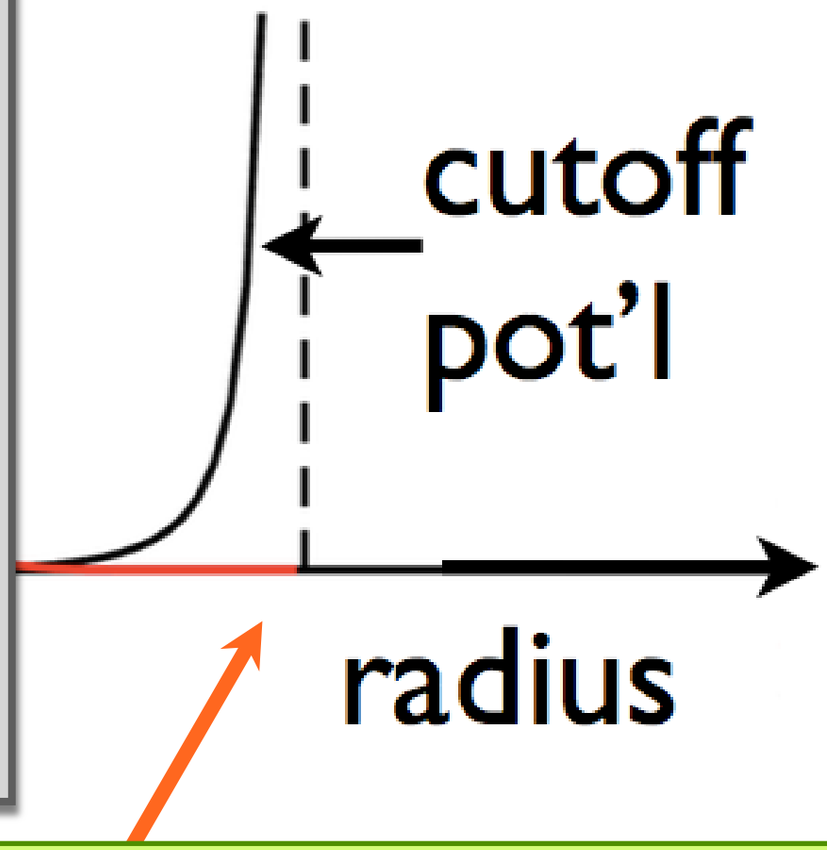
FHI-aims technical detail:

specification of the cut-off potential

cut_pot onset width scale

e.g.

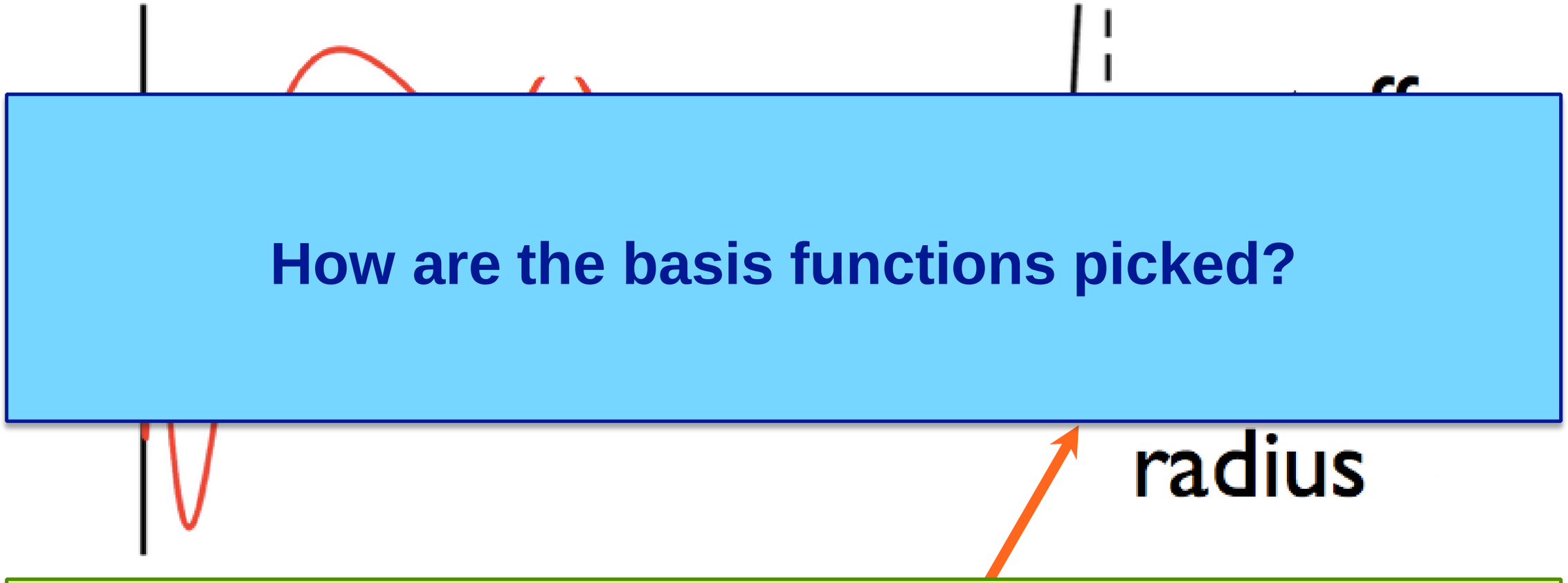
cut_pot 3.5 1.5 1.0



Necessary to localise basis functions in space
⇒ improves computational scaling!

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Basis functions in FHI-aims



Necessary to localise basis functions in space
⇒ improves computational scaling!

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Basis functions in FHI-aims

Wishlist:

- **element specific**
- **transferable**
- **from fast qualitative to meV-converged total energy accuracy**

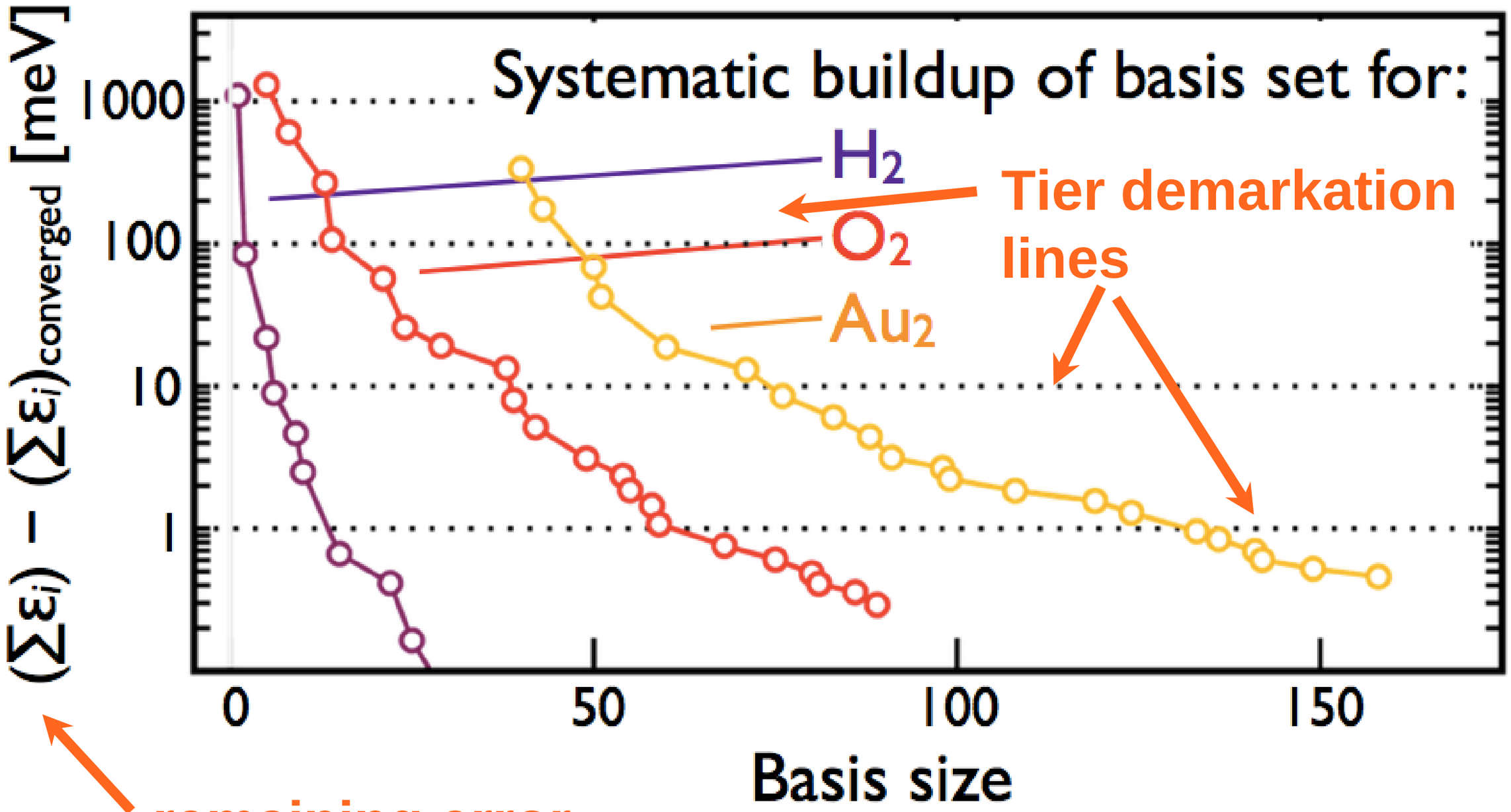
Good news! – FHI-aims developers prepared set of "Tiers" to systematically improve the accuracy!*

- **free atom like:** $v_i(r) = v^{\mathrm{DFT}}_{\text{free atom}}(r)$
- **Hydrogen like:** $v_i(r) = Z/r$
- **free ions, harm. osc. (Gaussians), ...**

*more detailed solution at the end of the presentation

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Basis function selection in FHI-aims



Aalto University
School of Science

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Result: Hierarchical Basis Set Library for All Elements

	H	C	O	Au
minimal	1s	[He]+2s2p	[He]+2s2p	[Xe]+6s5d4f
Tier 1	H(2s,2.1)	H(2p,1.7)	H(2p,1.8)	Au^{2+}(6p)
	H(2p,3.5)	H(3d,6.0)	H(3d,7.6)	H(4f,7.4)
		H(2s,4.9)	H(3s,6.4)	Au^{2+}(6s)
				H(5g,10)
				H(6h,12.8)
				H(3d,2.5)
Tier 2	H(1s,0.85)	H(4f,9.8)	H(4f,11.6)	H(5f,14.8)
	H(2p,3.7)	H(3p,5.2)	H(3p,6.2)	H(4d,3.9)
	H(2s,1.2)	H(3s,4.3)	H(3d,5.6)	H(3p,3.3)
	H(3d,7.0)	H(5g,14.4)	H(5g,17.6)	H(1s,0.45)
		H(3d,6.2)	H(1s,0.75)	H(5g,16.4)
				H(6h,13.6)
Tier 3	H(4f,11.2)	H(2p,5.6)	O^{2+}(2p)	H(4f,5.2)*
	H(3p,4.8)	H(2s,1.4)	H(4f,10.8)	H(4d,5.0)
	...	...	...	...

Systematic hierarchy of basis (sub)sets, iterative *automated* construction based on *dimers*

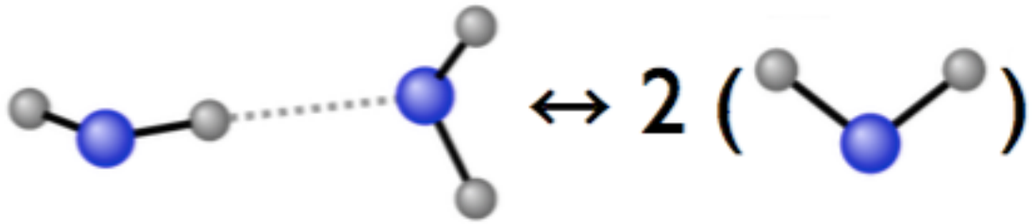
"First *tier* (level)"

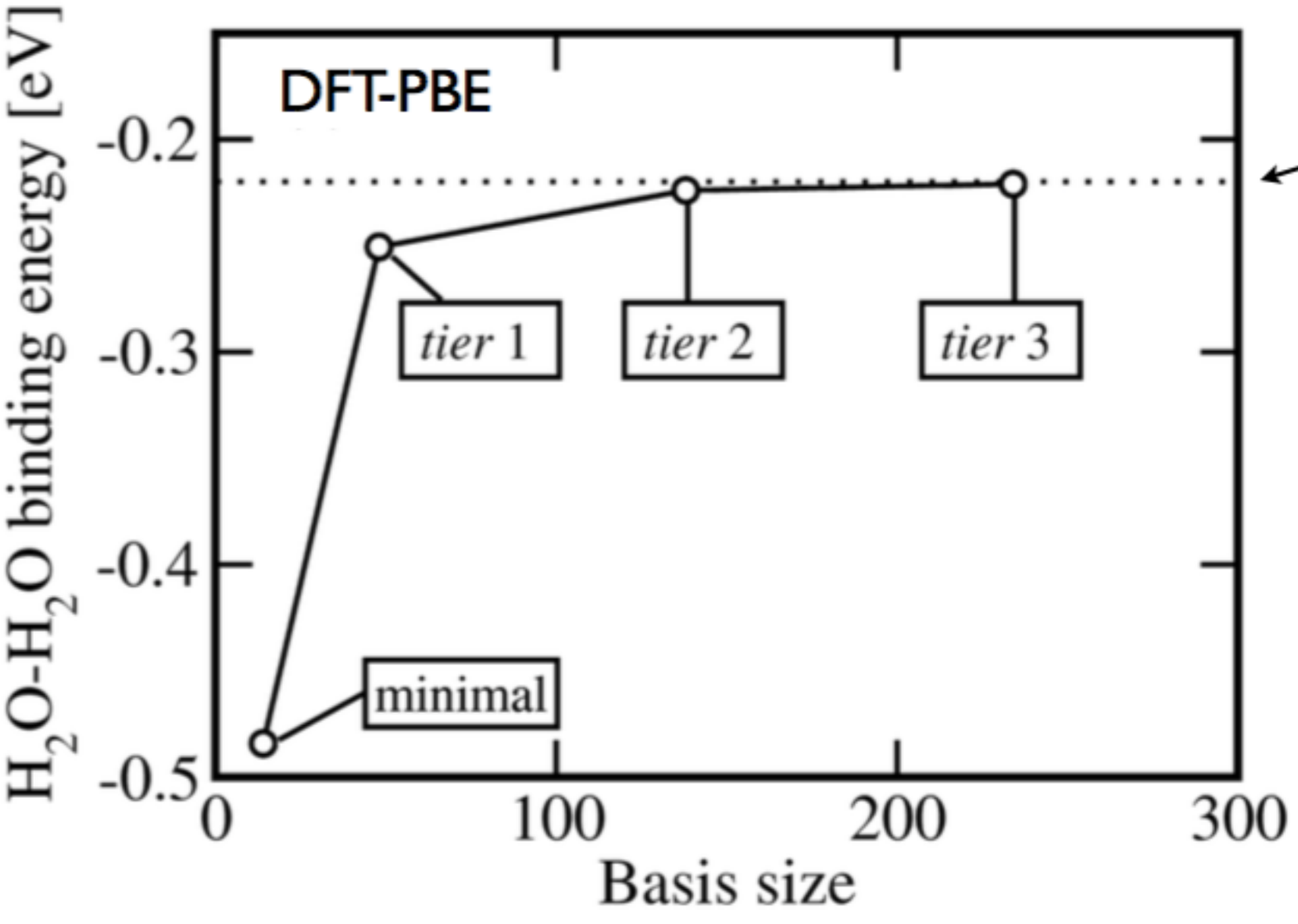
"Second *tier*"

"Third *tier*"

...

Accuracy: $(H_2O)_2$ Hydrogen Bond Energy





Basis set limit (independent):
E_{Hb} = −219.8 meV

Basis sets: Radial fn. character

	H	C,N,O
minimal	1s	[He]+2s2p
tier 1	*s,p*	*s,p,d*
tier 2	*s,p,s,d*	*s,p,d,f,g*
tier 3	*s,p,d,f*	*s,p,d,f*

Aalto University
School of Science

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Kohn-Sham equations in a basis

Pick basis set {φ$_i$} and expand:

$$\phi_n(\mathbf{r}) = \sum_i c_{ni}\varphi_i(\mathbf{r})$$

Solve generalised eigenvalue problem:

$$\mathbf{hc}_n = \epsilon_n \mathbf{sc}_n$$

$$h_{ij} = \langle \varphi_i | \hat{h} | \varphi_j \rangle$$

$$s_{ij} = \langle \varphi_i | \varphi_j \rangle$$

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Kohn-Sham equations in a basis

Two advantages:

1. number of $\{\varphi_i\}$ << number of r points
⇒ smaller matrices
2. matrix algebra very efficient on computers

$$\phi_n(\mathbf{r}) = \sum_i c_{ni}\varphi_i(\mathbf{r})$$

$$\mathbf{hc}_n = \epsilon_n \mathbf{sc}_n$$

$$h_{ij} = \langle \varphi_i | \hat{h} | \varphi_j \rangle$$

$$s_{ij} = \langle \varphi_i | \varphi_j \rangle$$

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Kohn-Sham self-consistency cycle

Initial guess $c_{ni}^{(0)}$

New $n^{(m)}(\mathbf{r}) = \sum_{nij} c_{ni}^{(m)} c_{nj}^{(m)} \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r})$

Update $v_{Hartree}^{(m)}(r)$, $v_{xc}^{(m)}(r)$

$$h_{ij}^{(m)} = \int d\mathbf{r} \varphi_i(\mathbf{r}) \hat{h}_{\mathrm{KS}}^{(m)}(\mathbf{r}) \varphi_j(\mathbf{r})$$

Solve $\mathbf{h}\mathbf{c}_n = \epsilon_n \mathbf{s}\mathbf{c}_n$

repeat until $n^{(m)} = n^{(m-1)}$

grid based

matrix algebra

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

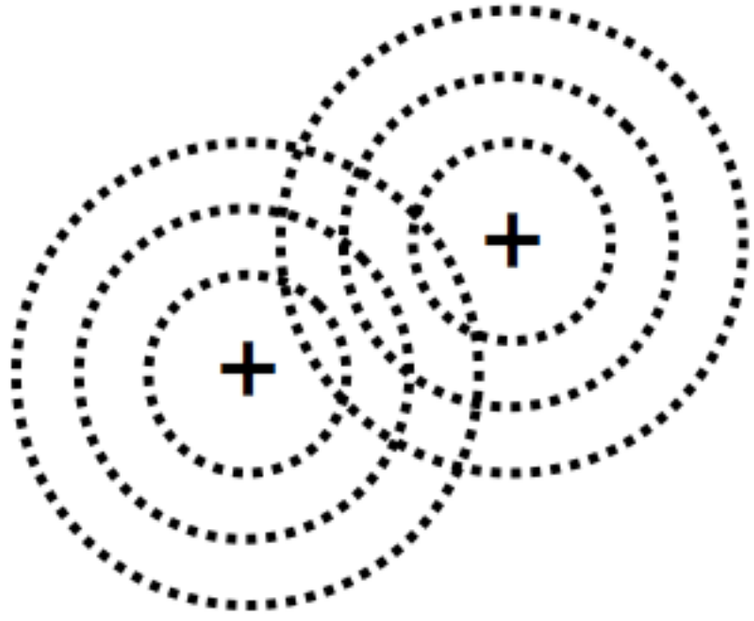
Grid-based operations

$$h_{ij}^{(m)} = \int d\mathbf{r} \varphi_i(\mathbf{r}) \hat{h}_{\mathrm{KS}}^{(m)}(\mathbf{r}) \varphi_j(\mathbf{r})$$

Discretise to integration grid:

$$\int d\mathbf{r} f(\mathbf{r}) \rightarrow \sum_{\mathbf{r}} w(\mathbf{r}) f(\mathbf{r})$$

FHI-aims uses overlapping atom-centered grids:



V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Grid-based operations

FHI-aims technical detail:

FHI-aims uses logarithmic grids with the following settings:

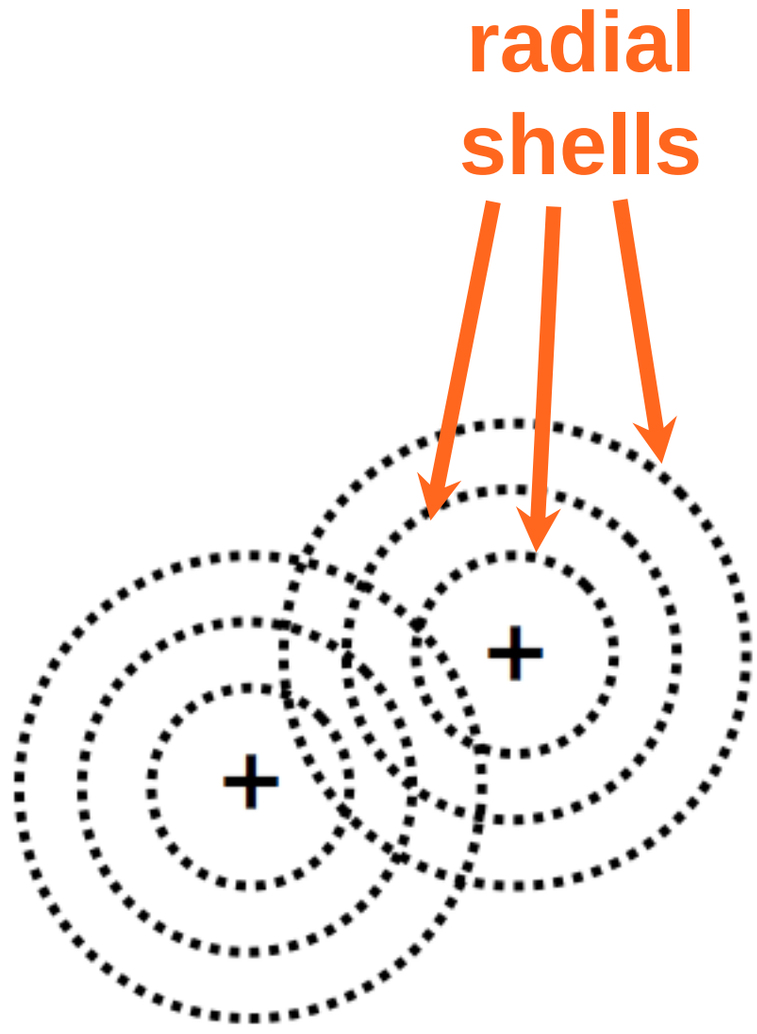
radial_base : 36 5.0

radial_multiplier : 1

 # points

max. radius

multiplies # points



FHI-aims uses overlapping atom-centered grids:

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Grid-based operations

FHI-aims technical detail:

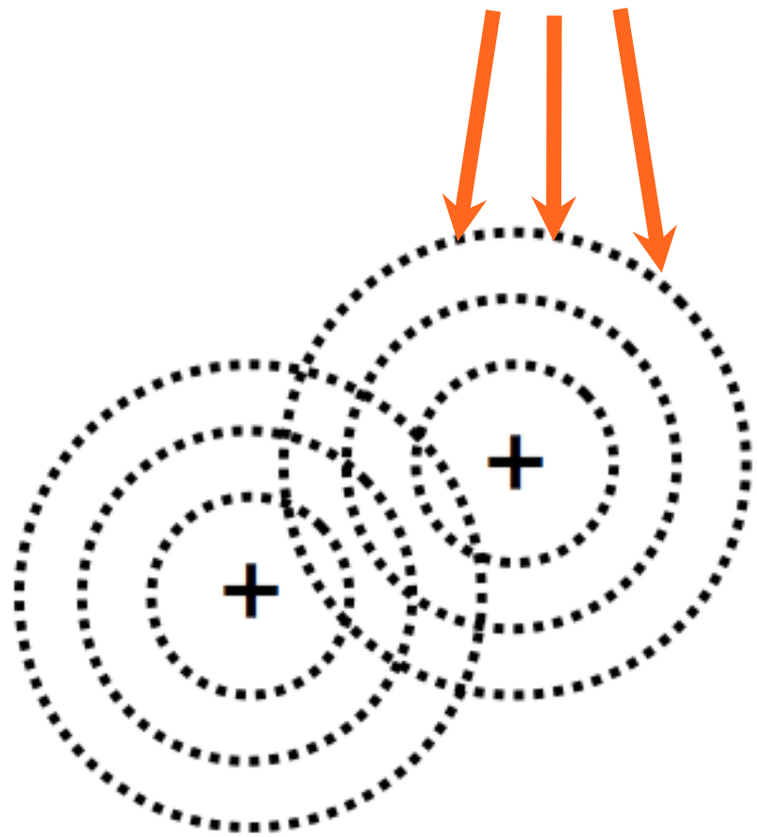
Lebedev grids can be made denser in outer regions:

```
angular_grids specified
      division   0.2659   50
      division   0.4451   110
      division   0.6052  194
#     division   0.7543  302
      outer_grid 194
```

 # points

radius

Specific angular point distribution (“Lebedev”)



Aalto University
School of Science

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

FHI-aims grid accuracy settings

FHI-aims technical detail:

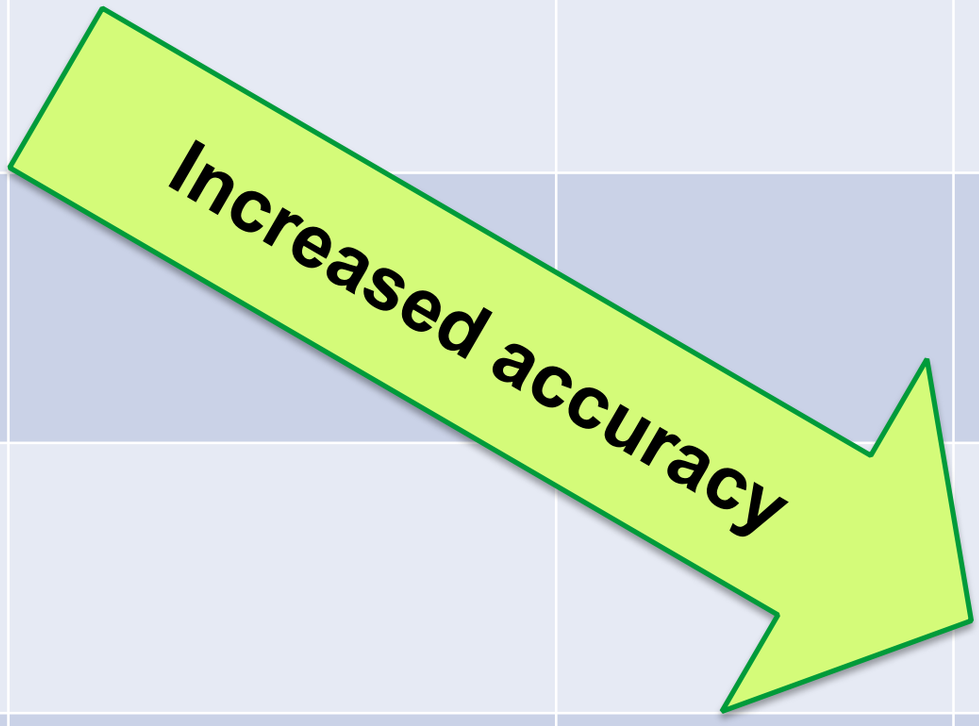
grid settings can be pre-defined:

light	:	computationally cheap, out-of-the-box settings for fast prerelaxations, structure searches, etc.
intermediate	:	For *hybrid-XC*: improved accuracy (derived from tight), but with lower computation costs.
tight	:	safe, guaranteeing meV-level accurate energy differences also for large structures.
really tight	:	for most purposes, strongly overconverged settings for convergence verification beyond tight.

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

FHI-aims basis set overview

	light	intermediate	tight	really tight
Tier 1				
Tier 2				
Tier 3				
Tier 4				



V. Blum et al. Computer Physics Communications 180, 2175 (2009)

FHI-aims basis set overview

	light	intermediate	tight	really tight
Tier 1		***New – for hybrid XC with improved accuracy, but keeping the computational cost down***		
Tier 2	***these combi-nations don't make much sense***		***Usually sufficient***	
Tier 3				
Tier 4		***This combination don't make much sense***		

Aalto University
School of Science

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Questions?

Enjoy our “solid-state & surface modelling intro” tutorial:

- **Download from Mycourses**
- **/work/courses/unix/PHYS/E0546/TUTORIALS**
- **Ask for printouts**

Interesting links related to the tutorial:

Bilbao crystallographic server – https://www.cryst.ehu.es/
Materials project – https://materialsproject.org
Web of Elements - https://www.webelements.com/

Don’t forget to put your name in the list of attendance!

Basis functions in FHI-aims

Wishlist:

- **element specific**
- **transferable**
- **from fast qualitative to meV-converged total energy accuracy**

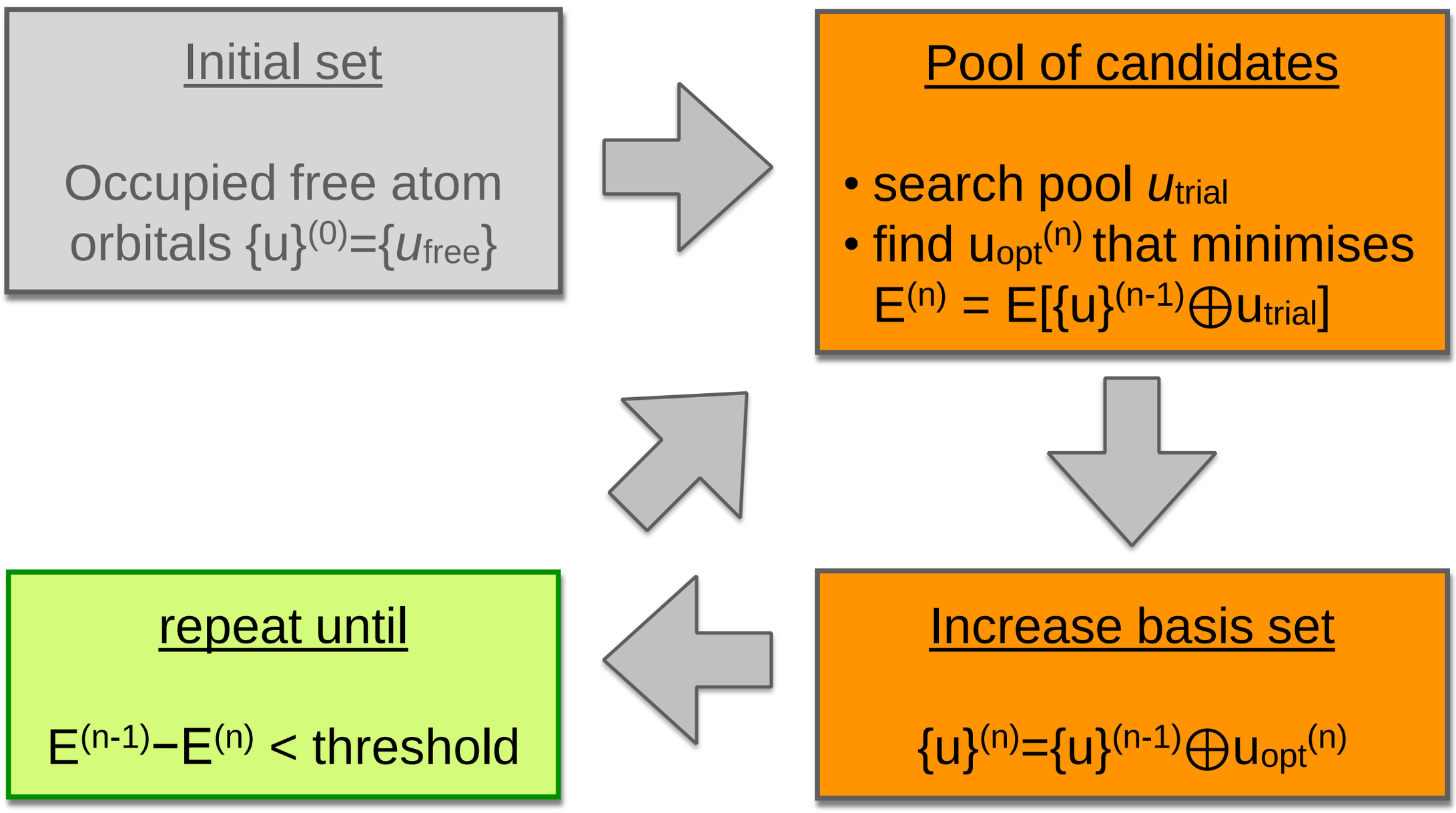
Maybe the computer can help us pick a good basis set.

- **free atom like:** $v_i(r) = v^{\mathrm{DFT}}_{\text{free atom}}(r)$
- **Hydrogen like:** $v_i(r) = Z/r$
- **free ions, harm. osc. (Gaussians), ...**

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Basis function selection in FHI-aims

Robust iterative selection strategy (e.g., Delley 1990)



V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Basis function selection in FHI-aims

Pool of trial functions u(r):

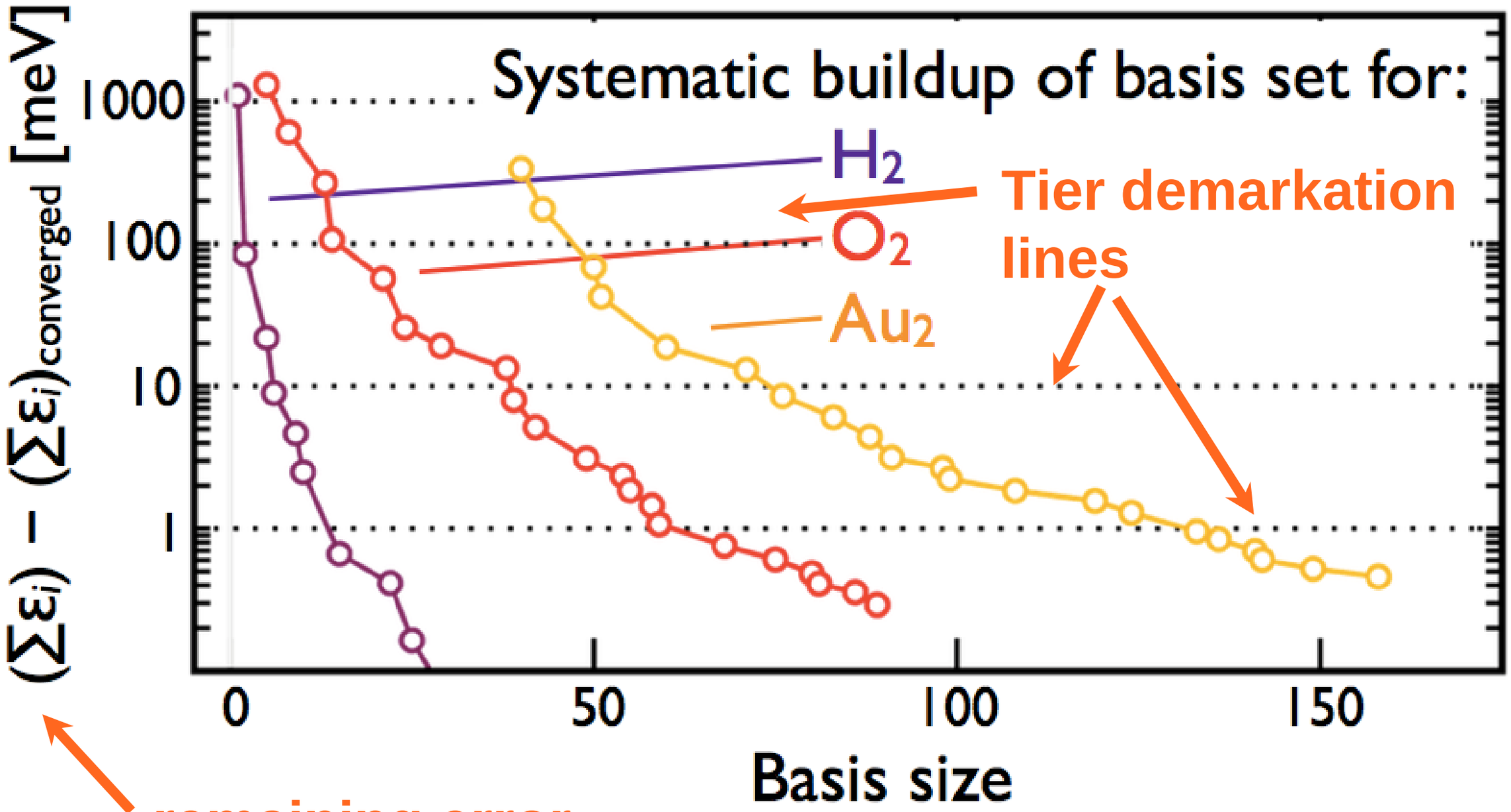
- 2+ ionic
- Hydrogen-like for z=0.1-20

Optimisation target:

Non-self-consistent symmetric dimers, averaged for different bonding distances

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Basis function selection in FHI-aims



Aalto University
School of Science

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Result: Hierarchical Basis Set Library for All Elements

	H	C	O	Au
minimal	1s	[He]+2s2p	[He]+2s2p	[Xe]+6s5d4f
Tier 1	H(2s,2.1)	H(2p,1.7)	H(2p,1.8)	Au^{2+}(6p)
	H(2p,3.5)	H(3d,6.0)	H(3d,7.6)	H(4f,7.4)
		H(2s,4.9)	H(3s,6.4)	Au^{2+}(6s)
				H(5g,10)
				H(6h,12.8)
				H(3d,2.5)
Tier 2	H(1s,0.85)	H(4f,9.8)	H(4f,11.6)	H(5f,14.8)
	H(2p,3.7)	H(3p,5.2)	H(3p,6.2)	H(4d,3.9)
	H(2s,1.2)	H(3s,4.3)	H(3d,5.6)	H(3p,3.3)
	H(3d,7.0)	H(5g,14.4)	H(5g,17.6)	H(1s,0.45)
		H(3d,6.2)	H(1s,0.75)	H(5g,16.4)
				H(6h,13.6)
Tier 3	H(4f,11.2)	H(2p,5.6)	O^{2+}(2p)	H(4f,5.2)*
	H(3p,4.8)	H(2s,1.4)	H(4f,10.8)	H(4d,5.0)
	...	...	...	...

Systematic hierarchy of basis (sub)sets, iterative *automated* construction based on *dimers*

"First *tier* (level)"

"Second *tier*"

"Third *tier*"

...

Grid-based operations

FHI-aims technical detail:

FHI-aims uses logarithmic grids with the following settings:

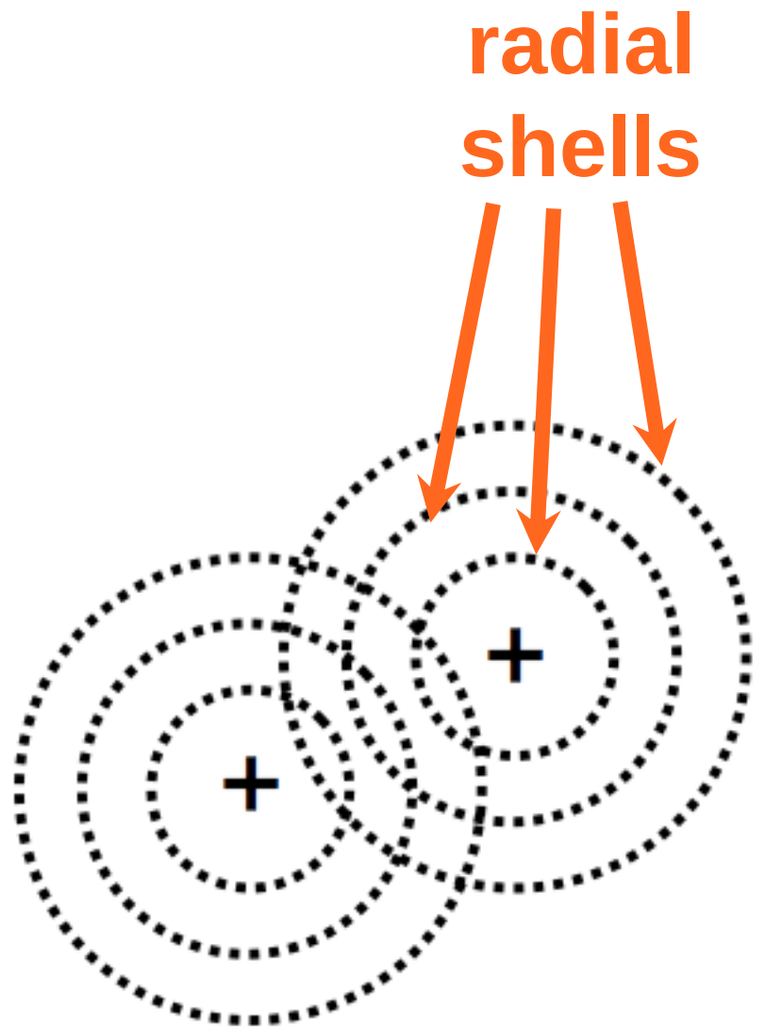
radial_base : 36 5.0

radial_multiplier : 1

 # points

max. radius

multiplies # points



FHI-aims uses overlapping atom-centered grids:

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Grid-based operations

FHI-aims technical detail:

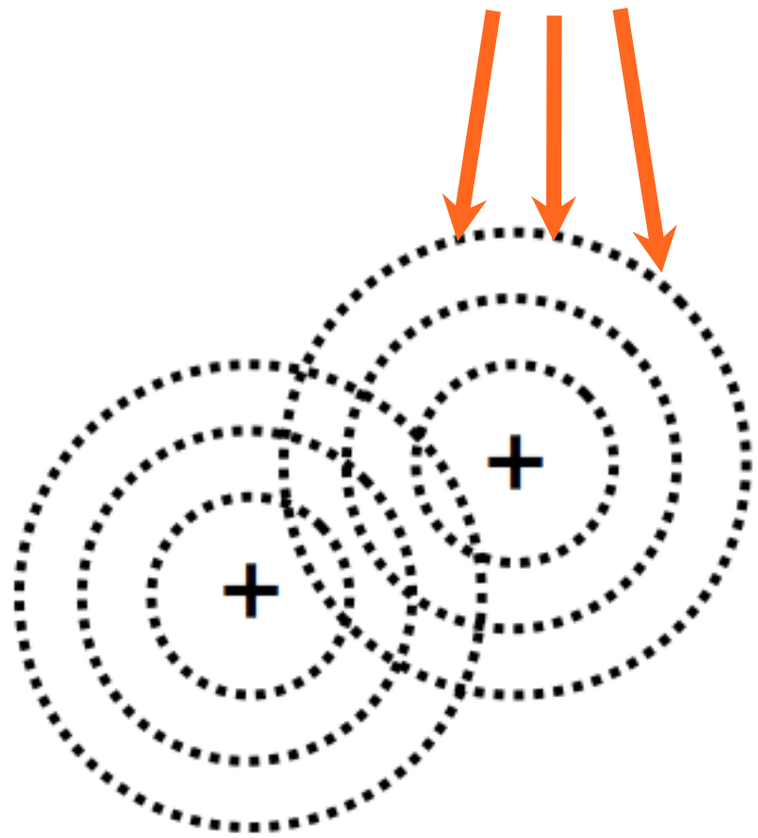
Lebedev grids can be made denser in outer regions:

 # points

```
angular_grids specified
      division   0.2659   50
      division   0.4451   110
      division   0.6052  194
#     division   0.7543  302
      outer_grid 194
```

radius

Specific angular point distribution ("Lebedev")



Aalto University
School of Science

V. Blum et al. Computer Physics Communications 180, 2175 (2009)