

# Density functional theory in solid state physics

## Lecture 6

- My stupidity: RRZE does not send emails with initial passwords for the HPC
- You can set your password for the HPC account yourself by logging into your IdM page (<https://www.idm.fau.de/go>)
- Under „Special services“, you should find an entry with „Username phyv\*\*\*\*“. By clicking on the wheel symbol, you can change your password
- I will update the tutorial on StudOn accordingly

- Which exchange-correlation functional to choose depends on requirements and available computational power
- Local exchange-correlation functionals:
  - Computationally cheap
  - Especially good for structural properties, also for phonons. Workhorses of practical DFT.
  - Bad electronic properties for systems with strong electron-electron interaction
  - metaGGAs in principle the best local functionals can achieve, but difficult to implement
- Non-local (hybrid) functionals:
  - Expensive
  - Good for electronic properties, especially band gaps and accurate single-electron energies
  - Similar accuracy for structural properties as good GGAs and metaGGAs

# Kohn-Sham DFT for periodic systems

- (Infinite) crystalline solid: Periodicity with lattice vectors  $\vec{a}_1, \vec{a}_2, \vec{a}_3$
- $v(\vec{r})$  has the same periodicity, shifting by vector  $\vec{T}_{lmn} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$  transforms  $v(\vec{r})$  into itself,

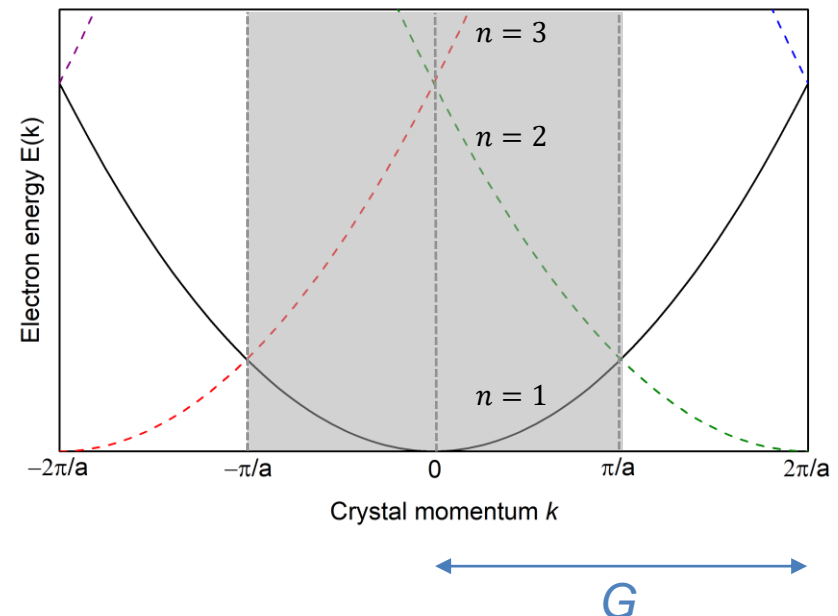
$$v(\vec{r} + \vec{T}_{lmn}) = v(\vec{r})$$

- Electron density  $n(\vec{r})$  and single-particle orbitals  $\varphi_i(\vec{r})$  are also periodic, Bloch functions (in the periodic directions)

$$F_k(r) = f_k(r)e^{ikr} \quad (k \text{ goes over whole reciprocal space})$$

- Reducible scheme: Only consider  $k$ -vectors in first Brillouin zone
- We now describe orbitals in terms of three numbers:  $k$ -vector, band index  $n$ , spin direction  $\sigma$ :

$$\varphi_{kn\sigma}(\vec{r}) = u_{kn\sigma}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$$



- Kohn-Sham equations for periodic systems:

$$\left( -\frac{1}{2} \nabla^2 + v(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{XC}^\sigma(\vec{r}) \right) \varphi_{kn\sigma}(\vec{r}) = \varepsilon_{kn\sigma} \varphi_{kn\sigma}(\vec{r})$$

- Electron density will then be an integral over Brillouin zone

$$n(\vec{r}) = \sum_{i,\sigma}^{occ} f_{occ}(\varepsilon_i) |\varphi_{i\sigma}(\vec{r})|^2 \rightarrow n(\vec{r}) = \sum_{n,\sigma}^{occ} \int f_{occ}(\varepsilon_{kn\sigma}) |u_{kn\sigma}(\vec{r})|^2 dk$$

Occupation of state  $i$

- Similarity for other properties, such as total energy:

$$E_{tot} = \sum_{n,\sigma}^{occ} \int f_{occ}(\varepsilon_{kn\sigma}) \varepsilon_{kn\sigma} dk$$

- In practice, integrals cannot be done analytically  $\rightarrow$  numerical integration

## Mean value k-point

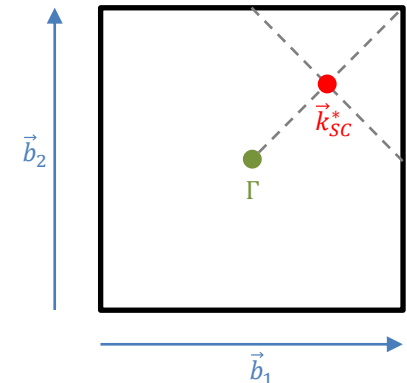
- Approximate integral by sum over set of  $N$  discrete points, i.e.

$$n(\vec{r}) \approx \sum_{n,\sigma}^{occ} \sum_k^N f_{occ}(\varepsilon_{kn\sigma}) |u_{kn\sigma}(\vec{r})|^2 w_k$$

Weight of „k-point“  $k$

- For computational reasons: Want  $N$  to be as small as necessary
- Simplest approximation: take one or a few „special“ points for the integration
- $\Gamma$  point usually is a bad choice
- Baldereschi's „mean-value point“ (*Phys. Rev. B* 7, 5212 (1973)): special point in Brillouin zone that approximates the average value  $\bar{f}$  of a  $k$ -periodic function.

$$I = \int_{BZ} f(\vec{k}) dk = V_{BZ} \bar{f}$$



- Dictated by crystal symmetry, tabulated for cubic and hexagonal lattices
- For simple cubic:  $\vec{k}_{SC}^* = \frac{\pi}{a}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , for FCC:  $\vec{k}_{FCC}^* = \frac{2\pi}{a}(0.6223, 0.2953, 0)$

## „Special k-points“ sets

- Sets of „special points“ to give optimally fast convergence

- Chadi & Cohen (*Phys. Rev. B* 8, 5747 (1973)):  $f(\vec{k}) = \underbrace{f_0}_{\vec{f}} + \sum_{m=1}^{\infty} f_m \sum_{|R|=C_m} e^{i\vec{k}\cdot\vec{R}}$

Sum over all all vectors that are equivalent by symmetry

Contributions decrease strongly with  $m$

$$f_0 = \sum_{i=1}^N \alpha_i f(\vec{k}_i) - \underbrace{\sum_m \sum_{i=1}^N \alpha_i f_m \sum_{|R|=C_m} e^{i\vec{k}\cdot\vec{R}}}_{\text{choose } \vec{k}_i \text{ such that } \approx 0}$$

- k-point set dependent on crystal symmetry

- For simple cubic: Single k-point

$$\vec{k}_1 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \quad (\text{in units of } 2\pi/a)$$

Four k-points set

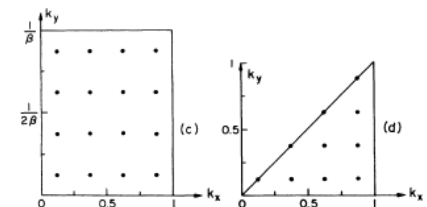
$$\vec{k}_1 = (\frac{1}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_1 = \frac{1}{8}; \quad \vec{k}_2 = (\frac{3}{8}, \frac{1}{8}, \frac{1}{8}), \quad \alpha_2 = \frac{3}{8};$$

$$\vec{k}_3 = (\frac{3}{8}, \frac{3}{8}, \frac{1}{8}), \quad \alpha_3 = \frac{3}{8}; \quad \vec{k}_4 = (\frac{3}{8}, \frac{3}{8}, \frac{3}{8}), \quad \alpha_4 = \frac{1}{8}.$$

Higher  $N$  k-point set

$$\vec{k}_i = \frac{1}{8} (1/2^n, 1/2^n, 1/2^n)$$

- Similar sets for 2D BZ: Cunningham (*Phys. Rev. B* 10, 4988 (1974))

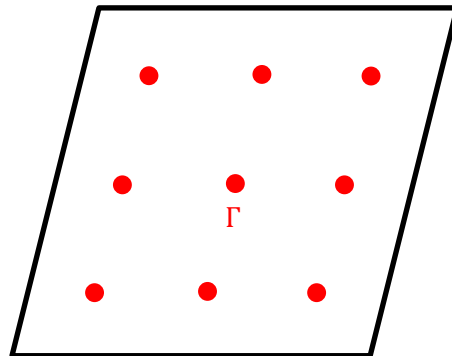


# Monkhorst-Pack grids

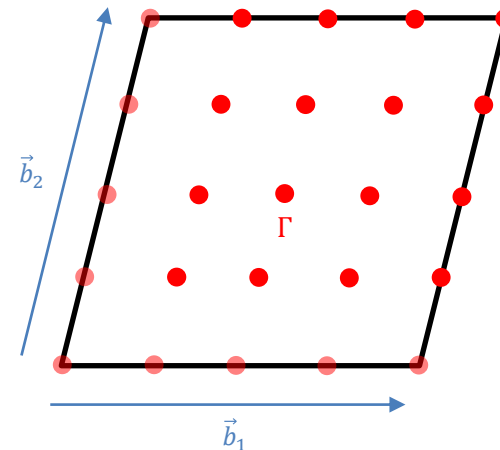
- Most relevant nowadays: Monkhorst-Pack grids (*Phys. Rev. B* 13 5188 (1976))
- Uniformly spaced grid of  $n_1 \times n_2 \times n_3$  k-points
- $\Gamma$ -centered (unshifted) grid:  $\vec{k}_{l,m,n} = \frac{l}{n_1} \vec{b}_1 + \frac{m}{n_2} \vec{b}_2 + \frac{n}{n_3} \vec{b}_3$  with  $l = -\frac{n_1-1}{2}, \dots, 0, 1, \dots, \frac{n_1-1}{2}$

Only included if  $l$  is even

3x3 grid



4x4 grid

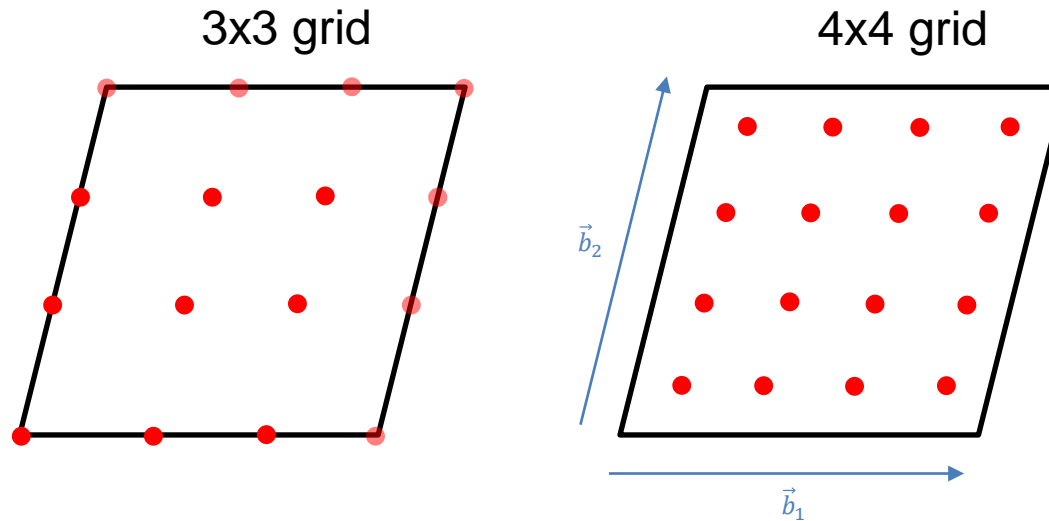


- Advantage: an easy-to-generate set of k-points, yields an approximate function  $\tilde{f}(\vec{k})$  with the correct symmetry



# Shifted Monkhorst-Pack grids

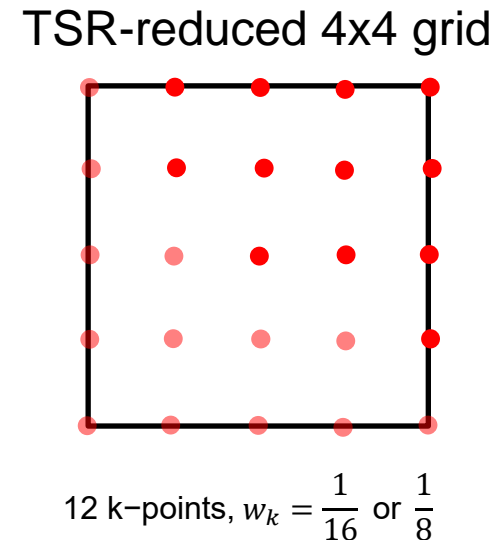
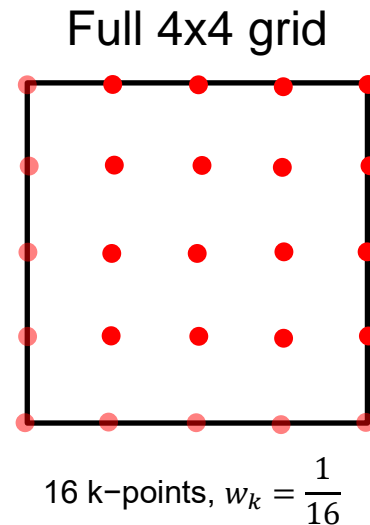
- „Shifted“ grids:  $\vec{k}_{l,m,n} = \frac{l-1}{n_1} \vec{b}_1 + \frac{m-1}{n_2} \vec{b}_2 + \frac{n-1}{n_3} \vec{b}_3$



- (Fully) shifted grids do not contain the  $\Gamma$ -point
- Do we need to use the full k-point grid in calculations?
- Use unshifted or shifted grids for calculations?

# Time-reversal symmetry

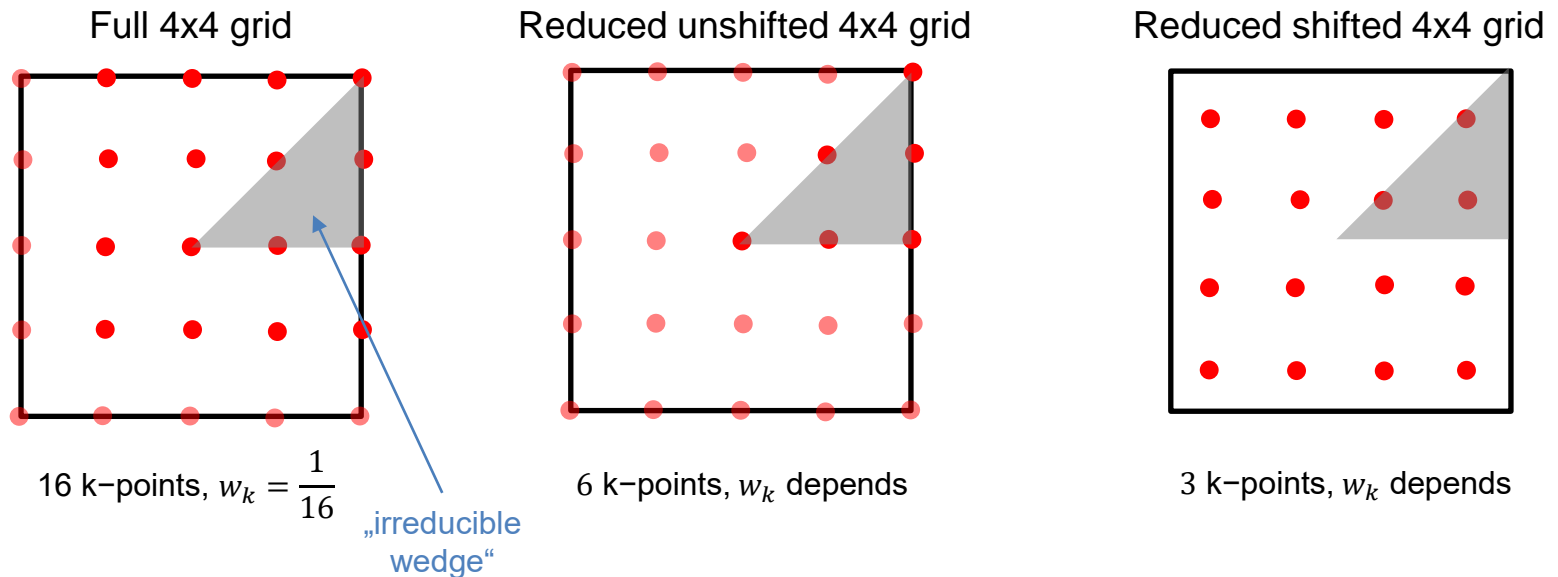
- Use symmetry operations to reduce full k-point grid
- Time-reversal symmetry: Contribution of  $-\vec{k}$  to properties is equal to that of  $\vec{k}$



- Electron density: 
$$n(\vec{r}) \approx \sum_{n,\sigma}^{occ} \sum_k^{N_{red}} f_{occ}(\epsilon_{kn\sigma}) |u_{kn\sigma}(\vec{r})|^2 w_k$$
- TRS is essentially always applicable, reduction of k-points in grid typically by factor 1.5-2

# Irreducible k-points set

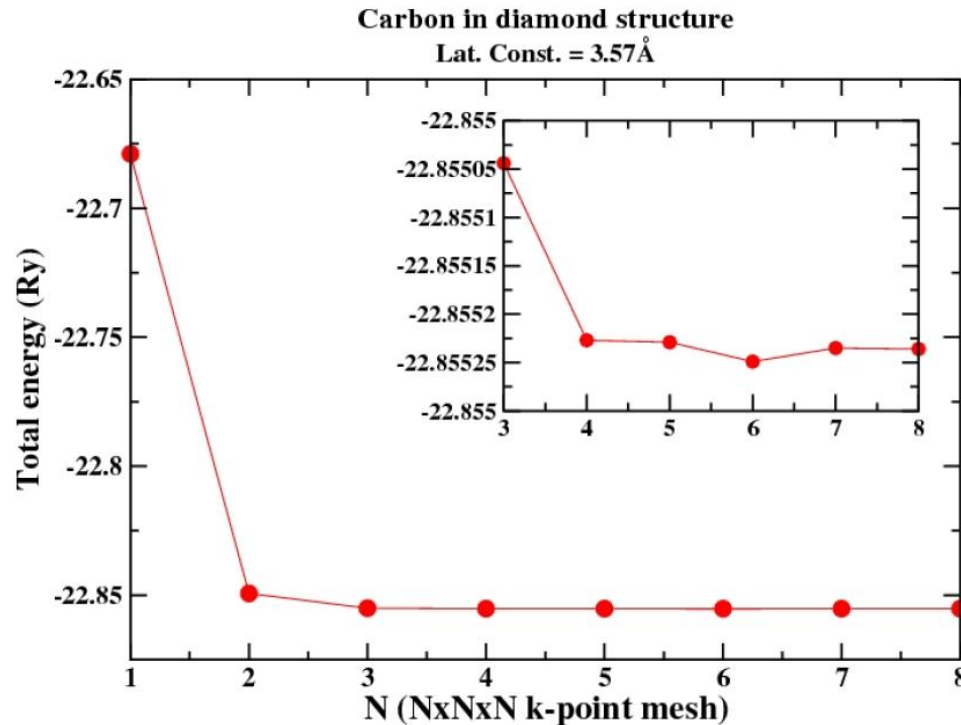
- Similarly: Crystal symmetry determines sets of  $\vec{k}$ -points that contribute equally, define „irreducible“ set of k-points.
- For example a square/cubic lattice with full symmetry:



- Degree of reduction depends on crystal symmetry, large speed gains for highly symmetric materials
- Bravais lattice determines whether a shifted or an unshifted grid gives less irred. k-points

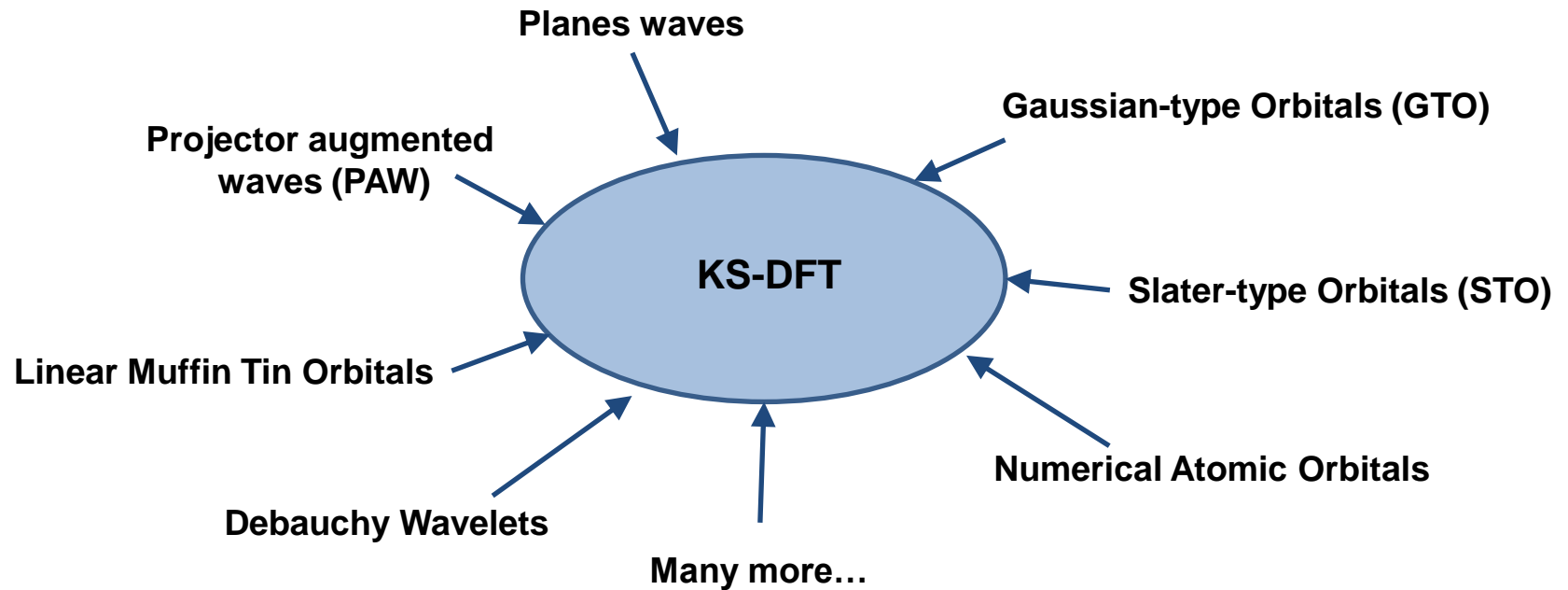
# Convergence of k-point sampling

- How dense should the sampling be? Depends on the material
- Good practice to do a 'convergence test' for each new material to ensure meaningful results



- Total energy differences usually converge faster than the absolute total energy, due to error cancellation

- How do we describe the single-particle orbitals? Typically using a basis set



# The planewave basis

- „Solid state point of view“: Atoms are a perturbation to the homogeneous electrons gas
- Idea: Use a basis set that inherently mirrors the 3D translation symmetry of the crystal
- Bloch wave-type orbitals in crystals:  $\varphi_{kn\sigma}(\vec{r}) = u_{kn\sigma}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$
- $u_{kn\sigma}(\vec{r})$  is periodic in space, so we can expand it in terms of plane waves:

$$u_{kn\sigma}(\vec{r}) = \sum_{\vec{G}} c_{kn\sigma}(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

Reciprocal lattice vector,  $\vec{G} = l\vec{b}_1 + m\vec{b}_2 + n\vec{b}_3$

- In real space:  $\varphi_{kn\sigma}(\vec{r}) = \sum_{\vec{G}} c_{kn\sigma}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$
- In reciprocal space:  $c_{kn\sigma}(\vec{G}) = FT \{ \varphi_{kn\sigma}(\vec{r}) \}$



- In principle, have to sum over infinitely many  $\vec{G}$
- In practice, this is not possible. But: contributions of „longer“  $\vec{G}$ 's become smaller
- Define „cutoff energy“ for the largest  $\vec{G}$  that is still included:

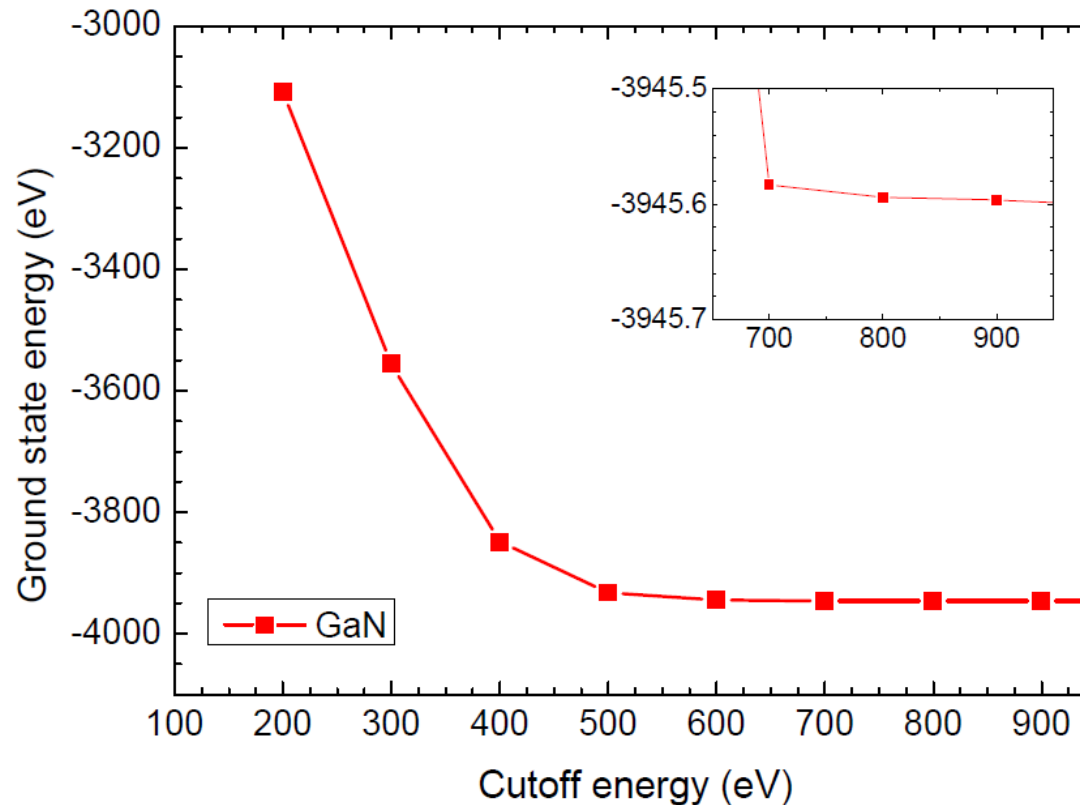
$$E_{cut} = \frac{|\vec{G}_{max}|^2}{2}$$

$$\varphi_{kn\sigma}(\vec{r}) \approx \sum_{\vec{G}}^{\vec{G}_{max}} c_{kn\sigma}(\vec{G}) e^{i(\vec{k}+\vec{G}) \cdot \vec{r}}$$

- Advantage: Plane waves are easy to handle and unbiased.
- It is simple to improve the basis set quality by increasing  $E_{cut}$
- The smoother the electron density of the system, the lower  $E_{cut}$  can be chosen

# Convergence test for cutoff energy

- Good practice: convergence test for the cutoff energy for every new system





- Plane wave basis allows for simple treatment of all terms in KS Eq.
- Kinetic energy and Hartree potential/energy are more easily evaluated in a plane wave basis

- Kinetic energy: 
$$T^S = \sum_{k,n,\sigma} \int \varphi_{kn\sigma}^*(\vec{r}) \frac{1}{2} \nabla^2 \varphi_{kn\sigma}(\vec{r}) d\vec{r}$$
$$= \frac{1}{2} \sum_{k,n,\sigma} \sum_{\vec{G}} \sum_{\vec{G}'} \int \left( c_{kn\sigma}^*(\vec{G}) e^{-i(\vec{k}+\vec{G}')\cdot\vec{r}} \right) \nabla^2 \left( c_{kn\sigma}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \right) d\vec{r}$$
$$= \frac{1}{2} \sum_{k,n,\sigma} \sum_{\vec{G}} |\vec{k} + \vec{G}|^2 c_{kn\sigma}^*(\vec{G}) c_{kn\sigma}(\vec{G})$$

- Hartree potential: 
$$v_H(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' = \dots = FT^{-1} \underbrace{\left[ \frac{4\pi n(\vec{G})}{V G^2} \right]}_{v_H(\vec{G})}$$

G=0 terms are excluded,  
they cancel with the average  
electrostatic potential of the  
nuclei

- Hartree energy: 
$$E_H = \int \int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r} = \frac{4\pi}{2V} \sum_{\vec{G} \neq 0} \frac{n(\vec{G}) n(\vec{G})}{G^2}$$

- In most codes: Kohn-Sham equation in reciprocal space

$$\sum_{\vec{G}'} \left[ \frac{1}{2} |\vec{k} + \vec{G}|^2 \delta_{\vec{G}\vec{G}'} + v(\vec{G} - \vec{G}') + v_H(\vec{G} - \vec{G}') + v_{XC}(\vec{G} - \vec{G}') \right] c_{ik}(\vec{G}') = \varepsilon_{ik} c_{ik}(\vec{G})$$

- $v(\vec{G} - \vec{G}')$  and  $v_{XC}(\vec{G} - \vec{G}')$   $c_{ik}(\vec{G}')$  from Fourier transformation, solve for  $c_{ik}$
- Plane wave basis also allows efficient implementation of exact exchange

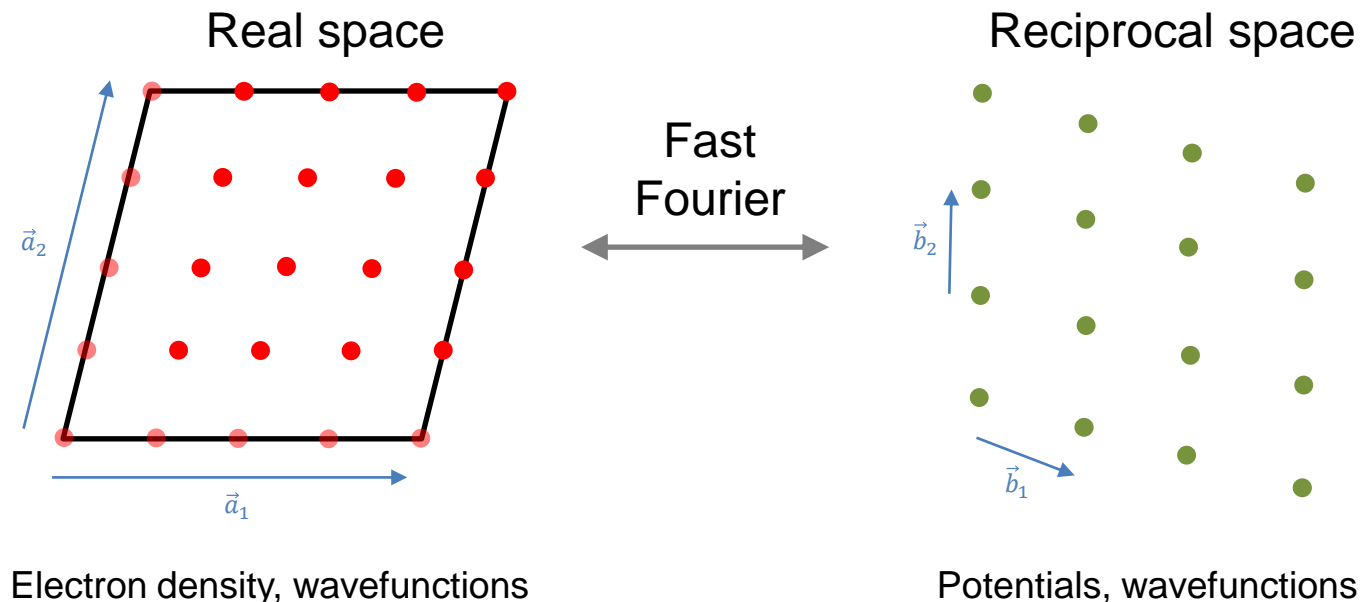
$$E^{HF} = -\frac{1}{2} \sum_{i,j,k,q} \int \int \frac{\varphi_{ik}^*(\vec{r}) \varphi_{jq}^*(\vec{r}') \varphi_{ik}(\vec{r}') \varphi_{jq}(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' d\vec{r} = \dots = -\frac{4\pi}{2V} \sum_{i,j,k,q} \sum_{\vec{G}} \frac{|C_{ikjq}(\vec{G})|^2}{|\vec{q} - \vec{k} + \vec{G}|^2}$$

$$\text{with } C_{ikjq}(\vec{G}) = \sum_{\vec{G}'} c_{ik}^*(\vec{G}') c_{jq}(\vec{G} + \vec{G}') = \sqrt{V} FT[\varphi_{ik}^*(\vec{r}) \varphi_{jq}(\vec{r})]$$

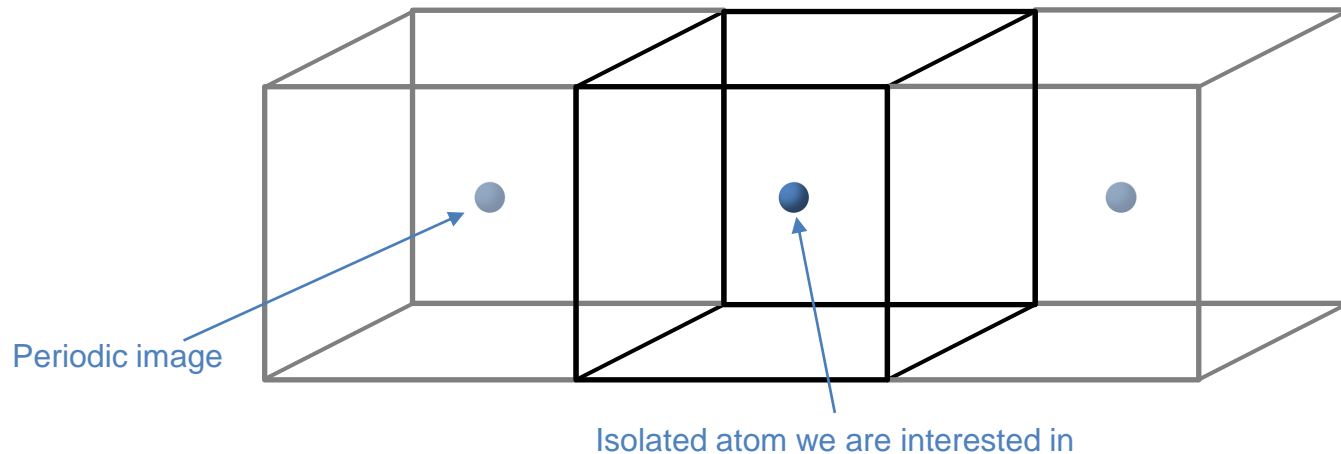
- Similar expression for non-local exact exchange potential  $\frac{dE^{HF}}{dc_{ik}^*(\vec{G}')}$ , solve GKS in rec. space

# Discrete Fourier Transforms

- Planewave basis allows efficient DFT calculations through use of Fast Fourier Transforms ( $N_{PW}$  is chosen as a product of small prime numbers)
- FFT reduces scaling from  $O(N_{PW}^2) \rightarrow O(N_{PW} \log(N_{PW}))$
- Substantial reduction, as  $N_{PW}$  is of order 10000-100000 in most practical calculations
- Fourier transformation between discrete grids in real and reciprocal space.



- A weakness of planewaves: Satisfaction of 3D periodic boundary conditions is required in all calculations
- For lower dimensional materials (atoms, molecules, surfaces): need to „pad“ system with vacuum layer to reduce residual interaction between periodic images

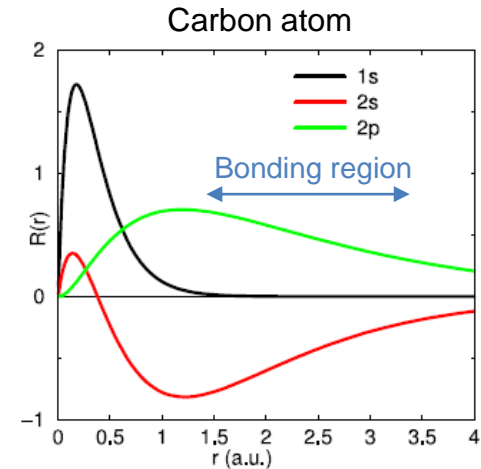


- For low-dimensional systems, this leads to an unfavourable increase in the basis size, as  $N_{PW} \propto V$  for a given  $E_{cut}$
- Vacuum thickness is chosen as a tradeoff between efficiency and accuracy
- (in exchange, we can sample only 1 k-point in the „non-periodic“ directions)

- A general problem of planewave basis: Best suited for rather smooth electron densities or single-particle wavefunctions.

- But: Electron density varies strongly around the nuclei, wavefunctions of core electrons are quite localized and can oscillate in the core region strongly due to orthogonality constraints

→ very high  $E_{cut}$  required to properly describe this behaviour, i.e. massive basis set size



- On the other hand: Core electrons provide little to no direct contribution to chemical or physical properties
- Core electrons contribute indirectly to properties through interaction with valence electrons

**C (Z=6)**

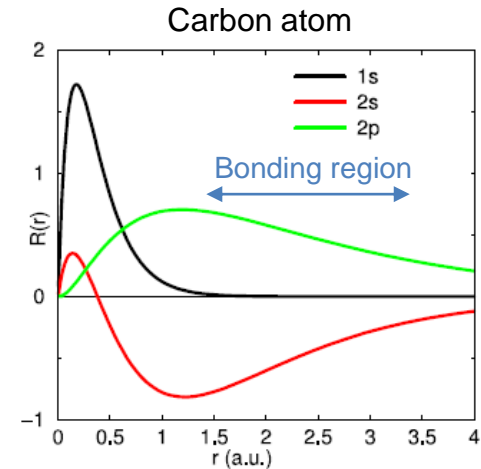
2p	$E_{1s} = -0.5$
2s	$E_{2s} = -0.7$
1s	$E_{1s} = -11.0$

(in a.u.)

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- On the other hand: Core electrons provide little to no direct contribution to chemical or physical properties
- Core electrons contribute indirectly to properties through interaction with valence electrons
- Idea: Smooth things out in the core region by not treating core electrons explicitly anymore

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