Basics II: electronic convergence and BZ sampling

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Outline

Determination of the Electronic Groundstate

Overview

- eigenvalue problem to be solved
- general strategies to solve the KS-equations
- algorithms used in VASP
- choice of the appropriate input parameters
- strategies if concergence fails, error handling

the Kohn-Sham Groundstate

the Free Energy Functional

- electronic contribution of the Kohn-Sham free energy F_{KS} at finite T:

$$\begin{aligned} F_{KS}[\phi, f, \vec{R}] &= \sum_n f_n < \phi_n | \hat{T} | \phi_n > - \sum_n \sigma S(f_n) \\ &+ E_H[\rho] + E_{xc}[\phi, f] + \int V_{\text{ion}}(\vec{r}) \rho(\vec{r}) d^3\vec{r} \end{aligned}$$

- with contributions of the kinetic energy,
- entropy of non-interacting e^-,
- Hartree term,
- exchange-correlation energy and the
- ionic potential

Electronic Convergence

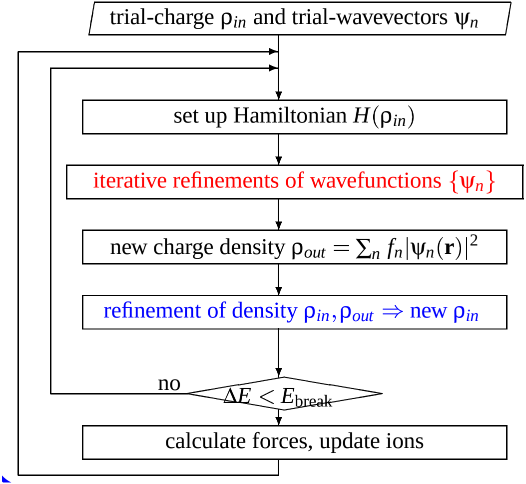
the Free Energy Functional

$$F_{KS}[\phi, f, \vec{R}] = \sum_n f_n < \phi_n|\hat{T}|\phi_n > - \sum_n \sigma S(f_n) + E_H[\rho] + E_{xc}[\phi, f] + \int V_{\rm ion}(\vec{r})\rho(\vec{r})d^3\vec{r}$$

- $\vec{R}$: ions' positions,
- f_n: levels' occupancies,
- $\phi : 1 - e^-$ orbitals
- electron density $\rho = \sum_{n=1}^{occ} f_n|\psi_n(\vec{r})|^2$
- going beyond DFT,

$$E_{xc}[\phi, f] = \underbrace{E_{xc}^{\rm loc}[\rho]}_{\rm LDA,GGA} + \underbrace{E_x^{\rm nl}[\phi, f]}_{\rm XXC}$$

the Self-Consisteny Cycle



trial-charge ρ_{in} and trial-wavevectors ψ_n

set up Hamiltonian $H(\rho_{in})$

iterative refinements of wavefunctions $\{\psi_n\}$

new charge density $\rho_{out} = \sum_n f_n |\psi_n(\mathbf{r})|^2$

refinement of density $\rho_{in}, \rho_{out} \Rightarrow$ new ρ_{in}

no

$\Delta E < E_{\text{break}}$

calculate forces, update ions

2 optimization loops

- inner (el): refinement of wavefunctions: optimization of $\{\psi_n\}$
- outer (el): refinement of ρ_{in} charge density mixing
- outer (ionic) refinement of atoms' positions: minimisation of the forces

Numerical Determination of the electronic groundstate

Iteration to Self-Consistency

self-consistent solution of $\mathbf{H}\Psi = E\Psi$

- old-fashioned:
  1. start with a trial ρ_{in}^{0}
  2. solve the Schrödinger eqn.
  3. calculate the new density $\rho_{out} = \sum^{occ} |\psi_n|^2$
  4. mix charge densities: $\rho_{new} = n\rho_{in} + (n-1)\rho_{out}$
  5. construct the new Schrödinger eqn. using ρ_{new}
  6. iterate 2-5 until convergence is reached

– slow

Numerical Determination of the electronic groundstate

Direct Minimization of the Functional

- modern, based on the method of Car-Parrinello:
- used if the diagonalization of **H** is the bottleneck of the calculation
- minimize the value of the functional $F_n(\vec{r})$

$$\text{gradient}: \quad F_n(\vec{r}) = [-\frac{\hbar^2}{2m_e}\nabla^2 + V^{\mathrm{eff}}(\vec{r}, \rho(\vec{r'})) - \epsilon_n]\phi_n$$

- start with a set of trial wavefunctions $\phi_n^0(\vec{r})$ with $n = 1, \ldots N_e(/2)$ (eg random numbers)
- converge each band iteratively, starting from ϕ_n^0, diagonalizing the Hamiltonian
- supported by VASP (versions up from vasp.4.6)

Basic Algorithms used in VASP

Overview

- almost all algorithms used by VASP are based on iterative matrix diagonalization schemes
  1. blocked Davidson (DAV)
  2. conjugate gradient (CG)
  3. residual minimization (RMM), direct inversion in the iterative subspace (DIIS)
- a small amount of a residual vector $|R_n>$ is added to the function f to refine f $(f = |\phi_n>, \rho, ...)$
- in iterative diagonalization methods, $|R(\phi_n)>$ is used to update the wavefunction: $\phi'_n = \phi_n + \lambda R_n$ (in the sense of a steepest descent approach)
- minimize the norm of $|R_n>$

Basic Algorithms used in VASP

Residual Vectors: wavefunction ($|\phi_n>$)

- start with some trial ϕ_n for an eigenstate n of $\hat{H}$
- variation of the Rayleigh quotient with respect to $<\phi_n| \longrightarrow$ residual vector $|R(\phi_n)>$:

$$\epsilon_n^{\mathrm{appr.}} = \frac{<\phi_n|\mathbf{H}|\phi_n>}{<\phi_n|\mathbf{S}|\phi_n>} \longrightarrow |R(\phi_n)> = (\mathbf{H} - \epsilon_n^{\mathrm{appr.}}\mathbf{S})|\phi_n>$$

- aim: find a matrix **K** which gives the exact error of the wavefunction (preconditioning), to find the optimal $|R_n>$

Basic Algorithms used in VASP

Preconditioning (I)

- aim: find a unitary matrix ("rotation matrix") **K** that yields:
- the exact error in the trial wavefunction (ideally in a single step)
- a preconditioned residual vector $|p_n\rangle = \mathbf{K}|R_n\rangle$
- based on the ansatz of Teter *et.al*:
  as E_{kin} dominates **H** for large $\vec{G}$, $\longrightarrow \mathbf{K} = \mathbf{K}(\frac{3}{2}E_{kin}(\vec{R}))$
  G. Kresse, J. Furthmüller, Phys. Rev. **B 54**, 11169, (1996),

$$\begin{aligned} \langle \mathbf{G}|\mathbf{K}|\mathbf{G}'\rangle &= \delta_{\mathbf{GG}'} \frac{27+18x+12x^2+8x^3}{27+18x+12x^2+8x^3+16x^4}, \quad \text{with} \\ x &= \frac{\hbar^2}{2m}\frac{G^2}{\frac{3}{2}E^{\mathrm{kin}}(\vec{R})} \end{aligned}$$

Basic Algorithms used in VASP

Preconditioning (II)

- preconditioning using hybrid functionals (M. Marsman, G. Kresse, to be published): the optimal **K** to optimize

$$\begin{aligned}\bar{F}[\mathbf{K}, f'] &= \sum_n \sum_{kl} f'_n \mathbf{K}^*_{nl} \mathbf{K}_{nk} < \phi_l | \hat{T} | \phi_k > - \sum_n \sigma S(f'_n) \\ &+ E_H[\rho] + \bar{E}_{xc}[\mathbf{K}, f'] + \int V_{\mathrm{ion}(\vec{r})} \rho(\vec{r}) d^3\vec{r}\end{aligned}$$

  with $\rho(\vec{r}) = \sum_n \sum_{kl} f'_n \mathbf{K}^*_{nl} \mathbf{K}_{nk} \phi^*_l(\vec{r}) \phi_k(\vec{r})$
- $\phi'_n = \sum_m \mathbf{K}_{nm} \phi_m$
- linearization of E_{XC} around the present set of orbitals:
- matrix elements for a fixed, non-local Fock V_{xc} calculated at the start of the self-consisteny procedure, not updated during the search of the optimal $\mathbf{K}_{nm}$.

Basic Algorithms used in VASP

Blocked Davidson Scheme (DAV)

1. select subset $\{\phi_k^1 | k = 1, .., n_1\}$ of all bands $\{\phi_n | n = 1, .., N_{\text{bands}}\}$
2. optimize ϕ_k^1 by adding the orthogonalized preconditioned $|R_n>$ $(|p_n>)$ to the presently considered subspace
3. Rayleigh Ritz optimization in the space spanned by these vectors ("sub-space" rotation in the $2 * n_1$ dim. space)
4. determine n_1 lowest vectors $\{\phi_k^2 | k = 1, ..., n_1\}$
5. iterate 2-4 if required
6. store the optimized w.f. back in the set $\{\phi_k | k = 1, ..n_1, .., N_{\text{bands}}\}$.
7. continue steps 1-4 with next sub-block $\{\phi_k^1 | k = n_1 + 1, .., 2n_1\}$
8. after each block of band has been optimized:
   Rayleigh Ritz optimization in the space $\{\phi_k | k = 1, .., N_{\text{bands}}\}$
9. approximately a factor of 1.5-2 slower than RMM-DIIS, but always stable.

Basic Algorithms used in VASP

Blocked Davidson (DAV)

1. $\{\phi_n | n = 1, .., N_{\mathrm{bands}}\} \Rightarrow \{\phi_k^1 | k = 1, .., n_1\}$
2. optimize this subset

$$\phi_k^1 \,/\, g_k^1 = \underbrace{\left(1 - \sum_{n=1}^{N_{\mathrm{bands}}} |\phi_n\rangle\langle\phi_n|\mathbf{S}\right)}_{\mathrm{orthonormalization\ \ operator}} \mathbf{K}\left(\mathbf{H} - \epsilon_{\mathrm{app}}\mathbf{S}\right)\phi_k^1 \,|\, k = 1, .., n_1 >$$

3. Rayleigh Ritz optimization $\longrightarrow \{\phi_k^2 | k = 1, n_1\}$
4. add additional preconditioned residuals

$$\phi_k^2 \,/\, g_k^1 \,/\, g_k^2 = (1 - \sum_{n=1}^{N_{\mathrm{bands}}} |\phi_n >< \phi_n|\mathbf{S})\mathbf{K}(\mathbf{H} - \epsilon_{\mathrm{app}}\mathbf{S})\phi_k^2 >, |\, k = 1, .., n_1$$

5. add a fourth set of preconditioned vectors if required,. . .

Basic Algorithms used in VASP

Conjugate Gradient (CG)

- strictly sequential: bands are optimized one after another
- optimization of F_{KS} with respect to the wavefunctions yields a gradient $|g_n>$

$$|g_n>= \underbrace{f_n\left(1-\sum_m |\phi_m><\phi_m|\right)\hat{H}|\phi_n>}_{1} + \underbrace{\sum_m \frac{1}{2}\mathbf{H}_{nm}(f_n-f_m)|\phi_m>}_{2}$$

with $\hat{H} = \hat{T} + \hat{V}_{\mathrm{ion}} + \hat{V}_H(\rho) + \hat{V}_{xc}[\phi, f]$

- $\hat{V}_{xc}$ includes the local V_{xc} (and the non-local screened Fock-exchange).
- 1: changes in F_{KS} with respect of changes in the ϕ orthogonal to the subspace spanned by the current ϕ
- 2: changes in F_{KS} with the subspace spanned by the current ϕ (=0 if only occupied orbitals are included)

Basic Algorithms used in VASP

Conjugate Gradient (CG)

- search direction determined by using Loewdin's perturbation theory:

$$\mathbf{U}_{nm} = \delta_{nm} - \Delta s \frac{\mathbf{H}_{nm}}{\mathbf{H}_{mm} - \mathbf{H}_{nn}}, \quad \phi'_n = \sum_m \mathbf{U}_{nm} \phi_m$$

$\mathbf{U}$… unitary matrix, chosen such that $< \phi'_n | \mathbf{H} | \phi'_m >= \epsilon_m \delta_{nm}$

- step direction $\approx \mathbf{H}_{mm} - \mathbf{H}_{nn}$
- Δs step width along the search direction
- implemented algorithms include:
  - (preconditioned) steepest descent
  - (preconditioned) conjugated gradient

Basic Algorithms used in VASP

Residual Minimization - direct inversion in the iterative subspace (RMM-DIIS)

- most time consuming step in CG: orthonormalization of the preconditioned residual vector to the current set of trial wavefunctions (for each single band update)
- avoided by minimizing the norm of the residual vector instead of the Rayleigh Ritz quotient
  P. Pulay, Chem. Phys. Lett.**73**,393 (1980), D.M. Wood, A. Zunger, J. Phys **A**, 1343 (1985)).
- each vector is optimized individually
- fast
- drawback: always finds the vector which is closest to the initial trial vector: $\longrightarrow$ if the initial set does not span the real ground state, some states may be "missing" in the final solution.

Basic Algorithms used in VASP

Residual Minimization - direct inversion in the iterative subspace (RMM-DIIS)

1. calculate a preconditioned residual vector $\mathbf{K}|R_m^0>=\mathbf{K}|R(\phi_m^0)>$
2. perform a trial step with width λ along this direction: $|\phi_m^1>=|\phi_m^0>+\lambda\mathbf{K}|R_m^0>$
3. $\longrightarrow$ new residual vector $|R_m^1>=|R(\phi_m^1)>$
4. search for the linear combination of $|\phi_m^0>$ and $|\phi_m^1>$, $|\phi_m^M>=\sum_{i=0}^M \alpha_i|\phi_m^i>$ (here: $M=1$), yielding $|R_m^M>=\sum_{i=0}^M \alpha_i|R_m^i>$ minimize $||R||$ by determining the lowest eigenvector/eigenvalue of $\sum_{j=0}^M<R_m^i|R_m^j>\alpha_j=\epsilon\sum_{j=0}^M<\phi_m^i|\mathbf{S}|\phi_m^j>\alpha_j$
5. start from 1, using $|\phi_m^M>$ and $|R_m^M>$

Basic Algorithms used in VASP

Further Algorithms

- based on CG: simultaneous update of all orbitals
- MD-like Damped velocity friction algorithm (see lecture 3) (requires the definition of a timestep)
- exact diagonalization: whenever there is a substantial amount ($>$ 30-50%) of unoccupied bands (eg for *GW* calculations)
- subspace rotation and diagonalization in the sub-space spanned by `NBANDS`

Parameters to be set in INCAR

choice of the electronic convergence algorithms

- `ALGO` algorithms to be used (alternative: `IALGO`):
  implemented in vasp.4.6 and vasp.5
  Normal (DAV) | Fast (DAV+RMM-DIIS) | VeryFast (RMM-DIIS) |
  implemented in vasp.5 only
  | Damped (damped MD) | All (damped MD+precond. CG) | Exact | Diag | Subrot | Eigenval | None | Nothing |
- for Hybrid functionals, always use direct optimization (A, Exact)
- `LDIAG` (True | False): perform subspace diagonalization
- `TIME` time step for damped MD-based algorithms

Outline

1. Electronic Convergence
   - Introduction
   - the SCF-scheme
   - Basic Algorithms used in VASP
2. Charge Density Mixing
3. Sampling the Brillouin Zone
   - Basics
   - BZ Sampling
   - Files and Parameters, Problem Handling

Charge Density Mixing

DIIS Mixing Algorithms

- calculation of the input density for the next el. step from $\rho_{new} = m\rho_{in} + (m-1)\rho_{out}$:
- minimize the norm of the residual vector $R[\rho_{\mathrm{in}}] = \rho_{\mathrm{out}}[\rho_{\mathrm{in}}] - \rho_{\mathrm{in}}$
- assume R can be linearized around ρ_{sc}:

$$
\begin{aligned}
R[\rho] &= -\mathbf{J}(\rho - \rho_{\mathrm{sc}}) \\
R[\rho] &\approx R[\rho]^{(m)} - \mathbf{J^{(m)}}(\rho^{(m)} - \rho_{\mathrm{sc}}) \\
\rho^{(m+1)} &= \rho^{(m)} + \mathbf{G^{(m)}}(\rho_{out}^{(m)} - \rho_{in}^{(m)}) \\
\mathbf{G^{(m)}} &= -\mathbf{J^{(m)-1}}
\end{aligned}
$$

Charge Density Mixing

DIIS Mixing

- $\mathbf{J} = 1 - \chi\mathbf{U}$: "charge dielectric" (Jacobian) matrix:
- in a system with a dielectric susceptibility χ, an external charge perturbation $(\Delta\rho)$ leads to a change in the potential $\mathbf{U} = \frac{4\pi e^2}{\mathbf{q}^2}$.
- model dielectric function implemented in VASP: G.P. Kerker, Phys.Rev.B**23**, 3082 (1981):

$$\begin{aligned} \mathbf{J} &\approx \mathtt{AMIX} \cdot \max\left(\frac{q^2}{q^2 + \mathtt{BMIX}}, \mathtt{AMIN}\right) \\ \mathtt{BMIX} &\ldots \ \mathbf{q} - \text{cutoff wavevector for the Kerker approx.} \end{aligned}$$

Charge Density Mixing

DIIS Mixing

- the convergence behaviour is determined by the width of the eigenvalue spectrum of $\mathbf{J} = 1 - \chi \frac{4\pi e^2}{\mathbf{q}^2}$
- insulators, semiconductors: constant, indepedent of the system size $L \Rightarrow$ good convergence
- metals:
  - short wavelength limit (large $\mathbf{q}$) $\longrightarrow \mathbf{J} \approx \mathbf{1}$: no screening
  - long wavelength limit: the screening term dominates $\mathbf{J}$:
    $\longrightarrow \mathbf{J} \approx \mathbf{q}^{-2} \sim L^2$
    $\Rightarrow$ the width of the spectrum is proportional to the square of the longest dimension of the lattice
    $\Rightarrow$ poor convergence, possibly charge sloshing.

Charge Density Mixing

Available Mixing Algorithms

- Linear Mixing ($n = \texttt{AMIX}$)
  $\rho_{in}^{(m+1)} = n\rho_{in}^{(m)} + (n-1)\rho_{out}^{(m)}$
- Kerker Mixing (`BMIX`)

$$\rho_{mix}(G) = \rho_{in}(G) + \texttt{AMIX} \cdot \max\left(\frac{G^2}{G^2 + \texttt{BMIX}}, \texttt{AMIN}\right)[\rho_{out}(G) - \rho_{in}(G)]$$

- Broyden Mixing, ($\texttt{WC} = 0$)
  D.D.Johnson, Phys.Rev.B**38**, 12807 (1988)
  information of the current iteration (m) updates $\mathbf{J}^{-1}$ but also overrides information of from previous iterations
- Pulay Mixing ($\texttt{WC} > 0$)
  P.Pulay,Chem.Phys.Lett**73**, 393 (1980)
  information from all previous iterations is included with equal weights.

Charge Density Mixing

Available Mixing Algorithms

- Tchebycheff mixing via a 2^{nd} order equation of motion, using a simple velocity Verlet algorithm
  H.Akai and P.H.Dederichs, J.Phys.C **18**, 2455 (1985)

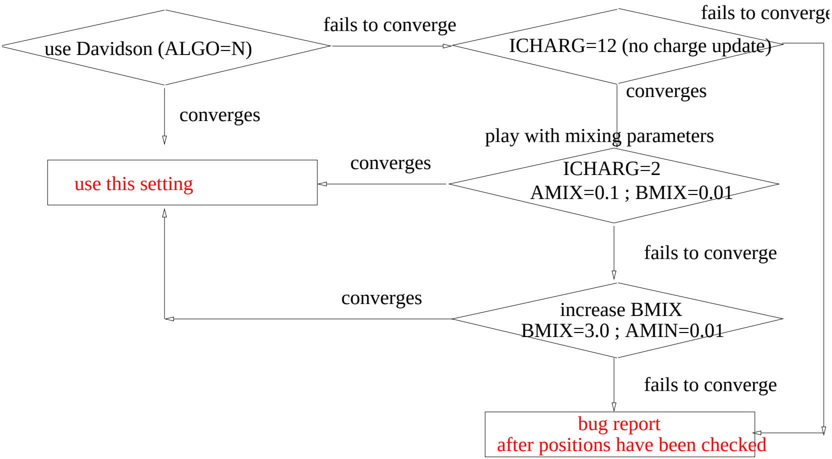
$$\begin{aligned} \ddot{\rho}_{mix}(G) &= 2 \cdot \mathbf{J}(\mathbf{G})[\rho_{out}(G) - \rho_{in}(G)] - \mu \dot{\rho}_{in}(G) \\ \mu &= \text{friction (damping) factor} \end{aligned}$$

Charge Density Mixing

Parameters to be set in INCAR

- `IMIX`: Mixing type:
  0 (no mixing) | 1 (Kerker) | 2 (Tchebycheff) |
  4 Broyden (WC=0) or Pulay (WC>0)
- Kerker mixing `BMIX, BMIX_MAG`: cutoff wavevectors
- for Boyden-type mixing: `INIMIX, MIXPE, MAXMIX, WC`
  - `INIMIX` functional form of the initial mixing matrix
  - `MIXPRE` metric for the Broyden scheme
  - `MAXMIX` max. # of steps stored in the Broyden scheme
  - `WC` weight factor for each iteration

what to do if convergence fails (DFT-level)



use Davidson (ALGO=N)

fails to converge

ICHARG=12 (no charge update)

fails to converge

converges

converges

use this setting

play with mixing parameters

converges

ICHARG=2
AMIX=0.1 ; BMIX=0.01

fails to converge

converges

increase BMIX
BMIX=3.0 ; AMIN=0.01

fails to converge

bug report
after positions have been checked

Outline

Some Basics

Periodicity

- perfect periodic lattices: translational symmetry: each unit cell is repeated at $\vec{R}$ by shifting it by $N \cdot \vec{a}$ ($\vec{a} = n_1\vec{a_1} + n_2\vec{a_2} + n_3\vec{a_3}$ lattice vector) with respect to some “origin of the lattice”:
- applying a translation operator $\hat{T}_{\vec{a_i}}$: $\hat{T}_{\vec{a_i}}(\vec{0}) = \vec{R}$
- $\hat{T}$ and $\hat{H}$ commute ($[\hat{T}, \hat{H}] = 0$)
  $\Rightarrow$ $\hat{T}$ and $\hat{H}$ have the same eigenfunctions.

$$\begin{aligned}
\hat{T}_{\vec{R}} \left|\vec{0}\right\rangle &= \left|\vec{R}\right\rangle = \lambda \cdot \left|\vec{0}\right\rangle \\
\left\langle\vec{R}|\vec{R}\right\rangle &= \lambda^*\lambda \cdot \left\langle\vec{0}|\vec{0}\right\rangle \\
\Rightarrow \lambda^*\lambda &= 1 \\
\Rightarrow \lambda &= e^{i\vec{k}}, \quad k \in \mathbf{R}
\end{aligned}$$

Some Basics (continued)

periodicity (continued)

- translation by a lattice vector $\vec{R}$

$$\hat{T}_{\vec{R}} \left|\vec{0}\right\rangle = \left|\vec{R}\right\rangle = e^{i\cdot\vec{k}\cdot\vec{R}} \cdot \left|\vec{0}\right\rangle$$

- $\Rightarrow$ for any Ψ that satisfies the Schrödinger equation in a periodic potential, $\exists\vec{k}$ such, that a translation by $\vec{R}$ is equivalent to a multiplication by the phase factor $e^{i\cdot\vec{k}\cdot\vec{R}}$, eg. for e^{-}-waves

$$\Psi(\vec{r}+\vec{R}) = e^{i\cdot\vec{k}\cdot\vec{R}}\Psi(\vec{r}).$$

periodicity: Range of $\vec{k}$

- for any lattice vector of the reciprocal lattice defined by unit vectors $\left(\vec{b_i} = \frac{2\pi}{\Omega}\vec{a_j} \times \vec{a_k}\right)$
  $\vec{G_n} = m_1\vec{b_1} + m_2\vec{b_2} + m_3\vec{b_3}$,
- let $\vec{k'} = \vec{k} + \vec{G_n}$,

$$\Psi_{\vec{k'}}(\vec{r}+\vec{R}) = e^{i\cdot\vec{k'}\cdot\vec{R}}\Psi(\vec{r}) = e^{i\cdot\vec{k}\cdot\vec{R}}\underbrace{e^{i\cdot\vec{G_n}\cdot\vec{R}}}_{\equiv 1}\Psi(\vec{r})$$

- range of allowed values for $\vec{k}$: within the first Brillouin zone (BZ)

$$0 < k \leq \frac{2\pi}{a} \text{ or } -\frac{\pi}{a} < k \leq \frac{\pi}{a}$$

- for finite crystals: $\# \ \vec{k} \neq \infty$
  $\rightarrow$? allowed number of $\vec{k}$ $\rightarrow$ quantization of $\vec{k}$

Some Basics (continued)

Quantisation of $\vec{k}$

- cyclic Born-von Kármán boundary conditions ($l = N_1 a_1$)
- unperturbed (ideal) crystal (eg 1D chain with length l),
- N_1: number of unit cells of the macroscopic crystal along x
- N_1: large enough to provide that effects of the crystal shape are negligible.

$$\Psi(\vec{x} + N_1\vec{a}_1) = \Psi(\vec{x}), \qquad \vec{\nabla}\Psi(\vec{x} + N_1\vec{a}_1) = \vec{\nabla}\Psi(\vec{x})$$

$$\Psi(x + N_1 a_1) = e^{ik_1 N_1 a_1}\Psi(x) \quad \Rightarrow \quad e^{ik_1 N_1 a_1} = 1$$

$$k_1 N_1 a_1 = 2\pi m_1 \quad \Rightarrow \quad k_1 = \frac{2\pi m_1}{N_1 a_1}, \quad m_1 \in Z$$

$$0 < m_1 \leq N_1 \quad \text{or} \quad -\frac{N_1}{2} < m_1 \leq \frac{N_1}{2}$$

Some Basics (continued)

energy bands

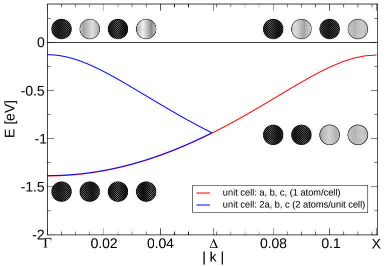
- proper wavefunctions in a periodic lattice: $\Psi_{\vec{k}}(\vec{r}) = \underbrace{e^{i\vec{k}\vec{r}}}_{\text{BlochFactor}} \cdot u(\vec{r})$ where $u(\vec{r})$ is a cell-periodic function of the lattice
- the eigenvalues $\epsilon_n(\vec{k})$ of a crystal of *fixed, finite* volume V: *discrete* spectrum of $\hat{H}$:

$$\hat{H}\Psi_{\vec{k}+\vec{G}_n}(\vec{r}) = \hat{H}\Psi_{n\vec{k}}(\vec{r}) = \epsilon_{\vec{k}+\vec{G}_n}\Psi_{n\vec{k}}(\vec{r}), \quad \epsilon_{\vec{k}+\vec{G}_n} = \epsilon_n(\vec{k})$$

- $\forall n$: the set of electronic levels $\epsilon_n(\vec{k})$ is the "n^{th} **energy band**".
- the eigenstates and -values are periodic with $\vec{k}$ in the reciprocal lattice ("extended zone sheme")

Some Basics (continued)

s-like bands for a primitive cell and a supercell with 2 atoms



Supercells

- example: bandstructure of (super)cells containing 1 (2) atoms with 2 *s*-electrons
- $\vec{a}' = 2\vec{a} \Rightarrow \vec{k}_1' = \frac{1}{2}\vec{k}_1$
- folding of the bandstructure

cell size	$1a$	$2a$
# bands	1	2
$\vec{k}$-pts	Γ	Γ
	Δ	X
	X	Γ

- $\Rightarrow$ for constant $\vec{k}$-grid-density: $N(\vec{k'}) = \frac{1}{2}N(\vec{k})$

Sampling of the Brillouin Zone

Integrals over the Brillouin zone I_{BZ}:

- for the calculation of e.g. Density of states (DOS), Charge densities, ...
- Integrals over the Brillouin zone are usually replaced by sums over special $\vec{k}$-points:
- $$I(\epsilon) = \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\mathrm{BZ}} F(\epsilon)\delta(\epsilon_{n\vec{k}} - \epsilon) d\vec{k} \longrightarrow \sum_{\vec{k}} w_{\vec{k}_i} F(\epsilon)\delta(\epsilon_{n\vec{k}} - \epsilon)$$
- Symmetry of the lattice: BZ ⟶ irreducible BZ (IBZ)

$$\Omega_{\mathrm{IBZ}} = \frac{\Omega_{\mathrm{BZ}}}{N_{\hat{R}}}$$

- $N_{\hat{R}}$: number of symmetry operations of the point group

Sampling of the Brillouin Zone

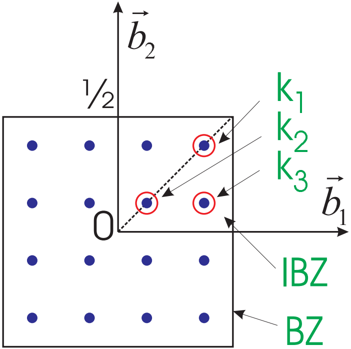
$\vec{k}$-mesh generation

- the BZ should be covered by equally-spaced $\vec{k}$-point grids, e.g. Monkhorst-Pack meshes
  H.J. Monkhorst, J.D. Pack, PRB **13**, 5188, (1976)

$$\vec{k} = \vec{b}_1 \frac{n_1 + s_1}{N_1} + \vec{b}_2 \frac{n_2 + s_2}{N_2} + \vec{b}_3 \frac{n_3 + s_3}{N_3}$$

- $\vec{b}$ unit vector of the BZ
- s_i optional shift along direction i
- N_i number of subdivisions along i

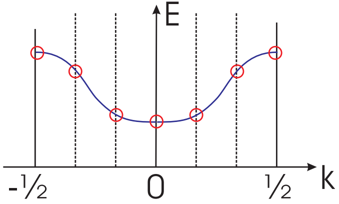
example of a MP-mesh of a 2D square lattice



Mesh data

- full BZ: $N_1 = N_2 = 4 \Rightarrow n_{\vec{k}}(\mathrm{BZ}){=}16$
- $N_{\hat{R}} = 4 \Rightarrow n_{\vec{k}}(\mathrm{IBZ}) = 4$
- $w_{\vec{k}_1} = w_{\vec{k}_2}(\mathrm{IBZ}) = \frac{4}{16} = \frac{1}{4}$
- $w_{\vec{k}_3} = \frac{8}{16} = \frac{1}{2}$
- $\frac{1}{\Omega_{\mathrm{BZ}}} \int\limits_{BZ} F(\vec{k}) d\vec{k} \longrightarrow \frac{1}{4}F(\vec{k}_1) + \frac{1}{4}F(\vec{k}_2) + \frac{1}{2}F(\vec{k}_3)$

example: bandstructure energy

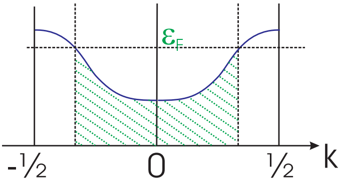


e.g: one *s*-like band

- $F(\vec{k}) = \epsilon(\vec{k})$
- $E = \sum_k w_{k_i}\epsilon_{k_i}$
- Γ: no nodes in Ψ ⇒ ϵ=min
- X: max # of nodes in Ψ ⇒ ϵ=max
- to increase the accuracy:
- increase the density of the $\vec{k}$-mesh

Smearing Methods

problem in metallic systems: some bands cross the Fermi level $E_F = \mu$
$\Rightarrow$ discontinuity of the occupancy f of bands at $E_F = \mu$



band n crossing E_f

- eg: bandstructure energy

$$E_b = \sum_{n,\vec{k}_i} w_{\vec{k}_i} \epsilon(\vec{k}_i, n) f(\epsilon(\vec{k}_i, n) - \mu)$$

- ocupancy of state $(\vec{k}_i, n)$

$$f(\epsilon(\vec{k}_i, n) - \mu) = \begin{cases} 1 & \ldots \quad \epsilon(\vec{k}_i, n) \leq \mu \\ 0 & \ldots \quad \epsilon(\vec{k}_i, n) > \mu \end{cases}$$

Smearing Methods

Fermi-Dirac smearing

- $$f\left(\frac{\epsilon_{(n,\vec{k})}-\mu}{\sigma}\right)=\frac{1}{\exp\left(\frac{\epsilon_{(n,\vec{k})}-\mu}{\sigma}\right)+1}$$
- $\sigma = k_B T$ ...smearing parameter ($\approx$ electronic T of the system)
- energy E is no longer variational with respect to the partial occupacies f
- the new variational functional is the Free energy F
  $F = E - \sum_n \sigma S(f_n)$
- S: entropy of a system of non-interacting electrons at a finite temperature T
- $S(f) = -[f\ln f + (1-f)\ln(1-f)]$

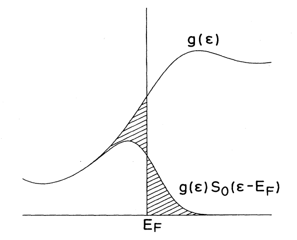
Smearing Methods

Gaussian Smearing

- levels are broadened with a Gaussian function
- f is the integral of the Gaussian function:
- $f\left(\frac{\epsilon_{n,\vec{k}}-\mu}{\sigma}\right) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp^{\left(\frac{\epsilon_{n,\vec{k}}-\mu}{\sigma}\right)^2}, \quad \int f = \frac{1}{2}\left[1 - \mathrm{erf}\left(\frac{\epsilon_{n,\vec{k}}-\mu}{\sigma}\right)\right]$
- analytical inversion of the error-function erf does not exist
- $\Rightarrow$ S and F cannot be written in terms of f,
- $S\left(\frac{\epsilon-\mu}{\sigma}\right) = \frac{1}{2\sqrt{\pi}} \exp^{-\left(\frac{\epsilon-\mu}{\sigma}\right)^2}$
- σ has no physical interpretation.
- variational functional $F(\sigma)$ differs from $E(0)$.
- Forces: $\vec{F}(F(\sigma))$ are not necessarily equal to $\vec{F}(E(0))$.
- workaround: extrapolation to $\sigma \longrightarrow 0$:

Smearing Methods

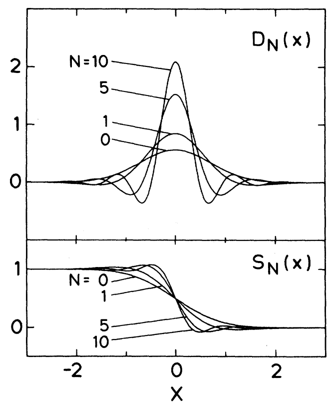
Methfessel-Paxton smearing



- generalization of Gaussian broadening with functions of higher order
- expansion of stepfunction in a complete set of orthogonal functions:
- Hermite polynomials of order N
- term of $N = 0$: integral over Gaussians

Smearing Methods

Methfessel-Paxton smearing



MP smearing

- Hermite-polynomial of order N
  $f_0(x) = \frac{1}{2}(1 - \mathrm{erf}(x))$
  $f_N(x) =$
  $f_0(x) + \sum_{m=1}^{N} A_m H_{2m-1}(x) e^{-x^2}$
  $S_N(x) = \frac{1}{2} A_N H_{2N}(x) e^{-x^2}$
- deviation of $F(\sigma)$ from $E(0)$ only of order 2+N in σ
- extrapolation for $\sigma \to 0$ usually not necessary, but possible:
- $E(0) \approx \hat{E}(\sigma) = \frac{1}{N+2}((N+1)F(\sigma) + E(\sigma))$

Smearing Methods

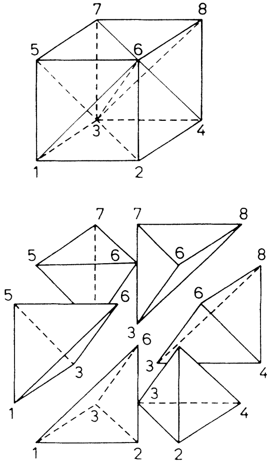
Methfessel-Paxton Smearing

- MP of order N leads to a negligible error, if $F(\epsilon)$ is representable as a polynomial of degree $2N$ around ϵ_{F}.
- linewidth σ can be increased for higher order N to obtain the same accuracy
- "entropy term": $S = \sigma \sum_n S_N(f_n)$ describes deviation of $F(\sigma)$ from $E(\sigma)$.

  $\Rightarrow$ if $S <$ few meV: $\hat{E}(\sigma) \approx F(\sigma) \approx E(\sigma) \approx E(0)$.

  $\Rightarrow$ forces correct within that limit.
- in practice: smearings of order N=1 or 2 are sufficient

Tetrahedron Intrgration



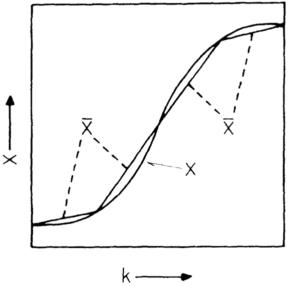
The Linear Tetrahedron Method

- (I)BZ is subdivided into tetrahedra spanned by the $\vec{k}$-points
- function X to be integrated: linearly interpolated between the tetrahedra $\longrightarrow \bar{X}$
- tetrahedra are remapped onto the $\vec{k}$-points, $\vec{k}$-points have effective weights ($\approx$ occupancies)

  $$w_{nj} = \frac{1}{\Omega_{\mathrm{BZ}}} \int\limits_{\Omega_{\mathrm{BZ}}} d\vec{k} c_j(\vec{k}) f\left(\epsilon_n(\vec{k})\right)$$

- $\bar{X} = \sum_{j=1}^{4} c_j(\vec{k}) X(\vec{k}_j) \quad \longleftarrow \int \bar{X}$

Tetrahedron Intrgration



Possible Drawbacks of the Linear T.M.

- $\geq 4\vec{k}$-pts necessary, Γ must be included
- tetrahedra can break the symmetry of the Bravais lattice
- linear interpolation of f may under- or overestimate the real curve
- the errors due to this linear interpolation only cancel for full bands (problem for metals)
- the afforded density of the $\vec{k}$-mesh (# of tetrahedra) can be large

T.M., Blöchl Corrections

improvements, drawbacks

P.Blöchl *et.al.*, PRB**49**, 16223 (1994)

- for metals: correction of quadratic errors is possible

  $$\delta w_{\vec{k}n} = \sum_{\mathrm{T}} \frac{1}{40} D_{\mathrm{T}}(E_F) \sum_{j=1}^{4} (\epsilon_{jn} - \epsilon_{\vec{k}n})$$

  ($T \ldots$ tetrahedra, $D \ldots$ DOS of T at $E = E_F$)
- best $\vec{k}$ -point convergence for energy
- drawbacks (if used for metals):
  - w_{nj}: not variational with the cange of ionic positions
  - $\Rightarrow$ the new effective partial occupancies do not minimize the groundstate total energy
  - $\Rightarrow$ variation of occupancies $w_{n\vec{k}}$ w.r.t. the ionic positions would be necessary
  - with US-PP and PAW practically impossible

$\vec{k}$-point generation

choice of $\vec{k}$-points as implemented in VASP

- used files: KPOINTS, INCAR
- generate equally spaced $\vec{k}$- mesh
- shift it by s_i (if shift is defined in KPOINTS)
- apply the symmetry operations of the symmetry group of the lattice if `ISYM` > 0: this includes the symmetries of the
  - Bravais lattice (`POSCAR`) ,
  - atomic positions (`POSCAR`) ,
  - pre-set MD-velocities (`POSCAR`) ,
  - magnetic ordering (`INCAR`)
- extract the $\vec{k}$ points lying in the IBZ ($\longrightarrow$ IBZKPT)
- calculate the proper weights $w_{\vec{k}_i}$

Input files: KPOINTS

specifies the $\vec{k}$ mesh to be used

```
Automatic mesh
0
G (M)
4 4 4
0.  0.  0.
```

general format for scf runs, DOS

1. header (comment)
2. $N_{\vec{k}} = 0$: automatic generation scheme
3. Γ (M)-centered MP grid
4. # of subdivisions N_i along b_i
5. optional shift of the mesh (s_i)

Input files: KPOINTS

```
high symm.  lines
10
Line-mode
rec
0 0 0
0.5 0.0 0

0.5 0.0 0
0.5 0.5 0.0

0.5 0.5 0.0
0.5 0.5 0.5
```

for bandstructure plots (DFT only)

eg for a simple cubic structure

1. header (comment)
2. intersections along each given symmetry line in the BZ
3. Γ–X
4. X–M
5. M–R

this format must not be used for hybrid functional band structures

Input files: INCAR

BZ-integration related Input Parameters

- `ISMEAR=`: BZ integration method :
  -1 (Fermi) | 0 (Gaussian) | 1,2 MP | -5 (Blöchl)
  for relaxation of metals use 1 or 2
- `SIGMA`: smearing width σ:
  S-contribution to F should not exceed a few meV/atom
  small-gap semiconductors!: $\sigma < \frac{1}{2} E_{gap}$
- `ISYM`: use of symmetrisation ($\vec{k}$-mesh spans the BZ or the IBZ)
  -1 | 0 (no symm) | 1,2 (symmetry used)

Setup of a proper $\vec{k}$-mesh

Some Hints

- always check for proper $\vec{k}$-mesh convergence before the production runs
- supercells: rescale the $\vec{k}$-mesh (preserve the density of the mesh)
- slabs (long axis $\perp$ to the surface, eg z) : $N_1 \times N_2 \times 1$
- free atoms, molecules $1\times1\times1$ (Γ-point only)
- $\vec{k}$ meshes for tetrahedra BZ-integration have to include Γ and the $\vec{k}$- points at the BZ-edges
- the KPOINTS - file format for DFT band-structure plots must not be used for calculations using hybrid functionals.