

# Plane-wave pseudopotential method

## 4<sup>th</sup> lecture

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# Outline

- Introduction
- k-point sampling
- smearing methods
- ground-state property

# Density Functional Theory

- The ground-state energy of a system of electrons under the influence of some external potential is a **unique functional** of the electron density  $\rho(\vec{r})$ .

$$E[\rho(\vec{r})] = G[\rho(\vec{r})] + \int V_{ext}(\vec{r})\rho(\vec{r})d^3r + \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' d^3r$$

$G[\rho(\vec{r})]$  : kinetic energy + the rest ... **the exact form is unknown**

- The energy is a minimum for the correct density function  $\rho(\vec{r})$ .

$$\left. \frac{\delta E[\rho(\vec{r})]}{\delta \rho(\vec{r})} \right|_{\rho_0(\vec{r})} = 0 \quad \text{subject to the condition} \quad \int \delta \rho(\vec{r}) d^3r = 0$$

# Kohn-Sham equation

- The electron density is written as a set of one-electron orbitals :

$$\rho(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$

- $G[\rho]$  in terms of the kinetic energy of a noninteracting electron system

$$G[\rho] = T_s[\rho] + E_{xc}[\rho]$$

$$T_s[\rho] = \sum_i \langle \phi_i | -\frac{\hbar^2}{2m} \nabla^2 | \phi_i \rangle$$

$E_{xc}[\rho]$  : exchange-correlation energy ... the exact form is unknown

-The Kohn-Sham equation can be obtained from the minimal property of  $E[\rho]$  subject to the condition of  $\int \delta\rho(\vec{r})d^3r = 0$

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' + \mu_{xc}[\rho(\vec{r})] \right\} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$

$$V_{eff}(\vec{r}, \rho(\vec{r}))$$

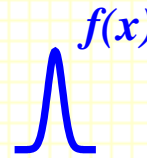
$$\mu_{xc}[\rho(r)] = \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})} \quad : \text{exchange-correlation potential}$$

$\varepsilon_i$  : Lagrange multiplier : one-electron energy

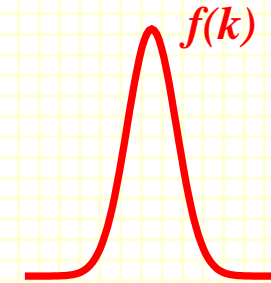
- In practice,  $V_{ext}(\vec{r})$  is the electron-nucleus interaction or the electron-ion interaction

# Fourier Transformation

$$f(x) = \int f(k) e^{ikx} dk$$

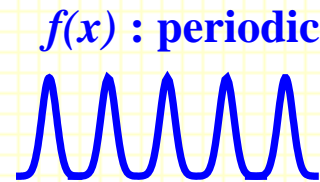


$\xrightarrow{F.T}$

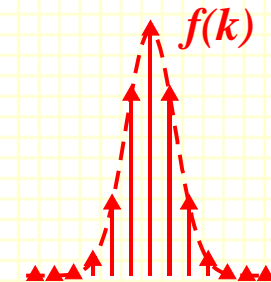


- A periodic function results in a discrete spectrum

$$f(x) = \sum_G f(G) e^{iGx}$$



$\xrightarrow{F.T}$



- **Sampling** a **periodic** function leads to a **periodic discrete** spectrum :  
possible error from **aliasing**

## Periodic Systems

- **Periodic arrangement of atoms gives periodic electron density**

$$V(\vec{r} + \vec{R}) = V(\vec{r}) \quad \rho(\vec{r} + \vec{R}) = \rho(\vec{r})$$

- **The wavefunctions of a periodic system satisfy Bloch theorem**

$$\Psi_{\vec{k}n}(\vec{r}) = e^{i\vec{k}\vec{R}} u_{\vec{k}n}(\vec{r}) \quad u_{\vec{k}n}(\vec{r} + \vec{R}) = u_{\vec{k}n}(\vec{r}); \quad \Psi_{\vec{k}n}(\vec{r} + \vec{R}) = e^{i\vec{k}\vec{R}} \Psi_{\vec{k}n}(\vec{r})$$

- **Periodic functions give discrete spectrum in momentum space**

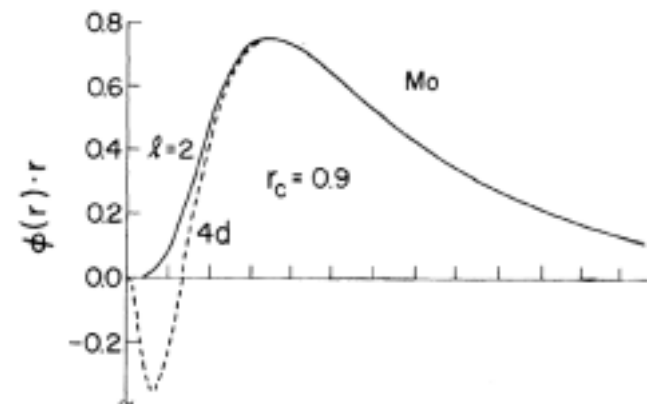
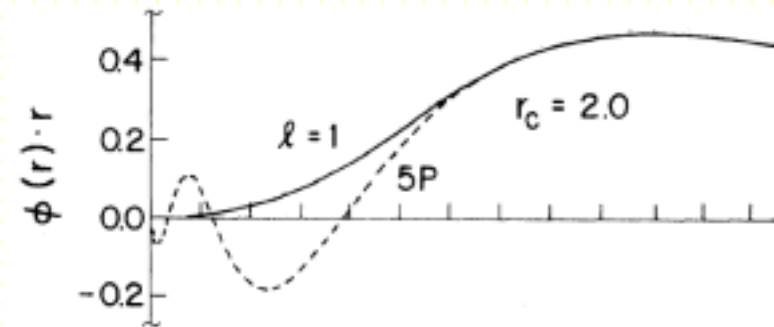
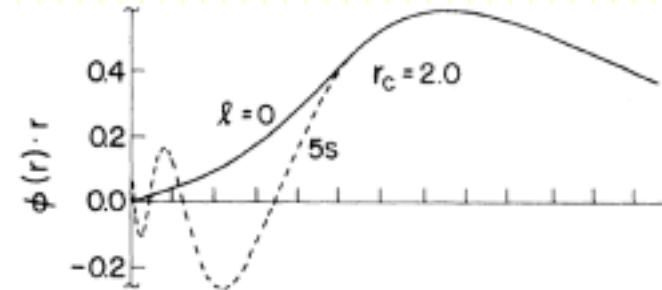
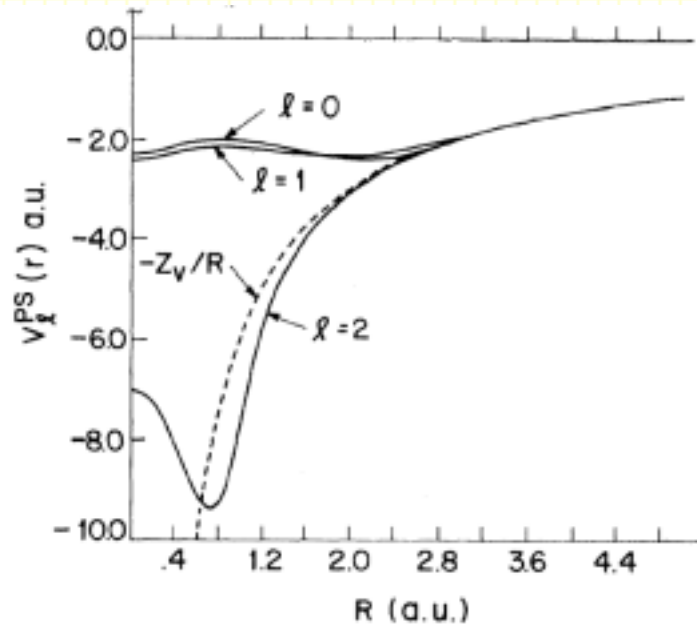
$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\vec{r}} \quad \rho(\vec{r}) = \sum_{\vec{G}} \rho_{\vec{G}} e^{i\vec{G}\vec{r}} \quad u_{\vec{k}n}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}n\vec{G}} e^{i\vec{G}\vec{r}}$$

- **Convenient and natural to use plane waves for wavefunction expansion**

## Pseudopotentials

- **Frozen-core approximation** : in most systems, core electrons do not contribute to the system's physical properties ... considering only valence electrons
- **Strong electron-nucleus potential usually leads to wiggled valence-electron wavefunctions : orthogonality of the wavefunctions**
- **Difficult, if not impossible, to use a reasonably small number of plane waves in the expansion to describe the wavefunctions faithfully**
- **Pseudopotentials : generate softer electron-nucleus potential in the core region from smooth and wiggless valence-electron wavefunctions which give the same electron-ion scattering properties as the original wavefunctions**

From Hamann, Schluter & Chiang PRL 43 1494 (1979)



## Solving Kohn-Sham equation

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\vec{r}, \rho(\vec{r}))\right\}\psi_{\vec{k}n}(\vec{r}) = \varepsilon_{\vec{k}n}\psi_{\vec{k}n}(\vec{r})$$

$$\psi_{\vec{k}n}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}n\vec{G}} e^{i(\vec{k}+\vec{G})\vec{r}}$$

- For every  $\vec{k}$  point in the 1<sup>st</sup> Brillouin zone, we can set up one matrix whose secular equation exists and equals to zero.

- Matrix elements are easy to evaluate when using plane-wave basis set.

$$\langle \vec{k} + \vec{G}' | -\frac{\hbar^2}{2m}\nabla^2 | \vec{k} + \vec{G} \rangle = \frac{\hbar^2}{2m} |\vec{k} + \vec{G}|^2 \delta_{\vec{G}'\vec{G}} \quad : \text{kinetic energy}$$

$$\langle \vec{k} + \vec{G}' | V_{loc} | \vec{k} + \vec{G} \rangle = V_{loc, \vec{G}-\vec{G}'} \quad : \text{local potential, its Fourier component}$$

- **The number of plane waves included in the basis for the wavefunction of a particular  $k$  wavevector is determined by the energy cutoff  $E_{\text{cutoff}}$**

$$\frac{\hbar^2}{2m} |\vec{k} + \vec{G}|^2 \leq E_{\text{cutoff}}$$

- **The magnitude of  $E_{\text{cutoff}}$  is decided by the physical property of the pseudopotential used in the calculation**

- **One numerical error which one should always bear in mind and check when necessary is the error from using an incomplete basis set : checking it by increasing  $E_{\text{cutoff}}$ , i.e. ENCUT in VASP, and redo the calculations.**

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\vec{r}, \rho(\vec{r})) \right\} \psi_{\vec{k}n}(\vec{r}) = \epsilon_{\vec{k}n} \psi_{\vec{k}n}(\vec{r})$$

- The potential  $V_{eff}$  depends on the charge density which is constructed from the wavefunctions of the occupied states : solving a problem whose question depends on the solution
- Use self-consistent scheme. Need an initial guessed charge density and wavefunctions to start with and update them at the end of each cycle for next input.
- The second numerical error in the calculations is from the error in the self-consistent loops, i.e. the convergence in the electronic energy which is controlled by EDIFF in VASP.

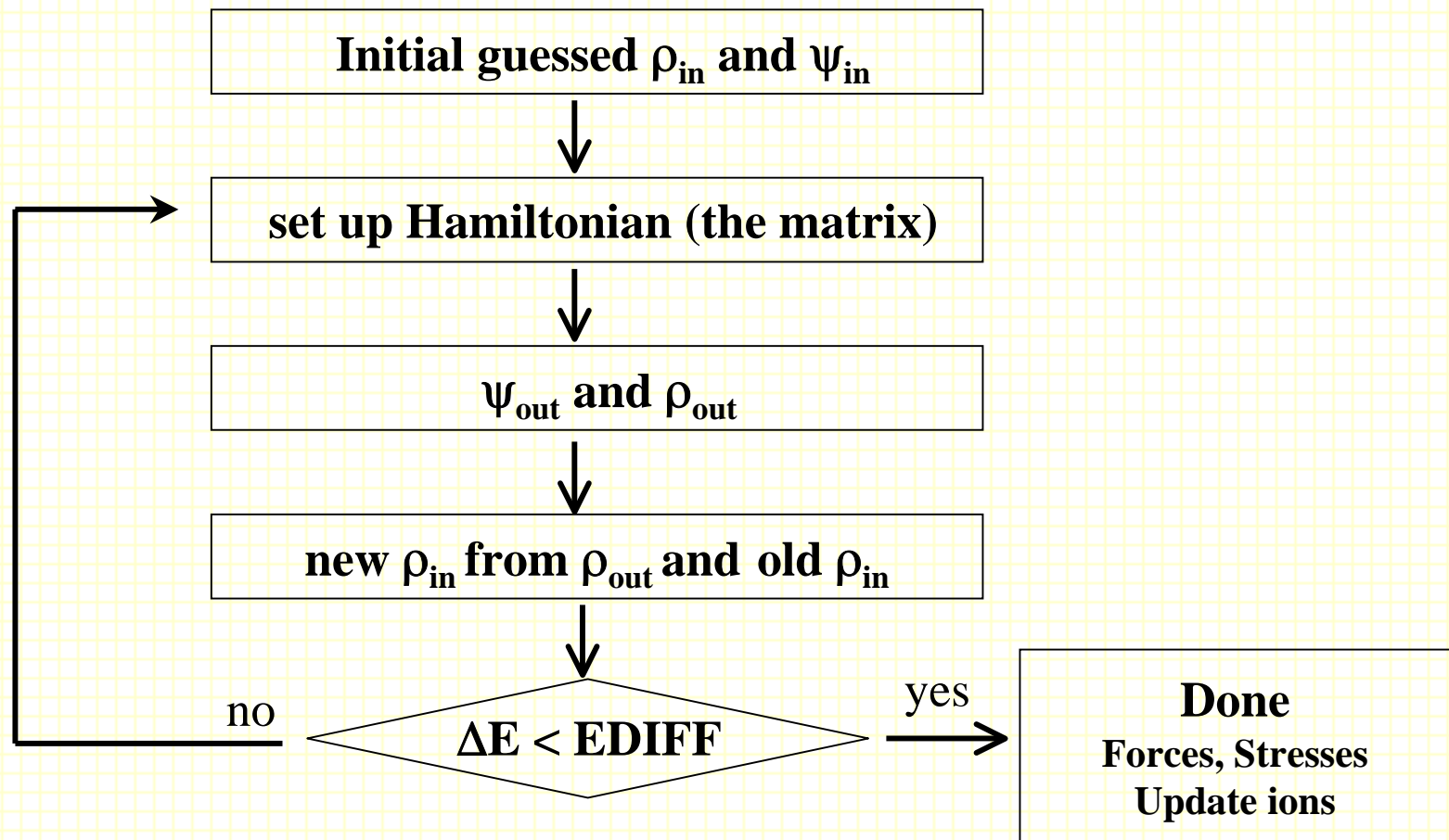
## Total Energy

- The total electronic energy, i.e. from the electron-ion and the electron-electron interaction, can be written as the summation of the one-electron energy while taking care of the double-counting corrections

$$\sum_{\vec{k}n} \varepsilon_{\vec{k}n} - \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' d^3r + E_{xc}[\rho(\vec{r})] - \int \mu_{xc}(\vec{r})\rho(\vec{r}) d^3r$$

- Total energy of the system has to include the ion-ion interaction.
- The total energy in VASP is relative to the atomic energy.

# Self-consistency loop : electronic iteration



## Concept of Special $k$ points

- Many physical properties involve integration over the Brillouin zone, e.g. the band energy of the occupied electron states.

- Considering a periodic system; the function  $f(k)$  has full lattice symmetry:

$$f(\vec{k} + \vec{G}) = f(\vec{k}) \longrightarrow f(\vec{k}) = \sum_m f(\vec{R}_m) e^{i\vec{k}\vec{R}_m}$$

- The Brillouin-zone integrated quantity  $f_0$  is in fact the  $R_m=0$  component of the Fourier spectrum of  $f(k)$

$$f(\vec{R}_m) = \frac{1}{\Omega_{BZ}} \int f(\vec{k}) e^{-i\vec{k}\vec{R}_m} d^3k \longrightarrow f_0 = \frac{1}{\Omega_{BZ}} \int f(\vec{k}) d^3k$$

- **Group those  $R_m$  which have the same length and are related to each other by lattice symmetry (stars), i.e. having the same Fourier component :**

$$f(\vec{k}) = f_0 + \sum_{m=1}^{\infty} f(\vec{R}_m) A_m(\vec{k})$$

$$A_m(\vec{k}) = \sum_{\{\vec{R}_m\} \in C_m} e^{i\vec{k}\vec{R}_m}$$

- **If there exists a particular  $k=k_i$  such that  $A_m(k)=0$  for every  $m$ , then the required quantity  $f_0$  is equal to  $f(k_i)$  and can be easily evaluated.**

- **But there exists no such magic  $k$  point!**

- Considering a set of  $k$  points such that

$$\sum_{i=1}^n \alpha_i A_m(\vec{k}_i) = 0 \quad \text{for } m = 1, 2, \dots, N \quad \text{and} \quad \sum_{i=1}^n \alpha_i = 1$$

- The required quantity  $f_0$  can then be written as

$$f_0 = \sum_{i=1}^n \alpha_i f(\vec{k}_i) - \sum_{m>N}^{\infty} f(\vec{R}_m) A_m(\vec{k})$$

- If the magnitude of the Fourier spectrum  $f(\vec{R}_m)$  decrease rapidly as  $m$  gets larger, which is usually the case :

$$f_0 \approx \sum_{i=1}^n \alpha_i f(\vec{k}_i)$$

## One-dimensional example

- In a one-dimensional periodic system,  $R_m = ma$  where  $a$  is the repeating length and let  $f_m$  denoting  $f(R_m)$

$$f(k) = f_0 + \sum_{m=1}^{\infty} f_m A_m(\vec{k}) \xrightarrow{f(R_m)=f(-R_m)} f_0 + \sum_{m=1}^{\infty} f_m \cos(kR_m)$$

- Considering two  $k$  points, each has different set of  $m$  satisfying  $A_m = 0$

$$k_1^0 = \pi/2a \longrightarrow \cos k_1^0 R_m = 0 \quad \text{for } m \in \{1, 3, 5, \dots\}$$

$$k_2^0 = \pi/4a \longrightarrow \cos k_2^0 R_m = 0 \quad \text{for } m \in \{2, 6, 10, \dots\}$$

- A  $k$ -point mesh of two can be chosen so that the set of  $m$  which satisfy  $A_m = 0$  including the previous two sets of  $m$  : larger first failure star

$$\text{choose } \begin{array}{l} k_1 = k_1^0 + k_2^0 \\ k_2 = k_1^0 - k_2^0 \end{array} \xrightarrow{\alpha_1 = \alpha_2 = 1/2} \alpha_1 \cos k_1 R_m + \alpha_2 \cos k_2 R_m = 0$$

for  $m \in \{1, 2, 3, 5, 6, 10, \dots\}$

## Monkhorst-Pack Method

- Sampling equally spaced  $k$  points in the parallelepiped formed by the primitive reciprocal translational vectors using the following rules :

- Choose three integer numbers  $N_1 N_2 N_3$  (Monkhorst-Pack parameters)
- The sampled  $k$  points satisfy

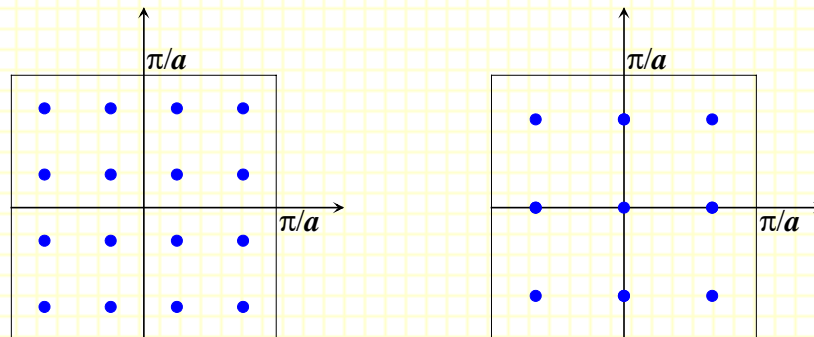
$$\vec{k}_{lmn} = t_l \vec{B}_1 + t_m \vec{B}_2 + t_n \vec{B}_3 \quad l = 1, 2, \dots, N_1 \quad m = 1, 2, \dots, N_2 \quad n = 1, 2, \dots, N_3$$

$$t_l = \frac{2l - N_1 - 1}{2N_1} \quad t_m = \frac{2m - N_2 - 1}{2N_2} \quad t_n = \frac{2n - N_3 - 1}{2N_3}$$

- for examples:

$$N_1 = N_2 = 4$$

$$N_1 = N_2 = 3$$



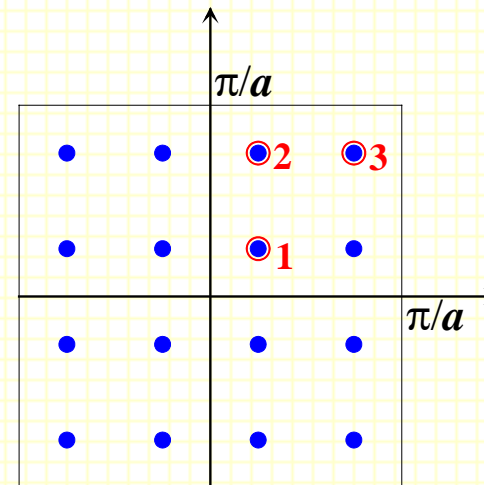
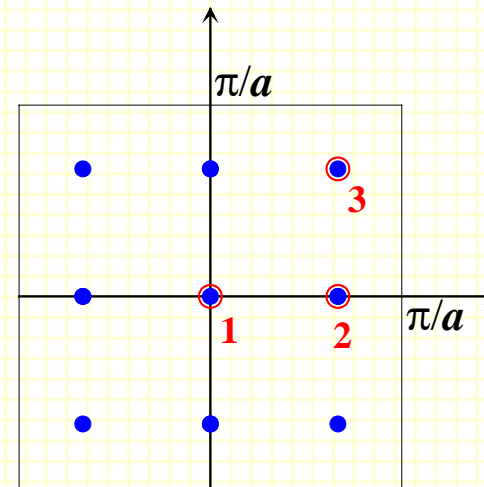
- **Folding those outside of the 1<sup>st</sup> Brillouin zone back to the 1<sup>st</sup> Brillouin zone**
- **Symmetrize the mesh according the point-group symmetry of the system**
- **Extract the  $k$  points which are not related by the point-group symmetry of the system:  $k$  points in the irreducible Brillouin zone**
- **Calculate the proper weighting factors**

## Examples

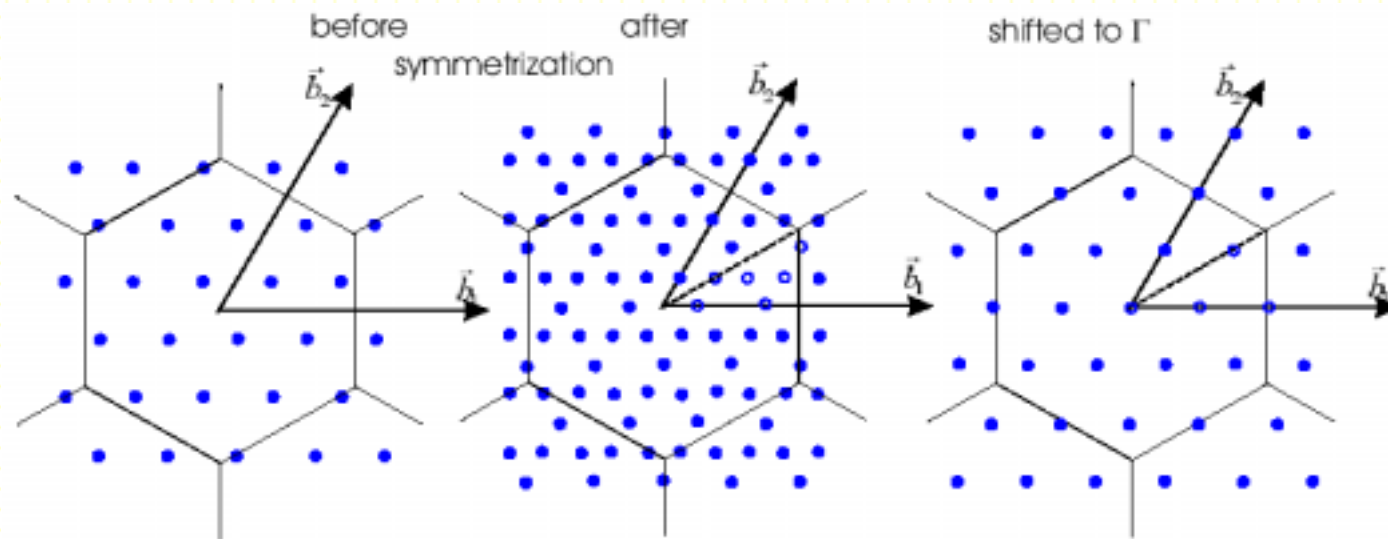
- $N_1=N_2=3$  total 9 k points
- including  $\Gamma$  point
- 3 irreducible points
- weighting factors  
 $\alpha_1 = 1/9, \alpha_2 = 4/9, \alpha_3 = 4/9$

- $N_1=N_2=4$  total 16 k points
- excluding  $\Gamma$  point
- 3 irreducible points
- weighting factors  
 $\alpha_1 = 1/4, \alpha_2 = 1/2, \alpha_3 = 1/4$

- Which one has the higher first failure star?



- Symmetrization might lead to non-equally spaced mesh, e.g. hexagonal cell with a mesh not including the  $\Gamma$  point, which is likely to be an inefficient mesh, i.e. considerably more number of irreducible k points with the same or lower first failure star



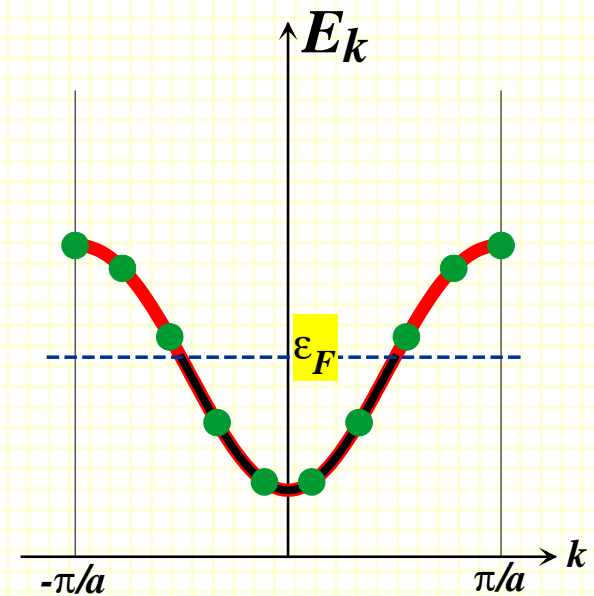
From VASP course by A. Eichler

- The third numerical error in the calculations is from using discrete k points for the Brillouin-zone integration.

## Determine Fermi Level in Metals

- In metallic systems, the continuous one-electron energy states around Fermi level imply the necessity of a dense grid of  $k$  points to be able to accurately determine Fermi level as well as the total energy and all related physical properties.

- Equivalently to say, the discontinuity of the electron density of state at Fermi level implies an oscillating and slowly decreasing magnitudes in its Fourier spectrum : high Fourier components are needed



## Solution

- Replacing the step function by a smoother one (denoted by  $f$ ) during the course of electronic self-consistent calculations should ease the problem.

- Original step-function formulation in evaluating the total number of electrons of the system

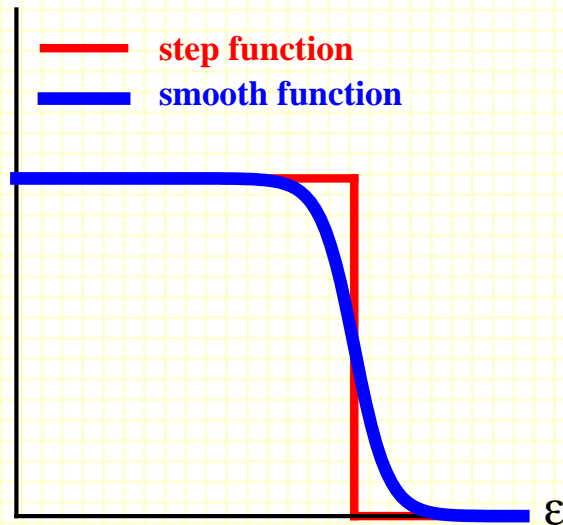
$$N_0 = \sum_n \sum_{\vec{k}} \Theta(\varepsilon_{\vec{k}n} - \mu) \quad \Theta(x) = \begin{cases} 1 & x \leq 0 \\ 0 & x > 0 \end{cases}$$

- $N_0$  : product of the number of electrons in one unit cell and the number of sampled  $k$  points in the 1<sup>st</sup> Brillouin zone

- Smooth-function formulation

$$N_0 = \sum_n \sum_{\vec{k}} f\left(\frac{\varepsilon_{\vec{k}n} - \mu}{\sigma}\right)$$

$\sigma$  : smearing parameter



**-The Fermi level in a metallic system ( $E_F = \mu$ ) is determined by this condition and  $f$  can be interpreted as partial occupations, in certain situations.**

## Solution 1 : ISMEAR = -1

- One of the most obvious solutions is to replace the step function by the Fermi-Dirac function as if the system is at finite temperature :

$$f_{FD}(\varepsilon_{\vec{k}n}, \sigma) = [1 + \exp(\frac{\varepsilon_{\vec{k}n} - \varepsilon_F}{\sigma})]^{-1}$$

-It leads to a new variational functional :

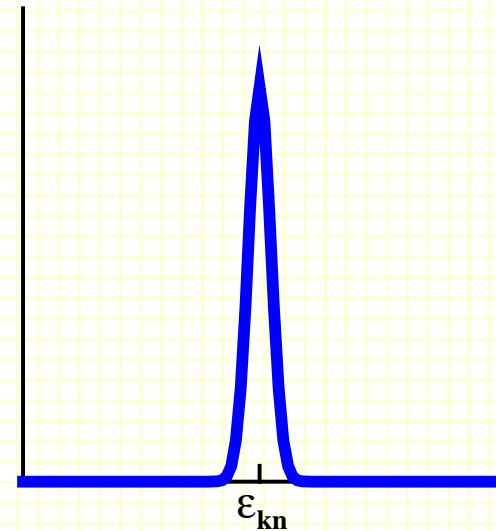
$$F = E - \sum_n \sigma S(f_n)$$

where  $S$  is the entropy of a non-interacting electron gas at finite temperature and  $\sigma$  can be interpreted as finite temperature, i.e.  $\sigma = k_B T$

## Solution 2 : ISMEAR = 0

- A second method is to broaden the one-electron energy level with a Gaussian function : Gaussian smearing.

$$N_0 = \sum_{k,n} \left[ \frac{1}{\sigma\sqrt{\pi}} \int_{-\infty}^{\mu} \exp\left[-\left(\frac{\varepsilon - \varepsilon_{kn}}{\sigma}\right)^2\right] d\varepsilon \right]$$



- $\sigma$  has no physical interpretation.
- Calculated forces are no necessarily equal to the correct forces
- Should extrapolate the results to those of  $\sigma \rightarrow \infty$

### Solution 3 : ISMEAR > 0

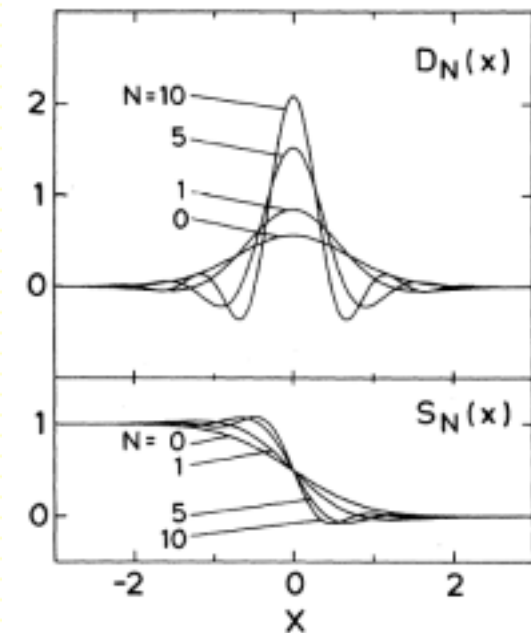
-Expanding the step function in a complete set of orthogonal functions, i.e. Hermite polynomial : method of Methfessel and Paxton (1989)

- The term of order zero corresponds to the gaussian broadening.

-“entropy term” describes deviation from  $E(\sigma)$

- Forces correct when the deviation < a few meV

- In practice : expansion of order 1 or 2 are sufficient, i.e. ISMEAR = 1 or 2



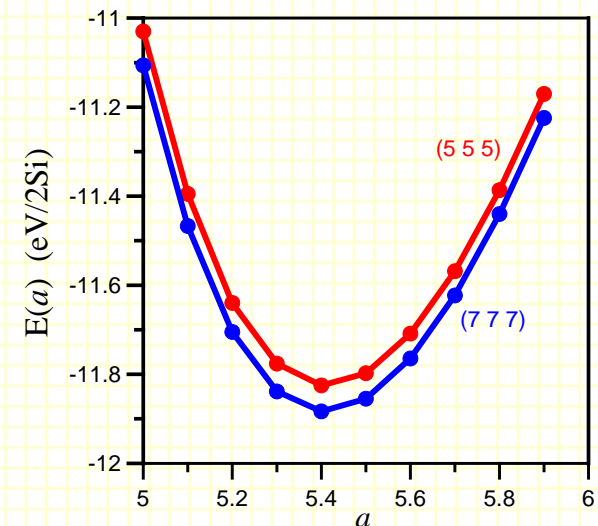
From VASP course by A. Eichler

#### **Solution 4 : ISMEAR = -5**

- **Linear interpolation, with possible correction of quadratic errors, of the function within the tetrahedra obtained by dividing the Brillouin zone : linear tetrahedron method with Blochl correction (1994).**
- **Safer to use k-point mesh including  $\Gamma$  : either choose odd Monkhorst-Pack parameters or generat a  $\Gamma$ -center mesh.**
- **It provides the best k-point convergence for the total energy**
- **Not to be used for relaxing metallic systems : large error in atomic forces**
- **Require at least four  $k$  points in the mesh : can not be applied to large-cell systems**

# Ground-State Properties

- The most basic ground-state property is the structure : including the structural parameters and compressibility (bulk modulus)
- Usually the  $E(V)$  is evaluated and fitted to the equation of state to obtain the ground-state volume and bulk modulus
- Different sets of  $k$  points and energy cutoffs are considered to estimate the errors from using discrete  $k$  points and finite basis set



- The Murnaghan equation of state is used in the present exercise :

$$E(V) = E(V_0) - \frac{B_0 V}{B'_0} \left[ \frac{\left(\frac{V}{V_0}\right)^{1-B'_0}}{1-B'_0} - \frac{V}{V_0} + 1 \right]$$

$$P = -\frac{\partial E}{\partial V} = \frac{B_0}{B'_0} \left[ \left(\frac{V}{V_0}\right)^{-B'_0} - 1 \right]$$

## **And it all follows from here**

- Proceed with the study (condensed-matter related systems, e.g. surface, interface) on condition that the ground-state property of the bulk can be specified correctly by the pseudopotentials**
- To be consistent, the successive studies should be done in the same energy cutoffs as that used to obtain the ground-state properties and similarly the corresponding density of k points (exception : one has gap while the other doesn't)**