BASIC CONCEPTS OF SOLID STATE THEORY

INTRODUCTION TO COURSE

•) Condensed matter physics is the largest branch of physics and probably also the most diverse
→ numerous undergraduate and graduate text books

•) Selected Literature
- C. Kittel : Introduction to Solid State Physics
- Ashcroft and Mermin : Solid State Physics
- Madelung, ... and many more ...
- THIS COURSE: (i) Cohen and Louie (mainly)
  (ii) Lecture notes of Sormann / Schachinger (TU Graz)

•) A few words about the "Cohen / Louie" book
- Title: "Fundamentals of Condensed Matter Physics"
- Author: Steven G. Louie (University of California, Berkeley)
  Computational condensed matter physicist (DFT, GW, BSE, ...)
  ≥ 100 000 citations, h-index = 159 (!)
- Content of book: It is the basis for a 2-semester graduate physics course at Berkeley
  It covers ≈ 90 hours of lectures + additional weekly discussions on the problem section

=> In this course, we will only treat a selection of topics covered by the book.

CONTENT OF LECTURE (tentative)

PART I: BASIC CONCEPTS: electrons and phonons

1. Concept of a solid: qualitative introduction and overview
2. Electrons in crystals
3. Electronic energy bands
4. Lattice vibrations and phonons

PART II: Electron interactions, dynamics and responses

5. Electron dynamics in crystals
6. Homogeneous electron gas
7. Density Functional Theory

} => Separate course "Fundamentals of electronic structure theory"

8. The dielectric function for solids

PART III: Optical and Transport phenomena

(9) Electronic transitions and optical properties of solids

(10) Electron–Phonon Interactions

(11) Dynamics of crystal electrons in a magnetic field

(12) Fundamentals of transport phenomena in solids

PART IV: Many-body effects, superconductivity, magnetism, lower-dimensional systems

(13) Many-body techniques (Green's functions)

(14) Superconductivity

(15) Magnetism

(16) Reduced-dimensional systems and nanostructures (graphene will be discussed in (3) (4))

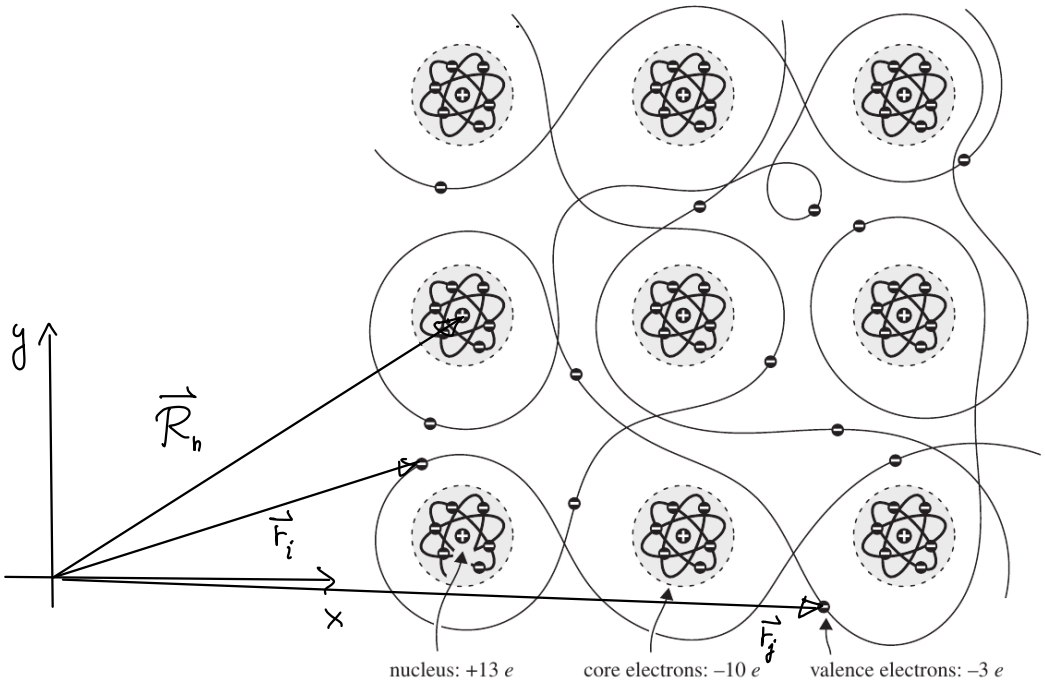
1 Concept of a Solid: qualitative introduction and overview

Possible definitions of a solid:

•) "stable shape, not liquid or fluid, some rigidity" (from dictionary)

•) "collection of interacting atoms with some fixed arrangement"

e.g.: fcc-Al Al: $\underbrace{1s^2\,2s^2\,2p^6}_{\text{core-electrons}}\,\underbrace{3s^2\,3p^1}_{\text{valence electrons}}$



$$\hat{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{n=1} \frac{\vec{P}_n^{\,2}}{2M_n} + \frac{1}{2}\sum_{i,j}{}' \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}\sum_{n,n'}{}' \frac{Z_n \cdot Z_{n'} \cdot e^2}{|\vec{R}_n - \vec{R}_{n'}|}$$

$$- \sum_i \sum_n \frac{Z_n e^2}{|\vec{r}_i - \vec{R}_n|} + \hat{H}_{rel.}$$

$$\hat{H}\,\Psi\left(\{\vec{r}_i\},\{\vec{R}_n\}\right) = E_\ell\,\Psi\left(\{\vec{r}_i\},\{\vec{R}_n\}\right)$$

E_0 ... ground state

1.3 A second model: ELEMENTARY EXCITATIONS

→ Change the description of a system when discussing excited states

→ quantized excitations emerge when the system is not in the ground state $|\Psi_0\rangle$ with energy E_0

Two classes of elementary excitations

Quasi-particles

- usually fermions
- quasi-electrons: m^*, $-|e|$, $\frac{1}{2}$ spin, $E = E(\vec{k})$ } $\simeq 5$ eV
- holes: m^*, $+|e|$, $\frac{1}{2}$ spin, $E = E(\vec{k})$ }
- polaron: electron + lattice deformation
- exciton (boson): bound electron-hole pair

Collective excitations

- usually bosonic
- phonons $\simeq$ $E \simeq 25$ meV

$\omega = \omega(\vec{q})$

- plasmons: charge density wave

$\omega_p = \sqrt{\frac{4\pi n e^2}{m}} \simeq 10$ eV

- magnon: spin excitation

1.5 EXTERNAL PROBES: photons, electrons, positrons neutrons, atoms, ...

Dispersion curves for free particles

$$E(k) = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4}$$

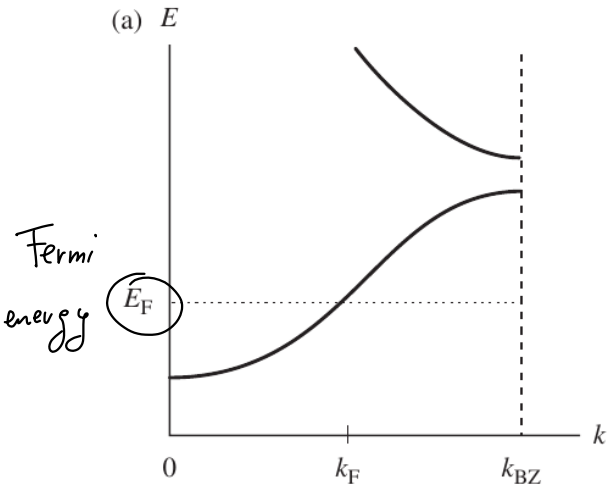
k: wavenumber $\quad p = \hbar k$

→ Photons: $\hbar\omega = \hbar k c$

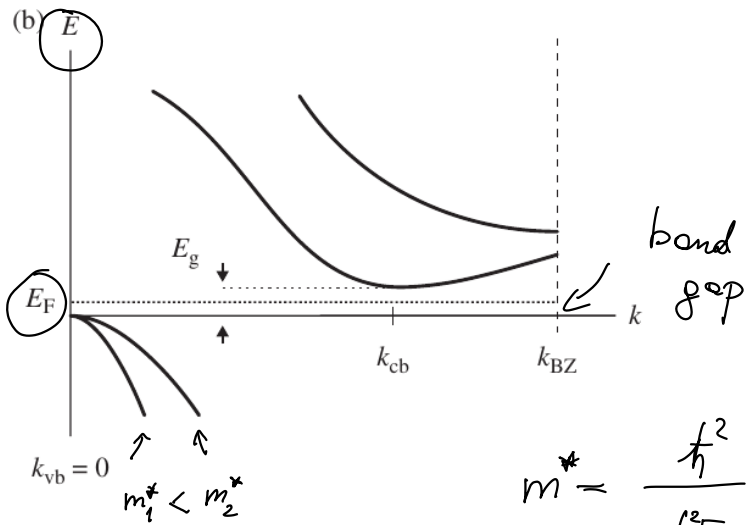
$\omega = k \cdot c$

→ Electrons: $E(k) = \frac{\hbar^2 k^2}{2m}$ (non-relativ.)

DISPERSION CURVES FOR ELEMENTARY EXCITATIONS IN SOLIDS (Fig. 1.3)



electronic band structure of a simple metal



band gap

$$m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}}$$

Semi-conductor

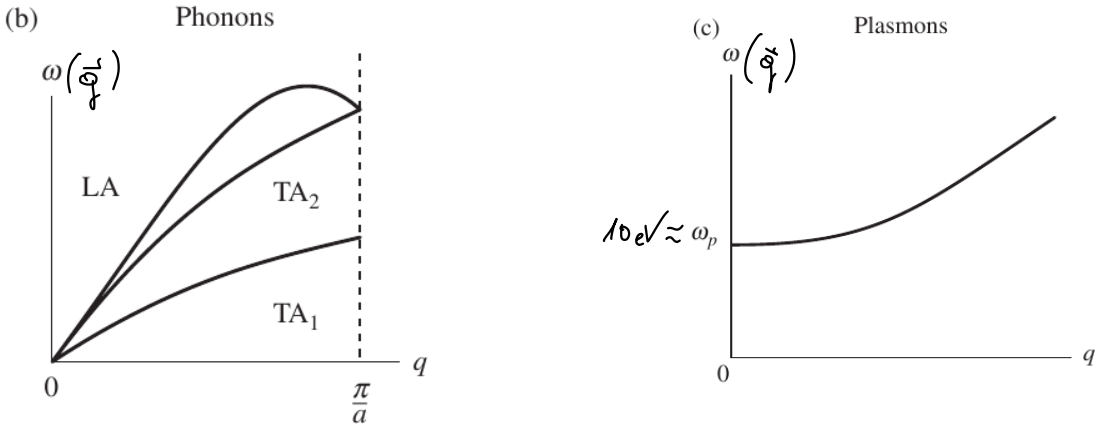
e.g.: InSb $m^* = 0.01\, m_e$

DISPERSION CURVES FOR COLLECTIVE EXCITATIONS (Fig. 1.4)

$\vec{k}$ ... electrons

$\vec{q}$ ... phonons

$q = \frac{2\pi}{\lambda}$



GENERAL APPROACH:

ordinary QM:

1.) Definition of bare elementary excitations → Hamiltonian

2.) Solving the equations of motions → dispersion curves

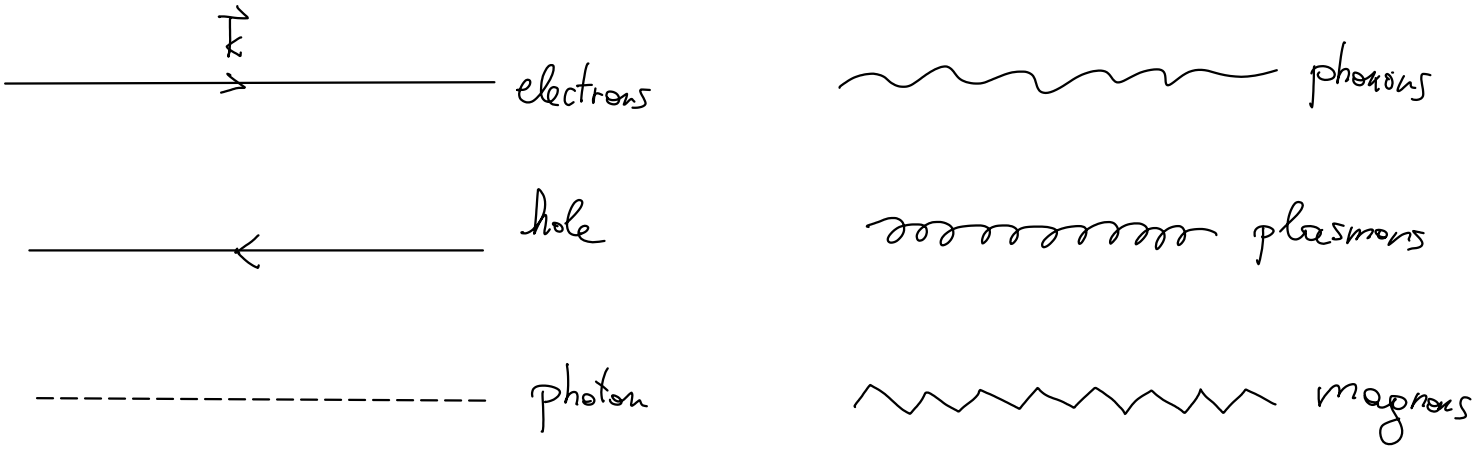
many-body physics:

3.) Inclusion of interactions between excitations

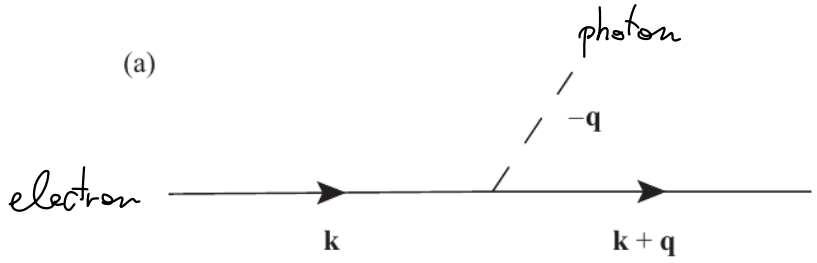
4.) Including effects of external probes

5.) Solution of new coupled equations

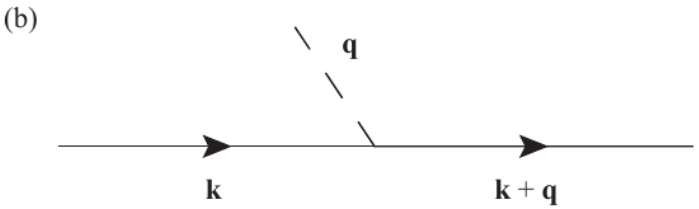
1.7 DIAGRAMMATIC REPRESENTATION



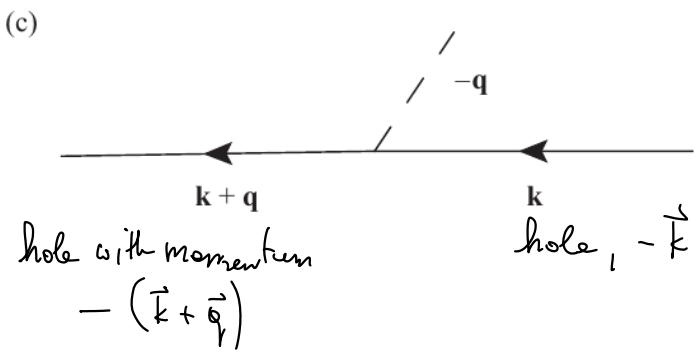
1.8 INTERACTIONS AMONG PARTICLES (Fig. 1.6)



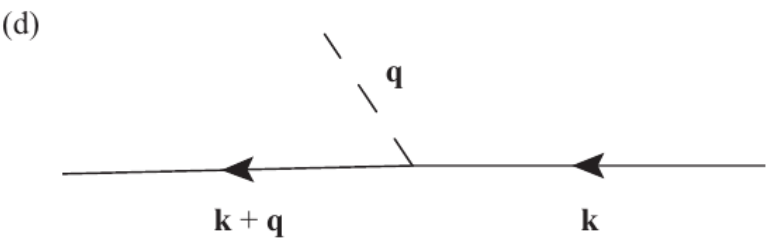
photon emission



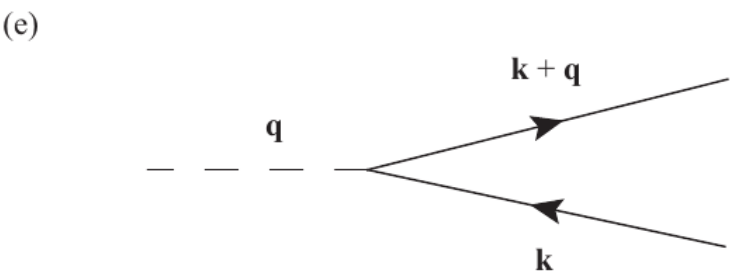
photon absorption



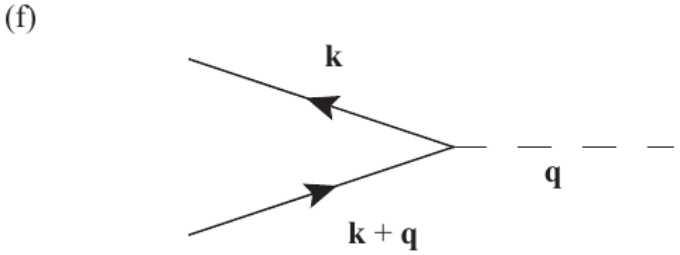
hole emits a photon



hole absorbs a photon

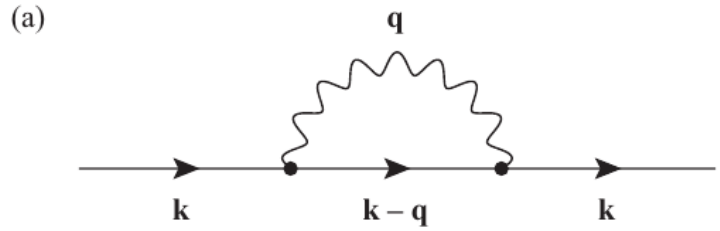


photon creates an electron-hole pair

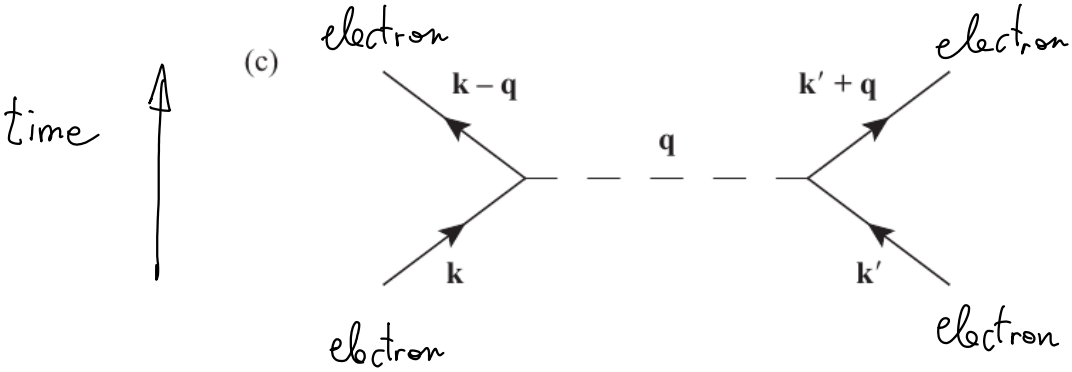


electron-hole annihilation

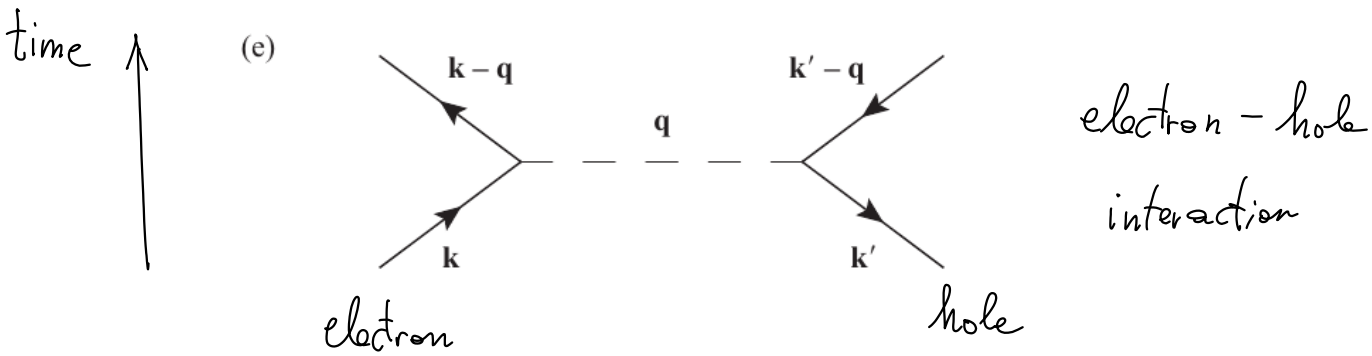
1.8.2 QUASIPARTICLE – QUASIPARTICLE INTERACTIONS (Fig. 1.8)



boson "dresses" the bare quasi-electron

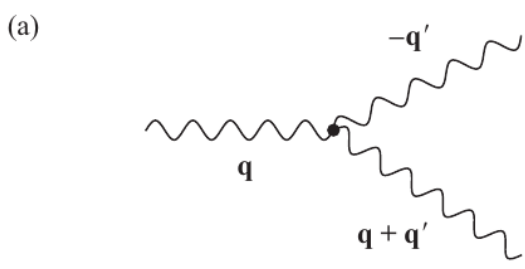


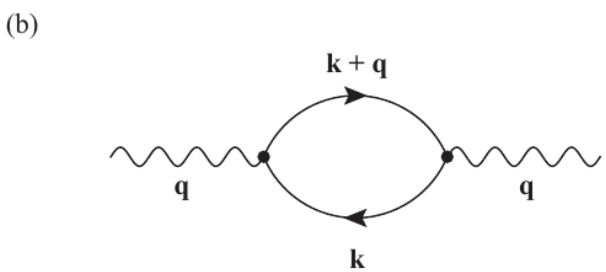
exchange a photon



electron – hole interaction

1.8.3 COLLECTIVE EXCITATION INTERACTIONS (Figs. 1.9/1.10)





2 ELECTRONS IN CRYSTALS

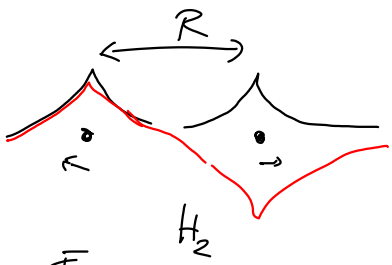
GOAL: Derive properties of quasi-electrons and holes in crystals by using an appropriate Hamiltonian and make a number of approximations leading to $E = E(\vec{k})$

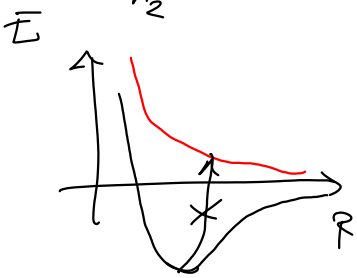
2.1 GENERAL HAMILTONIAN

(i) Solid is a collection of ion cores at positions $\vec{R}_n$ and itinerant electrons with coordinates $\vec{r}_i$.

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{\vec{p}}_i^{\,2}}{2m} + \sum_{n=1} \frac{\vec{P}_n^{\,2}}{2M_n} + \frac{1}{2}{\sum_{i,j}}' \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2}{\sum_{n,n'}}' \frac{Z_{n'} \cdot Z_n \cdot e^2}{|\vec{R}_n - \vec{R}_{n'}|}$$

$$- \sum_i \sum_n \frac{Z_n e^2}{|\vec{r}_i - \vec{R}_n|} + \hat{H}_{rel.}$$





(ii) BORN-OPPENHEIMER APPROXIMATION

$$\psi(\{\vec{r}_i\}, \{\vec{R}_n\})$$

↑ only parameters

$$\Rightarrow \hat{H}_e = \sum_i \left[\frac{\hat{\vec{p}}_i^{\,2}}{2m} + V(\vec{r}_i) \right] + \frac{1}{2}{\sum_{i,j}}' \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \hat{H}_r$$

$\hat{H}_e$: electronic Hamiltonian; bracketed term: 1-electron; $\hat{H}_r$: relativistic corrections

"crystal potential": $V(\vec{r}_i) = -\sum_n \frac{Z_n \cdot e^2}{|\vec{r}_i - \vec{R}_n|}$

(I) Electronic part:

$$\hat{H}_e \, \psi\left(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N ; \{\vec{R}_n\}\right) = E_e^{\ell}\left(\{\vec{R}_n\}\right) \cdot \psi\left(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N ; \{\vec{R}_n\}\right)$$

(ℓ: quantum numbers; E_e^{ℓ}: electronic part)

$\Rightarrow$ leads to: ·) electron and hole excitations

·) excitons (electron - hole pairs)

·) plasmons

·) magnons

electronic ground state: $E_e^0 = E_e^0(\{\vec{R}_n\})$

"Born-Oppenheimer surface"

(II) Core part: $E_e^0(\{\vec{R}_n\})$ .... defines potential energy surface for cores ($\hat{=} V_{ec}$)

$$\Rightarrow \hat{H}_c = \sum_n \frac{\vec{P}_n^2}{2M_n} + \frac{1}{2}{\sum_{nn'}}' \frac{Z_n Z_{n'} e^2}{|\vec{R}_n - \vec{R}_{n'}|} + V_{ec}(\{\vec{R}_n\})$$

$\Rightarrow$ leads to: phonons (lattice vibrations)

Combination of (I) + (II) leads to:

↳ ·) polarons

·) superconductivity (BCS-model)

·) resistivity

2.3 THE MEAN FIELD APPROXIMATION

Assumption that each electron moves in the average or mean field created by the cores together with all the other electrons.

examples: •) Hartree approximation: $\psi(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) = \varphi_1(\vec{r}_1) \cdot \varphi_2(\vec{r}_2) \dots \varphi_N(\vec{r}_N)$

•) Hartree-Fock approximation $\psi(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) =$ "Slater Determinant"

•) Density Functional Theory

$$\hat{H}_e = \sum_i \hat{H}(\vec{r}_i; \{\vec{R}_n\}) \quad \rightarrow \quad \boxed{\hat{H}(\vec{r}) = \frac{\vec{p}^2}{2m} + V(\vec{r}; \{\vec{R}_n\})}$$

One-electron Hamiltonian

2.4 THE PERIODIC POTENTIAL APPROXIMATION

→ The cores form an ordered, periodic array

→ Perfect crystal without any defects

cores $\{\vec{R}_n\}$ are fixed $\Rightarrow$ $\boxed{\text{Crystal potential } V(\vec{r}) = V(\vec{r}; \{\vec{R}_n\})}$

$V(\vec{r})$ contains: •) chemical composition

•) crystal structure

•) averaged electron-electron interactions

$\Rightarrow$ One-electron periodic potential model

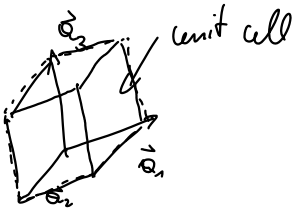
$$\hat{H} = \frac{\vec{p}^2}{2m} + V(\vec{r}) \qquad V(\vec{r} + \vec{R}_n) = V(\vec{r})$$

$V(\vec{r})$: translationally symmetric

$\vec{R}_n$: translational vector

2.5 TRANSLATIONAL SYMMETRY, PERIODICITY, LATTICES

Bravais lattice: $\vec{R}_n := \vec{R}_{n_1 n_2 n_3} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$, $n_1, n_2, n_3 \in \mathbb{Z}$



$\vec{a}_1, \vec{a}_2, \vec{a}_3$ ... unit cell vectors

$\Omega_p = (\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3$ ... unit cell volume

A few terms (that you most likely know already)

- Lattice vectors: $\vec{R}_n$; $V(\vec{r} + \vec{R}_n) = V(\vec{r})$
- primitive cell: contains 1 lattice point
- unit cell:
- basis: set of atoms at positions $\vec{r}_\mu$ $(\mu = 1, 2, \dots N_b)$ within one unit cell
- Wigner-Seitz cell: special type of primitive cell
- reciprocal lattice: $\vec{G}_m = m_1 \vec{g}_1 + m_2 \vec{g}_2 + m_3 \vec{g}_3$

$m_1 m_2 m_3 \in \mathbb{Z}$

$\vec{g}_i \cdot \vec{a}_j := 2\pi \delta_{ij}$

$\vec{G}_m \cdot \vec{R}_n = 2\pi \cdot \gamma$ (γ: integer)

$$\vec{g}_i = 2\pi \cdot \frac{\vec{a}_j \times \vec{a}_k}{(\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3}$$

$i, j, k = 1, 2, 3$ (+ cyclic permutations)

$$V(\vec{r} + \vec{R}) = V(\vec{r}) = \sum_{\vec{G}} \tilde{V}_{\vec{G}} e^{i \vec{G} \vec{r}}$$

- periodic functions:

$$u(\vec{r} + \vec{R}_n) = u(\vec{r}) = \sum_m \tilde{u}_m e^{i \vec{G}_m \cdot \vec{r}} = \sum_G \tilde{u}_{\vec{G}} e^{i \vec{G} \vec{r}}$$

discrete Fourier Series

– Brillouin zone: "Wigner-Seitz cell for reciprocal lattice"

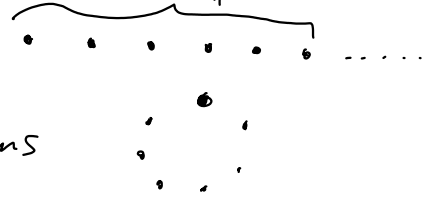
$$\Omega_{BZ} = (\vec{g}_1 \times \vec{g}_2) \cdot \vec{g}_3 = \ldots = \frac{(2\pi)^3}{\Omega_p}$$

– Periodic boundary conditions ($\hat{=}$ Born-von-Karmann boundary conditions)

Motivation:

-) finiteness is essential for defining a crystal volume
-) we want to avoid the presence of surfaces

Wolfgang Pauli: "God made the bulk; the surface was created by the devil."

$\Rightarrow$ crystal closes onto itself: 

-) 1D $\rightarrow$ closed chain (ring) of atoms
-) 2D $\rightarrow$ a sheet is closed to a torus
-) 3D $\rightarrow$ the crystal facets close to a "saper-torus"

number of unit cells: $N = N_1 \cdot N_2 \cdot N_3$

crystal volume: $\Omega_x = N \cdot \Omega_p$

periodic boundary conditions: $\begin{cases} f(\vec{r} + N_1 \vec{a}_1) = f(\vec{r}) \\ f(\vec{r} + N_2 \vec{a}_2) = f(\vec{r}) \\ f(\vec{r} + N_3 \cdot \vec{a}_3) = f(\vec{r}) \end{cases}$ enforce

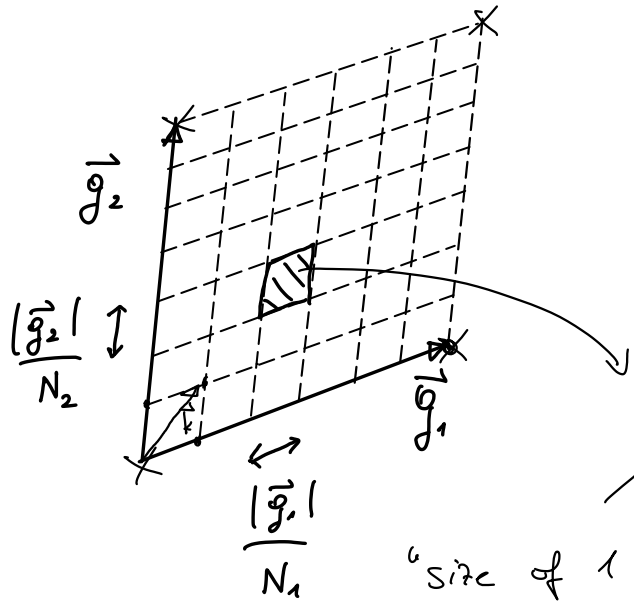
e.g.: $f(\vec{r}) = e^{i \vec{k} \vec{r}}$

$$e^{i\vec{k}(\vec{r} + N_i \vec{a}_i)} \stackrel{!}{=} e^{i\vec{k}\vec{r}} \quad \Rightarrow \quad e^{i \vec{k} N_i \vec{a}_i} = 1$$

$$\Rightarrow \quad N_i (\vec{k} \cdot \vec{a}_i) = 2\pi m_i \qquad m_i \in \mathbb{Z}$$

$$\vec{k} = \sum_{j=1}^{3} \alpha_j \vec{g}_j$$

$$N_i \sum_{j=1}^{3} \alpha_j \underbrace{\vec{g}_j \cdot \vec{a}_i}_{2\pi \delta_{ij}} = 2\pi m_i \quad \Rightarrow \quad \boxed{\alpha_i = \frac{m_i}{N_i}}$$



$$\vec{k} = \sum_{i=1}^{3} \frac{m_i}{N_i} \vec{g}_i$$

$$V_{cell} = \frac{(\vec{g}_1 \times \vec{g}_2) \cdot \vec{g}_3}{N_1 N_2 N_3} = \frac{(2\pi)^3}{\underbrace{\Omega_p \cdot N}_{\Omega_x}}$$

"size of 1 $\vec{k}$-point" $= \frac{(2\pi)^3}{\Omega_x}$

$$N_k = \frac{\Omega_x}{\Omega_p} = N \quad \text{... number of } \vec{k}\text{-points}$$

– Bloch's Theorem : $\underbrace{\left[-\frac{\hbar^2}{2m}\Delta + V(\vec{r})\right]}_{\hat{H}} \cdot \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$

Translational operator $\hat{T}_{\vec{R}}$ $\quad \boxed{\hat{T}_{\vec{R}}\, \varphi(\vec{r}) := \varphi(\vec{r}+\vec{R})}$

$$\hat{T}_{\vec{R}} \hat{V}(\vec{r}) \varphi(\vec{r}) = \underbrace{V(\vec{r}+\vec{R})}_{V(\vec{r})} \varphi(\vec{r}+\vec{R}) = V(\vec{r}) \cdot \underbrace{\varphi(\vec{r}+\vec{R})}_{\hat{T}_{\vec{R}}\varphi(\vec{r})} = \hat{V}(\vec{r}) \cdot \hat{T}_{\vec{R}} \varphi(\vec{r})$$

$$[\hat{T}_{\vec{R}}, \hat{V}] = [\hat{T}_{\vec{R}}, \hat{H}] = 0 \quad \Rightarrow \quad \text{common eigenvectors for } \hat{H}, \hat{T}_{\vec{R}} \text{ !!}$$

also the electron density $n(\vec{r}+\vec{R}) = n(\vec{r})$ is lattice periodic

$$n(\vec{r}) \sim |\varphi(\vec{r})|^2$$

$$n(\vec{r}) = \sum_{i=1}^{N} |\varphi_i(\vec{r})|^2$$

(A) $|\varphi(\vec{r}+\vec{R})|^2 \overset{!}{=} |\varphi(\vec{r})|^2$ ✓

$\varphi(\vec{r}+\vec{R}) = \alpha(\vec{R})\ \varphi(\vec{r})$ $\qquad |\alpha(\vec{R})| = 1$ (I)

moreover: $\hat{T}_{\vec{R}_1} \cdot \hat{T}_{\vec{R}_2} = \hat{T}_{\vec{R}_1+\vec{R}_2}$ $\quad / \varphi(\vec{r})$

$\varphi(\vec{r}+\vec{R}_1+\vec{R}_2) = \alpha(\vec{R}_1+\vec{R}_2)\cdot\varphi(\vec{r})$

$= \alpha(\vec{R}_2)\,\varphi(\vec{r}+\vec{R}_1) = \alpha(\vec{R}_2)\cdot\alpha(\vec{R}_1)\,\varphi(\vec{r})$ (II)

(I) + (II) fullfilled by the following ansatz: $\boxed{\alpha(\vec{R}) = e^{i\vec{k}\vec{R}}}$

$\vec{k} \in \mathbb{R}^3$

$\Rightarrow \boxed{\hat{T}_{\vec{R}}\,\varphi(\vec{r}) = \varphi(\vec{r}+\vec{R}) = e^{i\vec{k}\vec{R}}\,\varphi(\vec{r})}$ (B)

↑ eigenvalues of $\hat{T}_{\vec{R}}$

(i) $\hat{T}_{\vec{R}}^{+} = \hat{T}_{-\vec{R}}$

(ii) $\vec{k} \in 1^{st}$ BZ: because $e^{i(\vec{k}+\vec{G})\vec{R}} = e^{i\vec{k}\vec{R}}$

Bloch-Ansatz: $\varphi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}\,u_{\vec{k}}(\vec{r})$ fulfills (A) + (B)

with $u_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r})$ (lattice periodic)

$\vec{r} \to \vec{r}+\vec{R}$ $\qquad \varphi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\vec{r}}\, e^{i\vec{k}\vec{R}}\, u_{\vec{k}}(\vec{r})$

$\varphi_{\vec{k}}(\vec{r})$

•) Bloch-Theorem in words: $\boxed{\varphi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_{\vec{k}}(\vec{r})}$

"Any eigenfunction of the translational operator can be expressed as the product of a plane wave $e^{i\vec{k}\vec{r}}$ and a lattice-periodic function $u_{\vec{k}}(\vec{r})$."

•) lattice-periodic part can be expressed as a Fourier series:

$$\boxed{u_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega_x}} \sum_{\vec{G}} \tilde{u}_{\vec{k}}(\vec{G})\, e^{i\vec{G}\vec{r}}}$$

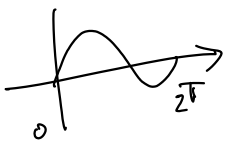
$$\langle \vec{r} | \vec{k} \rangle = \varphi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})\, e^{i\vec{k}\vec{r}} = \frac{1}{\sqrt{\Omega_x}} \cdot \sum_{\vec{G}} \tilde{u}_{\vec{k}}(\vec{G})\, e^{i(\vec{k}+\vec{G})\vec{r}}$$

•) What is the physical meaning of the Bloch vector $\vec{k}$?

$\hbar\vec{k}$ has units of momentum, but it is not a momentum quantum number!

$$[\hat{H}, \hat{T}_R] = 0 \qquad \text{but} \qquad [\hat{H}, \hat{P}] \neq 0$$

$$\langle \hat{\vec{P}} \rangle_{\vec{k}} = \langle \vec{k} | -i\hbar\vec{\nabla} | \vec{k} \rangle = -i\hbar \int_{\Omega_x} d^3r\, \varphi^*_{\vec{k}}(\vec{r})\, \vec{\nabla}\, \varphi_{\vec{k}}(\vec{r}) =$$



$$= -\frac{i\hbar}{\Omega_x} \sum_{\vec{G},\vec{G}'} \tilde{u}^*_{\vec{k}}(\vec{G}')\, \tilde{u}_{\vec{k}}(\vec{G}) \int_{\Omega_x} d^3r\, e^{-i(\vec{k}+\vec{G}')\vec{r}}\, \underbrace{\vec{\nabla}\, e^{i(\vec{k}+\vec{G})\vec{r}}}_{= i(\vec{k}+\vec{G})\cdot e^{i(\dots)}}$$

$$= \frac{\hbar}{\Omega_x} \sum_{\vec{G}\vec{G}'} (\vec{k}+\vec{G})\, \tilde{u}^*_{\vec{k}}(\vec{G}')\, \tilde{u}_{\vec{k}}(\vec{G}) \underbrace{\int_{\Omega_x} d^3r\, e^{+i(\vec{G}-\vec{G}')\cdot\vec{r}}}_{\Omega_x \cdot \delta_{\vec{G},\vec{G}'}}$$

$$= \hbar \sum_{\vec{G}} (\vec{k}+\vec{G}) \left|\tilde{u}_{\vec{k}}(\vec{G})\right|^2 \quad \parallel$$

3 ELECTRONIC ENERGY BANDS

$$\hat{H}\,\psi_{\vec{k}}(\vec{r}) = E_{\vec{k}}\,\psi_{\vec{k}}(\vec{r})$$

where: $\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})\cdot e^{i\vec{k}\vec{r}}$ (Bloch wave)

and $\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})$

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

$$\vec{\nabla}^2\left[e^{i\vec{k}\vec{r}}\cdot u_{\vec{k}}(\vec{r})\right] = \ldots =$$

$$\ldots = e^{i\vec{k}\vec{r}}\left[\left(\vec{\nabla}+i\vec{k}\right)^2 u_{\vec{k}}(\vec{r})\right]$$

$$\left[-\frac{\hbar^2}{2m}\left(\vec{\nabla}+i\vec{k}\right)^2 + V(\vec{r})\right] u_{\vec{k}}(\vec{r}) = E(\vec{k})\,u_{\vec{k}}(\vec{r})$$

$H = H(\vec{k})$ $\Rightarrow$ Bloch vector $\vec{k}$ is a parameter in the differential eq.

eigenvalues: $E_\nu(\vec{k})$ $\Rightarrow$ "band structure"

ν: band index; $\vec{k}$: Bloch vector

eigenvectors: $u_{\nu\vec{k}}(\vec{r})$

band; Bloch vector

Bloch function $\psi_{\nu,\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}\cdot u_{\nu\vec{k}}(\vec{r})$

Orthonormality:

$$\langle \psi_{\nu'\vec{k}'} \,|\, \psi_{\nu\vec{k}} \rangle = \int_{\Omega_x} d^3r\, \psi^*_{\nu'\vec{k}'}(\vec{r})\,\psi_{\nu\vec{k}}(\vec{r}) = \delta_{\vec{k},\vec{k}'}\,\delta_{\nu,\nu'}$$

Ω_x: crystal volume

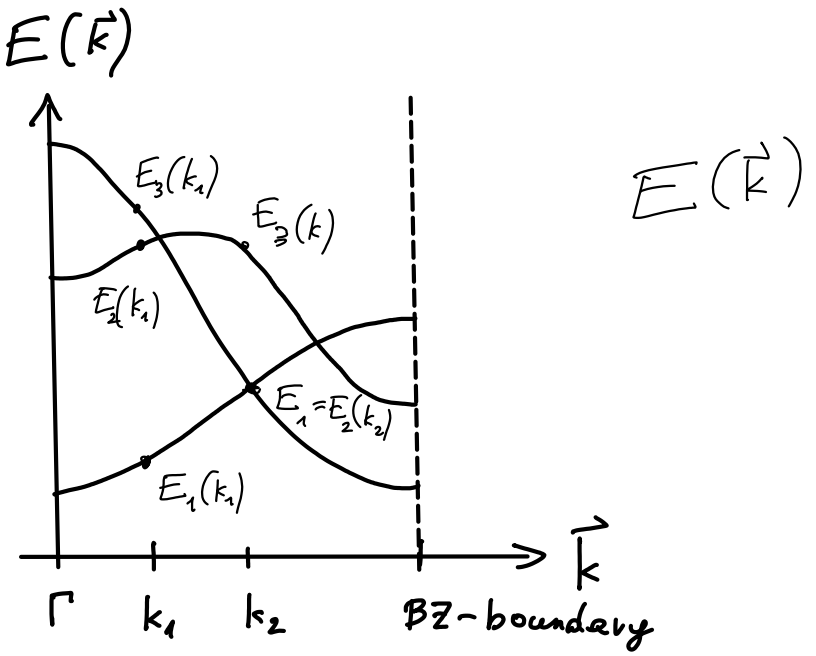
$$\frac{1}{\Omega_p}\int_{\Omega_p} d^3r\, u^*_{\nu\vec{k}}(\vec{r})\,u_{\nu'\vec{k}}(\vec{r}) = \delta_{\nu\nu'}$$

"Electronic Band Structure"

•) eigenvalues $E(\vec{k}) \longrightarrow E_\nu(\vec{k})$

•) eigenvectors $u_{\vec{k}}(\vec{r}) \longrightarrow u_{\nu\vec{k}}(\vec{r})$

Orthonormality of Bloch-functions: $\psi_{\nu\vec{k}}(\vec{r}) = \frac{1}{\sqrt{\Omega_x}} e^{i\vec{k}\vec{r}} u_{\nu\vec{k}}(\vec{r})$



3.2 SYMMETRIES AND ENERGY BANDS

① Periodicity in reciprocal space :

$$E_\nu(\vec{k}+\vec{G}) = E_\nu(\vec{k}) \quad \checkmark$$

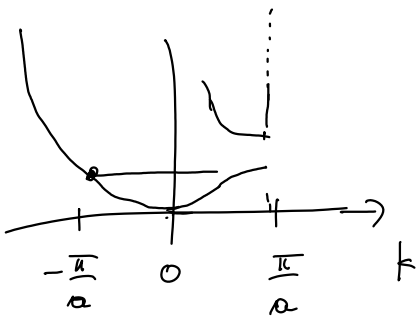
$$\psi_{\nu,\vec{k}+\vec{G}}(\vec{r}) = \psi_{\nu,\vec{k}}(\vec{r}) \quad \checkmark$$

$$\hat{H}\psi_{\nu\vec{k}} = E(\vec{k})\psi_{\nu\vec{k}}$$

$$e^{i\vec{G}\cdot\vec{R}} = 1$$

Proof: (1) $\hat{T}_{\vec{R}}\,\psi_{\nu\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{R}}\,\psi_{\nu\vec{k}}(\vec{r})$

$\vec{k} \to \vec{k}+\vec{G}$: (2) $\hat{T}_{\vec{R}}\,\psi_{\nu\vec{k}+\vec{G}}(\vec{r}) = e^{i\vec{k}\vec{R}}\,\psi_{\nu\vec{k}+\vec{G}}(\vec{r})$



$$G = \frac{2\pi}{a}$$

② KRAMER's Theorem (Time-reversal symmetry)

$$E_\nu(-\vec{k}) = E_\nu(\vec{k}) \quad \checkmark$$

$$\psi_{\nu,-\vec{k}}(\vec{r}) = \psi^*_{\nu,\vec{k}}(\vec{r}) \quad \checkmark$$

Proof :

$$\left[-\frac{\hbar^2}{2m}\left(\vec{\nabla}+i\vec{k}\right)^2 + V(\vec{r})\right] u_{\vec{k}}(\vec{r}) = E(\vec{k})\,u_{\vec{k}}(\vec{r}) \qquad \Big|^*$$

$$\left[-\frac{\hbar^2}{2m}\left(\vec{\nabla}-i\vec{k}\right)^2 + V(\vec{r})\right] u^*_{\vec{k}}(\vec{r}) = E(\vec{k})\,u^*_{\vec{k}}(\vec{r}) \qquad \Big| \vec{k} \to -\vec{k}$$

$$\left[-\frac{\hbar^2}{2m}\left(\vec{\nabla}+i\vec{k}\right)^2 + V(\vec{r})\right] u^*_{-\vec{k}}(\vec{r}) = E(-\vec{k})\,u^*_{-\vec{k}}(\vec{r})$$

③ Space group symmetry

$$E_\nu(\hat{\alpha}\vec{k}) = E_\nu(\vec{k})$$

$$\psi_{\nu,\hat{\alpha}\vec{k}}(\vec{r}) = \psi_{\nu\vec{k}}[\alpha\vec{r}+\vec{t}]$$ ✓

$$\hat{S}_{\{\hat{\alpha},\vec{t}\}} f(\vec{r}) := f\left(\{\hat{\alpha}|t\}\vec{r}\right) = f(\hat{\alpha}\vec{r}+\vec{t})$$

$$\hat{S}_{\{\hat{\alpha},\vec{t}\}} V(\vec{r}) = V(\hat{\alpha}\vec{r}+\vec{t}) \equiv V(\vec{r}) \Rightarrow \left[\hat{S}_{\{\alpha,\vec{t}\}}, \hat{H}\right] = 0$$

$$\hat{T}_{\vec{R}}\left[\hat{S}_{\{\hat{\alpha},\vec{t}\}}\psi_{\vec{k}}(\vec{r})\right] = \hat{T}_{\vec{R}}\psi_{\vec{k}}(\hat{\alpha}\vec{r}+\vec{t}) = \psi_{\vec{k}}(\hat{\alpha}\vec{r}+\vec{t}+\vec{R}) =$$

$$= \psi_{\vec{k}}\left(\hat{\alpha}(\vec{r}+\hat{\alpha}^{-1}\vec{R})+\vec{t}\right) =$$

$$= \hat{S}_{\{\alpha,\vec{t}\}}\psi_{\vec{k}}(\vec{r}+\hat{\alpha}^{-1}\vec{R}) =$$

$$= \hat{S}_{\{\alpha,\vec{t}\}}\hat{T}_{\hat{\alpha}^{-1}\vec{R}}\psi_{\vec{k}}(\vec{r}) =$$

$$= \hat{S}_{\{\alpha,\vec{t}\}}\underbrace{e^{i\vec{k}\cdot(\hat{\alpha}^{-1}\vec{R})}}_{= e^{i(\hat{\alpha}\vec{k})\cdot\vec{R}}}\psi_{\vec{k}}(\vec{r}) \qquad \hat{\alpha}^{-1} = \hat{\alpha}^{T}$$

$$\hat{T}_{\vec{R}}\left[\hat{S}_{\{\hat{\alpha},\vec{t}\}}\psi_{\vec{k}}(\vec{r})\right] = e^{i\hat{\alpha}\vec{k}\vec{R}}\left[\hat{S}_{\{\alpha,\vec{t}\}}\psi_{\vec{k}}(\vec{r})\right]$$

$$\hat{T}_{\vec{R}}\psi_{\alpha\vec{k}}(\vec{r}) = e^{i\alpha\vec{k}\vec{R}}\cdot\psi_{\alpha\vec{k}}(\vec{r})$$

$$\Rightarrow \boxed{\psi_{\alpha\vec{k}}(\vec{r}) = \psi_{\vec{k}}(\alpha\vec{r}+\vec{t})}$$

$$E(\alpha\vec{k}) = \langle \psi_{\alpha\vec{k}} | \hat{H} | \psi_{\alpha\vec{k}} \rangle =$$

$$= \langle \psi_{\vec{k}} | \hat{S}^{\dagger}_{\{\alpha,t\}} \hat{H} \hat{S}_{\{\alpha,t\}} | \psi_{\vec{k}} \rangle =$$

$$= \langle \psi_{\vec{k}} | \underbrace{\hat{S}^{\dagger}_{\{\alpha,t\}} \hat{S}_{\{\alpha,t\}}}_{\hat{1}} \hat{H} | \psi_{\vec{k}} \rangle = E(\vec{k})$$

Important example : inversion symmetry : $\hat{\alpha} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

$$\Rightarrow \begin{cases} E(-\vec{k}) = E(\vec{k}) \\ \psi_{-\vec{k}}(\vec{r}) = \psi_{\vec{k}}(-\vec{r}) \end{cases} \Rightarrow \boxed{\psi_{\vec{k}}(-\vec{r}) = \psi^{*}_{\vec{k}}(\vec{r})}$$

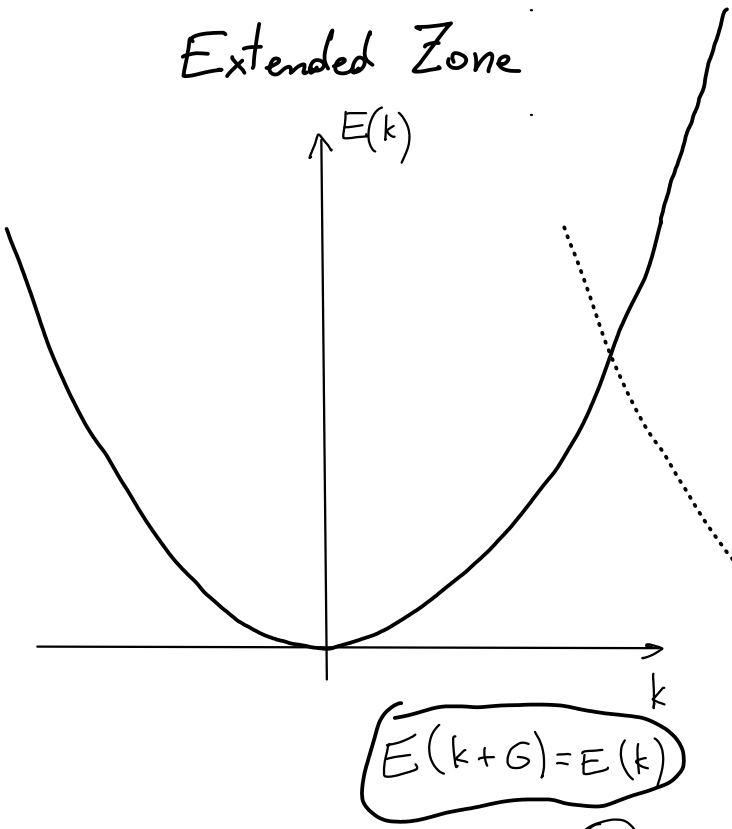
+ Kramer's theorem $\quad \psi_{-\vec{k}}(\vec{r}) = \psi^{*}_{\vec{k}}(\vec{r})$

3.1 Free Electron Model

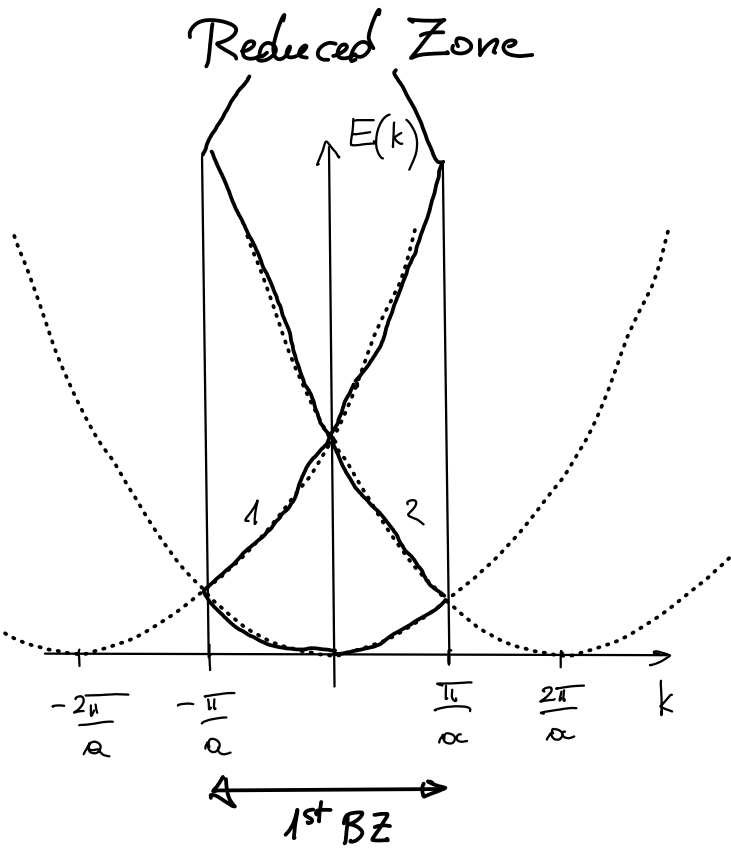
$$\left[-\frac{\hbar^2}{2m}\Delta + \phi\right]\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\psi_{\vec{k}}(\vec{r})$$

$V(\vec{r}) = 0$, but assume periodicity in $\vec{k}$-space in anticipation of a non-vanishing crystal potential

in 1D: $E(k) = \frac{\hbar^2}{2m}k^2$



vs.



$E(k+G) = E(k)$

$G = \ldots, -\frac{4\pi}{a}, -\frac{2\pi}{a}, 0, \frac{2\pi}{a}, \frac{4\pi}{a}, \ldots$

$$E_1(k) = \frac{\hbar^2}{2m}\left(k + \frac{2\pi}{a}\right)^2$$

$$E_2(k) = \frac{\hbar^2}{2m}\left(k - \frac{2\pi}{a}\right)^2$$

I.9

I, 22 ←

3.3 NEARLY-FREE ELECTRON MODEL (NFEM)

$$\underbrace{\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})\right]}_{\hat{H}}\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\,\psi_{n\vec{k}}(\vec{r})$$

treat lattice-periodic potential as a weak perturbation

$$\hat{H} = \hat{H}_0 + \hat{V}$$

$\hat{H}_0$: $-\frac{\hbar^2}{2m}\vec{\nabla}^2$; $\hat{V}$: perturbation

$$\Rightarrow E(\vec{k}) = E^{(0)}(\vec{k}) + \underbrace{E^{(1)}(\vec{k})}_{=\overline{V}} + E^{(2)}(\vec{k})$$

unperturbed system = free electrons $\quad E^{(0)}(\vec{k}) = \frac{\hbar^2}{2m}k^2$

$$\langle \vec{r}\,|\,\vec{k}\rangle = \frac{1}{\sqrt{\Omega_x}}e^{i\vec{k}\vec{r}}$$

$$E^{(1)}(\vec{k}) = \langle \vec{k}\,|\,V(\vec{r})\,|\,\vec{k}\rangle = \frac{1}{\Omega_x}\int d^3r\, e^{-i\vec{k}\vec{r}}\,V(\vec{r})\,e^{i\vec{k}\vec{r}} = \overline{V} \quad \ldots \text{ average potential}$$

non-degenerate perturbation

$$E^{(2)}(\vec{k}) = \sum_{\vec{k}'\neq\vec{k}} \frac{\left|\langle \vec{k}'\,|\,\hat{V}(\vec{r})\,|\,\vec{k}\rangle\right|^2}{E^{(0)}(\vec{k}) - E^{(0)}(\vec{k}')}$$

$$V(\vec{r}) = \sum_{\vec{G}} V(\vec{G})\,e^{i\vec{G}\vec{r}}$$

$$V_{\vec{k}'\vec{k}} = \langle \vec{k}'\,|\,\hat{V}\,|\,\vec{k}\rangle = \frac{1}{\Omega_x}\int d^3r\, e^{-i\vec{k}'\vec{r}}\,V(\vec{r})\,e^{i\vec{k}\vec{r}} =$$

$\vec{k} - \vec{k}' + \vec{G} \doteq 0$

$$= \frac{1}{\Omega_x}\sum_{\vec{G}} V(\vec{G}) \underbrace{\int d^3r\, e^{i(\vec{k}-\vec{k}'+\vec{G})\vec{r}}}_{\Omega_x \cdot \delta_{\vec{k}',\vec{k}+\vec{G}}} = \sum_{\vec{G}} V(\vec{G})\,\delta_{\vec{k}',\vec{k}+\vec{G}}$$

$$\Rightarrow E^{(2)}(\vec{k}) = \sum_{\vec{G}\neq 0} \frac{|V(\vec{G})|^2}{E^{(0)}(\vec{k}) - E^{(0)}(\vec{k}+\vec{G})} \qquad E(\vec{k}+\vec{G}) = E(\vec{k})$$

denominator: $\quad \frac{\hbar^2}{2m}k^2 - \frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 \overset{!}{\doteq} 0$

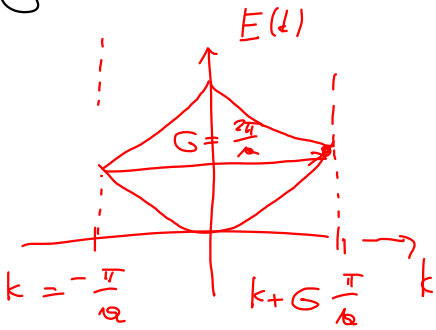
$$k^2 - \left(k^2 + 2\vec{k}\cdot\vec{G} + G^2\right) = 0$$

This defines the BZ-boundary: $\boxed{2\vec{k}\cdot\vec{G} + G^2 = 0}$ Bragg-condition

Degenerate perturbation theory of the 1D-case:

Nov. 28th 2021

$k = \pm \frac{\pi}{a}$ $\quad E(+\frac{\pi}{a}) = E(-\frac{\pi}{a})$ (doubly degenerate at BZ-boundary)



$\Rightarrow$ ansatz: $|\varphi\rangle = a|k\rangle + b|k+G\rangle$

$\rightarrow$ insert into $\hat{H}|\varphi\rangle = E|\varphi\rangle$

$\hat{H} = \hat{H}_0 + V$ $\qquad E = E^{(0)} + E^{(1)}$

$$\left(\hat{H}_0 + \hat{V} - E^{(0)} - E^{(1)}\right)\left(a|k\rangle + b|k+G\rangle\right) = 0$$

(i) $\cdot \langle k|$ $\qquad$ (ii) $\langle k+G|$

(i) $a\langle k|\hat{V}|k\rangle - aE^{(1)} + b\langle k|\hat{V}|k+G\rangle = 0$

(ii) $a\langle k+G|\hat{V}|k\rangle + b\langle k+G|\hat{V}|k+G\rangle - bE^{(1)} = 0$

$\Rightarrow$
$$\begin{pmatrix} V_{kk} - E^{(1)} & V_{k,k+G} \\ V_{k+G,k} & V_{k+G,k+G} - E^{(1)} \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$V_{kk} = V_{k+G,k+G} = V_0$ ... average potential

$V_{k,k+G} = V^*_{k+G,k} = \tilde{V}_G$ ... Fourier coefficient of potential

$\Rightarrow \left[V_0 - E^{(1)}\right]^2 - |V_G|^2 \overset{!}{=} 0$

$$\boxed{E^{(1)} = V_0 \pm |V_G|}$$

$\Rightarrow$ at BZ-boundary an energy gap of $2\cdot|V_G|$ opens up.

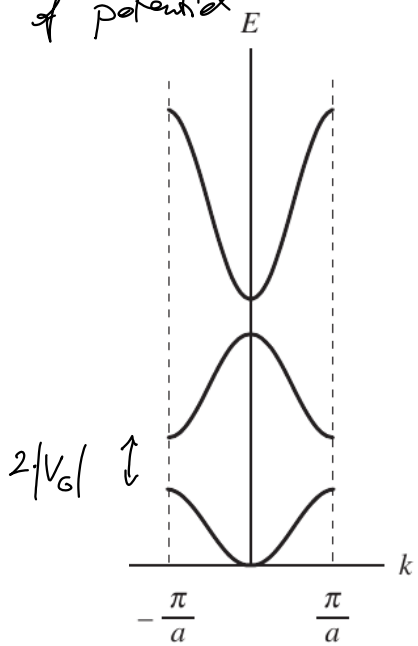
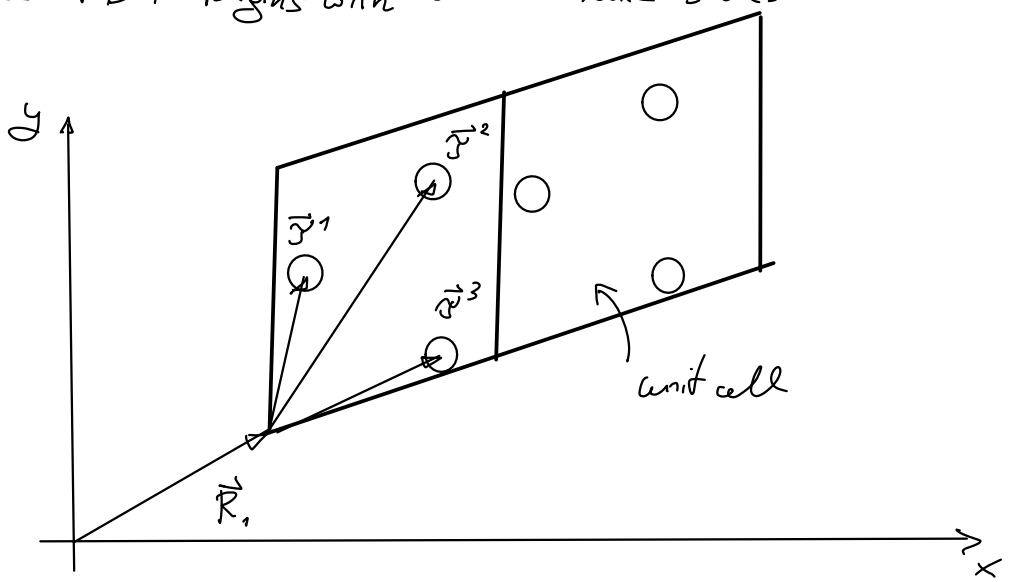


Fig. 3.5 (page 42)

3.4 TIGHT-BINDING MODEL (TBM)

→ model at the other limit of the NFEM, that is, useful for solids where the constituent atoms resemble slightly perturbed free atoms

→ The TBM begins with atomic-like states



The crystal potential is constructed as a sum over atomic-like potentials:

$$V(\vec{r}) = \sum_{l} \sum_{a} V_a\left(\vec{r} - \vec{R}_l - \vec{r}_a\right)$$

l: unit cell; a: atoms in basis

atomic wave functions ϕ_{ta} satisfy the equation:

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V_a(\vec{r})\right] \varphi_{ta}(\vec{r}) = E_{ta} \cdot \varphi_{ta}(\vec{r})$$

t_a: atom type; labels atomic states (nlm)

Linear Combination of Atomic Orbitals (LCAO)

$$\phi_{\vec{k}}^{t_a}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}\vec{R}_n} \varphi(\vec{r} - \vec{R}_n - \vec{\tau}_a)$$

(t_a: atom type; $\vec{k}$: Bloch vector; N: number of unit cells in crystal)

Bloch wave?

$$\phi_{\vec{k}}^{t_a}(\vec{r} + \vec{R}_m) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}\vec{R}_n} \varphi\left[\vec{r} - \underbrace{(\vec{R}_n - \vec{R}_m)}_{:=\vec{R}_\ell} - \vec{\tau}_a\right] =$$

relabel sum by introducing $\vec{R}_\ell = \vec{R}_n - \vec{R}_m$

$$= e^{i\vec{k}\vec{R}_m} \cdot \underbrace{\frac{1}{\sqrt{N}} \sum_\ell e^{i\vec{k}\vec{R}_\ell} \varphi(\vec{r} - \vec{R}_\ell - \vec{\tau}_a)}_{\phi_{\vec{k}}^{t_a}(\vec{r})}$$

✓

Bloch theorem ✓

Now: The crystalline electron wave function $\psi_{\vec{k}}(\vec{r})$ is expanded in terms of the LCAO functions $\phi_{\vec{k}}^{t_a}(\vec{r})$

$$\boxed{\psi_{\vec{k}}(\vec{r}) = \sum_{t,a} \alpha_{t_a}(\vec{k})\, \phi_{\vec{k}}^{t_a}(\vec{r})}$$

insert into Schrödinger equation: $\hat{H}\, \psi_{\vec{k}}(\vec{r}) = E(\vec{k})\, \psi_{\vec{k}}(\vec{r})$

simplify notation: $(t,a) \to j \Rightarrow \psi_{\vec{k}}(\vec{r}) = \sum_j \alpha_j(\vec{k})\, \phi_{\vec{k}}^{j}(\vec{r})$

$$\Rightarrow \quad \sum_j \alpha_j(\vec{k})\, \hat{H}\, \phi^j_{\vec{k}}(\vec{r}) = E(\vec{k}) \sum_j \alpha_j(\vec{k})\, \phi^j_{\vec{k}}(\vec{r}) \qquad \Big/ \int_{\Omega_\kappa} d^3r\, \phi^{i*}_{\vec{k}}(\vec{r})$$

$\Rightarrow$ Hamilton matrix: $H_{ij}(\vec{k}) = \int_{\Omega_\kappa} d^3r\, \phi^{i*}_{\vec{k}}(\vec{r})\, \hat{H}\, \phi^j_{\vec{k}}(\vec{r})$

Overlap matrix: $S_{ij}(\vec{k}) = \int_{\Omega_\kappa} d^3r\, \phi^{i*}_{\vec{k}}(\vec{r})\, \phi^j_{\vec{k}}(\vec{r})$

$\Rightarrow$

$$\boxed{\sum_j H_{ij}(\vec{k})\, \alpha_j(\vec{k}) = E(\vec{k}) \sum_i S_{ij}(\vec{k})\, \alpha_j(\vec{k})}$$

generalized matrix eigenvalue equation ($\hat{=}$ "secular equation")

M = dimension of H_{ij} = total number of atomic orbitals in the atomic basis

For illustrating the TBM, we demonstrate it with several examples

(1) – Crystal with 1 atom per unit cell and
– only one relevant atomic state (see also I.13)
$\Rightarrow M = 1$

(2) TBM for the graphene π-bands
(2 atoms per cell and 1 atomic p_z orbital per atom)

$\Rightarrow M = 2$

(3) Cu-O_2 planes in high-T_c superconductors

→ problem I.15, here: $M = 3$

ad (1) 1 atom / cell, 1 relevant atomic orbital $\Rightarrow$ $M=1$

$$\phi^1_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_u e^{i\vec{k}\vec{R}_u} \varphi_1(\vec{r}-\vec{R}_u) \qquad \hat{H}(\vec{r}+\vec{R}) = \hat{H}(\vec{r})$$

$$H_{11}(\vec{k}) = \langle \phi^1_{\vec{k}} | \hat{H} | \phi^1_{\vec{k}} \rangle = \frac{1}{N} \sum_{n,m} e^{i\vec{k}(\vec{R}_n - \vec{R}_m)} \int_{\Omega_x} \varphi_1^*(\vec{r}-\vec{R}_m)\, \hat{H}(\vec{r})\, \varphi_1(\vec{r}-\vec{R}_n)\, d^3r =$$

$\left[\vec{r}' = \vec{r} - \vec{R}_m \rightarrow d^3r' = d^3r \,,\quad \vec{r}-\vec{R}_m \rightarrow \vec{r}' - \underbrace{(\vec{R}_n - \vec{R}_m)}_{\vec{R}_p} \right]$

$$\Rightarrow H_{11}(\vec{k}) = \sum_p e^{i\vec{k}\vec{R}_p} \underbrace{\int_{\Omega_x} d^3r'\, \varphi_1^*(\vec{r}')\, \hat{H}(\vec{r}')\, \varphi_1(\vec{r}'-\vec{R}_p)}_{h_{11}(\vec{R}_p)}$$

$h_{11}(\vec{R}_p)$ .... "hopping integral"

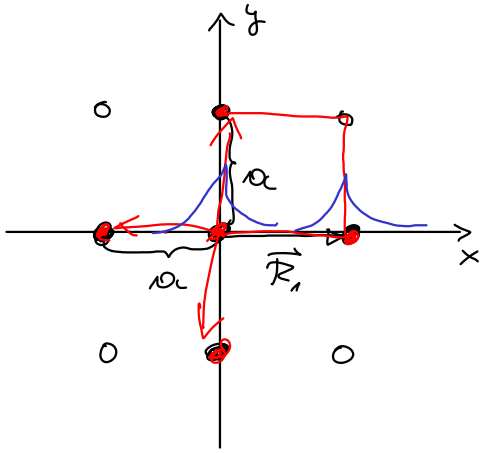
$$S_{11}(\vec{k}) = \sum_p e^{i\vec{k}\vec{R}_p} \underbrace{\int_{\Omega_x} d^3r'\, \varphi_1^*(\vec{r}')\, \varphi_1(\vec{r}'-\vec{R}_p)}_{S_{11}(\vec{R}_p)}$$

$S_{11}(\vec{R}_p)$ .... "overlap integral"

$M=1$ $\Rightarrow$ $H_{11}\alpha = E \cdot \alpha S_{11}$

$\Rightarrow$ $$\boxed{E(\vec{k}) = \frac{H_{11}(\vec{k})}{S_{11}(\vec{k})}}$$

Consider a simple cubic lattice with only nearest-neighbour interactions



$$H_{11}(\vec{k}) = \sum_p e^{i\vec{k}\vec{R}_p} \cdot h_{11}(\vec{R}_p) =$$

$$= \underbrace{h_{11}(\vec{0})}_{:=\varepsilon_a} + \underbrace{h_{11}(\vec{R}_1)}_{:=h} \cdot \sum_{\text{nearest neighbors}} e^{i\vec{k}\vec{R}_p}$$

$\hat{=}$ on-site energy

$\hat{=}$ hopping integral = transfer integral

6 nearest neighbors:

$$\vec{R}_{1,2} = \begin{pmatrix} \pm a \\ 0 \\ 0 \end{pmatrix}, \quad \vec{R}_{3,4} = \begin{pmatrix} 0 \\ \pm a \\ 0 \end{pmatrix}, \quad \vec{R}_{5,6} = \begin{pmatrix} 0 \\ 0 \\ \pm a \end{pmatrix}$$

$$H_{11}(\vec{k}) = \varepsilon_a + h \cdot \left[e^{ik_x a} + e^{-ik_x a} + \dots \right]$$

$$= \varepsilon_a + 2h \cdot \left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a) \right]$$

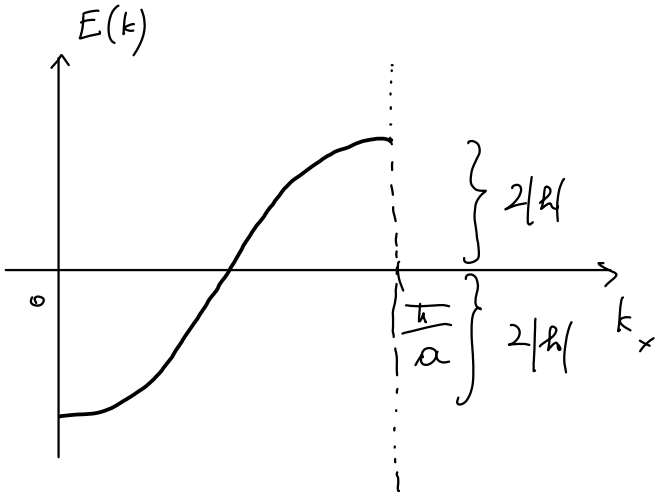
$$S_{11}(\vec{k}) = \sum_p e^{i\vec{k}\vec{R}_p} \cdot S_{11}(\vec{R}_p) \approx \underbrace{S_{11}(0)}_{=1} + 0 = 1$$

neglect overlaps with neighboring orbitals

$(M=1)$ $\quad E(\vec{k}) = \dfrac{H_{11}(\vec{k})}{S_{11}(\vec{k})}$

$$\Rightarrow \boxed{E(\vec{k}) = \varepsilon_a + 2h \left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a) \right]}$$

total band width $= 12 \cdot |h|$ note that $h < 0$



e.g.:

$\varepsilon_a + 4h$

in the plot: $(k_y = k_z = 0)$

Example (2): TBM for graphene π-bands

-) 1 p_z-orbital on each atomic site
-) Orthogonal orbitals (overlap matrix $= \hat{1}$)
-) Consider only nearest-neighbor interactions

C: $1s^2 2s^2 2p^2$

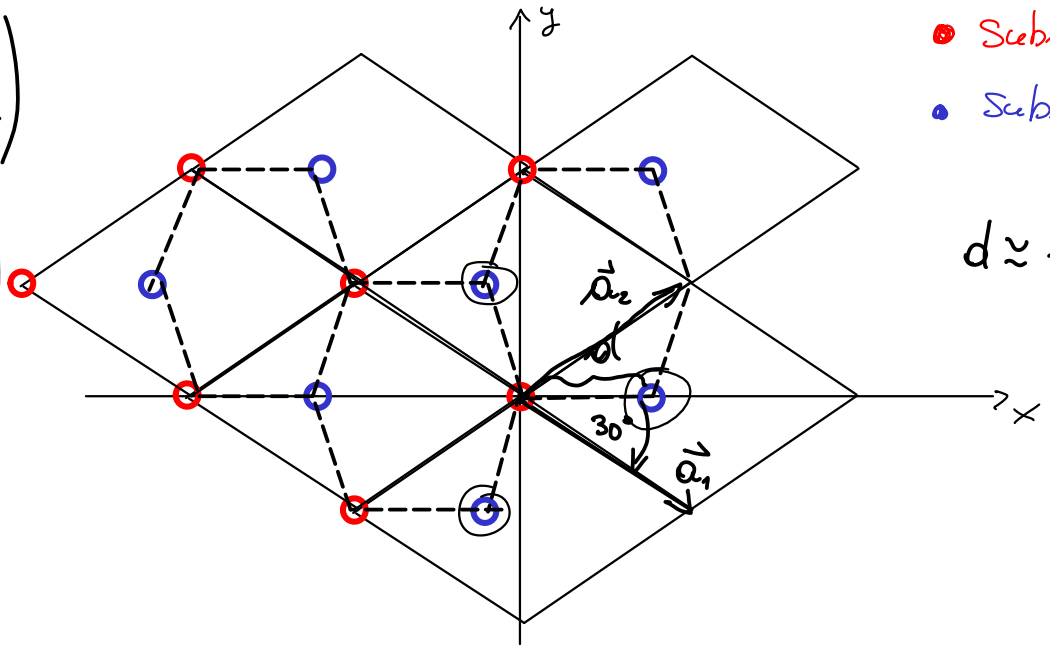
sp^2-hybridization

$$\vec{a}_1 = a \cdot \begin{pmatrix} 3/2 \\ -\sqrt{3}/2 \end{pmatrix}$$

$$\vec{a}_2 = a \cdot \begin{pmatrix} 3/2 \\ +\sqrt{3}/2 \end{pmatrix}$$

$$\vec{r}_A = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\vec{r}_B = \begin{pmatrix} a \\ 0 \end{pmatrix}$$



- Sublattice A
- Sublattice B

$a \approx 1{,}4\,\text{Å}$

2 Bloch-basis functions — atomic $2p_z$-orbital

$$\phi^A_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}(\vec{R}_n + \vec{r}_A)} \cdot \varphi(\vec{r} - \vec{R}_n - \vec{r}_A)$$

$$\phi^B_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}(\vec{R}_n + \vec{r}_B)} \cdot \varphi(\vec{r} - \vec{R}_n - \vec{r}_B)$$

LCAO wave function $\psi_{\vec{k}}(\vec{r}) = c_A(\vec{k})\,\phi^A_{\vec{k}}(\vec{r}) + c_B(\vec{k})\,\phi^B_{\vec{k}}(\vec{r})$

$$\begin{pmatrix} H_{AA}(\vec{k}) & H_{AB}(\vec{k}) \\ H_{BA}(\vec{k}) & H_{BB}(\vec{k}) \end{pmatrix} \cdot \begin{pmatrix} c_A \\ c_B \end{pmatrix} = E(\vec{k}) \cdot \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

By symmetry: $H_{AA} = H_{BB}$, $H_{BA} = H_{AB}^*$

$$H_{AA}(\vec{k}) = \int_{\Omega_x} d^3r\, \phi_{\vec{k}}^{A*}(\vec{r}) \cdot \hat{H}\, \phi_{\vec{k}}^{A}(\vec{r}) =$$

assume only nearest neighbor interactions

$$= \frac{1}{N} \sum_n \sum_m e^{i\vec{k}(\vec{R}_m - \vec{R}_n)} \cdot \int d^3r\, \varphi^*(\vec{r} - \vec{R}_n)\, \hat{H}\, \varphi(\vec{r} - \vec{R}_m) =$$

$$\approx \cancel{N} \cdot \frac{1}{\cancel{N}} \underbrace{\int d^3r\, \varphi^*(\vec{r})\, \hat{H}\, \varphi(\vec{r})}_{:= \varepsilon_0} = \varepsilon_0 \quad \ldots \text{ on-site energy} \neq f(\vec{k})$$

$$H_{AB}(\vec{k}) = \int_{\Omega_x} d^3r\, \phi_{\vec{k}}^{A*}(\vec{r})\, \hat{H}\, \phi_{\vec{k}}^{B}(\vec{r}) =$$

$$= \frac{1}{N} \sum_n \sum_m e^{i\vec{k}(\vec{R}_m - \vec{R}_n + \vec{\tau}_B)} \int d^3r\, \varphi^*(\vec{r} - \vec{R}_n)\, \hat{H}\, \varphi(\vec{r} - \vec{R}_m - \vec{\tau}_B) =$$

$$= \left| \begin{array}{ll} \vec{r}\,' = \vec{r} - \vec{R}_n & \vec{r} - \vec{R}_m = \vec{r}\,' - \underbrace{(\vec{R}_m - \vec{R}_n)}_{\vec{R}_p} \\ d^3r' = d^3r & \end{array} \right| =$$

Consider only 3 nearest neighbors

$$= \sum_p e^{i\vec{k}(\vec{R}_p + \vec{\tau}_B)} \cdot \underbrace{\int d^3r'\, \varphi^*(\vec{r}\,')\, \hat{H}\, \varphi(\vec{r}\,' - \vec{R}_p - \vec{\tau}_B)}_{\gamma} \approx$$

3 neighbours:

(i) $\vec{l}_1 = \vec{R}_p + \vec{\tau}_B = \vec{0} + \vec{\tau}_B = \begin{pmatrix} d \\ 0 \end{pmatrix}$

(ii) $\vec{l}_2 = -\vec{a}_1 + \vec{\tau}_B = \ldots = \begin{pmatrix} -d/2 \\ +\frac{\sqrt{3}}{2} d \end{pmatrix}$

(iii) $\vec{l}_3 = -\vec{a}_2 + \vec{\tau}_B = \ldots = \begin{pmatrix} -d/2 \\ -\frac{\sqrt{3}}{2} d \end{pmatrix}$

$$H_{AB}(\vec{k}) = \underbrace{\left[e^{i\vec{k}\vec{l}_1} + e^{i\vec{k}\vec{l}_2} + e^{i\vec{k}\vec{l}_3} \right]}_{f(\vec{k})} \cdot \gamma = \Gamma(\vec{k})$$

γ ↑ hopping integral

$$\begin{pmatrix} \varepsilon_0 & \gamma f(\vec{k}) \\ \gamma f^*(\vec{k}) & \varepsilon_0 \end{pmatrix} \cdot \begin{pmatrix} c_A \\ c_B \end{pmatrix} = E(\vec{k}) \cdot \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

$$\det \begin{vmatrix} \varepsilon_0 - E & \gamma f(\vec{k}) \\ \gamma f^*(\vec{k}) & \varepsilon_0 - E \end{vmatrix} \stackrel{!}{=} 0 \qquad \vec{k} = \begin{pmatrix} k_x \\ k_y \end{pmatrix}$$

$$(\varepsilon_0 - E)^2 - \gamma^2 |f(\vec{k})|^2 = 0$$

$$\Rightarrow \boxed{E(\vec{k}) = \varepsilon_0 \pm |\gamma| \cdot |f(\vec{k})|}$$

$$E(k_x, k_y) = \dots = \sqrt{1 + 4\cos\left(\frac{\sqrt{3}d}{2} k_x\right)\cos\left(\frac{\sqrt{3}d}{2} \cdot k_y\right) + 4\cos^2\left(\frac{\sqrt{3}d}{2} k_y\right)}$$

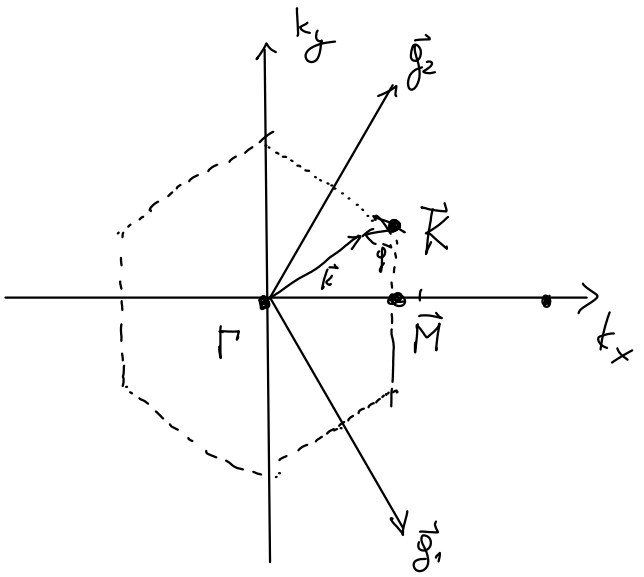
$\vec{Q}_1, \vec{Q}_2 \Rightarrow$ reciprocal basis vectors

$$\vec{g}_1 = \frac{2\pi}{d} \begin{pmatrix} 1/3 \\ -\frac{1}{\sqrt{3}} \end{pmatrix}$$

$$\vec{g}_2 = \frac{2\pi}{d} \begin{pmatrix} 1/3 \\ +\frac{1}{\sqrt{3}} \end{pmatrix}$$

$$\boxed{\vec{K} = \frac{\vec{g}_1 + 2\vec{g}_2}{3}}$$

$$\vec{M} = \frac{1}{2}(\vec{g}_1 + \vec{g}_2)$$



$$f(K) = e^{i\vec{K}\cdot\vec{\ell}_1} + e^{i\vec{K}\cdot\vec{\ell}_2} + e^{i\vec{K}\cdot\vec{\ell}_3} = e^{i\frac{2\pi}{3}} + 1 + e^{-i\frac{2\pi}{3}} =$$

$$\vec{K}\cdot\vec{\ell}_1 = \frac{1}{3}(\vec{g}_1 + 2\vec{g}_2)\cdot\vec{\tau}_B = \dots = \frac{2\pi}{3}$$

$$\vec{K}\cdot\vec{\ell}_2 = \frac{1}{3}(\vec{g}_1 + 2\vec{g}_2)\cdot(-\vec{a}_1 + \vec{\tau}_B) = -\frac{2\pi}{3} + \frac{2\pi}{3} = 0$$

$$\vec{K}\cdot\vec{\ell}_3 = \frac{1}{3}(\vec{g}_1 + 2\vec{g}_2)\cdot(-\vec{a}_2 + \vec{\tau}_B) = -\frac{2}{3}\cdot 2\pi + \frac{2\pi}{3} = -\frac{2\pi}{3}$$

$$f(K) = 2\underbrace{\cos\left(\frac{2\pi}{3}\right)}_{=-\frac{1}{2}} + 1 = 0$$

$$E(K) = \varepsilon_0 \pm \underbrace{\gamma\cdot f(K)}_{\Gamma(k)} = \varepsilon_0$$

valence and conduction bands touch
$\Rightarrow$ no gap

$$\vec{k} = \vec{K} + \vec{q}$$

$$\Gamma(K+\vec{q}) = \underbrace{\Gamma(K)}_{=0} + \frac{\partial\Gamma}{\partial\vec{q}}\cdot\vec{q} + \dots = \gamma\cdot\frac{3}{2}d\cdot(q_x - iq_y)$$

$\varepsilon_0 \stackrel{!}{=} 0$

$$\hat{H}(\vec{q}) = \underbrace{\frac{3}{2}\gamma d}_{:=\hbar v_0}\cdot\begin{pmatrix} 0 & q_x - iq_y \\ q_x + iq_y & 0 \end{pmatrix} =$$

$\vec{p} = \hbar\vec{q}$

$$= \hbar v_0\cdot\left[q_x\cdot\underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\hat{\sigma}_x} + q_y\cdot\underbrace{\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}}_{\hat{\sigma}_y}\right] = \hbar v_0\cdot\hat{\vec{\sigma}}\cdot\vec{q} = v_0\,\hat{\vec{\sigma}}\cdot\vec{p}$$

$\Rightarrow$ 2D-Version of Dirac equation for massless Fermions.

$\hbar v_0 = \frac{3}{2} \gamma \cdot d$ $\qquad d \simeq 1.4 \text{ Å} = 2.65 \text{ Bohr}$

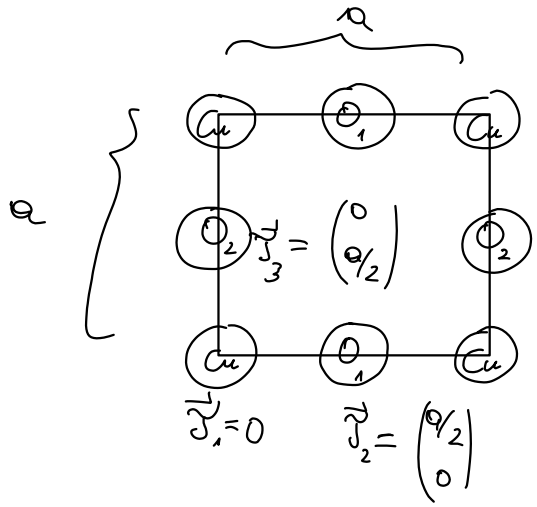
$\gamma \approx 2.7 \text{ eV} \cong 0.1 \text{ Ha}$

$v_0 \approx \frac{3}{2} \cdot 0,1 \cdot 2,65 = 0,3975$ atomic units

$\approx \frac{0,3975}{137} \cdot c \approx \underline{0,003 \cdot c}$

Dirac-Hamiltonian: $H = c \cdot \hat{\vec{\alpha}} \cdot \hat{\vec{p}} + \hat{\beta} mc^2$

Exercise for TBH: I.15 Cu-O planes



Cu: $d_{x^2-y^2}$

O_1: p_x :

O_2: p_y :

3.7 (Empirical) Pseudopotential Method

(Page 59 ff)

→ efficient method to obtain the electronic bandstructure of group IV or III-V semiconductors

→ idea: eg. Si: $\underbrace{1s^2 2s^2 2p^6}_{\text{core}} \,|\, \underbrace{3s^2 3p^2}_{\text{valence}}$

construct a "pseudo-potential" for the valence electrons that takes into account the atomic nuclei and the rest of the electrons (= core electrons)

→ empirical pseudo-potential ⇒ parameters are fitted experimental bandstructure
or ab-initio ——— no fits (→ see lecture F.E.S.T)

$$V_p(\vec{r}) = \sum_{\vec{R},\vec{J}} V_a(\vec{r}-\vec{R}-\vec{J})$$

↑ atomic pseudo potential

$$V_p(\vec{r}+\vec{R}) = V_p(\vec{r})$$

$$V(\vec{r}) = \sum_{\vec{G}} \tilde{V}(\vec{G}) e^{i\vec{G}\vec{r}}$$

$$\frac{N}{\Omega_x} = \frac{1}{\Omega_0}$$

$$\tilde{V}(\vec{G}) = \frac{1}{\Omega} \int_{\Omega_x} d^3r\, V(\vec{r}) e^{-i\vec{G}\vec{r}} = \frac{1}{\Omega_x} \sum_{\vec{R},\vec{J}} \int V_a(\overbrace{\vec{r}-\vec{R}-\vec{J}}^{\vec{r}'}) e^{-i\vec{G}\vec{r}}\, d^3r =$$

$$= \dots = \frac{1}{\Omega_0} \sum_{\vec{J}} e^{-i\vec{G}\cdot\vec{J}} \underbrace{\int_{\Omega_0} d^3r\, V_{\vec{J}}(\vec{r}) e^{-i\vec{G}\vec{r}}}_{\tilde{V}_{\vec{J}}(\vec{G})}$$

$\tilde{V}_{\vec{J}}(\vec{G})$ ... Fourier coefficient of atomic pseudo-potential

$$\tilde{V}_{\vec{J}}(\vec{G}) = \tilde{V}_{\vec{J}}(|\vec{G}|)$$

↑ assume spherical symmetric potentials

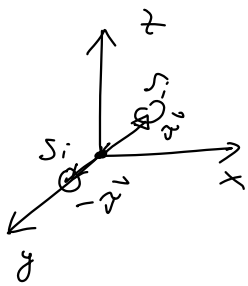
$$\Rightarrow \quad \tilde{V}(\vec{G}) = \frac{1}{w} \sum_{\vec{r}} e^{-i\vec{G}\vec{r}} \, \tilde{V}_{\vec{r}}(|\vec{G}|)$$

w: unit cell volume per atom

$$\tilde{V}(\vec{G}) = \sum_{\ell} \underbrace{S_\ell(\vec{G})}_{\text{structure factor}} \cdot \underbrace{\tilde{V}_\ell(|\vec{G}|)}_{\text{form factor}}$$

ℓ: sum over different atom types

e.g.: Si in diamond structure:



$$S(\vec{G}) = \frac{1}{2}\left[e^{i\vec{G}\vec{r}} + e^{-i\vec{G}\vec{r}}\right] = \cos(\vec{G}\cdot\vec{r})$$

see I.12

$$\vec{r} = a \cdot \begin{pmatrix} 1/8 \\ 1/8 \\ 1/8 \end{pmatrix}$$

a: lattice parameter

$$\vec{g}_1 = \frac{2\pi}{a}\begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix} \qquad \vec{g}_2 = \frac{2\pi}{a}\begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix} \qquad \vec{g}_3 = \frac{2\pi}{a}\begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix}$$

$$|\vec{G}_{hkl}|^2 = \left(\frac{2\pi}{a}\right)^2 \cdot \left[(-h+k+\ell)^2 + (h-k+\ell)^2 + (h+k-\ell)^2\right]$$

$$\vec{G}\cdot\vec{r} = \ldots = \frac{\pi}{4}(h+k+\ell)$$

$$\Rightarrow S(\vec{G}) = \cos\left[\frac{\pi}{4}(h+k+\ell)\right]$$

$$\vec{G}_{hkl} = h\cdot\vec{g}_1 + k\cdot\vec{g}_2 + \ell\cdot\vec{g}_3$$

	h	k	ℓ	$\lvert\vec{G}\rvert^2/\left(\frac{2\pi}{a}\right)^2$	$h+k+\ell$	$S(\vec{G})$	$\tilde{V}(\lvert\vec{G}\rvert)$ (Ry)
1	0	0	0	0	0	1	const.
2	1	0	0	3	1	$\sqrt{2}/2$	−0,23
3	1	1	1	3	3	$-\sqrt{2}/2$	−0,23
4	1	1	0	4	2	0	—
5	2	1	1	8	4	−1	+0.01
6	2	1	0	11	3	$-\sqrt{2}/2$	+0.06

Solution of Schrödinger-Equation $\hat{H}_p \psi_{\vec{k}} = E(\vec{k}) \psi_{\vec{k}}$

$\int \cdot \phi^*_{\vec{k}+\vec{G}}$

Hamiltonian: $\hat{H} = -\frac{1}{2}\Delta + V(\vec{r})$ $\left(\hbar = m = \frac{e^2}{4\pi\varepsilon_0} = 1 \right)$ atomic units

1 Bohr $\hat{=}$ 0.529 Å

1 Ha $\hat{=}$ 27.2 eV

Plane-wave basis: $\langle \vec{r} | \vec{k}+\vec{G} \rangle = \frac{1}{\sqrt{\Omega_x}} e^{i(\vec{k}+\vec{G})\vec{r}} = \phi_{\vec{k}+\vec{G}}(\vec{r})$

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}'} \alpha_{\vec{k}}(\vec{G}) \cdot \phi_{\vec{k}+\vec{G}'}(\vec{r})$$

$$\Rightarrow \boxed{H_{\vec{G}\vec{G}'}(\vec{k})} = \langle \vec{k}+\vec{G} | \hat{H} | \vec{k}+\vec{G}' \rangle \quad \rightsquigarrow \quad \sum_{\vec{G}'} \hat{H}_{\vec{G}\vec{G}'}(\vec{k}) \cdot \alpha_{\vec{G}'}(\vec{k}) = E(\vec{k})\, \alpha_{\vec{G}}(\vec{k})$$

$\hat{H} = \hat{T} + \hat{V}$

$$\hat{T}_{\vec{G}\vec{G}'}(\vec{k}) = \frac{1}{\Omega_x} \int_{\Omega_x} d^3r\, e^{-i(\vec{k}+\vec{G})\cdot\vec{r}} \underbrace{\left(-\frac{1}{2}\Delta\right) e^{i(\vec{k}+\vec{G}')\vec{r}}}_{+\frac{|\vec{k}+\vec{G}'|^2}{2} \cdot \text{—}} = \frac{|\vec{k}+\vec{G}'|^2}{2} \cdot \Omega_x \underbrace{\int_{\Omega_x} d^3r\, e^{-i(\vec{G}-\vec{G}')\vec{r}}}_{=\Omega_x \cdot \delta_{\vec{G},\vec{G}'}}$$

$$\boxed{\hat{T}_{\vec{G}\vec{G}'}(\vec{k}) = \frac{|\vec{k}+\vec{G}|^2}{2} \cdot \delta_{\vec{G}\vec{G}'}}$$

$$\hat{V}_{\vec{G}\vec{G}'} = \frac{1}{\Omega_x} \int d^3r\, e^{-i(\vec{k}+\vec{G})\vec{r}} V(\vec{r})\, e^{i(\vec{k}+\vec{G}')\vec{r}} = \sum_{\vec{G}''} \tilde{V}(\vec{G}'') \underbrace{\frac{1}{\Omega_x} \int d^3r\, e^{i[\vec{G}'' - (\vec{G}-\vec{G}')]\vec{r}}}_{\Omega_x \cdot \delta_{\vec{G}'', \vec{G}-\vec{G}'}} =$$

$V(\vec{r}) = \sum_{\vec{G}''} \tilde{V}(\vec{G}'') \cdot e^{i\vec{G}''\vec{r}}$

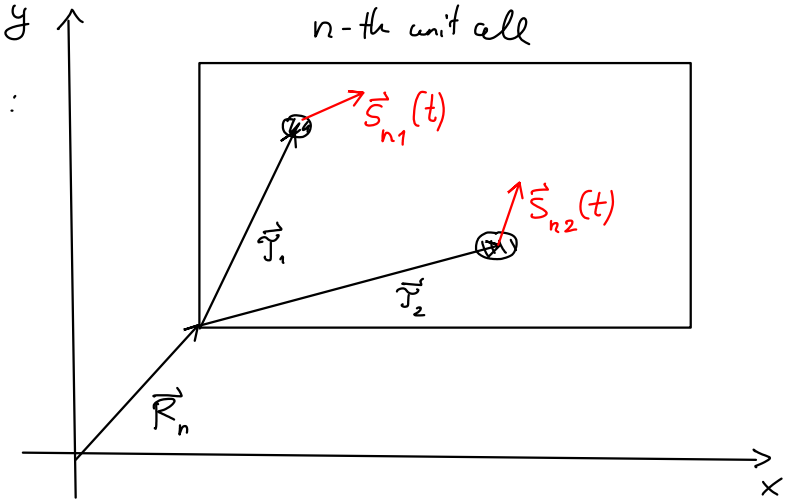
$$V_{\vec{G}\vec{G}'} = \tilde{V}(\vec{G}-\vec{G}') \quad \|$$

4.) LATTICE VIBRATIONS AND PHONONS

4.1 LATTICE VIBRATIONS (classical mechanics)

Equilibrium positions of atomic nuclei:

$$\vec{R}^{(0)}_{n,\alpha} = \vec{R}_n + \vec{r}_\alpha$$



$\vec{s}_{n\alpha}$ ... displacement of atom α in unit cell n.

Classical Equations of Motion:

$$\left\{\vec{s}_{n,\alpha}\right\}_i = s_{n\alpha i}$$

Kinetic Energy: $T = \sum_n \sum_\alpha \frac{M_\alpha}{2} \cdot \left|\dot{\vec{s}}_{n,\alpha}\right|^2$

Potential Energy: $U = U\left(\vec{R}^{(0)}_{n,\alpha}\right) + \sum_{n,\alpha} \left.\frac{\partial U}{\partial \vec{s}_{n,\alpha}}\right|_{\vec{R}^{(0)}_{n,\alpha}} \cdot \vec{s}_{n,\alpha} +$ ($= 0$)

$$+ \frac{1}{2} \sum_{n\alpha i} \sum_{n'\alpha' j'} \left.\frac{\partial^2 U}{\partial s_{n\alpha i}\, \partial s_{n'\alpha' j'}}\right|_{\vec{R}^{(0)}_{n\alpha}} \cdot s_{n\alpha i}\, s_{n'\alpha' j'} + \text{anharmonic terms}$$

$$\Phi^{n'\alpha' j'}_{n\alpha i}$$ ... spring constant matrix

$U = \frac{1}{2} k x^2$

$\Phi^{n'\alpha' j'}_{n\alpha i}$ ... force in direction i on atom α in unit cell n, if atom α' in unit cell n' is displaced in direction j' by an unit length.

•) $\Phi^{n'\alpha'i'}_{n\alpha i} = \Phi^{n\alpha i}_{n'\alpha'i'}$ ... Newton's actio = reactio

•) $\Phi^{n'\alpha'i}_{n\alpha i} = \Phi^{\alpha'i'}_{\alpha i}(\vec{R}_n - \vec{R}_{n'})$ translational periodicity

=> Equations of Motion: $d \cdot r \cdot N$ ← number of unit cells
↑ spatial dimensions ↑ ← number of atoms/cell

$$M_\alpha \ddot{s}_{n\alpha i}(t) = -\sum_{n'\alpha'i'} \Phi^{n'\alpha'i'}_{n\alpha i} s_{n'\alpha'i'}$$

$m\ddot{x} = -kx$

(i) harmonic ansatz: $s_{n\alpha i}(t) = \frac{1}{\sqrt{M_\alpha}} u_{n\alpha i} \cdot e^{-i\omega t}$ | $\ddot{s}_{n\alpha i} = -\omega^2 s_{n\alpha i}$

$$\Rightarrow -M_\alpha \omega^2 \frac{1}{\sqrt{M_\alpha}} u_{n\alpha i} e^{-i\omega t} = -\sum_{n'\alpha'i'} \Phi^{n'\alpha'i'}_{n\alpha i} \frac{1}{\sqrt{M_{\alpha'}}} u_{n'\alpha'i'} e^{-i\omega t} \quad / \cdot \frac{1}{\sqrt{M_\alpha}}$$

$$\sum_{n'\alpha'i'} \underbrace{\frac{\Phi^{n'\alpha'i'}_{n\alpha i}}{\sqrt{M_\alpha \cdot M_{\alpha'}}}}_{\text{dynamical matrix: } D^{n'\alpha'i'}_{n\alpha i}} \cdot u_{n'\alpha'i'} = \omega^2 \cdot u_{n\alpha i}$$

Size of matrix: $d \cdot r \cdot N$

(ii) Make use of translational symmetry
→ Bloch-wave ansatz:

$$u_{n\alpha i} = C_{\alpha i} \cdot e^{i\vec{q}\cdot(\vec{R}_n + \vec{\tau}_\alpha)} \qquad \vec{q} \in 1^{st}\ BZ$$

$$= C_{\alpha i} e^{i\vec{q}\vec{\tau}_\alpha} \cdot e^{i\vec{q}\vec{R}_n}$$

(translational symmetry)

$$\sum_{n\alpha' i'} \frac{\Phi_{\alpha i}^{\alpha' i'}(\vec{R}_n - \vec{R}_{n'})}{\sqrt{M_\alpha \cdot M_{\alpha'}}} \cdot u_{n'\alpha' i'} = \omega^2 \cdot u_{n\alpha i} \qquad u_{n\alpha i} = C_{\alpha i} e^{i\vec{q}\vec{r}_\alpha} \cdot e^{i\vec{q}\vec{R}_n}$$

$$\sum_{\alpha' i'} \left[e^{-i\vec{q}(\vec{r}_\alpha - \vec{r}_{\alpha'})} \sum_{n'} \frac{\Phi_{\alpha i}^{\alpha' i'}(\vec{R}_n - \vec{R}_{n'})}{\sqrt{M_\alpha M_{\alpha'}}} \cdot e^{-i\vec{q}(\vec{R}_n - \vec{R}_{n'})} \right] C_{\alpha' i'} = \left[\omega(\vec{q})\right]^2 C_{\alpha i}(\vec{q})$$

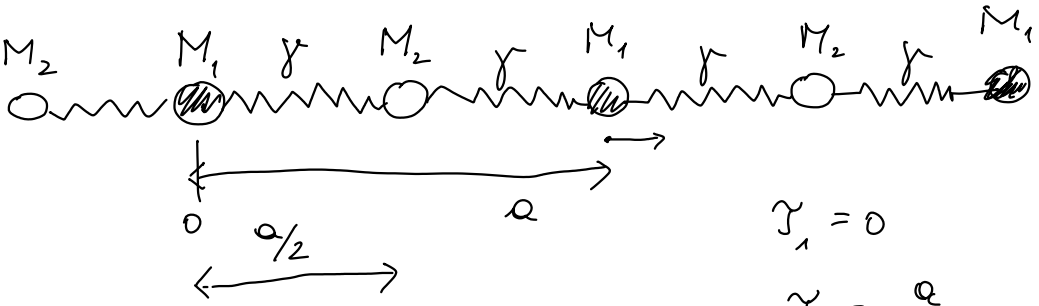
$$:= D_{\alpha i}^{\alpha' i'}(\vec{q}) \quad \text{... dynamical matrix}$$

$\vec{q}$: wave vector $\in 1^{st}$ BZ

$\omega_\lambda(\vec{q})$

λ: phonon branch $\lambda = 1, 2, \ldots$ dof

Example 1 — Diatomic 1D-chain of atoms



$d = 1$

$r = 2$

$\Downarrow$

2 phonon branches

$\gamma_1 = 0$

$\gamma_2 = \frac{a}{2}$

$$D_{\alpha}^{\alpha'}(\vec{q}) = e^{-iq\cdot(\gamma_\alpha - \gamma_{\alpha'})} \cdot \sum_{n'} \frac{\Phi_{\alpha}^{\alpha'}(na - n'a)}{\sqrt{M_\alpha M_{\alpha'}}} e^{-iq(na-n'a)}$$

assume only forces due to nearest neighbor atoms

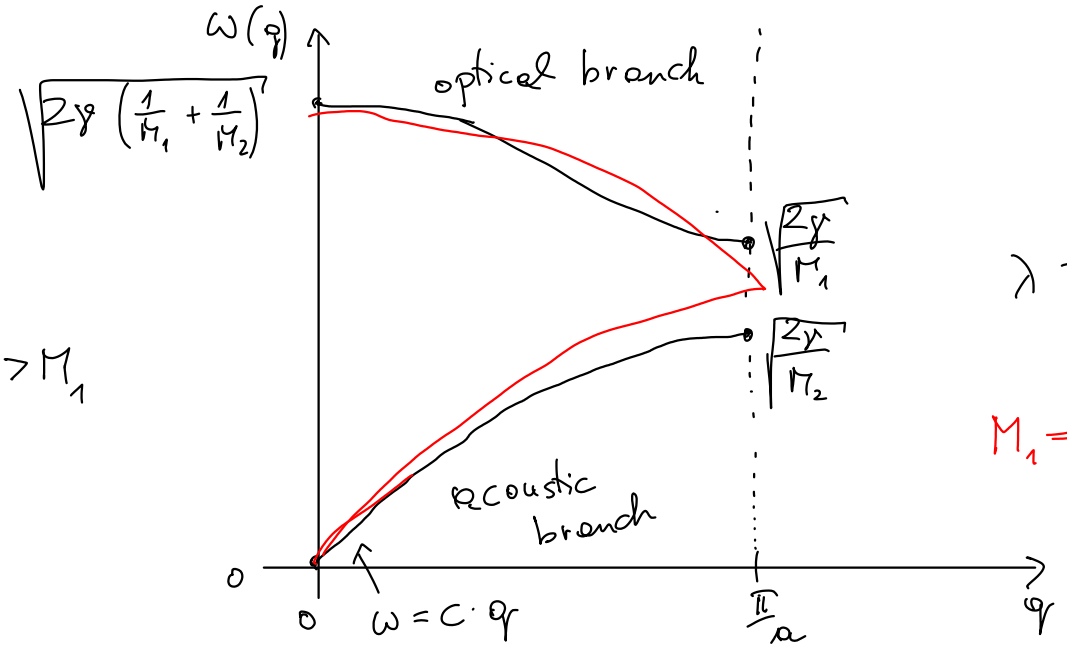
$$D_1^1(q) = 1 \cdot \frac{2\gamma}{M_1} \qquad D_2^2(\vec{q}) = 1 \cdot \frac{2\gamma}{M_2}$$

$$D_1^2(q) = e^{-iq\cdot(-\frac{a}{2})} \cdot \left[\frac{\overbrace{\Phi_1^2(-1)}^{-\gamma}}{\sqrt{M_1 M_2}} \cdot e^{-iqa} + \frac{\overbrace{\Phi_1^2(0)}^{-\gamma}}{\sqrt{M_1 M_2}} \cdot 1 \right] =$$

$$= -\frac{\gamma}{\sqrt{M_1 M_2}} \underbrace{\left[e^{-iq\frac{a}{2}} + e^{iq\frac{a}{2}} \right]}_{2\cos(q\cdot\frac{a}{2})}$$

$$\hat{D}(\vec{q}) = \begin{pmatrix} \frac{2\gamma}{M_1} & -\frac{2\gamma}{\sqrt{M_1 M_2}} \cdot \cos(q\frac{a}{2}) \\ -\frac{2\gamma}{\sqrt{M_1 M_2}} \cos(q\frac{a}{2}) & \frac{2\gamma}{M_2} \end{pmatrix} \qquad \hat{D}(\vec{q}) \cdot \vec{c} = \omega^2 \cdot \vec{c}$$

$$\omega^2_{1,2} = \gamma\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \gamma\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2\left(q\frac{a}{2}\right)}{M_1 M_2}}$$



$M_2 > M_1$

$q \to 0$

$\lambda = \frac{2\pi}{q}$

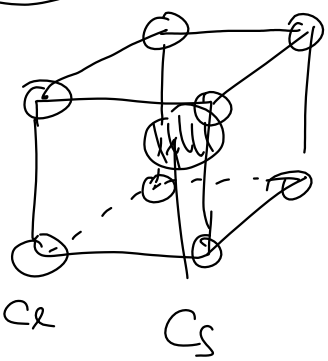
$M_1 = M_2$

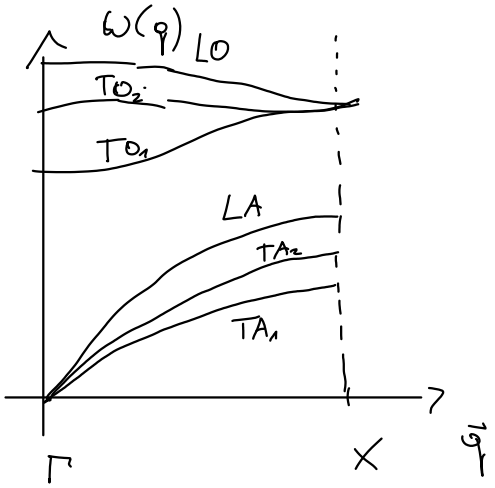
Example (2): Lattice dynamics in CsCl

$r = 2$ atoms/cell

$d = 3$

$r \cdot d = 6$ phonon branches



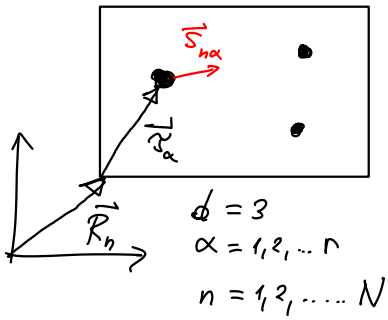


Example (3) graphene

4.2 Second Quantization and Phonons

Hamilton function $H = H(s_{n\alpha i}, \dot{s}_{n\alpha i})$

$$H(s_{n\alpha i}, \dot{s}_{n\alpha i}) = \overbrace{\sum_{n\alpha j} \frac{M_\alpha}{2} \dot{s}^2_{n\alpha i}}^{T} + \overbrace{\frac{1}{2} \sum_{n\alpha i} \sum_{n'\alpha' j'} \Phi^{n'\alpha' i'}_{n\alpha i} s_{n\alpha i} s_{n'\alpha' i'}}^{U}$$



GOAL: decouple the $d \times r \times N$ degrees of freedom and decompose the vibrations into $d \times r \times N$ independent (collective) harmonic oscillators by making use of the eigenmodes.

$$\hat{H} = \sum \hbar \omega_{j\vec{q}} \left(\hat{a}^\dagger_{j\vec{q}} \hat{a}_{j\vec{q}} + \frac{1}{2} \right)$$

$j | \vec{q}$ ← wave vector $\in$ BZ

↗ phonon branch

$$\left[\hat{a}_{j'\vec{q}'}, \hat{a}_{j\vec{q}} \right] = 0 \qquad \left[\hat{a}_{j'\vec{q}'}, \hat{a}^\dagger_{j\vec{q}} \right] = \delta_{jj'} \delta_{\vec{q}\vec{q}'}$$

$$\left[\hat{a}^\dagger_{j'\vec{q}'}, \hat{a}^\dagger_{j\vec{q}} \right] = 0$$

$\Rightarrow$ Louie / Cohen book p. 71–76

or Sormann / Schrödinger p. 257–259

Specific case: $S_{n\alpha i}(t) = \frac{1}{\sqrt{M_\alpha}} C_{\alpha i}^{(j)}(\vec{q}) \cdot e^{i\vec{q}\vec{R}_n} \cdot e^{-i\omega_j(\vec{q})\cdot t}$

most general displacement:

$$S_{n\alpha i}(t) = \frac{1}{\sqrt{M_\alpha}} \sum_{j\vec{q}} \underbrace{\beta_{j\vec{q}} \cdot e^{-i\omega_j(\vec{q})t}} \cdot C_{\alpha i}^{(j)}(\vec{q})\, e^{i\vec{q}\cdot\vec{R}_n}$$

$S \in \mathbb{R}$
$S^* = S$

$\frac{1}{\sqrt{N}} \cdot Q_j(\vec{q},t)$ .... collective (phonon) displacement vectors for phonon branch j at wave vector $\vec{q}$

To Do: make a canonical transformation from $S_{n\alpha i}(t) \longrightarrow Q_j(\vec{q},t)$

•) from $S_{n\alpha i} = S_{n\alpha i}^*$ $\Longrightarrow$

$$\boxed{\begin{aligned} C_{\alpha i}^{*(j)}(\vec{q}) &= C_{\alpha i}^{(j)}(-\vec{q}) \\ Q_j^*(\vec{q},t) &= Q_j(-\vec{q},t) \end{aligned}}$$

•) insert - $S_{n\alpha i}(t) = \frac{1}{\sqrt{NM_\alpha}} \sum_{j\vec{q}} Q_j(\vec{q},t)\, C_{\alpha i}^{(j)}(\vec{q})\, e^{i\vec{q}\cdot\vec{R}_n}$ $\Big/ \frac{d}{dt}$

$$\dot{S}_{n\alpha i}(t) = \frac{1}{\sqrt{NM_\alpha}} \sum_{j\vec{q}} \dot{Q}_j(\vec{q},t)\, C_{\alpha i}^{(j)}(\vec{q})\, e^{i\vec{q}\cdot\vec{R}_n}$$

into $H(S_{n\alpha i}, \dot{S}_{n\alpha i}) = T + U$

$$T = \sum_{n\alpha i} \frac{M_\alpha}{2} \dot{S}^2_{n\alpha i} =$$

$$= \sum_{n\alpha i} \frac{M_\alpha}{2} \frac{1}{NM_\alpha} \sum_{j\vec{q}} \sum_{j'\vec{q}'} \dot{Q}_{j\vec{q}} \dot{Q}_{j'\vec{q}'} C^{j\vec{q}}_{\alpha i} C^{j'\vec{q}'}_{\alpha i} e^{i(\vec{q}+\vec{q}')\vec{R}_n}$$

$\vec{q} = -\vec{q}$

$$= \frac{1}{2N} \sum_{j\vec{q}} \sum_{j'\vec{q}'} \dot{Q}^*_{j\vec{q}} \dot{Q}_{j'\vec{q}'} \underbrace{\sum_{\alpha i} C^{*j\vec{q}}_{\alpha i} C^{j'\vec{q}'}_{\alpha i}}_{\delta_{jj'}} \underbrace{\sum_n e^{-i(\vec{q}-\vec{q}')\vec{R}_n}}_{N \cdot \delta_{\vec{q},\vec{q}'}}$$

$$\boxed{T(\dot{Q}_{j\vec{q}}) = \frac{1}{2} \sum_{j\vec{q}} \dot{Q}^*_{j\vec{q}} \dot{Q}_{j\vec{q}}}$$

$$U = \frac{1}{2} \sum_{n\alpha i} \sum_{n'\alpha' i'} \Phi^{n'\alpha' i'}_{n\alpha i} \frac{1}{N} \frac{1}{\sqrt{M_\alpha M_{\alpha'}}} \sum_{j\vec{q}} \sum_{j'\vec{q}'} Q_{j\vec{q}} Q_{j'\vec{q}'} C^{j\vec{q}}_{\alpha i} C^{j'\vec{q}'}_{\alpha' i'} e^{i\vec{q}\vec{R}_n} \cdot e^{i\vec{q}'\vec{R}_{n'}}$$

$$e^{i\vec{q}\vec{R}_n} \cdot e^{i\vec{q}'\vec{R}_{n'}} = e^{i(\vec{q}+\vec{q}')\cdot\vec{R}_n} \cdot e^{i\vec{q}'(\underbrace{\vec{R}_{n'} - \vec{R}_n}_{\vec{R}_\nu})}$$

$$\Phi^{\alpha' i'}_{\alpha i}(n - n')$$

$$n - n' = \nu$$

$$\sum_n e^{i(\vec{q}+\vec{q}')\vec{R}_n} = N \cdot \delta_{\vec{q}, -\vec{q}'}$$

$$U = \frac{1}{2} \sum_{jj'\vec{q}} Q^*_{j\vec{q}} Q_{j'\vec{q}} \sum_{\alpha i} C^{*j\vec{q}}_{\alpha i} \sum_{\alpha' i'} \underbrace{\left[\sum_\nu \frac{\Phi^{\alpha' i'}_{\alpha i}(\vec{R}_\nu)}{\sqrt{M_\alpha M_{\alpha'}}} \cdot e^{i\vec{q}\vec{R}_\nu} \right]}_{D^{\alpha' i'}_{\alpha i}(\vec{q})} \cdot C^{j'\vec{q}}_{\alpha' i'}$$

$$\sum_{\alpha i} C^{*j\vec{q}}_{\alpha i} \cdot C^{j'\vec{q}}_{\alpha i} = \delta_{jj'}$$

$$= \omega^2_{j'\vec{q}} \cdot C^{j'\vec{q}}_{\alpha i}$$

$$\boxed{U = \frac{1}{2} \sum_{j\vec{q}} Q^*_{j\vec{q}} Q_{j\vec{q}} \cdot \omega^2_{j\vec{q}}}$$

$$\mathcal{L}(Q, \dot{Q}) = T - U$$

$$= \sum_{j\vec{q}} \left[\frac{1}{2} \dot{Q}^{*}_{j\vec{q}} \dot{Q}_{j\vec{q}} - \frac{1}{2} \omega^2_{j\vec{q}} Q^{*}_{j\vec{q}} Q_{j\vec{q}} \right]$$

$\Rightarrow$ decoupling accomplished!

•) Canonical Transformation

$$P_{j\vec{q}} = \frac{\partial \mathcal{L}}{\partial \dot{Q}^{*}_{j\vec{q}}} = \dot{Q}_{j\vec{q}}$$

$$H(Q_{j\vec{q}}, P_{j\vec{q}}) = \frac{1}{2} \sum_{j\vec{q}} \left[P^{*}_{j\vec{q}} P_{j\vec{q}} + \omega^2_{j\vec{q}} Q^{*}_{j\vec{q}} Q_{j\vec{q}} \right]$$

$$\dot{P}_{j\vec{q}} = - \frac{\partial H}{\partial Q^{*}_{j\vec{q}}} \Rightarrow \boxed{\ddot{Q}_{j\vec{q}} = -\omega^2_{j\vec{q}} Q_{j\vec{q}}}$$

$\Rightarrow$ independent harmonic oscillators

$\Rightarrow$ Quantization: replace classical variables by operators

$$\left[\hat{Q}_{j\vec{q}}, \hat{P}_{j'\vec{q}'} \right] = i\hbar \, \delta_{\vec{q},\vec{q}'} \, \delta_{jj'}$$

Creation operator: $\hat{a}^{\dagger}_{j\vec{q}} = \frac{1}{\sqrt{2\hbar\omega_{j\vec{q}}}} \cdot \left[\omega_{j\vec{q}} \hat{Q}^{\dagger}_{j\vec{q}} - i \hat{P}_{j\vec{q}} \right]$

annihilation operator: $\hat{a}_{j\vec{q}} = \frac{1}{\sqrt{2\hbar\omega_{j\vec{q}}}} \cdot \left[\omega_{j\vec{q}} \hat{Q}_{j\vec{q}} + i \hat{P}^{\dagger}_{j\vec{q}} \right]$

$$\boxed{\hat{H} = \sum_{j\vec{q}} \hbar\omega_{j\vec{q}} \left(\underbrace{\hat{a}^{\dagger}_{j\vec{q}} \hat{a}_{j\vec{q}}}_{\hat{n}} + \frac{1}{2} \right)}$$

Properties of the ladder operators $\hat{a}_i^\dagger$, $\hat{a}$

(i) $[\hat{a}_{j\vec{q}}, \hat{a}^\dagger_{j'\vec{q}'}] = \delta_{jj'}\,\delta_{\vec{q}\vec{q}'}$

(ii) $[\hat{a}_{j\vec{q}}, \hat{a}_{j'\vec{q}'}] = [\hat{a}^\dagger_{j\vec{q}}, \hat{a}^\dagger_{j'\vec{q}'}] = 0$

(iii) $\hat{a}_{j\vec{q}}|0\rangle = 0$ $\quad$ $\hat{a}$ ... annihilation operators

$|0\rangle$ ↑ vacuum state

(iv) $\hat{a}^\dagger_{j\vec{q}}|0\rangle = |1_{j\vec{q}}\rangle$ $\quad$ $\hat{a}^\dagger_{j\vec{q}}$ ... creates a phonon in state $(j\vec{q})$

(v) $|n_{j\vec{q}}\rangle = \frac{1}{\sqrt{n_{j\vec{q}}!}}\left(\hat{a}^\dagger\right)^{n_{j\vec{q}}}|0\rangle$

(vi) $|n_{j_1\vec{q}_1}\, n_{j_2\vec{q}_2} \ldots\rangle = \frac{1}{\sqrt{n_{j_1\vec{q}_1}!\; n_{j_2\vec{q}_2}! \ldots}}\left(\hat{a}^\dagger_{j_1\vec{q}_1}\right)^{n_{j_1\vec{q}_1}}\left(\hat{a}^\dagger_{j_2\vec{q}_2}\right)^{n_{j_2\vec{q}_2}}\ldots|0\rangle$

(vii) $\hat{a}_{j\vec{q}} + \hat{a}^\dagger_{j,-\vec{q}} = \sqrt{\frac{2\omega_{j\vec{q}}}{\hbar}}\cdot\hat{Q}_{j\vec{q}}$

$$\Rightarrow \boxed{\hat{S}_{n\alpha_i}(t) = \sum_{j\vec{q}}\sqrt{\frac{\hbar}{NM_i 2\omega_{j\vec{q}}}}\, c^{j\vec{q}}_{\alpha_i}\left[\hat{a}_{j\vec{q}} + \hat{a}^\dagger_{j,-\vec{q}}\right]e^{i\vec{q}\vec{R}_n}}$$

$$\boxed{\hat{H} = \sum_{j\vec{q}}\hbar\omega_{j\vec{q}}\left(\underbrace{\hat{a}^\dagger_{j\vec{q}}\,\hat{a}_{j\vec{q}}}_{\hat{n}_{j\vec{q}}} + \frac{1}{2}\right)}$$

4.3 VIBRATIONAL ENERGY / HEAT CAPACITY

Total Hamiltonian $\hat{H}_T$

$$\hat{H}_T = E_0 + \underbrace{\sum_{j\vec{q}} \hbar\omega_{j\vec{q}} \left(\hat{n}_{j\vec{q}} + \frac{1}{2} \right)}_{\text{phonons (bosons)}} + \underbrace{\sum_{j}^{\text{bands BZ}} \sum_{\vec{k}} \hat{n}_{j\vec{k}} E_j(\vec{k})}_{\text{electronic excitations (Fermions)}} +$$

E_0: ground state energy

$$+ \text{electron-electron-interactions}$$
$$+ \text{phonon-phonon-interactions}$$
$$+ \text{electron-phonon-interaction}$$
$$+ \dots$$

Fermions:

$$\langle \hat{n}_{j\vec{k}} \rangle (T) = \frac{1}{\exp\left\{ \frac{E_j(\vec{k}) - \mu(T)}{k_B T} \right\} + 1}$$

chemical potential $\sum_{j\vec{k}} n_{j\vec{k}} \overset{!}{=} N \Rightarrow \mu$

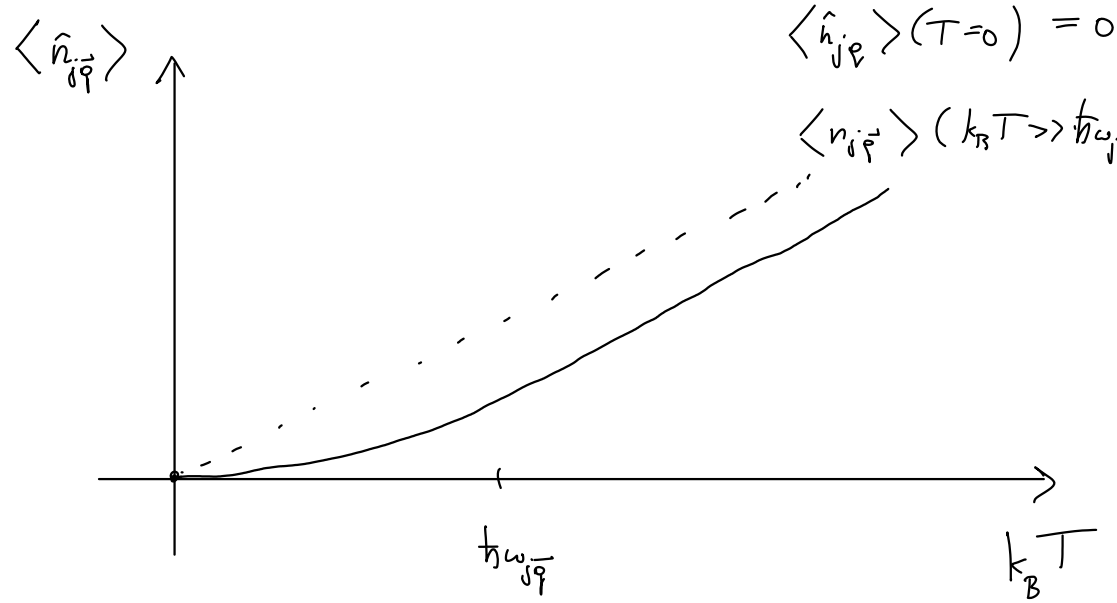
Bosons

$$\langle \hat{n}_{j\vec{q}} \rangle (T) = \frac{1}{\exp\left\{ \frac{\hbar\omega_{j\vec{q}}}{k_B T} \right\} - 1}$$

Phonon energy (vibrational energy)

$$U_{vib}(T) = \sum_{j\vec{q}} \hbar\omega_{j\vec{q}} \left[\langle \hat{n}_{j\vec{q}} \rangle (T) + \frac{1}{2} \right]$$

$$\sum_{j\vec{q}} 1 = 3 \cdot r \cdot N$$



$\langle \hat{n}_{j\vec{q}} \rangle (T=0) = 0$

$\langle n_{j\vec{q}} \rangle (k_B T \gg \hbar\omega_{j\vec{q}}) \propto \frac{k_B T}{\hbar\omega} + \dots$

$T = 0K$ $\quad U(0) = \frac{1}{2} \sum_{j\vec{q}} \hbar\omega_{j\vec{q}}$ ... "zero-point energy"

$k_B T \gg \hbar\omega_{j\vec{q}}$ $\quad \underline{U(T)} = \sum_{j\vec{q}} \hbar\omega_{j\vec{q}} \left[\frac{k_B T}{\hbar\omega_{j\vec{q}}} + \frac{1}{2} \right] =$

$= U(0) + \underline{k_B T \cdot 3 \cdot r \cdot N}$

$\Rightarrow$ classical limit ($\hat{=}$ Dulong-Petit law)

$$C_V(T) = \left(\frac{\partial U}{\partial T} \right)_V = 3 \cdot r \underbrace{N_A \cdot k_B}_{= R} = \text{const.}$$

4.4 PHONON DENSITY OF STATES

Schematically:

$$\sum_{j\vec{q}} f(\omega_{j\vec{q}}(\vec{q})) \to \frac{V}{(2\pi)^3}\sum_j \int d^3q\, f(\omega_{j\vec{q}}(\vec{q})) \to \int f(\omega)\cdot D(\omega)\,d\omega$$

$D(\omega)$: total phonon density of states

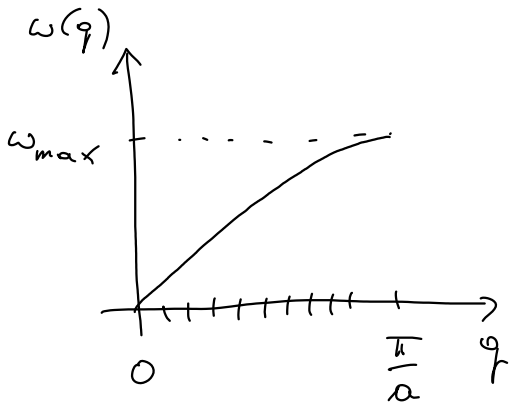
total DOS: $D(\omega) := \sum_{j,\vec{q}} \delta(\omega - \omega_{j\vec{q}}) = \sum_j \underbrace{D_j(\omega)}$

$D_j(\omega)$: DOS for phonon branch j

$D(\omega)\,d\omega \triangleq$ number of states with frequencies in the interval $[\omega, \omega + d\omega]$

Example: 1D monoatomic chain of atoms

$$\omega(q) = \sqrt{\frac{4\gamma}{M}}\,\sin\left(\frac{qa}{2}\right), \qquad \omega_{max} = \sqrt{\frac{4\gamma}{M}}$$



$$D(\omega)\,d\omega = \underbrace{W(q)}_{2\cdot\frac{L}{2\pi}}\,dq$$

$$L = N\cdot a$$

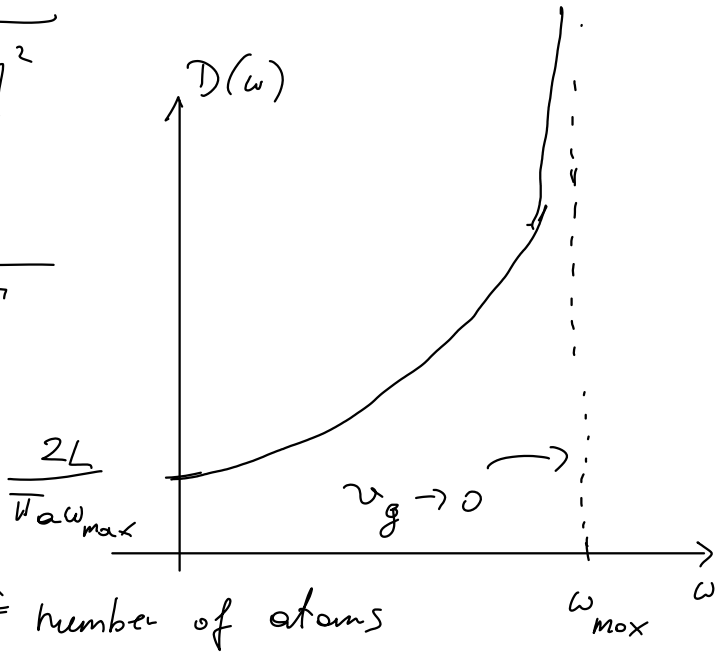
$$D(\omega) = \frac{L}{\pi}\cdot\frac{dq}{d\omega} = \frac{L}{\pi}\cdot\frac{1}{\frac{d\omega}{dq}}$$

$\frac{d\omega}{dq} \triangleq v_g$ ... group velocity

$$v_g = \frac{d\omega}{dq} = \omega_{max}\cdot\frac{a}{2}\cos\left(\frac{qa}{2}\right) = \frac{a}{2}\,\omega_{max}\sqrt{1-\sin^2\left(\frac{qa}{2}\right)} =$$

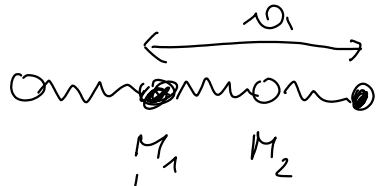
$$\frac{d\omega}{dq} = \frac{a}{2}\sqrt{\omega_{max}^2 - \underbrace{\omega_{max}^2 \cdot \sin^2\left(\frac{qa}{2}\right)}_{[\omega(q)]^2}}$$

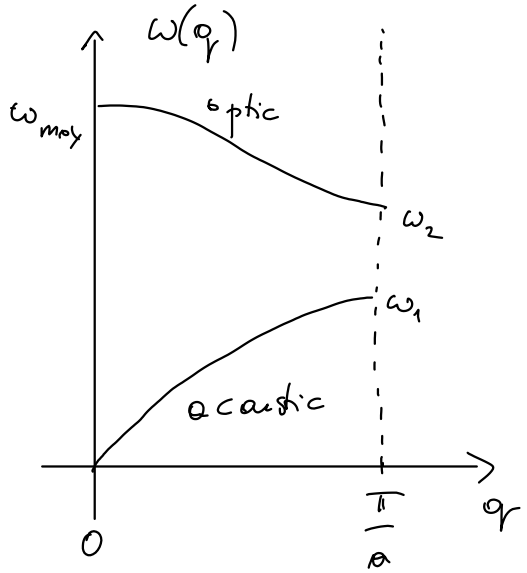
$$D(\omega) = \frac{2L}{\pi a \sqrt{\omega_{max}^2 - \omega^2}}$$



Excercise: $\int_0^{\omega_{max}} D(\omega)\,d\omega = \ldots = \frac{L}{a} \hat{=}$ number of atoms

Example II 1D diatomic chain of atoms





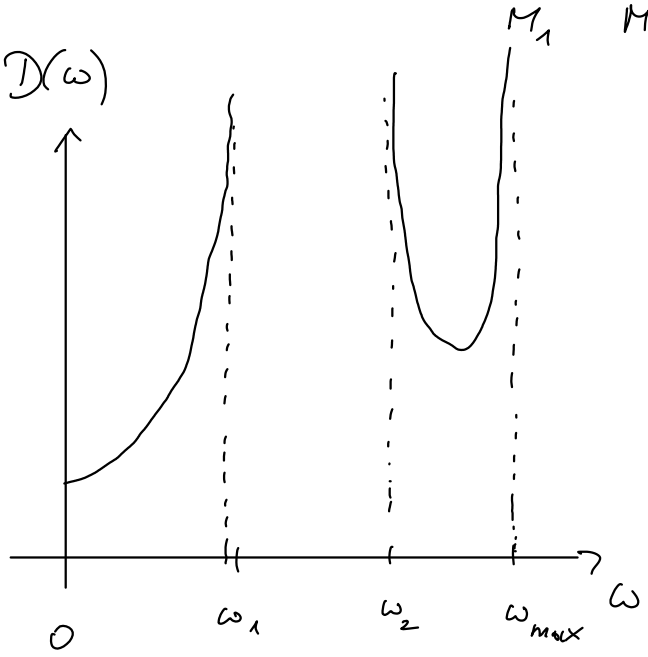
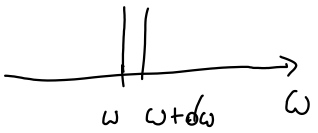


Fig 4.11, p. 81

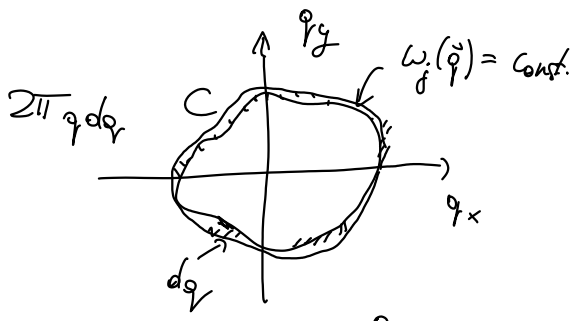
4.4.1 THE DEBYE APPROXIMATION

Generalize DOS from 1D → 2D → 3D

1D $$D_j(\omega) = 2 \cdot \frac{L}{2\pi} \cdot \frac{1}{\frac{d\omega_j}{dq}}$$

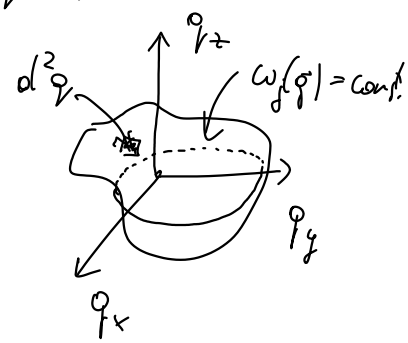


2D $$D_j(\omega) = \frac{A}{(2\pi)^2} \oint_C \frac{dq}{\left|\frac{d\omega_j}{d\vec{q}}\right|}$$



3D $$D_j(\omega) = \frac{V}{(2\pi)^3} \oint_S \frac{d^2q}{\left|\frac{d\omega_j}{d\vec{q}}\right|}$$

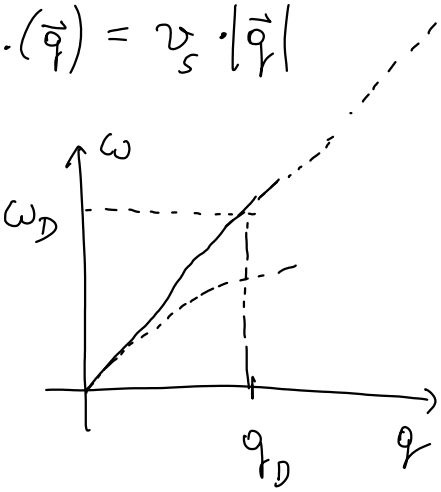
$4\pi q^2 dq$



Debye-Model: Assume a constant and isotropic sound velocity v_s: $\omega_j(\vec{q}) = v_s \cdot |\vec{q}|$

$$\left|\frac{d\omega_j}{d\vec{q}}\right| = \left|v_s \cdot \frac{\vec{q}}{q}\right| = v_s$$

Debye-frequency $\rightarrow \omega_D$



$$D_j(\omega) = \frac{V}{(2\pi)^3} \cdot \frac{4\pi q^2}{v_s} = \frac{V}{2\pi^2} \frac{\omega^2}{v_s^3}$$

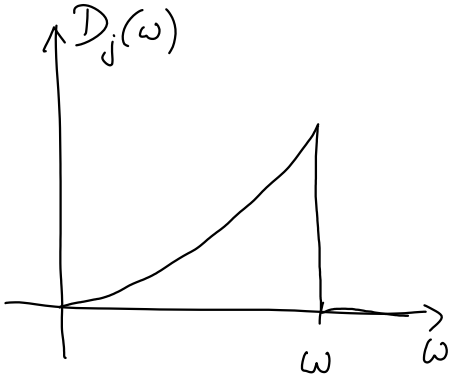
$\omega = v_s \cdot q$ ↑ Debye wave vector

$$\int_0^{\omega_D} D_j(\omega)\,d\omega \stackrel{!}{=} N \Rightarrow \frac{V}{2\pi^2} \cdot \frac{\omega_D^3}{3 v_s^3}$$

↑

$$\omega_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3} \cdot v_s \qquad q_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3}$$

$$D_j(\omega) = 3N \frac{\omega^2}{\omega_D^3}$$



Vibrational energy and heat capacity in Debye model:

$$U_{vib} = \sum_{j\vec{q}} \hbar\omega_{j\vec{q}} \left[\frac{1}{\exp\left[\frac{\hbar\omega_{j\vec{q}}}{k_B T}\right] - 1} + \frac{1}{2} \right] = U(T) + U_0$$

$$U_0 = \frac{1}{2} \sum_{j\vec{q}} \hbar\omega_{j\vec{q}} = \frac{1}{2} \underbrace{\sum_j}_{=3} \int_0^{\omega_D} D(\omega)\, \hbar\omega\, d\omega =$$

$$= \frac{3\hbar}{2} \frac{3N}{\omega_D^3} \int_0^{\omega_D} \omega^3 d\omega = \frac{9N}{2} \hbar \frac{\omega_D^4}{4\omega_D^3} = \frac{9N}{8} \hbar\omega_D$$

$$U(T) = \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^3 d\omega}{\exp\left[\frac{\hbar\omega}{k_B T}\right] - 1} =$$

$$x = \frac{\hbar\omega}{k_B T} \qquad dx = \frac{\hbar\, d\omega}{k_B T}$$

$$x_D = \frac{\hbar\omega_D}{k_B T} = \frac{T_D}{T} \quad \text{... Debye temperature}$$

$$U(T) = \frac{9N\hbar}{\omega_D^3} \cdot \frac{(k_B T)^4}{\hbar^4} \int_0^{x_D} \frac{x^3 dx}{e^x - 1}$$

$$U(T) = 9N \frac{(k_B T)^4}{(\hbar\omega_D)^3} \int_0^{x_D} \frac{x^3 dx}{e^x - 1}$$

$$e^x = 1 + x + \dots$$

(i) high-temperature limit: $T >> T_D = \frac{\hbar\omega_D}{k_B} \Rightarrow x << 1$

$$U(T) = 9N \cdot \frac{(k_B T)^4}{(\hbar\omega_D)^3} \cdot \underbrace{\int_0^{x_D} \frac{x^3}{x} dx}_{\frac{x_D^3}{3}} = 3N \frac{(k_B T)^4}{(\hbar\omega_D)^3} \cdot \frac{(\hbar\omega_D)^3}{(k_B T)^3} = 3N k_B T$$

$$C_V = \frac{\partial U}{\partial T} = 3N k_B \quad \ldots \text{ Dulong-Petit law}$$

(ii) low-T limit $T << T_D \Rightarrow x_D \longrightarrow \infty$

$$U(T) = \frac{3\pi^4 N}{5} \cdot \frac{(k_B T)^4}{(\hbar\omega_D)^3}$$

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

$$C_V(T) = \frac{\partial U}{\partial T} = \ldots = \frac{12\pi^4}{5} N k_B \cdot \left(\frac{T}{T_D}\right)^3 \sim T^3$$

T^3: phonon contribution

electronic DOS at E_F

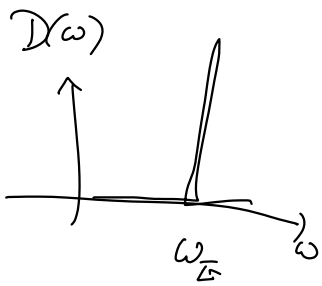
$$C_V(T) = \underbrace{\alpha \cdot T}_{\text{electronic contribution}} + \underbrace{\gamma \cdot T^3}_{\text{phonon contribution}}$$

relevant for metals

4.4.2 | THE EINSTEIN MODEL

Assumption: all phonon modes have the same frequency ω_E

$$\rightarrow D_J(\omega) = N \cdot \delta(\omega - \omega_E)$$



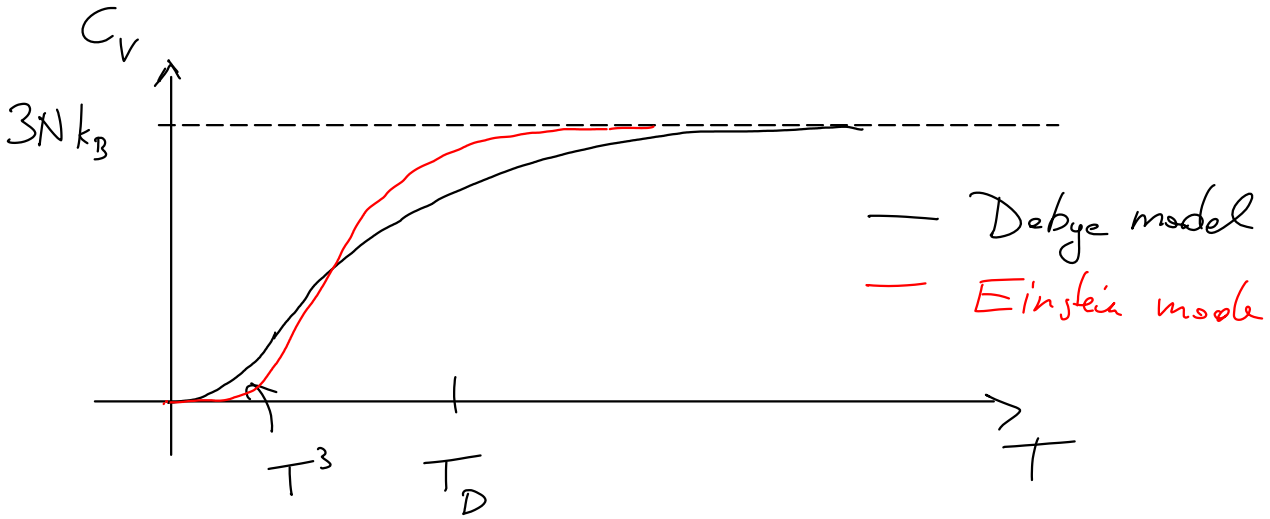
$$U(T) = 3Nk_B \frac{T_E}{\exp\left[\frac{T_E}{T}\right] - 1}$$

$$k_B T_E = \hbar\omega_E$$

$T \gg T_E$: $U(T) = \ldots = 3Nk_B T$

$T \ll T_E$: $U(T) = 3Nk_B T_E e^{-\frac{T_E}{T}}$

$e^{-\frac{1}{x}}$



EXERCISES I.27 I.28 I.30 I.31 I.32

5. ELECTRON DYNAMICS IN CRYSTALS

So far: electrons in a perfect, undisturbed crystal potential

now: behaviour of electrons under non-periodic perturbation

topics:
- Wannier functions and effective Hamiltonian
- Equation of motion for crystal electrons
- group velocity $\vec{v}$ and effective mass m^*
- Concept of Berry phase and Berry curvature

Time-dependant Schrödinger eq.

$$i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = \left[\hat{H}_0 + \hat{U}(\vec{r}) \right] \psi(\vec{r},t)$$

$\hat{H}_0$: perfect crystal Hamiltonian

$\hat{U}(\vec{r})$: static perturbation

•) $U(\vec{r})$ is slowly varying (compared atomic distances)

e.g.: uniform field $\vec{E}$ → $U(\vec{r}) = -e\vec{E}\cdot\vec{r}$

or magnetic fied $\vec{B}$ → $\vec{A} = \frac{1}{2}\vec{B}\times\vec{r}$

Problem: $U(\vec{r})$ becomes very large

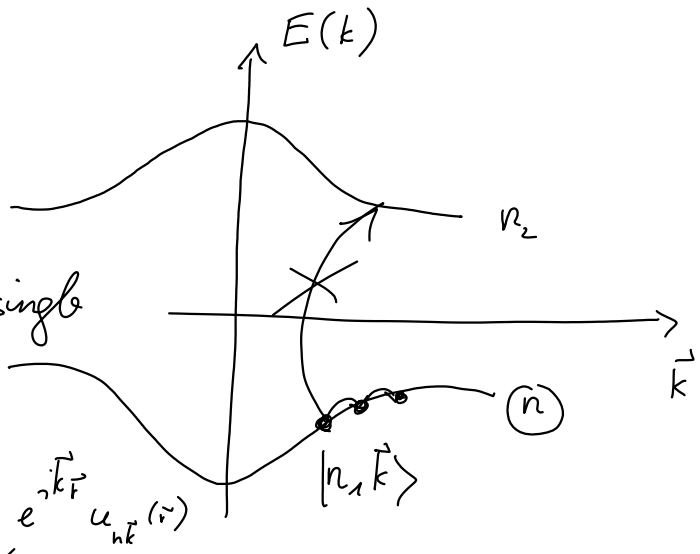
⇒ perturbation cannot be applied.

5.1 WANNIER FUNCTIONS and EFFECTIVE HAMILTONIAN

$U = U(\vec{r})$

$\Rightarrow$ adiabatic approximation

$\hat{=}$ electron stays within a single band.

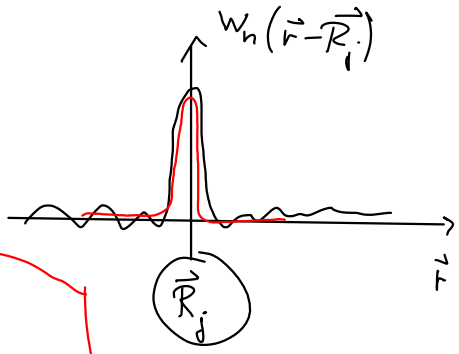


WANNIER FUNCTIONS w_n // $e^{i\vec{k}\vec{r}}\, u_{n\vec{k}}(\vec{r})$

$$w_n(\vec{r}-\vec{R}_j) = \frac{1}{\sqrt{N}} \sum_{\vec{k}}^{BZ} e^{-i\vec{k}\vec{R}_j}\, \phi_{n\vec{k}}(\vec{r})$$

↑ Wannier function at site $\vec{R}_j$

↑ Bloch state



maximally localized Wannier functions $e^{i\partial_{\vec{k}}}$

Marzari, Vanderbilt, Phys. Rev. B 56, 12847 (1997).

Rev. Mod. Phys.

Properties of Wannier functions:

(i) $$\phi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{k}\vec{R}_j}\, w_n(\vec{r}-\vec{R}_j)$$

(ii) $$\langle w_{n'}(\vec{R}_i) \,|\, w_n(\vec{R}_j) \rangle = \delta_{nn'}\, \delta_{ij}$$

(iii) $w_n(\vec{r}-\vec{R}_j)$ is localized around $\vec{R}_j$

(iv) $w_n(\vec{r}-\vec{R}_j)$ form a complete set of basis functions

5.2 Electron dynamics in the effective Hamiltonian approach

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = [\hat{H}_0 + \hat{U}]\, |\psi(t)\rangle$$

state vector $|\psi(t)\rangle$ can be expanded in any complete set of basis functions:

$$\hat{1} = \underbrace{\sum_{\vec{r}} |\vec{r}\rangle\langle\vec{r}|}_{\text{real space basis}} = \underbrace{\sum_{n\vec{k}} |\phi_{n\vec{k}}\rangle\langle\phi_{n\vec{k}}|}_{\text{Bloch basis}} = \underbrace{\sum_{n\vec{R}_j} |w_n(\vec{R}_j)\rangle\langle w_n(\vec{R}_j)|}_{\text{Wannier basis}}$$

$$|\psi(t)\rangle = \sum_{\vec{r}} |\vec{r}\rangle \underbrace{\langle\vec{r}|\psi(t)\rangle}_{\psi(\vec{r},t)} = \sum_{\vec{r}} \psi(\vec{r},t)\,|\vec{r}\rangle =$$

$$\overset{\text{or}}{=} \sum_{n\vec{k}} |\phi_{n\vec{k}}\rangle \underbrace{\langle\phi_{n\vec{k}}|\psi(t)\rangle}_{\psi_n(\vec{k},t)} = \sum_{n\vec{k}} \psi_n(\vec{k},t)\,|\phi_{n\vec{k}}\rangle$$

$$|\psi(t)\rangle \overset{\text{or}}{=} \sum_{n\vec{R}_j} |w_n(\vec{R}_j)\rangle \underbrace{\langle w_n(\vec{R}_j)|\psi(t)\rangle}_{\psi_n(\vec{R}_j,t)} = \sum_{n\vec{R}_j} \psi_n(\vec{R}_j,t)\,|w_n(\vec{R}_j)\rangle$$

↑ envelope function which only depends on $\vec{R}_j$.

Internal structure (varies on an atomic scale) is given by Wannier function $w_n(\vec{r}-\vec{R}_j)$

•) $U(\vec{r})$ is slowly varying

$\Rightarrow$ electron stays within a single band

$$|\psi(t)\rangle \simeq \sum_j \psi_n(\vec{R}_j, t) \cdot |w_n(\vec{R}_j)\rangle \qquad / \langle \vec{r}|$$

$$\psi(\vec{r}, t) = \sum_j \psi_n(\vec{R}_j, t) \cdot w_n(\vec{r} - \vec{R}_j)$$

Next goal: Define quantum operators in Wannier representation

Reminder:

$$\hat{\vec{r}}\,|\vec{r}\rangle = \vec{r}\,|\vec{r}\rangle$$

$$\hat{\vec{p}}\,|\vec{p}\rangle = \vec{p}\,|\vec{p}\rangle$$

$$[r_i, p_j] = i\hbar\,\delta_{ij}$$

$$\hat{\vec{p}} = -i\hbar \frac{\partial}{\partial \vec{r}}$$

$$\hat{\vec{r}} = i\hbar \frac{\partial}{\partial \vec{p}}$$

Define operators $\hat{\vec{R}}$ and $\hat{\vec{k}}$ in analogous manner:

$$\hat{\vec{R}}\,|w_n(\vec{R}_j)\rangle = \vec{R}_j\,|w_n(\vec{R}_j)\rangle$$

$$\hat{\vec{k}}\,|\phi_{n\vec{k}}\rangle = \vec{k}\,|\phi_{n\vec{k}}\rangle$$

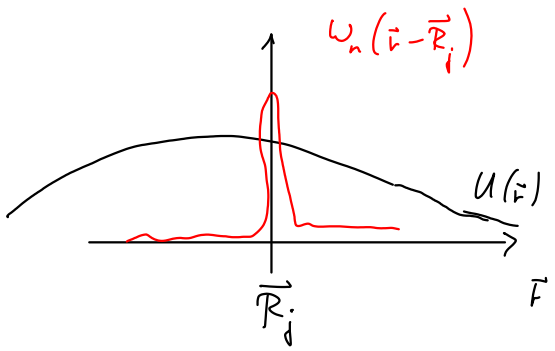
$$[\vec{R}, \vec{k}] = i \qquad \boxed{[\hat{R}_\ell, \hat{k}_m] = i\,\delta_{\ell m}}$$

$$\boxed{\hat{\vec{R}} = i \frac{\partial}{\partial \vec{k}}} \quad \text{and} \quad \boxed{\vec{k} = -i \frac{\partial}{\partial \vec{R}_j}}$$

$$\hat{U}(\vec{r})\,|w(\vec{R}_j)\rangle = \sum_{\vec{r}} U(\hat{\vec{r}})\,|\vec{r}\rangle\langle\vec{r}|\,w(\vec{R}_j)\rangle$$

$$\hat{\mathbb{1}} = \sum_{\vec{r}} |\vec{r}\rangle\langle\vec{r}|$$

$\langle w(\vec{r}-\vec{R}_j)$



$$\boxed{\hat{U}(\vec{r})\,|w(\vec{R}_j)\rangle \simeq U(\vec{R}_j)\,|w(\vec{R}_j)\rangle}$$

$/\langle w(\vec{R})|$

a) make use of single-band approximation in $i\hbar\frac{\partial}{\partial t}|\psi\rangle = (\hat{H}_0 + \hat{U})|\psi\rangle$

$$i\hbar\frac{\partial}{\partial t}\underbrace{\langle w(\vec{R})|\,\psi(t)\rangle}_{\psi(\vec{R},t)} = \langle w(\vec{R})|\hat{H}_0|\psi(t)\rangle + \underbrace{\langle w(\vec{R})|\,\hat{U}\,|\psi(t)\rangle}_{U(\vec{R})\cdot\langle w(\vec{R})|}$$

$$\langle w(\vec{R})|\,\hat{H}_0\,|\psi(t)\rangle = \sum_{\vec{R}'}\langle w(\vec{R})|\,\hat{H}_0\,|w(\vec{R}')\rangle\underbrace{\langle w(\vec{R}')|\,\psi(t)\rangle}_{\psi(\vec{R}',t)} = E_n\left(-i\frac{\partial}{\partial\vec{R}}\right)$$

$$\hat{\mathbb{1}} \simeq \sum_{\vec{R}'}|w(\vec{R}')\rangle\langle w(\vec{R}')|$$

$$\boxed{\hat{H}_0 = E_n(\hat{\vec{k}})}$$

$$\langle w(\vec{R})|\,\hat{H}_0\,|w(\vec{R}')\rangle = \langle w(\vec{R})|\,E_n(\hat{\vec{k}})\,|w(\vec{R}')\rangle = E_n\left(-i\frac{\partial}{\partial\vec{R}}\right)\cdot\delta_{\vec{R},\vec{R}'}$$

(*) $\langle\vec{r}'|\,G(\hat{\vec{p}})\,|\vec{r}\rangle = G\left(-i\hbar\frac{\partial}{\partial\vec{r}}\right)\cdot\delta(\vec{r}-\vec{r}')$

$$\boxed{i\hbar\frac{\partial}{\partial t}\psi(\vec{R},t) = \underbrace{\left[E_n\left(-i\frac{\partial}{\partial\vec{R}}\right) + U(\vec{R})\right]}_{\hat{H}_{\text{eff}}}\psi(\vec{R},t)}$$

Effective Hamiltonian for wavepacket envelope function $\psi(R,t)$

(1) $\hat{H}_{eff} = E_n\left(-i\frac{\partial}{\partial \vec{R}}\right) + U(\vec{R})$ .... $\vec{R}$-representation

$\langle \phi_{nk} | \ldots$ (2) $\hat{H}_{eff} = E_n(\vec{k}) + U\left(i\frac{\partial}{\partial \vec{k}}\right)$ ... $\vec{k}$-representation

→ electron coordinate $\vec{r}$ has been eliminated

→ effects of crystal are incorporated into $E(\vec{k})$

→ electrons move in potential $U(\vec{R})$ but with a renormalized kinetic energy operator.

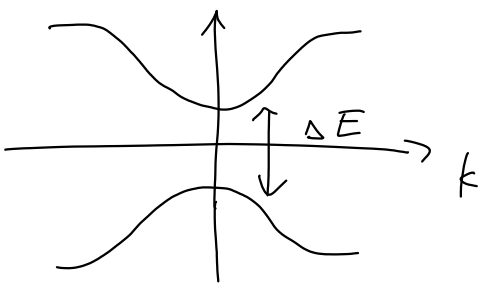
Validity of approximation ?

a.) $|\vec{\nabla} U| \cdot d \ll$ bandwidth of band $E(\vec{k})$

(d: interatomic distance)

b.) $U = U(t)$: $\hbar\omega \ll$ interband transition energies $= \Delta E$

a.) + b.)



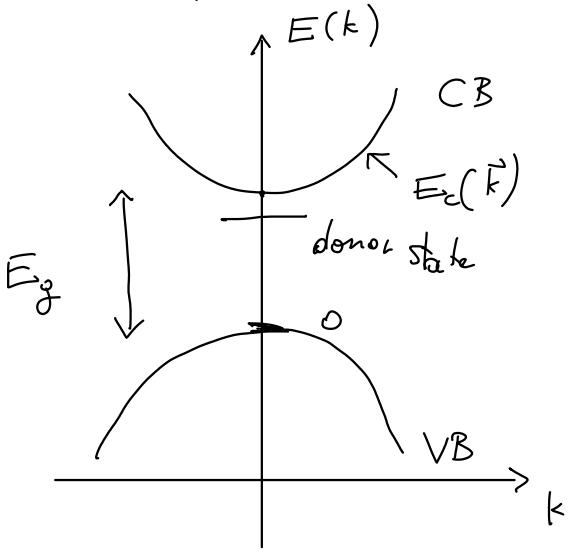
5.3 SHALLOW IMPURITY STATES IN SEMICONDUCTORS

→ application of effective Hamiltonian approach

→ example: substitutional impurity Si in GaAs crystal where Si replacing a Ga-site

Ga: $[Ar]\ 4s^2 4p^1$ Si: $[Ne]\ 3s^2 3p^2$

As: $[Ar]\ 4s^2 4p^3$



impurity wave function of donor state:

$$\Psi(\vec{r}) = \sum_{\vec{k}} \gamma(\vec{k})\ \phi_{c\vec{k}}(\vec{r})$$

$$= \sum_{\vec{R}} \gamma(\vec{R}) \cdot W_c(\vec{r}-\vec{R})$$

$$\hat{H}_{eff} = E_n\left(-i\frac{\partial}{\partial \vec{R}}\right) + U(\vec{R})$$

$$E_c(\vec{k}) = E_g + \frac{\hbar^2 k^2}{2m^*}$$

$$\left[E_c\left(-i\frac{\partial}{\partial \vec{R}}\right) - \frac{e^2}{4\pi\varepsilon\varepsilon_0}\frac{1}{R}\right]\gamma(\vec{R}) = E\,\gamma(\vec{R})$$

$$U(\vec{R}) = -\frac{e^2}{4\pi\varepsilon\varepsilon_0}\cdot\frac{1}{R}$$

↑ dielectric constant of GaAs

$$\left[E_g - \frac{\hbar^2}{2m^*}\vec{\nabla}_{\vec{R}} - \frac{e^2}{4\pi\varepsilon\varepsilon_0}\frac{1}{R}\right]\gamma(\vec{R}) = E\,\gamma(\vec{R})$$

$$E_n = E_g - \frac{R_{Rydberg}}{n^2} \Leftarrow \varepsilon \quad (\Leftarrow m^*)$$

↑ principal quantum number

5.4 MOTION IN EXTERNAL FIELDS

Here, we consider the motion of crystal electrons in a static, slowly-varying external electric field.

GOAL: derive effective equation of motion for the operators $\hat{\vec{R}}$ and $\hat{\vec{k}}$

REMINDER:

$$\hat{\vec{R}} \,|\, w_n(\vec{R}_j)\rangle = \vec{R}_j \,|\, w_n(\vec{R}_j)\rangle$$

$$\hat{\vec{k}} \,|\, \phi_{n\vec{k}}\rangle = \vec{k} \,|\, \phi_{n\vec{k}}\rangle$$

$$\hat{H}_{eff} = E_n(\hat{\vec{k}}) + U(\hat{\vec{R}}) \quad \dots \text{ effective Hamiltonian}$$

$E_n(\hat{\vec{k}})$: unperturbed crystal electrons; $U(\hat{\vec{R}})$: external perturbation

Heisenberg-picture:

$$\frac{d\hat{\vec{A}}}{dt} = \frac{\partial \hat{\vec{A}}}{\partial t} + \frac{1}{i\hbar}\left[\hat{\vec{A}}, \hat{H}\right]$$

$$i\hbar \frac{d\hat{\vec{R}}}{dt} = \left[\hat{\vec{R}}, H_{eff}\right] = \left[\hat{\vec{R}}, E_n(\hat{\vec{k}}) + \hat{U}(\hat{\vec{R}})\right] = \left[\hat{\vec{R}}, E_n(\hat{\vec{k}})\right]$$

Remember:

(i) $[\hat{x}, \hat{p}] = i\hbar \hat{1}$

(ii) $[\hat{x}, g(\hat{p})] = i\hbar \frac{\partial g}{\partial p}$

(iii) $[\hat{p}, f(\hat{x})] = -i\hbar \frac{\partial f}{\partial x}$

$[R_l, k_m] = i\delta_{lm}$

$$i\hbar \underbrace{\frac{d\hat{\vec{R}}}{dt}} = i \frac{\partial E_n(\vec{k})}{\partial \vec{k}} \qquad / : \hbar$$

$$\boxed{\hat{\vec{v}} := \frac{d\hat{\vec{R}}}{dt} = \frac{1}{\hbar} \cdot \frac{\partial E_n(\vec{k})}{\partial \vec{k}}}$$

$$i\hbar \frac{d\hat{\vec{k}}}{dt} = \left[\hat{\vec{k}}, \hat{H}_{eff}\right] = \left[\hat{\vec{k}}, E_n(\hat{\vec{k}}) + U(\hat{\vec{r}})\right] = \left[\hat{\vec{k}}, U(\hat{\vec{r}})\right]$$

$$= -i\frac{\partial U}{\partial \vec{r}} = -\vec{\nabla}_{\vec{r}} U(\vec{r})$$

$$\boxed{\hbar \frac{d\vec{k}}{dt} = \underbrace{-\vec{\nabla}_{\vec{r}} U(\vec{r})}_{\vec{F}} = \hat{\vec{F}}}$$

Apply to: crystal electrons in a constant electric field $\vec{F}_0 = -|e| \cdot \vec{\mathcal{E}}$

($\vec{\mathcal{E}}$: electric field)

$$\hbar \dot{\vec{k}} = \vec{F} = \text{const.}$$

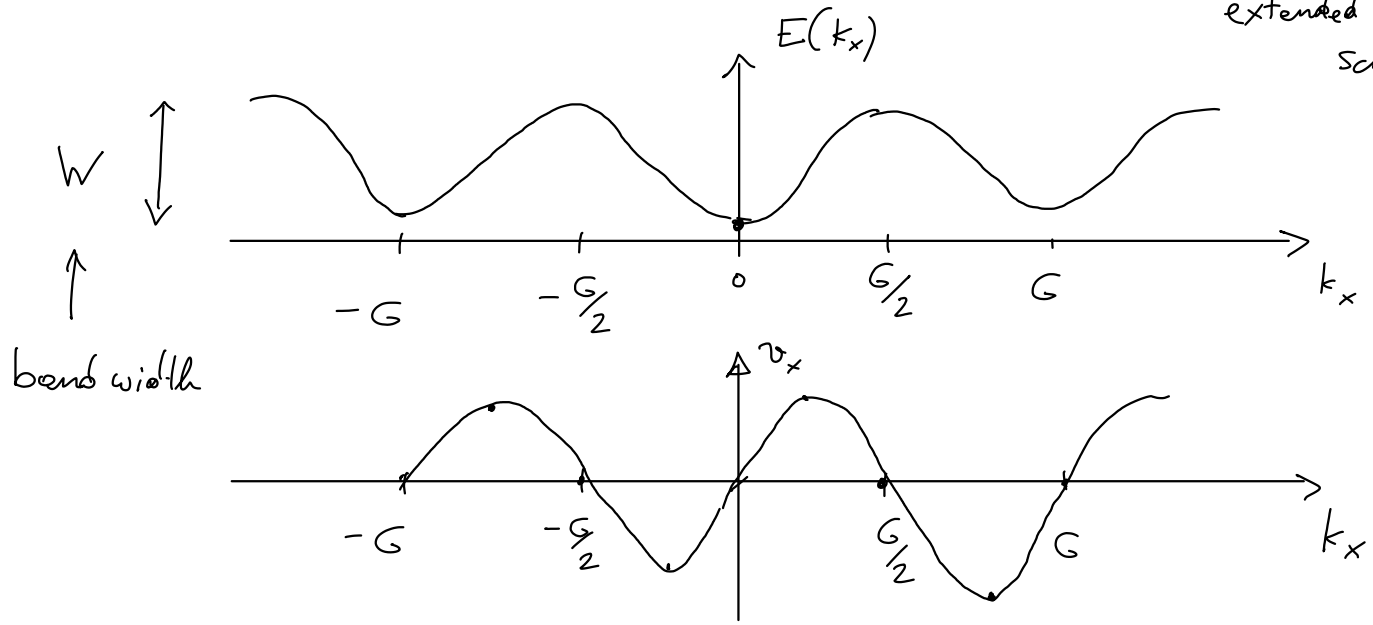
$$\vec{k}(t) = \vec{k}_0 + \frac{1}{\hbar}\vec{F} \cdot t$$

assume: $\vec{\mathcal{E}} = \mathcal{E}_x \vec{e}_x$ and $\vec{k}_0 = \vec{0}$

$$\vec{k}(t) = -\frac{|e|\,\mathcal{E}_x \cdot t}{\hbar} \cdot \vec{e}_x$$

group velocity: $v_x = \frac{1}{\hbar}\frac{\partial E(k)}{\partial k_x}$ $\qquad E(k+G) = E(k)$

extended zone scheme

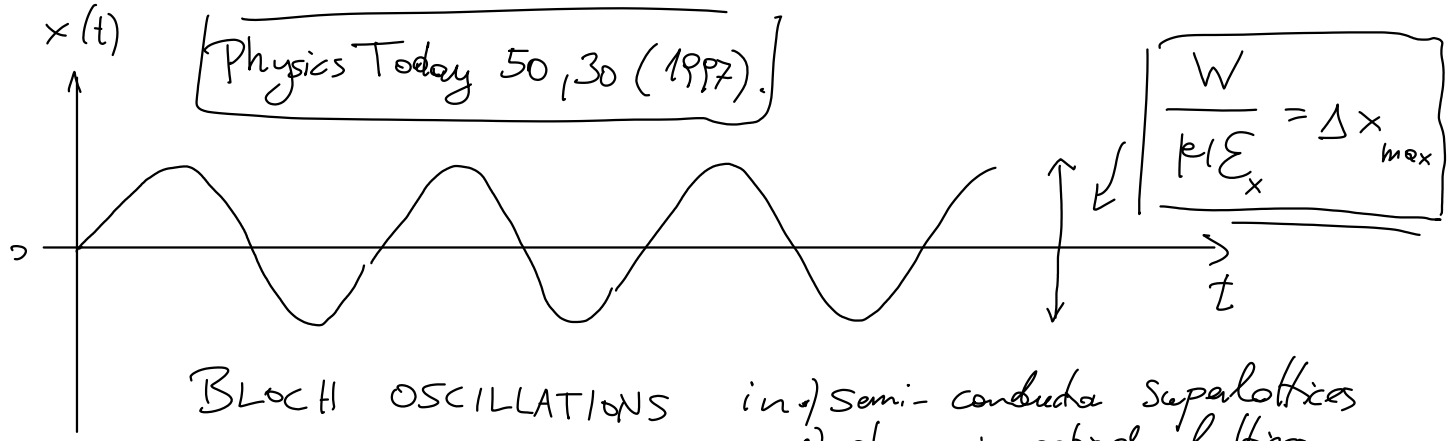


Position of wave-packet $x(t) = ?$

$$x(t) = \int_0^t v_x(t')\,dt' = \frac{1}{\hbar}\int_0^t dt'\,\frac{dE}{dk_x}(t')$$

$$t' = -\frac{\hbar}{|e|\mathcal{E}_x}k_x \quad \rightarrow \quad dt' = -\frac{\hbar}{|e|\mathcal{E}_x}dk_x$$

$$x(t) = -\frac{1}{|e|\mathcal{E}_x}\int_0^{k_x(t)} dk_x\,\frac{dE}{dk_x} = -\frac{1}{|e|\mathcal{E}_x}\left[E(k_x(t)) - E(k_x(0))\right]$$



Physics Today 50, 30 (1997).

BLOCH OSCILLATIONS in •) semi-conductor superlattices
•) atoms in optical lattices

Can we observe such Bloch oscillations ?

Example: •) metal with a bandwidth of $W = 10\,eV$

•) $\mathcal{E}_x = 1\,V/mm = 10^3\,V/m$

$$\Delta x_{max} = \frac{W}{|e|\cdot\mathcal{E}_x} = \frac{10\,\cancel{e}\cdot V}{\cancel{e}\,10^3} = 10^{-2}\,m = 10\,mm$$

on the other hand: $\sigma = \dfrac{e^2 \cdot n \cdot \tau}{m^*}$ (n: charge carrier density; τ: scattering time; m^*: effective mass)

$$\tau \simeq 10^{-13}\,sec$$

mean free path: $\lambda = v_{Fermi} \cdot \tau \approx 10^6\,m/s \cdot 10^{-13} \approx 10^{-7}\,m$

5.5 EFFECTIVE MASS TENSOR

$$\vec{F} = m\vec{a} \qquad \text{or} \qquad \vec{a} = \frac{1}{m}\cdot\vec{F}$$

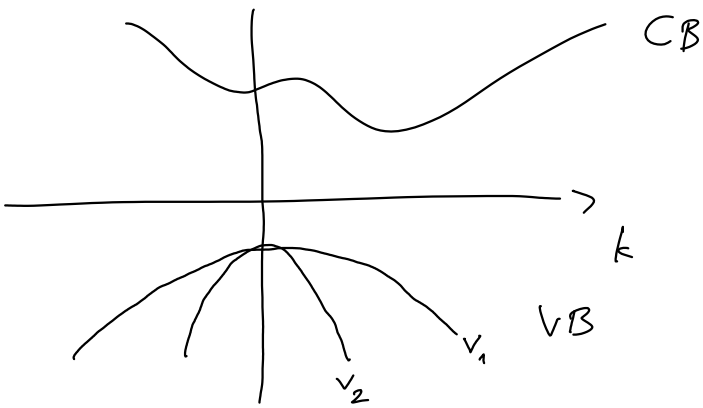
in a crystal: $\qquad a_\alpha =: \left[\frac{1}{m^*}\right]_{\alpha\beta} F_\beta \qquad \alpha = 1,2,3$

$$v_\alpha = \frac{1}{\hbar}\frac{\partial E}{\partial k_\alpha} \qquad \Big| \frac{d}{dt}$$

$$\dot{v}_\alpha = \left[a_\alpha = \frac{1}{\hbar}\frac{d}{dt}\frac{\partial E}{\partial k_\alpha} = \frac{1}{\hbar}\frac{\partial^2 E}{\partial k_\alpha \partial k_\beta}\cdot\underbrace{\frac{dk_\beta}{dt}}_{\frac{1}{\hbar}\cdot F_\beta} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_\alpha \partial k_\beta}\cdot F_\beta\right]$$

$$\left[\frac{1}{m^*}\right]_{\alpha\beta} = \frac{1}{\hbar^2}\frac{\partial^2 E(\vec{k})}{\partial k_\alpha \partial k_\beta}$$

effective mass tensor



Problem: II.2 Band structure and dynamics of electrons

Problem II.4 Velocity and effective mass of crystal electrons

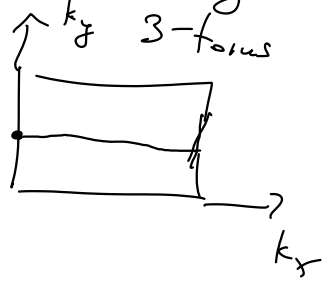
Problem II.5 Electron dynamics in fcc crystal
Bloch oscillations

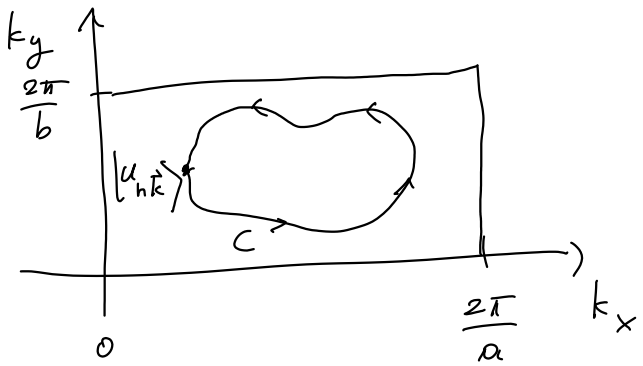
5.6 BERRY PHASE and BERRY CURVATURE

The equation of motion $\hat{\vec{v}} = \frac{d\hat{\vec{R}}}{dt} = \frac{1}{\hbar}\frac{\partial E}{\partial \vec{k}}$

What is this Berry (or geometric) phase?

- the potential $U(\vec{R})$ lets the electron drift adiabatically in $\vec{k}$-space





First we need: ADIABATIC THEOREM OF QUANTUM MECHANICS

(*) e.g.: D. J. Griffiths, Introduction to QM
Chapter 10 (see moodle page)

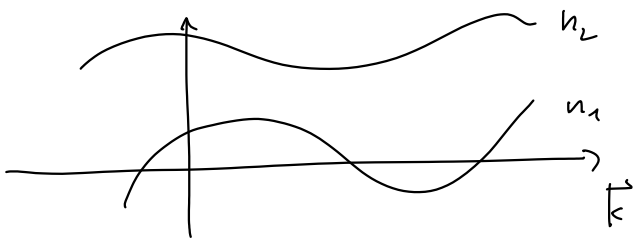
QUANTUM ADIABATIC THEOREM:

Assume a Hamiltonian $\hat{H}(\vec{R}(t))$

$$\hat{H}(\vec{R})\,|n(\vec{R})\rangle = E_n(\vec{R})\,|n(\vec{R})\rangle$$

Examples for $\vec{R}$:
(i) $\vec{R} \to \vec{B}$ ... magnetic field
(ii) $\vec{R} \to \vec{R}_\alpha$ ... nuclear coordinates
(iii) $\vec{R} \to \vec{k}$ ... Bloch vector in effective Hamiltonian

Adiabatic condition
-) The n-th eigenvalue $E_n(\vec{R})$ remains everywhere non-degenerate along the path $\vec{R}(t)$
-) The variation of $\vec{R}(t)$ is sufficiently slow such that a system initially in state $|n(\vec{R}(0))\rangle$ remains in the n-th eigenstate $|n(\vec{R}(t))\rangle$ up to a phase factor

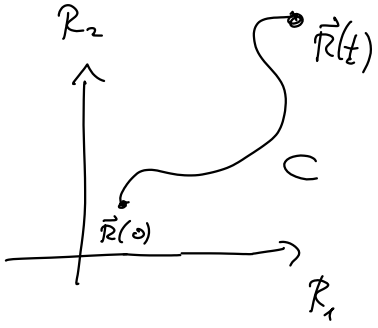


Under these conditions:

$$|\psi_n(t)\rangle = \underbrace{e^{i\gamma_n(t)}}_{\text{geometric}} \underbrace{e^{-\frac{i}{\hbar}\int_0^t dt' E_n(\vec{R}(t'))}}_{\text{dynamical phase factor}} |n(R(t))\rangle$$

or: BERRY phase (*)

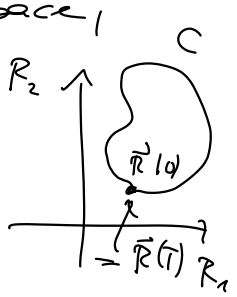
(*) Michael Berry, Proc. Royal Soc. A, 392, 45 (1984)



Insert into $i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$

Berry phase: $\gamma_n(t) = i \int_{\vec{R}(0)}^{\vec{R}(t)} d\vec{R} \cdot \langle n(\vec{R}) | \vec{\nabla}_{\vec{R}} | n(\vec{R}) \rangle$

$\Rightarrow$ $\gamma_n(t)$ only depends on the path in parameter space, but not on the rate of change



specifically for a cyclic evolution $\vec{R}(T) = \vec{R}(0)$

BERRY phase

$$\gamma_n = i \oint_C \langle n(\vec{R}) | \vec{\nabla}_{\vec{R}} | n(\vec{R}) \rangle \cdot d\vec{R} \qquad \gamma_n \in \mathbb{R}$$

BERRY CONNECTION

$$\vec{A}_n := i \langle n(\vec{R}) | \vec{\nabla}_{\vec{R}} | n(\vec{R}) \rangle$$ or Berry vector potential

$$\gamma_n = \oint_C d\vec{R} \cdot \vec{A}_n(\vec{R})$$

Is $\vec{A}_n$ gauge invariant?

Let's make a gauge transformation: $|\tilde{n}(\vec{R})\rangle = e^{-i\beta(\vec{R})} |n(\vec{R})\rangle$

$$\vec{A}_n \to \tilde{\vec{A}}_n = i \langle \tilde{n}(\vec{R}) | \vec{\nabla}_{\vec{R}} | \tilde{n}(\vec{R}) \rangle =$$

$$= i \langle \tilde{n}(\vec{R}) | \vec{\nabla}_{\vec{R}} | e^{-i\beta(\vec{R})} \cdot n(\vec{R}) \rangle$$

$$- i \left(\vec{\nabla}_{\vec{R}} \beta \right) | \tilde{n}(\vec{R}) \rangle + e^{-i\beta} \vec{\nabla}_{\vec{R}} | n(\vec{R}) \rangle$$

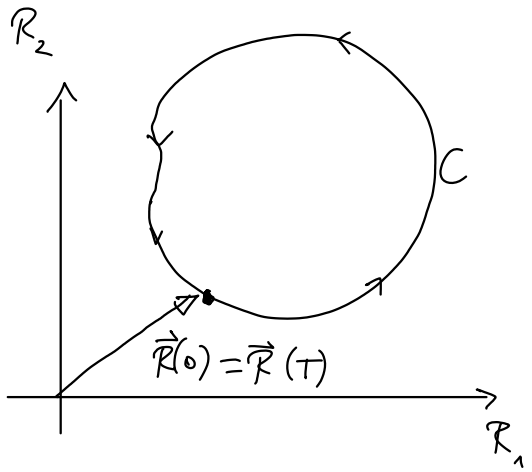
$$\boxed{\tilde{\vec{A}}_n = \vec{A}_n + \vec{\nabla}_{\vec{R}} \beta(\vec{R})}$$ gauge transformation

today: BERRY PHASE γ_n, BERRY CONNECTION $\vec{A}_n$ and BERRY CURVATURE $\vec{\Omega}_n$ and its consequences for the dynamics of crystal electrons.

$$\tilde{\gamma}_n = \gamma_n$$

$$\oint_C d\vec{R} \cdot \tilde{\vec{A}}_n = \oint_C d\vec{R} \cdot \vec{A}_n$$

$$\oint_C d\vec{R} \cdot \vec{\nabla} \beta(\vec{R}) = 0$$



$$\beta(\vec{R}(T)) - \beta(\vec{R}(0)) = 0 \quad \text{or} \quad 2\pi \times \text{integer}$$

$e^{i\beta}$

$e^{i\beta}$

(1) $\tilde{\gamma}_n = \gamma_n + 2\pi \cdot \text{integer}$

$\Rightarrow$ γ_n can only be changed by integer multiples of 2π by a gauge transformation, so we cannot remove the Berry phase in all cases

(2) For a closed path γ_n is gauge invariant and it is only dependent on the geometry of the path.

BERRY CURVATURE $\hat{=}$ „BERRY MAGNETIC FIELD"

now assume $\vec{R} \in \mathbb{R}^3$ (3D-parameter space)

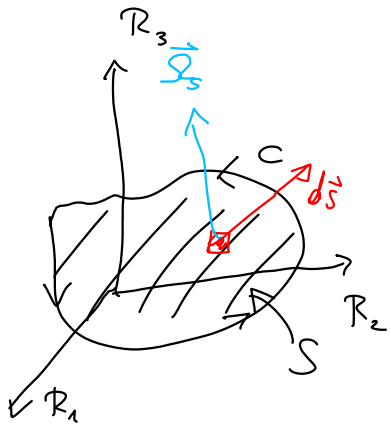
$$\boxed{\vec{\Omega}_n(\vec{R}) := \vec{\nabla}_{\vec{R}} \times \vec{A}_n(\vec{R})} \rightarrow \gamma_n = \oint_{C=\partial S} d\vec{R} \cdot \vec{A}_n = \int_S d\vec{S} \cdot \underbrace{\text{rot}\, \vec{A}_n}_{\vec{\Omega}_n}$$

Stokes' Theorem

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

$$\gamma_n = \int_S d\vec{s} \cdot \vec{\Omega}_n(\vec{R})$$

$$\boxed{\tilde{\vec{A}}_n = \vec{A}_n + \vec{\nabla}\beta(\vec{R})}$$



Berry curvature is gauge invariant

$$\tilde{\vec{\Omega}}_n = \vec{\nabla}_{\vec{R}} \times \left(\vec{A}_n + \vec{\nabla}\beta \right) = \vec{\nabla}_{\vec{R}} \times \vec{A}_n = \vec{\Omega}_n$$

•) $\vec{\Omega}_n$ ... can be viewed as a "magnetic field" in the the parameter space

•) Berry curvature is a truly local quantity and it provides a local description of the geometric properties of the parameter space.

Let us return to the dynamics of crystal electrons:

$$\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r}) \qquad V(\vec{r}+\vec{R}) = V(\vec{r})$$

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_{n\vec{k}}(\vec{r})$$

$$\hat{H}(\vec{k}) = \frac{\left(-i\hbar\vec{\nabla} + \vec{k}\right)^2}{2m} + V(\vec{r})$$

$$\hat{H}(\vec{k})\, u_{n\vec{k}}(\vec{r}) = E_n(\vec{k})\, u_{n\vec{k}}(\vec{r})$$

↑

Bloch vector $\vec{k}$ ≙ Parameter space "$\vec{R}$"

so $$\boxed{\hat{H}(\vec{k})\,|n\vec{k}\rangle = E_n(\vec{k})\,|n\vec{k}\rangle}$$

•) Berry phase: $$\gamma_n = \oint_C d\vec{k}\, \underbrace{\langle n\vec{k}|\, i\vec{\nabla}_{\vec{k}}\, |n\vec{k}\rangle}$$

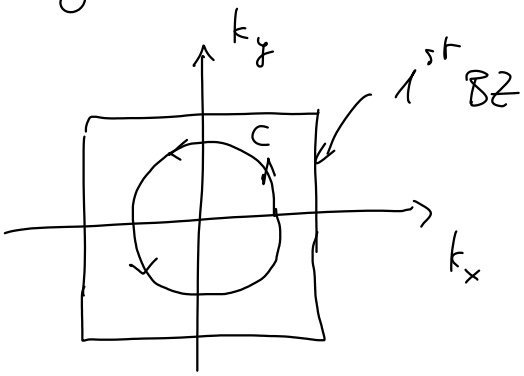
•) Berry connection: $$\vec{A}_n(\vec{k}) = \langle n\vec{k}|\, i\vec{\nabla}_{\vec{k}}\, |n\vec{k}\rangle$$

dimension of $\vec{A}_n$ = length

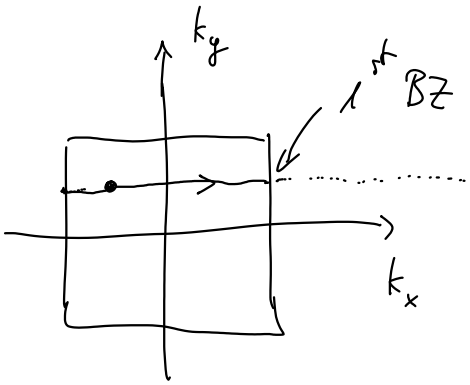
•) Berry curvature: $\vec{\Omega}_n = \vec{\nabla}_{\vec{k}} \times \vec{A}_n(\vec{k})$ .... dimension of an area

so $\gamma_n = \oint_{C=\partial S} d\vec{k} \cdot \vec{A}_n(\vec{k}) = \int_S d\vec{s} \cdot \Omega_n(\vec{k})$

(i) apply a magnetic field → cyclotron motion



(ii) Linear variation of $\vec{k}$ due to an electric field



Now examine the effect of the Berry curvature on equation of motion for crystal crystals

Remember: $\hat{H} = E_n(\hat{\vec{k}}) + U(\hat{\vec{R}})$ ... effective 1-band Hamiltonian

$$|\phi_{n\vec{k}}\rangle \longrightarrow e^{-i\gamma_n(\vec{k})} |\phi_{n\vec{k}}\rangle = |\tilde{\phi}_{n\vec{k}}\rangle$$

$$\hat{\vec{R}} = i\vec{\nabla}_{\vec{k}} \longrightarrow i\vec{\nabla}_{\vec{k}} \left[e^{-i\gamma_n(\vec{k})} \cdot |\phi_{n\vec{k}}\rangle \right] =$$

$$= e^{-i\gamma_n(\vec{k})} \, i\vec{\nabla}_{\vec{k}} \left| \phi_{n\vec{k}} \right\rangle + \left(\vec{\nabla}_{\vec{k}} \gamma_n(\vec{k}) \right) \cdot e^{-i\gamma_n(\vec{k})} \left| \phi_{n\vec{k}} \right\rangle$$

$$\boxed{\hat{\vec{R}} \longrightarrow \hat{\vec{R}} + \underbrace{\vec{\nabla}_{\vec{k}} \gamma_n(\vec{k})}_{\vec{A}_n(\vec{k})} = \hat{\vec{R}} + \vec{A}_n(\hat{\vec{k}})}$$

$$\gamma_n(\vec{k}) = \int_{\vec{k}_0}^{\vec{k}} d\vec{k}' \, \vec{A}_n(\vec{k}')$$

Compare: „minimal coupling principle"

$$\hat{\vec{p}} \longrightarrow \hat{\vec{p}} - q\vec{A}(\hat{\vec{r}})$$

$$\boxed{\hat{\vec{R}} \longrightarrow \hat{\vec{R}} + \vec{A}(\hat{\vec{k}}) = \hat{\vec{X}}}$$

$$\hat{H} \longrightarrow \hat{H}'$$

$$E_n(\hat{\vec{k}}) + U(\hat{\vec{R}}) \longrightarrow E_n(\hat{\vec{k}}) + U(\underbrace{\hat{\vec{R}} + \vec{A}(\hat{\vec{k}})}_{\hat{\vec{X}}})$$

Equations of Motion for the gauge-transformed $\hat{H}'$:

① $$i\hbar \frac{d\hat{\vec{X}}}{dt} = \left[\hat{\vec{X}}, \hat{H}' \right] = \left[\hat{\vec{X}}, E(\hat{\vec{k}}) + \hat{U}(\hat{\vec{X}}) \right]$$

② $$i\hbar \frac{d\hat{\vec{k}}}{dt} = \left[\hat{\vec{k}}, \hat{H}' \right] = \left[\hat{\vec{k}}, E(\vec{k}) + U(\hat{\vec{X}}) \right]$$

$$\left[\hat{\vec{k}}, U(\vec{R}) \right] = -i\vec{\nabla}_{\vec{R}} U(\vec{R})$$

add ② $$\left[\hat{k}_\ell, \hat{R}_m \right] = -i\delta_{\ell m}$$

now: $$\left[\hat{k}_\ell, \hat{X}_m \right] = \left[\hat{k}_\ell, \hat{R}_m + A(\hat{\vec{k}}) \right] = \left[\hat{k}_\ell, \hat{R}_m \right] = -i\delta_{\ell m}$$

$$\left[\hat{\vec{k}}, U(\hat{\vec{X}}) \right] = -\vec{\nabla}_{\vec{R}} U(\vec{R})$$

$$\Rightarrow \boxed{i\hbar \frac{d\hat{\vec{k}}}{dt} = -\vec{\nabla}_{\vec{R}} U(\vec{R})}$$ ... remains unchanged

add (1) $\left[\hat{\vec{X}},\, E(\hat{\vec{k}}) + U(\hat{\vec{X}})\right] = \underbrace{\left[\hat{\vec{X}},\, E(\hat{\vec{k}})\right]}_{(i)} + \underbrace{\left[\hat{\vec{X}},\, U(\hat{\vec{X}})\right]}_{(ii)}$

(i) $\left[\hat{\vec{X}},\, E(\hat{\vec{k}})\right] = \left[\hat{\vec{R}} + \vec{A}(\hat{\vec{k}}),\, E(\hat{\vec{k}})\right] = \left[\hat{\vec{R}},\, E(\hat{\vec{k}})\right] = i\,\vec{\nabla}_{\vec{k}} E(\vec{k})$

add (ii): $\left[\hat{x}_\ell, \hat{x}_m\right] = \left[\hat{R}_\ell + \hat{A}_\ell(\hat{\vec{k}}),\, \hat{R}_m + \hat{A}_m(\hat{\vec{k}})\right] =$

$= \left[\hat{A}_\ell(\hat{\vec{k}}),\, \hat{R}_m\right] + \left[\hat{R}_\ell,\, \hat{A}_m(\hat{\vec{k}})\right] =$

$= -i\,\frac{\partial A_\ell}{\partial k_m} + i\,\frac{\partial A_m}{\partial k_\ell} = i\left(\frac{\partial A_m}{\partial k_\ell} - \frac{\partial A_\ell}{\partial k_m}\right) = \ldots =$

$= i\,\varepsilon_{\ell m n}\,\Omega_n(\vec{k})$

$\left\{\vec{\Omega} = \vec{\nabla}_{\vec{k}} \times \vec{A}\right\}_n = \varepsilon_{nij}\,\frac{\partial}{\partial k_i} A_j = \Omega_n$

$\left[\vec{X},\, U(\hat{\vec{X}})\right] = \ldots = i\left(\vec{\nabla}_x U\right) \times \vec{\Omega}(\vec{k})$

Berry curvature

$\vec{E}$

$$\frac{d\hat{\vec{X}}}{dt} = \hat{\vec{v}} = \frac{1}{\hbar}\vec{\nabla}_{\vec{k}} E_n(\vec{k}) + \frac{1}{\hbar}\left(\vec{\nabla}_x \hat{U}\right) \times \vec{\Omega}_n(\vec{k})$$

normal velocity

(Luttinger) anomalous velocity

Compare: Xiao, Chang, Niu, Berry phase effects on electronic properties
Rev. Mod. Phys. 82, 1959 (2010).

Symmetry properties for Berry curvature $\vec{\Omega}$

→ assume $\vec{\nabla} U = -e\vec{\mathcal{E}}$

$$\vec{v} = \frac{1}{\hbar}\vec{\nabla}_{\vec{k}} E_n(\vec{k}) + \frac{e}{\hbar}\vec{\mathcal{E}} \times \vec{\Omega}_n(\vec{k})$$

$\vec{v}$ should be invariant under symmetry operations of the crystal

(i) time reversal symmetry : $t \to -t$

(ii) spatial inversal —"— : $\vec{r} \to -\vec{r}$

ad(i) $t \to -t$:

$$\left.\begin{array}{l} \vec{v} \to -\vec{v} \\ \vec{k} \to -\vec{k} \\ \vec{\mathcal{E}} \to \vec{\mathcal{E}} \end{array}\right\} \Rightarrow \vec{\Omega}_n(-\vec{k}) = -\vec{\Omega}_n(\vec{k})$$

ad(ii) $\vec{r} \to -\vec{r}$:

$$\left.\begin{array}{l} \vec{v} \to -\vec{v} \\ \vec{k} \to -\vec{k} \\ \vec{\mathcal{E}} \to -\vec{\mathcal{E}} \end{array}\right\} \Rightarrow \vec{\Omega}_n(-\vec{k}) = \vec{\Omega}_n(\vec{k})$$

for crystal with both, time and spatial inversion symmetry :

$$\Rightarrow \vec{\Omega}_n \equiv 0$$

Examples for non-vanishing $\vec{\Omega}_n$:

- magnetic systems, e.g. fcc-Fe
  → current $\perp \vec{\mathcal{E}}$ → anomalous Hall effect.
- Graphene with broken sublattice symmetry

- Transition metal dichalcogenides (2D-materials)

  WS_2, WSe_2
  MoS_2, $MoSe_2$

  "topological insulators"

Band Topology and Berry Curvature

Article: Ramirez, Skinner, Physics Today 31 (2020)

Topological invariants:

Example: 2D-surface can be characterized by its "genus"

Gauß-Bonnet-Theorem:

$$\frac{1}{2\pi}\int_S K \cdot dA = n = 2(1-g)$$

(K: local curvature; n: integer; g: genus)

example: sphere of radius R has curvature $K = \frac{1}{R^2}$

$$\frac{1}{2\pi}\int_{\text{sphere}} \frac{1}{R^2} dA = \frac{1}{2\pi R^2} 4\pi R^2 = 2 = 2(1-g)$$

$$\Rightarrow g = 0$$

Chern-theorem applied to $\vec{\Omega}_n$ and $\vec{k}$-space:

2D-BZ

$$\frac{1}{2\pi}\int_{BZ} \Omega_z(k_x, k_y)\, d^2k = C \quad \text{... integer number}$$

(C: Chern number)

-) 2D-materials with $C = 0$ are termed "topologically trivial"
-) 2D-material with $C \neq 0$ are "topological material"

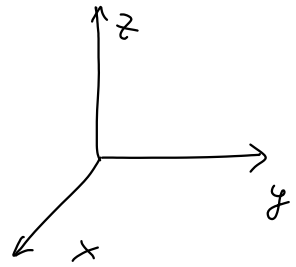
Relation to the integer Quantum Hall effect:

$$\vec{\mathcal{E}} = \mathcal{E}_x \vec{e}^{\,x}$$

$$\vec{\Omega} = \Omega_z \vec{e}^{\,z}$$

$$\vec{v} = v_y \vec{e}^{\,y}$$

$$\vec{v}_{an.} = -\frac{e}{\hbar} \vec{\mathcal{E}} \times \vec{\Omega}_n$$



$$v_y = \frac{e}{\hbar} \Omega_z(k_x, k_y) \cdot \mathcal{E}_x \qquad | \cdot e \left| \frac{1}{V} \sum_{BZ} \right. \qquad j = \sigma \cdot \mathcal{E}$$

$$n \cdot e \cdot v = \sigma \cdot \mathcal{E}$$

$$j_y = \underbrace{\frac{e^2}{\hbar} \left[\frac{1}{A} \sum_{BZ} \Omega_z(k_x, k_y) \right]}_{\sigma_{xy} \ \ldots \text{ Hall-conductivity}} \cdot \mathcal{E}_x$$

$$\frac{A}{(2\pi)^2} = \frac{1}{(\Delta k)^2}$$

$$\sigma_{xy} = \frac{e^2}{\hbar} \frac{1}{(2\pi)^2} \int_{BZ} d^2k \, \Omega_z(k_x, k_y)$$

$$\hbar = \frac{h}{2\pi}$$

$$\sigma_{xy} = \frac{e^2}{h} \cdot \underbrace{\frac{1}{2\pi} \int_{BZ} d^2k \, \Omega_z(k_x, k_y)}_{= C \ \ldots \text{ Chern number} \ = \ \text{integer}}$$