Solid State Physics IV

Exercises are extension to lecture

Electronic structure

Free electron: $\psi(r) = e^{i\vec{k}\cdot\vec{r}}$ $\vec{k}$: momentum

In crystal: translational symmetry / periodic potential

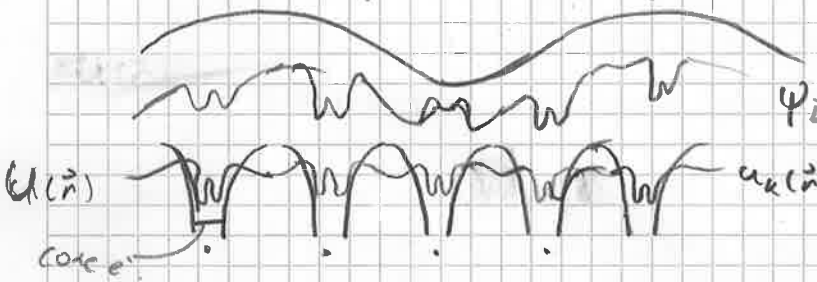
$U(\vec{r}) = U(\vec{r}+\vec{R})$ $\vec{R}$: Bravais vector (unit cell)

Schrödinger: $H\psi_{\vec{k}}(\vec{r}) = \left(-\frac{\hbar^2\nabla^2}{2m} + U(\vec{r})\right)\psi_{\vec{k}}(\vec{r}) = E_{\vec{k}}\psi_{\vec{k}}(\vec{r})$

Bloch theorem: $\psi_{\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi_{\vec{k}}(\vec{r})$

solutions Bloch wave: $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{\vec{k}}(\vec{r})$ ← periodic

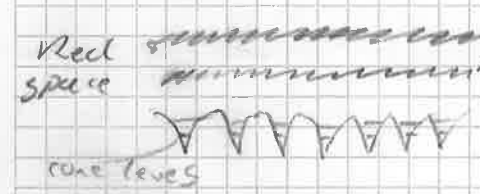
$\Rightarrow E(\vec{k})$ depends on $u_{\vec{k}}(\vec{r})$



[drawn as periodic in $\vec{r}$]

Real on direct space

What is a band? unique $E(\vec{k})$ (and spin (x2))
Separated by forbidden regions



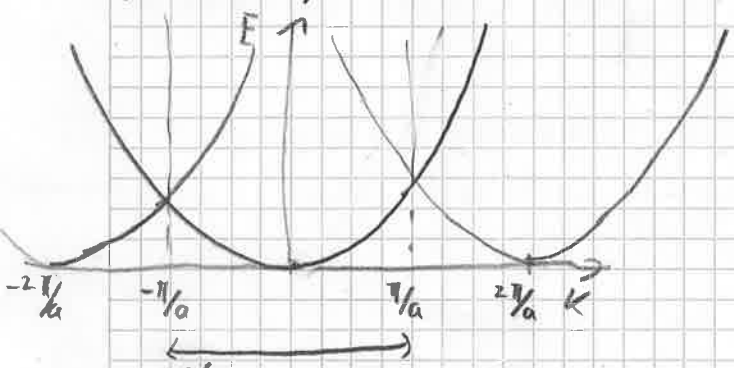
$|\psi(\vec{r})|^2$ probability density

$\left(\frac{2\pi}{R}\right)$

Reciprocal or momentum space: $\vec{k}' = \vec{k} + \vec{G}$ ← reciprocal lattice vector

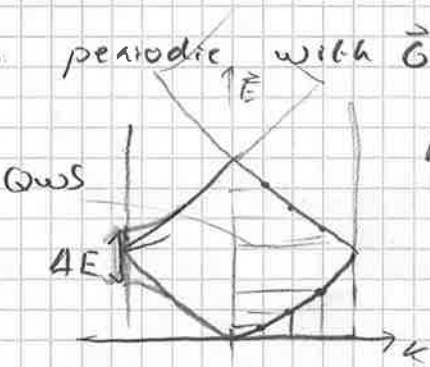
$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}} = \underbrace{u_{\vec{k}}(\vec{r})\, e^{-i\vec{G}\cdot\vec{r}}}_{u_{\vec{k}'}(\vec{r})} e^{i\vec{k}'\cdot\vec{r}} = u_{\vec{k}'}(\vec{r})e^{i\vec{k}'\cdot\vec{r}} = \psi_{\vec{k}'}(\vec{r})$

$\Rightarrow$ wave function and bands periodic with $\vec{G}$



1st Brillouin zone

$\Rightarrow$



Free e⁻ model

$E(\vec{k}) = \frac{\hbar^2\vec{k}^2}{2m_e}$

finite crystal ↔ QW, slab → $\vec{k}$ discrete → $E(\vec{k})$ discrete

"infinite" crystal → $\vec{k}$ continuous (QWS)

* weak potential model: free e⁻ + correction

Energy gap ($\Delta E = 2U_G$) at zone boundary

$\Rightarrow$ Separation into bands ← valence

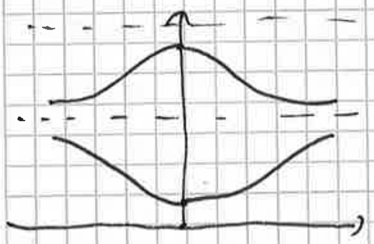
Filled bands: # e⁻ per unit cell /2 ← spin

$\left(U(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}\right)$ $\Rightarrow$ Fermi: E (E_F)

non integer band filling

Metal vs. insulator [other classifications possible]

↳ DOS at E_F ↳ no DOS at E_F



Do e^- in insulator move?

what determines velocity of e^- in metal?

? effective mass, direction ?

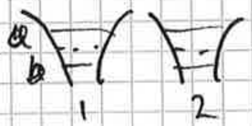
↳ tensor $\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j}$ in units of m_e

Main models: 1) quasi-free e^-: best for non-interacting

2) tight-binding: possible/easier to include interactions

for 1) Fermi sphere + backfolding

2) localized e^- + allow hopping (especially for d e^-)



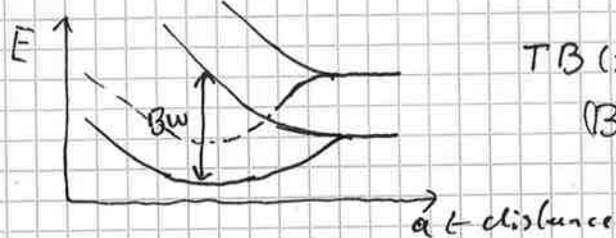
$|b\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$ $|a\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$

(bonding + anti-bonding)

N atoms $|k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot n} |n\rangle$ $|n\rangle$ state at n

Large hopping probability (small distance): ~~broad~~ large band width

Small " " (large "): small band width



TB (2) typically used for (B)W < other E scales (band distance, interactions)

≈ Idea of lecture: add interactions + look at response

Hubbard model ($e^- e^-$ interaction)

TB model: lattice of atoms with 1 s level (non-degenerate → 1 e^-)

$$H = -t \sum_{\langle ij \rangle \sigma} c^\dagger_{i\sigma} c_{j\sigma}$$

σ: spin t: hopping matrix element

depends on dimension + Bravais — over nearest neighbours

$c^\dagger_{i\sigma}$ ← annihilation on site i; $c_{j\sigma}$ ← creation on site j } move e^- from i → j

FT → $H_1 = \sum_{k\sigma} E(\vec{k}) c^\dagger_{k\sigma} c_{k\sigma}$ (for 1 band)

Spectrum $E(\vec{k}) = -2t(\cos k_x + \cos k_y + \cos k_z)$ (3D)

$W = 2zt$

* ( ) N sites → 2N states N e^- → half-filled → metal

! Independent of distance on t ! ⇒ fix for $t \neq 0$ (tunneling never ≡ 0)

chain 2 / square 4 ...

(*) Total bandwidth $W = 2zt$ z: # of N.N.

Coulomb repulsion missing → pay Energy U for $2e^-$ on same site

$H_{int} = U \sum_i n_{i\uparrow} n_{i\downarrow}$ electron density $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ (σ: opposite spin)

full $H = -t \sum_{ij\sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$ U: Hubbard U

Pay U, gain kinetic energy (hole + doublon move freely)

↳ half bandwidth $\overset{(*)}{=} -2zt$ $\times 2 \Rightarrow -2zt\ (= W)$

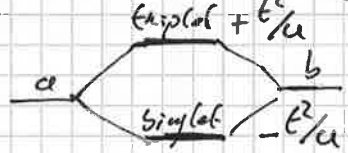
If $U > W$: insulating with gap $\Delta E = U - W$

Metal → insulator transition as function of U/t

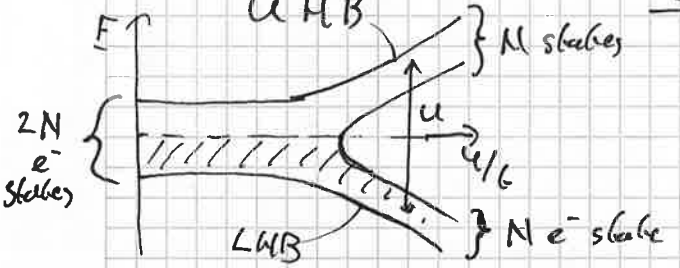
Mott (-Hubbard) insulator due to e^- correlations

Heitler-London state $|\psi_{HL}\rangle = \frac{1}{\sqrt{2}}(\psi_a(r_1)\uparrow \psi_b(r_2)\downarrow - \psi_a(r_1)\downarrow \psi_b(r_2)\uparrow)$

never on same site!



(explain singlet-triplet splitting next)



in band insulator (crystal structure) always $2N$ states / band

U/t changes if e^- from LHB → UHB or removed

Magnetic (spin) order in Mott insulator

Back to picture of localised e^- → localised spin ↑

(Rest only valid if spin is good Quantum #; collinear no SOI)

Mott insulator: hopping (delocalisation) as perturbation to localised ground state

[opposite from usual]

Not-ordered: 2^N degenerate (against thermodynamics)

⟹ spin order (certainly at $T = 0$K)

possibilities: ↑ ↑ or ↑ ↓

FM AFM

2nd order perturbation: $\Delta E = \sum_n \frac{|\langle 0|H'|n\rangle|^2}{E_0 - E_n}$ ← hopping

n: all excited states

FM: hopping forbidden (Pauli) $\Delta E = 0$

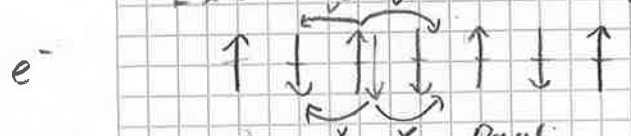
AFM: virtual transition: $2 \times t \to t^2$ | $1 \times U$ $\quad \Delta E = -\frac{2t^2}{U}$ (right↔left, left↔right)

Difference singlet ↔ triplet in Heitler-London

$\Rightarrow$ AFM has lower E!

Electron motion + spin order in Mott insulators

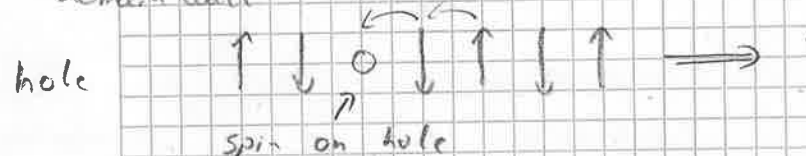
Extra e^- or hole to AFM ground state: U paid once

e^- 

AFM order blocks e^- motion? (in absence of spin flip)

Pauli: No ∀ e^- are indistinguishable → other e^- can hop

domain wall

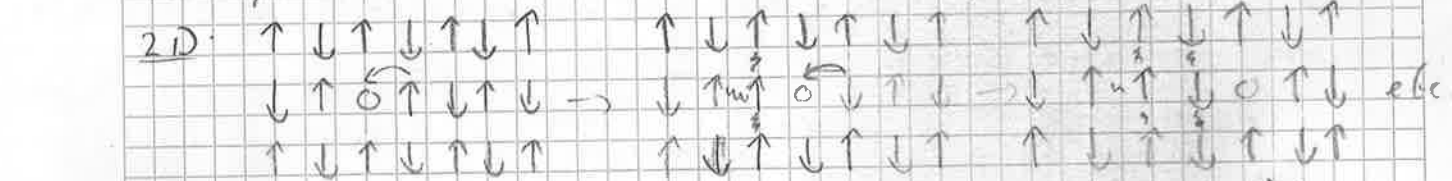
hole 

spin on hole

no spin ↳ spin-charge separation

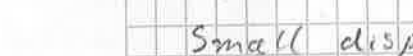
↳ domain wall ↳ energy cost J

only once in 1D ← (exchange)

2D: 

Extra DW energy with every movement $\hat{=} J|\vec{n}|$

Small displacement $\Rightarrow$ still insulator (all ok)

Assume FM:  No additional cost for e^- or h hopping (conductance)

Gain $\sim t\delta$ (δ: doping) loss: $\frac{t^2}{U} \cdot V$ (V: FM volume)

$\Rightarrow$ transition to FM metal with δ (doping)

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Transition metal ions

* Include atomic and orbital properties (mostly 3d TM)

Atomic quantum numbers:

- n energy level: 1, 2, 3 ...
- $\ell \leq n-1$ angular momentum
- s spin ($m_s = \pm 1/2$)

$\ell = 0$	s		2
$\ell = 1$	p	levels	6
$\ell = 2$	d	:	10
$\ell = 3$	f		14

On ℓ-shell → $2 \times (2\ell + 1)$ states

Filling periodic table: $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^2} 3d^{10} 4p^6$

* 3d-orbitals much smaller as s, p → localised (4d, 5d larger) Reduction $\frac{n+1}{n}$ p.T 4f smallest

Valence of ion in compound

Hund's rules (filling d- or f-shell)

1: Maximise total $S = \sum m_s$

2: For max S, maximise $L = \sum m_\ell$

Example: $3d^2$ [| | | ↑ | ↑] $m_\ell = -2\ -1\ 0\ 1\ 2$ $S = 1$ $L = 3$ $\Rightarrow {}^3F$ (total)

Atomic notation: ${}^{2S+1}L_J$ ← total angular momentum $J = L + S$

$L = 0, 1, 2, 3 \rightarrow S, P, D, F$

d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
${}^2D$	${}^3F$	${}^4F$	${}^5D$	${}^6S$	${}^5D$	${}^4F$	${}^3F$	${}^2D$

e^- - hole symmetry

consider e^- (d^1–d^5) consider holes (d^6–d^9)

* Origin of Hund's rules (2) in Coulomb interaction between orbitals (spherical harmonics) ⇒ make different

→ extra energy term: $U_{mn} = U_{mm} - 2J_H$ ← Hund's rule coupling

$J_H \approx 0.8 - 0.9\,eV$ (3d) $0.7/0.8\,eV$ (4d) $0.5\,eV$ (5d)

(different) (same orbitals (Hubbard U))

Only valid for spherical symmetry [refine]

Spin-orbit interaction (SOI)

Relativistic correction due to e^- motion in $\vec{E}$-field (↑ around nucleus)

(Zeeman) energy for magnetic moment in $\vec{B}$: $\Delta E = -\mu B$

For spin: $\mu_s = \frac{-2\mu_B}{\hbar}\vec{S}$ (spherical)

Lorentz transformation $\vec{B} = -\frac{\vec{v} \times \vec{E}}{c^2}$ $\vec{E} = \left|\frac{E}{r}\right| \vec{r}$ $\vec{p} = m_e \vec{v}$

$\vec{B} = \frac{\vec{r} \times \vec{p}}{m_e c^2} \left|\frac{E}{r}\right|$ angular momentum $\vec{L}$

Coulomb potential $|E| = \frac{1}{e}\frac{\partial U(r)}{\partial r}$

$\vec{B} = \frac{1}{m_e e c^2 r}\frac{\partial U(r)}{\partial r}\vec{L} \Longrightarrow \Delta E_{LS} = \frac{\mu_B}{\hbar m_e e c^2 r}\frac{\partial U(r)}{\partial r}\vec{L}\cdot\vec{S}$ [factor 1/2 relativistic cor]

Increase with Z, E_b $\left(\frac{\partial U}{\partial r}\right)$, $\vec{L}$, small orbitals $\left(\frac{1}{r}\right)$ λ (Z, valency, spin)

* Simplify for 3d: Russel-Saunders (LS) scheme

$\vec{J} = \vec{L} + \vec{S}$ with $\vec{L} = \sum \vec{\ell}_i$ $\vec{S} = \sum \vec{s}_i$ (contrast to jj-scheme)

$\mathcal{H}_{LS} = \lambda \vec{L}\cdot\vec{S}$ Extra term for Hund's rules:

(HR) 3) For e^- (up to d^5): minimise $\vec{J}$, for holes: maximise $\vec{J}$

	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
	${}^2D_{3/2}$	${}^3F_2$	${}^4F_{3/2}$	${}^5D_0$	${}^6S_{5/2}$	${}^5D_4$	${}^4F_{9/2}$	${}^3F_4$	${}^2D_{5/2}$
(Landé) g_J	$4/5$	$2/3$	$2/5$	—	2	$3/2$	$4/3$	$5/4$	$6/5$

$J = L+S, L+S-1, L+S-2 \ldots |L-S|$

$S = 1/2$ $L = 2$

$5/2\ (L+S)$ $3/2$

(Collog Monday graphene)

~ LS magnitude : 3d : 20-70 meV   4d : 100-300 meV   5d : 200-500 meV

In external B-field ; both S and L contribute

effective g-factor $g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$ ($M = g_J \mu_B J$)

isolated ion →   Zeeman : $-MH$

In crystals $g_J = \frac{g_L + g_S}{2} + \frac{L(L+1) - S(S+1)}{2J(J+1)} (g_L - g_S)$

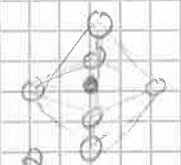
for $g_L = 1$ $g_S = 2$ ⟹ atom

Other effects of SOI

- Avoided crossing of bands
- Lifting spin degeneracy (broken inversion sym)

TM ions in a crystal : crystal field interaction

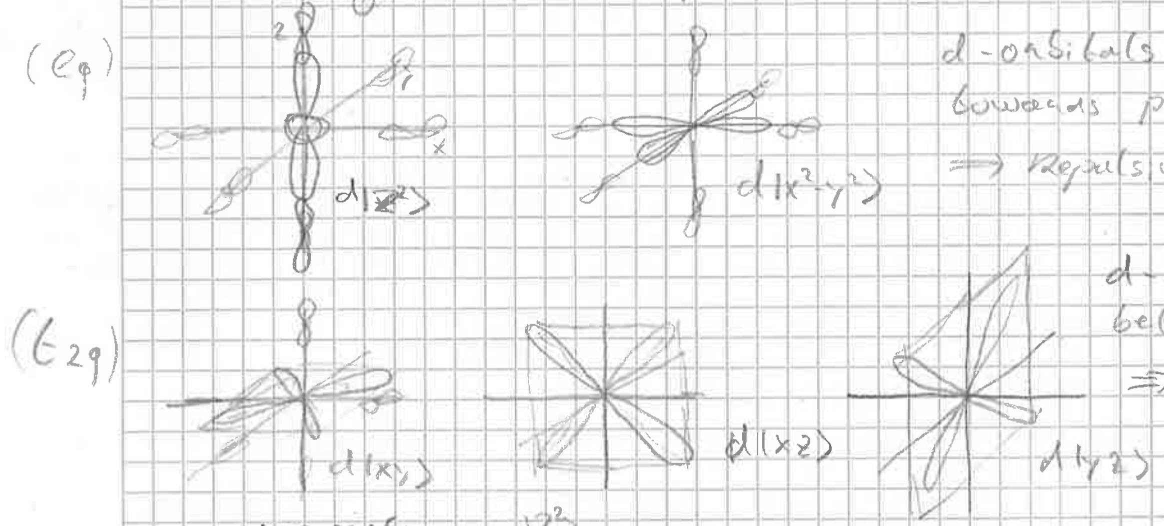
* TM typically in O tetrahedron



O : oxygen (p-orbitals)

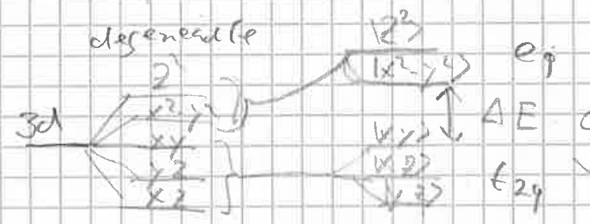
● : TM (d-orbitals)

Cubic symmetry



d-orbitals extend towards p-orbitals ⟹ Repulsion ⟹ higher E

d-orbitals between p ⟹ lower E



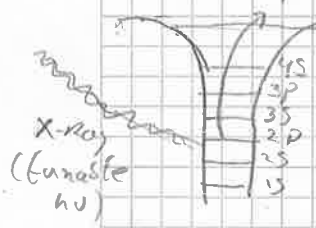
ΔE crystal field splitting ~ 10 Dq for tetragonal (eV)

Magnitude depends on atom, valence, spin ...

Change of level for distortions { tetragonal (elongated) axi / rhombohedral } orthorhombic

How to measure such effects?

X-ray absorption spectroscopy (XAS)



2p energy for 3d TM: 400 – 1000 eV

Dipole selection rules: $\Delta \ell = +/- 1$ $\Delta S = 0$

From s-state → unoccupied p DOS

From p → d unoccupied d DOS

Fermi golden rule: $W_{fi} \propto |\langle \Psi_f | T | \Psi_i \rangle|^2 \, \delta(E_f - E_i - h\nu)$ (only from occupied; T: transition matrix)

Dipole transitions: $W_{fi} \propto |\langle \Psi_f | \hat{\varepsilon}_q \cdot \hat{r} | \Psi_i \rangle|^2 \, \delta_{..}$ ($\hat{\varepsilon}_q$: E-field of $h\nu$; $\hat{r}$: e^- position; lifetime + exp. broadening)

* 2p → 3d transitions: overlap of 2p core hole with 3d DOS

⟹ interactions, change of Ψ_i and 3d DOS

Incorporated in (atomic) multiplet theory:

⟹ Identification of valence state + orbital occupancy + Crystal field splitting

XMCD: $q = +/- 1$ $\quad \hat{\varepsilon}_{\pm L} = \mp \frac{1}{\sqrt{2}} (\hat{x} \pm i\hat{y})$ $\quad (\hat{\varepsilon}_0 = \hat{z})$

dipole rule: $\Delta m_j = q$ (in spherical harmonics)

dichroism: $\frac{I_+ - I_-}{I_+ + I_-} \propto \langle L_z \rangle \neq 0$ for Ferro-, Ferri-, Altermagnets