Introduction

- What is the best language to describe the electronic structure in a solid?

  ⇝ start from free particles and switch on a weak periodic pot. Ⓘ

  ⇝ start from isolated atoms and let atomic wavefct. overlap Ⓘⓘ

How localized are the relevant degrees of freedom?

$E_{kin} \sim t$

$E_{pot}^{Coul} \sim U$

itinerant limit
Coulomb pot. energy small
kinetic Energy large
(good metals or band insulators)

DFT

localized limit (atomic)
Coulomb pot. dominat and
small kinetic energy
("Mott insulators")

Full structure of Coulomb rep important for certain cases

Coulomb int small pert. as {single particle limit

preview: DMFT

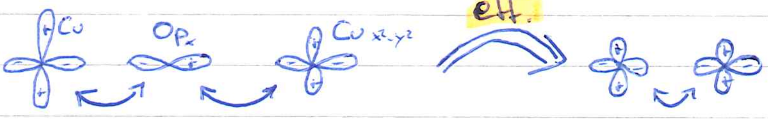
many-body physics

U/t

From bands to configurations : $\underset{[Xe]}{\overset{+III}{La_2}}\,\underset{[Ar]3d^9}{\overset{+II}{Cu}}\,\underset{[Ne]}{\overset{-II}{O_4}}$

La_2CuO_4 has an odd number of electrons in the unit cell ($3d^9$)
↳ metallic in the band picture! Experiment: very insulating ⚡

In a local picture on a lattice metalicity/charge transfer can be understood as "hopping" from one site to the next



in 2nd Quant. ⇒ $$t_{ij}\, c_i^+ c_j \xrightarrow{FT} \sum_{k,\sigma} E(k)\, c_{k\sigma}^+ c_{k\sigma} \qquad (1)$$

Now we start with $3d^9$ on every Cu site and let the electrons gain kinetic energy by hopping ⟹ this will produce the configurations $3d^8$ and $3d^{10}$

⟹ on average d^9 50% and d^8 / d^{10} 25% each

However, while E_{kin} gain is large we have to pay gigantic intra-atomic potential energy (Coulomb)
↳ hopping surpressed by Coulomb repulsion (Mott insulator)

⇒ in La_2CuO_4 we have a dominant $3d^9$ configuration

This situation is verified also by $\chi^{mag.}$ experiments
⇒ configurations have specific magnetic behaviour
↳ in the excersise we will calculate $\chi^{mag.}(T)$

Since we will be interested in specific configurations and local obserables we throw away the hopping for now completely
⇒ in (1) now k is not a good quantum number anymore when we look at an isolated atom/ion

So what are our quantum numbers of choice? ⇒ angular momentum

Atomic physics : "filling shells"

As you know well from highschool chemistry we describe atoms with main quantum numbers and angular momentum

↳ This picture originates from central-potential theories where the Coulomb repulsion is mean-field-type approximated by a single-particle potential : e.g. Hartree - Fock or Thomas Fermi

The many-particle-wavefunctions are constructed by Slater-determinants of single-electron wavefunctions obtained by solving the mean-field Schrödinger equation

includes eē repulsion ≙ screened core potential

$$H_{MF}\varphi = \left(-\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(r)\right)\varphi = \varepsilon^{MF}\varphi \qquad (2)$$

e.g. HF

Energies depend on main quantum number n and l

ε_{nl}^{MF} determines how the "shells" of the atom are filled

⇝ Observe the impression that this statement gives: Electrons are put in states which are "somehow" present ⇒ for correlated systems this is a dangerous picture!

A certain "filling" corresponds to a certain configuration
↳ this configuration is still highly degenerate since ε_{nl}^{MF} only depends on n and l

Let's estimate the degeneracy: p-shells

p^1 $\uparrow$ — — 6× degenerate ✓

p^2 6 for the first 5 for the second but indistinguishable $\frac{6\times5}{2} = 30/2 = 15\times$ deg.

p^3 $\frac{6\times5\times4}{2\times3} = 20\times$ deg. $\Longrightarrow$

$$\boxed{\binom{2(2l+1)}{k}}$$

l: angular momentum
k: # electrons

We will be interested in the 3d TM → assuming valence +II we find

$k=$	1	2	3	4	5	6	7	8	9
Ion	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
# deg	10	45	120	210	252	210	120	45	10

⌜The symmetry in this row can be atributed to the fact that you can make a particle-hole transformation (later more)⌟

These large degeneracies are partially lifted by the Coulomb interaction:

Full operator

$$H = \sum_{j=1}^{N}\left(-\frac{\hbar^2}{2m_e}\Delta_j - \frac{Ze^2}{r_j}\right) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|} \tag{3}$$

$$= \sum_{j=1}^{N} H^{MF}(j) + \left(\frac{1}{2}{\sum_{i\neq j}}'\frac{e^2}{|r_i-r_j|} - {\sum_j}'\left(V_{eff}(r_j) + \frac{Ze^2}{r_j}\right)\right)$$

The single particle picture sets the stage and we can treat the Coulomb repulsion $\underbrace{\text{only within partially filled shells}}$ as a first step

$\sum'$ means we replace only part of the mean-field Hamiltonian

↙ The theory as we will study here is actually not restricted to this

"Terms": Find splittings by symmetry

which makes the Hamiltonian a true many-body Hamiltonian

Hamiltonian (3) is, due to the Calomb interaction term, no longer invariant under rotations of single electrons but only the total orbital momentum

$L = \sum_{i=1}^{n} l_i$ is a conserved quantity.

$S = \sum_{i=1}^{n} s_i$ the total spin momentum

$$\Rightarrow \quad [H, L] = [H, S] = 0$$

good quantum numbers

$\Rightarrow$ Label states by means of $|L, L_z, S, S_z\rangle$

moreover $[H, L_\pm] = [H, S_\pm] = 0$ which means that the energy of the state does not depend on L_z and S_z (as long as there is no mag. field eg.)

$\Rightarrow$ Resulting levels are called "Terms" and are $(2L+1)(2S+1) \times$ deg.

These „Terms" are labeled in the form ${}^{2S+1}N_S(L)$, where

$N_S(\{1,2,3,4,5,6\}) = \{S,P,D,F,G,H,I\}$ (historic notation)

↳ In the case of a single electron in a subshell there is only one Term $L = l$ and $S = \frac{1}{2}$ and, of course, there is no Coulomb interaction ✓

↳ in a d-shell this term would be ${}^2D$

Let's now look at the configuration nl^2 ⇝ here we can use a symmetry of the Clebsch-Gordan-coefficients: Adding two equal angular momenta j (j being l or $s=\frac{1}{2}$) to total J results in eigenfunctions with

$$P_{12}|jj,JM\rangle = (-1)^{2j+J}|jj,JM\rangle$$

where P_{12} is the exchange of the particles.

⇒ Antisymmetry of the wave-function results in

Triplett ($S=1$) terms with $L = 2\lambda + 1$ $(\lambda = 0, 1, \dots, l-1)$
and
Singlett ($S=0$) terms with $L = 2\lambda$ $(\lambda = 0, 1, \dots, l)$

so for the configuration $3d^2$ we find the 5 terms

$$^3F, \ ^3P, \ ^1G, \ ^1D, \ ^1S$$

let's count:
$^3F \ (3 \times 7 = 21)$
$^3P \ (3 \times 3 = 9)$
$^1G \ (1 \times 9 = 9)$
$^1D \ (1 \times 5 = 5)$
$^1S \ (1 \times 1 = 1)$

45 states ✓

$\Rightarrow$ Coulomb-repulsion will split these Terms apart but not more (remark that "spin coupling" is included since we treat the full Coulomb operator and not a "Hubbard" U)

we found this simply by symmetry arguments!!
(we don't know the energies of those states)

For configurations with more than 2 electrons it becomes more cumbersome to find the Terms. It may even happen that terms occur more than once.

For d-shells we find the following number of terms

$k =$	1	2	3	4	5	6	7	8	9
#terms	1	5	8	16	16	16	8	5	1

↳ again we find the same symmetry in this row which we will now see is connected with the particle-hole-symmetry

Particle-hole-symmetry

$\{c_{m\mu}, c^{+}_{n\nu}\} = \delta_{mn}\delta_{\mu\nu}$ $\quad\{c_{m\mu}, c_{n\nu}\} = \{c^{+}_{m\mu}, c^{+}_{n\nu}\} = 0$

2^{nd} quantization $\quad \underset{\uparrow\ \text{anihilator}}{c_{m\mu}} \underset{\nwarrow\ \text{vacuum}}{|0\rangle_p} = 0 \quad \underset{\uparrow\ \text{creator}}{c^{+}_{m\mu}} |0\rangle_p = |m,\mu\rangle$

$m = l_z \quad \mu = s_z$

in 2^{nd} quantization the spin-operator looks like

$$\hat{S} = \sum_{m,\mu,\nu} c^{+}_{m\mu} S_{\mu,\nu} c_{m\nu} \,, \text{ were } \underline{\underline{S}} = \frac{1}{2}\underline{\underline{\sigma}} \qquad (\sigma: \text{Pauli-matrices}, \hbar = 1)$$

the orbital momentum looks like

$$\hat{L} = \sum_{m,n,\mu} c^{+}_{m\mu} L_{m,n} c_{n\mu} \,, \text{ where } L^{z}_{m,n} = m\,\delta_{m,n} \qquad \underset{\underset{L^{\pm} = L^{x} \pm i L^{y}}{\uparrow}}{L^{\pm}_{m,n}} = \sqrt{l(l+1) - mn}\;\delta_{m,n\pm 1}$$

because they fullfill the same commutation relations!

We can now make a canonical transformation from

"particle anihilator" → "hole creator" $a^{+}_{m\mu} := (-1)^{m+\frac{1}{2}-\mu} c_{-m-\mu}$ ⊛

"particle creator" → "hole anihilator" $a_{m\mu} := (-1)^{m+\frac{1}{2}-\mu} c^{+}_{-m-\mu}$

⇒ Now the "hole vacuum" $|0\rangle_h$ is the fully occupied state in the particle picture

$$|0\rangle_h = \prod_{m\mu} c^{+}_{m\mu} |0\rangle_p$$

So now $a_{m\mu} |0\rangle_h = 0$ ✓

Trafo ⊛ assures $S = \sum_{m,\mu,\nu} a^{+}_{m\mu} S_{\mu\nu} a_{m\nu}$ & $L = \sum_{mn\mu} a^{+}_{m\mu} L_{mn} a_{n\mu}$

⇒ $a^{+}_{m\mu}$ creates a hole with $L_z = m$ and $S_z = \mu$

Hund's rules I & II

The question remained how the terms that we found were split by the Coulomb repulsion...

For the ground state we have, in fact, very simple guidelines given by the famous Hunds rules:

1. maximize spin S
2. maximize orbital moment L

To understand these rules we can have a look at the expectation value of a given $|LS\rangle$ state for the Coulomb-operator

$$\langle LS | \sum_{i<j} \frac{e^2}{|r_i - r_j|} | LS \rangle = \frac{k(k-1)}{2} \int d^3x \int d^3y \, \frac{e^2}{|x-y|} \rho_{LS}(x,y)$$

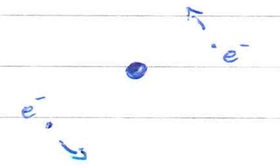
where $\rho_{LS}(x,y) = \sum_{\{s_i\}} \int d^3r_3 \ldots d^3r_k \, |\Psi_{LS}(x,s_1;y,s_2;r_3,s_3;\ldots;r_k,s_k)|^2$

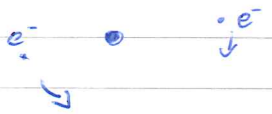
is the horribly complicated pair-correlation function

- Let's first look at the $k \leq 2l+1$ (less/equal half filled shell), then at maximal spin $|\uparrow\uparrow\ldots\uparrow\rangle$ the spin part of the wavefunktion is totally symmetric and the spatial part has to be totally antisymmetric and $\rho_{LS}(x,x) = 0$
  $\hookrightarrow$ Probability of two electrons "seeing" each other strongly surpressed.

1st rule ✓

The 2nd rule is less straight forward but can be understood with a semi-classical argument:
- At maximal $L_z = L$ the electrons "orbit" in the same direction and will less likely meet.





For more than half-filled shells we can look at the p-h trafo ⇒

Explicit form of the Coulomb-operator: Slater's integrals

At the end of the day we have to calculate

$$V^{nl}_{m_1,m_2,m_3,m_4} = \int d^3x \int d^3y \; \varphi^*_{nlm_1}(x)\, \varphi^*_{nlm_2}(y)\, \frac{e^2}{|x-y|}\, \varphi_{nlm_3}(y)\, \varphi_{nlm_4}(x) \qquad \textcircled{I}$$

inside the subshell nl $\Rightarrow$ $(2l+1)^4$ Matrixelements (625 for d-shells)

$\hookrightarrow$ can be reduced to $\underbrace{l+1 \text{ independent parameters}}_{\text{Slater's radial integrals}}$!

i) Expand to a Legendre series ($r_< = \min(|x|,|y|)$; $r_> = \max(|x|,|y|)$)

$$\frac{e^2}{|x-y|} = e^2 \sum_{\lambda=0}^{\infty} \frac{r_<^{\lambda}}{r_>^{\lambda+1}} \underbrace{P_\lambda(\cos(x,y))}_{\frac{4\pi}{2\lambda+1} \sum_{\kappa=-\lambda}^{\lambda} Y^*_{\lambda\kappa}(\Omega_x)\, Y_{\lambda\kappa}(\Omega_y)}$$

Multipole expansion (see eg Jackson classical ED)

- inserting this in Ⓘ and keeping in mind that we can factorize the wavefunctions to radial and angular parts we can see that also the integrals Ⓘ factorize to

i) radial Integrals

$$F^{\lambda} = e^2 \int_0^{\infty} dx \int_0^{\infty} dy \, \frac{r_<^{\lambda}}{r_{>+1}^{\lambda}} R_{nl}^2(x) R_{nl}^2(y) = 2e^2 \int_0^{\infty} dx \int_0^{x} dy \, \frac{y^{\lambda}}{x^{\lambda+1}} R_{nl}^2(x) R_{nl}^2(y)$$

ii) angular Integrals

$$G(l,\lambda;m_1,m_2,m_3,m_4,\kappa) = \int d\Omega_x \, Y_{lm_1}^*(\Omega_x) Y_{\lambda\kappa}^*(\Omega_x) Y_{lm_4}(\Omega_x)$$
$$\times \int d\Omega_y \, Y_{lm_2}^*(\Omega_y) Y_{\lambda\kappa}(\Omega_y) Y_{lm_3}(\Omega_y)$$

⇒ angular Integrals contain powerfull selection rules ⟹

Products of the form $Y^*_{l m_i} Y_{l m_j}$ are even and orthogonal to Spherical harmonics with $\lambda > 2l$

$$\Rightarrow \quad \lambda \text{ even} \quad \& \quad \lambda \leq 2l$$

Moreover the angular Integrals can be seen as addition of angular momenta and they can be expressed with Clebsch Gordan coeff. $\langle j_1 j_2 m_1 m_2 | J M \rangle$

$$\Rightarrow \quad G(l,\lambda; m_1, m_2, m_3, m_4, |\xi) = \langle l \lambda m_1 \xi | l m_4 \rangle \langle l \lambda m_3 \xi | l m_2 \rangle \cdot \underset{\uparrow}{M(l,\lambda)} \frac{1}{4\pi}$$

reduced matrix element only depending on λ and l

For d-electrons: $M(2,0) = 1 \quad M(2,2) = \frac{10}{7} \quad M(2,4) = \frac{18}{7}$

$\Rightarrow$ the angular part is completely analytical !

$$V^{nl}_{m_1,m_2,m_3,m_4} = \sum_{\lambda=0}^{l} \frac{F^{2\lambda}}{4\lambda+1} \sum_{\xi=-2\lambda}^{2\lambda} M(l,2\lambda) \langle l\,(2\lambda)\,m_1\xi \,|\, l m_4\rangle \langle l(2\lambda) m_3\xi \,|\, l m_2\rangle$$

⇒ as promised we remain with only three Slater-Integrals for a d-shell F^0, F^2, F^4 (for p-shells F^0, F^2; for f-shell F^0, F^2, F^4, F^6)

in 2^{nd}-Quant.
$$V^{nl}_{Coul} = \frac{1}{2} \sum_{\substack{m_1,m_2,m_3,m_4 \\ \mu,\nu}} c^{+}_{m_1\mu}\, c^{+}_{m_2\nu}\, V^{nl}_{\{m_i\}}\, c_{m_3\nu}\, c_{m_4\mu}$$

(the splitting is completely part-hole sym.)

it is easy now to understand F^0 since $\langle l0m0|ln\rangle = \delta_{mn}$
→ for k-electrons it will simply enhance the configuration energy
but it will not splitt the terms
(it is the "monopole" part) $\frac{1}{2}F^0 \cdot k(k-1)\,\mathbb{1}$ (i.e. it is a constant shift)

but also the other Slater integrals contribute to the averaged configuration energy

$$\langle C_{nl^k}\rangle = \underbrace{\left(F^0 - \frac{2}{63}\left(F^2+F^4\right)\right)}_{\text{Compare this to the Hubbard } U} \frac{k(k-1)}{2}$$

- Slater integrals can be evaluated with the radial wavefunctions from Hartree-Fock calculations.

- Keep in mind that we only treated the Coulomb interaction within a subshell ! If there are close by other configurations the Coulombic matrix elements can mix them in (if parity is conserved!)

  in atomic Cr or Cu you find as ground-state configurations

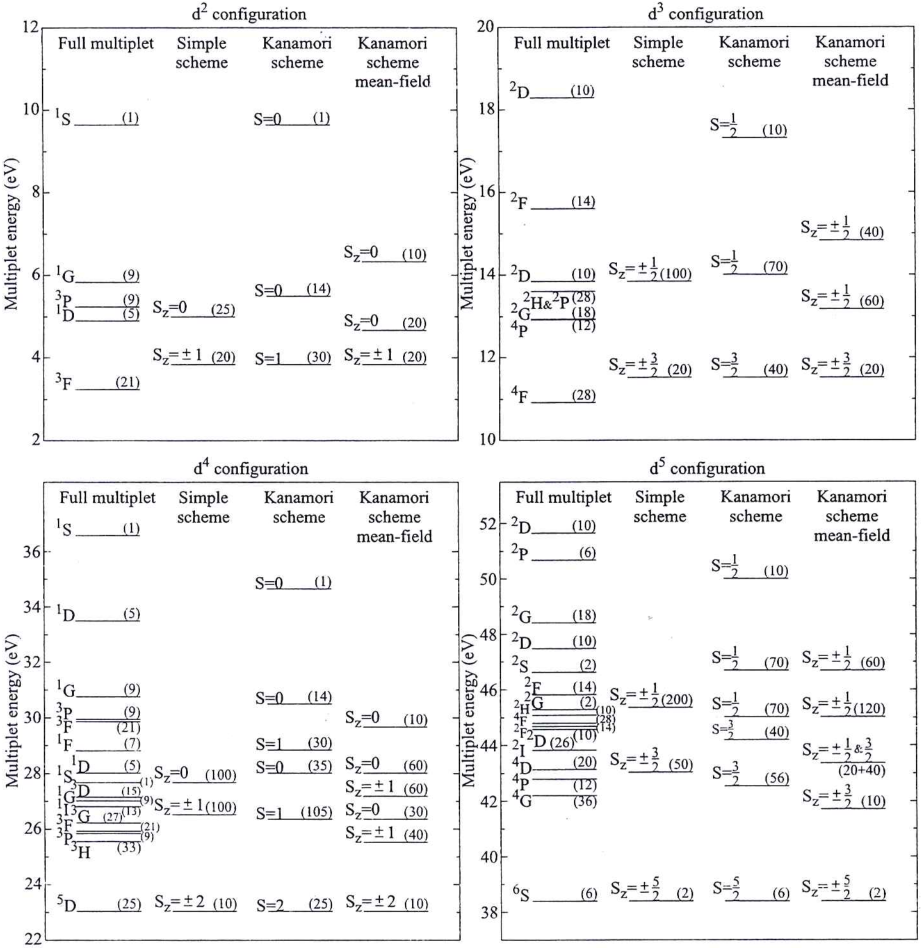
  $3d^5 4s^1$ and $3d^{10} 4s^1$ This is a result of Coulomb interaction!

Remark for experts:

Always be aware of the difference between the model Hamiltonian (possibly of Hubbard type) and the full multiplett structure. Ground state properties work nice most of the time but watch out when it comes to spectroscopy!

! Also extremely important: multiplett structure is NOT screened away! only the monopol part (corresponding to "U") can be effectively screened but not F^2 and F^4 or "J"

Comparison of Full multiplet structure to simple schemes (spherical)



taken from Maurits Haverkort PhD-thesis

Full multiplett : as we discussed

Simple scheme : Hubbard U
Hund's coupling J_H

Kanamori : U, U', J, J'

Kanamori MF : Kanamori Hamiltonians calculated in Hartree Fock approx.

Remark : Sometimes even ground state properties can depend on the scheme : spin-states in Cobaltates