

Transition Metal Oxides

①

"3d"
LaTiO₃ "Mott" Insulator. Insulator
when band theory says metal.
LaMnO₃: "Parent compound" "CMR" manganites
"Orbital Order"
La₂CuO₄: Mott Insulator. "Parent" compound"
High T_c Superconductors

"4d"
Sr₂RuO₃ Ferromagnet. Not understood
optical properties
Sr₃Ru₂O₇ Very nearly ferromagnetic.
"Metamagnetic" transition
Sr₂RuO₄ Triplet Superconductor

"5d" Largely unexplored

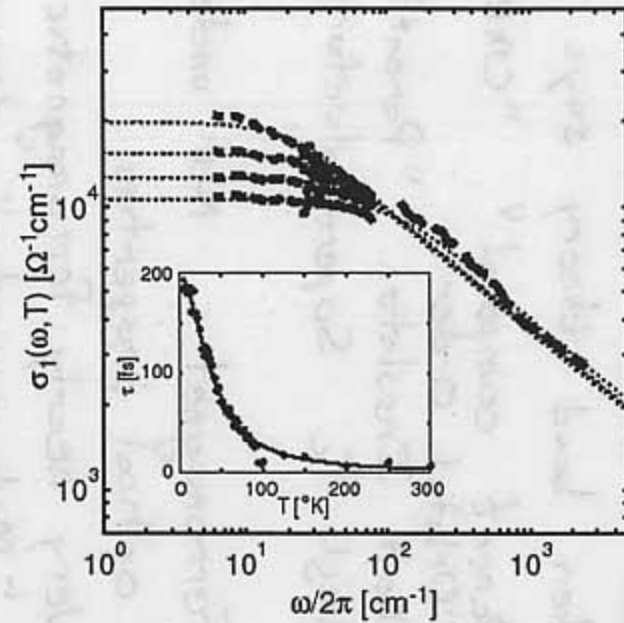
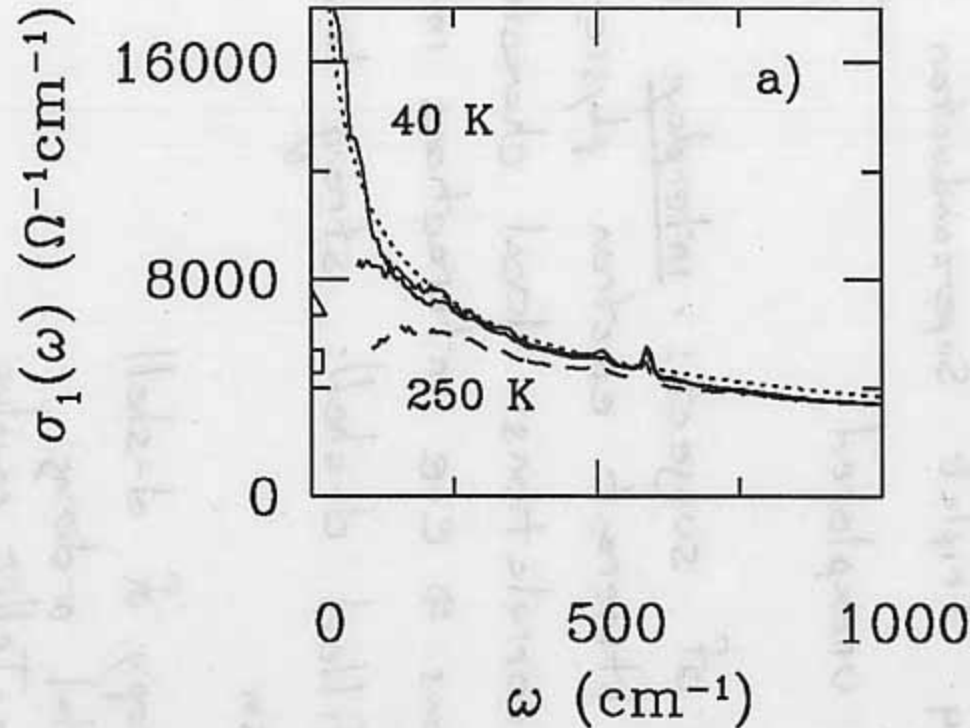
— Fig 1
(Ru oxides)

Interest of subject: interplay: local
moment + itinerant electron physics

- Strong correlations: local character of
d electrons \Rightarrow e-e interactions important
- Partly filled d-shell: strong tend. \rightarrow
magnetism
- anisotropy of d-shell
 - orbital ordering
 - Jahn-Teller coupling
 - Anisotropic conductivity (quasi 2d)

SrRuO₃: fractional power law conductivity

3



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Non-Fermi-Liquid Behavior of SrRuO₃: Evidence from Infrared Conductivity

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Fractional power-law conductivity in SrRuO₃ and its consequences

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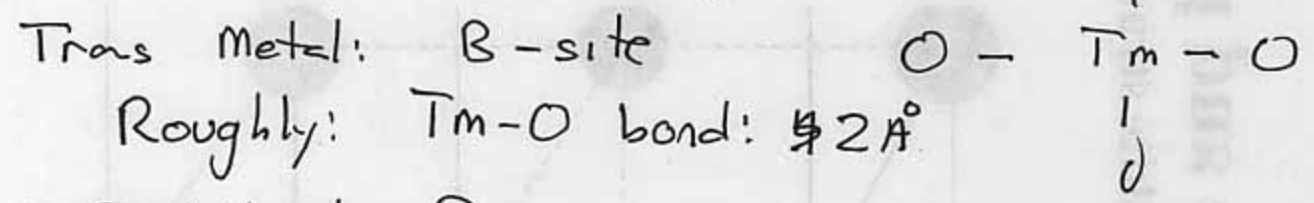
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(Date: July 10, 2003)

- These lectures:
- underlying physics of TMO
 - * \Rightarrow interaction physics of transition metal
 - relation: simple models + reality
 - Conceptual / computational technique "Dynamical Mean Field" method

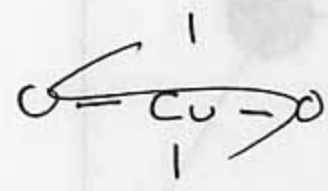
o Crystal Structure: variant of ABO_3 perovskite

- Simple perovskite: ~~Tm on B-site.~~ \rightarrow crystal str
- A, B interpenetrating cubic lattices



~~Ruddlesden-Popper~~

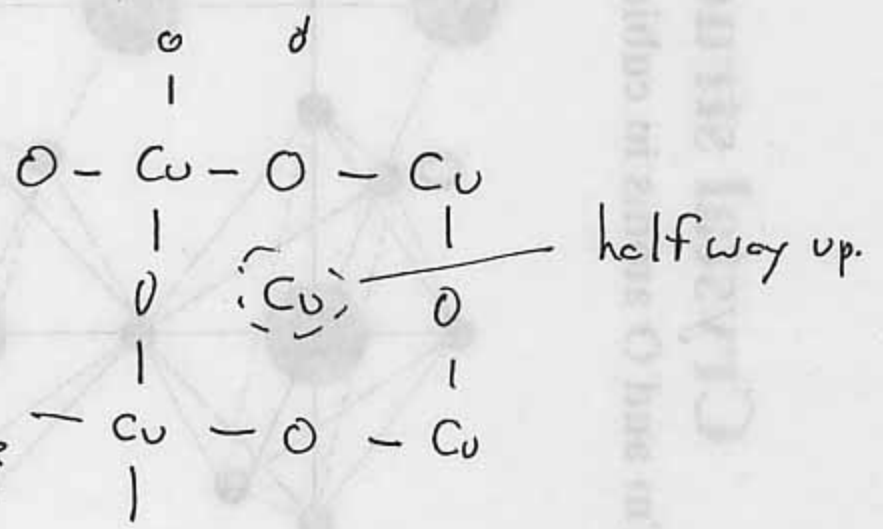
- Layered: La_2CuO_4 Sr_2RuO_4



Side view

Cu - displaced into pyro

Cu - O - Cu $\frac{1}{2}$ lattice const



Crystal structure and phase diagram

Tm and O atoms in cubic perovskite structure with doubled unit cell.

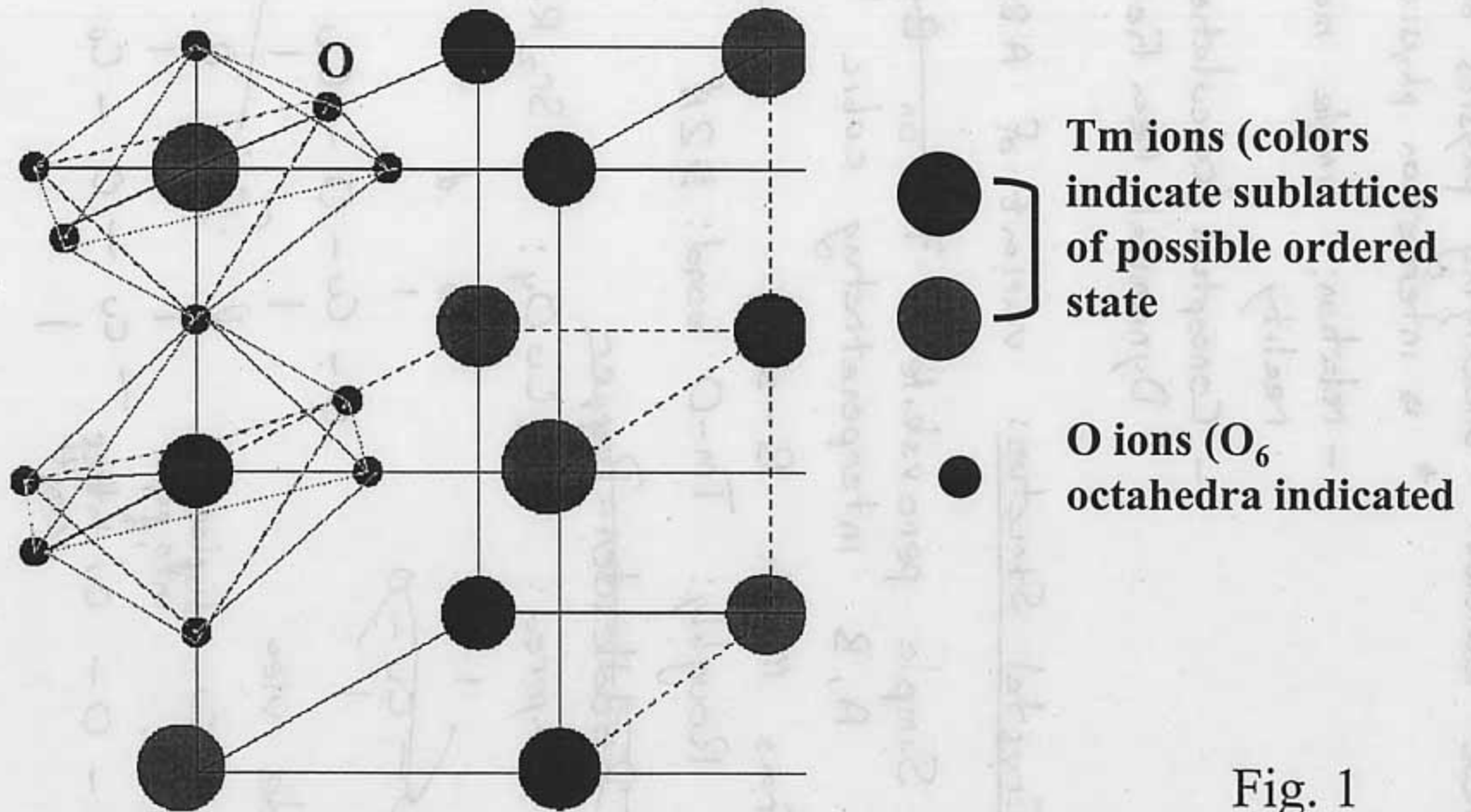


Fig. 1

Table 8-3

Radius of maximum radial charge density for the various wave functions of the light atoms as determined by self-consistent-field calculations. Since such calculations have been made for relatively few atoms, many of the values tabulated are interpolated but are believed to be fairly accurate. Values are given in angstroms.

	1s	2s	2p	3s	3p	3d	4s	4p
H	0.53							
He	0.30							
Li	0.20	1.50						
Be	0.143	1.19						
B	0.112	0.88	0.85					
C	0.090	0.67	0.66					
N	0.080	0.56	0.53					
O	0.069	0.48	0.45					
F	0.061	0.41	0.38					
Ne	0.055	0.37	0.32					
Na	0.050	0.32	0.28	1.55				
Mg	0.046	0.30	0.25	1.32				
Al	0.042	0.27	0.23	1.16	1.21			
Si	0.040	0.24	0.21	0.98	1.06			
P	0.037	0.23	0.19	0.88	0.92			
S	0.035	0.21	0.18	0.78	0.82			
Cl	0.032	0.20	0.16	0.72	0.75			
A	0.031	0.19	0.155	0.66	0.67			
K	0.029	0.18	0.145	0.60	0.63		2.20	
Ca	0.028	0.16	0.133	0.55	0.58		2.03	
Sc	0.026	0.16	0.127	0.52	0.54	0.61	1.80	
Ti	0.025	0.150	0.122	0.48	0.50	0.55	1.66	
V	0.024	0.143	0.117	0.46	0.47	0.49	1.52	
Cr	0.023	0.138	0.112	0.43	0.44	0.45	1.41	
Mn	0.022	0.133	0.106	0.40	0.41	0.42	1.31	
Fe	0.021	0.127	0.101	0.39	0.39	0.39	1.22	
Co	0.020	0.122	0.096	0.37	0.37	0.36	1.14	
Ni	0.019	0.117	0.090	0.35	0.36	0.34	1.07	
Cu	0.019	0.112	0.085	0.34	0.34	0.32	1.03	
Zn	0.018	0.106	0.081	0.32	0.32	0.30	0.97	
Ga	0.017	0.103	0.078	0.31	0.31	0.28	0.92	1.13
Ge	0.017	0.100	0.076	0.30	0.30	0.27	0.88	1.06
As	0.016	0.097	0.073	0.29	0.29	0.25	0.84	1.01
Se	0.016	0.095	0.071	0.28	0.28	0.24	0.81	0.95
Br	0.015	0.092	0.069	0.27	0.27	0.23	0.76	0.90
Kr	0.015	0.090	0.067	0.25	0.25	0.22	0.74	0.86

in wave mechanics from Eq. (7-22), in which the wave function is a function of $x = 2Zr/n$, so that the radius is inversely proportional to Z . With the shielding taken into account, we should expect that the size of the orbit should be equal to that of a corresponding hydrogenic orbit, divided by $Z - s$, where s is a shielding constant. In Table 8-1, we have

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There is one
from Table 8-3.
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reason for the dis
functions for the
different shapes.
groups of element
they are easily rem

everywhere

PROBLEMS

1. The helium atom, with two electrons, can be approximated fairly well by the self-consistent-field method, replacing the wave function of each electron by a hydrogen-

Wave Function values of $Z - s$ which
this way, for the 1s, 2s, and 2p orbits
quite different from the effective Z
the explanation of this discrepancy
this does not affect the fact that in
a radius which is approximately
a suitably chosen shielding con-
we get to $Z = 100$, the size of the
as in hydrogen, has shrunk to

as we go to higher atomic num-
dated inside an atom of about
electronic shell of the alkali
as we go from lithium to
In other words, the atoms
periodic table. Neverthe-
this is possible because
the same thing is observed
vs. For instance, in a
assuming that they act
the estimates of atomic
the figures of Table
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d the radii observed
radii of Table 8-3,
going from light to
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same function will behave properly both at $r = 0$ and at infinite r . This latter procedure is recommended by Hartree.

It is possible, in other words, to calculate the wave functions with quite moderate effort. They must be normalized, which can be done by Simpson's rule, and we then have the functions $P_{nl}(r_i)$ for one stage of the approximation. We next carry out the integrations necessary to get the functions $Y_0(n, l, r_i)$ from Eq. (9-20), by using Simpson's rule, and are ready to start another stage of the process. Detailed techniques for handling this procedure have been described by Hartree.¹ As we have stated before, the process can be made to converge by a considerable but quite finite amount of labor, and as we have indicated in Chap. 8 and Appendix 16, calculations have been made for a good many atoms, both by this method and by the Hartree-Fock method, which we have mentioned earlier, and which is somewhat more accurate, though not different in its fundamental concepts from the scheme we have been describing.

We must remember that a slightly different Schrödinger equation is solved for each orbital: the potential in each case is that of the nucleus and the spherically averaged potential of all orbitals except the one which is being calculated. Thus the ordinary proof of orthogonality does not apply. Two u_i 's corresponding to different l values will automatically be orthogonal on account of their functions of angle, but functions of the same l value will not be quite orthogonal. For some purposes involving the calculation of multiplet structure, according to methods which we shall discuss later, it is highly desirable to use orthogonal orbitals. In this case, the usual method of procedure, not an entirely satisfactory one, has been to make orthogonal linear combinations of the Hartree functions, using the Schmidt orthogonalization technique. For instance, for the s functions, one uses the $1s$ function; a linear combination of $1s$ and $2s$, chosen to be orthogonal to $1s$; a linear combination of $1s$, $2s$, and $3s$, chosen to be orthogonal to $1s$ and $2s$; and so on. This difficulty is not met with the Hartree-Fock method. In that method, though, as with Hartree's method each electron still moves in a different potential, nevertheless things are so arranged that the orbitals are automatically orthogonal to each other.

9-5. Examples of Calculation by the Self-consistent-field Method.

We now wish to illustrate the sort of results obtained by the self-consistent-field method, and as an example, we give in Fig. 9-2 the radial wave functions calculated by the Hartree-Fock method for Cu^+ , by Hartree and Hartree.² This is the heaviest atom for which the Hartree-Fock calculation has been carried out. For comparison, in Fig. 9-3 we

¹ D. R. Hartree, "The Calculation of Atomic Structures," John Wiley & Sons, Inc., New York, 1957.

² D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)*, A157:490 (1936).

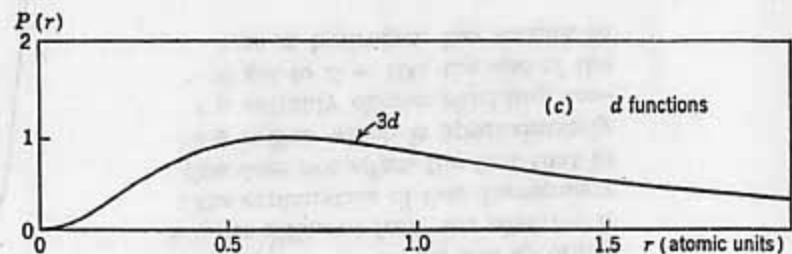
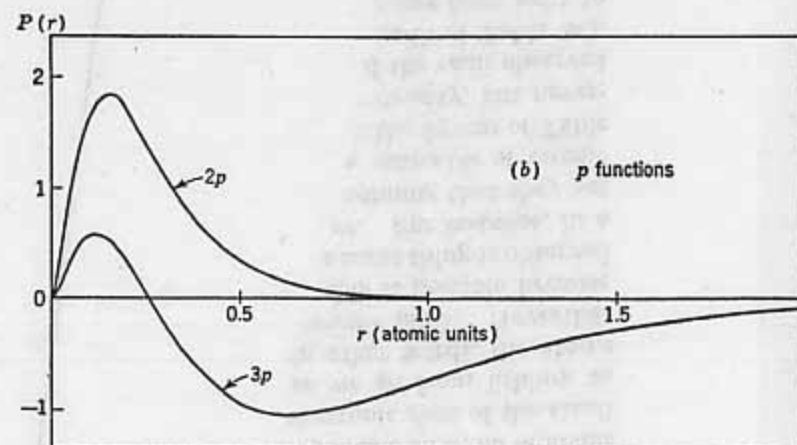
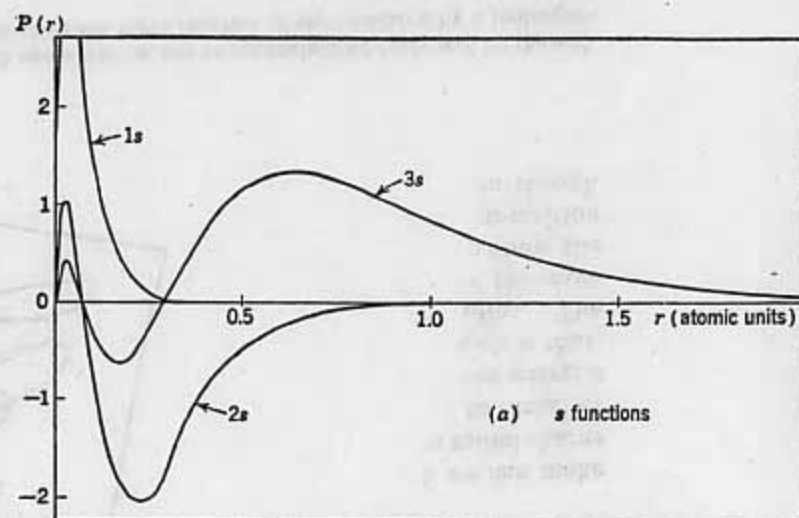


FIG. 9-2. Radial wave functions $P_{nl}(r)$ for Cu^+ , as determined by the Hartree-Fock method by Hartree and Hartree.

Key Feature of TMO- d electrons.

(3)

Recall atomic physics - build up atoms

H: $1s$ $\psi(r) \sim e^{-r/a_B}$ a_B : Bohr radius
 $S_{el} = 1/2$ 0.5 \AA

He: $1s^2$ Size a little larger: mutual repulsion
 $S=0$ (filled shell)

- excited states: $1s' 2p'$

Li: $1s^2 2s'$ (pays to put 2nd el in 2s not?)
 $1s' 2s'$

Note: 2s must be orthogonal to 1s \Rightarrow sits further out from nucleus ψ

Be: $1s^2 2s^2$

B: $1s^2 2s^2 2p^1 \dots B$

C, N, O, F Fill up 2p-shell! Ne

Na Mg Al Si P S Cl Ar. Fill 3s, then 3p

K $4s^1$ Ca $4s^2$ Sc $3d^1 4s^2$ Ti V Cr Mn Fe Co Ni Cu Zn
Fill 3d shell, keeps $4s^2$

3d: 1st time fill up d shell.

Can sit close to nucleus; doesn't have to be \perp to other orbitals

(but not too close) - centrifugal barrier

Typical size of d-orbitals, $.5 - .3 \text{ \AA} \approx a_B$

d's sit inside $4s$, but \approx as strongly bound well
 $r_{4s} \approx 1 \text{ \AA}$

4d

Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd

4d must be \perp 3d \Rightarrow wave fn larger (relatively)
 \Rightarrow more delocalized. Bigger hyb

3d: 1st fill 4f shell.... even more deloc.

Expect: 3d: more localized behavior

4d: more itinerant behavior

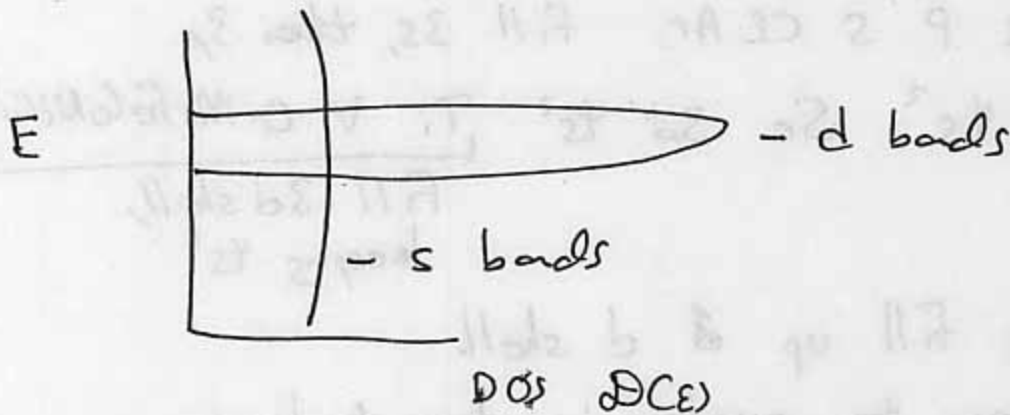
Ni, Co F.M. ~~Co~~, Rh, Pd. Not (maybe near)

Make atoms into solid: - Reminds tight binding

(1) s & 4s s: Very spread out: delocalize

\Rightarrow ~~very~~ very broad bands 10eV

(2) d: small - narrow band, high DOS



Where is Fermi level: - in d-bands

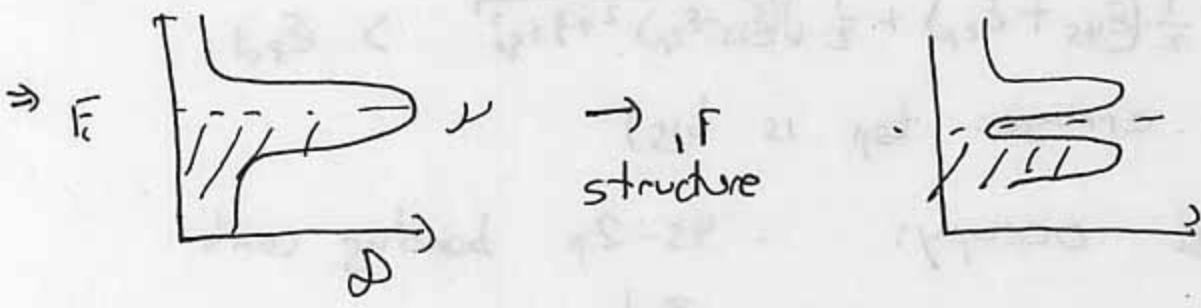
idea: 3 4s²; Filled shell.

But hyb. big \Rightarrow broad band. - some

4s go far up in energy \Rightarrow want to dump
some e⁻ in d: but typically not too much - counts

- Obvious point: arrangement of atoms in crystal \Rightarrow structure in DOS.

xx Very xx rough estimate: $E = \int d\epsilon \epsilon D(\epsilon)$



Gain energy (filled states \downarrow)

\Rightarrow very often in band theory of T.M. compounds: chemical potential in or near DOS minimum [interesting consequence for Stoner Theory]

- Transition Metal Oxides: O is very electronegative
 Wants to grab 2 e^- O_{3s}
 Simple picture $3d$ $4s$ O_{2p}

Simple H: $\epsilon_{3d} d^\dagger d + \epsilon_{4s} s^\dagger s + \epsilon_{O_{2p}} p^\dagger p$
 $- t_{dp} (d^\dagger p + hc) - t_{sp} (s^\dagger p + hc)$

Matrix: $H = \begin{bmatrix} \epsilon_{3d} & & t_{dp} \\ & \epsilon_{4s} & t_{sp} \\ t_{dp} & t_{sp} & \epsilon_{2p} \end{bmatrix}$

$t_{sp} \gg t_{dp}$. Set $t_{dp} = 0$

Eigenvalues: $\epsilon_{3d} = \frac{1}{2} (\epsilon_{4s} + \epsilon_{2p}) \pm \sqrt{(\epsilon_{4s} - \epsilon_{2p})^2 + 4t_{sp}^2}$

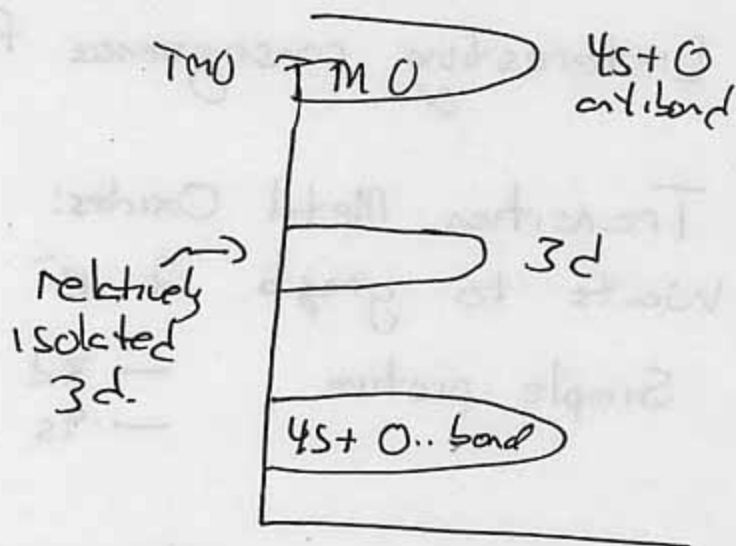
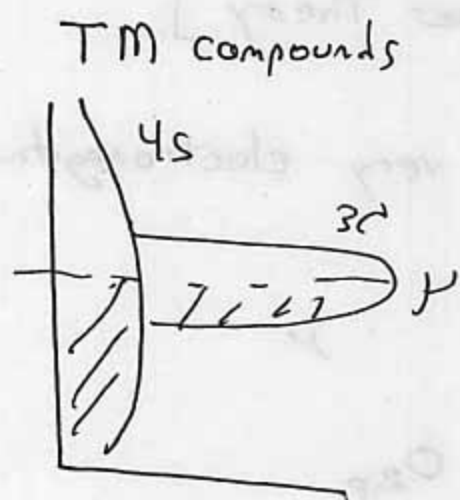
\Rightarrow if $\frac{1}{2} (\epsilon_{4s} + \epsilon_{2p}) + \frac{1}{2} \sqrt{(\epsilon_{4s} - \epsilon_{2p})^2 + 4t_{sp}^2} > \epsilon_{3d}$

easy to arrange: t_{sp} is big)

then ~~part~~ occupy:
• 4s-2p bonding comb
• 3d

even though in atom 3d is higher

— This is (roughly) what happens in TMOs



Picture grossly oversimplified
Will see real band theory later

- Next point: relative electronegativity of Tm rel to O decreases as move across Tm row.

Sc, Ti: d "far" from 4s/O bonding

Mn \rightarrow Cu d "near" to 4s/O bonding

- Key gn: what do you mean by density of states (7)

① Density as function of chemical potential: $n(\mu)$

$$\Rightarrow \mathcal{D}(\epsilon) = \left. \frac{dn}{d\mu} \right|_{\mu=\epsilon}$$

$$\text{B } F = E - \mu N \Rightarrow E - \int d^3r \mu(r) n(r) \Rightarrow \text{local dos } \frac{\delta E}{\delta \mu(r)}$$

② 1 electron removal spectrum $T=0$

$\epsilon_{\text{pos}} \rightarrow c_{\alpha} \cdot$ removes 1 electron from normalized state (soln of some single particle schrodinger eq)
 $\phi_{\alpha}(r)$

$$G_{\alpha\alpha'}(t) = -i \langle T c_{\alpha}(t) c_{\alpha'}^{\dagger}(0) \rangle$$

$\langle \rangle =$ ground state expectation value.

T : time ordering symbol. $t > 0 \Rightarrow T c_{\alpha}(t) c_{\alpha'}^{\dagger}(0)$

$$= c_{\alpha}(t) c_{\alpha'}^{\dagger}(0)$$

$$t < 0 \Rightarrow T c_{\alpha}(t) c_{\alpha'}^{\dagger}(0)$$

$$= -c_{\alpha'}^{\dagger}(0) c_{\alpha}(t)$$

Write $G_{\alpha\alpha'}$ in basis of exact eigenstates of problem

$|n\rangle$: energy E_n

Define: E_{α} & $E_{\alpha'}$

~~$$G_{\alpha\alpha'}(t) = -i \langle 0 | c_{\alpha} | n \rangle \langle n | c_{\alpha'}^{\dagger} | 0 \rangle$$~~

$$G_{\alpha\alpha'}(t > 0) = -i \sum_n \langle 0 | e^{+iHt} c_{\alpha} e^{-iHt} | n \rangle \langle n | c_{\alpha'}^{\dagger} | 0 \rangle$$

$$G_{\alpha\alpha'}(t > 0) = -i \sum_{n_e} e^{-i(E_{n_e} - E_0)t} B_{n_e\alpha}^* B_{n_e\alpha'} \quad B_{n_e\alpha} = \langle n | c_{\alpha} | 0 \rangle$$

$$G_{\alpha\alpha'}(t < 0) = +i \sum_{n_h} e^{i(E_{n_h} - E_0)t} B_{n_h\alpha}^* B_{n_h\alpha'} \quad B_{n_h\alpha} = \langle n | c_{\alpha}^\dagger | 0 \rangle$$

Note: distinguish "electron" (particle addition) states, reachable by adding e^- to s , "hole" states, reachable by removing

Define:
$$G_{\alpha\alpha'}(\omega) = \int_0^{\infty} dt e^{i\omega t - \varepsilon t} G_{\alpha\alpha'}(t) + \int_{-\infty}^0 dt e^{i\omega t + \varepsilon t} G_{\alpha\alpha'}(t)$$

ε : infinitesimal convergence factor put to make ints converge

$$G_{\alpha\alpha'} = \sum_{n_e} \frac{B_{n_e\alpha}^* B_{n_e\alpha'}}{\omega - (E_{n_e} - E_0) + i\varepsilon} + \sum_{n_h} \frac{B_{n_h\alpha}^* B_{n_h\alpha'}}{\omega + (E_{n_h} - E_0) - i\varepsilon}$$

$$\text{Im } G_{\alpha\alpha'} = \pi \sum_{n_e} B_{n_e\alpha}^* B_{n_e\alpha'} \delta(\omega - (E_{n_e} - E_0)) - \pi \sum_{n_h} B_{n_h\alpha}^* B_{n_h\alpha'} \delta(\omega + (E_{n_h} - E_0))$$

Spectral function: same thing with a +

i.e.
$$\text{Im } G_{\alpha\alpha'}^R = \sum_{n_e} \frac{B_{n_e\alpha}^* B_{n_e\alpha'}}{(\omega - E_{n_e} - E_0 - i\varepsilon)} + \sum_{n_h} \frac{B_{n_h\alpha}^* B_{n_h\alpha'}}{(\omega + E_{n_h} - E_0 - i\varepsilon)}$$

• Mathematics: define $G_{\lambda\lambda'}(z)$ \hookrightarrow complex

$$G_{\lambda\lambda} = \sum_{n_e} \frac{-B_e^2}{z - (E_{n_e} - E_0)} + \sum_{n_h} \frac{B_h^2}{z - (E_{n_h} - E_0)}$$

G: analytic, $\text{Im } z \neq 0$ singularities at z real.

diff G: diff choices abt decay with sus

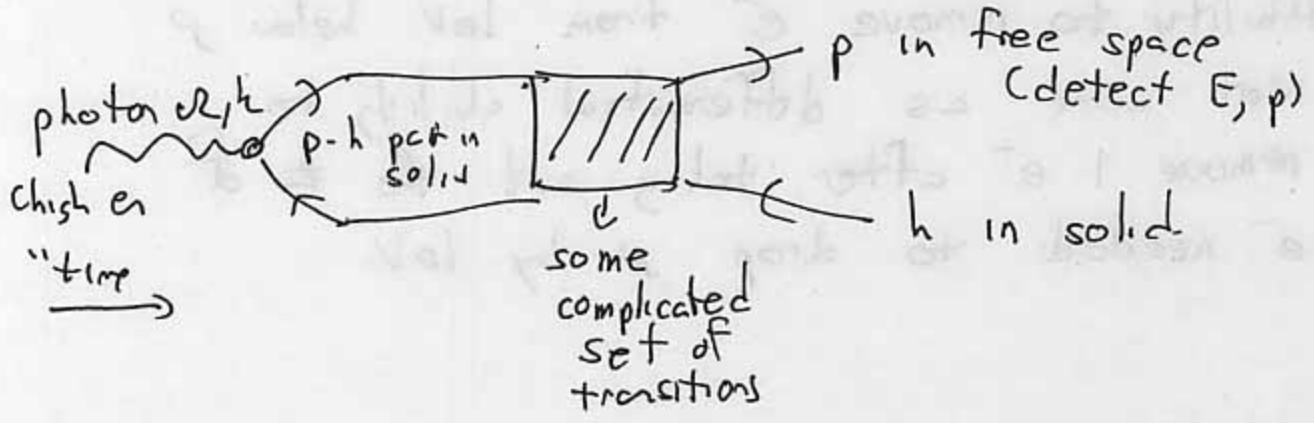
• Very convenient: consider z purely imaginary

$$z = (2n+1)i\pi T \quad \rightarrow \text{temperature}$$

\Rightarrow G in "imaginary time": nice analytical properties
($e^{iE_n t} \rightarrow e^{-E_n \tau}$)

• Physics - Photoemission photon in electron out

typically: complicated + ill-understood intermediate states; final state ~~transfer~~ straight forward



\Rightarrow Idea: if $\omega - E$ is small, \square is index of $\omega - E$
 \Rightarrow ampl. of getting $p \Rightarrow M_{\omega} C_{p-\hbar k} \Rightarrow \text{signal} \sim \text{Im } G_{\lambda\lambda}$

Spectral function $A_{\lambda\lambda'}$ (ν).

$\omega > 0$: peaks at electron addition levels
 $\omega < 0$: peaks at electron removal levels

Amplitudes: overlaps of states $\lambda\lambda'$ with ground state

Isolated

Atom: series of lines: electron ~~removal~~ removal energies

Solid: continuum: broadened peaks & conn to atomic removal energies

Measurable: photoemission: reasonably good
- removal levels

inverse photoemission: addition:
not so easy

Points: non-interacting system: $\frac{dn}{d\nu}$ same as $A(\omega)$

Interacting system: not same - energetics changes as you change occupancy.

Ability to remove e^- from level below μ
Not same as differential ability to remove 1 e^- after taking out the # of e^- needed to drop μ by level.

Simple example: already covered by Cox

Anderson Impurity Model

$$H = - \sum_{p\sigma} \epsilon_p c_{p\sigma}^\dagger c_{p\sigma} + \sum_p V (c_{p\sigma}^\dagger d_\sigma + hc) + \epsilon_d d_\sigma^\dagger d_\sigma + U n_{d\uparrow} n_{d\downarrow}$$

Solution: discussed in detail in Mahan

Here: simple approach via functional integral

Ex rederive via eqn of motion

$$Z = \int \mathcal{D}c^\dagger c \mathcal{D}d^\dagger d \exp \int_{\beta}^0 [\partial_\tau - H] d\tau$$

Contains some c into c-source $\eta_c^\dagger + \eta_c$

Action in ω -space:

$$c_p^\dagger d_p \begin{pmatrix} i\omega - \epsilon_p & V \\ V & i\omega - \epsilon_d \end{pmatrix} \begin{pmatrix} c_p \\ d_p \end{pmatrix} + U n_{d\uparrow} n_{d\downarrow}$$

Shift: $c_p \rightarrow c_p - \frac{V}{i\omega - \epsilon_p} d_p \Rightarrow$ c's decouple (Z_{imp})

$$Z = Z_c \cdot \int \mathcal{D}d^\dagger d \exp \left[d^\dagger \left[i\omega - \epsilon_d - \sum_p \frac{V_p^2}{i\omega - \epsilon_p} \right] d \right] + U n_{d\uparrow} n_{d\downarrow}$$

"self energy". Expresses physics that d can go into c-electron bath \rightarrow some form as unper. c- but contains some d-correl. (exp. of op. like $d^\dagger d$)

Shift not ~~innocent~~ as innocent as it seems. To obtain c-electron Green function, must introduce "source term" ηc_p^\dagger

Shift: $\eta c_p^\dagger \rightarrow \eta \left(c_p^\dagger - \frac{V d^\dagger}{i\omega - \epsilon_p} \right) + \frac{\eta V d^\dagger}{i\omega - \epsilon_p}$

\Rightarrow some of what we calculate from shifted partition fn Z_{imp} is actually c-c correlation

Non-interacting:

$$F_{imp} = kT \ln Z_{imp} = \sum_{\sigma} \int \frac{d\epsilon}{\pi} f(\epsilon) \tan^{-1} \left[\frac{\text{Im} \Sigma(\epsilon)}{\epsilon - \epsilon_d - \text{Re} \Sigma(\epsilon)} \right]$$

$$\Rightarrow \delta n_{imp} = - \frac{\delta F}{\delta \mu} \Big|_{T=0} = \sum_{\sigma} \frac{1}{\pi} \tan^{-1} \frac{\text{Im} \Sigma(\mu)}{\mu - \epsilon_d - \text{Re} \Sigma(\mu)} \quad \text{"Friedel sum rule"}$$

But

$$N_d = \int \frac{d\epsilon}{\pi} f(\epsilon) \frac{\text{Im} \Sigma(\epsilon)}{(\epsilon - \epsilon_d - \text{Re} \Sigma)^2 + \text{Im} \Sigma^2}$$

$\neq N_{imp}$ unless $\text{Im} \Sigma(\epsilon) = \text{const.}$
 $\text{Re} \Sigma(\epsilon) = \text{const.}$

Difference: effect of impurity on c's

" d-electron Greens function

$$G_{dd}^{\sigma} = \langle T d_{\sigma}^{\dagger}(0) d_{\sigma}(0) \rangle$$

Imp result: General express E as functional of G_{dd} (11)

$$N_d = \int \frac{d\omega}{\pi} \text{Im } G_{dd}$$

$$E_d = \int d\omega \omega \text{Im } G_{dd}(\omega)$$

U=0

$$G_{dd} = \frac{1}{\omega - \epsilon_d - \Sigma_d^{(0)}(\omega) - i\Gamma}$$

$$\Sigma_d^{(0)}(\omega) = \sum_p \frac{V_p^2 \delta(\omega - \epsilon_p)}{\omega - \epsilon_p - i\epsilon}$$

[Non-interacting formula]

$$\text{Im } \Sigma_d = \pi \sum_p V_p^2 \delta(\omega - \epsilon_p)$$

$\sim \pi N_0 V^2$ (if not much STR in ϵ_p)

IF V_0 not too big, ..

$$\text{Im } G_{dd} \sim \frac{\Gamma}{(\omega - \epsilon_d^*)^2 + \Gamma^2}$$

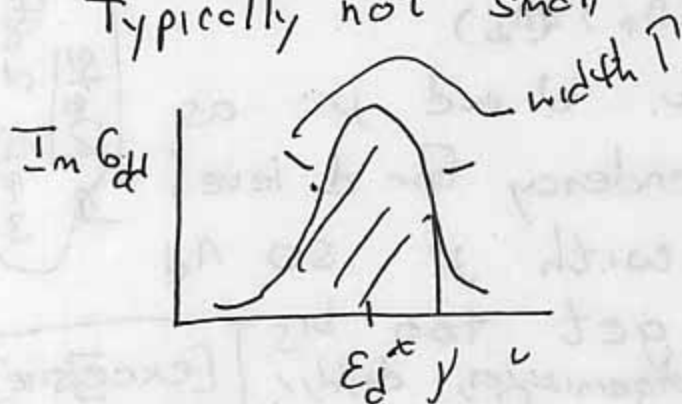
$$\Gamma = \text{Im } \Sigma_d^{(0)}(\omega = \epsilon_d^*)$$

$$\epsilon_d^* : \omega = \text{Re } \Sigma(\omega)$$

Soln of $\epsilon_d^* : \omega = \epsilon_d + \text{Im } \Sigma(\omega)$
 $\omega - \text{Re } \Sigma(\omega) = \epsilon_d$

$\Rightarrow \epsilon_d^*$: shift of level by coupling to solid.

Typically not small



Non-interacting:

Removal/addition spectrum "same" as $dn/d\epsilon$ (up to c-band part)

Note: $Z_{TOT} = Z_c Z_{imp} \Rightarrow F_{TOT} = kT \ln Z_{TOT} = F_c + F_{imp}$

hypothetical F of cond band w/ no impurity

F of impurity - coupled: ie. extra F due to imp

Hartree-Fock (v. easy to implement in Mathematica)
(here \equiv Hartree)

$$\epsilon_d \rightarrow \epsilon_{d\sigma} = \epsilon_d + U \langle n_{\bar{\sigma}} \rangle \quad (\bar{\sigma} \text{ is opp spin to } \sigma)$$

$$\Rightarrow \text{Egs} \quad n_{\uparrow} = \int \frac{d\nu}{\pi} \text{Im} \frac{1}{\omega - \epsilon_d - U n_{\downarrow} - \Sigma(\omega)}$$

$$n_{\downarrow} = \int \frac{d\nu}{\pi} \text{Im} \frac{1}{\omega - \epsilon_d - U n_{\uparrow} - \Sigma(\omega)}$$

Cesp. simple + relevant to thinking about simple metals: $\Sigma(\omega) \rightarrow i\Gamma$

Also amusing to consider structure in conduction band: e.g. V const, $\int (ct)^2 f(\nu - \epsilon_p)$

\Rightarrow HF: add (spdep) ω -indep term to Σ $= \sqrt{4t^2 - \omega^2} \text{ for } |\omega| < 2t$

Roughly: HF solns: shifted resonance.

2 classes: unpolarized: $\langle n_{\uparrow} \rangle = \langle n_{\downarrow} \rangle$

of soln

Interplay betw. U and μ : as charge μ : tendency for d level to float with μ so n_d does not get too big

Note as $\omega \rightarrow \mu$, 2 ddfs spec

\Rightarrow diff betw. photoemission, d/d, [exercise]

Band situation: high density of impurities

- each d you expel from impurity must go into band \Rightarrow raises $\mu \Rightarrow$ makes it less likely to expel next imp. More tendency of d to "float" with μ . \Rightarrow Why, in mag. TM, TMO, d bands partly filled, near FS

Simple case $\epsilon(\omega) = i\Gamma$ $\epsilon_d = 0$

$$n = 2 \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\Gamma}{(\omega - U_n)^2 + \Gamma^2} \Rightarrow n = \frac{2}{\pi} \tan^{-1} \frac{\Gamma}{\mu - U_n}$$

$$= \frac{2}{\pi} \left(1 + \frac{2}{\pi} \tan^{-1} \frac{\mu - U_n}{\Gamma} \right)$$

Mathematica: $n(\mu, U)$

or $\frac{dn}{d\mu} = \cancel{2 \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{2\Gamma}{(\mu - U_n)^2 + \Gamma^2}} + \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{2U_n \Gamma (\omega - U_n) n \frac{dn}{d\mu}}{((\omega - U_n)^2 + \Gamma^2)^2}$

$$\frac{dn}{d\mu} \left[1 + \frac{2U_n}{\pi} \frac{\mu - U_n \Gamma}{(\mu - U_n)^2 + \Gamma^2} \right] = \frac{2\Gamma}{\pi (\mu - U_n)^2 + \Gamma^2}$$

$$\Rightarrow \frac{dn}{d\mu} = \frac{\frac{2}{\pi} (\text{Im } G)}{1 + \frac{U_n}{\pi} \text{Im } G} \neq \text{Im } G$$

note: larger U : decreased $\frac{dn}{d\mu}$

Rough rule of thumb

Band theory: $\frac{dn}{d\mu}$ + very crude approx to $\text{Im } G$

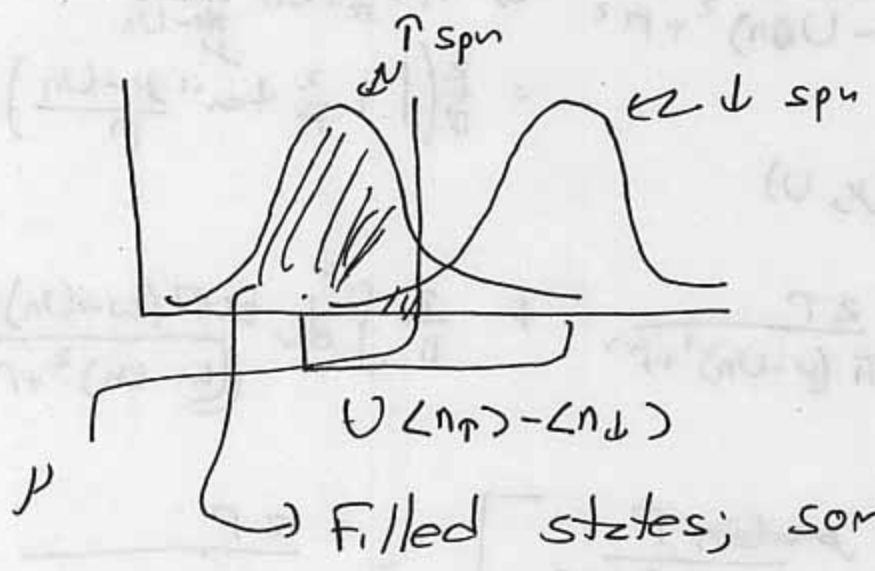
Observed $\text{Im } G$: different

General: as U increases, the transition shifts to lower energy.

Left order: linear order (not necessarily)

Single impurity problem: broken symm not allowed (exc in special case) for a mathematical (Kondo) \Rightarrow Kondo physics

• Polarized: U suff. large. Soln $n \uparrow / n \downarrow \neq n \downarrow$ favored



Now more tendency for level to "float" with μ
Bigger diff, photoemission, inv. ph. em

Linear instability criterion $n_{\uparrow} = \bar{n} + \delta n$
 $n_{\downarrow} = \bar{n} - \delta n$

$$\Rightarrow \delta n = U \int_{\mu}^{\omega} \frac{d\omega}{\pi} \text{Im} \frac{1}{[\omega - \epsilon_d - U\bar{n} - \Sigma(\omega)]^2}$$

$$\Sigma = i\Gamma : | = U \cdot \text{Im} \frac{1}{\mu - \epsilon_d - U\bar{n} - i\Gamma} = \frac{U\Gamma}{(\mu - \epsilon_d^*)^2 + \Gamma^2}$$

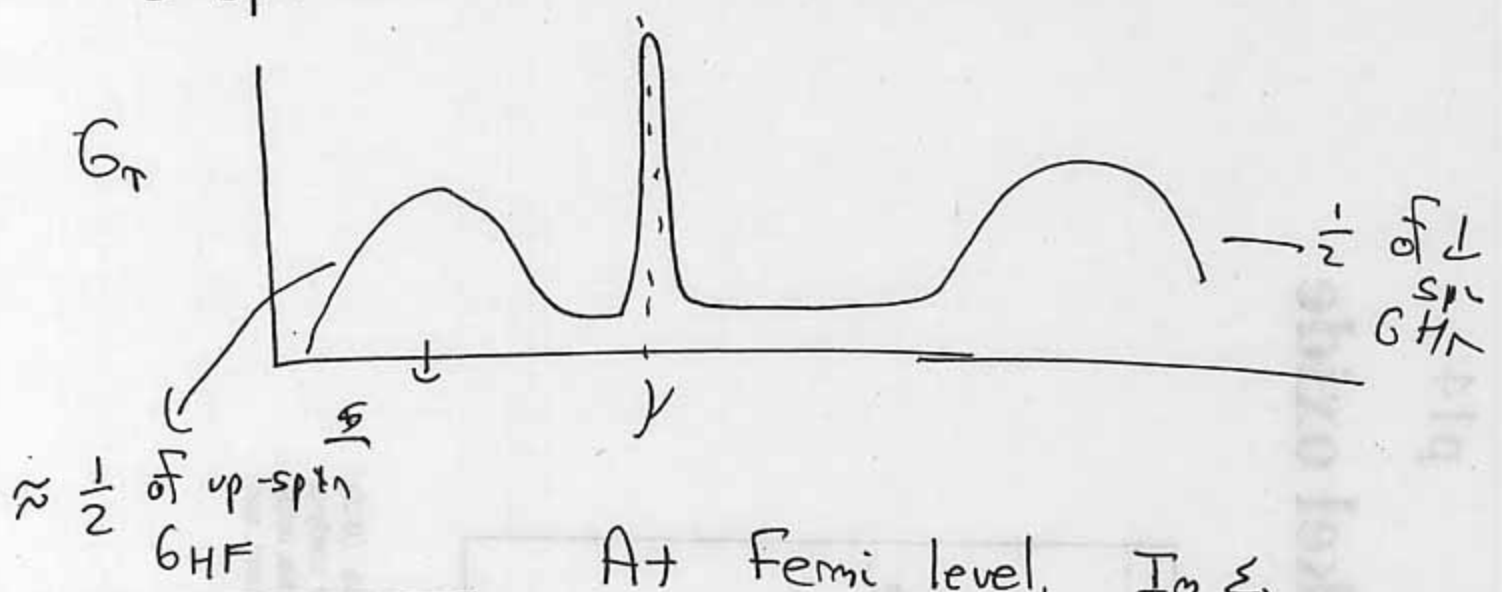
"Anderson criterion" = Stoner criterion = $U N_0^{HF}$

Easiest to polarize half-filled level.

Beware: as move μ away from ϵ_d^* or put structure in $\Sigma(\omega)$ transition tends to become 1st order. Linear instab. Not meaningful

Single impurity problem: broken symm not allowed (exc. in special circ., .e.s. FM or multichannel Kondo) \Rightarrow KONDO PHYSICS

Simple picture: 2 effects: spin fluct
 mean that you should average G_{HF} over
 2 spin dirs. • "Kondo resonance" (14)



At Fermi level, $\text{Im } \epsilon$,
 $\epsilon - \epsilon_0 - \text{Re } \epsilon$
 must be consistent w/ Friedel sum rule

Beyond simple pictures: Gumarson, Schaeferhauer

Above: large U picture. Decrease U : Kondo res. broadens, filled + empty peaks core together
 Rough rule of thumb: band theory - decent dI/dV , misses structure in $\text{Im } G$
 ϵ at 2ω

Summary: 2 things to be interested in
 (a) ground state energy, spin pol.
 (b) ~~etc~~ dynamics (simplest ex: spectral function)

(c) - ~~widely~~ used Quantum chemistry: finite (but getting larger) clusters "CI": Hartree Fock + corrections. \rightarrow exact diag for states of it!
 - DFT.

Photoemission—nickel oxide

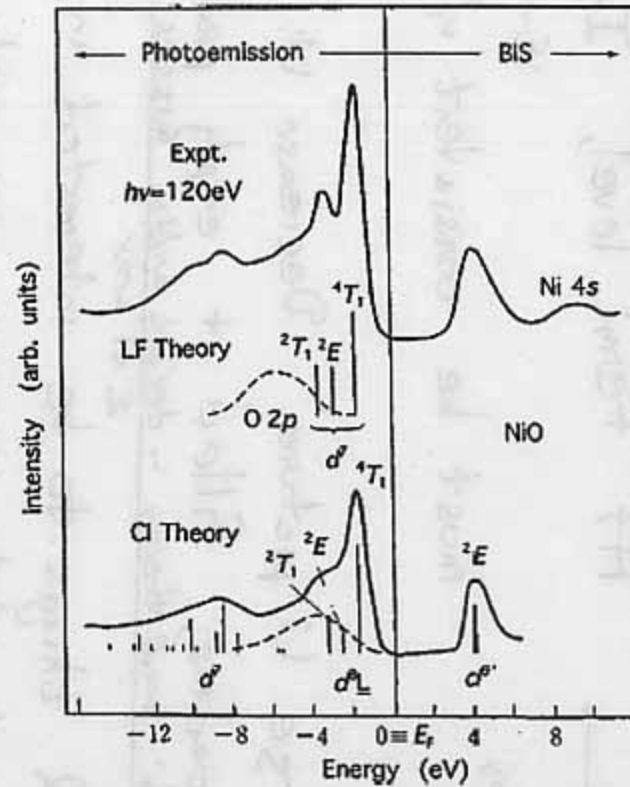


FIG. 39. Photoemission and inverse-photoemission (BIS) spectra of NiO (Sawatzky and Allen, 1984) and their analysis using ligand-field (LF) theory with the Ni^{2+} ion and that using CI theory for the NiO_6 cluster model (Fujimori, Minami, and Sugano, 1984).

Simple view of TMO band theory:

Impt e^- : ~~from~~ d-electrons $\begin{matrix} d_{xy} & d_{x^2-y^2} \\ d_{xz} & d_{3z^2-r^2} \\ d_{yz} \end{matrix}$

degen. in free space

In cubic symm: a rep not of $O(3)$ but O_h

\Rightarrow 5-plet splits into t_{2g} (3) and e_g (2) "Crystal field"
(better: "ligand field") - hyb w/ O

Emb: gns of point group theory: G.F. Koster + A

Dimmock: Table of the 32 Point Groups + Their Representations MIT Press 1963]

In general, keep one or other

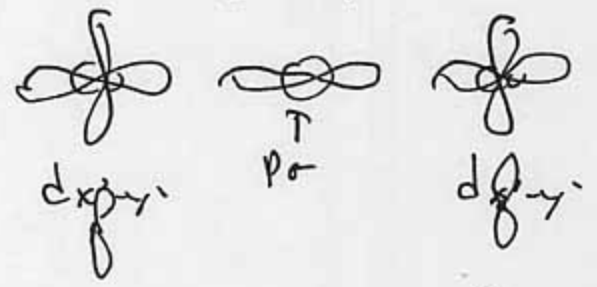
La_2CuO_4 $LaMnO_3$.. eg.

$LaTiO_3$, Sr_2FeMoO_6 ; Sr_2RuO_4 t_{2g}

Rule of thumb: eg orbitals: $d_{3z^2-r^2}$ $d_{x^2-y^2}$

"point towards O": hybridize strongly
hybridize w/ p_o

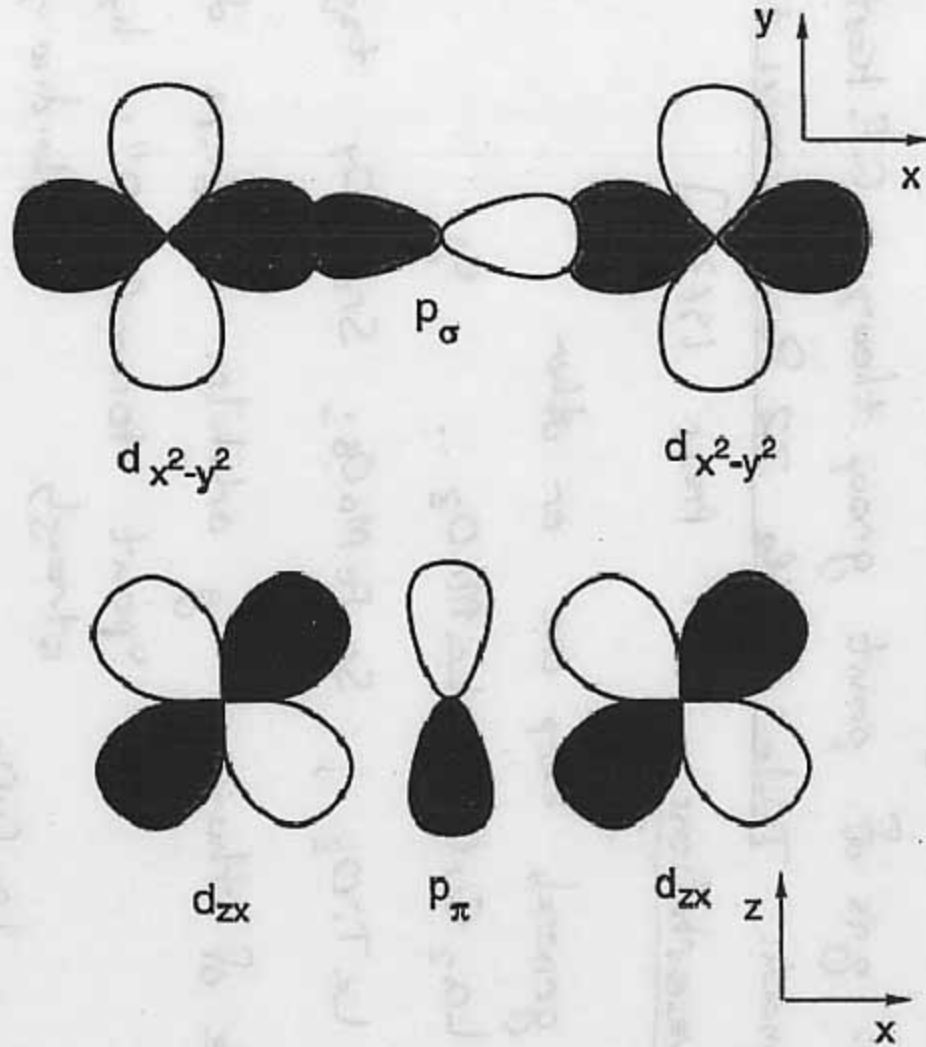
La_2CuO_4



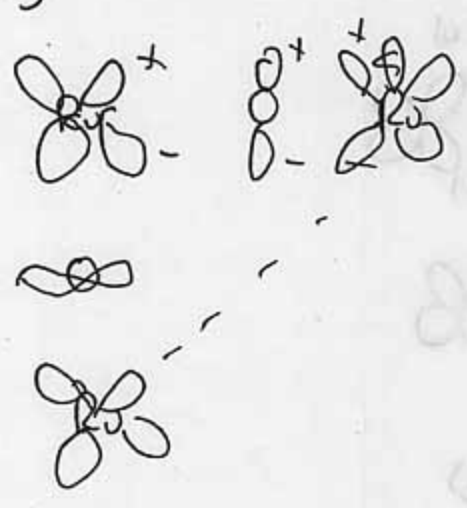
\Rightarrow strong hyb in-plane
weak hyb out-of-plane



Examples of p-d hopping



t_{2g}

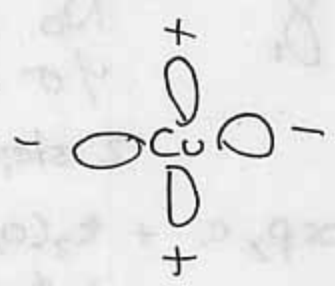


- Weaker along bond hopping
more diagonal hopping

- Planar nature of some orbitals \Rightarrow dominantly in-plane hopping.

Look down!

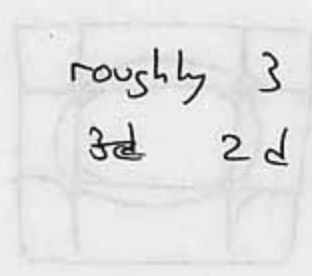
No overlap
of p or orbitals



\Rightarrow in-plane hopping much bigger than out of plane.

- Additional subtlety

LaTiO_3 : d_{xy} bands: ~~dominant~~
 d_{yz}
 d_{xz}



roughly 3 interpenetrating
3d 2d bands

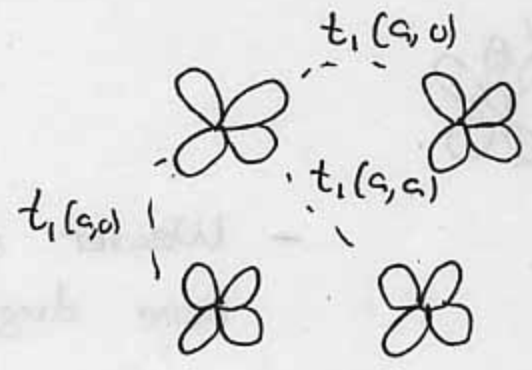
Additional subtlety: many quasi 2d materials: TM's stripes



Apply rules to Sr_2RuO_4 - very planar

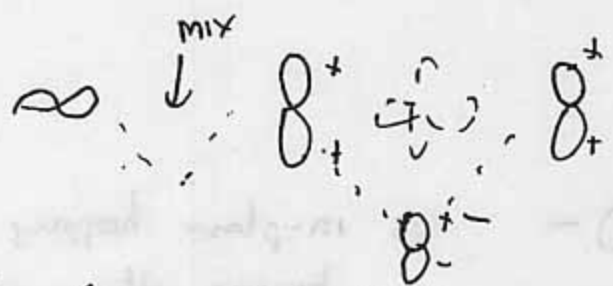
xy orbital

Planar



$$\Rightarrow \epsilon - 2t_1(a,0) (\cos p_x a + \cos p_y a) - 4t_1(a,a) (\cos p_x a \cos p_y a) \dots$$

xz yz linear



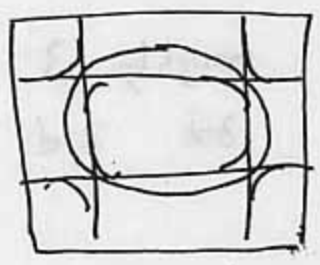
No overlap
y or x

2 step hop is possible

$$\Rightarrow 1d \text{ band } - 2t_2(a,0) \cos p_y a + t_2(a,a) \cos p_x a + t_{mix} \Rightarrow dt_1$$

$$1d \text{ band } - 2t_2(a,0) \cos p_x a$$

Sketch



Now look at details of FS.

Compare LDA

LDA Band Theory

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Recall ~~Kohn~~-Hohenberg-Kohn-Shan theorem

- \exists some functional of ~~ground state~~ density $\rho(r)$ s.t. ground state is minimized.
- Can cast minimization problem as soln of Schroedinger Eqn with some nonlocal potential V_{xc} :

$$\text{Solve! } \left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{latt}}(r) + \int d^3r' \frac{\rho(r')}{|r-r'|} \right] \psi_n(r)$$

$$+ \int d^3r' V_{xc}(r, r') \psi_n(r') = E_n \psi_n(r)$$

Obtain N lowest e.v. ; $E = \sum_n E_n$

* Exact if know exact V_{xc} .

In practice, have a variety of uncontrolled approximations, tested in various circumstances

- Very good for light electrons.

? d-electrons? How to test

(1) Nature of ground state - mag. or not
metal or ins.

(2) If metal, shape of Fermi surface

(3) Excitation spectrum

(i) Fermi velocities

(ii) excitation speed

Note! comparison depends on choice of V_{xc}

LDA, GGA, ...

LCS)DA

- Nature of ground state: overpredicts FM; underpredicts AFM.

- ~~In FM to Sr3~~

- Several "near FM" (Sr3Ru2O7, Pd, MnSi) or weak FM

- too large a moment is predicted or G.S. is wrongly predicted to be FM

- Old functionals: tend to predict "correlated insulators" (NiO, LaTiO3; La2CuO4) to be metals. Newer, more difficult to implement (e.g. "B3LYP") seem to do better

[(But have other controversial features incl. id-like z^2 base)

[Perry, Tahn-Kheli, Goddard, PRB 63 144510]?

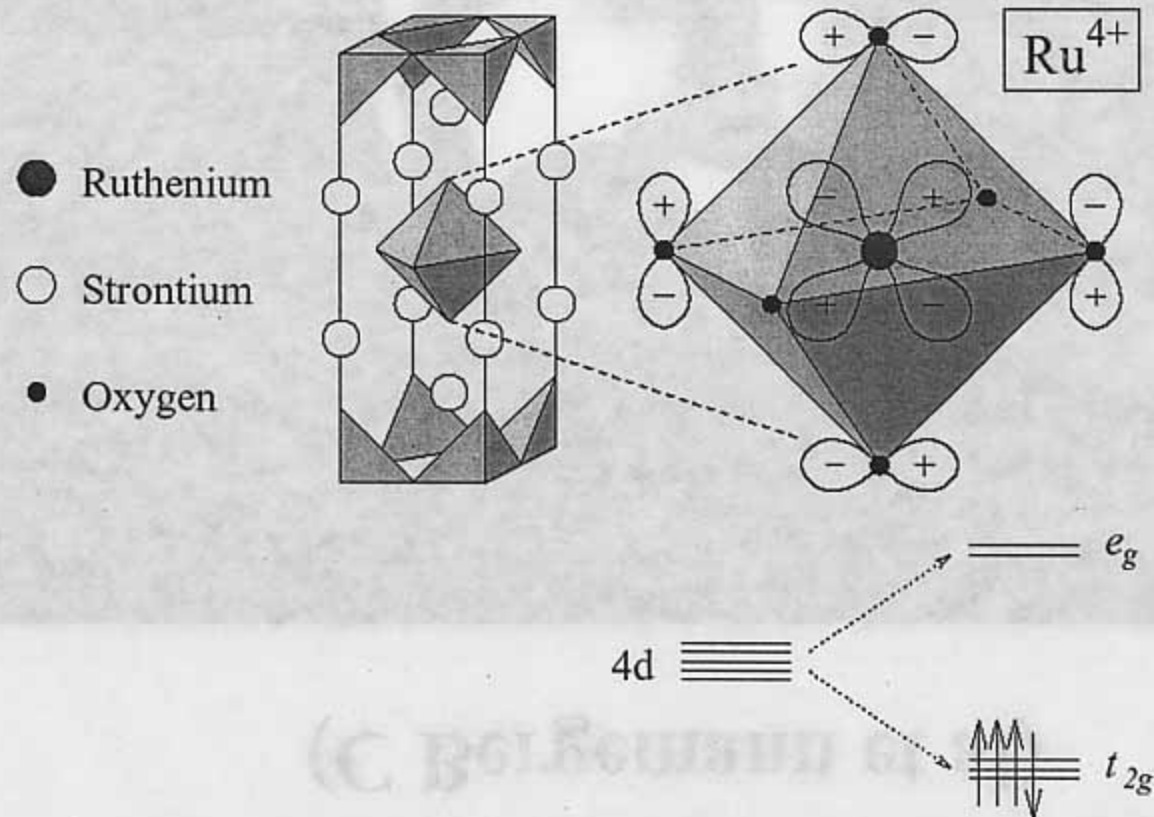
- Nature of fermi surface: few expt. studies

- Photoemission-cuprates
- Quantum Oscillations: Sr2RuO4

Works well: CaVO3 Inoue et al PRL 88 236403
 ReVO3 236403
 C. N. K. et al (LCS) 2666
 (C. Bergman)

- 4d. Triplet Sc. v. high purity samples

Sr₂RuO₄-crystal structure (Bergmann)



Sr₂RuO₄-dHvA fermi surface p17
(C Bergemann et al)

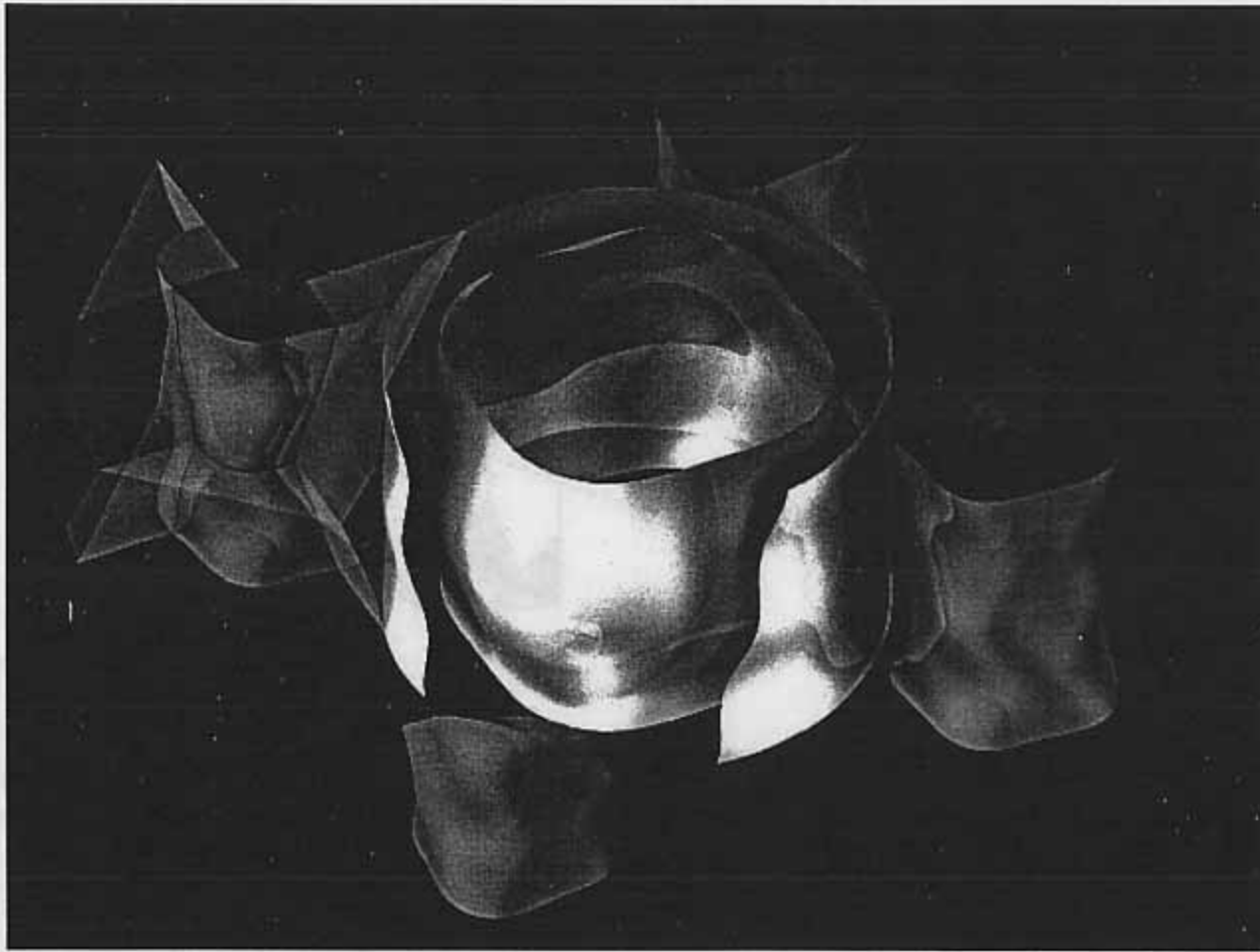
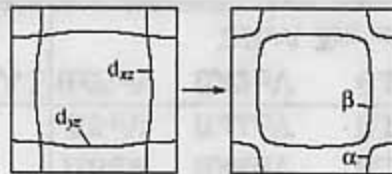
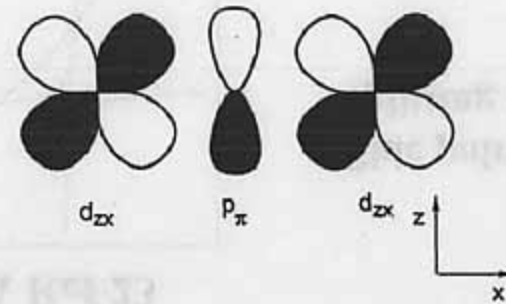
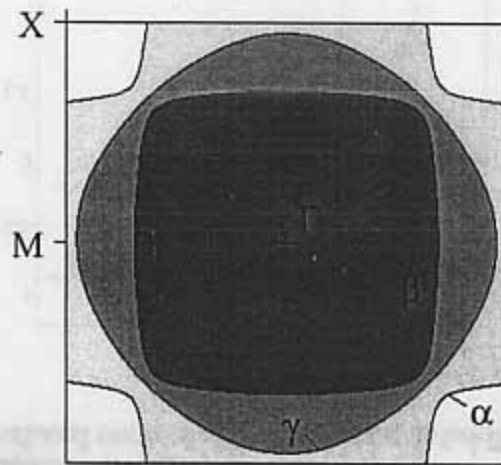


FIG. 28: Visualization of the Fermi surface of Sr₂RuO₄. The *c*-axis corrugation is exaggerated by a factor of 15 for clarity.

Qualitative view of Sr₂RuO₄ fermi surface



--2d: d_{xy} : hop in 2 in-plane dir
 , --1d: cant go in z-direction

FIG. 3: Qualitative sketch of the Fermi surface in Sr₂RuO₄. The lower panel shows how the d_{xz} and d_{yz} bands regroup to form the α and β surfaces.

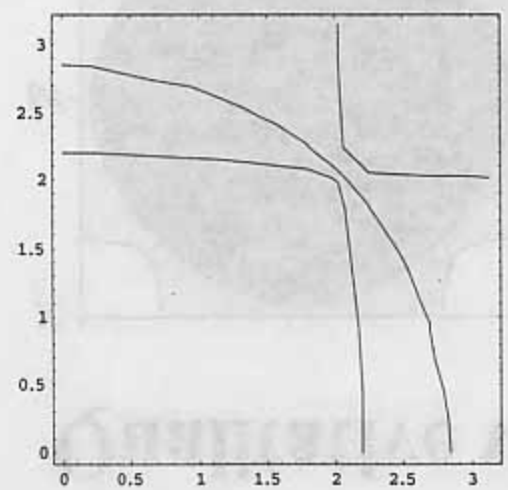
Values of tight binding parameters band theory and dHvA

Ref.	$t_{xx}(0)^a$	$t_{xx}(a, 0, 0)$	$t_{xx}(a, a, 0)$	F_T	$t_{zz}(0)^a$	$t_{zz}(a, 0, 0)$	$t_{zz}(0, a, 0)$	$t_{zz}(a, a, 0)$	$t_{zz}(\frac{a}{2}, \frac{a}{2}, \frac{a}{2})$	$t_{zz}(a, a, 0)$
22	0.4eV	0.4eV	0.12eV	16.1 kT	0.3eV	0.25eV	—	—	0.025eV	—
23	0.5eV	0.44eV	0.14eV	16.9 kT	0.24eV	0.31eV	0.045eV	0.01eV	—	—
24	0.5eV	0.44eV	0.14eV	16.9 kT	0.24eV	0.31eV	0.045eV	0.01eV	—	0.1eV ^b
Section VIA 1 3	0.65eV	0.42eV	0.17eV	18.65kT	0.33eV	0.30eV	0.031eV	—	0.002eV	0.041eV
		dHvA Experiment: 18.65kT								

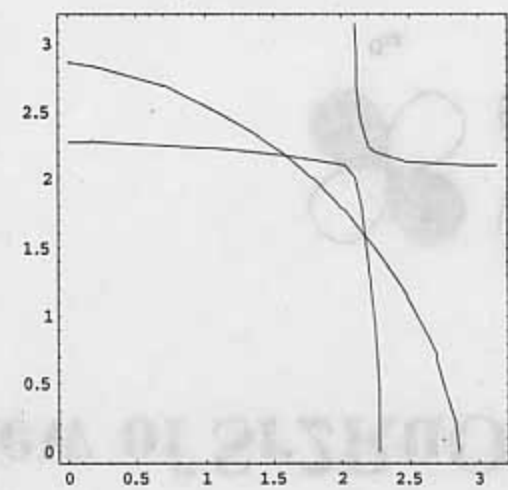
^aMeasured from ρ_F .

^bIntroduced unphysically as constant hybridisation $t_{xz}(0, 0, 0)$.

dHvA FS

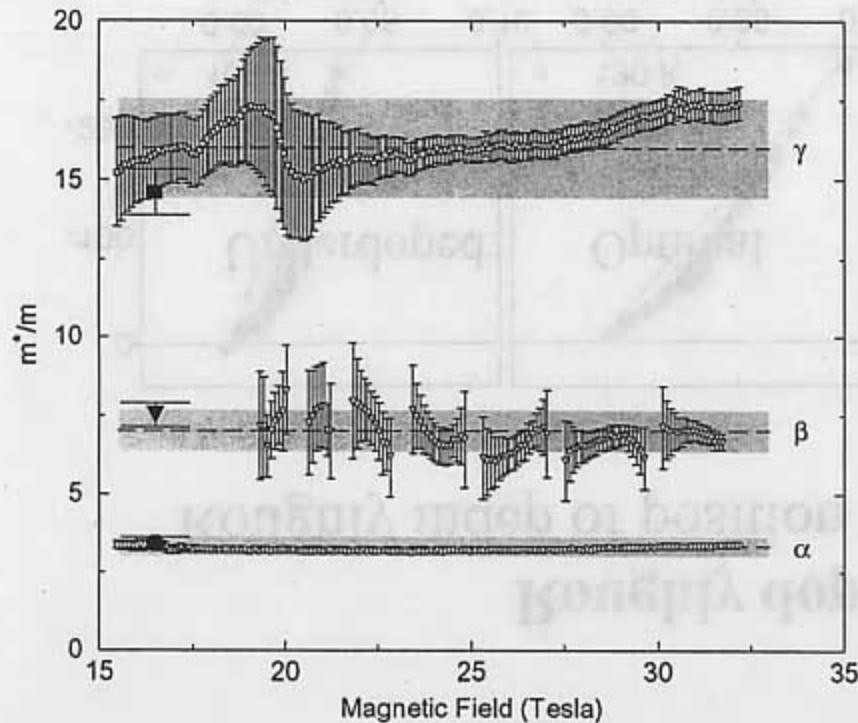


FS, LDA Ref 23



Side point: Jahn-Teller splitting $xz, yz :: xy$ 0.3eV

Quasiparticle mass enhancements over band results

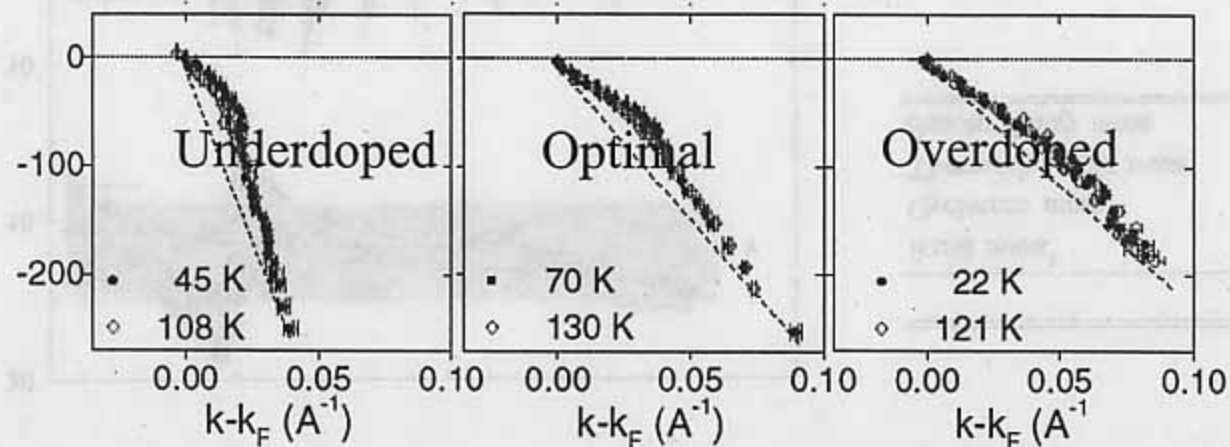


		α	β	γ
Band mass ⁷	m_b/m	1.1	2.0	2.9
Cyclotron mass	m_c/m	2.1	4.3	5.8
Thermodynamic mass	m^*/m	3.3	7.0	16
Susceptibility mass	m_{susc}^*/m	4.1	8.6	25

LDA overpredicts band masses (qp dispersion) by factors of 3-5.

Photoemission: $v_F = 1.8 \text{ eV-Å}$

Roughly doping-independent
 Roughly indep of position on fermi surface (opt BSCCO)



**Focus on blue (sc)
 and on near fermi
 surface. Note
 $v_{\text{band}} = 4 \text{ eV-Å}$**

**Zone diagonal dispersion,
 Johnson et al PRL87 177007 (2001)**

TMO: electronic structure.

In principle, must solve for 10^{23} particles

$$H = \underbrace{- \sum_i \frac{\hbar^2}{2m} \nabla_i^2 - \sum_i \sum_j \frac{z_j e^2}{|r_i - R_j|}}_{\text{"Single particle" part } H_0} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}}_{\text{interaction } H_I}$$

In practice: (a) can't solve (b) soln would have TMI

- Very useful way to think abt diff approx solns

Electron Greens Function. $-i \langle T c c^\dagger \rangle$

IF $H_I = 0$, $G \rightarrow G_n(p) = \frac{1}{\omega - \epsilon_n^0(p)} = \frac{1}{\omega - \underbrace{\epsilon_n^0(p)}_{\substack{\text{matrix} \\ \text{in band} \\ \text{indices}}}}$

ϵ_n p in 1st BZ, n = band index

In presence of H_I

$$G = [\omega - \epsilon_n^0(p) \delta_{nn'} - \Sigma_{nn'}(p, \omega)]^{-1} = [\omega - H_0 - \underline{\Sigma}]^{-1}$$

As matter of principle G diagonal in p, matrix in band indices (or in space $p + n \vec{G} \rightarrow$ recip. lat. vect.) ind. energy

As matter of principle, can derive all phys. quantities from "Luttinger Ward" functional $\Phi[G]$ - ∞ sum of diagrams

In practice, can't evaluate sum exc. in special cases

$\Sigma(\omega)$: complex function. $\text{Im} \Sigma_{nn'}(p, \omega)$: scattering

$$\text{Re} \Sigma = \int \frac{dx}{\pi} \frac{\text{Im} \Sigma(x)}{\omega - x} \text{ (Kramers-Kronig)}$$

~~BAND THEORY: $\Sigma_{nn'}(p, \omega) \rightarrow \Sigma_{nn'}(p)$~~

Make connection precise:

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$\Phi[G]$: sum of vacuum-vacuum skeleton diagrams

Note $\frac{\delta \Phi}{\delta G} = \Sigma$

$\rightarrow G + \Sigma \Rightarrow 1 - \text{Tr} \Sigma G$

Then $F = -\text{Tr} \ln \underline{G}^{-1} + \Phi[G] - \frac{1}{4} \text{Tr} [G_0^{-1} G]$

$\frac{\delta F}{\delta G} = 0 \Rightarrow$ Dyson $\Sigma G + G^{-1} + \Sigma \cdot \frac{1}{4} G_0^{-1} = 0$

G_0 : carries info abt lattice. Φ : info abt int's

In Kohn-Sham approach.

know $G = \frac{1}{\omega - H_0} \omega$

$G = [\omega - H_0 - V_{KS}]^{-1}$

Also know F

$\Rightarrow \Phi_{KS}[G] = E_{xc}[\rho] + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r' - \text{Tr} \underbrace{\Sigma_{KS} G}_{\text{in LDA} \Rightarrow \Sigma V_{KS,j}}$ $= \int V_{KS}(r) \rho(r) d^3r$
 $\Sigma_{KS} G$

Extensions:

$\Sigma = \Sigma_{KS}(\rho) + \Sigma^{ext}(\omega)$: local fn

\Rightarrow as above but $\Phi_{KS} \rightarrow \Phi_{KS} - G_0 \text{Tr} [\Sigma(\omega) G(\omega)] + \Phi[G_\omega] - \Phi_{DC}$

remove part of energy already included in DFT

Band Theory $\sum_{nn'}(\rho, \omega) \rightarrow \sum_{nn'}(\rho)$ (no Im part)

$$G_{band} = [\omega - H_0 - \sum_{nn'}(\rho)]^{-1}$$

Eigenvalues of $H_0 + \sum_{nn'}(\rho) \rightarrow$ Band dispersions ϵ_n
 $\epsilon_n(\rho)$

Kohn-Shan theory: prescription for evaluating part of $\Phi[G]$ having to do w/ ground state energy

Effects beyond band theory; ω -dep. of
 $\sum_{nn'}(\rho, \omega)$

- to study:
 - ① perturbation theory..
 - ② Diagonalise small systems
 - ③ Dynamical mean field
($\sum_{nn'}(\rho, \omega) \rightarrow \sum_{nn'}(\omega)$).

Comparison to Sr_2RuO_4 , La_2CuO_4

• Metals: FS close to but not ex. right
Excitations (e.g. velocity) off
by factor ≈ 2

Many implementations miss "Mott insulating" behavior