Transition Metal Oxides

3d

LaMnO$_3$: "Parent compound" "CMR" manganites
"Orbital Order"
La$_2$CuO$_4$: Mott Insulator. "Parent" compound
High T$_c$ Superconductors

4d

Sr$_2$RuO$_3$: Ferromagnet. Not understood
optical properties
Sr$_3$Ru$_2$O$_7$: Very nearly ferromagnetic.
"Metamagnetic" transition
Sr$_2$RuO$_4$: Triplet Superconductor

5d

Largely unexplored

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 orders
  - Jahn-Teller couplings
  - Anisotropic Conductivity (quasi 2d)
These lectures: underlying physics of TMO
- interaction physics of transition metals
- relation: simple models + reality
- Conceptual/calculational technique
  "Dynamical Mean Field" method

Crystal Structure: variant of ABO$_3$ perovskite

- Simple perovskite: Tm on B-site.
- A, B interpenetrating cubic lattices
  Trans Metal: B-site
  O - Tm - O
- Roughly: Tm-O bond: 4.2 Å
- Rattlesden-Pepper
- Layered: La$_2$CuO$_4$: Sr$_2$RuO$_4$

Side view
Cu - displaced into paper
Cu - O - Cu lattice const
Cu - O - Cu halfway up
Crystal structure and phase diagram

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

Tm ions (colors indicate sublattices of possible ordered state)

O ions (O$_6$ octahedra indicated)

Fig. 1
in wave mechanics from Eq. (7-29), in which the wave function is a function of \( r = 2 \sqrt{z}/n \), so that the radius is inversely proportional to \( n \). With the shielding taken into account, we should expect that the size of each orbit should be equal to that of a corresponding hydrogenic orbit divided by \( Z - 2 \), where \( Z \) is the shielding constant.

In Table 8.3, we have listed the radial quantum numbers for the various wave functions of the hydrogenic atom. The values are given for each shell of electrons, and they are derived from the quantum numbers given in Table 8.2. The values are not always integers, and they are given in scientific notation. The values are also given for the various shells of electrons, and they are derived from the quantum numbers given in Table 8.2. The values are not always integers, and they are given in scientific notation.

Table 8.4

<table>
<thead>
<tr>
<th>Shell</th>
<th>Curve</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>2s</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>2p</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>3s</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>3p</td>
<td>0.22</td>
<td></td>
</tr>
</tbody>
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The values in Table 8.4 are the radial quantum numbers for the various wave functions of the hydrogenic atom. The values are given for each shell of electrons, and they are derived from the quantum numbers given in Table 8.2. The values are not always integers, and they are given in scientific notation.

As we go from lithium to sodium, the effective potential of the electron shell of the alkali metal is decreased by the shielding effect. Thus, we should expect that the size of the orbit will be smaller for the alkali metals than for the noble gases. This is indeed the case, as we can see from the figures of Table 8.3. The radius of the orbit for the 1s shell of lithium is 0.10 a.u., while the radius of the orbit for the 1s shell of sodium is 0.08 a.u. This is because the shielding effect is stronger for the alkali metals than for the noble gases.

In general, the orbital radii for the 2s and 2p levels are smaller than the orbital radii for the 1s level. This is because the 2s and 2p levels have a smaller effective potential than the 1s level. As we go to higher atomic numbers, the size of the orbit will decrease further, as the shielding effect becomes more and more important.

The orbital radii for the 3s and 3p levels are also smaller than the orbital radii for the 2s and 2p levels. This is because the 3s and 3p levels have a smaller effective potential than the 2s and 2p levels. As we go to higher atomic numbers, the size of the orbit will decrease further, as the shielding effect becomes more and more important.

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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 \( P_{n\ell}(r) \) for one stage of the approximation. We next carry out the integrations necessary to get the functions \( Y_\ell(n_l l, n_\ell l, l/r) \) 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 \( \psi \)'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 \( \text{Cu}^+ \), by Hartree and Hartree.\(^1\) This is the heaviest atom for which the Hartree-Fock calculation has been carried out. For comparison, in Fig. 9-3 we


Key Feature of TMO- d electrons.

Recall atomic physics - build up atoms

H: $1s \psi(r) = e^{-r/\alpha}$ \(\alpha \approx \text{Bohr radius} = 0.5 \text{Å}

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

Li: $1s^2 2s^1$ (pays to put 2nd el in 2s not 1s)
Note: 2s must be orthogonal to 1s \(\Theta\) sits farther out from nucleus

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

B: $1s^2 2s^2 2p^1$ \(\Theta\) \(\Theta\)

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

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

K $4s^1$ Ca $4s^2$ Sc $3d^1 4s^3$ Ti $3d^0 4s^2$ V $3d^1 4s^2$ Cr $3d^5 4s^1$ Mn $3d^6 4s^1$ Fe $3d^6 4s^2$ Ni $3d^8 4s^2$ Cu $3d^9 4s^2$

Fill 3d shell, keeps $4s^2$

3d: 1st time fill up & d shell
Can sit close to nucleus \(\Theta\) doesn't have to be \(\perp\) to other orbitals
But not too close\(\Theta\) - centrifugal barrier
Typical size of d-orbitals 
\(0.5 - 0.3 \text{Å} \approx \alpha\)

d's sit inside $4s$, but \(\alpha\) as strongly bound well $4 \text{Å}$
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, Fe Fm. 180, Rh, Pd, not (maybe near)

Make atoms into solid: - Remull, tight bonds
1. & 4s & 5s: Very spread out: delocalize
   \( \Rightarrow \) broad bands (100eV
2. d: small - narrow band, high DOS

Where is Fermi level? - in d-bands
deal? & 4s? Filled shell.
But hyb. big \( \Rightarrow \) broad band. - Sore
4s go for up in energy \( \Rightarrow \) want to dump
some \( e^- \) in d: but typically not too much - counts
- Obvious point: \( \text{arrangement of atoms in crystal} \Rightarrow \text{structure in DOS.}\)

\[ E = \int dE \text{DCE} \]

\( \begin{array}{c}
\text{F} \\
\text{D}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{structure} \\
\end{array} \quad \begin{array}{c}
\text{S}
\end{array} \]

Gain energy (filled states)

\( \Rightarrow \text{very often in band theory of T.M. compounds: chemical potential in or near DOS minimum.} \)

[Interesting consequence for Stoner Theory]

- Transition Metal Oxides: \( O \) is very electronegative.

\( \text{Wants to grab} \ 2e^- \text{ O} \quad \text{Oss} \)

Simple picture

\[
\begin{array}{c}
\text{3d} \\
\text{4s}
\end{array}
\]

\[ -\quad \begin{array}{c}
\text{O}_{2p}
\end{array} \]

Simple H:

\[ E_{3d} d^+d + E_{4s} s^+s + E_{2p} p^+p \]

\[ - t_{dp} (d^+p + hc) - t_{sp} (s^+p + hc) \]

Matrix:

\[
H = \begin{bmatrix}
E_{3d} & t_{dp} \\
E_{4s} & t_{sp} \\
t_{dp} & t_{sp} & E_{2p}
\end{bmatrix}
\]
tsp > tdp. Set \( t_{dp} = 0 \)

Eigenvalues:
\[
\varepsilon_{3d} \quad \frac{1}{2} \varepsilon_{3s} + \varepsilon_{3p} + \sqrt{\left(\varepsilon_{3s} - \varepsilon_{3p}\right)^2 + 4t_{sp}^2}
\]

i.e. if \( \frac{1}{2} (\varepsilon_{3s} + \varepsilon_{3p}) + \frac{1}{2} \sqrt{\left(\varepsilon_{3s} - \varepsilon_{3p}\right)^2 + 4t_{sp}^2} > \varepsilon_{3d} \)

(easy to arrange: tsp is large)

then \( \varepsilon_{3d} \) occupy: \( 4s - 2p \) bond is comb., \( 3d \)

even though in atom \( 3d \) is higher

This is (roughly) what happens in TMOs

- **TM compounds**

<table>
<thead>
<tr>
<th></th>
<th>TMO</th>
<th>TMO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 4s + 0 )</td>
<td>( 4s + 0 )</td>
</tr>
</tbody>
</table>

\( \text{relatively isolated} \ 3d.\)

- **Picture grossly oversimplified**
- Will see real bond theory later
- Next point: relative electronegativity of \( Tm \) relative to \( O \) decreases as move across \( Tm \) row.
- \( Sc, Ti: \text{d "for" from } 4s/0 \text{ bonds} \)
- \( Mn \rightarrow Cu: \text{d "near" to } 4s/0 \text{ bonds} \)
- Key qn: what do you mean by density of states?

1. Density as function of chemical potential: \( n(\mu) \)  
   \( \Delta(\varepsilon) = \left. \frac{d n}{d \varepsilon} \right|_{\mu = \varepsilon} \)  

2. \( F = E - \mu N \rightarrow E = \int d^3r \psi(r) N(r) \psi(r) \) \( \Rightarrow \) local dos  
   \( \frac{\delta E}{\delta \psi(r)} \)

2.1 electron removal spectrum \( \gamma = 0 \)
   
   \( \langle \rho_{\text{ex}} \rangle \): removes 1 electron from normalized state (so in of same single particle Schroedinger)
   \( \phi_{\text{ex}}(r) \)

   \( G_{\text{ex}}(t) = -i \langle T \phi_{\text{ex}}(t) \phi_{\text{ex}}(0) \rangle \)

\( \langle \rangle = \) ground state expectation value.

\( T: \) time ordering symbol. \( t > 0 \)
   \[ T \phi_{\text{ex}}(t) \phi_{\text{ex}}(0) = \phi_{\text{ex}}(t) \phi_{\text{ex}}(0) \]
   \( t < 0 \)
   \[ T \phi_{\text{ex}}(t) \phi_{\text{ex}}(0) = -\phi_{\text{ex}}(0) \phi_{\text{ex}}(t) \]

Write \( G_{\text{ex}} \) in basis of exact eigenstates of problem \( \langle n \rangle \): energy \( E_n \)

Define: \( E_0 \) \&

\( G_{\text{ex}}(t > 0) = -i \sum_{n} \langle n | e^{-iHt} \phi_{\text{ex}}(0) c_a \ker n \rangle \phi_{\text{ex}}(t) c_a^0 \rangle \)
Note: distinguish “electron” (positive addition) states, reachable by adding $e^{-}$ to $s$

hole states, reachable by removals

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

\[ + \int_{-\infty}^{0} dt \ e^{i\omega t + \varepsilon t} G_{aa'}(t) \]

$\varepsilon$: infinitesimal convergence factor put to make $\int$s converge

$G_{aa'} = \sum_{n_{e}} \frac{B_{n_{e}a}^{*} B_{n_{e}a'}^{*}}{\omega - (E_{n_{e}} - E_{0}) + i\varepsilon} + \sum_{n_{h}} \frac{B_{n_{h}a}^{*} B_{n_{h}a'}^{*}}{\omega + (E_{n_{h}} - E_{0}) - i\varepsilon}$

$\text{Im} \ G_{aa'} = \pi \sum_{n_{e}} \frac{B_{n_{e}a}^{*} B_{n_{e}a'}^{*} \delta(\omega - (E_{n_{e}} - E_{0}))}{\omega - (E_{n_{e}} - E_{0}) - i\varepsilon}$

$- \pi \sum_{n_{h}} \frac{B_{n_{h}a}^{*} B_{n_{h}a'}^{*} \delta(\omega + (E_{n_{h}} - E_{0}))}{\omega + (E_{n_{h}} - E_{0}) + i\varepsilon}$

Spectral function: some thing with $a^{+}$

I.e. $\text{Im} \ G_{a^{+}a} = \sum_{n_{e}} \frac{B_{n_{e}a}^{*} B_{n_{e}a'}^{*}}{(\omega - E_{n_{e}} - E_{0} - i\varepsilon)} + \sum_{n_{h}} \frac{B_{n_{h}a}^{*} B_{n_{h}a'}^{*}}{\nu + E_{n_{h}} - E_{0} - i\varepsilon}$
Mathematics: define $G_{aa'}(z) \rightarrow \text{complex}$

$G_{aa} = \sum_e \frac{B_e^2}{z - (E_{ae} - E_0)} + \sum_{h} \frac{B_h^2}{z - (E_{ah} - E_0)}$

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

diff $G$: diff choices ebt delays with sus

- Very convenient: consider $z$ purely imaginary
  $z = (2n+1) i \pi$ $\rightarrow$ temperature.

$\Rightarrow$ $G$ in "imaginary time": nice analytical properties

$(e^{iEn_t} \Rightarrow e^{-En_t})$

Physics - Photoemission

- Photon in electron out

Typically: complicated + ill-understood intermediate states: final state $\rightarrow$ straight forward

Idea: if $\nu L - E$ is small, $\mathcal{M}$ is indep. of $\nu - E$  

$\Rightarrow$ ampl. of getting $p \rightarrow M_{\nu L} C_{p-h} \Rightarrow$ signal $\rightarrow \text{Im} G_{aa}$
Spectral function $A_{\pi}(\omega)$.

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

Amplitudes: overlaps of states $\pi_j^*$ with ground state.

Isolated Atom: series of lines: electron removal energies.

Solid: continuum; broadened peaks correspond to atomic removal energies.

Measureable: photoemission: reasonably good
inverse photoemission: addition:
not so easy

Points: non-interacting system: $\frac{d\nu}{d\nu}$ same as $A_{\pi}(\omega)$
Interacting system: not same - energetics change as you chase occupancy.
Ability to remove $e^-$ from lev below $\nu$
Not same as differential ability to remove 1 $e^-$ after taking out the # of $e^-$ needed to drop $\nu$ by lev.
Simple example: already covered by Cox

Anderson Impurity Model

\[ H = - \sum_{\sigma} \epsilon_{\sigma} c_{\sigma}^+ c_{\sigma} + \frac{1}{2} \sum_{\sigma \neq \sigma'} V(c_{\sigma}^+ c_{\sigma'}) + \varepsilon_d \sum_{\sigma} n_\sigma + U \sum_{\sigma \neq \sigma'} n_{\sigma} n_{\sigma'} \]

Solution: discussed in detail in Mahan

Here: simple approach via functional integral

**Ex rederive via eqn of motion**

\[ Z = \int Dc_c Dd_d \exp \left[ \frac{1}{i} \int \left( c_{\sigma}^+ c_{\sigma} - V n_{\sigma} \right) + \varepsilon_d \sum_{\sigma} n_\sigma + U \sum_{\sigma \neq \sigma'} n_{\sigma} n_{\sigma'} \right] d \]

Action in \( \omega \)-space:

\[ c_{\sigma}^+ d_\sigma \left( i\omega - \epsilon_{\sigma} + V \right) c_{\sigma} \quad + \quad U \sum_{\sigma \neq \sigma'} \]

Shift: \( c_{\sigma} \rightarrow c_{\sigma} - \frac{V}{i\omega - \epsilon_{\sigma}} d \) ⇒ c's decouple

\[ Z = Z_c \cdot \int Dd_d \exp \left[ i \int \left( \omega - \epsilon_d - \frac{1}{2} \frac{V^2}{\omega - \epsilon_{\sigma}} \right) \right] d + \text{other terms} \]

"self energy". Expresses physics that \( d \) can go into c-electron left some form as un Mart c-

but contains some d-correl.
Shift not innocent as it seems. To obtain c-electron Green function, must introduce "source term" \( \gamma C_f \)

Shift: \( \gamma C_f \rightarrow \gamma(C_f - \frac{V_d^+}{i\omega - \epsilon_f}) + \gamma V_d^+ \)

\( \Rightarrow \) some of what we calculate from shifted partition \( \hat{Z}_{\text{imp}} \) is actually c-c correlation

Non-interacting:

\[
F_{\text{imp}} = kT \ln \hat{Z}_{\text{imp}} = \frac{\epsilon}{\hbar} \int \frac{de}{\pi} f(\epsilon) + \text{c.c.} \left[ \frac{\text{Im } \epsilon(\epsilon)}{\epsilon - \epsilon_i - \text{Re } \epsilon(\epsilon)} \right]
\]

\( \Rightarrow \) \( \delta n = \frac{-6F}{\epsilon_0} = \frac{\epsilon'}{\pi} + \text{c.c.} \left[ \frac{\text{Im } \epsilon(\epsilon)}{\mu - \epsilon_0 - \text{Re } \epsilon(\epsilon)} \right] \) "Friedel Sum Rule"

But

\[
\gamma_d = \int \frac{de}{\pi} f(\epsilon) \frac{\text{Im } \epsilon(\epsilon)}{(\epsilon - \epsilon_i - \text{Re } \epsilon)^2 + \text{Im } \epsilon^2}
\]

\( \neq \text{N}_{\text{imp}} \) unless \( \text{Im } \epsilon(\epsilon) = \text{const.} \)

\( \text{Re } \epsilon(\epsilon) = \text{const.} \)

\textbf{Difference: effect of impurity on c's}
\[ G_{dd} = \langle T \rho_{dd}^+(\omega) \rangle \]

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

\[ U = 0 \]

\[ G_{dd} = \frac{1}{\omega - \epsilon_d - \frac{\omega}{\omega - \epsilon_d + i \Gamma}} \]

[Non-interacting formula]

\[ \text{Im} \epsilon_d = \frac{\pi \nu^2}{\hbar} \delta(\omega - \epsilon_d) \]

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

\[ \Gamma = \text{Im} \epsilon_d(\omega = \epsilon_d^*) \]

\[ \epsilon_d^* = \text{shift of level by coupling to solid. Typically not small} \]

\[ \text{Non-interacting: Removal/addition spectrum \"smeared\" as \text{dn/dy cusp to c-band part}} \]

Note: \[ Z_{\text{tot}} = Z_c Z_{\text{imp}} \]

\[ F_{\text{tot}} = kT \ln Z_{\text{tot}} = F_c + F_{\text{imp}} \]

\[ \text{hypothetical } F \text{ of cond. band } \text{w/o impurity} \]

\[ F \text{ of impurity - coupled: } \text{i.e. extra } F \text{ due to } \nu \]
Hartree–Fock (cf. easy to implement in Mathematica) (Here \( \equiv \) Hartree)

\[ \varepsilon_d \to \varepsilon_d^0 = \varepsilon_d + U\langle \sigma \rangle \] (\( \sigma \) is opp spin too)

\[ E_{\uparrow} = \int \frac{d\nu}{\pi} \text{Im} \frac{1}{\nu - \varepsilon_d - U\langle \sigma \rangle - \varepsilon(\omega)} \]

\[ E_{\downarrow} = \int \frac{d\nu}{\pi} \text{Im} \frac{1}{\nu - \varepsilon_d - U\langle \sigma \rangle + \varepsilon(\omega)} \]

Cesp. simple + relevant to thinking about simple metals: \( \varepsilon(\omega) \to i\gamma \)

Also amusing to consider structure in conduction band: e.g. \( V \) const, \( \int \text{cst} \) \( \eta(\nu - \varepsilon_p) \)

\[ HF: \text{add (spin dep) } \nu \text{-indep term to } \varepsilon \]

Roughly: HF solns: shifted resonance.

2 classes: unpolarized: \( \langle \eta\sigma \rangle = \langle \nu \sigma \rangle \)

Interplay betw. \( U \) and \( \mu \): as \( \mu \) tends to float with \( \mu \) so \( d \) does not get too high \( \Rightarrow \) diff betw. photoemission, cold!

Bnd situation: high density of impurities
- each \( d \) you expel from impurity must go into bnd \( \Rightarrow \) raises \( \mu \) \( \Rightarrow \) makes it less likely to expel next imp. More tendency of \( d \) to “float” with \( \mu \) \( \Rightarrow \) Why, in may TM, TMO, \( d \) bnds partly filled, near FP
Simple case \[ E^{(0)} = \Gamma \] \[ e_d = 0 \]

\[ n = 2 \int \frac{dw}{\pi} \frac{\Gamma}{(\omega - U\eta)^2 + \eta^2} \Rightarrow n = \frac{2}{\pi} \text{cn}^{-1} \frac{\Gamma}{\omega - U\eta} \]

Mathematica: \[ n(\nu, U) \]

or \[ \frac{dn}{d\nu} = \frac{2}{\pi} \frac{\Gamma}{(\nu - U\eta)^2 + \eta^2} + \frac{2}{\pi} \int d\omega \frac{2U\Gamma (\omega - U\eta) n}{(\omega - U\eta)^2 + \eta^2} \]

\[ \frac{dn}{d\nu} \left[ 1 + \frac{2U\eta}{\pi} \frac{\text{sn} \frac{\Gamma}{\nu - U\eta}}{(\nu - U\eta)^2 + \eta^2} \right] = \frac{2}{\pi} \frac{\Gamma}{(\nu - U\eta)^2 + \eta^2} \]

\[ \frac{dn}{d\nu} = \frac{2}{\pi} (\text{Im} \, G) \quad + \text{Im} \, G \quad + \text{Im} \, G \quad \text{note: lower } U: \frac{dn}{d\nu} \text{ decreased} \]

Rough rule of thumb

Band theory: \[ \frac{dn}{d\nu} \] + very crude approx to \[ \text{Im} \, G \]

Observed \[ \text{Im} \, G \]: different
* Polarized: $U$ suff. large, $\text{Soln } u / u \neq u$ favored!

```latex
\begin{align*}
\text{Fg.} & \quad \text{Filled states: some up, some down} \\
\text{Linear instability criterion} & \quad \eta_0 = \bar{\eta} + \Delta \eta \\
& \quad \eta_0 = \bar{\eta} - \Delta \eta \\
\Rightarrow & \quad \Delta n = U \int \frac{d\epsilon}{\pi} \text{Im} \left[ \frac{1}{\omega - \epsilon - \bar{\eta} - \Sigma(\omega)} \right]^2 \\
\Sigma & = i \Pi: \quad I = u \cdot \text{Im} \left[ \frac{1}{\mu - \epsilon - \bar{\eta} - i\Pi} \right] = \frac{U}{\Pi} \frac{\Pi}{(\epsilon - \epsilon^*)^2 + \Pi^2} \\
\text{Anderson criterion} & = \text{Stoner criterion} = U N_0 \frac{\Pi}{\epsilon^*} \\
\text{Easiest to polarize half-filled level.} \\
\text{Beware! as move } \mu \text{ away from } \epsilon^* \text{ or put} \\
\text{structure in } \Sigma(\omega) \text{ transition tends to become} \\
1\text{st order. Linear unstable. Not meaningful.} \\
```

Single impurity problem: broken symm not allowed (exc. in special cases, i.e., FM or multichannel Kondo) $\Rightarrow$ KONDO PHYSICS
Simple picture: 2 effects: $\theta$ spin fluctuates, mean spin that you should average $G_{HF}$ over 2 spin dvs. "Kondo resonance"

\[ \begin{array}{c}
\frac{1}{2} \text{ of up–spin} \\
6_{HF}
\end{array} \]

Beyond simple pictures: Gummerson, Schoenhauser

At Fermi level, $\Im \xi$ must be consistent w/ Friedel sum rule.


Rough rule of thumb: back theory – decent dispersion misses structure in $2 \xi$.

Summary: 2 things to be interested in:

(a) ground state energy, spin pol.
(b) state dynamics (simplest ex: spectral function)

(c) – widely used Quantum chemistry: Finite (but getting larger) clusters, "CI"! Hartree-Fock + corrections. (c) exact dgs for states of $U$

– 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 TM0 band theory:

Imp't e\(^{-}\): p\(_\pi\), d-electrons \[\begin{align*} d_{xy} & \ \\ d_{x^2-y^2} & \ \\ d_{z^2} & \ \\ d_{3z^2-r^2} & \ \\ d\_y & \end{align*}\] degen. in free space

In cubic symm: rep not of O(3) but Oh

\(\ \\\ \ \\) 5-plet splits into \(3\), \(2\)

“Crystal Field” (better “Ligand Field”, \(d\)-hyb \(\rightarrow\) O

CMB: gns of point group theory: C.F. Koster + A. Dimmock: Table of the 32 Point Groups + Their Representations MIT Press 1963]

In general, keep one or other

La\(_2\)CuO\(_4\)  LaMn\(_2\)O\(_3\)... eg.

LaTi\(_2\)O\(_3\), Sr\(_2\)FeMoO\(_6\), Sr\(_2\)RuO\(_4\) t\(_{2g}\)

Rule of thumb: eg orbitals: \(d\_z^2\), \(d\_xy\)

“pont towards \(O\)”; hybridize strongly

\(\ \\ \ \ \\) strong hyb n-plane

weak hyb out-of-plane

\(\ \\ \ \ \\) \(\ \\ \ \ \\) \(\ \\ \ \ \\)
Examples of p-d hopping
- Weak long bond hopping more diagonal hopping

- Planar nature of some orbitals ⇒ dominance in-plane hoppings.
  Look down: \( \text{CuO}_2 \) ⇒ in-plane hoppings much bigger than out of plane.
  No overlap
  \( \uparrow \text{p}_{\Delta} \text{ or } \uparrow \text{p}_{\Delta} \)

- Additional subtlety
  \( \text{LaTiO}_3 \): dy \( \uparrow \text{bds} \):
  \( d_{\Delta} \) and \( d_{\Delta} \) roughly 3 interpenetrate 2 \( d \) bds

Additional subtlety: many quasi 2d materials: \( \uparrow \text{p}_{\Delta} \text{ or } \uparrow \text{p}_{\Delta} \)
Apply rules to $\text{Sr}_2\text{RuO}_4$ - very planar $t_1(\pi,0)$

$xy$ orbital $t_1(\pi,\pi)$

$$\Rightarrow a \cdot -2t_1(\pi,0) \cos p_x c + \cos p_y c$$

$$-4t_1(\pi,0) \cos p_x c \cos p_y c$$

$X^2 Y Z$ linear $\rightarrow$ 8 mix 8 $t_1$

$X^2 Y Z$ linear $\rightarrow$ 8 mix 8 $t_1$

No overlap $\gamma/0$ or $\pi$

2 step hop is pass

$1d$ band $-2t_2(\pi,0) \cos p_x c + t_2(\pi,0) \cos p_x c$

$1d$ band $-2t_2(\pi,0) \cos p_x c$

Sketch

Now look at details of FS.

Compare LOA
LDA Bond Theory

Recall Kohn–Hohenberg–Kohn–Sham theorem:

If some functional of ground state density \( \rho(r) \), s.t. ground state is minimized.

Can cast minimization as problem as solution of Schroedinger Eqn. with some nonlocal potential \( V_{xc} \):

Solve:

\[
\left[ -\frac{1}{2m} \nabla^2 + V_{latt}(r) + \int \frac{d^3r'}{r-r'} \rho(r') \right] \Psi_n(r) \\
+ \int d^3r' \ V_{xc}(r,r') \Psi_n(r') = E_n \Psi_n(r)
\]

Obtain \( N \) lowest c.v.; \( E = \sum E_n \).

* Exact if knew 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—magn. or not

(2) If metal, shape of Fermi surface

(3) Excitation spectrum

(i) Fermi velocities (ii) excitation spec

Note: comparison depends on choice of \( V_{xc} \)

LDA, GGA, ...
- Nature of ground state: overpredicts FM, underpredicts AFM.
  \[ \text{In FM \& SD} \]

- Several "near FM" (Sr₂Ru₂O₇, Pd, Mn Si) or weak FM
  - too large a moment is predicted or C.G. is wrongly predicted to be FM

- Old functionals tend to predict "correlated insulators" (e.g., La₂TiO₃, La₂CuO₄) to be metals. Newer, more difficult to implement (e.g., "B3LYP") seem to do better

  \[ \text{(But have no other controversial feature incl. 1d-like e}^2 \text{ bond)} \]

  [Perry, Tahir-Kheli, Goddard, PAB 63 144 510 J]

- Nature of Fermi surface: few exp. studies
  - Photoemission - cuprates
  - Quantum Oscillations: Sr₂Ru₂O₄
    \[ \text{C. Bergeman} \]

- 4d. Triplet Sc. vs. high purity samples
Sr$_2$RuO$_4$-crystal structure (Bergmann)

- Ruthenium
- Strontium
- Oxygen

$\text{Ru}^{4+}$

$4d \rightarrow e_g$

$4d \rightarrow t_{2g}$
Sr2RuO4-dHvA fermi surface
(C Bergemann et al)

FIG. 28: Visualization of the Fermi surface of Sr2RuO4. The c-axis corrugation is exaggerated by a factor of 1.5 for clarity.
Qualitative view of Sr$_2$RuO$_4$ 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 Sr$_2$RuO$_4$. The lower panel shows how the $d_{xz}$ and $d_{yz}$ bands re-group to form the $\alpha$ and $\beta$ surface.
Values of tight binding parameters, band theory, and dHvA

<table>
<thead>
<tr>
<th>Ref.</th>
<th>$t_{11}(0,0)$</th>
<th>$t_{12}(0, a_0, 0)$</th>
<th>$t_{22}(a_0, 0, 0)$</th>
<th>$E_T$</th>
<th>$t_{12}(0, 0, a_0)$</th>
<th>$t_{22}(0, a_0, 0)$</th>
<th>$t_{22}(a_0, a_0, 0)$</th>
<th>$t_{22}(a_0, a_0, 0)$</th>
<th>$t_{22}(a_0, a_0, 0)$</th>
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<tbody>
<tr>
<td>22</td>
<td>0.4 eV</td>
<td>0.4 eV</td>
<td>0.12 eV</td>
<td>14.1 kT</td>
<td>0.3 eV</td>
<td>0.25 eV</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>23</td>
<td>0.5 eV</td>
<td>0.44 eV</td>
<td>0.14 eV</td>
<td>16.9 kT</td>
<td>0.24 eV</td>
<td>0.31 eV</td>
<td>0.045 eV</td>
<td>0.01 eV</td>
<td>—</td>
</tr>
<tr>
<td>24</td>
<td>0.5 eV</td>
<td>0.44 eV</td>
<td>0.14 eV</td>
<td>16.9 kT</td>
<td>0.24 eV</td>
<td>0.31 eV</td>
<td>0.045 eV</td>
<td>0.01 eV</td>
<td>0.1 eV</td>
</tr>
<tr>
<td>Section VIA 1</td>
<td>0.65 eV</td>
<td>0.42 eV</td>
<td>0.17 eV</td>
<td>18.65 kT</td>
<td>0.33 eV</td>
<td>0.30 eV</td>
<td>0.031 eV</td>
<td>—</td>
<td>0.002 eV</td>
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<tr>
<td>3</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

- Measured from c.w.
- Introduced unphysically as constant hybridization $t_{12}(0, 0, 0)$.

**dHvA FS**

**FS, LDA Ref 23**

Side point: Jahn-Teller splitting $xz, yz :: xy 0.3 eV
Quasiparticle mass enhancements over band results

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
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</thead>
<tbody>
<tr>
<td>Band mass</td>
<td>$m_0/m$</td>
<td>1.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Cyclotron mass</td>
<td>$m_e/m$</td>
<td>2.1</td>
<td>4.3</td>
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<tr>
<td>Thermodynamic mass</td>
<td>$m^*/m$</td>
<td>3.3</td>
<td>7.0</td>
</tr>
<tr>
<td>Susceptibility mass</td>
<td>$m^*_\text{susc}/m$</td>
<td>4.1</td>
<td>8.6</td>
</tr>
</tbody>
</table>

LDA overpredicts band masses (qp dispersion) by factors of 3-5.
Photoemission: $v_F = 1.8$ eV-A

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

Zone diagonal dispersion,
Johnson et al PRL87 177007 (2001)
TMD: electronic structure.

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

$$H = -\sum \frac{\hbar^2}{2m} \nabla_i^2 - \sum \frac{Z_i e^2}{|r_i - r_j|} + \sum \frac{e^2}{|r_i - r_j|}$$

"Single particle" part $H_0$

interaction $H_I$

In practice: (e) can't solve (b) soln would have TMD

- Very useful way to think abt diff approx solns

Electron Green's Function: $-i \langle T C C^+ \rangle$

If $H_I = 0$, $G_{n\sigma} \rightarrow G_n \left( p \right) = \frac{1}{w - \varepsilon_n(p)} = \frac{1}{w - H_0}$

$G_n p$ in $1^{st}$ BZ, $n$ = band index

In presence of $H_I$

$$G = \left[ \omega - \varepsilon_n(p) S_{nn'} - \varepsilon_{nn'}(p, \omega) \right]^{-1} = \left[ \omega - H_0 - \Sigma \right]^{-1}$$

As matter of principle $G$ diagonal in $p$, matrix in band indices (or in space $p + n \mathbf{G}$ recip. latt. vect.) incl. energy

As matter of principle can derive all phys. quantities from "Luttinger-Ward Functional" $\Phi \left[ G \right]$ - do sum of diagrams

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

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

$\text{Re} \Sigma = \int \frac{d\mathbf{x}}{2\pi} \frac{\text{Im} \Sigma(x)}{w - x}$ (Kramers-Kronig)

BAND THEORY: $\Sigma_{nm}(p, \omega) \rightarrow \Sigma_{nm}(p)$
Make connection precise:

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

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

Then $F = -Tr \ln G^{-1} + \Phi [G] G^{-1} [G^{-1} G]^{-1}$

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

$G_0$: carries info abt lattice. $\Phi$: info abt ints.

In Kohn-Sham approach. $G = G_0 - H_0 - V_{ks}$

Also know $F$

$\Rightarrow \Phi [G]$: Exc $\Phi [G] + \frac{1}{2} \sum \frac{p(r) \cdot p(r')}{|r-r'|}$ $\Phi [G] G^{-1}$

$E_{ks} G$

Extensions:

$E = E_{ks} (\rho) + E_{exx} (\omega)$: local $F_n$

$\Rightarrow$ as above but $\Phi_{ks} \Rightarrow \Phi_{ks} - G_0^{-1} [E (\omega)] G_0^{-1} G_0^{-1}$

$\Phi [G_{ws}] - \Phi_{DC}$

remove part of energy already included in DFT
Band Theory \( \Sigma_{n \to} (p, \omega) \to \Sigma_{n \to} (p) \) (No Impart)

\[ G_{\text{band}} = [\omega - H_0 - \Sigma_{n \to} (p)]^{-1} \]

Eigenvalues of \( H_0 + \Sigma_{n \to} (p) \to \) Band dispersions \( \Sigma_{n \to} (p) \)

Kohn-Sham theory: prescription for evaluating part of \( \mathcal{G} [G] \) having to do \( \nu \) ground state energy

Effects beyond band theory: \( \nu \)-dep. of \( \Sigma_{n \to} (p, \omega) \)

- to study:
  1. Perturbation theory...
  2. Diagonalize small systems
  3. Dynamical mean field

\( \Sigma_{n \to} (p, \omega) \to \Sigma_{n \to} (\omega) \)

Comparison to \( \text{Sr}_2 \text{RuO}_4 \), \( \text{La}_2 \text{CuO}_4 \)

- Metals: FS close to but not ex. right
- Excitations (e.g., velocity) off by factor \( \approx 2 \)

Many implementations miss "Mott insulating" behavior