Band structures of known families of HTSC cuprates;


can we engineer them to get further?

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The crackpot contribution at the end of an otherwise serious school
The quest for high-temperature superconductivity
In order to get better superconductors, do we need to understand the mechanism?

and if we do, does it help?
What can be learned about high T\textsubscript{c} from the LDA?


1988 - 91 LDA+U calculations for undoped compounds. Parameters of the 3-band Hubbard model supporting the Emery and t-J models.

1988 - 92 Fermi surfaces for many cuprates. Agreement with positron anihilation and early ARPES.

1994 - 95 Extract low-energy TB models explaining the "chemistry". Predict \( t'/t \), bi-layer splitting \( t_{\text{perp}}(k_x,k_y) \propto (\cos k_x - \cos k_y)^2 \) and interplane exch-coupling \( J_{\text{perp}} \propto \int t_{\text{perp}}(k)t_{\text{perp}}(k+Q)dk/U \)

1995 - 96 Phonon frequencies and linewidths for all \( q \)'s in \( s \)- and \( d \)-wave channels. Analytical \( g(k,k') \)

2000- Who cares! ARPES sees the FS and the dressed band structure!

We do, because ARPES from overdoped systems do confirm the LDA FS predictions.

2001 \( t'/t \) for 15-20 families of HTSC; correlation with \( T_{c,\text{max}} \)

2003- Numerically exact Wannier functions, 1- and 3-band Hubbard Hamiltonians. DMFT, DCA and other many-body calculations.

2009- After 23 years, the mechanism of HTSC remains an unsolved problem
YBa$_2$Cu$_3$O$_7$
$\text{YBa}_2\text{Cu}_3\text{O}_7$

Stoichiometric at optimal doping

LDA

Bi-layer splitting:
La$_{2-n}$Sr$_n$CuO$_4$

Electron count: $+3 \times 2 - n + 11 - 2 \times 4 = 9 - n \rightarrow$ Cu $d^{9-n}$
Tl$_2$Ba$_2$CuO$_{6+\delta}$
Hussey et al.

Angular magnetoresistance oscillations (AMRO)
Where does this materials dependence come from?

There is presently no accepted theory of high-temperature superconductivity in the cuprates

Electronic structure $\rightarrow$ $H = \sum t_{ij} c_i^\dagger c_j + U \sum n_{i\uparrow} n_{i\downarrow}$
$\text{YBa}_2\text{Cu}_3\text{O}_7$

Stoichiometric at optimal doping

LDA

Bi-layer splitting:
The Materials Trend, PRL 87, 047003 (2001)

Cuprates $3d^{9-x} = 3d_{x^2-y^2}^{1-x}$

LDA conduction-band $(x^2-y^2)$ shapes and ARPES Fermi surfaces for overdoped HTSCs
Which structural elements determine $r$?
One-orbital LDA Wannier-like function

$\text{La}_2\text{CuO}_4$

$T_c = 40 \text{ K}, \ r=0.17$

$\text{HgBa}_2\text{CuO}_4$

$T_c = 90 \text{ K}, \ r=0.33$
One-orbital LDA Wannier-like function

La$_2$CuO$_4$
The materials trend is best understood in terms of a tight-binding model with two orbitals:

\[ d = \text{Cu } x^2-y^2 \]
dressed with

\[ \text{O } p \]

and

\[ s = \text{axial orbital } = \text{Cu } 4s \]
dressed with

\[ \text{Cu } 3z^2-1, \]
\[ \text{O}_a z, \]
\[ \text{La } 3z^2-1, \text{ a.s.o.} \]

The material-dependent parameter is \( \varepsilon_s - \varepsilon_F (>0) \). The smaller it is, the larger is \( r \sim t'/t \).
\begin{align*}
H_4 & 
\begin{array}{c|cccc}
\langle d, k \rangle & |d, k\rangle & |s, k\rangle & |x, k\rangle & |y, k\rangle \\
\langle d, k \rangle & \epsilon_d & 0 & 2t_{pd} \sin \frac{k_x}{2} & -2t_{pd} \sin \frac{k_y}{2} \\
\langle s, k \rangle & 0 & \epsilon_s & 2t_{sp} \sin \frac{k_x}{2} & 2t_{sp} \sin \frac{k_y}{2} \\
\langle x, k \rangle & 2t_{pd} \sin \frac{k_x}{2} & 2t_{sp} \sin \frac{k_x}{2} & \epsilon_p & 0 \\
\langle y, k \rangle & -2t_{pd} \sin \frac{k_y}{2} & 2t_{sp} \sin \frac{k_y}{2} & 0 & \epsilon_p \\
\end{array}
\end{align*}
Löwdin downfolding to 2 orbitals:

\[
\begin{align*}
H_4 & \begin{pmatrix}
|d, k\rangle \\
|s, k\rangle \\
|x, k\rangle \\
|y, k\rangle
\end{pmatrix} \\
\langle d, k | & \epsilon_d 0 2t_{pd} \sin \frac{k_x}{2} -2t_{pd} \sin \frac{k_y}{2} \\
\langle s, k | & 0 \epsilon_s 2t_{sp} \sin \frac{k_x}{2} 2t_{sp} \sin \frac{k_y}{2} \\
\langle x, k | & 2t_{pd} \sin \frac{k_x}{2} 2t_{sp} \sin \frac{k_x}{2} \epsilon_p 0 \\
\langle y, k | & -2t_{pd} \sin \frac{k_y}{2} 2t_{sp} \sin \frac{k_y}{2} 0 \epsilon_p
\end{align*}
\]

\[
H_2 (\varepsilon) \begin{pmatrix}
|d, \varepsilon, k\rangle \\
|s, \varepsilon, k\rangle
\end{pmatrix} = \\
\begin{align*}
\langle d, \varepsilon, k | & \epsilon_d + \frac{4t_{pd}^2}{\varepsilon - \epsilon_p} \left( \sin^2 \frac{k_x}{2} + \sin^2 \frac{k_y}{2} \right) \\
\langle s, \varepsilon, k | & \frac{4t_{sp}^2 t_{pd}}{\varepsilon - \epsilon_p} \left( \sin^2 \frac{k_x}{2} - \sin^2 \frac{k_y}{2} \right) \\
\langle x, \varepsilon, k | & \frac{4t_{sp}^2 t_{pd}}{\varepsilon - \epsilon_p} \left( \sin^2 \frac{k_x}{2} - \sin^2 \frac{k_y}{2} \right) \\
\langle y, \varepsilon, k | & \epsilon_s + \frac{4t_{pd}^2}{\varepsilon - \epsilon_p} \left( \sin^2 \frac{k_x}{2} + \sin^2 \frac{k_y}{2} \right)
\end{align*}
\]
Hybridization between $x^2-y^2$ and axial orbital Cu $4s$, apical O $2p_z$, etc.

Hybridization $\sim (\cos k_x - \cos k_y)^2$
\[ H2(\varepsilon) = |d, \varepsilon, k\rangle \quad \frac{4t^2_{pd}}{\varepsilon - \varepsilon_p} \left( 1 - \frac{\cos k_x + \cos k_y}{2} \right) \quad \frac{4t_{sp} t_{pd}}{\varepsilon - \varepsilon_p} \cos k_x - \cos k_y \]

\[ \langle s, \varepsilon, k | = -\frac{4t_{sp} t_{pd}}{\varepsilon - \varepsilon_p} \cos k_x - \cos k_y \quad \frac{4t^2_{sp}}{\varepsilon - \varepsilon_p} \left( 1 - \frac{\cos k_x + \cos k_y}{2} \right) \]

**Downfolding to 1 orbital:**

\[ H1(\varepsilon) = \langle \tilde{d}, \varepsilon, k | H | \tilde{d}, \varepsilon, k \rangle = \]

\[ = \varepsilon_d + \frac{4t^2_{pd}}{\varepsilon - \varepsilon_p} \left( 1 - \frac{\cos k_x + \cos k_y}{2} \right) + \frac{4t^2_{sp}}{\varepsilon - \varepsilon_p} \left( \frac{\cos k_x - \cos k_y}{2} \right)^2 \]

\[ = \varepsilon_d + \frac{4t^2_{pd}}{\varepsilon - \varepsilon_p} \left( 1 - \frac{\cos k_x + \cos k_y}{2} \right) + \frac{t^2_{sp}}{\varepsilon - \varepsilon_p} \left( 1 - 2 \cos k_x \cos k_y + \frac{\cos 2k_x + \cos 2k_y}{2} \right) \]

\[ = \varepsilon_0 - 2t (\cos k_x + \cos k_y) + 4t' \cos k_x \cos k_y - 2t'' (\cos 2k_x + \cos 2k_y) + \ldots \]

\[ t = \frac{t^2_{pd}}{\varepsilon - \varepsilon_p}, \quad \frac{t'}{t} \approx \frac{2t_{sp}}{\varepsilon - \varepsilon_p} \quad \frac{t''}{t'} = \frac{1}{2} \equiv r(\varepsilon) \]
From the nearest-neighbor 4-orbital model \((\varepsilon_p, \varepsilon_d, \varepsilon_s, t_{pd}, t_{sp})\) to the longer-ranged 1-orbital model \((t, t', t'', ...)\)
$T_{c \text{ max}} = 40K$, $r = 0.17$  

$T_{c \text{ max}} = 90K$, $r = 0.33$  

$r = \frac{1}{2} \sin (\pi \Delta \kappa)$
$r = \frac{1}{2} \cos (\pi k_{\Gamma M}/\Gamma M) + \sin^2 \left(\frac{\pi k_{XM}/XM}{2}\right) [2 + \cos (\pi k_{\Gamma M}/\Gamma M)]$

Angular magnetoresistance oscillations (AMRO)

Tl$_2$Ba$_2$CuO$_{6+\delta}$

Hussey et al.

Wannier function for the cuprate conduction band

The materials trend is best understood in terms of a tight-binding model with two orbitals:

\[ d = \text{Cu } x^2-y^2 \]

dressed with

\[ \text{O } p \]

and

\[ s = \text{axial orbital} = \text{Cu } 4s \]

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\[ \text{Cu } 3z^2-1, \]

\[ \text{O}_a z, \]

\[ \text{La } 3z^2-1, \text{a.s.o.} \]

The material-dependent parameter is \( \varepsilon_s - \varepsilon_F (> 0) \). The smaller it is, the larger is \( r \sim t'/t \).
One-orbital LDA Wannier-like function

La$_2$CuO$_4$

Four-orbital model

Axial

La $\varepsilon_s$

Cu 4s $\varepsilon_F$

O$_c$ 2p$_z$

Cu 3d$_{3z^2-1}$

La$_2$CuO$_4$
One-orbital LDA Wannier-like function
The Materials Trend, PRL 87, 047003 (2001)

- Hg Ba$_2$Ca$_2$Cu$_3$O$_8$
- Hg Ba$_2$Ca Cu$_2$O$_6$
- Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}^k$
- Tl$_2$Ba$_2$Ca Cu$_2$O$_8$
- Y Ba$_2$Cu$_3$O$_7$
- Hg Ba$_2$Cu O$_4$
- Tl$_2$Ba$_2$Cu O$_6$

- Pb$_2$Sr$_2$Y Cu$_3$O$_8$
- La$_2$Ca Cu$_2$O$_6$
- La Ba$_2$Cu$_3$O$_7$
- La$_2$Cu O$_4$

- Bi$_2$Sr$_2$Cu O$_6$
- Pb$_2$Sr$_2$Cu$_2$O$_6$
- Ca$_2$Cu O$_2$Cl$_2$

- r ~ t'/t
That the axial orbital is the channel for coupling the CuO$_2$ layer to its surroundings is supported by the experimental observations that $c$-axis transport is strongly suppressed by the opening of a pseudogap with a $(\cos k_x - \cos k_y)^2$-dependence and that the scattering in the normal state has a similar $k_\parallel$-dependence.

At the same time, the axial orbital is the vehicle for coupling between neighboring oxygens inside the layer. It therefore seems plausible that contraction of the axial orbital around the CuO$_2$-layer, away from the non-stoichiometric layers, will strengthen the phase coherence and thus increase $T_{c\ max}$.

It was completely unexpected that for multi-layer materials, the $T_{c\ max}$ trend is followed the Fermi-surface sheet with the largest $r$-value, i.e. with the lowest $\epsilon_{\text{axial}}$ and, hence, with the smallest hole volume.

How $r$ determines $T_{c\ max}$ remains to be understood.
Current approximations to ab initio Density-Functional Theory (LDA) are insufficient for conduction bands with strong electronic correlations, e.g. they do not account for the Mott metal-insulator transition.

On the other hand, LDA Fermi surfaces are accurate for most metals, including overdoped high-temperature superconductors.

Presently, we therefore start with the LDA. For the few correlated bands, we then construct localized Wannier orbitals and a corresponding low-energy Hubbard Hamiltonian. The latter is solved in the Dynamical Mean-Field Approximation.
Low-energy multiband Hubbard Hamiltonian

\[ \hat{H} = \sum_{i m \sigma, i' m' \sigma'} \delta_{\sigma, \sigma'} h_{i m, i' m'} c_{i m \sigma} ^\dagger c_{i' m' \sigma'} + \frac{1}{2} \delta_{i, i'} \sum'_{i m m' \sigma \sigma'} U_{i m m'} \hat{n}_{i m \sigma} \hat{n}_{i m' \sigma'} - \text{d.c.} \]

\( h_{i m, i' m'} \) is the LDA one-electron part. For the two-electron, on-site term, we use:

\[
\frac{1}{2} \sum_{m=1} \sum_{m' = 1} \sum_{\sigma} \sum_{\sigma'} U_{i m m'} \hat{n}_{i m \sigma} \hat{n}_{i m' \sigma'} \approx \]

\[ U_i \sum_{m} \hat{n}_{i m \uparrow} \hat{n}_{i m \downarrow} + (U_i - 2J_i) \sum_{m \neq m'} \sum_{\sigma \sigma'} \hat{n}_{i m \uparrow} \hat{n}_{i m' \downarrow} + (U_i - 3J_i) \sum_{m \neq m'} \sum_{\sigma, \sigma'} \left( \hat{n}_{i m \uparrow} \hat{n}_{i m' \uparrow} + \hat{n}_{i m \downarrow} \hat{n}_{i m' \downarrow} \right) \]

for two electrons in

same orbital

different orbitals and spins

same spin
Mott transition in cuprate HTSCs

Wannier orbitals and conduction band, LDA

Hubbard model, LDA+DMFT
T=2000K, undoped

U = 2.1
U = 3.0 eV

T. Saha-Dasgupta and OKA 2002
Cuprates $3d^{9-x} = 3d_{x^2-y^2}^{1-x}$

Conduction band LDA

One-band Hubbard model LDA+DMFT

$U = 2.1$ eV
undoped

$U = 3.0$ eV
undoped

10% doped

T. Saha-Dasgupta and OKA 2002
La$_2$CuO$_4$

Axial 4s-like orbital and $x^2-y^2$
How to make a cuprate Fermi surface out of a nickelate heterostructure, in theory

$3z^2-1 \quad 3d^7 (e_g^1) \quad x^2-y^2$

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$^2$ Institute for Solid State Physics, Vienna University of Technology
Khaliullin’s idea: Make Ni$^{3+}$(d$^7$)-based HTSCs by sandwiching hole doped LaO-NiO$_2$ layers between insulating layers through heterostructuring (orbital engineering)

- The confinement together with the electronic correlations should make it possible to localize or empty the 3z$^2$-1 band thus leaving the conduction electron in the x$^2$-y$^2$ band

- If the 3z$^2$-1 orbital can be manipulated to lie above x$^2$-y$^2$, it might play the role of the axial orbital in the cuprate d$^9$ HTSCs

- Charge disproportionation (d$^6$+d$^8$) must be avoided

Confinement:

Paramagnetic LDA bands in (1 -1 0) plane

Cubic

Mn 3d \(e_g\)

LaMnO\(_3\)

La 4f

La 5d

O 2p

\(\Gamma(000)\) Z(00½) R(10½) A(11½) Z(00½) X(001) M(101) R(111) X(001)

Cubic

LaNiO\(_3\)

\(x^2-y^2\)

\(3z^2-1\)
$d^7$ nickelates

Simplified $e_g$ conduction-band structure in 2D square lattice:
Ni 4s, La 5d, Al 3p

Ni t<sub>2g</sub>, O 2p, Al 3s

Cubic

LaNiO<sub>3</sub>

x<sup>2</sup>-y<sup>2</sup>

3z<sup>2</sup>-1

1/1

LaAl

Ni 4s, La 5d, Al 3p

(eV)
The Coulomb correlations enhance the crystal-field splitting and simplifies the Fermi surface to one sheet when $\varepsilon_{3z^2-1}(\Gamma) > \varepsilon_F$, i.e. with a shape ($r \sim \frac{1}{2}$), like that in the cuprates with the highest $T_{c_{\text{max}}}$.
Cuprates $3d^{9-x} = 3d_{x^2-y^2}^{1-x}$

Conduction band LDA

One-band Hubbard model LDA+DMFT

$U = 2.1 \text{ eV}$

undoped

$U = 3.0 \text{ eV}$

undoped

10% doped

T. Saha-Dasgupta and OKA 2002
FIG. 3 (color online). Energy levels for the unstrained two-site model with $U = 6.4$ eV as a function of the splitting $\Delta$ between the energies of the $3z^2 - 1$ and $x^2 - y^2$ Wannier orbitals. The LDA value of $\Delta$ is indicated by the dashed line. $O_F$ ($O_{AF}$) denotes a configuration with the same (different) orbital(s) on the two sites.
Control by the chemistry (Al, Ti, Sc) of the insulating layers.

Control by lattice constant of the substrate.

1-sheet FS: $5.7 < U < 6.5$ eV

Control by the chemistry (Al, Ti, Sc) of the insulating layers.
Phase diagram of 3D RNiO$_3$ perovskites

FIG. 5. The phase diagram of transition temperatures vs bandwidth $W^2$ at room temperature. $T_{IM}$ and $T_N$ are taken from Refs. [23,25,29,30]. Lines inside the figure are guides to the eyes. Inset: definition of the angle $\omega$ used to obtain $W \sim \cos \omega/(\text{Ni-O})^{3.5}$.

Chemical control by the A and B cations and the thickness of the insulating layer. This is also a tool for avoiding charge disproportionation.
Adding insulating neighbor layers

promissing
Adding a NiO$_2$ nearest-neighbor layer (bilayer) less good
On stock:
(H-U Habermeier)
Thank you for listening

and

thank you to Nicola, Claudia and Mac for organizing this exciting summer school