3-orbital LDA Hamiltonian

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I. ORBITALS

The single-particle Wannier basis consists of the following three Bloch-summed in-plane orbitals:

$$\begin{aligned} |d,\mathbf{k}\rangle &\equiv \sum_{\mathbf{T}} \left|\mathrm{Cu}\; x^2-y^2\right\rangle \exp\left(i\mathbf{k}\cdot\mathbf{T}\right) \\ |x,\mathbf{k}\rangle &\equiv \sum_{\mathbf{T}} \left|\mathrm{O_a}\; x\right\rangle i^{-1} \exp\left(ik_x/2\right)\exp\left(i\mathbf{k}\cdot\mathbf{T}\right) \\ |y,\mathbf{k}\rangle &\equiv \sum_{\mathbf{T}} \left|\mathrm{O_b}\; y\right\rangle i^{-1} \exp\left(ik_y/2\right)\exp\left(i\mathbf{k}\cdot\mathbf{T}\right) \end{aligned}$$

Here, the phases have been chosen in such a way that the Hamiltonian and its eigenvectors $\left[c_{d,j}\left(\mathbf{k}\right),\, c_{s,j}\left(\mathbf{k}\right),\, ...c_{zy,j}\left(\mathbf{k}\right)\right]$ are real. Moreover, in the Bloch sums, we have omitted the usual prefactor $N^{-1/2}$ so that the Bloch orbitals are normalized to one over the primitive cell, rather than over the crystal with N cells. Accordingly, we take $\sum_{\mathbf{k}}$ to mean the average, rather than the sum, over the Brillouin zone. In the following we set $a=b=1$.

II. PARAMETERS OF THE 3-ORBITAL MODEL IN THE LDA

We have obtained a 3-orbital LDA Hamiltonian (electron energies) for La_2CuO_4, $Tl_2Ba_2CuO_6$, and $HgBa_2CuO_4$ from *numerical* LDA-NMTO *Wannier-like orbitals* (N=0, ϵ_0=ε_F). Its parameters obtained by Fourier transformation of the downfolded and symmetrically orthonormalized 3-orbital NMTO Hamiltonian are given in the tables. Here, $\begin{smallmatrix}\chi'\mathbf{R}'\\ \chi\mathbf{R}\end{smallmatrix}$ is the hopping integral from orbital $\chi\left(\mathbf{r}-\mathbf{R}\right)$ to orbital $\chi'\left(\mathbf{r}-\mathbf{R}'\right)$. Numerical energies are in meV.

	ϵ_d	$\epsilon_d-\epsilon_p$	$\begin{smallmatrix}d(100)\\ d(000)\end{smallmatrix}$	$\begin{smallmatrix}d(110)\\ d(000)\end{smallmatrix}$
La		431	−102	34
Tl		415	−91	30
Hg		444	−84	27

	$\begin{smallmatrix}x(\frac12 00)\\ d(000)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac12 10)\\ d(000)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac32 00)\\ d(000)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac32 10)\\ d(000)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac12 20)\\ d(000)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac32 20)\\ d(000)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac52 00)\\ d(000)\end{smallmatrix}$
La	961	−103	−1	22	1	−5	1
Tl	917	−104	1	12	1	−3	7
Hg	894	−102	1	14	3	−1	4

	$\begin{smallmatrix}y(0\frac12 0)\\ x(-\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}y(1\frac12 0)\\ x(-\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}y(1\frac32 0)\\ x(-\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}y(1\frac52 0)\\ x(-\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}y(\frac12 11)\\ x(-\frac12 00)\end{smallmatrix}$ bct	$\begin{smallmatrix}y(0\frac12 1)\\ x(-\frac12 00)\end{smallmatrix}$ sc
La	154	−26	18	−4	34	
Tl	377	−15	15		0	
Hg	401	−11	24			1

	$\begin{smallmatrix}x(\frac12 00)\\ x(-\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac12 10)\\ x(\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac12 10)\\ x(-\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac32 00)\\ x(-\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac12 20)\\ x(-\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac32 10)\\ x(-\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac32 20)\\ x(-\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac12 20)\\ x(\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac12 30)\\ x(\frac12 00)\end{smallmatrix}$	$\begin{smallmatrix}x(\frac52 00)\\ x(-\frac12 00)\end{smallmatrix}$
La	−241	19	107	−19	−20	−10	3	−19	7	−1
Tl	1	15	141	−16	−31	−8	1	−41	16	−5
Hg	1	0	127	−5	24	1	3	−41	11	

	$^{x\left(0\frac{1}{2}01\right)}_{x\left(-\frac{1}{2}00\right)}$ bct	$^{x\left(1\frac{1}{2}01\right)}_{x\left(-\frac{1}{2}00\right)}$ bct	$^{x\left(\frac{1}{2}01\right)}_{x\left(\frac{1}{2}00\right)}$ sc	$^{x\left(\frac{1}{2}01\right)}_{x\left(-\frac{1}{2}00\right)}$ sc	$^{x\left(\frac{1}{2}11\right)}_{x\left(-\frac{1}{2}00\right)}$ sc
La	−36	30			
Tl	0	0			
Hg			−5	4	3

III. THE 3-ORBITAL TIGHT-BINDING LDA HAMILTONIAN

With the on-site energies and hopping integrals given above, i.e. the Fourier components of $H\left(\mathbf{k}\right)$,

$$
H\left(\mathbf{k}\right)=\begin{array}{|ccc|}
\hline
\boxed{\epsilon_d\left(\mathbf{k}\right)} & \boxed{\left(\begin{array}{l} 2^{x\left(\frac{1}{2}00\right)}_{d(000)} \\ +2^{x\left(\frac{3}{2}00\right)}_{d(000)}\cos k_x+4^{x\left(\frac{1}{2}10\right)}_{d(000)}\cos k_y \\ +4^{x\left(\frac{3}{2}10\right)}_{d(000)}\cos k_x\cos k_y \\ +2^{x\left(\frac{5}{2}00\right)}_{d(000)}\cos 2k_x+4^{x\left(\frac{1}{2}20\right)}_{d(000)}\cos 2k_y \end{array}\right)\sin\frac{k_x}{2}} & \boxed{-\left(\begin{array}{l} 2^{x\left(\frac{1}{2}00\right)}_{d(000)} \\ +2^{x\left(\frac{3}{2}00\right)}_{d(000)}\cos k_y+4^{x\left(\frac{1}{2}10\right)}_{d(000)}\cos k_x \\ +4^{x\left(\frac{3}{2}10\right)}_{d(000)}\cos k_x\cos k_y \\ +2^{x\left(\frac{5}{2}00\right)}_{d(000)}\cos 2k_y+4^{x\left(\frac{1}{2}20\right)}_{d(000)}\cos 2k_x \end{array}\right)\sin\frac{k_y}{2}} \\
\boxed{c.c.} & \boxed{\begin{array}{l} \epsilon_p+2^{x\left(\frac{1}{2}00\right)}_{x\left(-\frac{1}{2}00\right)}\cos k_x+2^{x\left(\frac{1}{2}10\right)}_{x\left(\frac{1}{2}00\right)}\cos k_y \\ +4^{x\left(\frac{1}{2}10\right)}_{x\left(-\frac{1}{2}00\right)}\cos k_x\cos k_y \\ +2^{x\left(\frac{3}{2}00\right)}_{x\left(-\frac{1}{2}00\right)}\cos 2k_x+2^{x\left(\frac{1}{2}20\right)}_{x\left(\frac{1}{2}00\right)}\cos 2k_y \\ +4^{x\left(\frac{3}{2}10\right)}_{x\left(-\frac{1}{2}00\right)}\cos k_y\cos 2k_x+4^{x\left(\frac{1}{2}20\right)}_{x\left(-\frac{1}{2}00\right)}\cos k_x\cos 2k_y \\ +4^{x\left(\frac{3}{2}20\right)}_{x\left(-\frac{1}{2}00\right)}\cos 2k_x\cos 2k_y, \end{array}} & \boxed{-4\left(\begin{array}{l} ^{y\left(0\frac{1}{2}0\right)}_{x\left(-\frac{1}{2}00\right)} \\ ^{y\left(1\frac{1}{2}0\right)}_{x\left(-\frac{1}{2}00\right)}\left(\cos k_x+\cos k_y\right) \\ +^{y\left(1\frac{3}{2}0\right)}_{x\left(-\frac{1}{2}00\right)}\cos k_x\cos k_y \end{array}\right)\sin\frac{k_x}{2}\sin\frac{k_y}{2}} \\
\boxed{c.c.} & \boxed{c.c.} & \boxed{H_{xx}\left(k_x\leftrightarrow k_y\right)} \\
\hline
\end{array}
$$

with

$$\epsilon_d\left(\mathbf{k}\right)=\epsilon_d+2^{d(100)}_{d(000)}\left(\cos k_x+\cos k_y\right)+4^{d(110)}_{d(000)}\cos k_x\cos k_y$$

and where we still need to add small hoppings.

IV. MODEL HAMILTONIAN

Hamiltonian for electrons:

$$H_{im\sigma,i'm'\sigma'}=H^{LDA}_{i\neq i'}+\delta_{i,i'}\left(\varepsilon_{ep}n_{ep}+\varepsilon_{ed}n_{ed}+Un_{ed\uparrow}n_{ed\downarrow}\right)$$

For U (and J) constrained LDA-LMTO calculations give:

	s_{Cu}	U_d	J_d	n_{hd}	$\epsilon_{hp}-\epsilon_{hd}$
	Boh rradii	eV	eV		eV
La	2.50	9.37	0.94	0.479	2.68
Tl	2.50	9.53	0.95	0.456	2.59
Hg	2.50	9.46	0.95	0.452	2.58

Here the radii, s, of the Cu spheres have been chosen such that the number of Cu d holes is (approximately) the same as in the 3-orbital model, namely

$$n_{hd} = 2\sum_k \theta\left(\varepsilon_{3k}-\varepsilon_F\right)\left|u_{3k,d}\right|^2,$$

where 3 denotes the antibonding pd band. In the last column, we give the size of the pd-gap:

$$\epsilon_{hp}-\epsilon_{hd} = \epsilon_{ed}-\epsilon_{ep}+U = \epsilon_{ed}^{LDA}\left(n_{ed}\right)-\epsilon_{ep}^{LDA}+U\left(1-\frac{1}{2}n_{ed}\right) = \frac{1}{2}Un_{hd}+\left[\epsilon_{ed}-\epsilon_{ep}\right]^{LDA},$$

where $\left[\epsilon_{ed}-\epsilon_{ep}\right]^{LDA}$ is $\epsilon_d-\epsilon_p$ in the LDA table.

V. INTERPRETATION OF THE LDA BANDS: FIRST-NEAREST-NEIGHBOR 6-ORBITAL MODEL ($S\Pi$ MODEL)

For interpretation of the accurate numerical results, we have used the 1st-nearest-neighbor 6-orbital model down-folded analytically to an orthonormal 3-orbital Hamiltonian. The results of this analytical axial-plus-$p\pi$-orbital ($s\pi$) model are given below. In the first rows, d is the interatomic distance.

	ϵ_d	$\epsilon_p-\epsilon_d$	$\frac{d(100)}{d(000)}$	$\frac{d(110)}{d(000)}$
d	0	0	1	1.41
$s\pi$	ε_d	$\varepsilon_p-\varepsilon_d+4\tau\left[\varepsilon_p\right]-2t\left[\varepsilon_p\right]+12\dot{\tau}\left(3\tau-t\right)-2\dot{t}\left(6\tau-5t\right)$	0	0

	$\frac{x\left(\frac{1}{2}00\right)}{d(000)}$	$\frac{x\left(\frac{1}{2}10\right)}{d(000)}$	$\frac{x\left(\frac{3}{2}00\right)}{d(000)}$	$\frac{x\left(\frac{3}{2}10\right)}{d(000)}$	$\frac{x\left(\frac{1}{2}20\right)}{d(000)}$	$\frac{x\left(\frac{3}{2}20\right)}{d(000)}$	$\frac{x\left(\frac{5}{2}00\right)}{d(000)}$
d	0.5	1.12	1.5	1.80	2.06	2.5	2.5
$s\pi$	$\left(1+2\dot{\tau}\right)t_{pd}$	$\left(\dot{\tau}-\frac{1}{2}\dot{t}\right)t_{pd}$	$-\left(2\dot{\tau}-\dot{t}\right)t_{pd}$	$-\dot{\tau}t_{pd}$	0	0	0

	$\frac{y\left(0\frac{1}{2}0\right)}{x\left(-\frac{1}{2}00\right)}$	$\frac{y\left(1\frac{1}{2}0\right)}{x\left(-\frac{1}{2}00\right)}$	$\frac{y\left(1\frac{3}{2}0\right)}{x\left(-\frac{1}{2}00\right)}$	$\frac{y\left(1\frac{5}{2}0\right)}{x\left(-\frac{1}{2}00\right)}$	$\frac{y\left(\frac{1}{2}11\right)}{x\left(-\frac{1}{2}00\right)}$ bct	$\frac{y\left(0\frac{1}{2}1\right)}{x\left(-\frac{1}{2}00\right)}$ sc
d	0.71	1.58	2.12	2.92	2.25	2.55
$s\pi$	$t\left[\varepsilon_p\right]+2\left(\dot{\tau}t+\dot{t}\tau-2\dot{t}t\right)$	$2\dot{t}t$	$-2\left(\dot{\tau}t+\dot{t}\tau\right)$	0		

	$\frac{x\left(\frac{1}{2}00\right)}{x\left(-\frac{1}{2}00\right)}$	$\frac{x\left(\frac{1}{2}10\right)}{x\left(\frac{1}{2}00\right)}$	$\frac{x\left(\frac{1}{2}10\right)}{x\left(-\frac{1}{2}00\right)}$
d	1	1	1.41
$s\pi$	$-2\tau\left[\varepsilon_p\right]+t\left[\varepsilon_p\right]-8\dot{\tau}\left(3\tau-t\right)+2\dot{t}\left(4\tau-3t\right)$	$2\tau\left[\varepsilon_p\right]+6\dot{\tau}\left(4\tau-t\right)-2\dot{t}\left(3\tau+t\right)$	$-\tau\left[\varepsilon_p\right]-2\dot{\tau}\left(8\tau-2t\right)+\dot{t}\left(4\tau+t\right)$

	$\frac{x\left(\frac{3}{2}00\right)}{x\left(-\frac{1}{2}00\right)}$	$\frac{x\left(\frac{1}{2}20\right)}{x\left(-\frac{1}{2}00\right)}$	$\frac{x\left(\frac{3}{2}10\right)}{x\left(-\frac{1}{2}00\right)}$	$\frac{x\left(\frac{3}{2}20\right)}{x\left(-\frac{1}{2}00\right)}$	$\frac{x\left(\frac{1}{2}20\right)}{x\left(\frac{1}{2}00\right)}$	$\frac{x\left(\frac{1}{2}30\right)}{x\left(\frac{1}{2}00\right)}$	$\frac{x\left(\frac{5}{2}00\right)}{x\left(-\frac{1}{2}00\right)}$
d	2	2.24	2.24	2.53	2	3	3
$s\pi$	$2\dot{\tau}\left(3\tau-t\right)-\dot{t}\left(2\tau-t\right)$	$-4\dot{\tau}\tau$	$\dot{\tau}\left(4\tau-t\right)-\dot{t}\tau$	$\dot{\tau}\tau$	$6\dot{\tau}\tau$	0	0

The parameters describing the downfolded s and π orbitals, together with rough estimates of their values, are:

$$t \equiv \frac{t_{sp}^2}{\varepsilon_s - \varepsilon_F} = \frac{1}{2}\frac{r}{1-2r}\left(\varepsilon_F - \varepsilon_p\right) \sim \begin{bmatrix} 0.15 \\ 0.4 \end{bmatrix} \text{ eV} \quad \text{for} \quad \begin{array}{r} \text{La} \\ \text{Tl and Hg} \end{array},$$

$$\tau \equiv \frac{t_{p\pi}^2}{\varepsilon_F - \varepsilon_\pi}$$

$$\dot{t} = \left(\frac{t_{sp}}{\varepsilon_s - \varepsilon_F}\right)^2 \quad \text{and} \quad \dot{\tau} = -\left(\frac{t_{p\pi}}{\varepsilon_F - \varepsilon_\pi}\right)^2,$$

$$t\left[\varepsilon_p\right] \equiv t + \dot{t}\left(\varepsilon_p - \varepsilon_F\right) = \left(1 - \frac{\varepsilon_F - \varepsilon_p}{\varepsilon_s - \varepsilon_F}\right) t < t \quad \text{and} \quad \tau\left[\varepsilon_p\right] \equiv \tau + \dot{\tau}\left(\varepsilon_p - \varepsilon_F\right) = \left(1 + \frac{\varepsilon_F - \varepsilon_p}{\varepsilon_F - \varepsilon_\pi}\right)\tau \sim 2\tau$$

$$\tau \approx \frac{1}{2}\tau\left[\varepsilon_p\right] \sim 0.1 \text{ eV}, \quad \dot{\tau} \approx \frac{\tau}{\varepsilon_p - \varepsilon_F} \sim \begin{bmatrix} -0.05 \\ -0.10 \end{bmatrix} \quad \text{for} \quad \begin{array}{r} \text{La} \\ \text{Tl and Hg} \end{array}$$

$$t_{pd} \sim 1.1 \text{ eV}.$$

By comparison with the numerical NMTO results given in the previous section, we realize that also O $3d$ and Ba and La $5d$ orbitals not taken into account in the $s\pi$ model, do play a minor role, in particular by providing direct dd hopping.