Single-particle basis sets for realistic theories of correlated materials

NMTOs:

intelligible (minimal, local-orbital) basis sets obtained from scattering theory.

Direct generation of Wannier-like orbitals

Application to high-temperature superconductors

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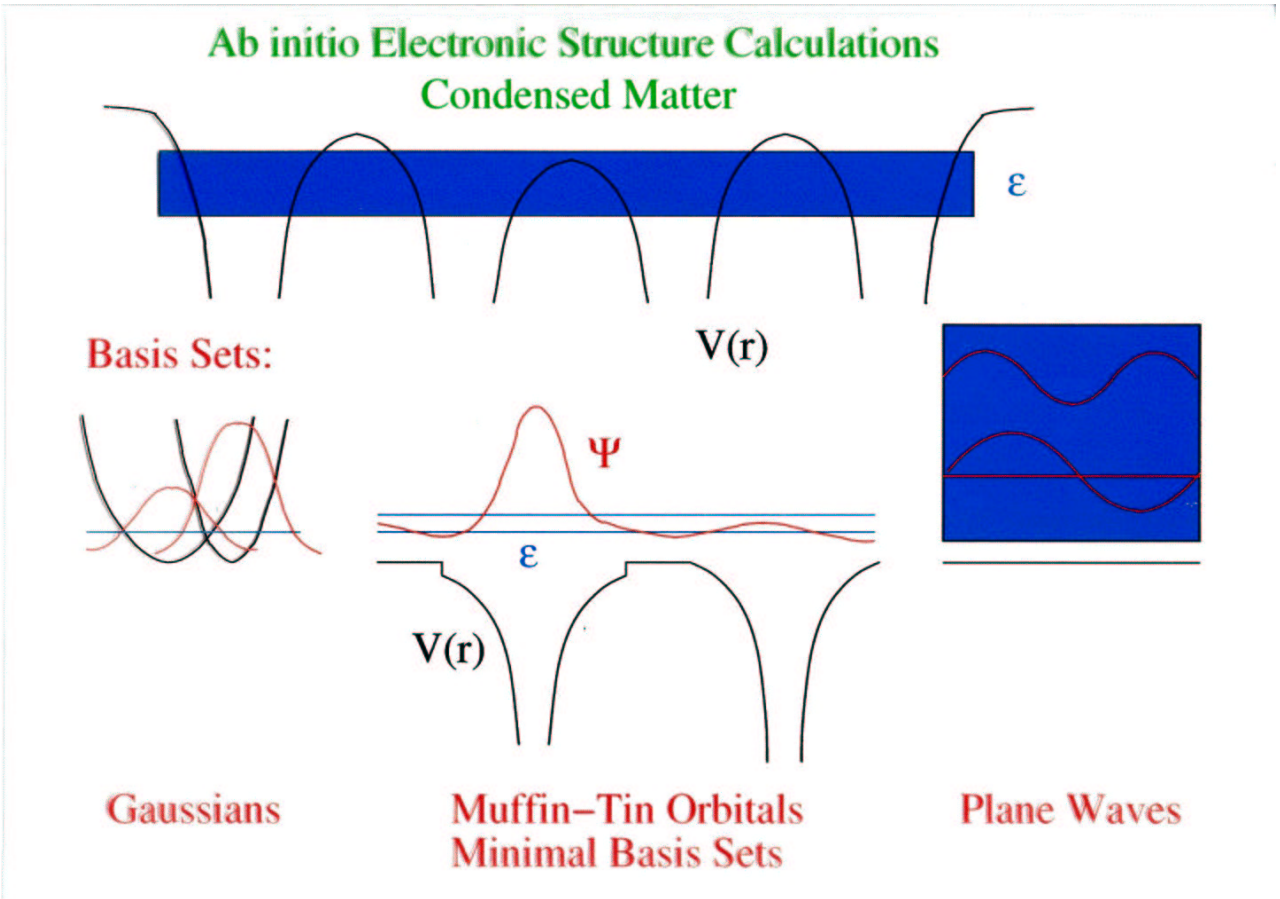
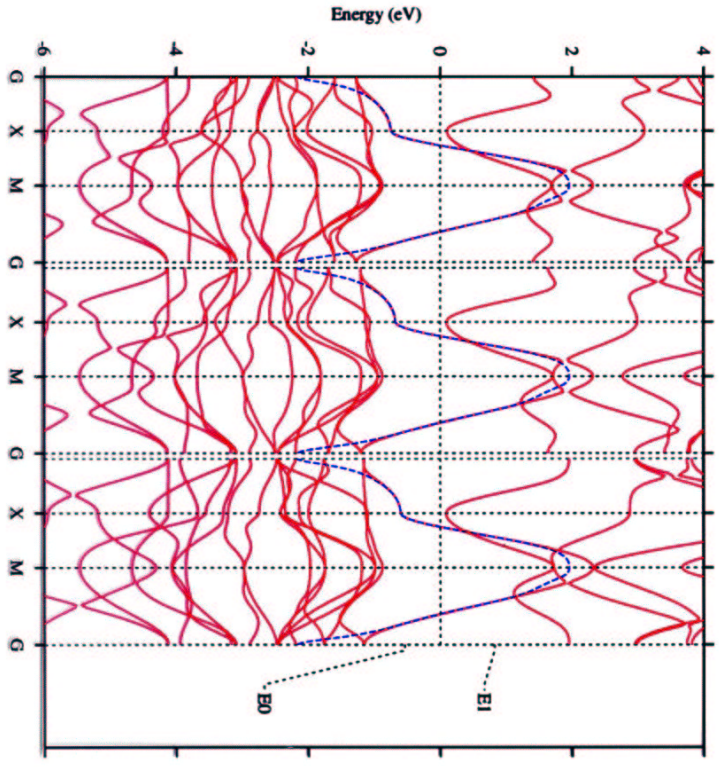


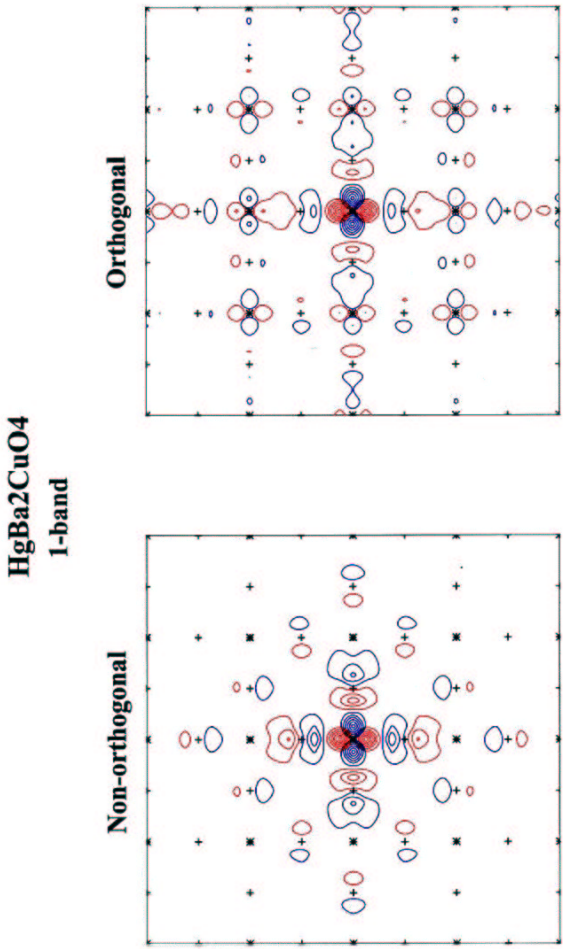
We derive the single-particle Hilbert space from a Kohn-Sham potential. For the *correlated* electrons, we separate a subspace $\{n\}$ of *local* orbitals.

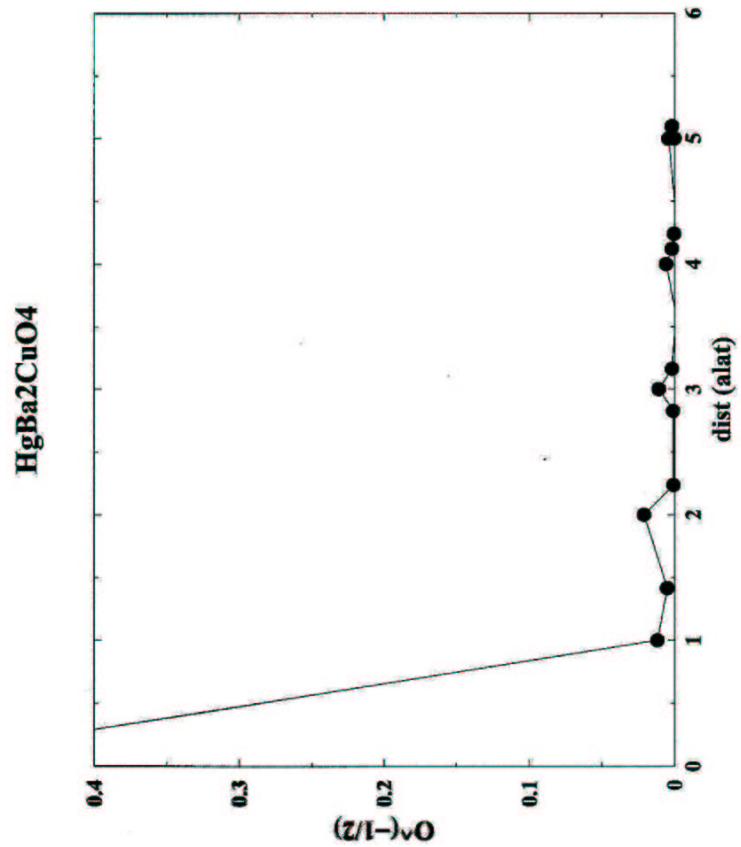
For an *isolated* set of bands, the *Wannier functions*, $w_n(\mathbf{r}-\mathbf{T})$, can be obtained from the Bloch states, $\psi_n^{\mathbf{k}}(\mathbf{r})$, computed with *any* basis set:

$$w_{n'}(\mathbf{r}) = \int d\mathbf{k} \sum_n U_{n'n}^{\mathbf{k}} \psi_n^{\mathbf{k}}(\mathbf{r}) .$$

Here, $U_{n'n}^{\mathbf{k}}$ is a *unitary* matrix [$U^{\mathbf{k}} = e^{i\phi(\mathbf{k})}$ if there is only one band], which is chosen in such a way that the $w_n(\mathbf{r})$ are (maximally) localized. This is done, by choosing the *local* projection of $\sum_n U_{n'n}^{\mathbf{k}} \Psi_n^{\mathbf{k}}(\mathbf{r})$ to be *real*. For plane-wave basis sets, this is essential and should even be augmented by minimization of e.g. $|\mathbf{r} - \langle \mathbf{r} \rangle|^2$. For local-orbital sets, this is hardly needed.




HgBa2CuO4
1-band
Orthogonal
Non-orthogonal


HgBa2CuO4
dist (alat)
0
1
2
3
4
5
6
0.1
0.2
0.3
0.4

By construction, the NMTO is very localized, but has an overlap matrix

$$\langle\chi|\chi\rangle = O \equiv 1 + o: \quad \int \chi(\mathbf{r}-\mathbf{T})^* \chi\left(\mathbf{r}-\mathbf{T}'\right) d\mathbf{r} = \delta_{\mathbf{T},\mathbf{T}'} + o_{\mathbf{T}-\mathbf{T}'}$$

Symmetrical (Loewdin) orthonormalization:

$$\begin{aligned} \left|\chi^{\perp}\right\rangle &= |\chi\rangle\, O^{-1/2} \approx |\chi\rangle\,(1-o/2): \\ \chi^{\perp}(\mathbf{r}) &\approx \chi(\mathbf{r}) - \sum_{\mathbf{T}>\mathbf{0}} (o_{\mathbf{T}}/2)\,[\chi(\mathbf{r}-\mathbf{T}) + \chi(\mathbf{r}+\mathbf{T})] \end{aligned}$$

where we have used that O is Hermitian (symmetric), $o_{\mathbf{T}} = o_{-\mathbf{T}}$.

Can we use $U^{\mathbf{k}} = e^{i\phi(\mathbf{k})}$ to localize the orthonormal NMTO better, *i.e.* can we undo the orthonormalization delocalization?

The transformation between Wannier-functions of different $\phi(\mathbf{k})$ is:

$$|w\rangle = \left|\chi^{\perp}\right\rangle U: \qquad w\left(\mathbf{r}-\mathbf{T}'\right) = \sum_{\mathbf{T}} \chi^{\perp}(\mathbf{r}-\mathbf{T})\, U_{\mathbf{T}-\mathbf{T}'}$$

where the translationally invariant transformation matrix satisfies:

$$U^{\dagger}U = 1: \qquad \sum_{\mathbf{T}} U^*_{\mathbf{T}-\mathbf{T}'} U_{\mathbf{T}} = \delta_{\mathbf{T}',\mathbf{0}}.$$

By construction, $\chi^{\perp}(\mathbf{r})$ is quite localized. We may therefore limit ourselves to consider *infinitesimal* unitary transformations:

$$U \equiv \mathbf{1}+u; \quad U^{\dagger} = 1+u^{\dagger} = U^{-1} \approx 1-u; \implies u^{\dagger} = -u: \quad u^*_{-\mathbf{T}} = -u_{\mathbf{T}}$$

Since u is *anti-Hermitian,*

$$w(\mathbf{r}) = \chi^{\perp}(\mathbf{r}) + \sum_{\mathbf{T}>\mathbf{0}} \left[u_{\mathbf{T}}\chi^{\perp}(\mathbf{r}-\mathbf{T}) - u^*_{\mathbf{T}}\chi^{\perp}(\mathbf{r}+\mathbf{T})\right],$$

it is impossible to choose $u_{\mathbf{T}}$'s that will undo the $o_{\mathbf{T}}$'s:

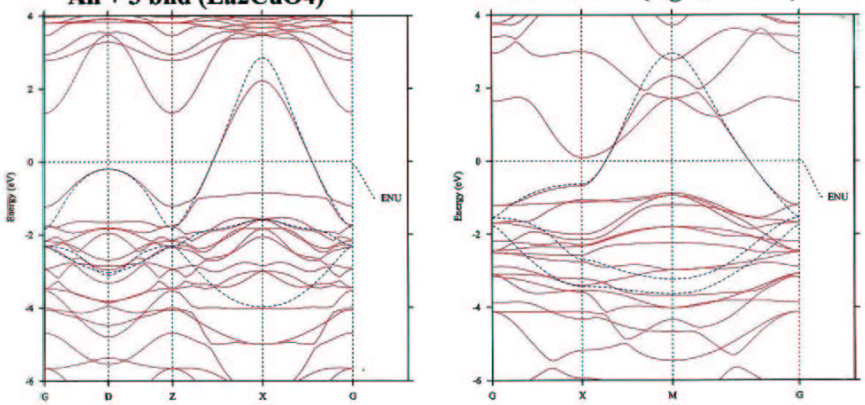
$$|w\rangle \;=\; \left|\chi^{\perp}\right\rangle U \;=\; |\chi\rangle\, O^{-1/2} U \;\approx\; |\chi\rangle\,(1+u-o/2)\,:$$

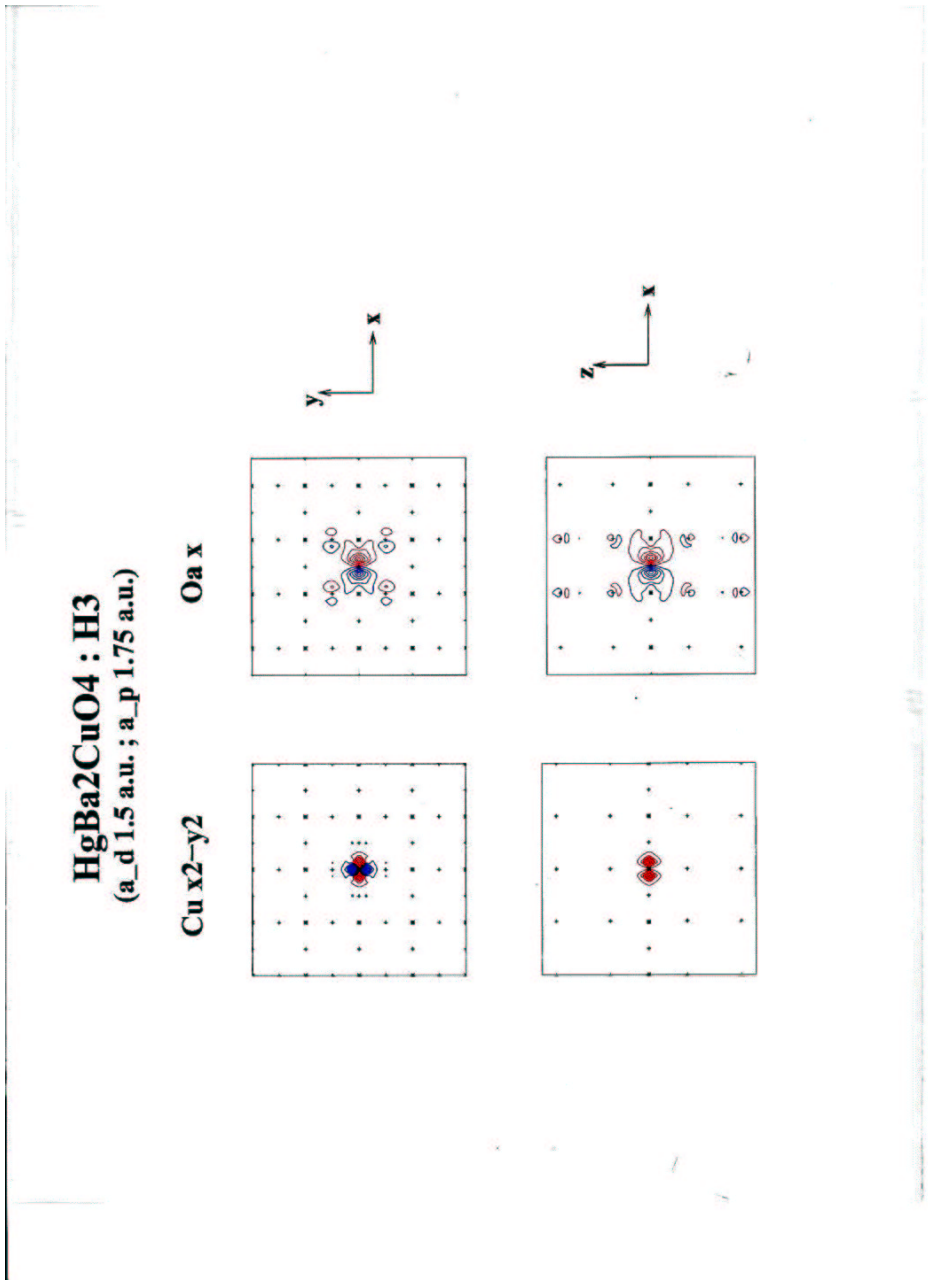
$$w(\mathbf{r}) \;=\; \chi(\mathbf{r}) - \sum_{\mathbf{T}>\mathbf{0}} \left[(o_{\mathbf{T}}/2 - u_{\mathbf{T}})\,\chi(\mathbf{r}-\mathbf{T}) + (o_{\mathbf{T}}/2 + u^{*}_{\mathbf{T}})\,\chi(\mathbf{r}+\mathbf{T})\right]$$

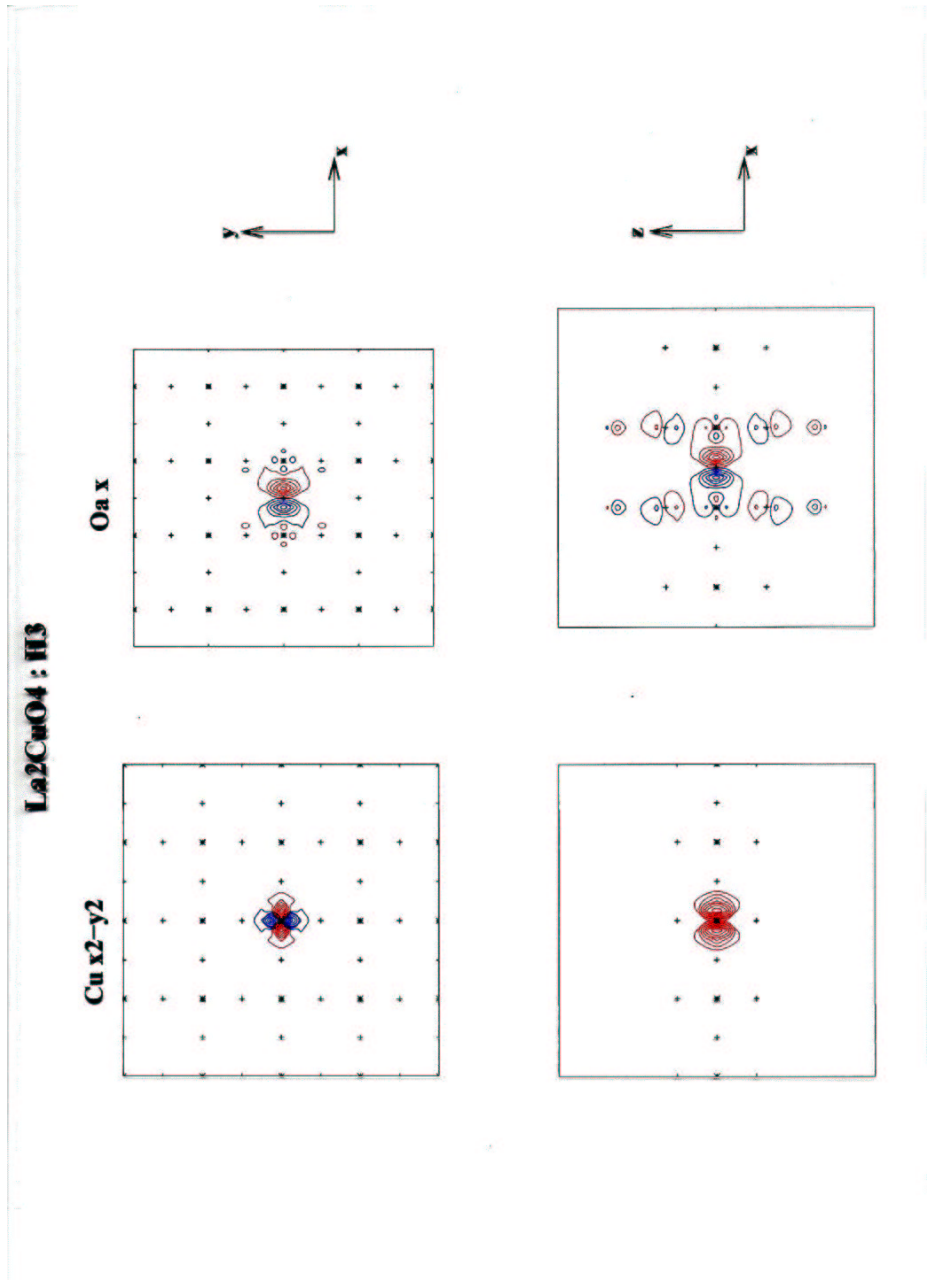
Conclusion: The NMTO is "maximally" localized.

But of course, by expanding the low-energy basis to include the two O p NMTOs, the Cu $d_{x^2-y^2}$ orbital becomes much more localized. However, that means going to a 3-band model.

LMTO




HgBa2CuO4 : H3
(a_d 1.5 a.u. ; a_p 1.75 a.u.)
Oa x
Cu x2−y2
y
x
z
x


La2CuO4 : H3
Oa x
Cu x2−y2
y
x
z
x