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

T. Saha-Dasgupta, E. Pavarini, D. Savrasov, O. K. Andersen
We derive the single-particle Hilbert space from a Kohn-Sham potential. For an isolated set of bands, the Wannier functions, \( w_n(r - \Gamma) \), can be obtained from the Bloch states, \( \psi_n^k(r) \), computed with any basis set:

\[
\psi_n^k(r) = \frac{1}{\sqrt{N}} \sum_{n} U_{nk} \psi_n^k(r).
\]

Here, \( U_{nk} \) is a unitary matrix \( U_{nk} = e^{i\phi(k)} \) if there is only one band, which is chosen in such a way that the \( w_n(r) \) are (maximally) localized. This is done by choosing the local projection of \( \sum_n U_{nk}^* \psi_n^k(r) \) to be real. For plane-wave basis sets, this is essential and should even be augmented by minimization of e.g. \( |r - \tau|^2 \). For local-orbital sets, this is hardly needed.
Minimal local-orbital sets, direct generation of Wannier-like functions, and...

HgBa₂CuO₄

Orthogonal

Non-orthogonal

1-band

HgBa₂CuO₄

dist (a|t)

(2|1)\_O
By construction, the NMTO is very localized, but has an overlap matrix
\[ \langle \chi | \chi \rangle = \mathcal{O} \equiv 1 + o : \int \chi(r - T)^* \chi(r - T') \, dr = \delta_{T, T'} + o_{T - T'} \]

Symmetrical (Loewdin) orthonormalization:
\[ \chi_{\perp} \approx \chi \cdot \mathcal{O}^{-1/2} \approx \chi (1 - o/2) : \]
\[ \chi_{\perp}(r) \approx \chi(r) - \sum_{T > 0} (o_T/2) [\chi(r - T) + \chi(r + T)] \]
where we have used that \( \mathcal{O} \) is Hermitian (symmetric), \( o_T = o_{-T} \).

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

The transformation between Wannier-functions of different \( \phi(k) \) is:
\[ |w \rangle = |\chi_{\perp} \rangle U : \quad w(r - T') = \sum_T \chi_{\perp}(r - T) \cdot U_{T - T'} \]
where the translationally invariant transformation matrix satisfies:
\[ U^{\dagger} U = 1 : \quad \sum_T U_{T - T'}^* U_T = \delta_{T', 0}. \]

By construction, \( \chi_{\perp}(r) \) is quite localized. We may therefore limit ourselves to consider infinitesimal unitary transformations:
\[ U \equiv 1 + u; \quad U^\dagger = 1 + u^\dagger = U^{-1} \approx 1 - u; \quad \Rightarrow u^\dagger = -u; \quad u^*_{-T} = -u_T \]
Since \( u \) is anti-Hermitian,
\[ w(r) = \chi_{\perp}(r) + \sum_{T > 0} [u_T \chi_{\perp}(r - T) - u_T^* \chi_{\perp}(r + T)], \]
\[ \text{it is impossible to choose } u_T \text{'s that will undo the } o_T \text{'s:} \]
\[|\psi\rangle = \left| \chi \right\rangle \equiv O^{-1/2} U \approx |\chi\rangle(1 + u_o/2)\]

\[|\psi\rangle = x(r) = \sum_{T>0} (\alpha T/2 - u_T) \chi(r - T) + (\alpha T/2 + u_T) \chi(r + T)\]

Conclusion:

The NMTO is "maximally" localized.

But of course, by expanding the low-energy basis to include the two \(O_p\) NMTO, the Cu \(d_{2s}+d_{2p}\) orbital becomes much more localized. However, that means going to a 3-band model.