Wannier functions
theory and selected applications

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Dynamical Mean-Field Approach with Predictive Power for Strongly Correlated Materials
Outline

• Motivation

• Fourier transform

• Exponential localization and band topology

• Examples

• Crystal field parameters for rare earths in oxides
Electrons in periodic potential

Bloch theorem

\[-\nabla^2 \psi(r) + V(r)\psi(r) = \epsilon\psi(r)\]

\[\psi_{n,k}(r) = e^{-i\mathbf{k} \cdot \mathbf{r}} u_{n,k}(r)\]

Bloch waves are not necessarily the best basis for further developments, e.g. perturbative treatment of the interaction.
Localized and orthonormal orbitals

- Useful basis for treatment of local perturbations (impurities, defects, on-site interaction)
- Obey canonical commutation relations
- Explicit translational symmetry
- Compromise between localization in space and ‘localization’ in the energy domain (minimal basis)
- Analytic tool - chemist’s view
Orthogonal atomic orbitals

Bloch sum (Fourier series)

\[ \phi(k, x) = \frac{A(k)}{N^{1/2}} \sum_{R} e^{i k \cdot R} v(x - R) \]

Normalization

\[ \frac{1}{A(k)^2} = \sum_{R} e^{i k \cdot R} \int dx v^*(x) v(x - R) \]

Fourier coefficient

\[ w(R, x) = \frac{1}{N^{1/2}} \sum_{k} e^{-i k \cdot R} \phi(k, x) \]
\[ = \sum_{R'} c(R - R') v(x - R') \]
Wannier functions

- Single isolated band
- Isolated composite band
- Entangled band 

$E(k)$
WF of single isolated band

Fourier coefficient

\[ w_n(r - R) = \frac{V}{(2\pi)^d} \int_{BZ} dke^{-ik \cdot R} \psi_{n,k}(r) \]

Fourier series

\[ \psi_{n,k}(r) = \sum_{R} e^{ik \cdot R} w_n(r - R) \]

\[ \psi_{n,k}(r) \rightarrow e^{i\phi(k)} \psi_{n,k}(r) \]

Gauge freedom
WF of isolated composite band

Fourier coefficient

\[ w(r - R) = \frac{V}{(2\pi)^d} \int_{BZ} dk U(k) \psi_k(r) e^{-ik \cdot R} \]

Fourier series

\[ \tilde{\psi}_k(r) = \sum_R e^{ik \cdot R} w(r - R) \]

\[ \psi'_{n,\mathbf{k}}(r) = U_{nm}(\mathbf{k}) \psi_{\bar{m},\mathbf{k}}(r) \]

Gauge freedom
WF properties

Explicit periodicity
\[ w_R(r) = w(r - R) \]

Orthogonality
\[ \langle w(r - R) | w(r - R') \rangle = \delta_{R,R'} \]

Uniqueness of Wannier center
\[ \tilde{\psi} = e^{i\phi} \psi \]

\[ \langle \tilde{w} | r | \tilde{w} \rangle = \langle w | r | w \rangle + \frac{V}{(2\pi)^d} \int_{BZ} dk \nabla_k \phi(k) \]
\[ = \langle w | r | w \rangle + R \]
Convergence of Fourier coefficients

\[ f(x) \]

\[ a_n = \frac{1}{2\pi} \int_0^{2\pi} dx e^{-inx} f(x) \]

\[ (1 - \frac{x}{\pi})^4 (1 + \frac{x}{\pi})^4 \]

\[ \sim n^{-5} \]

\[ (1 + \cos(x)) \sqrt{1.1 + \cos(x)} \]

\[ \sim e^{-\alpha n} \]

\[ \exp\left(-\frac{1}{1-(x/\pi)^2}\right) \]

\[ \sim |\pi n|^{-3/4} \exp\left(-\sqrt{|\pi n|}\right) \]
Convergence of Fourier coefficients

\[ f(x) \quad a_n = \frac{1}{2\pi} \int_{0}^{2\pi} dx e^{-inx} f(x) \]

\((1 - \sqrt{1 + \cos(x)})\)
Exponential localization of WFs

Can we make $\psi_k$ analytic?

$\psi_k$ can be made locally analytic - $k \cdot p$ expansion:

Can it be done globally?

This is a non-trivial topological question.
Brief excursion to topology

(Berry) connection

\[ A_{mn}^\alpha(k) = \langle u_n,k | \frac{\partial}{\partial k_\alpha} u_{m,k} \rangle \]

gauge dependent

(Berry) curvature

\[ B^{\alpha\beta}(k) = \text{tr} \left( \frac{\partial A^\beta}{\partial k_\alpha} - \frac{\partial A^\alpha}{\partial k_\beta} - [A^\alpha, A^\beta] \right) \]

\[ = 2 \text{Im} \sum_{n=n_{\text{min}}}^{n_{\text{max}}} \langle u_{n,k} | \frac{\partial}{\partial k_\alpha} u_{n,k} \langle \frac{\partial}{\partial k_\beta} u_{n,k} \rangle \]

gauge invariant

Exponentially localized WF exist if all Chern numbers associated with \( B^{\alpha\beta}(k) \) are zero.
Construction of WFs

Localization of WF reflects the variation of $u_k(r)$ through BZ.

$$\psi_{n,k}(r) = e^{-ik \cdot r} u_{n,k}(r)$$

Projection technique - aligns the phase of Bloch waves on a given site

- always works in 1D
- in 2D and 3D there are system where finite projection everywhere in BZ is not possible (QHE)
Construction of WFs

Maximum localization method - minimizes 2nd moment of WF

- Formulated in basis independent way

- Input: \[ M_{mn}^{(k,b)} = \langle u_{mk}|u_{nk+b}\rangle = \langle \psi_{mk}|e^{-ib\cdot r}|\psi_{nk+b}\rangle \]

- Additional input: \[ A_{mn}^{(k)} = \langle \psi_{mk}|g_n\rangle \]

- Output: \( U(k) \) unitary transformation between the Bloch and WF basis

Technical difficulty - to find a discrete approximation of \( \langle u_{n,k}|\frac{\partial}{\partial k_\alpha}u_{m,k}\rangle \) in terms of \( M_{mn}^{(k,b)} \)
Examples - large vs small energy window

SrVO$_3$

V-$d$ e$_g$

V-$d$ t$_{2g}$

O-$p$

V-centered

$xy$ orbital
Examples - symmetries and tight-binding representation

How to make use of weakly broken symmetries?

• We want to treat symmetry breaking term as perturbation and need to identify it and quantify
• TB Hamiltonian has higher symmetry than underlying the crystal structure

<table>
<thead>
<tr>
<th>Ising ferromagnet</th>
<th>anti-ferromagnet</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Diagram of Ising ferromagnet]</td>
<td>[Diagram of anti-ferromagnet]</td>
</tr>
</tbody>
</table>

Change meaning of up and down on even sites
Examples - symmetries and tight-binding representation

LaOFeAs - construction of model with 1 f.u. per u.c

Hoppings have higher translational symmetry than the crystal structure in proper basis!

Information about the crystal symmetry is ‘hidden’ in the shape of WF's
Examples - spin-orbital coupling

Sr$_2$IrO$_4$ (hypothetical symmetrized structure)

We want to construct J=1/2-like WFs out of t$_{2g}$ band.

$$w(r) \sim \left( \begin{array}{c} \alpha z (x + iy) \\ xy \end{array} \right)$$
Examples - spin-orbital coupling

Sr$_2$IrO$_4$ (hypothetical symmetrized structure)

\[
\langle \psi | \psi' \rangle = \int d\mathbf{r} \psi^*(\mathbf{r}) \psi'(\mathbf{r})
\]

\[
\langle \psi | \psi' \rangle = \sum_{\sigma} \int d\mathbf{r} \psi^*_\sigma(\mathbf{r}) \psi'_\sigma(\mathbf{r})
\]

\[w(\mathbf{r}) \sim \begin{pmatrix}
\alpha x + iy \\
xy
\end{pmatrix}\]

JK et al., Comput. Phys. Commun. 2010
Disentanglement

WFs are not unitary images of Bloch waves but an optimized projections.

\[ N_{WF} < N_{bands} \]

Projection method: Maximize overlap with a given subspace at each \( k \)-point

MALOC method: Find the smoothest \( N_{WF} \)-dimensional connection in a given \( N_{bands} \)-dimensional subspace
WFs and effective models

\[
H = \sum_k \left( [h^{dd}(k)]_{\alpha\beta} d^\dagger_{k\alpha} d_{k\beta} + [h^{pp}(k)]_{\gamma\delta} p^\dagger_{k\gamma} p_{k\delta} + [h^{dp}(k)]_{\alpha\gamma} d^\dagger_{k\alpha} p_{k\gamma} + [h^{pd}(k)]_{\gamma\alpha} p^\dagger_{k\gamma} d_{k\alpha} \right) \\
+ \sum_i U_{\alpha\beta\gamma\delta} d^\dagger_{i\alpha} d^\dagger_{i\beta} d_{i\gamma} d_{i\delta} - H_{dc}.
\]

Converge LDA, get \( \psi_k \) and \( \epsilon_k \)

Compute WFs for chosen Hilbert subspace

Construct \( h(k) \) in WF basis

Compute \( U_{\alpha\beta\gamma\delta} \) in WF basis

Solve model (compute correlation functions), e.g. with DMFT

Construct transition amplitudes (matrix elements) in WF basis

Compute observables
WFs and effective models

\[
H = \sum_k \left( [h^{dd}(k)]_{\alpha \beta} d^\dagger_{k\alpha} d_{k\beta} + [h^{pp}(k)]_{\gamma \delta} p^\dagger_{k\gamma} p_{k\delta} + [h^{dp}(k)]_{\alpha \gamma} d^\dagger_{k\alpha} p_{k\gamma} + [h^{pd}(k)]_{\gamma \alpha} p^\dagger_{k\gamma} d_{k\alpha} \right) \\
+ \sum_i U_{\alpha \beta \gamma \delta} d^\dagger_{i\alpha} d^\dagger_{i\beta} d_{i\gamma} d_{i\delta} - H_{dc}.
\]

Converge LDA, get \( \psi_k \) and \( \epsilon_k \)

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Construct \( h(k) \) in WF basis

Compute \( U_{\alpha \beta \gamma \delta} \) in WF basis

By choosing WFs we specify which interactions are treated explicitly and for which (static) mean-field decoupling is used.
Crystal field parameters: R in YAlO$_3$

15 crystal field parameters:

- 2
- 4
- 6
- 0
- 2
- 4
- 6

Nd, Tb, Er

Experiment: optical transitions between multiplet states
Theory: exact diagonalization for 4f shell in crystal field (CF)

How to get the CF parameters?
Crystal field parameters: R in YAlO$_3$

4f weakly coupled to the crystal environment - hybridization treated perturbatively

\[ \hat{H} = \sum_{i,j} (\hat{h}_{ij}^{at} + \sum_k \frac{V_{ik} V_{kj}}{\Delta_{fp}}) \hat{f}_i^\dagger \hat{f}_j + \hat{W}_f \]

Extracting CF parameters

old way

using WFs

- converge Wien2k with 4f in core
- get band structure with 4f in valence and shifted Op orbitals
- construct WFs from 4f window
- expand

\[ \hat{H}_{CF} = \sum_{k=0}^{k_{max}} \sum_{q=-k}^k B_{q}^{(k)} \hat{C}_{q}^{(k)} \]
Crystal field parameters: R in YAlO$_3$

Theory vs experiment: CF splittings of various multiplets

**Nd:YAlO$_3$**

**Er:YAlO$_3$**

**experiment:** Duan *et al.*, PRB 2007
Donlan&amp;Santiago, J. Chem. Phys. 1972

**theory:** Novák *et al.*, PRB 2013
Novák *et al.*, arXiv:1306.5948
Summary

- There is a close relationship between $k$-smoothness of Bloch waves and localization of Wannier functions.

- Existence of exponentially localized WFs is a topological property of a given (composite) band.

- Larger energy window $\Rightarrow$ more localized WFs.

- For typical applications in LDA+DMFT (i.e. large energy windows) the projection and MALOC methods give similar WFs.
Construction of WFs using w2w and wannier90

1) complete wien2k scf calculation
2) prepare a uniform k-mesh
   prepare case.ksym with 1 sym. operation
   x kgen -so -> case.klist
3) prepare case.w2win and w2w.def
   choose bands
   choose initial projections
   write_w2win case
   write_w2wdef case
4) prepare case.win
   chose band and orbitals
   add the list of k-points
   write_win case
5) prepare the list of k-connections case.nnkp
   wannier90.x -pp case
6) prepare $\psi_{nk}$ on a uniform k-mesh
   x lapw1 -> case.vector
7) run w2w w2w.def -> case.mmn, case.amn, case.eig
8) run wannier90.x case -> case.wout, case_band.dat, case_hr.dat
9) wplot case
10) convert Hamiltonian case
Construction of WFs using w2w and wannier90

case.w2win:

BOTH
21 23  # min band Nmin, max band Nmax
3 3  # LJMAX max in exp(ibr) expansion, #Wannier functions
2  #d-xy orbital
2 2 -2 0.00000000 0.70710677  # index of atom, L, M, coefficient (complex)
2 2 2 0.00000000 -0.70710677  # index of atom, L, M, coefficient (complex)
2  #d-yz orbital
2 2 -1 0.00000000 0.70710677  # index of atom, L, M, coefficient (complex)
2 2 1 0.00000000 0.70710677  # index of atom, L, M, coefficient (complex)
2  #d-xz orbital
2 2 -1 0.70710677 0.00000000  # index of atom, L, M, coefficient (complex)
2 2 1 -0.70710677 0.00000000  # index of atom, L, M, coefficient (complex)

\[ Y_{22} - Y_{2-2} \]
\[ Y_{21} + Y_{2-1} \]
\[ Y_{21} - Y_{2-1} \]
Construction of WFs using w2w and wannier90

**case.nnkp:**

```plaintext
... begin kpoints
  125
  0.00000000  0.00000000  0.00000000
  0.00000000  0.00000000  0.20000000
  0.00000000  0.00000000  0.40000000

... end kpoints

begin projections
end projections

begin nnkpts
  6
  1  2  0  0  0
  1  6  0  0  0
  1  26 0  0  0
  1  5  0  0  -1
  1  21 0  -1  0
  1  101 -1  0  0
  1  101 -1  0  0
  2  1  0  0  0
...```
Construction of WFs using w2w and wannier90

```plaintext
case.win:
 iprint = 3
 num_bands = 3
 num_wann = 3
 num_iter = 1000
 num_print_cycles = 100
...
begin kpoint_path
 R 0.50 0.5 0.5 GAM 0. 0. 0.
 GAM 0.00 0.00 0.00 X 0.50 0.00 0.00
 X 0.50 0.00 0.00 M 0.50 0.50 0.00
 M 0.50 0.50 0.00 GAM 0.00 0.00 0.00
end kpoint_path
...
bands_plot = .true.
!restart = plot
hr_plot = .true.
...
mp_grid : 5 5 5
begin kpoints
 0.000000000 0.000000000 0.0000000000
 0.000000000 0.000000000 0.200000003
...
```
Disentanglement

Cu

Energy (eV)

Window

Energy (eV)

(a)

(b)