Band Structure: Bulk and Surface

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3D Crystals: Bloch’s theorem

Crystal Hamiltonian:

\[ H = -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{eff}}(\mathbf{r}) \]

Hamiltonian eigenstates:

The solutions of the Schrödinger equation

\[ H \psi_{n\mathbf{k}}(\mathbf{r}) = E_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}) \]

are the Bloch functions:

\[ \psi_{n\mathbf{k}}(\mathbf{r}) = \text{“Bloch function”} \]

where \( n \) is a counting (band) index and \( \mathbf{k} \) labels transformation properties under translations:

\[ \psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}) \]
Bulk bandstructure

\[ \psi_{nk}(r) = \text{“Bloch function”} \]

**Note:**
- \( \mathbf{k} \) is a wavevector.
- Units = \((\text{length})^{-1}\)

**Occupation**

Metal

Insulator

**vanderbilt Lecture, Surface Science, 3/4/2013**
Bloch’s Theorem

Wavefunction labels are $n$, $k$.

$n = 1, 2, 3, \ldots$; $k \in \text{B.Z.}$

Two equivalent versions of translational symmetry:

(i) $\psi_{nk}(r + R) = e^{ik \cdot R} \psi_{nk}(r)$

(ii) $\psi_{nk}(r) = e^{ik \cdot r} u_{nk}(r)$ where $u_{nk}(r + R) = u_{nk}(r)$
Bulk bandstructure of diamond (C)
Real space and reciprocal space

\[ \mathbf{R} = \text{Lattice Vectors:} \quad \mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \]

\[ \mathbf{G} = \text{Reciprocal Lattice Vectors:} \quad \mathbf{G}_m = m_1 \mathbf{A}_1 + m_2 \mathbf{A}_2 + m_3 \mathbf{A}_3 \]

where \( \mathbf{A}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} \) or \( e^{i\mathbf{G}_m \cdot \mathbf{R}_n} = 1 \)

**Example:**

**Real Space**

**Reciprocal Space**

Unit cell

Brillouin zone
Beware alternate notations

\[ \mathbf{R}_n = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \]

Previous \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) now \( \mathbf{a}, \mathbf{b}, \mathbf{c} \)

\[ \mathbf{G}_m = m_1 \mathbf{A} + m_2 \mathbf{B} + m_3 \mathbf{C} \]

Previous \( \mathbf{A}_1, \mathbf{A}_2, \mathbf{A}_3 \) now \( \mathbf{A}, \mathbf{B}, \mathbf{C} \)

\[ \mathbf{A} \cdot \mathbf{a} = 2\pi, \quad \mathbf{A} \cdot \mathbf{b} = 0, \ldots \]
Periodicity in reciprocal space

Recall that \( \psi_{nk}(r) \) is the \( H \) eigenstate having boundary condition

\[
\psi_{nk}(r + R) = e^{i k \cdot R} \psi_{nk}(r)
\]

But then it follows that

\[
\psi_{n,k+G}(r) = \psi_{nk}(r)
\]

since

\[
e^{i(G+k) \cdot R} = e^{iG \cdot R} e^{ik \cdot R} = e^{ik \cdot R}
\]

which follows because \( G \cdot R = 2\pi \times \text{integer} \)

BZ is unit cell in reciprocal space
Summary: 3D crystals
Surface periodicity

Top view of surface unit cell in real space:

Si (001)  
\[ \begin{align*}
  &\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \Quad
Surface Brillouin zone

Conventional labels of points in the BZ:
Bulk Bloch state of wavevector $k$

$k_{\perp}$: 1D wavenumber

$k_{\parallel}$: 2D wavevector
Bulk band-structure from surface viewpoint

Let $k_\parallel$ be the component of $k$ parallel to the surface.

Let $k_\perp$ be the component of $k$ normal to the surface.

Bulk $\epsilon_{n_k} \rightarrow \epsilon_{n,k_\perp,k_\parallel} \rightarrow \epsilon_{\alpha,k_\parallel}$

$\alpha = (n, k_\perp)$ (combined index)

For given $k_\parallel$, plot the range of energies covered as $\alpha$ runs over all possible values.
Projected bulk bands at surface

Example

This is the conventional representation

Cubic crystal: Tight binding, 1 band

A simple tight-binding model with one $s$ state per site gives:

$$\epsilon(k) = \epsilon_s - 2V_s \cos(k_x a) - 2V_s \cos(k_y a) - 2V_s \cos(k_z a)$$

3D BZ:

Bulk Band Structure:

$$\Gamma = (0, 0, 0) \quad M = \left(\frac{\pi}{a}, \frac{\pi}{a}, 0\right) \quad X = \left(\frac{\pi}{a}, 0, 0\right) \quad R = \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right)$$
Cubic crystal: Tight binding, 1 band

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$$\epsilon(k) = \epsilon_s - 2V_s \cos(k_x a) - 2V_s \cos(k_y a) - 2V_s \cos(k_z a)$$

3D BZ: Look down

Bulk band structure:

$\Gamma = (0, 0, 0)$  $M = (\frac{\pi}{a}, \frac{\pi}{a}, 0)$  $\xi_s - 6V_s$

$X = (\frac{\pi}{a}, 0, 0)$  $R = (\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a})$

Cubic crystal: Tight binding, 1 band

Now plot surface BZ for (001) surface:

\[ \bar{\Gamma} = (0, 0) \]
\[ \bar{X} = (\frac{\pi}{a}, 0) \]
\[ \bar{M} = (\frac{\pi}{a}, \frac{\pi}{a}) \]
Cubic crystal: Tight binding, 1 band

Now plot surface BZ for (001) surface:

\[ \overline{\Gamma} = (0, 0) \]
\[ \overline{X} = \left(\frac{\pi}{a}, 0\right) \]
\[ \overline{M} = \left(\frac{\pi}{a}, \frac{\pi}{a}\right) \]
Cubic crystal: Tight binding, 1 band

Now plot surface BZ for (001) surface:

\[ \Gamma = (0, 0) \]
\[ \bar{X} = \left( \frac{\pi}{a}, 0 \right) \]
\[ \bar{M} = \left( \frac{\pi}{a}, \frac{\pi}{a} \right) \]
Cubic crystal: Add second band

Add $p$ bands, etc:

$\gamma_s$ bands

$p$ bands
Cubic crystal: Redraw
Sometimes you will see:

What are these solid and dashed lines?
Surface bandstructure of diamond (111)

Bloch’s theorem for a surface

\[ \psi_{\alpha,k||}(z, r||) = u_{\alpha,k||}(z, r||) e^{i k || \cdot r||} \]

where

\[ u_{\alpha,k||}(z, r||) = u_{\alpha,k||}(z, r|| + R||) \]

Energy bands are labeled as \( \epsilon_{\alpha,k||} \)

Index ‘\( \alpha \)’ is like the \( n \) index of a state \( \psi_{nlm} \) of the H atom: it can be either discrete or continuous.
Surface states and resonances

$\alpha$ is discrete:

$u_\alpha(z) \to 0$ as $z \to (+\infty)$ or $(-\infty)$

"Surface state"

$\alpha$ is continuous:

$u_\alpha(z)$ still decays for $z \to (+\infty)$

but penetrates indefinitely into the bulk

"Bulk state" or "Resonance"
How do various states look at the surface?

Bulk state

Surface state

Resonance
Experiments

Angle Resolved Photo-Emission Spectroscopy

Angle Resolved Inverse Photo-Emission Spectroscopy

Experiments

Angle Resolved Photo-Emission Spectroscopy

Angle Resolved Inverse Photo-Emission Spectroscopy

Experiments: Photoemission

Evidence for a New Broadening Mechanism in Angle-Resolved Photoemission from Cu(111)

S. D. Kevan
Bell Laboratories, Murray Hill, New Jersey 07974

FIG. 1. Experimental energy distribution curves for the Cu(111) sp surface state for several angles near normal emission in the ΓLUX plane. The second peak is due to the Ar \dagger doublet.

FIG. 2. Energy dispersion relation for the surface state. The solid curve is a parabolic least-squares fit. The shaded region is the projected bulk continuum of states. Note that the surface state enters the bulk continuum just above the Fermi level.
Experiments: Inverse Photoemission

A. Goldman, V. Dose and G. Borstel
Recent: Topological insulators

Observation of a large-gap topological-insulator class with a single Dirac cone on the surface


Spin-Orbit Coupling

Theoretical calculations

Energy (eV)

Bulk
- No SOC
- SOC

Surface
- No SOC
- SOC

Spin-Orbit Coupling
How do various states look at the surface?

- **Bulk state**
- **Surface state**
- **Resonance**
Typically, surface states exist if:

1. Character is similar to a bulk state, but shifted in energy by the surface perturbation

Usually $\Delta'$ is small (or at least $< \Delta$)
Typically, surface states exist if:

2. State of new character, e.g., a “broken bond” or “adsorbate state”, is created at the surface.

Typically the state is near the middle of the gap and is very localized (e.g., within one or a few atom distances from the surface in real space).

Example: Si (111) 1x1:
Surface bandstructure of diamond (111)
Surface bandstructure of diamond (111)

Summary

• Bulk bandstructure
  - 3D Real space and reciprocal space
  - Bloch’s theorem for 3D crystals
• Surface bandstructure
  - 2D Real space and reciprocal space
  - Projected bulk bandstructure
  - Surface bands
  - Resonances