From Atoms to Materials: Predictive Theory and Simulations

Week 2: Electronic Structure and Bonding of Molecules and Crystals
Lecture 2.5: Electronic Band Structures

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Electronic bands in crystals

How do we describe the $\sim 10^{24}$ crystal wavefunctions?
Background: Bravais lattice and basis

Bravais lattice: collection of points generated by three non-collinear vectors

\[ r_{lmn} = l \cdot \vec{a}_1 + m \cdot \vec{a}_2 + n \cdot \vec{a}_3 \]

Two dimensional Bravais lattice

Perfect crystal: Bravais lattice + basis (atoms)
Background: Crystal structures

Face centered cubic

Body centered cubic

Diamond

Zincblende
Background: Reciprocal space

Functions with the periodicity of the Bravais lattice can be written using plane waves as a basis set:

\[ e^{i \boldsymbol{G} \cdot \boldsymbol{r}} \]

With:

\[ \boldsymbol{G} \left( n_1 \boldsymbol{a}_1 + n_2 \boldsymbol{a}_2 + n_3 \boldsymbol{a}_3 \right) = n' 2\pi \]

The vectors that satisfy that condition also make a Bravais lattice in k-space: the reciprocal lattice with basis set \( \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3 \)

\[ \boldsymbol{G} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3 \]

\[ \boldsymbol{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \]
Background: Dirac’s notation

Wavefunction $\psi(r)$ Represented with a *ket*: $|\psi\rangle$

Complex conjugate of wavefunction: $\psi^*(r)$ *bra*: $\langle \psi |$

When a *braket* is formed integration is implied:

$$\langle \psi_1 | \psi_2 \rangle = \int \psi_1^*(r) \psi_2(r) \, d^3r$$

Expectation values

$$\langle \psi_1 | O | \psi_2 \rangle = \int \psi_1^*(r) O \psi_2(r) \, d^3r$$
How do we describe the $\sim 10^{24}$ crystal wavefunctions?
LCAO in crystals

Atomic orbital centered in atom \( n \)

\[
|\psi_{\text{xtal}}\rangle = \sum_n a_n |n\rangle = a_n |n\rangle
\]

Sum is implied for repeated indexes

\[
H a_n |n\rangle = E a_n |n\rangle \quad \text{Schrödinger Equation}
\]

Multiply by: \( \langle m | \)

\[
\langle m | H a_n |n\rangle = \langle m | E a_n |n\rangle
\]

\[
a_n \langle m | H | n\rangle = E a_n \langle m | n\rangle
\]

Only interactions between nearest neighbors + neglect overlap

\[
a_{m-1} \langle m | H | m-1\rangle + a_m \langle m | H | m\rangle + a_{m+1} \langle m | H | m+1\rangle = a_m E
\]
LCAO in crystals

\[-V_2a_{m-1} + h_0a_m - V_2a_{m+1} = a_mE\]

\[\psi_m = \omega_m\]

Ansatz: \[a_m(k) = e^{ikR_m} = e^{ikam}\]

\[-V_2e^{ik(m-1)a} + h_0e^{ikma} - V_2e^{ik(m+1)a} = Ee^{ikma}\]

\[-V_2e^{-ika} + h_0 - V_2e^{ika} = E\]

\[-V_2e^{-ika} + h_0 - V_2e^{ika} = E = h_0 - V_2(e^{-ika} + e^{ika})\]

\[E(k) = h_0 - 2V_2 \cos(ka)\]
First Brillouin Zone

Are all k values allowed or physically meaningful?

\[ \psi_{xtal}(k) = e^{ikan} |n\rangle \]

\[ \psi_{xtal}(k + \frac{2\pi}{a}) = e^{i(k + \frac{2\pi}{a})an} |n\rangle = e^{i\frac{2\pi}{a}an} e^{ikan} |n\rangle \]

\[ \psi_{xtal}(k) = \psi_{xtal}(k + \frac{2\pi}{a}) \]

Values of k: \(-\frac{\pi}{a} < k \leq \frac{\pi}{a}\)

- In 3D values of k are restricted to the First Brillouin Zone
- Points in k-space that are closer to the origin than to any other point of the reciprocal lattice
Band diagrams AKA E-k diagrams

s-type orbitals

\[ E_{1s}(k) = h_{0,1s} - 2V_{2,1s} \cos(ka) \]

p-type orbitals

- Each band denotes an atomic orbital
- K tells you how the WF changes from unit cell to unit cell