6.730 Physics for Solid State Applications

Lecture 13: Electrons in a Periodic Solid

Outline

• Brillouin-Zone and Dispersion Relations
• Introduce Electronic Bandstructure Calculations
• Example: Tight-Binding Method for 1-D Crystals

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Approaches to Calculating Electronic Bandstructure

**Nearly Free Electron Approximation:**
- Superposition of a few plane waves
  \( \psi(r) = \sum_{\mathbf{R}} c_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{r}} \)

**Cellular Methods (Augmented Plane Wave):**
- Plane wave between outside \( r_s \)
- Atomic orbital inside \( r_s \) (core)

**Pseudopotential Approximation:**
- Superposition of plane waves coupled by pseudopotential

**\( k.p \):**
- Superposition of bandedge (\( k=0 \)) wavefunctions

**Tight-binding Approximation (LCAO):**
- Superposition of atomic orbitals

\[ \psi_r(r) = \sum_{\alpha} c_{\alpha} \sum_{\mathbf{R}_n} c_{\alpha,\mathbf{R}_n} \phi_{\alpha}(r - \mathbf{R}_n) \]
Band Formation in 1-D Solid

- Simple model for a solid: the one-dimensional solid, which consists of a single, infinitely long line of atoms, each one having one s orbital available for forming molecular orbitals (MOs).

When the chain is extended:

- The range of energies covered by the MOs is spread
- This range of energies is filled in with more and more orbitals
- The width of the range of energies of the MOs is finite, while the number of molecular orbitals is infinite: This is called a band.

Tight-binding (LCAO) Band Theory

\[ -\frac{\hbar^2 \nabla^2}{2m} + V(r) \bigg| \psi_l(r) = E_l \psi_l(r) \]

\[ V(r) = V_0(r) + \Delta V(r) \]

\[ \left[ -\frac{\hbar^2 \nabla^2}{2m} + V_0(r) + \Delta V(r) \right] \psi_l(r) = E_l \psi_l(r) \]

\[ \Delta V(r) = \sum_{R_n \neq 0} V_0(r + R_n) \]

\[ V(r) = \sum_{R_j} V_0(r + R_j) \]
LCAO Wavefunction

\[ \tilde{\mathcal{H}} = \frac{\mathbf{p}^2}{2m} + V_0(\mathbf{r}) + \Delta V(\mathbf{r}) \]

\[ \frac{\mathbf{p}^2}{2m} \phi_i(\mathbf{r}) + V_0(\mathbf{r}) \phi_i(\mathbf{r}) = E_i \phi_i(\mathbf{r}) \]

Write general LCAO: Sum over types of orbitals (\( \alpha = 1s, 2s, 2p \), etc.) within a unit cell and sum over unit cells

\[ \psi_i(\mathbf{r}) = \sum_\alpha \sum \phi_{i,\alpha}(\mathbf{r} - \mathbf{R}_n) \]

Special case: take only one type of s-orbital per unit cell

\[ \psi(\mathbf{r}) = \sum_{n=-\infty}^{\infty} e[n] \phi(\mathbf{r} - n\mathbf{a}_x) \]

Energy for LCAO Bands with one-orbital per unit cell

Finite-basis set approximation gives:

\[ \sum_{m=-\infty}^{\infty} \tilde{H}(n, m) c[m] = E \sum_{p=-\infty}^{\infty} \tilde{S}(n, p) c[p] \]

\[ \tilde{H}(n, m) = \langle \phi(\mathbf{r} - n\mathbf{a}_x) | \tilde{\mathcal{H}} | \phi(\mathbf{r} - m\mathbf{a}_x) \rangle \]

\[ \tilde{S}(n, p) = \langle \phi(\mathbf{r} - n\mathbf{a}_x) | \phi(\mathbf{r} - p\mathbf{a}_x) \rangle \]

Z-transform, just like lattice waves!

\[ c[p+1] = c[p] z^{-1} \text{  and  } c[p] = c[0] z^{-p} \]

\[ \left( \sum_{m=-\infty}^{\infty} \tilde{H}(n, m) e^{-ik(n-m)a} \right) \epsilon = E \left( \sum_{p=-\infty}^{\infty} \tilde{S}(n, p) e^{-ik(n-p)a} \right) \epsilon \]
Energy for LCAO Bands

\[ \left( \sum_{m=-\infty}^{\infty} \tilde{H}(n, m)e^{-i(k(n-m)a)} \right) \epsilon = E \left( \sum_{p=-\infty}^{\infty} \tilde{S}(n, p)e^{-i(k(n-p)a)} \right) \epsilon \]

\[ \tilde{H}(n, m) = \tilde{H}^*(m, n) = \tilde{H}(n-m) \]

\[ \tilde{S}(n, m) = \tilde{S}^*(m, n) = \tilde{S}(n-m) \]

**Reduced Hamiltonian Matrix:**

\[ H(k) = \sum_{p=-\infty}^{\infty} \tilde{H}(p)e^{-ikpa} \]

**Reduced Overlap Matrix:**

\[ S(k) = \sum_{p=-\infty}^{\infty} \tilde{S}(p)e^{-ikpa} \]

\[ H(k) \epsilon = E S(k) \epsilon \]

\[ E(k) = \frac{H(k)}{S(k)} \]

Reduced an NxN eigen value problem to a 1x1

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**Reduced Overlap Matrix for 1-D Lattice**

Single s-orbital, single atom basis

\[ S(k) = \sum_{p=-\infty}^{\infty} \tilde{S}(p)e^{-ikpa} \]

\[ \tilde{S}(0) = \langle \phi(r)|\phi(r) \rangle = 1 \]

\[ \tilde{S}(1) = \langle \phi(r - a|x)|\phi(r) \rangle \]

\[ \tilde{S}(1) = \tilde{S}(-1) \]

\[ S(k) = 1 + \tilde{S}(1)(e^{ika} + e^{-ika}) \]
Reduced Hamiltonian Matrix for 1-D Lattice
Single s-orbital, single atom basis

\[ H(k) = \sum_{p=-\infty}^{\infty} \tilde{H}(p)e^{-ikpa} \]

\[ \tilde{H}(0) = \langle \phi(r) | \frac{\hat{p}^2}{2m} + V_0 + \Delta V(r) | \phi(r) \rangle \]
\[ = E_s^0 + \langle \phi(r) | \Delta V(r) | \phi(r) \rangle \]
\[ = E_s \]

\[ \tilde{H}(1) = \langle \phi(r - ai_x) | \frac{\hat{p}^2}{2m} + V_0 + \Delta V(r) | \phi(r) \rangle \]
\[ = \tilde{H}(-1) \]
\[ H(k) = E_s + V_{ss\sigma}(e^{ika} + e^{-ika}) \]

Energy Band for 1-D Lattice
Single orbital, single atom basis

\[ H(k) \epsilon = E S(k) \epsilon \]

\[ E(k) = \frac{H(k)}{S(k)} = \frac{E_s + V_{ss\sigma}(e^{ika} + e^{-ika})}{1 + \tilde{S}(1)(e^{ika} + e^{-ika})} \]
\[ E(k) = E(k + n2\pi/a) \]
\[ \tilde{S}(1) \ll 1 \]
\[ E(k) \approx E_s + 2V_{ss\sigma}\cos ka \]
LCAO Wavefunction for 1-D Lattice
Single s-orbital, single atom basis

\[ \psi(r) = \sum_{n=-\infty}^{\infty} c[n] \phi(r - n a_i x) \]

\[ c[n] = e^{-i k n a} \]

\[ \psi_k(r) = e \sum_{n=-\infty}^{\infty} e^{-i k n a} \phi(r - n a_i x) \]

\[ \psi_k(r) = \psi_{k+K_x}(r) \]
LCAO Wavefunction for 1-D Lattice

Single orbital, single atom basis

\[ \psi_k(r) = \epsilon \sum_{n=-\infty}^{\infty} e^{-i kna} \phi(r - na_i x) \]

\( k = 0 \)

\[ \psi_{k=0}(r) = \epsilon [\cdots + \phi(r + ai_x) + \phi(r) + \phi(r - ai_x) + \phi(r - 2ai_x) + \phi(r - 3ai_x) + \cdots] \]

\( k = \pi/\alpha \)

\[ \psi_{k=\pi/\alpha}(r) = \epsilon [\cdots - \phi(r + ai_x) + \phi(r) - \phi(r - ai_x) + \phi(r - 2ai_x) - \phi(r - 3ai_x) + \cdots] \]

<table>
<thead>
<tr>
<th><strong>LCAO LCAO Wavefunction</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Highest energy (most nodes)</strong></td>
</tr>
<tr>
<td><strong>Lowest energy (fewest nodes)</strong></td>
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</tbody>
</table>

Bloch’s Theorem

LCAO gives: 

\[ \psi_k(r) = \epsilon \sum_{n=-\infty}^{\infty} e^{-i kna} \phi(r - na_i x) \]

Translation of wavefunction by a lattice constant...

\[ \psi_k(r + ai_x) = \epsilon \sum_{n=-\infty}^{\infty} e^{i kna} \phi(r + ai_x - na_i x) \]

\[ = e^{ika} \epsilon \sum_{n=-\infty}^{\infty} \phi(r - (n-1)ai_x) \]

...yields the original wavefunction multiplied by a phase factor

\[ \psi_k(r + ai_x) = e^{ika} \psi_k(r) \]

Consistent that the probability density is equal at each lattice site

This is not a proof of Bloch’s theorem, only showing that LCAO satisfies Bloch’s Theorem
Wavefunction Normalization

Using periodic boundary condition for a crystal with N lattice sites between boundaries...

\[
\psi_k(r) = \frac{1}{\sqrt{Na}} e^{i k \cdot x} u_k(r)
\]

\[
1 = \int_{V_{\text{box}}} \psi_k^*(r) \psi_k(r) \, d^3r = \frac{1}{Na} \int_{V_{\text{box}}} u_k^*(r) u_k(r) \, d^3r = \frac{1}{a} \int_{\text{unit cell}} u_k^*(r) u_k(r) \, d^3r
\]

Counting Number of States in a Band

Combining periodic boundary condition...

\[
\psi_k(r + Na x) = \psi_k(r)
\]

...with Bloch's theorem...

\[
\psi_k(r + Na x) = e^{i k Na} \psi_k(r)
\]

...yields a discrete set of \( \mathbf{k} \)-vectors

\[
k = \frac{m 2\pi}{Na} \quad \text{where} \quad m = 0, \pm 1, \pm 2, \ldots
\]

Within the 1st Brillouin Zone there are \( N \) states or \( 2N \) electrons
Overview

2N electrons each for \( p_x, p_y, p_z \)

2N electrons

Tight-binding and Lattice Wave Formalism

Electrons (LCAO)

\[
\langle S^{-1}(k) H(k) \rangle \tilde{\epsilon} = E \tilde{\epsilon}
\]

\[
H_{\beta,\alpha}(k) = \sum_{R_p} \langle \phi_\beta(r - R_s - R_p) | \hat{\rho} | \phi_\alpha(r - R_s) \rangle e^{-i \mathbf{k} \cdot \mathbf{r}_p}
\]

\[
S_{\beta,\alpha}(k) = \sum_{R_p} \langle \phi_\beta(r - R_s - R_p) | \phi_\alpha(r - R_s) \rangle e^{-i \mathbf{k} \cdot \mathbf{r}_p}
\]

\[
E(k) = E(k + n2\pi/a)
\]

Lattice Waves

\[
\langle M^{-1} D(k) \rangle \tilde{\epsilon} = \omega^2 \tilde{\epsilon}
\]

\[
D_{i,j}(k) = \sum_{R_p} \left( \frac{\partial^2 V}{\partial \mathbf{u}_i \partial \mathbf{u}_j |_{\mathbf{R}_s, t}} \right) e^{-i \mathbf{k} \cdot \mathbf{r}_p}
\]

\[
\omega(k) = \omega(k + n2\pi/a)
\]