3.23 Electrical, Optical, and Magnetic Properties of Materials
Fall 2007

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Last time

1. Explicit solution of the Bloch equation, energy bands
2. Brillouin zone, Fermi surface
3. Energy of molecules and solids
4. Mean field approaches – Hartree and Hartree-Fock
5. Spin-statistics, Slater determinant, Pauli principle
6. Huckel approach (LCAO for aromatic compounds)
Study

- Chap. 5 Singleton
- Read Chap. 6 Singleton

**Tight-binding (LCAO for solids)**

- **Hamiltonian**
\[ \hat{H} = \hat{H}_{\text{t}} + \Delta U(r) \psi \]
Tight-binding (LCAO for solids)

- Bloch eigenstates of an ATOMIC CRYSTAL

$$\Psi_{nk}^\ast (\vec{r}) = \sum_{\vec{R}} \exp(i\vec{k} \cdot \vec{r}) \psi_n (\vec{r})$$

$$\Psi_{nk} (\vec{r} + \vec{R}) = \sum \exp(i\vec{k} \cdot \vec{r}) \phi_n (\vec{r} + \vec{R})$$

- Bloch eigenstates of a REAL CRYSTAL

$$\Psi_{nk} (\vec{r}) = \sum_{\vec{R}} \exp(i\vec{k} \cdot \vec{r}) \phi_n (\vec{r})$$

$$\phi (\vec{r}) = \sum_n b_n \psi_n (\vec{r})$$

$$\int \phi_m^\ast (H_{AT} + A) \phi_n = \int \delta (\vec{k}) \langle \phi_{nk} | \phi_{nk} \rangle$$
Some despicable algebraic workout

\[ \int \psi_m^* \hat{H} \psi_k = \int (\hat{H} \psi_m) \psi_k^* \psi = E_m \int \psi_m^* \psi_k \]
\[ \int \psi_m^* \Delta V \psi_k = (E(k) - E_m) \int \psi_m^* \psi_k \]
\[ \int \psi_m^* (r) \psi_n (r') = \sum_R e^{i \mathbf{k} \cdot \mathbf{R}} \int \psi_m^* (r) \sum_R \psi_n (r - \mathbf{R}) e^{i \mathbf{k} \cdot \mathbf{R}} \]
\[ = b_m + \sum_R \sum_n b_n \int \psi_m^* (r) \psi_n (r - R) e^{i \mathbf{k} \cdot \mathbf{R}} \]

More workout

\[ (E(k) - E_m) b_n = - (E(k) - E_m) \sum_R \left( \sum_n \psi_m^* (r) \psi_n (r - R) e^{i \mathbf{k} \cdot \mathbf{R}} \right) \]
\[ b_m \neq 0 \Rightarrow E(k) \neq E_m \]
\[ \sum_R \sum_n \psi_m^* (r) \Delta V(r) \psi_n (r) \]
\[ + \sum_R \sum_n b_n \int \psi_m^* (r) \Delta V(r) \psi_n (r) \]

More

\[ \int \psi_m^*(r) \Delta V(r) \psi_m(r) \]
\[ \text{\textcolor{red}{\( y = -\beta \)}} \]
\[ \int \psi_m^*(r) \psi_m(r) \alpha(\mathbf{R}) \]
\[ \text{\textcolor{red}{\( \alpha(\mathbf{R}) \)}} \]
\[ \int \psi_m^*(r) \Delta V(r) \psi_m(r) \alpha(\mathbf{R}) \]
\[ \text{\textcolor{red}{\( -\beta \)}} \]

More

\[ \varepsilon(k) = E_m - \left( \sum_{\mathbf{R} \neq 0} \varepsilon(\mathbf{R}) e^{i \mathbf{R} \cdot \mathbf{b} \cdot \mathbf{b}} + \sum_{\mathbf{R} \neq 0} \varepsilon(\mathbf{R}) e^{i \mathbf{R} \cdot \mathbf{b} \cdot \mathbf{b}} \right) \]
\[ = E_m - \beta - \sum_{\mathbf{R} \neq 0} \varepsilon(\mathbf{R}) e^{i \mathbf{R} \cdot \mathbf{b} \cdot \mathbf{b}} \]
From s level to s bands

\[ \varepsilon(\mathbf{k}) = E_s - \beta - \sum_{\text{nearest neighbor}} \gamma(\mathbf{R}) \cos(\mathbf{k} \cdot \mathbf{r}) \]

\[ N_a = \mathbf{R} = \frac{q}{2} \left( \pm 1, \pm 1, 0 \right) \]

\[ \mathbf{R} = (b_x^a, b_y^a, b_z^a) \]

\[ \varepsilon(\mathbf{R}) = E_s - \beta - \gamma \mathbf{x} \left( \sum_{\text{all the points}} \left( b_x^a \mathbf{R} a + b_y^a \mathbf{R} a \right) \right) \]

From s level to s bands

Figure by MIT OpenCourseWare.

Tight-binding vs. empirical psp


A comparison of the band structure of Ge as calculated by (a) the tight-binding, (b) the empirical pseudopotential, and (c) the nearly free electron methods.
Bands in Ge

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Ferroelectric perovskites

Ferroelectric perovskites

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