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

3.23 Fall 2007 – Lecture 11

FERMI $\nearrow \frac{e^2}{\hbar c}$

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

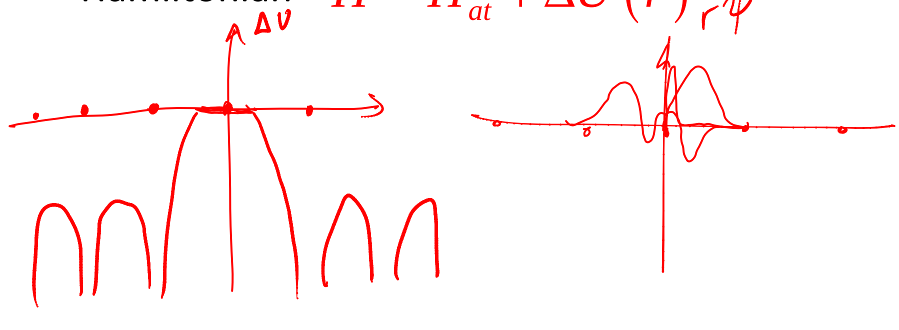
POST PROF. FINK → FREE ELECTRON GAS

FRIDAY 4pm 13-5066

MONDAY 4pm 13-5066

Tight-binding (LCAO for solids)

- Hamiltonian $\hat{H} \stackrel{PER}{=} \hat{H}_{at} + \Delta\hat{U}(\vec{r})$



Tight-binding (LCAO for solids)

- Bloch eigenstates of an ATOMIC CRYSTAL

ATOMIC ORBITALS

$$\Psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} \exp\left(i\vec{k}\cdot\vec{R}\right)\psi_n\left(\vec{r}-\vec{R}\right)$$

BLOCH SUM

$$\Psi_{n\vec{k}}(\vec{r}+\vec{R}) = \sum_{\vec{R}'} e^{i\vec{k}\cdot\vec{R}'}\psi_n(\vec{r}-\vec{R}'+\vec{R})$$

$$= e^{i\vec{k}\cdot\vec{R}}\sum_{R'} e^{i\vec{k}\cdot(\vec{R}'-\vec{R})}\psi_n(\vec{r}-(\vec{R}'-\vec{R}))$$

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Tight-binding (LCAO for solids)

- Bloch eigenstates of a REAL CRYSTAL

$$\Psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} \exp\left(i\vec{k}\cdot\vec{R}\right)\phi\left(\vec{r}-\vec{R}\right)$$

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

LCAO

$$\int \psi_m^* (H_{AT} + \Delta V)\psi_{nk} = \int E_n(k)\,\psi_{nk}\,\psi_m^*$$

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Some despicable algebraic workout

$$\int \psi_m^* H_{AT} \psi_{nk} = \int (H_{AT} \psi_m)^* \psi = E_m \int \psi_m^* \psi_{nk}$$

$$\int \psi_m^* \Delta U \psi_{nk} = \left(E(k) - E_m\right) \int \psi_m^* \psi_{nk}$$

$$\int \psi_m^*(\vec{r})\, \psi_{nk}(\vec{r}) = \sum_R e^{i\vec{k}\cdot\vec{R}} \int \psi_m^*(\vec{r}) \left(\sum_n b_n \psi_n(\vec{r}-\vec{R})\right)$$

$$= b_m + \sum_{R\neq 0} \sum_n b_n \int \psi_m^*(r)\, \psi_n(\vec{r}-\vec{R})\, e^{i\vec{k}\cdot\vec{R}}$$

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More workout

$$\left(E(k) - E_m\right) b_m = -\left(E(k) - E_m\right) \sum_n b_n \left(\sum_{R\neq 0} \int \psi_m^*(r)\, \psi_n(r-R)\, e^{ikR} \right)$$

$$+ \sum_n b_n \int \psi_m(r)\, \Delta U(r)\, \psi_n(r)$$

$$+ \sum_n b_n \left(\sum_{R\neq 0} \int \psi_m^*(r)\, \Delta U(r)\, \psi_n(r-R) \right)$$

$b_m \neq 0 \Rightarrow E(k) \simeq E_m$

$b_{n\neq m} = 0$

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More

$$\int \psi_m^*(r)\,\Delta U(r)\,\psi_m(r)$$
$$(1) = -\beta$$

$$\int \psi_m^*(r)\,\psi_m(r-\vec{R})$$
$$\alpha(\vec{R})$$

$$\int \psi_m^*(r)\,\Delta U(r)\,\psi_m(\vec{r}-\vec{R})$$
$$= \gamma(\vec{R})$$

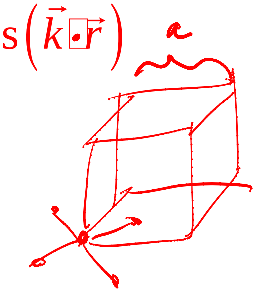
More

$$E(k) - E_m = -\left(E(k)-E_m\right)\sum_{R\neq 0} e^{i\vec{k}\cdot\vec{R}}\,\alpha(\vec{R})$$
$$-\beta - \sum_{R\neq 0}\gamma(\vec{R})\,e^{i\vec{k}\cdot\vec{R}}$$
$$\gamma(-\vec{R})$$

$$E(k) = E_m - \frac{\beta \sum_{R\neq 0}\gamma(\vec{R})\,e^{i\vec{k}\cdot\vec{R}}}{1+\sum_{R\neq 0}\alpha(\vec{R})\,e^{i\vec{k}\cdot\vec{R}}}$$

From *s* level to *s* bands

$$\varepsilon(\vec{k}) = E_s - \beta - \sum_{\substack{\text{nearest}\\ \text{neighb.}}} \gamma(\vec{R})\cos(\vec{k}\cdot\vec{r})$$



$$Na = \vec{R} = \frac{a}{2}(\pm 1, \pm 1, 0)$$
$$(\pm 1, 0, \pm 1)$$
$$(0, \pm 1, \pm 1)$$

$$\vec{k} = (k_x, k_y, k_z)$$

$$\varepsilon(\vec{k}) = E_s - \beta - 4\gamma\left(\cos\tfrac{1}{2}k_x a \cos\tfrac{1}{2}k_y a + \right.$$
$$\left. + \text{ ALL THE PERM}\right)$$

From *s* level to *s* bands

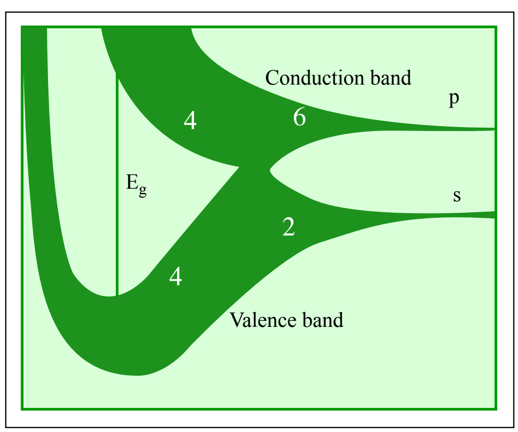


Figure by MIT OpenCourseWare.

Tight-binding vs. empirical psp

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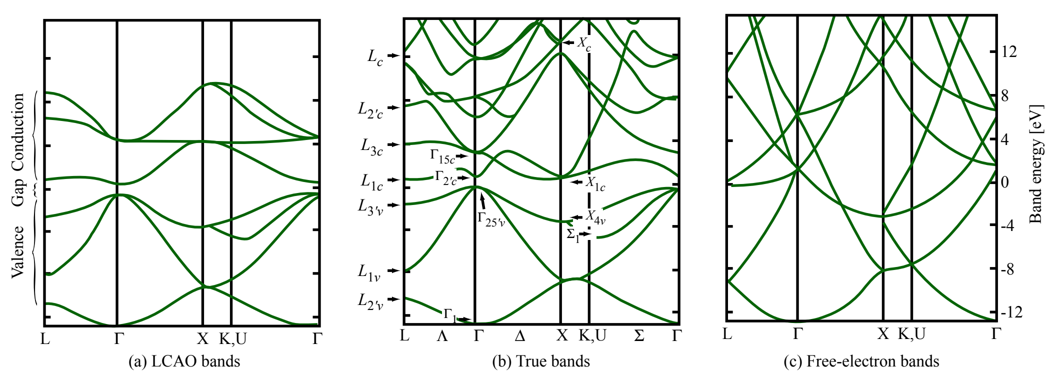
Yu, Peter Y., and Manuel, Cardona. *Fundamentals of Semiconductors: Physics and Materials Properties*. New York, NY: Springer, 2001.

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.

Figure by MIT OpenCourseWare.

Bands in Ge

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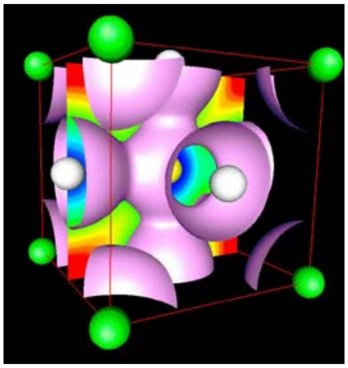
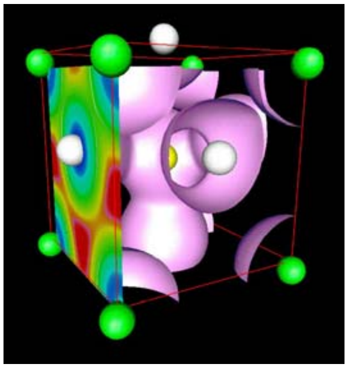
Ferroelectric perovskites





Ferroelectric perovskites

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King-Smith, R. D., and David Vanderbilt. "First-principles Investigation of Ferroelectricity in Perovskite Compounds." *Physical Review B* 49 (March 1994): 5828-5844.

Ferroelectric perovskites

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King-Smith, R. D., and David Vanderbilt. "First-principles Investigation of Ferroelectricity in Perovskite Compounds." *Physical Review B* 49 (March 1994): 5828-5844.