

ECE 595, Section 10  
Numerical Simulations  
Lecture 23: Electronic  
Bandstructures

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# Recap from Friday

- 3D Lattice Types
- Full 3D Photonic Bandgap Structures
  - Yablonovite
  - Woodpile
  - Inverse Opals
  - Rod-Hole 3D PhCs

# Outline

- Recap from Friday
- Electronic bandstructure overview
- Computational methods:
  - Nearly-free electron model
  - Wigner-Seitz method
  - Tight-binding
  - Pseudopotentials

# Electronic Bandstructure Overview

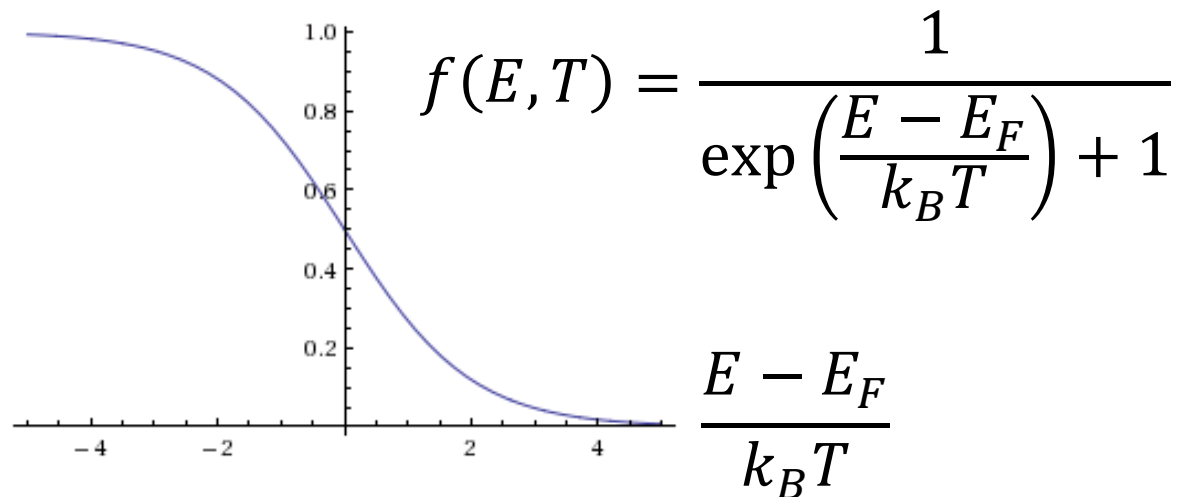
- Controlled by Schrodinger's equation:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(x) \right] \Psi(x) = E\Psi(x)$$

- In absence of potential,  $E = \hbar^2 k^2 / 2m$
- Electrons are fermions. At  $T=0$ , will fill all lowest-energy states up to the *Fermi energy*
- Can prove that the Fermi energy  
 $E_F = \hbar^2 (3\pi^2 n)^{2/3} / 2m$

# Electronic Bandstructure Overview

- At  $T=0$ , all states below  $E_F$  occupied, all states above are unoccupied
- When  $T>0$ , will have a Fermi-Dirac function for probability of occupying a state near the Fermi surface



# Electronic Bandstructure Overview

- In general, absolute electrostatic potentials become *extremely* large for electrons
- However, the inner core electrons screen the nuclear charge
- Thus for many problems, the core can be treated as a closed shell, creating a much weaker, delocalized potential

# Nearly Free Electron Model

- In this approach, one only considers potential to be a weak perturbation from empty lattice
- First, choose nearly-free basis functions:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

- Then, directly solve Schrodinger's equation with the Fourier coefficients of the potential:

$$\sum_{\mathbf{G}} V_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = \left[ E(k) - \frac{\hbar^2 k^2}{2m} \right] c_{\mathbf{k}}$$

# Nearly Free Electron Model

- For most k-values, only keep the average potential:

$$E(k) = \frac{\hbar^2 k^2}{2m} + V_o$$

- For nearly-degenerate values (e.g., BZB), only include 2 components:

$$E(k) = \frac{\hbar^2 k^2}{2m} + V_o \pm |V_G|$$

- Best suited for metals, e.g., aluminum



# Wigner-Seitz method

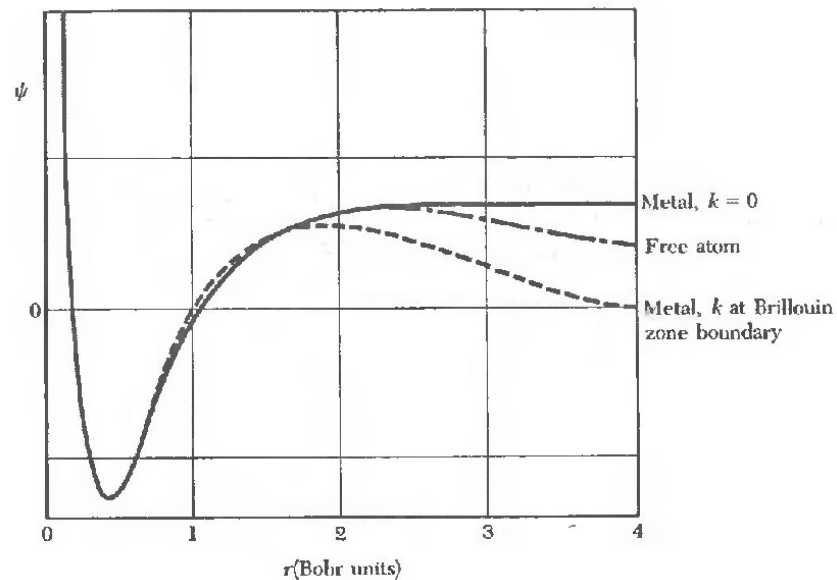
- Next approximation after NFE
- Assume solutions are of the form:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

- Can then solve Schrodinger's equation at  $\mathbf{k}=0$  using the Wigner-Seitz wavefunctions

# Wigner-Seitz method

- Wigner-Seitz wavefunctions developed for each individual atom and orbital
- Example: for 3s electrons in Na



# Tight-binding

- In this approach, consider electrons to be primarily localized around their atom of origin
- To treat hopping of electrons, employ linear combinations of atomic orbitals (LCAO):

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k} \cdot \mathbf{r}_j} \varphi(\mathbf{r} - \mathbf{r}_j)$$

- Widely used approach in chemistry

# Tight-binding

- Can evaluate mean-field energy using LCAO:

$$E = \langle \psi_{\mathbf{k}} | H | \psi_{\mathbf{k}} \rangle$$
$$E = \frac{\hbar^2 k^2}{2m} + \frac{1}{N} \sum_j \sum_m e^{i\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_m)} \langle \varphi_m | V | \varphi_j \rangle$$

- Ignoring all terms except for diagonal and nearest-neighbors, one obtains (in 1D):

$$E = \frac{\hbar^2 k^2}{2m} + V_0 + 2V_1 \cos(ka)$$

# Tight-binding

- Becomes slightly more complicated in 2D or 3D
- For a bcc lattice:

$$E = \frac{\hbar^2 k^2}{2m} + V_0 + 8V_1 \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right)$$

- For an fcc lattice:

$$E = \frac{\hbar^2 k^2}{2m} + V_0 + 4V_1 \left[ \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_z a}{2}\right) \right]$$

# Pseudopotentials

- As we observed previously, higher atomic orbitals tend to vary strongly near the core
- However, we can extract the energy from applying the Hamiltonian at any position
- Thus, we can replace the true screened potential with a weaker, so-called 'pseudopotential'
- Solutions will be valid outside of pseudopotential region in core

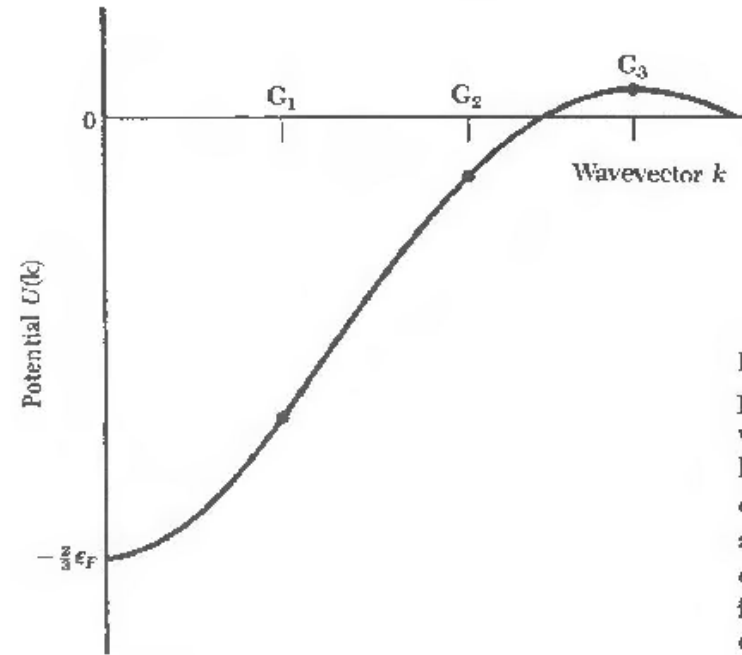
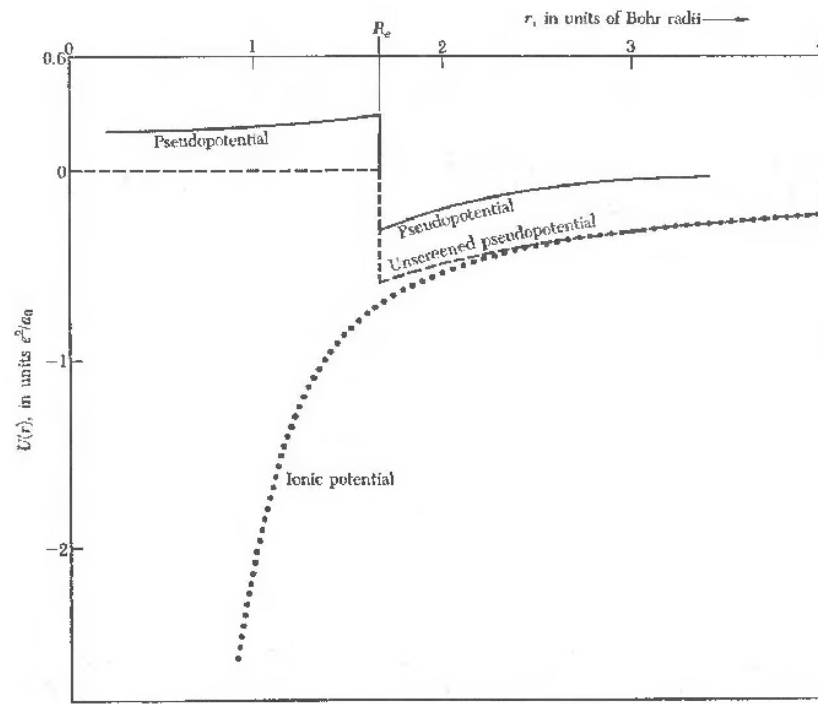
# Pseudopotentials

- Several options for pseudopotential.
- Example: empty core model:

$$V(r) = \begin{cases} 0, & r < R \\ e^2/r, & r > R \end{cases}$$

- Empirical pseudopotential model (EPM). For silicon:
  - $V_0 = (-2/3)E_F$
  - $V_{\sqrt{3}} = -0.2241 \text{ Ry}$
  - $V_{\sqrt{8}} = -0.052 \text{ Ry}$
  - $V_{\sqrt{11}} = -0.0724 \text{ Ry}$

# Pseudopotentials



- Pseudopotential in real space for Na atom

- Pseudopotential in reciprocal space



# Next Class

- Is on Wednesday, March 6
- Will continue on electronic bandstructures
- Recommended reading: Kittel, Intro to Solid State Physics, Chapter 10