Laws are like sausages; it is better not to see them being made.
- Otto von Bismarck

Making quality sausage requires watching the process.
- Tomás Arias, 2023

PRACTICAL APPROACHES AND APPROXIMATIONS II
THIS LECTURE

• Periodicity and aperiodic systems
• Specifying periodic systems
• The cost of periodicity: Bloch’s theorem
• Metals and effective electron temperatures
PERIODICITY AND SUPERCELL CONVERGENCE

- Periodicity replaces macroscopic crystal with manageable unit cell
- Aperiodic systems can be embedded in a periodic “supercell”
  - isolated molecules
  - impurities, vacancies, antisite defects
  - surfaces, grain boundaries
  - step edges, dislocations

- Always verify convergence with supercell size (😊)
• Periodicity and aperiodic systems
• **Specifying periodic systems**
• The cost of periodicity: Bloch’s theorem
• Metals and effective electron temperatures
**PERIODIC SYSTEMS**

- **Lattice**: Set of locations \( \{ \vec{R} \} \) of all equivalent unit cells
  - Generally, any \( \vec{R} \) can be written in terms of “primitive” lattice vectors \( \vec{R}_1, \vec{R}_2, \vec{R}_3 \): \( \vec{R} = n_1 \vec{R}_1 + n_2 \vec{R}_2 + n_3 \vec{R}_3 \)
  - Note: \( \vec{R}_1, \vec{R}_2, \vec{R}_3 \) can be *any* linearly independent vectors, need not be orthogonal or equal lengths!
**PERIODIC SYSTEMS**

- **Lattice**: Set of locations \( \{ \mathbf{R} \} \) of all equivalent unit cells
  - Generally, any \( \mathbf{R} \) can be written in terms of “primitive” lattice vectors \( \mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3 \): \( \mathbf{R} = n_1 \mathbf{R}_1 + n_2 \mathbf{R}_2 + n_3 \mathbf{R}_3 \)

- **Basis**: Locations \( \{ \mathbf{t} \} \) of atoms within each cell, relative to the origin of that cell: \( \mathbf{r}_{\text{atom}} = \mathbf{R} + \mathbf{t}_{\text{atom}} \)

- **Wyckoff/“lattice” coordinates**: Atomic locations expressed as fractions of primitive lattice vectors:
  \( \mathbf{t} = x_1 \mathbf{R}_1 + x_2 \mathbf{R}_2 + x_3 \mathbf{R}_3 \) (generally \( 0 \leq x_\alpha < 1 \))
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BLOCH’S THEOREM I AND K-POINT CONVERGENCE

- Periodicity $\Rightarrow$ all cells are physically identical
  
  $n(\vec{r} + \vec{R}_\alpha) = n(\vec{r})$ for lattice vectors $\vec{R}_\alpha$ ($\alpha = 1, 2, 3$)

- Wave functions have unobservable phase, so we can only say
  
  $|\psi_i(\vec{r} + \vec{R}_\alpha)|^2 = |\psi_i(\vec{r})|^2$

  $\Rightarrow \psi_i(\vec{r} + \vec{R}_\alpha) = e^{i\phi_\alpha} \psi_i(\vec{r})$ with $\phi_\alpha \in [0, 2\pi)$

- All $\phi_\alpha \in [0, 2\pi)$ possible and must be included: $\Sigma_i \leftarrow \iiint_{[0,2\pi]^3} d^3 \phi$

- Integrated by sampling of $[0,2\pi]^3$ with $N_1 \times N_2 \times N_3$ “k-point” grid

- **Always** verify convergence with $k$-point sampling (😊)
BLOCH’S THEOREM II AND K-POINT SCALING \textbf{CONVERGENCE}

- \( \psi_i(\vec{r} + \vec{R}_\alpha) = e^{i\phi_\alpha} \psi_i(\vec{r}) \) \ with \( \phi_\alpha \in [0,2\pi) \)

- Consider \( \psi_i(\vec{r}) \approx e^{i\vec{k} \cdot \vec{r}} \cdot e^{i\vec{k} \cdot (\vec{r} + \vec{R}_\alpha)} = e^{i\vec{k} \cdot \vec{R}_\alpha} e^{i\vec{k} \cdot \vec{r}} \)

- Physically, interpret \( \phi_\alpha = \vec{k} \cdot \vec{R}_\alpha \) and solve for \( \vec{k} \)

- All states \( \psi_i(\vec{r}) \) have an associated \( \vec{k} \)
  \( \Rightarrow \) index all with same \( \vec{k} \) with \( n=1,2,...: \psi_i(\vec{r}) \equiv \psi_{n\vec{k}}(\vec{r}) \)

- \textbf{PRO-TIP:} Keeping the same \( \Delta \vec{k}_\alpha \) gives same quality
  \( \Rightarrow \) upscaling \( \vec{R}_\alpha \) upscales \( \Delta \phi_\alpha \) and downscalers \( N_\alpha \) \( (\text{bigger supercell, fewer k-points!}) \)
BLOCH’S THEOREM III

- So far, for $\psi_i(\vec{r})$, $i = \{n\vec{k}\}$ and $\phi_{\alpha} = \vec{k} \cdot \vec{R}_{\alpha}$ ...

$$\psi_{n\vec{k}}(\vec{r} + \vec{R}_{\alpha}) = e^{i\vec{k} \cdot \vec{R}_{\alpha}} \psi_{n\vec{k}}(\vec{r}) \quad \text{[standard form 1]}$$

- Alternate form of Blocks theorem

$$\psi_{n\vec{k}}(\vec{r}) \equiv e^{i\vec{k} \cdot \vec{r}} u_{n\vec{k}}(\vec{r}), \ u_{n\vec{k}}(\vec{r} + \vec{R}_{\alpha}) = u_{n\vec{k}}(\vec{r}) \quad \text{[standard form 2]}$$

Proof:

$$u_{n\vec{k}}(\vec{r}) \equiv e^{-i\vec{k} \cdot \vec{r}} \psi_{n\vec{k}}(\vec{r})$$

$$\Rightarrow u_{n\vec{k}}(\vec{r} + \vec{R}_{\alpha}) = e^{-i\vec{k} \cdot (\vec{r} + \vec{R}_{\alpha})} \psi_{n\vec{k}}(\vec{r} + \vec{R}_{\alpha})$$

$$= e^{-i\vec{k} \cdot (\vec{r} + \vec{R}_{\alpha})} e^{i\vec{k} \cdot \vec{R}_{\alpha}} \psi_{n\vec{k}}(\vec{r}) = e^{-i\vec{k} \cdot \vec{r}} \psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r}) \quad \checkmark$$
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Fermi Occupancy & Electron Temperature Convergence

- Electron density (kinetic energy similar story)

\[ n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 = \sum_{n \mathbf{k}} f_{n \mathbf{k}} |\psi_{n \mathbf{k}}(\mathbf{r})|^2 \]

- At $T=0$, obtain min $E_0$ by filling lowest energy states first (Aufbau)

\[ f_{n \mathbf{k}} = \begin{cases} 
1, 2 & \text{if } \epsilon_{n \mathbf{k}} \leq \epsilon_{\text{Fermi}} \\
0 & \text{if } \epsilon_{n \mathbf{k}} > \epsilon_{\text{Fermi}} 
\end{cases} \]
FERMI OCCUPANCY & ELECTRON TEMPERATURE CONVERGENCE

\[ f_{n\vec{k}} = \begin{cases} 
1,2 & \text{if } \epsilon_{n\vec{k}} \leq \epsilon_{\text{Fermi}} \\
0 & \text{if } \epsilon_{n\vec{k}} > \epsilon_{\text{Fermi}}
\end{cases} \]

- Semiconductor: completely filled bands: all \( k \)-points contribute (😊)
- Metal: Fermi-level cuts band(s), contributing regions are complicated (😢)

\[ \epsilon_{n\vec{k}} = \epsilon_F \]

\[ \vec{k} \]

\[ \text{Nb} \]
For metals, contributing regions are complicated (😢)

DFT generalizes to $T>0$ !

\[ f_{n\vec{k}} = \frac{1}{e^{(\epsilon_{n\vec{k}} - \mu)/k_BT} + 1} \] (Fermi-Dirac distribution)

F-D distribution is smooth and easier to integrate (😊)!

Higher $T$ needs fewer k-points, with mild impact on results

⇒ Use elevated $T$ ($\sim 4T_{room}$), and **verify** $T\rightarrow0$ convergence (😡)
SUMMARY OF ISSUES TO MANAGE

- Choice of approximate functional \( E_{xc}^{\text{LDA}}[n(\vec{r})], E_{xc}^{\text{GGA}}[n(\vec{r})], \text{etc.} \)
  - GGA is usually sufficient (maybe DFT+U for oxides, hybrid for subtle chemistry)
- Iterative convergence (always)
- Plane-wave cutoff \( E_{\text{cut}} \) (always, once for each new element/pseudopotential)
- Pseudopotential choice (once for each new element, especially exotica)
  - Verify against experimental data for first use
- Supercell (aperiodic systems only)
- k-points (always, but scales inversely with supercell size)
- Electron Temperature (metals only, for every new compound)
THANK YOU!

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