PRACTICAL APPROACHES AND APPROXIMATIONS II

Laws are like sausages; it is better not to see them being made.

-Otto von Bismarck

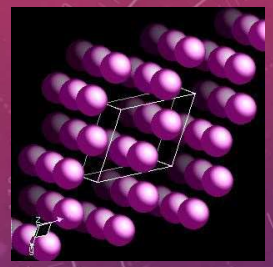
Making quality sausage requires watching the process.

-Tomás Arias, 2023

THIS LECTURE

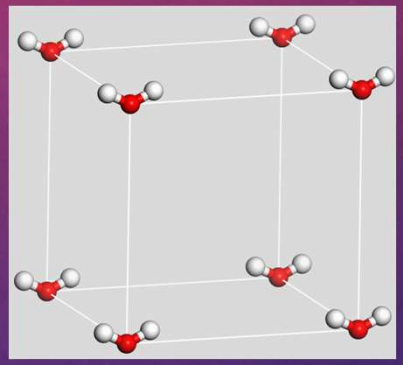
- Periodicity and aperiodic systems
- Specifying periodic systems
- The cost of periodicity: Bloch’s theorem
- Metals and effective electron temperatures

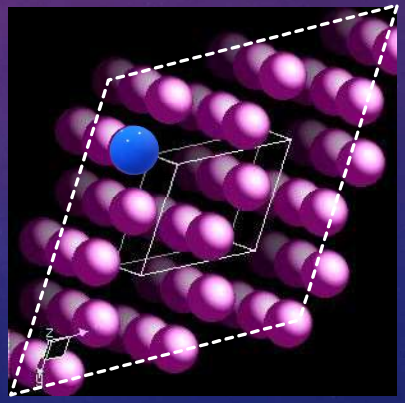
PERIODICITY AND SUPERCELL *CONVERGENCE*

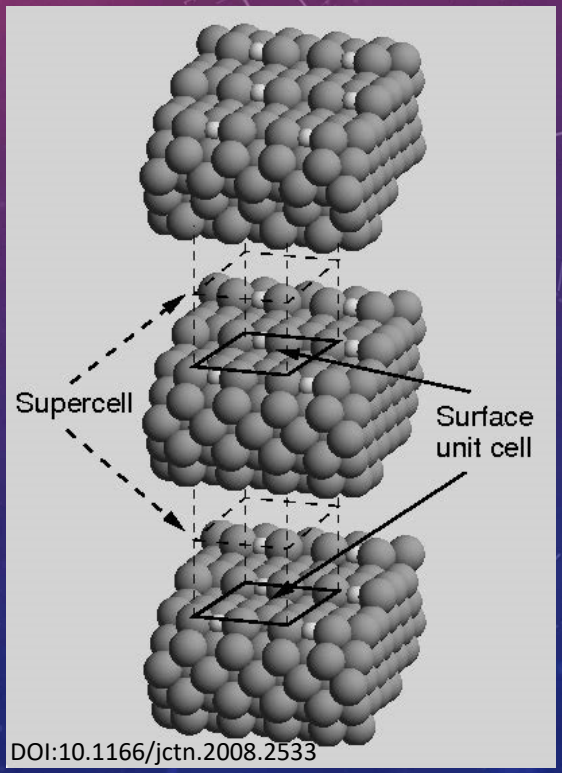


- Periodicity replaces macroscopic crystal with manageable unit cell
- Aperiodic systems can be embedded in a periodic "supercell"
  - isolated molecules
  - impurities, vacancies, antisite defects
  - surfaces, grain boundaries
  - step edges, dislocations

- *Always* verify convergence with supercell size (😠)







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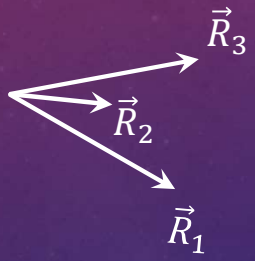
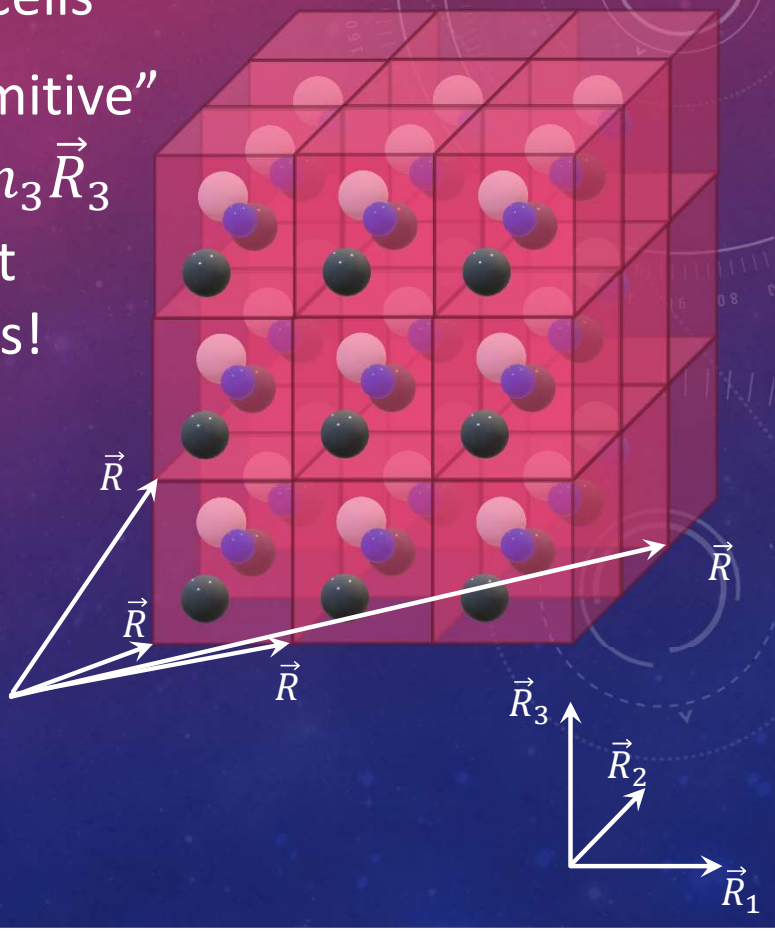
- Periodicity and aperiodic systems
- **Specifying periodic systems**
- The cost of periodicity: Bloch's theorem
- Metals and effective electron temperatures

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 lenghts!





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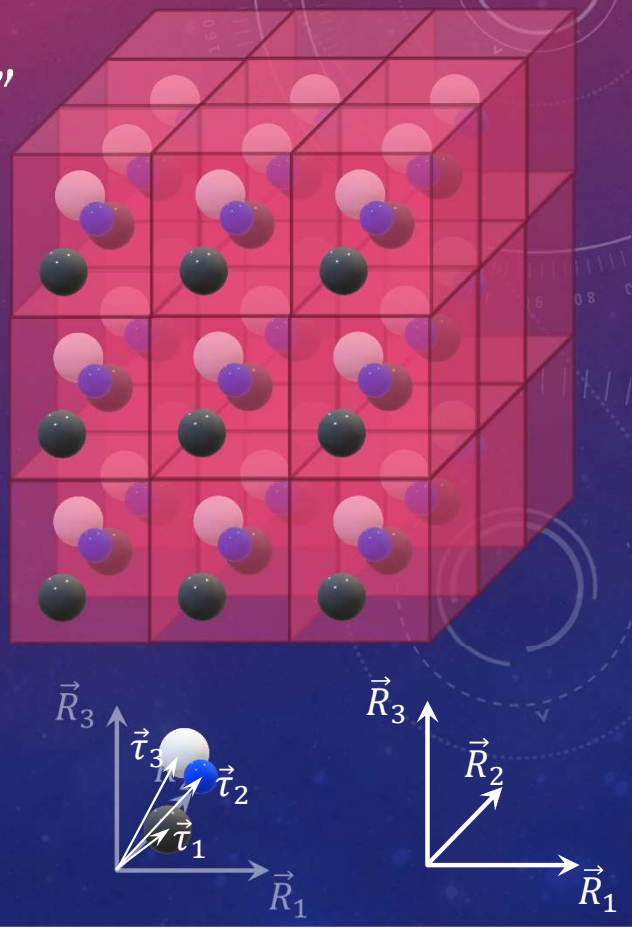
- *Basis*: Locations $\{\vec{\tau}\}$ of atoms within each cell, **relative to the origin of that cell**: $\vec{r}_{\text{atom}} = \vec{R} + \vec{\tau}_{\text{atom}}$

- *Wyckoff/"lattice" coordinates*: atomic locations **expressed as fractions of primitive lattice vectors**: $\vec{\tau} = x_1\vec{R}_1 + x_2\vec{R}_2 + x_3\vec{R}_3$ (generally $0 \leq x_\alpha < 1$)



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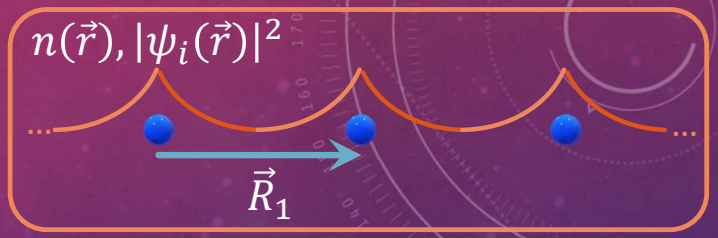
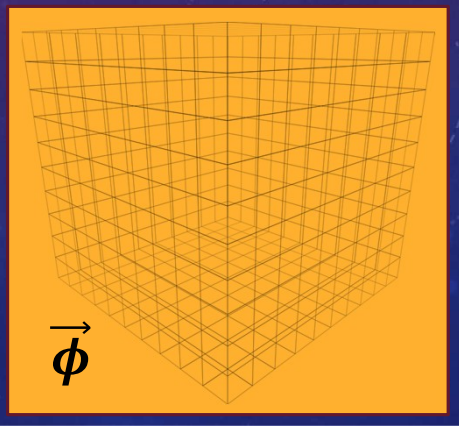
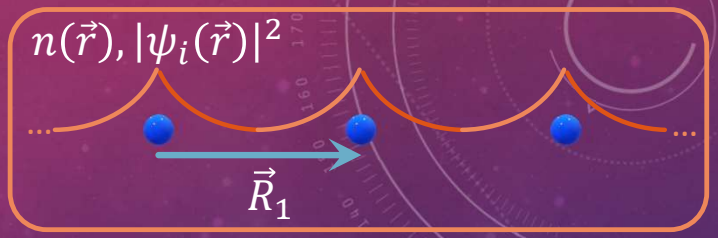
BLOCH'S THEOREM I AND K-POINT *CONVERGENCE*



- Periodicity ⇒ 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
  $$\left|\psi_i\left(\vec{r} + \vec{R}_\alpha\right)\right|^2 = |\psi_i(\vec{r})|^2$$
  $$\Rightarrow \psi_i\left(\vec{r} + \vec{R}_\alpha\right) = e^{i\phi_\alpha}\,\psi_i(\vec{r}) \text{ with } \phi_\alpha \in [0,2\pi)$$
- All $\phi_\alpha \in [0,2\pi)$ possible and must be included: $\sum_i \leftarrow \iiint_{[0,2\pi]^3} d^3\phi$
- 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 (😠)



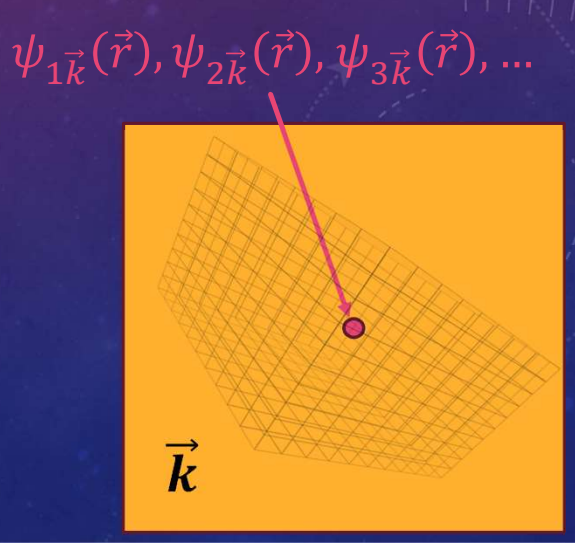
BLOCH'S THEOREM II AND K-POINT SCALING *CONVERGENCE*



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

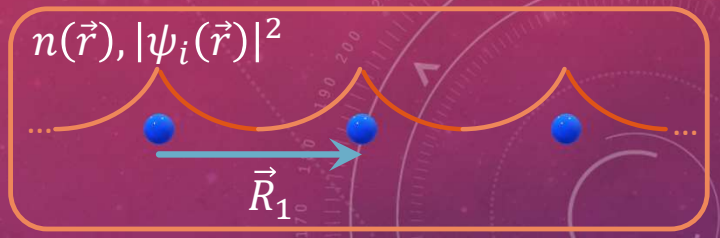
- Consider $\psi_i(\vec{r}) \sim e^{i\vec{k}\cdot\vec{r}}$: $e^{i\vec{k}\cdot(\vec{r}+\vec{R}_\alpha)} = e^{i\vec{k}\cdot\vec{R}_\alpha}\, e^{i\vec{k}\cdot\vec{r}}$
- Physically, interpret $\phi_\alpha = \vec{k}\cdot\vec{R}_\alpha$ and solve for $\vec{k}$

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



- **PRO-TIP:** Keeping the same $\Delta\vec{k}_\alpha$ gives same quality
  ⇒ upscaling $\vec{R}_\alpha$ upscales $\Delta\phi_\alpha$ and downscales N_α (😳)
  (bigger supercell, fewer k-points!)

BLOCH'S THEOREM III

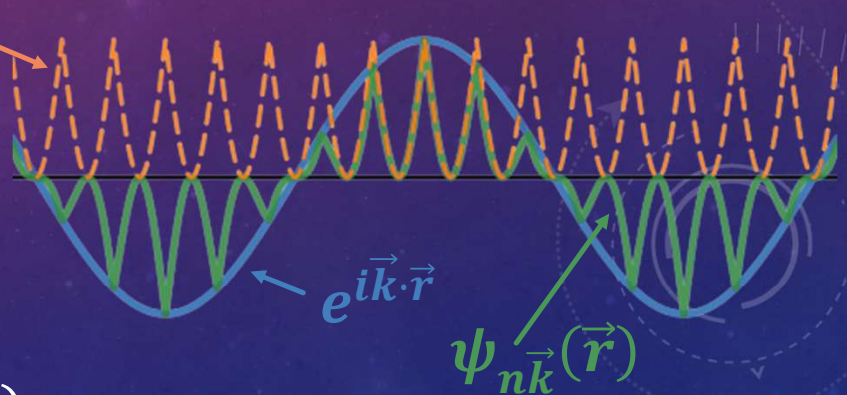


- So far, for $\psi_i(\vec{r})$, $i = \{n\vec{k}\}$ and $\phi_\alpha = \vec{k} \cdot \vec{R}_\alpha$ …

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

- Alternate form of Blocks theorem

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



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

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

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

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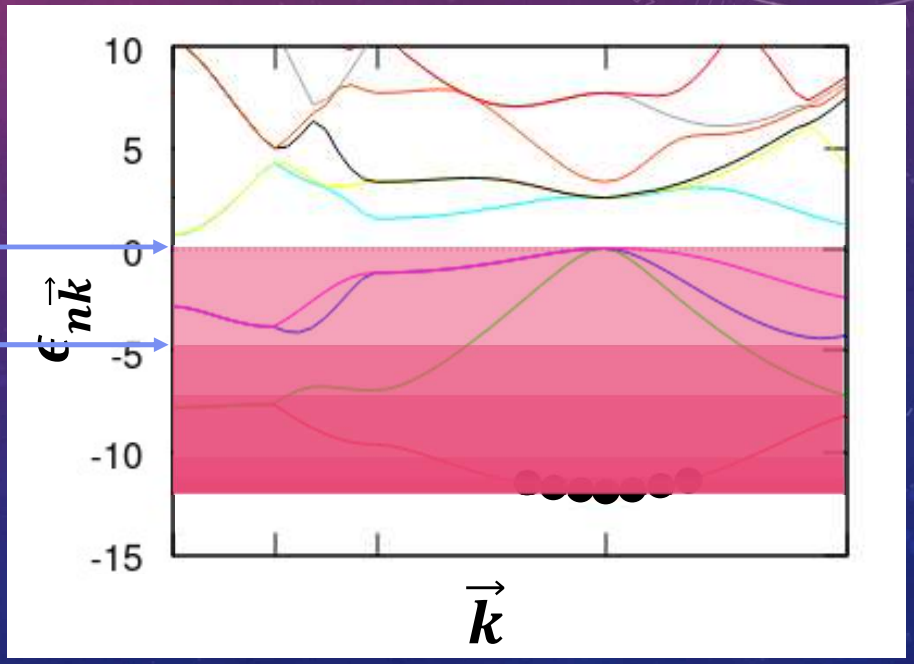
FERMI OCCUPANCY & ELECTRON TEMPERATURE *CONVERGENCE*

- Electron density (kinetic energy similar story)

$$n(\vec{r}) = \sum_i f_i |\psi_i(\vec{r})|^2 = \sum_{n\vec{k}} f_{n\vec{k}} \left|\psi_{n\vec{k}}(\vec{r})\right|^2$$

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

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



FERMI OCCUPANCY & ELECTRON TEMPERATURE *CONVERGENCE*

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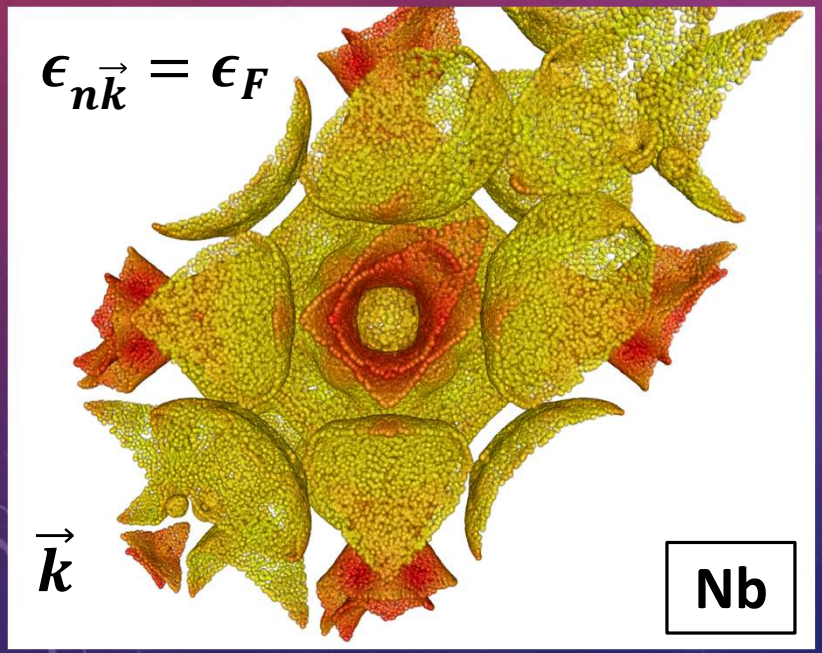
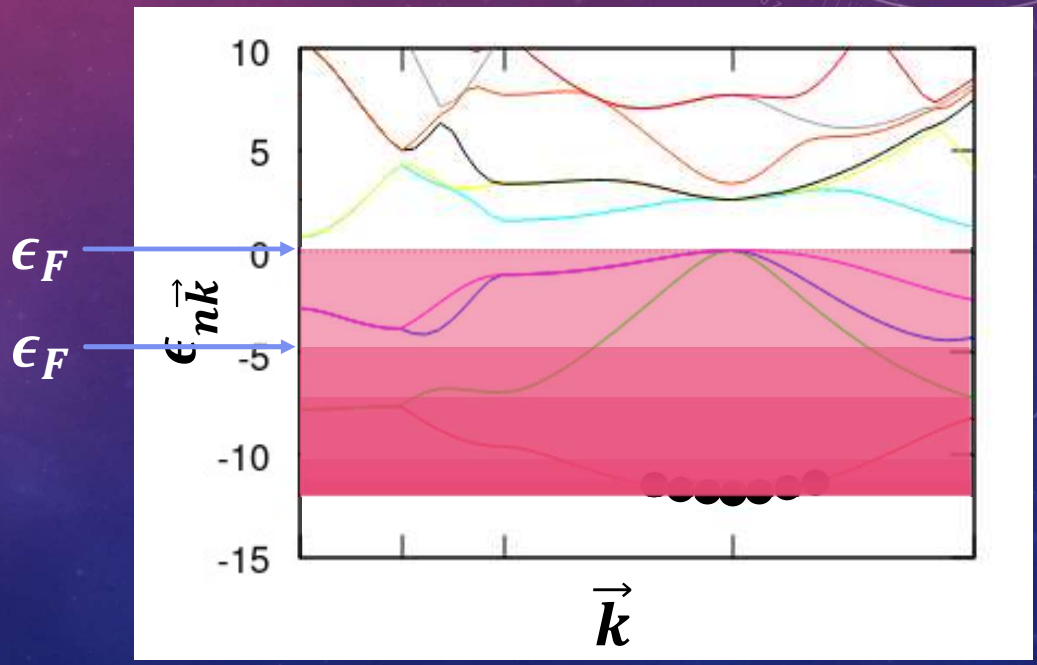
- Semiconductor: completely filled bands: all k=points contribute (😳)
- Metal: Fermi-level cuts band(s), contributing regions are complicated (😐)

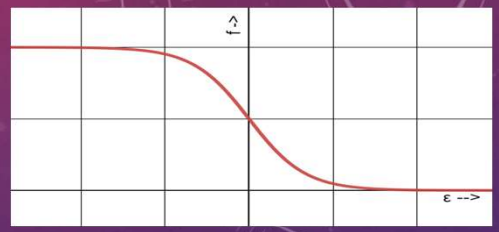




FERMI OCCUPANCY & ELECTRON TEMPERATURE *CONVERGENCE*

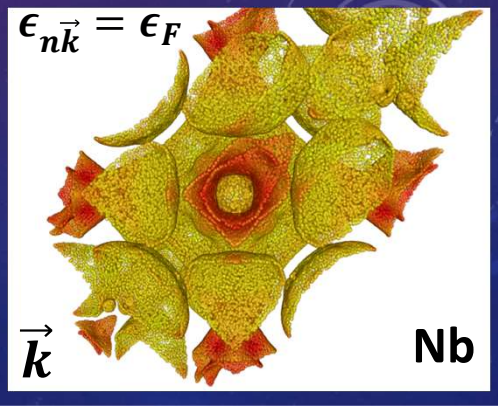
- For metals, contributing regions are complicated (😐)
- DFT generalizes to T>0 !

$$\Rightarrow f_{n\vec{k}} = \frac{1}{e^{(\epsilon_{n\vec{k}}-\mu)/k_B T}+1}$$ (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 (~$4T_{room}$), and *verify* $T \rightarrow 0$ convergence (😠)



SUMMARY OF ISSUES TO MANAGE

- Choice of approximate functional $\left(E_{xc}^{LDA}[n(\vec{r})], E_{xc}^{GGA}[n(\vec{r})], etc.\right)$
  - GGA is usually sufficient (maybe DFT+U for oxides, hybrid for subtle chemistry)
- Iterative convergence (always)
- Plane-wave cutoff E_{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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