ELECTRONIC STRUCTURE: BANDS AND WANNIER FUNCTIONS

Everything we call real is made of things that cannot be regarded as real.

– Niels Bohr

THIS LECTURE

- DFT and excited states
- Band structures from experiment
- Band structures from DFT
- Density of states and quantum capacitance
- Comparison of *ab initio* results and ARPES for a complex system

- Direct uses for Kohn-Sham wave functions
- From Kohn-Sham wave functions to Wannier functions

DENSITY-FUNCTIONAL THEORY AND EXCITED STATES

DFT is *not* just an electronic ground-state theory

The proof we gave was for ground-states, but …

- Directly generalizes to $T>0$ [minimum *free energy* over *density matrices*]
- For specific excited states, search instead for stationary points [not min's]
- Also, can get excited states from time-dependent DFT (TDDFT)
  [based on different type of theorem]
- Some excited states can be related to ground states (band structure)

🤔?

DENSITY-FUNCTIONAL THEORY AND EXCITED STATES

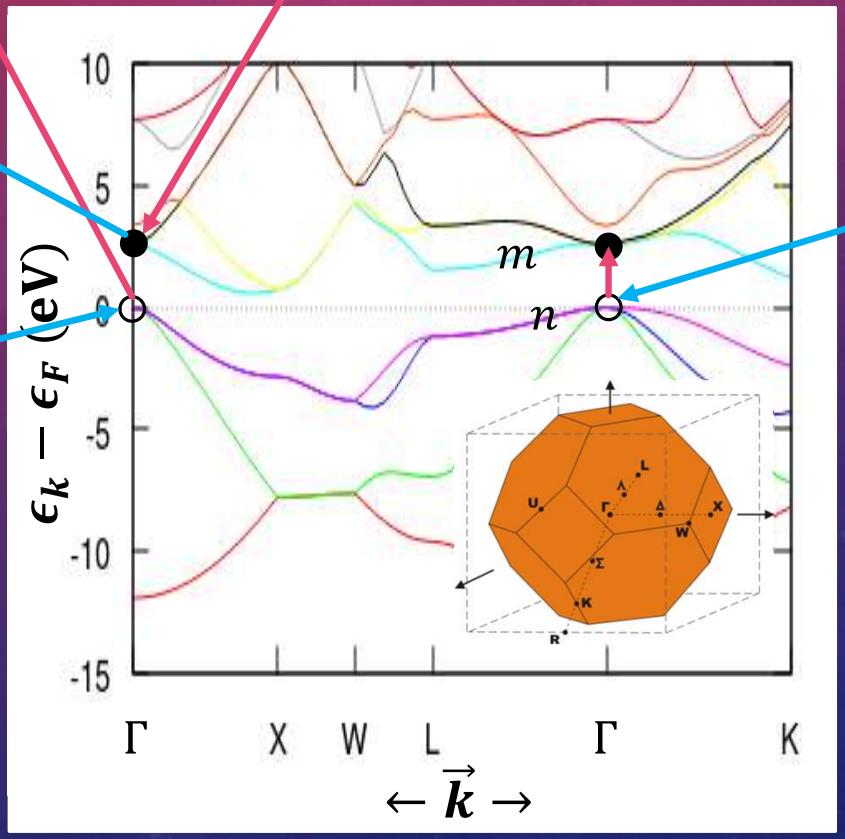
Band structures give excited state information

***Inverse* Photoemission:**

$$\Delta E_{\text{solid}} = +\epsilon_{m\vec{k}}$$
$$= E_0(\mathrm{N}+1) - E_0(\mathrm{N})$$

Photoemission:

$$\Delta E_{\text{solid}} = -\epsilon_{n\vec{k}}$$
$$= E_0(N-1) - E_0(N)$$
$$\Rightarrow \epsilon_{n\vec{k}} = E_0(N) - E_0(N-1)$$



$h\nu$

$h\nu$

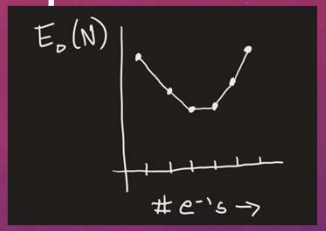
Photoadsorption:

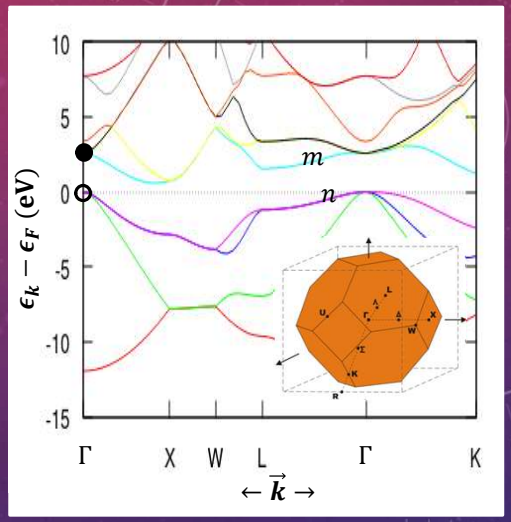
$$\Delta E_{\text{solid}} = \epsilon_{m\vec{k}} - \epsilon_{n\vec{k}}$$

(*)
Technically, only for top (bottom) of valence (conduction) band, but can restrict to states with a given net $\vec{k}$.

DENSITY-FUNCTIONAL THEORY AND EXCITED STATES

$\epsilon_{n\vec{k}}$ = changes in E_0 with changes in occupancies





$\epsilon_{m\vec{k}} = E_0(N+1) - E_0(N)$

$\epsilon_{n\vec{k}} = E_0(N) - E_0(N-1)$

- Idea:

$$E_0(f_{n\vec{k}}) = \min_{\psi_{n\vec{k}}} E_0(\psi_{n\vec{k}}, f_{n\vec{k}})$$

$$E_0(N+1) - E_0(N) \cong \frac{d}{df_{n\vec{k}}} E_0(f_{n\vec{k}}) \cdot \Delta f_{n\vec{k}} = \frac{d}{df_{n\vec{k}}} E_0(f_{n\vec{k}})$$

- Now, usual Hellmann-Feynman argument gives

$$\frac{dE_0}{df_{n\vec{k}}} = \frac{\partial}{\partial f_{n\vec{k}}} E_0(\psi^{(0)}_{n\vec{k}}(f_{n\vec{k}}), f_{n\vec{k}})$$

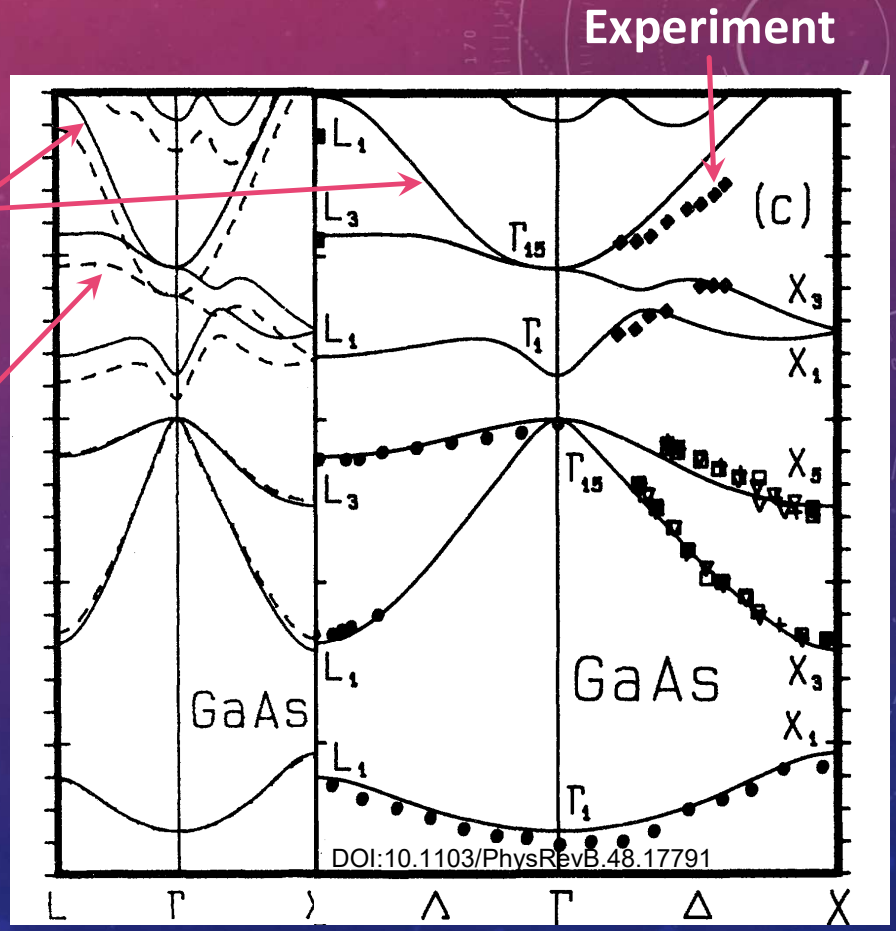
$$= \int d^3r\, \psi^*_{n\vec{k}}(\vec{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{sc}}(\vec{r})\right) \psi_{n\vec{k}}(\vec{r}) = \epsilon^{(KS)}_{n\vec{k}}$$ (😳!!) [Janak Theorem]

where, $V_{\text{sc}}(\vec{r}) = V_{\text{nuc}}(\vec{r}) + \int d^3r' \frac{n(r')}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})} \equiv V_{\text{nuc}}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r})$

- Thus, $\epsilon_{n\vec{k}} = E_0(N+1) - E_0(N) \cong \frac{dE_0}{df_{n\vec{k}}} = \epsilon^{(KS)}_{n\vec{k}}$

DFT BAND STRUCTURES AND "SCISSORS" OPERATOR

- In general, excellent match!
- Issue is that $\frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}$ is not continuous as e^-'s are added / subtracted
- Easily corrected by rigid upward shift of empty bands ("scissoring")
- Can get shift from experiment or higher-level theories (GW, etc.)



DENSITY OF STATES (DOS) AND QUANTUM CAPACITANCE

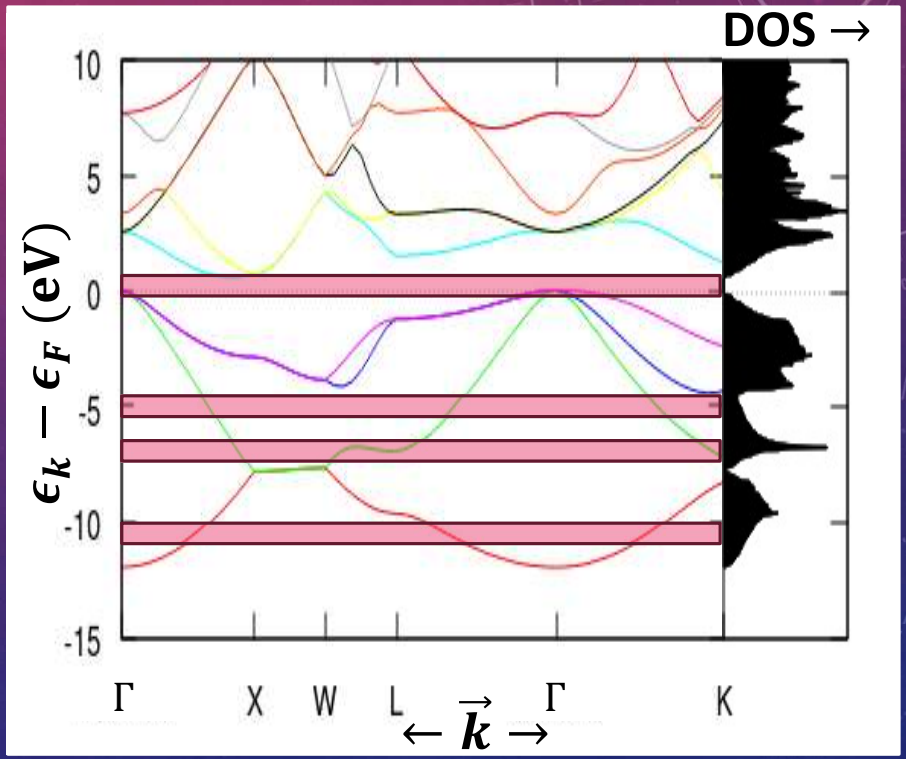
- DOS measures states/unit energy

$$g(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{\#\ \text{states: } \epsilon < \epsilon_{n\vec{k}} < \epsilon + d\epsilon}{d\epsilon}$$

  - Tends to be high where bands are flat
  - Tends to be low where bands are steep
  - Zero inside band gaps

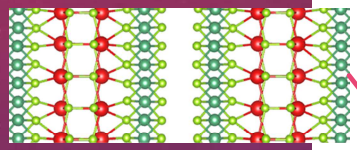
- Changing potential varies Fermi level and charge in the system:

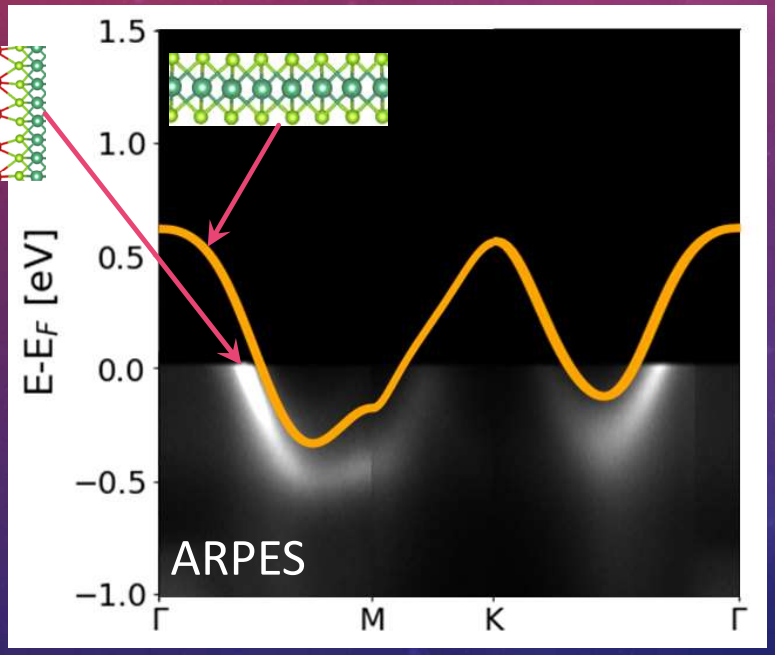
$$C_{\text{quant}} \equiv \frac{dQ}{dV} = \frac{-e \cdot dN}{d\epsilon/(-e)} = e^2 \frac{dN}{d\epsilon} = e^2 g(\epsilon)$$

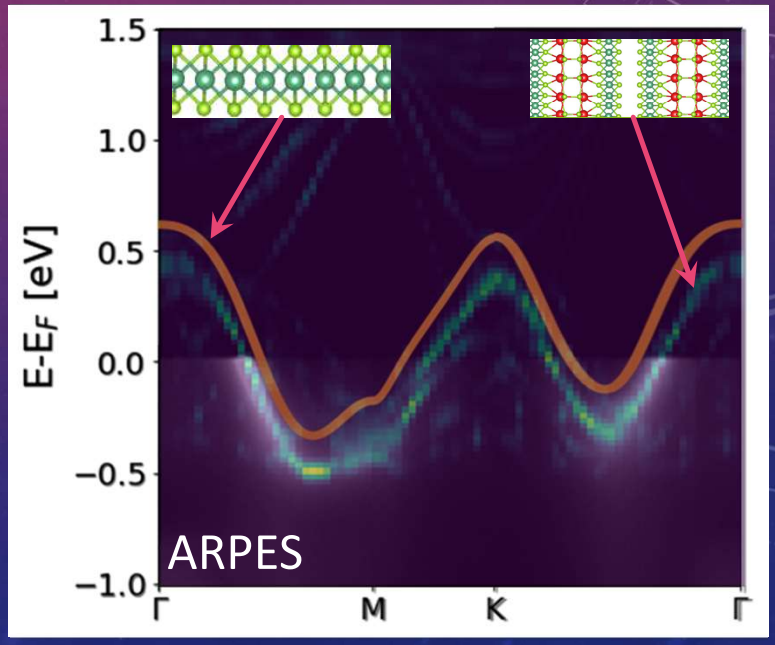


DFT BAND-STRUCTURES II

Direct comparison with
Angular resolved photoemission spectroscopy (ARPES)





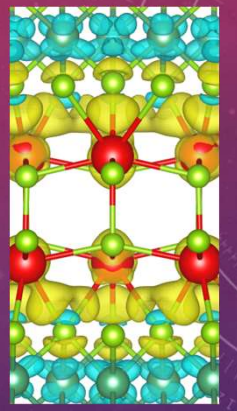


From Niedzielski, Faeth, Goodge, Sinha, McQueen, Kourkoutis and Arias, APS Bulletin: bit.ly/3Og42Tf

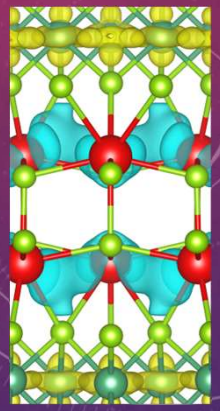
USES FOR THE KOHN-SHAM ORBITALS $\psi_{n\vec{k}}(\vec{r})$

- Sum densities in different energy ranges

$$n(\vec{r}) = \sum_{\epsilon_0 < \epsilon_{n\vec{k}} < \epsilon_1} f_{n\vec{k}} \left|\psi_{n\vec{k}}(\vec{r})\right|^2$$

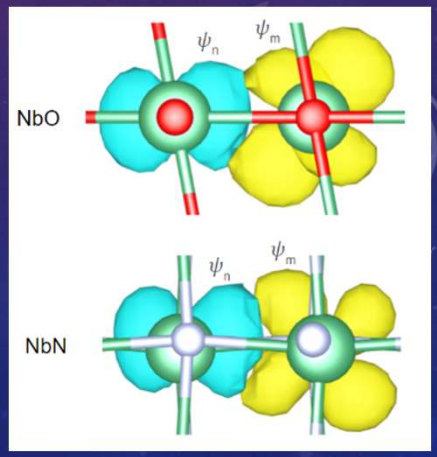


valence bands



Fermi level

- Construct local representation of orbitals ("Wannier functions") to understand physical chemistry and for more efficient computation



FROM ORBITALS $\psi_{n\vec{k}}(\vec{r})$ TO WANNIER FUNCTIONS $W_n(\vec{r})$

- Recall Bloch's theorem

  $\psi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\,\psi_{n\vec{k}}(\vec{r})$ where $e^{i\vec{k}\cdot\vec{R}} = e^{i\phi}$

- ϕ and $\phi + 2\pi N$ are equivalent $\Rightarrow \psi_{n\vec{k}}(\vec{r})$ is periodic in $\vec{k}$

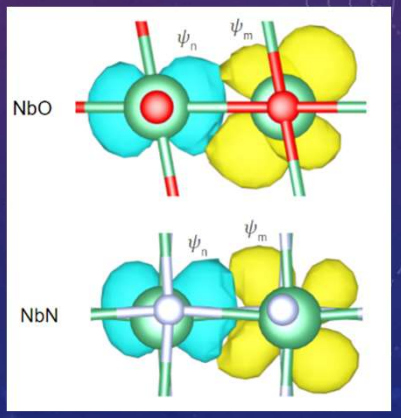
- Expand $\psi_{n\vec{k}}(\vec{r})$ in a Fourier series in $\vec{k}$

$$\psi_{\cdot\vec{k}}(\cdot) = \sum_{\vec{R}} W_{\cdot\vec{R}}(\cdot)\, e^{i\vec{k}\cdot\vec{R}}$$

$$W_{\cdot\vec{R}}(\cdot) = \frac{1}{\Omega_{BZ}} \int d^3k\, e^{-i\vec{k}\cdot\vec{R}} \psi_{\cdot\vec{k}}(\cdot)\ ;\ \Omega_{BZ} = \int d^3k$$

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} W_{n\vec{R}}(\vec{r}) e^{i\vec{k}\cdot\vec{R}}$$

$$W_{n\vec{R}}(\vec{r}) = \frac{1}{\Omega_{BZ}} \int d^3k\, e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r})$$



THANK YOU!

TAA2@CORNELL.EDU