

The background features a dark red to blue gradient with several circular patterns. A prominent scale on the left side ranges from 140 to 260 in increments of 10. Other circles contain arrows and partial arcs, suggesting a technical or scientific theme.

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

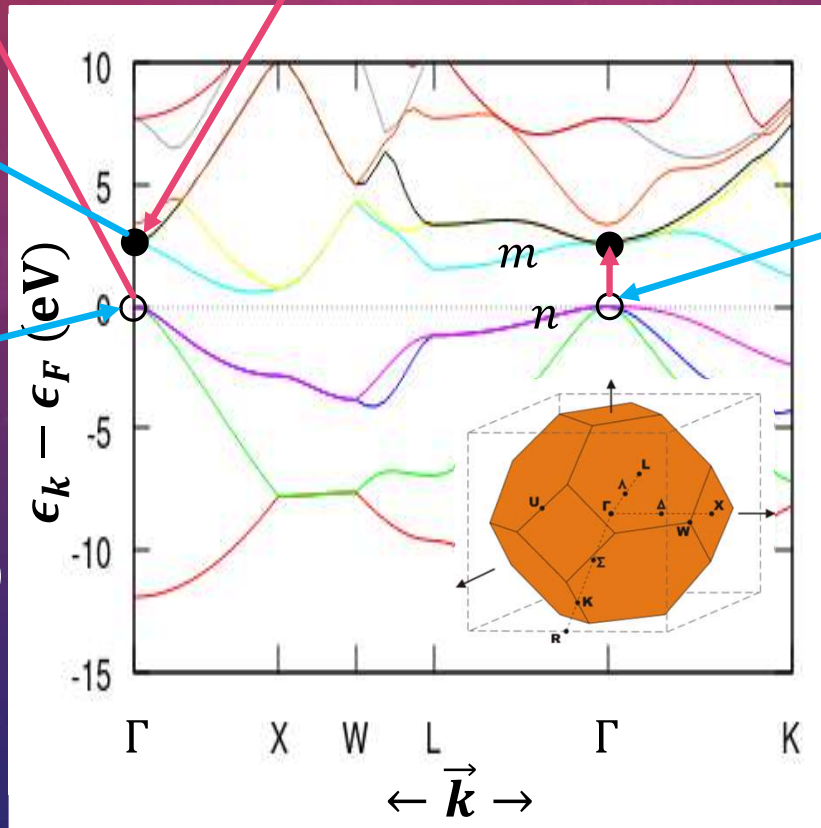
Band structures give excited state information

Inverse Photoemission:

$$\begin{aligned} \Delta E_{\text{solid}} &= +\epsilon_{m\vec{k}} \quad hv \\ &= E_0(N+1) - E_0(N) \end{aligned}$$

Photoemission: hv

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



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} .

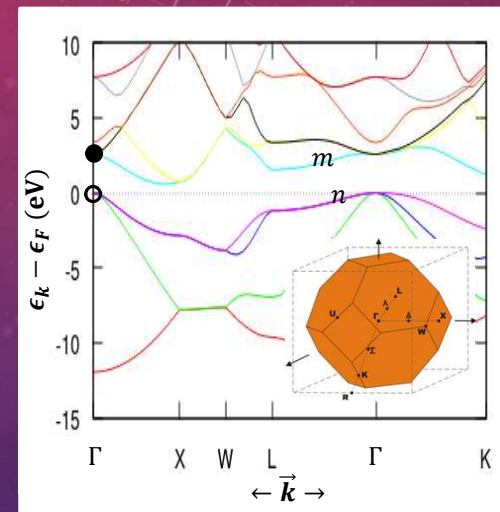
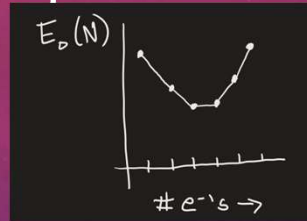
DENSITY-FUNCTIONAL THEORY AND EXCITED STATES

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

• Idea:

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

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



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

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

• Now, usual Hellmann-Feynman argument gives

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

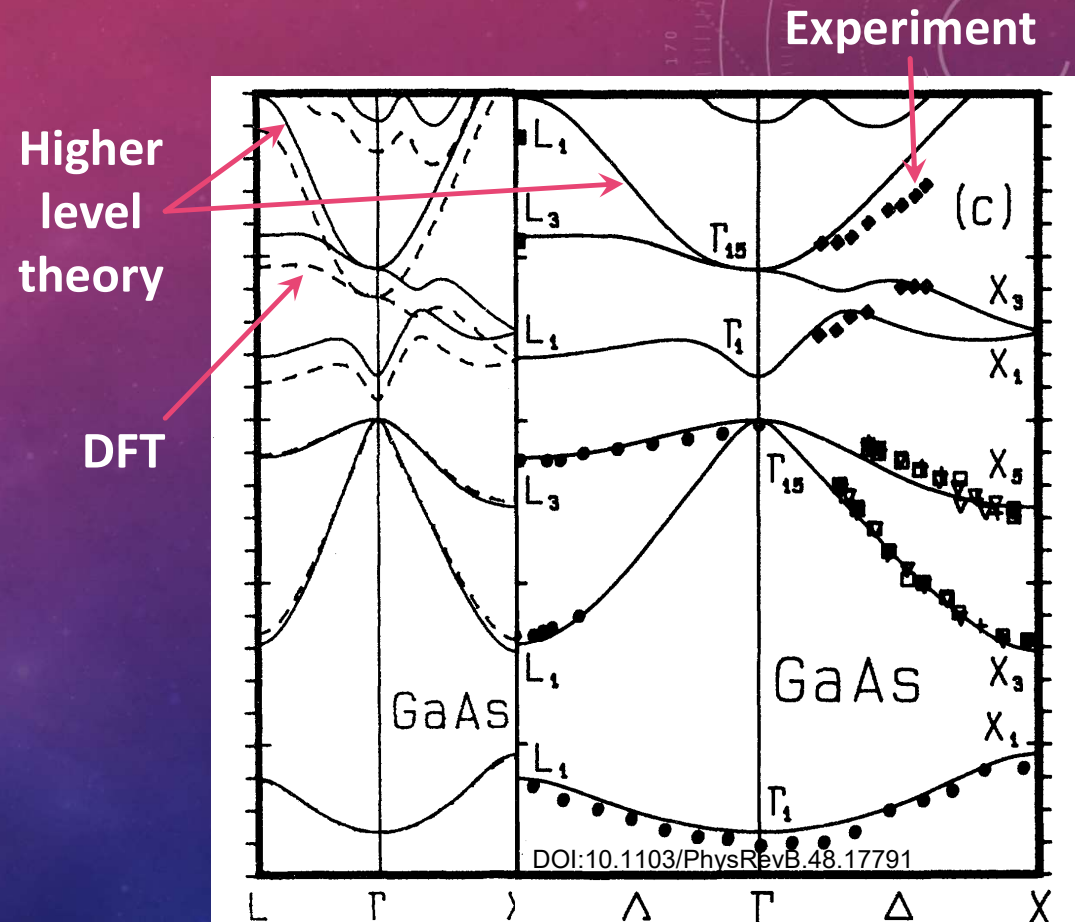
$$= \int d^3r \psi_{n\vec{k}}^*(\vec{r}) \left(-\frac{1}{2} \nabla^2 + V_{sc}(\vec{r}) \right) \psi_{n\vec{k}}(\vec{r}) = \epsilon_{n\vec{k}}^{(KS)} (\text{🤪!!}) \text{ [Janak Theorem]}$$

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

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

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

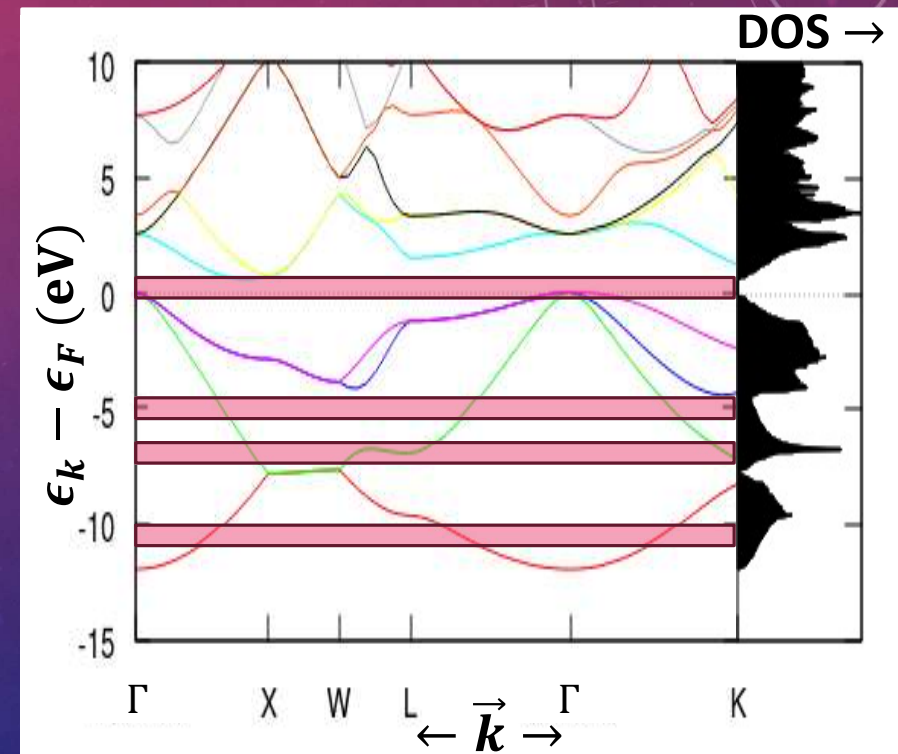
- DOS measures states/unit energy

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

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

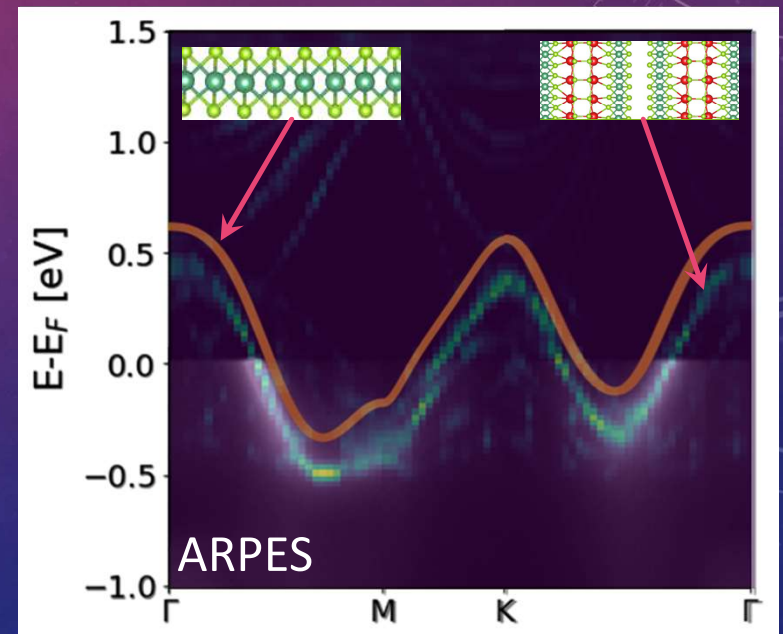
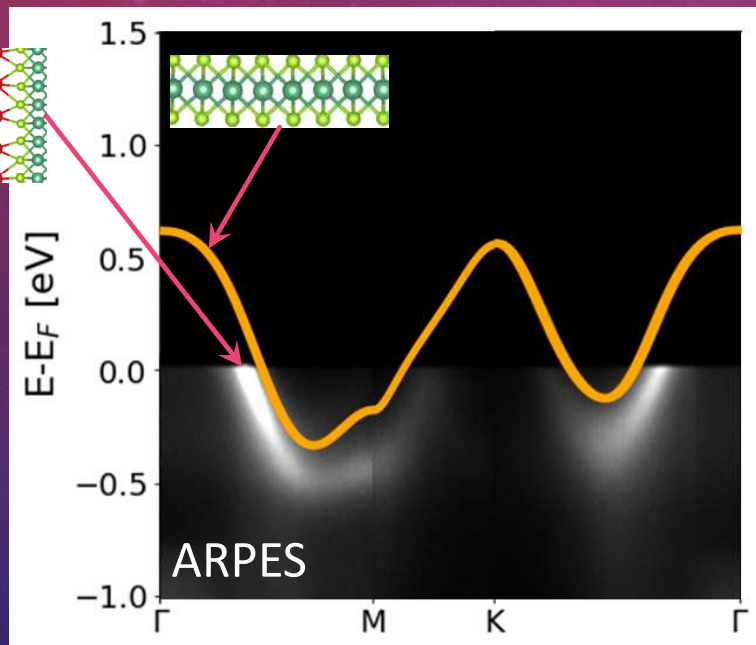
- Changing potential varies Fermi level and charge in the system:

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



DFT BAND-STRUCTURES II

Direct comparison with
Angular resolved photoemission spectroscopy (ARPES)



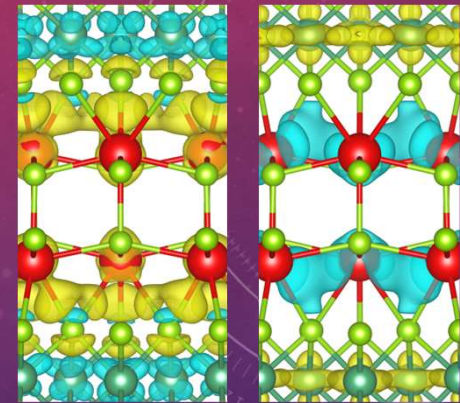
From Niedzielski, Faeth, Goodge, Sinha, McQueen, Kourkoutis and Arias, APS Bulletin: [bit.ly/3Og42Tf](https://arxiv.org/abs/1508.07411)

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

- Sum densities in different energy ranges

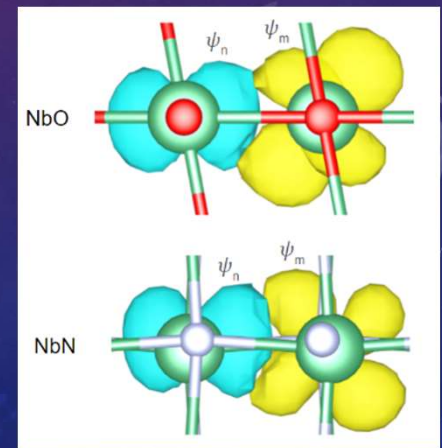
$$n(\vec{r}) = \sum_{\epsilon_0 < \epsilon_{n\vec{k}} < \epsilon_1} f_{n\vec{k}} |\psi_{n\vec{k}}(\vec{r})|^2$$

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



valence
bands

Fermi
level



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

- Recall Bloch's theorem

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

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

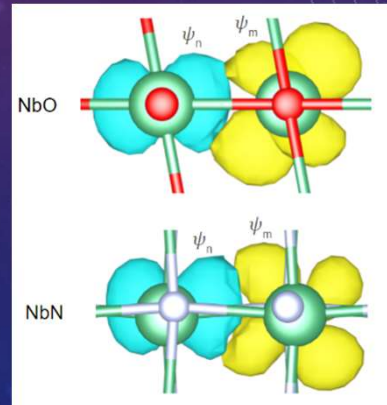
- Expand $\psi_{n\vec{k}}(\vec{r})$ in a Fourier series in \vec{k}

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

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

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

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



The background is a gradient of purple and blue, featuring bokeh light effects and technical diagrams. On the left side, there are several circular diagrams with dashed lines and arrows, resembling a technical drawing or a schematic. One prominent diagram has a scale from 140 to 260. The text 'THANK YOU!' is centered in the lower right quadrant in a white, sans-serif font.

THANK YOU!

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