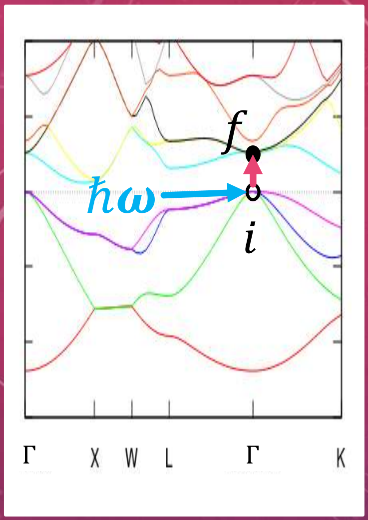


FROM WANNIER FUNCTIONS TO OPTICAL ABSORPTION

The changing of bodies into light, and light into bodies, is very conformable to the course of Nature, which seems delighted with transmutations.

-Isaac Newton

THIS LECTURE

- Properties of and uses for Wannier functions
- Optical absorption
  - Connecting measurements to quantum processes
  - An example: Photoemission from PbTe

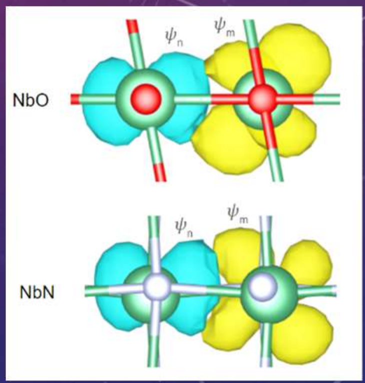
FROM LAST TIME …

$\psi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi_{n\vec{k}}(\vec{r})$ has the same $\vec{\mathrm{k}}$ periodicity as the $e^{i\vec{k}\cdot\vec{R}}$'s

$\Rightarrow$ Expand $\psi_{n\vec{k}}(\vec{r})$ in a Fourier series in $\vec{k}$ holding $n, \vec{r}$ (temporarily) fixed:

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

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

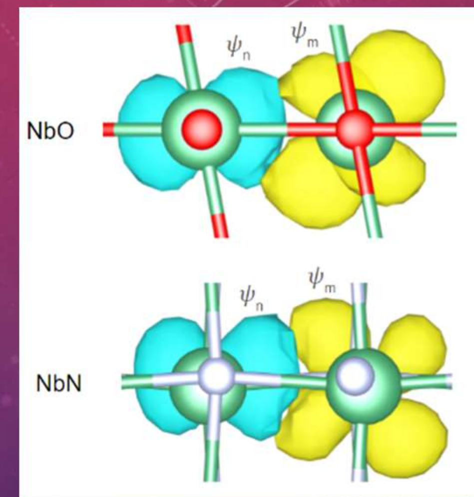


Now, do separately for all $n, \vec{r}$ to restore full dependencies:

$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} W_{n\vec{R}}(\vec{r}) e^{i\vec{k}\cdot\vec{R}}$; $\Rightarrow W_{n\vec{R}}(\vec{r})$'s are a basis for the $\psi_{n\vec{k}}(\vec{r})$'s!

$W_{n\vec{R}}(\vec{r}) = \frac{1}{\Omega_{BZ}}\int_{BZ} d^3k\, e^{-i\vec{k}\cdot\vec{R}}\psi_{n\vec{k}}(\vec{r})$; Defines the $W_{n\vec{R}}(\vec{r})$'s

PROPERTIES OF WANNIER FUNCTIONS $W_n(\vec{r})$



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

- Using Bloch's theorem

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

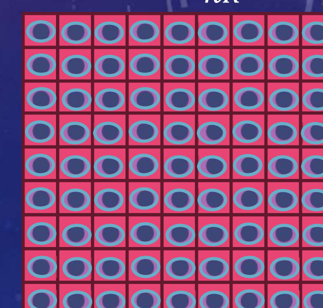
$$\equiv W_n(\vec{r}-\vec{R})$$

- Fourier analysis: ***if*** $\psi_{n\vec{k}}(\vec{r})$ is a smooth function of $\vec{k}$,

  $W_{n\vec{R}}(\vec{r}) = W_n(\vec{r}-\vec{R})$ decays rapidly with $\vec{R}$

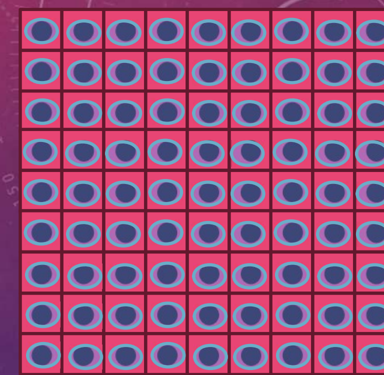
  $\Rightarrow$ $W_n(\vec{r})$ is well localized

(ellipse) $= W_{n\vec{R}}(\vec{r})$



MAXIMALLY LOCALIZED WANNIER FUNCTIONS (MLWFS)

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



- $\psi_{n\vec{k}}(\vec{r})$ enters only as $\left|\psi_{n\vec{k}}(\vec{r})\right|^2$ and $\psi^*_{n\vec{k}}(\vec{r})\nabla^2\psi_{n\vec{k}}(\vec{r})$
  $\Rightarrow$ phase is undetermined and varies *randomly* (not smoothly)
- Include adjustable compensatory phases $\psi_{n\vec{k}}(\vec{r}) \leftarrow e^{-i\phi_{n\vec{k}}}\,\psi_{n\vec{k}}(\vec{r})$
  and optimize to "maximally localize" $W_n(\vec{r})$: $\min_{\phi_{n\vec{k}}} \langle W_n | r^2 | W_n \rangle$

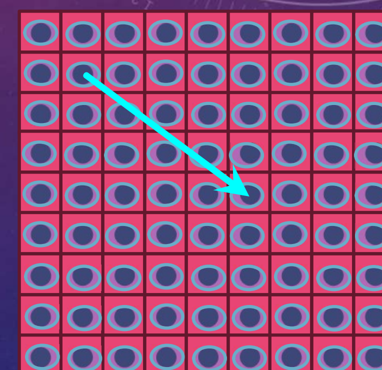
* Sometimes benefit by combining multiple bands, all handled by code
* Sometimes need to play with initial "guess" for minimization

WANNIER-FUNCTION ACCELERATED BAND-STRUCTURES

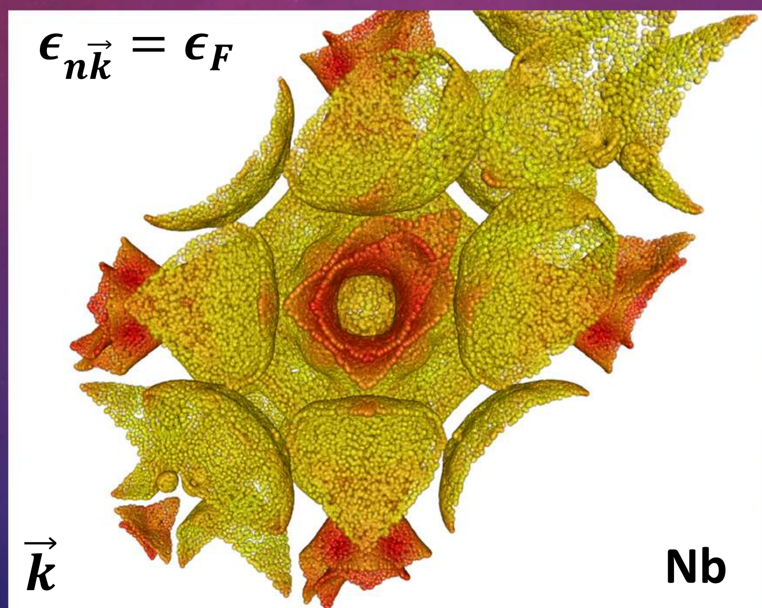
- Once localized, $W_n(\vec{r})$ enable extremely rapid calculations from very sparse matrix:

$$\epsilon_{n\vec{k}} = \mathrm{eig}\,\underbrace{\left\langle W_{n_1\vec{R}_1}(\vec{r}) \middle| -\frac{1}{2}\nabla^2 + V_{sc}(\vec{r}) \middle| W_{n_2\vec{R}_2}(\vec{r}) \right\rangle}$$

Depends only on $\vec{R}_2$- $\vec{R}_1$



- Dense sampling of k-space (10^9 k-points 🤓!):



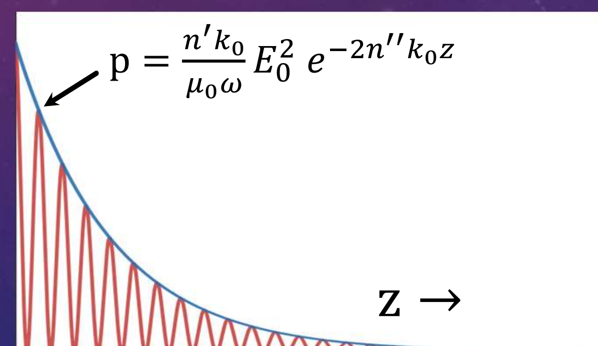
FROM MACROSCOPIC PROPERTIES TO MICROSCOPIC PROCESSES: OPTICAL ABSORPTION AS AN EXAMPLE

FROM OPTICAL CONSTANTS TO PHOTON ABSORPTION

Relate optical constants to energy flow in the material

- $\epsilon = n^2 = (n' + i\, n'')^2 \;\Rightarrow \epsilon' = n'^2 - n''^2, \epsilon'' = 2n'n''$
- $\vec{E}(z) = \vec{E}_0\, e^{i\,k\,z} = \vec{E}_0\, e^{i(\omega/c_{\text{material}})z} = \vec{E}_0 e^{in(\omega/c)z}$
  $= \vec{E}_0\, e^{ink_0 z} = \vec{E}_0\, e^{in'k_0 z} e^{-n''k_0 z}$
- power/area $\mathrm{p} = \frac{k}{\mu_0 \omega}\left|\vec{E}\right|^2 = \frac{1}{2}\frac{n'k_0}{\mu_0\omega} E_0^2\, e^{-2n''k_0 z}$

  (1/2 for time average)
- energy loss/volume $\frac{du}{dt} = \hbar\omega\, w, \quad w \equiv \frac{\text{adsorbed photons/time}}{\text{volume}}$



FROM OPTICAL CONSTANTS TO PHOTON ABSORPTION

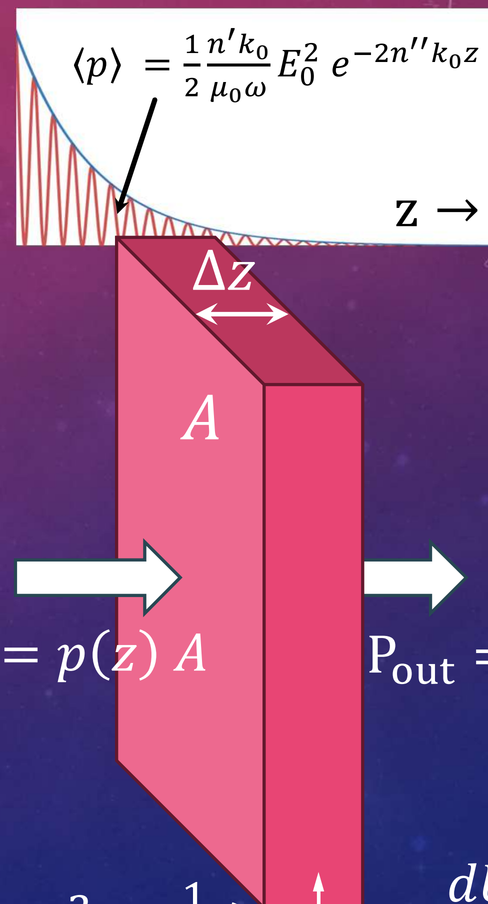
$$P_{in} - P_{out} = \frac{dU}{dt}$$

$$p(z)A - p(z+\Delta z)A = \frac{du}{dt}(A\,\Delta z)$$

- $\frac{du}{dt} = -\frac{p(z+\Delta z) - p(z)}{\Delta z} = -\frac{dp}{dz}$ ← (continuity eq.)
- $\epsilon'' = 2n'n''$
- $\mathrm{p} = \frac{n' k_0}{2\mu_0 \omega} E_0^2\, e^{-2n'' k_0 z}$
- $\frac{du}{dt} = \hbar\omega\, w$

$$= -\frac{dp}{dz} = 2n'' k_0 \cdot \frac{n' k_0}{2\mu_0\omega}\mathrm{E}^2 = 2n'n'' \frac{k_0^2 E^2}{2\mu_0\omega}$$

$$\Rightarrow \epsilon'' = 2n'n'' = \frac{2\hbar\mu_0\omega^2}{k_0^2}\frac{w}{E^2} = \frac{2\hbar}{\epsilon_0}\frac{w}{E^2} \text{ (🤓!)} \quad \left(\frac{\mu_0\omega^2}{k^2} = \mu_0 c^2 = \frac{1}{\epsilon_0}\right)$$



FROM OPTICAL CONSTANTS TO PHOTON ABSORPTION

- $w \equiv \frac{\text{adsorbed photons/time}}{\text{volume}}$

standard quantum rate for perturbation $\frac{e}{m}\vec{A}\cdot\vec{\mathrm{p}}$

$$= \frac{1}{V}\sum_{fi}\delta\left(\epsilon_f - \epsilon_i - \hbar\omega\right)\left\{(1-f_f)f_i - (1-f_i)f_f\right\}\frac{2\pi}{\hbar}\left|\left\langle f\left|\frac{e}{m}\vec{A}\cdot\vec{p}\right|i\right\rangle\right|^2$$

all transitions — that conserve energy — forward and reverse processes must go from filled to empty state

$N_{\vec{k}}\langle\ldots\rangle_{\vec{k}} = N_{\text{cell}}\langle\ldots\rangle_{\vec{k}}$

¼ for time *and* space averages

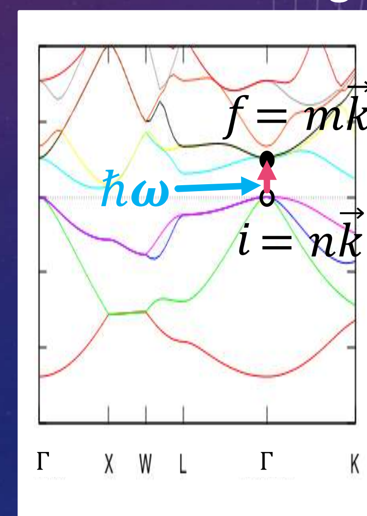
⅓ for orientation average

$$= \frac{1}{V}\sum_{\vec{k}}\sum_n\sum_m \delta\left(\epsilon_{m\vec{k}} - \epsilon_{n\vec{k}} - \hbar\omega\right)\left\{f_{n\vec{k}} - f_{m\vec{k}}\right\}\frac{2\pi e^2}{\hbar m^2}\frac{A^2}{4}\frac{1}{3}\left|\langle f|\vec{p}|i\rangle\right|^2$$

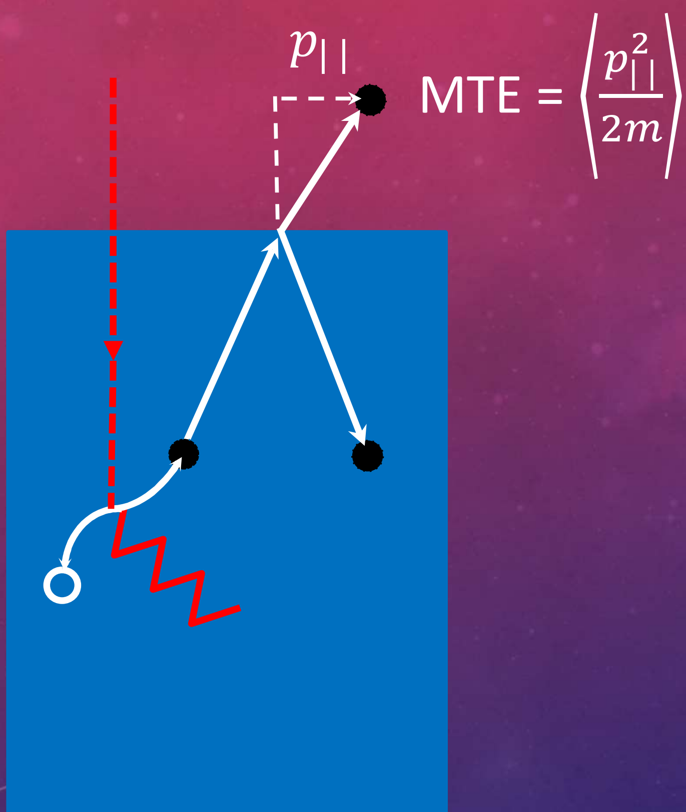
$$= \frac{\pi e^2 E^2}{6\hbar m^2\omega^2}\frac{1}{\mathrm{V_{cell}}}\int\frac{d^3k}{\Omega_{BZ}}2\sum_{nm}\delta\left(\epsilon_{m\vec{k}} - \epsilon_{n\vec{k}} - \hbar\omega\right)\left\{f_{n\vec{k}} - f_{m\vec{k}}\right\}\left|\langle f|\vec{p}|i\rangle\right|^2$$

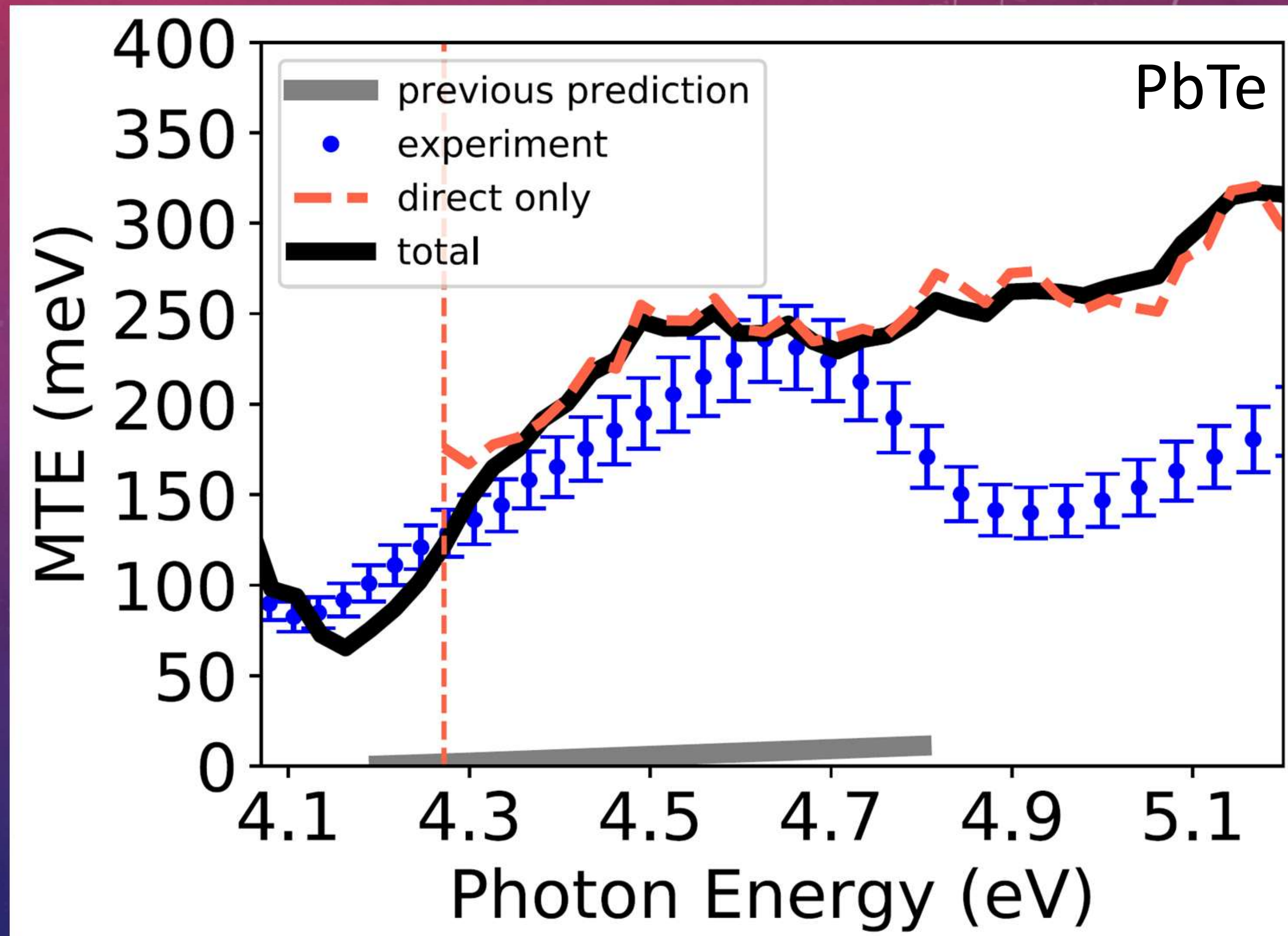
for spin ↑,↓

$$\Rightarrow \epsilon'' = \frac{2\hbar}{\epsilon_0}\frac{w}{E^2} = \frac{\pi e^2}{3\epsilon_0 m^2\omega^2}\frac{1}{\mathrm{V_{cell}}}\int\frac{2d^3k}{\Omega_{BZ}}\sum_{nm}\delta\left(\epsilon_{m\vec{k}} - \epsilon_{n\vec{k}} - \hbar\omega\right)\left\{f_{n\vec{k}} - f_{m\vec{k}}\right\}\left|\langle f|\vec{p}|i\rangle\right|^2$$



DISTRIBUTION OF PHOTOEMITTED ELECTRONS





Nangoi, … , Arias, …, PRB (201)

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←**Survey!!!** 🤓

THANK YOU!

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--- LAST SLIDE ---
(BACKUPS BELOW)

FROM IMAGINARY PART TO ALL CONSTANTS

- Kramers-Kronig relation

$$\epsilon'(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\epsilon''(\omega')}{\omega' - \omega} d\omega'$$

- Index of refraction $(n' + in'') = \sqrt{\epsilon' + i\epsilon''}$