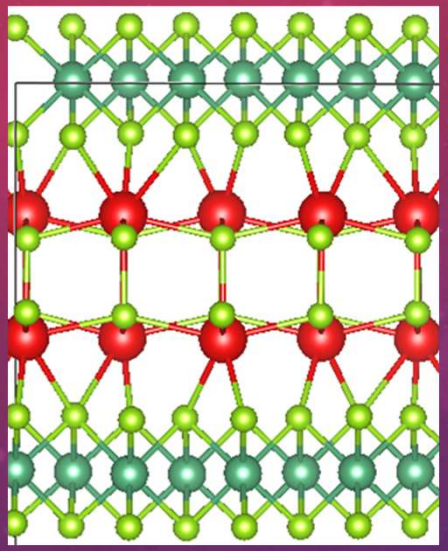
MISMATCHED INTERFACE THEORY (MINT)

What to do when there is no good supercell?

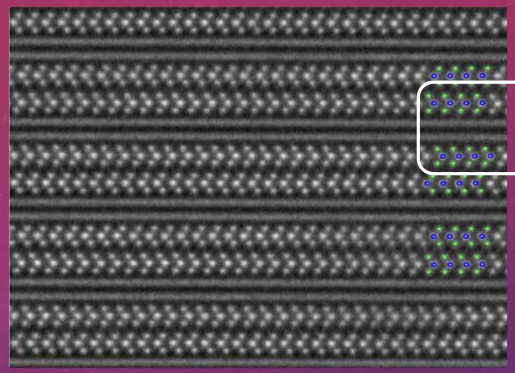
Taken extensively from
Niedzielski, Faeth, Goodge, Sinha, McQueen, Kourkoutis and Arias
APS Bulletin: bit.ly/3Og42Tf

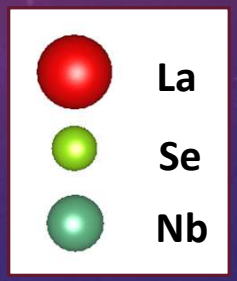
MISFIT MATERIALS

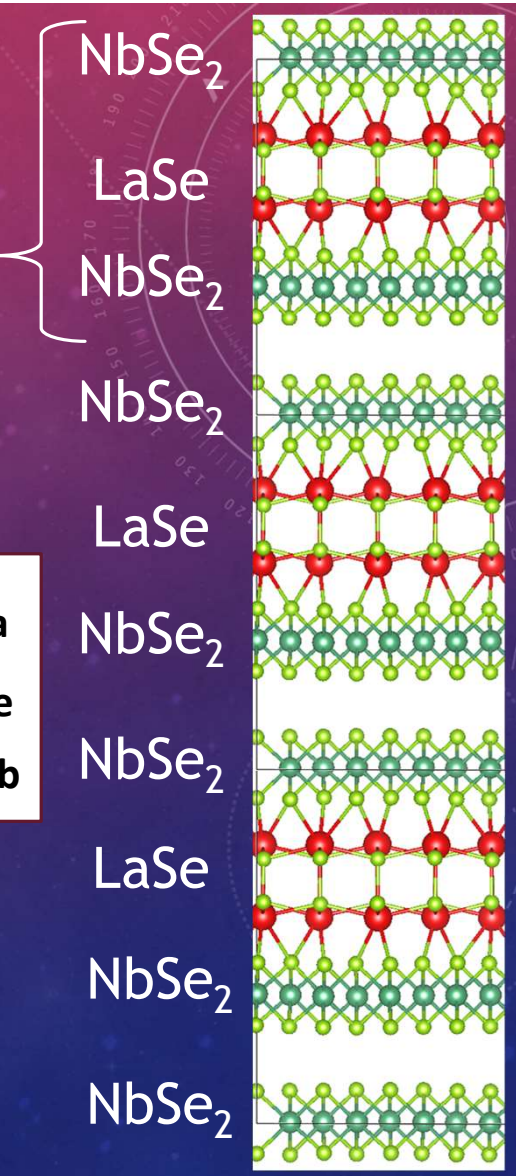
$(LaSe)_{1.14}(NbSe_2)_2$



$(LaSe)_{1.14}(NbSe_2)_2$



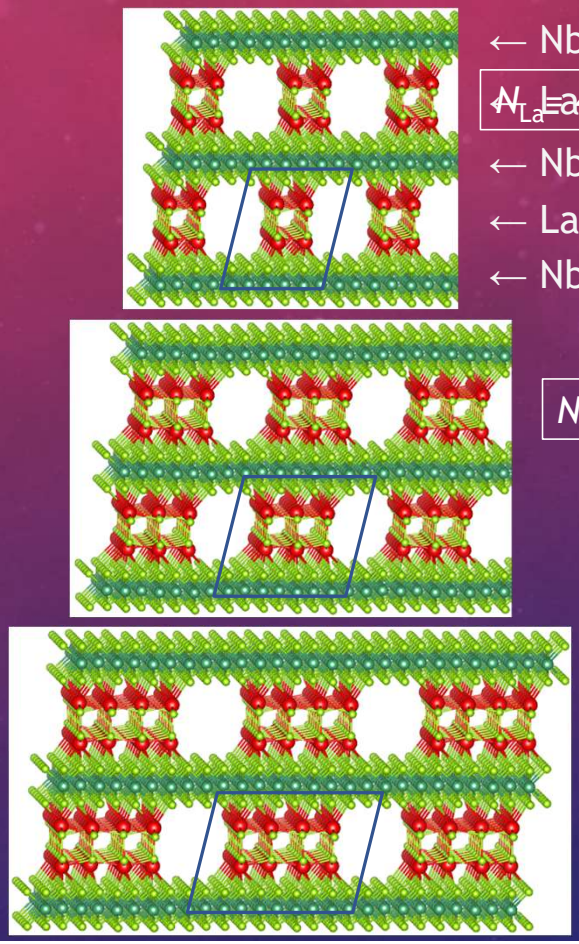




- Chemical formula is irrational
- Layers remain intact, no misfit dislocations
- Horizontal lattice constants mismatched
- There is no overall periodicity (forms horizontal Moiré pattern)
- Any supercell will strain one or both types of layers (🤔 ?)

MINT-SANDWHICH

Sequence of periodic prototype materials (with voids)

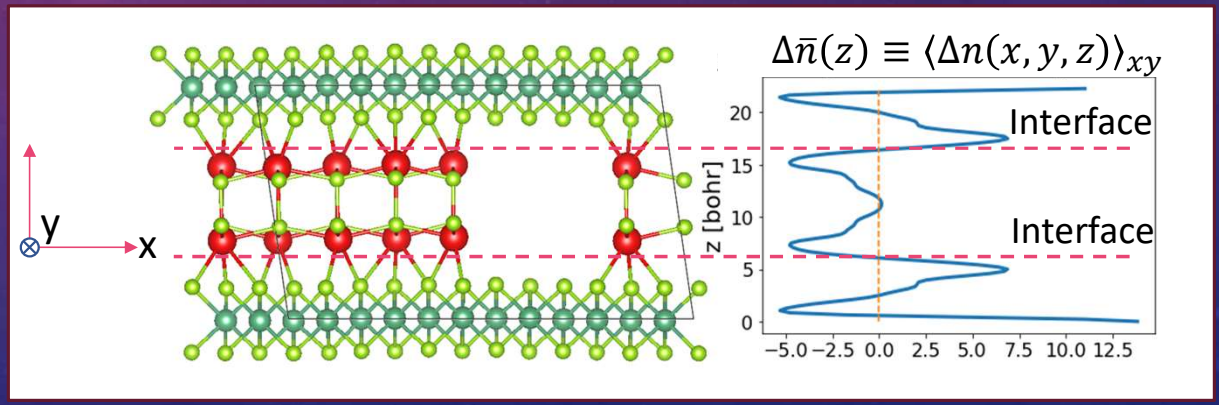


$(LaSe)_{1.14}NbSe_2$

Convergent sequence for desired material property

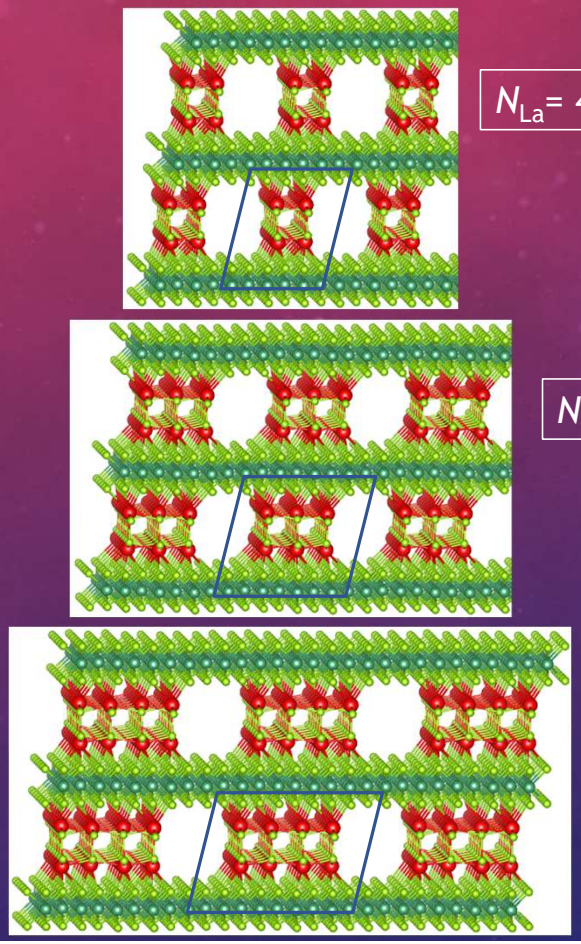
Charge transfer

- Compute $n(\vec{r})$ for combined and isolated systems
- $\Delta n(\vec{r}) \equiv n_{(\mathrm{LaSe})(\mathrm{NbSe_2})}(\vec{r}) - n_{\mathrm{LaSe}}(\vec{r}) - n_{\mathrm{Nb}\ \ _2}(\vec{r})$
- $\Delta N \equiv \int_{\mathrm{LaSe}} n(\vec{r})\, d^3r$

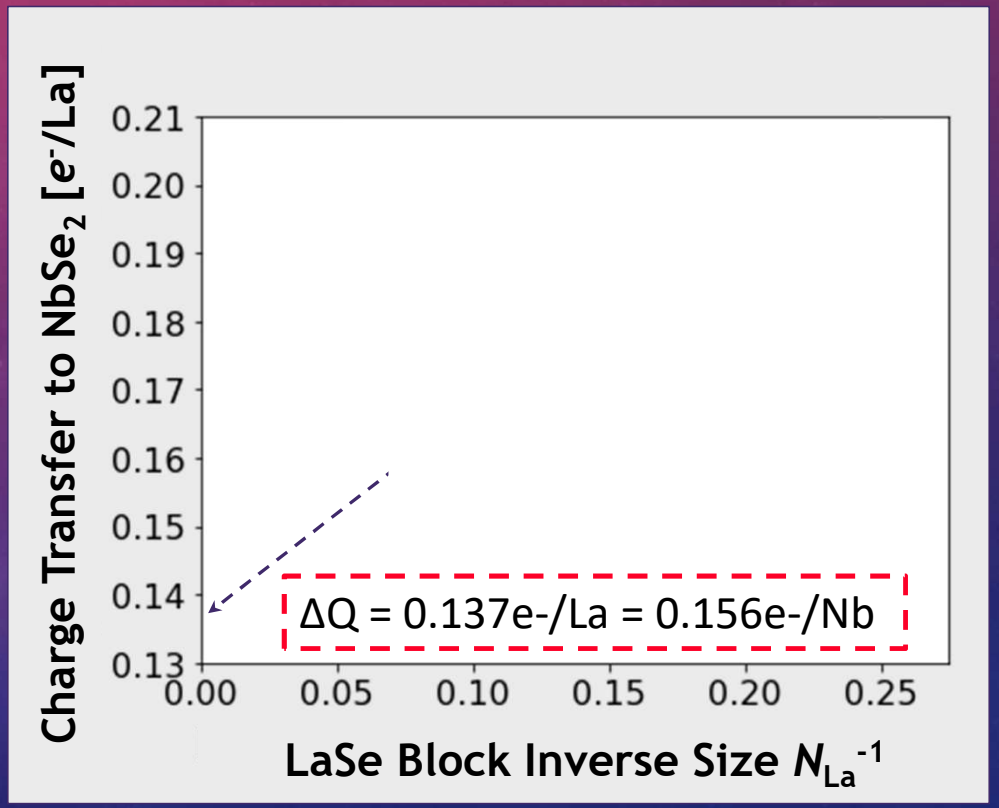


MINT-SANDWICH

Sequence of periodic prototype materials (with voids)



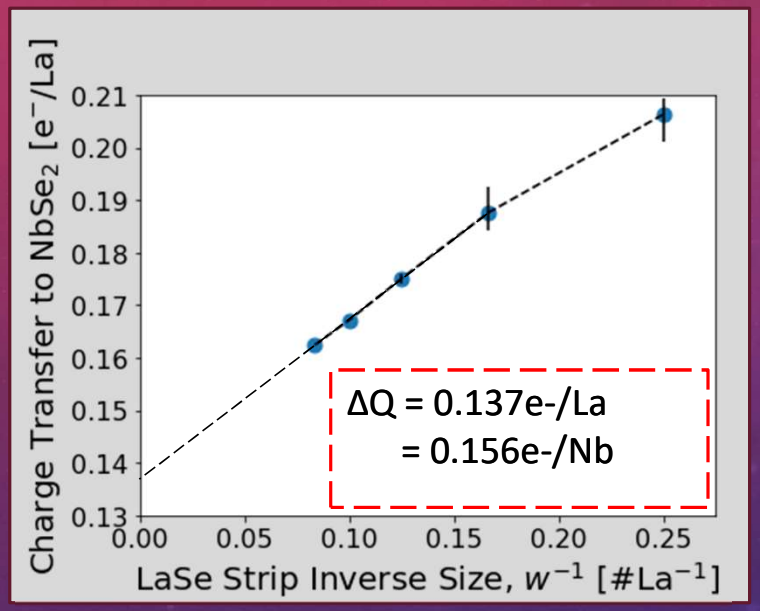
Charge transfer

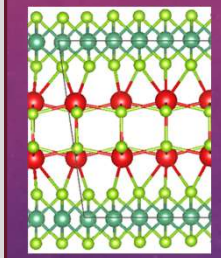


☆ Misfit charge transfer determined!

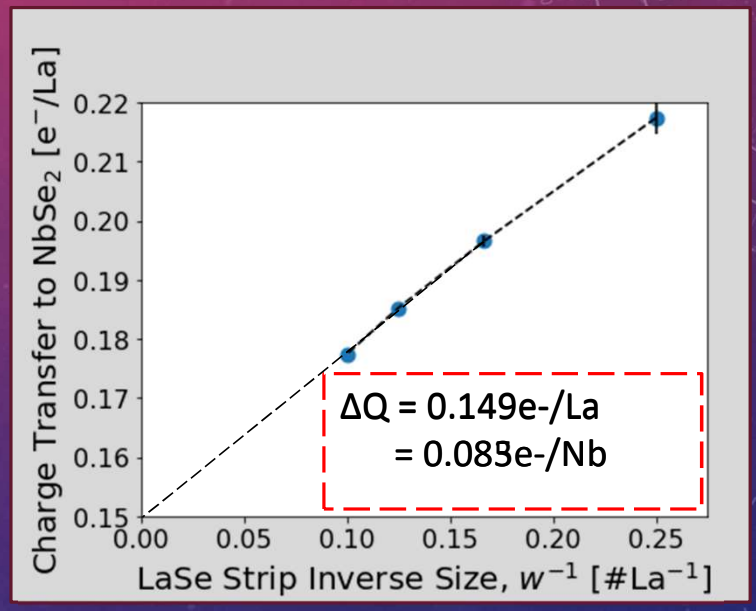
INTERLAYER CHARGE TRANSFER

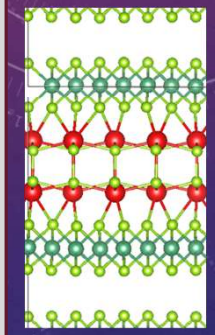
LaSe $NbSe_2$





LaSe $(NbSe_2)_2$

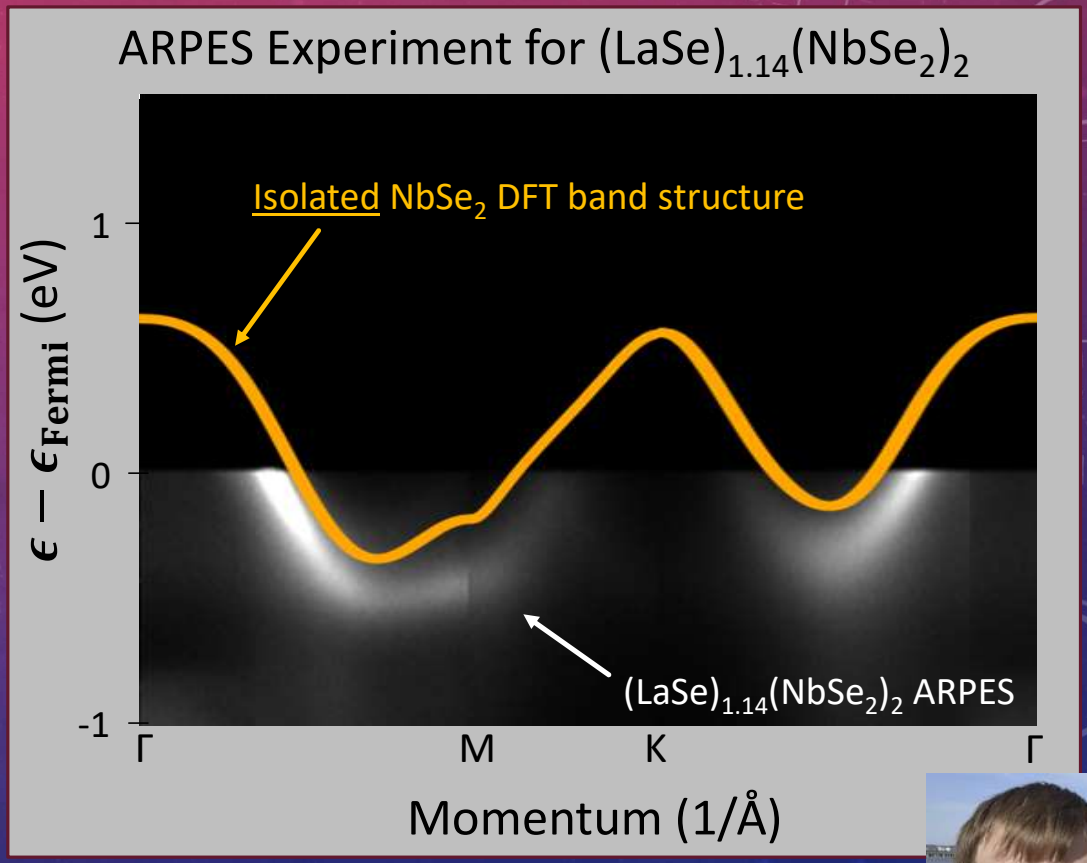




⇒ Compare to ARPES d-band shift!

ARPES CHARGE TRANSFER

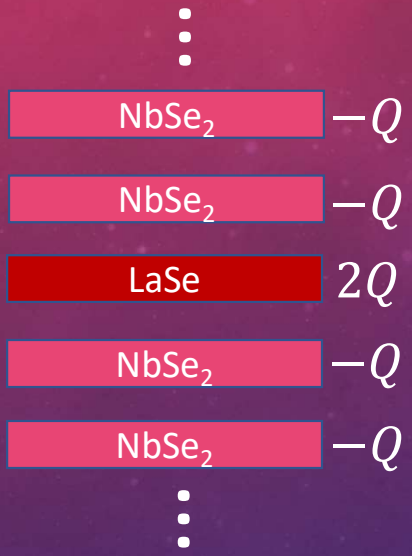
- ARPES measures filled states only
- Compute charge transfer from movement of Fermi level Nb-d band
- Luttinger Volume Analysis: ΔQ_{ARPES} = 0.51(5)e-/Nb
- *Ab initio* ΔQ_{MINT} = 0.082(6)e-/Nb << ΔQ_{ARPES} ???
- Correct MINT electronic structure?



Experimental Data from Brendan Faeth

QUANTUM CAPACITOR MODEL:

Capacitor Model



$$\Delta Q = C_{\text{quantum}} \frac{\epsilon_{F2} - \epsilon_{F1}}{e}$$

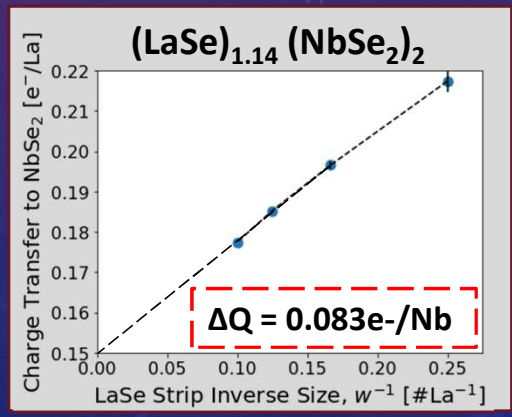
$$C_{\text{quantum}} = \left[\frac{1}{C_{\text{geom}}} + \frac{1}{g_1 e^2} + \frac{1}{g_2 e^2} \right]^{-1}$$

Ab initio data

	g (eV^{-1}/A)	ϵ_F (eV)
LaSe	0.102	-2.75
NbSe2	0.115	-5.54

$$\Rightarrow dQ = 0.064 \text{ e-/Nb}$$

From MINT:

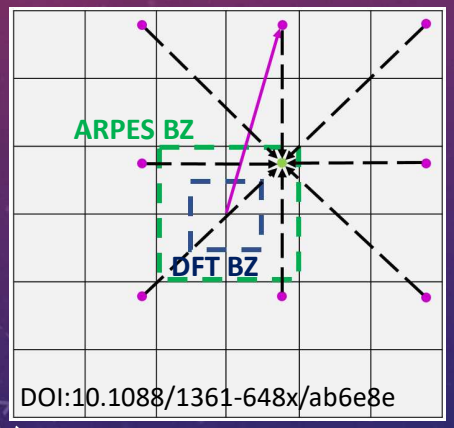


ARPES BAND-STRUCTURE WITHOUT PERIODICITY?

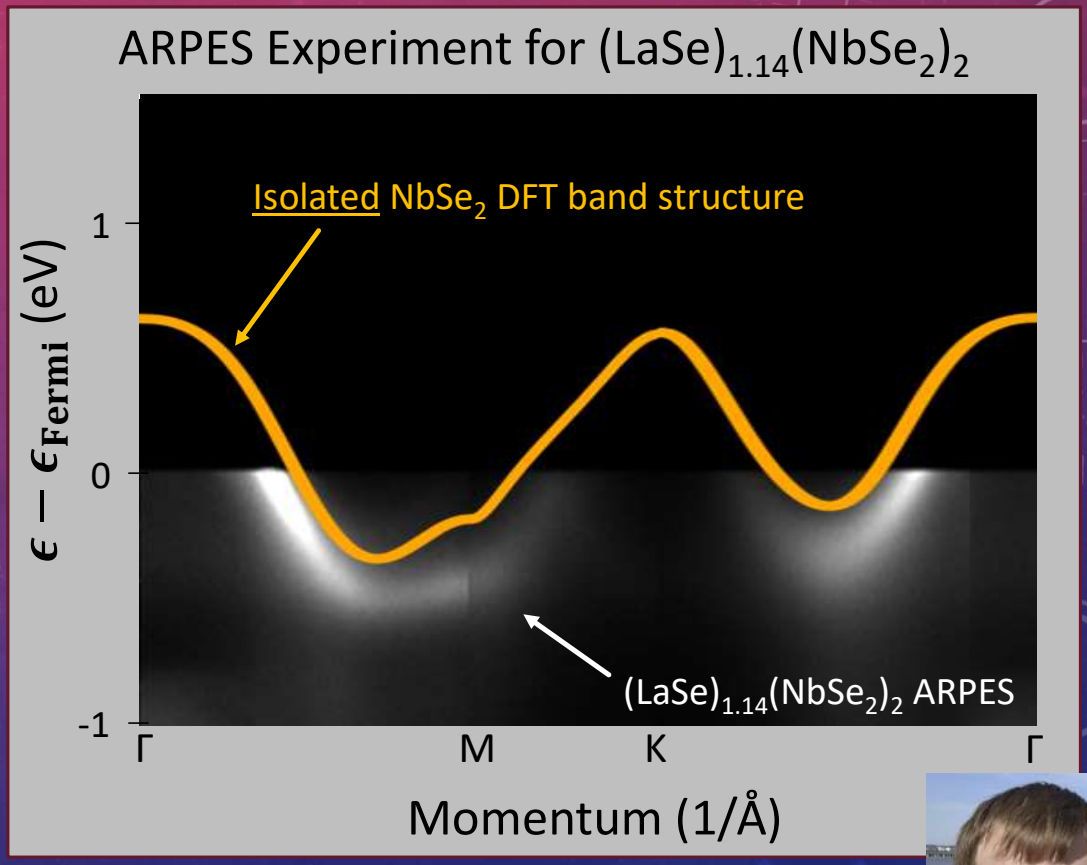
- ARPES actually measures energy-momentum distribution of e^-'s

$$n_{\mathrm{ARPES}}(\vec{q},\epsilon) = \sum_i \left|\hat{\psi}_i(\vec{q})\right|^2 \delta(\epsilon - \epsilon_i)$$

- For display, experimentalists *mapped* $\vec{q}$'s to periodicity of $NbSe_2$
- We can do the same for each member of prototype sequence:

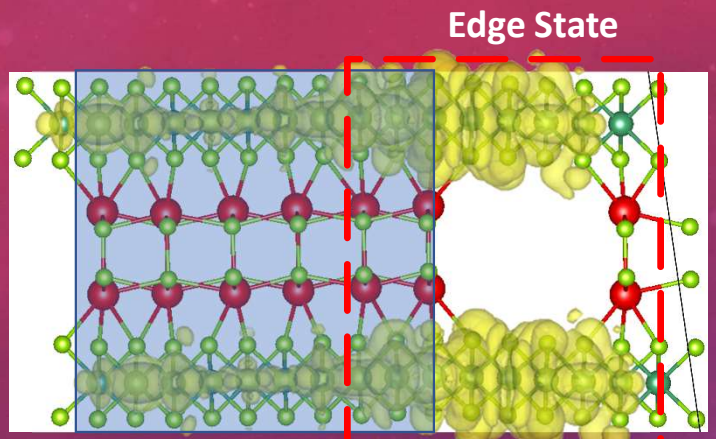


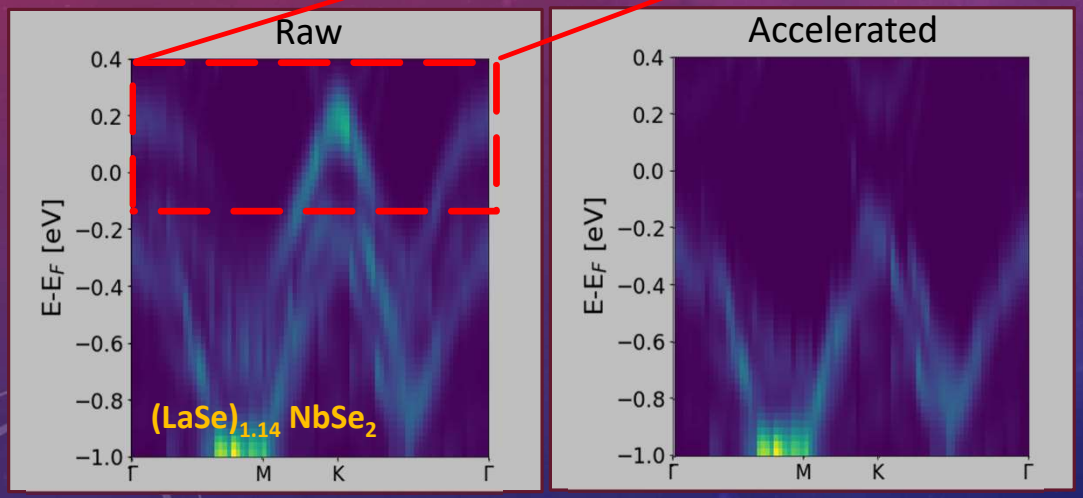
$$n_{\mathrm{final}}(\vec{k},\epsilon) = \sum_{\vec{G}\ \mathrm{NbSe_2}} n_{\mathrm{ARPES}}\left(\vec{k}+\vec{G},\epsilon\right)$$



Experimental Data from Brendan Faeth

ACCELERATING CONVERGENCE





Issue

- Appearance of ghost band
- Become negligible as prototype grows, but undesirably slowly
- Cause: vacuum regions lead to edge states

Solution

- Compute probablilty of each state in bulk region:

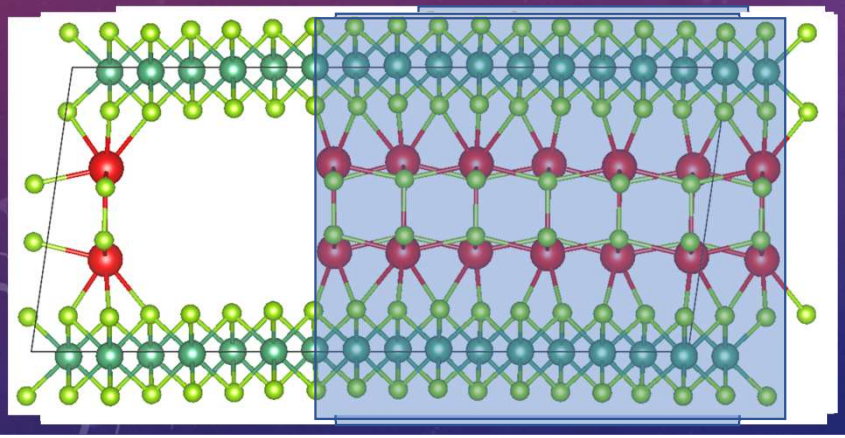
$$W_i \equiv \int_{\text{bulk}} \left|\psi_{n\vec{k}}(\vec{r})\right|^2 d^3r$$

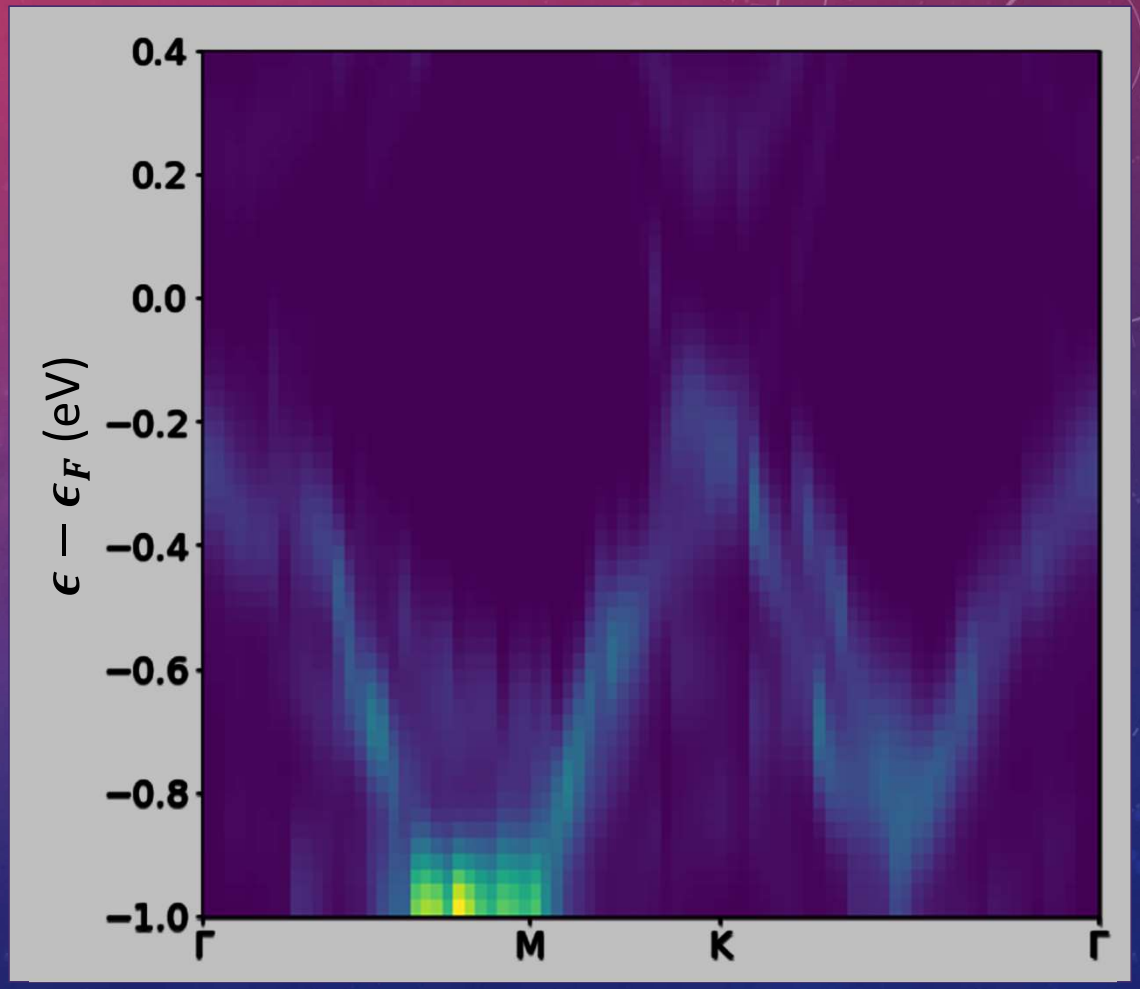
- Weigh each state accordingly:

$$n_{\text{ARPES}}(\vec{q},\epsilon) = \sum_i W_i \left|\hat{\psi}_i(\vec{q})\right|^2 \delta(\epsilon - \epsilon_i)$$

FIRST *AB INITIO* INCOMMENSURATE ARPES PREDICTIONS

Single layer material
$(LaSe)_{1.14}NbSe_2$



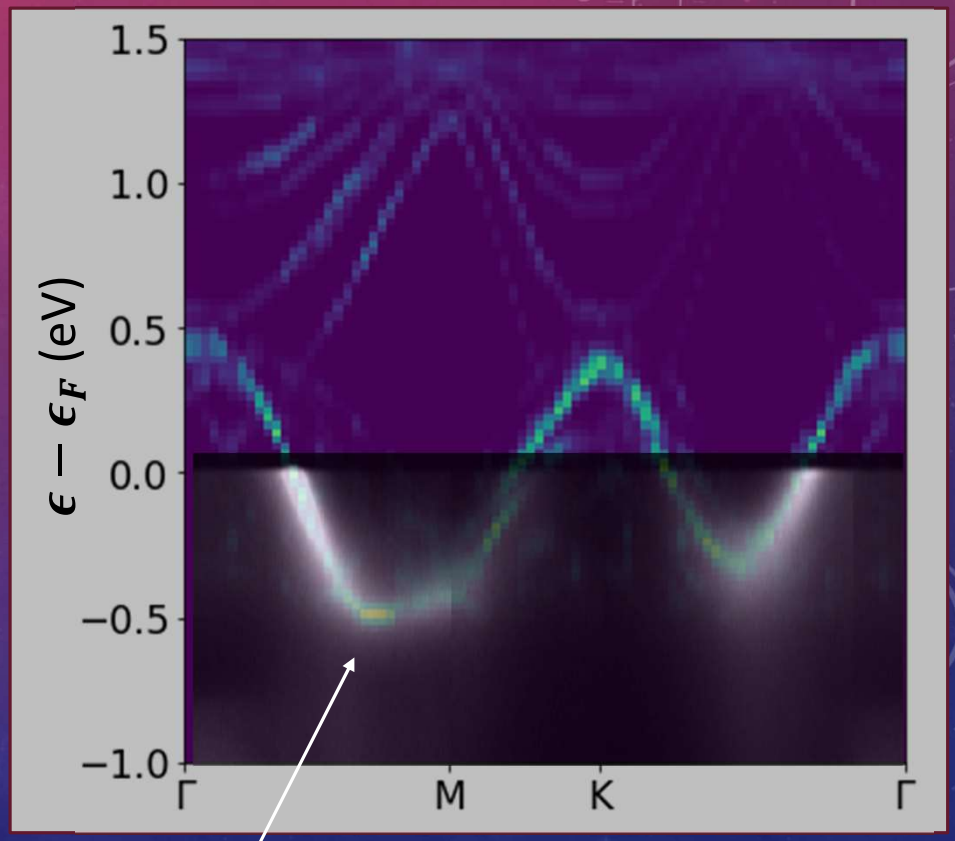


RESULT FOR DOUBLE-LAYER MATERIAL

$(LaSe)_{1.14}(NbSe_2)_2$

- **Excellent Agreement (!!!)** with ARPES measurements on $(LaSe)_{1.14}$ $(NbSe_2)_2$.
- Fully consistent with ARPES result of **0.51(5)e-/Nb** into Nb d-band
- However, our calculated interlayer charge transfer is **0.082(6)e-/Nb**
- Resolution is *pseudodoping!*

MINT Prediction

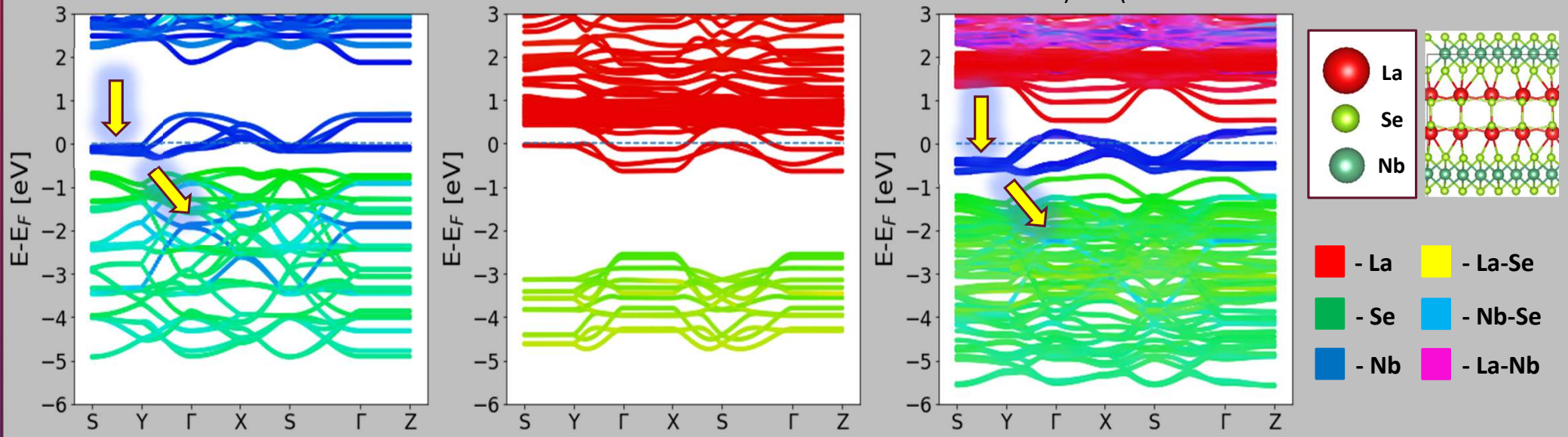


$(LaSe)_{1.14}$ $(NbSe_2)_2$ measurement overlay

PSEUDODOPING I

Orbital Projected Band Structures

Isolated $NbSe_2$ | Isolated LaSe | $(LaSe_{)1.14(}NbSe_2)_2$

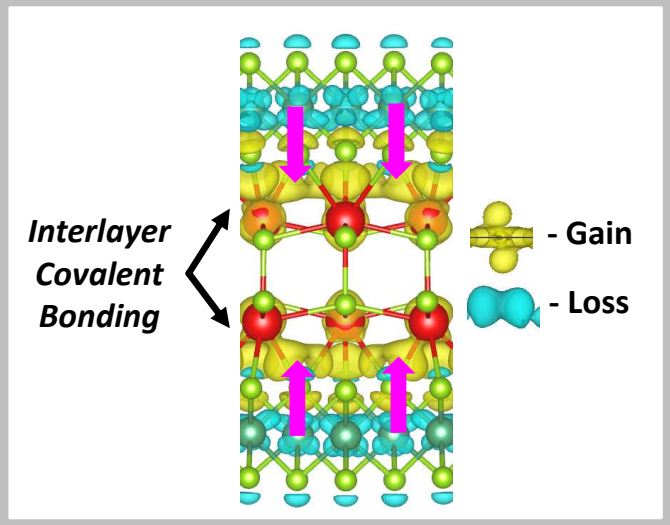


- Nb d-bands (blue) drop below ϵ_F and gain electrons ✓
- Se p-bands (green/cyan, -3 eV $< \epsilon <$ -1 eV) lose significant Nb character, Nb also loses e^-'s …

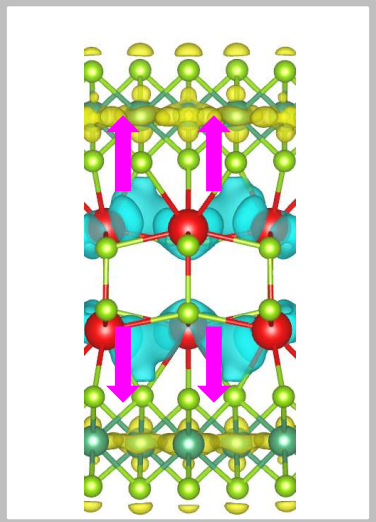
PSEUDODOPING II

Electron density changes: $\Delta n(\vec{r})$

$\Delta Q_{\text{valence}} \approx -0.4\ e^-/\text{Nb}$



$\Delta Q_{\text{Fermi}} \approx +0.5\ e^-/\text{Nb}$



- Covalent bonding shifts $\approx -0.4\ e^-/\text{Nb}$ away from valence Nb-d orbitals
- Charge imbalance nearly compensated by $\approx +0.5\ e^-/\text{Nb}$ gain in Femi-level Nb-d orbital (explains ARPES observation)
- Net gain in layer is $\approx +0.1\ e^-/\text{Nb}$ (explains MINT charge transfer)

THANK YOU!

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