*Ab initio* many-body photoemission theory of transverse momentum distributions of photoelectrons from single-crystal materials: PbTe(111) as a case study*

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Why need *ab initio* theory?

- To understand fundamental processes relevant to MTE, e.g.
  - scattering between electrons and phonons (crystal vibrations)
  - bulk & surface effects: emission of bulk & surface electrons

Outline

- Motivation for *ab initio* studies of photoemission from PbTe(111)
- *Ab initio* bulk photoemission theory including phonon effects
- Results & interpretations, comparison with our experiments
- Further improvements to theory by including surface effects
- Summary
Motivation for PbTe(111)

- Previous predictions* yield MTE ≤ 15 meV
  - Emission directly to vacuum
- Our experiments 10–20× larger and shows photoemission below threshold
  - Light penetration depth ~200 Å
    ⇒ bulk emission important?
  - Phonons can affect e⁻ momenta
    ⇒ phonon effects on MTE important?
- Need new ab initio photoemission theory including bulk emission & phonon effects

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*W. A. Schroeder, T. Li, and B. Rickman, P3 2016.
Ab initio Bulk Photoemission Theory*

More bulk e\(^-\) than surface e\(^-\)

1. **Photon** excites bulk e\(^-\)-h\(^+\) pair at rate \(\nu\)
   - Direct: photon \(\rightarrow\) e\(^-\)-h\(^+\)
   - Phonon-mediated: photon + phonon \(\rightarrow\) e\(^-\)-h\(^+\)

2. e\(^-\) in a **coherent** outgoing scattering state
   - Conservation of energy and transverse momentum gives rise to transmission probability \(t(q)\)
     - Calculate photoexcitation transition rates \(\nu\) and transmission probabilities \(t\)
     - MTE = \(\langle \frac{\hbar^2}{2m} q_{||}^2 \rangle\) weighted by \(\nu \cdot t(q)\)

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Results: Calculated MTE from PbTe(111)

- Direct only reproduces magnitude, but has higher threshold

*Bulk emission important!*

Results: Calculated MTE from PbTe(111)

- **Direct + phonon** reproduces photoemission below threshold

**Phonon effects important below threshold!**

Results: Calculated MTE from PbTe(111)

- **Direct + phonon** reproduces photoemission below threshold

With two big questions answered, smaller questions to explore:

1. Phonon effects above direct threshold significant?
2. Reason for observed MTE dip centered at 4.9 eV?

First exploration: Significance of phonon effects

- Phonon effects above direct threshold significant!

First exploration: Significance of phonon effects

- Phonon effects above direct threshold **significant!**

For PbTe(111), phonon effects on photoemission important & significant below & above direct threshold

Second exploration: MTE dip at 4.9 eV

Calculations include emission of only bulk electrons
Second exploration: MTE dip at 4.9 eV

⇒ Contributions at 0 TE likely due to emission of *surface* electrons
Second exploration: MTE dip at 4.9 eV

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⇒ Contributions at 0 TE likely due to emission of surface electrons

Need to combine bulk and surface contributions to photoemission on equal footing through a unified photoemission theory.
Why need *ab initio* theory?

- To understand fundamental processes relevant to MTE, e.g.
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  - bulk & surface effects: emission of bulk & surface electrons

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Unified Photoemission Theory: One-step Model*

Instead of treating photoexcitation and surface transmission separately ...

\[ \hbar \Omega: K \approx 0 \]

Bulk photoexcitation

Surface transmission

Surface

\[ \hbar \omega: \alpha, k_p \]

\[ b', k_f \]

\[ b, -k \]
Unified Photoemission Theory: One-step Model*

... treat them both *simultaneously* in a single step

- Requires expressing electronic states in *full* space
  = material half-space + vacuum half-space
  - Bulk, surface, vacuum states on equal footing
- **Challenge**: non-periodic boundaries in surface normal direction

New *ab initio* one-step photoemission theory

- Developed new technique combining electron Green’s function approach with plane-wave DFT to handle non-periodic boundaries
- Currently implementing direct photoemission; will implement phonon-mediated photoemission
  - Then, apply to PbTe(111) and others e.g. Cs-Sb, Cs-GaAs, etc.
- Ultimately, plan to study photoemission from e.g. *photocathodes coated with 2D materials* (talks in Session A yesterday)
Summary

- Ab initio many-body photoemission theory for predicting MTE
- Case study on single-crystal PbTe(111):
  - Calculated MTEs same/similar magnitude as observed MTEs
  - Phonon effects important & significant
  - Surface emission seems significant at higher photon energies
    ⇒ Need to include bulk and surface contributions on equal footing

Developing new ab initio one-step photoemission theory to include bulk and surface emissions in a unified framework
- Plan to study photocathodes coated with 2D materials

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