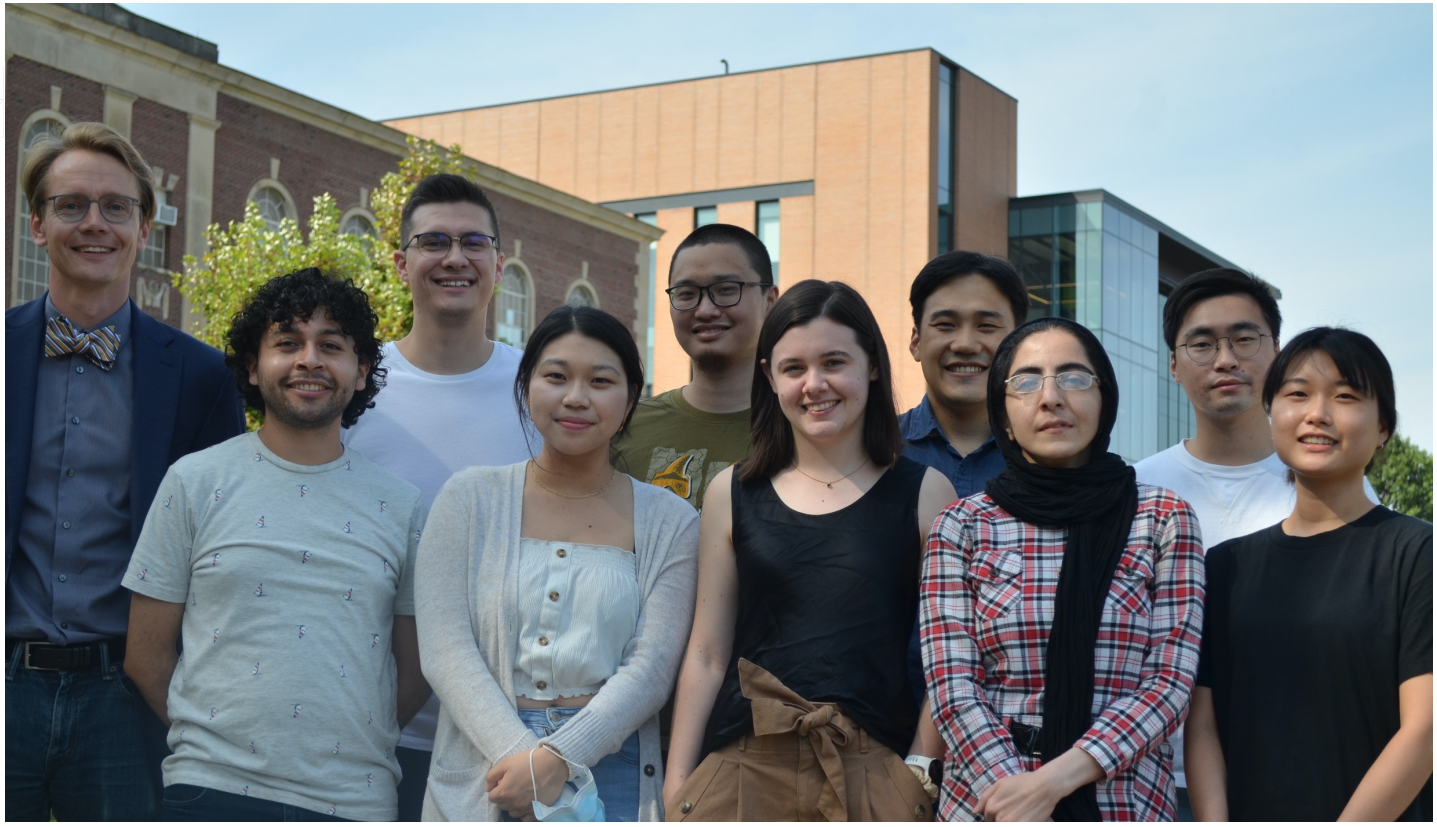
Theoretical spectroscopy of semiconductors from first principles

André Schleife

Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign

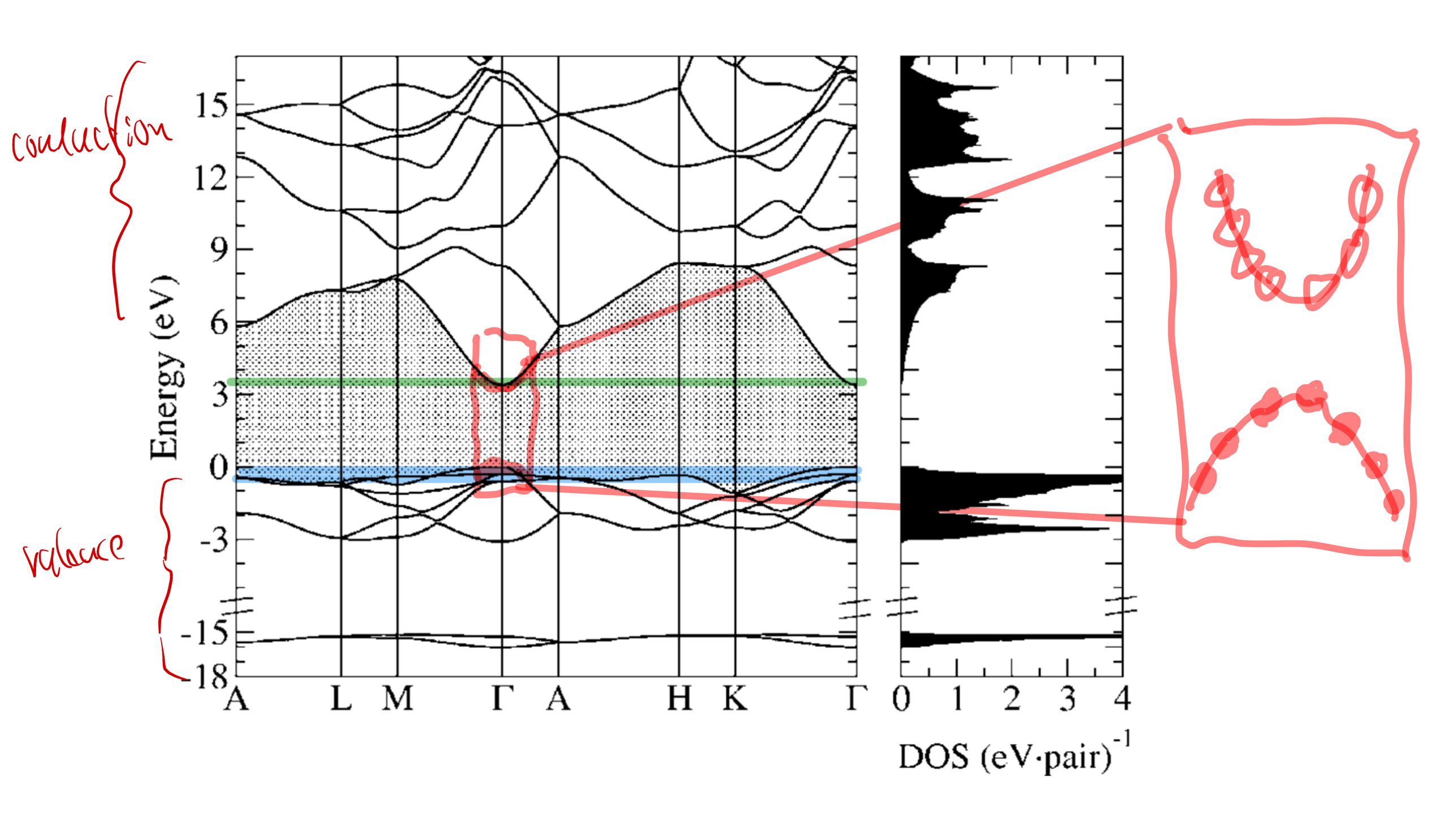
Mercator Fellow, SFB1242

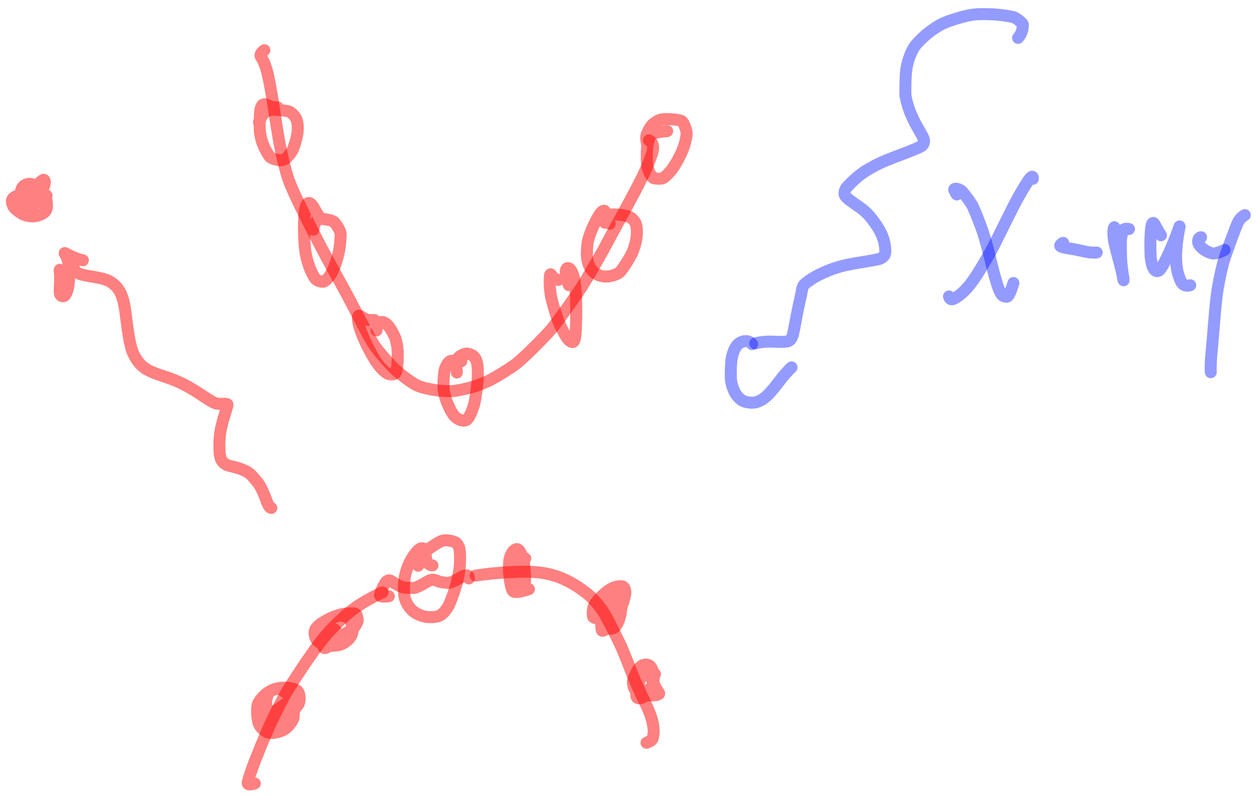
ASESMA 2023, Kigali, Rwanda, Jun 19, 2023



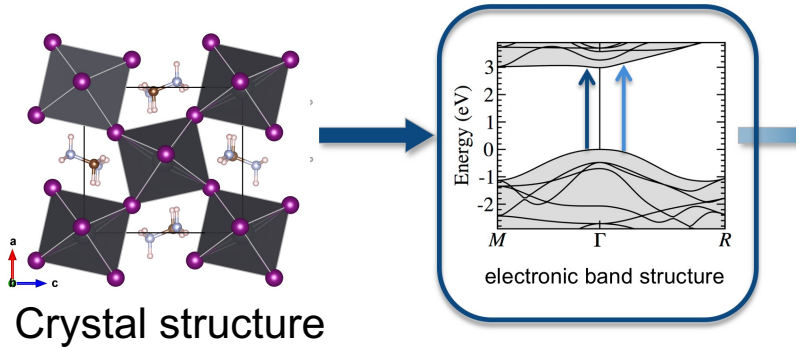
Schleife Group

Department of Materials Science and Engineering

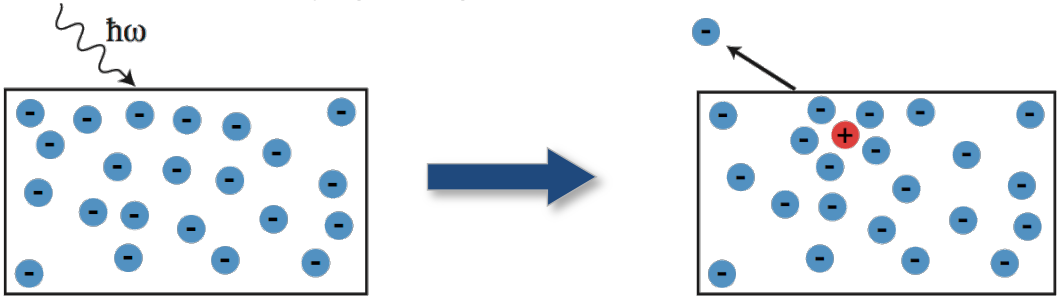

conduction
valence
Energy (eV)
15
12
9
6
3
0
-3
-15
-18
A
L
M
Γ
A
H
K
Γ
0
1
2
3
4
DOS (eV·pair)$^{-1}$


X-ray
XPS

How to predict single-particle excitations?



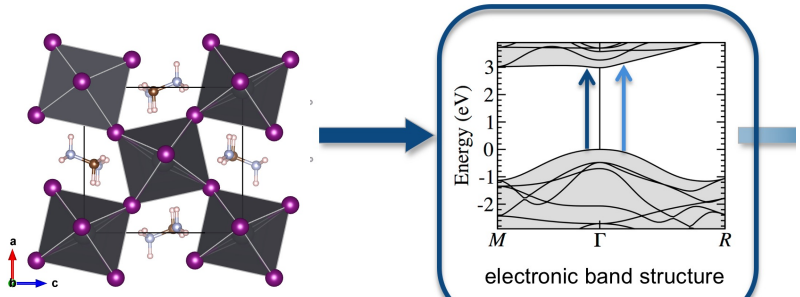
- Photoemission spectroscopy (PES)



- Removal (PES) or addition (inverse PES) of an electron
- Important: Reaction of the electrons of the system

- approximation of the electronic self energy: $\Sigma = GW$ $\quad W = v\epsilon^{-1}$
- quasiparticle energies from one step of perturbation theory
- HSE hybrid functional: non-local treatment of exchange and correlation

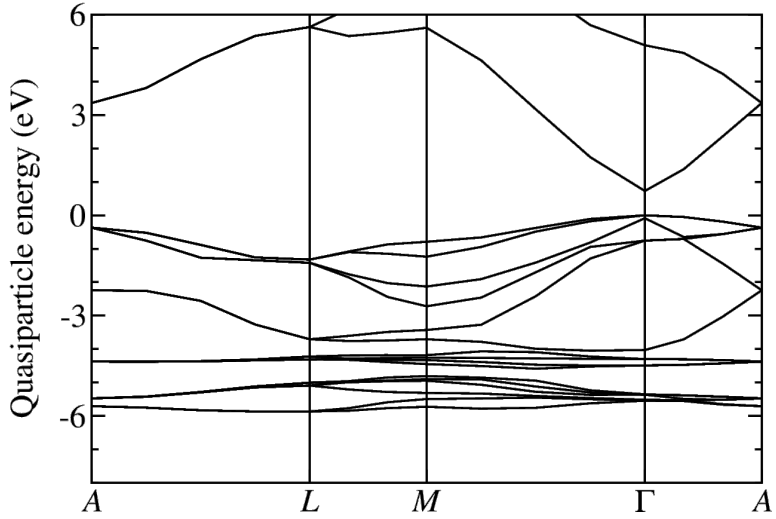
How to predict single-particle excitations?



Crystal structure

- Photoemission spectroscopy (PES)

wurtzite ZnO: local-density approximation



- Local-density approximation insufficient for electronic properties

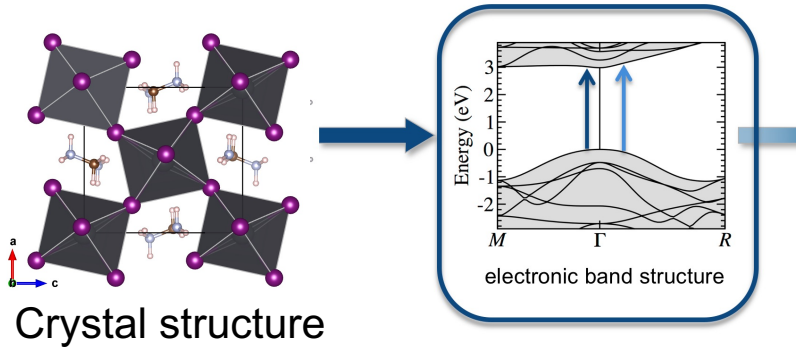
← band gap too small

E_g^{LDA}=0.7 eV

E_g^{exp}=3.4 eV

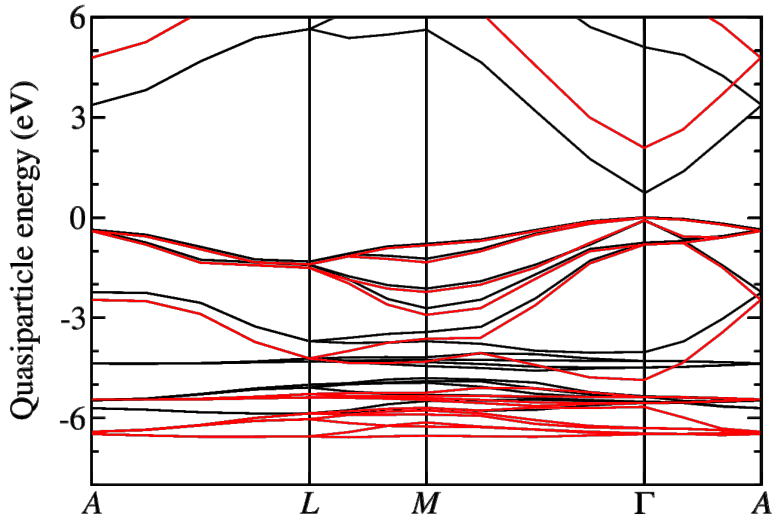
← *d*-bands too high

How to predict single-particle excitations?



- Photoemission spectroscopy (PES)

wurtzite ZnO: HSE hybrid functional



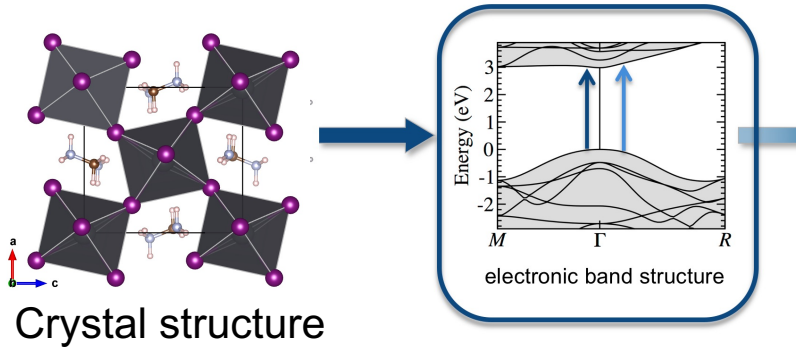
band gap improved

E_g^{HSE}=2.1 eV

E_g^{exp}=3.4 eV

d-bands improved

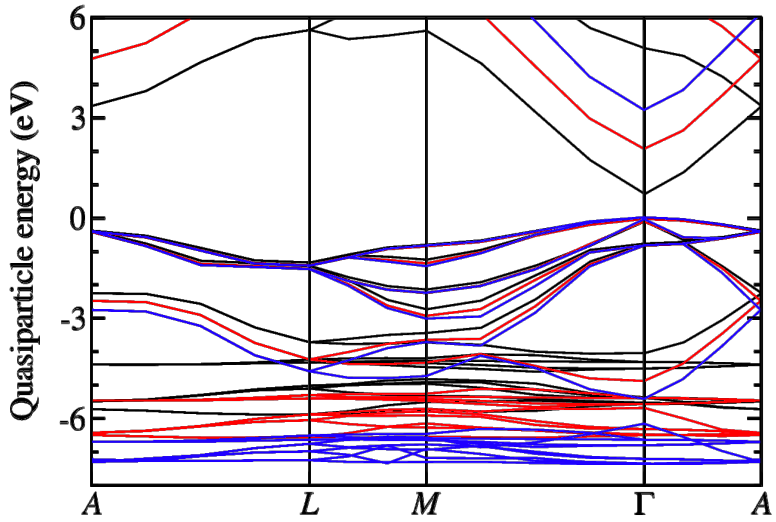
How to predict single-particle excitations?



Crystal structure

- Photoemission spectroscopy (PES)

wurtzite ZnO: hybrid functional and quasiparticle effects

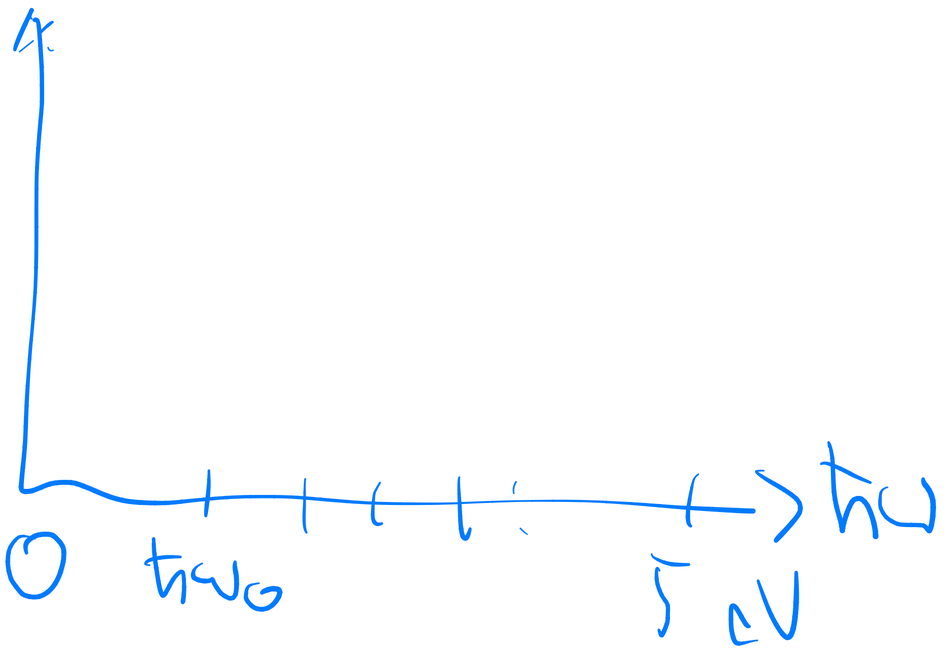


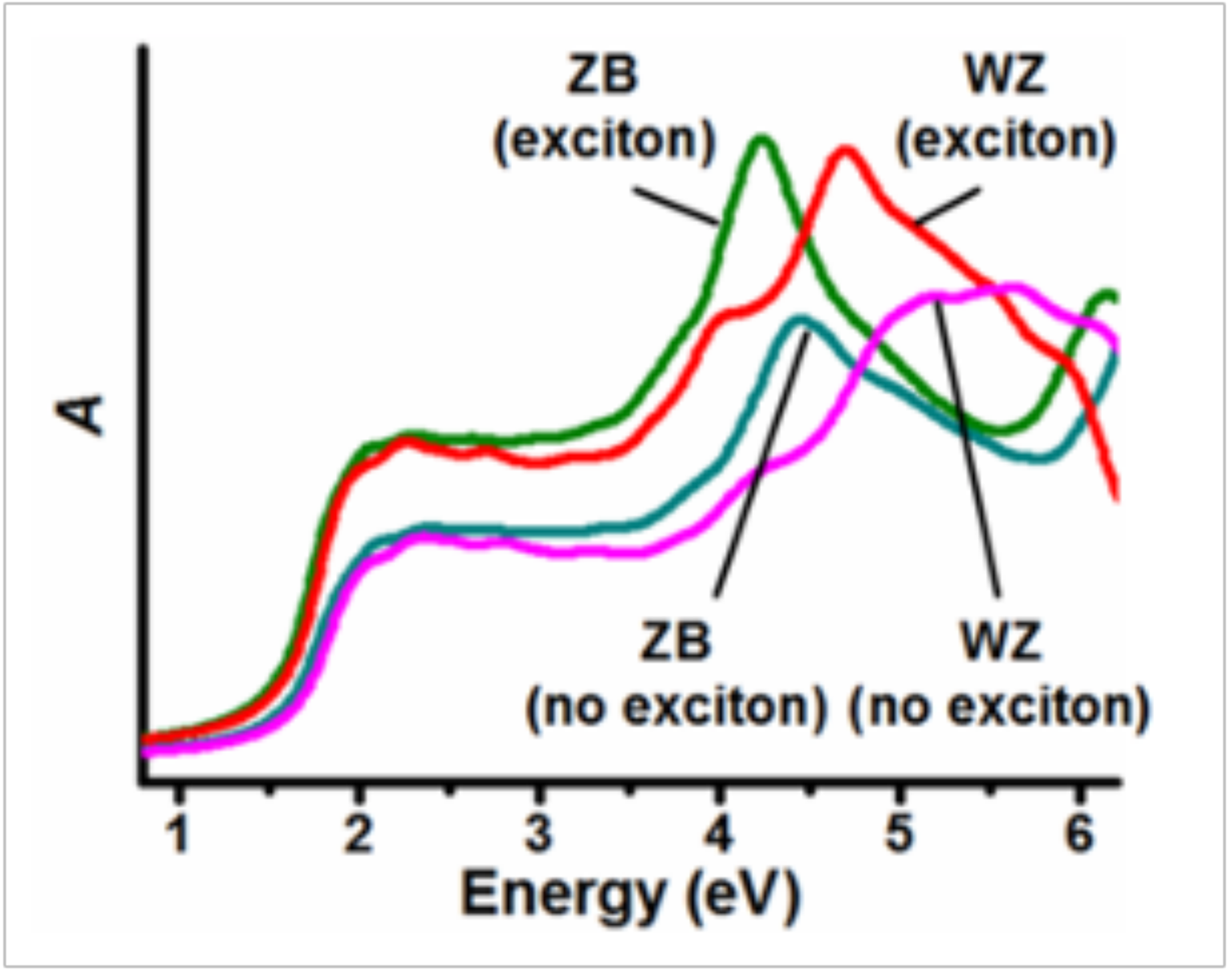
E_g^{HSE+GW}=3.2 eV

E_g^{exp}=3.4 eV

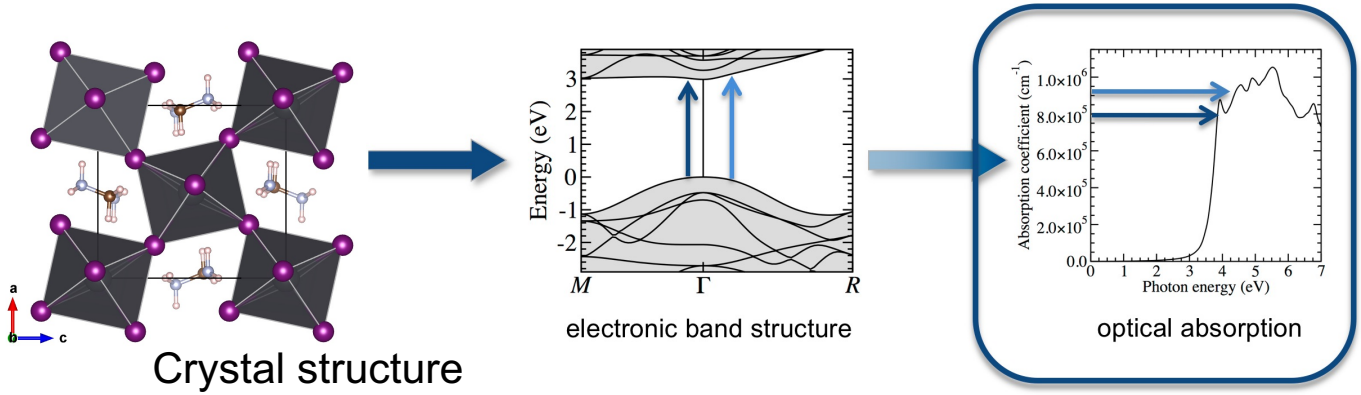
optical spectroscopy

optical absorption




ZB
(exciton)
WZ
(exciton)
A
ZB
(no exciton)
WZ
(no exciton)
1
2
3
4
5
6
Energy (eV)

How to predict two-particle excitations?



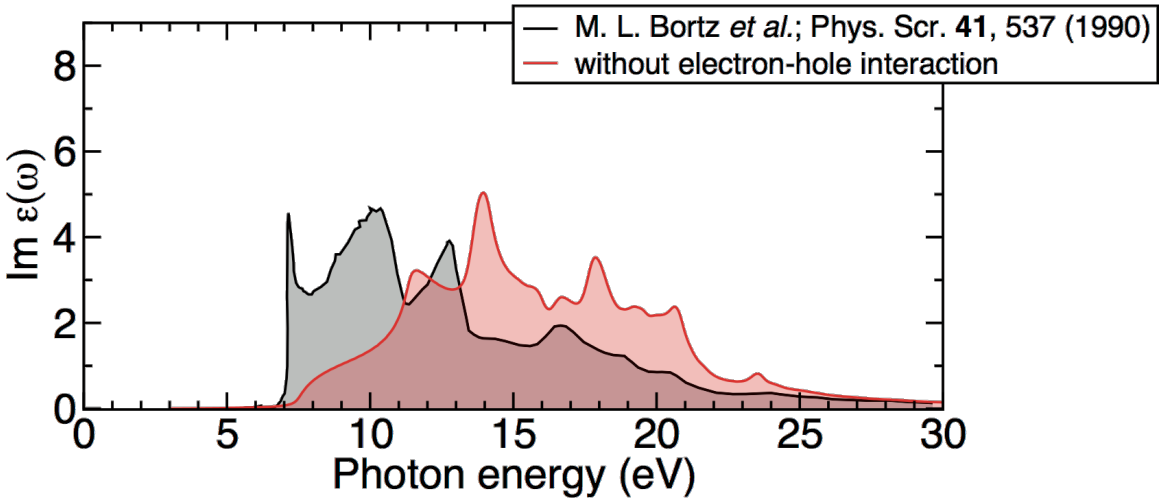
Crystal structure

electronic band structure

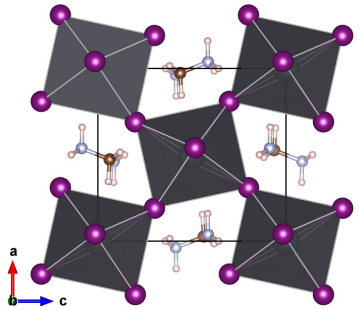
optical absorption

- Optical absorption/Ellipsometry:
- Electron-hole interaction ignored

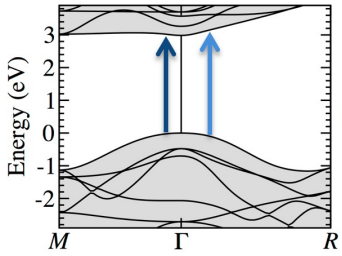
MgO:



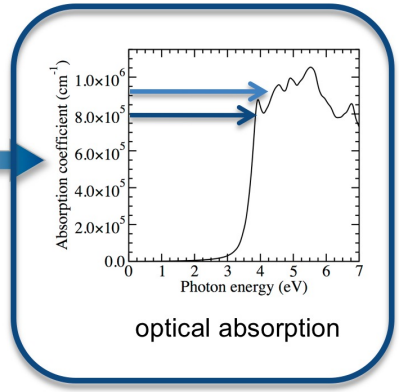
How to predict two-particle excitations?



Crystal structure

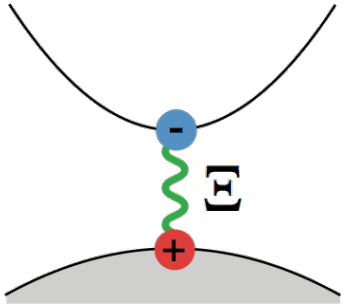


electronic band structure

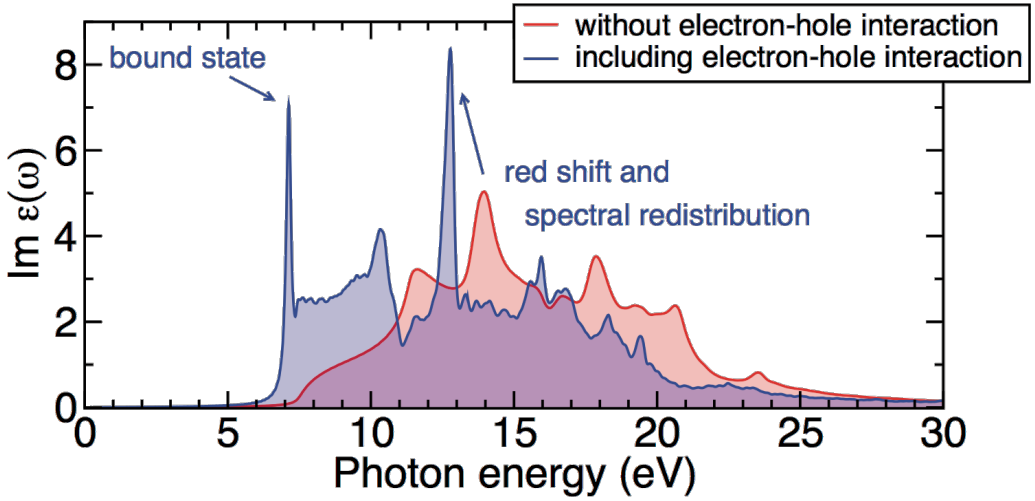


optical absorption

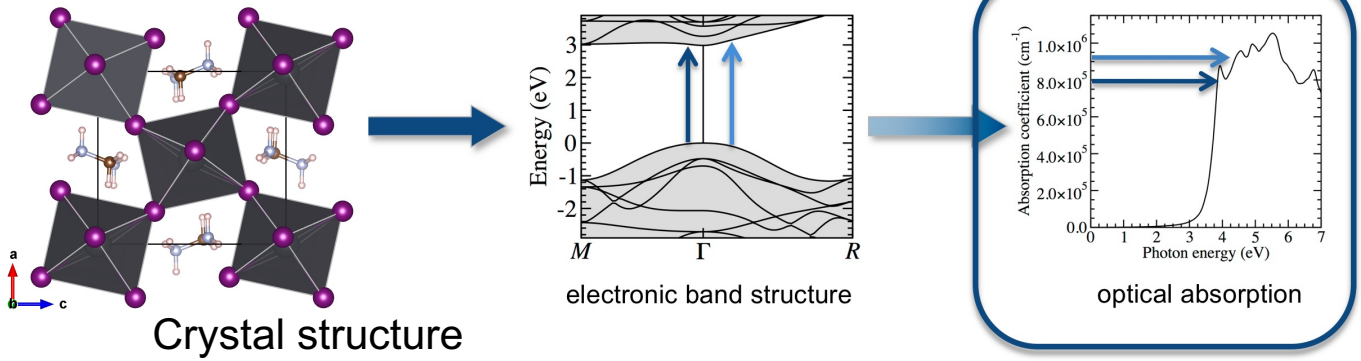
- Optical absorption/Ellipsometry:
- Bethe-Salpeter equation for optical polarization function
  - Electron-hole interaction: Ξ



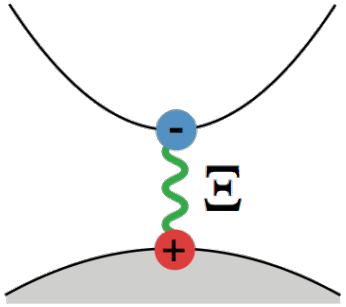
MgO:



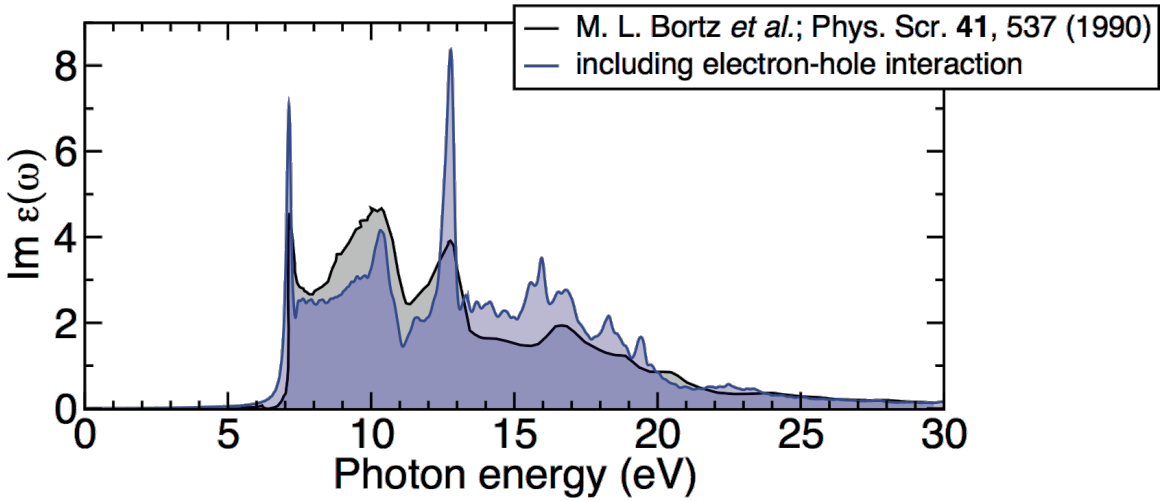
How to predict two-particle excitations?



- Optical absorption/Ellipsometry:
- Bethe-Salpeter equation for optical polarization function
  - Electron-hole interaction: Ξ

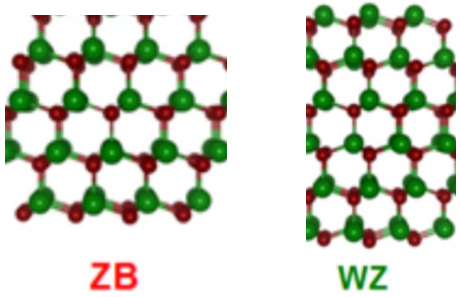


MgO:

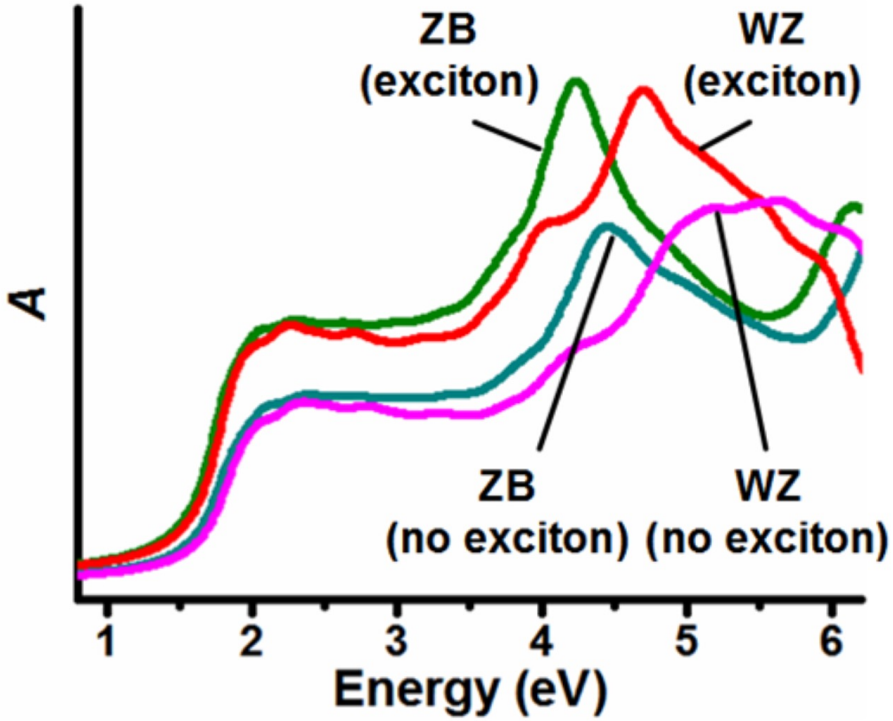


Connecting structural and optical properties

CdSe →



Bulk zinc-blende and wurtzite CdSe: Excitonic effects small



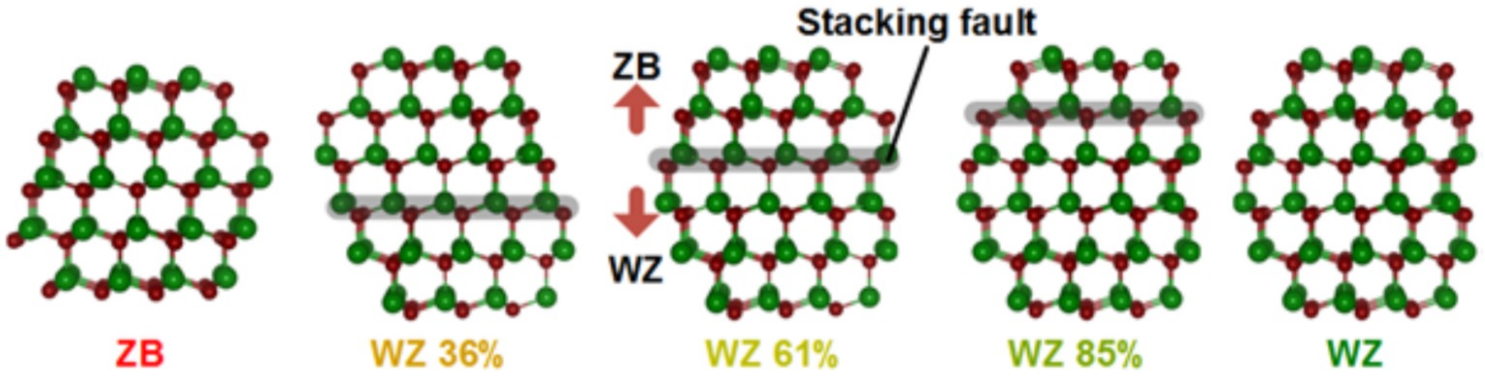
- Red shift of peaks still present, but excitonic effects similar in wz and zb
- Electronic screening much larger (static electronic dielectric constant: 14)

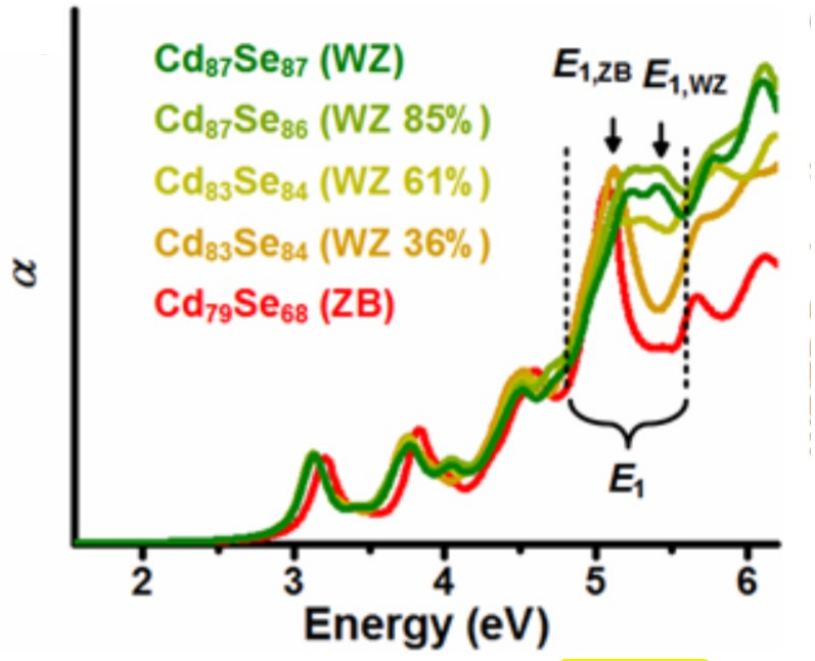
- Found that this allows to distinguish phase (zb vs. wz) spectroscopically

Lim, Schleife, Smith, Nat. Comm. **8**, 14849 (2017)

Connecting structural and optical properties

Nanocrystals: zinc-blende vs. wurtzite



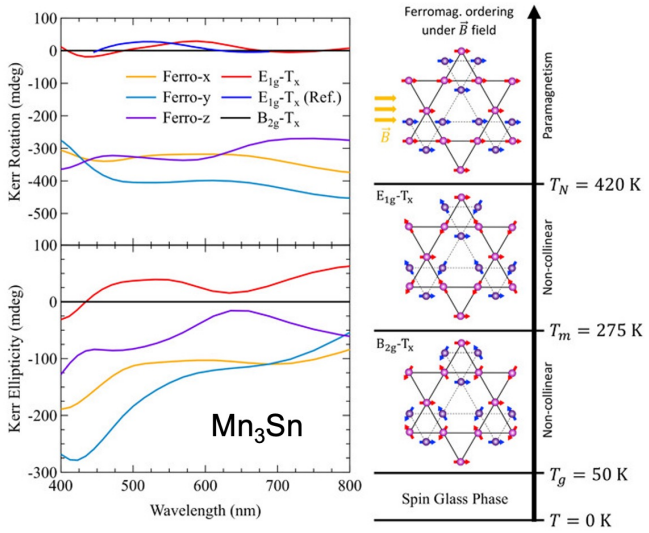


- Difficult around band gap
- Much easier around the E_1 peaks
- Also correlates very well with wz/zb ratio
- Spectral/optical distinction is amenable to high-throughout experimentation

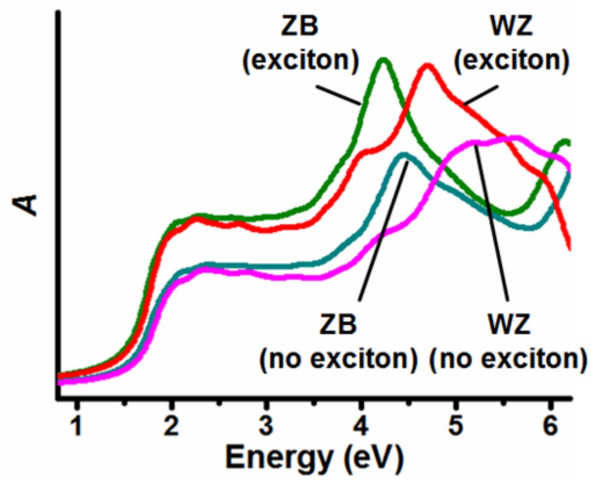
Lim, Schleife, Smith, Nat. Comm. **8**, 14849 (2017)

My group: Overview

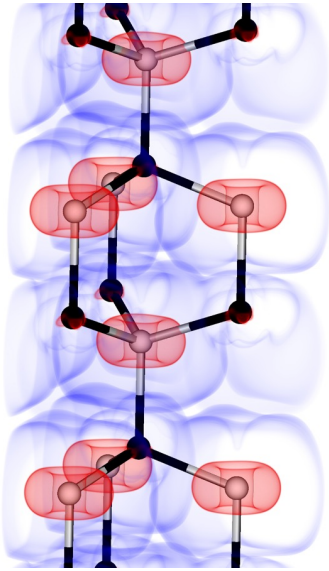
Electronics, Optoelectronics, Spintronics (Magneto-Optical spectra, Pump-probe spectra, Nanocrystals, Disorder via Alloys or Temperature)



S. Siddiqui *et al.*, J. Appl. Phys. **128**, 040904 (2020)



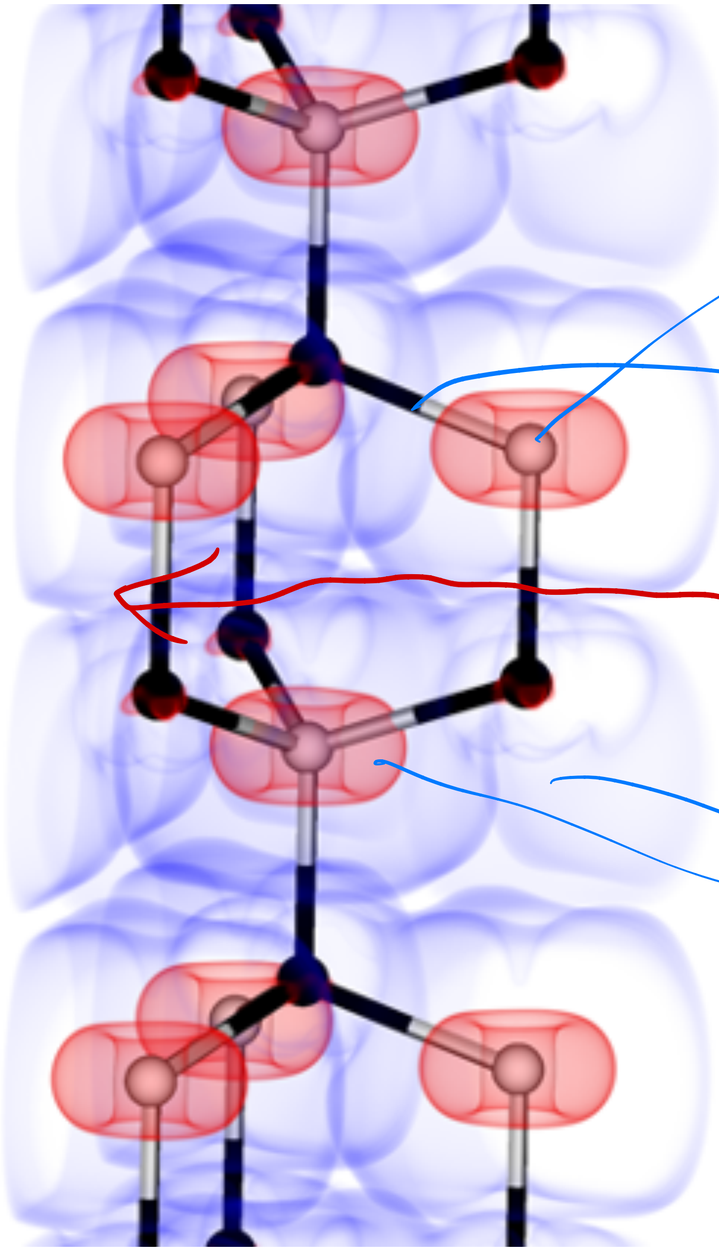
CdSe

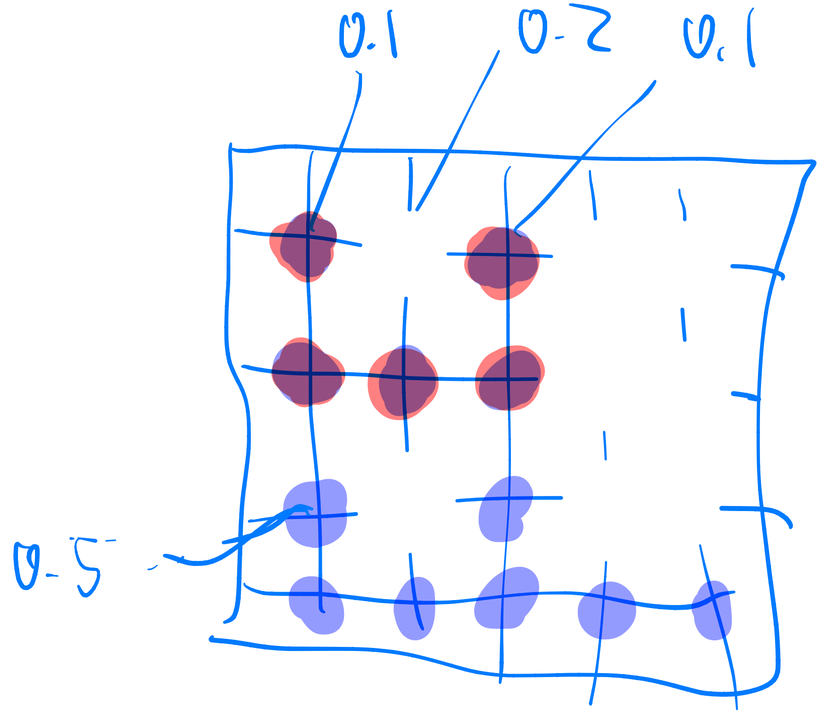


(Crystal-)structure identification

Computational Methods

- First-principles theoretical spectroscopy (RT-TDDFT, GW+BSE)
- Non-equilibrium dynamics (Boltzmann transport equation)
- Data-driven materials discovery/selection, Machine learning
- Magnetic structure, magneto-optics, magnons
- Cluster expansion, Frozen-phonon approximation

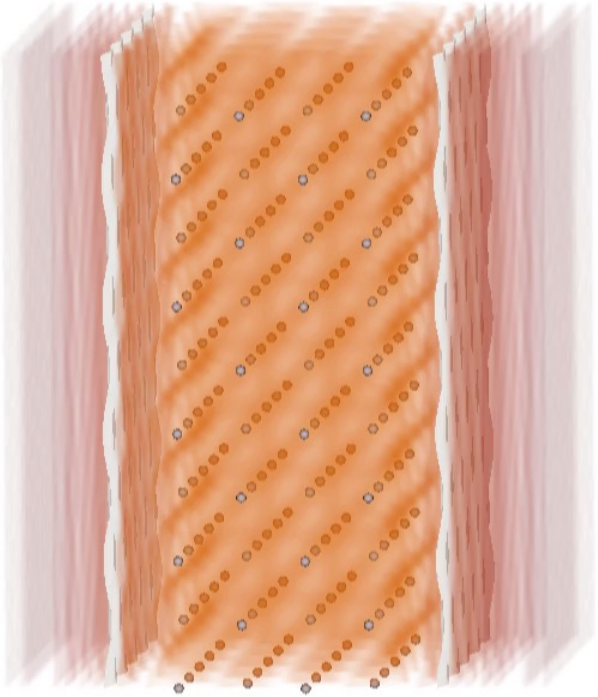




$$n(r) = n(x, y, z)$$

$n(x, y, z, t)$ $E(t)$

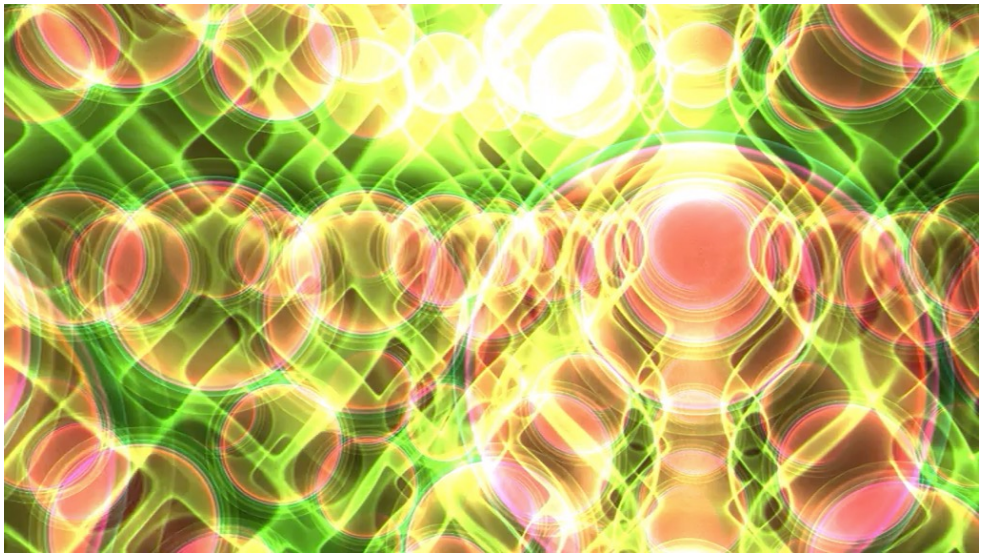
Excited electrons: Time dependence



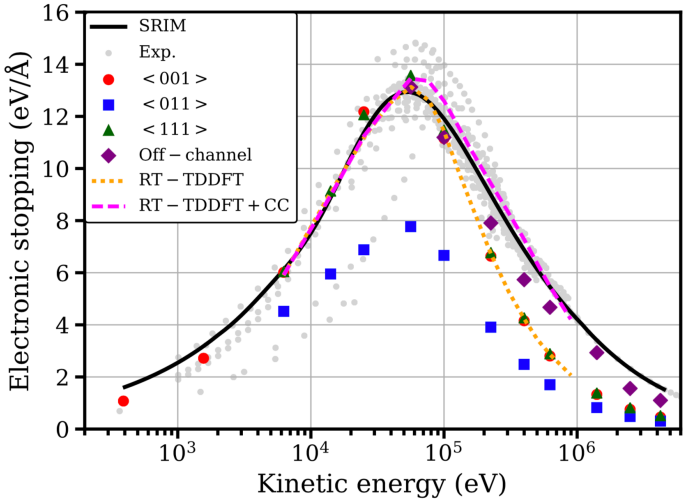
- Interesting physics: Non-adiabatic electron-ion dynamics
- Exciting applications: Materials modification, Ion implantation for Qbits

My group: Overview

Extreme Environments (radiation damage/electronic stopping, dynamical projectile charge state, secondary electron emission)



Proton-irradiated MgO



C. Lee, J. A. Stewart, R. Dingreville, S. M. Foiles, and A. Schleife, Phys. Rev. B **102**, 024107 (2020)

Computational Methods

- First-principles theoretical spectroscopy (RT-TDDFT, GW+BSE)
- Data-driven materials discovery/selection, Machine learning

Defect Excitations: Real-time TDDFT

Time-dependent Kohn-Sham equations:

$$\mathrm{i}\hbar\frac{\partial\varphi_i(t)}{\partial t} = \hat{H}[n]\varphi_i(t) = \left[\hat{T} + v_{\mathrm{ext}}(\mathbf{r},t) + v_{\mathrm{H}}[n](\mathbf{r}) + v_{\mathrm{XC}}[n](\mathbf{r})\right]\varphi_i(t)$$

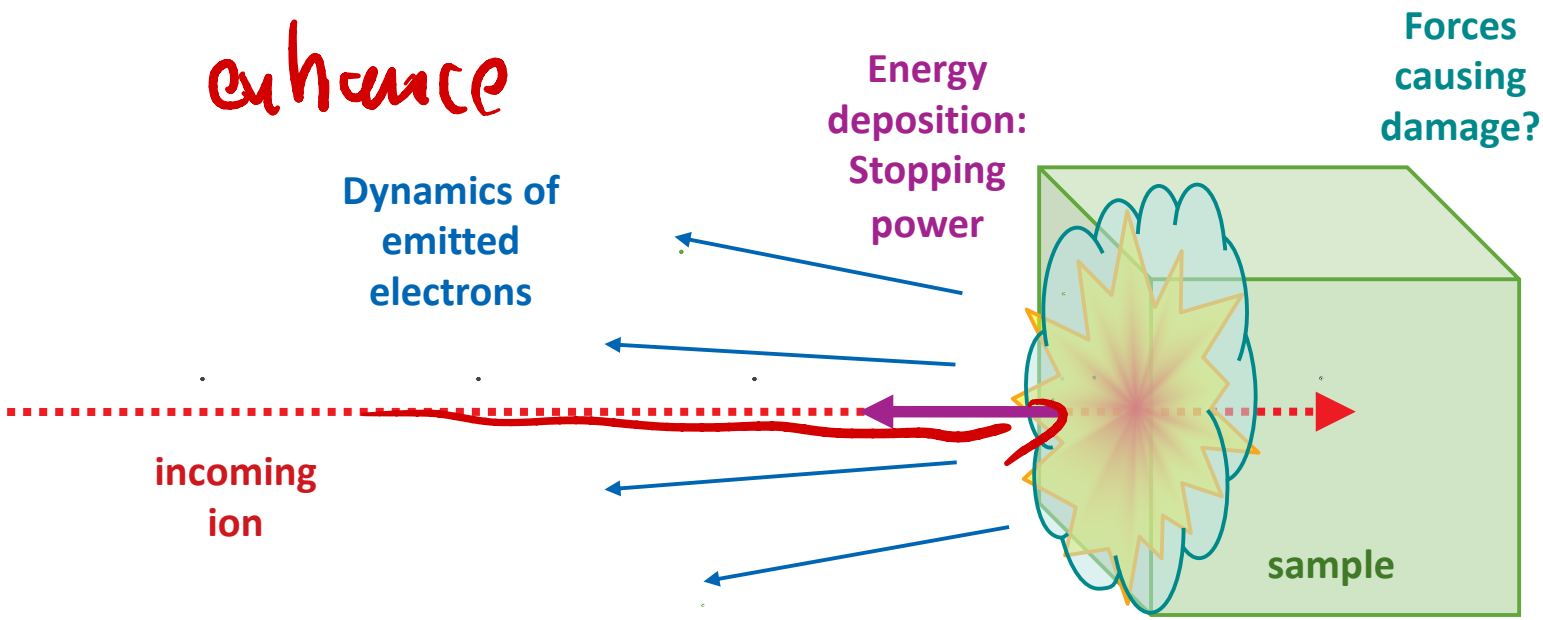
- Periodic systems: Plane-wave expansion of wave functions: $\psi_i(\mathbf{r},t) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{G}} C_i(\mathbf{G},t)e^{\mathrm{i}\mathbf{G}\cdot\mathbf{r}}$
- Electron-ion interaction: Norm-conserving pseudopotentials
- Exchange-correlation: Time-dependent local-density approximation
- Enforced Time-Reversal Symmetry (ETRS) Method

- Computationally challenging: Highly parallel implementation
- Excellent strong scaling: Qbox/Qb@ll code

- Compute forces at each time step and update positions of the atoms

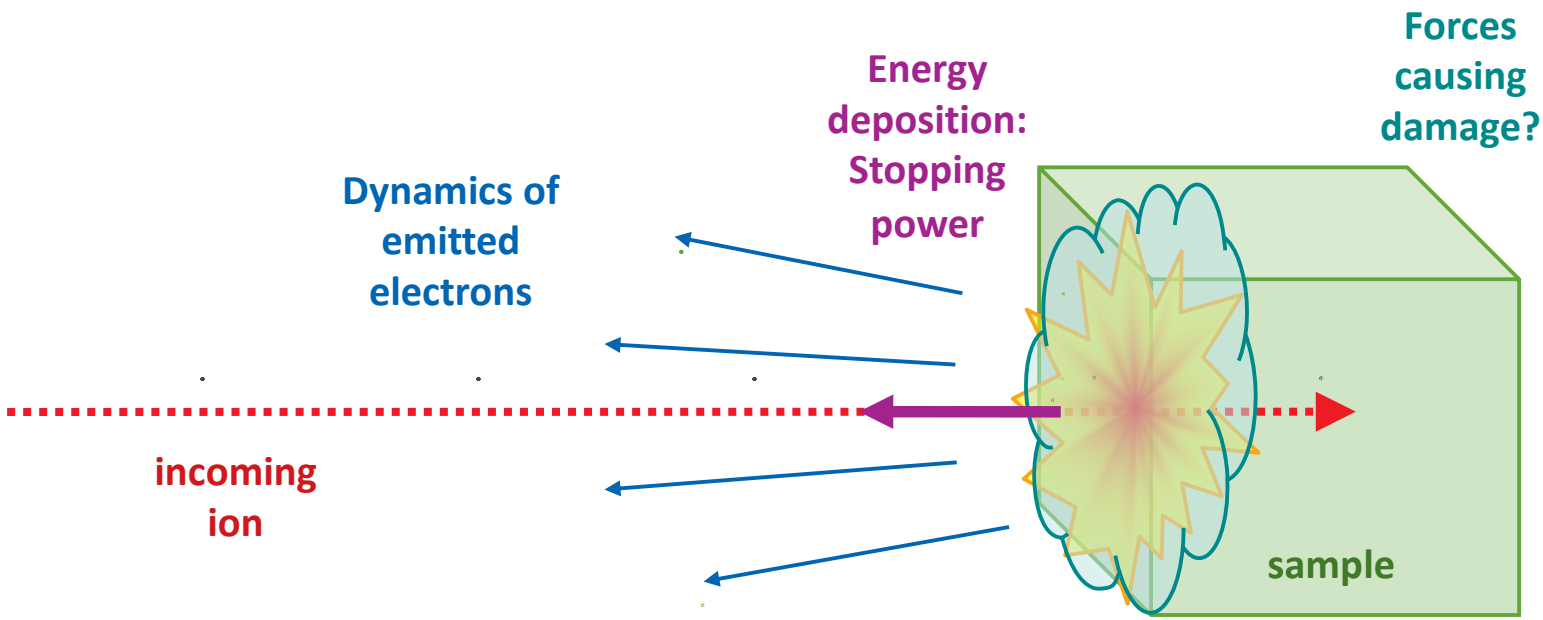
→ Ehrenfest molecular dynamics

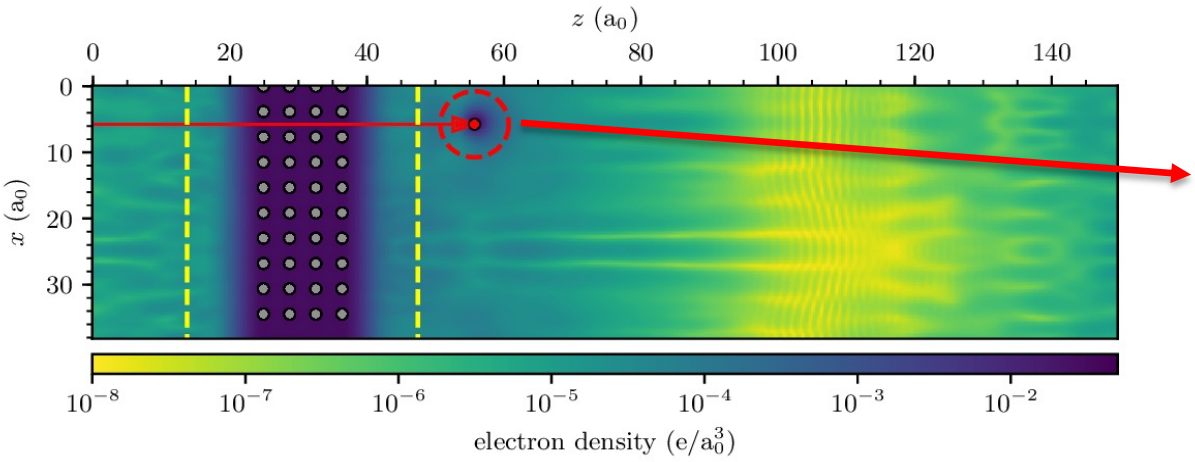
Excitations in 2D Materials: Simulation setup

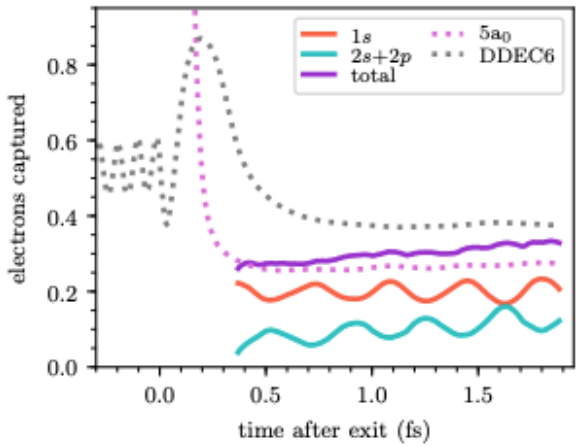


Kononov, Schleife; PRB **102**, 165401 (2020)

Excitations in 2D Materials: Simulation setup



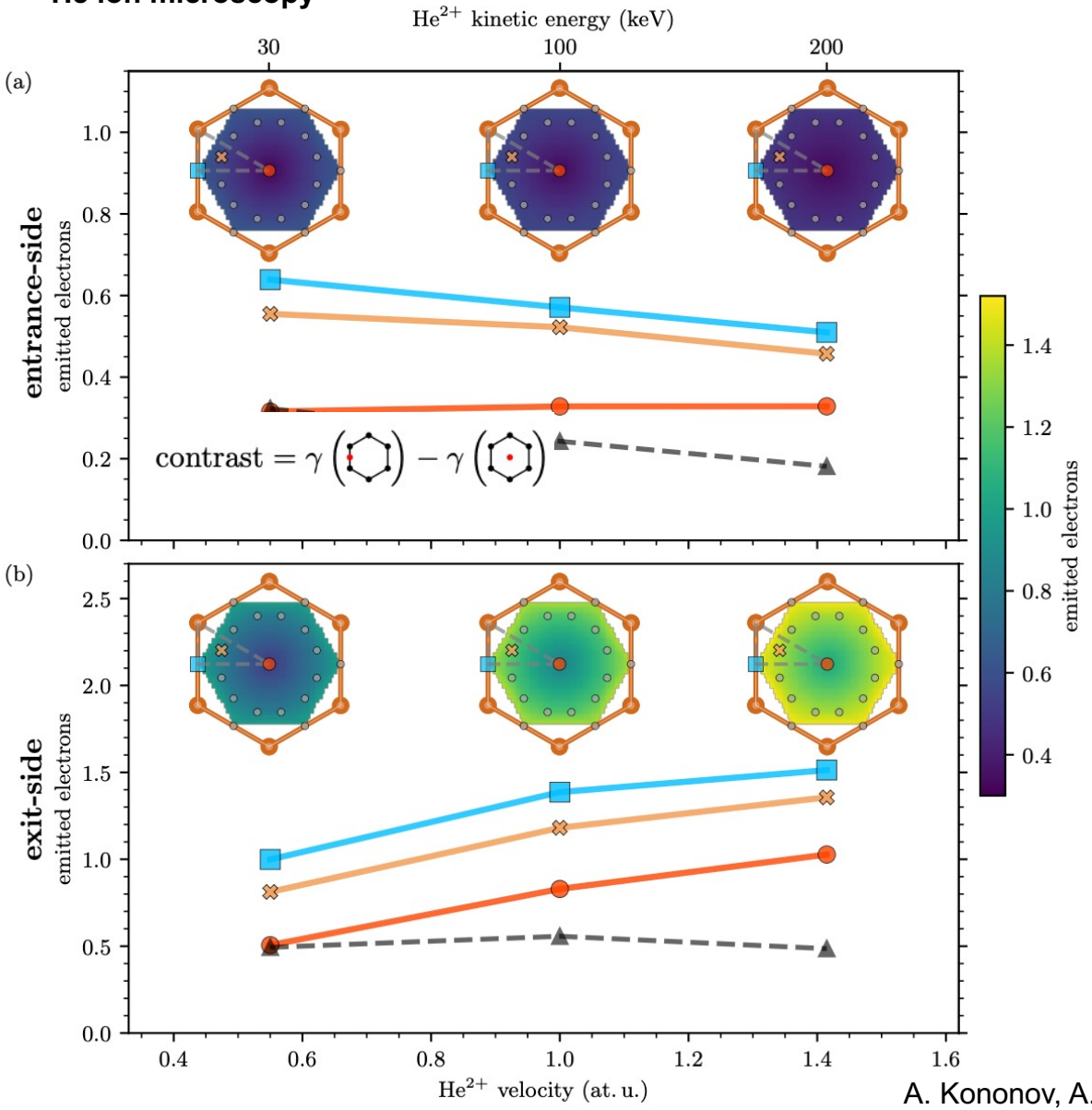




Kononov, Schleife; PRB **102**, 165401 (2020)

Excitations in 2D Materials: Protons in Graphene

He ion microscopy



- emitted-electron yield

$$\gamma_j(\mathbf{x}) = \lim_{t\to\infty} \int_{V_j} n_{\mathbf{x}}(\mathbf{r}, t)\, dr^3$$

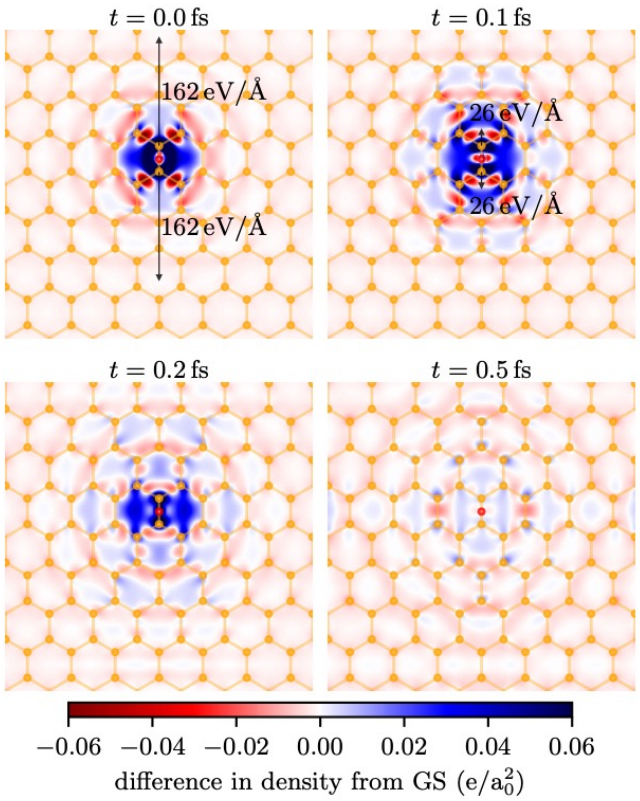
- exit-side electron emission produces higher contrast than entrace side
- beam energies of 50 – 100 keV achieve maximal contrast (exit-side)
- more energetic ions deposit less energy into the nuclear subsystem (less damage)
- stronger exit-side electron emission could allow lower ion doses (less damage)

A. Kononov, A. Olmstead *et al.*, 2D Materials **9**, 045023 (2022)

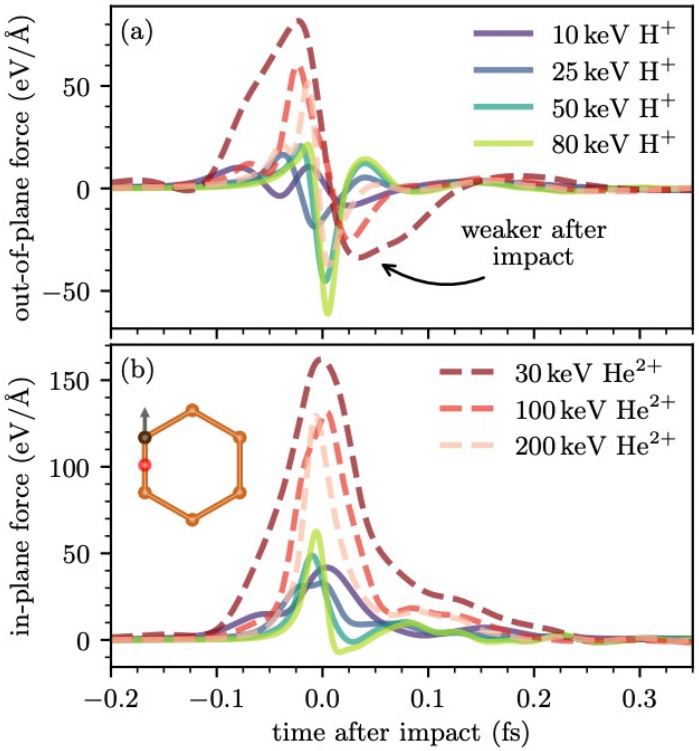
Excitations in 2D Materials: Protons in Graphene

Excited-State Forces

He^{2+} (30 keV)



- Charge dissipates on fs timescale
- Not localized long enough for defect creation



- Large forces only for few fs
- Energy transfer less than 0.01 eV
- Too small to overcome formation energy of defects, but bond deformation possible

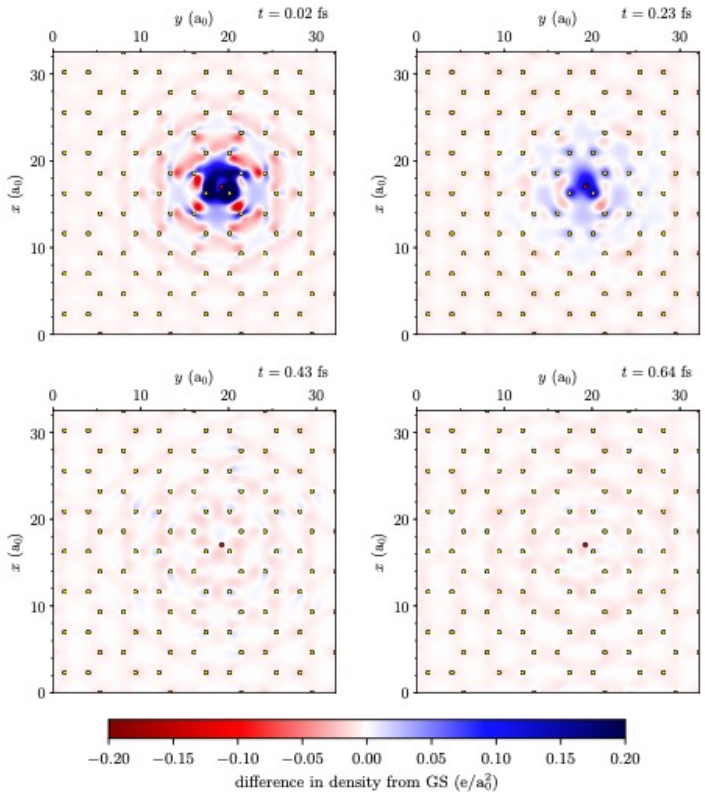
A. Kononov, A. Olmstead *et al.*, 2D Materials **9**, 045023 (2022)

Excitations in 2D Materials: Protons in Graphene

Excited-State Forces

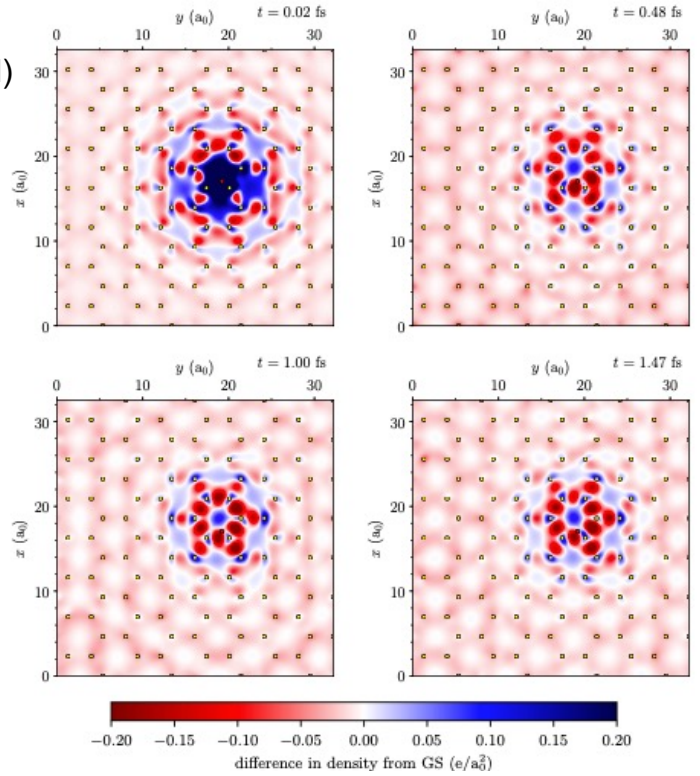
Si^{4+}:

(centroid)

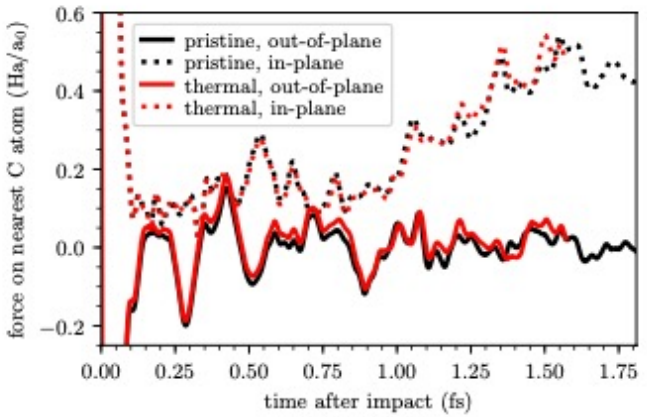


Si^{12+}:

(centroid)



- Excitation depends on charge of the projectile
- Finite size effects (in plane) unclear
- No significant (net) out of plane force in excited state (Si^{12+}, centroid)



Acknowledgments

- **Alina Kononov**
- **Cheng-Wei Lee**
- **Alexandra Olmstead**
- Xavier Andrade
- Emil Constantinescu
- Alfredo Correa

SNL grant
1736375

N00014-18-1-2605

OAC 17-40219
DMR-1555153

OCI-0725070
ACI-1238993

DOE INCITE:
DE-AC02-06CH11357

Advertisement

- **Please fill out form (name, e-mail, level of study, research interests)**
- Postdoc? Email your CV: pmartin9@illinois.edu
- Any other question: schleife@Illinois.edu

DMR-2326558

I-MRSEC

DMR-1720633