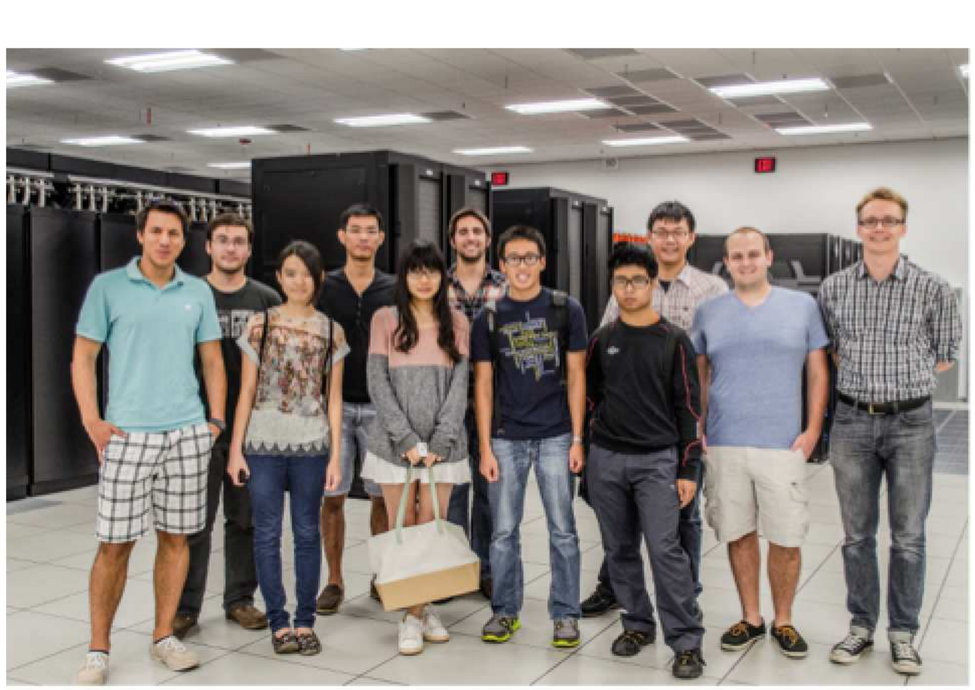
Optical Absorption Spectra of In_2O_3 and Ga_2O_3 from First-principles Calculations

Joel Varley, Condensed Matter and Materials Division, Lawrence Livermore National Laboratory

André Schleife, Department of Materials Science and Engineering, Univ. of Illinois at Urbana-Champaign



Blue Waters Symposium 2015: 5/11/2015, Sun River, OR

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Acknowledgments:

- Martin Feneberg
- Klaus Irmscher
- Anderson Janotti
- Chris G. Van de Walle

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Applications of Oxide Semiconductors

Why it Matters:

Optoelectronics and semiconductor technology:

- Lasers and light-emitting diodes
- Transparent electronics

Plasmonics

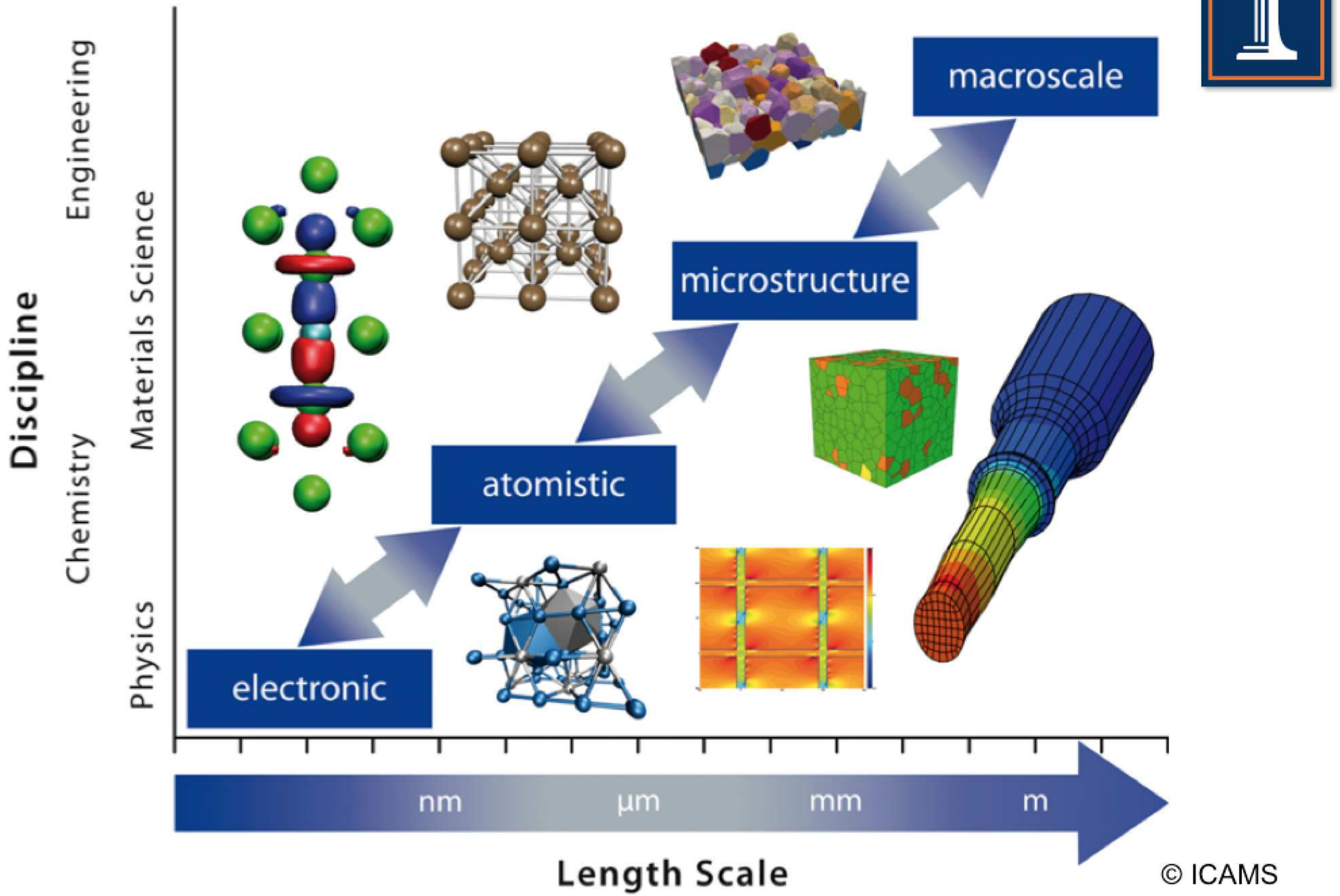
Energy-related applications:

- Photocatalytic water splitting
- Transparent electrodes: Solar cells
- Piezoelectronics

Some fundamentals not well understood/Key Challenges:

- Optical absorption?
- Excitonic effects?
- Anisotropy?
- Outlook: Understand influence of free electrons

Here: Atomistic Length (and Time) Scales



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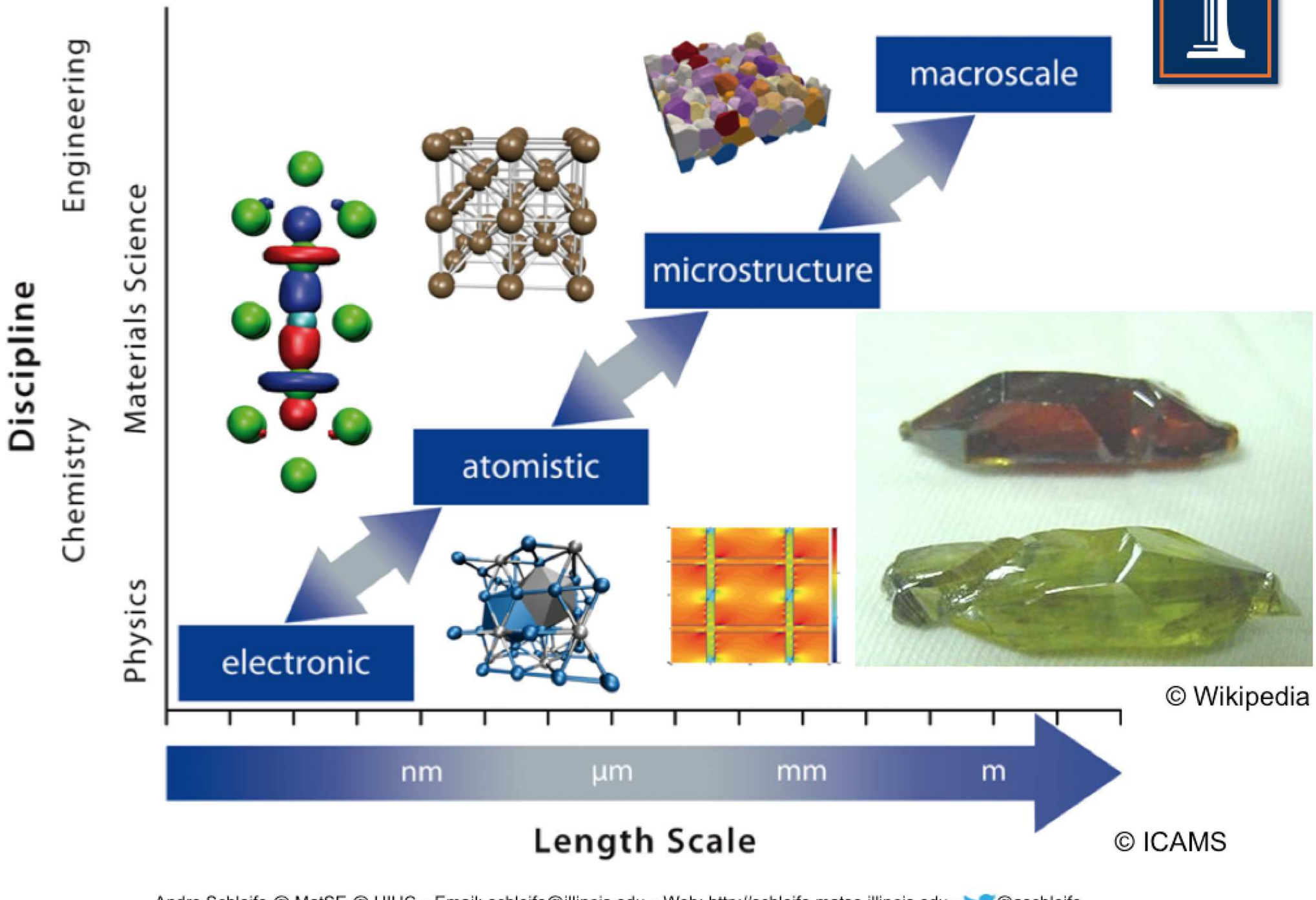

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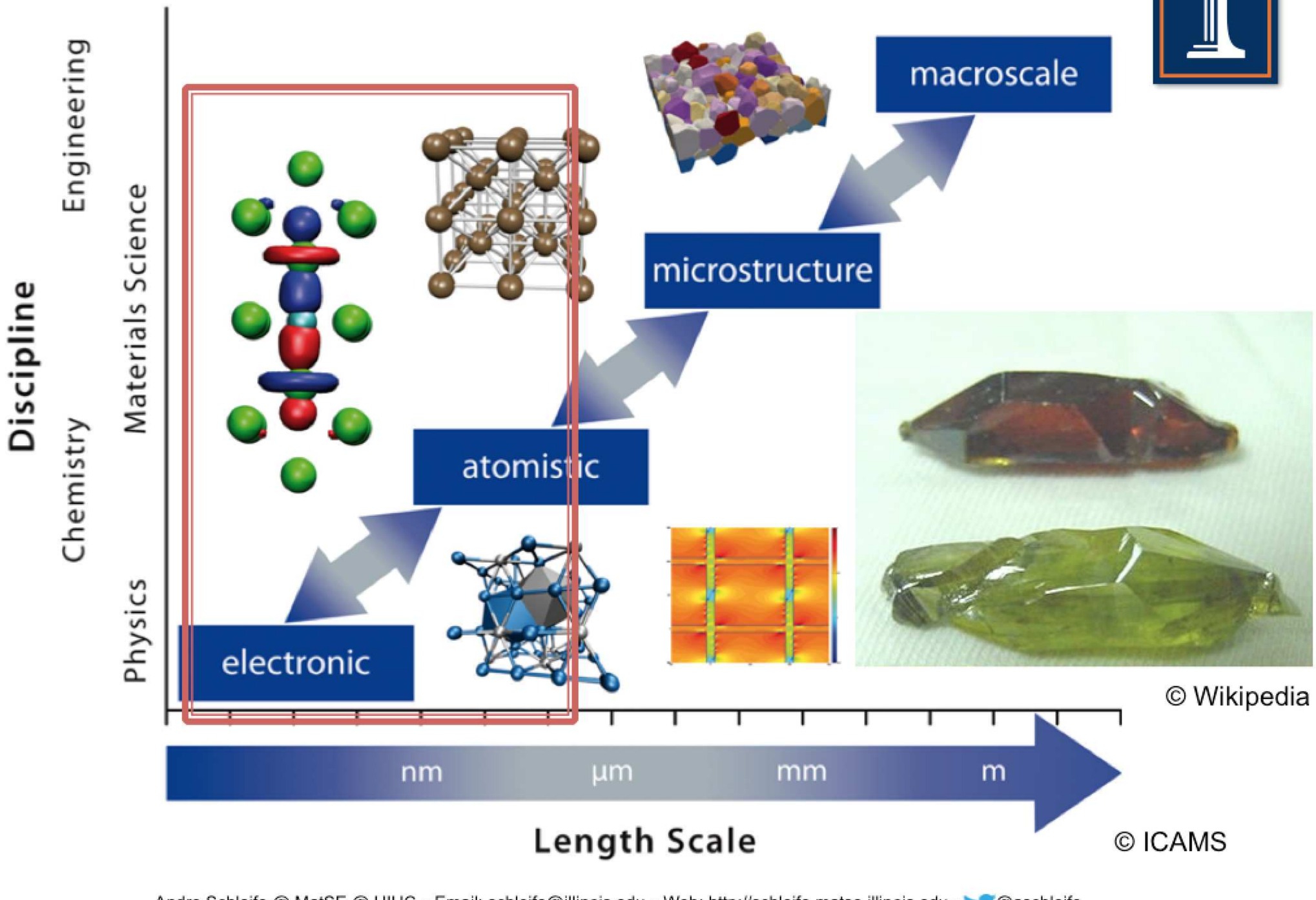

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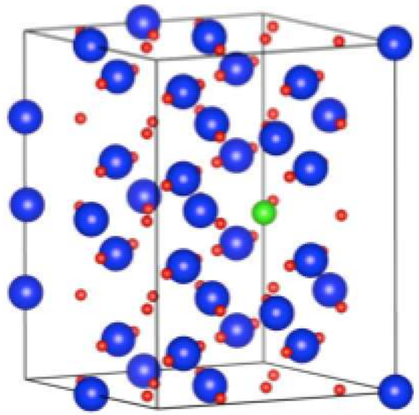
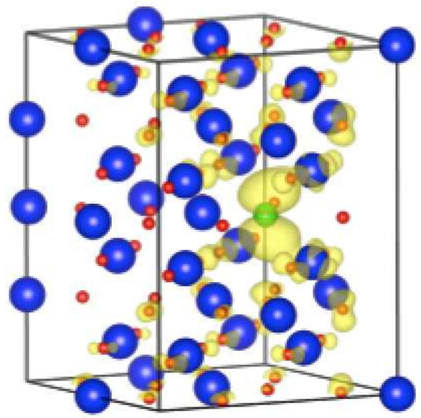
Optoelectronics from First-Principles Theory



Atomic Geometry

Optoelectronics from First-Principles Theory



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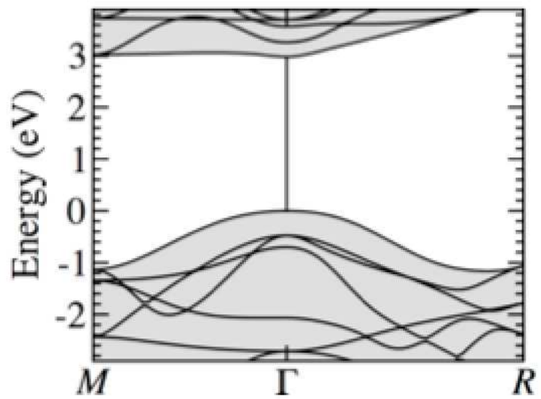
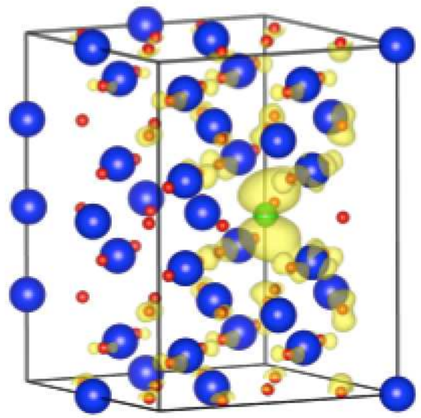


Electronic Band Structure

Optoelectronics from First-Principles Theory



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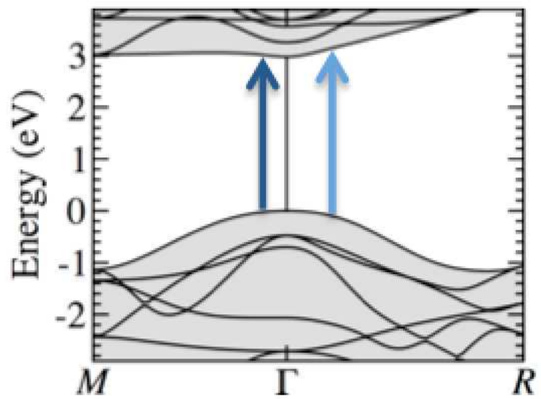

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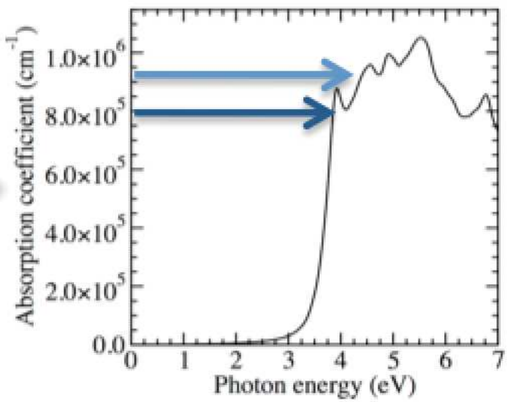

Optical Absorption

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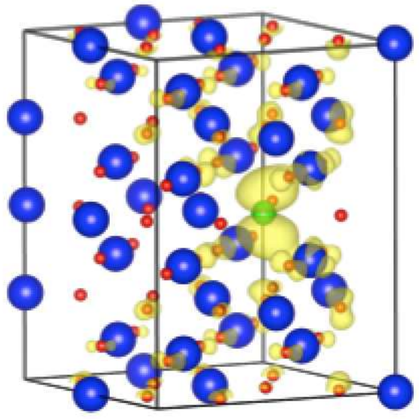
Optoelectronics from First-Principles Theory

Excited electronic states



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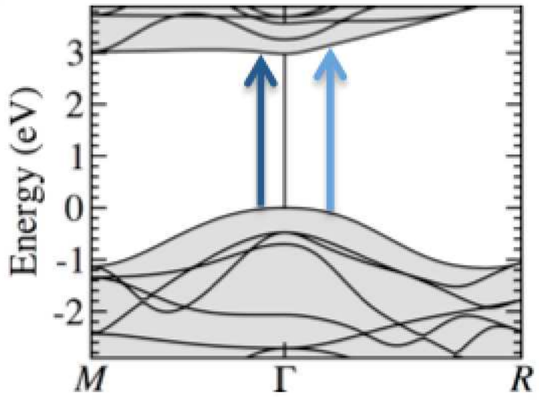

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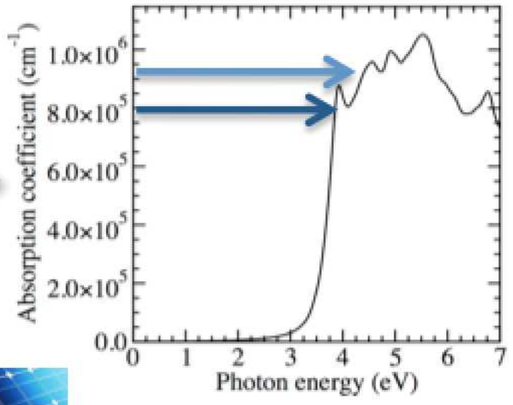

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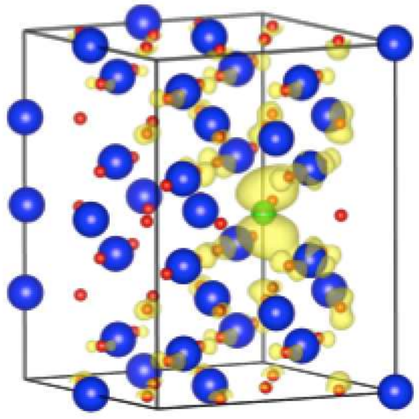

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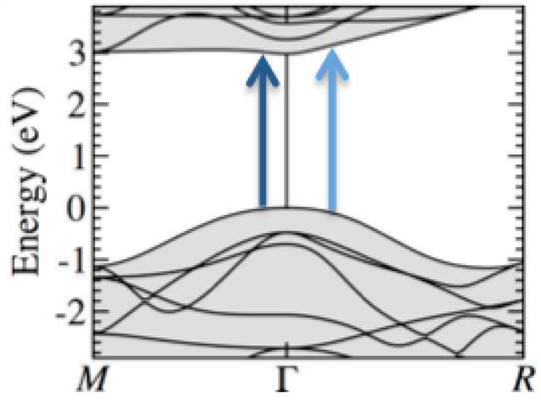

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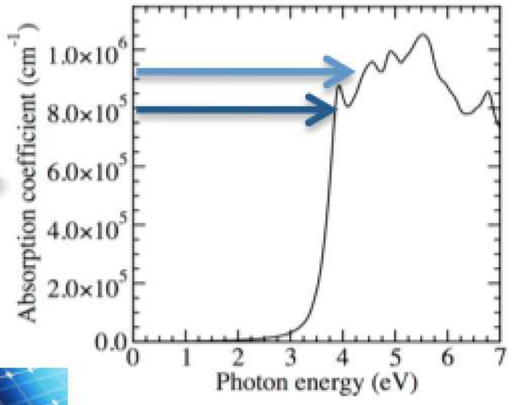
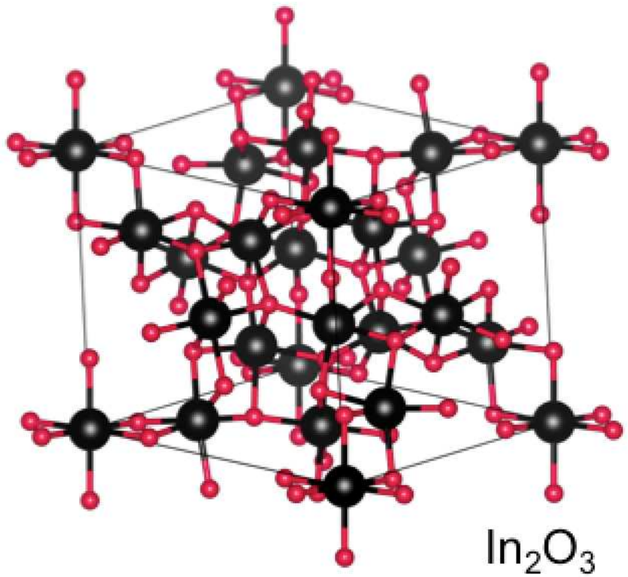


Optical Absorption

Problems/Key Challenges:

- Computationally expensive techniques
- Limitations of approximations used?
- Large unit cells to simulate
- Experiment: High-quality single crystals are rare



In_2O_3

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Single-Particle Excitations: Background

Photoemission spectroscopy (PES)

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

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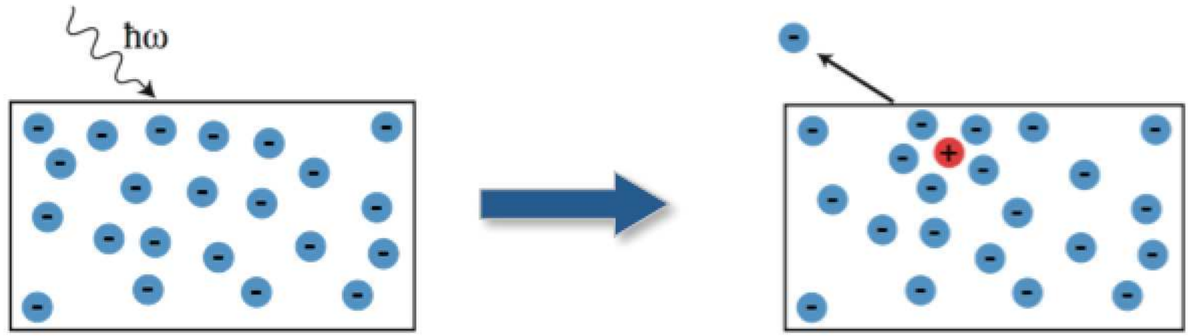
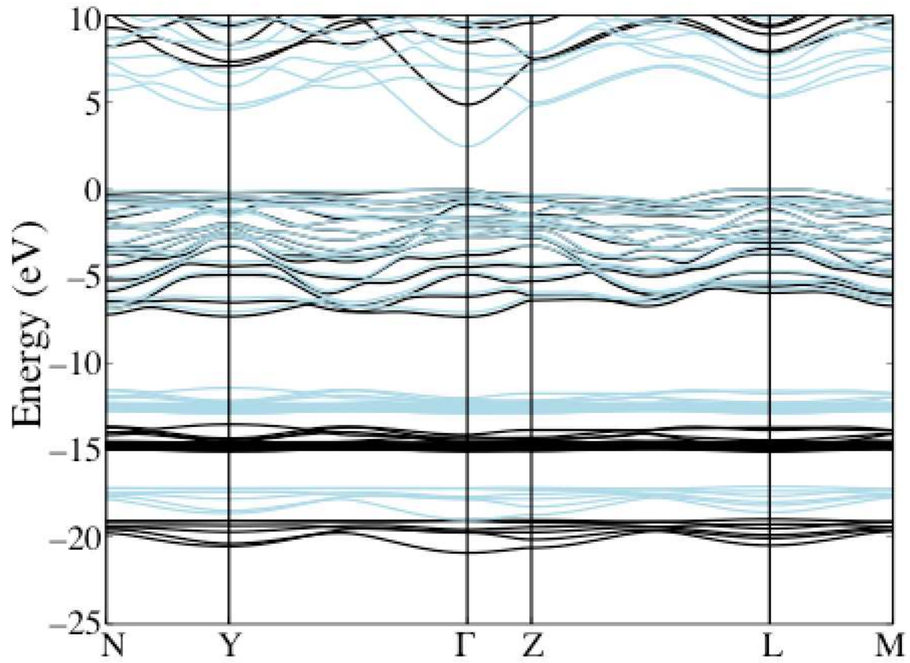


- Removal (PES) or addition (inverse PES) of an electron
- Important: Reaction of the electrons of the system

Example: beta-Ga_2O_3

- DFT-PBE band gap too small: 2.5 eV
- HSE reproduces experiment well (4.86 eV)

- Here: PBE+Δ
- Agrees well with HSE (valence band width: 7.07 eV vs. 7.33 eV, Exp: 7.37 eV)
- (small) Mismatch at higher energies



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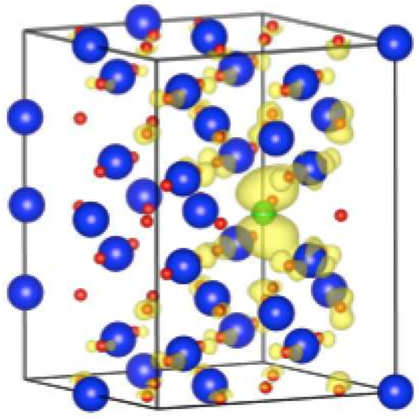

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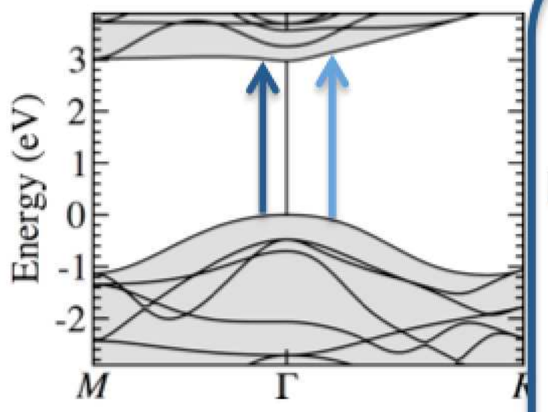

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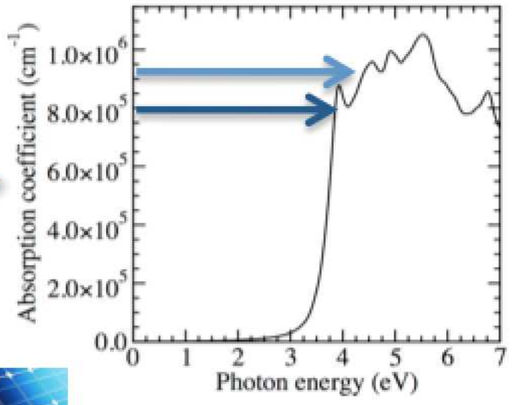

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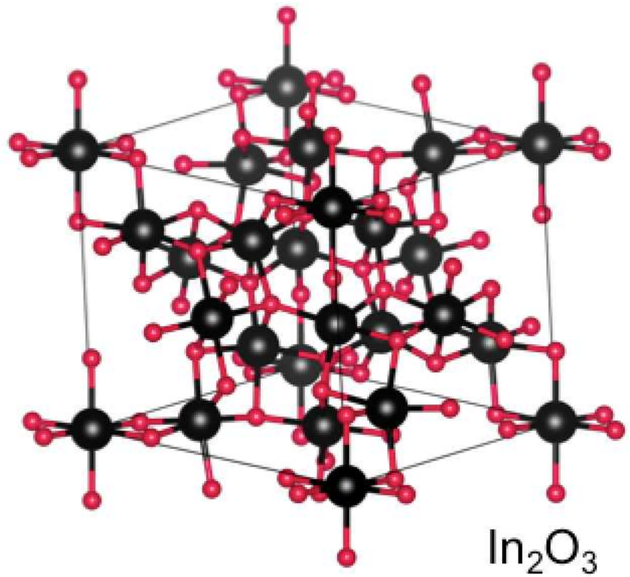

In_2O_3

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Two-Particle Excitations: Background

Optical Absorption:

- Electron from valence band excited into conduction band
- Electron-hole attraction (screened Coulomb potential)
- Macroscopic dielectric function: Local-field effects

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- Bethe-Salpeter equation for optical polarization function

→ Electron-hole interaction: Ξ

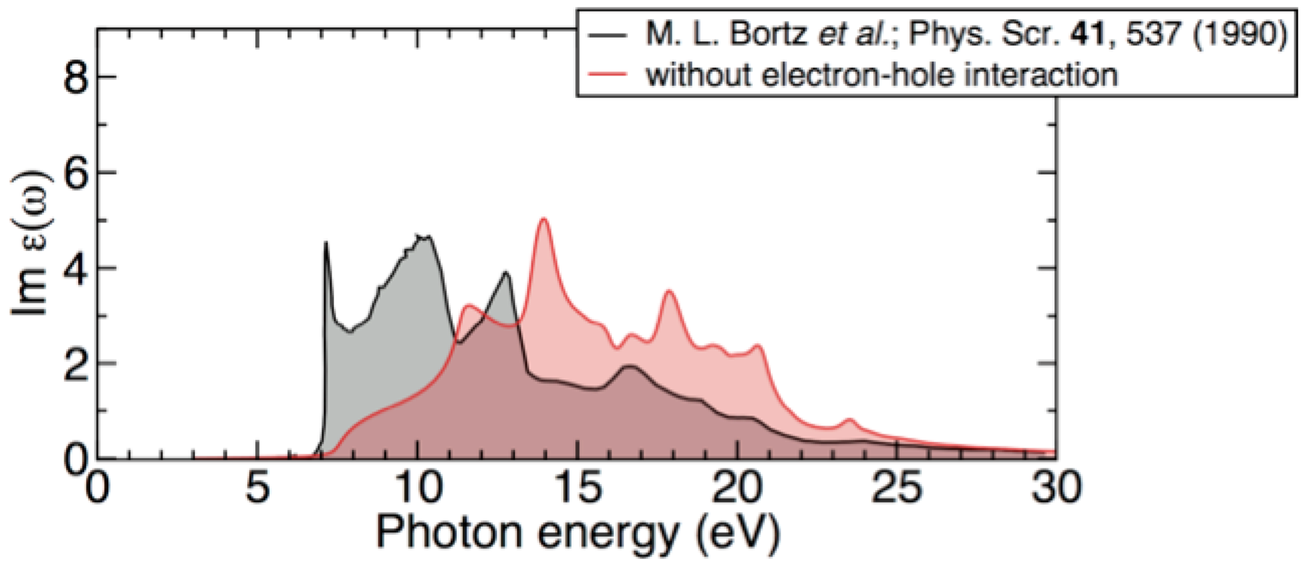
$$P(11',22') = P_0(11',22') + \iiint \mathrm{d3}\,\mathrm{d4}\,\mathrm{d5}\,\mathrm{d6}\,P_0(11',43)\,\Xi(34,65)\,P(56,22')$$

$$\varepsilon(11') = \delta(1-1') - \int \mathrm{d2}\,v(1-2)\,P(22^+,1'1'^+)$$

$1 := \mathbf{r}_1, t_1$

Why BSE? Why Blue Waters?

Example: MgO



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J. Varley and A. Schleife; Semicond. Sci. Tech. **30**, 024010 (2015)

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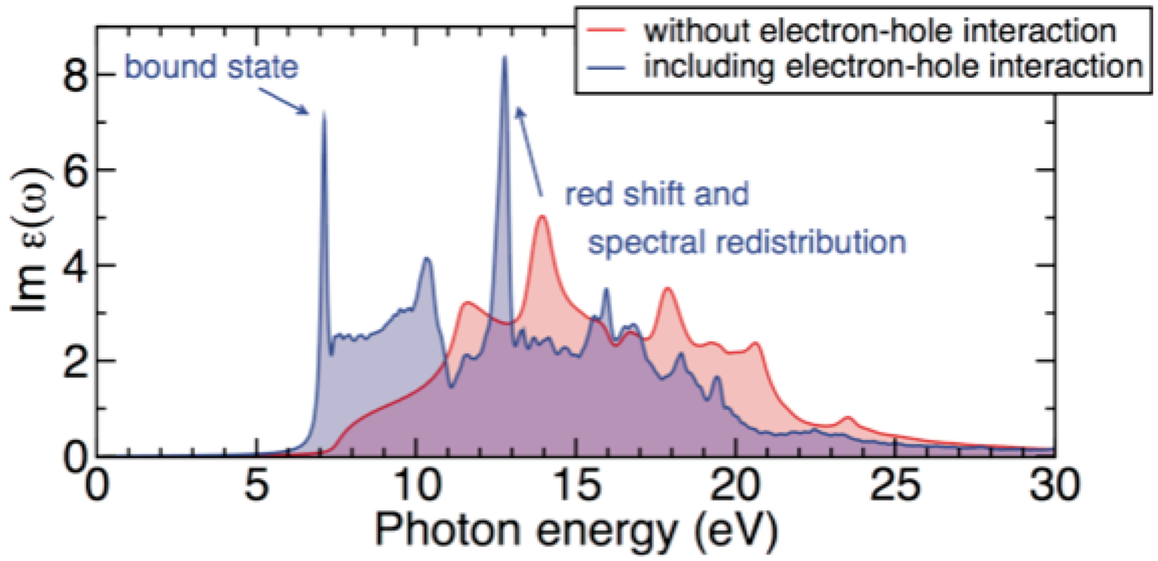

Excitonic effects: Solution of the Bethe-Salpeter equation

- Leads to eigenvalue problem (“excitonic Hamiltonian”)
- Huge matrix: Rank > 50k (MgO)
- Time-propagation approach to calculate the dielectric function

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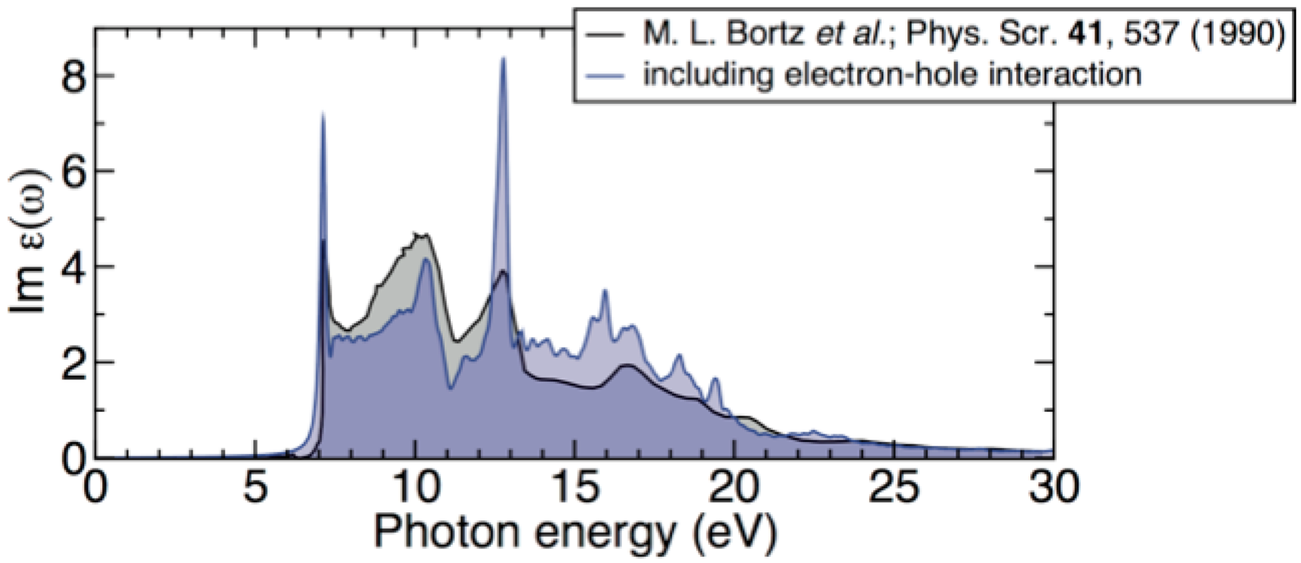

Excitonic effects: Solution of the Bethe-Salpeter equation

- Leads to eigenvalue problem ("excitonic Hamiltonian")
- Huge matrix: Rank > 50k (MgO)
- Time-propagation approach to calculate the dielectric function
- Excellent description of the optical properties of the oxides

→ Predictive power (e.g. for In_2O_3, Ga_2O_3, …)

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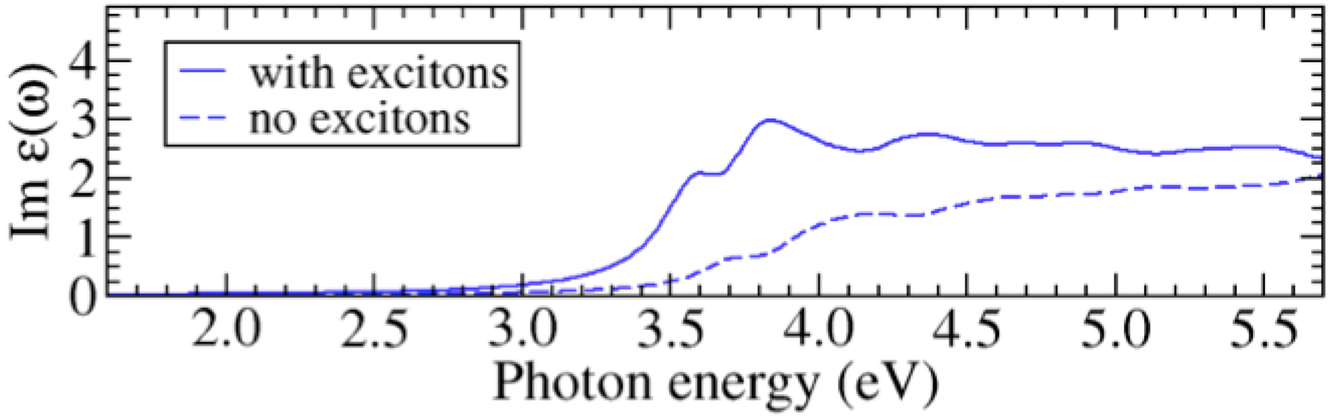
Results: Excitons in cubic In_2O_3

Accomplishments:

DFT vs. BSE near band edge:



- Slight red shift of absorption edge: Exciton binding energy
- Sampling of Brillouin zone is biggest computational challenge
- Shape of onset strongly affected: Bound excitonic state

- Cubic material: No anisotropy of the dielectric function

- Description of screening??

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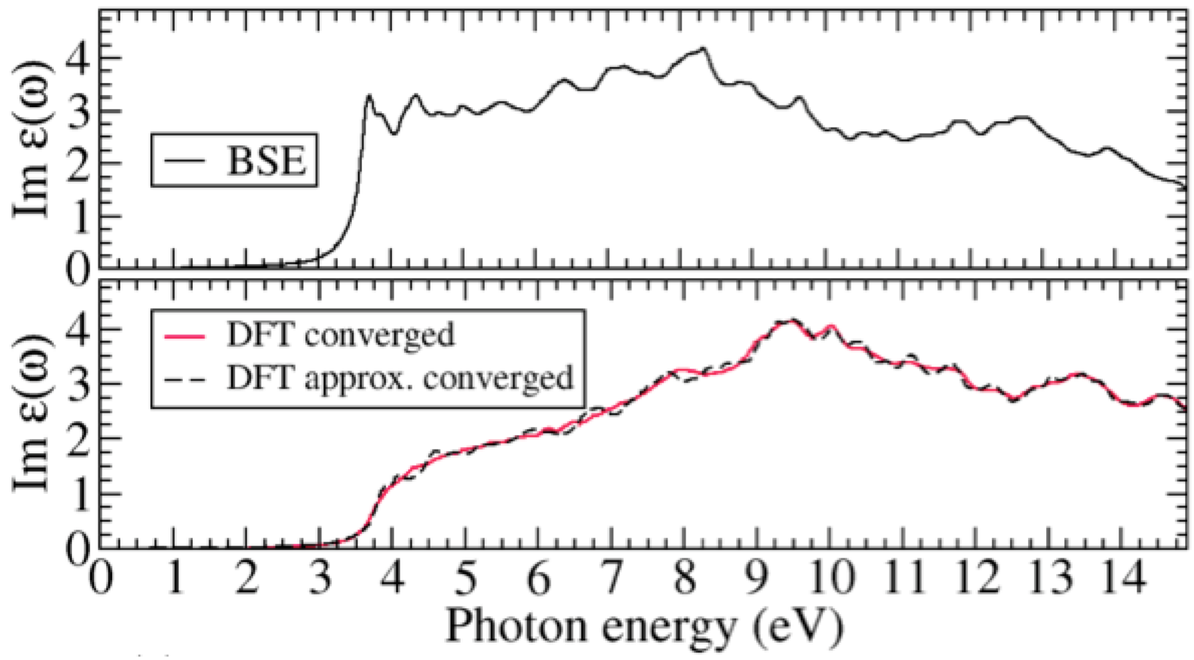
Results: Excitons in cubic In_2O_3

Accomplishments:

DFT and BSE: Large photon energy range



- Pronounced difference across entire energy range
- DFT peaks tend to be red-shifted in BSE
- Computationally challenging: Matrix ranks reach 360k (In_2O_3) – i.e. up to about 1 TB

- Influence of screening?
- Influence of quasiparticle corrections?

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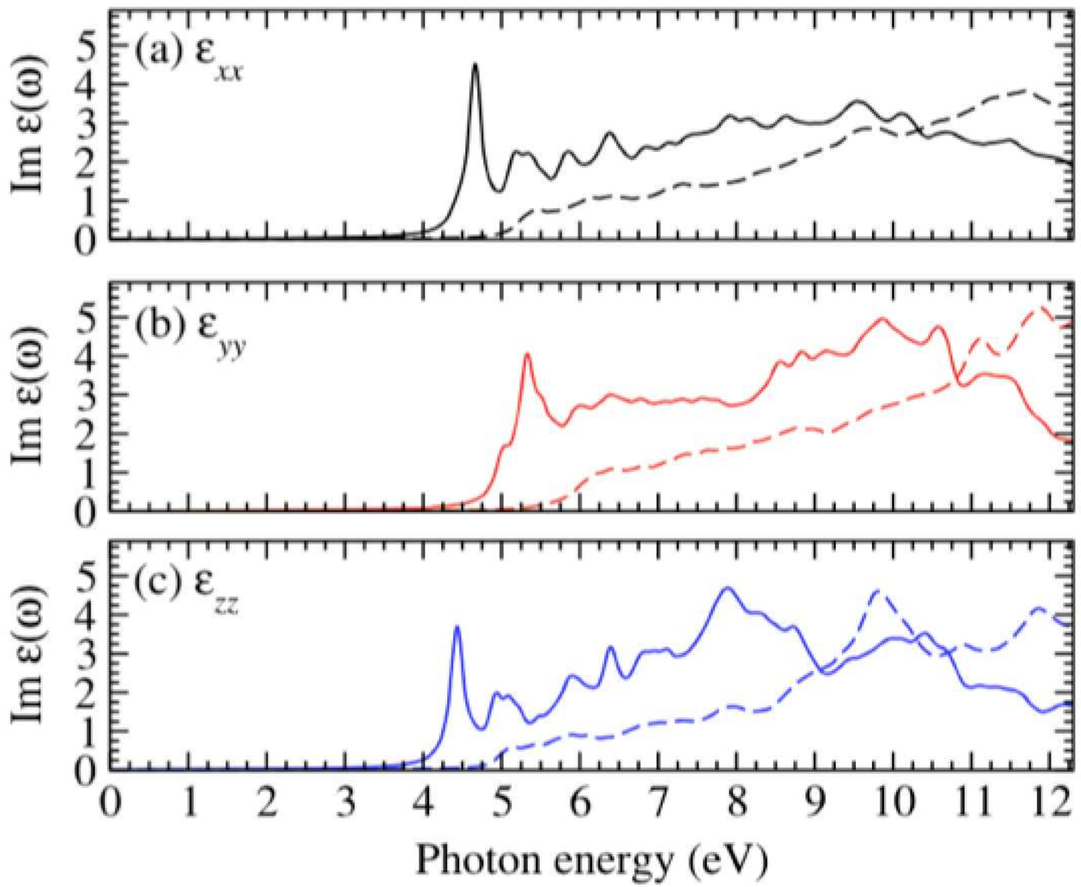
Two-Particle Excitations: monoclinic Ga_2O_3

Accomplishments:

Optical spectrum across large photon energy range:



- Screening smaller than in In_2O_3 (ε_0=4.05 vs. 4.80): Excitonic effects more pronounced
- Strong excitonic bound state dominates onset

- Very strong optical anisotropy
- Excitonic effects do not affect anisotropy significantly

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Summary and Outlook

Summary

- Study of optical properties of complex, technologically relevant materials
- Impact: High (predictive) accuracy for computational materials design, Develop understanding of exciton physics

- Computationally expensive and approximations are involved
- Blue Waters extremely useful in order to tackle high memory/data throughput requirements

- Accurate results over large photon energy range
- Strong influence of excitonic effects and anisotropy

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Outlook

- Code that can explore:
  - Influence of free carriers (e.g. for plasmonics)
  - Influence of screening due to electron-phonon coupling
  - Multiple length scales