

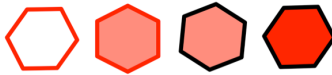
# Summary: School on Electron-Phonon Physics, Many-Body Perturbation Theory, and Computational Workflows

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July 24, 2024

THEOS, EPFL





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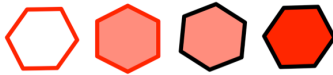
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# Overview

- Date: June 10-16, 2024
- Location: Austin, TX
- Focus: Electron-phonon interactions, many-body perturbation theory, and computational workflows
- Structure: Lectures, hands-on tutorials, workshops

- Electron-Phonon Interactions
- Density Functional Perturbation Theory (DFPT)
- Many-Body Perturbation Theory (GW and BSE)
- Wannier Functions and Their Applications
- Electron Transport and Superconductivity
- High-Performance Computing and Special Methods

- Quantum ESPRESSO: Setup and execution
- Wannier90 for Wannier function generation
- EPW: Band structure interpolation, electron-phonon matrix elements
- Mobility and Superconductivity Calculations
- GW and BSE: Practical applications
- Automated Workflows: EPWpy, Wannierizations



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# Wannier function

- Wannier functions provide a localized representation of electronic states in crystalline solids. (Gregory Wannier 1937)
- Wannier functions  $|\mathbf{R}j\rangle$  are constructed from Bloch functions  $|\psi_{n\mathbf{k}}(\mathbf{r})\rangle$ :

$$|\mathbf{R}j\rangle = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_{n=1}^J U_{\mathbf{k},nj} |\psi_{n\mathbf{k}}\rangle \quad (1)$$

where  $V_{\text{cell}}$  is the volume of the unit cell and the integral is over the Brillouin zone (BZ).

- Useful for understanding electronic structure, polarization, and electron localization.

- Localization: Wannier functions are exponentially localized in insulators.
- Orthogonality: Wannier functions are orthogonal:

$$\langle \mathbf{R}_m i | \mathbf{R}_n j \rangle = \delta_{ij} \delta_{\mathbf{R}_m \mathbf{R}_n} \quad (2)$$

- Completeness: They form a complete basis set for the Hilbert space of electronic states.



# Maximally Localized Wannier Functions (MLWFs)

- The most popular way to the gauge: Maximally-localized Wannier Functions (MLWF).
- We minimize the quadratic spread of the position operator of a manifold

$$\Omega = \sum_{j=1}^J [\langle \mathbf{0}j | r^2 | \mathbf{0}j \rangle - |\langle \mathbf{0}j | \mathbf{r} | \mathbf{0}j \rangle|^2] \quad (3)$$

through the optimization of the unitary matrices  $U_{\mathbf{k},nj}$

- This minimization ensures that Wannier functions are as localized as possible.
- Optimal smoothness in reciprocal space: good localization in real space  
N. Marzari and D. Vanderbilt, PRB 56, 12847 (1997)

# Computational Echo-system for Wannier Functions

- Wannier90: A widely used software package for computing MLWFs.

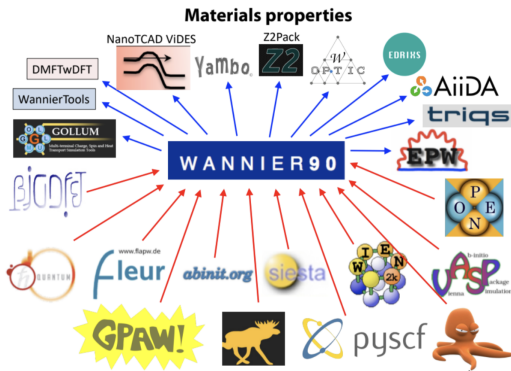


Figure: Ab initio engines using Wannier90.

*Computer Physics Communications*, 178(9), 685-699 (2009).

Wannier90:<http://www.wannier.org/>

- Electronic Structure:
  - Provides insight into the bonding and electronic properties of materials.
  - Used for band structure interpolation and analysis.
- Polarization and Berryology:
  - Electronic polarization, Berry phases, Berry curvature, optical and anomalous Hall conductivity, orbital magnetization
- Topological Insulators:
  - Used to study topological invariants, properties and edge states.
- Electron-Phonon Interactions:
  - Facilitate the calculation of electron-phonon coupling matrices.
- Ballistic transport and nanostructures:
  - Landauer conductance, embedding self-energies, large-scale tight binding
- Beyond DFT with localized orbitals:
  - Koopmans-Wannier spectral functionals, strongly correlated systems with DMFT.

# Example: Band Structure Interpolation

- Wannier functions allow for efficient interpolation of band structures.
- Essential for calculating accurate electronic properties over the Brillouin zone.
- Example: Interpolated band structure of silicon using MLWFs.

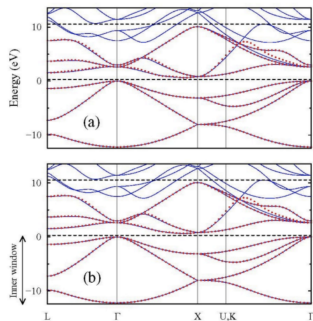
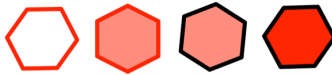


Figure: Interpolated band structure of silicon using Wannier functions.

- Wannier functions provide a localized representation of electronic states in solids.
- They are essential for various applications, including electronic structure, polarization, and topological properties.
- Computational tools like Wannier90 facilitate the practical use of Wannier functions.



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# GW and BSE

- GW is a many-body perturbation theory method used to calculate the electronic structure of materials.
- Theoretical framework: the many-body perturbation theory. The Green's function ( $G$ ) and the screened Coulomb interaction ( $W$ ).
- Beyond DFT method: Provides more accurate quasiparticle energies compared to Density Functional Theory (DFT).
- Moderately correlated systems may be solved numerically from first principles using many-body perturbation theory (e.g., GW and GW-BSE approaches, and beyond)

- The quasiparticle energy  $E_n$  is given by:

$$E_n = \epsilon_n + \langle \psi_n | \Sigma(E_n) - V_{xc} | \psi_n \rangle \quad (4)$$

where  $\epsilon_n$  are the Kohn-Sham energies,  $\Sigma$  is the self-energy, and  $V_{xc}$  is the exchange-correlation potential.

- The self-energy  $\Sigma$  in the GW approximation is:

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = i \int \frac{d\omega'}{2\pi} G(\mathbf{r}, \mathbf{r}'; \omega + \omega') W(\mathbf{r}, \mathbf{r}'; \omega') \quad (5)$$

where  $G$  is the Green's function and  $W$  is the screened Coulomb interaction.



- Start with a DFT calculation to obtain Kohn-Sham eigenvalues and eigenfunctions.
- Compute the dielectric function  $\epsilon(\mathbf{q}, \omega)$  and the screened Coulomb interaction  $W(\mathbf{q}, \omega)$ .
- Construct the Green's function  $G(\mathbf{r}, \mathbf{r}'; \omega)$ .
- Calculate the self-energy  $\Sigma(\mathbf{r}, \mathbf{r}'; \omega)$ .
- Solve for the quasiparticle energies  $E_n$ .

# Introduction to Bethe-Salpeter Equation (BSE)

- BSE is used to calculate the optical properties of materials by including electron-hole interactions.
- Derived from the two-particle Green's function.
- Provides accurate excitonic effects and optical spectra.

- The BSE describes the correlated motion of an electron-hole pair:

$$(\epsilon_c - \epsilon_v)A_{vc} + \sum_{v'c'} K_{vc,v'c'} A_{v'c'} = \Omega A_{vc} \quad (6)$$

where  $\epsilon_c$  and  $\epsilon_v$  are the energies of conduction and valence bands,  $A_{vc}$  are the exciton amplitudes,  $K$  is the electron-hole interaction kernel, and  $\Omega$  are the exciton energies.

- The kernel  $K$  includes the direct Coulomb interaction and the exchange interaction.

- Perform a GW calculation to obtain quasiparticle energies and wavefunctions.
- Construct the electron-hole interaction kernel  $K$ .
- Solve the BSE to obtain exciton energies  $\Omega$  and amplitudes  $A_{vc}$ .
- Calculate the optical absorption spectrum using the exciton amplitudes.

- Electronic Structure:
  - Provides accurate band gaps and quasiparticle energies.
  - Essential for studying semiconductors and insulators.
- Optical Properties:
  - BSE captures excitonic effects in optical spectra.
  - Important for understanding light absorption and emission in materials.
- Materials Design:
  - GW and BSE are used to predict and design new materials with desired electronic and optical properties.

# Example: Band Gap of Silicon

- GW calculation corrects the underestimated band gap from DFT.
- Results show excellent agreement with experimental values.

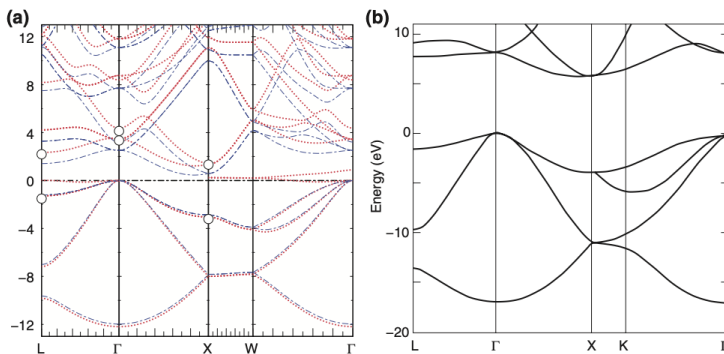


Figure: Comparison of GW (left) and DFT (right) band gaps for silicon.

## Example: Optical Spectrum of MoS<sub>2</sub>

- BSE captures excitonic peaks in the optical absorption spectrum of monolayer MoS<sub>2</sub>.
- Matches experimental spectra and reveals excitonic binding energies.

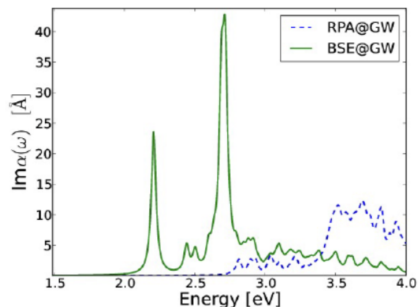
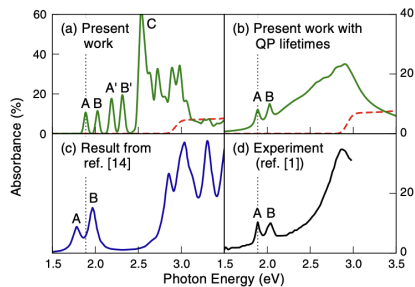


Figure: Absorption spectrum of MoS<sub>2</sub> calculated with the RPA and BSE using the  $G_0W_0$  quasiparticle band structure. (Thygesen PRB 2013)

## Example: Optical Spectrum of MoS<sub>2</sub>

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**Figure:** Absorption spectrum of MoS<sub>2</sub> computed using BSE in comparison with experiment. (Diana PRL 2013)



- BerkeleyGW:
  - <http://www.berkeleygw.org/>
  - A software package for GW and BSE calculations.
  - Interfaces with DFT codes like Quantum ESPRESSO and VASP.
- Yambo:
  - <http://www.yambo-code.org/>
  - Another package for many-body calculations including GW and BSE.
  - Capable of handling large systems and complex materials.

- GW provides accurate quasiparticle energies, improving upon DFT results.
- BSE includes electron-hole interactions, essential for accurate optical spectra.
- These methods are critical for studying electronic and optical properties of materials.



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# DFPT

- DFPT is an extension of Density Functional Theory (DFT) for studying the response of a system to small perturbations.
- It allows for the calculation of phonons, dielectric properties, and electron-phonon interactions.
- Developed to overcome the limitations of finite-difference methods in calculating response functions.

- DFT provides the ground-state properties of a many-electron system using the electron density  $\rho(\mathbf{r})$ .
- DFPT extends DFT to linear response theory, allowing the calculation of changes in  $\rho(\mathbf{r})$  due to a perturbation.
- The perturbation can be an external electric field, atomic displacement, etc.

- The response of the electron density  $\rho(\mathbf{r})$  to a perturbation  $V_{\text{ext}}(\mathbf{r})$  can be expressed as:

$$\delta\rho(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \delta V_{\text{ext}}(\mathbf{r}') d\mathbf{r}' \quad (7)$$

where  $\chi(\mathbf{r}, \mathbf{r}')$  is the density-density response function.

- DFPT calculates  $\chi(\mathbf{r}, \mathbf{r}')$  using perturbation theory within the DFT framework.

- The self-consistent field (SCF) equations in DFT are modified to include the perturbation:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}[\rho_0](\mathbf{r}) + \delta V_{\text{eff}}[\delta\rho](\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (8)$$

- Here,  $V_{\text{eff}}$  is the effective potential, and  $\delta V_{\text{eff}}$  is its variation due to the perturbation.

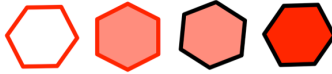
- Phonon Calculations:
  - Determines the vibrational modes and frequencies of a crystal.
  - Used to study thermal properties and stability of materials.
- Dielectric Properties:
  - Calculates the dielectric constant and piezoelectric tensors.
  - Important for understanding material responses to electric fields.
- Electron-Phonon Interactions:
  - Computes electron-phonon coupling constants.
  - Essential for studying superconductivity and electrical conductivity.

Baroni, S., de Gironcoli, S., Dal Corso, A., & Giannozzi, P. (2001). Phonons and related crystal properties from density-functional perturbation theory. *Reviews of Modern Physics*, 73(2), 515.



- DFPT extends DFT to study the response of systems to small perturbations.
- It is crucial for calculating phonons, dielectric properties, and electron-phonon interactions.
- Widely used in material science to predict and understand physical properties.

- Comprehensive coverage of electron-phonon physics and computational methods
- Balance of theoretical lectures and practical tutorials
- Importance of hands-on experience with state-of-the-art tools



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# Supplimentary and Misc.

- Frontiers in many-body excited-state dynamics from first principles



This is to certify that

**LIU Binbin**

attended in-person the following workshop:

**Frontiers in many-body excited-state dynamics from first principles**

Location: CECAM-HQ-EPFL, Lausanne, Switzerland

Date: July 15 – 17, 2024

Organized by:

**Marina Filip**, University of Oxford, United Kingdom

**Alejandro Molina Sanchez**, University of Valencia, Spain

**Diana Qiu**, Yale University, United States

**Sivan Refaely-Abramson**, Weizmann Institute of Science, Israel

Prof. Andrea CAVALLI  
CECAM Director



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# Wannierize Excitonic Bands (from the CECAM workshop)

- Maximally-Localized Exciton Wannier Functions (Haber, Qiu, da Jornada, Neaton, Phys. Rev. B 108, 125118 (2023)).
- A new representation of excitons enabling tight-binding models, geometric phases, interpolation, and physical interpretation
- Interface with Wannier90 different workflows. (Special treatment to the non-analytic term.)
- → MLXWFs can be a good localized basis for exciton-polaron physics. (Dai, Lian, Lafuente-Bartolome, Giustino, Phys. Rev. B 109, 045202 (2024))

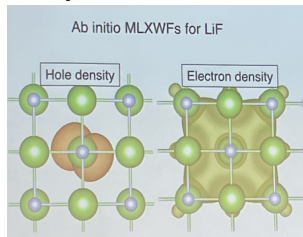


Figure: Ab initio MLXWFs for LiF (From: Neaton's group at Berkeley.)

- Thermoelectric: Practical efforts to achieve low-temperature thermoelectrics using nodal loop semimetals may therefore find it fruitful to identify materials with a nearly flat nodal line. (PRXEnergy.3.023007)
- Exitonic effects in Weyl semimetals.
- Exiton in Weyl phonons: no research paper on this so far!

# Applications of Direct Band Gap Semiconductor

Optoelectronic devices: Direct band gap materials, with their high radiative recombination rates and strong absorption of light, are widely used in the development of lasers, LEDs, and photodetectors. These devices rely on efficient light emission and absorption for their operation. Solar cells: Direct band gap materials are also utilized in solar cells, where their high absorption coefficient enables efficient conversion of sunlight into electricity.



Figure: Solar city (Tesla)

- The GW method, F Aryasetiawan and O Gunnarsson, 1998 Rep. Prog. Phys. 61 237
- Electronic excitations: density-functional versus many-body Green's-function approaches, REVIEWS OF MODERN PHYSICS, VOLUME 74, APRIL 2002
- Calculating excitons, plasmons, and quasiparticles in 2D materials and van der Waals heterostructures, Kristian Sommer Thygesen
- The GW approximation: content, successes and limitations, Lucia Reining
- The GW Compendium: A Practical Guide to Theoretical Photoemission Spectroscopy Dorothea Golze\* Marc Dvorak and Patrick Rinke