



# Optical Properties of Nanomaterials from *ab-initio* Calculations

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# Outline

## Introduction

- What do we want to calculate?
- How do we calculate from first-principles?

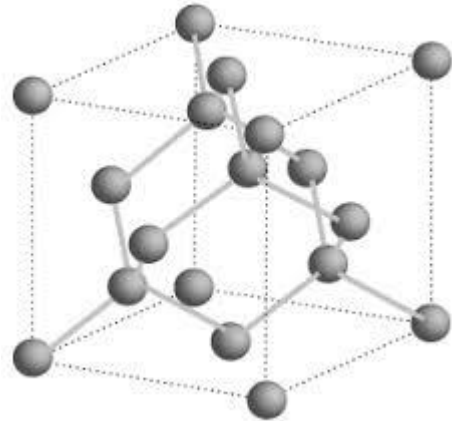
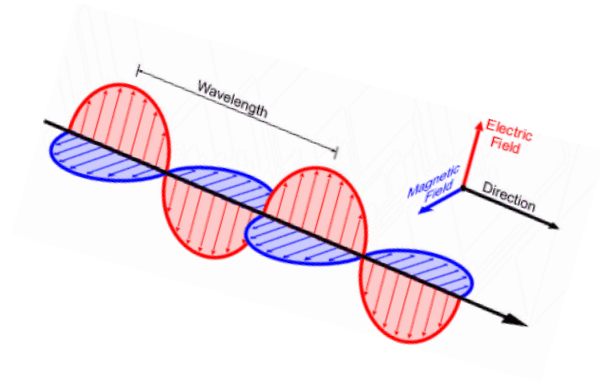
## Ground state calculations

- Basic approximations and ground state Density Functional Theory (DFT)
- Advantages and deficiencies of ground state DFT

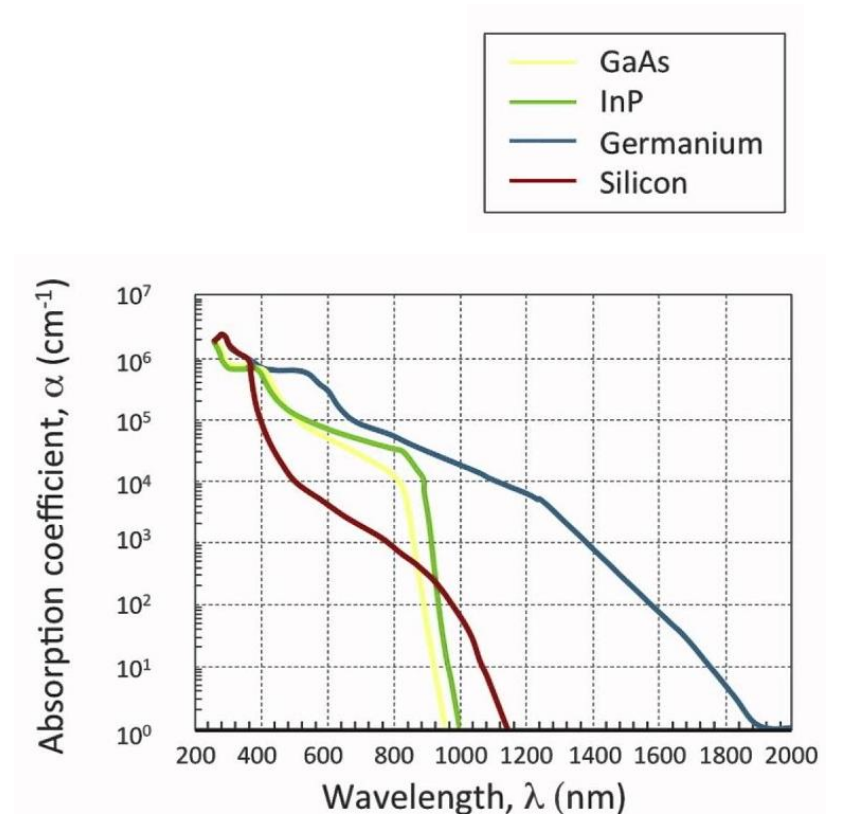
## Excited state calculations

- Many-body perturbation theory (MBPT) and the GW approximation
- **Applications:** quasiparticle effects in bulk and 2D materials
- Excitonic effects and the Bethe-Salpeter equation (BSE)
- **Applications:** absorption spectra and excitonic effects in bulk and 2D materials
- **Future prospects:** excitonic effects in non-linear optical properties
- Our research on GW/BSE and non-linear optical properties

# What do we want to calculate?



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How to calculate absorption or reflectance spectra from first-principles calculations?

# How do we calculate?

The absorption coefficient for frequency  $\omega$  and normal incidence is commonly defined as:

$$\alpha(\omega) = \frac{2\omega\kappa(\omega)}{c}$$

where  $\kappa(\omega)$  is the extinction coefficient, which is the imaginary part of the complex refractive index.

It can be expressed in terms of the complex dielectric function  $\varepsilon(\omega)$  as:

$$\kappa(\omega) = \text{Im} \left[ \sqrt{\varepsilon(\omega)} \right] = \sqrt{\frac{\varepsilon_1(\omega)}{2}} \sqrt{\sqrt{1 + \left[ \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)} \right]^2} - 1}$$

where  $\varepsilon_1$  and  $\varepsilon_2$  are its real and imaginary parts, respectively.

# How do we calculate?

In quantum mechanics, the function  $\varepsilon_2(\omega)$  can be extracted from perturbation theory. In a non-interacting picture, it may be expressed as:

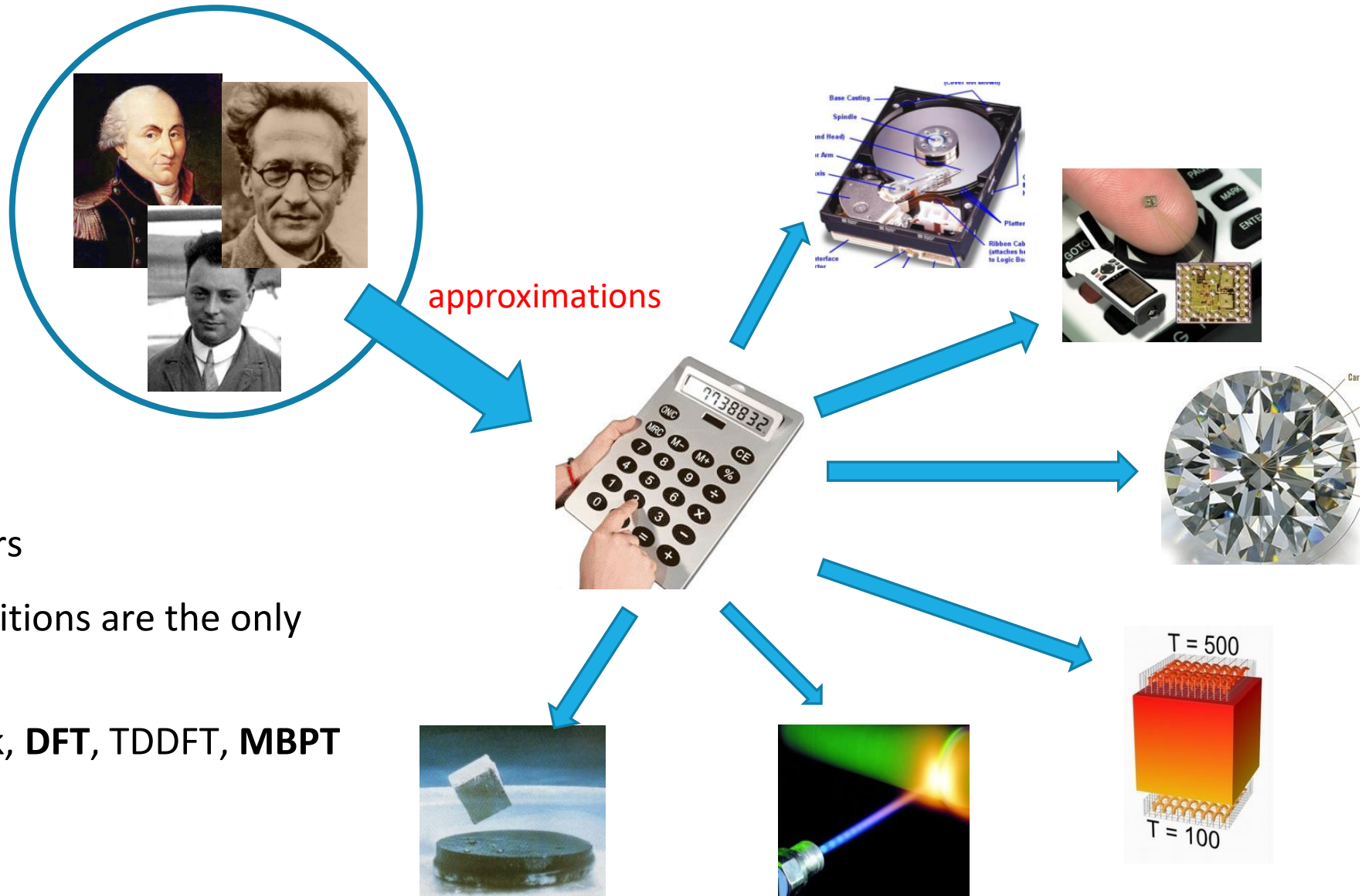
$$\varepsilon_2(\omega) = \frac{16\pi}{\omega^2} \sum_{v, c} |\langle v | \mathbf{v} \cdot \boldsymbol{\lambda} | c \rangle|^2 \delta(\omega - (E_c - E_v))$$

where:

- $\mathbf{v}$  is the velocity operator of the electron and  $\boldsymbol{\lambda}$  the polarization vector of the incident light.
- $v$  and  $c$  denote occupied and empty single-electron states, respectively, of energies  $E_c$  and  $E_v$ .
- The real part can be calculated from  $\varepsilon_2(\omega)$  by using causality (Kramers-Kronig) relations.

Therefore, in principle, we can compute optical properties from first-principles if we are able to obtain the electron wavefunctions and energies!

# Ab-initio calculations



- No empirical parameters
- Atomic species and positions are the only required inputs
- Examples: Hartree-Fock, **DFT**, TDDFT, **MBPT (GW/BSE)**, CI, ...

# Fundamental approximations

## **Born-Oppenheimer approximation:**

- Separates ionic and electronic degrees of freedom (ions are much slower)
- Ionic coordinates appear as fixed parameters for the electronic problem
- Electronic energy appears as an effective potential for the ionic problem

## **One-electron approximation:**

- Electronic problem is still a many-body problem (interacting electrons)
- We would like to map this problem into a series of one-electron problems under the action of an effective potential that includes the effects of interactions
- How do we do this and justify this approximation? → **DFT, GW, ...**

# Density Functional Theory (DFT)

P. Hohenberg e W. Kohn, Phys. Rev **136**, 864B (1964)

W. Kohn e L. J. Sham, Phys. Rev. **140**, 1133A (1965)



W. Kohn  
Nobel Prize  
(1998)

- ▶ **Hohenberg - Kohn:** Total energy of the system can be expressed as a functional of the electronic density  $n(\mathbf{r})$ . The ground state is determined by the global minimum of this functional. Therefore, the density replaces the many-electron wavefunction  $\Psi(\mathbf{r}_1 \dots \mathbf{r}_N)$  as the fundamental variable of the system:  $n \rightarrow \Psi, E_0$ .
- ▶ **Kohn – Sham:** Ground state may be exactly obtained (in principle) from an auxiliary system of non-interacting electrons, with the same density, under the action of an effective potential (which is unknown).

**Computational Implementation:** Quantum-Espresso, SIESTA, VASP, Abinit ...




# Kohn-Sham (KS) equations

By minimizing the HK functional in the auxiliary system, we obtain a set of one-electron equations:

$$\left[ -\frac{1}{2}\nabla^2 + V_{KS}^\sigma(\mathbf{r}) \right] \phi_i^\sigma(\mathbf{r}) = \epsilon_i^\sigma \phi_i^\sigma(\mathbf{r})$$

one-electron  
wavefunctions (wfcs)



where:

$$V_H(\mathbf{r}) = \frac{\delta E_H[n]}{\delta n(\mathbf{r}, \sigma)} = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$V_{KS}^\sigma(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}^\sigma(\mathbf{r})$$

$$V_{xc}^\sigma(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r}, \sigma)}$$

- $V_{ext}(\mathbf{r})$  is the potential due to interactions between the electron and the ions and external fields.
- $V_H(\mathbf{r})$  is the Hartree potential (classical electrostatic electron-electron repulsion).
- $V_{xc}^\sigma(\mathbf{r})$  is the exchange-correlation potential. It includes the quantum effects coming from the Pauli principle (exchange) and anything beyond it (correlation). **Its exact form is unknown.**

# Solving the KS equations

**Basis:** One-electron wfcs are expanded in a convenient basis set, such as plane-waves (QE, VASP), pseudoatomic orbitals (SIESTA), etc. Convergence with respect to basis size needs to be checked.

**K-points:** Integrations over the Brillouin zone are replaced with summations over a sufficiently dense **k**-point grid.

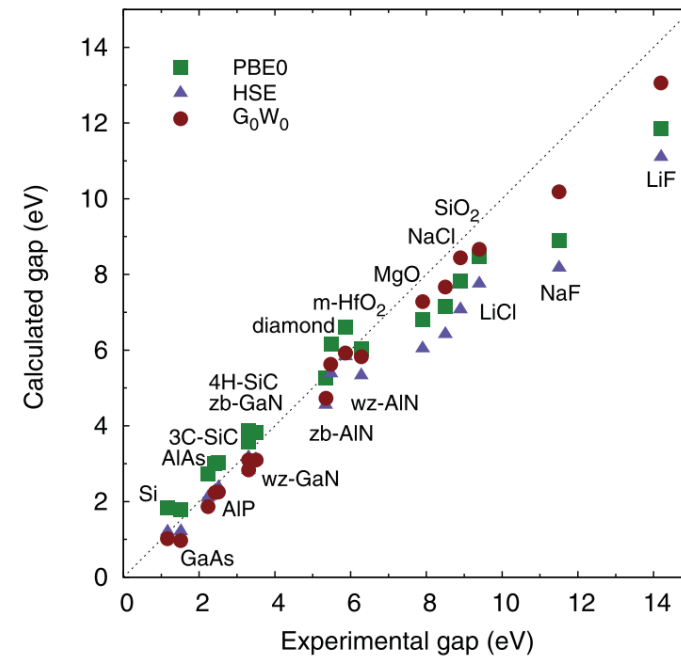
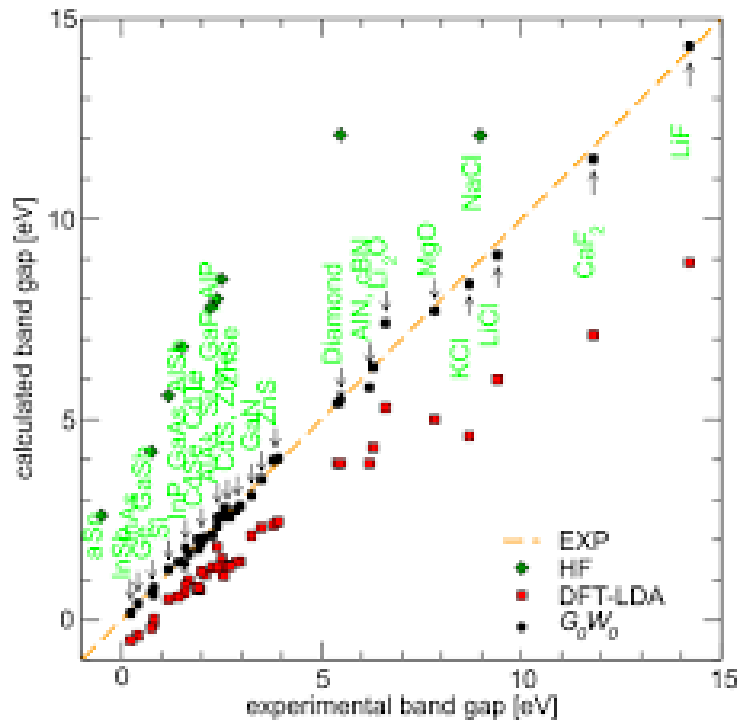
**Ion-electron interaction ( $V_{ext}$ ):** Exact all-electron potential is replaced with a pseudopotential (PP) that reproduces the valence (bonding) properties and provides smoother pseudowfcs near the atomic cores.

**Exchange-correlation ( $V_{xc}$ ):** Since its exact form is unknown, approximations are required. The most common functionals are LDA, GGA, meta-GGA and Hybrid.

**Self-consistency:**  $V_{KS}$  is a functional of the density, which depends on the wfcs we need to calculate. Therefore, the problem needs to be solved iteratively.

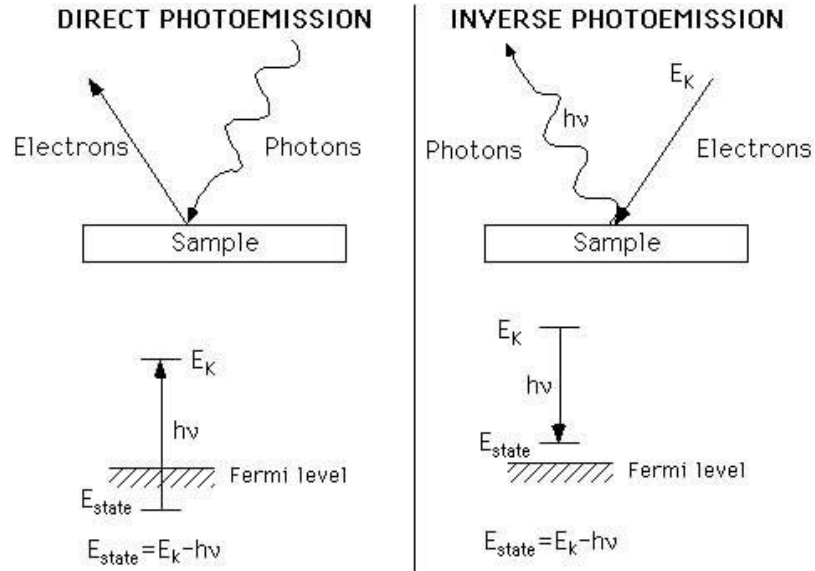
# Advantages and deficiencies of ground-state DFT

- Properties that are calculated from total energies are accurately described by the formalism: cohesive energies, formation energies of defects, vibrational frequencies, ...
- Properties that are calculated from KS energies are **not** properly described by the formalism: **band gaps**, photoemission and absorption spectra, binding energies, ...



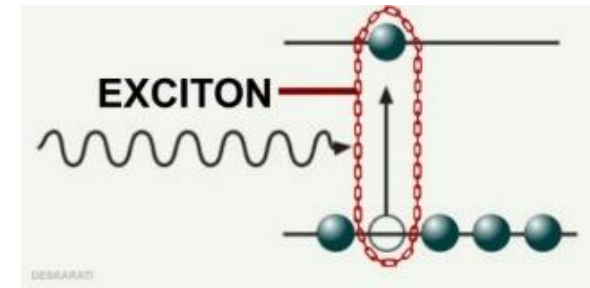
Van-Schilfgaarde, Kotani, and Faleev, Phys. Rev. Lett. **96**, 22640 (2006)  
W. Chen and A. Pasquarello, Phys. Rev. B **86**, 035134 (2012)

## Photoemission



Addition/removal of electrons:  
 $N \rightarrow N \pm 1$

Excitations with the same number of electrons:  
 $N \rightarrow N$



- Band gaps and optical properties are related to excited states of a system! As such, they cannot be fully described with a ground state theory.
- New formalisms that include excited states are required, such as many-body perturbation theory (MBPT) or time-density functional theory (TDDFT).

# Many-body perturbation theory (MBPT)

The first important quantity of the theory is the **single-electron Green's function**:

$$G(\mathbf{x}, t, \mathbf{x}', t') = -i \langle N | T [\psi_H(\mathbf{x}, t) \psi_H^\dagger(\mathbf{x}', t')] | N \rangle$$

- $|N\rangle$  is the ground state of the many-electron interacting system, described by a **time-independent** Hamiltonian  $H$ .
- $\psi_H^\dagger(\mathbf{x}, t)$  and  $\psi_H(\mathbf{x}, t)$  are electron creation and annihilation field operators in the Heisenberg representation.
- $T$  is the time-order operator. It ensures electron propagation for  $t > t'$  and hole propagation for  $t < t'$ .
- The electron density can be obtained from  $G$  as  $n(\mathbf{x}, t) = G(\mathbf{x}, t, \mathbf{x}, t^+)$ . Other properties can also be extracted from it.

# Spectral representation of $G$

By noting that  $G(\mathbf{x}, t, \mathbf{x}', t') = G(\mathbf{x}, \mathbf{x}', t - t')$  and doing a Fourier transform from time to energy domain, we obtain:

$$G(\mathbf{x}, \mathbf{x}', \epsilon) = \sum_s \left[ \frac{f_s(\mathbf{x})f_s^*(\mathbf{x}')}{\epsilon - \epsilon_s + i\eta} + \frac{f_s(\mathbf{x})f_s^*(\mathbf{x}')}{\epsilon - \epsilon_s - i\eta} \right]$$

- The sum is done over all excited states  $s$  of the system with  $N + 1$  (first term) and  $N - 1$  (second term) electrons.
- **Poles of  $G$  correspond to excitation energies of the system:**  $\epsilon_s = E_s(N + 1) - E(N)$  in the first term and  $\epsilon_s = E(N) - E_s(N - 1)$  in the second term.
- $f_s(\mathbf{x}) = \langle N | \psi(\mathbf{x}) | N + 1, s \rangle$  or  $\langle N - 1, s | \psi(\mathbf{x}) | N \rangle$  are probability amplitudes for transitions between the ground and excited states.
- $\eta \rightarrow 0^+$  is a small real factor to ensure convergence.
- The first term is the causal/retarded part of the function, while the second is the advanced part.

# Equations of motion

The equation of motion for the field operator is:

$$i\partial_t\psi_H(\mathbf{x},t) = [\psi_H(\mathbf{x},t), H] = \left[ h(\mathbf{x}) + \int dx' v(\mathbf{r}, \mathbf{r}') \psi_H^\dagger(\mathbf{x}',t) \psi_H(\mathbf{x}',t) \right] \psi_H(\mathbf{x},t)$$

From this equation, we obtain the corresponding equation of motion for the Green's function:

$$\begin{aligned} [i\partial_t - h(\mathbf{x})]G(\mathbf{x},t,\mathbf{x}',t') + i \int d\mathbf{x}'' v(\mathbf{r}, \mathbf{r}'') \langle N | T [\psi_H^\dagger(\mathbf{x}'',t) \psi_H(\mathbf{x}'',t) \psi_H(\mathbf{x},t) \psi_H^\dagger(\mathbf{x}',t')] | N \rangle \\ = \delta(\mathbf{x} - \mathbf{x}') \delta(t - t') \end{aligned}$$

where:

$$h(\mathbf{x}) = -\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{x}) \qquad v(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

- Note that the expectation value in the second term has the structure of a two-electron Green's function!
- A similar equation can be built for this function and involves the three-electron Green's function, and so on...

# Self-energy

Instead of working with high-order Green's functions and a chain of equations of motion, it is more convenient to introduce a **self-energy operator  $\Sigma$**  such that

$$[i\partial_t - h(\mathbf{x}) - V_H(\mathbf{x})]G(\mathbf{x}, t, \mathbf{x}', t') - \int d\mathbf{x}'' dt'' \Sigma(\mathbf{x}, t, \mathbf{x}'', t'')G(\mathbf{x}'', t'', \mathbf{x}', t') = \delta(\mathbf{x} - \mathbf{x}')\delta(t - t')$$

where:

$$V_H(\mathbf{x}) = \int d\mathbf{x}' v(\mathbf{r}, \mathbf{r}') G(\mathbf{x}', t, \mathbf{x}', t) = \int d\mathbf{x}' \frac{n(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|}$$

is the Hartree potential, the same we have seen in DFT!

Note that:

- $V_H$  represents the average potential in the system. As we have seen, it corresponds to the classical electrostatic electron-electron repulsion.
- **$\Sigma$  represents the effects of exchange and correlation in the system**, but it is more general than the exchange-correlation potential  $V_{xc}$  from DFT, as it is non-local and time-dependent!



# Quasiparticle equations

By Fourier transforming the equation of motion for  $G$ , we arrive at:

$$[\epsilon - h(\mathbf{x}) - V_H(\mathbf{x})]G(\mathbf{x}, \mathbf{x}', \epsilon) - \int d\mathbf{x}'' \Sigma(\mathbf{x}, \mathbf{x}'', \epsilon)G(\mathbf{x}'', \mathbf{x}', \epsilon) = \delta(\mathbf{x} - \mathbf{x}')$$

By using its spectral representation, we obtain the **quasiparticle equations**:

$$[\epsilon_s - h(\mathbf{x}) - V_H(\mathbf{x})]f_s(\mathbf{x}) - \int d\mathbf{x}'' \Sigma(\mathbf{x}, \mathbf{x}'', \epsilon_s)f_s(\mathbf{x}'') = 0$$

Note that:

- $\Sigma$  is energy dependent, so it includes dynamical effects from excitations. The many-body nature of the problem is encoded in this dependence.
- $\Sigma$  is non-Hermitian, so the eigenvalues  $\epsilon_s$  are complex. The real parts correspond to excitation energies, as we have discussed, and the (inverse) imaginary parts are related to lifetimes.
- When the lifetimes are long, we can think of quasiparticles with energy  $\text{Re}(\epsilon_s)$  and wavefunctions  $f_s(\mathbf{x})$ .

# Hedin's equations

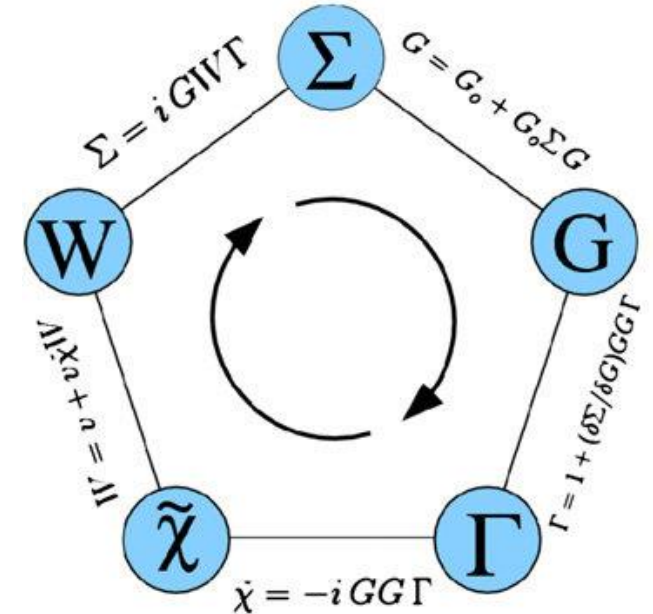
It can be shown that  $\Sigma$  satisfies a set of four coupled integral equations:

$$W(12) = v(1,2) + \int d(34)v(13)P(34)W(42),$$

$$P(12) = -i \int d(34)G(13)G(41^+)\Gamma(34; 2),$$

$$\Sigma(12) = i \int d(34)G(13)\Gamma(32; 4)W(41^+),$$

$$\Gamma(12; 3) = \delta(12)\delta(13) + \int d(4567)\frac{\delta\Sigma(12)}{\delta G(45)}G(46)G(75)\Gamma(67; 3).$$



- They relate the self-energy  $\Sigma$  to the Green's function  $G$ , the screened Coulomb interaction  $W$ , the polarizability  $P$  (or  $\tilde{\chi}$ ) and the vertex function  $\Gamma$ .
- In these equations (and in the following),  $1 = \mathbf{x}_1, t_1$  is a short notation for spatial, spin and time variables.

# GW approximation

Hedin's equations provide a perturbation expansion for  $\Sigma$  in powers of  $W$ . The first-order term is found by setting the vertex function to:

$$\Gamma^{GW}(12; 3) = \delta(12)\delta(13)$$

which results in:

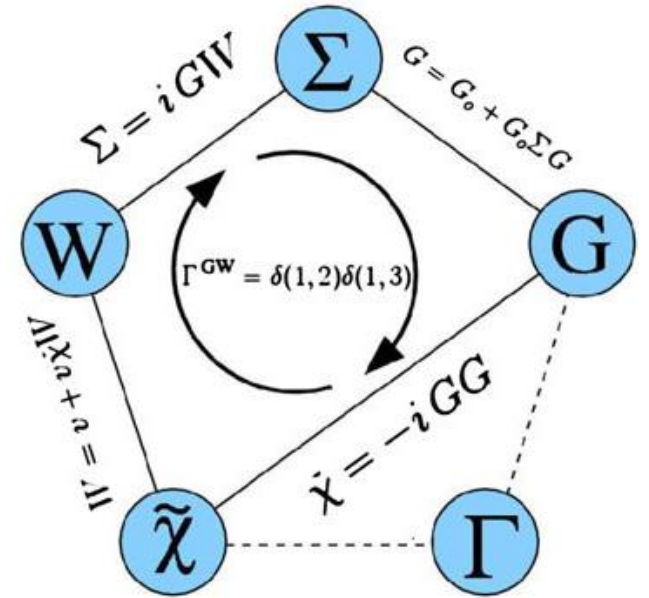
$$\Sigma^{GW}(12) = iG(12)W(1^+2)$$

This is the GW approximation for  $\Sigma$ , named after its form.

The polarization reduces to

$$P^{GW}(12) = -iG(12^+)G(21)$$

which consists in excitations of non-interacting electron-hole pairs (bubble approximation).



# Dielectric function

We may define a dielectric function  $\varepsilon$  such that

$$W(12) = \int d(3) \varepsilon^{-1}(13) v(32)$$

From the previous equation for  $W$ , we may also write:

$$\varepsilon(12) = \delta(12) - \int d(3) v(13) P(32)$$

such that  $\varepsilon$  and  $W$  can also be directly evaluated from the Green's function  $G$ .

- Physically,  $\varepsilon$  describes the effects of screening in the system.
- Since  $\Sigma^{GW} \sim GW$ , we see that the effects of correlation, contained in  $\Sigma$ , are related to screening.
- If correlation effects are neglected, we would not have screening and  $\Sigma^{HF} \sim Gv$ . This corresponds to the Hartree-Fock approximation!

# GW in practice

In routine calculations, it is common practice to start with a DFT calculation, which provides KS single-particle wavefunctions  $\phi_s(x)$  and energies  $\varepsilon_s^{DFT}$ .

With these ingredients, we build an initial expression for the single-particle Green's Function:

$$G_0(\mathbf{x}, \mathbf{x}', \varepsilon) = \sum_s \left[ \frac{\phi_s(\mathbf{x})\phi_s^*(\mathbf{x}')}{\varepsilon - \varepsilon_s^{DFT} + i\eta} + \frac{\phi_s(\mathbf{x})\phi_s^*(\mathbf{x}')}{\varepsilon - \varepsilon_s^{DFT} - i\eta} \right]$$

Comparing with the exact spectral representation shown before, note that:

- We replace the quasi-particle wavefunctions  $f_s$  with the KS wavefunctions  $\phi_s$ .
- We replace the excitation energies from the ground state with  $N$  electrons to excited states with  $N \pm 1$  electrons with the KS energies  $\varepsilon_s$ .

With  $G_0$ , we may build initial expressions for  $P$ ,  $\varepsilon$  and  $W$ , resulting in a self-energy  $\Sigma_0 \sim G_0 W_0$ .

# GW in practice

Following this approach, it is convenient to rewrite the quasiparticle equations as:

$$[\varepsilon_s^{GW} - h(\mathbf{x}) - V_H(\mathbf{x}) - V_{xc}(\mathbf{x})]f_s(\mathbf{x}) - \int d\mathbf{x}'' [\Sigma_0^{GW}(\mathbf{x}, \mathbf{x}', \varepsilon_s^{GW}) - V_{xc}(\mathbf{x}')\delta(\mathbf{x} - \mathbf{x}')]f_s(\mathbf{x}') = 0$$

where  $V_{xc}$  is the exchange-correlation potential from DFT.

Treating  $\Sigma - V_{xc}$  as a perturbation, first-order perturbation theory yields:

$$\varepsilon_s^{GW} = \varepsilon_s^{DFT} + \langle \phi_s | \Sigma_0(\varepsilon_s^{GW}) - V_{xc} | \phi_s \rangle$$

which may be solved for  $\varepsilon_s^{GW}$ .

We may obtain a solution consistent with a first-order correction by making a Taylor expansion of  $\Sigma$ :

$$\Sigma_0(\varepsilon_s^{GW}) = \Sigma_0(\varepsilon_s^{DFT}) + \left. \frac{d\Sigma_0(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\varepsilon_s^{DFT}} (\varepsilon_s^{GW} - \varepsilon_s^{DFT})$$

# GW in practice

By combining the two equations, we obtain an expression for the quasiparticle energies:

$$\varepsilon_s^{GW} = \varepsilon_s^0 + \frac{d\Sigma_0(\varepsilon)/d\varepsilon}{1 - d\Sigma_0(\varepsilon)/d\varepsilon} \Big|_{\varepsilon=\varepsilon_s^{DFT}} (\varepsilon_s^0 - \varepsilon_s^{DFT}) \qquad \varepsilon_s^0 = \varepsilon_s^{DFT} + \langle \phi_s | \Sigma_0(\varepsilon_s^{DFT}) - V_{xc} | \phi_s \rangle$$

We also assume that  $f_s(\mathbf{x}) \approx \phi_s(\mathbf{x})$ , such that the quasiparticle wavefunctions do not differ substantially from the DFT wavefunctions.

Note that:

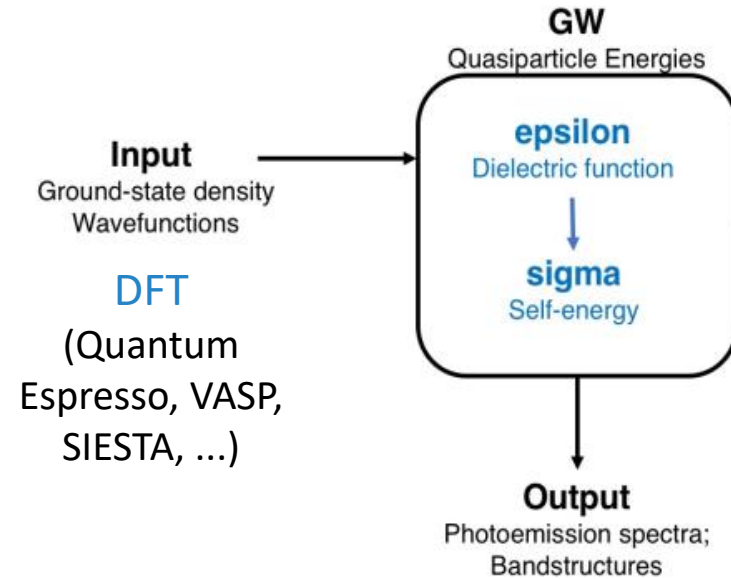
- We could build a new expression for the Green's function by inserting  $f_s(\mathbf{x})$  and  $\varepsilon_s^{GW}$  in the spectral representation.
- The new function  $G_1$  could be used to update  $W$  and/or  $\Sigma$  and the resulting  $\Sigma_1$  could be used to obtain a new set of quasiparticle energies.
- This procedure could be iterated until self-consistency is achieved.
- However, in most calculations, the first iteration is enough to produce accurate quasiparticle energies. Such an approach is called single-shot GW or  $G_0W_0$ .

# Overview of a typical $G_0W_0$ calculation



BerkeleyGW

<https://berkeleygw.org/>



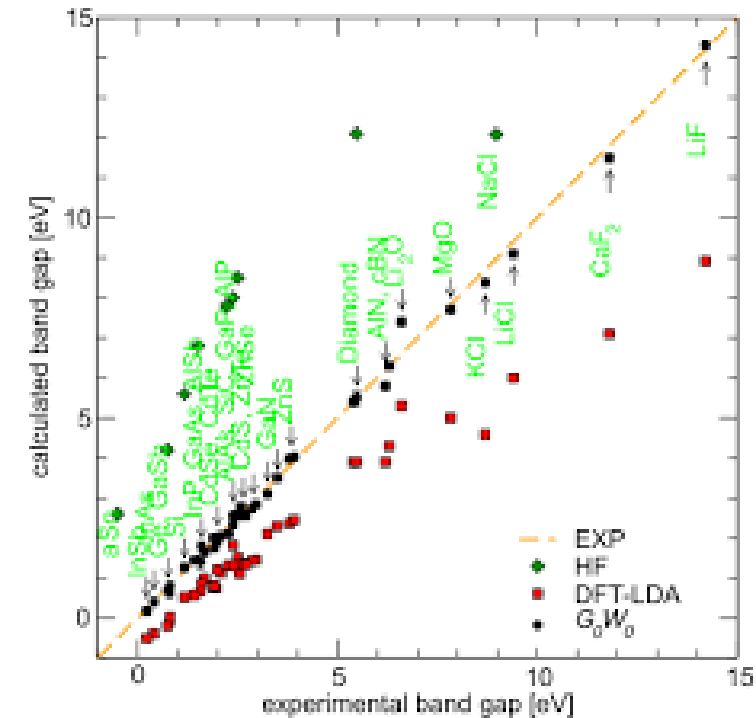
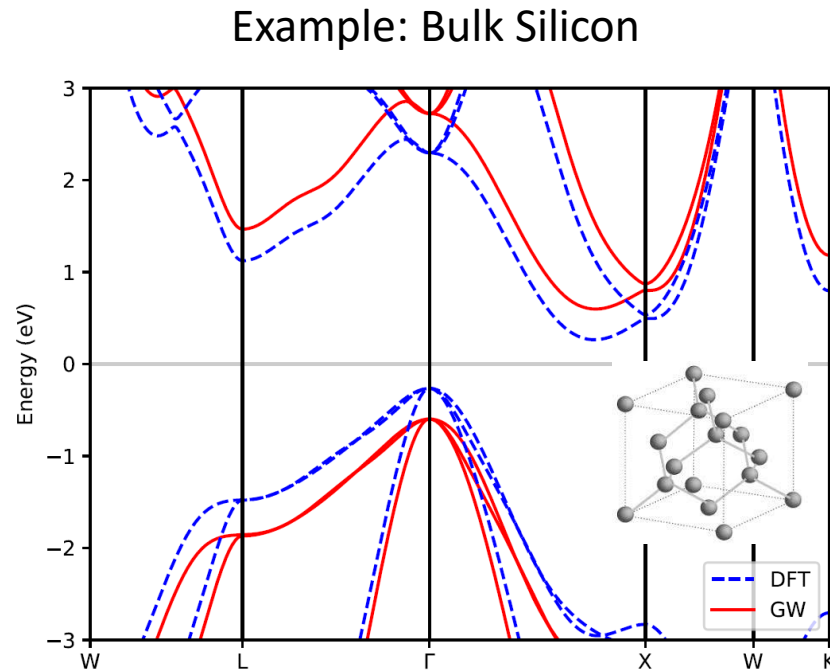
- **Computational implementation:** BerkeleyGW, Yambo, ABINIT, ...
- **Convergence parameters:** number of empty bands, **k**-point sampling and cutoff energy of the dielectric function (in reciprocal space)
- **Typical bottlenecks:** memory (RAM) and number of CPUs

Mark S. Hybertsen and Steven G. Louie, Phys. Rev. B 34, 5390 (1986)

Jack Deslippe *et. al.*, Comput. Phys. Commun. 183, 1269 (2012)

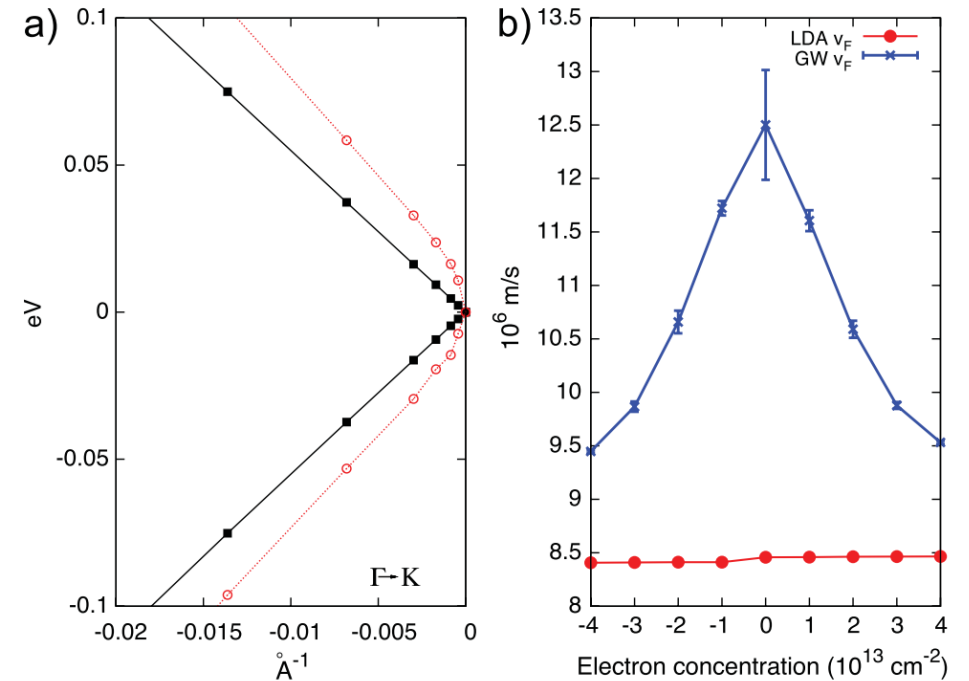
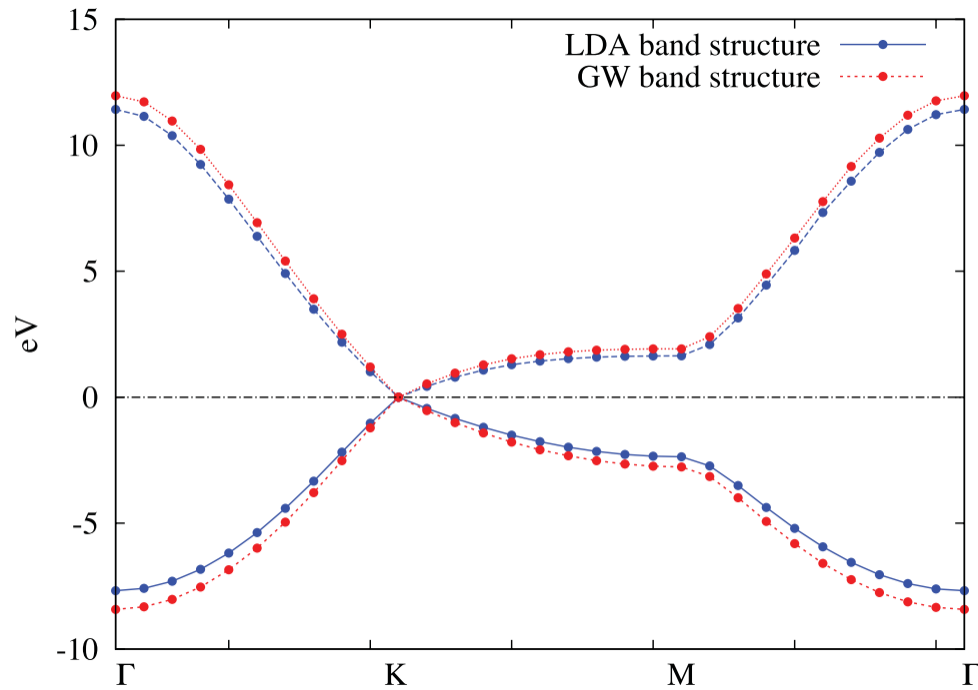


# Application: Gap renormalization in semiconductors and insulators



- Main effect of the quasiparticle corrections is a rigid shift of the unoccupied states, increasing the band gap and bringing it to close agreement with experiment.

# Application: Fermi velocity renormalization in graphene

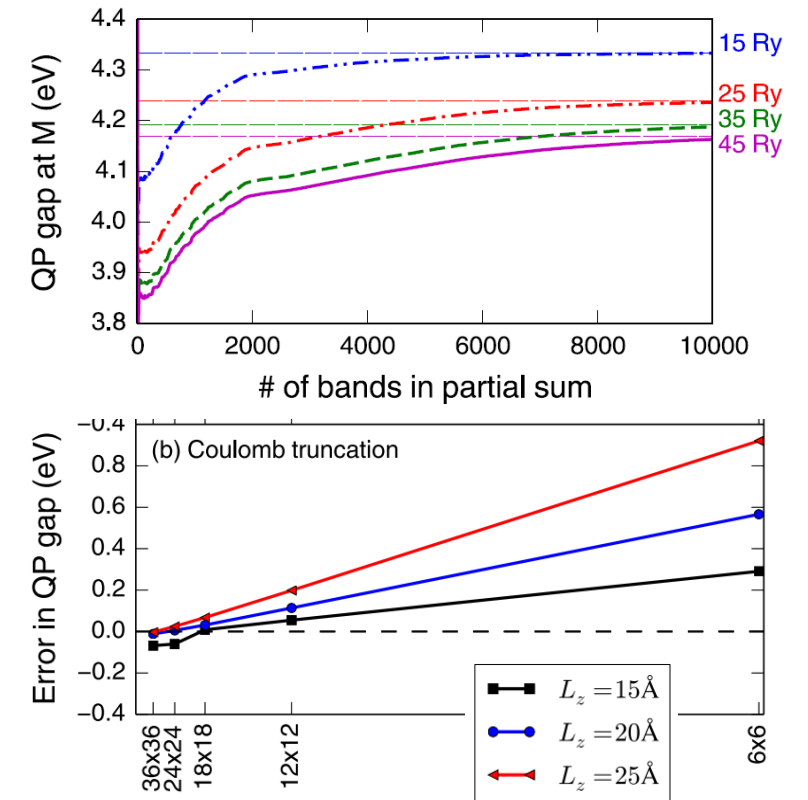
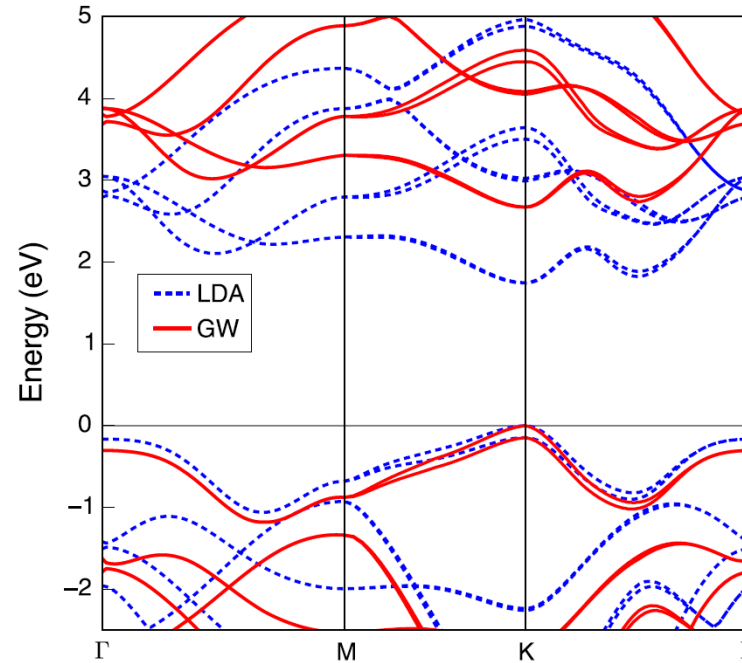
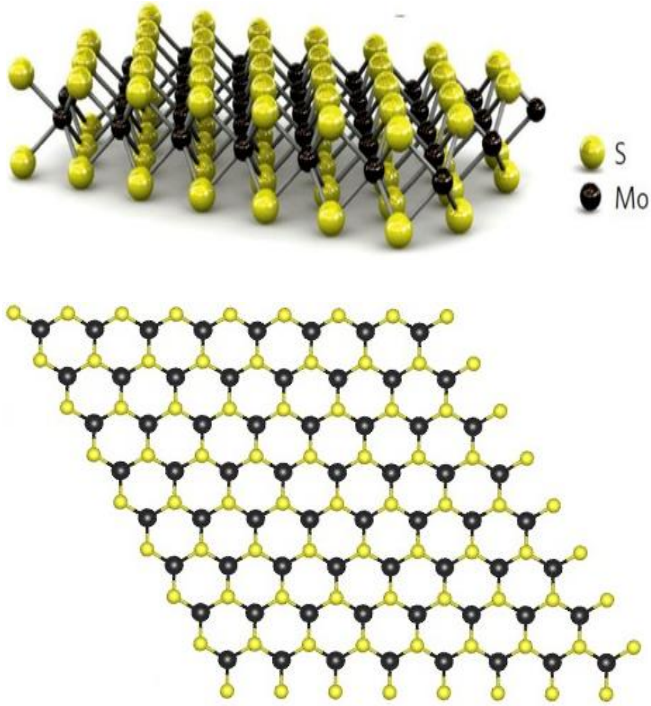


- Fermi velocity (slope of linear dispersion) increases due to quasiparticle effects.
- Magnitude of renormalization decreases as the system is doped.

Paolo E. Trevisanutto *et. al.*, Phys. Rev. Lett. **101**, 226405 (2008)

C. Attaccalite and A. Rubio, Phys. Status Solidi B **246**, 2523 (2009)

# Challenges: Convergence in low-dimensional systems



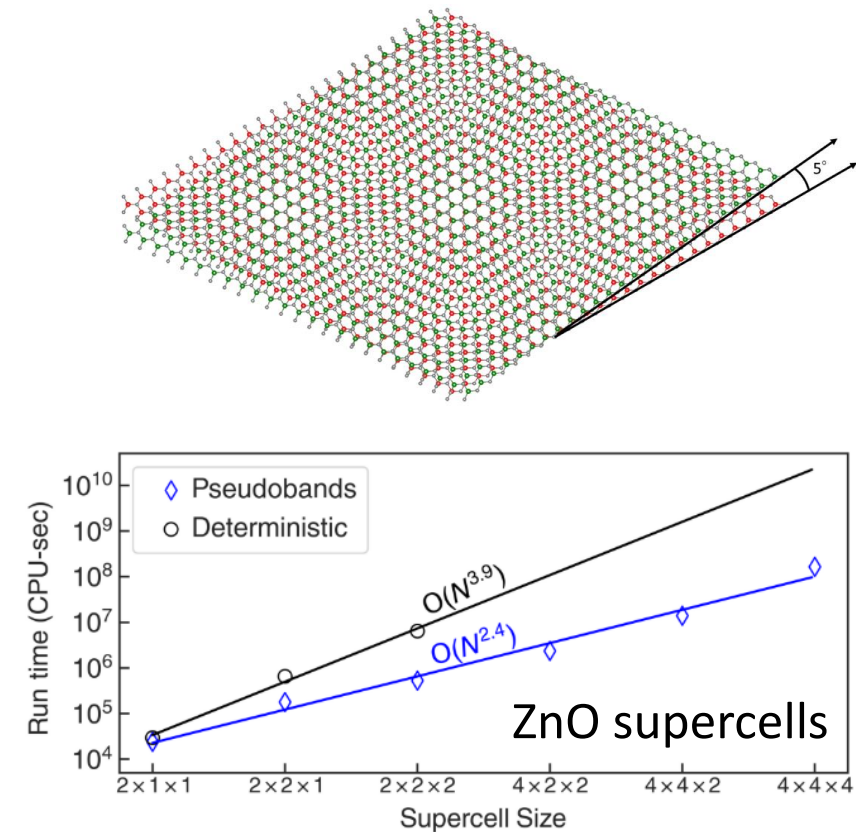
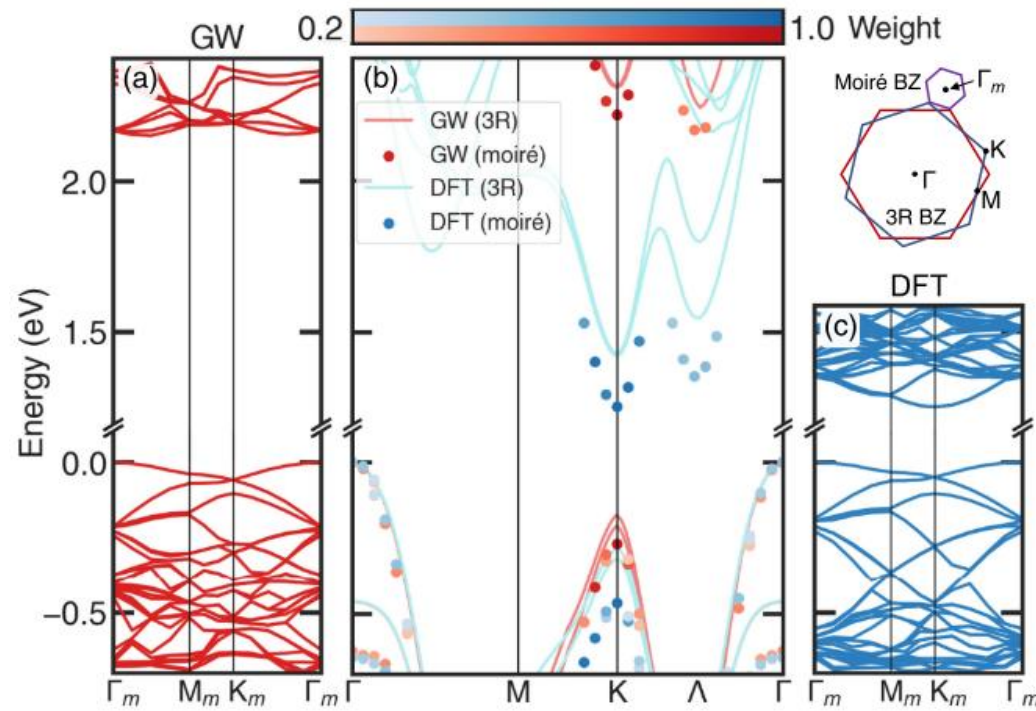
- Calculations in such systems typically require very dense k-point grids and thousands of empty bands.
- Recent developments have accelerated these calculations considerably.

Diana Y. Qiu, Felipe H. da Jornada, and Steven G. Louie, Phys. Rev. B **93**, 235435 (2016)

Felipe H. da Jornada, Diana Y. Qiu, and Steven G. Louie, Phys. Rev. B **95**, 035109 (2017)

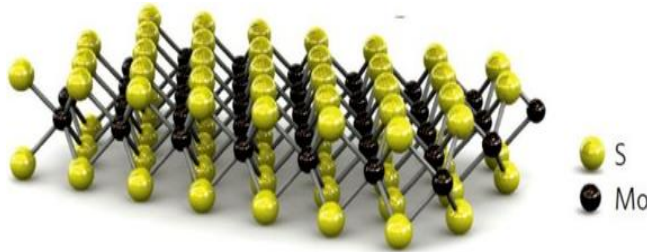
# Application: GW band structure of Moiré systems and other supercells

Twisted MoS<sub>2</sub> bilayer (5,75° – 546 atoms)

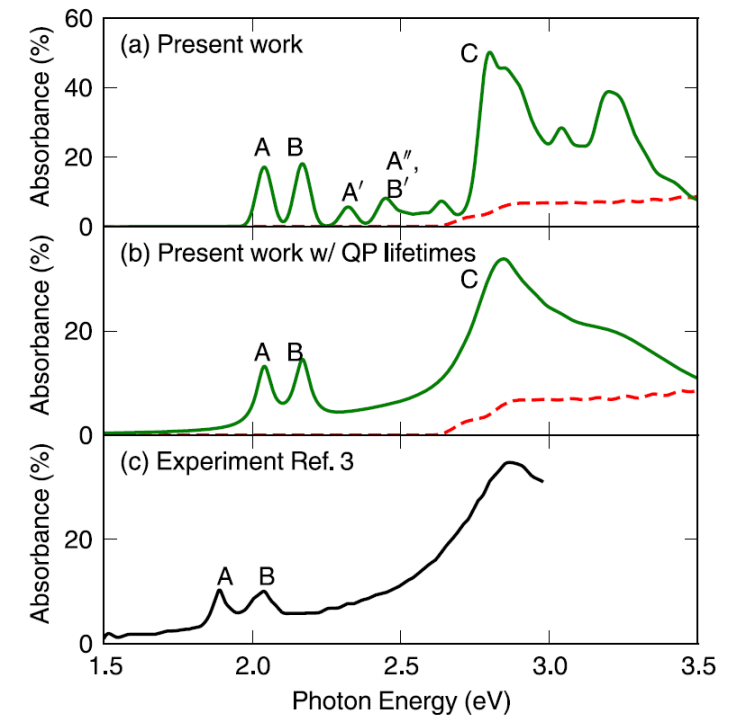


➤ GW calculations in supercells are now more feasible using mixed stochastic-deterministic approaches.

# The necessity to go beyond GW

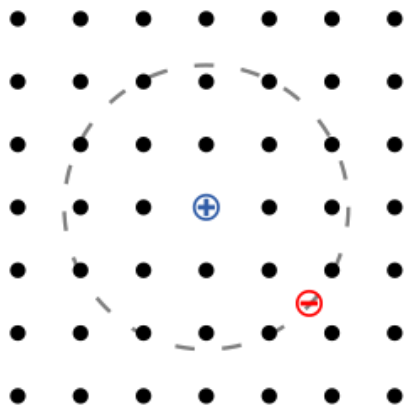
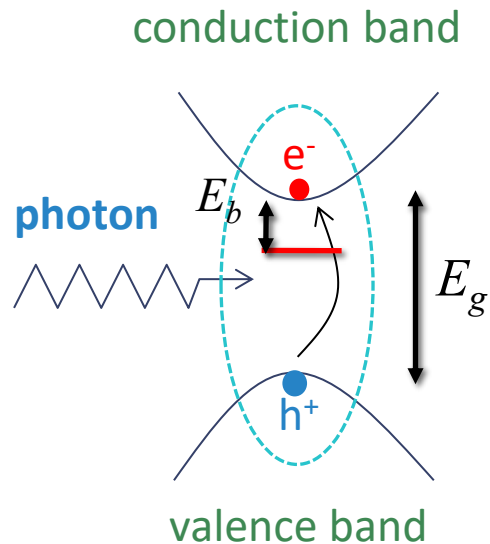


$$\varepsilon_2(\omega) = \frac{16\pi}{\omega^2} \sum_{v,c} |\langle v | \mathbf{v} \cdot \boldsymbol{\lambda} | c \rangle|^2 \delta(\omega - (E_c - E_v))$$



- If we plug the GW band structure and wavefunctions in the formula for the dielectric function, we obtain a non-interacting absorption spectrum such as the red dashed curve above.
- This curve clearly does not agree with experiment. What are we missing?

# Excitonic effects



- A photon may excite an electron from the valence to the conduction band.
- The electron leaves a hole behind, which acts as a positive charge center.
- The electron and hole attract each other, forming a bound quasiparticle known as the **exciton**.
- In many materials, the exciton behaves as a hydrogen-like atom with a very large radius (Wannier exciton) due to the screening environment.
- The binding energy of the pair ( $E_b$ ) reduces the actual excitation energy of the exciton. Therefore, bound excitons typically appear in absorption spectra as sharp peaks below the single-particle band gap.
- In 2D materials, binding energies are much larger due to reduced screening, thus excitonic effects are extremely important!

# MBPT description of excitons

Since the exciton is a two-particle bound state, we need to introduce a **two-particle Green's function**:

$$G_2(1, 2; 1', 2') = (-i)^2 \langle N | T [\psi_H(1) \psi_H(2) \psi_H^\dagger(2') \psi_H^\dagger(1')] | N \rangle$$

We will further assume that  $t_2, t_2' > t_1, t_1'$ , such that:

$$G_2(1, 2; 1', 2') = (-i)^2 \langle N | T [\psi_H(2) \psi_H^\dagger(2')] T [\psi_H(1) \psi_H^\dagger(1')] | N \rangle$$

- In this form,  $G_2$  describes the propagation of an electron-hole pair.
- We will also assume that the electron and the hole in a pair are created simultaneously, such that  $t_1' = t_1^+$  and  $t_2' = t_2^+$ .
- Finally, since the Hamiltonian is time-independent,  $G_2$  is a function only of the time difference  $t_1 - t_2$ .

Michael Rohlfing and Steven G. Louie, Phys. Rev. B 62, 4927 (2000)

G. Strinati, Rivista del Nuovo Cimento 11 (1988)



# Bethe-Salpeter equation (BSE)

In this framework, it is actually more convenient to work with a **two-particle correlation function**:

$$L(1, 2; 1', 2') = -G_2(1, 2; 1', 2') + G(1, 1')G(2, 2')$$

It can be shown that  $L$  satisfies the **Bethe-Salpeter equation**:

$$L(1, 2; 1', 2') = L_0(1, 2; 1', 2') + \int d(3456) L_0(1, 4; 1', 3) K(3, 5; 4, 6) L(6, 2; 5, 2')$$

where:

- $L_0(1, 2; 1', 2') = G(1, 2')G(2, 1')$  is the propagator for a non-interacting electron-hole pair
- $K(3, 5; 4, 6) = \frac{\delta[V_H(3)\delta(3,4) + \Sigma(3,4)]}{\delta G(6,5)}$  is the interaction kernel

Note that, when  $K = 0$ , we have  $L = L_0$ , as expected.



# Spectral representations

As in the single-particle case, it is more convenient to work in the energy space. For that end, we introduce spectral representations for the non-interacting correlation functions:

$$L_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \varepsilon) = \sum_{v,c} \left[ \frac{\phi_c(\mathbf{x}_1) \phi_v^*(\mathbf{x}'_1) \phi_v(\mathbf{x}_2) \phi_c^*(\mathbf{x}'_2)}{\varepsilon - (E_c - E_v)} - \frac{\phi_v(\mathbf{x}_1) \phi_c^*(\mathbf{x}'_1) \phi_c(\mathbf{x}_2) \phi_v^*(\mathbf{x}'_2)}{\varepsilon + (E_c - E_v)} \right]$$

where the wavefunctions and energies are known from a single-particle calculation (DFT or GW) and  $v$  and  $c$  denote occupied (hole) and empty (electron) states, respectively.

We then introduce a similar representation for the interacting correlation function:

$$L(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \varepsilon) = \sum_S \left[ \frac{\chi_S(\mathbf{x}_1, \mathbf{x}'_1) \chi_S^*(\mathbf{x}_2, \mathbf{x}'_2)}{\varepsilon - \Omega_S} - \frac{\chi_S(\mathbf{x}_2, \mathbf{x}'_2) \chi_S^*(\mathbf{x}_1, \mathbf{x}'_1)}{\varepsilon + \Omega_S} \right]$$

By solving the BSE, we are able to obtain the new excitation energies  $\Omega_S$  and the electron-hole (exciton) wavefunctions  $\chi_S(\mathbf{x}, \mathbf{x}')$ .

# BSE in a quasiparticle basis

In practical applications, we write the exciton wavefunctions in terms of the single-particle functions:

$$\chi_s(\mathbf{x}, \mathbf{x}') = \sum_{vc} A_{vc}^S \phi_c(\mathbf{x}) \phi_v^*(\mathbf{x}') + B_{vc}^S \phi_v(\mathbf{x}) \phi_c^*(\mathbf{x}')$$

In that basis, the BSE is transformed into an eigenvalue problem:

$$(E_c - E_v - \Omega_S) A_{vc}^S + \sum_{v'c'} K_{vc,v'c'}^{AA} (\Omega_S) A_{v'c'}^S + \sum_{v'c'} K_{vc,v'c'}^{AB} (\Omega_S) B_{v'c'}^S = 0$$

and an analogous equation for  $B_{vc}^S$ .

- It is common to assume that  $K_{vc,v'c'}^{AB} \approx 0$ , such that the two equations decouple and we deal only with the  $A_{vc}^S$  equation (where  $B_{vc}^S = 0$ ). This is known as the **Tamm-Dancoff approximation**.
- It works very well for semiconductors and insulators, but care must be taken for metals!

# The interaction kernel

By using the GW approximation for  $\Sigma$  and assuming that the derivative of  $W$  with respect to  $G$  may be neglected, we have:

$$\begin{aligned} K(3, 5; 4, 6) &= \frac{\delta[V_H(3)\delta(3, 4) + \Sigma(3, 4)]}{\delta G(6, 5)} = -i\delta(3, 4)\delta(5, 6)v(3, 6) + i\delta(3, 6)\delta(4, 5)W(3, 4) \\ &= K^x(3, 5; 4, 6) + K^d(3, 5; 4, 6) \end{aligned}$$

- $K^d$  corresponds to a **screened direct interaction**. It is responsible for the attractive nature of the e-h interaction and the formation of bound exciton states.
- $K^x$  corresponds to an **unscreened exchange interaction**. It is responsible for the fine details of the excitonic spectrum, such as the singlet-triplet splitting.

# Absorption with excitonic effects

By using the solutions of the BSE, we may now adapt the expression for the imaginary part of the dielectric function as:

$$\varepsilon_2(\omega) = \frac{16\pi}{\omega^2} \sum_S |\langle 0 | \mathbf{v} \cdot \boldsymbol{\lambda} | S \rangle|^2 \delta(\omega - \Omega_S)$$

where  $|0\rangle$  is the ground state and the sum runs over all excited states  $|S\rangle$ .

The matrix elements can be expressed in terms of the non-interacting ones:

$$\langle 0 | \mathbf{v} | S \rangle = \sum_{v,c} A_{vc}^S \langle v | \mathbf{v} | c \rangle$$

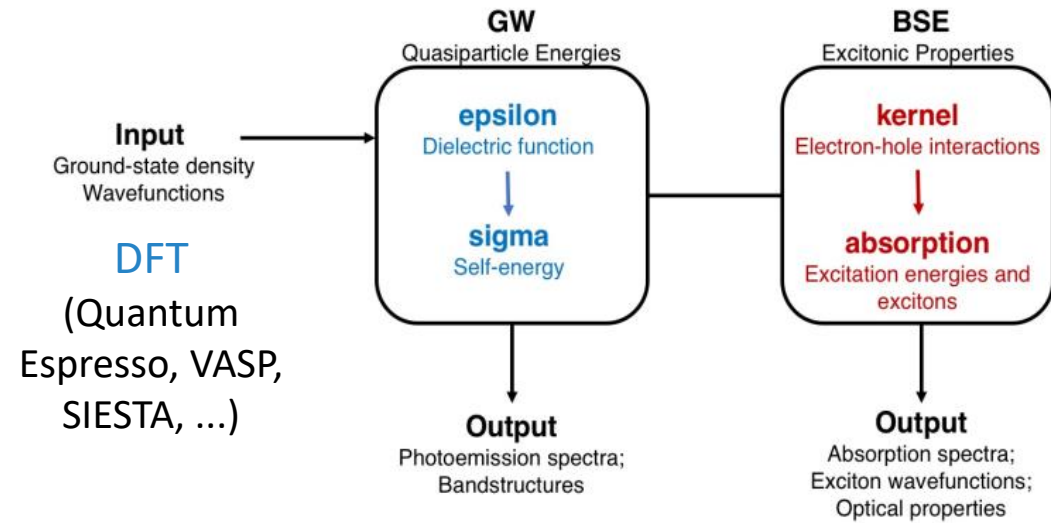
We are now fully equipped to obtain absorption spectra including excitonic effects from ab-initio calculations!

# Full overview of a typical GW/BSE calculation



BerkeleyGW

<https://berkeleygw.org/>



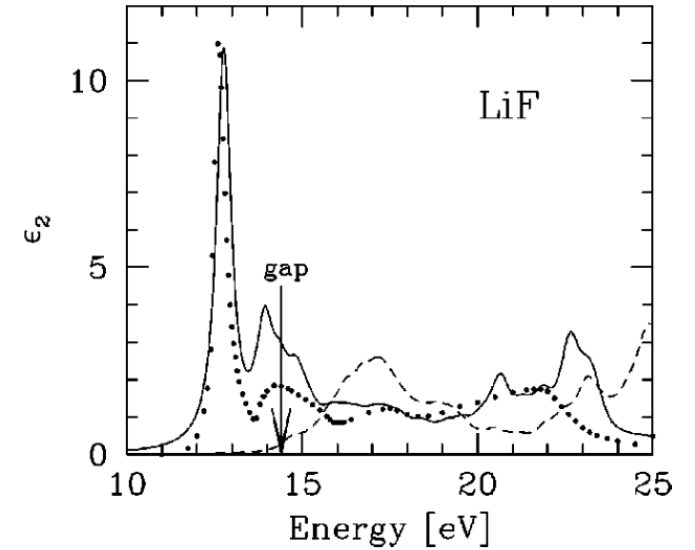
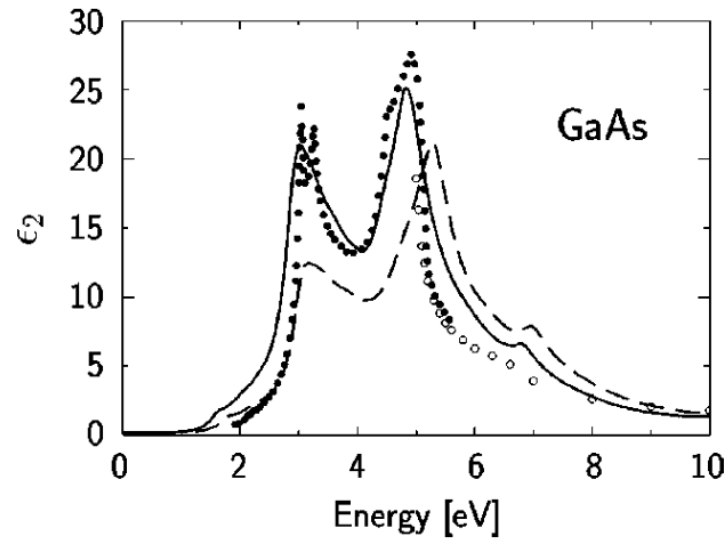
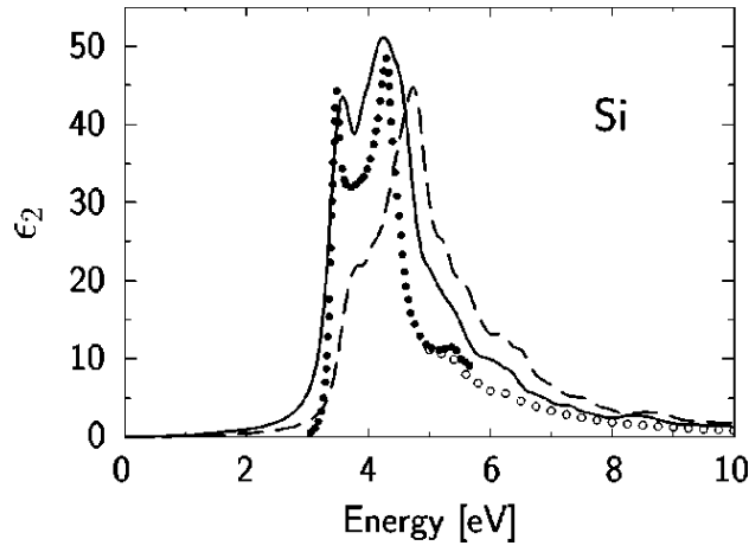
- **Computational implementation:** BerkeleyGW, Yambo, ABINIT, ...
- **Convergence parameters (BSE):** number of single-particle occupied ( $v$ ) and empty ( $c$ ) states included in the kernel and  $k$ -point sampling
- **Typical bottlenecks:** memory (RAM) and number of CPUs

Michael Rohlfing and Steven G. Louie, Phys. Rev. B 62, 4927 (2000)

Jack Deslippe *et. al.*, Comput. Phys. Commun. 183, 1269 (2012)

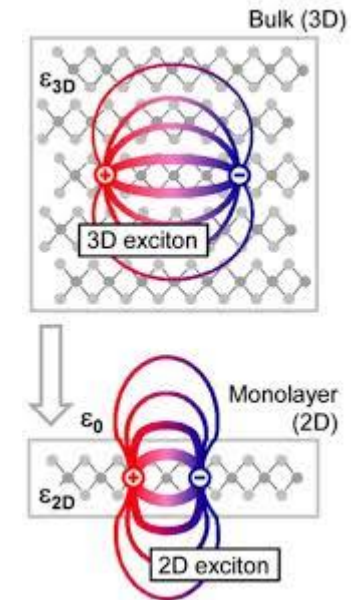
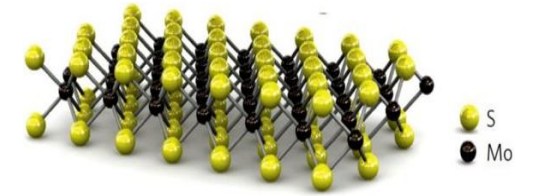
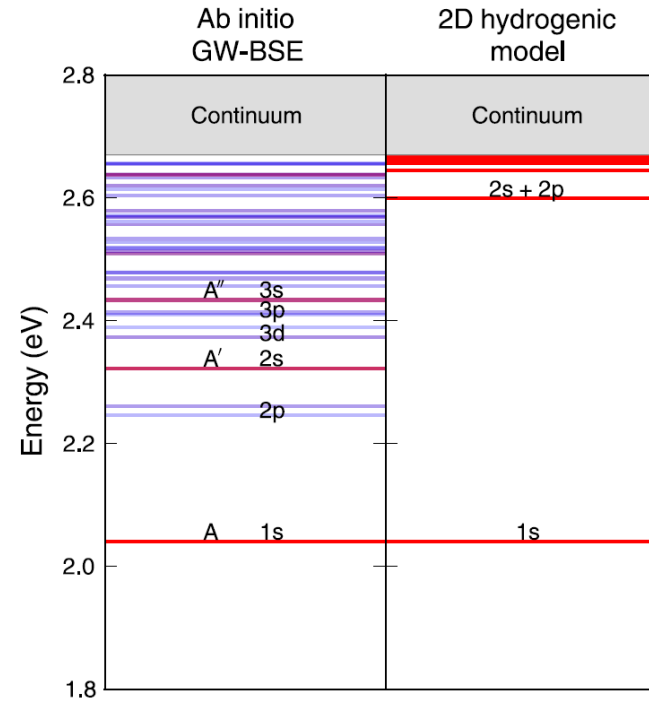
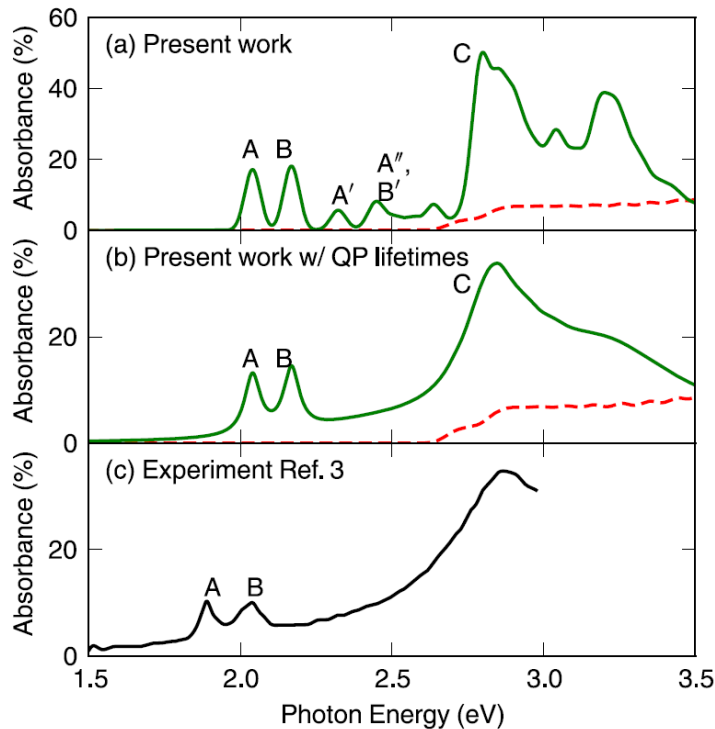
# Application: Bulk (3D) semiconductors and insulators

--- = no-eh  
.... = eh  
— = exp



- Excitonic effects bring the spectra to closer agreement with experiment.
- Excitonic effects are more important in insulators, where the gap is wider and the screening is weaker.

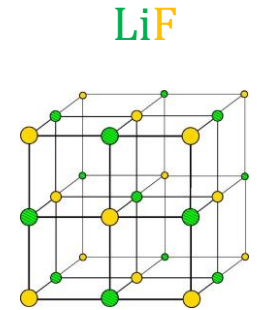
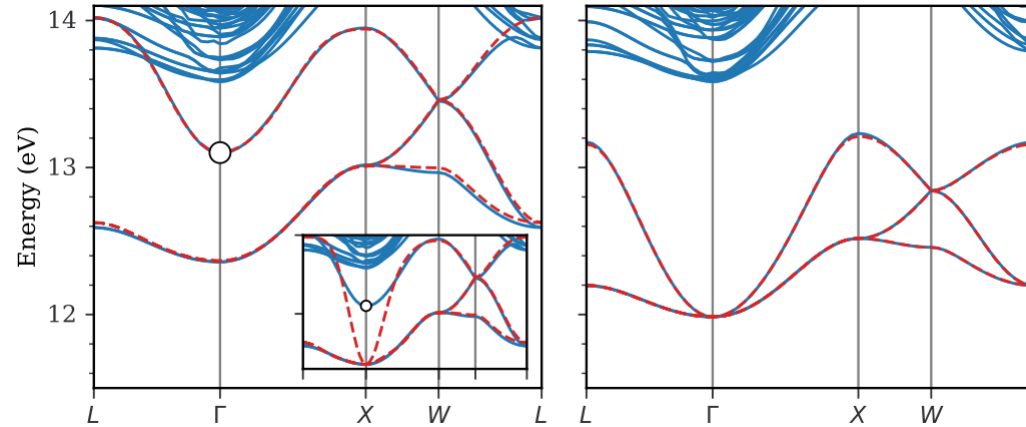
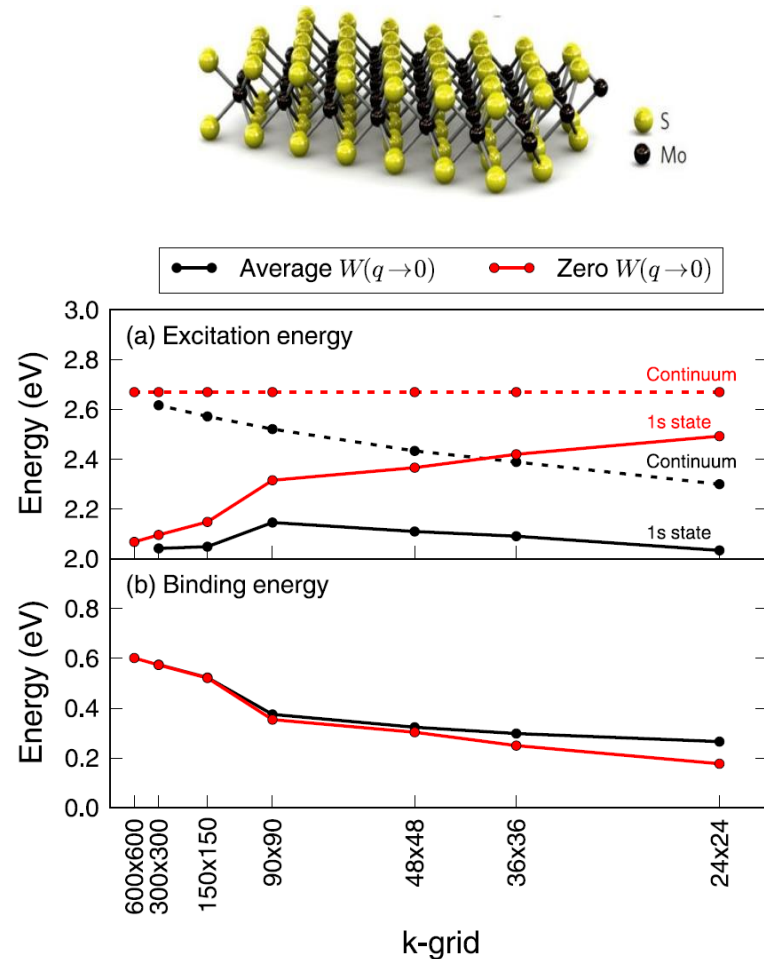
# Application: 2D semiconductors



- Excitonic effects are even more important in 2D materials, as screening is much weaker.
- Screening is also non-homogeneous, resulting in lifted degeneracies and reverse ordering of exciton states in comparison to hydrogenic models.

Diana Y. Qiu, Felipe H. da Jornada, and Steven G. Louie, Phys. Rev. B **93**, 235435 (2016)

# Challenges: Convergence in low-dimensional systems



- Typical calculations can be very hard to converge, requiring prohibitively dense **k**-point grids.
- Recent developments: cluster interpolation algorithms (CSI), BSE in a wannier basis, wannier interpolation, etc.

Diana Y. Qiu, Felipe H. da Jornada, and Steven G. Louie, Phys. Rev. B **93**, 235435 (2016)

Felipe H. da Jornada, Diana Y. Qiu, and Steven G. Louie, Phys. Rev. B **95**, 035109 (2017)

Jonah B. Haber, Diana Y. Qiu, Felipe H. da Jornada, and Jeffrey B. Neaton, Phys. Rev. B **108**, 125118 (2023)



# Future prospects: Non-linear optical properties with excitonic effects

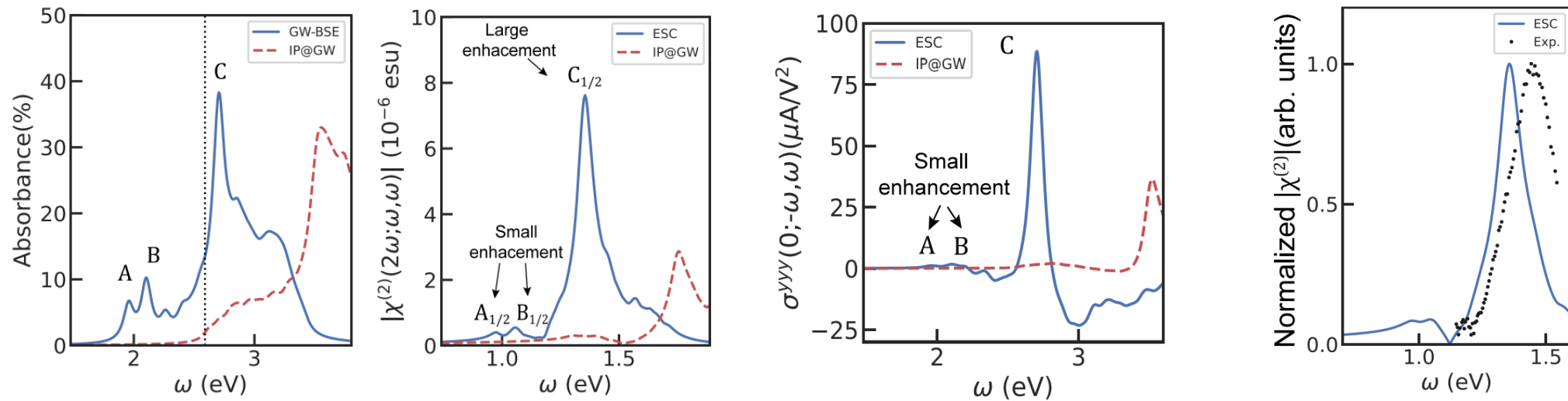
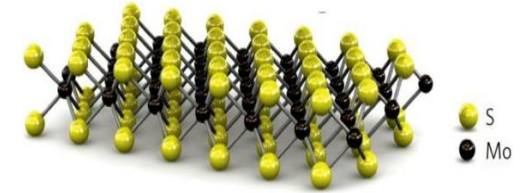
It can be shown that the BSE is, in fact, equivalent to a linear response theory of the optical properties of materials.

Going beyond linear-response and including excitonic effects is very challenging. Recent possibilities include:

- **Time-domain methods (TDDFT, TD-aGW, ...):** non-perturbative in external fields and excitonic effects are more easily included.
- **Perturbation methods (sum over excitonic states):** perturbation expansion is carried on a basis of excitonic states obtained from the solutions of the BSE. Typically, such methods are cheaper than time-domain methods, but much harder to go beyond second-order responses.

**Phenomena of interest:** second harmonic generation (SHG) and shift currents in non-centrosymmetric materials, high harmonic generation, ...

# Application: SHG and shift currents in 2D materials (MBPT)

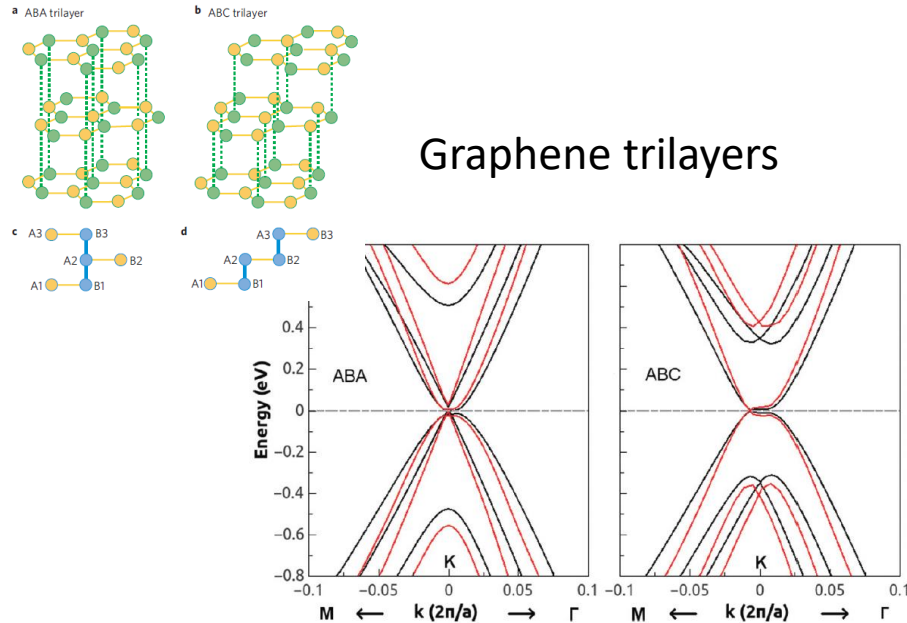
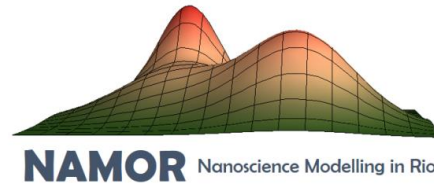


- Excitonic effects typically enhance linear and non-linear responses and bring results to closer agreement with experiments.

Yang-Hao Chan, Diana Y. Qiu, Felipe H. da Jornada, and Steven G. Louie, PNAS 118, e1906938118 (2021)

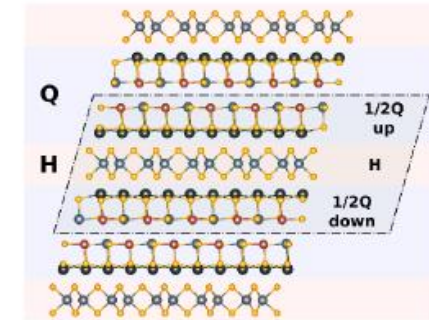
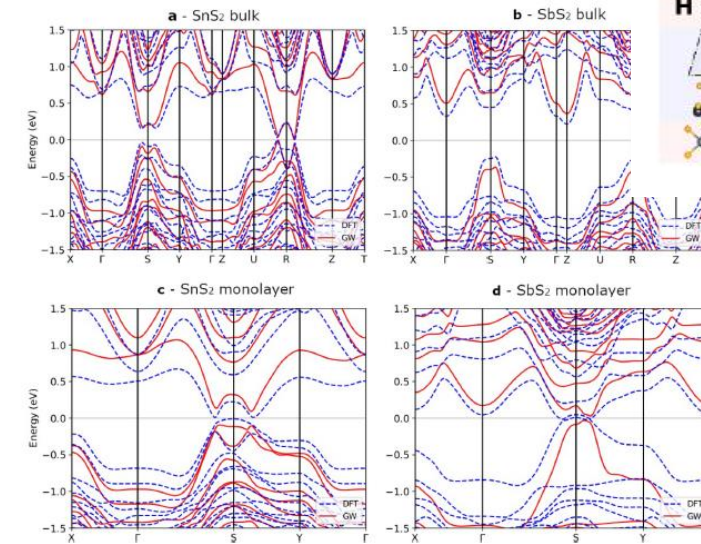
Jiawei Ruan, Yang-Hao Chan, and Steven G. Louie, Nano Lett. 24, 15533 (2024)

# Our research



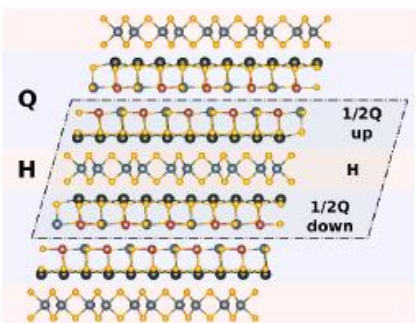
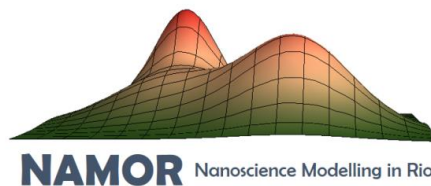
Marcos G. Menezes, Rodrigo B. Capaz, Steven G. Louie,  
Phys. Rev. B **89**, 035431 (2014)

## Franckeite as a topological insulator

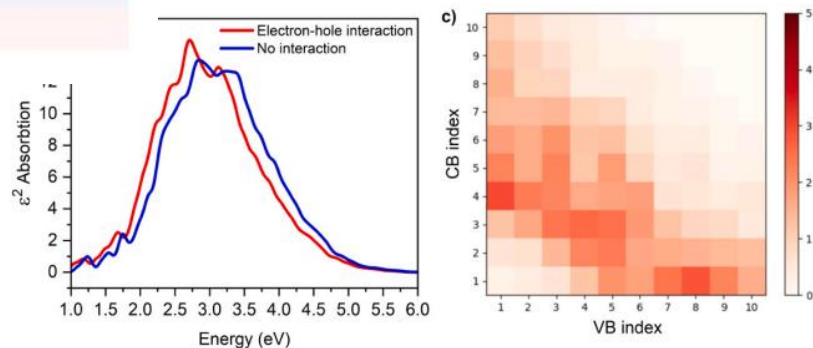


Wendel S. Paz, Marcos G. Menezes, Nathanael N. Batista,  
Gabriel Sanchez-Santolino, Matěj Velický, María Varela, Rodrigo  
B. Capaz, and Juan José Palacios, Nano Lett. **21**, 7781 (2021)

# Our research

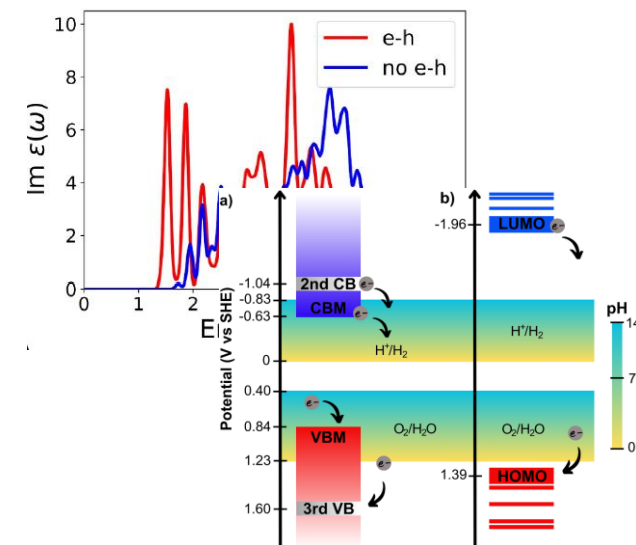
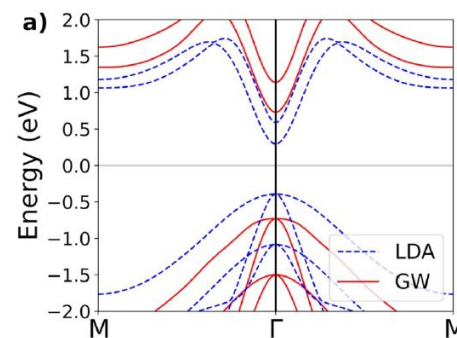
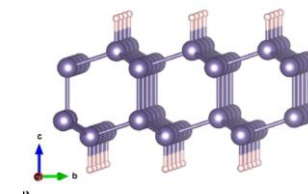


Francite as a photocatalyst  
for NO<sub>x</sub> abatement



Jefferson E. Silveira, Guilherme J. Inacio, Nathanael N. Batista, Wallace P. Morais, Marcos G. Menezes, Juan A. Zazo, Jose A. Casas, Wendel S. Paz, Journal of Environmental Chemical Engineering 12, 111998 (2024)

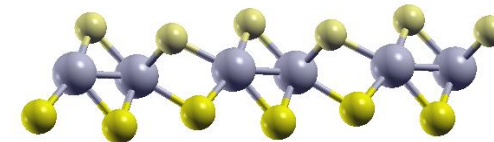
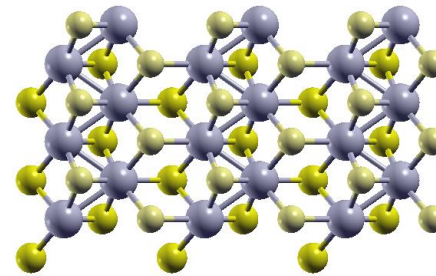
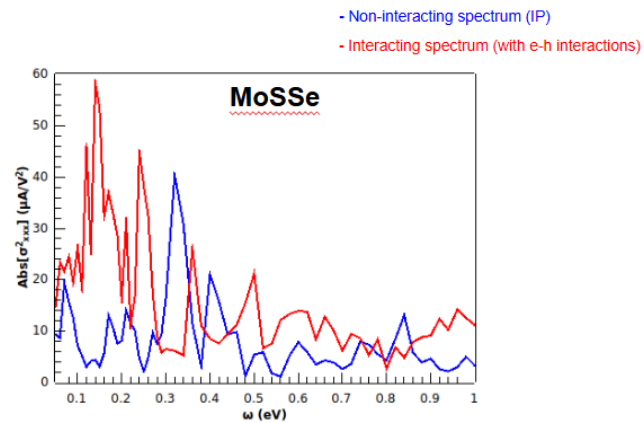
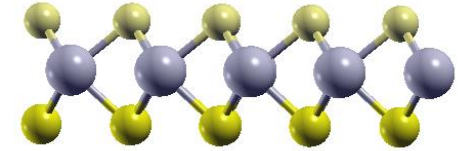
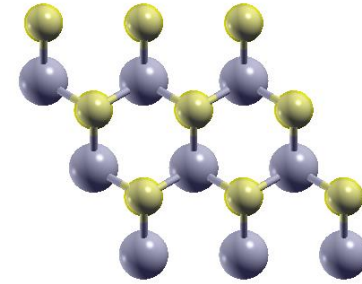
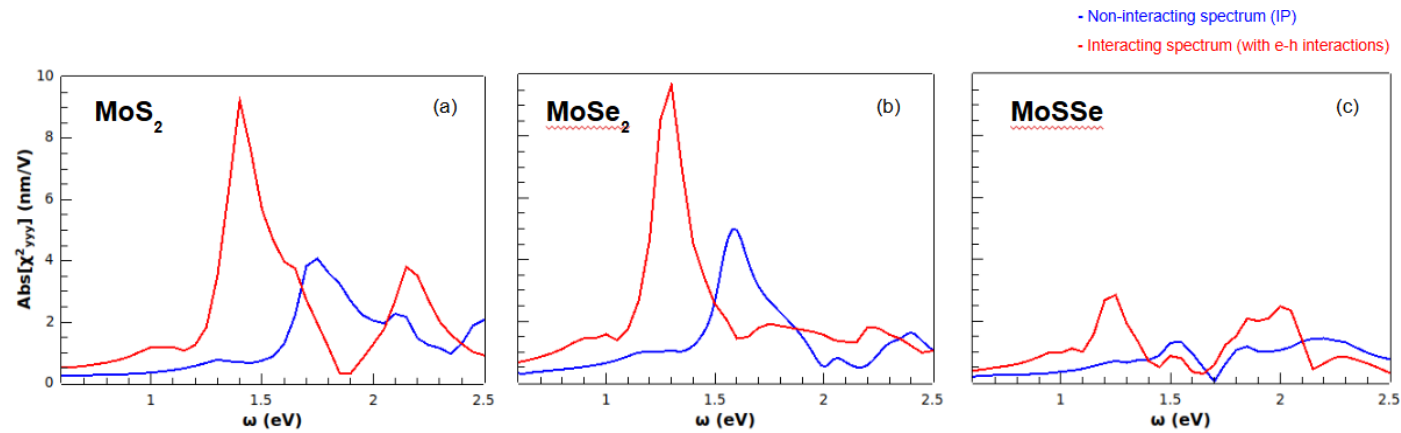
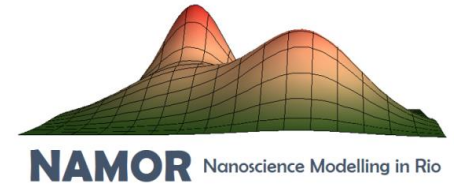
$\alpha$ -Ge (111) as a photocatalyst  
for water splitting



Vinícius G. Garcia, Guilherme J. Inacio, Luciano F. Filho, Luíza T. Pacheco, Fernando N.N. Pansini, Marcos G. Menezes, Wendel S. Paz, FlatChem 48, 100753 (2024)

# Our research

## SHG in Janus TMDs



Marcos G. Menezes, Yang-hao Chan, Felipe H. da Jornada, *in preparation* (2025)

# Summary

- Ground-state DFT is widely successful for the calculation of structural and electronic properties of nanomaterials, but it is typically insufficient to account for their optical properties.
- GW calculations provide a more accurate band structure, with renormalized band gaps in semiconductors and insulators and renormalized band velocities in linear dispersions (such as graphene).
- Excitonic effects are included through the solutions of the BSE. They are very important for an accurate description of absorption spectra of bulk insulators and low-dimensional systems in general, where screening is less effective.
- Convergence of GW/BSE calculations in low-dimensional systems is very challenging due to the required **k**-point grids and number of empty states. Recent developments (subsampling, CSI, stochastic bands, ...) have accelerated these calculations.
- Inclusion of excitonic effects in non-linear responses require approaches that go beyond the BSE, such as time-dependent methods (TDDFT, TD-aGW) or sum over exciton states.



# Our group

## Professors:

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Eduardo Pereira (IC)

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Leandro Benatto

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Juan Palacios (UAM/Spain)

Marcello Neto (UFRJ)

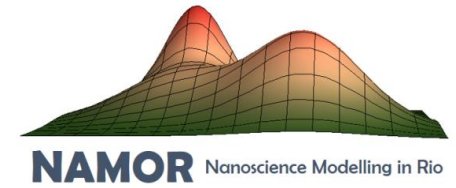
Saif Ullah (Wake Forest/USA)

Wendel Paz (UFES)

Yang-hao Chan (Academia Sinica/Taiwan)

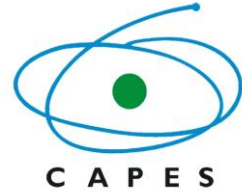
## Research areas:

- Quantum materials
- Semiconductors
- Defects, surfaces and interfaces
- Energy storage and conversion
- Quantum computation and information



**Contact:** [marcosgm@if.ufrj.br](mailto:marcosgm@if.ufrj.br)

# Acknowledgments



# Thank You!

Slides: <https://www.if.ufrj.br/~marcosgm/>

Contact: [marcosgm@if.ufrj.br](mailto:marcosgm@if.ufrj.br)



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EXTRAS



# Solving the KS equations

**Basis:** One-electron wfcs are expanded in a convenient basis set, such as plane-waves (QE, VASP), pseudoatomic orbitals (SIESTA), etc.

**K-points:** Integrations over the Brillouin zone are replaced with summations over a sufficiently dense **k**-point grid.

- Monkhorst-Pack algorithm is the most widely used for an efficient and accurate sampling.
- Convergence with respect to the density of the grid needs to be analyzed.

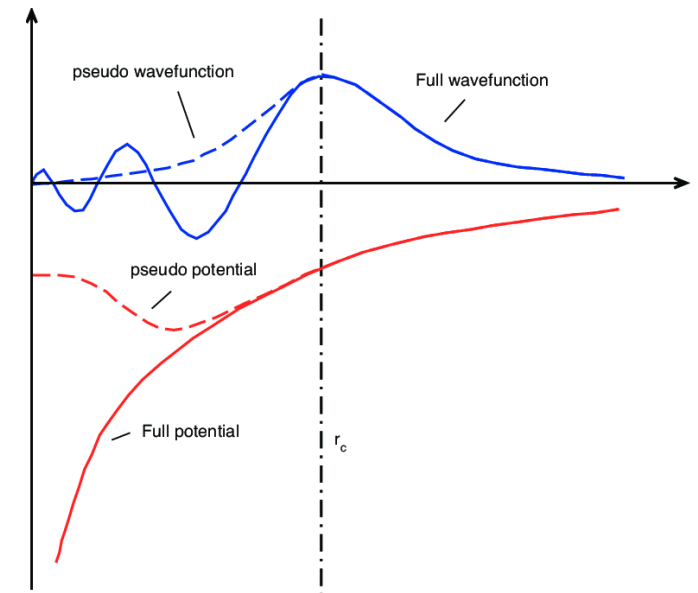
# Solving the KS equations

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**Ion-electron interaction ( $V_{ext}$ ):** Exact all-electron potential is replaced with a pseudopotential (PP) that reproduces the valence (bonding) properties and provides smoother pseudowfcs near the atomic cores.

- Different pseudization schemes: Norm-Conserving (NC), Ultrasoft (US), PAW, ...
- Different valence electronic configurations may be employed, such that the resulting PP is softer or harder to converge.



# Solving the KS equations

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**Exchange-correlation ( $V_{xc}$ ):** Since its exact form is unknown, approximations are required.

- Common parametrizations such as LDA and GGA are based on the 3D electron gas. Less accurate, but very cheap.
- Hybrid functionals (HSE, PBE0, B3LYP, ...) include some amount of exact exchange from Hartree-Fock theory. They are more accurate, but also more expensive.
- Meta-GGA functionals include additional corrections that depend on the kinetic energy density (and its derivatives). Intermediate accuracy and computational cost. Currently under implementation in most codes.

# Solving the KS equations

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**Exchange-correlation ( $V_{xc}$ ):** Since its exact form is unknown, approximations are required.

**Self-consistency:**  $V_{KS}$  is a functional of the density, which depends on the wfcs we need to calculate. Therefore, the problem needs to be solved iteratively.

- An initial guess is made for the density, typically a superposition of atomic densities.  $V_{KS}$  is calculated from that density.
- KS equations are solved and a new density is built from the wfcs.
- $V_{KS}$  is recalculated from that new density and KS equations are solved again.
- Procedure is repeated until new density does not differ substantially from the previous one.