MAX DRIVING THE EXASCALE TRANSITION

Quasi-particles and excitons using Yambo

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Università di Roma Tor Vergata

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eement 824143

Outline

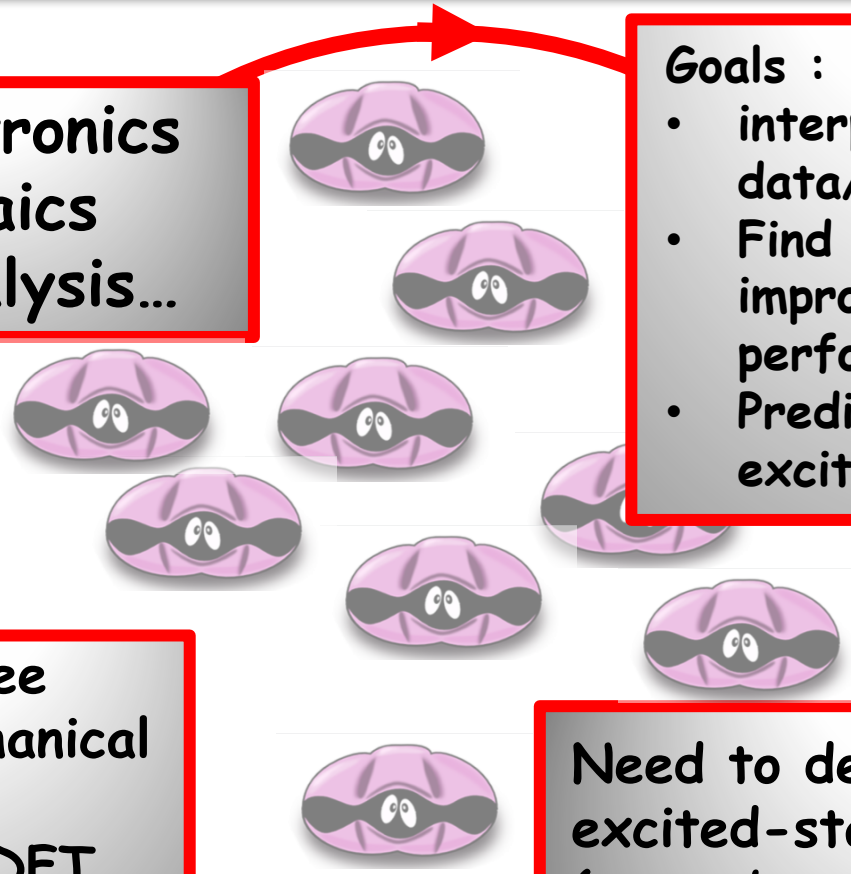
MAX DRIVING THE EXASCALE TRANSITION

- Why Yambo?

- From DFT to post-DFT (MBPT)
- Main implemented equations for QP and excitons: GW and BSE
- Examples of (my) recent research works done using Yambo

Why Yambo? Motivations & goals

Optoelectronics
Photovoltaics
Photocatalysis…



Goals :

- interpret spectroscopy data/experiments
- Find key parameters to improve devices performance w/o trial&error
- Predict new materials excited-state properties

Need to describe ground & excited-state properties (gaps, band-offsets, optical spectra..) in materials of different dimensionality

Parameter-free quantum-mechanical theories
DFT + post-DFT (MBPT/TDDFT)

DFT and post-DFT (MBPT) simulations

DFT

Kohn-Sham Equations

$$H_0(r)\varphi_{KS}(r) + v_{xc}(r)\varphi_{KS}(r) = \varepsilon_{KS}\varphi_{KS}(r)$$

Ground-state properties
KS gaps underestimate
the real QP ones

- ✓ **Quantum-espresso / p2y**
- ✓ **Abinit / a2y**

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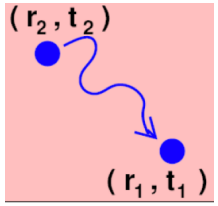
Yambo

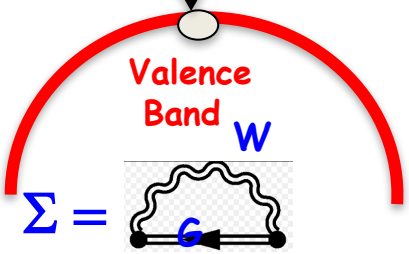
GW method

$$\varepsilon_i^{QP} \approx \varepsilon_i^{KS} + \langle \varphi_i^{KS} | \Sigma(\varepsilon_{nk}^{KS}) - V_{xc} | \varphi_i^{KS} \rangle$$

Electronic
(transport)
gaps



Quasi-particle
Bandstructures



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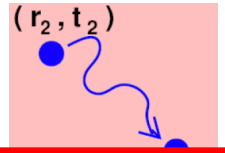
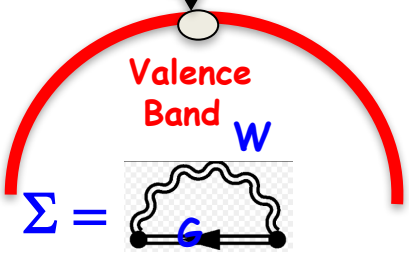


PES, IPES, ARPES, STS

Quasi-particle
Bandstructures



MAX DRIVING THE EXASCALE TRANSITION

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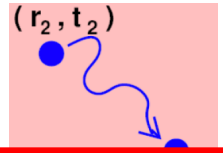

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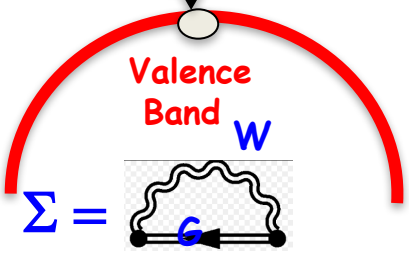
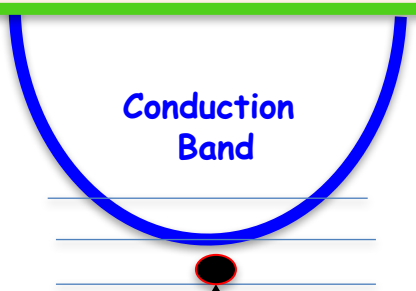


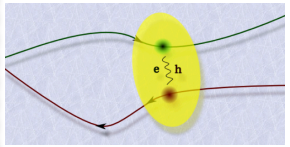
Bethe-Salpeter Equation (BSE)

$$[H_{el} + H_{hole} + H_{el-hole}]A_\lambda = E_\lambda A_\lambda$$

$$Abs(\omega) \propto \sum_\lambda \left| \sum_{vc} A_\lambda^{(vc)} \langle v|D|c \rangle \right|^2 \delta(E_\lambda - \omega)$$



Optical Gaps, spectra



A_λ = excitonic eigenfunctions
E_λ = excitonic Eigenvalues

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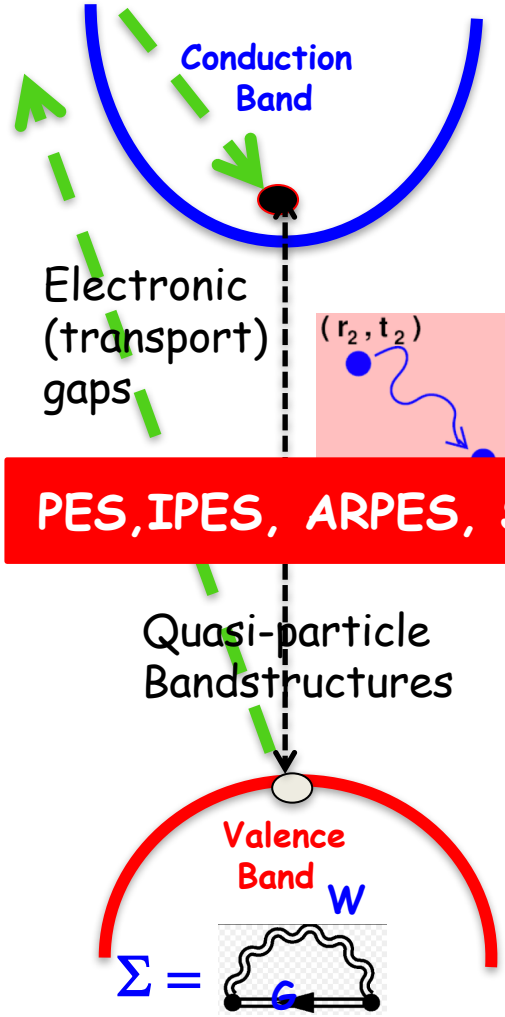

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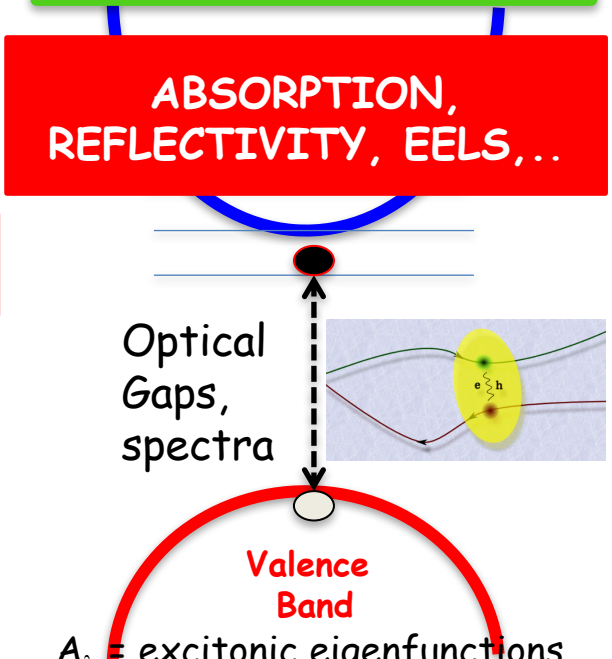

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MAX DRIVING THE EXASCALE TRANSITION

Quasi-particles with Yambo

yambo -g n DysSolver= "n" First order expansion around KS eigenvalue

$$E_{nk}^{QP} = \epsilon_{nk} + Z_{nk}\langle\psi_{nk}|\Sigma(\epsilon_{nk}) - V_{xc}|\psi_{nk}\rangle \qquad Z_{nk} = \left[1 - \frac{d\Sigma_{nk}(\omega)}{d\omega}\Big|_{\omega=\epsilon_{nk}}\right]^{-1}$$

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$$\Sigma^{GW} = GW = \boxed{Gv} + \boxed{G(W - v)}$$

Exchange-part of the self-energy Σ^{X}

Correlation-part of the self-energy Σ^{C}

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$$\Sigma^{GW} = GW = \underbrace{Gv}_{\Sigma^X} + \underbrace{G(W-v)}_{\Sigma^C}$$

Exchange-part of the self-energy

Correlation-part of the self-energy

- ✓ **GoWo from DFT-KS eigenvalues, eigenfunctions**
- ✓ **e- GWo** GWoIter
- ✓ **e- GW** GWIter

Self-consistent cycles updating only energies

- ✓ **Collinear** (no-spin/spin polarized calculations)
- ✓ **Non collinear** (when SOC is important)
- ✓ **Start from LDA/GGA (QE, abinit)**
- ✓ **Hybrids from QE**

MAX DRIVING THE EXASCALE TRANSITION

Exchange

$\Sigma^{x}_{n\mathbf{k}} - V^{xc}_{n\mathbf{k}}$

$\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G}) = \langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|m\mathbf{k}-\mathbf{q}\rangle$

yambo -x

Very fast!

$$-\sum_{m}^{occ}\int_{BZ} d\mathbf{q}\sum_{\mathbf{G}} v(\mathbf{q}+\mathbf{G})|\rho_{n,m}(\mathbf{k},\mathbf{q},\mathbf{G})|^2$$

GW corrections with Yambo

Exchange

$\Sigma^{x}_{n\mathbf{k}} - V^{xc}_{n\mathbf{k}}$

$\rho_{nm}(k,q,G) = \langle nk | e^{i(q+G)\cdot r} | mk-q \rangle$

yambo -x

Very fast!

$$-\sum_{m}^{occ} \int_{BZ} d\mathbf{q} \sum_{\mathbf{G}} v(\mathbf{q}+\mathbf{G}) |\rho_{n,m}(\mathbf{k},\mathbf{q},\mathbf{G})|^2$$

Correlation

$$\Sigma^{c}_{n\mathbf{k}} \quad \sum_{m} \int_{BZ} d\mathbf{q} \sum_{\mathbf{G},\mathbf{G}'} v(\mathbf{q}+\mathbf{G}) \ldots \int d\omega' \epsilon^{-1}_{G,G'}(q,\omega')$$

- ✓ Terminators for sum over m
  (F.Bruneval X. Gonze PRB 78 2008)
- ✓ Plasmon-Pole (PPA)
- ✓ Fully integration over ω'
- ✓ Restarting during dielectric screening calculation

Very time consuming!

Parallelization/HPC Helps a lot. .. See Andrea Ferretti talk!

- ✓ Random Integration Method (RIM)
- ✓ Coulomb-cutoff for non-periodic systems

BSE simulations with Yambo

In transition space

yambo -o b -k sex

$$H^{exc}_{t,t'} = \Delta E^{QP}_{t} \delta_{t,t'} + f_t (v - W)_{t,t'}$$

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$$H^{exc}_{t,t'} = \Delta E^{QP}_{t} \delta_{t,t'} + f_t (v - W)_{t,t'}$$

Resonant **coupling**

$$\begin{pmatrix} [\Delta E + (v-W)]_{cv,c'v'} & (v-W)_{cv,v'c'} \\ (v-W)_{vc,c'v'} & [\Delta E + (v-W)]_{vc,v'c'} \end{pmatrix}$$

coupling **Anti-Resonant**

✓ **No-TDA**

full matrix : molecules

Energy Loss

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Energy Loss

✓ **TDA**

Coupling neglected: extended systems, optics

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coupling

Anti-Resonant

✓ **No-TDA**

full matrix : molecules
Energy Loss

✓ **TDA**

Coupling neglected: extended systems, optics

✓ **Collinear** non spin-polarized, spin polarized systems

✓ **Non collinear** (perturbative/non perturbative SOC size 4 x4 w/o)

✓ Q=0 excitons

✓ Finite Q excitons

BSE simulations with Yambo

$$\epsilon_M(\omega) = (I\omega - H^{exc})^{-1}_{t,t'}$$

yambo -y h

$$\epsilon_M(\omega) = (I\omega - H^{exc})^{-1}_{t,t'}$$

Diagonalization

$$H^{exc}_{t,t'} A^{t'}_{\lambda} = E_{\lambda} A^{t}_{\lambda}$$

- ✓ **Excitonic eigenvalues/eigenvectors available**
- ✓ **Analysis of excitons (real/reciprocal space) using ypp post-processing code**

- **Lapack/scalapack** libraries
  All Eigenvectors/eigenvalues

  yambo –y d

- **Slepc/Petsc** libraries (for large-scale sparse eigenvalue problems). Only a limited number eigev/vectors

  yambo –y s

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Inversion

- ✓ Only spectrum

Lapack/scalapack
Libraries
yambo –y i

Recursive approach
Lanczos/Haydock
Very efficient
good MPI scalability
yambo –y h

QP energies and excitons in twisted Bilayers of BN using Yambo

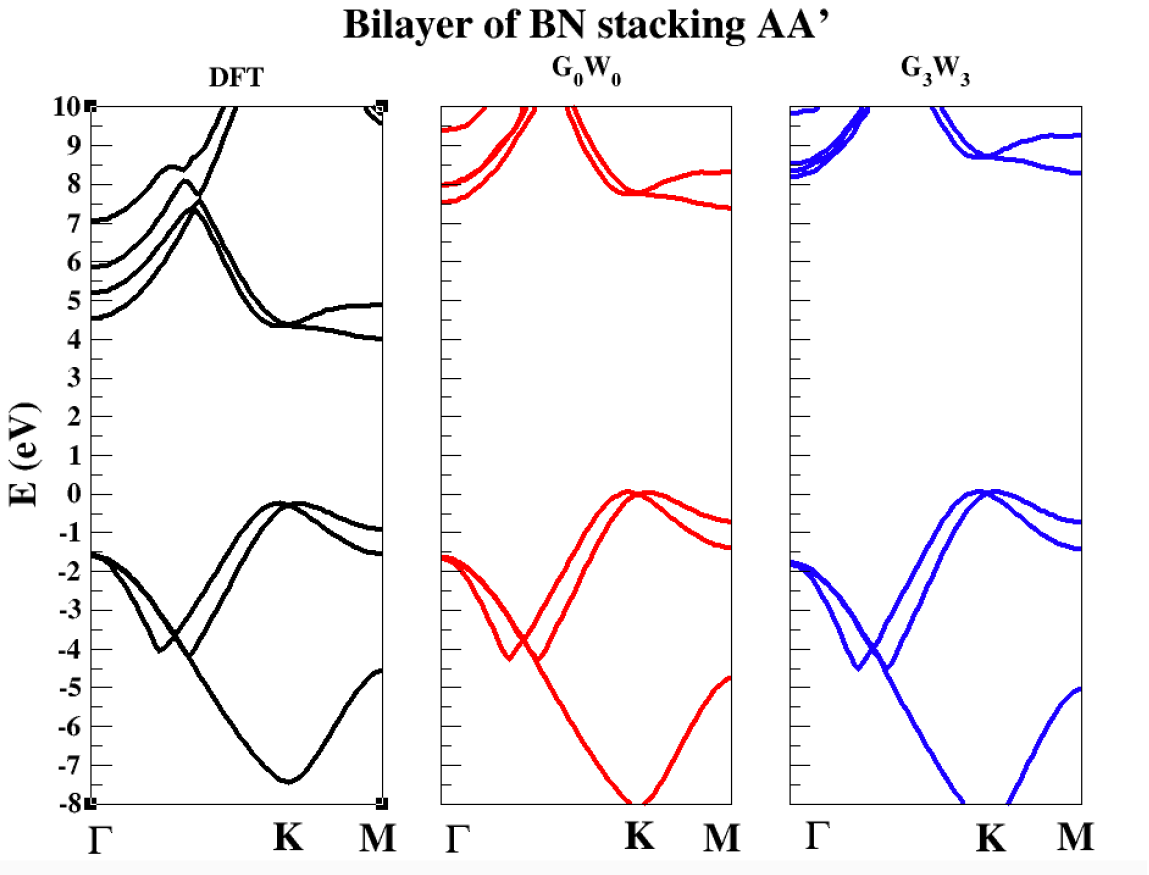
How do the QP bandstructure and excitons change with different stacking and twisting angles?

A.Zobelli et al. in preparation

QP energies and excitons in twisted Bilayers of BN using Yambo

-- use of iterative e-GW approach

-- use of post-processing ypp code to interpolate the QP energies (ypp -s b) obtained in a 18x18x1 k-grid, along high-simmetry directions



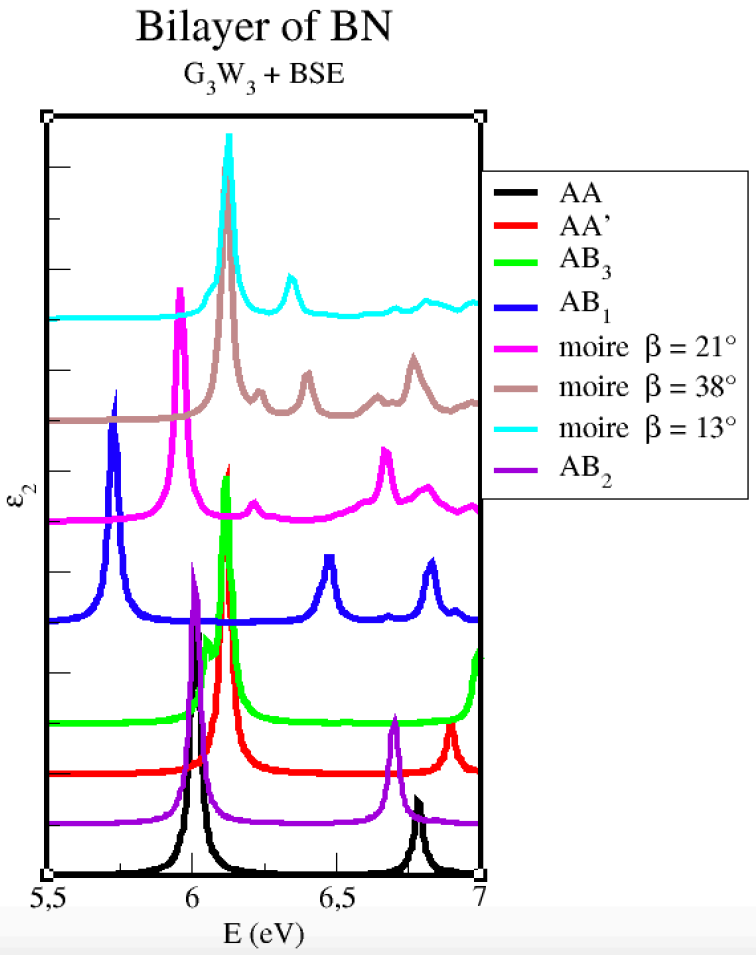
A.Zobelli et al. in preparation

MAX DRIVING THE EXASCALE TRANSITION

QP energies and excitons in twisted Bilayers of BN using Yambo

-- use of iterative approach to solve BSE

-- use of post-processing ypp code to analyze excitons properties



Largest Moire-structure (twisted bilayer) angle =13°
86 atoms

H_{exc} size up to

13000 x 13000
(16 s Haydock solver)

9000 x 9000
16 mins lapack diago solver)

marconi-knl 40 MPI CPU

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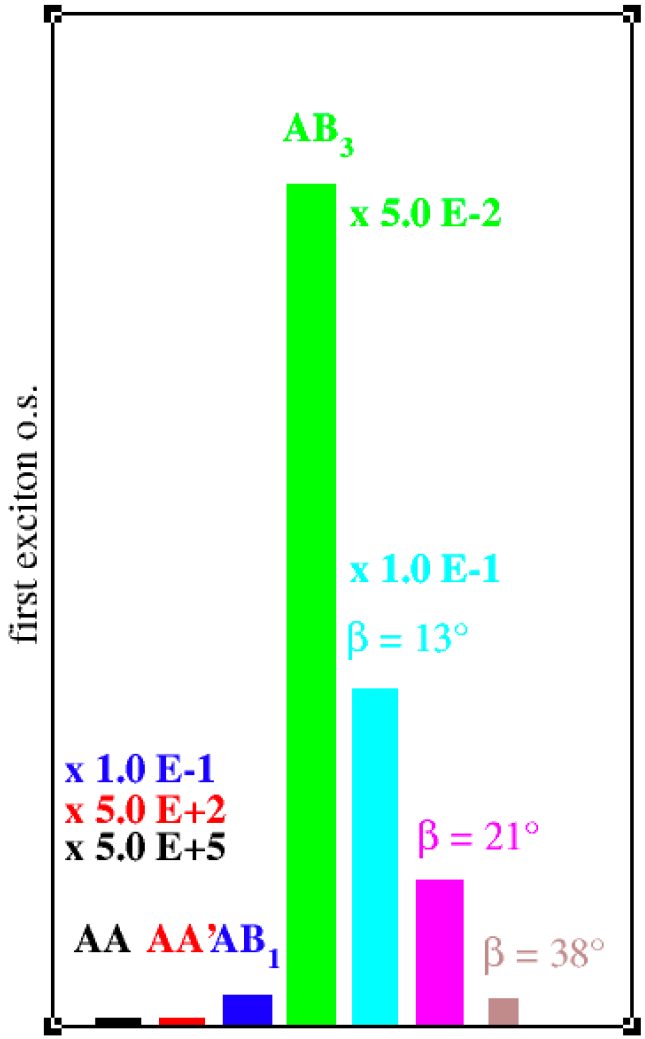
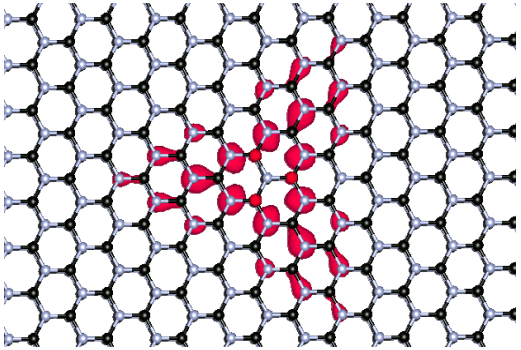
DARK -> BRIGHT



ypp -e s

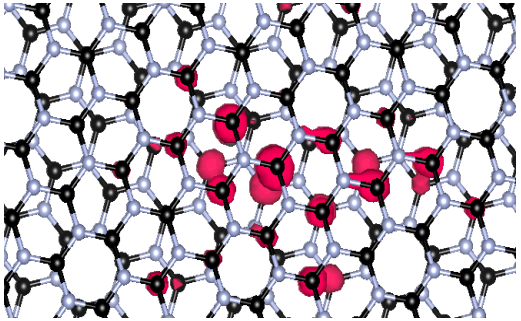
Exciton plot fixing the hole position

ypp -e w



AA' stacking

Different spatial localization



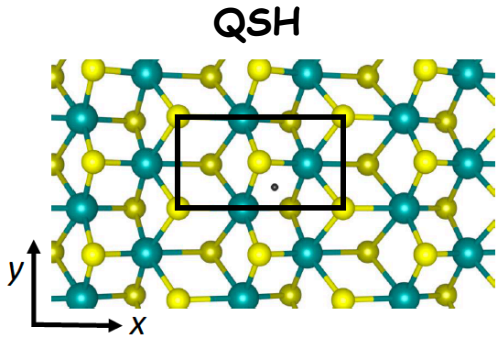
Twisted
β =13°

A.Zobelli et al. in preparation

MAX DRIVING THE EXASCALE TRANSITION

QP energies and excitons in 1 ML MoS_2-T' using Yambo

Is there any excitonic instability?



no-soc semi-metal
soc small-gap

D. Varsano, M.Palummo, E. Molinari, M.Rontani Nat. Nan. 15 (5), 367-372 2020

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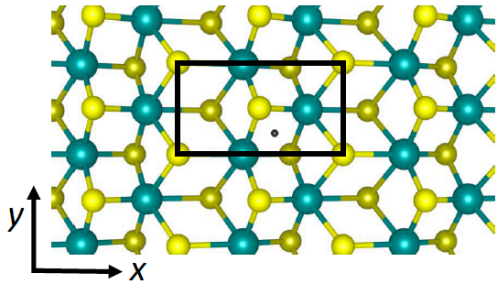
Is there any excitonic instability?

YES

QSH



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The exciton b.e exceeds 32meV the QP gap

Topological excitonic insulator (ab-initio + mean-field self-consistent model)

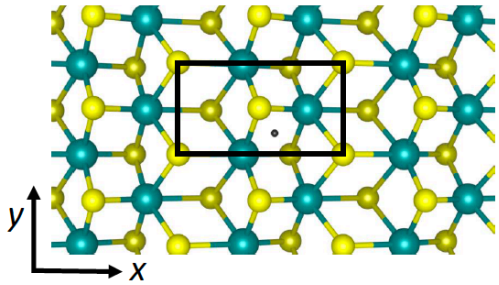
D. Varsano, M.Palummo, E. Molinari, M.Rontani Nat. Nan. 15 (5), 367-372 2020

QP energies and excitons in 1 ML MoS_2-T' using Yambo

We had to:

- GW-BSE (.With SOC /non collinear calaculation)
- use coulomb cutoff to avoid spurious replica interactions (ws 2D cutoff implementation similar to I.Beigi PRB 73 (2006))
- use terminators to converge over empty states. (F.Bruneval ;X. Gonze PRB 78 2008)
- use very dense k-meshes for GW and BSE to reach accuracy of about 10 meV

QSH



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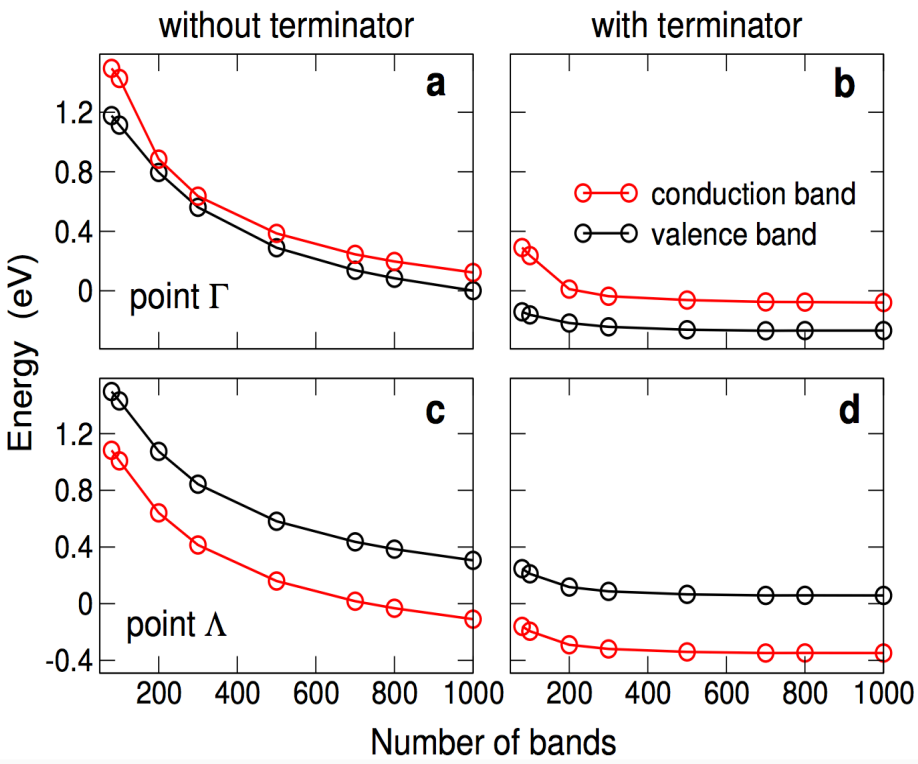
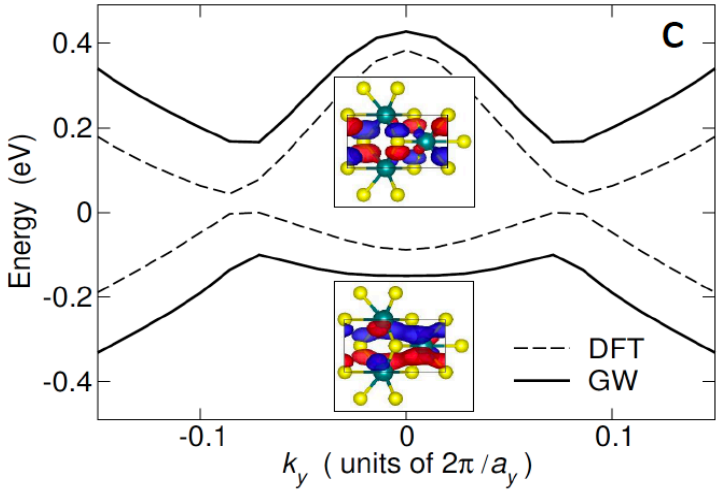
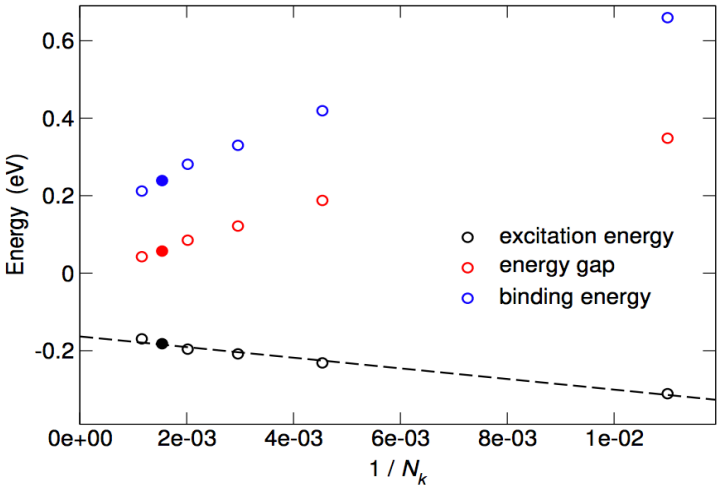




QP gap 0.2 eV > without cutoff



GW run on Marconi-knl

648 Q 10 Ry 300 b
X/Xo 4 mins/Q on 200 mpi CPU/16 threads

D. Varsano, M.Palummo, E. Molinari, M.Rontani Nat. Nan. 15 (5), 367-372 2020

QP energies and excitons in organic crystals using Yambo

Which is the origin of the optical anisotropy of porphyrine ZnTPP crystals if isolated molecules are isotropic ?

Localized or delocalized excitons Wannier or Frenkel or Charge-transfer?

M. Palummo , C. Hogan et al. in preparation

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We had to

go beyond GoWo
go beyond TDA
include many states in the BSE
analyze excitons

M. Palummo , C. Hogan et al. in preparation

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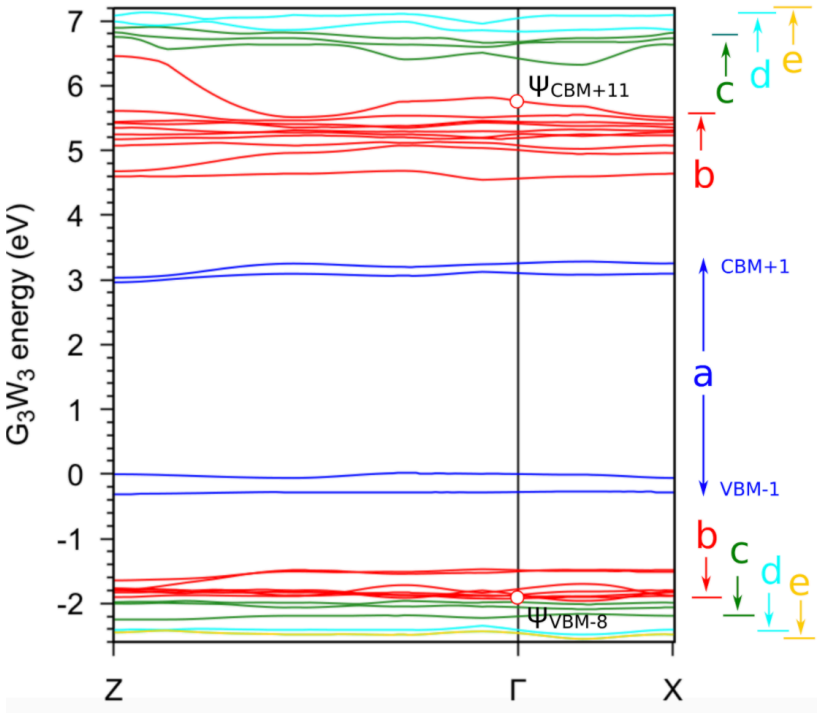
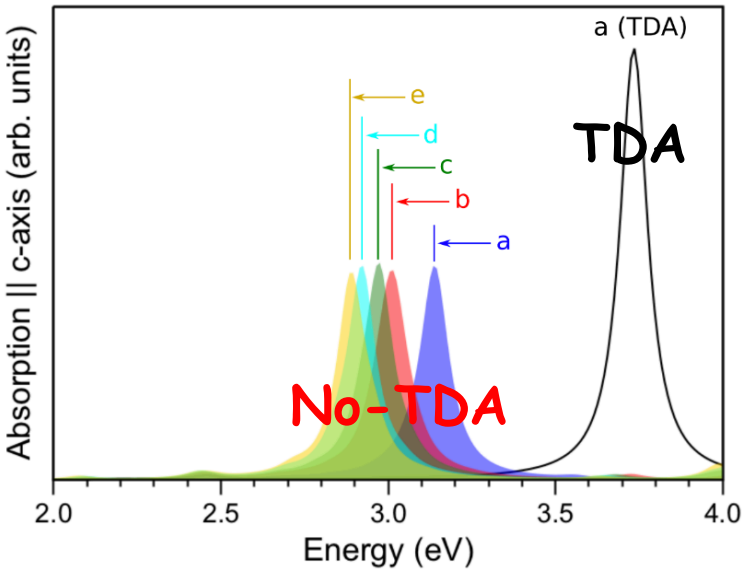


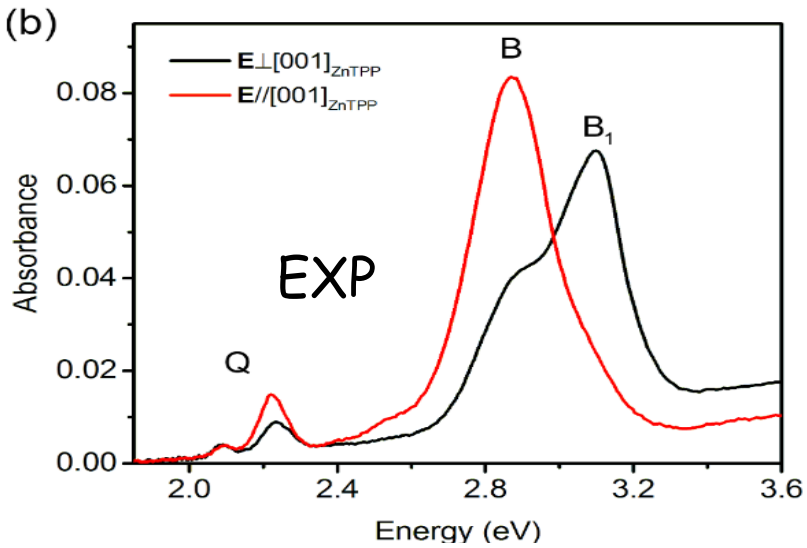
Gap at G_3W_3 level > 0.2 eV larger than Gap at G_0W_0 level



TDA does not reproduce the correct energetic position of the optical peak

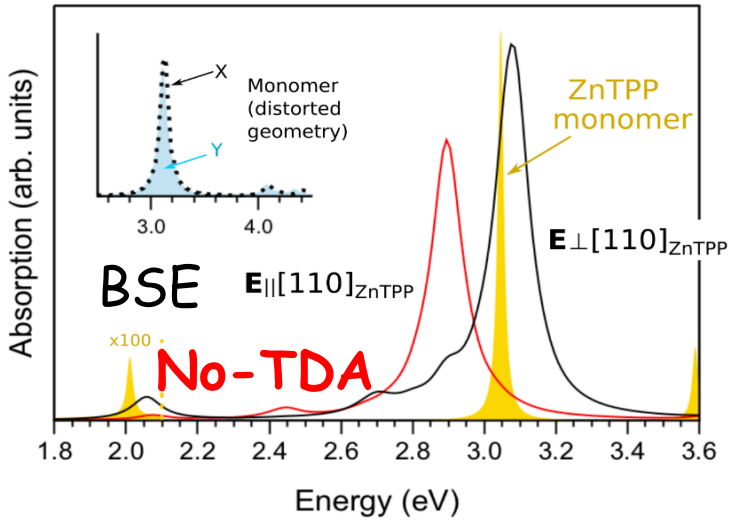
M. Palummo , C. Hogan et al. in preparation

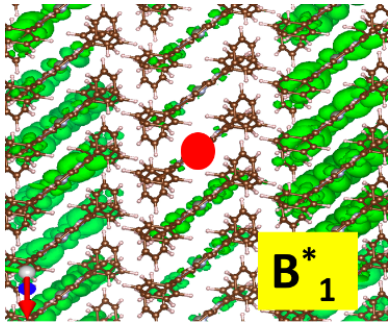
QP energies and excitons in organic crystals using Yambo



1-node/36 MPI-CPU
marconi-knl

BSE 26000X26000 7 hours
Iterative-solver 1 min.





ypp -e w

Very-delocalized excitons

M. Palummo , C. Hogan et al. in preparation

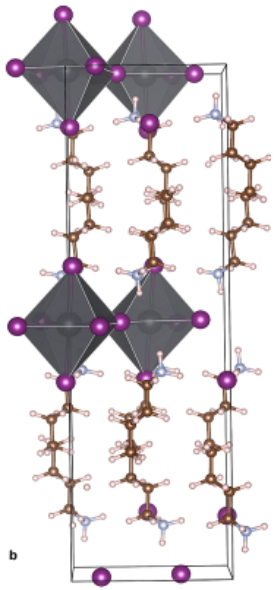
MAX DRIVING THE EXASCALE TRANSITION

QP energies and excitons in layered hybrid halide perovskites using Yambo

Are the HSE gaps a good estimation of the QP ones in layered 2D-perovskites (isolated sheets and repeated bulk structures) such as BA_2PbI_4 ?

Bound/localized excitons or free-carriers ?

BA_2PbI_4

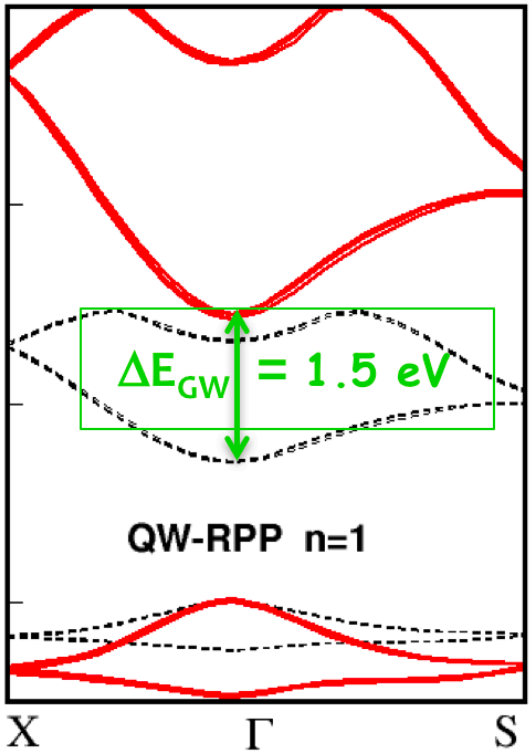


156 atoms in the unit cell

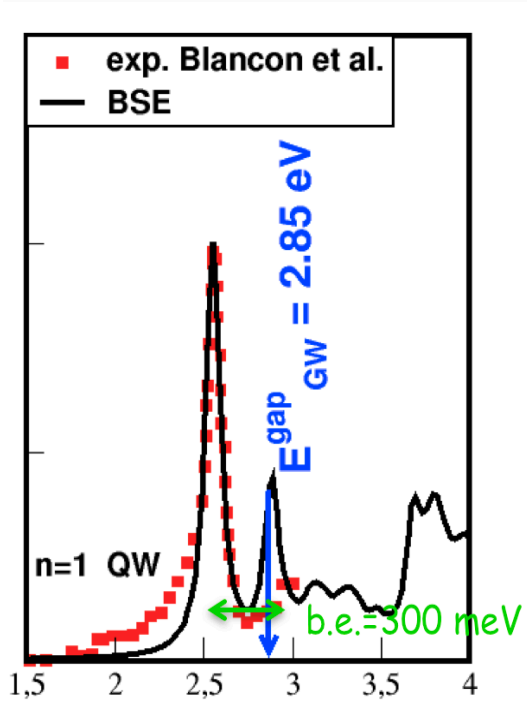
G.Giorgi,K.Yamashita,MP JPCL 2018

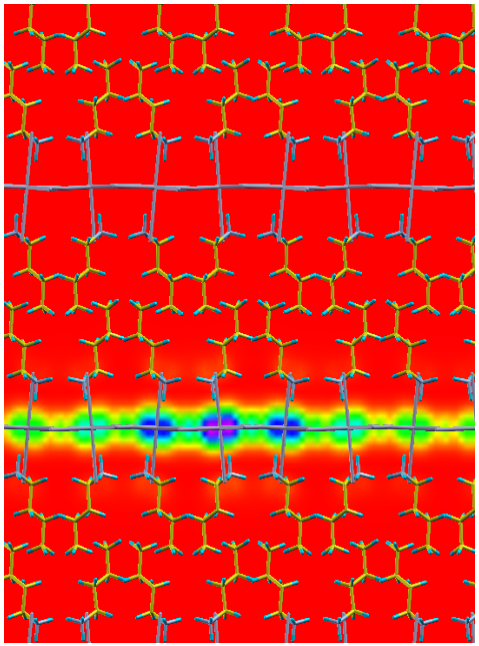
QP energies and excitons in layered hybrid halide perovskites using Yambo

HSE underestimate the QP gaps of about 1 eV



Strongly bound and very localized excitons





G.Giorgi,K.Yamashita,MP JPCL 2018

MAX DRIVING THE EXASCALE TRANSITION

QP energies and excitons in layered hybrid halide perovskites using Yambo

We had to:

include SOC in DFT, GW and BSE
use e-GW (self-consistent GW)
use terminators for empty bands
use Double grid technique to solve BSE

D. Kammerlander, et al PRB 86 (12), 125203 (2013)

On marconi knl

up to 20 Q-points /2000 b
40 nodes/10 mpi-cpu/6 threads X/Xo > 3 hours/Q point

On m100:

96 atoms PEA_2SnI_4. 25 nodes /4 mpi-cpu/ 32 threads 4 gpu
68 Q - 4000 b - X/Xo. 4.5 mins /Q point

G.Giorgi,K.Yamashita,MP JPCL 2018

MAX DRIVING THE EXASCALE TRANSITION

DRIVING THE EXASCALE TRANSITION

Follow on:

company/max-centre/

@max_center2

http://www.max-centre

the Yambo team

1. Many-body perturbation theory calculations using the yambo code
Journal of Physics: Condensed Matter 31, 325902 (2019)
2. Yambo: an ab initio tool for excited state calculations
Comp. Phys. Comm. 144, 180 (2009)

Example of Parallelism: Correlation part of self energy

$$\Sigma^c_{n\mathbf{k}}(\omega) = \langle n\mathbf{k}|\Sigma^c|n\mathbf{k}\rangle = i\sum_m \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G},\mathbf{G}'} \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\rho_{nm}(\mathbf{k},\mathbf{q},\mathbf{G})\rho^*_{nm}(\mathbf{k},\mathbf{q},\mathbf{G}') \times \int d\omega' G^0_{m\mathbf{k}-\mathbf{q}}(\omega-\omega')\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega')$$

QP states (MPI qp)

G bands (MPI b)

Q transferred momenta (MPI q)

Space DoF (OMP SE_Threads)

```
SE_ROLEs= "q qp b"     # [PARALLEL] CPUs roles (q,qp,b)
SE_CPU= "1 2 8"        # [PARALLEL] CPUs for each role
SE_Threads= 4          # [OPENMP/GW] Number of threads
                       # for  self-energy
```

num MPI tasks = 1 x 2 x 8
num threads/MPI-tasks = 4
Total num threads = 4 x (1 x 2 x 8)
MPI-b best memory distribution
MPI-qp no communication
MPI-q leads to load unbalance
OpenMP very efficient