Band gaps of 2D materials and van der Waals heterostructures

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GPAW meeting
Jyväskylä, June 7th, 2016

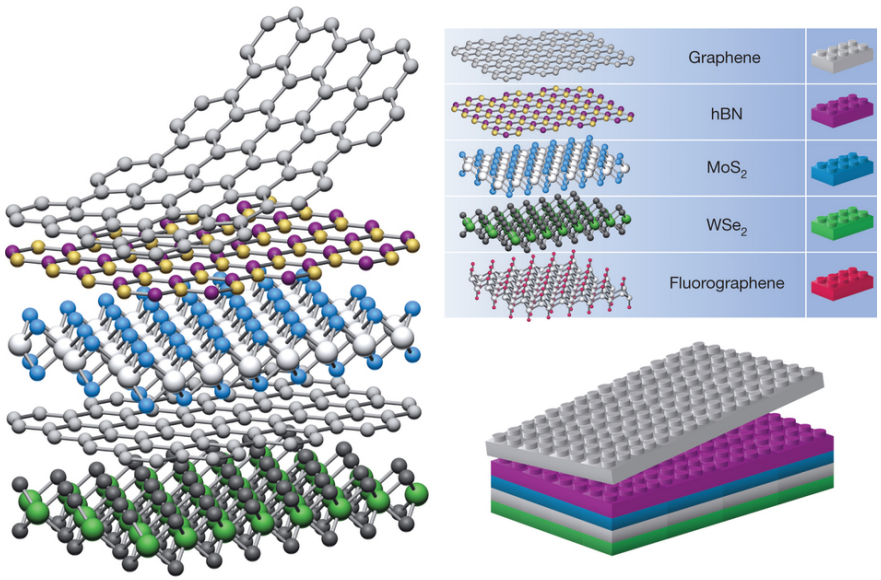
Van der Waals Heterostructures

- Engineer material properties by stacking different 2D layers.

- **Our Focus:** Calculate properties of electronic excitations (Plasmons, excitons, quasi-particles) in these materials.

- **Dielectric function:** Screening from surrounding layers.

LEGO brick picture



Geim & Grigorieva, *Nature* 499,419 (2013)

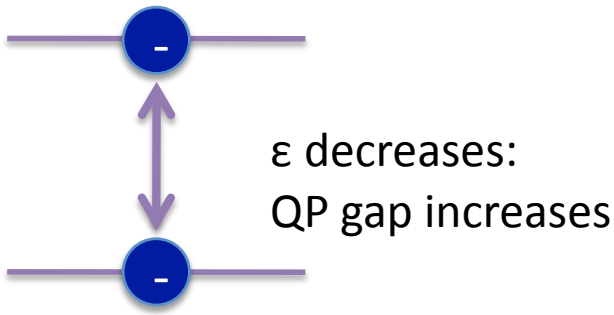
Outline

- Introduction: 2D materials and heterostructures
  - Calculating electronic excitations
  - Why we need other approaches for vdWh
- The 'Quantum electrostatic heterostructure' (QEH) model
  - The dielectric function of vdWh
- Calculating band gaps
  - Short introduction to the GW approximation
  - GW + QEH approach for band gaps of vdWh

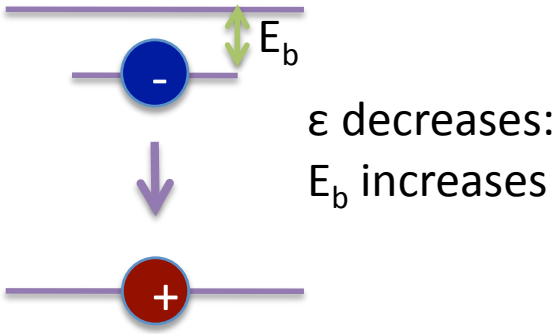
Screening and effect on excitations

- From 3D to 2D -> Screening decreases (smaller ε).

$$v_{\text{tot}}(\mathbf{r},\omega) = \int d\mathbf{r} \int d\mathbf{r}' \epsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) v_{\text{ext}}(\mathbf{r}',\omega).$$



- Smaller ε
  - larger band gap
  - larger exciton binding energy



- Different substrates -> tuning the screening and thereby the band gap.

Modeling heterostructures

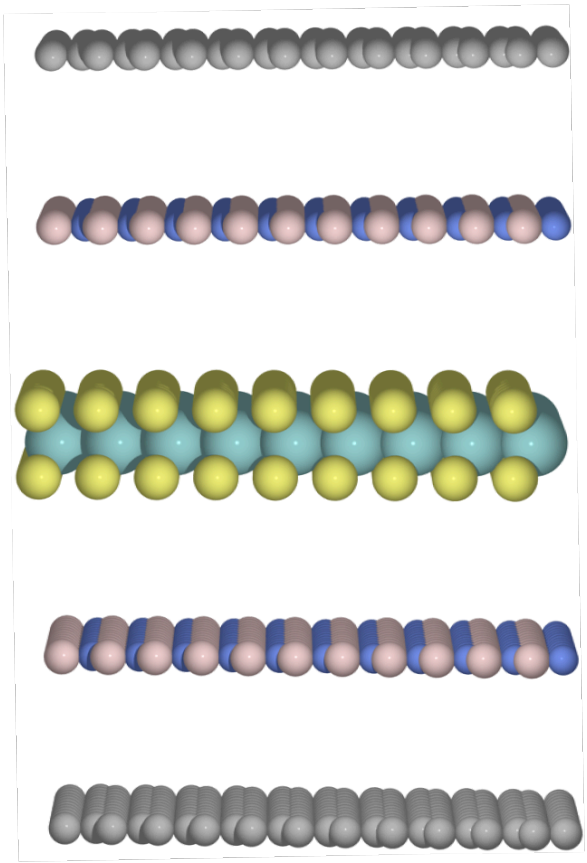
- **The Dielectric function:** Electronic excitations and screening from surrounding layers:

$$v_{\mathrm{tot}}(\mathbf{r},\omega) = \int d\mathbf{r} \int d\mathbf{r}' \epsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) v_{\mathrm{ext}}(\mathbf{r}',\omega).$$

- **Ab initio:** Linear response TDDFT in periodic supercell.

$$\epsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) = \delta(\mathbf{r}-\mathbf{r}') + \int \frac{1}{|\mathbf{r}-\mathbf{r}''|} \chi(\mathbf{r}'',\mathbf{r}',\omega) d\mathbf{r}''$$

- **Challenges:** Lattice mismatch & many layers -> Calculations are too costly.



First step: the QEH model

Breaking the Dyson-like equation:

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi^0(\mathbf{r},\mathbf{r}',\omega) + \int\int d\mathbf{r}_1 d\mathbf{r}_2 \chi^0(\mathbf{r},\mathbf{r}_1,\omega)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\chi(\mathbf{r}_2,\mathbf{r}',\omega)$$

.... into **two steps:**

Coulomb potential:

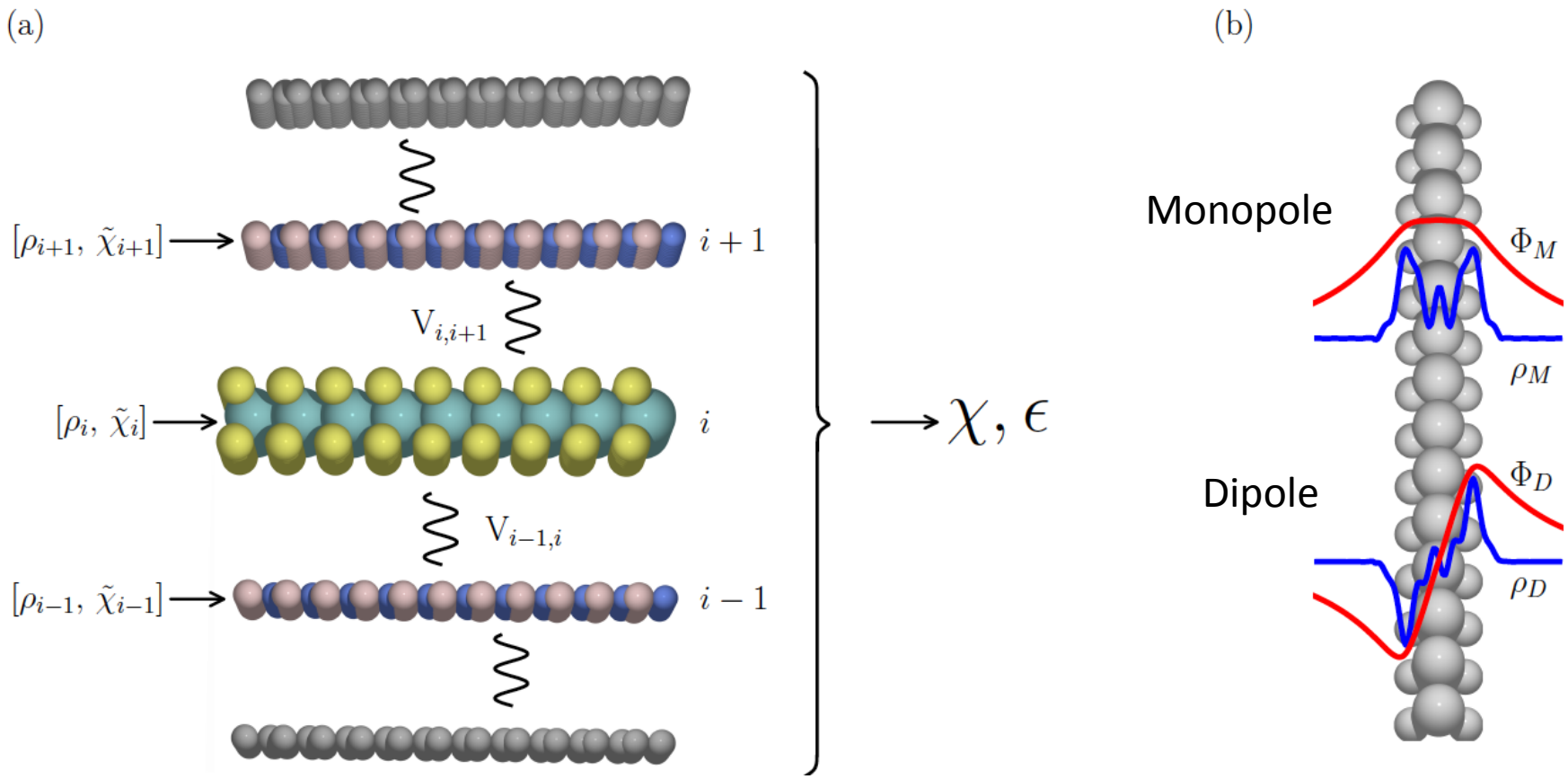
$$\mathbf{V} = \tilde{\mathbf{V}} + \mathbf{V}^{\mathbf{I}}$$

1. Intra-layer part: $\tilde{\chi} = \chi^{\mathbf{0}} + \chi^{\mathbf{0}}\tilde{\mathbf{V}}\tilde{\chi}$

2. Inter-layer part: $\chi = \tilde{\chi} + \tilde{\chi}\mathbf{V}^{\mathbf{I}}\chi$

K. Andersen, S. Latini, and K. S. Thygesen,
Nano Lett., 2015, 15 (7), pp 4616–4621.

The QEH model: overview

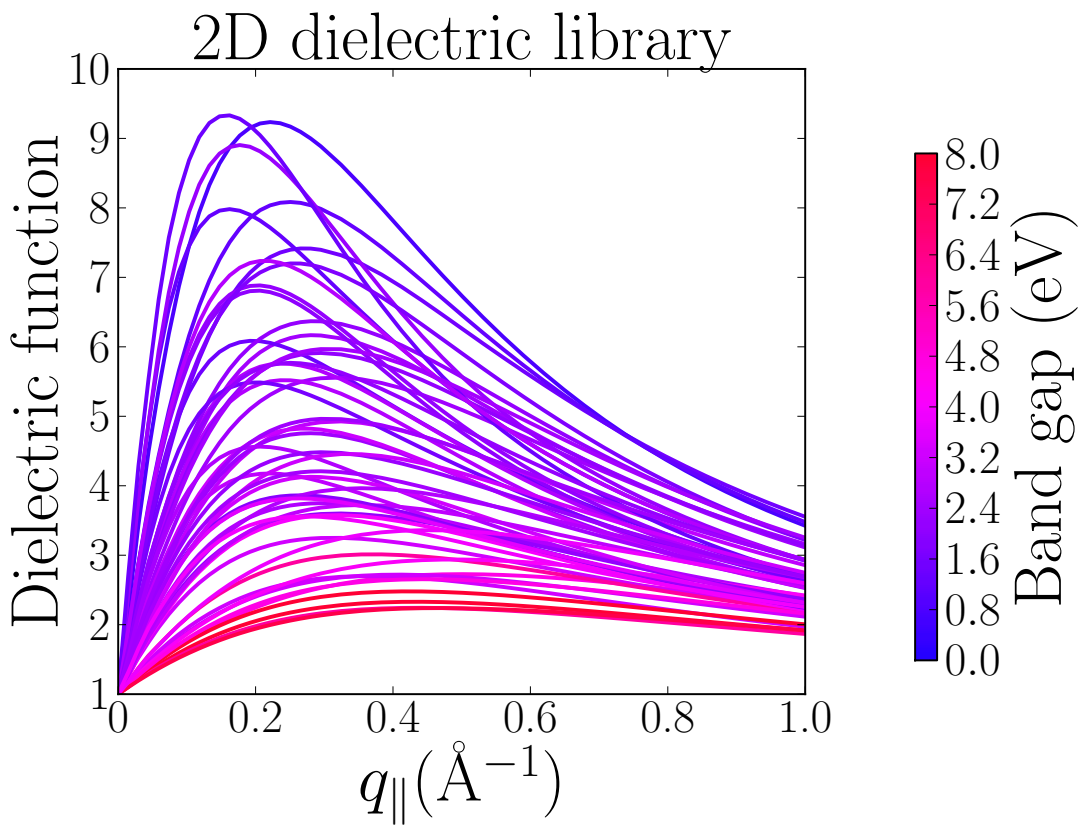


K. Andersen, S. Latini, and K. S. Thygesen,
Nano Lett., 2015, 15 (7), pp 4616–4621.

Dielectric building blocks

- 51 semiconducting TMDCs, graphene and hBN
- Magnitude of ε correlates with band gap
- 2D semiconductor: No screening in the optical limit.

$$\epsilon_{2D}(\mathbf{q}_{\parallel} \to 0) = 1$$



Database at: https://cmr.fysik.dtu.dk/vdwh/vdwh.html

Band gaps: F. Rasmussen and K. S. Thygesen, Journal of Phys. Chem. C, 2015

The dielectric function of multilayer MoS_2

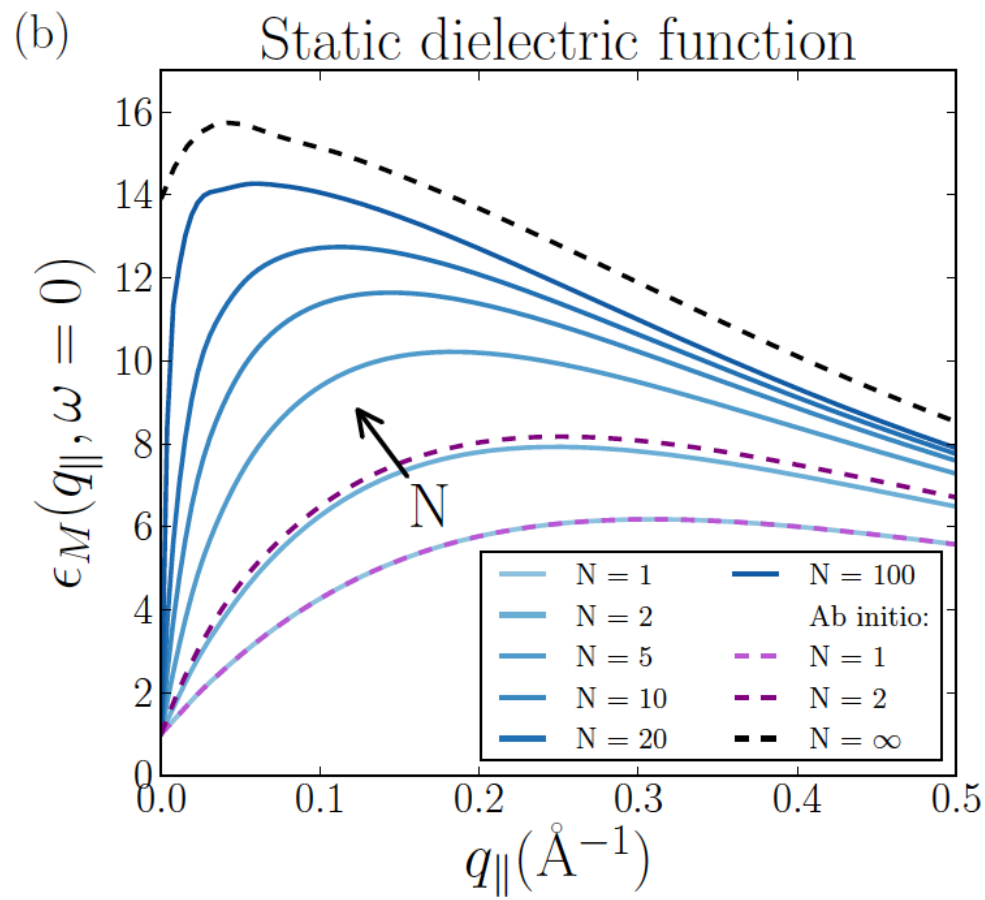
Test: Does the model capture the 2D - 3D transition of the dielectric function?

- **Yes!**

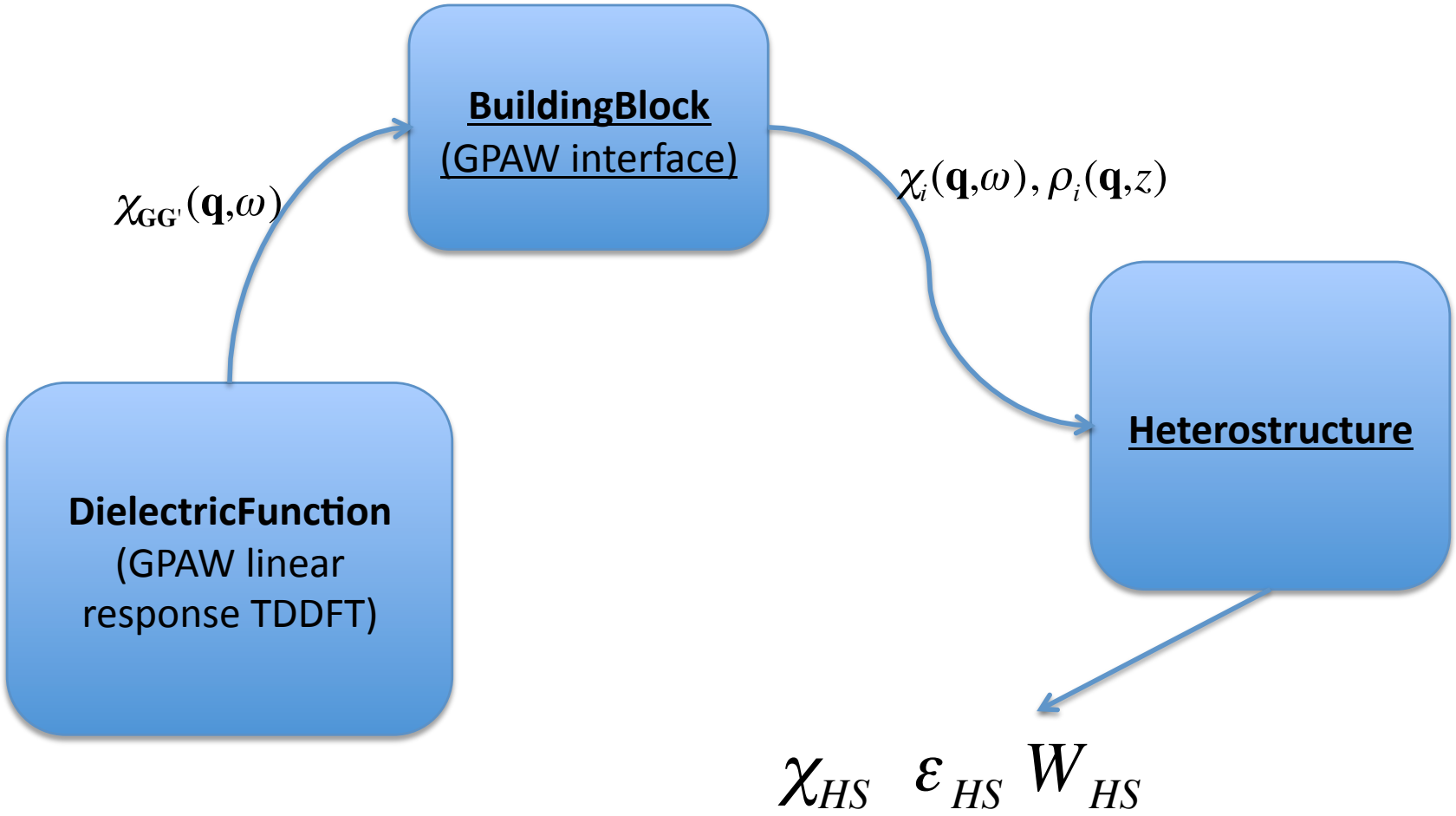
Large increase with the number of layers (N).

Good agreement with ab initio results

$$\frac{1}{\epsilon_M} = \frac{1}{V}\int d\mathbf{r}d\mathbf{r}'\epsilon^{-1}(\mathbf{r},\mathbf{r}')$$



GPAW implementation: Overview



Calculational example

- Calculate buildingblock with GPAW:

```
from gpaw.response.df import DielectricFunction
from gpaw.response.qeh import *

gspath = '../gs/gs_full-graphene.gpw'

df = DielectricFunction(calc=gspath,
                        name=name,
                        eta=0.1,
                        domega0=0.025,
                        omega2=10.0,
                        nblocks=1)

BB = BuildingBlock(df=df,
                   filename = name,
                   nq_inf=10,
                   isotropic_q=True)

BB.calculate_building_block()
```

- Use the Heterostructure class to calculate stuff:

```
from gpaw.response.qeh import *

d = [6.15, 6.15, 5, 5, 5, 5, 5]
HS = Heterostructure(structure=['3MoS2',
                                '2graphene',
                                '3hBN'],     # set up structure
                     d=d,                    # layer distance array
                     include_dipole=True,
                     wmax=0,                 # only include w=0
                     qmax=1,                 # q grid up to 1 Ang^{-1}
                     )
q, w, epsM = HS.get_macroscopic_dielectric_function()

q, w, eels = HS.get_eels()
```

Next step: Band gaps with GW

Idea: Calculate the screened potential of the heterostructure with QEH, and calculate the change for a given layer.

$$\Delta W_i(\mathbf{q},\omega) = W_{HS}(\mathbf{q},\omega) - W_i(\mathbf{q},\omega)$$

And use GW to calculate the change in Quasi particle band bap:

$$E_{n\mathbf{k}}(HS) = E_{n\mathbf{k}} + \Delta E_{n\mathbf{k}}(QEH)$$

The cost is only slightly larger than a full GW monolayer calculation.

Band gaps beyond DFT

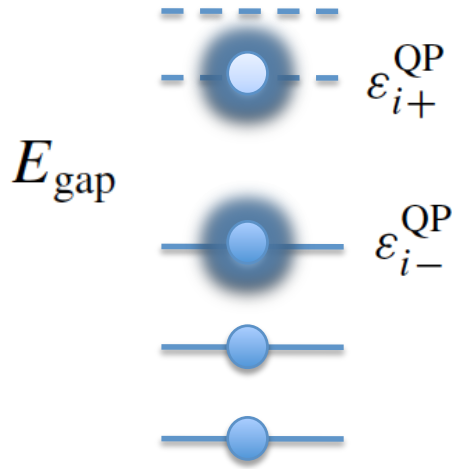
- Quasi particle energies:

$$\varepsilon_{i-}^{\mathrm{QP}} = E_0^N - E_i^{N-1}$$

$$\varepsilon_{i+}^{\mathrm{QP}} = E_i^{N+1} - E_0^N .$$

addition and removal energies.

$$E_{\mathrm{gap}} = \varepsilon_{0+}^{\mathrm{QP}} - \varepsilon_{0-}^{\mathrm{QP}}$$



- Quasiparticle equation:

$$\left\{H^0 + \Sigma(\varepsilon_{i\pm}^{QP})\right\}\left|\psi_{i\pm}^{QP}\right\rangle = \varepsilon_{i\pm}^{QP}\left|\psi_{i\pm}^{QP}\right\rangle$$

Self energy

Non-interacting Hamiltonian

The GW approximation

- The selfenergy is approximated as:

$$\Sigma_{GW}(r,r';\omega) = i\int d\omega' G(r,r';\omega')W(r,r';\omega-\omega')$$

Greens function:

$$G(\omega) = \sum_{i\pm} \frac{\left|\psi_{i\pm}^{QP}\right\rangle\left\langle\psi_{i\pm}^{QP}\right|}{\omega - \varepsilon_{i\pm}^{QP} + i\eta}$$

Screened potential:

$$W(r,r',\omega) = \int \epsilon^{-1}(r,r'',\omega)\frac{1}{|r''-r'|}dr''$$

- Most often G and W are evaluated from single-particle (Kohn Sham) states -> G_0W_0 approximation.

Note: Self-consistent GW is being implemented in GPAW by Per Schmidt (See also his poster later today on vertex corrections in GW)

GW implementation in GPAW

- Quasiparticle energies:

$$E_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k}} \cdot \mathrm{Re}\left(\Sigma_{n\mathbf{k}} + \epsilon_{n\mathbf{k}}^{\mathrm{EXX}} - V_{n\mathbf{k}}^{\mathrm{XC}}\right)$$

Renormalization factor

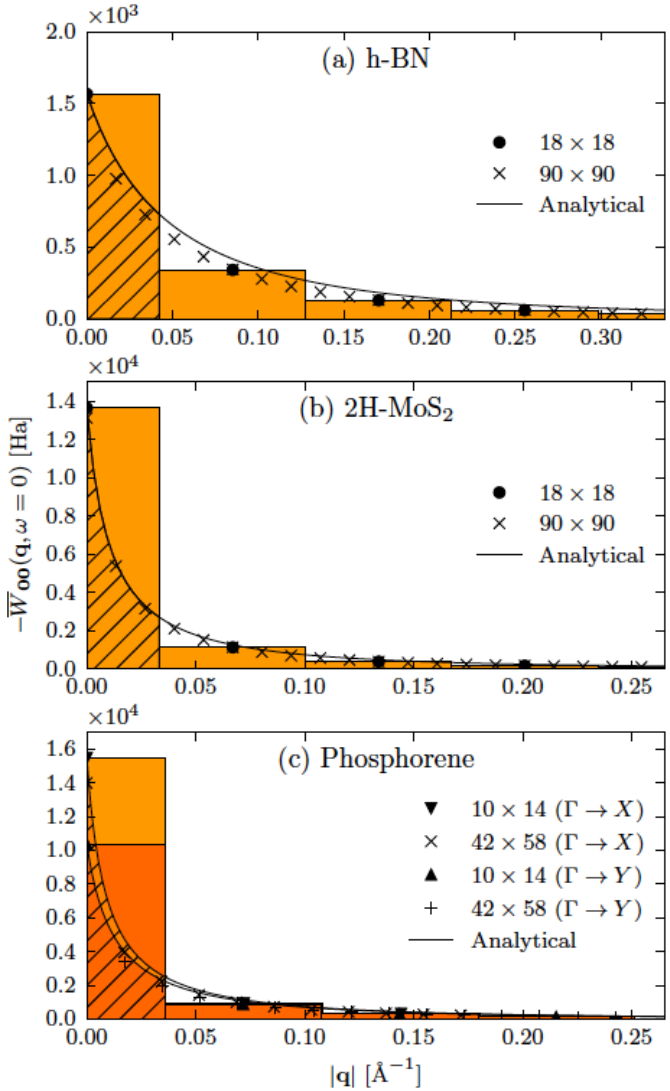
- Selfenergy:

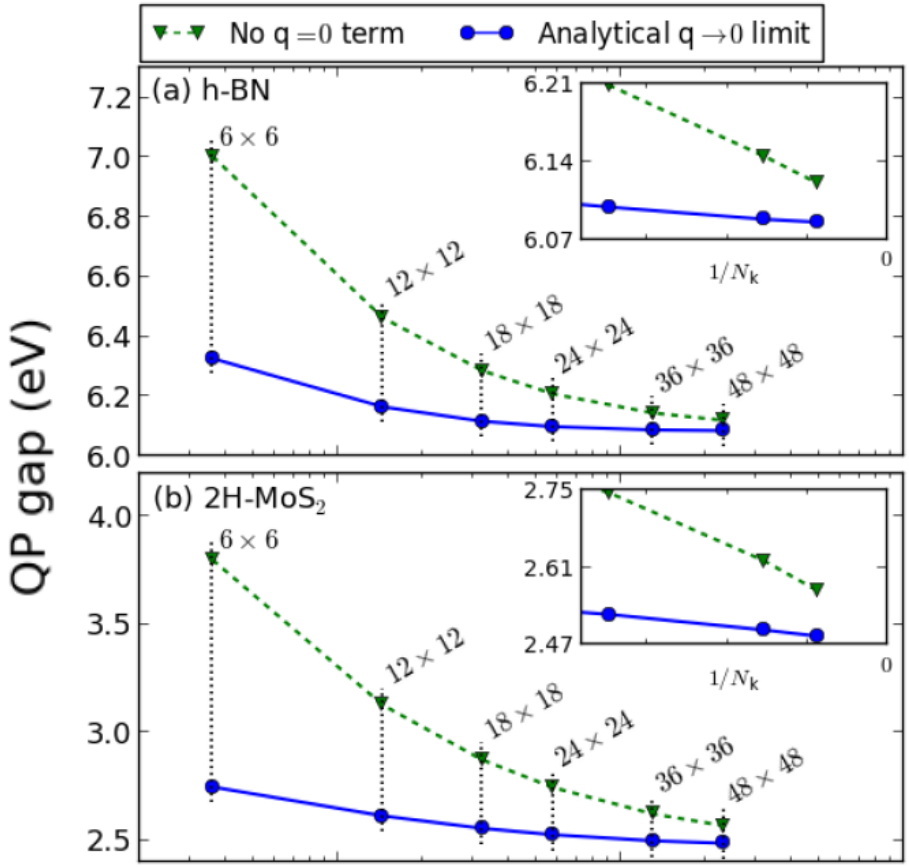
$$\langle n\mathbf{k}|\Sigma^c(\omega)|n\mathbf{k}\rangle = \frac{1}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{q} \sum_{\mathbf{G}\mathbf{G}'} \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega' \overline{W}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega')$$
$$\times \sum_m \frac{[\rho_{n,\mathbf{k}}^{m,\mathbf{k}+\mathbf{q}}(\mathbf{G})][\rho_{n\mathbf{k}}^{m,\mathbf{k}+\mathbf{q}}(\mathbf{G}')]^*}{\omega + \omega' - \epsilon_{m\mathbf{k}+\mathbf{q}} - i\eta\,\mathrm{sgn}(\epsilon_{m\mathbf{k}+\mathbf{q}} - \mu)},$$

- Screened Coulomb potential (symmetrized):

$$\overline{W}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \frac{4\pi}{|\mathbf{q}+\mathbf{G}|}\left(\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) - \delta_{\mathbf{G}\mathbf{G}'}\right)\frac{1}{|\mathbf{q}+\mathbf{G}'|}.$$

Recent work on the GW implementation: Improving the performance for 2D materials





Filip A. Rasmussen, Per S. Schmidt, Kirsten T. Winther, and Kristian S. Thygesen (Submitted)

Quasiparticle energies from QEH

- Use QEH to calculate the *change* in selfenergy:

$$\Sigma_{HS} = \Sigma_{N=1} + \Delta\Sigma_{QEH}$$

$$Z_{HS} = \left(1 - \mathrm{Re}\left\langle n\mathbf{k}\middle|\frac{\partial}{\partial\omega}\left(\Sigma_{N=1}(\omega) + \Delta\Sigma_{QEH}(\omega)\right)_{|\omega=\epsilon_{n\mathbf{k}}}\middle|n\mathbf{k}\right\rangle\right)^{-1}$$

- Used to calculate the change in quasi-particle energy:

$$E_{n\mathbf{k}}(HS) = \epsilon_{n\mathbf{k}} + Z_{n\mathbf{k},HS} \cdot \mathrm{Re}\left(\Sigma_{n\mathbf{k}} + \Delta\Sigma_{nk,QEH} + \epsilon_{n\mathbf{k}}^{\mathrm{EXX}} - V_{n\mathbf{k}}^{\mathrm{XC}}\right)$$

$$\boxed{\Delta E_{n\mathbf{k}} = Z_{n\mathbf{k},HS} \cdot \mathrm{Re}\ \Delta\Sigma_{n,QEH}}$$

Selfenergy from QEH

$$\Delta\Sigma_{n\mathbf{k}}(\omega=\epsilon_{n\mathbf{k}}) = \frac{1}{\Omega}\sum_{\mathbf{q}}^{1.\mathrm{BZ}}\sum_{m}^{\mathrm{all}}\frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega'\,\Delta W_{QEH}(\mathbf{q},\omega')\cdot \frac{\rho^{n\mathbf{k}}_{m\mathbf{k}-\mathbf{q}}(\mathbf{G}=\mathbf{0})\rho^{n\mathbf{k}*}_{m\mathbf{k}-\mathbf{q}}(\mathbf{G}=\mathbf{0}')}{\omega+\omega'-\epsilon_{m\,\mathbf{k}-\mathbf{q}}+i\eta\,\mathrm{sgn}(\epsilon_{m\,\mathbf{k}-\mathbf{q}}-\mu)}$$

Only **G=G'=0** component is included -> macroscopic part

- Change in screened potential from QEH:

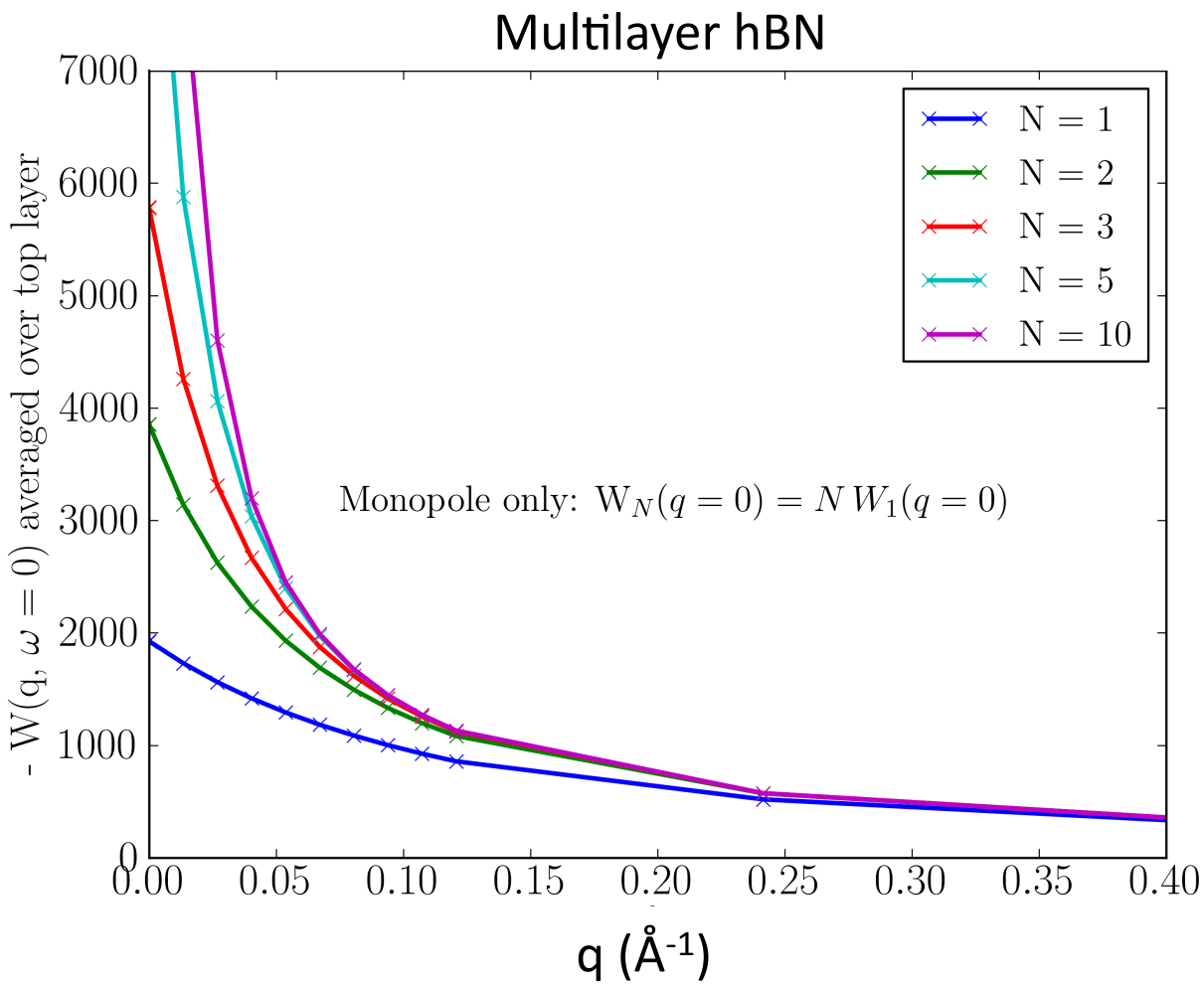
$$\Delta W_i(\mathbf{q},\omega) = W_{HS}(\mathbf{q},\omega) - W_i(\mathbf{q},\omega)$$

•Very cheap computationally compared to full GW calculation!

Screened potential from QEH

Potential averaged over top layer for stack of hBN.

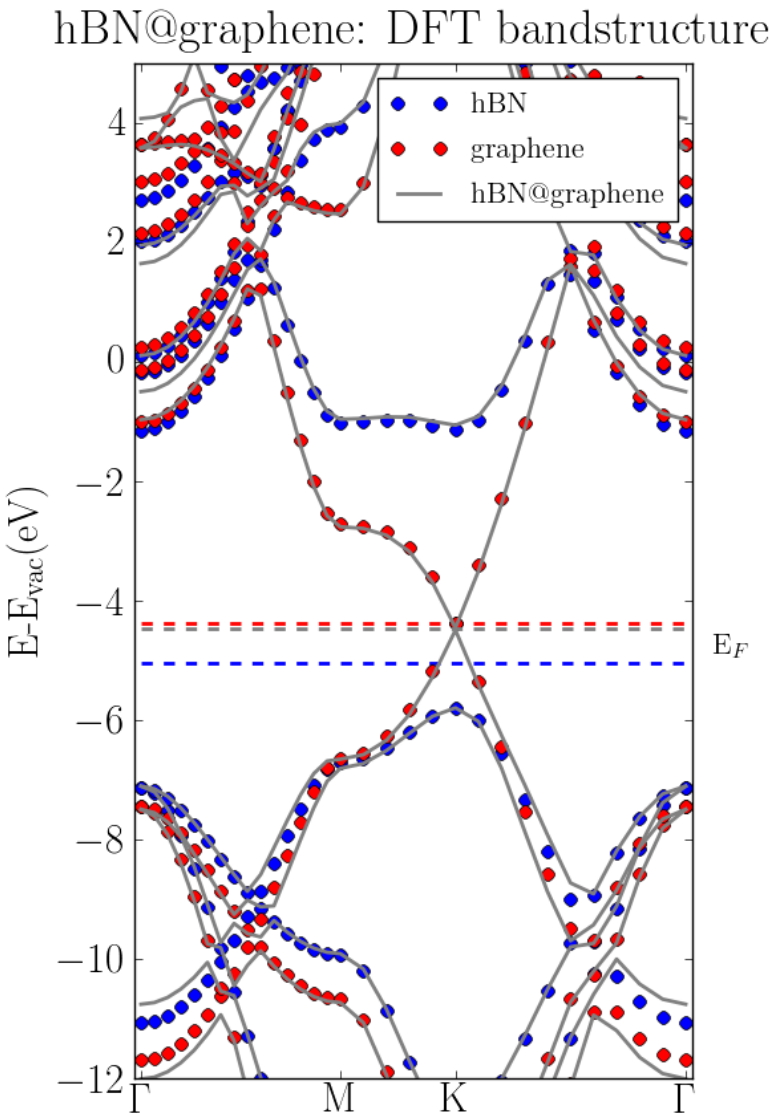
Increases proportional with N for q -> 0.



An example: hBN on graphene

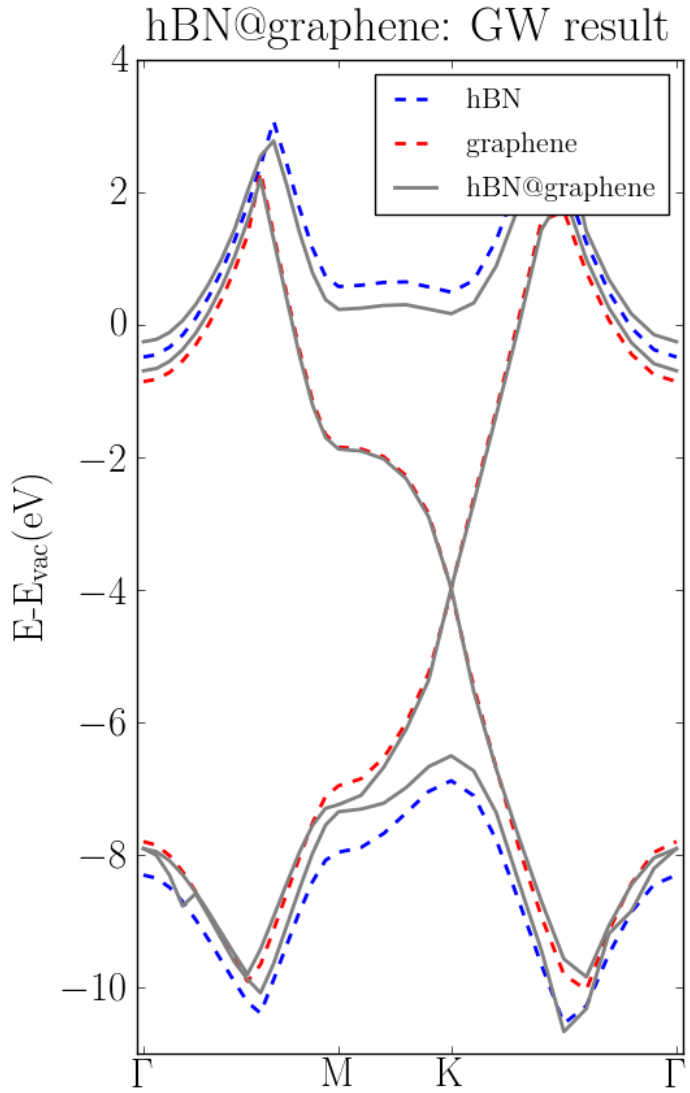
- DFT bandstructure: Small effect of hybridization (total bandstructure just the sum of the isolated layers).

- Bandgap of hBN of ~ 5eV is not affected by the presence of graphene in DFT.



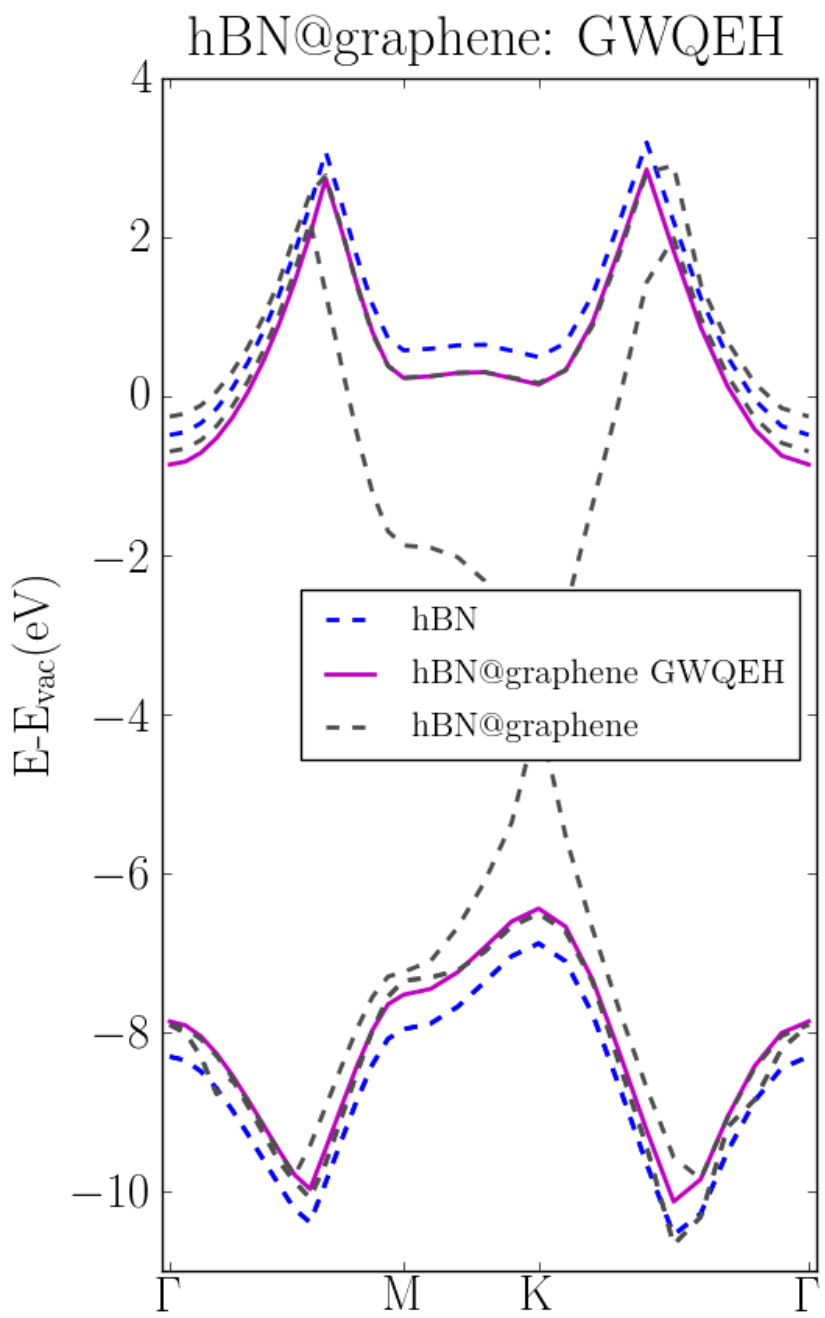
hBN@graphene: GW result

- Bandgap of freestanding hBN is opened to ~ 7 eV.
- With graphene: Reduction of the gap by ~0.7 eV!



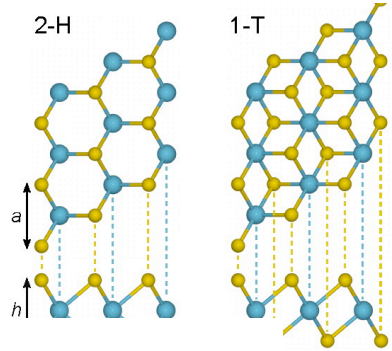
Performance of the GW+QEH approach

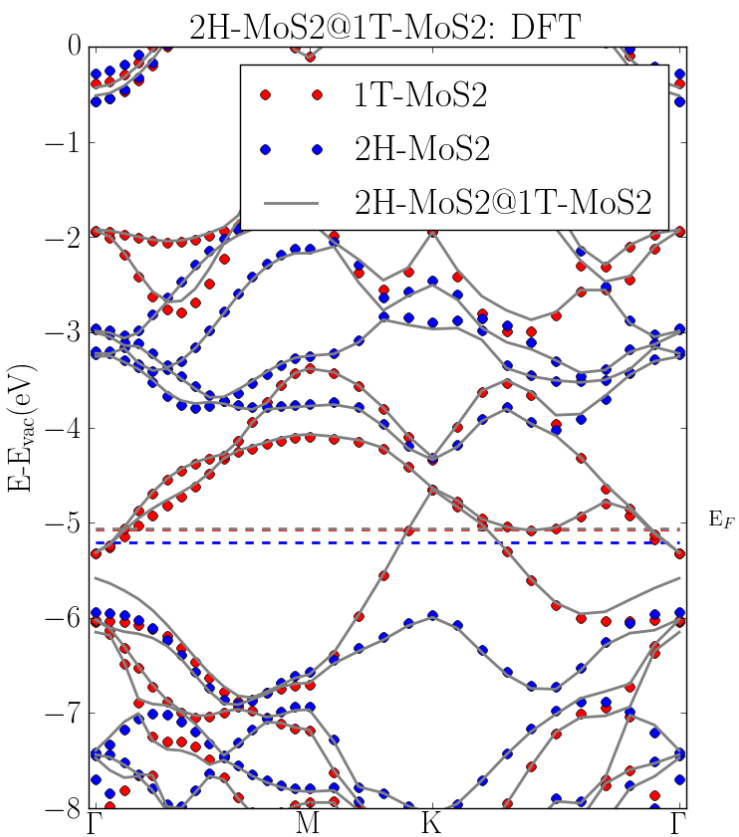
- The correction gives a constant shift to the hBN bands (almost constant in k-space)
- Direct gap in K is perfectly reproduced by the QEH approach!
- Problems whenever hybridization is taking place.

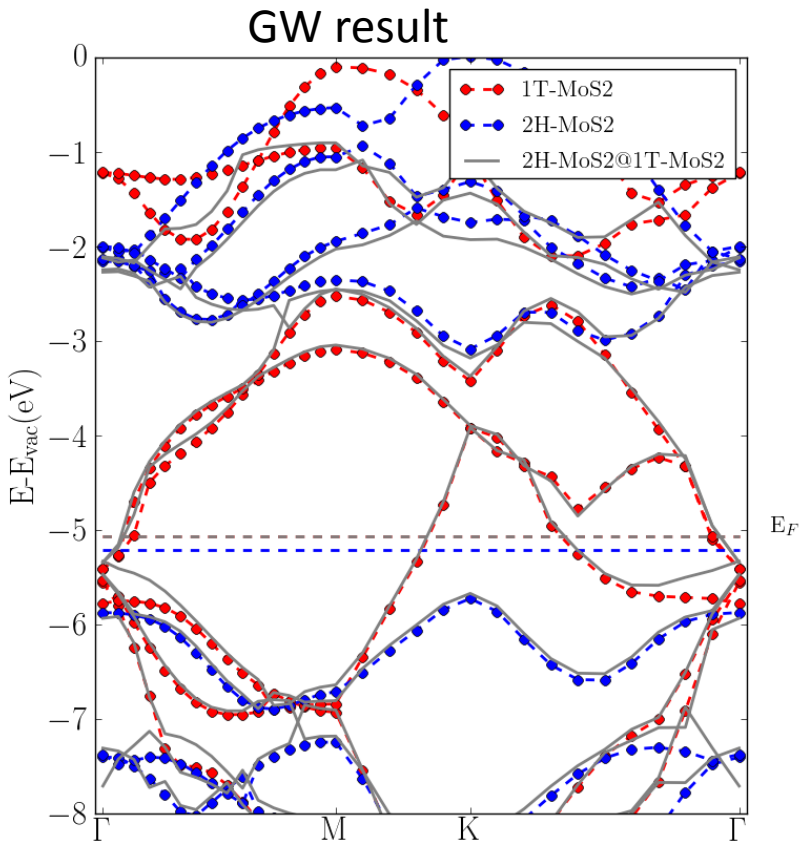


Other test-system: 2H-MoS2@1T-MoS2

- Semiconducting / metallic phase of MoS2

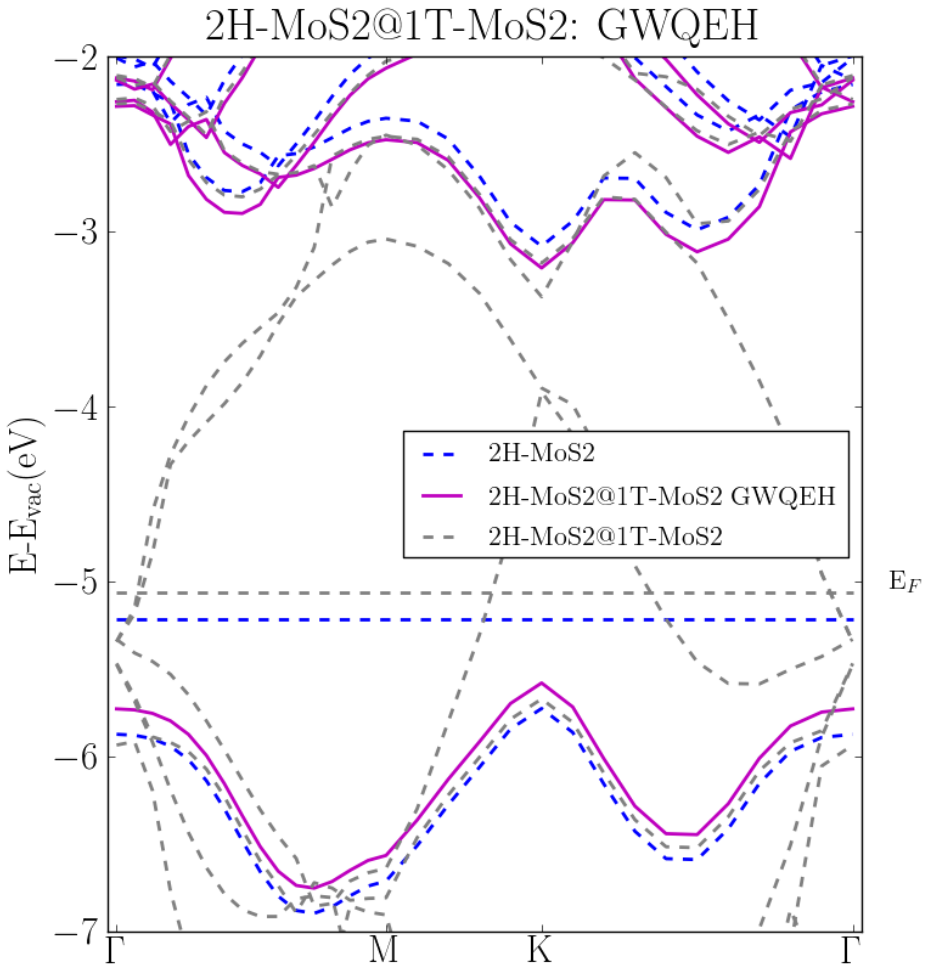




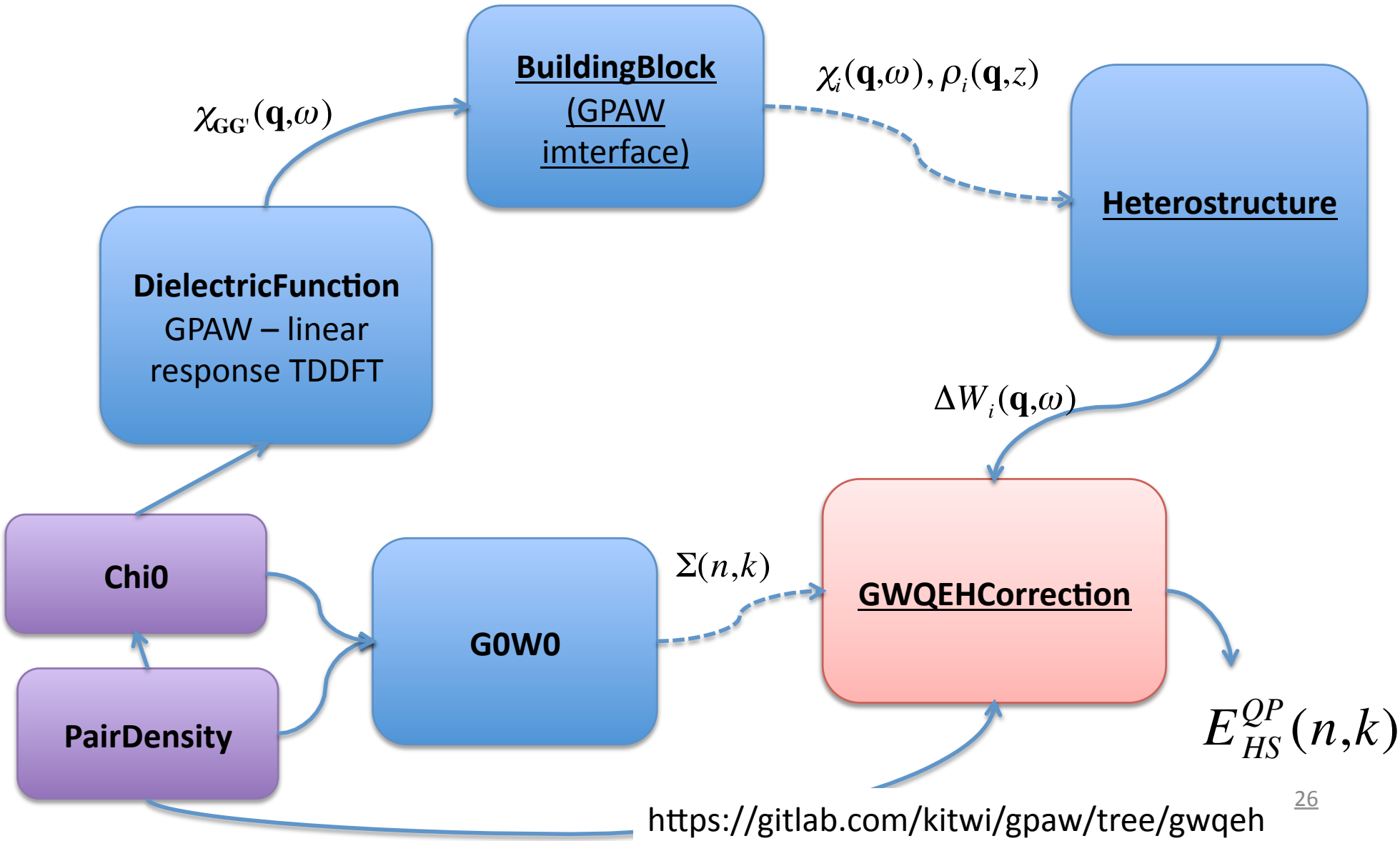


Performance of GWQEH approach

- GW gives a (direct) gap reduction of ~ 0.2 eV
- GWQEH overestimates the shift by 0.1 eV ->
-
- Hybridization / dipole formation



GPAW implementation



https://gitlab.com/kitwi/gpaw/tree/gwqeh

Calculation example

```
from gpaw.response.gwqeh import *

gspath = '../1/gs/gs_full-hBN.gpw'

GWQEH = GWQEHCorrection(calc=gspath,
                        structure=['hBN',
                                   'graphene'],
                        d = [3.326],
                        gwfile='../1/GW/gw-hBN_results.pckl',
                        bands=(3,5),
                        filename='gwqeh-hBN-graphene',
                        domega0=0.1,
                        omega2=10,
                        include_q0=False
                        )

qp = GWQEH.calculate_qp_energies()
```

Conclusion

- We have developed an efficient scheme for calculating the dielectric properties of vdWh.
- Enables calculations for much larger vdWh consisting of layers with different lattice constants.
- The approach has been extended to calculate band gaps of vdWhs:
  - Only describe systems where hybridization is weak + without charge transfer
  - More testing needed!

Thank you for your attention!

Kristian Thygesen

Simone Latini

Per Schmidt

GPAW!

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