GW calculations for molecules and solids: Theory and implementation in CP2K

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Overview

Quasiparticle energies in *GW*: Theory

- **Definition:**

  A quasiparticle energy ε_n is defined as energy which
  - is needed to remove an electron from the system to the vacuum or
  - is gained if one places an electron from the vacuum to the system

- In DFT and Hartree-Fock, there is no theoretical foundation that the eigenvalues ε_n from an SCF,

$$\left(-\frac{\nabla^2}{2} + v_{\text{el-core}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right) \psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r})$$

  have anything to do with quasiparticle energies.

- **Theorem:**

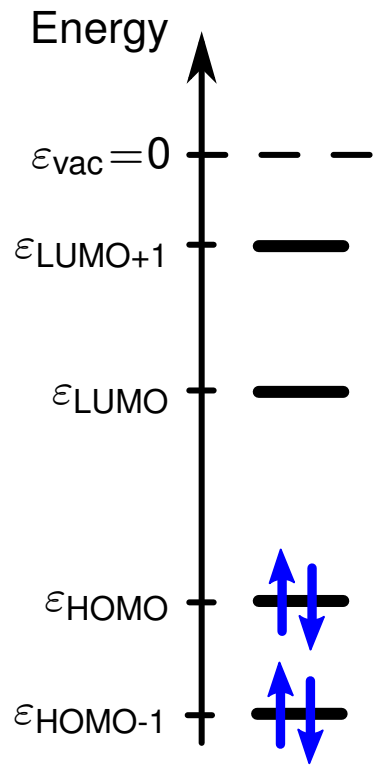
  A self-energy $\Sigma(\mathbf{r}, \mathbf{r}', \varepsilon)$ (non-local, energy-dependent) containing exchange and correlation effects exists, such that the solution of

$$\left(\frac{-\nabla^2}{2} + v_{\text{el-core}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right) \psi_n(\mathbf{r}) + \int d\mathbf{r}' \; \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_n) \psi_n(\mathbf{r}') = \varepsilon_n \psi_n(\mathbf{r})$$

  gives the correct quasiparticle energies ε_n of the interacting many-electron system.

- In the *GW* approximation, the self-energy reads

$$\Sigma^{GW}(\mathbf{r}, \mathbf{r}', \varepsilon) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\varepsilon' \; G(\mathbf{r}, \mathbf{r}', \varepsilon - \varepsilon', \{\varepsilon_n\}, \{\psi_n\}) \; W(\mathbf{r}, \mathbf{r}', \varepsilon', \{\varepsilon_n\}, \{\psi_n\})$$



Single-electron (quasiparticle) levels of a closed shell molecule

Quasiparticle energies in GW: G_0W_0 formalism in practice

G_0W_0: Start from DFT MOs $\psi_n^{\mathrm{DFT}}(\mathbf{r})$ and compute first-order correction to DFT eigenvalues:

1. Converge DFT SCF (e.g. PBE functional for solids "G_0W_0@PBE", PBE0 for molecules)

$$\Big(-\frac{\nabla^2}{2} + v_{\text{el-core}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \Big) \psi_n^{\mathrm{DFT}}(\mathbf{r}) = \varepsilon_n^{\mathrm{DFT}} \, \psi_n^{\mathrm{DFT}}(\mathbf{r}) \, .$$

2. Compute density response (most expensive step):

$$\chi(\mathbf{r}, \mathbf{r}', i\omega) = 2 \sum_{i}^{\text{occ}} \sum_{a}^{\text{virt}} \psi_a^{\mathrm{DFT}}(\mathbf{r}') \psi_i^{\mathrm{DFT}}(\mathbf{r}') \psi_i^{\mathrm{DFT}}(\mathbf{r}) \psi_a^{\mathrm{DFT}}(\mathbf{r}) \, \frac{\varepsilon_i^{\mathrm{DFT}} - \varepsilon_a^{\mathrm{DFT}}}{\omega^2 + \left(\varepsilon_i^{\mathrm{DFT}} - \varepsilon_a^{\mathrm{DFT}} \right)^2} \, . \qquad (\mathcal{O}(N^4))$$

3. Compute dielectric function with $v(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$

$$\epsilon(\mathbf{r}, \mathbf{r}', i\omega) = \delta(\mathbf{r}, \mathbf{r}') - \int d\mathbf{r}'' \, v(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}', i\omega) \, . \qquad (\mathcal{O}(N^3))$$

4. Compute screened Coulomb interaction

$$W_0(\mathbf{r}, \mathbf{r}', i\omega) = \int d\mathbf{r}'' \, \epsilon^{-1}(\mathbf{r}, \mathbf{r}'', i\omega) v(\mathbf{r}'', \mathbf{r}') \, . \qquad (\mathcal{O}(N^3))$$

5. Compute the self-energy

$$\Sigma(\mathbf{r}, \mathbf{r}', i\omega) = -\int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \, G_0(\mathbf{r}, \mathbf{r}', i\omega - i\omega') W_0(\mathbf{r}, \mathbf{r}', i\omega') \, , \; G_0(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{m}^{\text{all}} \frac{\psi_m^{\mathrm{DFT}}(\mathbf{r}') \psi_m^{\mathrm{DFT}}(\mathbf{r})}{i\omega + \varepsilon_{\mathrm{F}} - \varepsilon_m^{\mathrm{DFT}}} \, . \quad (\mathcal{O}(N^3))$$

6. Compute G_0W_0 quasiparticle energies (replace wrong XC from DFT by better XC from GW)

$$\varepsilon_n^{G_0W_0} = \varepsilon_n^{\mathrm{DFT}} + \langle \psi_n^{\mathrm{DFT}} | \mathrm{Re} \, \Sigma(\varepsilon_n^{G_0W_0}) - v^{\mathrm{xc}} | \psi_n^{\mathrm{DFT}} \rangle \qquad (\mathcal{O}(N^3))$$

Historical sketch of *GW*

- 1965: Proposition of the *GW* method

  Lars Hedin: New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem, Phys. Rev. **139**, A796 (1965), $\sim$ 3700 citations

- 1986: First G_0W_0@LDA calculation for diamond, Si, Ge, and LiCl

  M. S. Hybertsen and S. G. Louie: Electron correlation in semiconductors and insulators: Band gaps and quasiparticle energies, Phys. Rev. B **34**, 5390 (1986), $\sim$ 2700 citations

- 2005 – now: *GW* for solids in publicly available plane-waves codes

  Abinit: X. Gonze *et al.*, Z. Kristallogr. **220**, 558 – 562 (2005)

  VASP: M. Shishkin and G. Kresse, Phys. Rev. B **74**, 035101 (2006)

  Yambo: A. Marini, C. Hogan, M. Grüning, D. Varsano, Comput. Phys. Commun. **180**, 1392 – 1403 (2009)

  BerkeleyGW: J. Deslippe *et al.*, Comput. Phys. Commun. **183**, 1269 – 1289 (2012)

  GPAW: F. Hüser, T. Olsen, and K. S. Thygesen, Phys. Rev. B **87**, 235132 (2013)

  WEST: M. Govoni and G. Galli, J. Chem. Theory Comput. **11**, 2680 –2696 (2015)

- 2011 – now: *GW* with localized basis in publicly available codes

  FHI-aims: X. Ren *et al.*, New J. Phys. **14**, 053020 (2012)

  Turbomole: M. van Setten, F. Weigend, and F. Evers, J. Chem. Theory Comput. **9**, 232 – 246 (2012)

  molgw: F. Bruneval *et al.*, Comput. Phys. Commun. **208**, 149 – 161 (2016)

  CP2K: J. Wilhelm, M. Del Ben, and J. Hutter, J. Chem. Theory Comput. **12**, 3623 – 3635 (2016)

- Recent trend: Numerically converged results and agreement between codes

  J. Klimeš, M. Kaltak, and G. Kresse: Predictive *GW* calculations using plane waves and pseudopotentials, Phys. Rev. B **90**, 075125 (2014)

  M. van Setten *et al.*: *GW*100: Benchmarking G_0W_0 for Molecular Systems, JCTC **11**, 5665 – 5687 (2015)

Hedin's equations

- Hedin's equation: Complicated self-consistent equations which give the exact self-energy.

  Notation: $(1) = (\mathbf{r}_1, t_1)$, G_0: non-interacting Green's function, e.g. from DFT

  Self-energy: $$\Sigma(1,2) = i \int d(34) G(1,3) \Gamma(3,2,4) W(4,1^+)$$

  Green's function: $$G(1,2) = G_0(1,2) + \int d(34) G_0(1,3) \Sigma(3,4) G(4,2)$$

  Screened interaction: $$W(1,2) = V(1,2) + \int d(34) V(1,3) P(3,4) W(4,2)$$

  Bare interaction: $$V(1,2) = \delta(t_1 - t_2)/|\mathbf{r}_1 - \mathbf{r}_2|$$

  Polarization: $$P(1,2) = -i \int d(34) G(1,3) G(4,1^+) \Gamma(3,4,2)$$

  Vertex function: $$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int d(4567) \frac{\partial \Sigma(1,2)}{\partial G(4,5)} G(4,6) G(7,5) \Gamma(6,7,3)$$

- It can be shown that $\Sigma(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) = \Sigma(\mathbf{r}_1, \mathbf{r}_2, t_2 - t_1)$. After a Fourier transform of Σ from time $t \equiv t_2 - t_1$ to frequency (= energy), the self-energy $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$ can be used to compute the quasiparticle levels ε_n using

$$\left(\frac{-\nabla^2}{2} + v_{\text{el-core}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right) \psi_n(\mathbf{r}) + \int d\mathbf{r}' \; \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_n) \psi_n(\mathbf{r}') = \varepsilon_n \psi_n(\mathbf{r})$$

Hedin's equations: Hartree-Fock

Hartree-Fock is GV:

Self-energy: $$\Sigma(1,2) = i \int d(34) G(1,3) \Gamma(3,2,4) W(4,1^+) = G(1,2) V(2,1)$$

Green's function: $$G(1,2) = G_0(1,2) + \int d(34) G_0(1,3) \Sigma(3,4) G(4,2)$$

Screened interaction: $$W(1,2) = V(1,2) + \int d(34) V(1,3) \cancelto{\to 0}{P(3,4)} W(4,2) = V(1,2)$$

Bare interaction: $$V(1,2) = \delta(t_1 - t_2)/|\mathbf{r}_1 - \mathbf{r}_2|$$

Polarization: $$P(1,2) = \cancel{-i \int d(34) G(1,3) G(4,1^+) \Gamma(3,4,2)} = 0$$

Vertex function: $$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \cancel{\int d(4567) \frac{\partial \Sigma(1,2)}{\partial G(4,5)} G(4,6) G(7,5) \Gamma(6,7,3)}$$

Hedin's equations: *GW*

Self-energy: $\Sigma(1,2) = i \int d(34) G(1,3) \Gamma(3,2,4) W(4,1^+) = iG(1,2)W(2,1^+)$

Green's function: $G(1,2) = G_0(1,2) + \int d(34) G_0(1,3) \Sigma(3,4) G(4,2)$

Screened interaction: $W(1,2) = V(1,2) + \int d(34) V(1,3) P(3,4) W(4,2)$

Bare interaction: $V(1,2) = \delta(t_1 - t_2)/|\mathbf{r}_1 - \mathbf{r}_2|$

Polarization: $P(1,2) = -i \int d(34) G(1,3) G(4,1^+) \cancel{\Gamma(3,4,2)} = G(1,2)G(2,1^+)$

Vertex function: $\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \cancel{\int d(4567) \frac{\partial \Sigma(1,2)}{\partial G(4,5)} G(4,6) G(7,5) \Gamma(6,7,3)}$

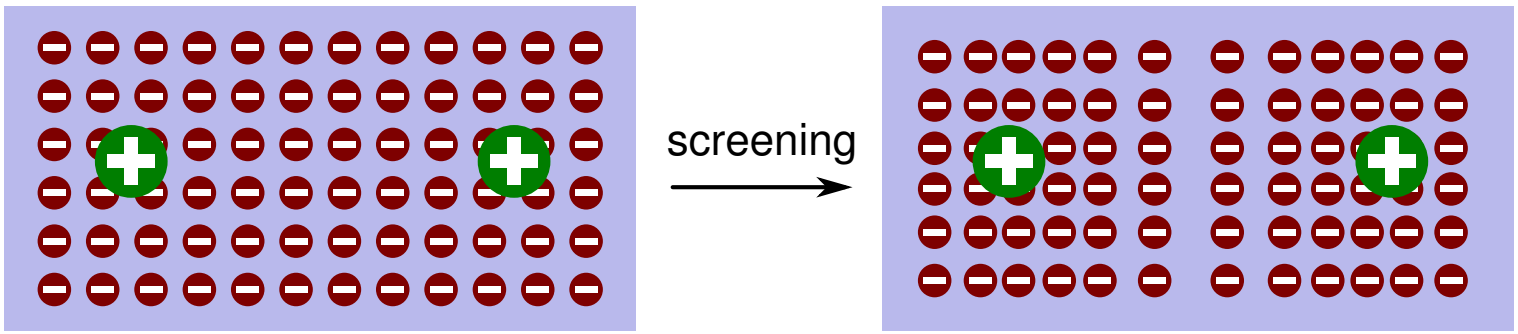
Screening

- In *GW*, the screened Coulomb interaction is appearing:

$$W(\mathbf{r}, \mathbf{r}', \omega) = \int d\mathbf{r}'' \epsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega) v(\mathbf{r}'', \mathbf{r}')$$

- Compare to screened Coulomb potential with spatially constant, static (ω=0) dielectric constant ϵ_r in SI units:

$$W(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$



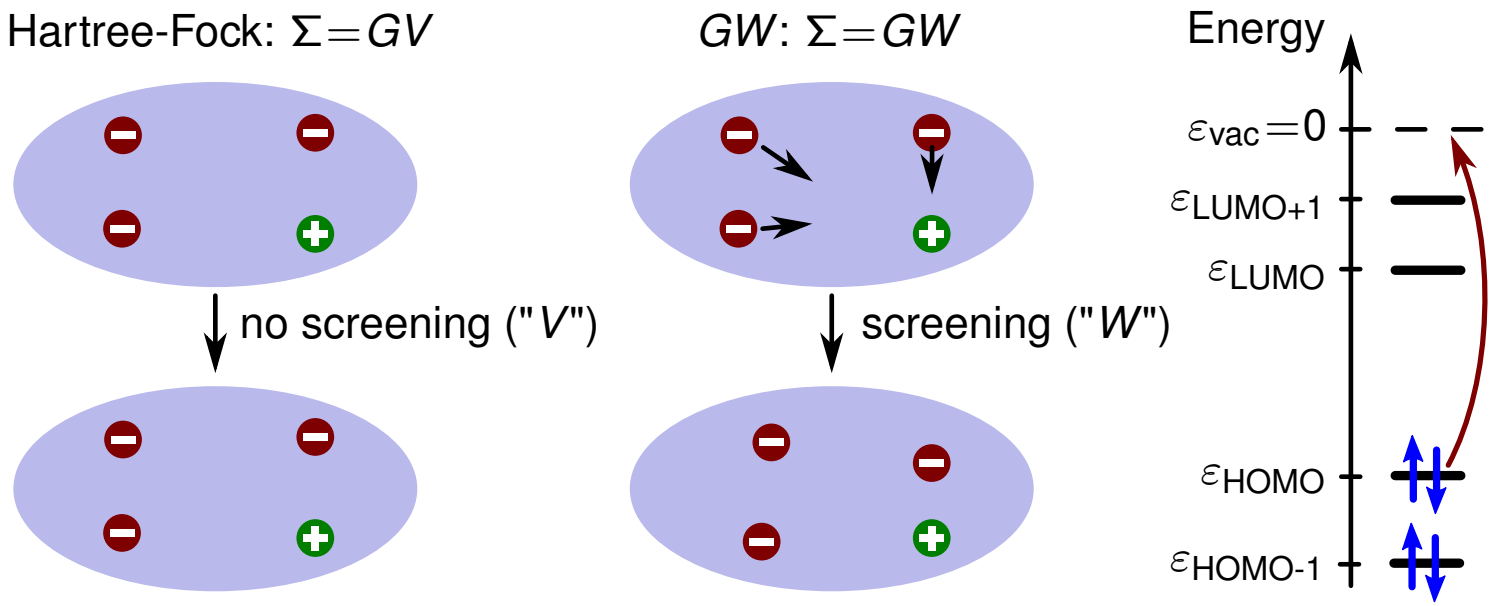
 charge which has been added to the system

 internal mobile charge carriers (e.g. electrons) which adapt due to the + charge

- screening: adaption of electrons due to additional charge, key ingredient in *GW* (next slide)

V in Hartree-Fock versus W in GW

- Gedankenexperiment: Ionization which leads to a hole (marked by "+")



- HF does not account for relaxation of electrons after adding an electron to an unoccupied MO or removing an electron from an occupied MO (only V in HF, no W or ϵ)
  $\Rightarrow$ occupied levels are too low, unoccupied levels are too high $\Rightarrow$ HOMO-LUMO gap too large
- In DFT, ε_n (besides $\varepsilon_{\text{HOMO}}$) do not have any physical meaning. Self-interaction error (SIE) in common GGA functionals $\Rightarrow$ HOMO far too high in DFT $\Rightarrow$ HOMO-LUMO gap too low in DFT
- Mixing HF and DFT (hybrids) can give accurate HOMO-LUMO gaps since two errors (SIE in DFT vs. absence of screening in HF) may compensate
- GW accounts for screening (since W is included) after adding an electron to an unoccupied MO or removing an electron from an occupied MO $\Rightarrow$ accurate ε_n^{GW}

Physics beyond *GW*

- *GW* does not account for the exact adaption of other electrons
  $\Rightarrow \varepsilon_n^{GW}$ can be improved by higher level of theory ("adding more diagrams")

- Analogy: Full CI contains all determinants (= diagrams), but is untractable for large systems.
  Way out: neglect unnecessary determinants leading to e.g. CCSD, CCSD(T), RPA, MP2

- Exact expansion of the self-energy:

$$\Sigma(1,2) = iG(1,2)W(2,1^+) - \int d(34)\, G(1,3)W(1,4)G(4,2)W(3,2)G(3,4) + \ldots$$

  $\Rightarrow$ *GW* approximation is good if W is small, otherwise higher order terms in W important

- Screening is high in systems with small bandgap (since MOs in occupied orbitals can scatter into unoccupied orbitals with low loss of energy)

  $\Rightarrow \epsilon$ is large in systems with small bandgap

  $\Rightarrow W$ is small in systems with small bandgap

  $\Rightarrow$ The *GW* approximation is good for systems with small bandgaps

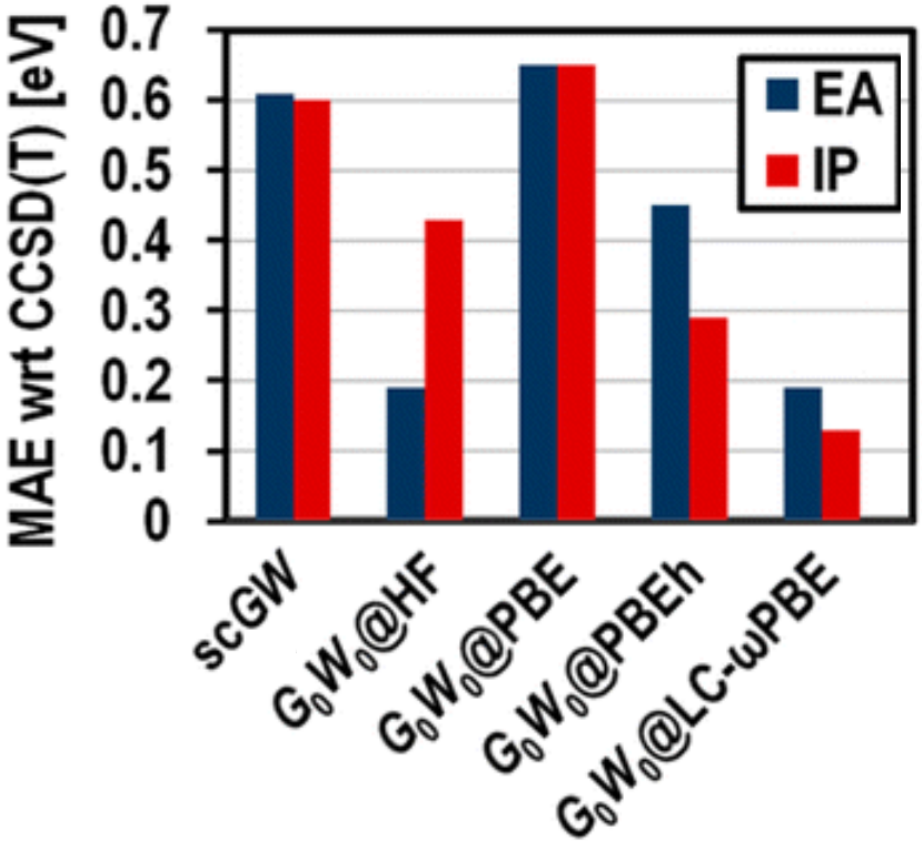
Accuracy of G_0W_0

	Band gap	
	G_0W_0@PBE	Expt.
Si	1.16	1.17
GaAs	1.34	1.52
SiC	2.31	2.40
C	5.50	5.48
BN	6.17	6.1-6.4
MgO	7.27	7.83
LiF	13.68	14.20

Benchmark for solids (VASP)

Bandgap = HOMO-LUMO gap

Liu *et al.*, PRB **94**, 165109 (2016)



Benchmark for molecules (FHI-aims)

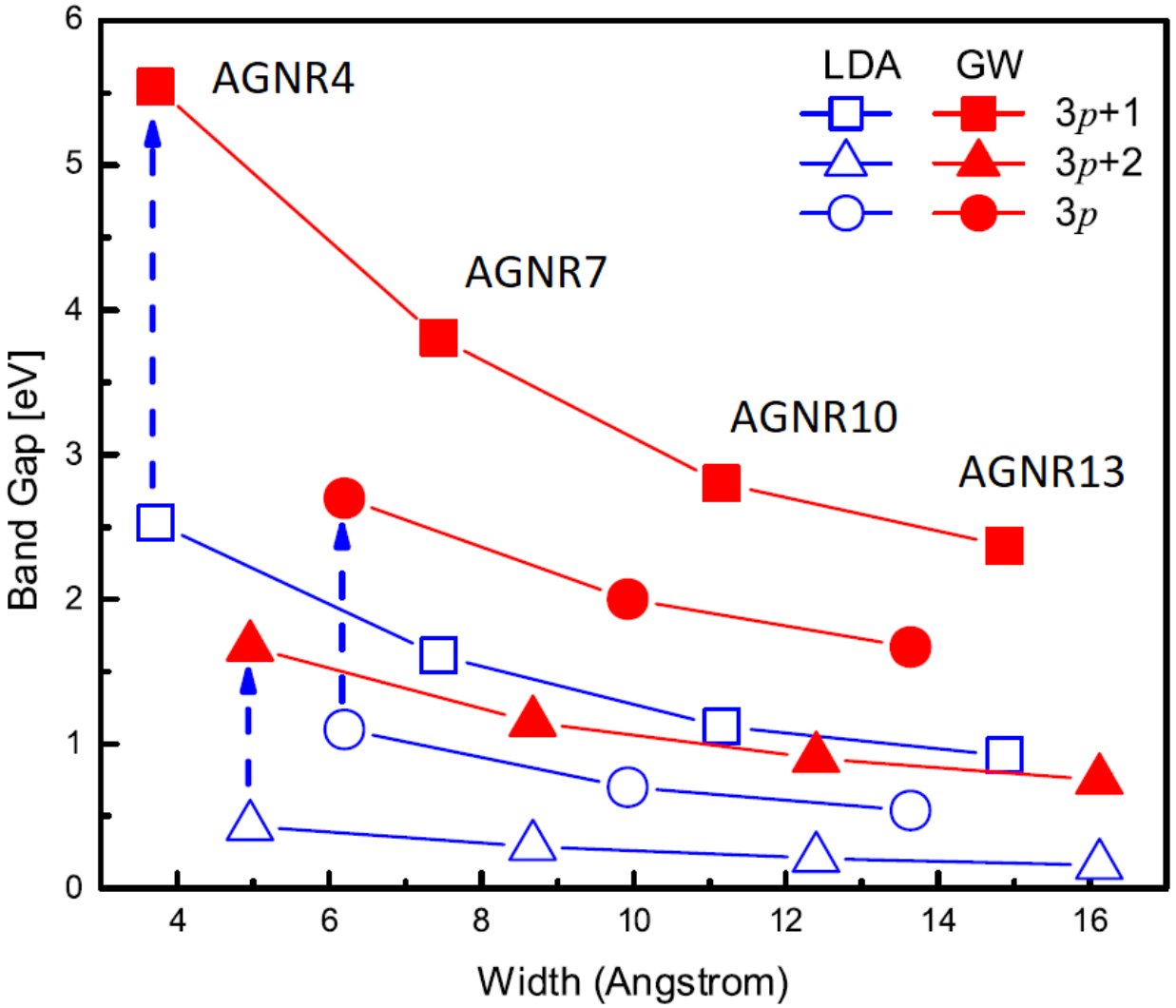
MAE = Mean absolute error

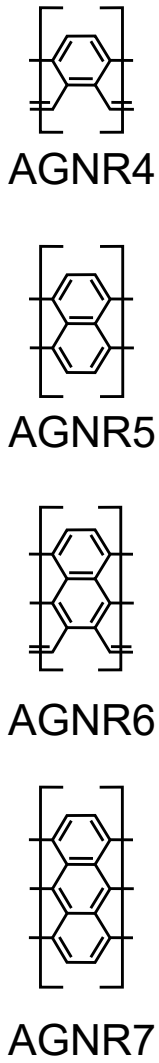
IP = Ionization potential = $|\varepsilon_{\text{HOMO}}|$

EA = Electron affinity = $|\varepsilon_{\text{LUMO}}|$

Knight *et al.*, JCTC **12**, 615 (2016)

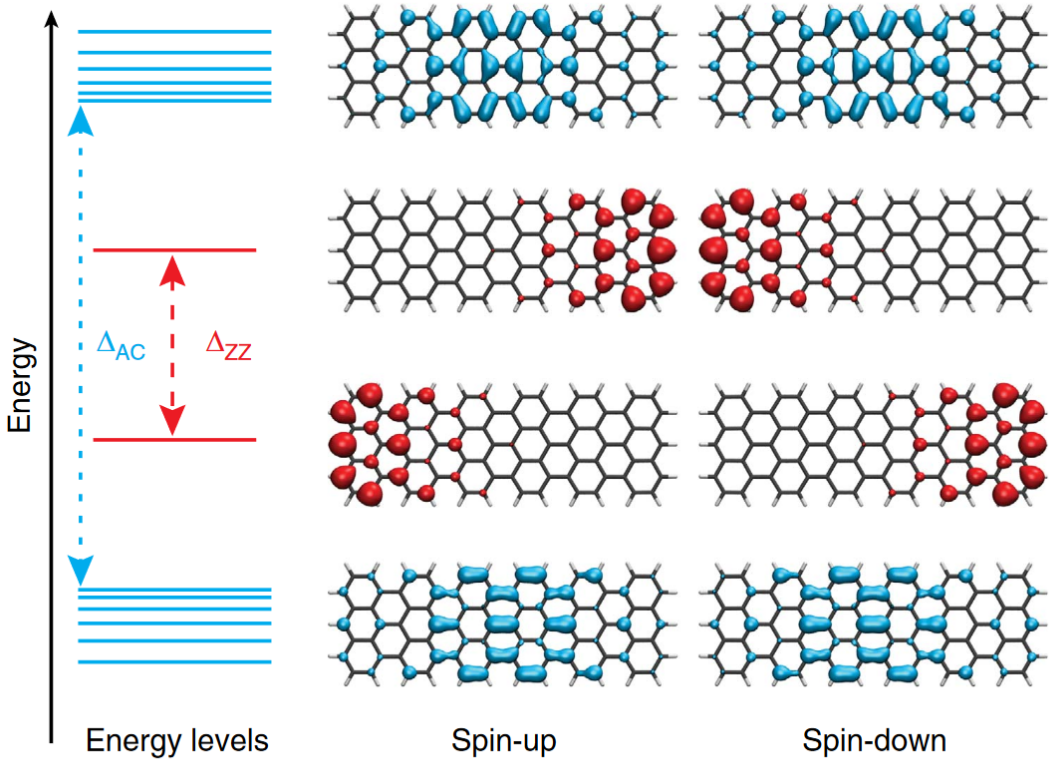
Application of G_0W_0 to periodic graphene nanoribbons

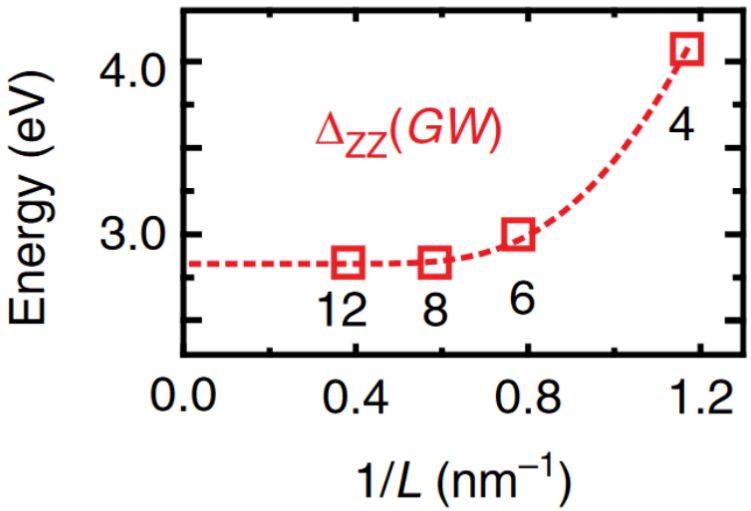




L. Yang, C.-H. Park, Y.-W. Son, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **99**, 186801 (2007)

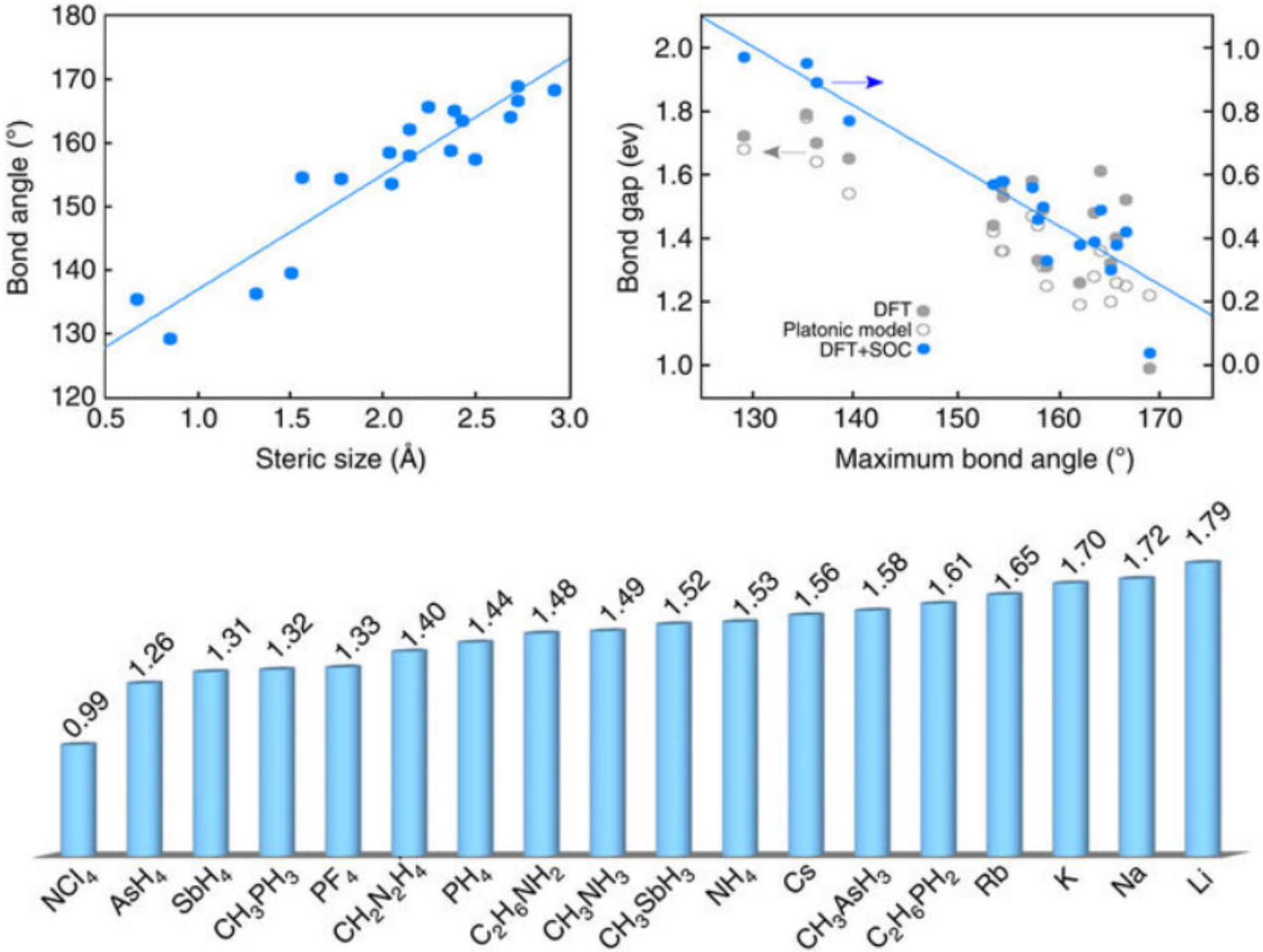
Application of G_0W_0 to novel graphene nanoribbons





S. Wang, L. Talirz, C. A. Pignedoli, X. Feng, K. Müllen, R. Fasel, P. Ruffieux, Nat. Commun. **7**, 11507 (2016)

Application of G_0W_0 to novel perovskite solar cells



M. R. Filip, G. E. Eperon, H. J. Snaith, and F. Giustino, Nat. Commun. **5**, 5757 (2014)

Literature: J. Wilhelm, M. Del Ben, and J. Hutter, J. Chem. Theory Comput. **12**, 3623 – 3635 (2016)

Resolution of the identity (RI) [Chem. Phys. Lett. **213**, 514-518 (1993)]

In post-DFT methods as *GW*, four-index Coulomb integrals are appearing:

$$(nm|kl) = \int d^3\mathbf{r}\, d^3\mathbf{r}'\, \psi_n(\mathbf{r})\psi_m(\mathbf{r})\, \frac{1}{|\mathbf{r}-\mathbf{r}'|}\, \psi_k(\mathbf{r}')\psi_l(\mathbf{r}')$$

RI with overlap metric

$$\mathrm{Id} = \sum_{PQ} |P\rangle\, S^{-1}_{PQ}\, \langle Q|$$

$$(nm|kl) = \sum_{PQRT} (nmP) S^{-1}_{PQ} V_{QR} S^{-1}_{RT} (Tkl)$$

$$(nmP) = \int d^3\mathbf{r}\, \psi_n(\mathbf{r})\psi_m(\mathbf{r})\varphi_P(\mathbf{r})$$

Resolution of the identity basis $\{\varphi_P\}$ with

- Overlap matrix
  $S_{PQ} = \int d^3\mathbf{r}\, \varphi_P(\mathbf{r})\varphi_Q(\mathbf{r})$
- Coulomb matrix
  $V_{PQ} = \int d^3\mathbf{r}\, d^3\mathbf{r}'\, \varphi_P(\mathbf{r})\varphi_Q(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$

RI with Coulomb metric

$$\mathrm{Id} = \sum_{PQ} |P\rangle\, V^{-1}_{PQ}\, \langle Q|\, \frac{1}{\hat{r}}$$

$$\begin{aligned}
(nm|kl) &= \sum_{PQRT} (nm|P) V^{-1}_{PQ} V_{QR} V^{-1}_{RT} (T|kl) \\
&= \sum_{PQ} (nm|P) V^{-1}_{PQ} (Q|kl) \\
&= \sum_{PQR} \underbrace{(nm|P) V^{-1/2}_{PQ}}_{= B^{nm}_Q} \underbrace{V^{-1/2}_{QR} (R|kl)}_{= B^{kl}_Q} \\
&= \sum_{Q} B^{nm}_Q B^{kl}_Q
\end{aligned}$$

$$(nm|P) = \int d^3\mathbf{r}\, d^3\mathbf{r}'\, \psi_n(\mathbf{r})\psi_m(\mathbf{r})\, \frac{1}{|\mathbf{r}-\mathbf{r}'|}\, \varphi_P(\mathbf{r}')$$

G_0W_0 in real space versus GW with RI

G_0W_0 in real space

1. Compute density response [$\mathcal{O}(N^4)$]

$$\chi(\mathbf{r},\mathbf{r}',i\omega)=\sum_{ia}\psi_a(\mathbf{r}')\psi_i(\mathbf{r}')\psi_i(\mathbf{r})\psi_a(\mathbf{r})\,\frac{2(\varepsilon_i-\varepsilon_a)}{\omega^2+(\varepsilon_i-\varepsilon_a)^2}$$

2. Compute dielectric function

$$\epsilon(\mathbf{r},\mathbf{r}',i\omega)=\delta(\mathbf{r},\mathbf{r}')-\int d\mathbf{r}''\,v(\mathbf{r},\mathbf{r}'')\chi(\mathbf{r}'',\mathbf{r}',i\omega)$$

3. Compute screened Coulomb interaction

$$W_0(\mathbf{r},\mathbf{r}',i\omega)=\int d\mathbf{r}''\,\epsilon^{-1}(\mathbf{r},\mathbf{r}'',i\omega)v(\mathbf{r}'',\mathbf{r}')$$

4. Compute self-energy (SE)

$$\Sigma(\mathbf{r},\mathbf{r}',i\omega)=-\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}G_0(\mathbf{r},\mathbf{r}',i\omega-i\omega')W_0(\mathbf{r},\mathbf{r}',i\omega')$$

5. Compute G_0W_0 quasiparticle energies

$$\varepsilon_n^{G_0W_0}=\varepsilon_n+\langle\psi_n|\mathrm{Re}\,\Sigma(\varepsilon_n^{G_0W_0})-v^{\mathrm{xc}}|\psi_n\rangle$$

G_0W_0 with RI

1. Compute Π_{PQ} matrix [Π equivalent to $v^{1/2}\chi v^{1/2}$, $\mathcal{O}(N^4)$ operations]

$$\Pi_{PQ}(i\omega)=\sum_{ia}B_P^{ia}\,\frac{2(\varepsilon_i-\varepsilon_a)}{\omega^2+(\varepsilon_i-\varepsilon_a)^2}\,B_Q^{ia}$$

2. Compute symmetrized dielectric function

$$\epsilon_{PQ}(i\omega)=\delta_{PQ}-\Pi_{PQ}(i\omega)$$

3. Compute SE $\Sigma_n(i\omega)\equiv\langle\psi_n|\Sigma(i\omega)|\psi_n\rangle$

$$\Sigma_n(i\omega)=-\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\sum_m^{\text{all}}\frac{1}{i(\omega-\omega')+\varepsilon_F-\varepsilon_m}\times\sum_{PQ}B_P^{nm}\epsilon_{PQ}^{-1}(i\omega')B_Q^{mn}$$

4. Compute G_0W_0 quasiparticle energies

$$\varepsilon_n^{G_0W_0}=\varepsilon_n+\langle\psi_n|\mathrm{Re}\,\Sigma(\varepsilon_n^{G_0W_0})-v^{\mathrm{xc}}|\psi_n\rangle$$

Exchange and correlation self-energy

The self-energy $\Sigma_n(i\omega)$ from the last slide,

$$\Sigma_n(i\omega) = -\int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \sum_m^{\text{all}} \frac{1}{i(\omega-\omega') + \varepsilon_F - \varepsilon_m} \sum_{PQ} B_P^{nm} \epsilon_{PQ}^{-1}(i\omega') B_Q^{mn} \,,$$

is split into an exchange part Σ_n^x [= (n,n)-diagonal element of the Fock matrix]

$$\Sigma_n^x = -\sum_m^{\text{occ}} \sum_P B_P^{nm} B_P^{mn} \,,$$

and a correlation part

$$\Sigma_n^c(i\omega) = -\int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \sum_m^{\text{all}} \frac{1}{i(\omega-\omega') + \varepsilon_F - \varepsilon_m} \sum_{PQ} B_P^{nm} [\epsilon_{PQ}^{-1}(i\omega') - \delta_{PQ}] B_Q^{mn} \,,$$

such that $\Sigma_n(i\omega) = \Sigma_n^x + \Sigma_n^c(i\omega)$. This procedure guarantees numerical stability.

Analytic continuation

The self-energy $\Sigma_n^c(i\omega)$ is computed for imaginary frequency and needed for real frequency (= energy) for solving the quasiparticle equation:

$$\varepsilon_n^{G_0W_0} = \varepsilon_n + \mathrm{Re}\,\Sigma_n(\varepsilon_n^{G_0W_0}) - v_n^{\mathrm{xc}}$$

where $v_n^{\mathrm{xc}} = \int d^3\mathbf{r}\,\psi_n(\mathbf{r})v_{\mathrm{xc}}(\mathbf{r})\psi_n(\mathbf{r})$.

$\Sigma_n(\omega)$ for a real-valued ω is obtained from $\Sigma_n(i\omega)$ by fitting an N-point Padé approximant

$$P(i\omega) = \frac{\sum_{j=0}^{N-1} a_j \cdot (i\omega)^j}{1 + \sum_{k=0}^{N} b_k \cdot (i\omega)^k}$$

to $\Sigma_n(i\omega)$ to determine the complex numbers a_j and b_k. Then, $\Sigma_n(\omega)$ is obtained by evaluating P:

$$\Sigma_n(\omega) = \frac{\sum_{j=0}^{N-1} a_j \cdot (\omega - \varepsilon_{\mathrm{F}})^j}{1 + \sum_{k=0}^{N} b_k \cdot (\omega - \varepsilon_{\mathrm{F}})^k}$$

where the Fermi level ε_{F} appears to obtain the correct offset.

Input for G_0W_0@PBE for the H_2O molecule I

DFT calculation to get the molecular orbitals ψ_n from a PBE calculation:

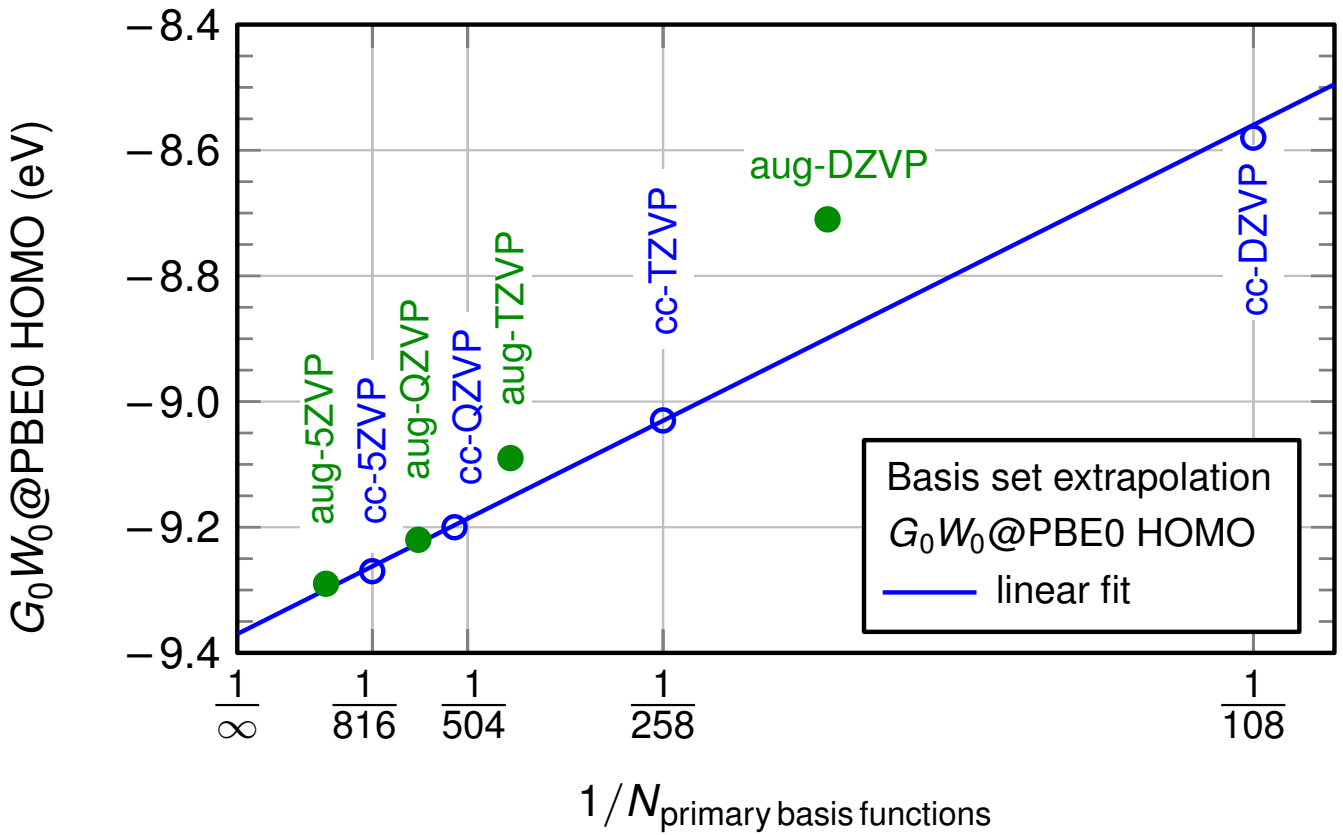
```
&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME BASIS_def2_QZVP_RI_ALL
    POTENTIAL_FILE_NAME POTENTIAL
    &MGRID
      CUTOFF 400
      REL_CUTOFF 50
    &END MGRID
    &QS
      ! all electron calculation since GW100
      ! is all-electron test
      METHOD GAPW
    &END QS
    &POISSON
      PERIODIC NONE
      PSOLVER MT
    &END
    &SCF
      EPS_SCF 1.0E-6
      SCF_GUESS ATOMIC
      MAX_SCF 200
    &END SCF
    &XC
      &XC_FUNCTIONAL PBE
      &END XC_FUNCTIONAL
      ! GW is part of the WF_CORRELATION section
      &WF_CORRELATION
        ...
      &END
    &END XC
  &END DFT
                    .
                    .
                    .
  &SUBSYS
    &CELL
      ABC 10.0 10.0 10.0
      PERIODIC NONE
    &END CELL
    &COORD
      O  0.0000 0.0000 0.0000
      H  0.7571 0.0000 0.5861
      H -0.7571 0.0000 0.5861
    &END COORD
    &TOPOLOGY
      &CENTER_COORDINATES
      &END
    &END TOPOLOGY
    &KIND H
      ! def2-QZVP: basis of GW100
      BASIS_SET def2-QZVP
      ! just very large RI basis to ensure good
      ! convergence in RI basis
      RI_AUX_BASIS RI-5Z
      POTENTIAL ALL
    &END KIND
    &KIND O
      BASIS_SET def2-QZVP
      RI_AUX_BASIS RI-5Z
      POTENTIAL ALL
    &END KIND
  &END SUBSYS
&END FORCE_EVAL
&GLOBAL
  RUN_TYPE      ENERGY
  PROJECT       ALL_ELEC
  PRINT_LEVEL   MEDIUM
&END GLOBAL
```

Input for G_0W_0@PBE for the H_2O molecule II

Parameters for the *GW* calculation:

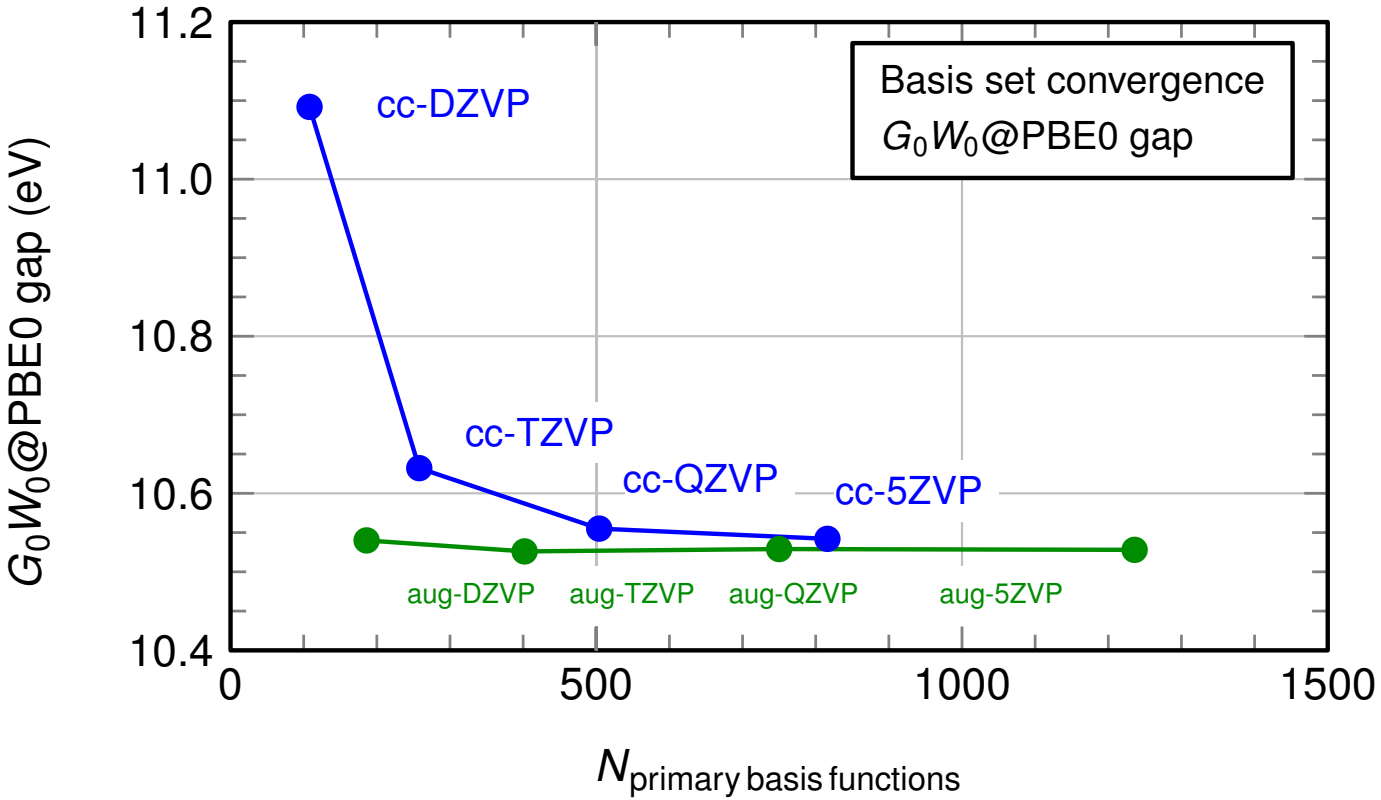
```
&XC

  &XC_FUNCTIONAL PBE
  &END XC_FUNCTIONAL

  ! GW is part of the WF_CORRELATION section
  &WF_CORRELATION

    ! RPA is used to compute the density response function
    METHOD RI_RPA_GPW

    ! Use Obara-Saika integrals instead of GPW integrals
    ! since OS is much faster
    ERI_METHOD OS

    &RI_RPA

      ! use 100 quadrature points to perform the
      ! frequency integration in GW
      RPA_NUM_QUAD_POINTS 100

      ! SIZE_FREQ_INTEG_GROUP is a group size for
      ! parallelization and should be increased for
      ! large calculations to prevent out of memory.
      ! maximum for SIZE_FREQ_INTEG_GROUP
      ! is the number of MPI tasks
      SIZE_FREQ_INTEG_GROUP 1

      GW

                .
                .
                .

      &RI_G0W0

       ! compute the G0W0@PBE energy of HOMO-9,
       ! HOMO-8, ... , HOMO-1, HOMO
       CORR_OCC   10

       ! compute the G0W0@PBE energy of LUMO,
       ! LUMO+1, ... , LUMO+20
       CORR_VIRT  20

       ! Pade approximant
       ANALYTIC_CONTINUATION PADE

       ! for solving the quasiparticle equation,
       ! the Newton method is used as in GW100
       CROSSING_SEARCH NEWTON

       ! use RI for the exchange self-energy
       RI_SIGMA_X

      &END RI_G0W0

    &END RI_RPA

    ! NUMBER_PROC is a group size for
    ! parallelization and should be increased
    ! for large calculations
    NUMBER_PROC 1

  &END WF_CORRELATION

&END XC
```

Basis set convergence for benzene: HOMO level



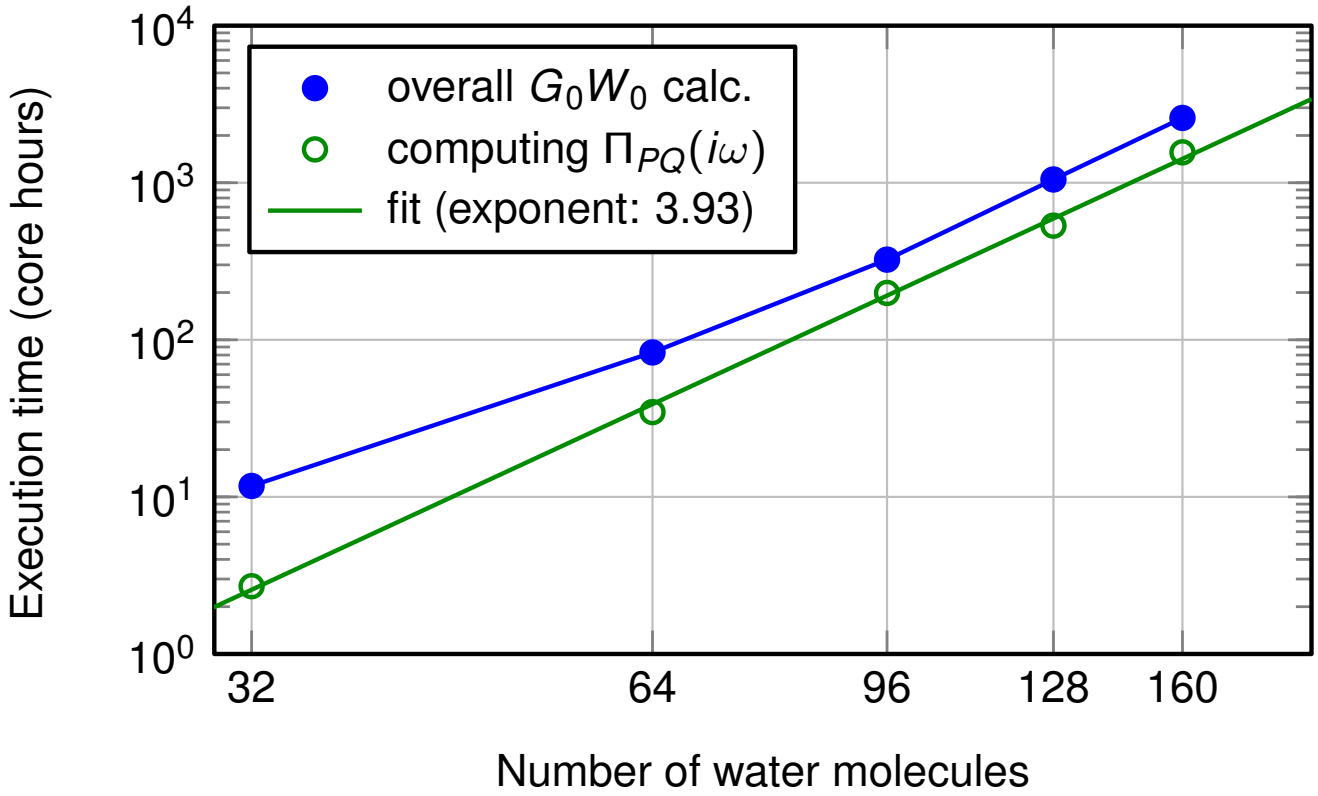
- Slow basis set convergence for the HOMO level
- Basis set extrapolation necessary

Basis set convergence for benzene: HOMO-LUMO gap



- Slow basis set convergence for the HOMO-LUMO gap in a correlation-consistent (cc) basis
- Fast basis set convergence for the HOMO-LUMO gap in an augmented (aug) basis

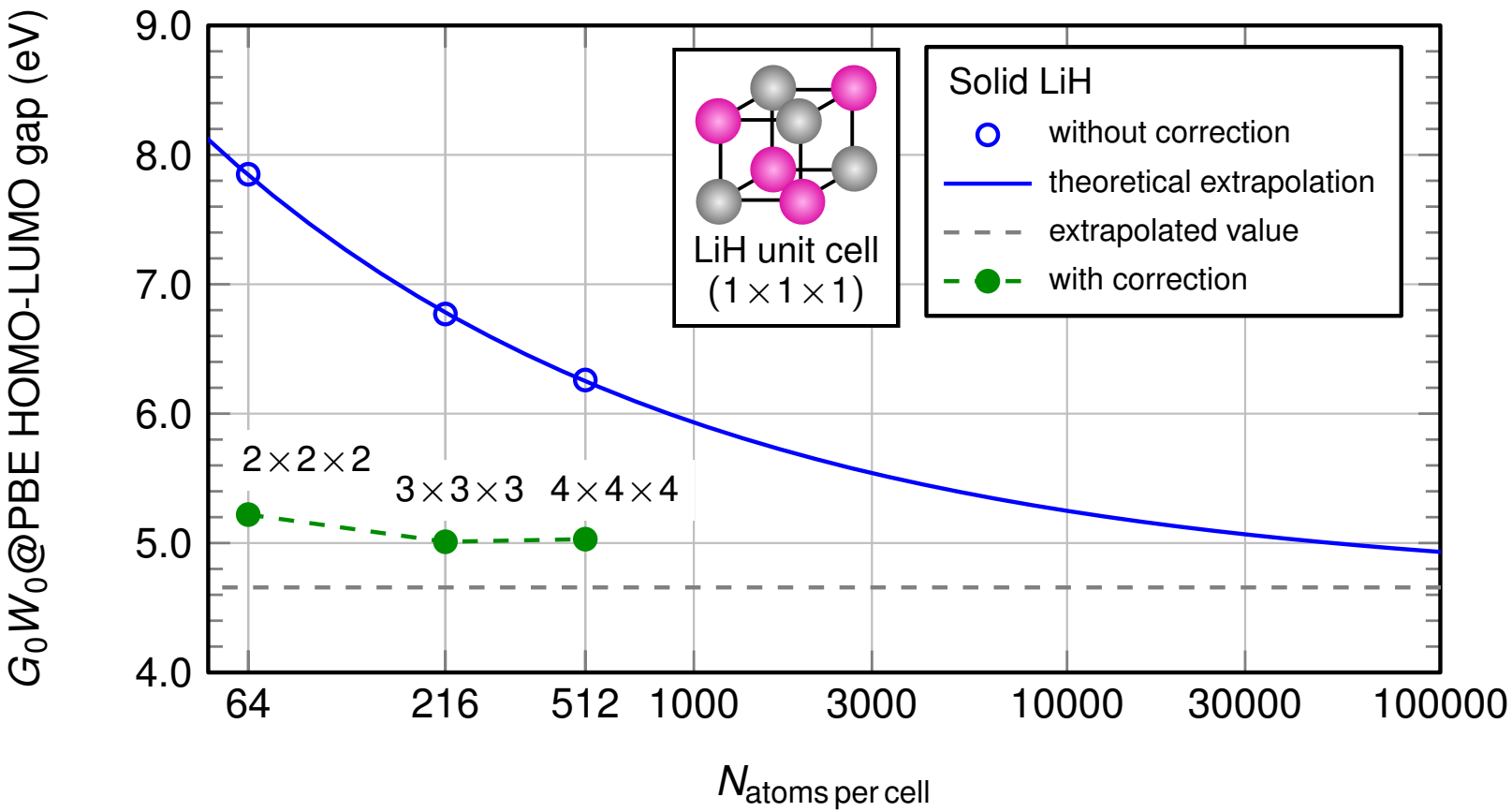
Computational cost for water in a cc-TZVP basis



- $\mathcal{O}(N^4)$ computational cost as expected
- massively parallel implementation

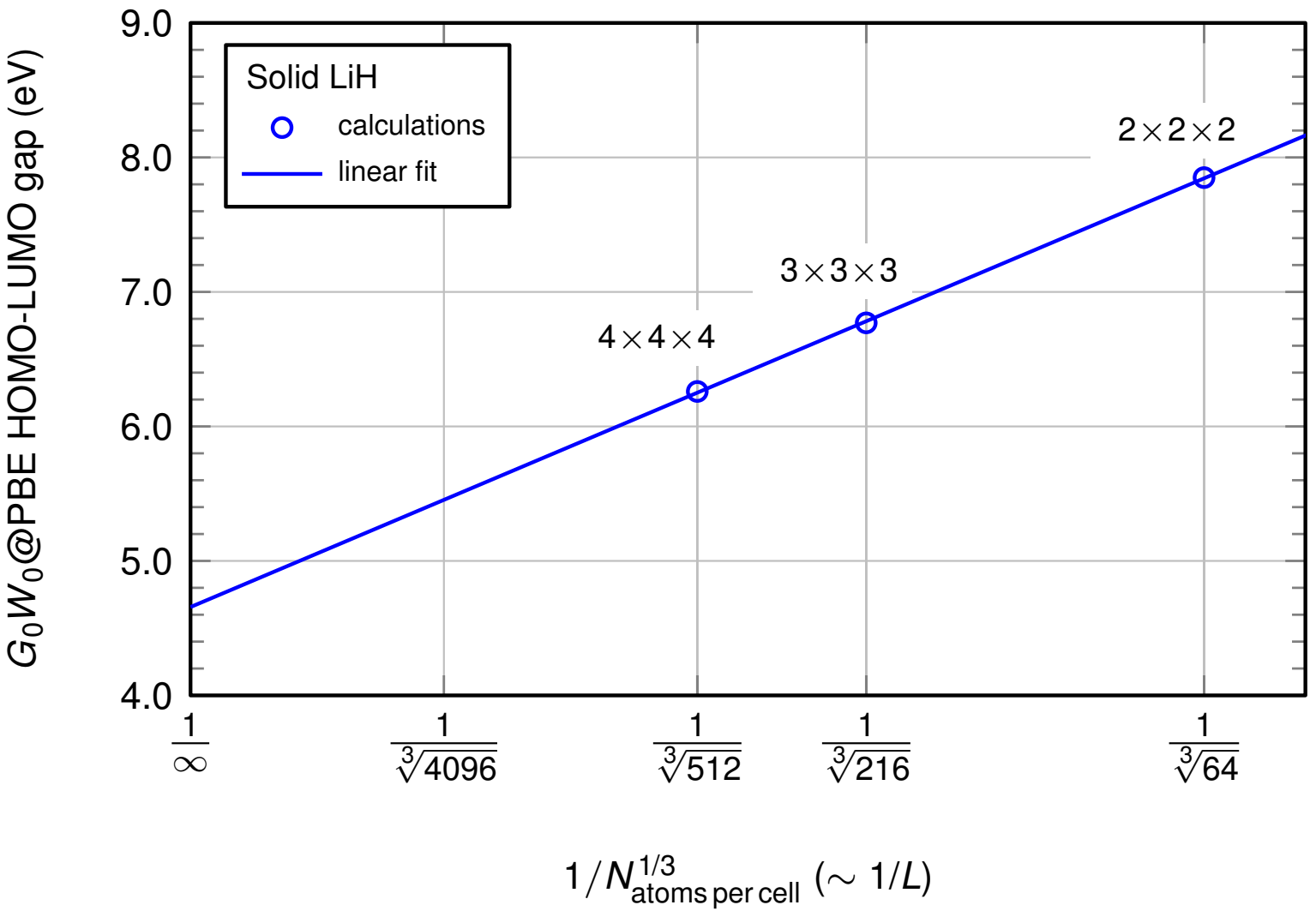
Literature: J. Wilhelm and J. Hutter, Phys. Rev. B **95**, 235123 (2017)

Motivation: Slow convergence of *GW* with the cell size

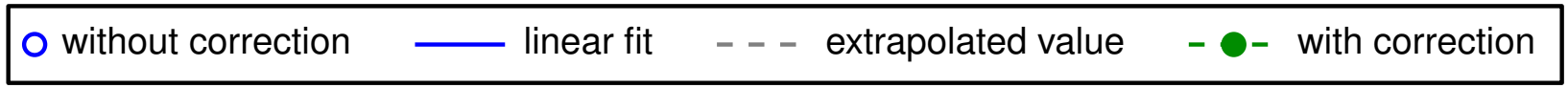


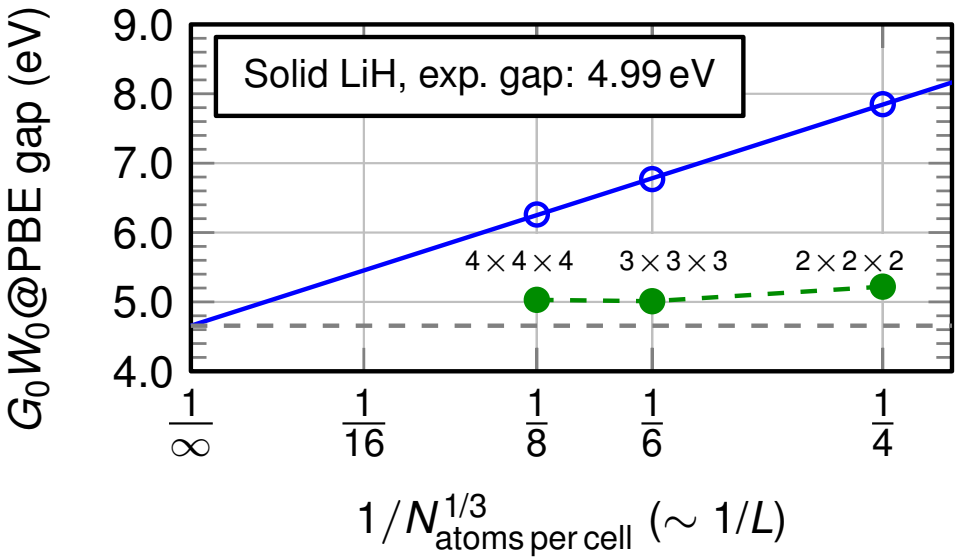
- Very slow convergence of the G_0W_0 HOMO-LUMO gap as function of the cell size
- The extrapolation (blue line) can be done with $1/N_{\text{atoms per cell}}^{1/3}$
- Comparison: Convergence of DFT gap with $\exp(-N_{\text{atoms per cell}})$ for non-metallic systems

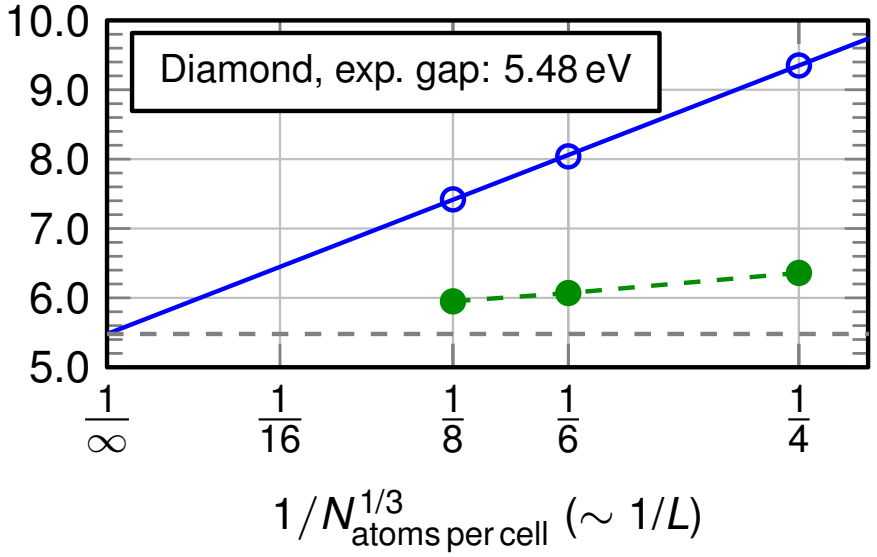
$1/L$ convergence of the HOMO-LUMO gap

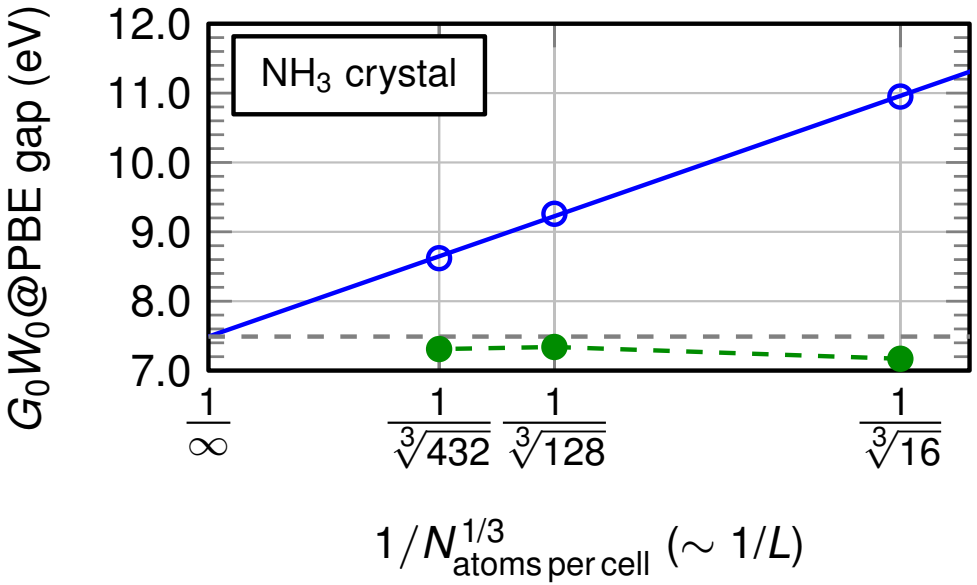


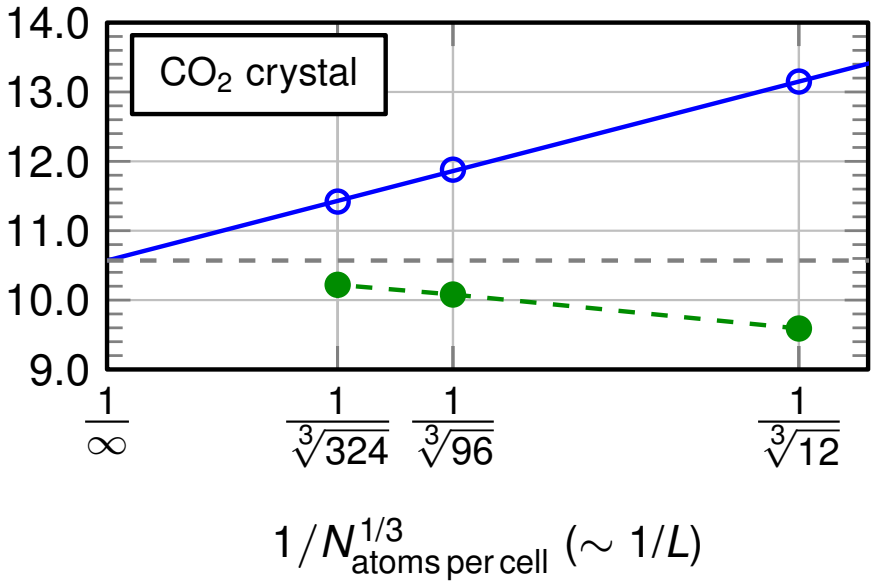
Benchmark calculations for solids











Input for periodic G_0W_0@PBE for solid LiH

```
                .
                .
                .
&XC

  &XC_FUNCTIONAL PBE
  &END XC_FUNCTIONAL

  &WF_CORRELATION

    METHOD  RI_RPA_GPW

    &RI_RPA

      RPA_NUM_QUAD_POINTS  100

      GW

      &RI_G0W0

       CORR_OCC  5
       CORR_VIRT 5

       ! activate the periodic correction
       PERIODIC

       ANALYTIC_CONTINUATION PADE

       CROSSING_SEARCH NEWTON

      &END RI_G0W0

                .
                .
                .
```

```
    ! HF calculation for the exchange self-energy
    ! Here, the truncation of the Coulomb operator works
    &HF

      &SCREENING
        EPS_SCHWARZ 1.0E-6
        SCREEN_ON_INITIAL_P TRUE
      &END

      &INTERACTION_POTENTIAL
        POTENTIAL_TYPE TRUNCATED
        ! the truncation radius is half the cell size
        CUTOFF_RADIUS  2.00
        T_C_G_DATA t_c_g.dat
      &END

      &MEMORY
        MAX_MEMORY  0
      &END

    &END

  &END RI_RPA

  NUMBER_PROC  1

 &END

&END XC

                .
                .
                .
```

Literature: J. Wilhelm, D. Golze, C. A. Pignedoli, and J. Hutter, in preparation

$\mathcal{O}(N^3)$ *GW* space-time method [Rojas *et al.*, PRL **74**, 1827 (1995)]

Canonical $\mathcal{O}(N^4)$ G_0W_0

1. Compute density response in $\mathcal{O}(N^4)$

$$\chi(\mathbf{r},\mathbf{r}',i\omega)=\sum_{ia}\psi_a(\mathbf{r}')\psi_i(\mathbf{r}')\psi_i(\mathbf{r})\psi_a(\mathbf{r})\,\frac{2(\varepsilon_i-\varepsilon_a)}{\omega^2+(\varepsilon_i-\varepsilon_a)^2}$$

2. Compute dielectric function

$$\epsilon(\mathbf{r},\mathbf{r}',i\omega)=\delta(\mathbf{r},\mathbf{r}')-\int d\mathbf{r}''\,v(\mathbf{r},\mathbf{r}'')\chi(\mathbf{r}'',\mathbf{r}',i\omega)$$

3. Compute screened Coulomb interaction

$$W_0(\mathbf{r},\mathbf{r}',i\omega)=\int d\mathbf{r}''\,\epsilon^{-1}(\mathbf{r},\mathbf{r}'',i\omega)v(\mathbf{r}'',\mathbf{r}')$$

4. Compute self-energy

$$\Sigma(\mathbf{r},\mathbf{r}',i\omega)=-\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\,G_0(\mathbf{r},\mathbf{r}',i\omega-i\omega')W_0(\mathbf{r},\mathbf{r}',i\omega')$$

5. Compute G_0W_0 quasiparticle energies

$$\varepsilon_n^{G_0W_0}=\varepsilon_n+\langle\psi_n|\mathrm{Re}\,\Sigma(\varepsilon_n^{G_0W_0})-v^{\mathrm{xc}}|\psi_n\rangle$$

$\mathcal{O}(N^3)$ G_0W_0 space-time method

1. Compute density response in $\mathcal{O}(N^3)$

$$\chi(\mathbf{r},\mathbf{r}',i\tau)=\sum_{ia}\psi_a(\mathbf{r}')\psi_i(\mathbf{r}')\psi_i(\mathbf{r})\psi_a(\mathbf{r})e^{-(\varepsilon_a-\varepsilon_i)\tau}$$

$$=\sum_{i}^{\mathrm{occ}}\psi_i(\mathbf{r}')\psi_i(\mathbf{r})e^{-|(\varepsilon_i-\varepsilon_\mathrm{F})\tau|}\sum_{a}^{\mathrm{virt}}\psi_a(\mathbf{r}')\psi_a(\mathbf{r})e^{-|(\varepsilon_a-\varepsilon_\mathrm{F})\tau|}$$

2. Compute dielectric function

$$\epsilon(\mathbf{r},\mathbf{r}',i\tau)=\delta(\mathbf{r},\mathbf{r}')-\int d\mathbf{r}''\,v(\mathbf{r},\mathbf{r}'')\chi(\mathbf{r}'',\mathbf{r}',i\tau)$$

3. Compute screened Coulomb interaction

$$W_0(\mathbf{r},\mathbf{r}',i\omega)=\int d\mathbf{r}''\,\epsilon^{-1}(\mathbf{r},\mathbf{r}'',i\omega)v(\mathbf{r}'',\mathbf{r}')$$

4. Compute self-energy

$$\Sigma(\mathbf{r},\mathbf{r}',i\tau)=-G_0(\mathbf{r},\mathbf{r}',i\tau)W_0(\mathbf{r},\mathbf{r}',i\tau)$$

5. Compute G_0W_0 quasiparticle energies

$$\varepsilon_n^{G_0W_0}=\varepsilon_n+\langle\psi_n|\mathrm{Re}\,\Sigma(\varepsilon_n^{G_0W_0})-v^{\mathrm{xc}}|\psi_n\rangle$$

Resolution of the identity (RI) II

RI with overlap metric

$$(\mu\nu|\lambda\sigma) = \sum_{PQRT} (\mu\nu P) S^{-1}_{PQ} V_{QR} S^{-1}_{RT} (T\lambda\sigma)$$

$$(\mu\nu P) = \int d^3\mathbf{r}\, \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})\varphi_P(\mathbf{r})$$

✓ $(\nu\mu P) = 0$ if one of $\phi_\mu, \phi_\nu, \varphi_P$ far-off

✗ slightly larger RI basis as for RI-Coulomb

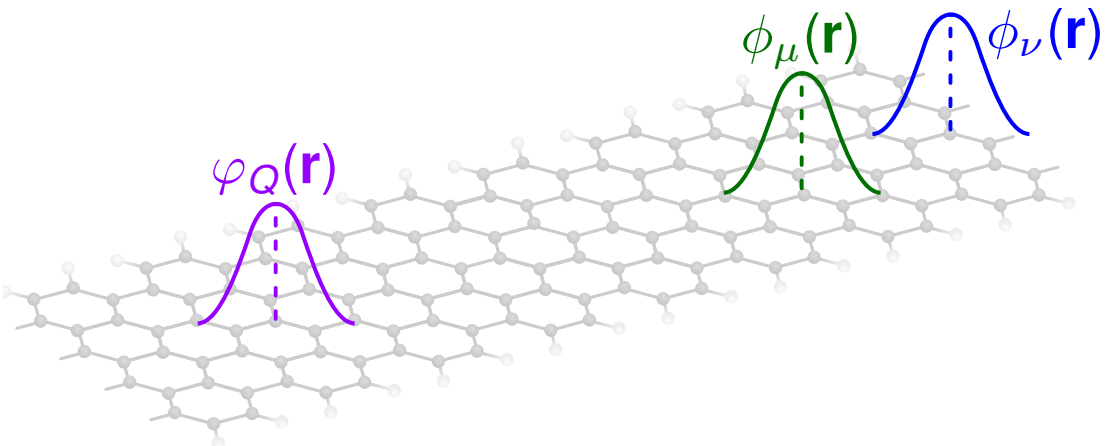
RI with Coulomb metric

$$(\mu\nu|\lambda\sigma) = \sum_{PQ} (\mu\nu|P) V^{-1}_{PQ} (Q|\lambda\sigma)$$

$$(\mu\nu|P) = \int d^3\mathbf{r}\, d^3\mathbf{r}'\, \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \varphi_P(\mathbf{r}')$$

✓ $(\nu\mu|P) = 0$ if ϕ_μ, ϕ_ν far-off

✗ No sparsity of $(\nu\mu|P)$ if φ_P far-off



$$(\mu\nu P) = \int d^3\mathbf{r}\, \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})\varphi_P(\mathbf{r}) \approx 0$$

$$(\mu\nu|P) = \int d^3\mathbf{r}\, d^3\mathbf{r}'\, \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \varphi_P(\mathbf{r}') \approx 1$$

Cubic-scaling *GW* in a Gaussian basis with overlap-metric RI

$$G_{\mu\nu}(i\tau) = \begin{cases} \sum_i C_{\mu i} C_{\nu i} e^{-|(\varepsilon_i - \varepsilon_F)\tau|}, & \text{if } \tau < 0 \\ -\sum_a C_{\mu a} C_{\nu a} e^{-|(\varepsilon_a - \varepsilon_F)\tau|}, & \text{if } \tau > 0 \end{cases}$$

$$\tilde{\chi}_{PQ}(i\tau) = \sum_{\mu\sigma} \sum_{\lambda} (\lambda\sigma P) G_{\mu\lambda}(i\tau) \times \sum_{\nu} (\mu\nu Q) G_{\nu\sigma}(-i\tau)$$

$\mathcal{O}(N^2)$, JW, P. Seewald, M. Del Ben, J. Hutter, JCTC **12**, 5851 – 5859 (2016)

$$\Sigma_n(i\tau) = -\sum_{\mu\nu PQ} G_{\mu\nu}(i\tau)(n\mu P) \times \tilde{W}_{PQ}(i\tau)(Q\nu n)$$

$\mathcal{O}(N^2 N_{GW})$

$$\chi(i\tau) = \mathbf{S}^{-1} \tilde{\chi}(i\tau) \mathbf{S}^{-1}$$

$\chi(i\omega)$

$\varepsilon(i\omega) = \mathbf{1} - \mathbf{V}\chi(i\omega)$

$\mathbf{W}(i\omega) = \varepsilon^{-1}(i\omega)\mathbf{V}$

$\tilde{\mathbf{W}}(i\omega) = \mathbf{S}^{-1}\mathbf{W}(i\omega)\mathbf{S}^{-1}$

$\tilde{\mathbf{W}}(i\tau)$

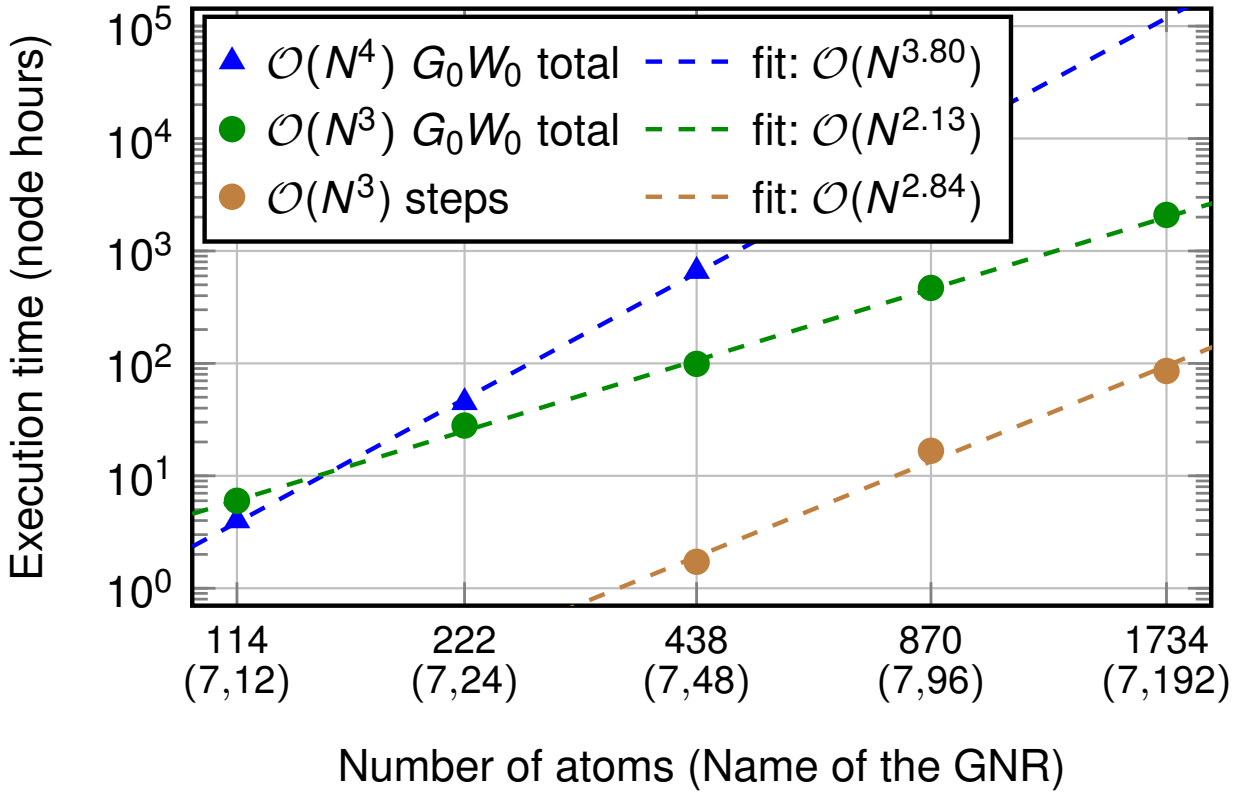
$\Sigma_n(i\omega)$

$\Sigma_n(\varepsilon)$

$$\varepsilon_n^{G_0W_0} = \varepsilon_n + \mathrm{Re}\,\Sigma_n(\varepsilon_n^{G_0W_0}) - v_n^{\mathrm{xc}}$$

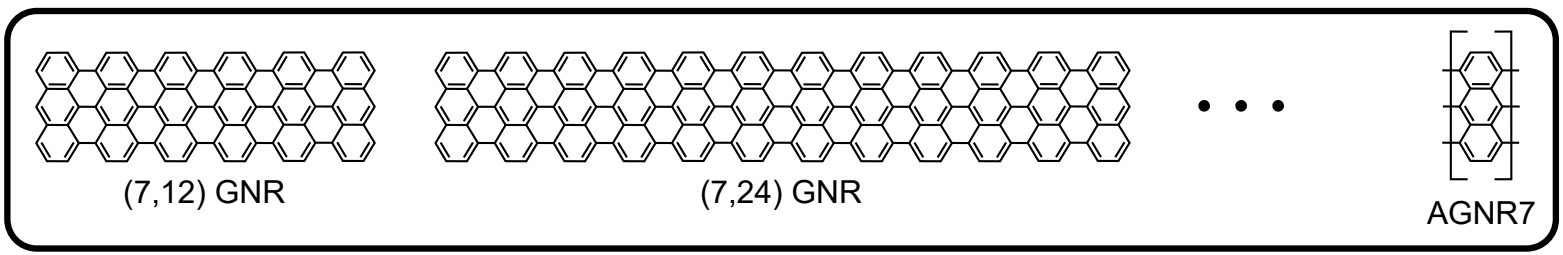
RI with overlap metric: $(\mu\nu|\lambda\sigma) = \sum_{PQRT} (\mu\nu P) S^{-1}_{PQ} V_{QR} S^{-1}_{RT} (T\lambda\sigma)$

Computational scaling of cubic-scaling *GW*



Cubic-scaling *GW* particularly efficient for systems with

- low dimensionality (best: one-dimensional chain, worst: spherical molecule, periodic system)
- local electronic structure (best: solution of small molecules, worst: extended π system)



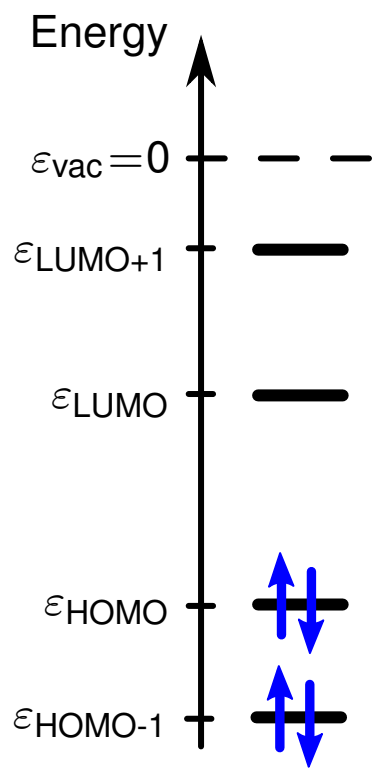
Input for cubic-scaling G_0W_0

- G_0W_0@PBE for the (7,192) GNR (1734 atoms, aug-DZVP basis)
- 400 Piz Daint MC nodes (4 OMP threads)

```
&WF_CORRELATION

  METHOD RI_RPA_GPW

  ! cubic-scaling GW only works with overlap metric RI
  RI OVERLAP

  ERI_METHOD OS

  &WFC_GPW

    ! EPS_FILTER should be tuned, computational cost
    ! strongly depends on EPS_FILTER
    EPS_FILTER  1.0E-9

    ! EPS_GRID may be tuned since memory is weakly
    ! dependent on it
    EPS_GRID 1.0E-6

  &END

  &RI_RPA

    ! cubic-scaling GW only works with the minimax grid
    ! in imag. time and frequency
    MINIMAX

    ! number of time and frequency points, at most 20
    RPA_NUM_QUAD_POINTS  12

    IM_TIME

              .
              .
              .

    ! parameters for computing chi(it)
    &IM_TIME

      ! EPS_FILTER_IM_TIME should be tuned
      EPS_FILTER_IM_TIME 1.0E-11

      ! for large systems, increase GROUP_SIZE_3C
      ! to prevent out of memory (OOM)
      GROUP_SIZE_3C 9

      ! for large systems, increase GROUP_SIZE_3C
      ! to prevent out of memory (OOM)
      GROUP_SIZE_P 1

      ! for larger systems, MEMORY_CUT must be
      ! increased to prevent out of memory (OOM)
      MEMORY_CUT  12

      GW

    &END

    &RI_G0W0
      CORR_OCC 15
      CORR_VIRT 15
      CROSSING_SEARCH NEWTON
      OMEGA_MAX_FIT 1.0
      ANALYTIC_CONTINUATION PADE
      RI OVERLAP
      RI_SIGMA_X
    &END RI_G0W0
  &END RI_RPA
&END
```

Summary

- *GW*: method to compute quasiparticle energies from first principles
- Accuracy of G_0W_0@PBE for solids, G_0W_0@PBE0 for molecules in the order of few hundreds of meV
- High $\mathcal{O}(N^4)$ computational cost
- Hundreds of atoms can be treated on supercomputers by G_0W_0 in CP2K
- Slow basis set convergence
- Correction scheme for periodic G_0W_0 calculations
- $\mathcal{O}(N^3)$ G_0W_0 method for big systems



Quasiparticle energies of a closed shell molecule