gw1rdm

GW 1-body reduced density-matrix

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1-body reduced density matrix

N-body wavefunction contains too much information $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$

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N-body wavefunction contains too much information $\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$

→ DFT works with the density:

$$\rho(\mathbf{r}) = N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \Psi^*(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)\Psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)$$

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1-body quantity sufficient to calculate many observables including

$$E_H = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}')$$

but not the kinetic energy $T \neq T[\rho]$

→ Kohn-Sham approach etc...

1-body reduced density matrix

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→ 1-body reduced density-matrix:

$$\gamma(\mathbf{r}, \mathbf{r}') = N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \Psi^*(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)\Psi(\mathbf{r}', \mathbf{r}_2, \cdots, \mathbf{r}_N)$$

can access the kinetic energy:

$$T[\gamma] = -\frac{\hbar^2}{2m} \int d\mathbf{r} \lim_{\mathbf{r}' \to \mathbf{r}} \nabla^2_{\mathbf{r}'} \gamma(\mathbf{r}, \mathbf{r}')$$

1-body reduced density matrix with non-interacting electrons

With non-interacting electrons (i.e. Kohn-Sham), one can easily calculate

→ the density:

$$\rho(\mathbf{r}) = \sum_i f_i \, \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r})$$

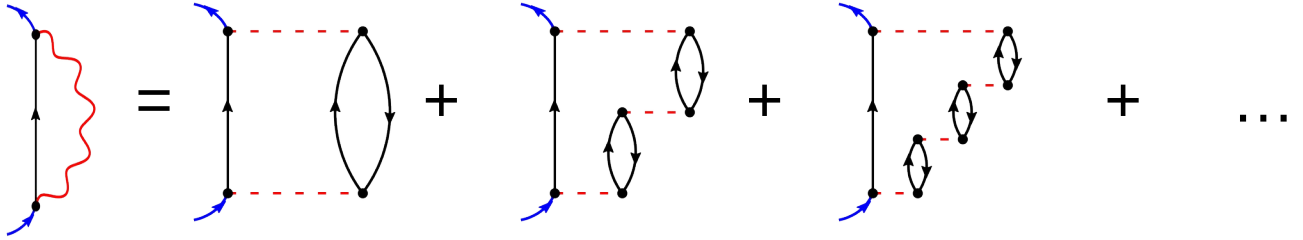
→ the density-matrix:

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i f_i \, \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}')$$

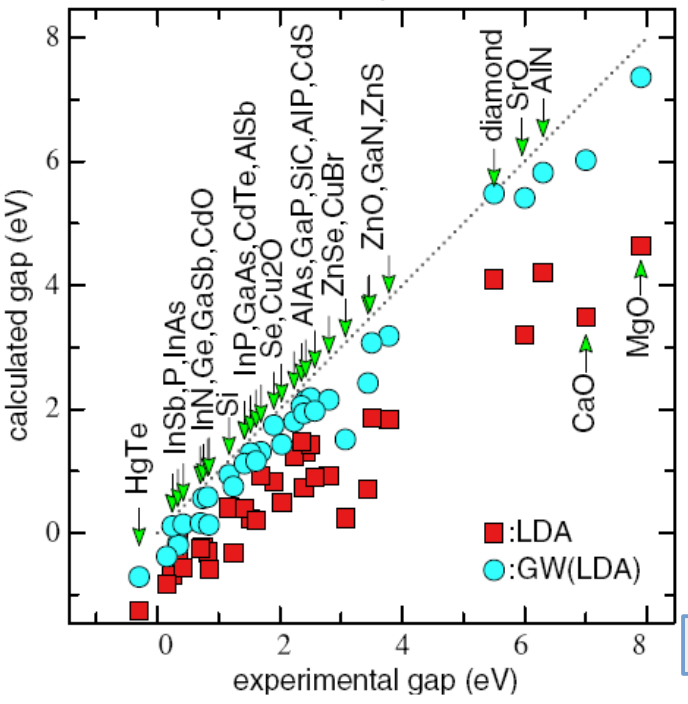
where the occupation numbers f_i are 0 or 2.

GW is known for the band gaps

Diagrammatic approach:



Band gaps of **solids**



See **`tutorial/gw1`**

van Schilfgaarde *et al.* PRL (2008)

GW can get you the full Green's function

The Green's function contains the density-matrix:

$$\gamma(\mathbf{r}, \mathbf{r}') = -iG(\mathbf{r}, \mathbf{r}', t - t' = 0^-)$$

in imaginary frequency domain:

$$\gamma(\mathbf{r}, \mathbf{r}') = -\frac{1}{2\pi} \int d\omega \, G(\mathbf{r}, \mathbf{r}', \mu + i\omega)$$

ABINIT work flow

The usual **one-shot procedure**:

1. Self-consistent Kohn-Sham for many many states

nband 200

$\varphi_{\mathbf{k}i}(\mathbf{r})$ $\epsilon_{\mathbf{k}i}$

ABINIT work flow

The usual **one-shot procedure**:

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for many many states
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2. Screening calculation
on imaginary frequencies
gwcalctyp 21

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$W(i\omega)$

ABINIT work flow

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gwcalctyp 21

WFK

$W(i\omega)$

SCR

3. *GW* calculation for the full self-energy
on imaginary frequencies
gwcalctyp 21

WFK

$\langle \mathbf{k}i | \Sigma^{GW}(\mu + i\omega) | \mathbf{k}j \rangle$

ABINIT work flow

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gwcalctyp 21

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3. *GW* calculation for the full self-energy
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_WFK

$\langle \mathbf{k}i|\Sigma^{GW}(\mu+i\omega)|\mathbf{k}j\rangle$

gw1rdm 1 or 2

$$\langle \mathbf{k}i|\gamma^{GW}|\mathbf{k}j\rangle = -\frac{1}{2\pi}\int d\omega \frac{\langle \mathbf{k}i|\Sigma^{GW}(\mu+i\omega)|\mathbf{k}j\rangle}{(\mu+i\omega-\epsilon_{\mathbf{k}i})(\mu+i\omega-\epsilon_{\mathbf{k}j})}$$

_WFK _DEN

Fun facts about the density-matrix

$\langle \mathbf{k}i | \gamma | \mathbf{k}j \rangle$

Diago

Natural orbitals $\phi_{\mathbf{k}i}(\mathbf{r})$

Natural occupations $0 < f_{\mathbf{k}i} < 2$

$$\sum_{\mathbf{k}i} w_{\mathbf{k}} f_{\mathbf{k}i} = N$$

Fun facts about the density-matrix

$\langle \mathbf{k}i|\gamma|\mathbf{k}j\rangle$ → Diago → Natural orbitals $\phi_{\mathbf{k}i}(\mathbf{r})$

Natural occupations $0 < f_{\mathbf{k}i} < 2$

$$\sum_{\mathbf{k}i} w_{\mathbf{k}} f_{\mathbf{k}i} = N$$

Silicon GW@PBE0

```
Occs. after updating with S_c correct. at k-point:    0.50000   0.00000   0.00000
   1.93854   1.92153   1.86156   1.86155   0.07995   0.05992   0.05991   0.02140   0.02140   0.02123
   0.02101   0.01904   0.01904   0.01191   0.00607   0.00529   0.00500   0.00500   0.00487   0.00487
   0.00370   0.00331   0.00331   0.00312   0.00312   0.00225   0.00140   0.00140   0.00125   0.00122
   0.00122   0.00105   0.00101   0.00101   0.00099   0.00097   0.00093   0.00093   0.00084   0.00083
   0.00070   0.00070   0.00060   0.00060   0.00056   0.00039   0.00032   0.00032   0.00027   0.00027
   0.00024   0.00024   0.00024   0.00024   0.00024   0.00024   0.00022   0.00020   0.00020   0.00020
   0.00020   0.00020   0.00020   0.00018   0.00018   0.00016   0.00014   0.00013   0.00013   0.00012
   0.00010   0.00010   0.00009   0.00009   0.00008   0.00007   0.00007   0.00007   0.00006   0.00006
   0.00005   0.00005   0.00005   0.00005   0.00005   0.00005   0.00005   0.00005   0.00004   0.00004
   0.00004   0.00004   0.00004   0.00004   0.00004   0.00003   0.00003   0.00003   0.00003   0.00003
   0.00002   0.00002   0.00002   0.00002   0.00002   0.00002   0.00002   0.00001   0.00001   0.00001
   0.00001   0.00001   0.00001   0.00001   0.00001   0.00001   0.00001   0.00001   0.00001   0.00000

Total occ. from band     1 to  120 at current k-point:    7.99342
```

→ All the occupations are between 0 and 2

Fun facts about the density-matrix

$\langle \mathbf{k}i|\gamma|\mathbf{k}j\rangle$ → Diago → Natural orbitals $\phi_{\mathbf{k}i}(\mathbf{r})$

Natural occupations $0 < f_{\mathbf{k}i} < 2$

$$\sum_{\mathbf{k}i} w_{\mathbf{k}} f_{\mathbf{k}i} = N$$

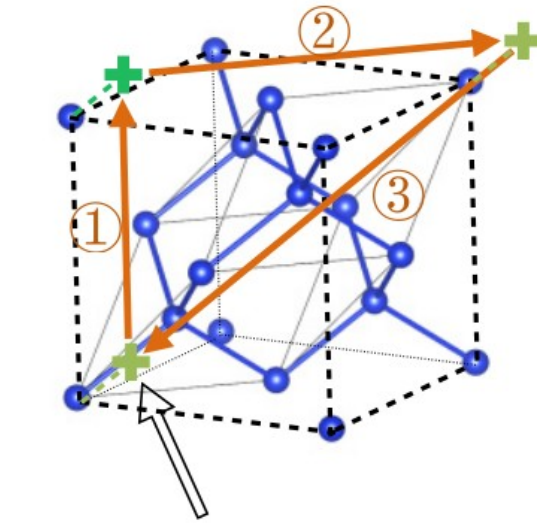
Silicon GW@PBE0

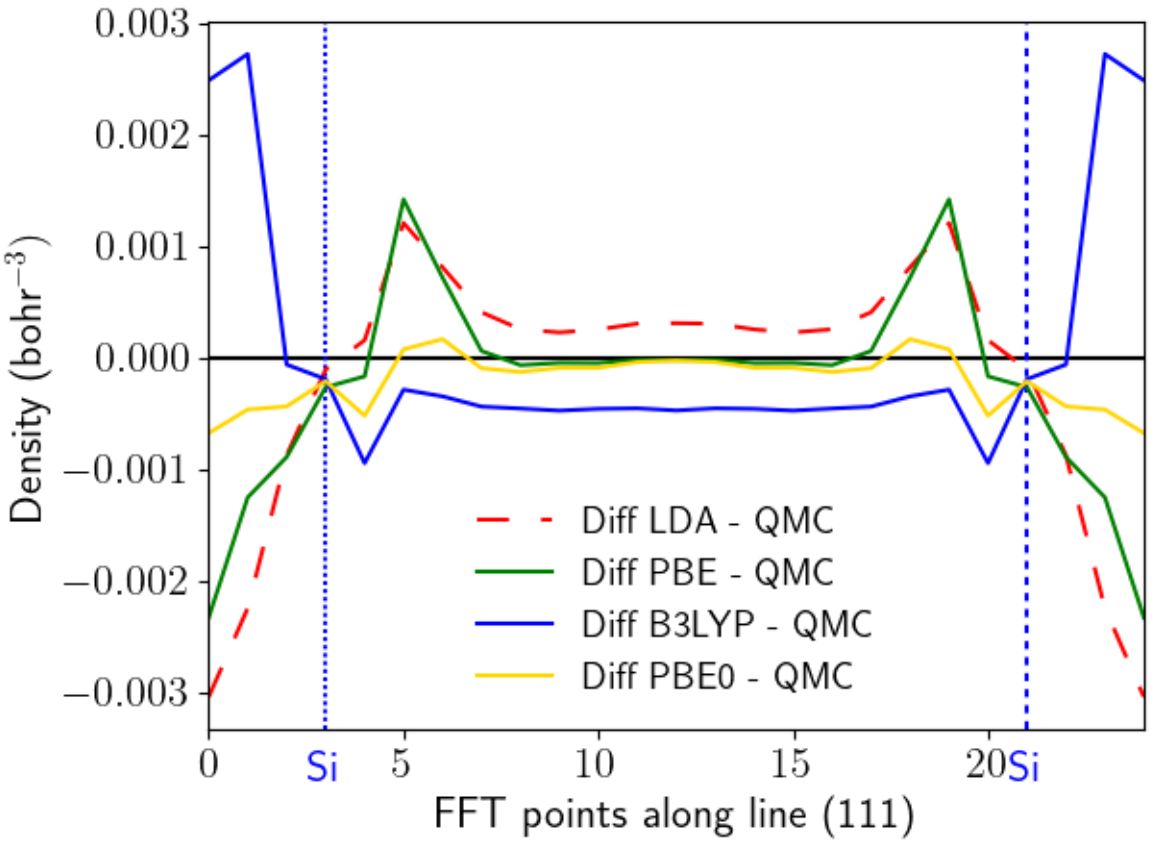
```
Total occ. from band     1 to  120 at current k-point:    7.99561
Total occ. from band     1 to  120 at current k-point:    7.99688
Total occ. from band     1 to  120 at current k-point:    8.00560
Total occ. from band     1 to  120 at current k-point:    8.00442
Total occ. from band     1 to  120 at current k-point:    7.98525
Total occ. from band     1 to  120 at current k-point:    7.99342

Total averaged occ. from all k-points:   7.99922
```

→ The number of electrons is conserved within 10^{-3}

→ Correlation induces **weight transfer** in between k-points

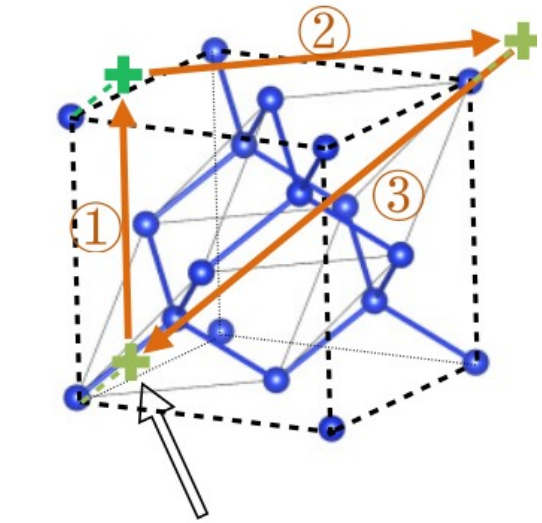
Silicon density

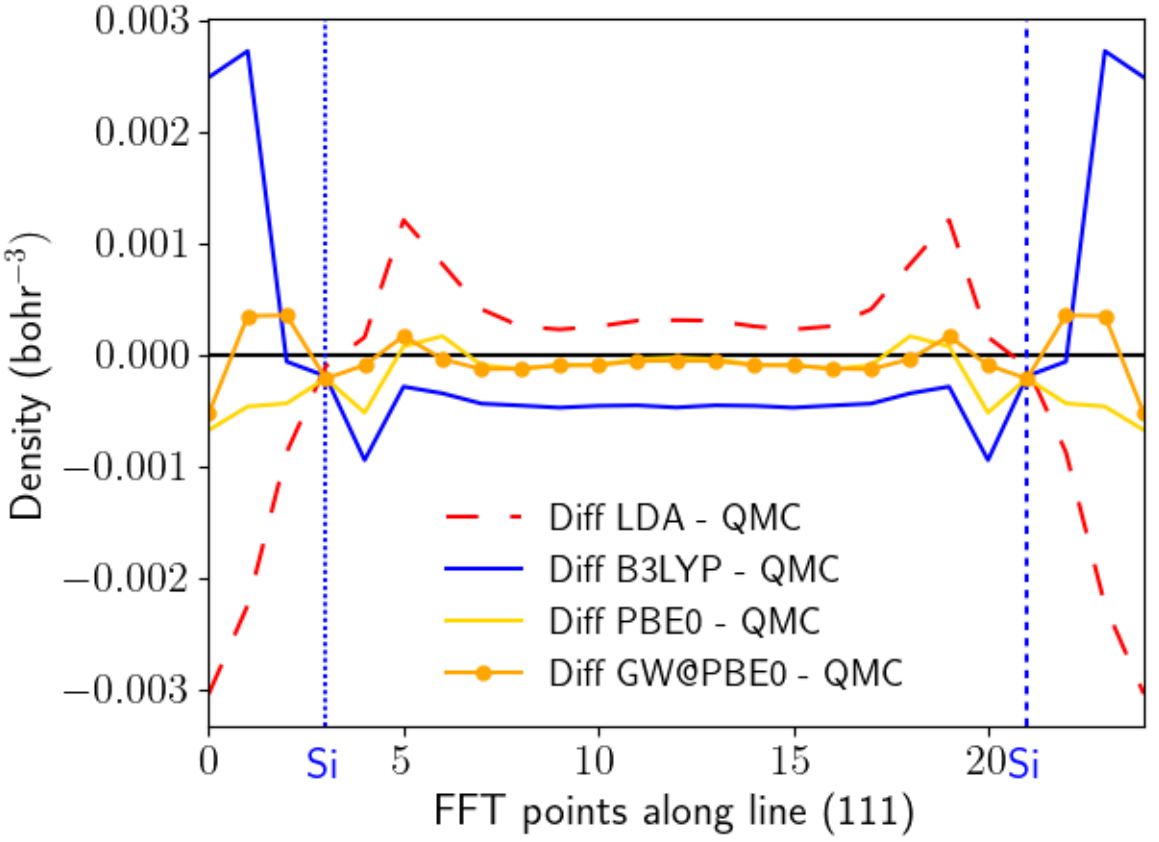




QMC: Chen *et al.* PRB (2021)

Silicon density





QMC: Chen *et al.* PRB (2021)

New *GW* total energy definition

$$T_s[\varphi^{\mathrm{KS}}] = 3.104 \text{ Ha}$$

$$T[\gamma^{GW}] = 3.385 \text{ Ha}$$

→ This one already includes the **"correlation part"** of the kinetic energy

We propose a new total energy formula:

$$E_{tot}^{GW} = E_{\mathrm{HF}}[\gamma^{GW}] + E_c^{GW}$$

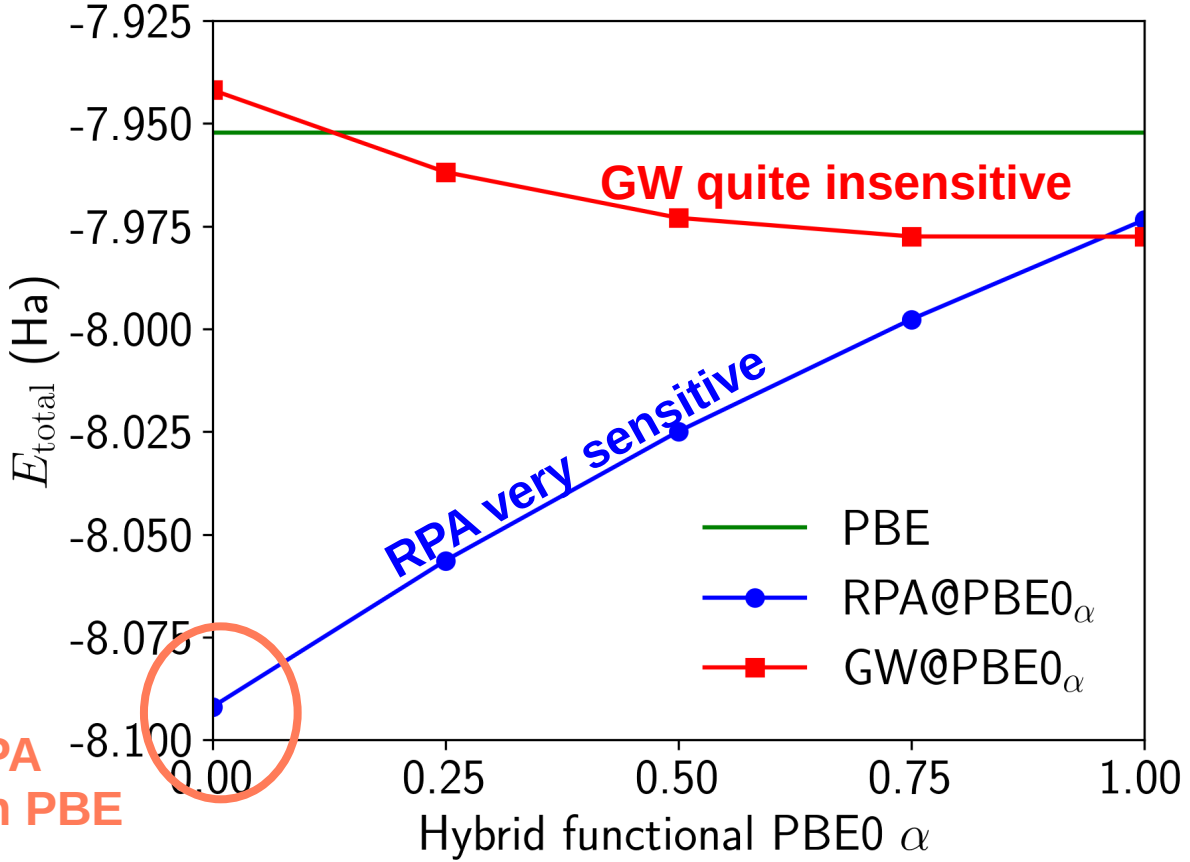
no adiabatic connection

to be compared with RPA formula:

$$E_{tot}^{\mathrm{RPA}} = E_{\mathrm{HF}}[\varphi^{\mathrm{KS}}] + E_c^{\mathrm{RPA}}$$

adiabatic connection

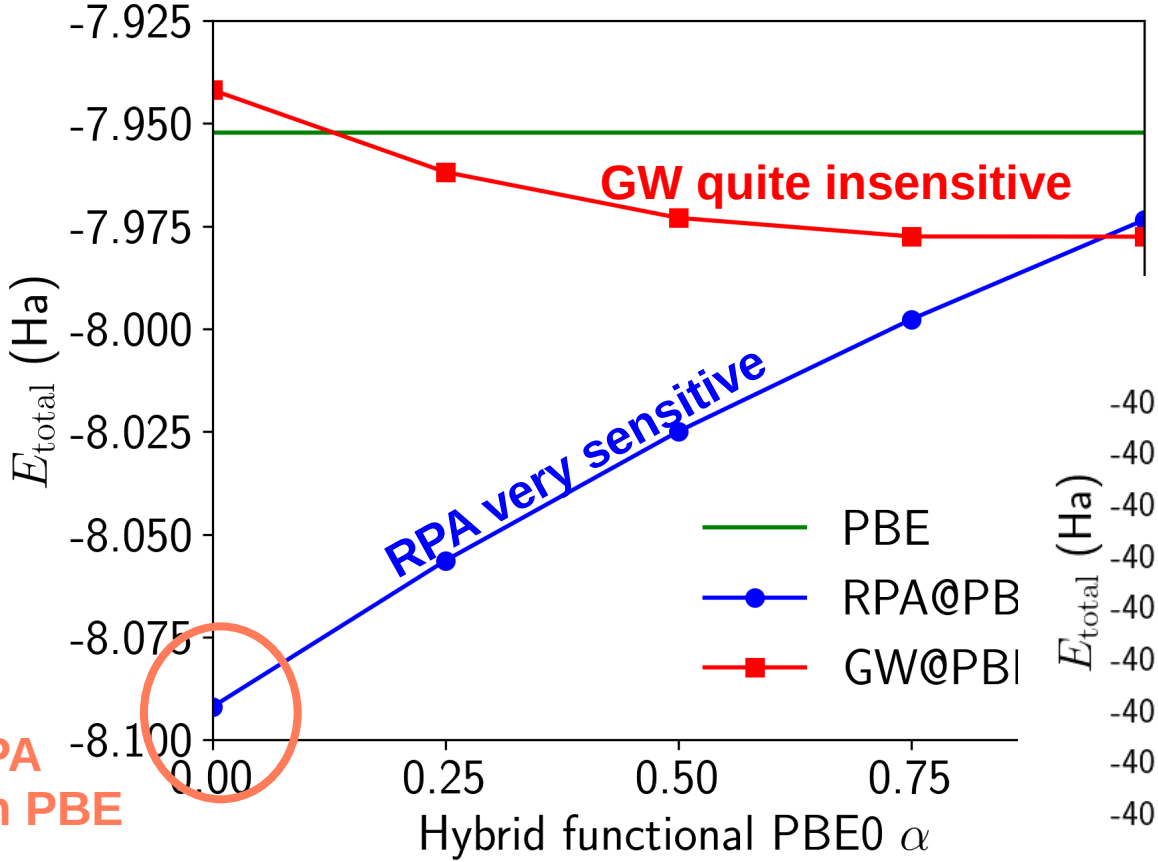
Silicon *GW* total energy



Usual RPA based on PBE

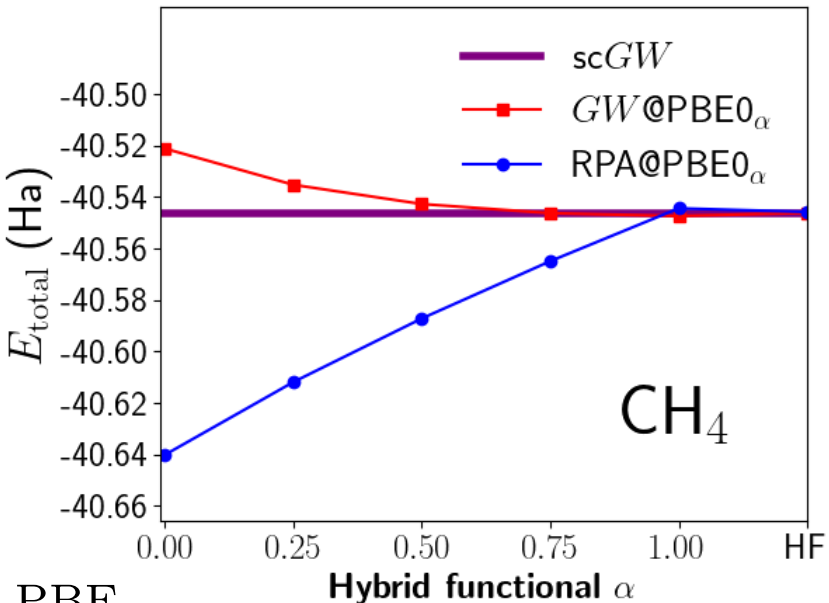
$$v^{\alpha}_{\text{PBE0}}(\mathbf{r},\mathbf{r}') = \alpha\Sigma_x + (1-\alpha)v_x^{\text{PBE}} + v_c^{\text{PBE}}$$

Silicon *GW* total energy



Usual RPA based on PBE

Same behavior for molecules obtained with a different code

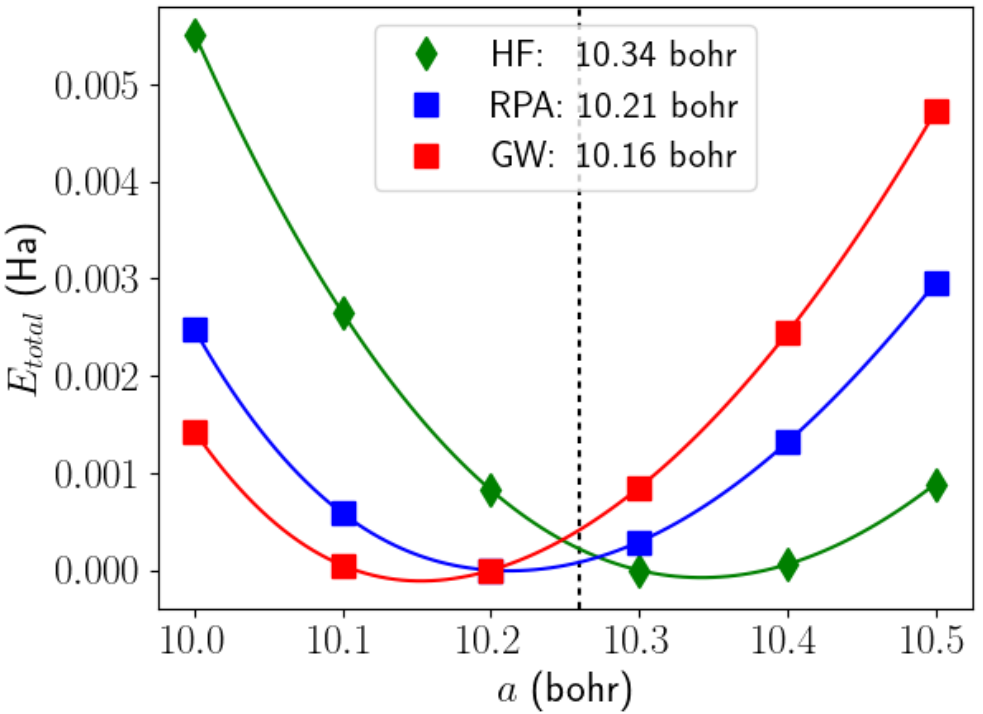


$$v^{\alpha}_{\text{PBE0}}(\mathbf{r},\mathbf{r}') = \alpha\Sigma_x + (1-\alpha)v_x^{\text{PBE}} + v_c^{\text{PBE}}$$

Bruneval *et al.* JCTC (2021)

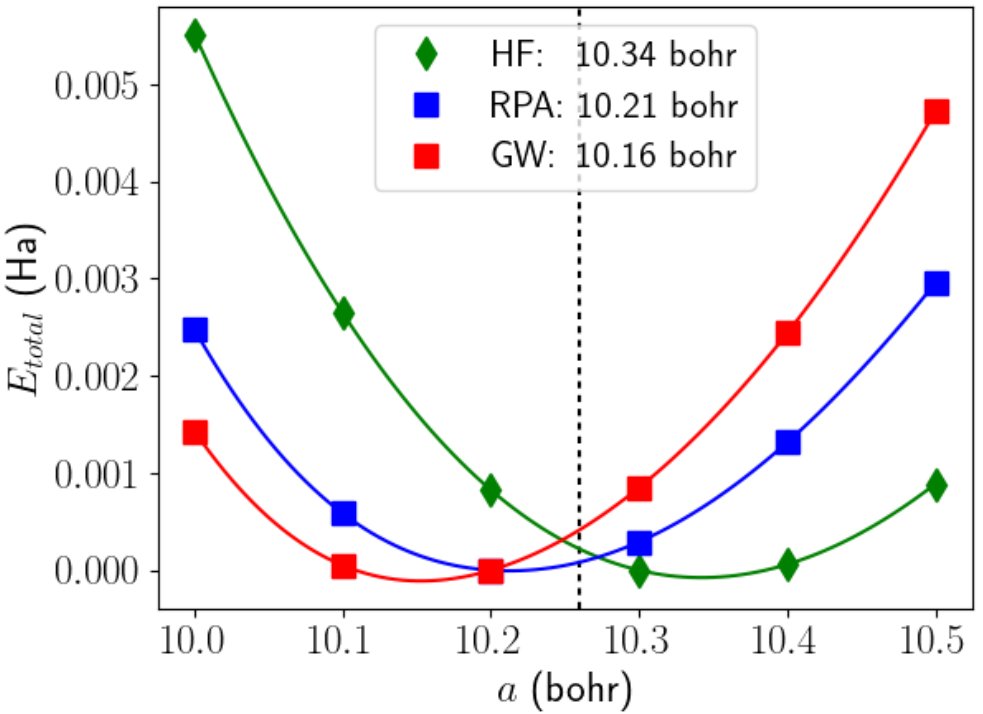
Silicon lattice constant

PBE input

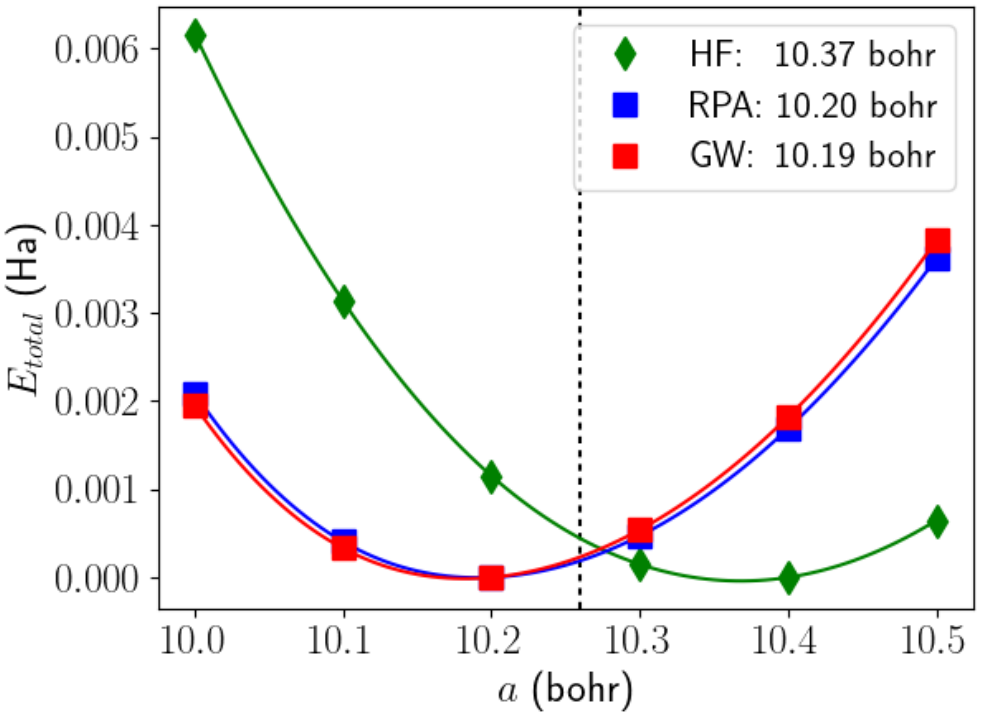


Silicon lattice constant

PBE input



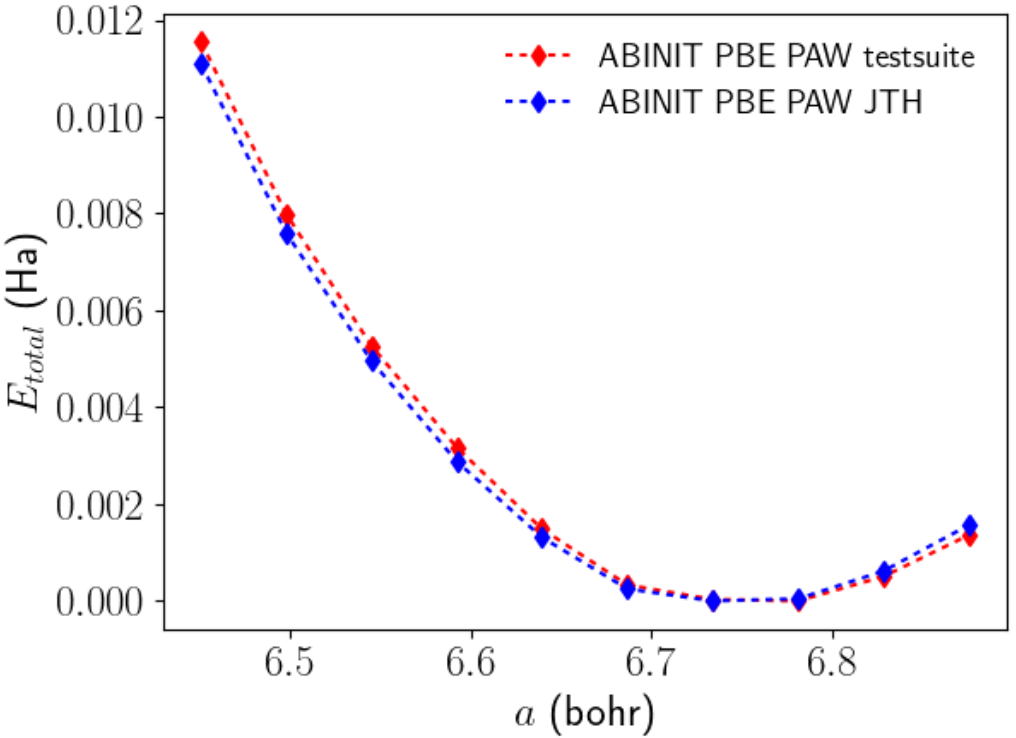
PBE0 75% input



RPA ~ GW → should be close to scGW

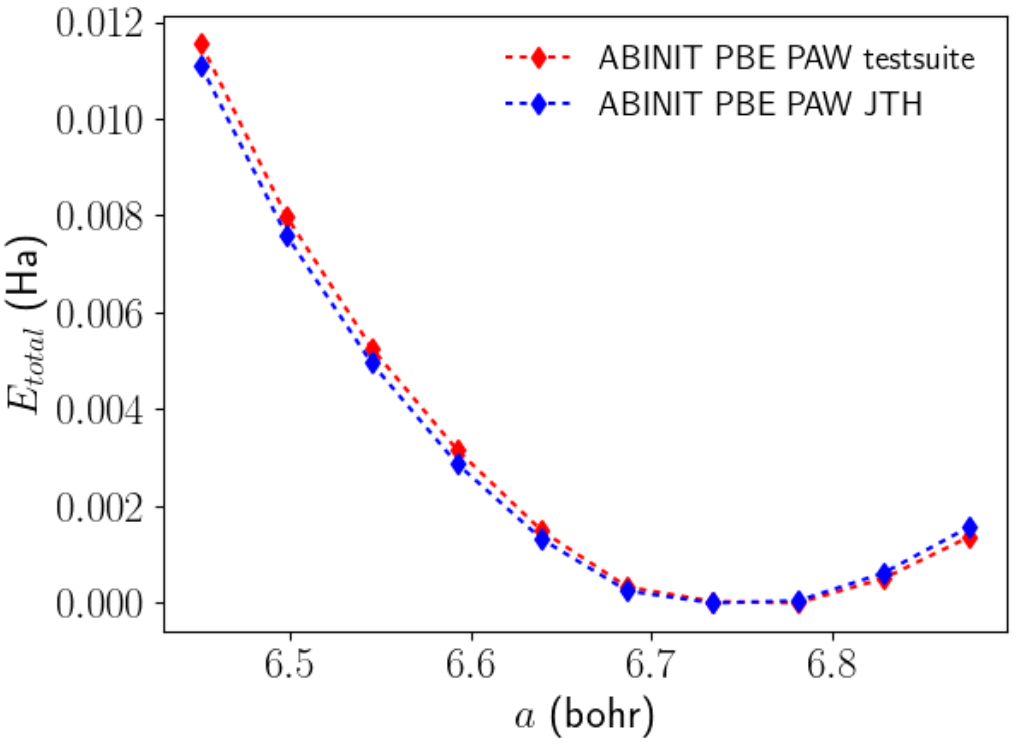
HF lattice constant nightmare

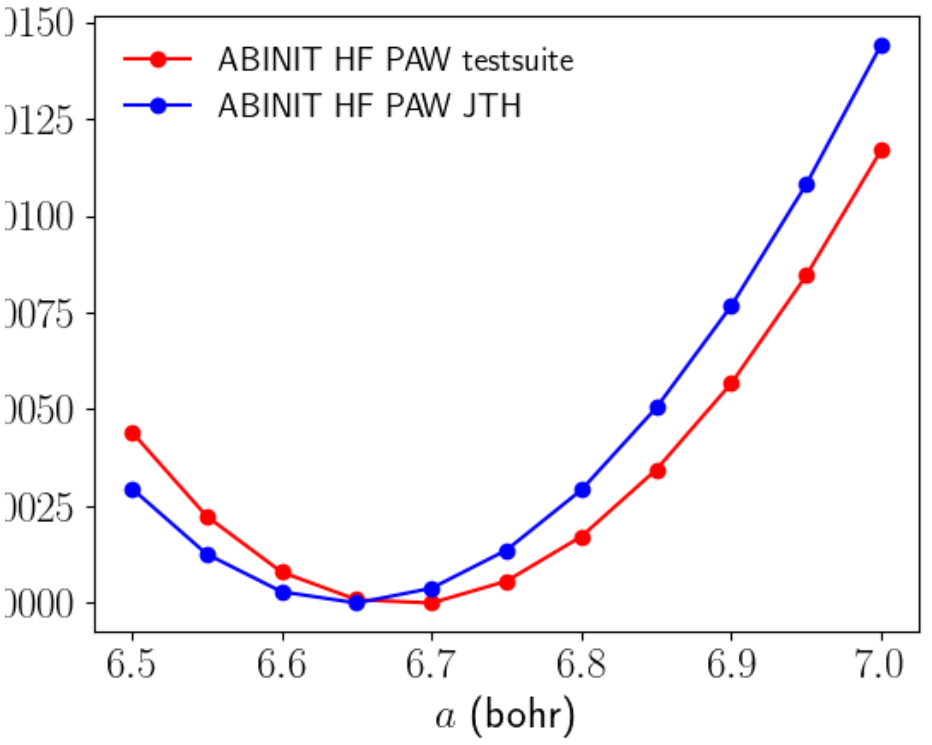
Remember: $E_{tot}^{\mathrm{RPA}} = E_{\mathrm{HF}}[\varphi^{\mathrm{KS}}] + E_c^{\mathrm{RPA}}$



Diamond

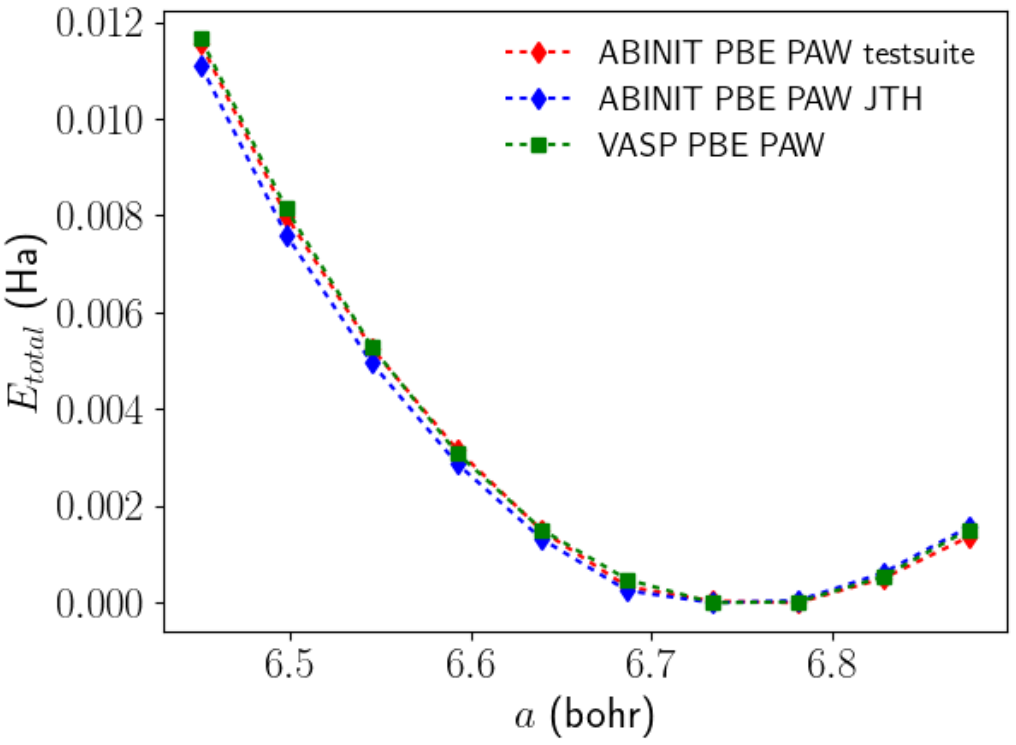
HF lattice constant nightmare

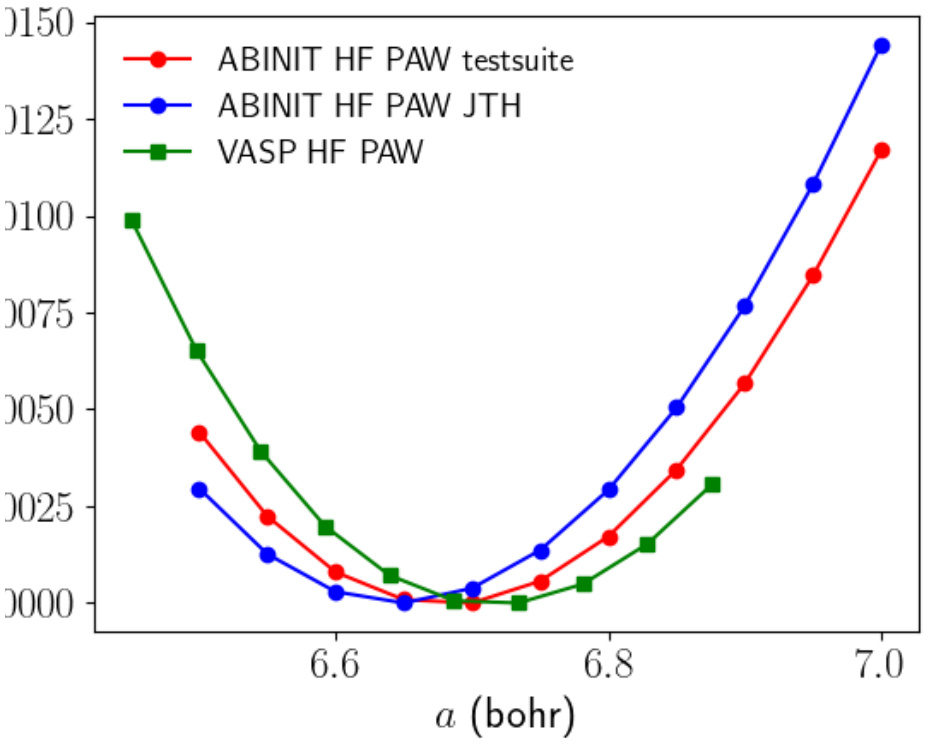




Diamond

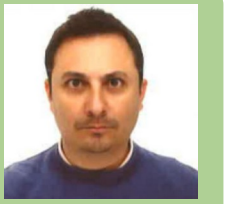
HF lattice constant nightmare





Diamond

Summary



Mauricio Rodriguez-Mayorga

Implementation of the *GW* 1body reduced density-matrix `gw1rdm`

New evaluation of

→ electronic density

→ natural orbitals, natural occupations (diagonalization)
differ from 0 or 2, but sum up to the correct *N*

→ total energy parts (kinetic energy including correlation)

→ Estimate of the self-consistent GW total energy for solids

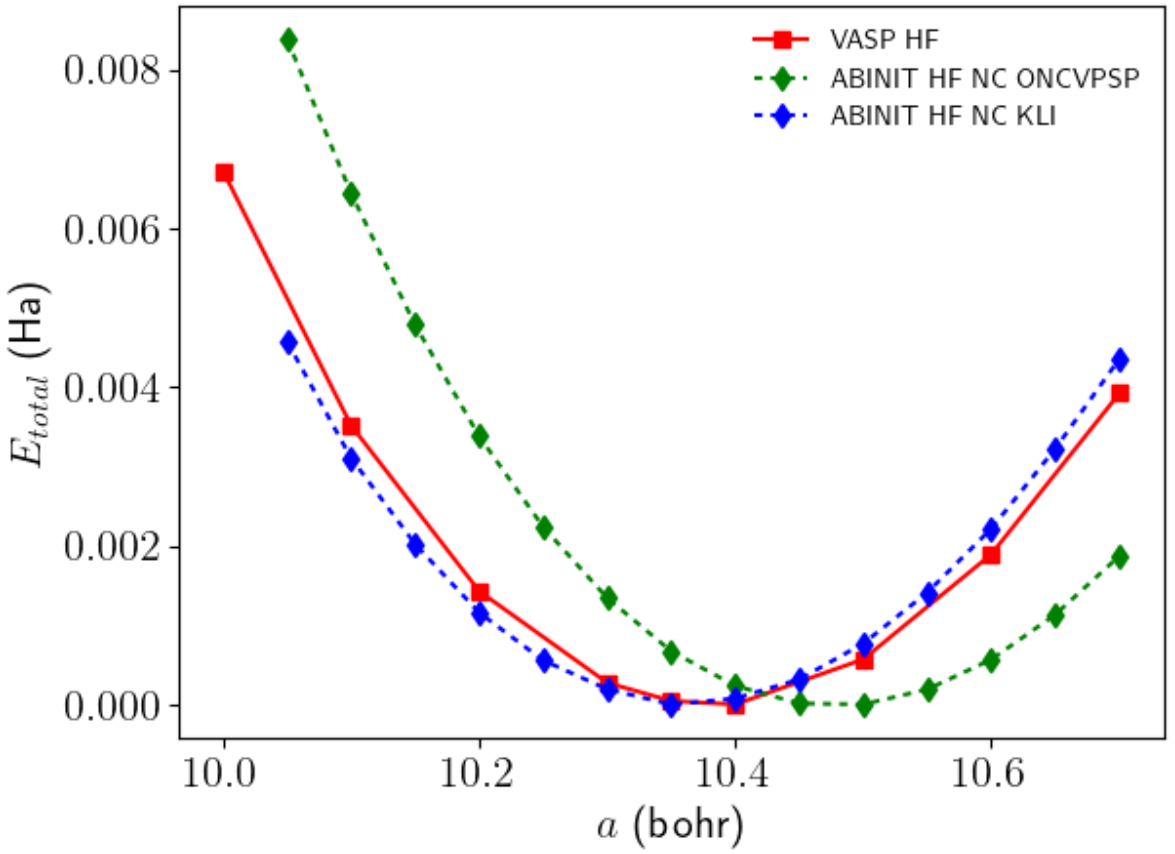
→ Estimate of scGW lattice constants ≠ RPA@PBE

→ then, can scGW capture van der Waals?

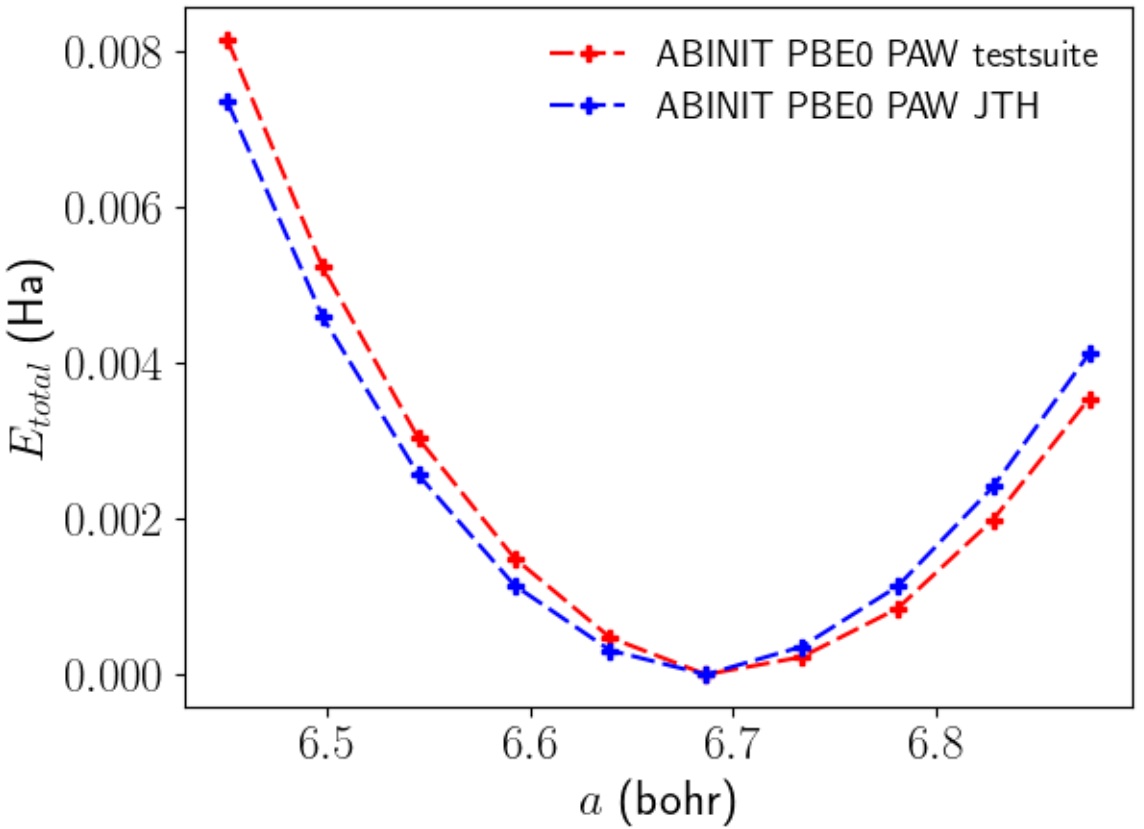
ONLY NC

Supplemental information

KLI NC pseudo potential as a workaround?

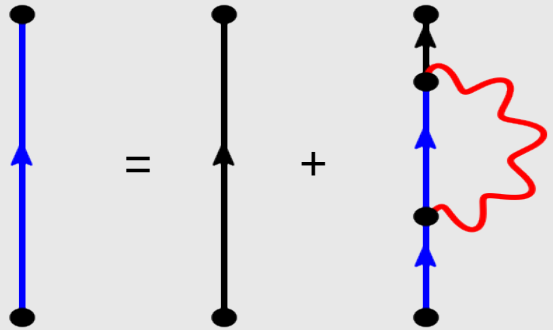


Diamond PBE0 PAW



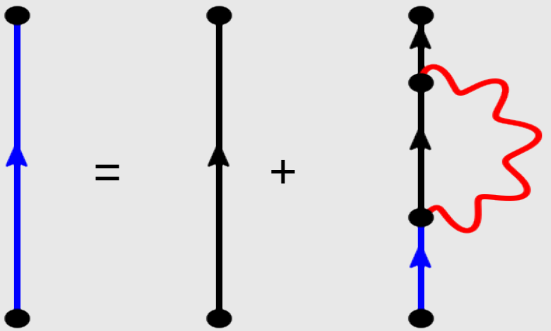
The linearized *GW* density matrix

Dyson equation
for the *GW* approximation



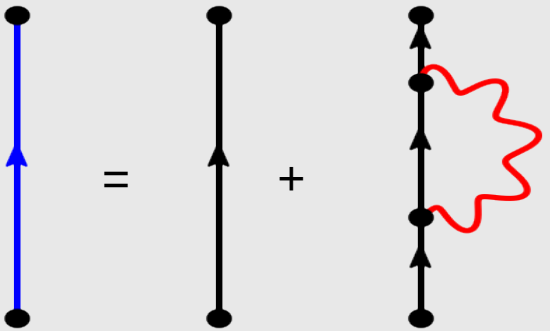
$$G = G_0 + G_0 (GW) G$$

One-shot G_0W_0



$$G = G_0 + G_0 (G_0W_0) G$$

Linearized Dyson



$$G = G_0 + G_0 (G_0W_0) G_0$$

3-step approximation: “linearized one-shot GW” approximation