Parameter-free exchange-correlation kernels and response functions in the framework of time-dependent density-functional theory

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PLAN

- **Derivation of a f_{xc}^{TDDFT}**
  $\hookrightarrow$ **TDDFT vs BSE**
- **Kernels and spectra analysis**
- **Application to realistic systems**
  $\hookrightarrow$ **Solid Si and SiC**
- **Future developments**
  $\hookrightarrow$ **Towards the bound excitons**

Electronic spectra - Absorption spectrum

$$\bar{\chi} = \chi^0 + \chi^0 \left[\bar{v} + f_{xc}\right] \bar{\chi}$$

$$\bar{v} = v - v(\mathbf{G} = 0)$$

$$\varepsilon_{\mathrm{M}}(\omega) = \lim_{\mathbf{q}\rightarrow 0} \left[1 - v_{\mathbf{G}=0}(\mathbf{q}) \bar{\chi}_{\mathbf{G}=\mathbf{G'}=0}(\mathbf{q}, \omega)\right]$$

$$\text{Absorption}\,(\omega) = \Im \left\{\varepsilon_{\mathrm{M}}(\omega)\right\}$$

Transition framework

$$\bar{\chi}^{(\mathrm{n_1 n_2})}_{(\mathrm{n_3 n_4})}(\omega) = \mathrm{M}^{-1}_{(\mathrm{n_1 n_2})(\mathrm{n_3 n_4})}(\omega) \left(f_{n_4} - f_{n_3} \right)$$

- $$\mathrm{M}^{(\mathrm{n_1 n_2})}_{(\mathrm{n_3 n_4})}(\omega) = (\epsilon_{n_2} - \epsilon_{n_1} - \omega)\delta_{n_1 n_3}\delta_{n_2 n_4} + \\ + \left(f_{n_1} - f_{n_2} \right) \Xi^{(\mathrm{n_1 n_2})}_{(\mathrm{n_3 n_4})}(\omega)$$

- $$\Xi^{(\mathrm{n_1 n_2})}_{(\mathrm{n_3 n_4})}(\omega) = 2 \int d\mathbf{r} d\mathbf{r}' \, \Phi(n_1 n_2, \mathbf{r}) \bar{v}(\mathbf{r} - \mathbf{r}') \Phi^*(n_3 n_4, \mathbf{r}') + \\ + \mathrm{F}^{(\mathrm{n_1 n_2})}_{(\mathrm{n_3 n_4})}(\omega)$$

- $$\Phi(n_1 n_2, \mathbf{r}) = \phi_{n_1}(\mathbf{r}) \phi^*_{n_2}(\mathbf{r})$$

TDDFT

BSE

TDDFT

$\epsilon_{n_i}^{\mathrm{DFT}}$ KS eigenvalues

BSE

$\epsilon_{n_i}^{\mathrm{QP}}$ Quasi-Particle energies

TDDFT

$\epsilon_{n_i}^{\mathrm{DFT}}$ KS eigenvalues

$\phi_{n_i}^{\mathrm{DFT}}(\mathbf{r})$ KS eigenfunctions

BSE

$\epsilon_{n_i}^{\mathrm{QP}}$ Quasi-Particle energies

$\phi_{n_i}^{\mathrm{QP}}(\mathbf{r})$ Quasi-Particle wavefunctions

TDDFT

$\epsilon_{n_i}^{\mathrm{DFT}}$ KS eigenvalues

$\phi_{n_i}(\mathbf{r})$ wavefunctions

BSE

$\epsilon_{n_i}^{\mathrm{QP}}$ Quasi-Particle energies

$\phi_{n_i}(\mathbf{r})$ wavefunctions

TDDFT

$\epsilon_{n_i}^{\mathrm{DFT}}$ KS eigenvalues

$\phi_{n_i}(\mathbf{r})$ wavefunctions

$$\mathrm{F}^{\mathrm{TDDFT}}_{(\mathrm{n_1 n_2})(\mathrm{n_3 n_4})}(\omega) = 2\int d\mathbf{r}d\mathbf{r}'\, \Phi(n_1 n_2, \mathbf{r}) f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \Phi^*(n_3 n_4, \mathbf{r}')$$

BSE

$\epsilon_{n_i}^{\mathrm{QP}}$ Quasi-Particle energies

$\phi_{n_i}(\mathbf{r})$ wavefunctions

$$\mathrm{F}^{\mathrm{BSE}}_{(\mathrm{n_1 n_2})(\mathrm{n_3 n_4})}(\omega) = -\int d\mathbf{r}d\mathbf{r}'\, \Phi(n_1 n_3, \mathbf{r}) W(\mathbf{r}, \mathbf{r}') \Phi^*(n_2 n_4, \mathbf{r}')$$

$$W(\mathbf{r}, \mathbf{r}', \omega = 0) = v\varepsilon^{-1}_{\mathrm{RPA}}(\omega = 0)$$

TDDFT and BSE give the same spectra if ~~and only if~~

$$^4\bar{\chi}^{\mathrm{TDDFT}}(\omega) = {}^4\bar{\chi}^{\mathrm{BSE}}(\omega)$$

$$\Downarrow$$

$$\mathrm{M}^{\mathrm{TDDFT}}(\omega) = \mathrm{M}^{\mathrm{BSE}}(\omega)$$

TDDFT and BSE give the same spectra if ~~and only if~~

$$(\epsilon^{\mathrm{DFT}}_{n_2} - \epsilon^{\mathrm{DFT}}_{n_1} - \omega)\delta_{n_1 n_3}\delta_{n_2 n_4} + (f_{n_1} - f_{n_2}) \Big[ct[\bar{v}] + \\ + 2\int d\mathbf{r}d\mathbf{r}'\, \Phi(n_1 n_2, \mathbf{r}) f_{xc}(\mathbf{r}, \mathbf{r}', \omega)\Phi^*(n_3 n_4, \mathbf{r}')\Big] =$$

$$= (\epsilon^{QP}_{n_2} - \epsilon^{QP}_{n_1} - \omega)\delta_{n_1 n_3}\delta_{n_2 n_4} + (f_{n_1} - f_{n_2}) \Big[ct[\bar{v}] + \\ - \int d\mathbf{r}d\mathbf{r}'\, \Phi(n_1 n_3, \mathbf{r}) W(\mathbf{r}, \mathbf{r}')\Phi^*(n_2 n_4, \mathbf{r}')\Big]$$

$$f_{xc}(\mathbf{q},\mathbf{G},\mathbf{G}') = \frac{1}{2}\sum_{\substack{(\mathrm{n}_1\mathrm{n}_2)\\(\mathrm{n}_3\mathrm{n}_4)}} \Phi^{-1}(n_1 n_2,\mathbf{G})\Big[(\epsilon^{\mathrm{QP}}_{n_2} - \epsilon^{\mathrm{QP}}_{n_1} - \epsilon^{\mathrm{DFT}}_{n_2} + \epsilon^{\mathrm{DFT}}_{n_1})\delta_{n_1 n_3}\delta_{n_2 n_4} \\ - (f_{n_1} - f_{n_2})\, \Phi(n_1 n_3,\mathbf{G}) W_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\Phi^*(n_2 n_4,\mathbf{G}')\Big](\Phi^*)^{-1}(n_3 n_4,\mathbf{G}')$$

`if it is possible to invert` $\Phi(n_1 n_2,\mathbf{G})$

Résumé

$$\bar{\chi}^{\text{TDDFT}}_{(\mathrm{n}_1\mathrm{n}_2)(\mathrm{n}_3\mathrm{n}_4)} = \bar{\chi}^{\text{BSE}}_{(\mathrm{n}_1\mathrm{n}_2)(\mathrm{n}_3\mathrm{n}_4)}$$

$$\phi^{\text{DFT}}_{n_i} = \phi^{\text{QP}}_{n_i}$$

$$W_{\mathbf{GG}'}(\mathbf{q},\omega) = v_{\mathbf{GG}'}\delta_{\mathbf{GG}'}\varepsilon^{-1}_{\text{RPA}}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega=0)$$

$$f_{xc}(\mathbf{q},\mathbf{G},\mathbf{G}') = \frac{1}{2}\Phi^{-1}\left[\mathrm{GW}_{\text{shift}} + \Phi W \Phi^*\right](\Phi^*)^{-1}$$

`if` $\Phi(n_1 n_2,\mathbf{G})$ `is invertible.`

How to implement this kernel

$$\bar{\chi} = \left(1 - \chi^0 \bar{v} - \chi^0 f_{xc}\right)^{-1} \chi^0$$

$$\bar{\chi} = \chi^0 \left(\chi^0 - \chi^0 \bar{v} \chi^0 - \chi^0 f_{xc} \chi^0\right)^{-1} \chi^0$$

$$\bar{\chi} = \chi^0 \left(\chi^0 - \chi^0 \bar{v} \chi^0 - K(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega)\right)^{-1} \chi^0$$

How to implement this kernel

$$f_{xc} = \frac{1}{2}\Phi^{-1}\left[\mathrm{GW}_{\mathrm{shift}} + \Phi W \Phi^*\right](\Phi^*)^{-1}$$

$$K = \chi^0 f_{xc} \chi^0$$

$$K(\mathbf{q},\mathbf{G},\mathbf{G}',\omega) = \frac{1}{2}\frac{\Phi^*}{\Delta\epsilon^{\mathrm{DFT}} - \omega}\left[\mathrm{GW}_{shift} + \Phi W \Phi^*\right]\frac{\Phi}{\Delta\epsilon^{\mathrm{DFT}} - \omega}$$

$$K(\mathbf{q},\mathbf{G},\mathbf{G}',\omega) = T_1 + T_2$$

`without explicit inversion of` Φ

$$f_{xc}^{\mathrm{eff}}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega) = (\chi^0)^{-1} K(\mathbf{q},\mathbf{G},\mathbf{G}',\omega)(\chi^0)^{-1}$$

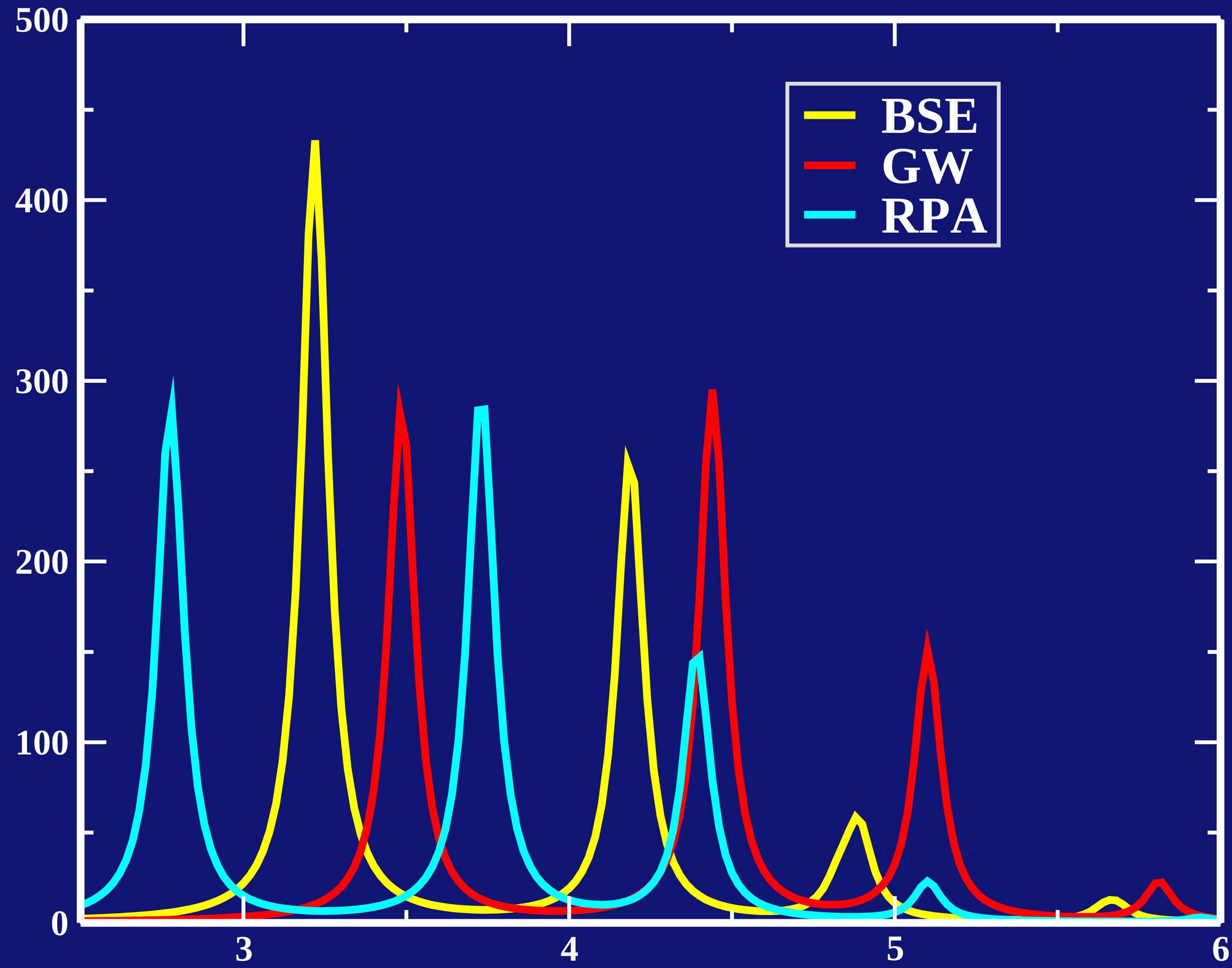
What do we expect then??

- K works (close to the BSE result!)
  - T_1 reproduces the GW corrections
  - T_2 reproduces the excitonic effects
- f_{xc}
  - f_{xc} static when $N_{\mathbf{G}} \sim N_t$
  - f_{xc} "strange" when invertibility problems for Φ occur

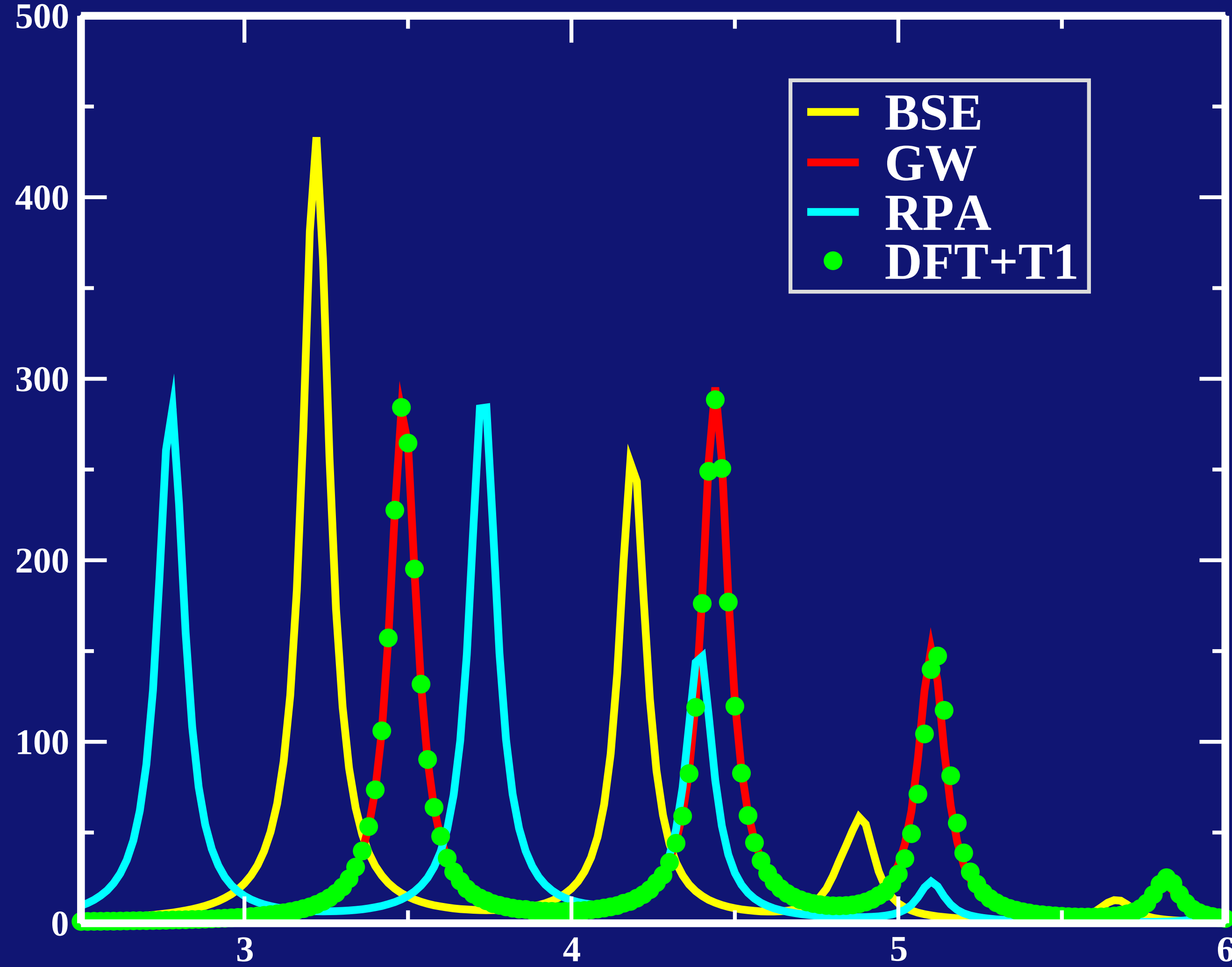
  $\longrightarrow$ $N_{\mathbf{G}} \ll N_t$ or $N_t \gg N_{\mathbf{G}}$

  $\longrightarrow$ linear dependencies in Φ due to the k sampling

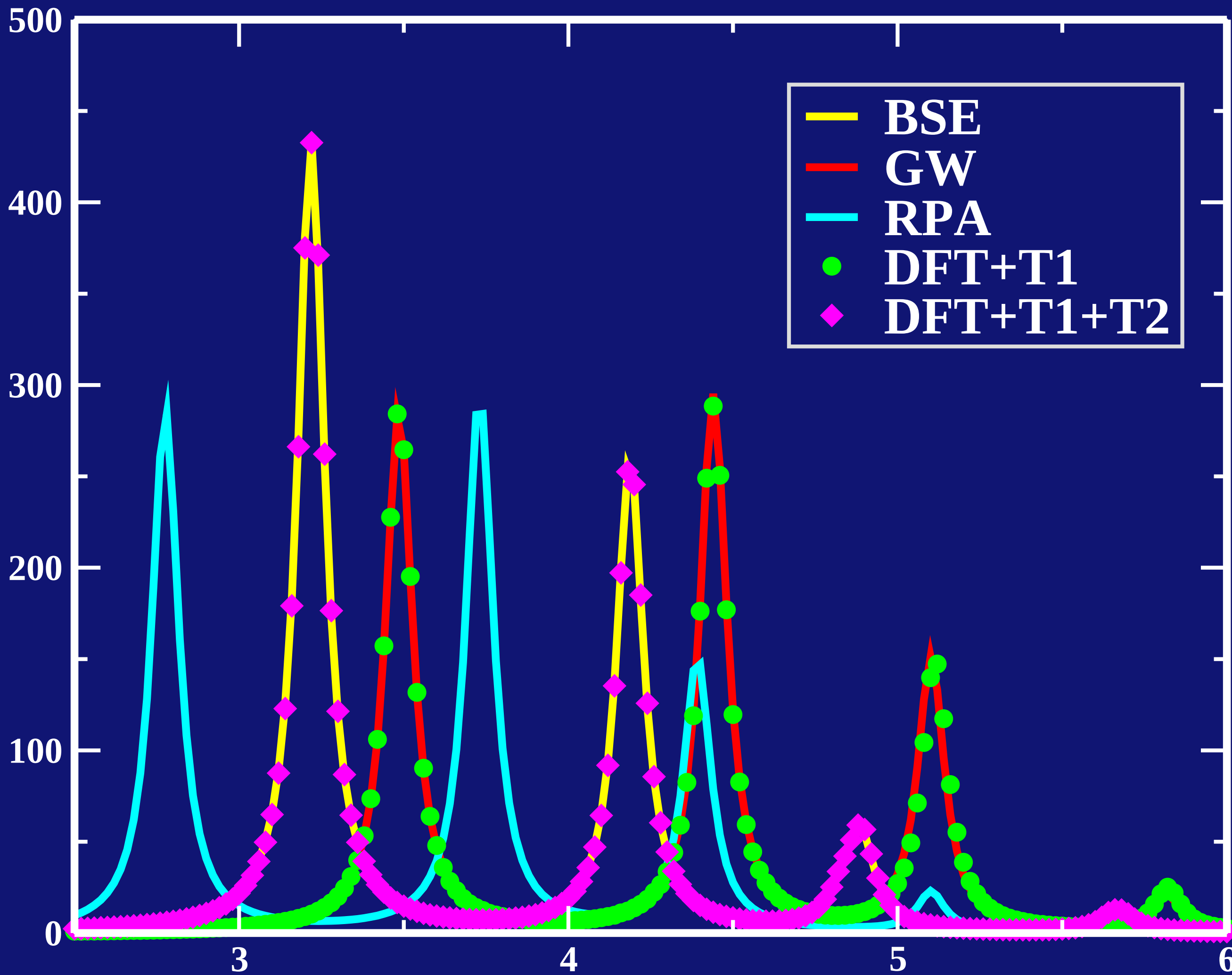
Silicon 2k



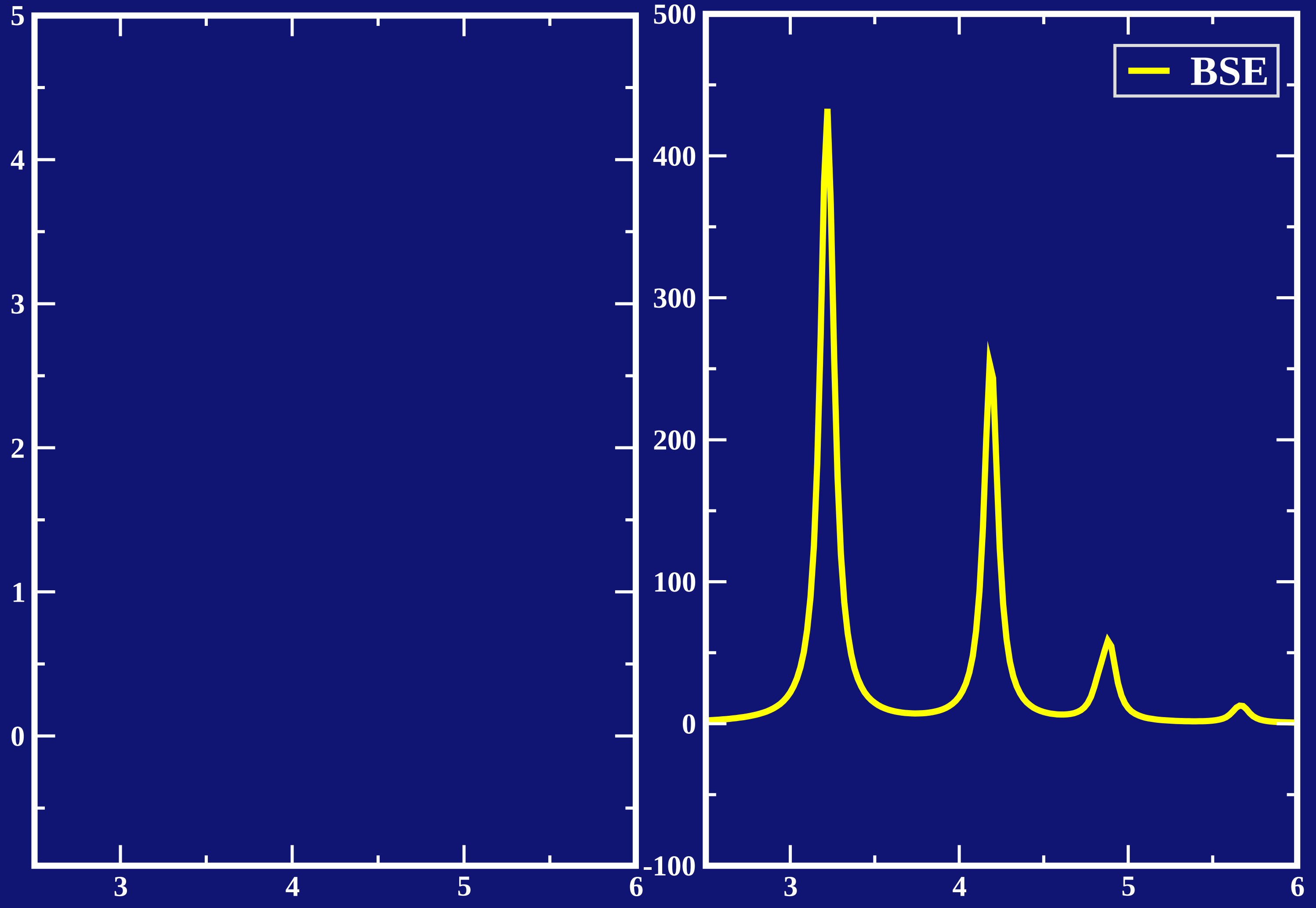
Silicon 2k



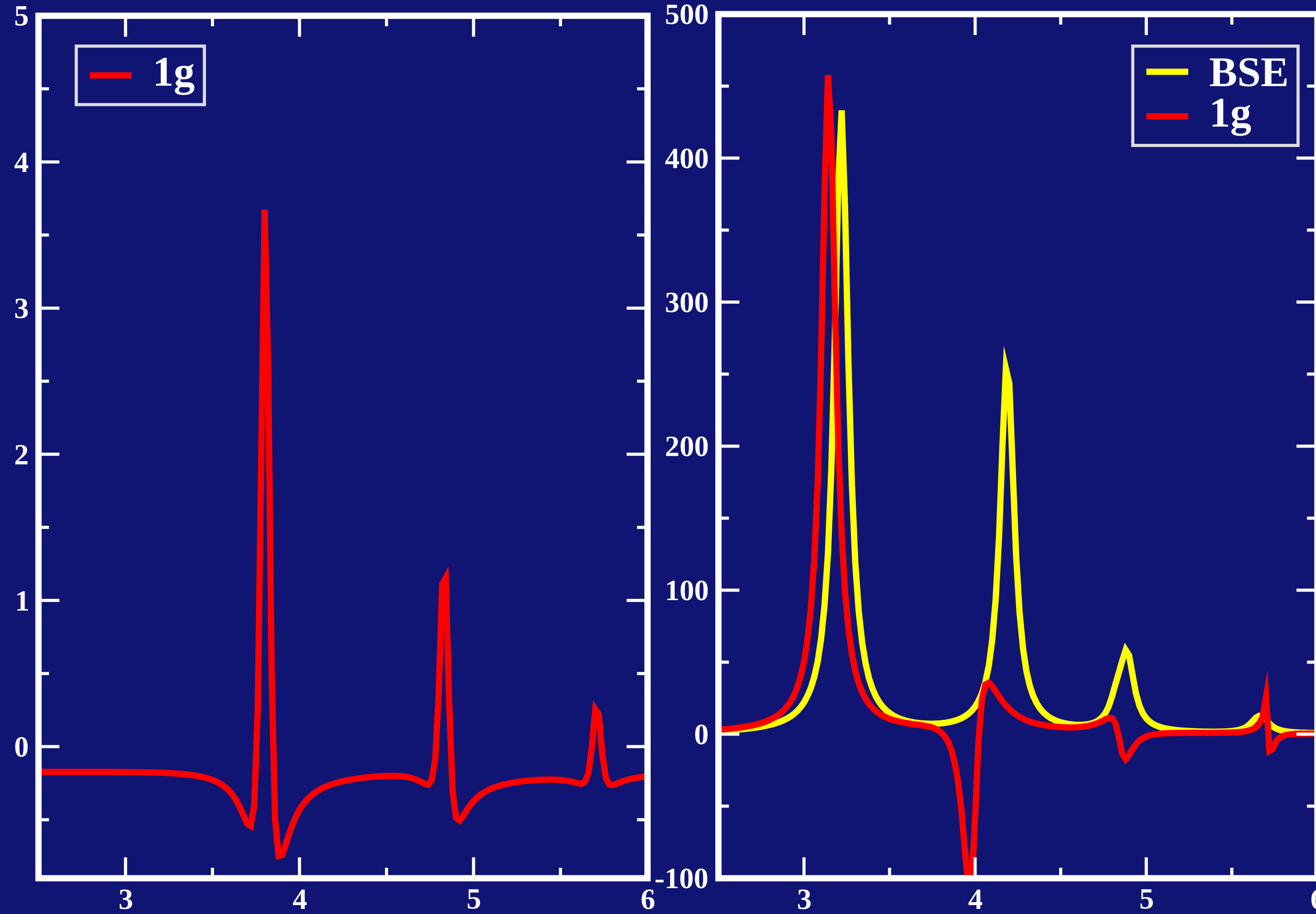
Silicon 2k



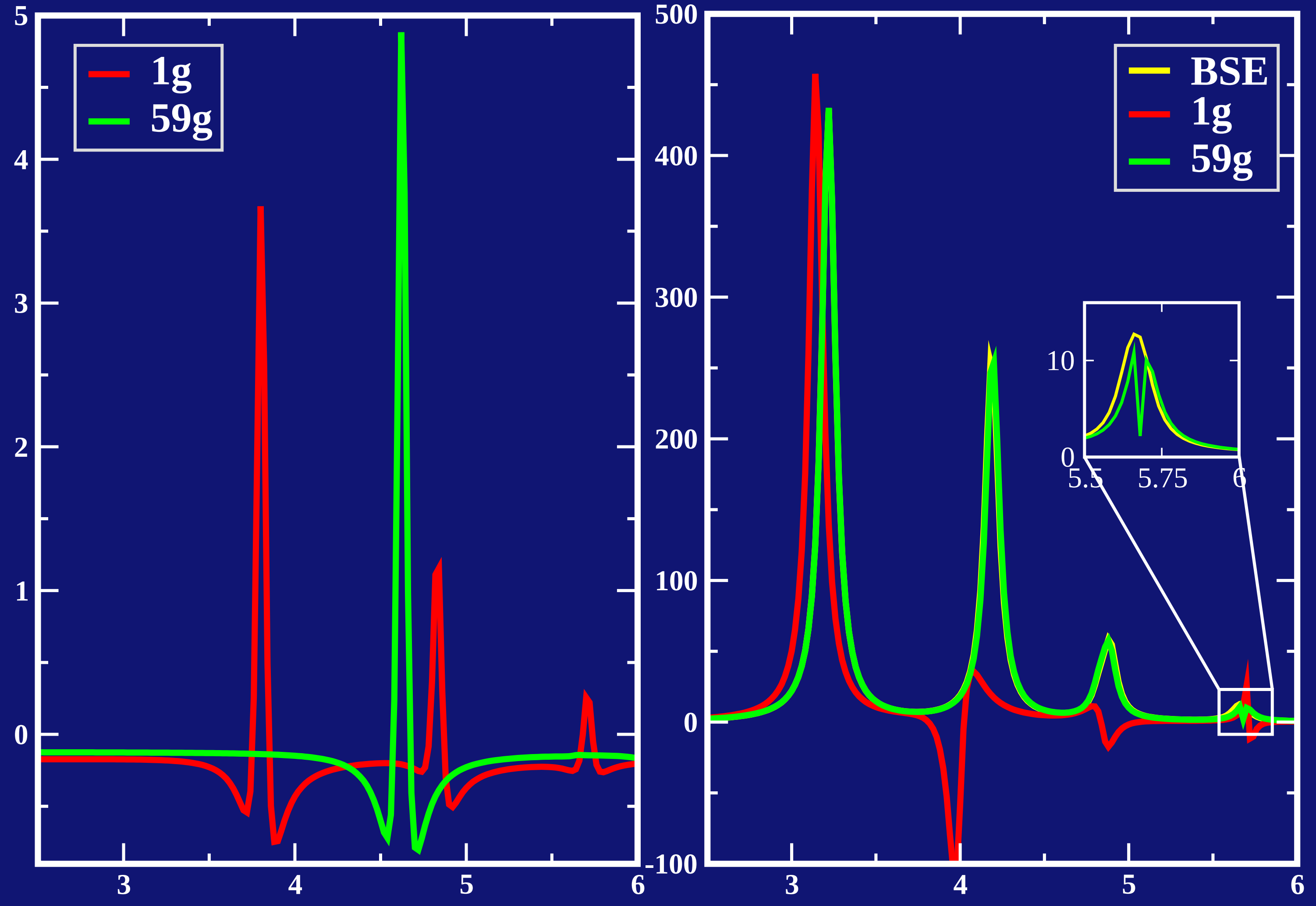
kernels $N_t = 288$ **spectra**



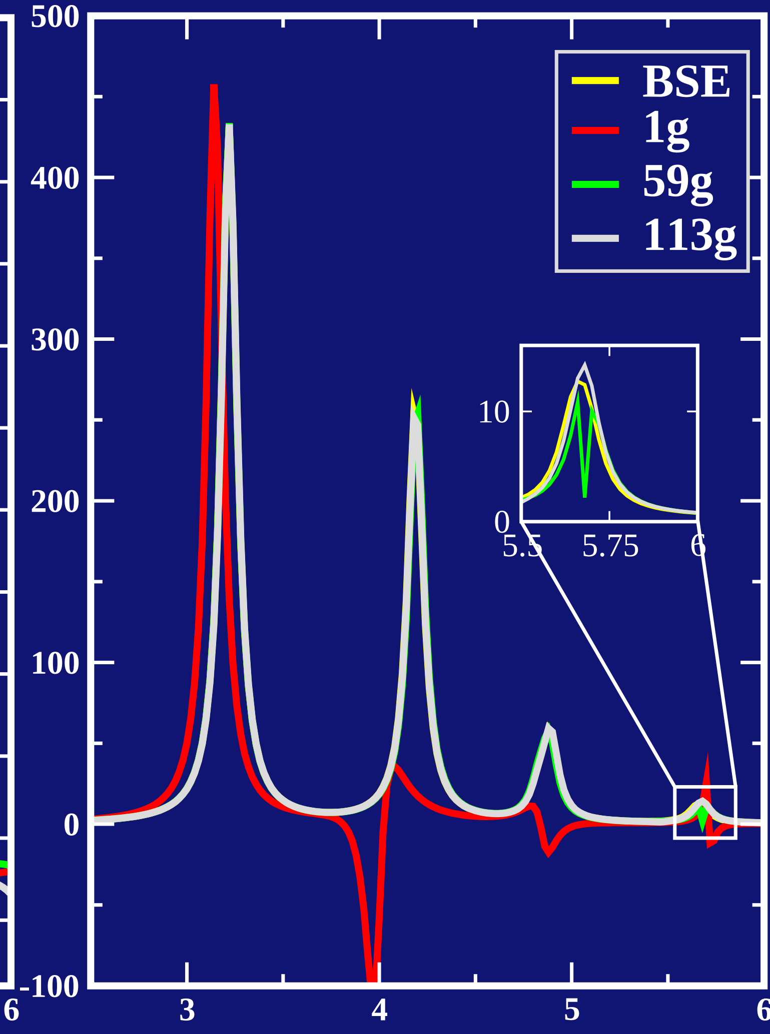
kernels $N_t = 288$ **spectra**



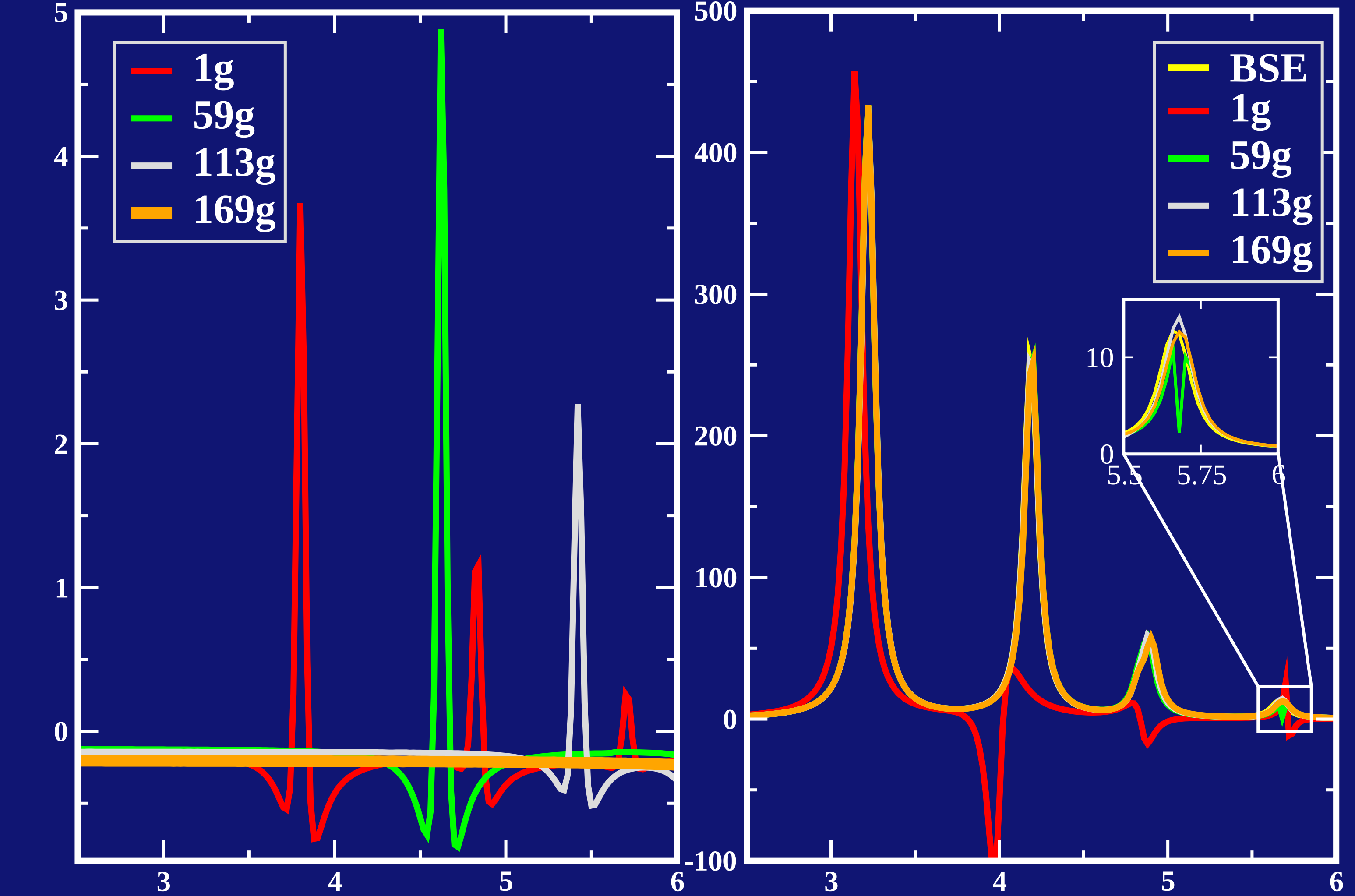
kernels $N_t = 288$ **spectra**



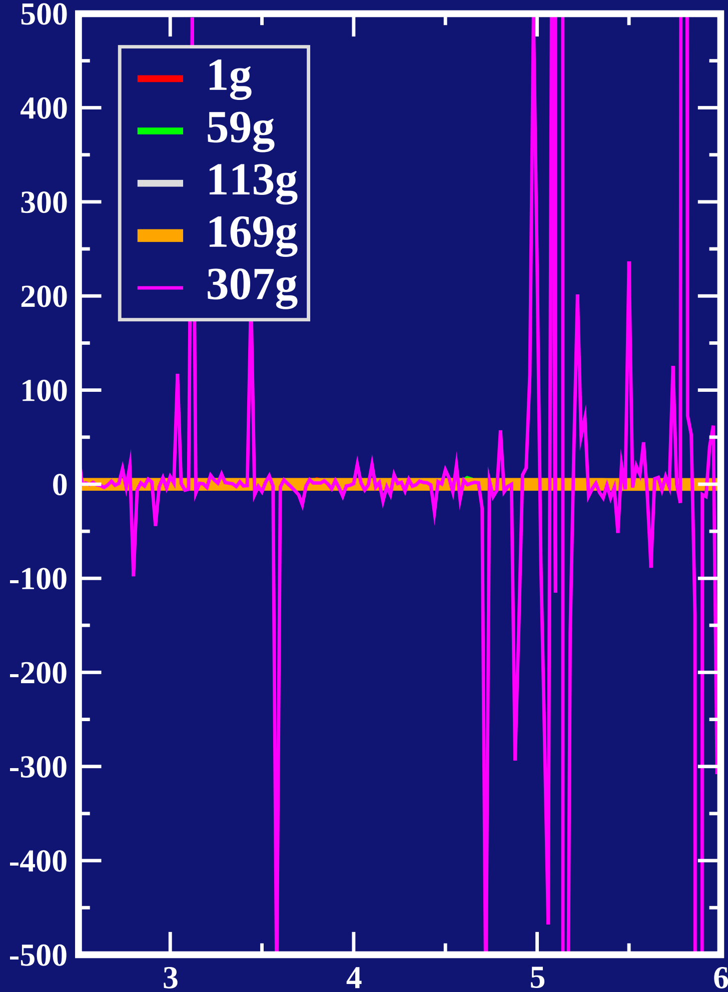
kernels $N_t = 288$ **spectra**

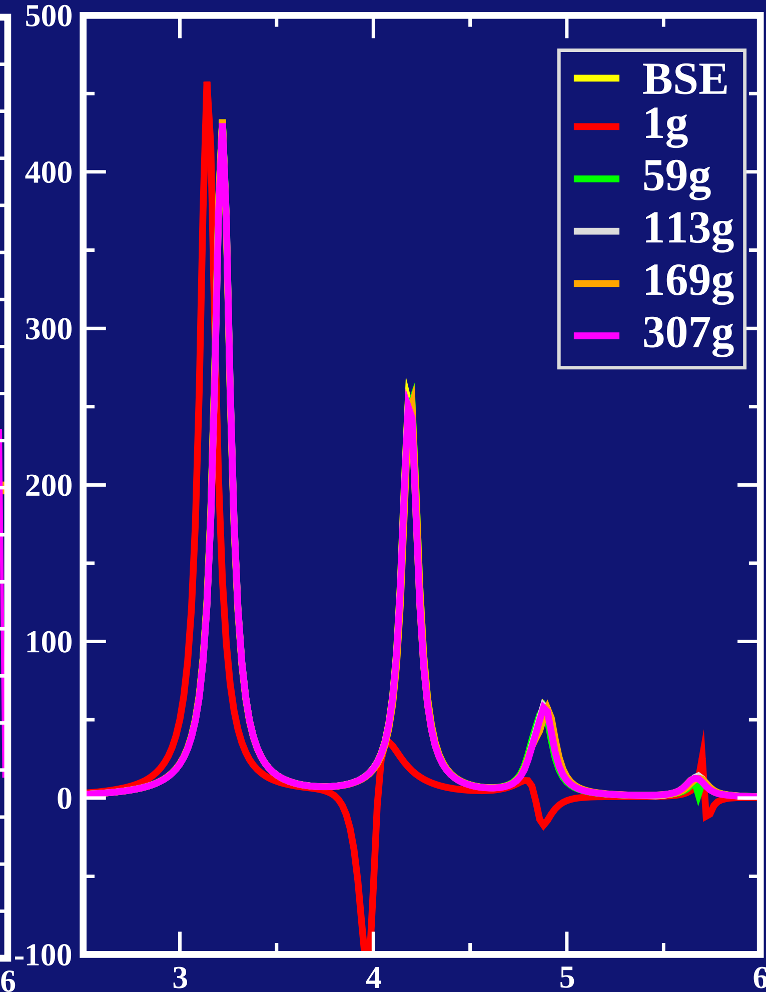


kernels $N_t = 288$ **spectra**



kernels $N_t = 288$ **spectra**





... so for Si and SiC with 2k ..

$\surd$ K works (close to the BSE result!)

$\surd$ T_1 reproduces the GW corrections

$\surd$ T_2 reproduces the excitonic effects

- f_{xc}

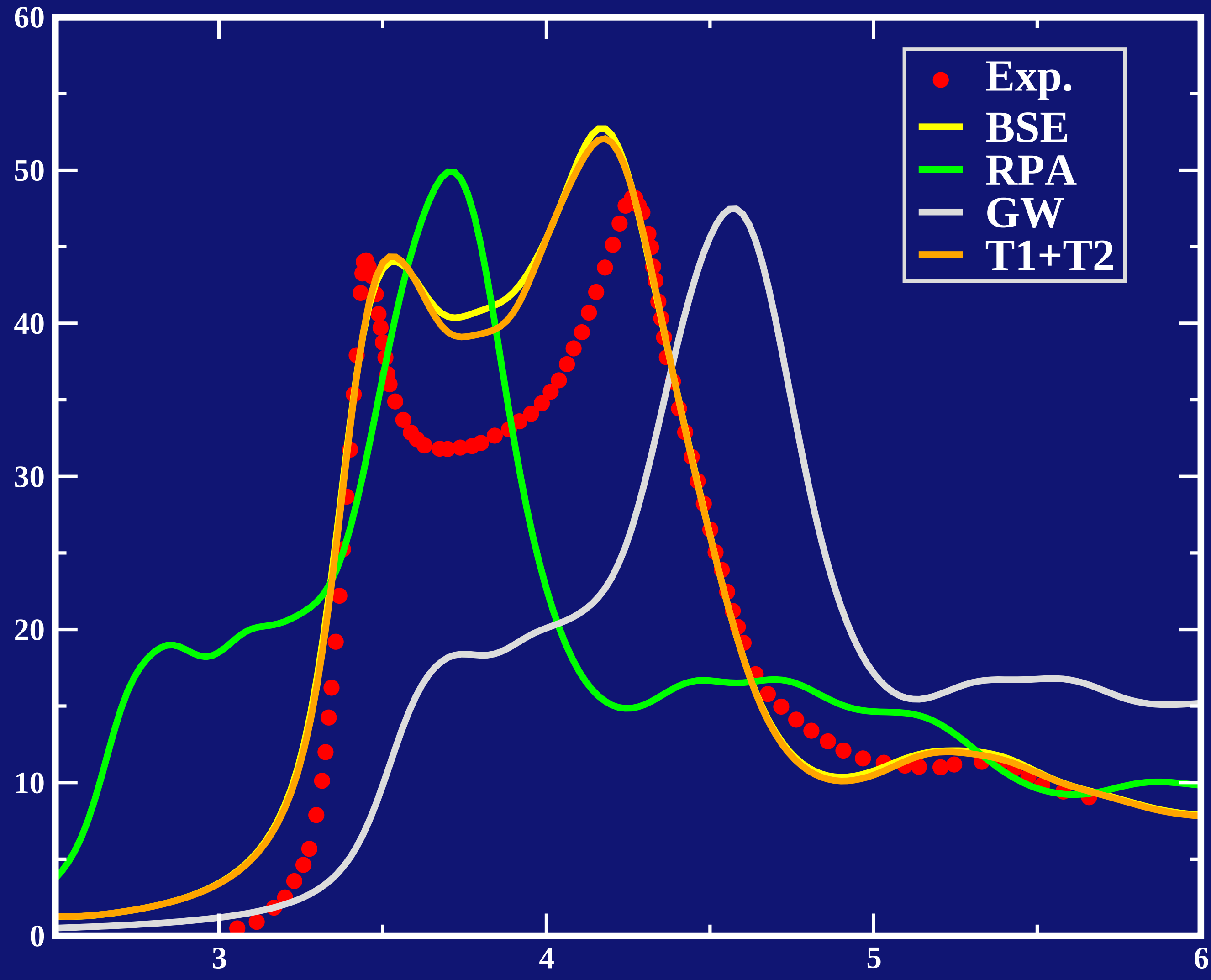
$\surd$ f_{xc} static when $N_{\mathbf{G}} \sim N_t$

$\surd$ f_{xc} dynamic when $N_{\mathbf{G}} \ll N_t$ but it can work

$\times$ f_{xc} "crazy" when Φ is no more invertible

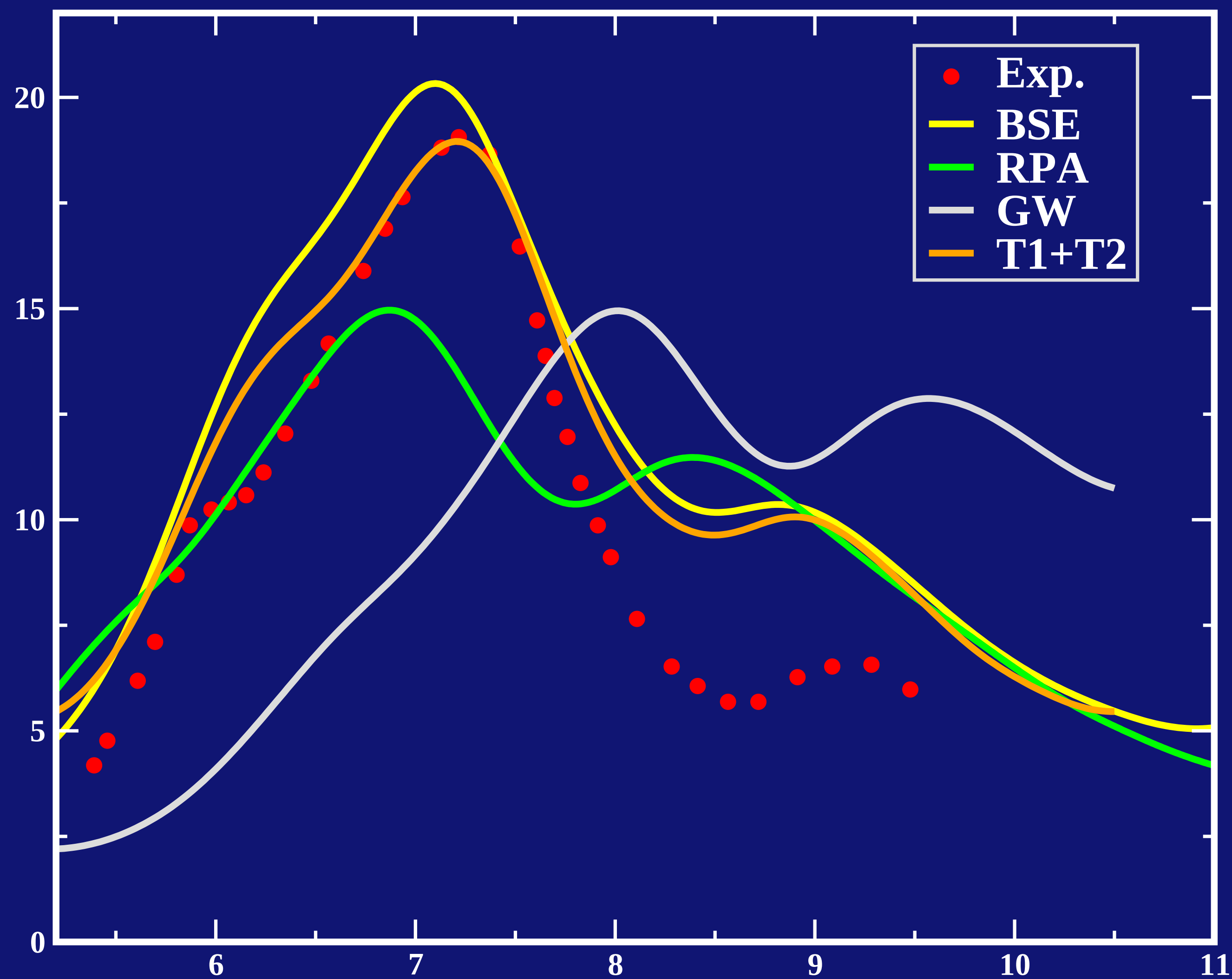
Solid Silicon - 256k

$N_t = 2304 \quad N_{\mathbf{G}} = 307$

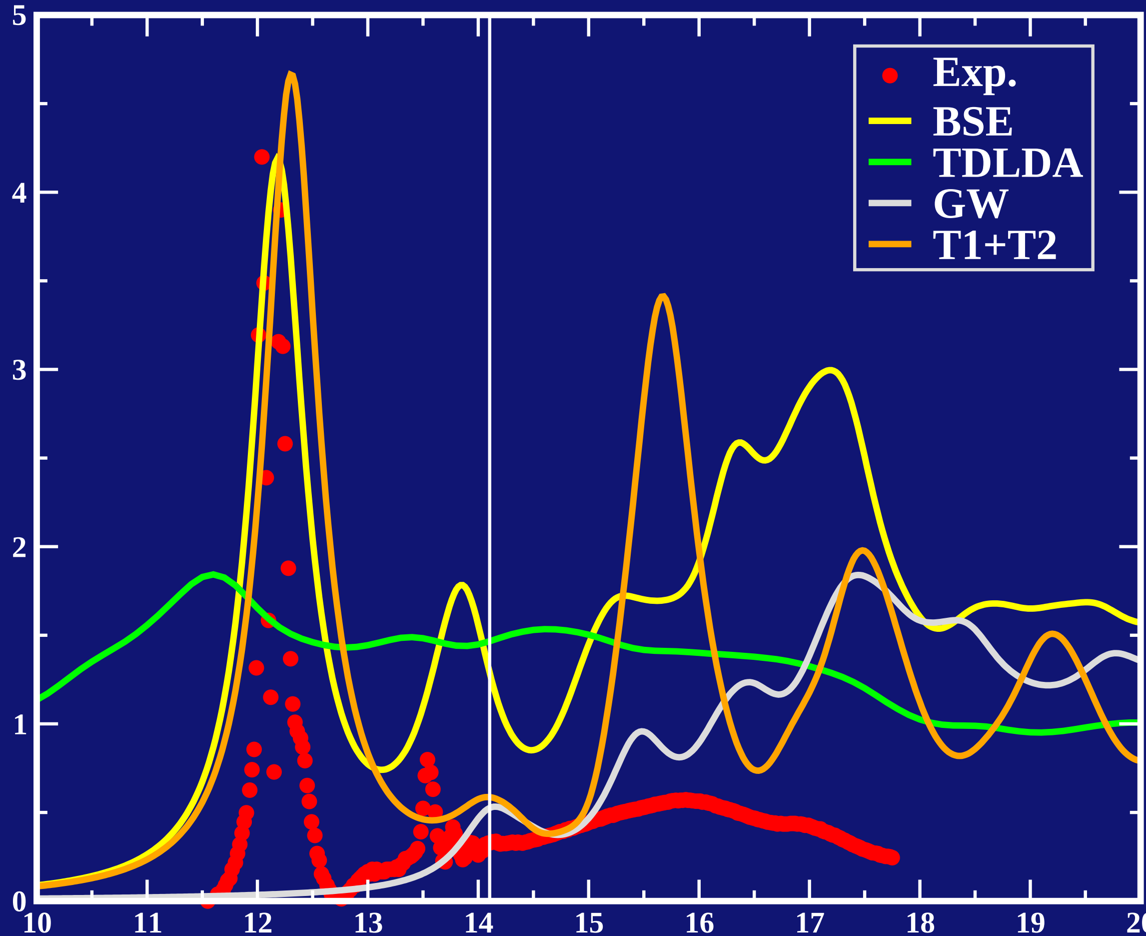


Solid Silicon Carbide - 256k

$N_t = 2304 \quad N_{\mathbf{G}} = 387$



… future developments : Bound exciton ⇒ Solid Argon



BSE: Argon, V.Olevano et al. in preparation

Conclusions

$$f_{xc}^{\mathrm{TDDFT}}$$

Conclusions

$$f_{xc}^{\mathrm{TDDFT}}$$

parameter-free

Conclusions

static in principle
dynamic in practice
reduced spacial complexity

$$f_{xc}^{TDDFT}$$

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it works!

f_{xc}^{TDDFT}

semi-conductors

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f_{xc}^{TDDFT}

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improvable

Conclusions

static in principle
dynamic in practice
reduced spacial complexity

invertibility problems

it works!

semi-conductors

$$f_{xc}^{\mathrm{TDDFT}}$$

parameter-free

promising

improvable

bound excitons

Conclusions

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Thank you for your attention!