Parameter-free calculation of response functions in time-dependent density-functional theory

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Ab initio Electrons Excitations Theory:
Towards Systems of Biological Interest

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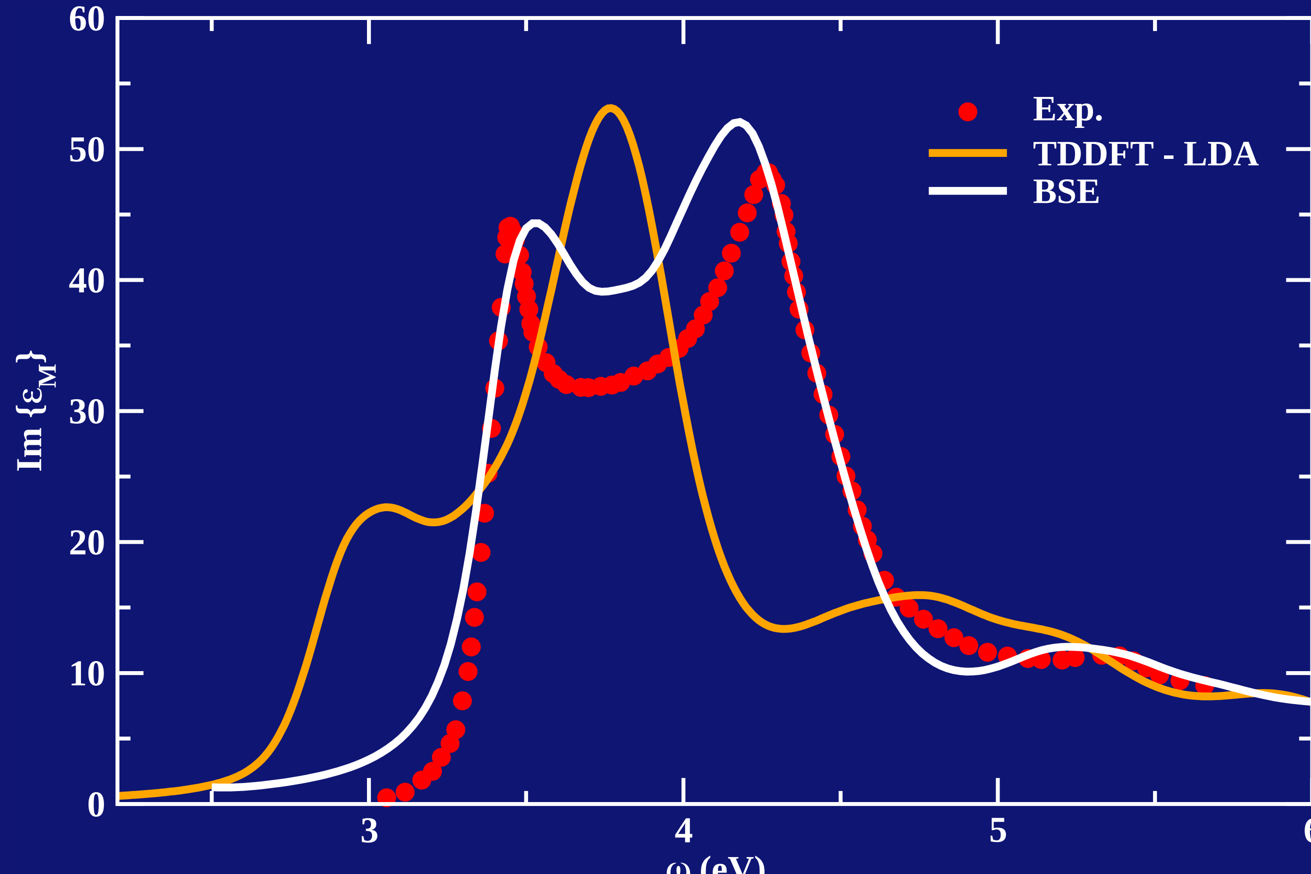
LaTeX 2_ε- Pdfscreen - JAVA powered

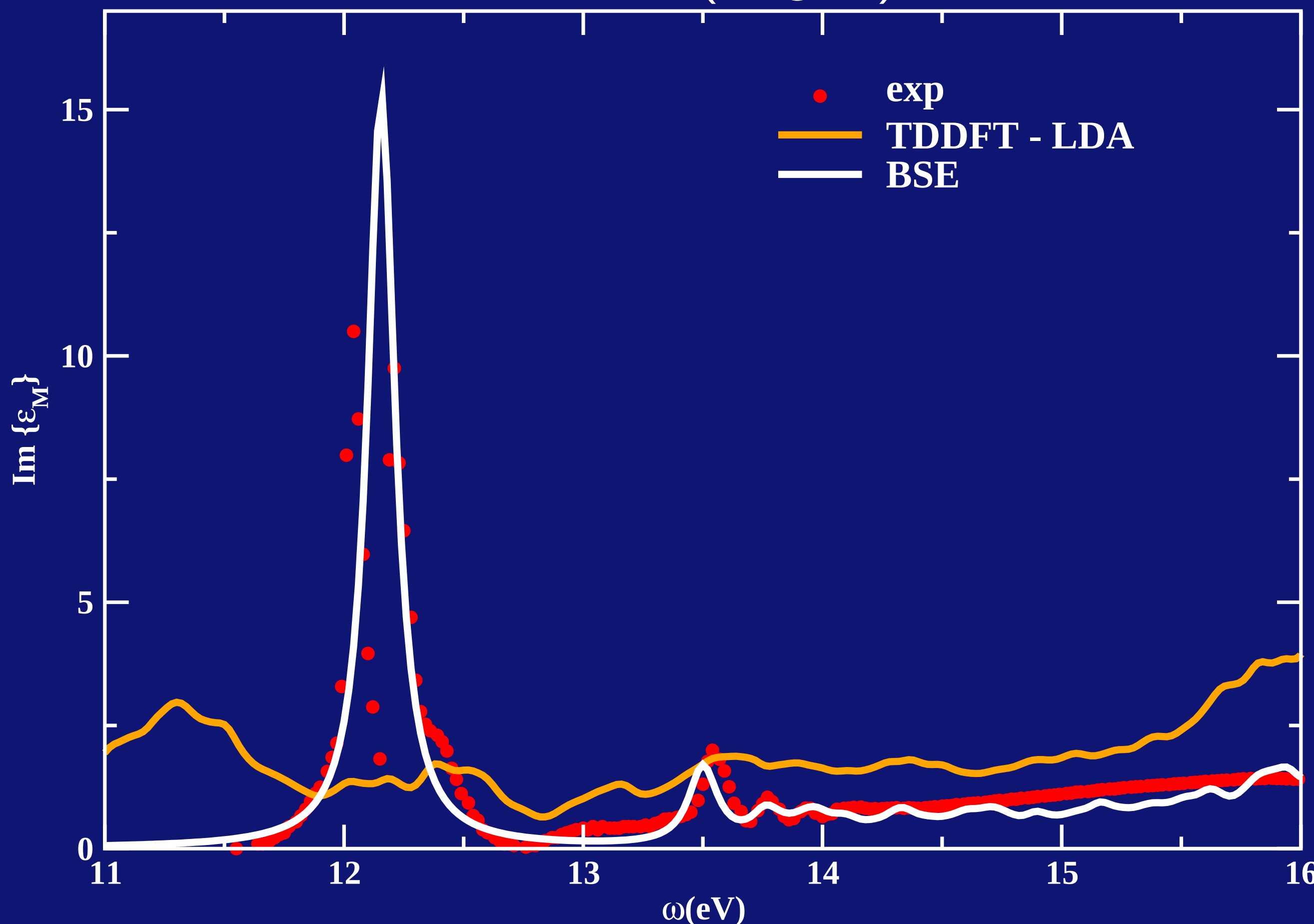
Absorption Spectra in solids

Semiconductors (Silicon)



Absorption Spectra in solids

Insulators (Argon)



V.Olevano *et al.*, unpublished.

Outline

- **Derivation of a f_{xc}^{TDDFT}**
  - $\hookrightarrow$ **TDDFT vs BSE**
- **Kernels and spectra analysis**
- **Application to realistic systems**
  - $\hookrightarrow$ **Semiconductors - Solid Si and SiC**
  - $\hookrightarrow$ **Bound excitons - Solid Argon**
- **Conclusions and perspectives**

Absorption spectrum

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

$$\varepsilon_{\text{M}}(\omega) = \lim_{\mathbf{q}\to 0}\left[1 - v_{\mathbf{G}\,=\,0}(\mathbf{q}) S_{\mathbf{G}\,=\mathbf{G}'\,=\,0}(\mathbf{q},\omega)\right]$$

$$S = \text{polarizability} = \begin{cases} \bar{L} \Rightarrow \text{BSE} \\ \bar{\chi} \Rightarrow \text{TDDFT} \end{cases}$$

Same spectra in TDDFT and BSE

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

$$\text{BSE} \quad \leftrightarrow \quad {}^4\bar{L} = {}^4P^0 + {}^4P^0 \left({}^4\bar{v} - {}^4W\right) {}^4\bar{L}$$

$$\text{TDDFT} \quad \leftrightarrow \quad \bar{\chi} = \chi^0 + \chi^0 \left(\bar{v} + f_{xc}\right) \bar{\chi}$$

$$^4\bar{\chi} = {}^4\chi^0 + {}^4\chi^0 \left({}^4\bar{v} + {}^4f_{xc}\right) {}^4\bar{\chi}$$

$$\bar{v} = v - v_0$$

$$^4\bar{v} = \delta(12)\delta(34)\bar{v}(13)$$

$$^4W = \delta(13)\delta(24)W(12)$$

$$^4f_{xc} = \delta(12)\delta(34)f_{xc}(13)$$

Transition framework

$$A_{(n_1 n_2)}^{(n_3 n_4)} = \int d(1234) \phi_{n_1}(1) \phi_{n_2}^*(2) A(1,2,3,4) \phi_{n_3}^*(3) \phi_{n_4}(4)$$

BSE $\Leftrightarrow \; {}^4\bar{L} = {}^4P^0 + {}^4P^0 \left({}^4\bar{v} - {}^4W \right) {}^4\bar{L}$

TDDFT $\Leftrightarrow \; \bar{\chi} = \chi^0 + \chi^0 \left(\bar{v} + f_{xc} \right) \bar{\chi}$

Transition framework

$$A_{(n_1 n_2)}^{(n_3 n_4)} = \int d(1234)\phi_{n_1}(1)\phi_{n_2}^*(2)A(1,2,3,4)\phi_{n_3}^*(3)\phi_{n_4}(4)$$

$$\text{BSE} \Leftrightarrow \left[\Delta E \; + < v > - < W > \right] A_\lambda = E_\lambda A_\lambda$$

$$\text{TDDFT} \Leftrightarrow \left[\Delta\epsilon \; + < v > + < f_{xc} > \right] A_\lambda = E_\lambda A_\lambda$$

Transition framework

$$A_{(n_1 n_2)}^{(n_3 n_4)} = \int d(1234)\phi_{n_1}(1)\phi^*_{n_2}(2)A(1,2,3,4)\phi^*_{n_3}(3)\phi_{n_4}(4)$$

BSE $\Leftrightarrow \left[\Delta E \;+ < v > - < W >\right] \; A_\lambda = E_\lambda A_\lambda$

TDDFT $\Leftrightarrow \; \left[\Delta\epsilon + < v > + < f_{xc} >\right] A_\lambda = E_\lambda A_\lambda$

$$< f_{xc} >= - < W > + (\Delta E - \Delta\epsilon)$$

How can we use $< f_{xc} >$ in a *2-point* equation ??

How can we use $< f_{xc} >$ in a *2-point* equation ??

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

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

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

$$T(1,2,\omega) = \int d(34)\, \chi^0(1,3,\omega) f_{xc}(3,4,\omega) \chi^0(4,2,\omega) =$$

$$= \int d(34) \sum_{\substack{n_1 n_2 \\ n_3 n_4}} \frac{\Phi^*(n_1 n_2, \mathbf{r}) \Phi(n_1 n_2, \mathbf{r}_1)}{\omega - (\epsilon_{n_2} - \epsilon_{n_1}) + i\eta} f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega) \frac{\Phi^*(n_3 n_4, \mathbf{r}_2) \Phi(n_3 n_4, \mathbf{r}')}{\omega - (\epsilon_{n_4} - \epsilon_{n_3}) + i\eta}$$

How can we use $< f_{xc} >$ in a *2-point* equation ??

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$$= \sum_{\substack{n_1 n_2 \\ n_3 n_4}} \frac{\Phi^*(n_1 n_2, \mathbf{r})}{\omega - (\epsilon_{n_2} - \epsilon_{n_1}) + i\eta} < f_{xc} > \frac{\Phi(n_3 n_4, \mathbf{r}')}{\omega - (\epsilon_{n_4} - \epsilon_{n_3}) + i\eta}$$

- $< f_{xc} >= - < W > + (\Delta E - \Delta\epsilon)$

- $< f_{xc} >= - < W > + (\Delta E - \Delta\epsilon)$

$$\bar{\chi} = \chi^0 \left(\chi^0 - \chi^0 \bar{v} \chi^0 - T_1 - T_2 \right)$$

$$T_1 = \sum_{n_1 n_2} \frac{\Phi^*(n_1 n_2, \mathbf{G}) \Phi(n_1 n_2, \mathbf{G}')}{[\omega - \Delta\epsilon + i\eta]^2} [\Delta E - \Delta\epsilon]$$ QP shift

$$T_2 = -\sum_{\substack{n_1 n_2 \\ n_3 n_4}} \frac{\Phi^*(n_1 n_2, \mathbf{G})}{\omega - \Delta\epsilon + i\eta} < W > \frac{\Phi(n_3 n_4, \mathbf{G}')}{\omega - \Delta\epsilon + i\eta}$$ excitonic effect

if $\chi^0(\{\epsilon_{n_i}\}) \longrightarrow \chi^0_{\mathrm{GW}}(\{E_{n_i}\})$

$$< f_{xc} >= - < W > \quad \Rightarrow \quad T = T_2$$

$$F^{\mathrm{BSE}}_{(n_1 n_2)(n_3 n_4)} = - < W >$$

$$F^{\mathrm{TDDFT}}_{(n_1 n_2)(n_3 n_4)} =< f_{xc} >$$

When the assumption $F^{\mathrm{TDDFT}}_{(\mathrm{n_1 n_2})(\mathrm{n_3 n_4})} = F^{\mathrm{BSE}}_{(\mathrm{n_1 n_2})(\mathrm{n_3 n_4})}$ cannot be fulfilled

$$F^{\mathrm{BSE,reso}}_{(vc)(vc)} = \int \phi_v(1)\phi_v(1) W \phi_c(2)\phi_c(2)$$

$$F^{\mathrm{TDDFT,reso}}_{(vc)(vc)} = \int \phi_v(1)\phi_c(1) f_{xc} \phi_v(2)\phi_c(2)$$

$$F^{\mathrm{BSE,coup}}_{(vc)(cv)} = \int \phi_v(1)\phi_c(1) W \phi_c(2)\phi_v(2)$$

$$F^{\mathrm{TDDFT,coup}}_{(vc)(cv)} = \int \phi_v(1)\phi_c(1) f_{xc} \phi_v(2)\phi_c(2)$$

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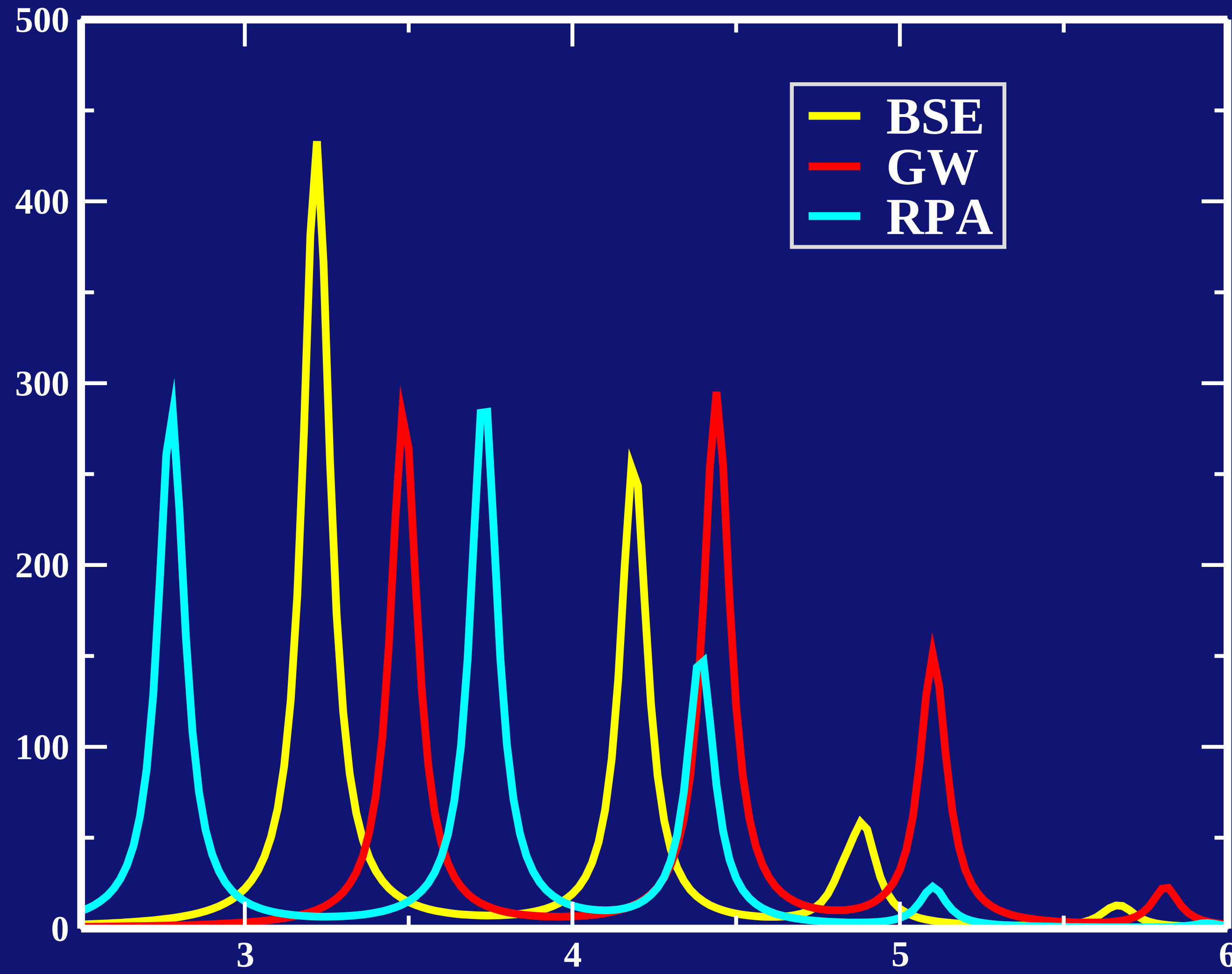
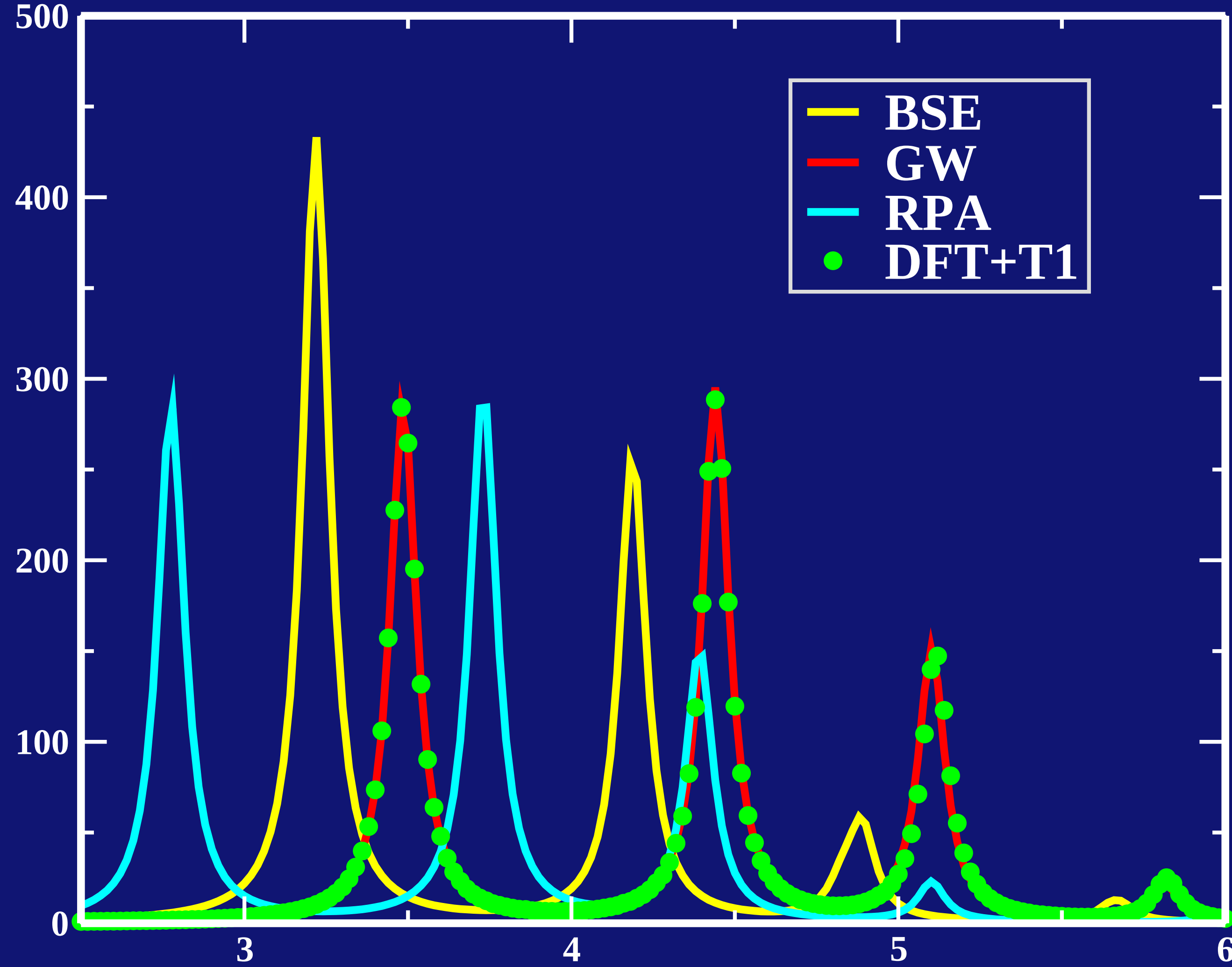
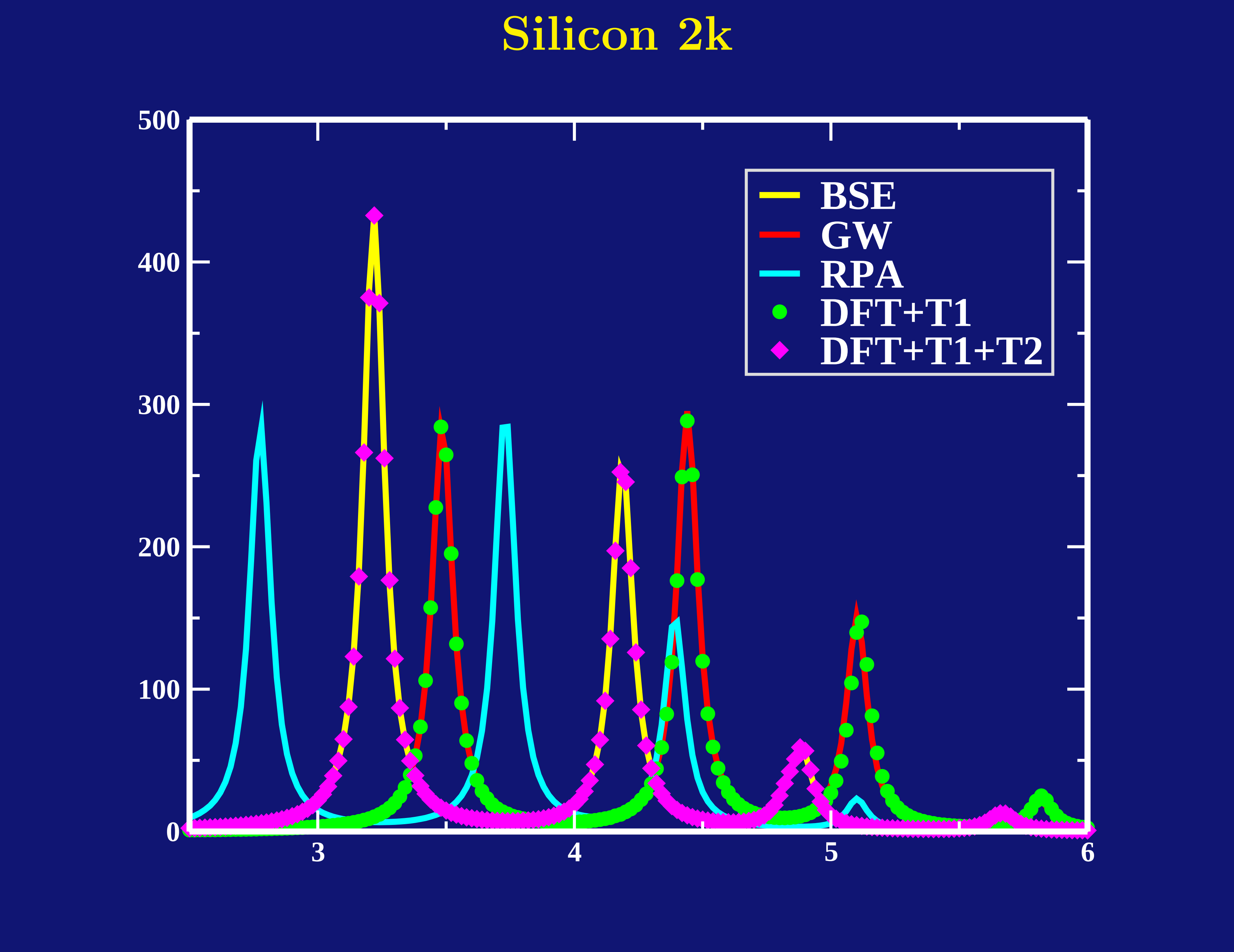
$F^{\mathrm{TDDFT}}_{(\mathrm{n_1 n_2})(\mathrm{n_3 n_4})}$ parameters

Silicon 2k



Silicon 2k




Silicon 2k
500
400
300
200
100
0
3
4
5
6
BSE
GW
RPA
DFT+T1
DFT+T1+T2

Problem of T_1

- Convergence of T_1 $\sim 300\textsc{g}$
- Convergence of the spectrum $< 100\textsc{g}$

$$(T_1)_{k,k} = (\Delta E_k - \Delta\epsilon_k)$$

$$(T_1)_{k,k+\Delta k} = 0 \quad \forall \Delta k \neq 0$$

Problem of T_1

- Convergence of T_1 ~ 300G
- Convergence of the spectrum < 100G

$$(T_1)_{k,k} = (\Delta E_k - \Delta \epsilon_k)$$

$$(T_1)_{k,k+\Delta k} = 0 \quad \forall \Delta k \neq 0$$

since

- T_1 worsens (if not prevents) the convergence of the spectrum
- T_1 does not avoid the calculation of the $E_{n_i}^{QP}$

the quasiparticle corrections will be included in the χ^0

The (useless?) kernel f_{xc}

1) $F^{\mathrm{TDDFT}}_{(\mathrm{n}_1\mathrm{n}_2)(\mathrm{n}_3\mathrm{n}_4)} = F^{\mathrm{BSE}}_{(\mathrm{n}_1\mathrm{n}_2)(\mathrm{n}_3\mathrm{n}_4)}$

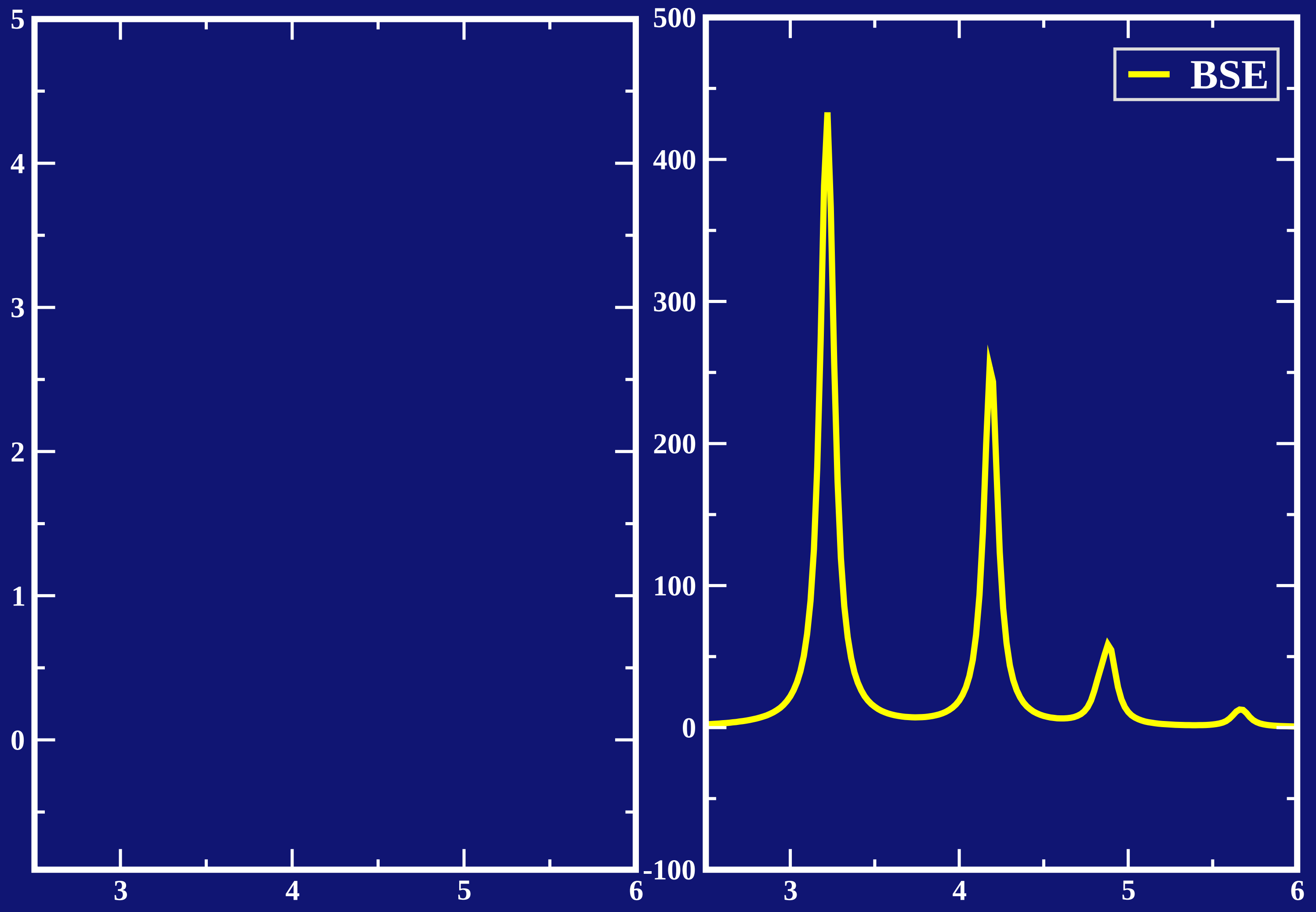
2) $T_2(\omega) = \frac{\Phi}{\omega - \Delta\epsilon} F^{\mathrm{BSE}} \frac{\Phi}{\omega - \Delta\epsilon} = \frac{\Phi\Phi}{\omega - \Delta\epsilon} f_{xc} \frac{\Phi\Phi}{\omega - \Delta\epsilon}$

3) $f_{xc}^{\mathrm{eff}} = (\chi^0)^{-1} T_2 (\chi^0)^{-1}$ should be static ?

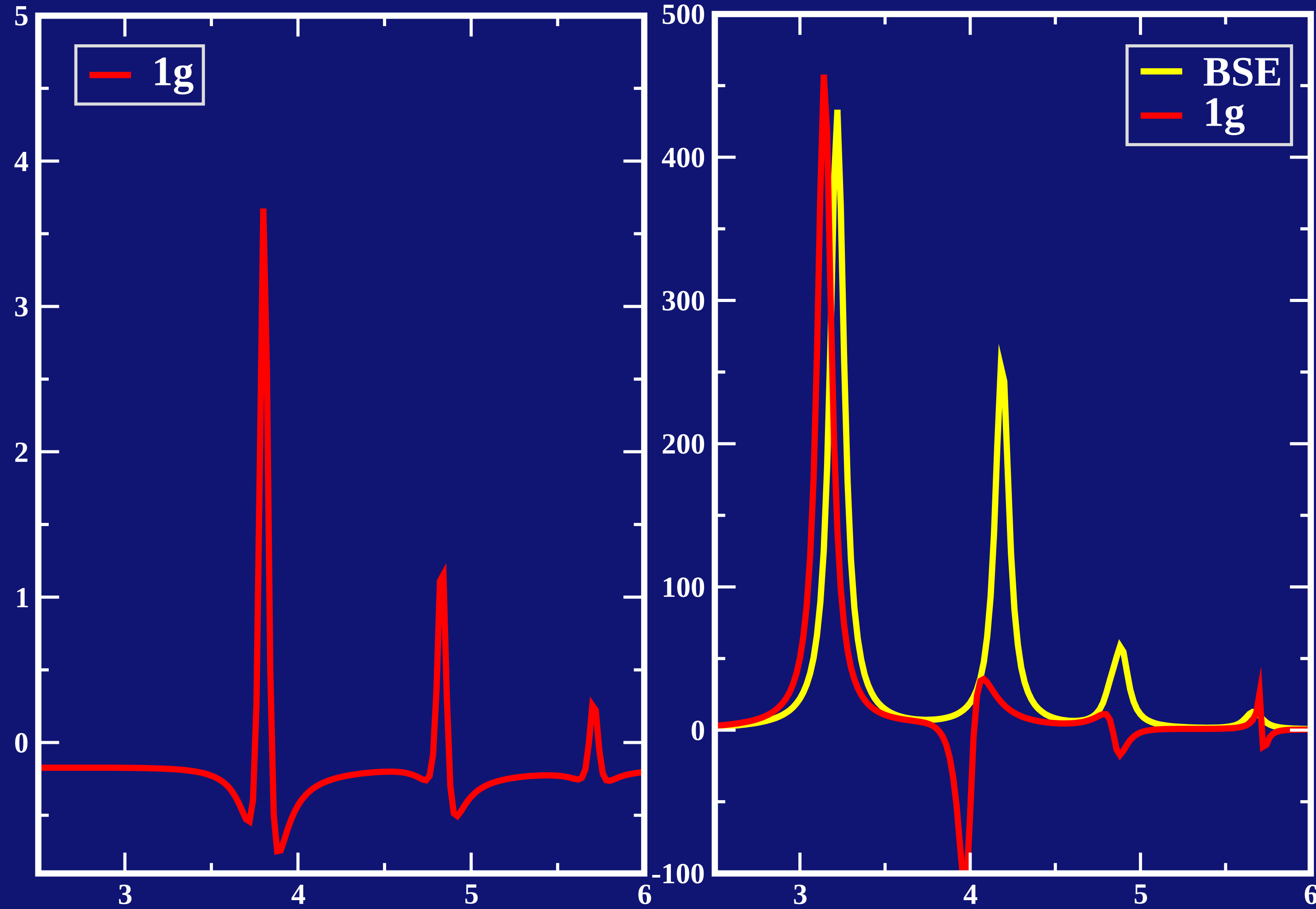
$\searrow$

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

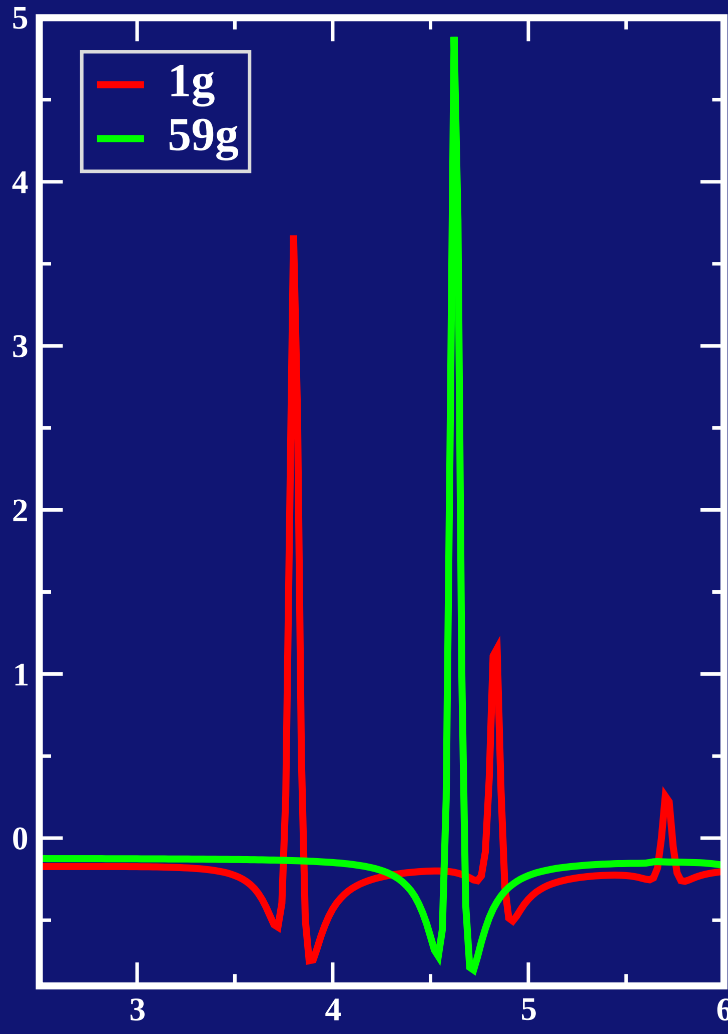
kernels $N_t = 288$ **spectra**

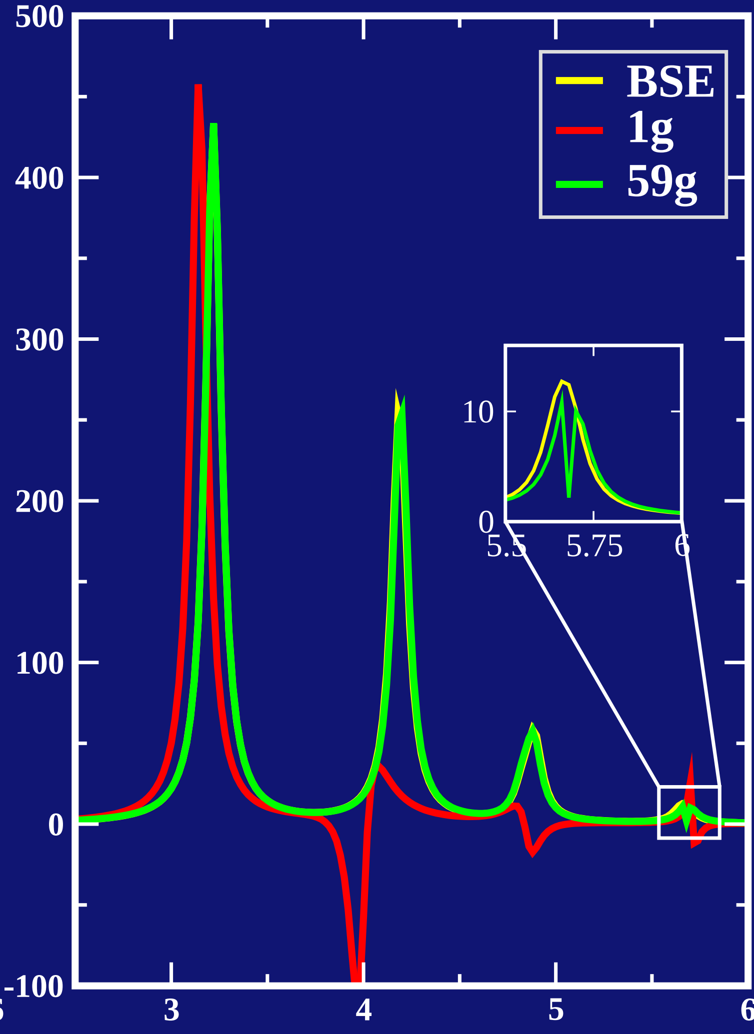


kernels $N_t = 288$ **spectra**

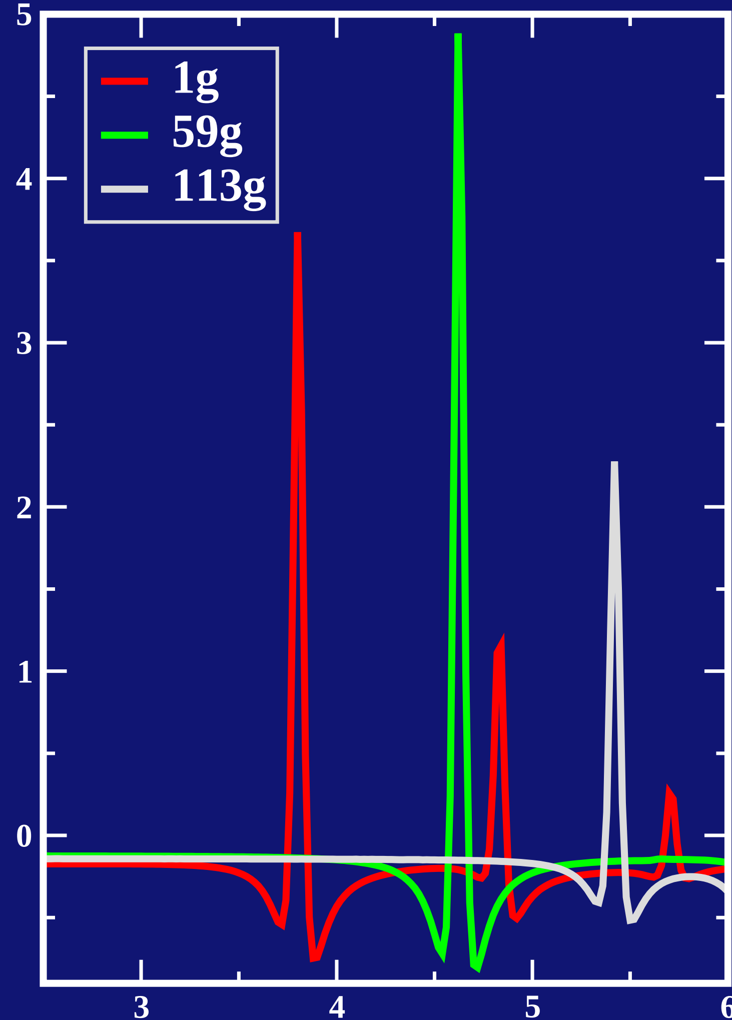


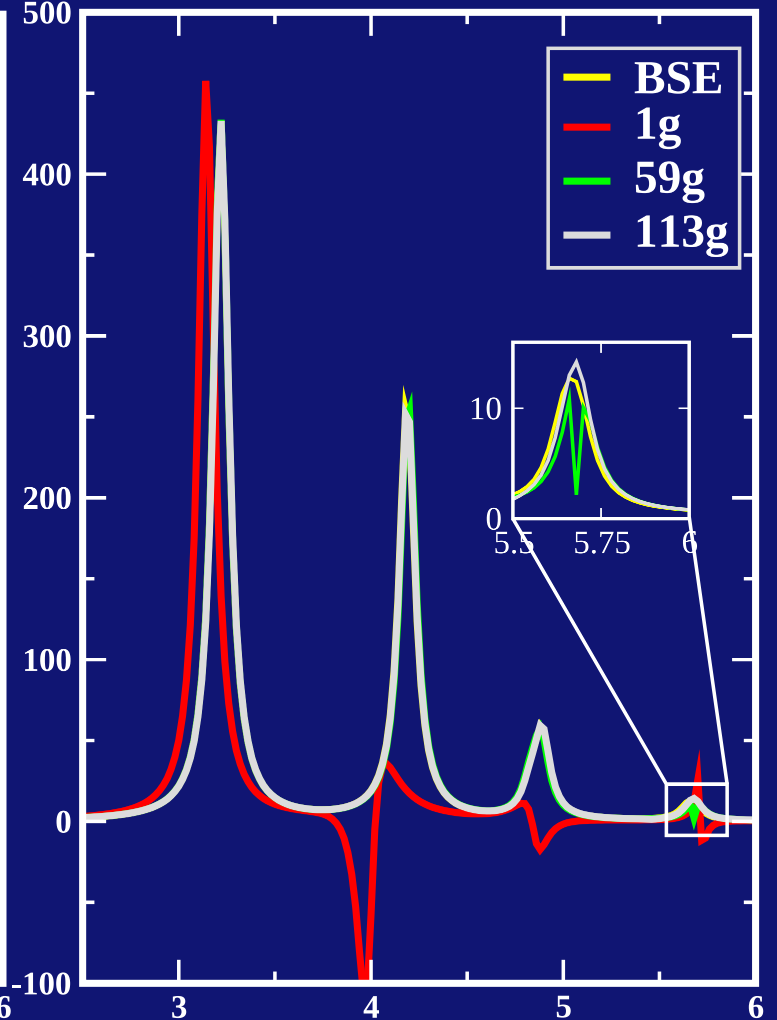
kernels $N_t = 288$ **spectra**



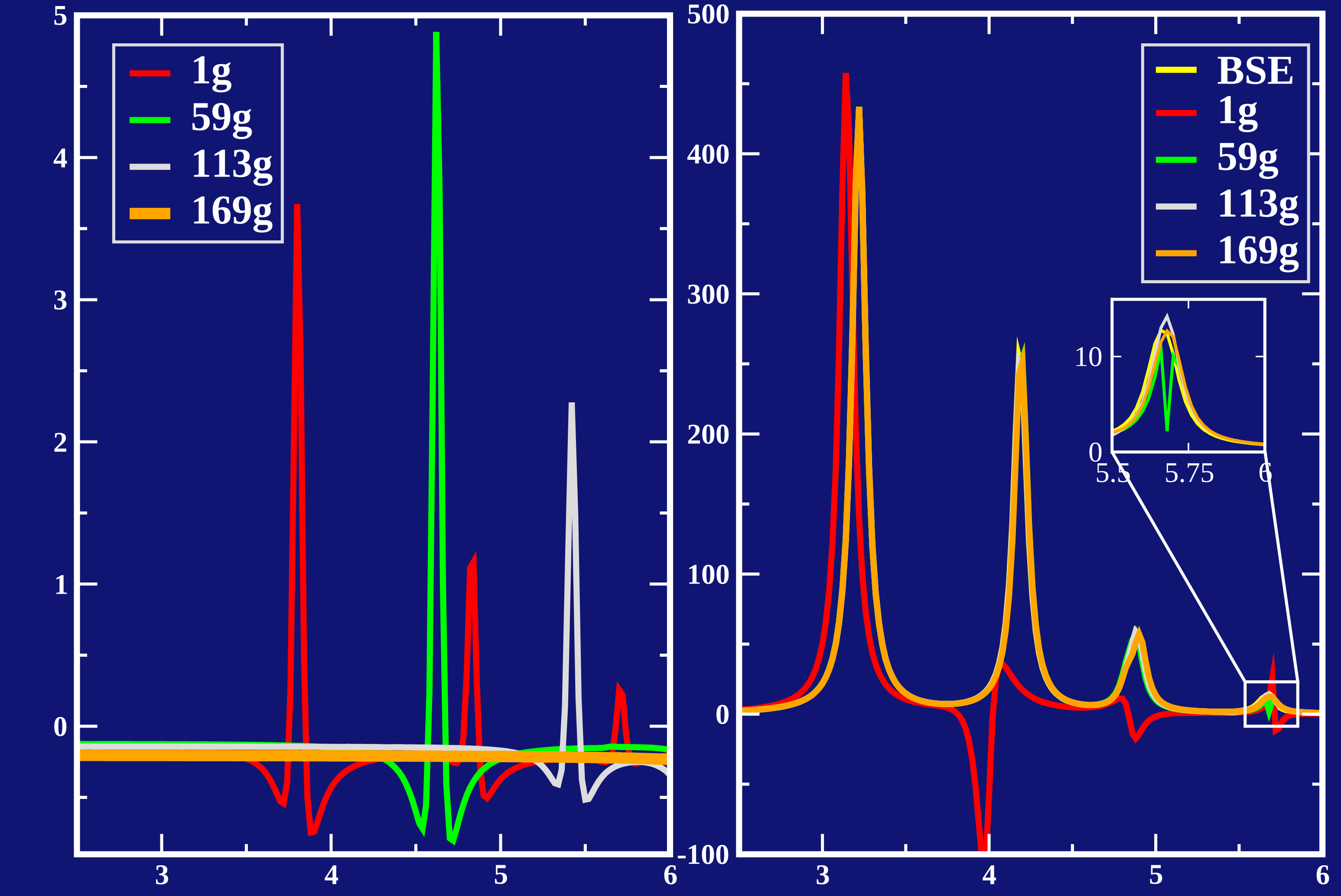


kernels $N_t = 288$ spectra

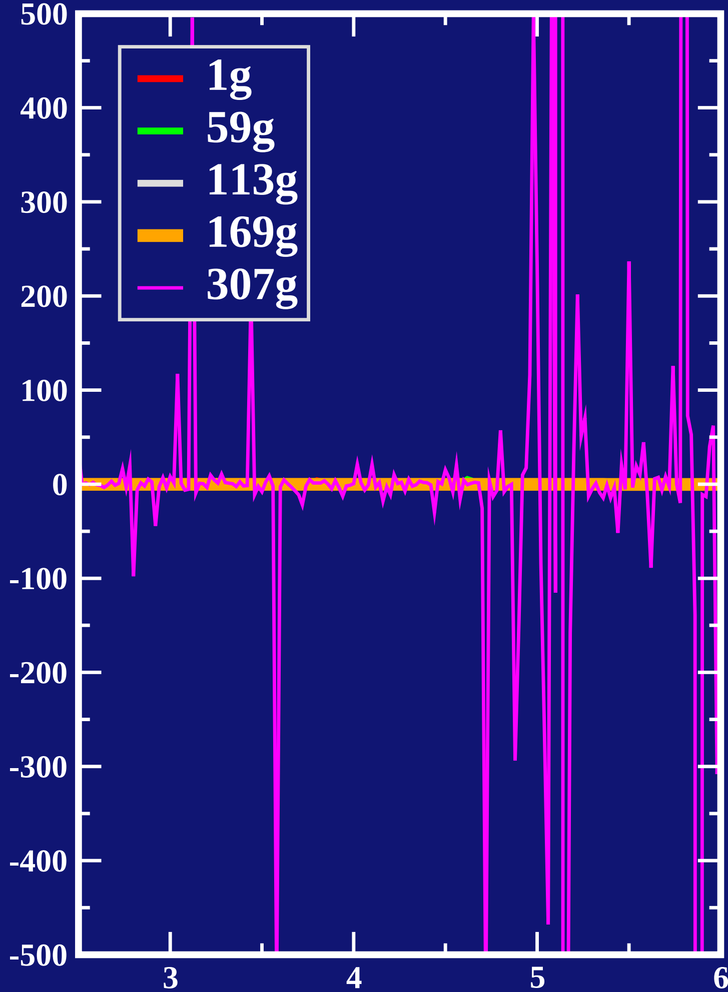


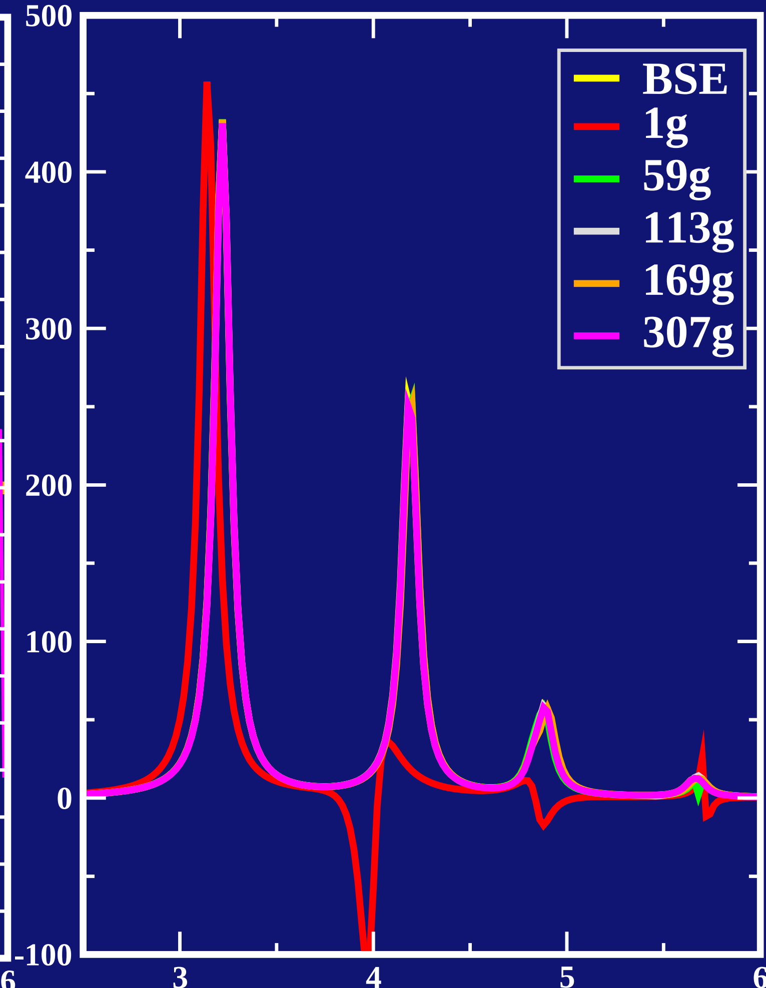


kernels $N_t = 288$ **spectra**



kernels $N_t = 288$ **spectra**





The (useless?) kernel f_{xc}

1) $F^{\rm TDDFT}_{(n_1n_2)(n_3n_4)} = F^{\rm BSE}_{(n_1n_2)(n_3n_4)}$ N_t^2 conditions

✓ $T_2(\omega) = \frac{\Phi}{\omega-\Delta\epsilon} F^{\rm BSE} \frac{\Phi}{\omega-\Delta\epsilon}$

3) $f_{xc}^{\rm eff} = (\chi^0)^{-1}\, T_2\, (\chi^0)^{-1}$ if χ^0 is invertible

f_{xc} is dynamic unless the three conditions above are fulfilled

but it is never calculated nor used in real calculations

Link with other works

$$\bar{\chi} = \chi^0 \left(\chi^0 - \chi^0 \bar{v} \chi^0 - \frac{\Phi}{\omega - \Delta\epsilon} < W > \frac{\Phi}{\omega - \Delta\epsilon} \right)^{-1} \chi^0$$

- $f_{xc}^{\mathrm{eff}} \sim \frac{\alpha}{q^2}$ Reining *et al*, PRL (2002)

- $f_{xc}^{\mathrm{eff}} \sim \frac{\alpha(\omega)}{q^2}$ Del Sole *et al*, PRB (2003)

- EXX, $W \longrightarrow \tilde{v}$, Kim and Görling, PRL (2002)

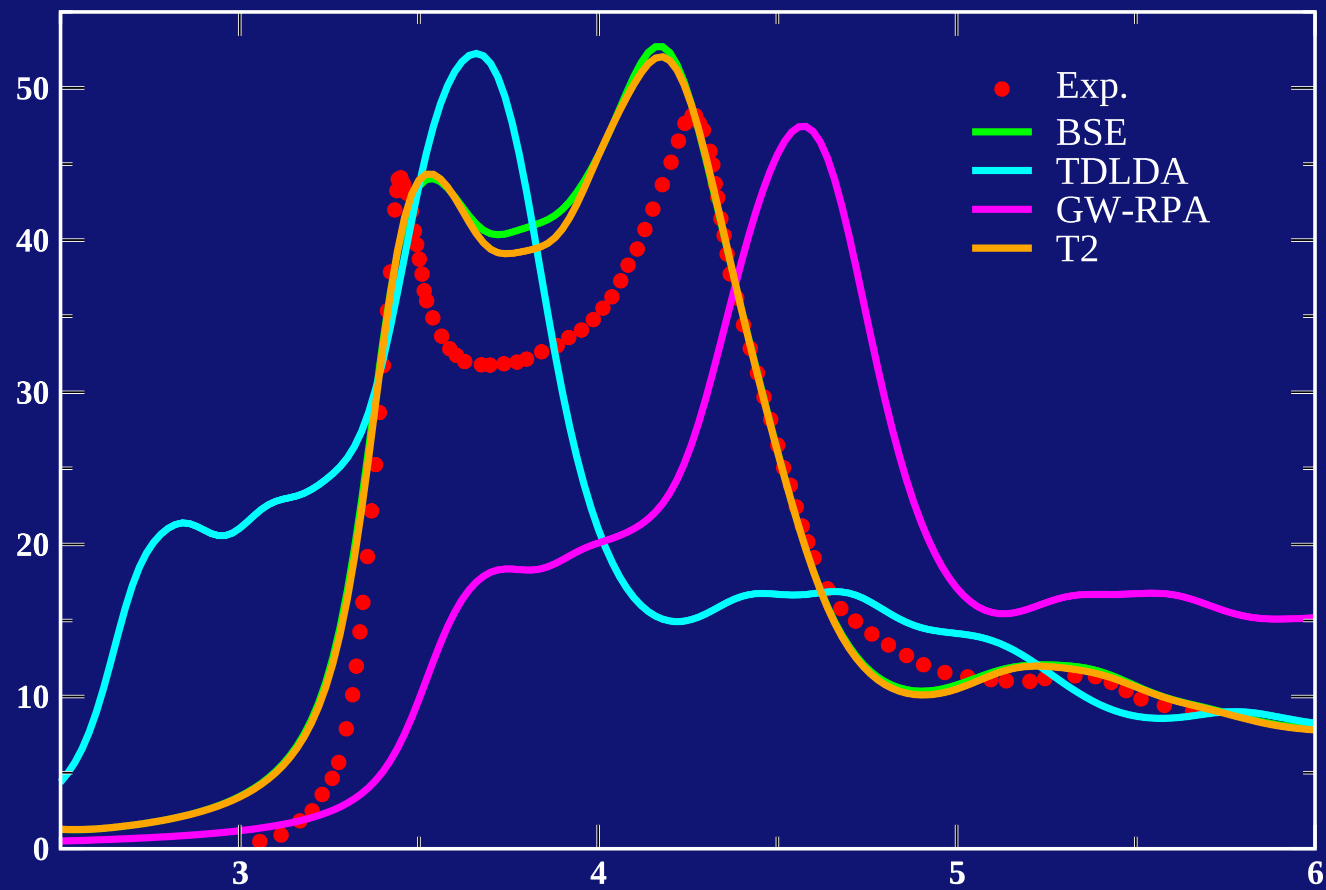
$\swarrow$ no parameters $\searrow$ 1 parameter

- Del Sole *et al.* (2003), Adragna's thesis (2002)

Realistic applications

Solid Silicon - 256k

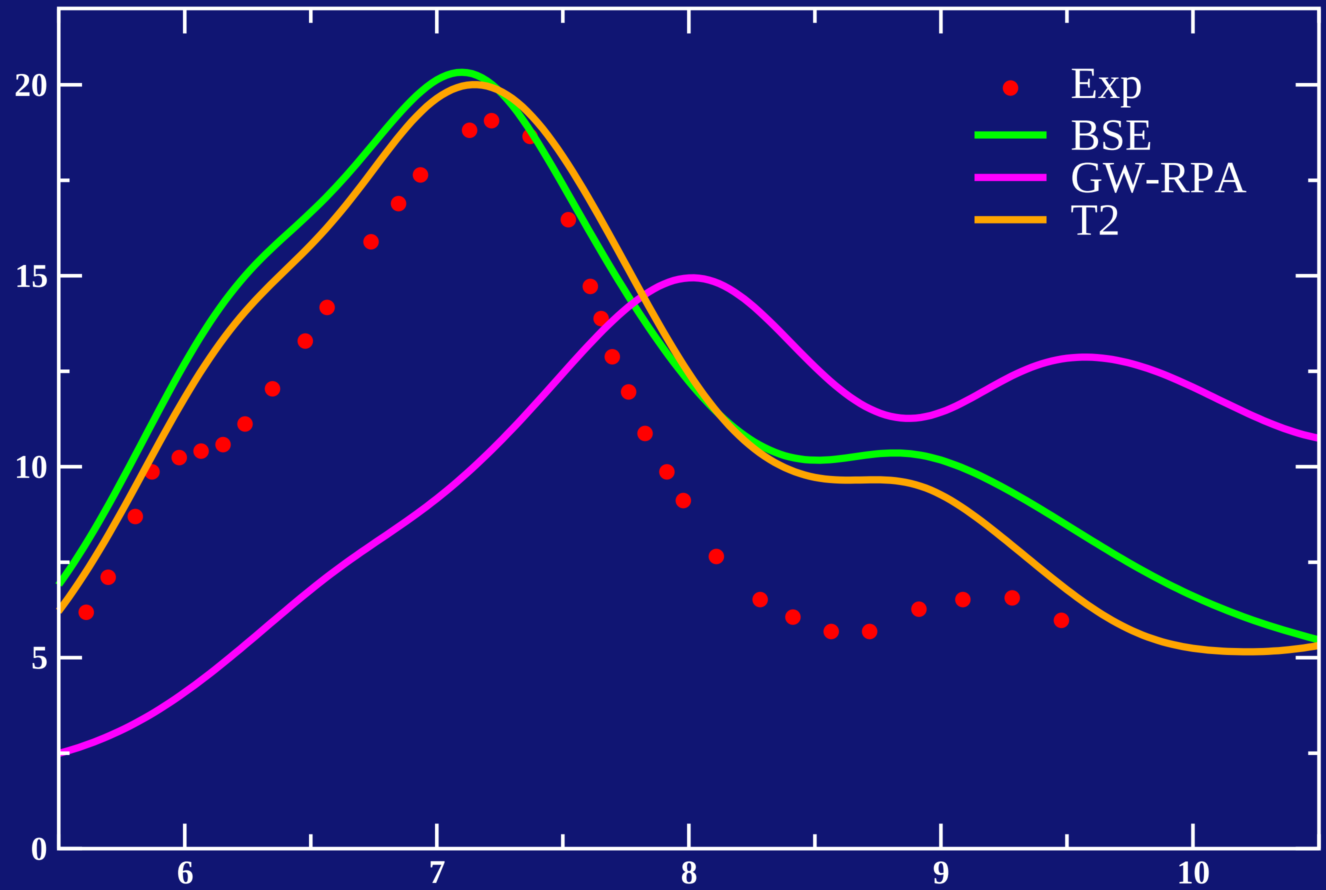
$N_t = 2304 \quad N_{\mathbf{G}} = 307$



Sottile, Olevano and Reining, PRL (2003)

Solid Silicon Carbide - 256k

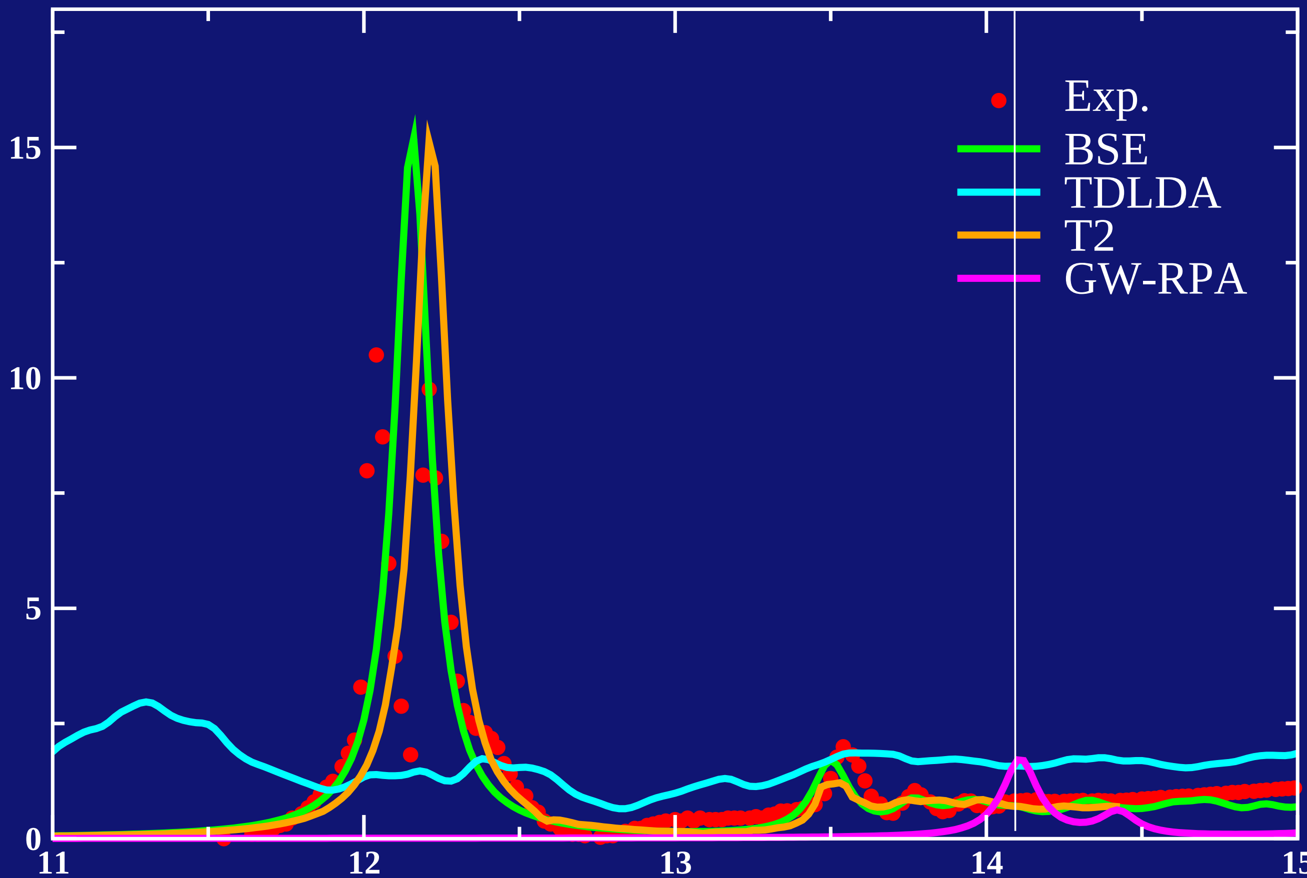
$N_t = 2304 \quad N_{\mathbf{G}} = 387$



Sottile, Olevano and Reining, PRL (2003)

Solid Argon - 2048k

$N_t = 6144 \quad N_{\mathbf{G}} = 307$



F. Sottile, PhD thesis.

Conclusions

- $T(\omega) \quad \longleftrightarrow \quad$ TDDFT $\leftrightarrow$ BSE

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

$\rightarrow T$ dynamic

$\rightarrow f_{xc}$ not necessary

$\rightarrow$ problems : T_1 (T_2^d) ; χ^0

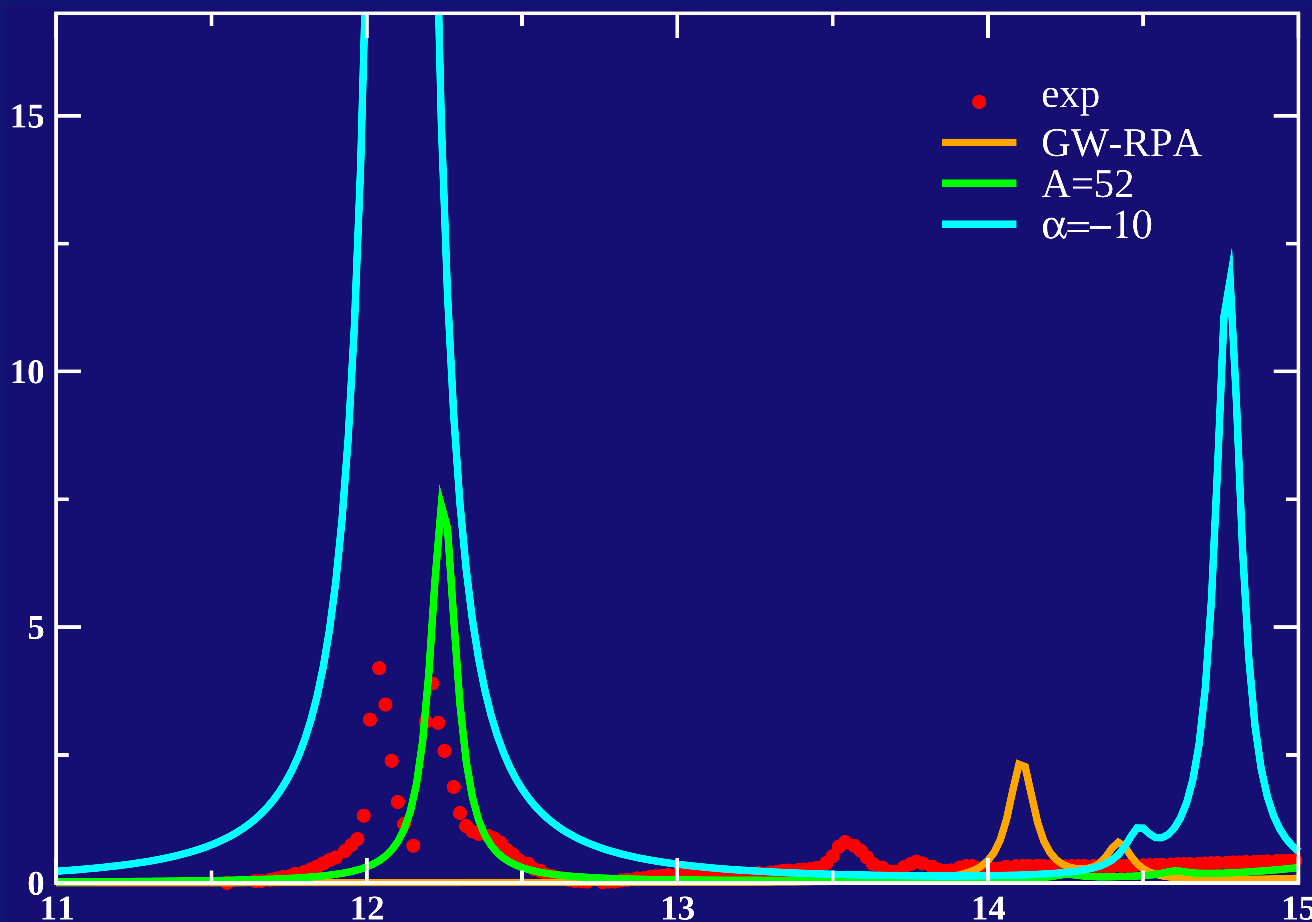
- it works for semiconductors (continuum exciton)

- it works for insulators (bound exciton)

What to do

- Quasiparticle corrections
- $W^{(n_3 n_4)}_{(n_1 n_2)}$
- towards complex (biological) systems $\left\{ \begin{array}{c} \textit{ab initio} \\ \text{models} \end{array} \right.$

Contact exciton model



Sottile, Karlsson, Reining and Aryasetiawan, (2003) to be published

Contact exciton model

$$W(\mathbf{G},\mathbf{G}') = \frac{A}{\Omega}\delta_{\mathbf{G},\mathbf{G}'}$$

$$\bar{\chi} = \bar{L} \quad \text{holds}$$

$$f_{xc} = -\frac{1}{2}W(\mathbf{G},\mathbf{G}')$$