# TDDFT and BSE in the HEG: some analytic considerations

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# TDDFT and BSE in the HEG: some analytic considerations

Motivation:

→ Understand more about TDDFT versus BSE

→ Understand more about electron-hole correlation functions

→ Insert analytical results into ab initio calculations

# TDDFT and BSE in the HEG: some analytic considerations

→ TDDFT and BSE

→ TDDFT and BSE in the HEG

→ Analyical solutions and approximations

→ Some results

## → TDDFT and BSE

$$\epsilon^{-1}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \delta(\mathbf{r}_1 - \mathbf{r}_2) + \int d\mathbf{r}_3\, v_c(|\mathbf{r}_1 - \mathbf{r}_3|)\, \chi(\mathbf{r}_3, \mathbf{r}_2; \omega)$$

$$\frac{\delta n(\mathbf{r}, t; [n])}{\delta v_{\mathrm{ext}}(\mathbf{r}', t')} = \chi(\mathbf{r}, \mathbf{r}', t, t')$$

$$n(\mathbf{r}t) = -iG(\mathbf{r}, t, \mathbf{r}t^{+}) \qquad \delta G/\delta v = -G\,[\delta G^{-1}/\delta v]\,G$$

$$\chi(1,2) = -iG(1,\bar{3})\,\frac{\delta G^{-1}(\bar{3},\bar{4})}{\delta v_{\mathrm{ext}}(2)}\,G(\bar{4},1^{+})$$

**Note: by definition, G can be either the exact G or the KS one!**

$$G^{-1} = G_0^{-1} - v_{\mathrm{ext}} - v_H - v_{xc}^{\mathrm{eff}}$$

$v_{xc}^{\mathrm{eff}}$ is either the KS xc potential or the xc self-energy

$$\chi = -iG\frac{\delta G^{-1}}{\delta v_{\text{ext}}}G \qquad G^{-1} = G_0^{-1} - v_{\text{ext}} - v_H - v_{xc}^{\text{eff}}$$

$$\chi = \chi_0 + \chi_0 v_c \chi - iG\frac{\delta v_{xc}^{\text{eff}}}{\delta v_{\text{ext}}}G$$

$$\chi_0 \equiv -iGG$$

$$v_{xc}^{\text{eff}} = v_{xc}^{\text{eff}}[n]$$

$$\chi = \chi_0 + \chi_0 v_c \chi - iG\frac{\delta v_{xc}^{\text{eff}}}{\delta n}\frac{\delta n}{\delta v_{\text{ext}}}G$$

$$\chi = \chi_0 + \chi_0 v_c \chi + \chi_0 \frac{\delta v_{xc}^{\text{eff}}}{\delta n}\chi$$

$f_{\text{xc}}$

$\rightarrow f_{\text{xc}}^{\text{mb}}$

**???**

(~ NQ kernel)

$v_{xc}^{\text{eff}} = v_{xc}^{KS}[n]$ : linear response in TDDFT

$v_{xc}^{\text{eff}} = \Sigma_{xc}[n]$ : linear response in GF framework

$$\chi = \chi_0 + \chi_0 v_c \chi + \chi_0 \frac{\delta v_{xc}^{\mathrm{eff}}}{\delta n} \frac{\delta n}{\delta v_{\mathrm{ext}}}$$

$$\Sigma_{xc}[n] = ???$$

$$\Sigma_{xc}[G] \approx iGW$$

$$\chi = \chi_0 + \chi_0 v_c \chi + \chi_0 \frac{\delta v_{xc}^{\mathrm{eff}}}{\delta G} \frac{\delta G}{\delta v_{\mathrm{ext}}}$$

$$-i\frac{\delta G}{\delta v_{\mathrm{ext}}} = {}^3\chi_0 + {}^3\chi_0 v_c \chi + {}^4\chi_0 \frac{\delta v_{xc}^{\mathrm{eff}}}{\delta G} \frac{\delta G}{\delta v_{\mathrm{ext}}}$$

$L$

$$v_{\mathrm{ext}}(1) \to v_{\mathrm{ext}}(1,2)$$

Bethe-Salpeter equation

$$\chi(1,2) = -i\frac{\delta G(1,1^+}{\delta v_{\mathrm{ext}(2^+,2)})} = -iL(1,2,1^+,2^+)$$

$$-i\frac{\delta G}{\delta v_{\mathrm{ext}}} = {}^3\chi_0 + {}^3\chi_0 v_c \chi + {}^4\chi_0 \frac{\delta v_{xc}^{\mathrm{eff}}}{\delta G}\frac{\delta G}{\delta v_{\mathrm{ext}}}$$

BSE yields variation of *G* wrt non-local potential

LR-TDDFT yields variation of *n* wrt local potential

But could we get more also out of LR-TDDFT, at least approx?

Usual strategy:
1. open the bubble
2. insert a few delta-functions
3. postulate that the results $L$

**Is this shaky or the thing to do?**

$$\chi = \chi_0 + \chi_0 v_c \chi + \chi_0 \frac{\delta v_{xc}^{\mathrm{eff}}}{\delta n} \frac{\delta n}{\delta v_{\mathrm{ext}}}$$

$$-i \frac{\delta G^{\mathrm{KS}}}{\delta v_{\mathrm{ext}}} = {}^3\chi_0 + {}^3\chi_0 v_c \chi + {}^3\chi_0 \frac{\delta v_{xc}^{\mathrm{KS}}}{\delta n} \frac{\delta n}{\delta v_{\mathrm{ext}}}$$

$$-i \frac{\delta G^{\mathrm{KS}}}{\delta v_{\mathrm{ext}}} = {}^3\chi_0 + {}^3\chi_0 v_c \chi + {}^3\chi_0 \frac{\delta v_{xc}^{\mathrm{KS}}}{\delta G^{\mathrm{KS}}} \frac{\delta G^{\mathrm{KS}}}{\delta v_{\mathrm{ext}}}$$

$$-i \frac{\delta G^{\mathrm{KS}}}{\delta v_{\mathrm{ext}}} = {}^4\chi_0 + {}^4\chi_0 v_c \chi + {}^4\chi_0\, \delta \frac{\delta v_{xc}^{\mathrm{KS}}}{\delta G^{\mathrm{KS}}} \frac{\delta G^{\mathrm{KS}}}{\delta v_{\mathrm{ext}}}$$

$L^{\mathrm{KS}}$

This is not $f_{\mathrm{xc}}$

Here, we have postulated a non-local external potential, i.e. an extended domain for the KS Green's function.

Have to define the KS Green's function.

$$-i\frac{\delta G^{\mathrm{KS}}}{\delta v_{\mathrm{ext}}} = {}^4\chi_0 + {}^4\chi_0 v_c \chi + {}^4\chi_0\,\delta\,\frac{\delta v_{xc}^{\mathrm{KS}}}{\delta G^{\mathrm{KS}}}\frac{\delta G^{\mathrm{KS}}}{\delta v_{\mathrm{ext}}}$$

$$L^{\mathrm{KS}} = {}^4\chi_0 + {}^4\chi_0\,\delta\,v_c\,\delta\,L^{\mathrm{KS}} + {}^4\chi_0\,\delta\,\frac{\delta v_{xc}^{\mathrm{KS}}}{\delta G^{\mathrm{KS}}}L^{\mathrm{KS}}$$

$$L^{\mathrm{ks}} = {}^4\chi_0 + {}^4\chi_0\,\delta\,v_c\,\delta\,L^{\mathrm{ks}} + {}^4\chi_0\,\delta\,\frac{\delta v_{xc}^{\mathrm{KS}}}{\delta n}\,\delta\,L^{\mathrm{ks}}$$

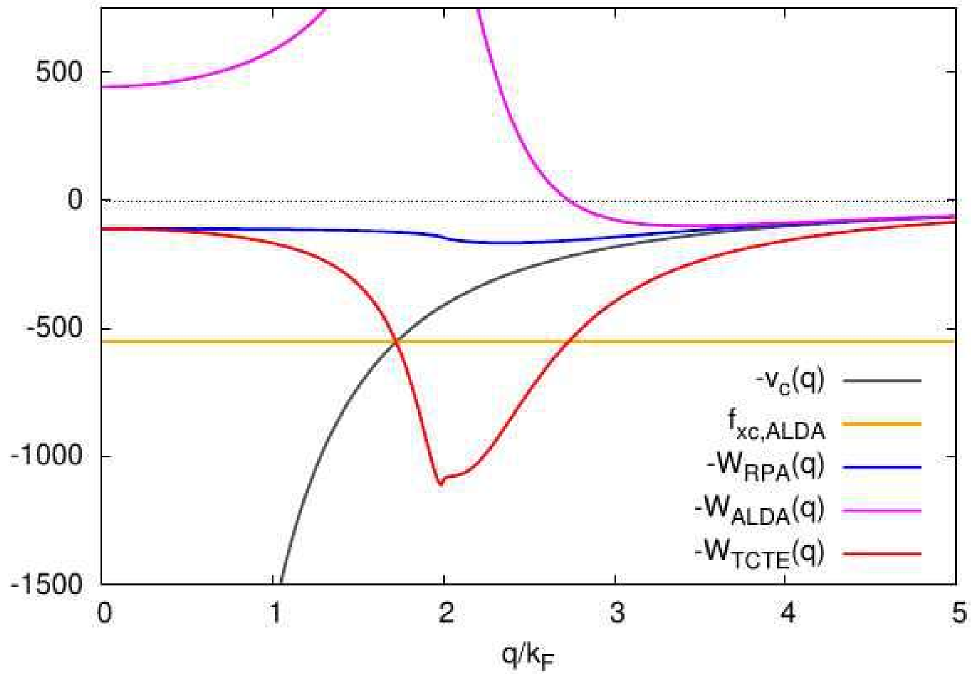
Still another one possible with $f_{\mathrm{xc}}^{\mathrm{mb}}$

$$L^{-1} = L_0^{-1} - \delta\delta v_c - \Xi$$

Some elements of kernel not important in inversion,
Or exact BSE kernel has delta-functions?

Effective exciton hamiltonian, diagonalisation.

$$L \approx \sum_{\lambda} \sum_{s} A_{\lambda}^{s} \Phi_{s}(r_1, r_2) \sum_{s'} A_{\lambda}^{s'*} \Phi_{s'}^{*}(r_3, r_4) e^{-iE_{\lambda}(t-t')}$$



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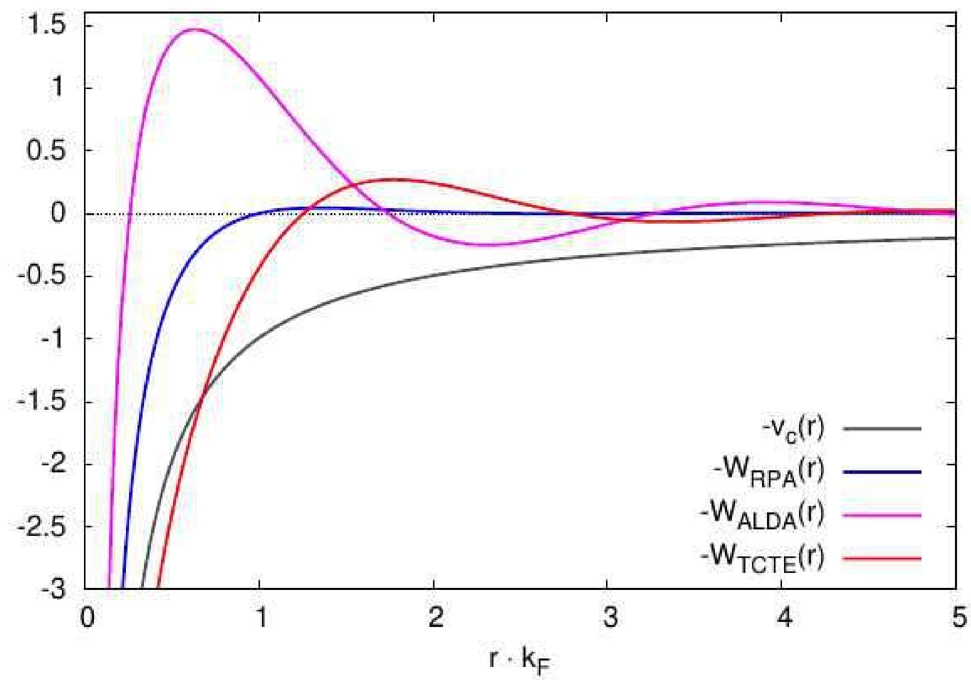
q/k$_F$
$-v_c(q)$
$f_{xc,ALDA}$
$-W_{RPA}(q)$
$-W_{ALDA}(q)$
$-W_{TCTE}(q)$

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5
$r \cdot k_F$
$-v_c(r)$
$-W_{RPA}(r)$
$-W_{ALDA}(r)$
$-W_{TCTE}(r)$

HEG, $L^{\mathrm{ks}}$ ("Casida"):

$$(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}}) A_\lambda^{\mathbf{k}\mathbf{k}+\mathbf{q}} + f_{Hxc}(\mathbf{q}) \Big( \sum_{\mathbf{k}'} A_\lambda^{\mathbf{k}'\mathbf{k}'+\mathbf{q}} + \sum_{\mathbf{k}'} A_\lambda^{\mathbf{k}'-\mathbf{q}\mathbf{k}'} \Big)$$

$$= E_\lambda A_\lambda^{\mathbf{k}\mathbf{k}+\mathbf{q}}$$

$$(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}-\mathbf{q}}) A_\lambda^{\mathbf{k}-\mathbf{q}\mathbf{k}} - f_{Hxc}(\mathbf{q}) \Big( \sum_{\mathbf{k}'} A_\lambda^{\mathbf{k}'\mathbf{k}'+\mathbf{q}} + \sum_{\mathbf{k}'} A_\lambda^{\mathbf{k}'-\mathbf{q}\mathbf{k}'} \Big)$$

$$= E_\lambda A_\lambda^{\mathbf{k}-\mathbf{q}\mathbf{k}},$$

"Simple", because f does not depend on kk'

$$(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}}) = q^2/2 + \mathbf{kq}$$

$$(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}-\mathbf{q}}) = -q^2/2 + \mathbf{kq}$$

$$\varepsilon_{-\mathbf{k}} - \varepsilon_{-\mathbf{k}-\mathbf{q}} = -q^2 - \mathbf{kq}$$

$$a_{\mathbf{k}} \equiv A_\lambda^{\mathbf{k}\mathbf{k}+\mathbf{q}}$$

$$b_{\mathbf{k}} \equiv A_\lambda^{-\mathbf{k}-\mathbf{q}-\mathbf{k}}$$

$$s \equiv \sum_{\mathbf{k}} a_{\mathbf{k}}$$

$$z \equiv \sum_{\mathbf{k}} b_{\mathbf{k}}\,.$$

$$(q^2/2 + \mathbf{kq})\, a_{\mathbf{k}} + f_{H\mathrm{xc}}(\mathbf{q})\Big(s + z\Big) = E a_{\mathbf{k}}$$

$$-(q^2/2 + \mathbf{kq})\, b_{\mathbf{k}} - f_{H\mathrm{xc}}(\mathbf{q})\Big(s + z\Big) = E b_{\mathbf{k}}$$

$$(a_{\mathbf{k}} + b_{\mathbf{k}}) = -\frac{2 f_{H\mathrm{xc}}(\mathbf{q})\Big(s + z\Big)}{(q^2/2 + \mathbf{kq}) - E^2/(q^2/2 + \mathbf{kq})}$$

$$(s + z) = -\sum_{\mathbf{k}} \frac{2(q^2/2 + \mathbf{kq})\, f_{H\mathrm{xc}}(\mathbf{q})\Big(s + z\Big)}{(q^2/2 + \mathbf{kq})^2 - E^2}$$

$$1 = -\sum_{\mathbf{k}} \frac{2(q^2/2 + \mathbf{kq}) f_{H\mathrm{xc}}(\mathbf{q})}{(q^2/2 + \mathbf{kq})^2 - E^2}$$

Max:

$$Q_{\mathbf{k}} = \pm E$$

$$Q_{\mathbf{k}} \equiv q^2/2 + \mathbf{kq}$$

$$a_{\mathbf{k}} = -\frac{f_{H\mathrm{xc}}(\mathbf{q})\Big(s + z\Big)}{Q_{\mathbf{k}} - E} \qquad b_{\mathbf{k}} = -\frac{f_{H\mathrm{xc}}(\mathbf{q})\Big(s + z\Big)}{Q_{\mathbf{k}} + E}$$

$$
(\varepsilon_{\mathbf{k+q}} - \varepsilon_{\mathbf{k}}) A_\lambda^{\mathbf{kk+q}} - \Big( \sum_{\mathbf{k'}} W(k-k') A_\lambda^{\mathbf{k'k'+q}}
$$

$$
+ \sum_{\mathbf{k'}} W(k-k'+q)(A_\lambda^{\mathbf{k'-qk'}} \Big) = E_\lambda A_\lambda^{\mathbf{kk+q}}
$$

$$
(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}}) A_\lambda^{\mathbf{k-qk}} + \Big( \sum_{\mathbf{k'}} W(k-k'-q) A_\lambda^{\mathbf{k'k'+q}}
$$

$$
+ \sum_{\mathbf{k'}} W(k-k') A_\lambda^{\mathbf{k'-qk'}} \Big) = E_\lambda A_\lambda^{\mathbf{k-qk}} .
$$

$$
Q_{\mathbf{k}} a_{\mathbf{k}} - \sum_{\mathbf{k'}} \Big( W(\mathbf{k}-\mathbf{k'}) a_{\mathbf{k'}} + W(\mathbf{k}+\mathbf{k'}+\mathbf{q}) b_{\mathbf{k'}} \Big)
$$

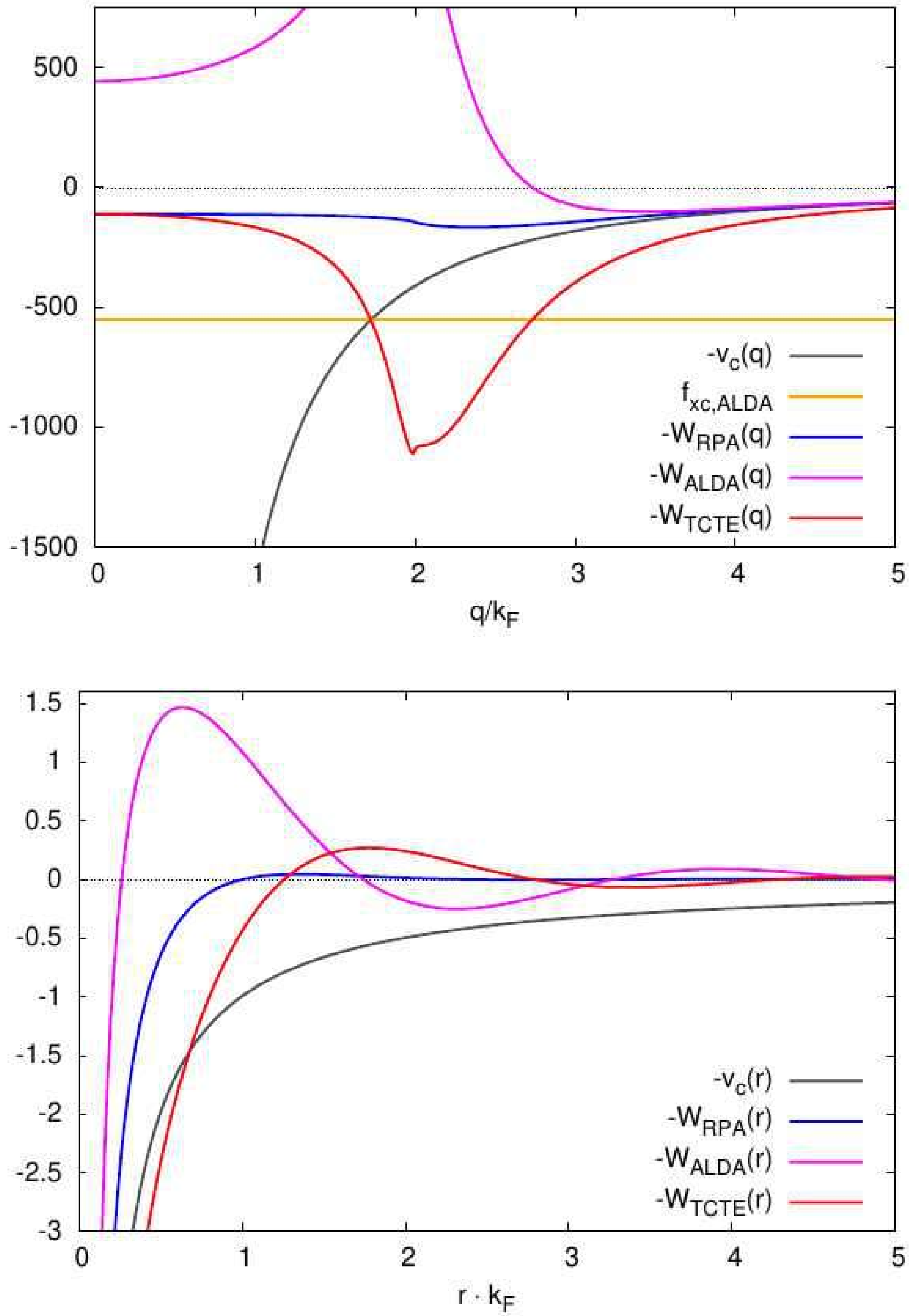
$$
= E_\lambda a_{\mathbf{k}}
$$

$$
-Q_{\mathbf{k}} b_{\mathbf{k}} + \sum_{\mathbf{k'}} \Big( W(\mathbf{k}+\mathbf{k'}+\mathbf{q}) a_{\mathbf{k'}} + W(\mathbf{k}-\mathbf{k'}) b_{\mathbf{k'}} \Big)
$$

$$
= E_\lambda b_{\mathbf{k}} ,
$$

(

Solution on the way (for certain *W*)



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-2.5
-3
r · k_F
-v_c(r)
-W_RPA(r)
-W_ALDA(r)
-W_TCTE(r)

BSE seems to priviledge similar k as TDDFT

HEG can be (partially) solved analytically

Write real material as HEG+ corrections?

$$1 = -\sum_{\mathbf{k}} \frac{2(q^2/2 + \mathbf{kq}) f_{Hxc}(\mathbf{q})}{(q^2/2 + \mathbf{kq})^2 - E^2}$$

$$a_{\mathbf{k}} = -\frac{f_{Hxc}(\mathbf{q})\Big(s + z\Big)}{Q_{\mathbf{k}} - E} \qquad b_{\mathbf{k}} = -\frac{f_{Hxc}(\mathbf{q})\Big(s + z\Big)}{Q_{\mathbf{k}} + E}$$

→ Work with true gap and corrections to diagonal kernel?

→ Compare TDDFT and BSE in case both are exact

We encounter the 2-body correlation function in the BSE

$$\begin{aligned} L(1,2,3,4) &= L^0(1,2,3,4) \\ &\quad + L^0(1,2,\bar{5},\bar{6})\left[v(\bar{5},\bar{7})\delta(\bar{5},\bar{6})\delta(\bar{7},\bar{8}) \right. \\ &\qquad \left. - W(\bar{5},\bar{6})\delta(\bar{5},\bar{7})\delta(\bar{6},\bar{8})\right] L(\bar{7},\bar{8},3,4). \end{aligned}$$

$$\chi(\mathbf{r}_1,\mathbf{r}_2;t_1-t_2) = -iL(\mathbf{r}_1,t_1,\mathbf{r}_1,t_1,\mathbf{r}_2,t_2,\mathbf{r}_2,t_2)$$

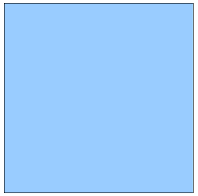
Analysis:

Travelling electron and hole

$$L(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_3, t_3, \mathbf{r}_4, t_4)$$

The Bethe-Salpeter equation $L = L_0 + L_0\,(v-W)\,L$ gives us:

$$L(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_3, t_3, \mathbf{r}_4, t_4)$$

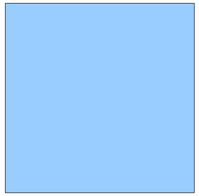


Here, two particles (an electron and a hole) are travelling

# Analysis → physical consequences:

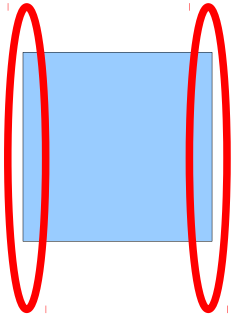
Travelling electron and hole

$$L(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_3, t_3, \mathbf{r}_4, t_4)$$



Electron and hole travelling together

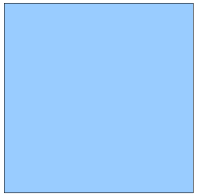
$$\chi(\mathbf{r}_1, \mathbf{r}_2; t_1 - t_2) = -iL(\mathbf{r}_1, t_1, \mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_2, t_2)$$



## Analysis → physical consequences:

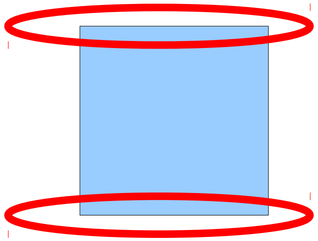
Travelling electron and hole

$$L(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_3, t_3, \mathbf{r}_4, t_4)$$



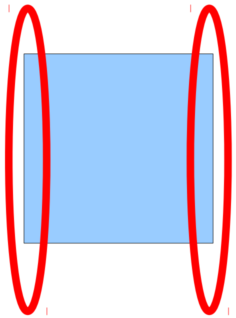
Density (probability) of electron in presence of hole

$$L(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_2, t_2^-, \mathbf{r}_1, t_1^+)$$



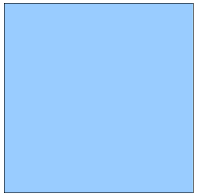
Electron and hole travelling together

$$\chi(\mathbf{r}_1, \mathbf{r}_2; t_1 - t_2) = -iL(\mathbf{r}_1, t_1, \mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_2, t_2)$$



# Analysis:
## Travelling electron and hole

$$L(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_3, t_3, \mathbf{r}_4, t_4)$$



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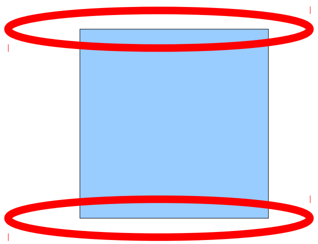
$$L(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_2, t_2^-, \mathbf{r}_1, t_1^+)$$



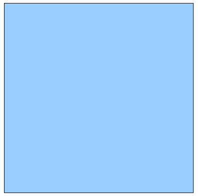
*Note: have to check +/-)*

Non-interacting: $G(11^+)G(22^-)$

Analysis:

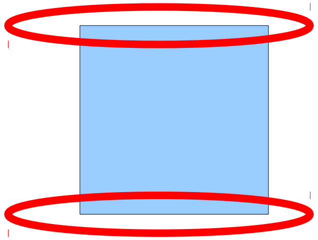
Travelling electron and hole

$$L(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_3, t_3, \mathbf{r}_4, t_4)$$



Density (probability) of electron in presence of hole

$$L(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2, \mathbf{r}_2, t_2^-, \mathbf{r}_1, t_1^+)$$



**This tells us about e-h correlation**

$$\frac{q^2}{2} a_\lambda + N_{\mathbf{k}} f_{H\mathrm{xc}}(\mathbf{q})(a_\lambda + b_\lambda) = E_\lambda a_\lambda$$

$$-\frac{q^2}{2} b_\lambda - N_{\mathbf{k}} f_{H\mathrm{xc}}(\mathbf{q})(a_\lambda + b_\lambda) = E_\lambda b_\lambda$$

$$\rightarrow \qquad E_\lambda^2 = \frac{q^4}{4} + 2\frac{q^2}{2} N_{\mathbf{k}} f_{H\mathrm{xc}}(\mathbf{q})$$

Note: * plasmon energy determined by $1/q^2$ in f (Hartree- RPA!!!!)
* without resonant-antiresonant coupling, divergent P.E.

$$A_\lambda^{\mathbf{k}\mathbf{k}+\mathbf{q}} = \frac{f_{H\mathrm{xc}}(\mathbf{q})(a+b)}{E_\lambda - (\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}})}$$

approximately indep. of k

$$A_\lambda^{\mathbf{k}-\mathbf{q}\mathbf{k}} = \frac{-f_{H\mathrm{xc}}(\mathbf{q})(a+b)}{E_\lambda - (\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}-\mathbf{q}})}$$

$$|\Psi_\lambda(\mathbf{r}_e,\mathbf{r}_h)|^2 = |\sum_{\mathbf{k}=occ} A_\lambda^{\mathbf{k}\mathbf{k}+\mathbf{q}} e^{-i(\mathbf{k}\mathbf{r}_h-(\mathbf{k}+\mathbf{q})\mathbf{r}_e)}$$

$$+A_\lambda^{\mathbf{k}-\mathbf{q}\mathbf{k}} e^{-i(\mathbf{k}\mathbf{r}_h-(\mathbf{k}-\mathbf{q})\mathbf{r}_e)}|^2$$

$$|\Psi_\lambda(\mathbf{r}_e,0)|^2 = |\frac{a_\lambda}{N_\mathbf{k}}\sum_{\mathbf{k}=occ} e^{i(\mathbf{k}+\mathbf{q})\mathbf{r}_e} + \frac{b_\lambda}{N_\mathbf{k}}\sum_{\mathbf{k}=occ} e^{i(\mathbf{k}-\mathbf{q})\mathbf{r}_e)}|^2$$

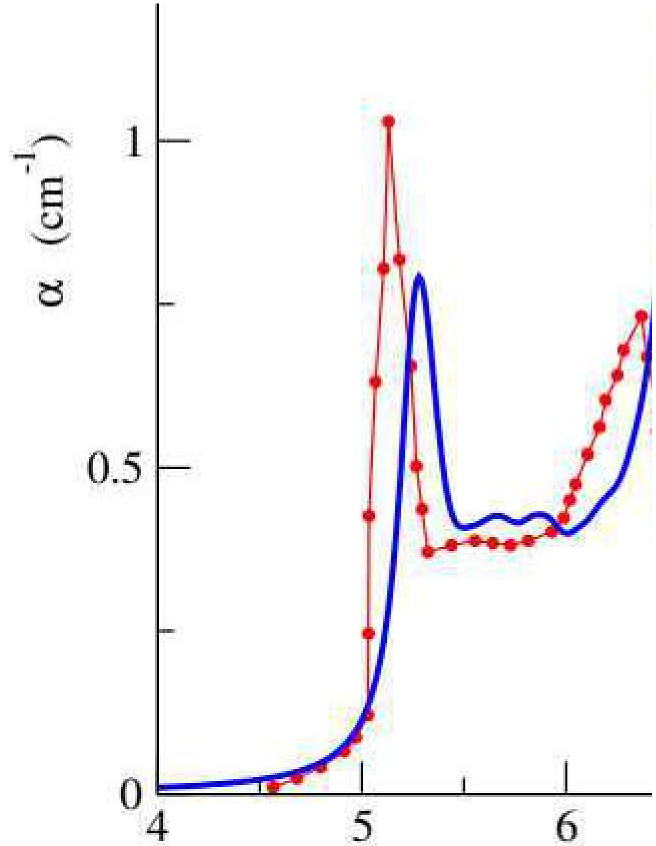
$$= |\frac{a_\lambda}{N_\mathbf{k}} s_+|^2 + |\frac{b_\lambda}{N_\mathbf{k}} s_-|^2 + 2\mathrm{Re}\,\frac{a_\lambda}{N_\mathbf{k}}\frac{b_\lambda^*}{N_\mathbf{k}} s_+ s_- e^{2i\mathbf{q}\mathbf{r}_e}$$

The (restricted, therefore s+,s- q-dep.) sums over k lead to localization.

Note: we did not use the sign of f

Question: Details (e.g., is coupling crucial), and Interpretation!

# Use this to study charge dynamics in silver chloride, AgCl


Arnaud Lorin, Matteo Gatti, Lucia Reining, Francesco Sottile, arXiv:2009.08699

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Spectrum = linear response

$$n(\mathbf{r},t) = \int d\mathbf{r}'dt'\,\chi(\mathbf{r},\mathbf{r}',t-t')v_{\mathrm{ext}}(\mathbf{r}',t')$$

In a periodic system:

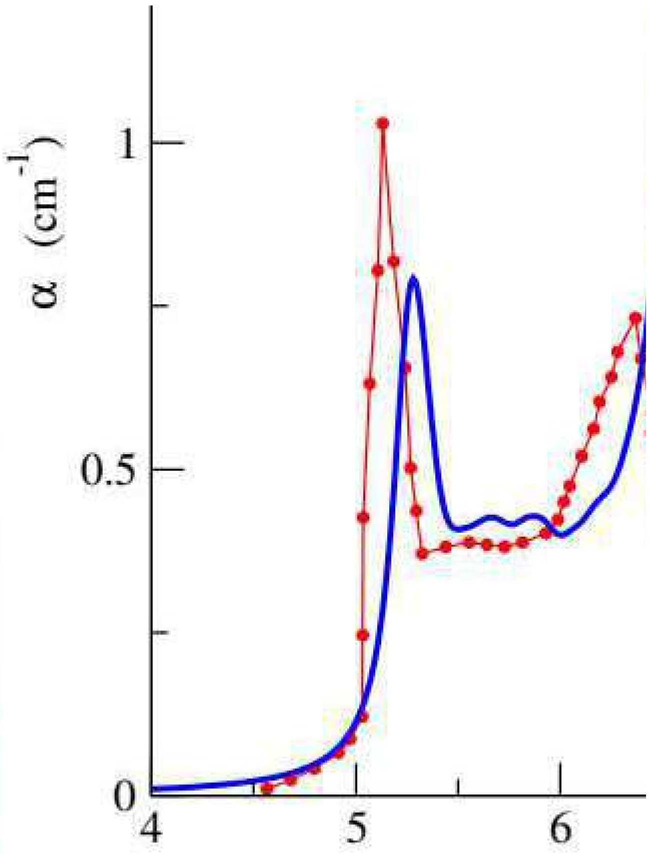
$$n(\mathbf{q}+\mathbf{G},\omega) = \sum_{\mathbf{G}'} \chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)v_{\mathrm{ext}}(\mathbf{q}+\mathbf{G}',\omega)$$

Coupling of Fourier components

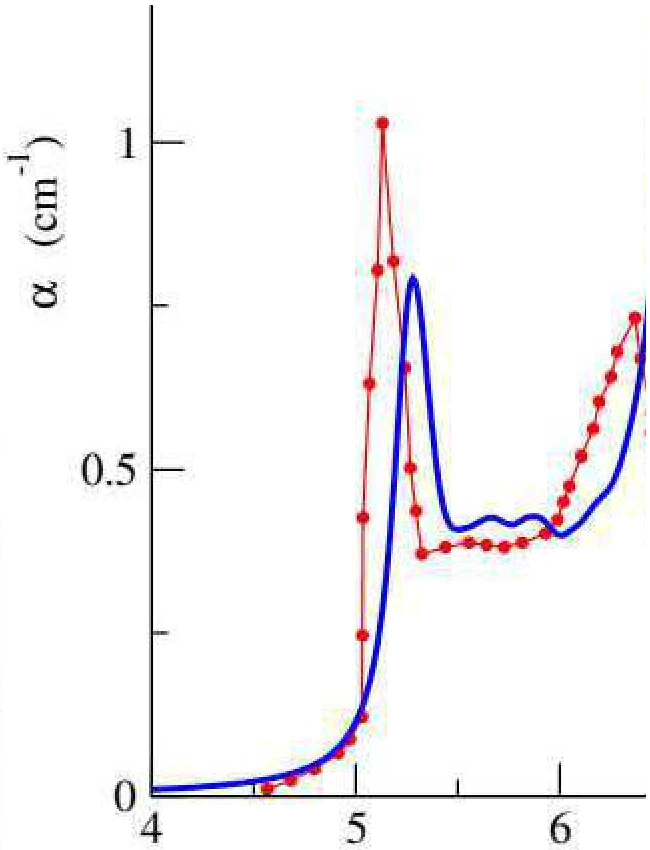
→ the induced density looks different from the potential

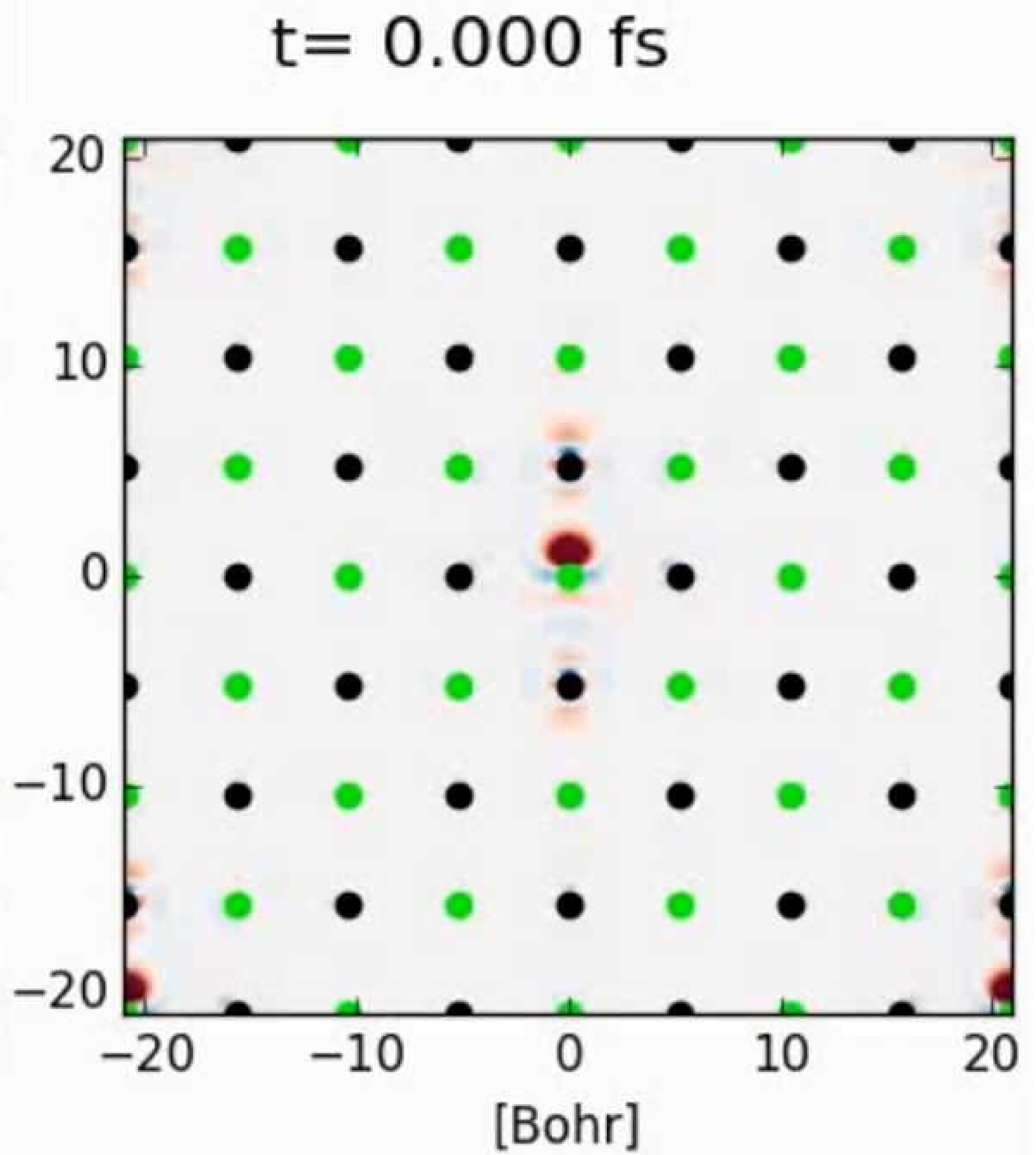
The information is contained in the full response matrix

Frequency in gap:

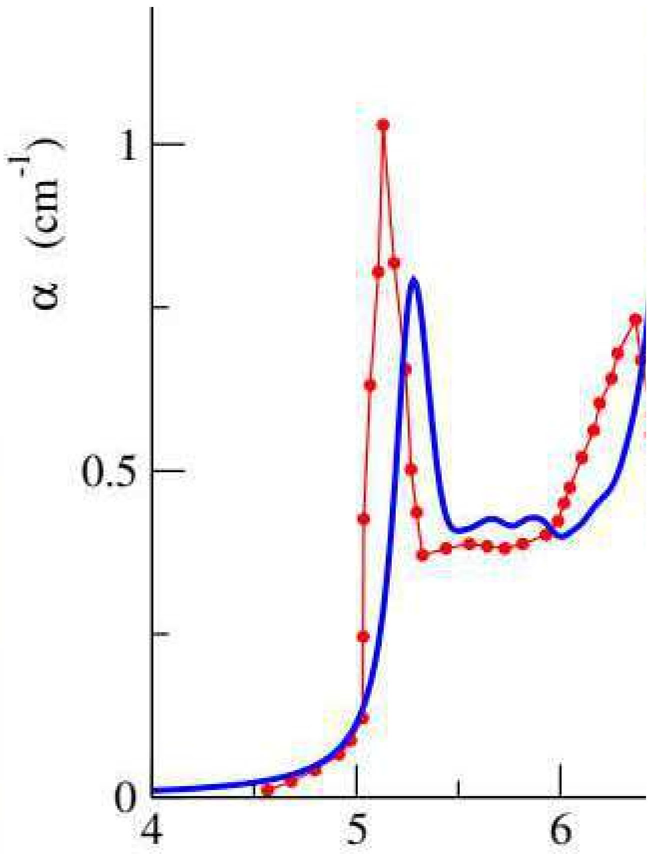


Frequency in gap:



Frequency on exciton:



# Electronic excitations: describing couplings in space and time

→ What do I mean by coupling

→ Coupling of spatial modes:
what happens in an excitation?

→ Coupling in time:

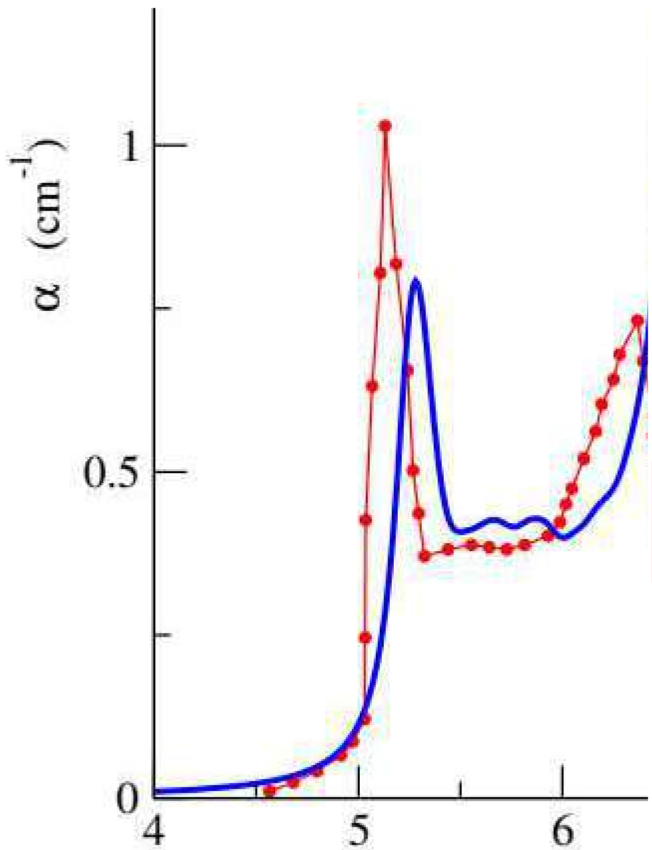
Coupling of elementary excitations in photoemission

……………………………...and in excitation spectra

→ Excursion to TDDFT

→ Conclusions

Example excitons: $H = H^{el} + H^{h} + H^{el\text{-}h}$ → mixing of transitions




Theo: A. Lorin et al., PhD thesis 2020
https://arxiv.org/abs/2009.08699

Exp: M. Yanagihara, Y. Kondo, H. Kanzaki,
J. Phys. Soc. Jpn. 52, 4397 (1983)

Absorption coefficient silver chloride

# Electronic excitations: describing couplings in space and time

→ What do I mean by coupling

→ Coupling of spatial modes:
what happens in an excitation?

→ Coupling in time:

Coupling of elementary excitations in photoemission

……………………………...and in excitation spectra

→ Excursion to TDDFT

→ Conclusions

Spectrum = linear response

$$n(\mathbf{r},t) = \int d\mathbf{r}' dt' \, \chi(\mathbf{r},\mathbf{r}',t-t') v_{\mathrm{ext}}(\mathbf{r}',t')$$

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$$n(\mathbf{q}+\mathbf{G},\omega) = \sum_{\mathbf{G}'} \chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) v_{\mathrm{ext}}(\mathbf{q}+\mathbf{G}',\omega)$$

Coupling of Fourier components

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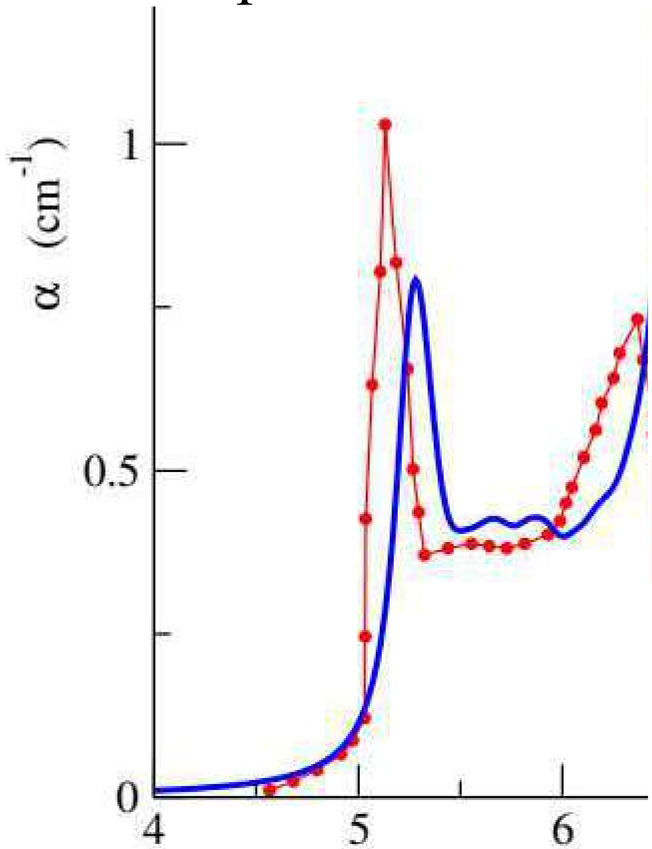
Coupling of Fourier components

→ the induced density looks different from the potential

The information is contained in the full response matrix

Example excitons: $H = H^{el} + H^{h} + H^{el\text{-}h}$ $\rightarrow$ mixing of transitions

Absorption coefficient silver chloride




Theo: A. Lorin et al., PhD thesis 2020
https://arxiv.org/abs/2009.08699

Exp: M. Yanagihara, Y. Kondo, H. Kanzaki, J. Phys. Soc. Jpn. 52, 4397 (1983)

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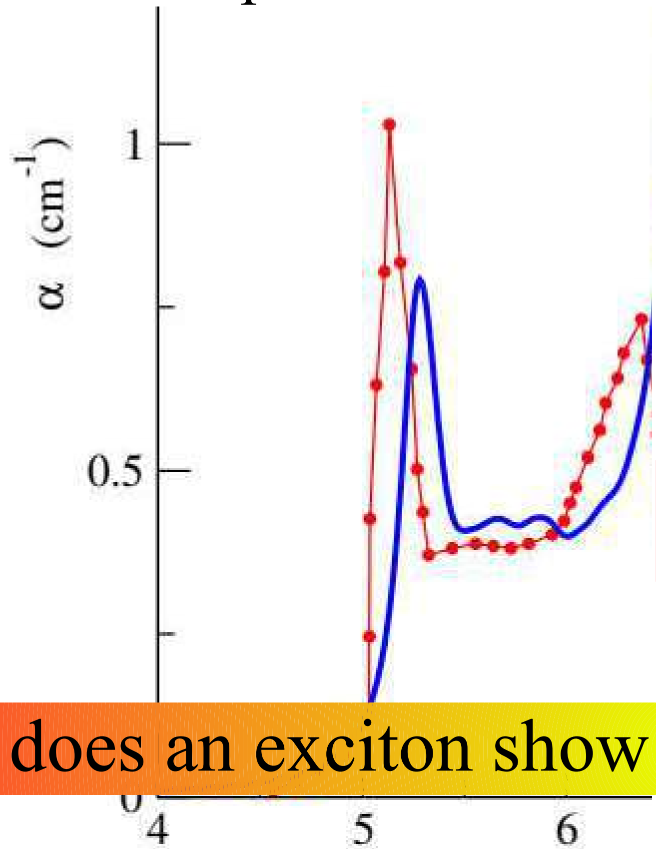


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How does an exciton show up in the charge response???

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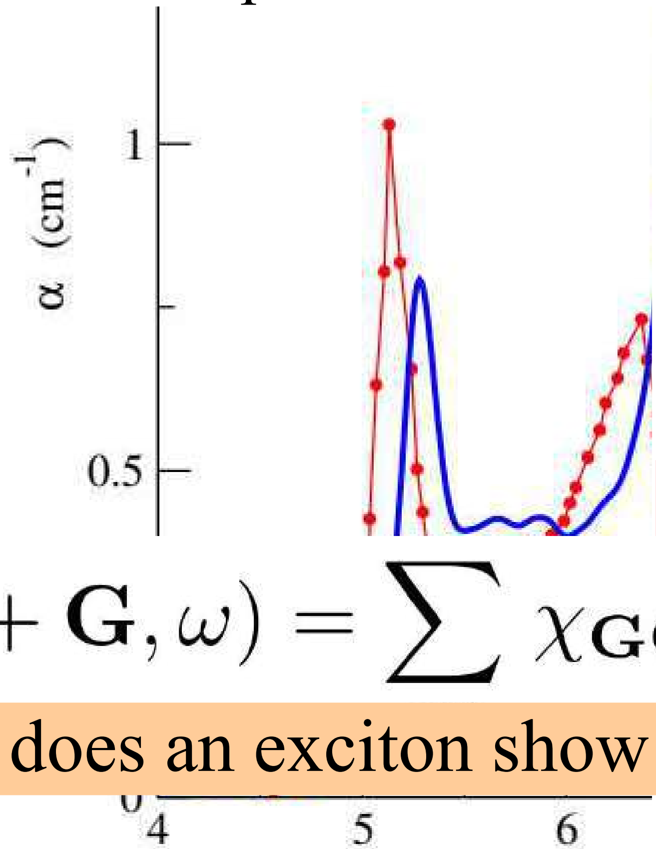


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Up to recently only for G=G’=0 (macroscopic experiments)

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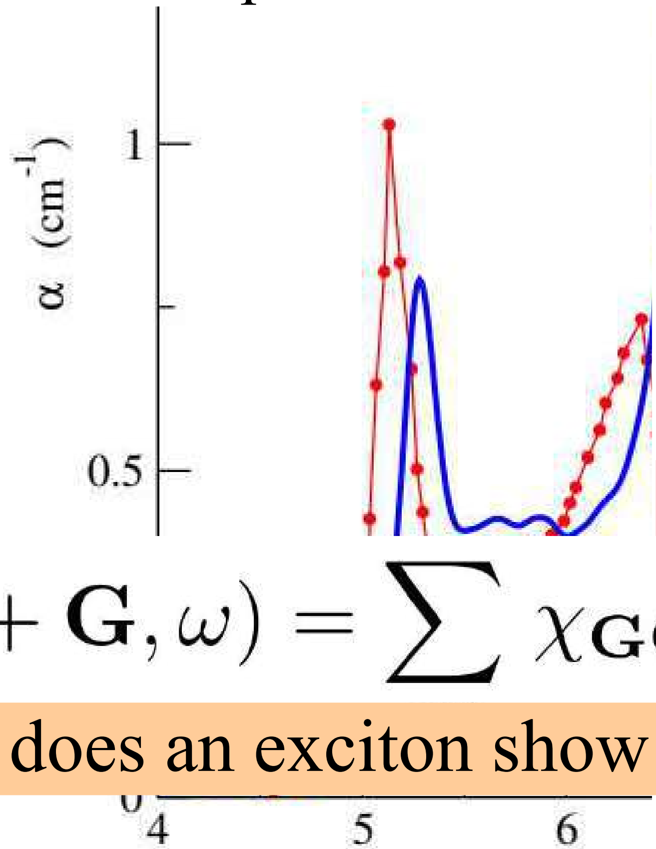


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How to get off-diagonal elements? What do they look like?

Igor Reshetnyak, Matteo Gatti, Francesco Sottile, and Lucia Reining, Phys. Rev. Research 1, 032010(R) (2019)

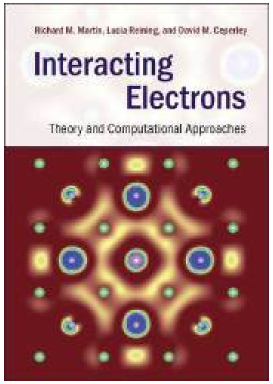
$\mathrm{H} = \mathrm{H}^{\mathrm{el}} + \mathrm{H}^{\mathrm{h}} + \mathrm{H}^{\mathrm{el\text{-}h}}$

$$\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \sum_{\lambda,\lambda'} \left[ \sum_t A_\lambda^{*t}(\mathbf{q}) \tilde{\rho}_t^*(\mathbf{q}+\mathbf{G}) \times \frac{O^{-1}_{\lambda,\lambda'}}{\omega - E_\lambda(\mathbf{q}) + i\eta} \sum_{t'} A_{\lambda'}^{t'}(\mathbf{q}) \tilde{\rho}_{t'}(\mathbf{q}+\mathbf{G}') \right]$$

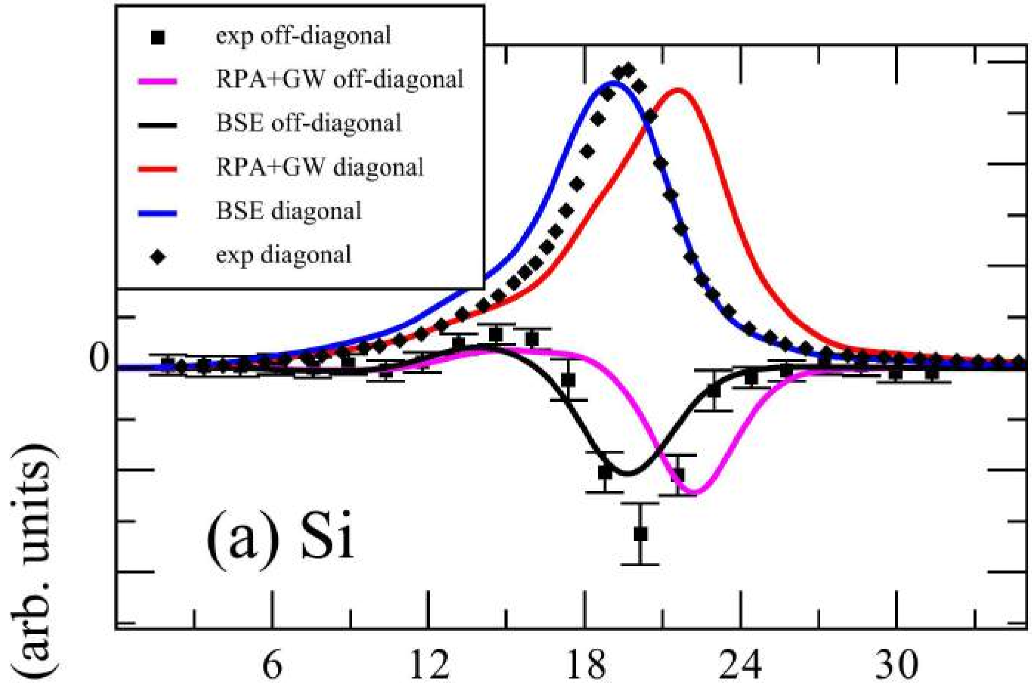
in terms of eigenvectors $A$ and eigenvalues $E$ of e-h hamiltonian

building on M. Gatti and F. Sottile, Phys. Rev. B 88, 155113 (2013)

Martin, Reining, Ceperley
Cambridge 2016



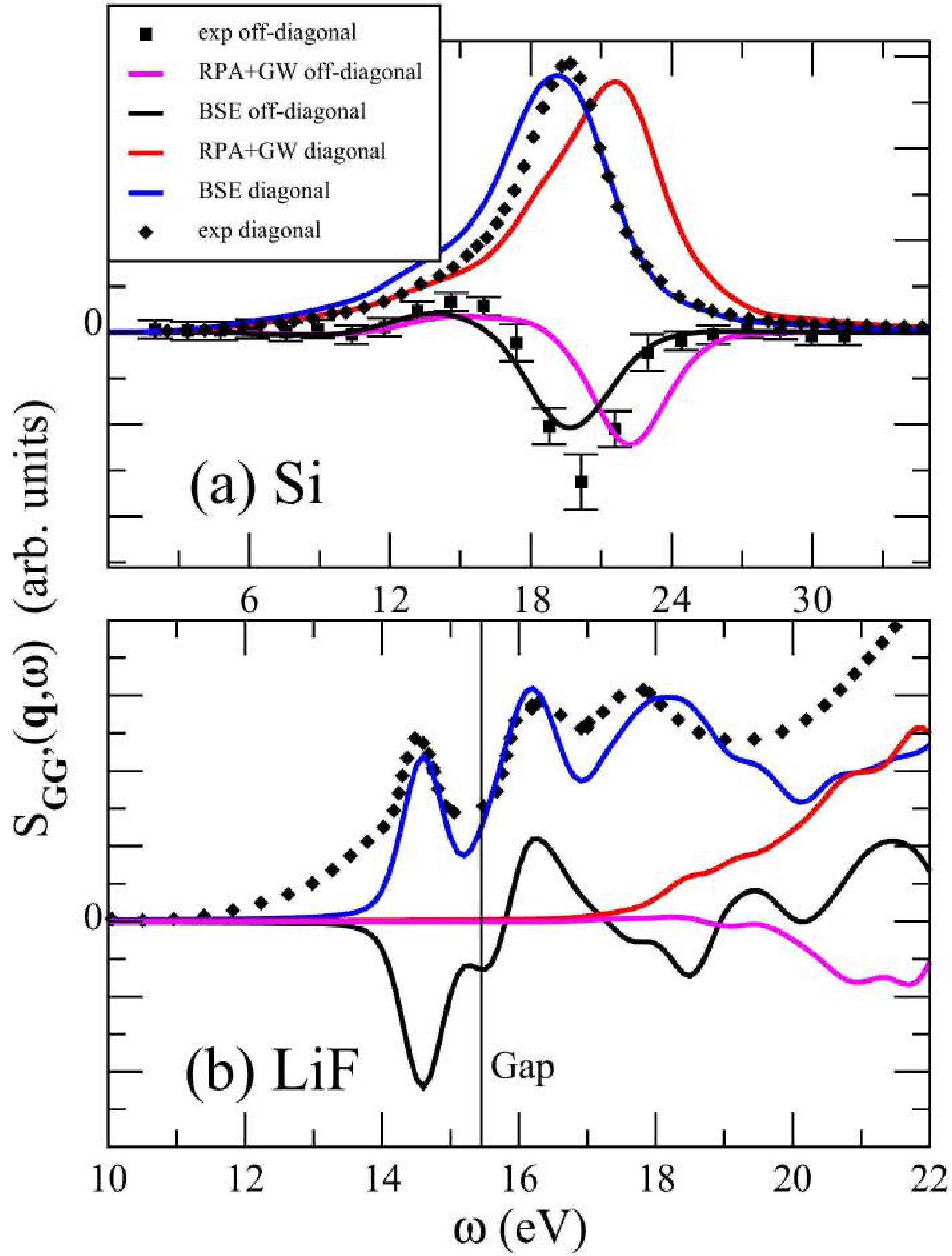
# IXS and CIXS Silicon




Exp: W. Schülke and A. Kaprolat, Phys. Rev. Lett. 67, 879 (1991)

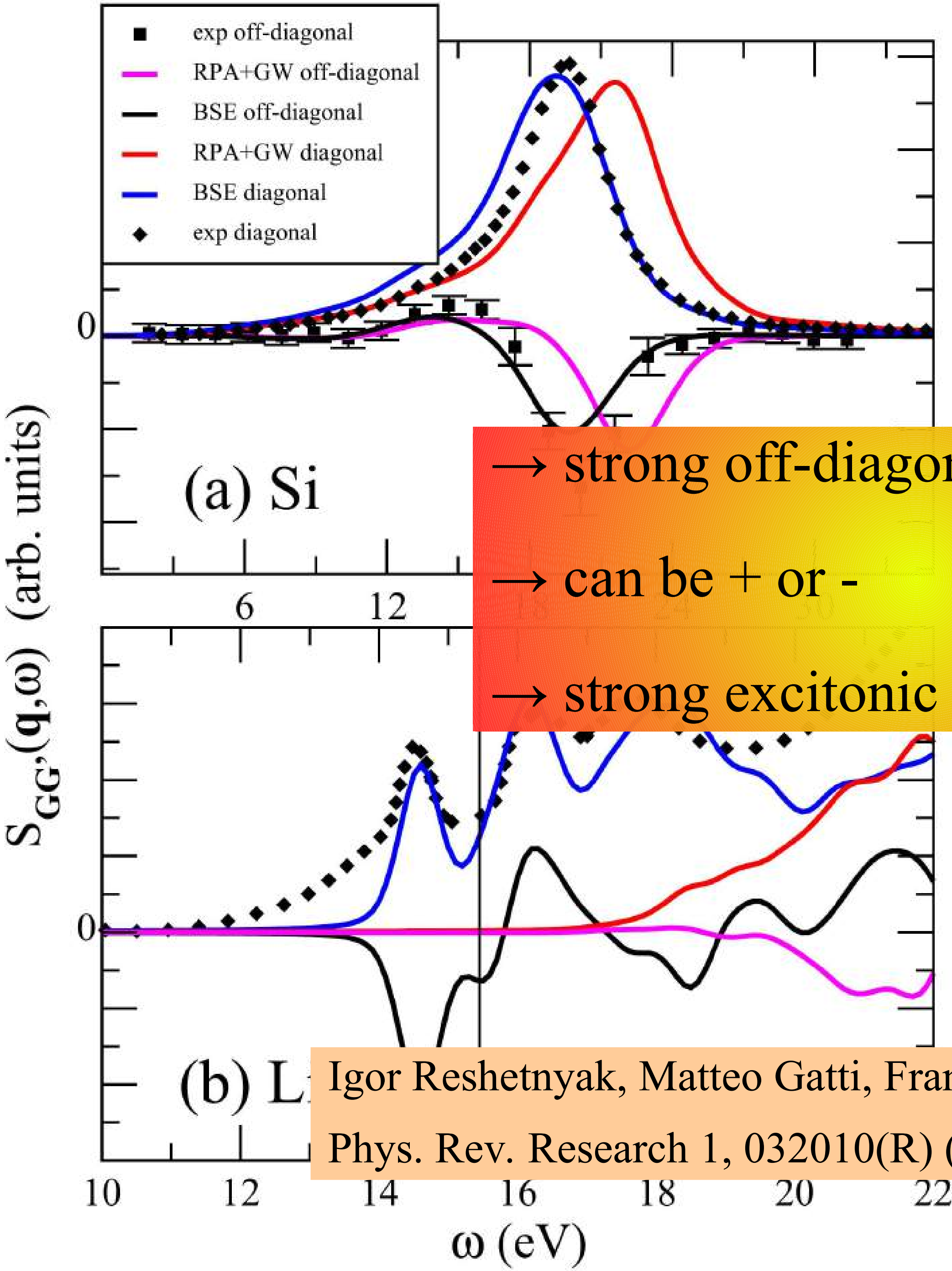
H. Weissker et al, Phys. Rev. Lett. 97, 237602 (2006),
Phys. Rev. B 81, 085104 (2010).

Igor Reshetnyak, Matteo Gatti, Francesco Sottile, and Lucia Reining,
Phys. Rev. Research 1, 032010(R) (2019)




# IXS and CIXS
# LiF

Exp diago: Fields, Gibbons, Schnatterly, Phys. Rev. Lett. 38, 430 (1977)




→ strong off-diagonal elements

→ can be + or -

→ strong excitonic effects off-diago

Exp diago: Fields, Gibbons, Schnatterly, Phys. Rev. Lett. 38, 430 (1977)

Igor Reshetnyak, Matteo Gatti, Francesco Sottile, and Lucia Reining, Phys. Rev. Research 1, 032010(R) (2019)

→ Bound excitons with electron localized close to hole

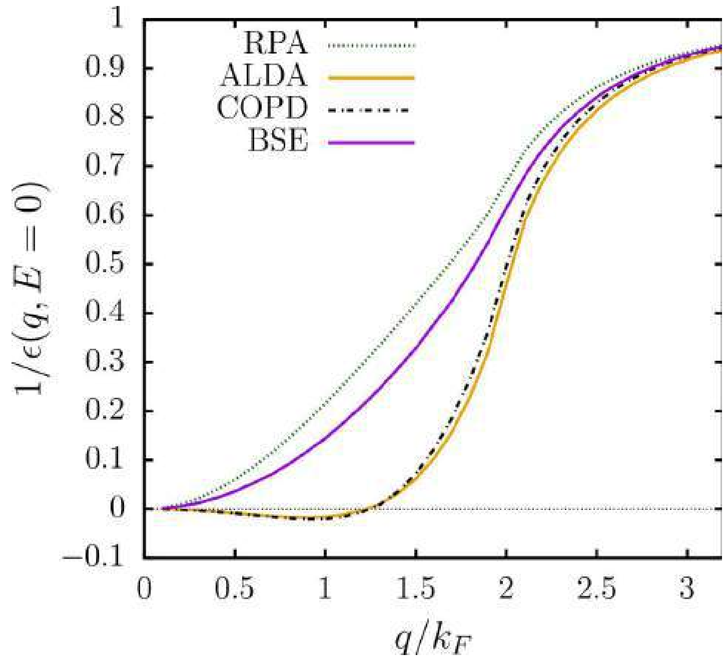
→ These resonances give a very strong
and long-ranged density response

→ More than beautiful pictures:
Charge dynamics for photovoltaics, photocatalysis & more

# How important is this? Look simply at the HEG…..
*Jaakko Koskelo, Matteo Gatti*

1. A matter of consistency:
Plasmon frequency

2. Intriguing effects:
Negative screening and more
cf J. Perdew




$r_s=6$

COPD: M. Corradini, et al., PRB 57, 14569 (1998)
S. Moroni, D. M. Ceperley, and G. Senatore, PRL 75, 6 (1995)

→ Lousy "BSE" results in low density HEG

→ Simple ALDA much better – some NL folded in

→ Better: 2p2h Panholzer, Gatti, Reining, PRL 120, 166402 (2018)