The Bethe-Salpeter Equation

Lucia Reining (using also material of Francesco Sottile)

Palaiseau Theoretical Spectroscopy Group & Friends

ETSF

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IP PARIS

The Bethe-Salpeter Equation

→ From linear response TDDFT to TD-GFT

→ Approximations to the BSE

→ BSE in practice

→ Examples and notes

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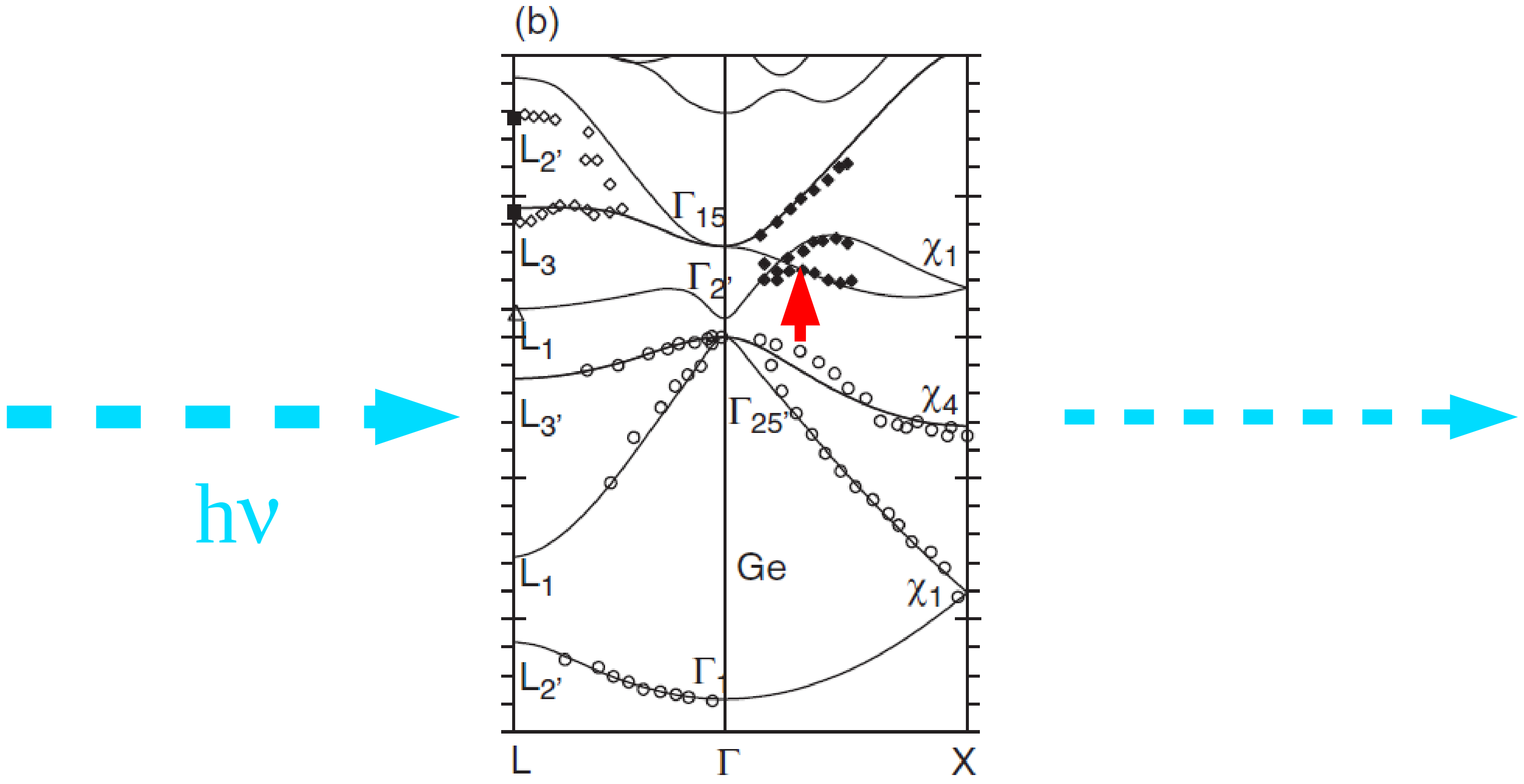
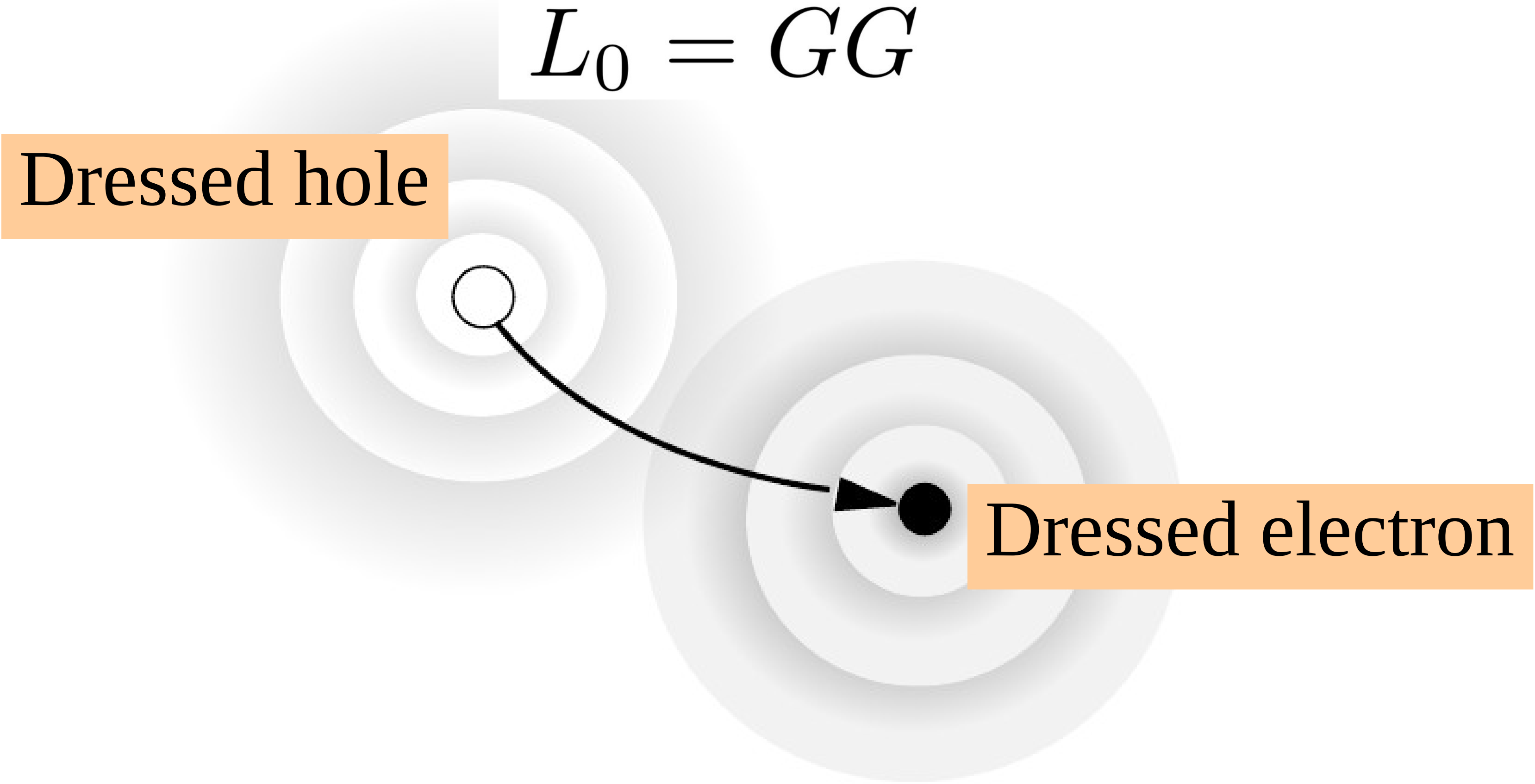
Absorption: measuring electron-hole pairs → 2-body GF



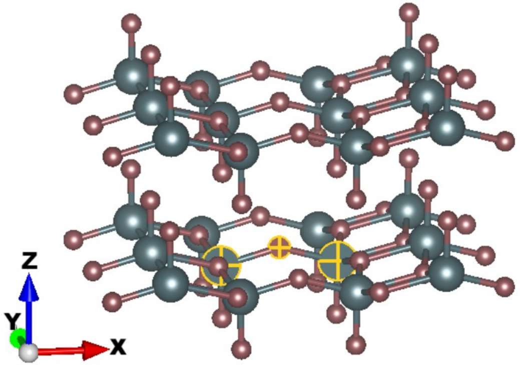
$$\Big(-\frac{\nabla^2}{2} + v_{\mathrm{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r}) \Big) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

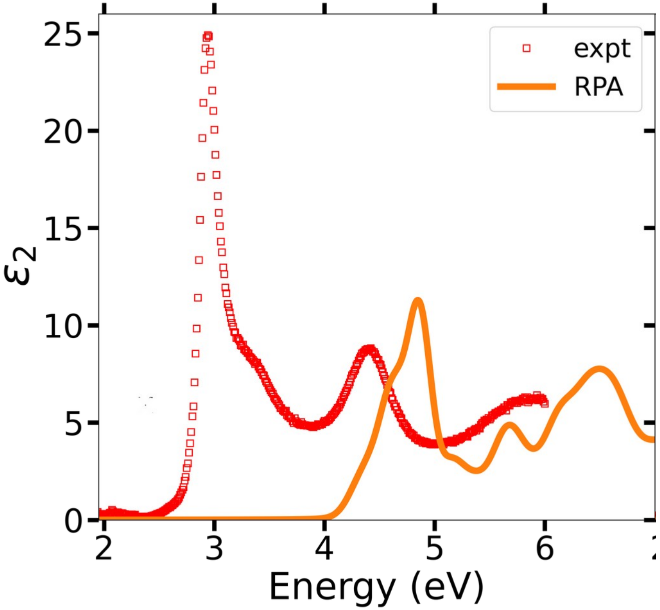
$$\Big(-\frac{\nabla^2}{2} + v_{\mathrm{ext}}(\mathbf{r}) + v_H(\mathbf{r}) \Big) \varphi_i(\mathbf{r};\omega) + \int d\mathbf{r}'\, \Sigma_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega)\varphi_i(\mathbf{r}';\omega) = \varepsilon_i(\omega)\varphi_i(\mathbf{r};\omega)$$


$L_0 = GG$
Dressed hole
Dressed electron

Optical absorption in the aux. system of electrons and holes (indep.)

V_2O_5: a layered bulk material



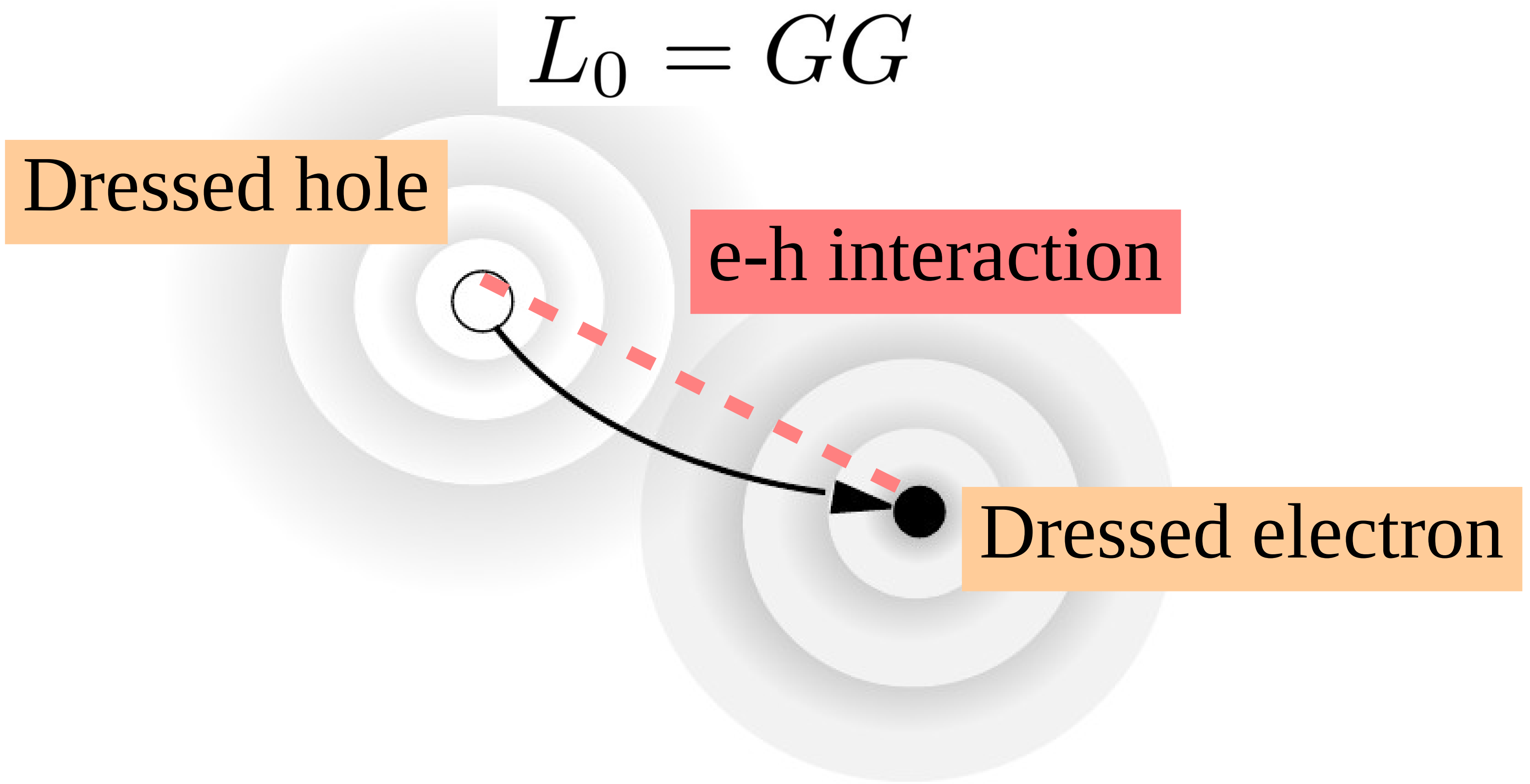


GW-RPA

Exp

Vitaly Gorelov
Reining, Feneberg, Goldhahn, Schleife, Lambrecht, Gatti

npj comp mat (2022)


$L_0 = GG$
Dressed hole
e-h interaction
Dressed electron

$$\chi = \frac{\delta n}{\delta v_{\mathrm{ext}}} = \frac{\delta n}{\delta v_{\mathrm{tot}}} \frac{(\delta v_{\mathrm{ext}} + \delta v_{\mathrm{H}} + \delta v_{\mathrm{xc}})}{\delta v_{\mathrm{ext}}}$$

$$\chi = \chi^0 + \left(\frac{\delta v_{\mathrm{H}} + \delta v_{\mathrm{xc}}}{\delta n}\right) \frac{\delta n}{\delta v_{\mathrm{ext}}} = \chi^0 + \chi^0 (v_c + f_{\mathrm{xc}}) \chi$$

$$\chi = \frac{\delta n}{\delta v_{\mathrm{ext}}} = \frac{\delta n}{\delta v_{\mathrm{tot}}} \frac{(\delta v_{\mathrm{ext}} + \delta v_{\mathrm{H}} + \delta v_{\mathrm{xc}})}{\delta v_{\mathrm{ext}}}$$

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$$\chi = \frac{\delta n}{\delta v_{\mathrm{ext}}} = \frac{\delta n}{\delta v_{\mathrm{tot}}} \frac{(\delta v_{\mathrm{ext}} + \delta v_{\mathrm{H}} + \delta \Sigma_{\mathrm{xc}})}{\delta n} \frac{\delta n}{\delta v_{\mathrm{ext}}}$$

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$$L = \frac{\delta G}{\delta v_{\text{ext}}} = \frac{\delta G}{\delta v_{\text{tot}}} \frac{(\delta v_{\text{ext}} + \delta v_{\text{H}} + \delta \Sigma_{\text{xc}})}{\delta G} \frac{\delta G}{\delta v_{\text{ext}}}$$

$$L_0 \equiv GG$$

$$\chi = \frac{\delta n}{\delta v_{\mathrm{ext}}} = \frac{\delta n}{\delta v_{\mathrm{tot}}} \frac{(\delta v_{\mathrm{ext}} + \delta v_{\mathrm{H}} + \delta v_{\mathrm{xc}})}{\delta v_{\mathrm{ext}}}$$

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$$L_0 \equiv GG$$

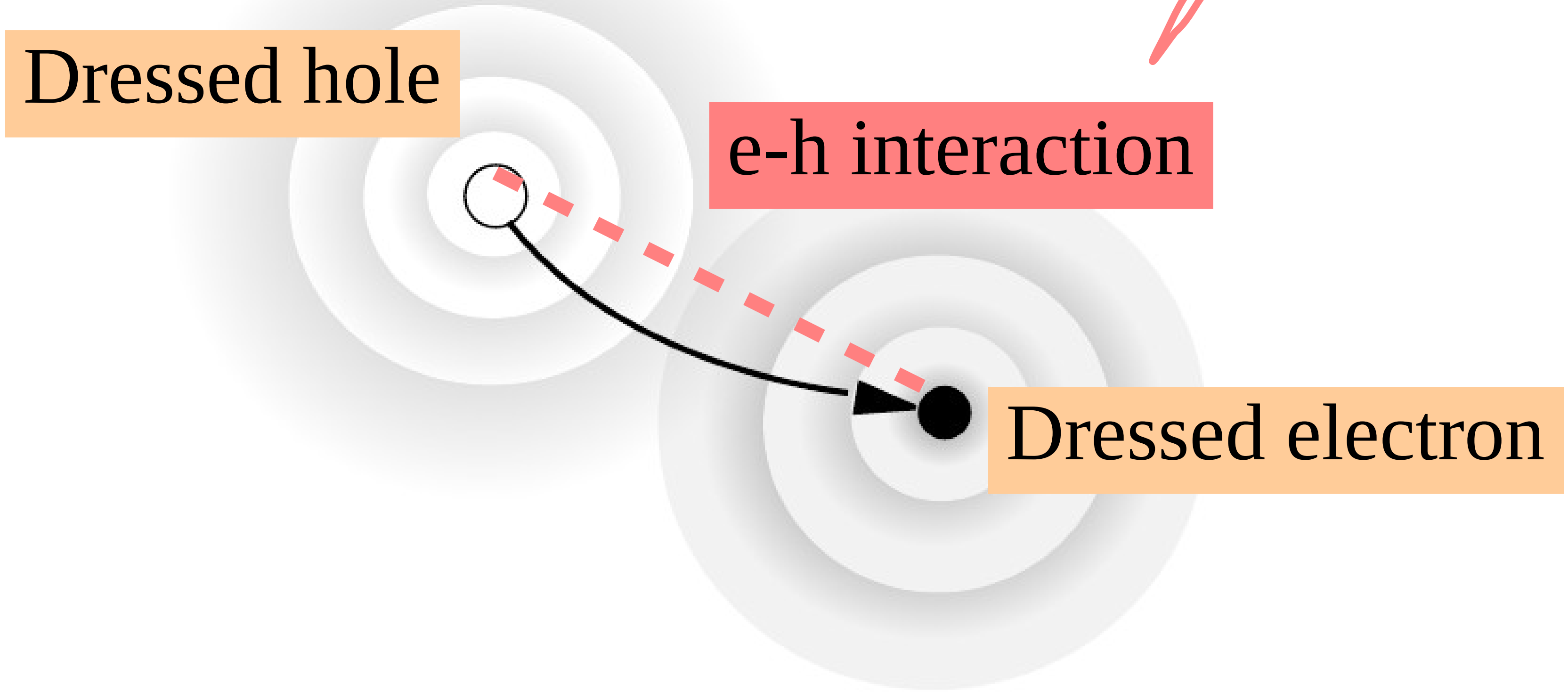
$$L = L_0 + L_0 \left(-i v_c + \frac{\delta \Sigma_{\mathrm{xc}}}{\delta G} \right) L$$

BSE

Bethe-Salpeter Equation

$$L = L_0 + L_0 \frac{\delta(v_H + \Sigma_{\mathrm{xc}})}{\delta G} L$$

$$L_0 = GG$$



Bethe-Salpeter Equation

$$L(1234) = L^0(1234) + L^0(1256)\left[v(57)\delta(56)\delta(78) + \frac{\delta\Sigma(56)}{\delta G(78)}\right]L(7834)$$

Comparison with Linear Response quantities

$$\chi(12) = \frac{\delta n(1)}{\delta V_{ext}(2)}$$

$$L(1234) = \frac{\delta G(12)}{\delta \tilde{V}_{ext}(34)}$$

Comparison with Linear Response quantities

$$\chi(12) = \frac{\delta n(1)}{\delta V_{ext}(2)}$$

$$L(1133) = \frac{\delta G(11)}{\delta \tilde{V}_{ext}(33)}$$

Comparison with Linear Response quantities

$$\chi(12) = \frac{\delta n(1)}{\delta V_{ext}(2)}$$

$$-i\, L(1133) = \frac{\delta n(1)}{\delta V_{ext}(3)}$$

$$n(\mathbf{r}, t) = -iG(\mathbf{r}, \mathbf{r}, t, t^{+})$$

Comparison with Linear Response quantities

$$\chi(12) = \frac{\delta n(1)}{\delta V_{ext}(2)}$$

$$-i\,L(1133) = \frac{\delta n(1)}{\delta V_{ext}(3)}$$

Bethe-Salpeter Equation

$$L(1234) = L^0(1234) + L^0(1256)\left[v(57)\delta(56)\delta(78) + \frac{\delta\Sigma(56)}{\delta G(78)}\right]L(7834)$$

Comparison with Linear Response quantities

$$\chi(12) = \frac{\delta n(1)}{\delta V_{ext}(2)}$$

Have to solve 4 point equation, then take a part!

Bethe-Salpeter Equation

$$L(1234) = L^0(1234) + L^0(1256)\left[v(57)\delta(56)\delta(78) + \frac{\delta\Sigma(56)}{\delta G(78)}\right]L(7834)$$

We have the (4-point)
Bethe-Salpeter equation.
And now ?

The Bethe-Salpeter Equation

→ From linear response TDDFT to TD-GFT

→ Approximations to the BSE

→ BSE in practice

→ Examples and notes

Approximations

First point: Choosing Σ

$$L(1234) = L^0(1234) + L^0(1256)\left[v(57)\delta(56)\delta(78) + \frac{\delta\Sigma(56)}{\delta G(78)}\right]L(7834)$$

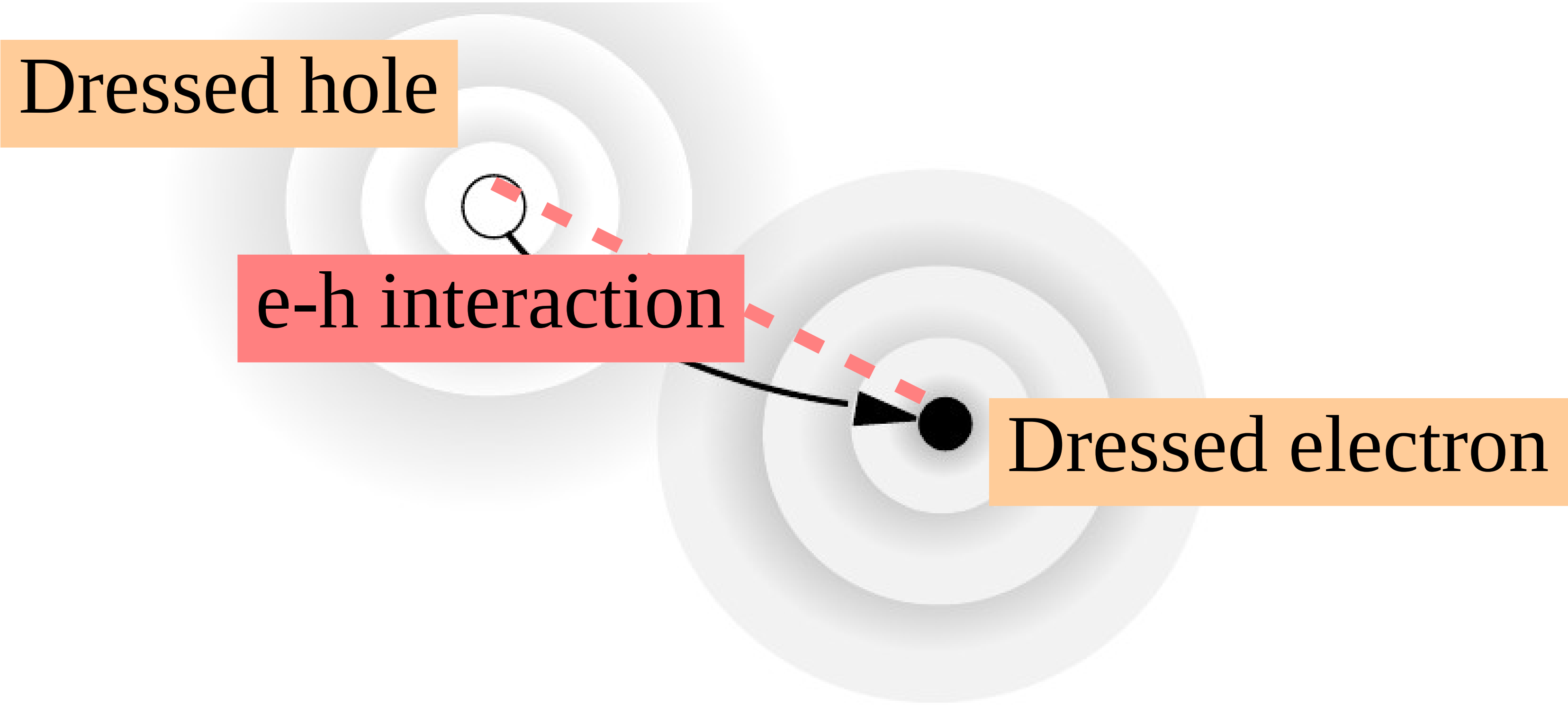
Hartree-Fock: $\Sigma_x(1,2) = iG(1,2)v_c(2,1^+)$

$$n(\mathbf{r},t) = -iG(\mathbf{r},\mathbf{r},t,t^+)$$

$$\rho(\mathbf{r},\mathbf{r}') = -iG(\mathbf{r},t,\mathbf{r}',t^+)$$

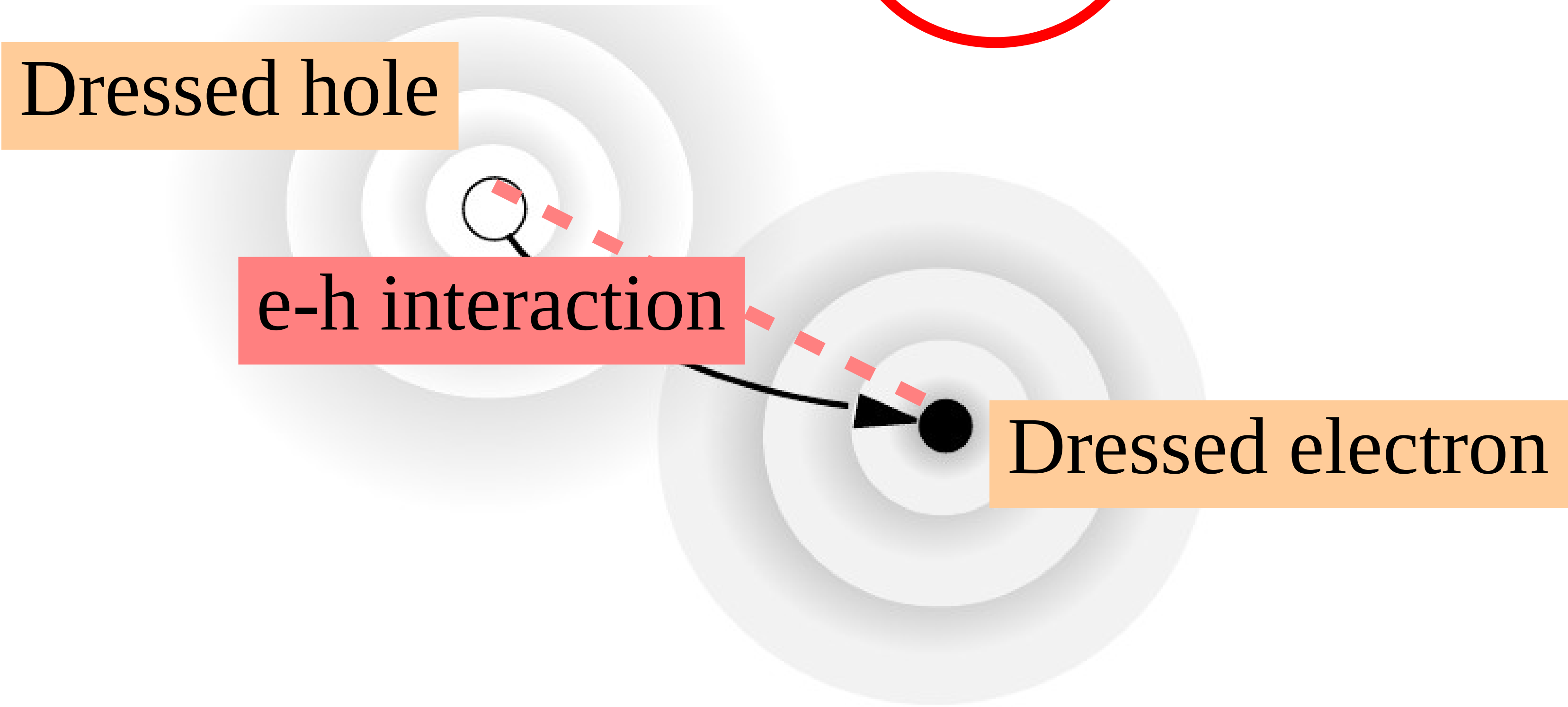
→ Linear response: Bethe-Salpeter equation

$$L = L_0 + L_0\left(-iv_c + \frac{\delta\Sigma_{\text{xc}}}{\delta G}\right)L$$

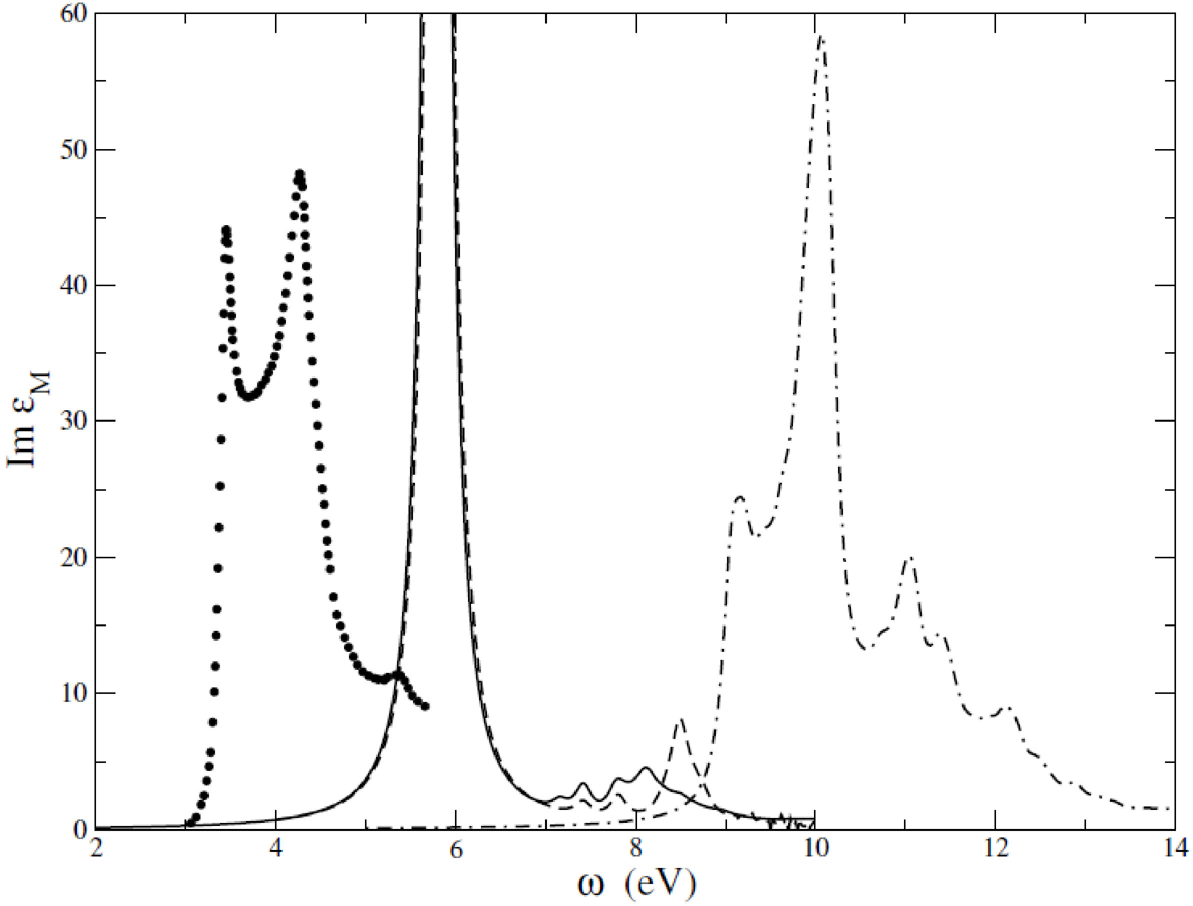


→ Linear response: Bethe-Salpeter equation

$$L = L_0 + L_0\Big(- iv_c + \frac{\delta \Sigma_{\text{xc}}}{\delta G} \Big) L$$



Silicon: TD-HF



Bruneval, Sottile, Olevano, Reining, J. Chem. Phys. 124, 144113 (2006)

Approximations

First point: Choosing Σ

$$L(1234) = L^0(1234) + L^0(1256)\left[v(57)\delta(56)\delta(78) + \frac{\delta\Sigma(56)}{\delta G(78)}\right]L(7834)$$

Screened Coulomb term

$$\Sigma^{GW}(1,2) = iG(12)W(21)$$

$\Rightarrow$ **Standard Bethe-Salpeter equation (Time-Dependent Screened Hartree-Fock)**

$$L = GG + GG\,[v - W]\,L$$

$\Rightarrow$ Approx. $\dfrac{\delta W}{\delta G} = 0$

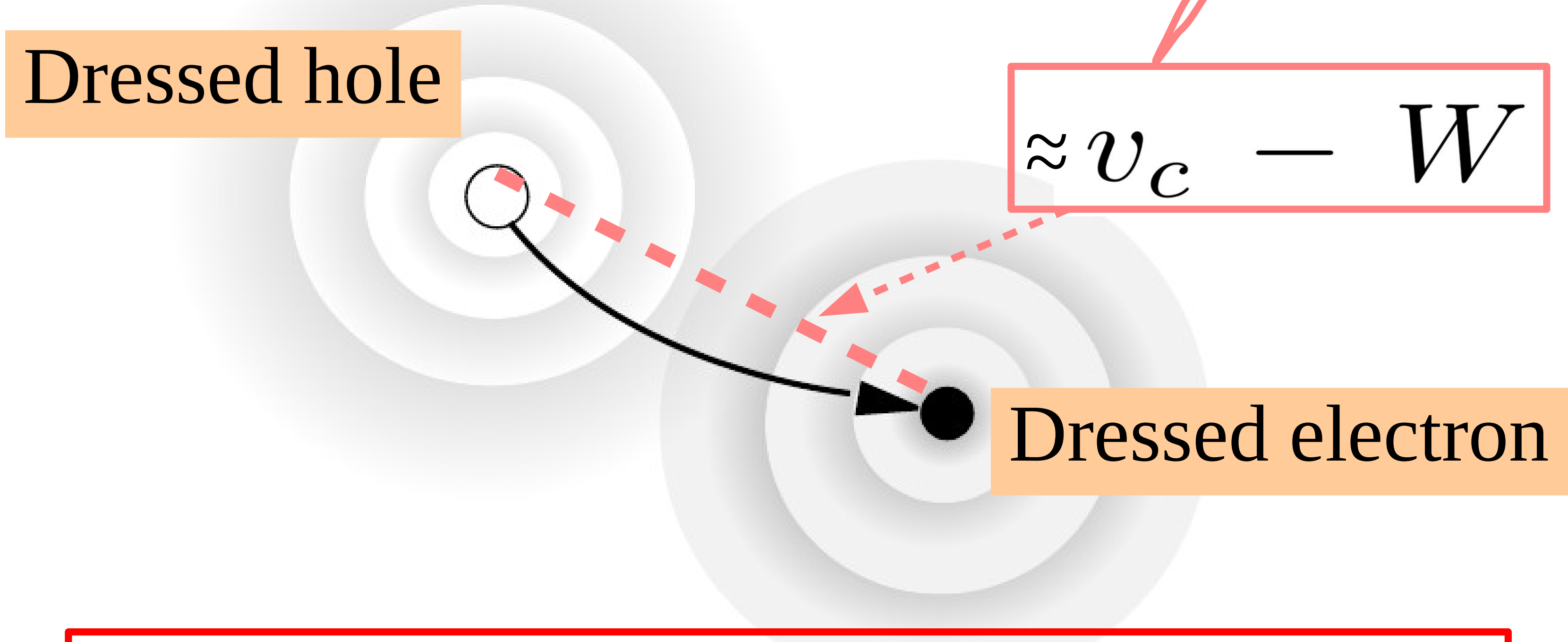
W instantaneous → static

Bethe-Salpeter Equation

$$L = L_0 + L_0 \frac{\delta(v_H + \Sigma_{\mathrm{xc}})}{\delta G} L$$

$$L_0 = GG$$

$$\approx v_c \; - \; W$$



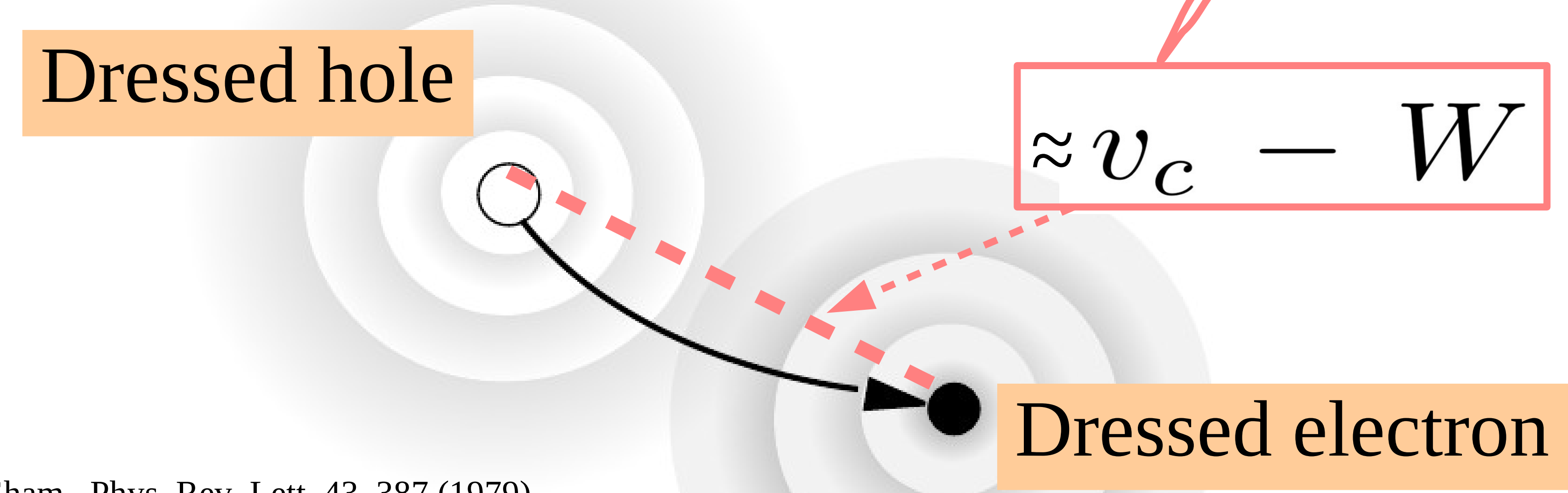
Can be seen as auxiliary system with effective interaction

Bethe-Salpeter Equation

$$L = L_0 + L_0 \frac{\delta(v_H + \Sigma_{\text{xc}})}{\delta G} L$$

$$L_0 = GG$$

$$\approx v_c \; - \; W$$



Hanke & Sham, Phys. Rev. Lett. 43, 387 (1979)
Strinati, Nuovo Cimento 11, 1 (1988)
Onida, et al., Phys. Rev. Lett. 75, 818 (1995)
Albrecht, Onida, Reining Phys. Rev. B 55, 10278 (1997); Albrecht et al. PRL 80, 4510 (1998)
Benedict, Shirley, Bohn, PRL 80, 4514 (1998)
Rohlfing & Louie, PRL 80, 3320 (1998); PRL 81, 2312 (1998)

The Bethe-Salpeter Equation

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In practice (for electron-hole BSE)

$$L(1234,\omega) = L^0(1234,\omega) + L^0(1256,\omega)K(5678)L(7834,\omega)$$

$$L_{(n_1 n_2)}^{(n_3 n_4)}(\omega) = L_{(n_1 n_2)}^{0\,(n_3 n_4)}(\omega) + L_{(n_1 n_2)}^{0\,(n_5 n_6)}(\omega)K_{(n_5 n_6)}^{(n_7 n_8)}L_{(n_7 n_8)}^{(n_3 n_4)}(\omega)$$

We work in transition space...

$$L(1234,\omega) \Rightarrow L_{(n_1 n_2)}^{(n_3 n_4)}(\omega) =$$

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

Clever choice of the basis ϕ_n

Mixing of transitions

The Excitonic Hamiltonian

$$L^{(n_3 n_4)}_{(n_1 n_2)}(\omega) = [(E_{n_2} - E_{n_1} - \omega)\delta_{n_1 n_3}\delta_{n_2 n_4} + \ll v \gg - \ll W \gg]^{-1}$$

$$L^{(n_3 n_4)}_{(n_1 n_2)}(\omega) = \frac{1}{H^{exc} - \omega}$$

$$H^{exc} = (E_{n_2} - E_{n_1})\delta_{n_1 n_3}\delta_{n_2 n_4} + \ll v \gg - \ll W \gg$$

Resonant vs Coupling

$n_1, n_2, n_3, n_4 = v, c \quad (\mathbf{k})$

$$H^{reso} = (E_c - E_v)\delta_{vv'}\delta_{cc'} + \ll v \gg - \ll W \gg$$

(or inverting)

BSE - creating and diagonalizing a (big) matrix

$$\Rightarrow H^{exc}_{(vc)(v'c')} A^{(v'c')}_{\lambda} = E^{exc}_{\lambda} A^{(vc)}_{\lambda}$$

$$\Rightarrow L^{(v'c')}_{(vc)}(\omega) = \sum_{\lambda} \frac{A^{(vc)}_{\lambda} A^{*(v'c')}_{\lambda}}{\omega - E^{exc}_{\lambda} + i\eta}$$

Spectrum in BSE (only resonant)

$$\text{Abs}^{\text{BSE}}(\omega) = Im \langle L(\omega) \rangle = \sum_{\lambda} \left| \sum_{vc} A_{\lambda}^{(vc)} \langle c|D|v \rangle \right|^2 \delta \left(\omega - E_{\lambda}^{exc} \right)$$

$$\text{Abs}^{\text{IP-RPA}}(\omega) = Im \left\langle \chi^0(\omega) \right\rangle = \sum_{vc} |\langle c|D|v \rangle|^2 \, \delta \left(\omega - (\epsilon_c - \epsilon_v) \right)$$

BSE in practice

Standard Approximations for BSE

- Ground-state
  - pseudopotential
  - V_{xc} local density approximation
- Quasi-particle Many-Body Theory
  - GW approximation for Σ
  - W rpa, plasmon-pole model
  - $\psi_{\mathrm{GW}} = \phi_{\mathrm{KS}}$
- Bethe-Salpeter equation
  - $\frac{\delta W}{\delta G} = 0$
  - W rpa, static
  - only resonant term

The Bethe-Salpeter Equation

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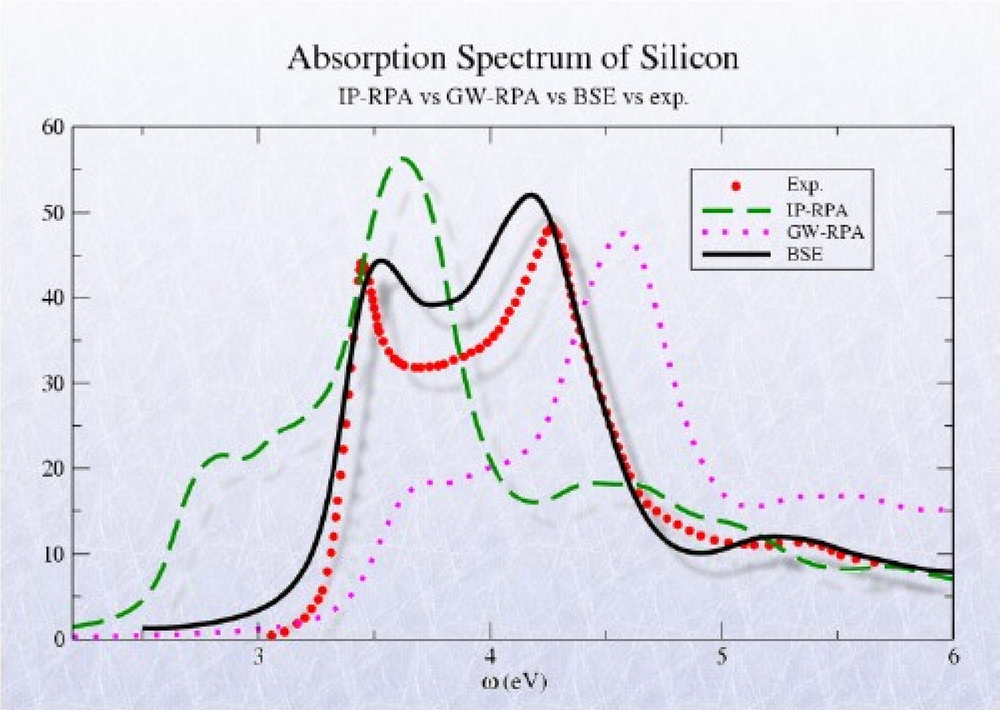
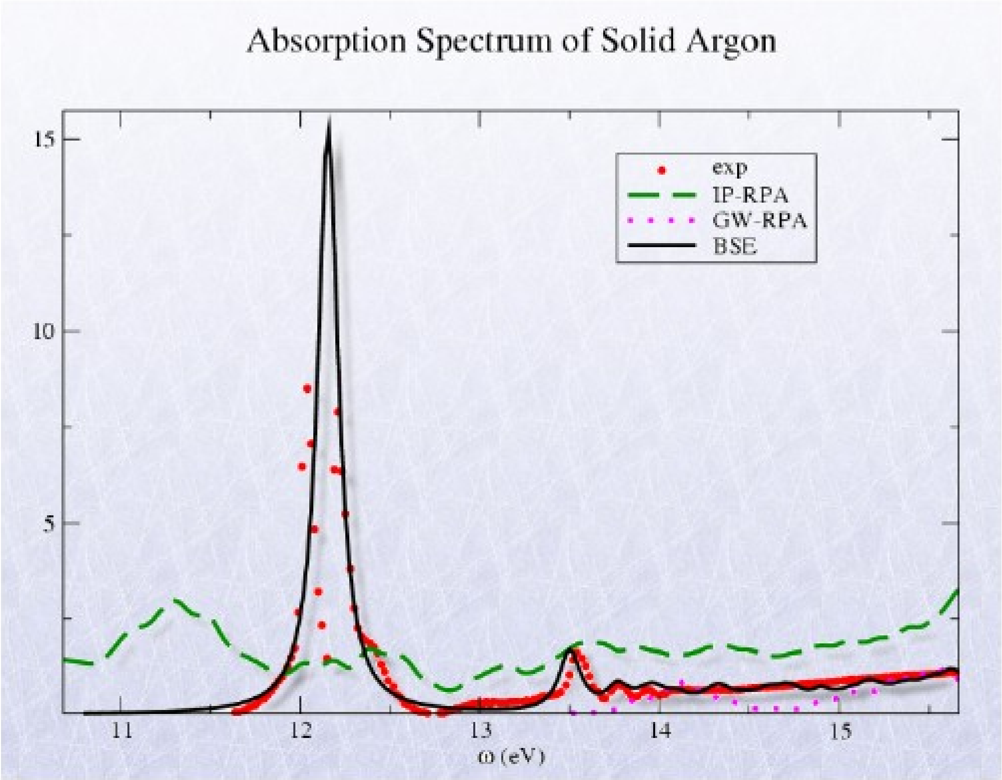


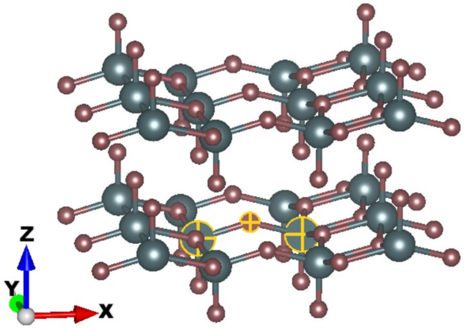
Albrecht *et al.*, PRL **80**, 4510 (1998)

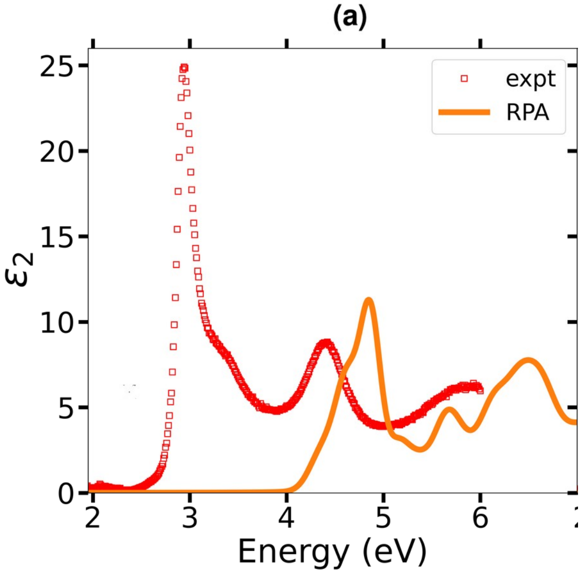


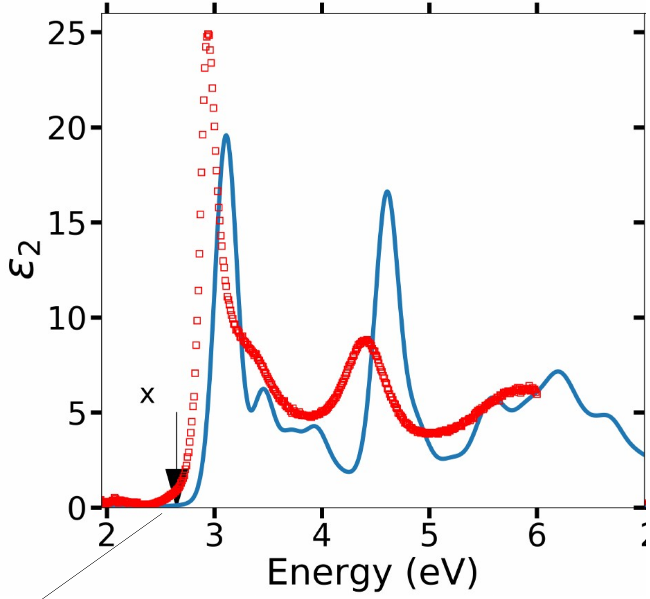
Sottile, Marsili, *et al.*, PRB (2007).

State-of-the-art Bethe-Salpeter

V_2O_5: a layered bulk material







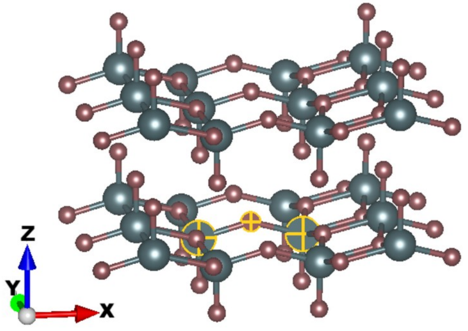
Dark exciton

Vitaly Gorelov et al.,
npj comp mat (2022)

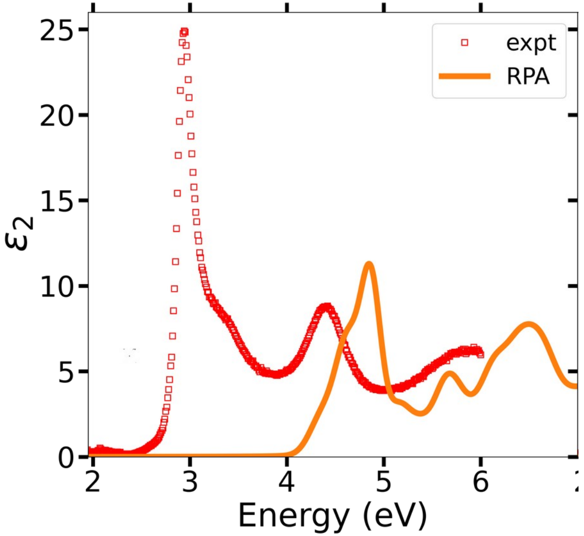
State-of-the-art Bethe-Salpeter

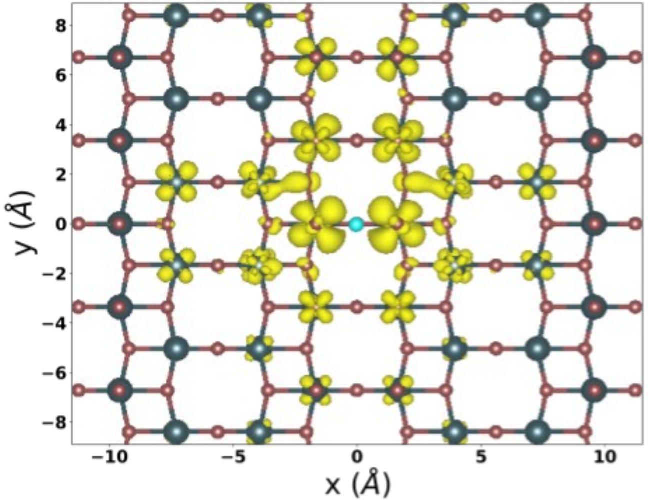
V_2O_5: a layered bulk material

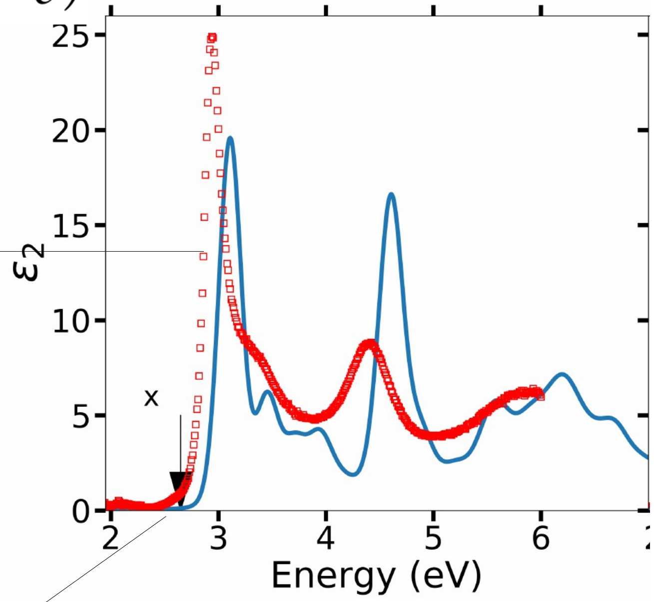
$$H_{\text{exc}}\Psi_\lambda(\mathbf{r}_h,\mathbf{r}_e) = E_\lambda\Psi_\lambda(\mathbf{r}_h,\mathbf{r}_e)$$



(a)



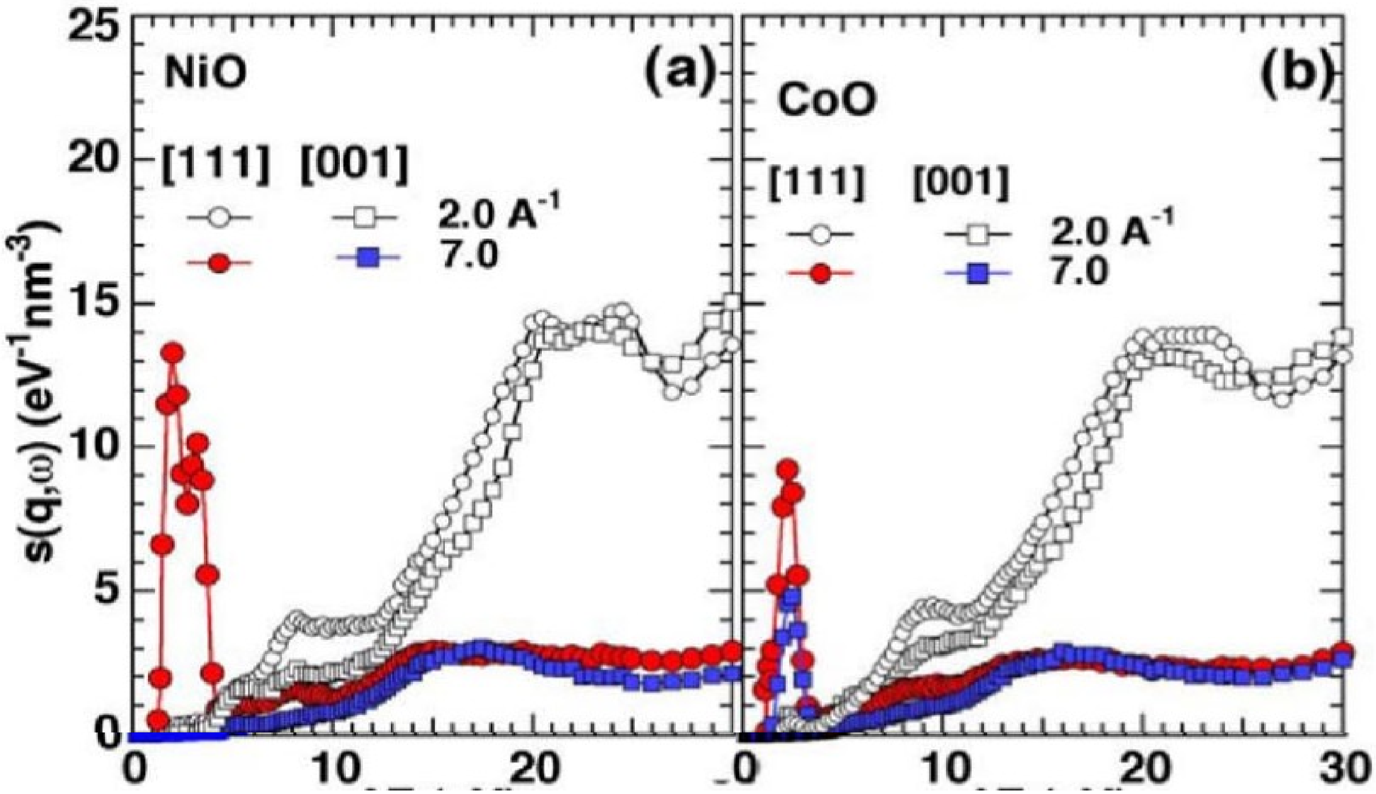




Dark exciton

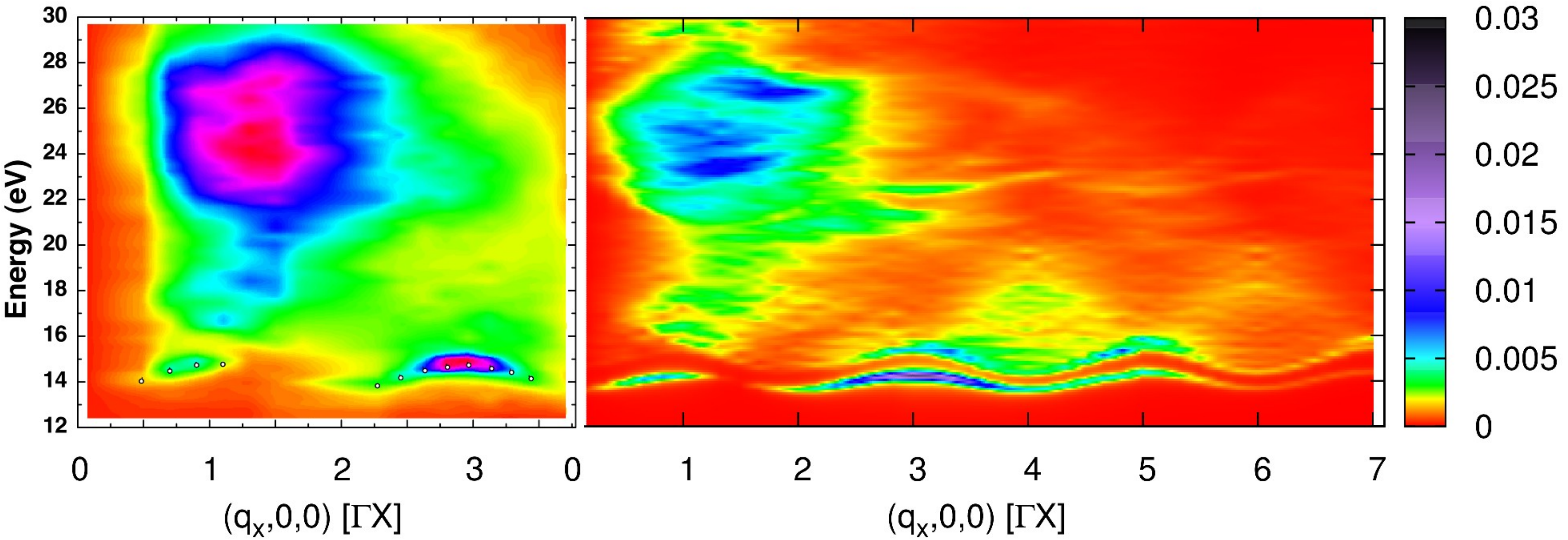
Vitaly Gorelov et al., *npj comp mat (2022)*

Excitons are important also at q different from 0!



Larson et al., Phys. Rev. Lett. 99:026401, 2007

Exciton dispersion in LiF



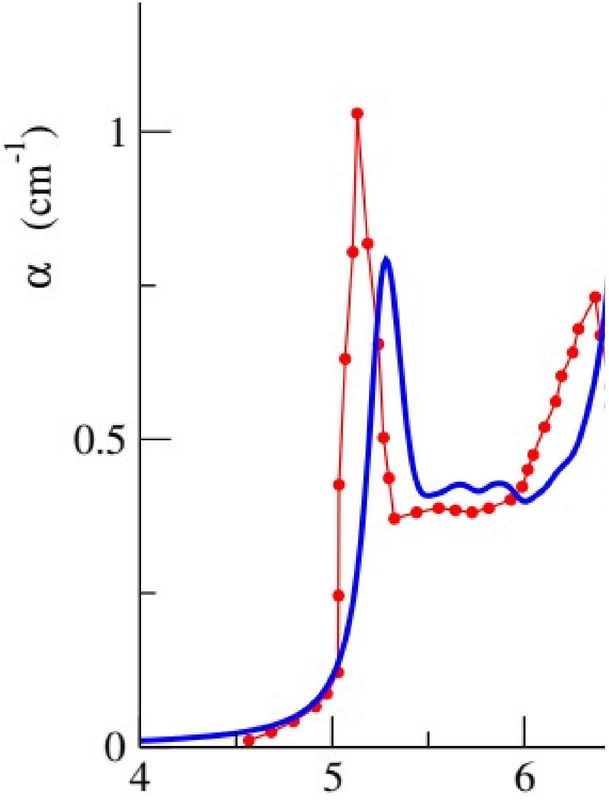
M. Gatti and F. Sottile, Phys. Rev. B 88, 155113
Exp. P. Abbamonte et al., Proc. Natl. Acad. Sci. USA 105, 12159 (2008).

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

Full microscopic response needed for charge dynamics

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

Use this to study charge dynamics in silver chloride, AgCl



Arnaud Lorin, Matteo Gatti, Lucia Reining, Francesco Sottile, PRB

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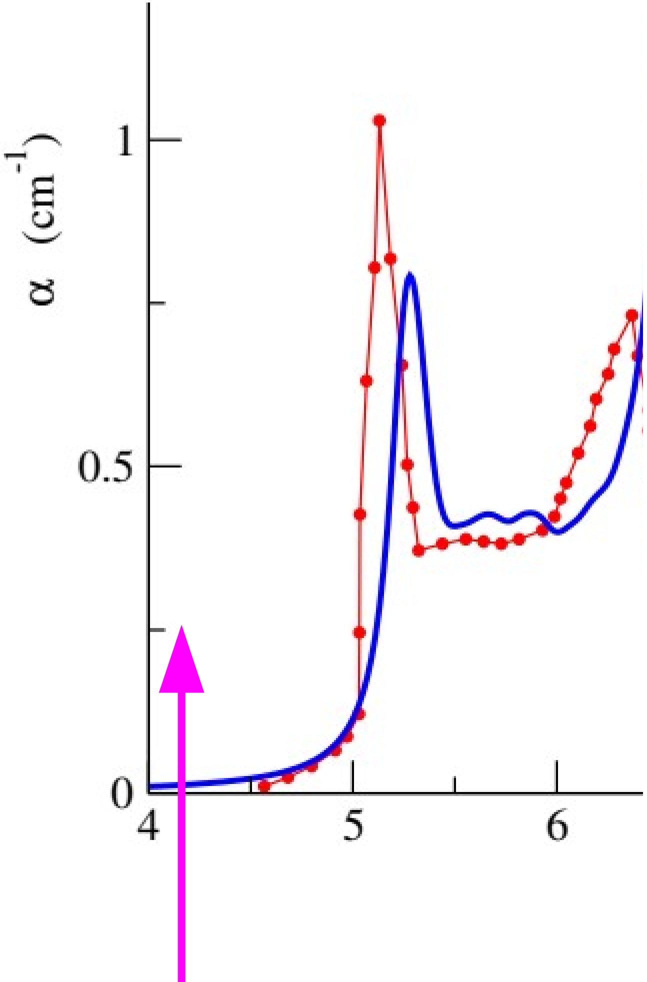
dim matériaux anciens et patrimoniaux

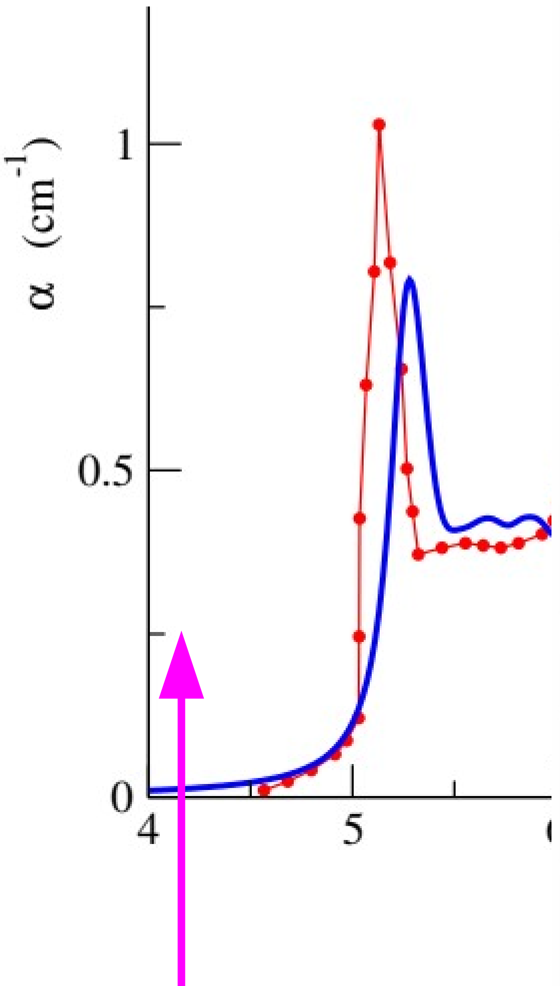
îledeFrance

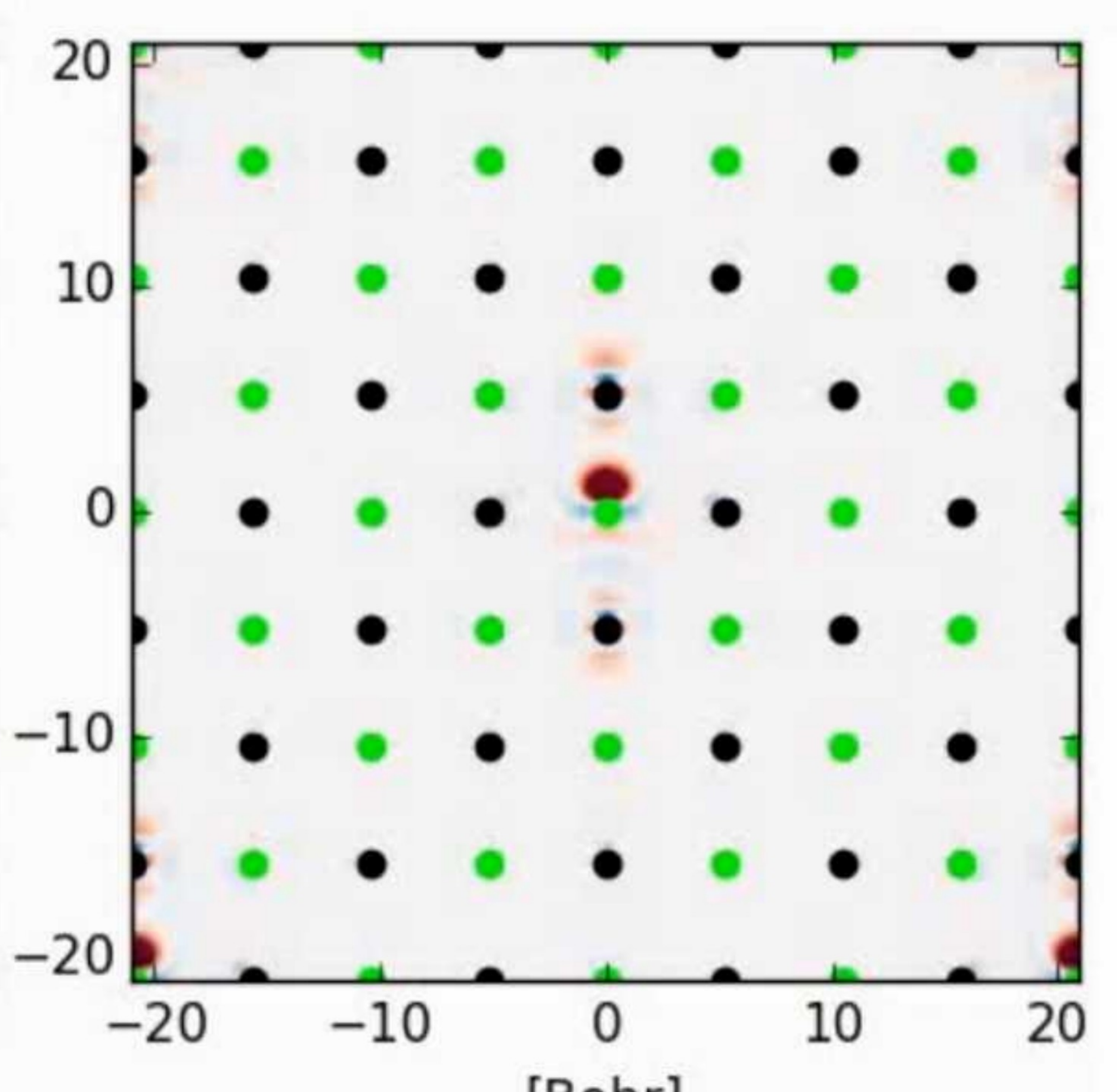
Exp: M. Yanagihara, Y. Kondo, H. Kanzaki, J. Phys. Soc. Jpn. 52, 4397 (1983)

Frequency in gap:

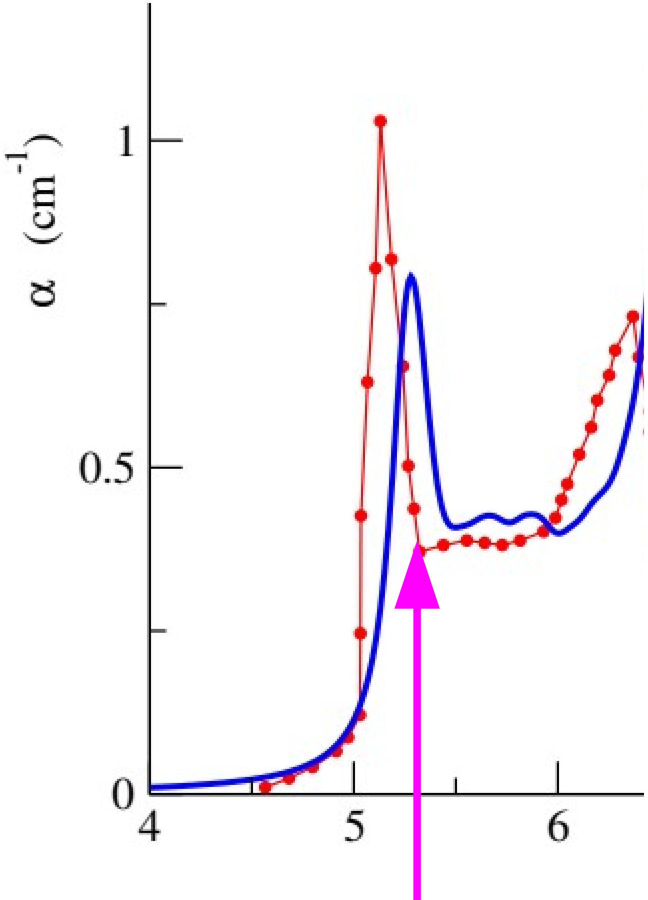


Frequency in gap:

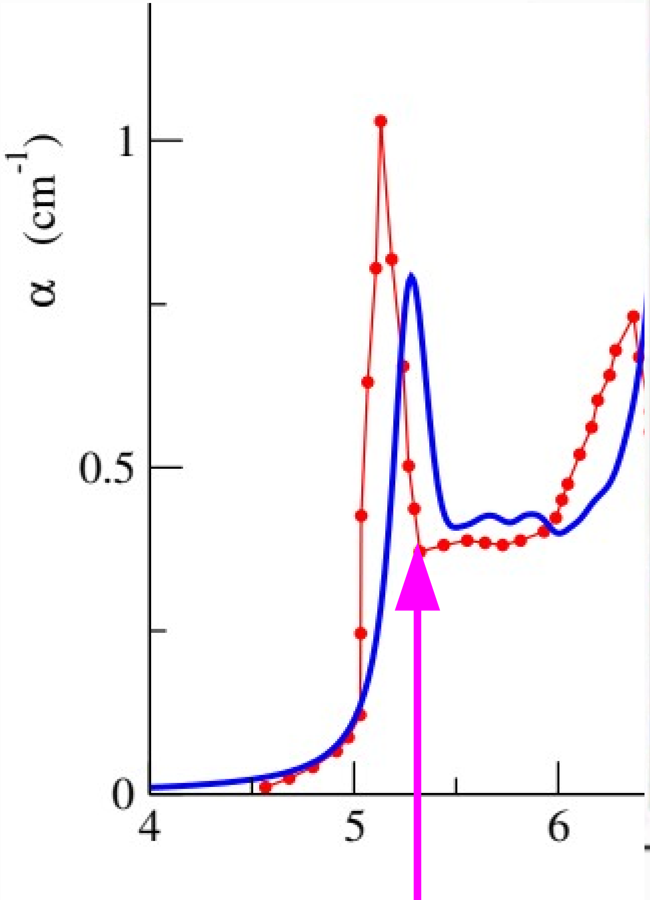


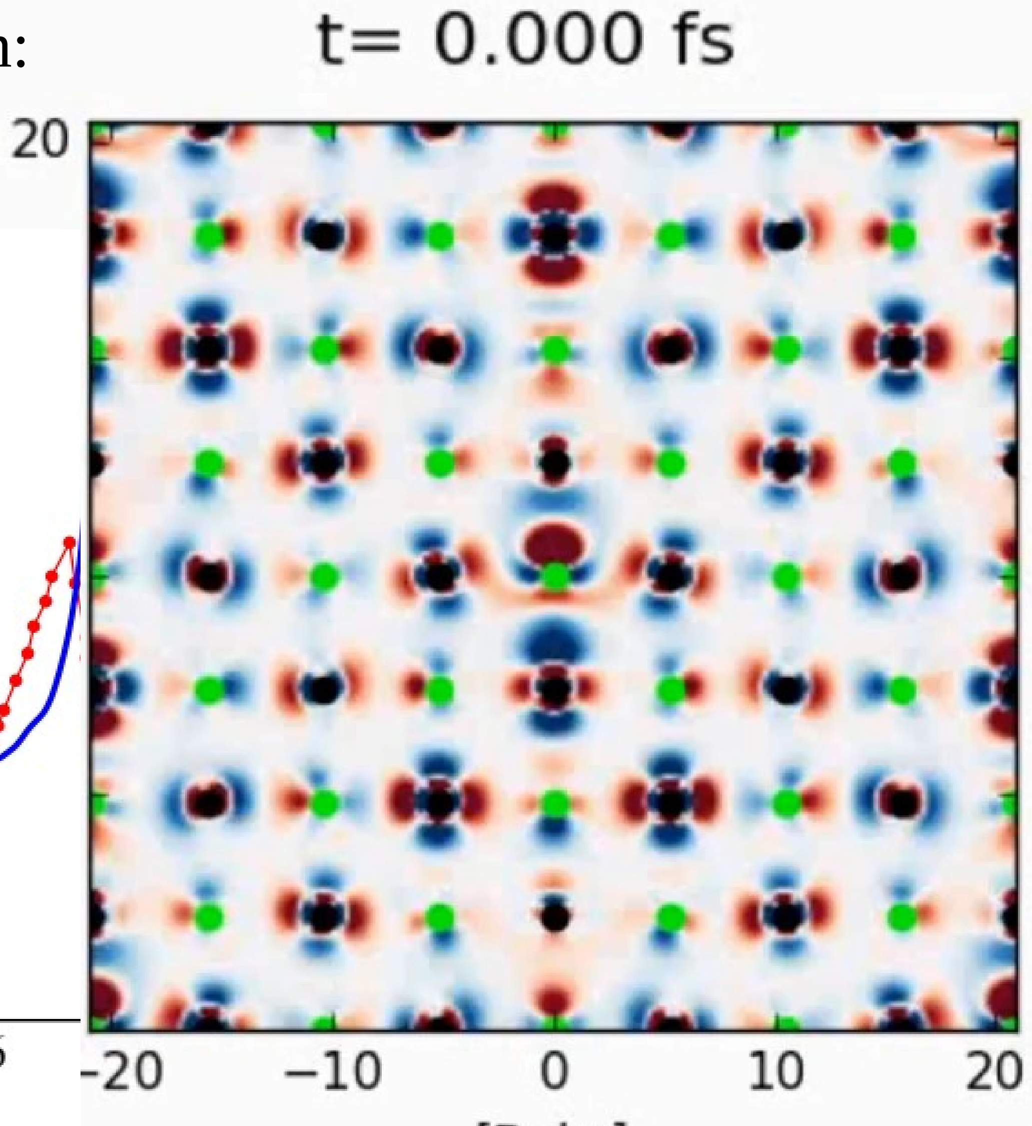


Frequency on exciton:

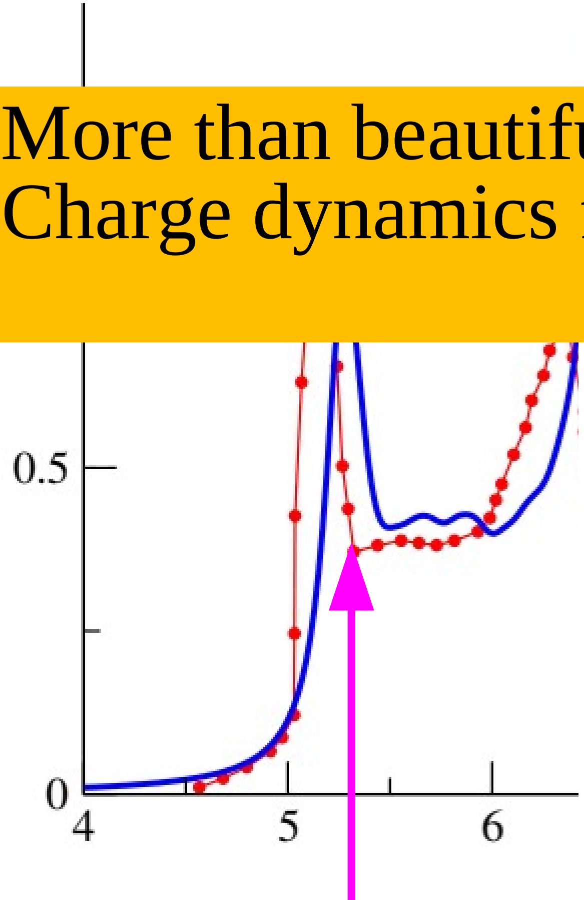


Frequency on exciton:





Frequency on exciton:

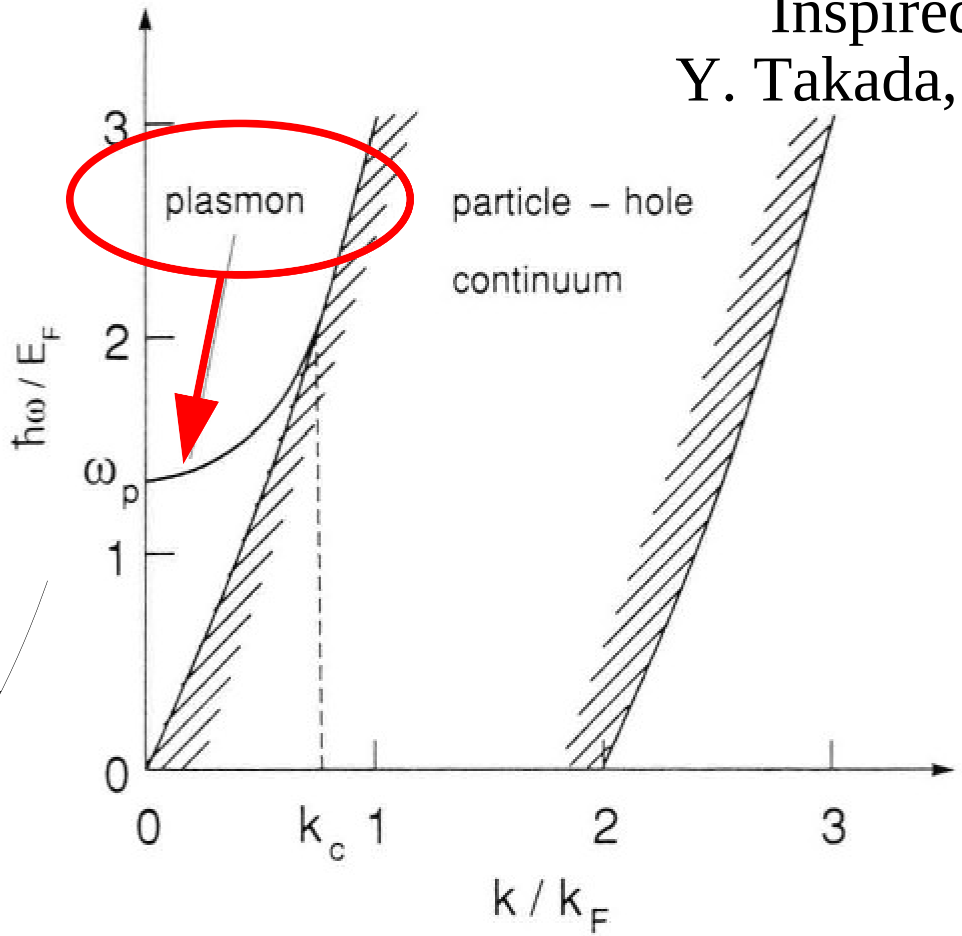


→ More than beautiful pictures:
Charge dynamics for photovoltaics, photocatalysis & more

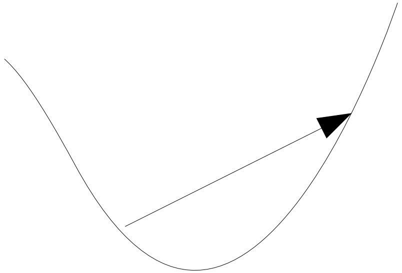
Excitations in the low-density homogeneous electron gas

Inspired by:
Y. Takada, PRB 94, 245106 (2016)

collective

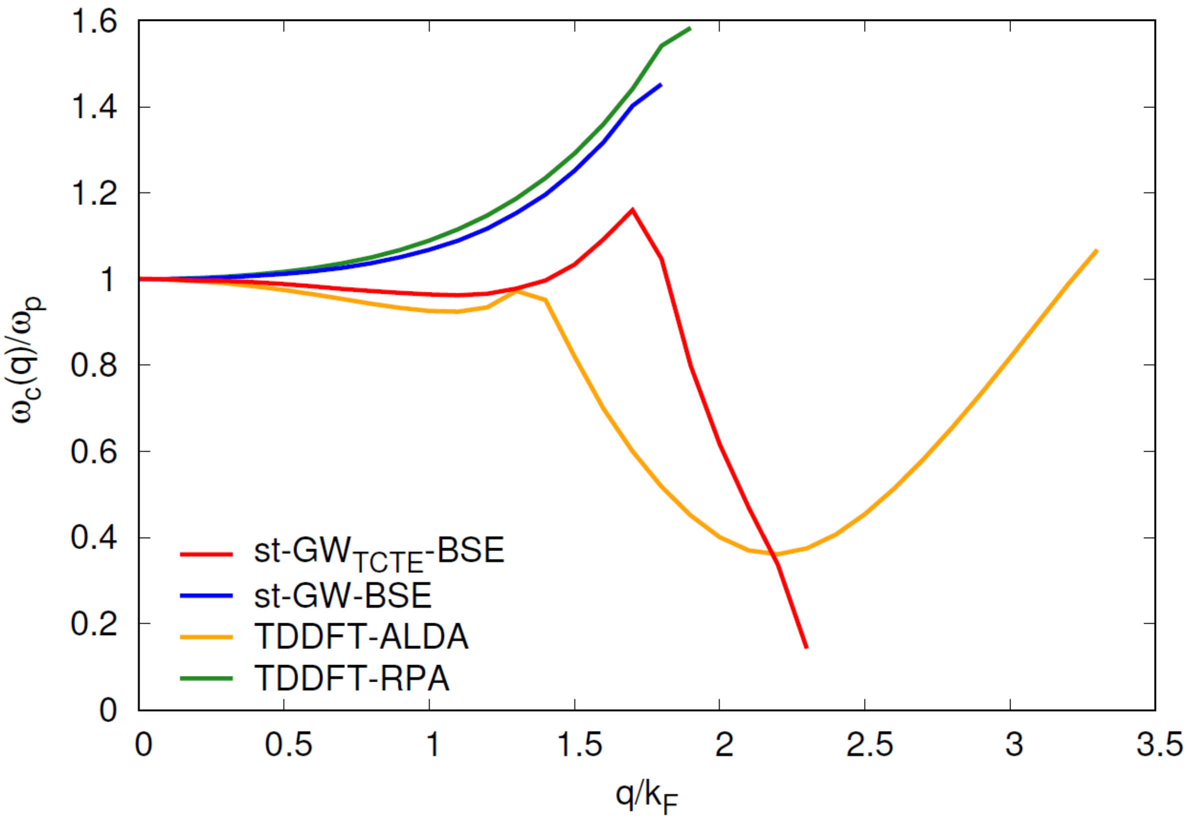


Poles in χ



from K. Sturm, "Dynamic Structure Factor: an Introduction", Zeitschrift für Naturforschung A (1993)

Collective modes: $\mathrm{Re}\,\epsilon(q,\omega_c(q)) = 0$



Koskelo, Reining, Gatti *https://doi.org/10.48550/arXiv.2301.00474*

The Bethe-Salpeter Equation

→ From linear response TDDFT to TD-GFT

To tell the truth, very similar!

→ Approximations to the BSE

Mostly GW-derived and instantaneous

→ BSE in practice

Mostly in form of e-h hamiltonian

→ Examples: optical and loss spectra, full response,

meets limits when short distance & time physics

Suggested Reading

Strinati, G., “Application of the Green’s function method to the study of the optical-properties of semiconductors,” Rivista del Nuovo Cimento 11, 1, 1988. *Pedagogical review of the theoretical framework underlying today’s Bethe–Salpeter calculations. Derivation of the main equations and link to spectroscopy.*

Rohlfing & Louie, “Electron-hole excitations and optical spectra from first principles”, Phys. Rev. B 62, 4927 (2000). *Good overview of BSE in practice as we still mostly do it today.*

Onida, G., Reining, L., and Rubio, A., “Electronic excitations: density-functional versus many-body Greens-function approaches,” Rev. Mod. Phys. 74, 601, 2002. *Review of ab initio calculations of electronic excitations with accent on optical properties and a comparison between Bethe–Salpeter and TDDFT*

R.M. Martin, L. Reining, D.M. Ceperley, “Interacting Electrons:
Theory and Computational Approaches, Cambridge May 2016
Quite recent book containing many-body perturbation theory, DMFT and QMC