# Introduction to many-body perturbation theory, GW band gap calculations and RPA energy calculations

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Palaiseau Theoretical Spectroscopy Group & Friends




# Linear response

→ Linear response Dyson-like equation: TDDFT

→ From TDDFT to the BSE

→ RPA: why and what

# Linear response

→ Linear response Dyson-like equation: TDDFT

→ From TDDFT to the BSE

→ RPA: why and what

# Linear Response……..

$$\delta n = \int \chi \delta v_{\mathrm{ext}}$$

*Density-density response fct*

$$\epsilon^{-1} = 1 + v_c \chi$$

$$\mathrm{Im}\,\epsilon^{-1}(\omega)$$

Energy Loss,
Dynamic Structure Factor (IXS)

$$v_{\mathrm{tot}} = \epsilon^{-1} v_{\mathrm{ext}}$$

$$W = \epsilon^{-1} v_c$$

e.g., for MBPT

$$\mathrm{Im}\,\epsilon(\omega)$$

Absorption

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

density response

density-density response function

perturbation

The time-dependent density gives us (directly or formally) access to response functions

TDDFT

$$\left( -\frac{\nabla^2}{2} + v_{\mathrm{aux}}(\mathbf{r}) \right) \varphi_\ell^{\mathrm{aux}}(\mathbf{r}) = \varepsilon_\ell^{\mathrm{aux}} \varphi_\ell^{\mathrm{aux}}(\mathbf{r})$$

TDDFT

$$\left( -\frac{\nabla^2}{2} + v_{\mathrm{aux}}(\mathbf{r}) \right) \varphi_\ell^{\mathrm{aux}}(\mathbf{r}) = \varepsilon_\ell^{\mathrm{aux}} \varphi_\ell^{\mathrm{aux}}(\mathbf{r})$$

$$\left( -\frac{\nabla^2}{2} + v_{\mathrm{aux}}(\mathbf{r}, t) \right) \varphi_\ell^{\mathrm{aux}}(\mathbf{r}, t) = i \frac{\partial}{\partial t} \varphi_\ell^{\mathrm{aux}}(\mathbf{r}, t)$$

TDDFT

$$\left( -\frac{\nabla^2}{2} + v_{\rm aux}(\mathbf{r}) \right) \varphi_\ell^{\rm aux}(\mathbf{r}) = \varepsilon_\ell^{\rm aux} \varphi_\ell^{\rm aux}(\mathbf{r})$$

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Ando, Z. Phys. B 26, 263 and Solid State Commun. 21, 133(1977).
Peuckert, J. Phys. C 11, 4945 (1978)
Zangwill and Soven, Phys. Rev. A 21, 1561 (1980)

TDDFT

$$\left( -\frac{\nabla^2}{2} + v_{\mathrm{aux}}(\mathbf{r}) \right) \varphi_\ell^{\mathrm{aux}}(\mathbf{r}) = \varepsilon_\ell^{\mathrm{aux}} \varphi_\ell^{\mathrm{aux}}(\mathbf{r})$$

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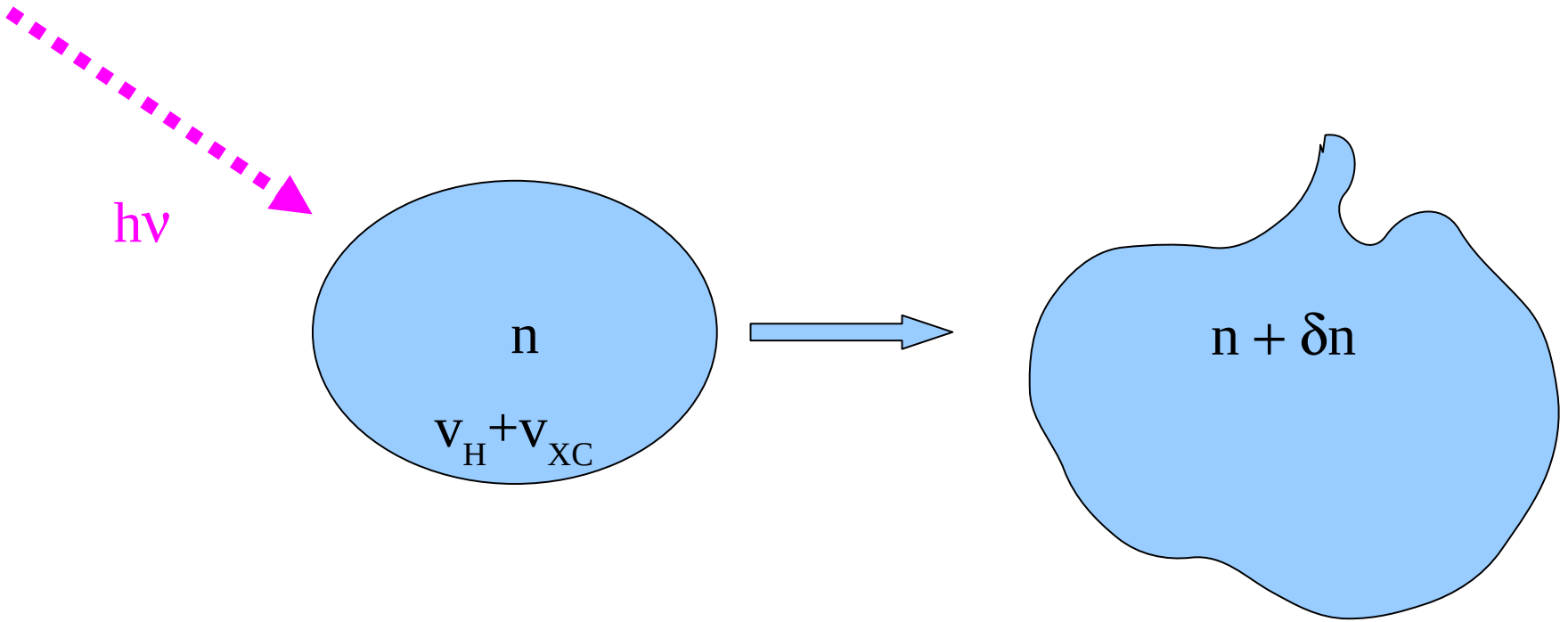
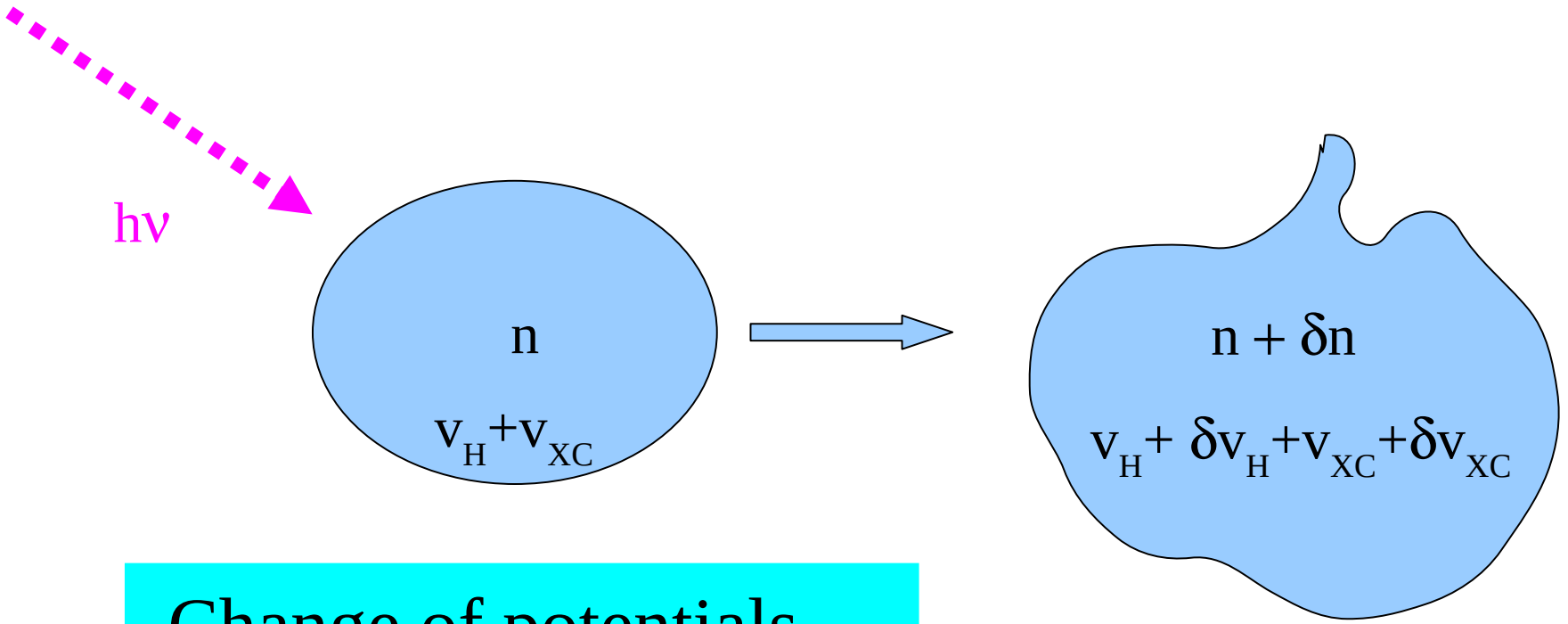
$$v_{\mathrm{aux}}(\mathbf{r}, t) = v_{\mathrm{aux}}([n], \mathbf{r}, t)$$

# TDDFT in linear response



Excitation ?

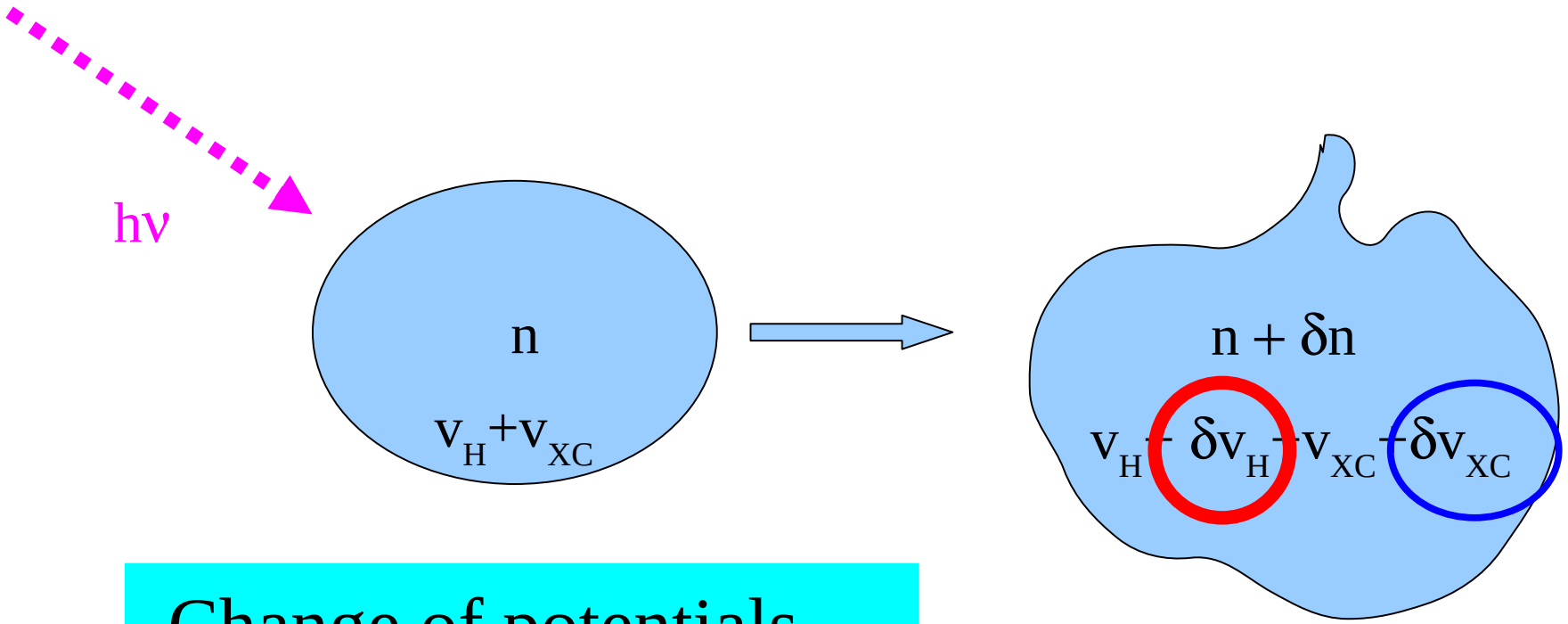
→ Induced potentials



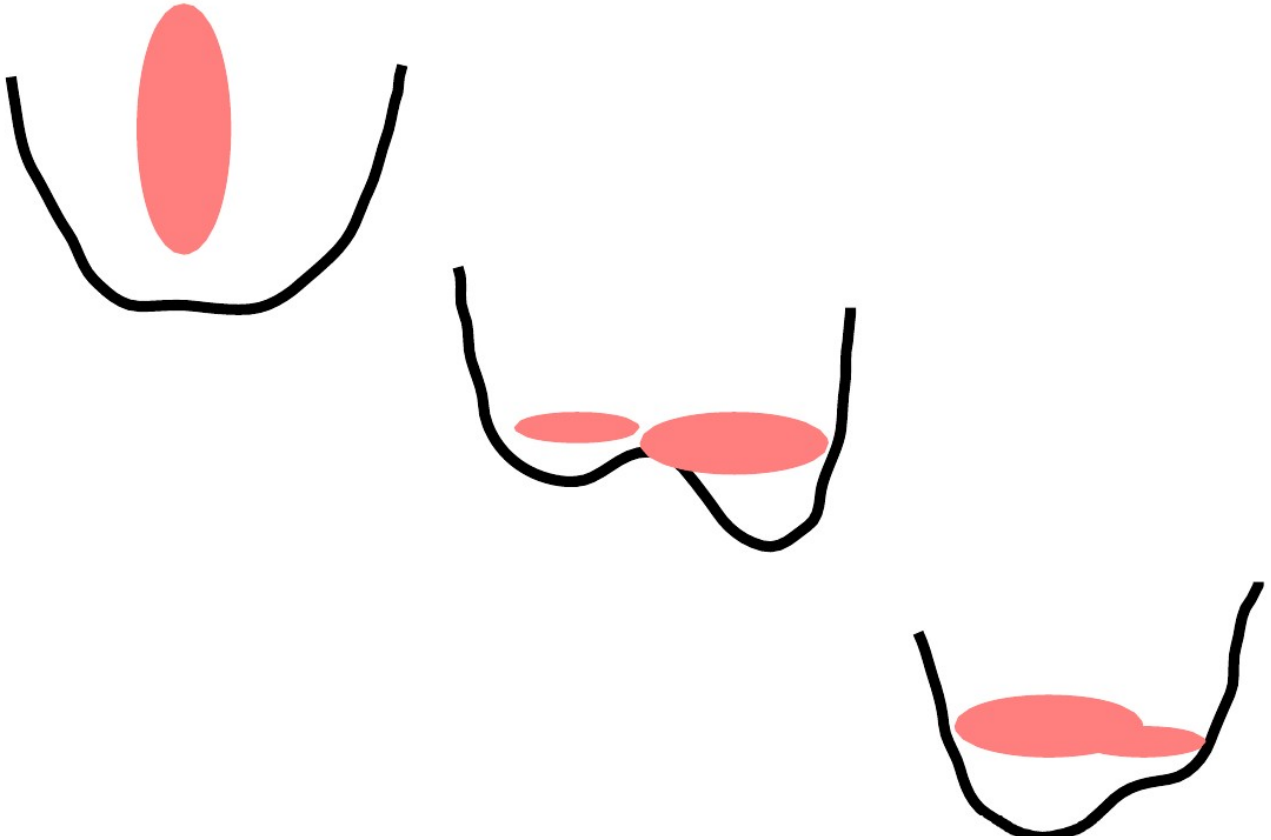

Change of potentials

Excitation ?

→ Induced potentials




Change of potentials



$$\chi = \chi^0 + \chi^0 \frac{\delta v_{\mathrm{Hxc}}}{\delta n} \chi^0 + \chi^0 \frac{\delta v_{\mathrm{Hxc}}}{\delta n} \chi^0 \frac{\delta v_{\mathrm{Hxc}}}{\delta n} \chi^0 + \ldots\ldots$$

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

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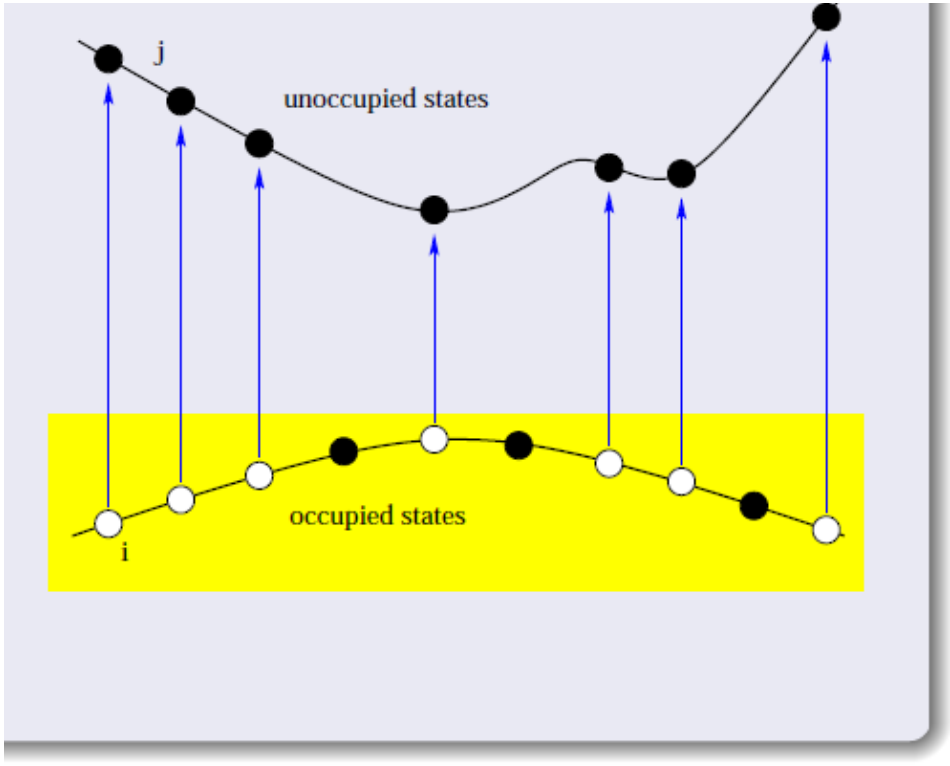
$$\chi^0$$

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{ij} (f_i - f_j) \frac{\varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_i(\mathbf{r}') \varphi_j^*(\mathbf{r}')}{\omega - (\varepsilon_i - \varepsilon_j)}$$



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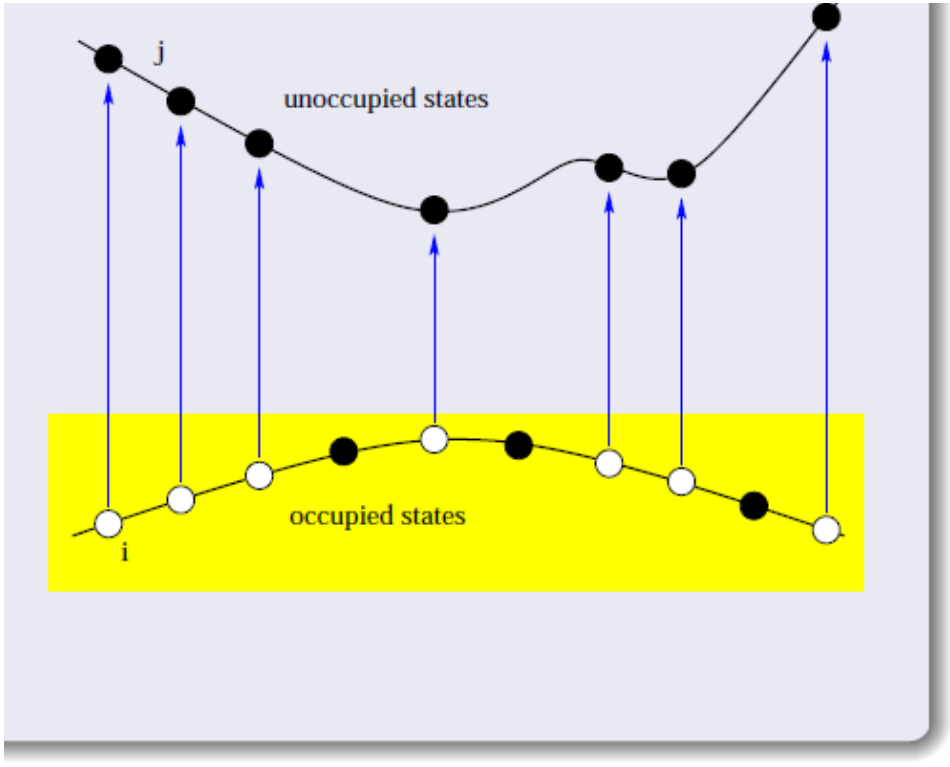
$$\chi_0 = -iG_{\mathrm{KS}} G_{\mathrm{KS}}$$



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$\chi^0$

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$$\chi^0$$

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

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

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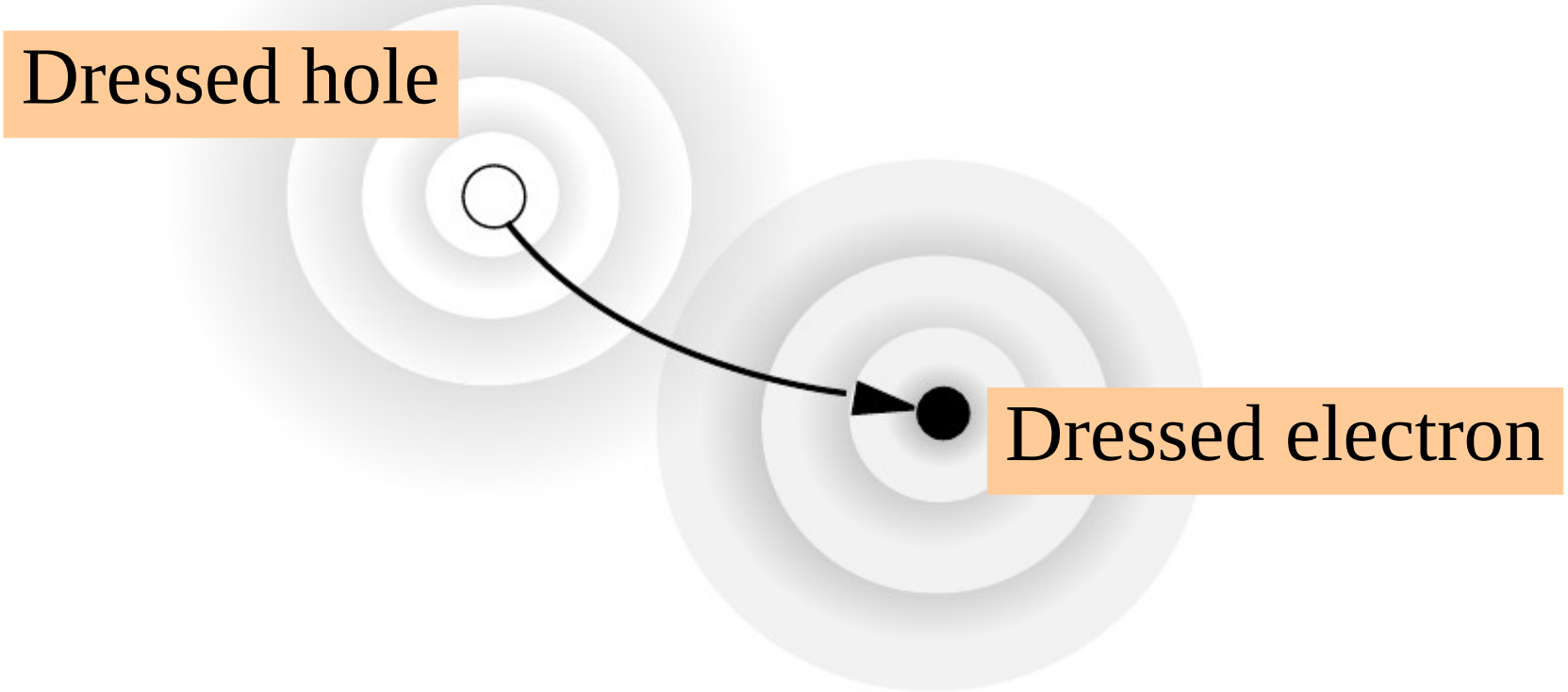
RPA: $f_{\mathrm{xc}} \rightarrow 0$

In the framework of Green's functions:

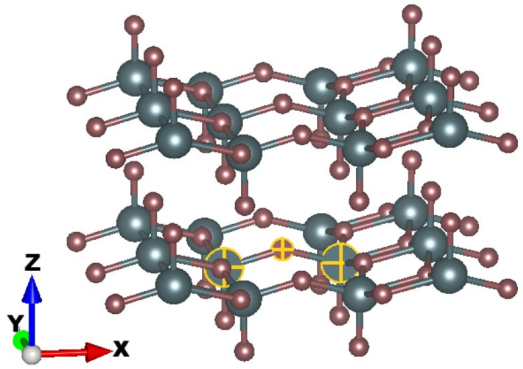
$$L_0 = GG$$

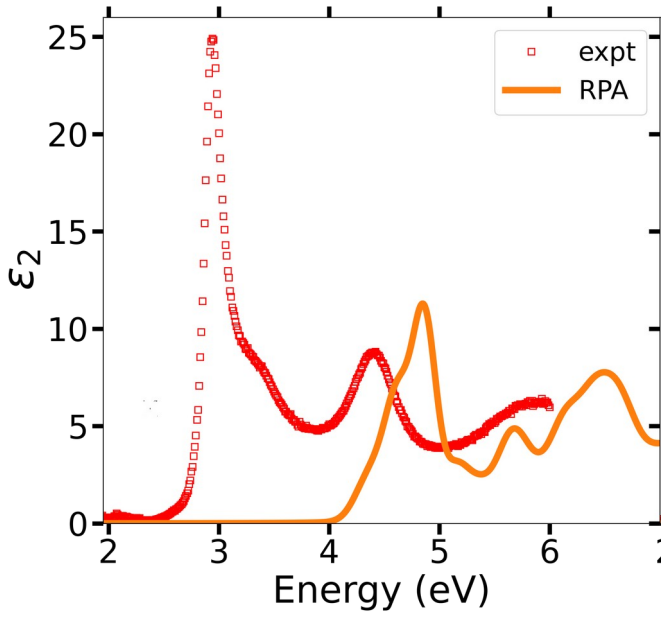


# Optical absorption in the aux. system of electrons and holes (indep.)

Chaire Énergies Durables
École polytechnique - EDF

$V_2O_5$: a layered bulk material

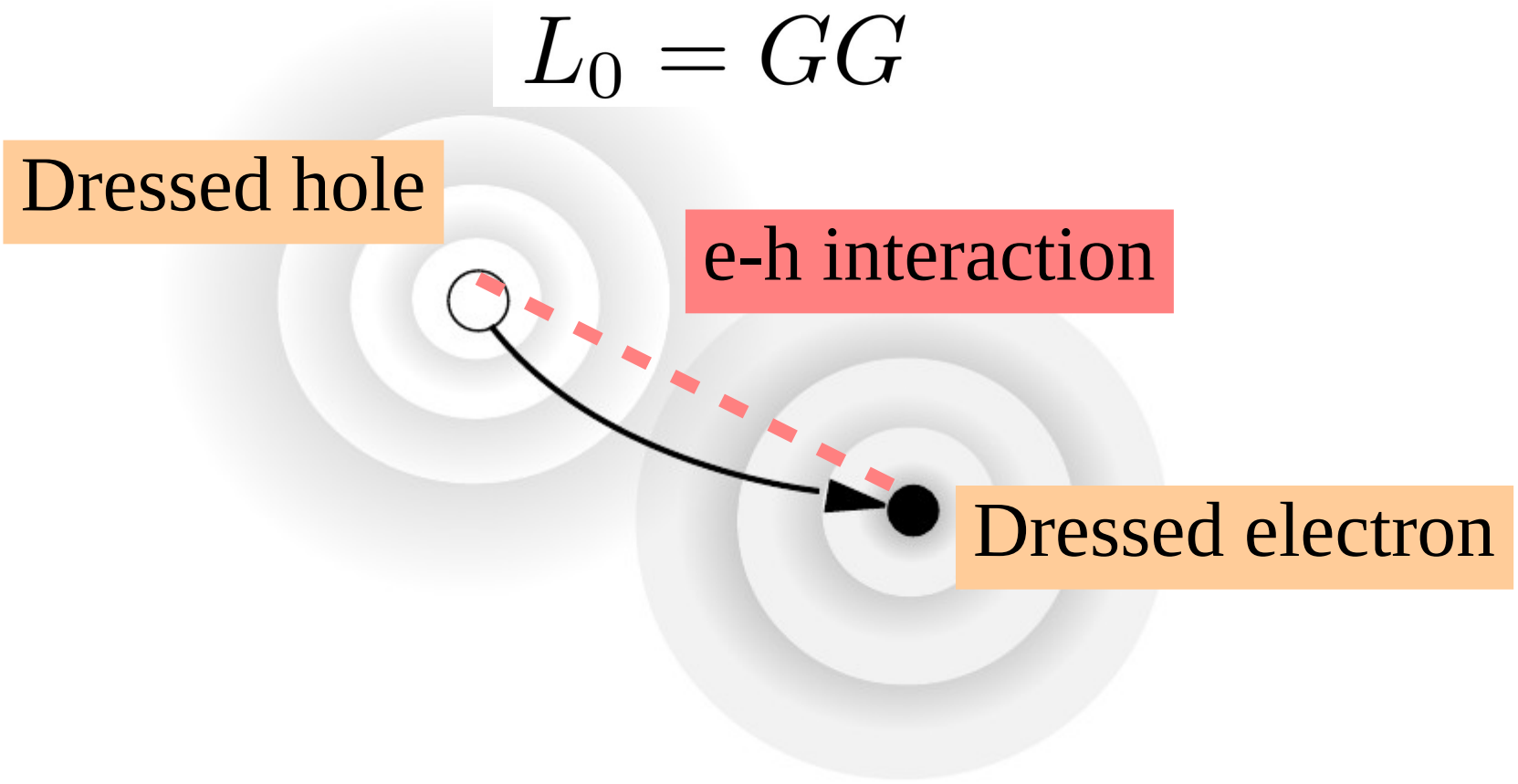



GW-RPA  Exp

Vitaly Gorelov
Reining, Feneberg, Goldhahn, Schleife, Lambrecht, Gatti
*npj comp mat (2022)*

$$L_0 = GG$$



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

$$L_0 \equiv GG$$

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

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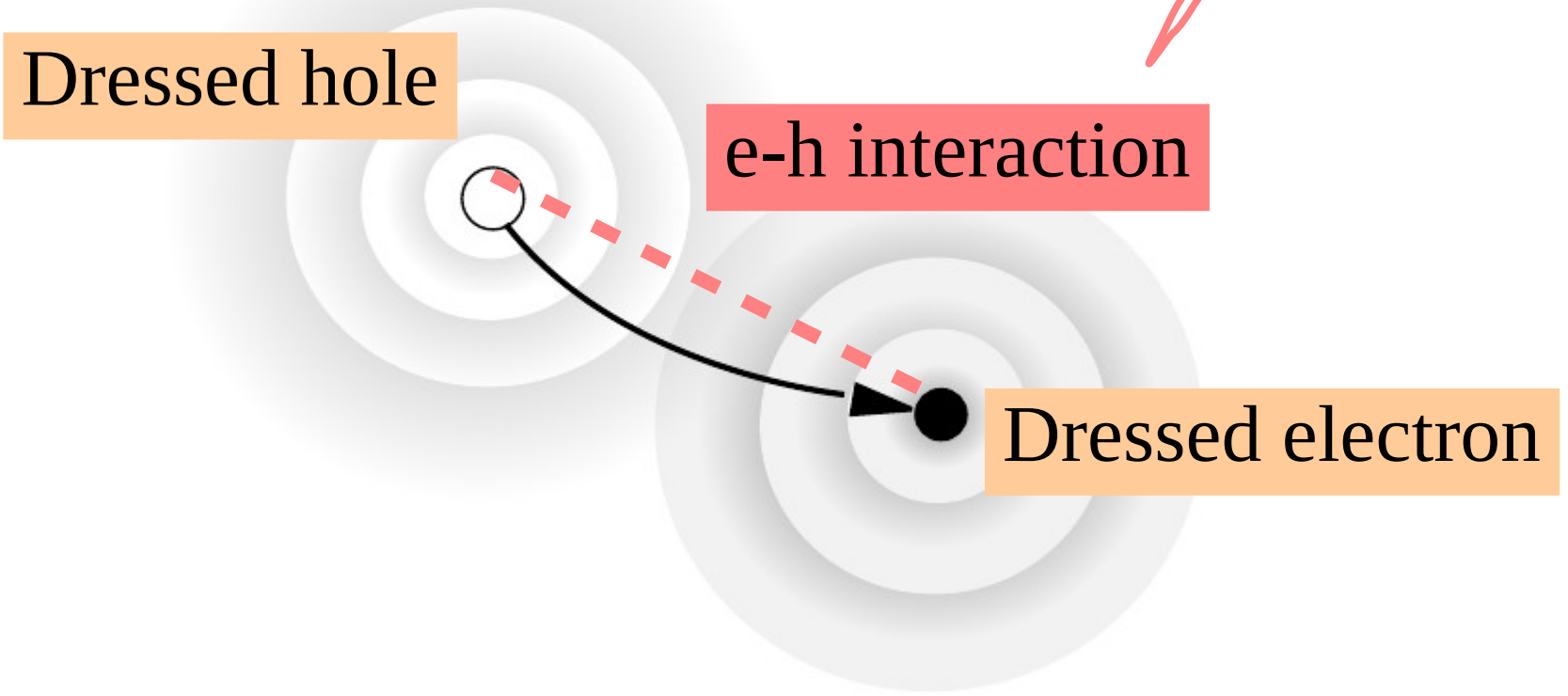
$$L_0 \equiv GG$$

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

Bethe-Salpeter Equation

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

$$L_0 = GG$$



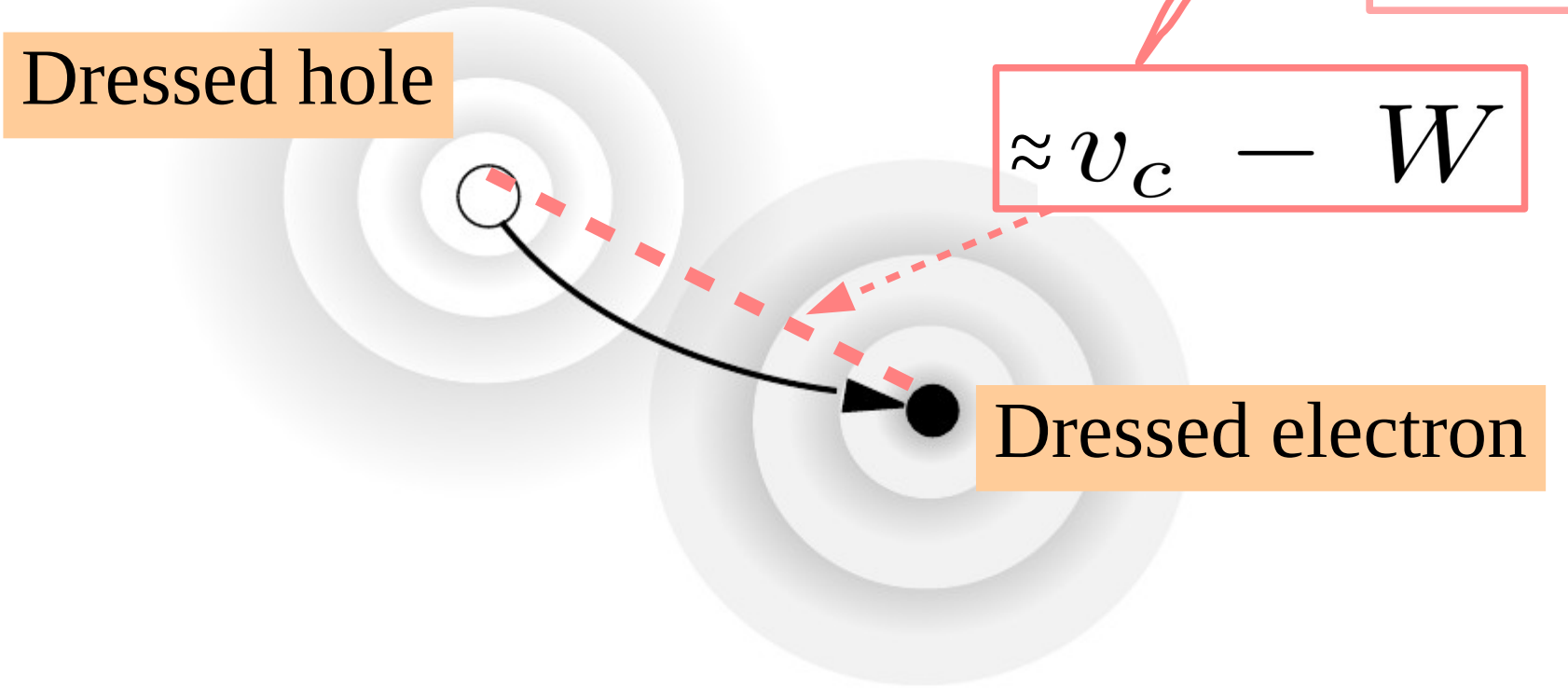
Bethe-Salpeter Equation

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

$$L_0 = GG$$

From GW

$$\approx v_c - W$$



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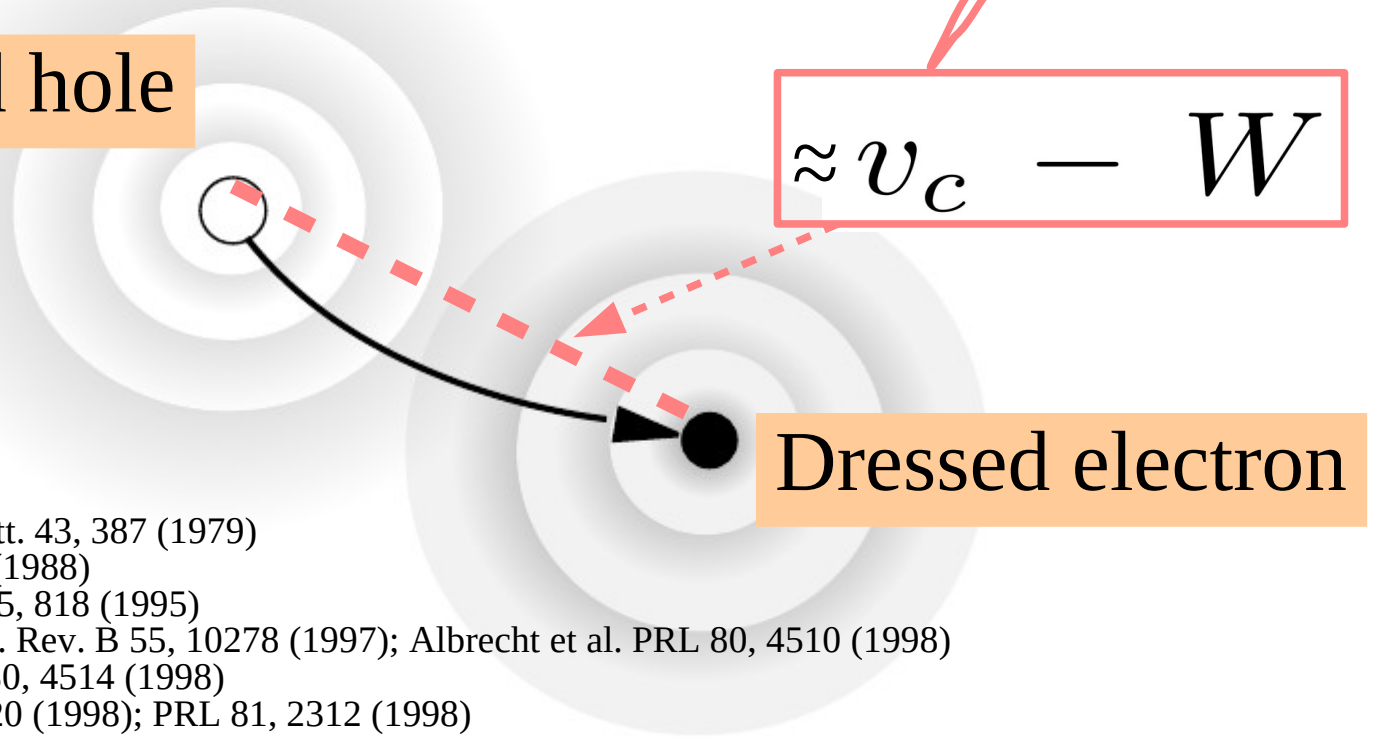


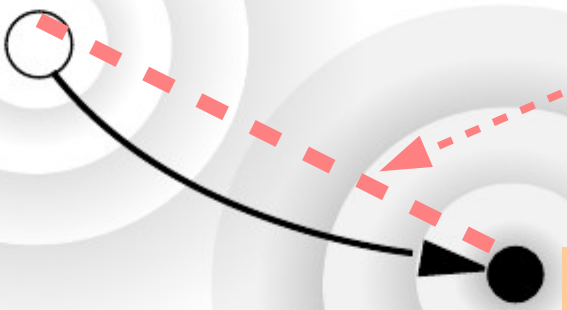

Hanke & Sham, Phys. Rev. Lett. 43, 387 (1979)
Strinati, Nuovo Cimento 11, 1 (1988)
Onida, et al., Phys. Rev. Lett. 75, 818 (1995)
Albrecht, Onida, Reining Phys. Rev. B 55, 10278 (1997); Albrecht et al. PRL 80, 4510 (1998)
Benedict, Shirley, Bohn, PRL 80, 4514 (1998)
Rohlfing & Louie, PRL 80, 3320 (1998);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

Bethe-Salpeter Equation

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

$$L_0 = GG$$

$$\frac{\delta(v_H + \Sigma_{xc})}{\delta G} \approx v_c - W$$



Dressed hole

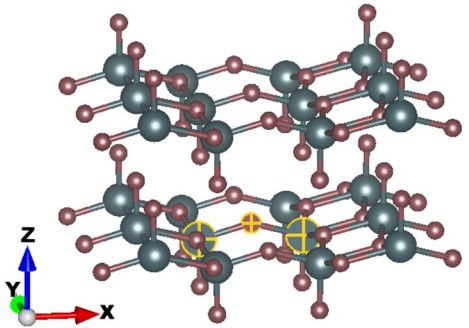
Dressed electron

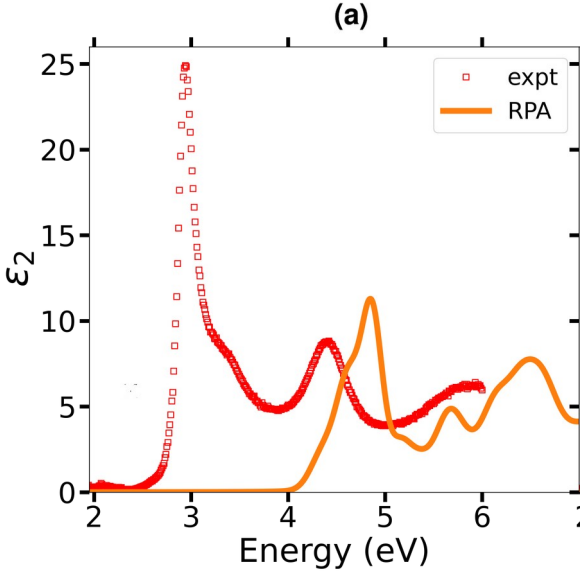
Neglect of interaction kernel: GW-RPA

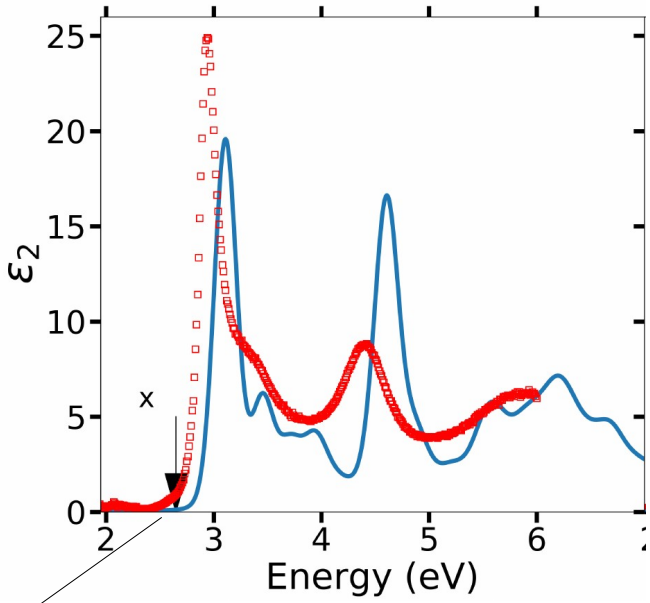
# State-of-the-art Bethe-Salpeter

Chaire Énergies Durables
École polytechnique - EDF

$V_2O_5$: a layered bulk material




Dark exciton

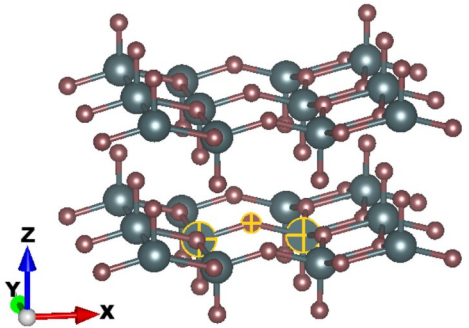
Vitaly Gorelov et al.,
*npj comp mat (2022)*

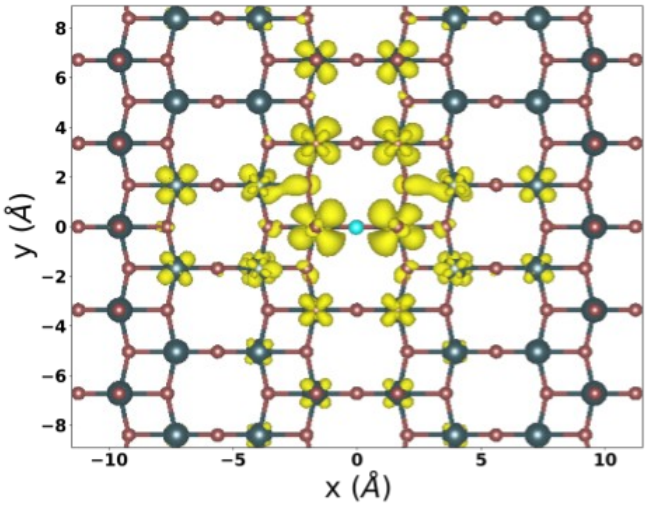
# State-of-the-art Bethe-Salpeter

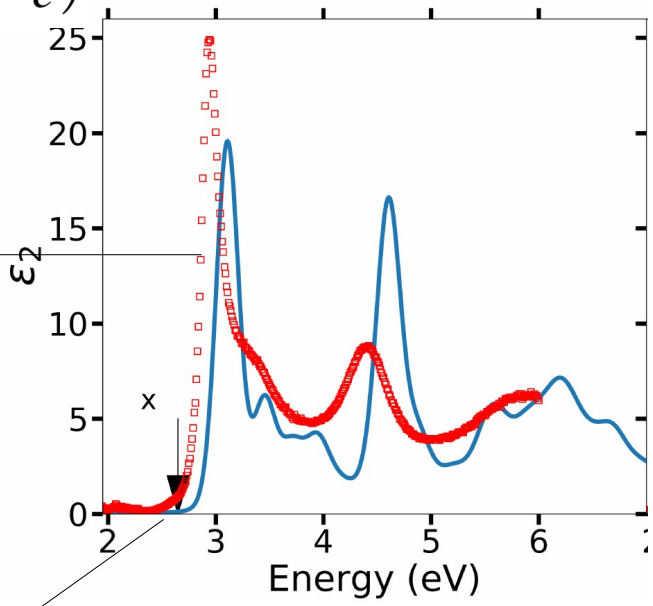
Chaire Énergies Durables
École polytechnique - EDF

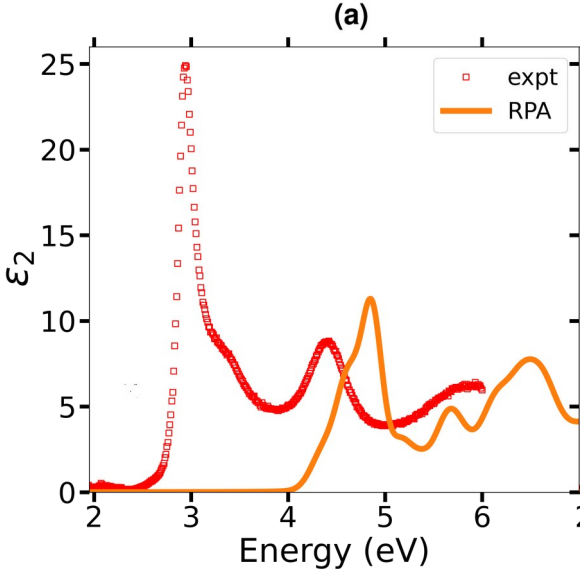
$V_2O_5$: a layered bulk material

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



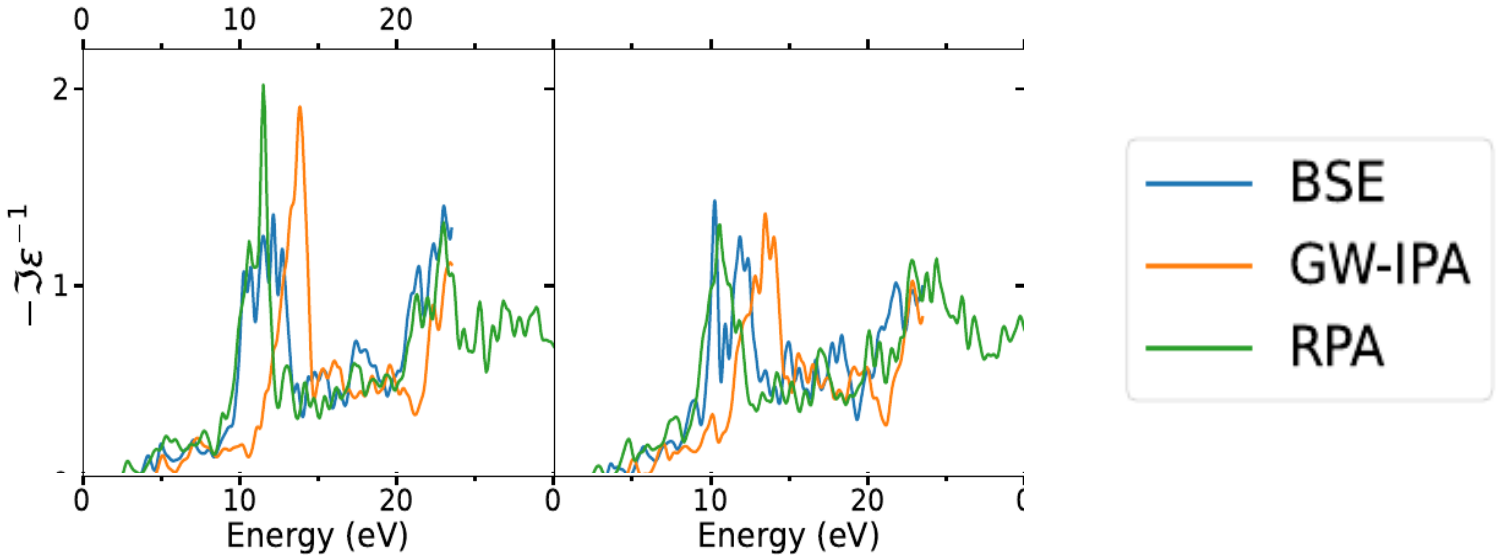




Dark exciton

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

→ BSE and TDDFT in principle exact

→ Approximations (GW!) for BSE kernel reliable, TDDFT depends




Loss function of vanadium pentoxide (and many other materials):

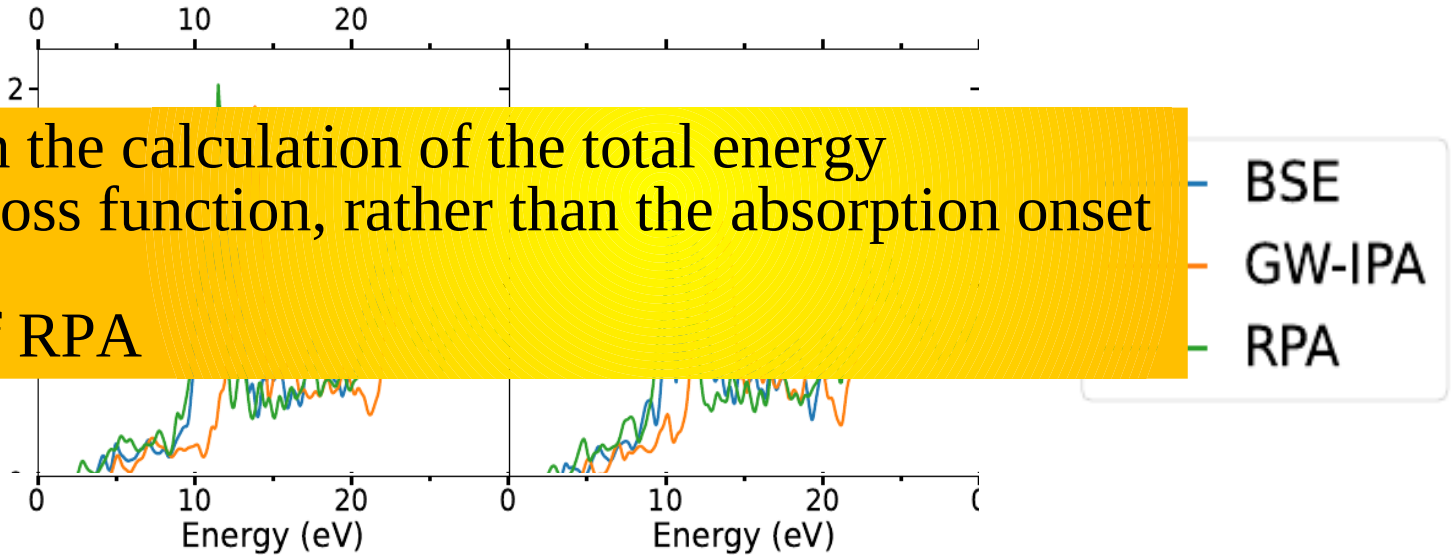
Cancellations → KS-RPA ok

→ BSE and TDDFT in principle exact

→ Approximations (GW!) for BSE kernel reliable, TDDFT depends

In GW and in the calculation of the total energy
we need the loss function, rather than the absorption onset

→ success of RPA




Loss function of vanadium pentoxide (and many other materials):

Cancellations → KS-RPA ok

The one-body Green's function also yields the total energy:

$$E_{\rm gs} = \frac{1}{2}\int dx \lim_{x'\to x} \lim_{t'\to t^+} \left[\frac{\partial}{\partial t} - ih(x)\right] G(x,x',t,t')$$

V.M. Galitskii, A. M. JETP 1950, 7, 96

This contains

→ the external potential energy (only the density needed)
→ the kinetic energy calculated with G,
→ and the interaction potential energy (Hartree + xc)

The xc contribution to the interaction potential energy can also be written as

$$E_{\rm xc} = E_{\rm x}^{KS} - \frac{1}{2\pi}\int d\mathbf{r}d\mathbf{r}' v_c(\mathbf{r},\mathbf{r}') \int_0^\infty d\omega \Big[\chi(\mathbf{r},\mathbf{r}';i\omega) - \chi_0(\mathbf{r},\mathbf{r}';i\omega)\Big]$$

(Fluctuation-dissipation theorem)

We could calculate the polarizability in TDDFT or BSE.

Problem: what about the kinetic energy? It still requires *G* (tbp, density matrix)

→ Adiabatic connection: scale Coulomb interaction keeping density fix

$$U_{\rm xc} = E_{\rm x}^{KS} - \frac{1}{2\pi}\int d\mathbf{r}d\mathbf{r}' v_c(\mathbf{r},\mathbf{r}') \int_0^\infty d\omega \int_0^1 d\lambda \Big[\chi_\lambda(\mathbf{r},\mathbf{r}';i\omega) - \chi_0(\mathbf{r},\mathbf{r}';i\omega)\Big]$$

$$E_{\rm xc} = E_{\rm x}^{KS} - \frac{1}{2\pi}\int d\mathbf{r}d\mathbf{r}' v_c(\mathbf{r},\mathbf{r}') \int_0^\infty d\omega \Big[\chi(\mathbf{r},\mathbf{r}';i\omega) - \chi_0(\mathbf{r},\mathbf{r}';i\omega)\Big]$$

$U_{\rm xc}$ also contains the difference between the full and KS kinetic energy

→ We “only” need a good approximation for the polarizability

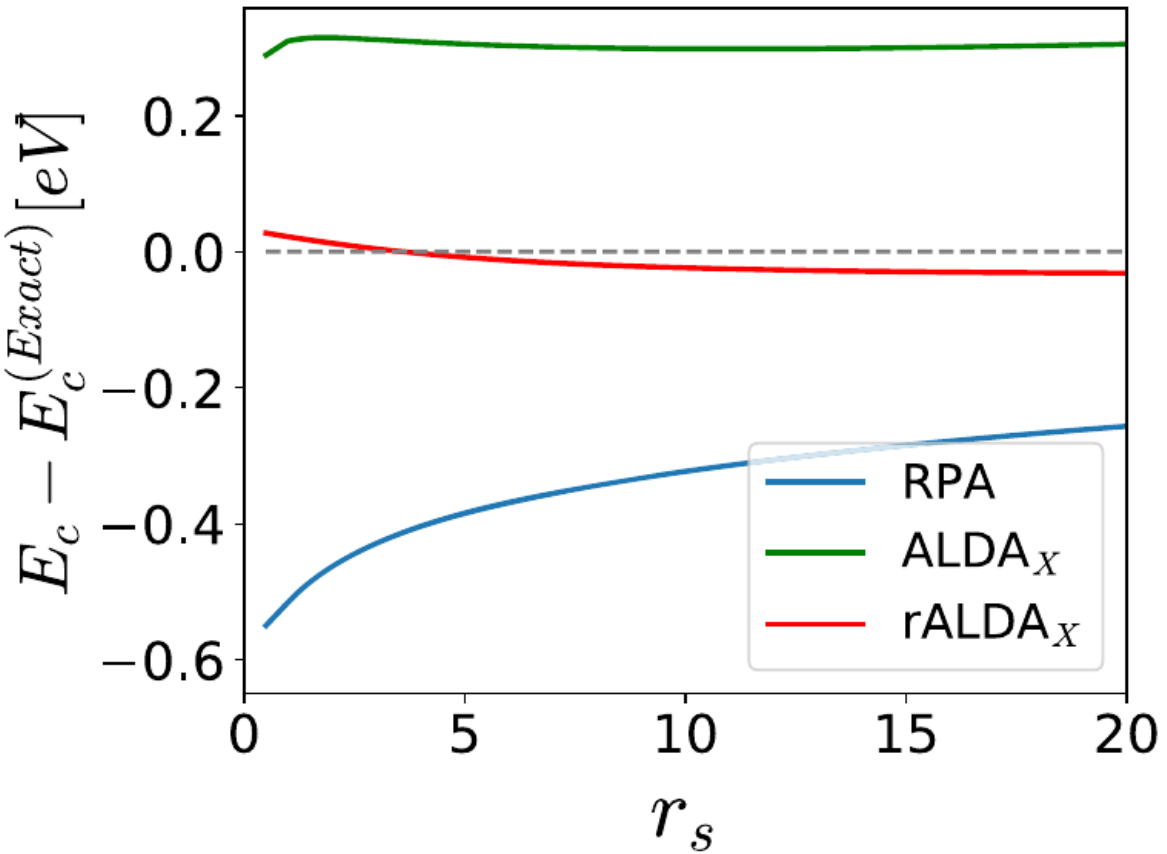
Simplest : RPA  Already has, e.g., van der Waals. Standard scaling $O(N^4)$

RPA correlation energy in GW context:

$$E_{\mathrm{c}}^{\mathrm{RPA}} = \frac{1}{2}\int_0^1 \frac{\mathrm{d}\lambda}{\lambda}\left(\frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega \mathrm{Tr}\left[G^0(i\omega)\Sigma_{\mathrm{c}}^{GW}(i\omega,\lambda)\right]\right)$$

Ren, X.; Rinke, P.; Joas, C.; Scheffler, M. Random-phase approximation and its applications in computational chemistry and materials science. Journal of Materials Science 47, 7447 (2012)

# HEG correlation energy




Olsen, T.; Patrick, C. E.; Bates, J. E.; Ruzsinszky, A.; Thygesen, K. S. npj Computational Materials 2019, 5, 106.

**Table 1.** Correlation energies of H, $H_2$, and He evaluated with different functionals

| | LDA | PBE | RPA | $ALDA_x$ | rALDA | Exact |
|---|---|---|---|---|---|---|
| H | −14 | −4 | −13 | 6 | −2 | 0 |
| $H_2$ | −59 | −27 | −51 | −16 | −28 | −26 |
| He | −70 | −26 | −41 | −19 | −27 | −26 |

Exact values are taken from ref. [101] All numbers are in kcal/mol

Lee, J. S. & Park, S. Y. J. Chem. Phys. 112, 10746–10753 (2000).

| | Atomization energies | | | |
|---|---|---|---|---|
| | ME (eV) | MAE (eV) | MAPE (%) | MaxAPE (%) |
| LDA | −0.74 | 0.74 | 18.0 | 32.7 |
| PBE | 0.15 | 0.17 | 4.5 | 15.4 |
| RPA | 0.30 | 0.30 | 7.3 | 13.5 |
| RPA+ | 0.35 | 0.35 | 8.7 | 15.0 |
| | Lattice constants | | | |
| | ME (Å) | MAE (Å) | MAPE (%) | MaxAPE (%) |
| LDA | −0.045 | 0.045 | 1.0 | 3.7 |
| PBE | 0.070 | 0.072 | 1.4 | 2.7 |
| RPA | 0.016 | 0.019 | 0.4 | 0.9 |
| RPA+ | 0.029 | 0.030 | 0.6 | 1.1 |
| | Bulk moduli | | | |
| | ME (GPa) | MAE (GPa) | MAPE (%) | MaxAPE (%) |
| LDA | 9 | 11 | 9.6 | 31.0 |
| PBE | −11 | 11 | 10.7 | 23.7 |
| RPA | −1 | 4 | 3.5 | 10.0 |
| RPA+ | −3 | 5 | 3.8 | 11.4 |

Harl J, Schimka L, Kresse G (2010) Phys Rev B 81:115126

# Linear response

→ Linear response Dyson-like equation: TDDFT

→ From TDDFT to the BSE

→ RPA: why and what

* Linear response is at the basis of much of our work

* RPA has its charme

* Actions needed to go beyond, and to speed up!

# 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*

Ren, X.; Rinke, P.; Joas, C.; Scheffler, M. “Random-phase approximation and its applications in computational chemistry and materials science”, Journal of Materials Science 47, 7447 (2012)
*Comprehensive review on RPA and beyond total energy calculations*