Neutral Electronic Excitations:

a Many-body approach to the optical absorption spectra

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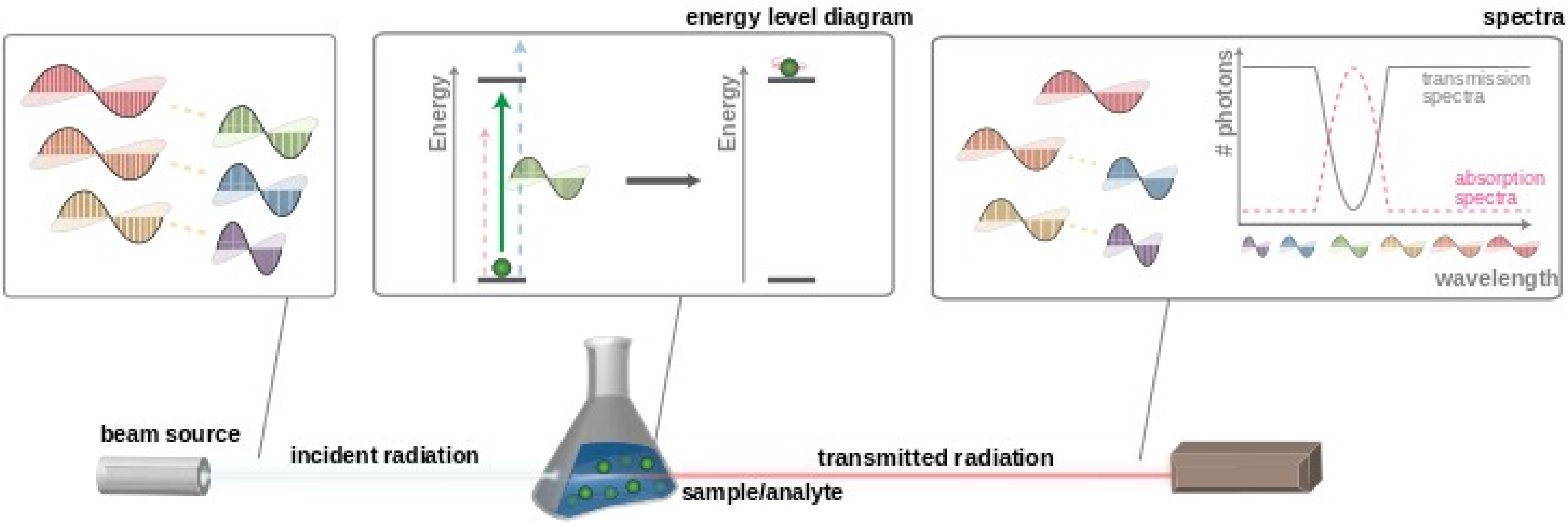
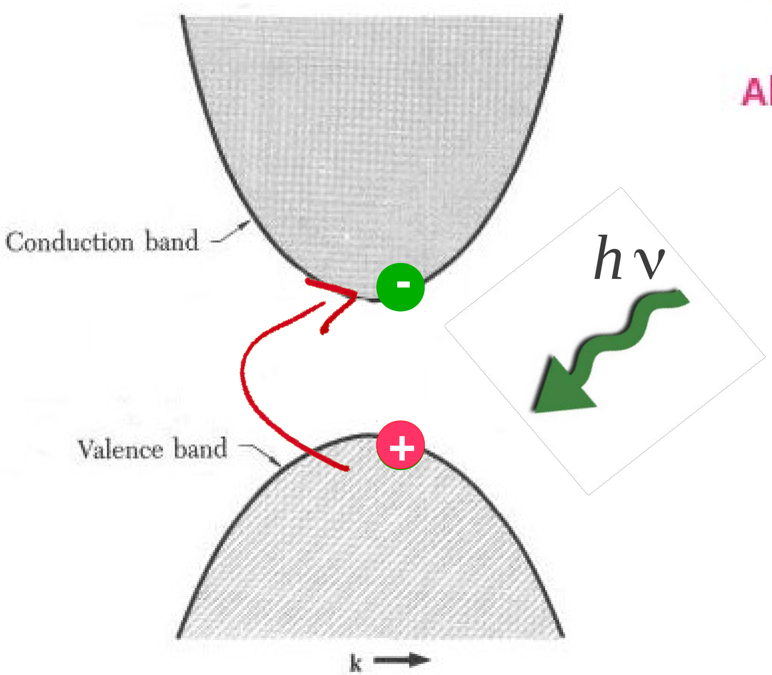
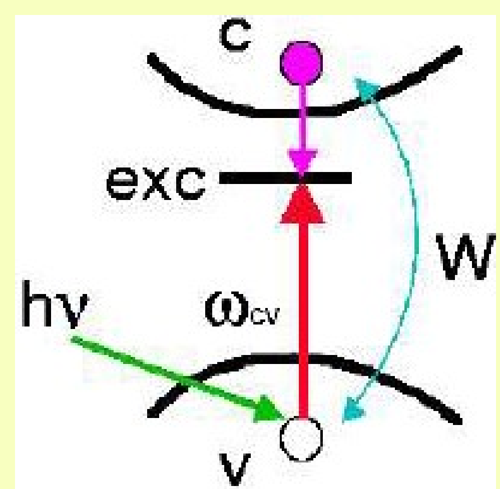
Motivations: Absorption Spectroscopy



Absorption **Transmission** **Detection**





Many Body Effects!!!

Outline

Response of the system to a perturbation → Linear Response Regime

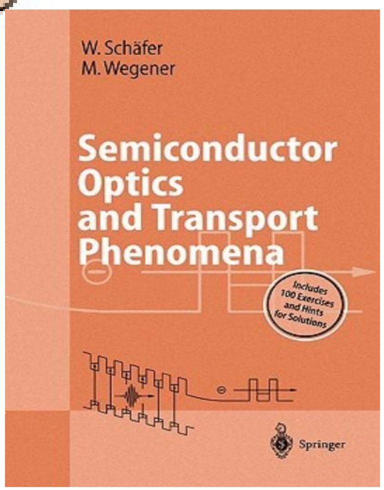
How can we calculate the response of the system? Time Dependent - DFT and Bethe Salpeter Equation

Conclusions

Linear Response Regime (I)

$$H_{tot} = H + H^{ext}(t) = H + \int d\mathbf{r}\,\rho(\mathbf{r})\,\phi^{ext}(\mathbf{r},t)$$

The external potential "induces" a (time-dependent) density perturbation



$$\rho^{ind}(\mathbf{r},t) \equiv \langle\Psi(t)|\rho(\mathbf{r})|\Psi(t)\rangle - \langle\rho\rangle \qquad \langle O\rangle \equiv \langle\Psi|O|\Psi\rangle$$

$$|\Psi(t)\rangle \equiv e^{-iHt}|\Psi_I(t)\rangle \approx |\Psi\rangle + i\int_{-\infty}^{t} dt'\,H_I^{ext}(t')\,|\Psi\rangle$$

$$\rho^{ind}(\mathbf{r},t) = \int_{-\infty}^{t} dt' \int_{-\infty}^{\infty} d\mathbf{r}'\,\chi_{\rho\rho}(\mathbf{r}\mathbf{r}',t-t')\,\phi^{ext}(\mathbf{r}',t')$$

Kubo Formula (1957)

Linear Response Regime (II)

The induced charge density results in a total potential via the Poisson equation.

$$V_{tot}(\vec{r}\,t) = V_{ext}(\vec{r}\,t) + \int dt' \int d\vec{r}\,'\, v(\vec{r}-\vec{r}\,')\,\rho_{ind}(\vec{r}\,'t')$$

Kubo Formula

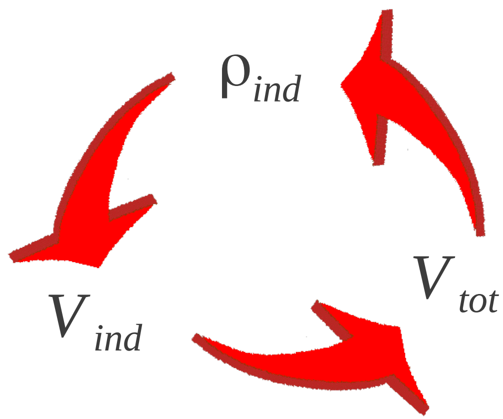
$$V_{tot}(\vec{r}\,t) = V_{ext}(\vec{r}\,t) + \int\int dt'\,dt'' \int\int d\vec{r}\,'\,d\vec{r}\,''\, v(\vec{r}-\vec{r}\,')\,\chi(\vec{r}\,',\vec{r}\,'')\,V_{ext}(\vec{r}\,''t'')$$

$$\rho_{ind}(\vec{r}) = \int dt' \int d\vec{r}\,'\, P(\vec{r},\vec{r}\,')\,V_{tot}(\vec{r}\,'t')$$

Variation of the charge density w.r.t. The total potential.

$$\chi(\vec{r}\,t,\vec{r}\,'t') = P(\vec{r}\,t,\vec{r}\,'t') + \int\int dt_1\,dt_2 \int\int d\vec{r}_1\,d\vec{r}_2\, P(\vec{r}\,t,\vec{r}_1 t_1)\,v(\vec{r}_1-\vec{r}_2)\,\chi(\vec{r}_2 t_2,\vec{r}\,'t')$$

Linear Response Regime (II)



Screening of the external perturbation

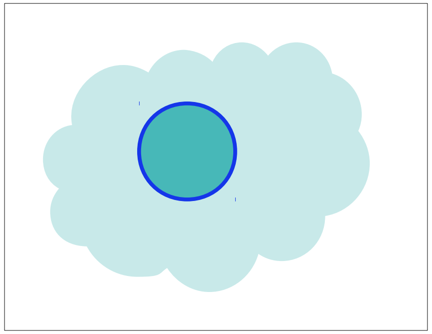
The screening is described by the inverse of the microscopic dielectric function

$$\epsilon^{-1}(\vec{r}\,t,\vec{r}\,'t') = \frac{\delta V_{tot}(\vec{r}\,t)}{\delta V_{ext}(\vec{r}\,t)}$$

$$= \delta(\vec{r}-\vec{r}\,') + \int dt''\, d\vec{r}\,''\, v(\vec{r}-\vec{r}\,'')\chi(\vec{r}\,'',\vec{r}\,')$$

Optical Absorption: Time Dependent DFT

$$\begin{cases} [-\frac{1}{2}\nabla^2 + V_{eff}(\boldsymbol{r},t)]\psi_i(\boldsymbol{r},t) = i\frac{\partial}{\partial t}\psi_i(\boldsymbol{r},t) \\ \rho(\boldsymbol{r},t) = \sum_{i=1}^{N} |\psi_i(\boldsymbol{r},t)|^2 \end{cases}$$



$$V_{eff}(\boldsymbol{r},t) = V_H(\boldsymbol{r},t) + V_{xc}(\boldsymbol{r},t) + V_{ext}(\boldsymbol{r},t)$$

Petersilka et al. Int. J. Quantum Chem. 80, 584 (1996)

$$\chi = \frac{\delta\rho_I}{\delta V_{ext}} \qquad \chi_0 = \frac{\delta\rho_{NI}}{\delta V_{eff}}$$

... by using ...

$$\delta\rho_I = \delta\rho_{NI}$$

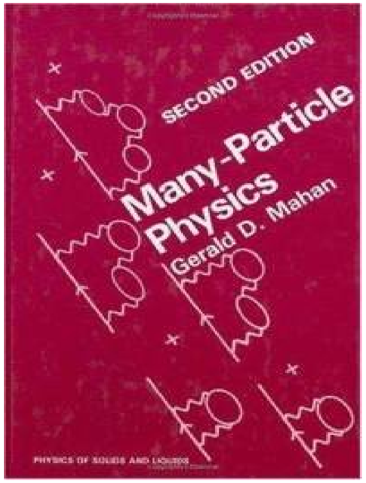
$$\chi\,\delta V_{ext} = \chi^0(\delta V_{ext} + \delta V_H + \delta V_{xc})$$

$$\chi = \chi^0\left(1 + \frac{\delta V_H}{\delta V_{ext}} + \frac{\delta V_{xc}}{\delta V_{ext}}\right)$$

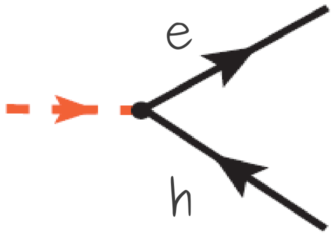
$\frac{\delta V_H}{\delta V_{ext}} \rightarrow v\chi$

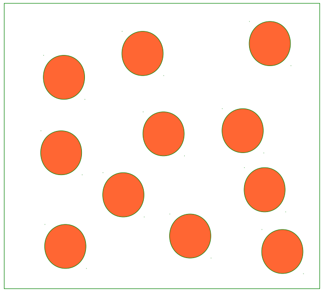
$\frac{\delta V_{xc}}{\delta V_{ext}} \rightarrow f_{xc}\chi$

Optical Absorption: Non Interacting (Quasi)Particles



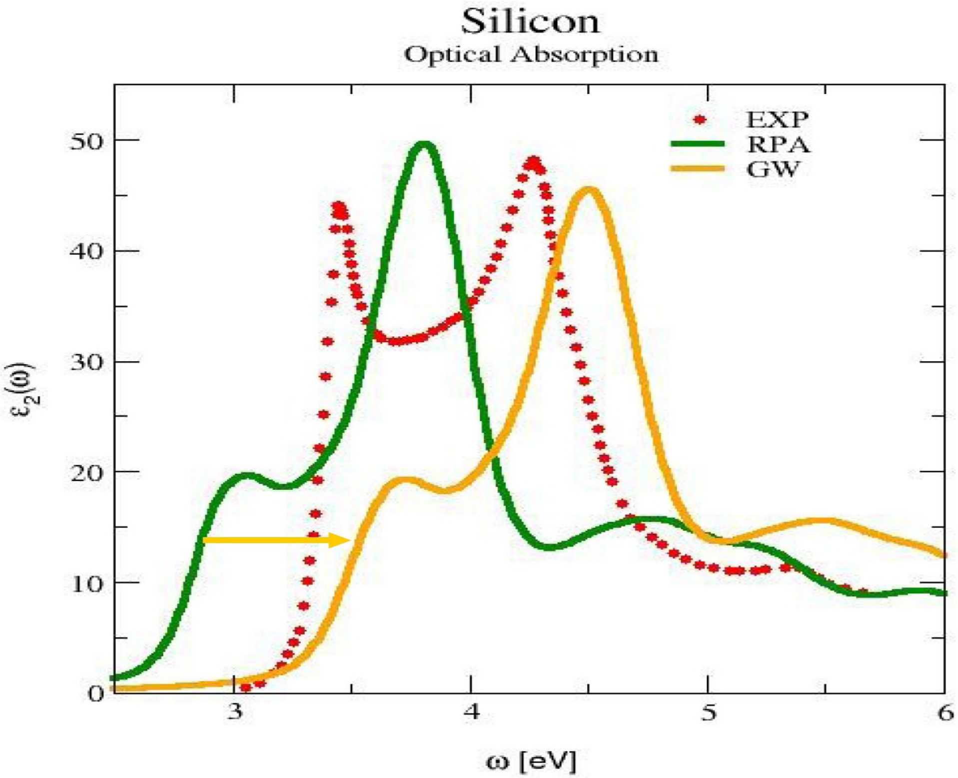
Elementary process of absorption:
Photon creates a single e-h pair



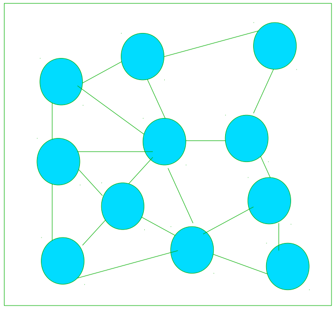


Non Interacting Particles

Hartree, HF, DFT

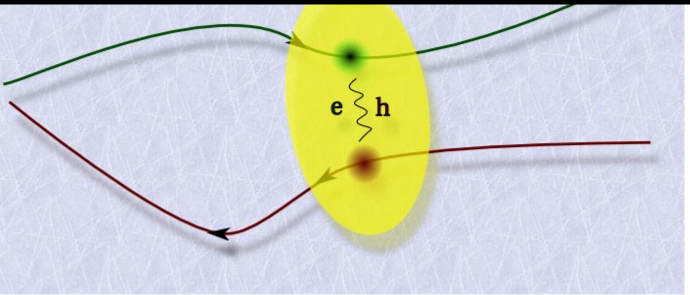


Independent transitions



Non Interacting quasi-particles GW

Derivation of the Bethe–Salpeter equation (1)



Two particle Green's Function

$$G_2(1,3;2,3^+) = G(1,2)G(3,3^+) - \frac{\delta G(1,2)}{\delta U(3)}$$

$$\chi(1,2) = \frac{\delta \rho(1)}{\delta U(2)} = i\hbar \left[G_2(1,2;1^+,2^+) - G(1,1^+)G(2,2^+) \right]$$

$$\chi(1,2) = -i\hbar L(1,2;1^+,2^+)$$

$$\chi(1,2) = P(1,2) + \int d34\, P(1,3) v(3,4) \chi(4,2)$$

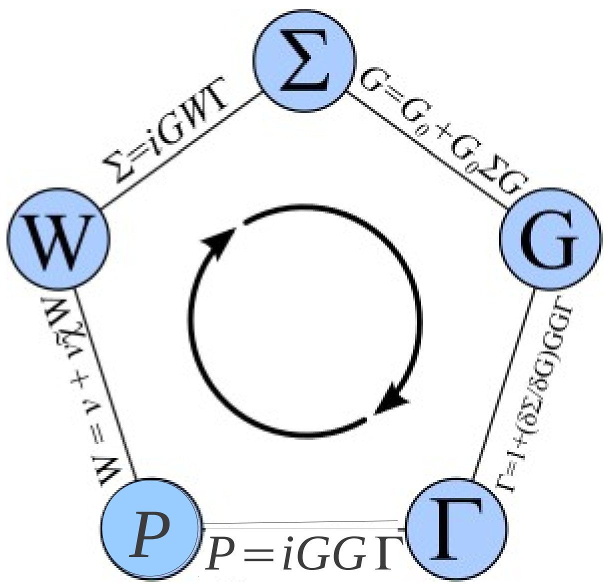
$$L = \ldots + \ldots v L$$

G. Strinati, Rivista del Nuovo Cimento, 11, 1 (1988)

Derivation of the Bethe-Salpeter equation (2)

$$\chi = P + P v \chi$$

$\chi = -i\hbar L$? $P = -i\hbar \bar{L}$ ⇒ $L = \bar{L} + \bar{L} v L$



$$P(1,2) = -i\hbar \int d(34)\, G(1,3)\, G(4,1^+)\, \Gamma(3,4,2)$$

$$\Gamma = 1 + \frac{\delta \Sigma}{\delta G} G G \Gamma \qquad G G \Gamma = G G + G G \frac{\delta \Sigma}{\delta G} G G \Gamma$$

$$\bar{L} = L_0 + L_0 \frac{\delta \Sigma}{\delta G} \bar{L}$$

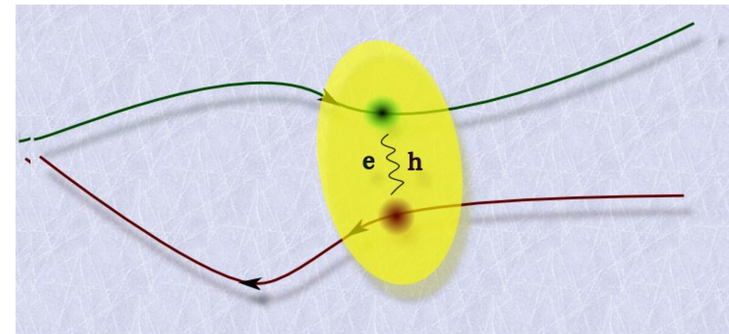
$$L = L_0 + L_0 \left[v + \frac{\delta \Sigma}{\delta G} \right] L$$

Bethe-Salpeter Equation!

Derivation of the Bethe-Salpeter equation (3)

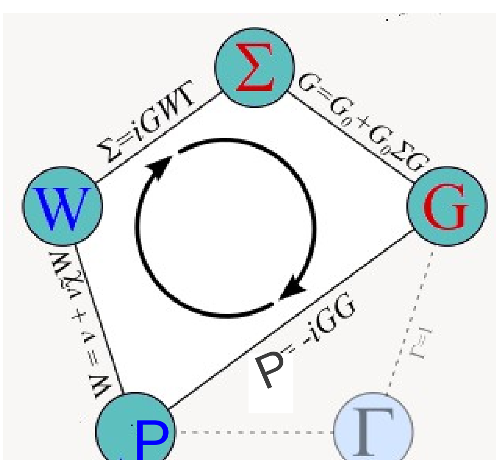
$$L = L_0 + L_0\left[v + \frac{\delta \Sigma}{\delta G}\right] L$$

Bethe-Salpeter Equation!



Screened Coulomb term

$\Sigma^{GW}(1,2) = -iG(1,2)W(2,1)$ => Standard Bethe-Salpeter equation (Time-Dependent Screened Hartree-Fock)



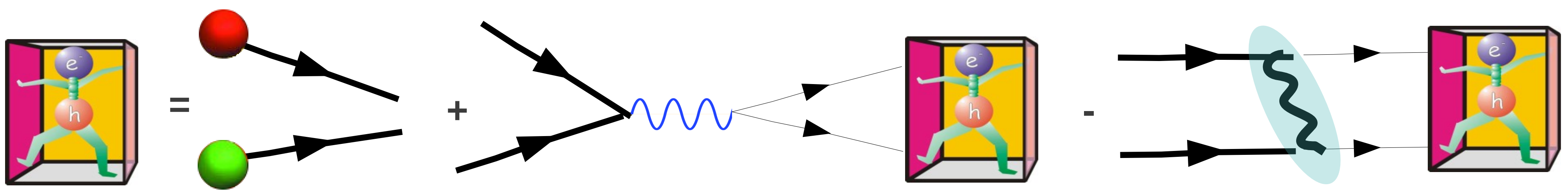
$$L = L_0 + L_0\left[v - \frac{\delta (GW)}{\delta G}\right] L$$

$$L = L_0 + L_0[v - W] L$$

Dynamical effects in the BS equation

$$L = L_0 + L_0[v - W]L$$

$$L(1234) = L_0(1234) +$$
$$+ L_0(1256)[v(57)\delta(56)\delta(78) - W(56)\delta(57)\delta(68)]L(7834)$$

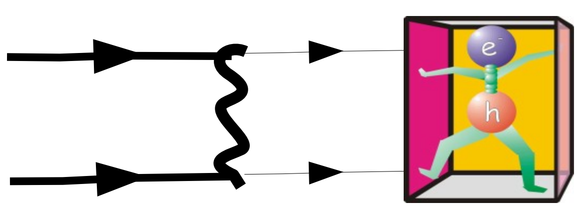


Quasihole and
quasielectron

Intrinsc 4-point equation.
It describes the (coupled) progation of two particles, the electron and the hole !

Retardation effects are neglected

$$W(1,2) = W(\mathbf{r}_1, \mathbf{r}_2)\delta(t_1, t_2)$$

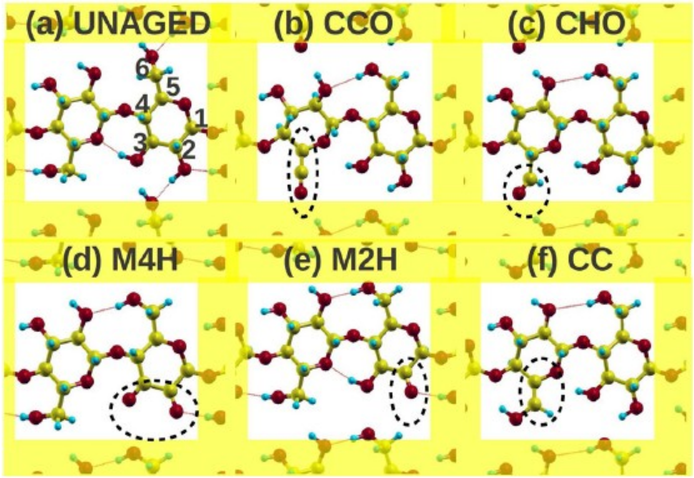


$$L(1,2,3,4) = L(\mathbf{r}_{1,}\mathbf{r}_{2,}\mathbf{r}_{3,}\mathbf{r}_4; t - t_0) = L(1,2,3,4,\omega)$$

Why does paper turn yellow?

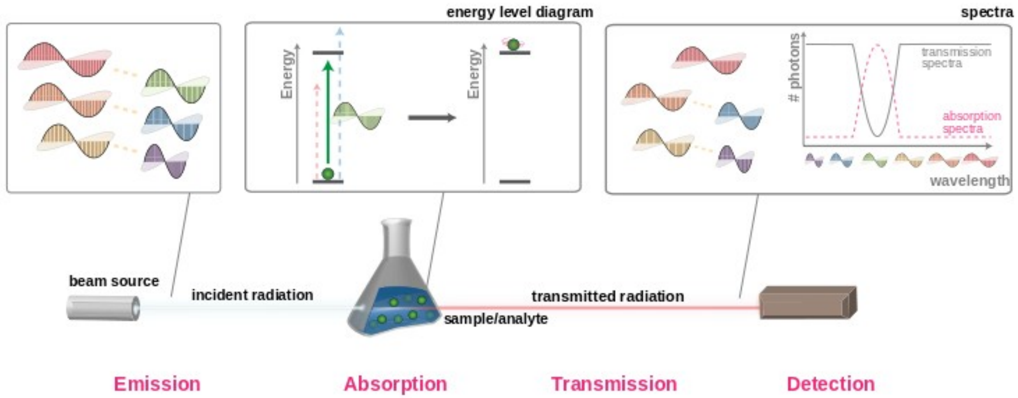
Treasure map

By comparing ultraviolet-visible reflectance spectra of ancient and artificially aged modern papers with *ab-initio* TD-DFT calculations, it was possible to identify and estimate the abundance of **oxidized functional groups acting as chromophores and responsible of paper yellowing.**



A. Mosca Conte et al.,
Phys. Rev. Lett. 108, 158301 (2012)

Conclusions



$$\epsilon^{-1}(\vec{r}\,t,\vec{r}\,'t') = \frac{\delta V_{tot}(\vec{r}\,t)}{\delta V_{ext}(\vec{r}\,t)}$$

$$= \delta(\vec{r}-\vec{r}\,') + \int dt''\, d\vec{r}\,''\, v(\vec{r}-\vec{r}\,'')\,\underline{\chi(\vec{r}\,'',\vec{r}\,')}$$

Thank you for your attention