Theoretical approaches to the many-body electronic problem: an introduction

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Palaiseau Theoretical Spectroscopy Group

Theoretical approaches to the many-body electronic problem: an introduction

→ Theoretical Spectroscopy: aims and observations

→ Theoretical Spectroscopy: tools

→ Interaction leads to........... coupling

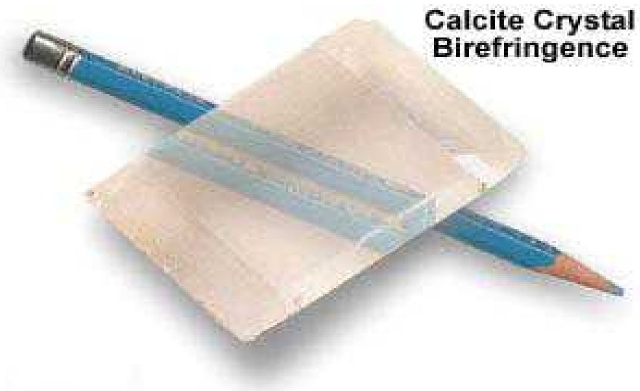
→ Interaction leads to........... decay

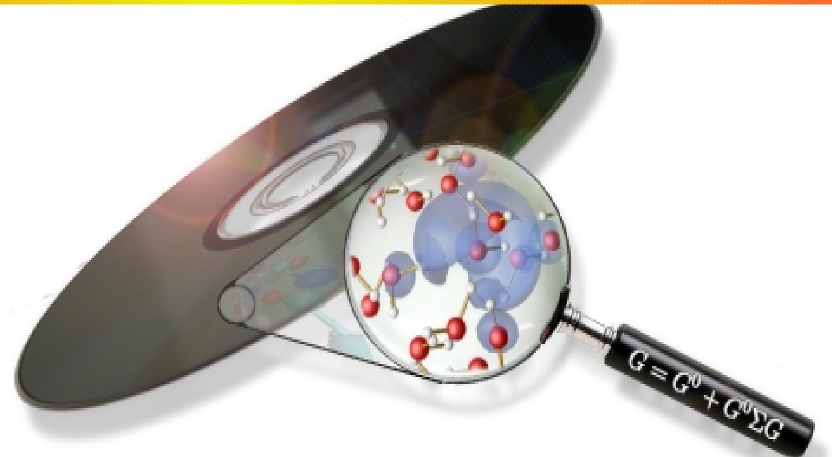
→ Interaction leads to........... additional excitations

→ Electron-hole correlation

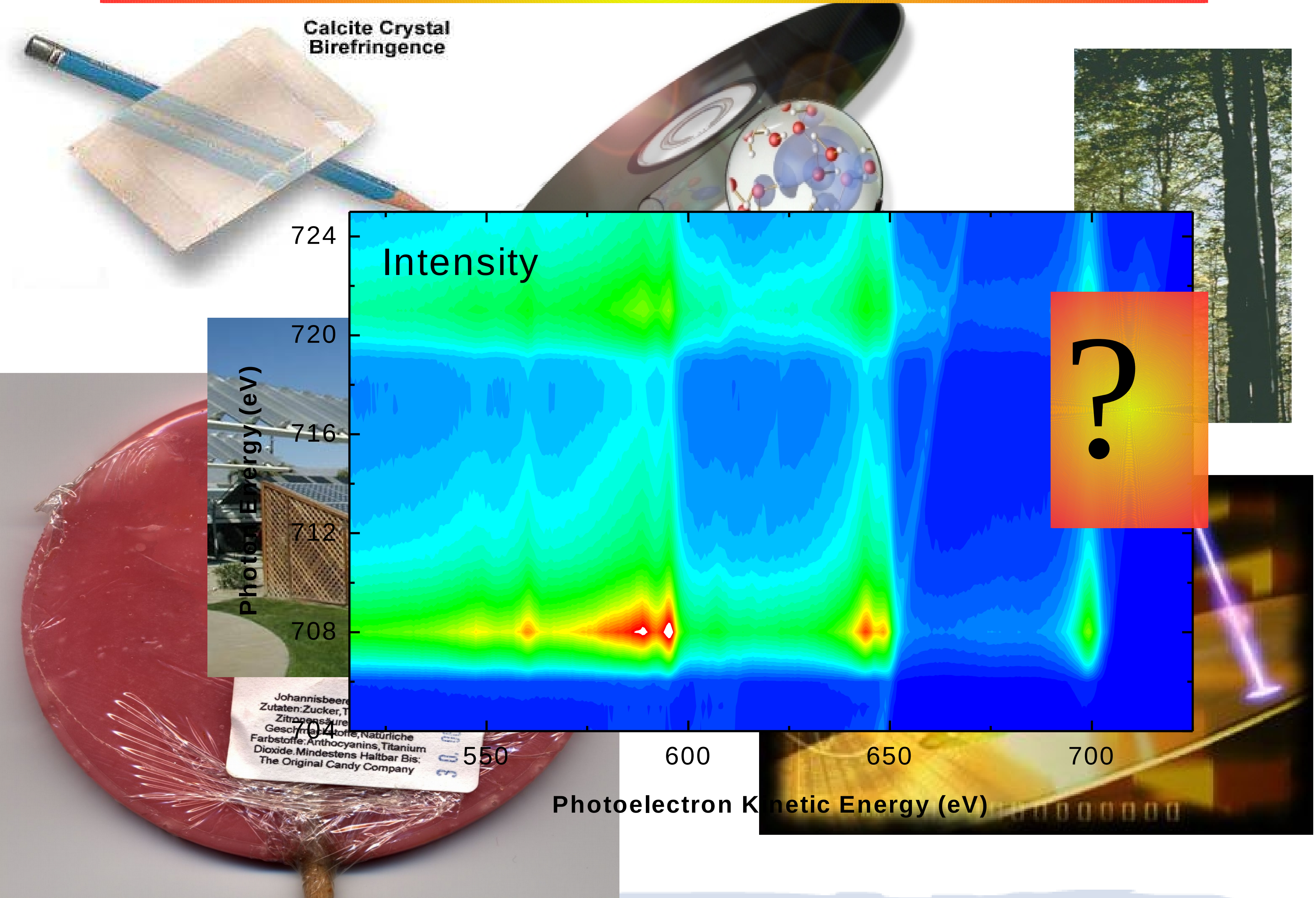
→ Outlook

→ Theoretical Spectroscopy: aims and observations





→ Theoretical Spectroscopy: aims and observations



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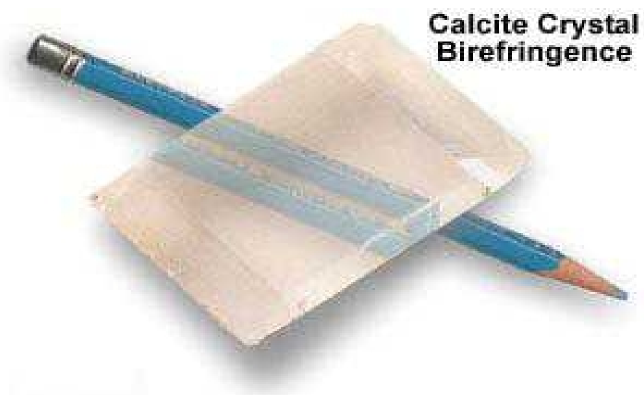
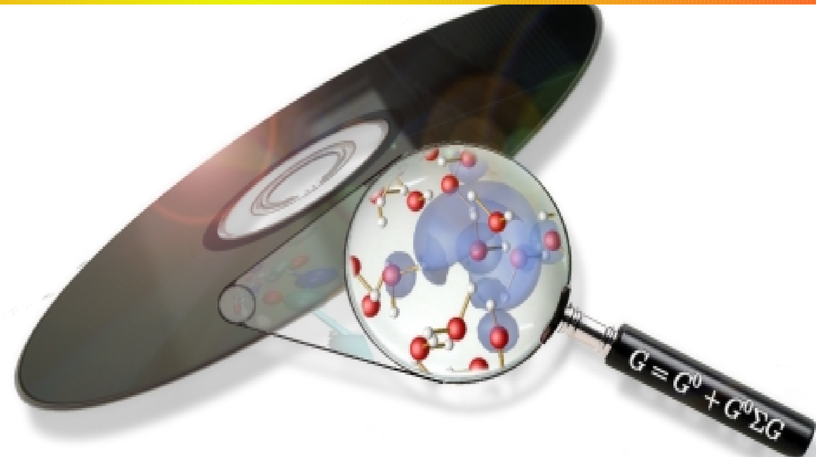
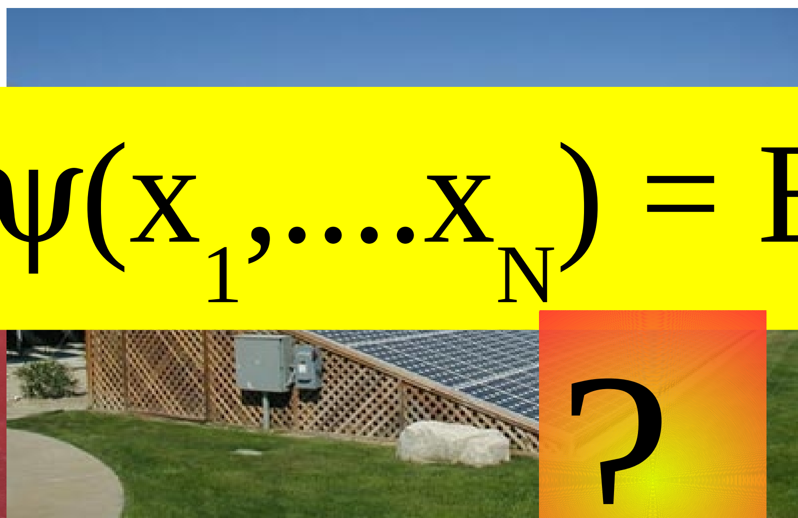
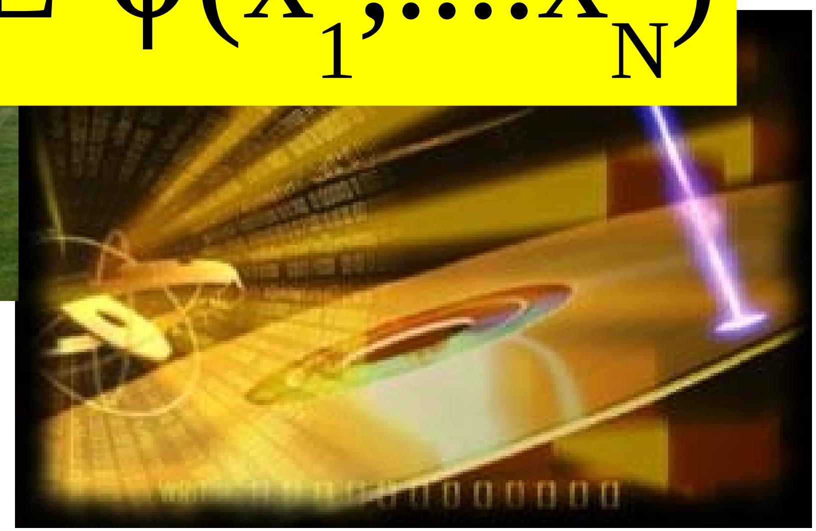




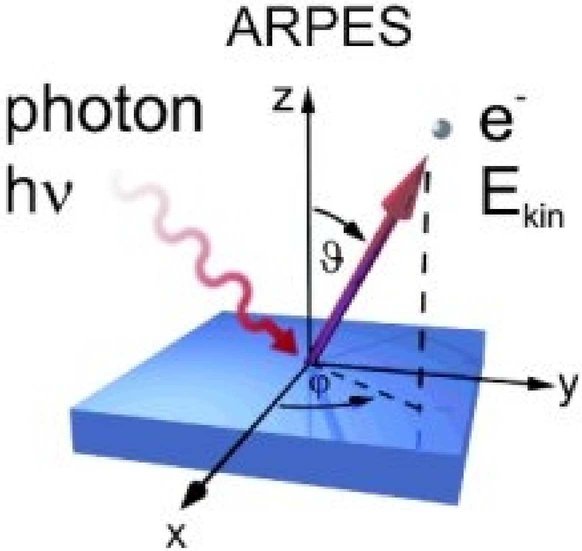


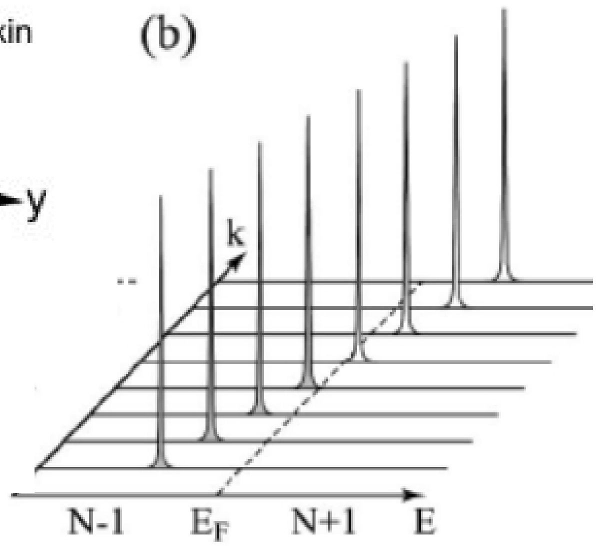


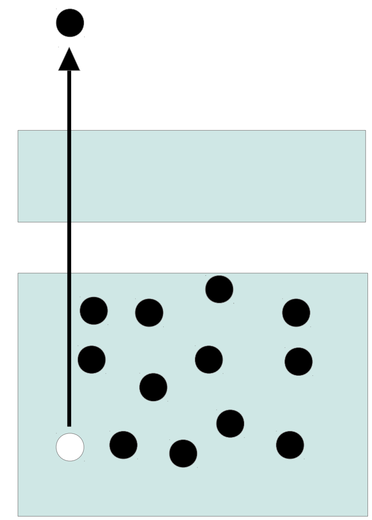
$$H\psi(x_1,\ldots x_N) = E\,\psi(x_1,\ldots x_N)$$

?

→ Theoretical Spectroscopy: aims... and observations!





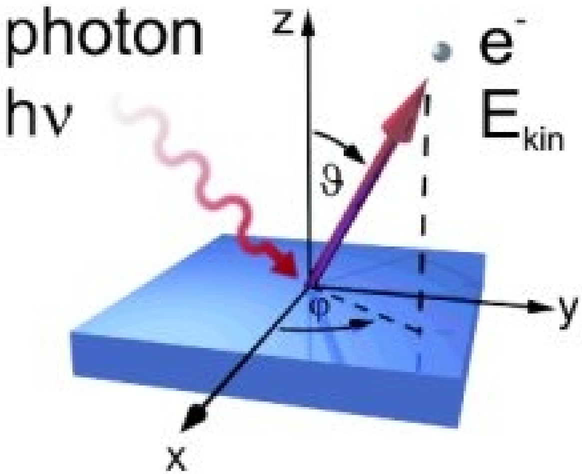


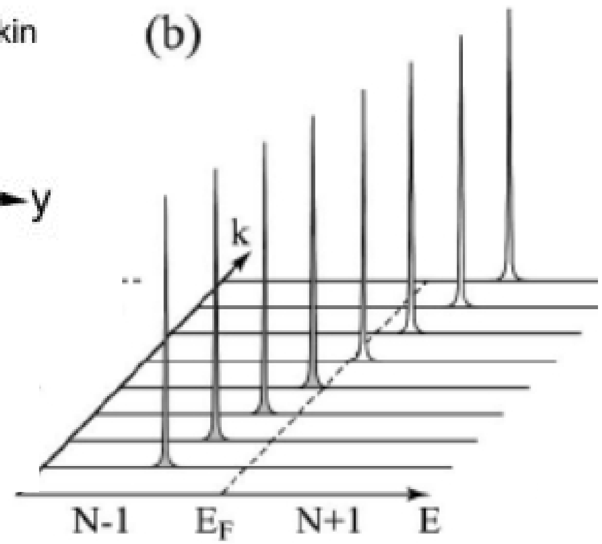
From Damascelli et al., RMP 75, 473 (2003)
and http://www.ieap.uni-kiel.de/surface/ag-kipp/arpes/arpes.htm

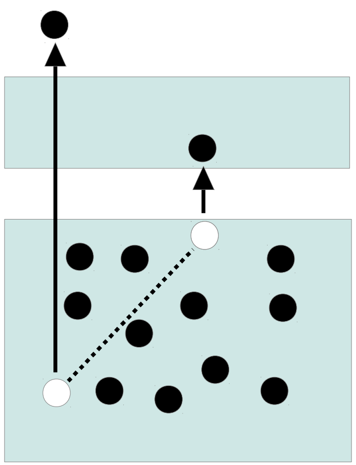
+......

→ Theoretical Spectroscopy: aims... and observations!

ARPES







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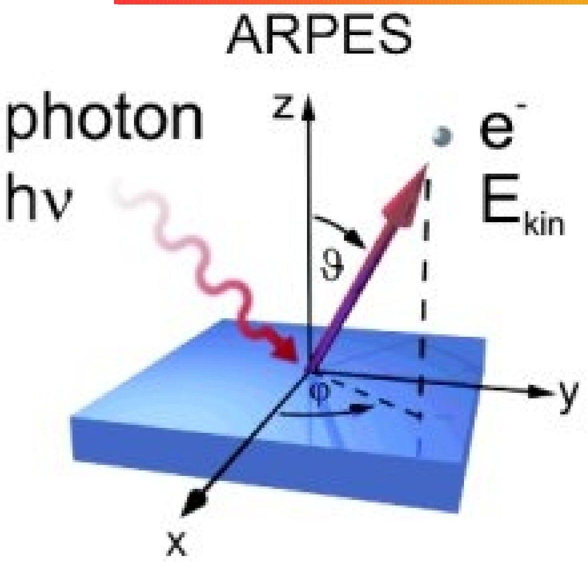
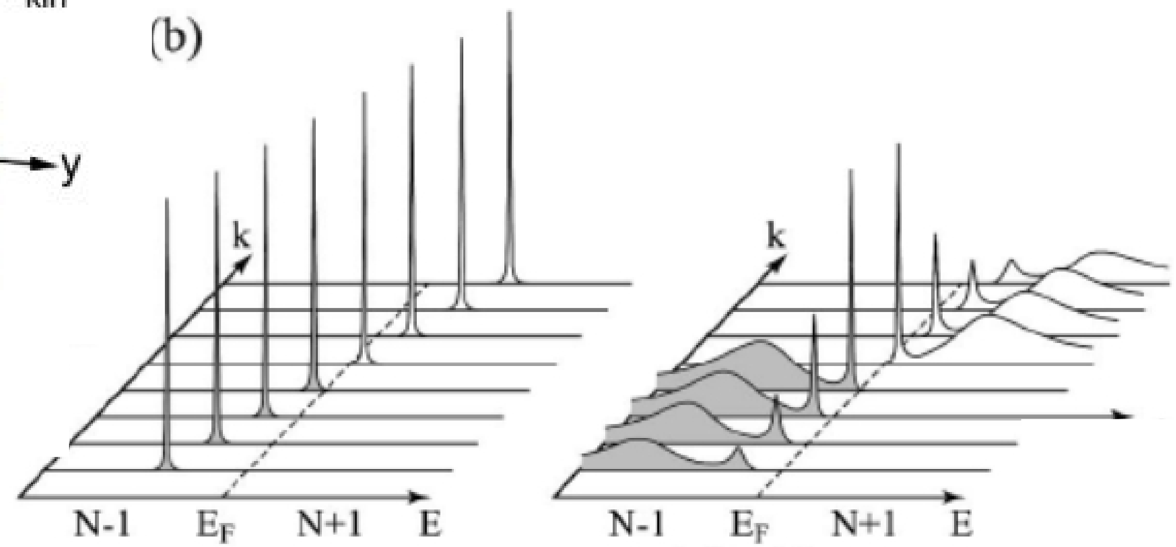
+......

→ Theoretical Spectroscopy: aims... and observations!





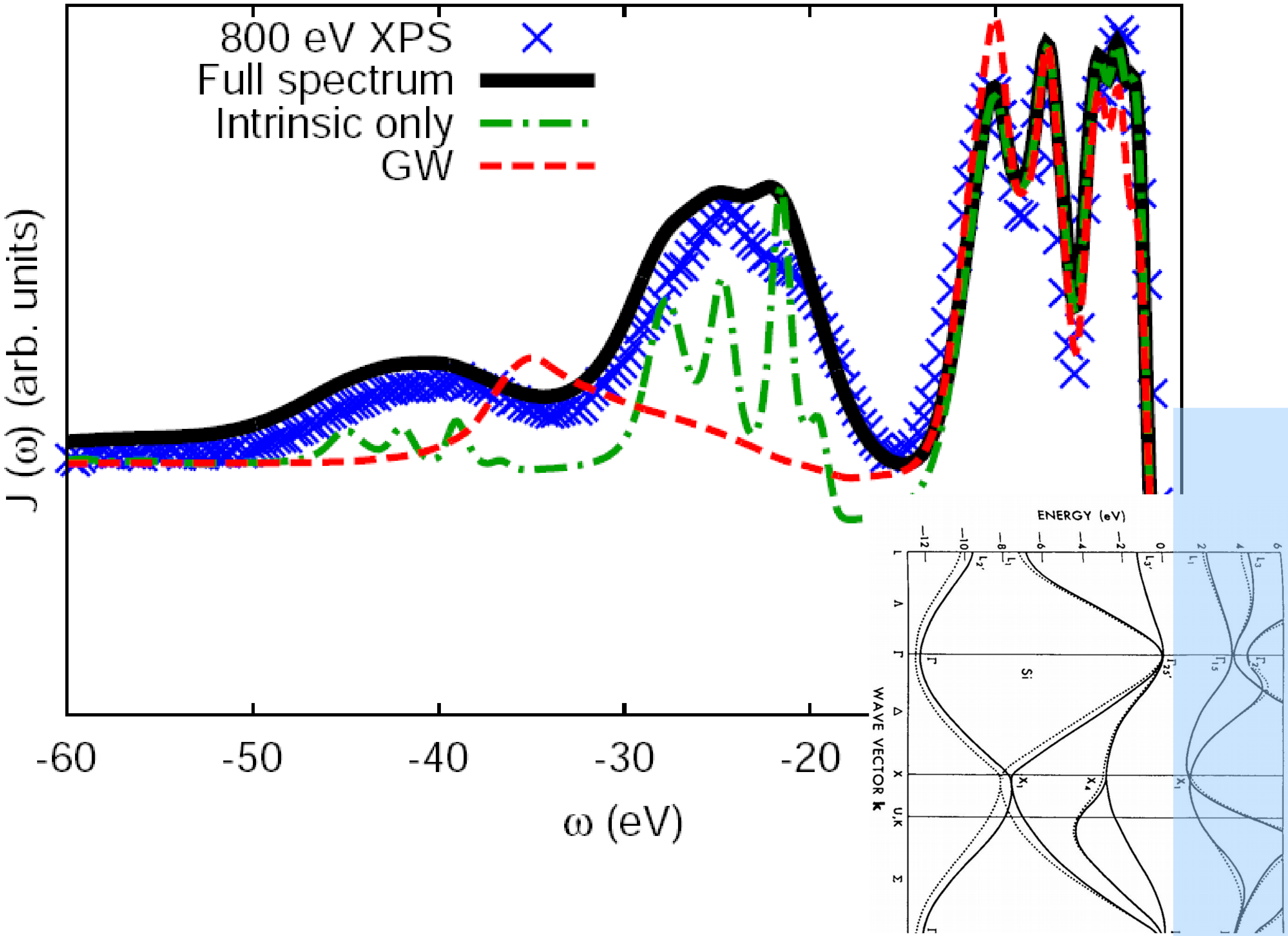
From Damascelli et al., RMP 75, 473 (2003)
and http://www.ieap.uni-kiel.de/surface/ag-kipp/arpes/arpes.htm

This is not what we expect (in an i.p. picture)!

+......

→ ARPES of simple bulk silicon:

Obviously far from an i.p. picture!



Cohen and Chelikowsky: "Electronic Structure and Optical Properties of Semiconductors" Solid-State Sciences 75, Springer-Verlag 1988)

Exp.: F. Sirotti et al., TEMPO beamline SOLEIL

→ Theoretical Spectroscopy: tools

Calculate only what you want,.....so that you can understand!

$$H\psi_n(x_1,....x_N) = E_n\ \psi_n(x_1,....x_N)$$

Want: → total energy E_0

→ expectation values like

* density
* spectral functions
* dielectric function

$$V_{tot}(\omega) = \varepsilon^{-1}(\omega) V_{ext}(\omega)$$

Do not want: → *all many-body* $\psi_n(x_1,....x_N)$

→ Theoretical Spectroscopy: tools

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Want: → total energy E_0

→ expectation values like

* density
* spectral functions
* dielectric function

Small systems: CI

Larger: Stochastic (QMC)

$$V_{tot}(\omega) = \varepsilon^{-1}(\omega)V_{ext}(\omega)$$

Do not want: → *all many-body* $\psi_n(x_1,....x_N)$

→ Theoretical Spectroscopy: tools

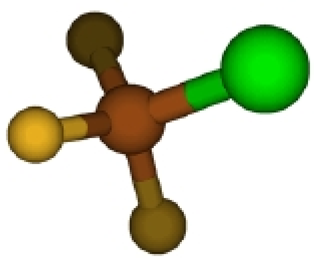
Effective quantities in an effective world

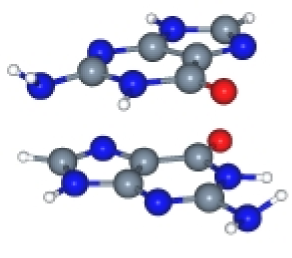
A practical example, simulate zero gravity

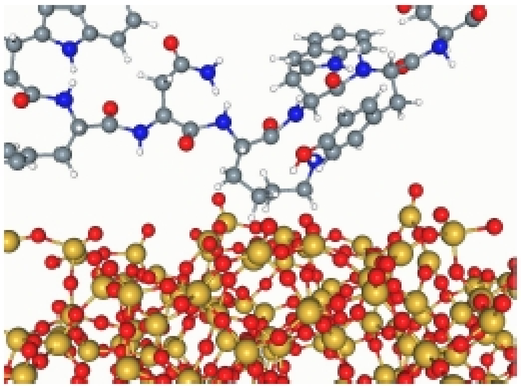
→ The effective quantities:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N, t) \quad \longrightarrow \quad G(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) \quad \longrightarrow \quad \rho(\mathbf{r}, t)$$

CI, QMC — GF methods (GW, BSE) — DF







Importance of the density

Example: atom of Nitrogen (7 electron)

$$\Psi(\mathbf{r}_1, .., \mathbf{r}_7) \quad \text{21 coordinates}$$

$$10 \text{ entries/coordinate} \Rightarrow 10^{21} \text{ entries}$$
$$8 \text{ bytes/entry} \Rightarrow 8 \cdot 10^{21} \text{ bytes}$$
$$5 \cdot 10^{9} \text{ bytes/DVD} \Rightarrow 10^{12} \text{ DVDs}$$

Importance of non-interacting

The Kohn-Sham one-particle equations

$$H_i(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i(\mathbf{r})\psi_i(\mathbf{r})$$

→ The effective world:

$$\left(-\frac{1}{2}\boldsymbol{\nabla}^2 + v_{\text{eff}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

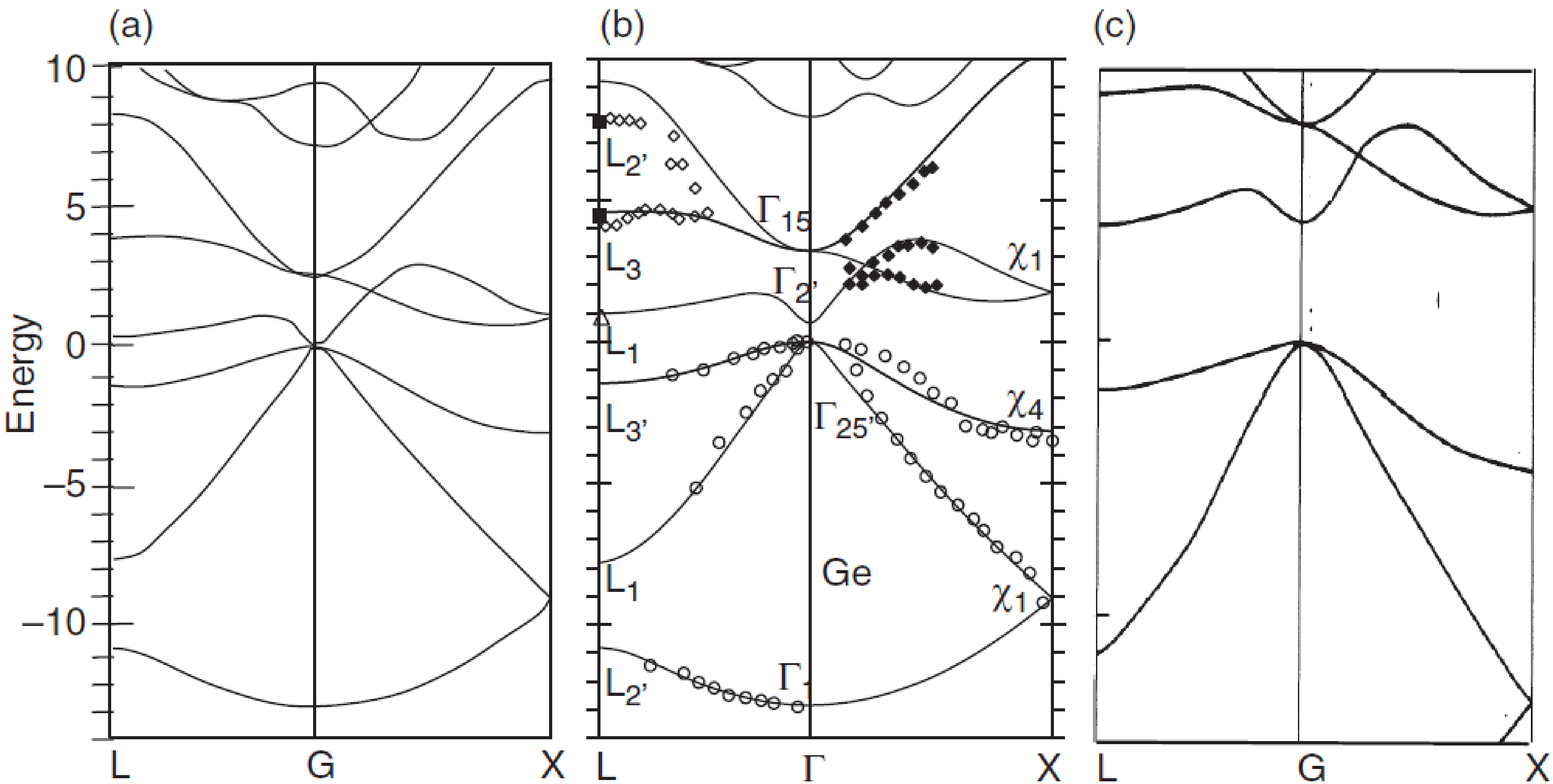
LDA or so

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}([n],\mathbf{r}) + v_{\text{xc}}([n],\mathbf{r})$$

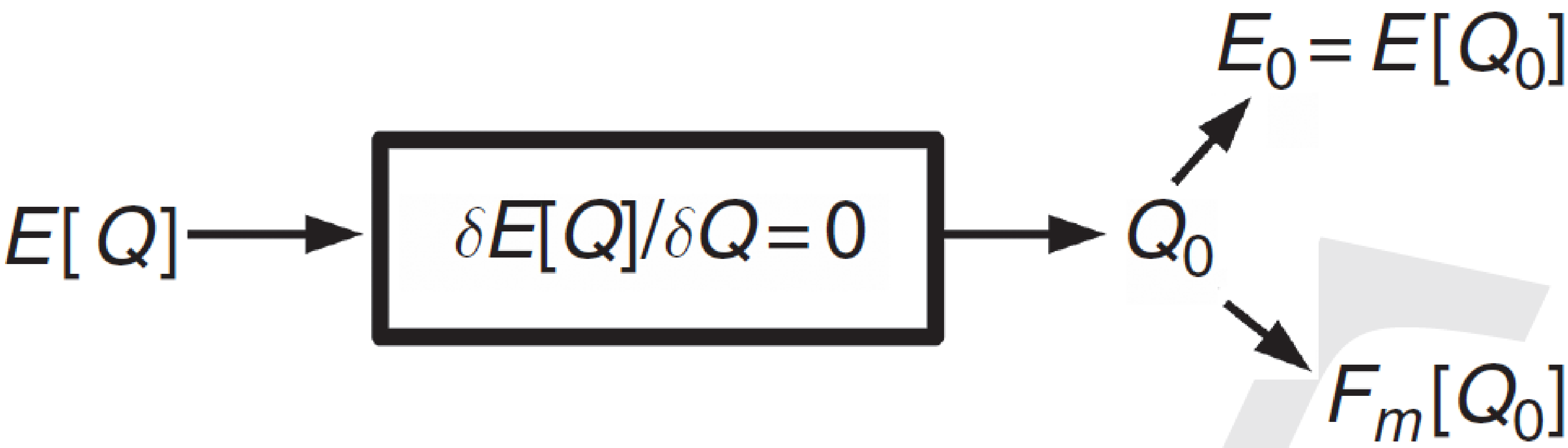
Designed for density and top valence
NOT for bandgaps, for example!!!

Hohenberg-Kohn-Sham

Band structure of germanium



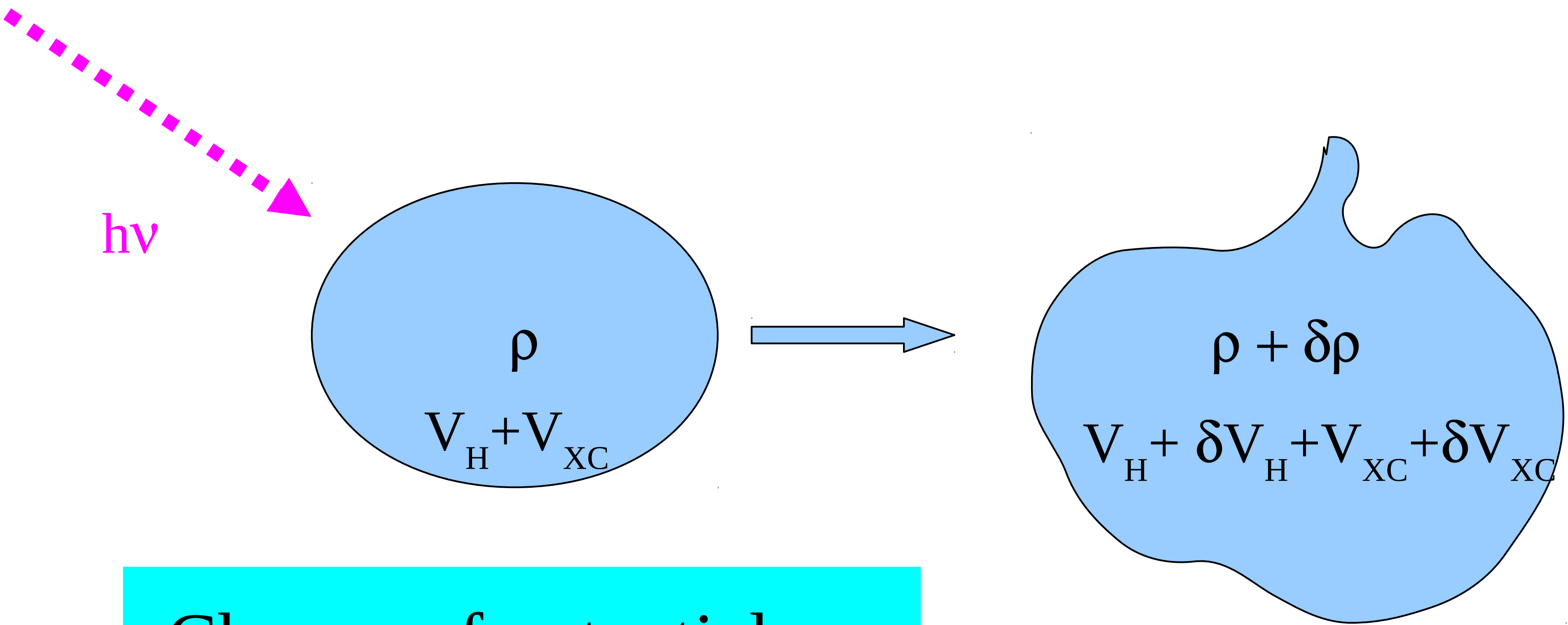
Rohlfing et al., PRB 48, 17791 (1993)
A. Svane, PRB 35, 5496 (1987)



DFT:

$$E[n] \rightarrow \delta E / \delta n = 0 \rightarrow n_0 \rightarrow E_0 = E[n_0]$$
$$\rightarrow F_0 = F[n_0] \text{ ???}$$

(TD)DFT point of view: moving density

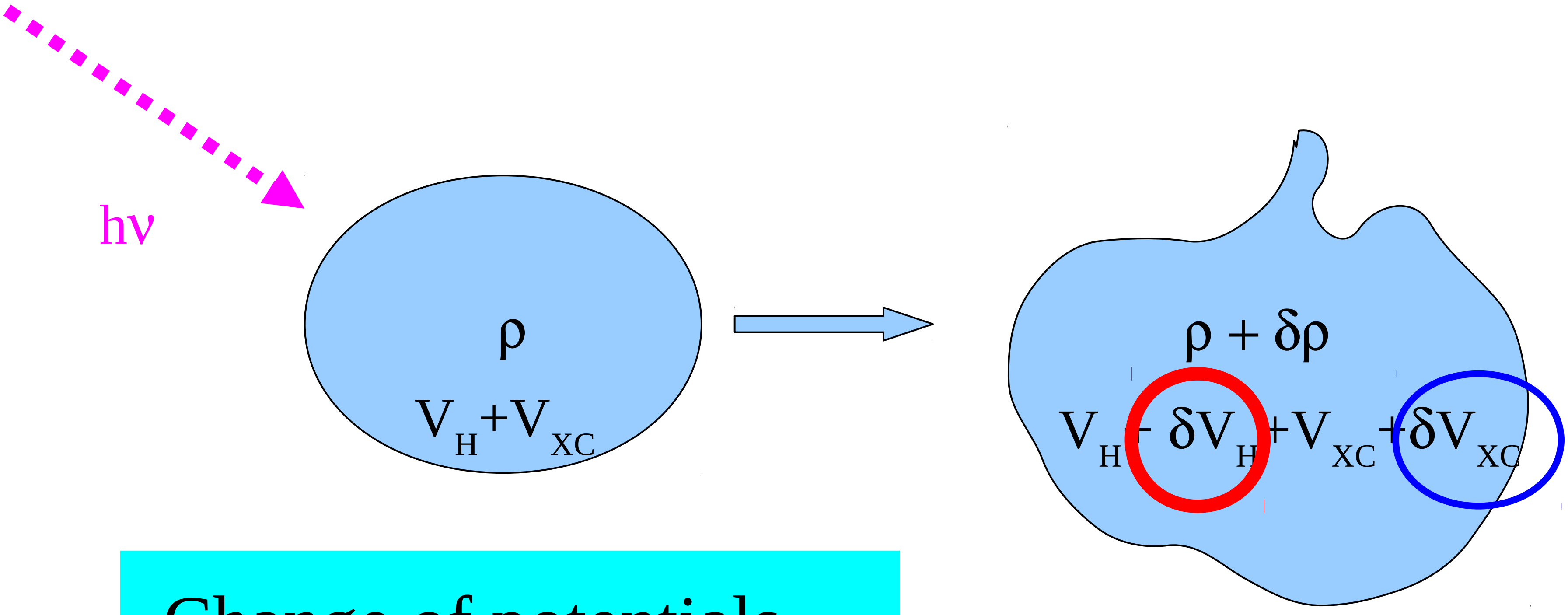


Change of potentials

$$V_{tot}(\omega) = \varepsilon^{-1}(\omega) V_{ext}(\omega)$$

Excitation ?

→ Induced potentials



Change of potentials

RPA

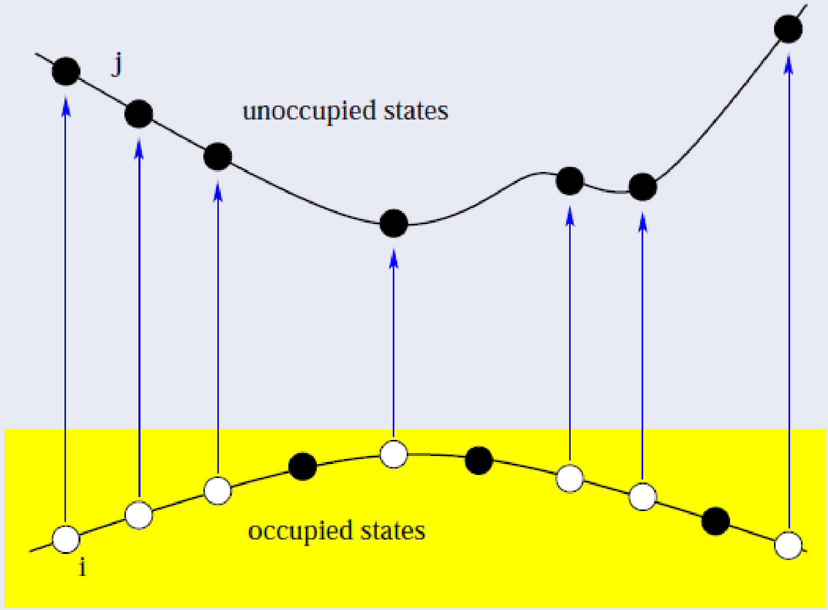
TDLDA, ….

Polarizability

interacting system $\delta n = \chi \delta V_{ext}$

non-interacting system $\delta n_{n-i} = \chi^0 \delta V_{tot}$

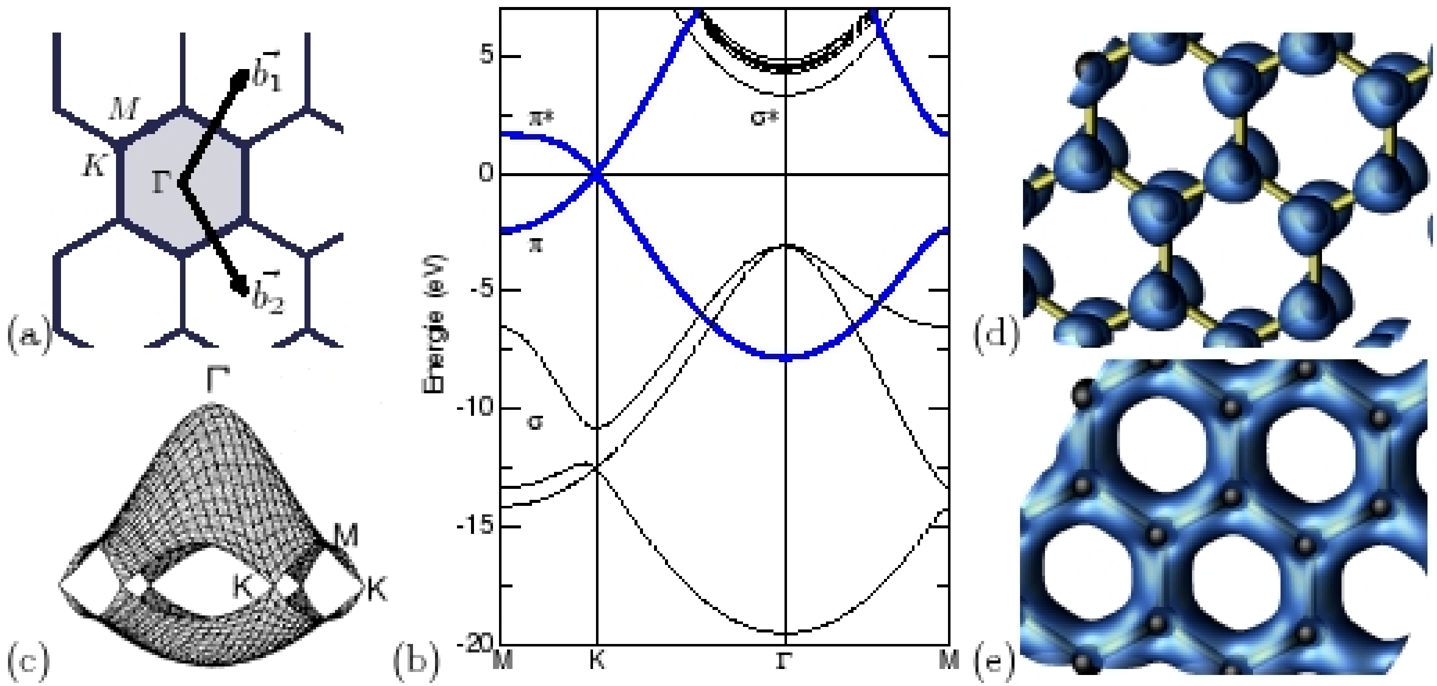
$$\chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega - (\epsilon_i - \epsilon_j)}$$



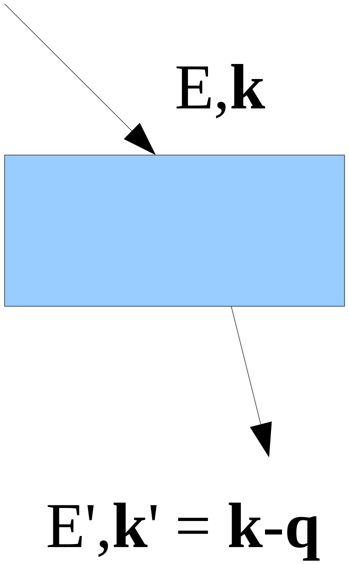
Polarizability χ in TDDFT

1. DFT ground-state calc. $\rightarrow \quad \phi_i, \epsilon_i \qquad [V_{xc}]$
2. $\phi_i, \epsilon_i \quad \rightarrow \quad \chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega-(\epsilon_i-\epsilon_j)}$
3. $\left.\begin{array}{l} \frac{\delta V_H}{\delta n} = v \\ \frac{\delta V_{xc}}{\delta n} = f_{xc} \end{array}\right\}$ variation of the potentials
4. $\chi = \chi^0 + \chi^0 (v + f_{xc}) \chi$

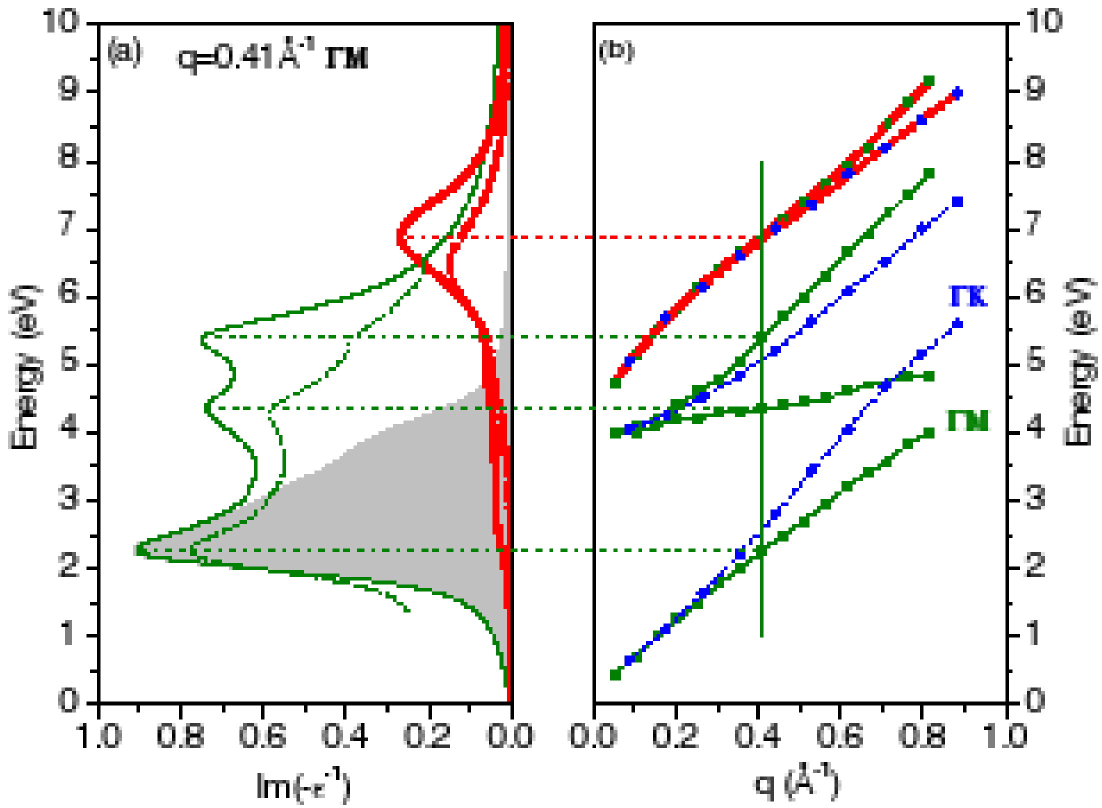
Graphene, π plasmon



R. Hambach, Diplomarbeit and PhD thesis

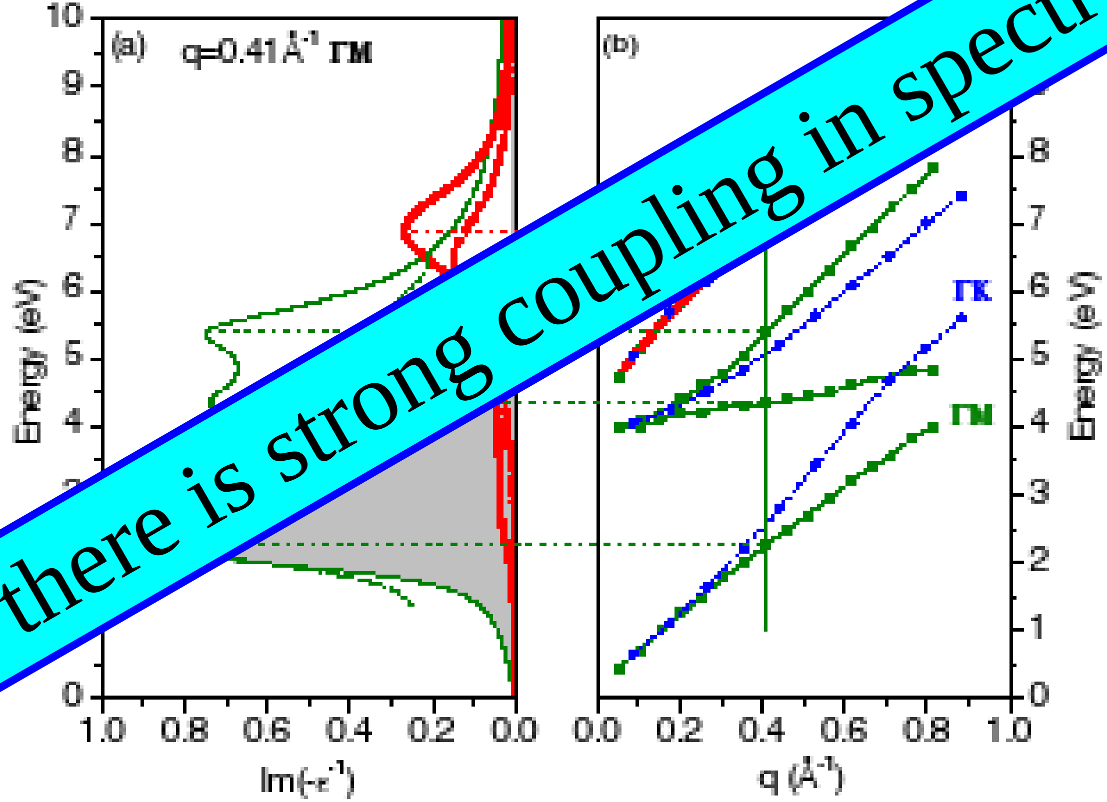


Graphene, π plasmon



C. Kramberger et al., PRL 100, 196803 (2008)

Graphene, π plasmon

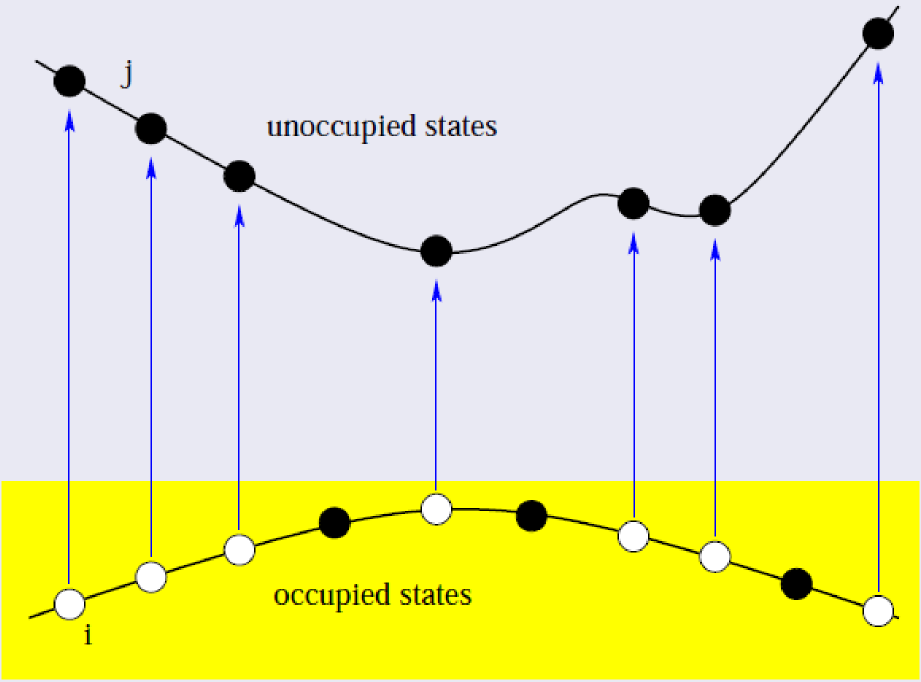


Usually there is strong coupling in spectroscopy

C. Kramberger et al., PRL 100, 196803 (2008)

Reciprocal space

$$\chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) = \sum_{vc\mathbf{k}} \frac{\left\langle \phi_{v\mathbf{k}} \middle| e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} \middle| \phi^*_{c\mathbf{k}+\mathbf{q}} \right\rangle \left\langle \phi_{c\mathbf{k}+\mathbf{q}} \middle| e^{-\imath(\mathbf{q}+\mathbf{G}')\mathbf{r}'} \middle| \phi^*_{v\mathbf{k}} \right\rangle}{\omega - \left(\epsilon_{c\mathbf{k}+\mathbf{q}} - \epsilon_{v\mathbf{k}}\right) + \imath\eta}$$



Reciprocal space

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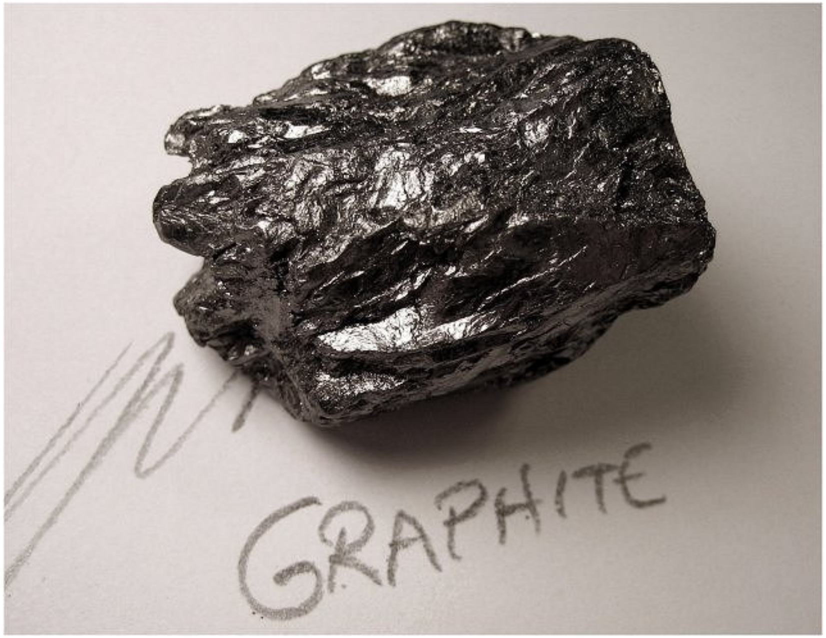
$$\chi_{\mathbf{GG}'}(\mathbf{q},\omega) = \chi^0 + \chi^0 \left(v + f_{xc}\right) \chi$$

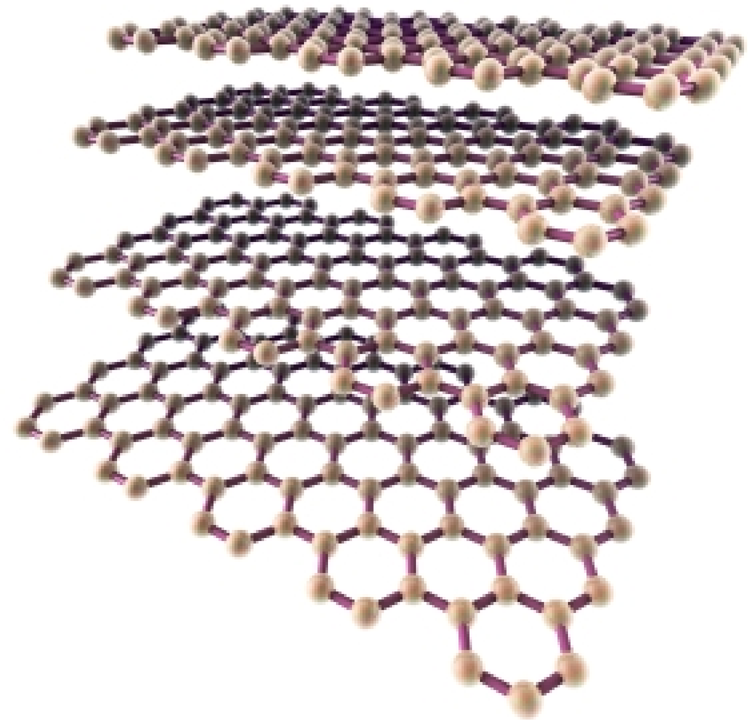
$$\varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega) = \delta_{\mathbf{GG}'} + v_{\mathbf{G}}(\mathbf{q}) \chi_{\mathbf{GG}'}(\mathbf{q},\omega)$$

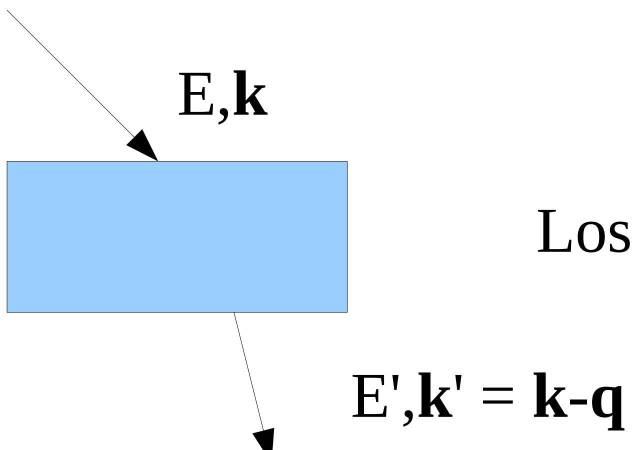
GG_1

G_1G_2

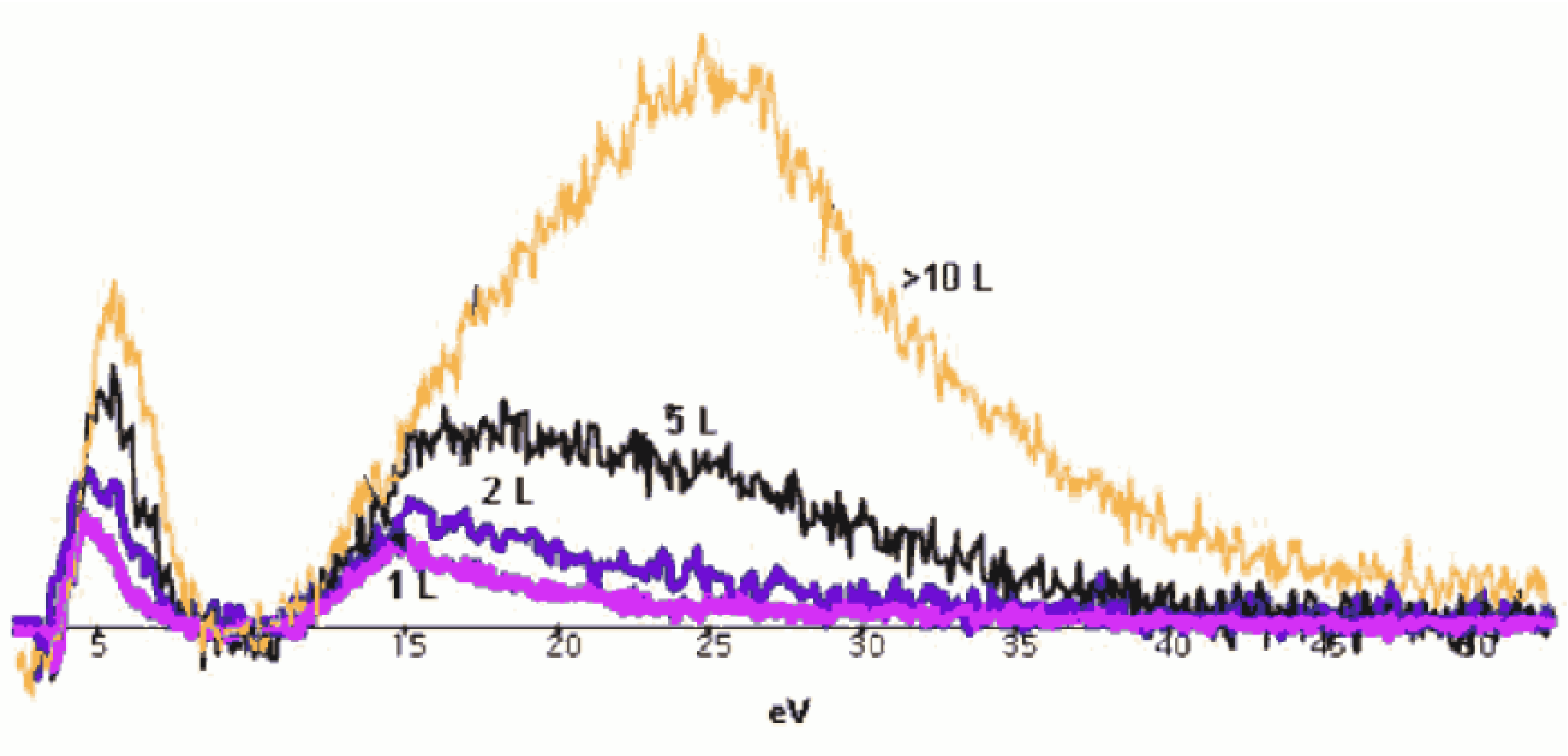
→ Interaction leads to........... coupling





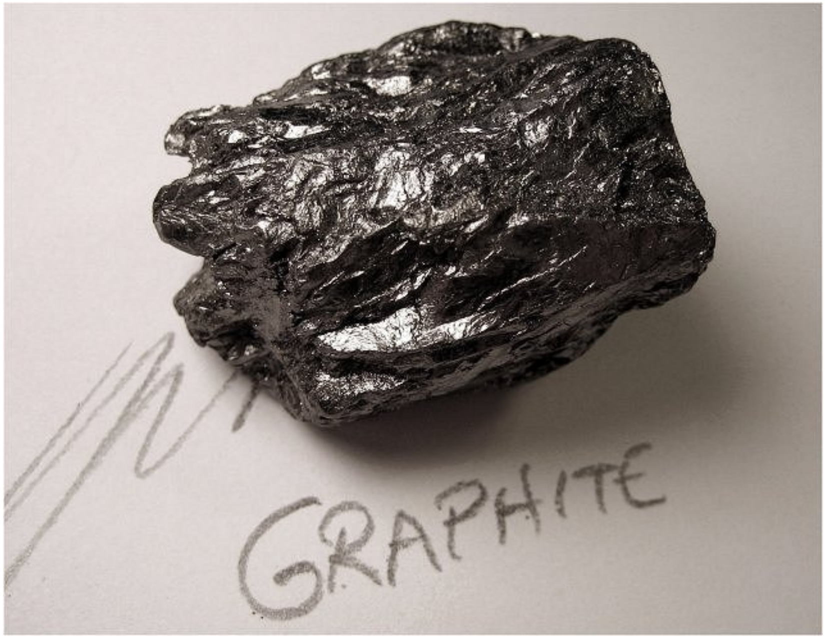


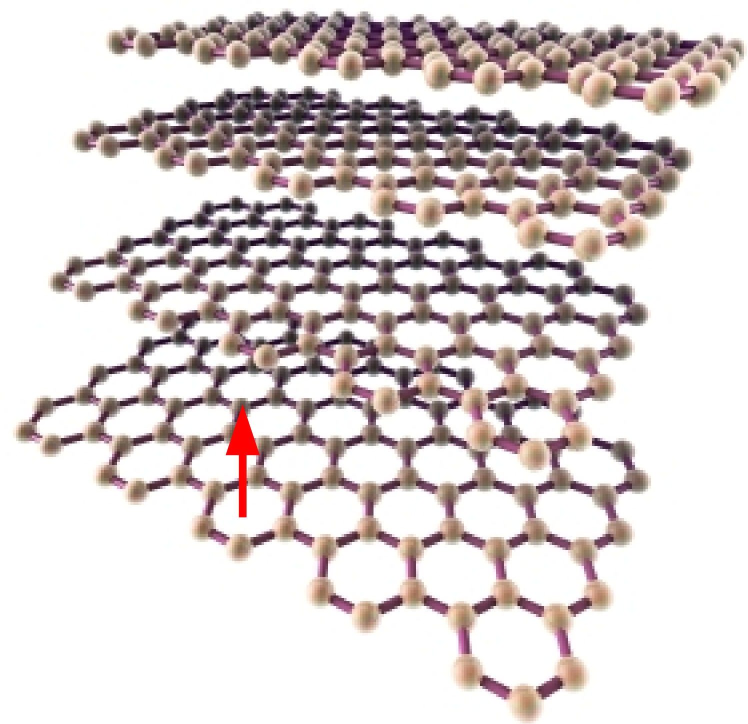
Loss spectroscopy



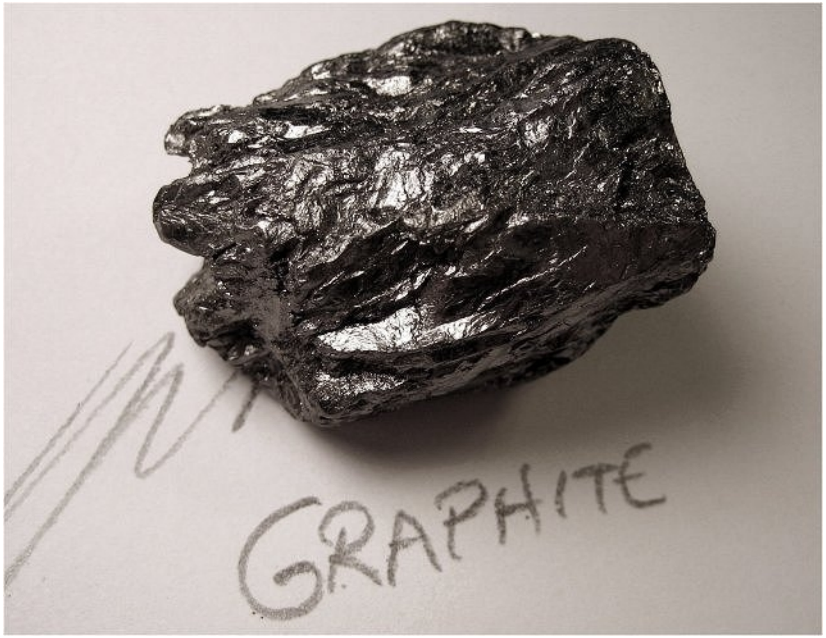
Exp: Eberlein et al., Phys. Rev. B 77, 233406 (2008)

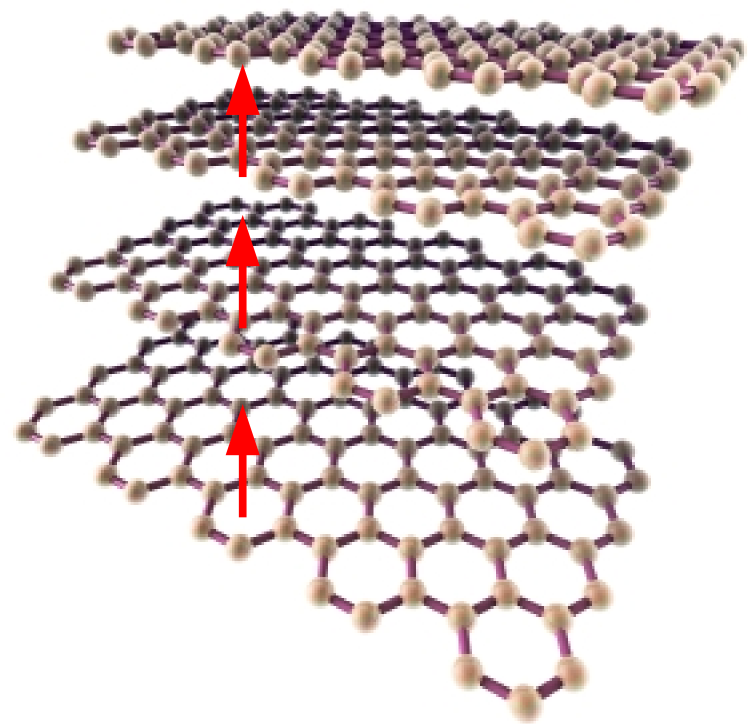
→ Interaction leads to........... coupling





→ Interaction leads to.......... coupling





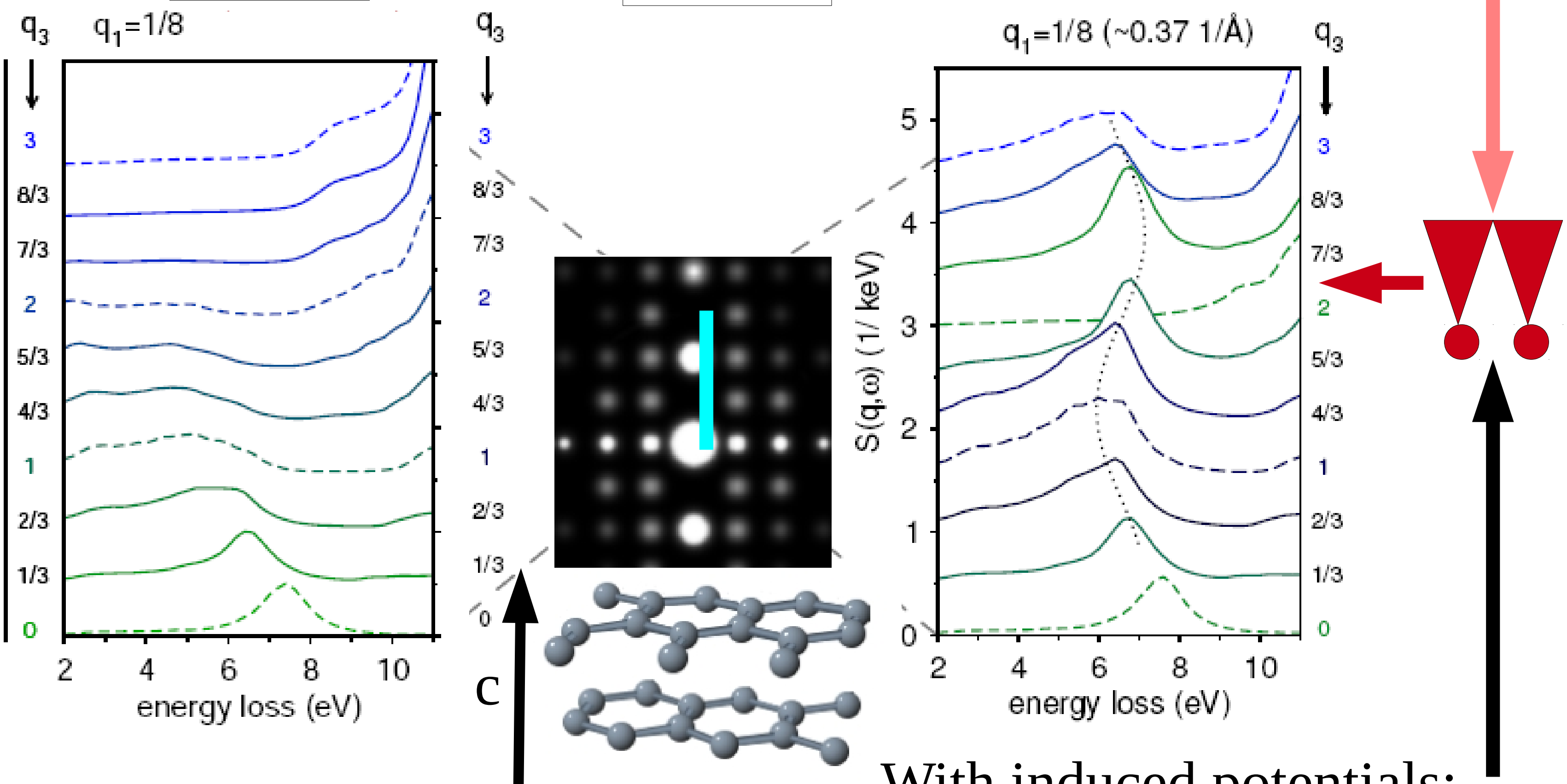
Why study this? * Unexpected effects!
* Guideline for experiments

Close to Bragg point

inelastic

elastic

inelastic

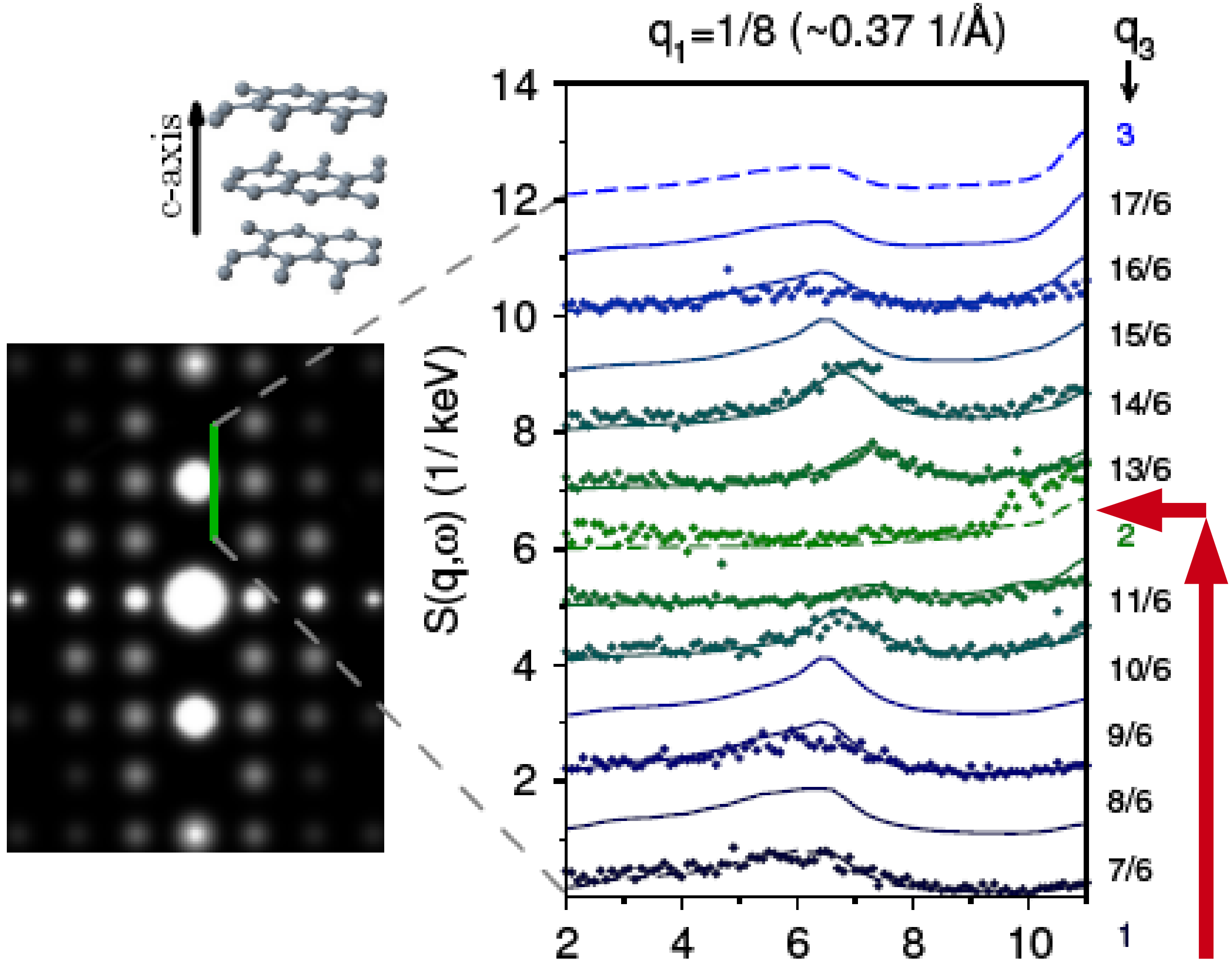


Independent particles

With induced potentials:
Induced modes

Ralf Hambach et al., Phys. Rev. Lett. **101**, 266406 (2008)

Experimental verification, N. Hiraoka et al., Spring8 Taiwan/Japan

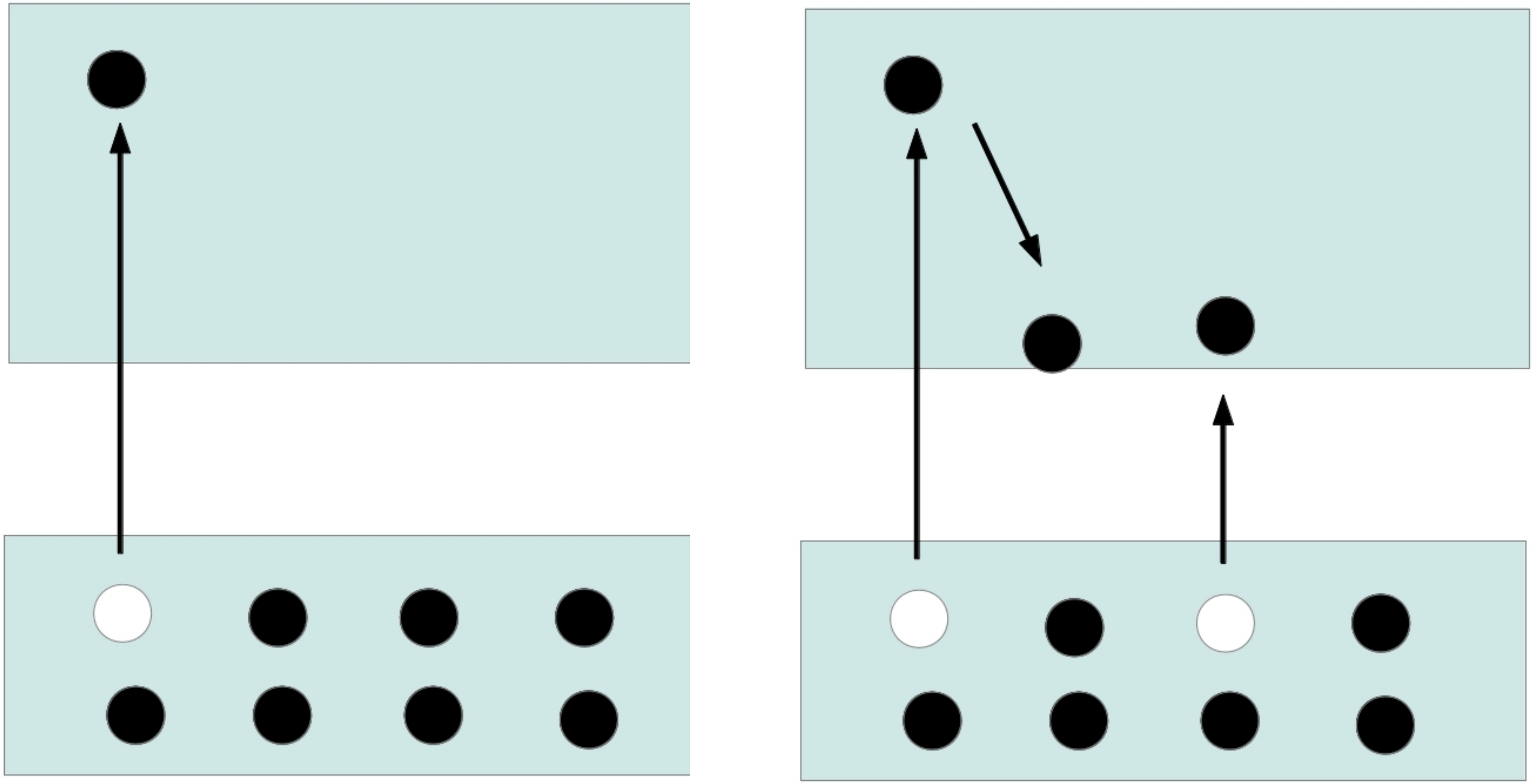


Strong changes close to Bragg reflex!

Ralf Hambach et al., Phys. Rev. Lett. **101**, 266406 (2008)

→ Interaction leads to.......... decay

Why study this?   * Closer to experiment
* Example carrier lifetime



Reciprocal space

$$\chi^0_{\mathbf{GG}'}(\mathbf{q},\omega) = \sum_{vc\mathbf{k}} \frac{\langle \phi_{v\mathbf{k}} | e^{\imath(\mathbf{q}+\mathbf{G})\mathbf{r}} | \phi^*_{c\mathbf{k}+\mathbf{q}} \rangle \langle \phi_{c\mathbf{k}+\mathbf{q}} | e^{-\imath(\mathbf{q}+\mathbf{G}')\mathbf{r}'} | \phi^*_{v\mathbf{k}} \rangle}{\omega - (\epsilon_{c\mathbf{k}+\mathbf{q}} - \epsilon_{v\mathbf{k}}) + \imath\eta}$$

$$\chi_{\mathbf{GG}'}(\mathbf{q},\omega) = \chi^0 + \chi^0 (v + f_{xc})\,\chi$$

$$\varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega) = \delta_{\mathbf{GG}'} + v_{\mathbf{G}}(\mathbf{q})\chi_{\mathbf{GG}'}(\mathbf{q},\omega)$$

GG_1

G_1G_2

(ω)

Dynamic coupling difficult in TDDFT

→ Theoretical Spectroscopy: tools

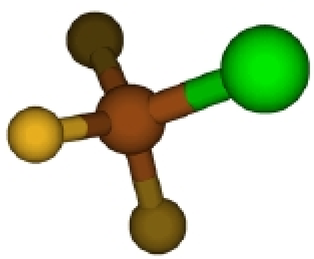
Effective quantities in an effective world

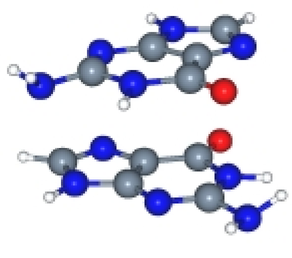
How do we get this one?

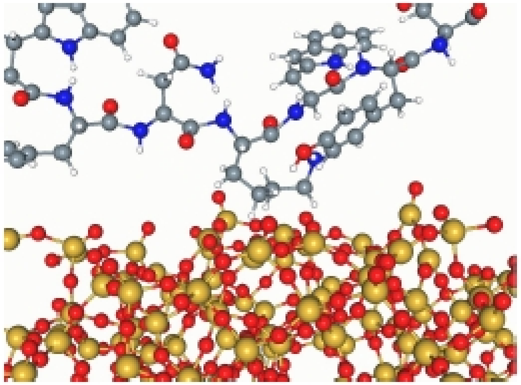
→ The effective quantities:

$\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N, t) \quad \longrightarrow \quad G(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) \quad \longrightarrow \quad \rho(\mathbf{r}, t)$

CI, QMC — GF methods (GW, BSE) — DF

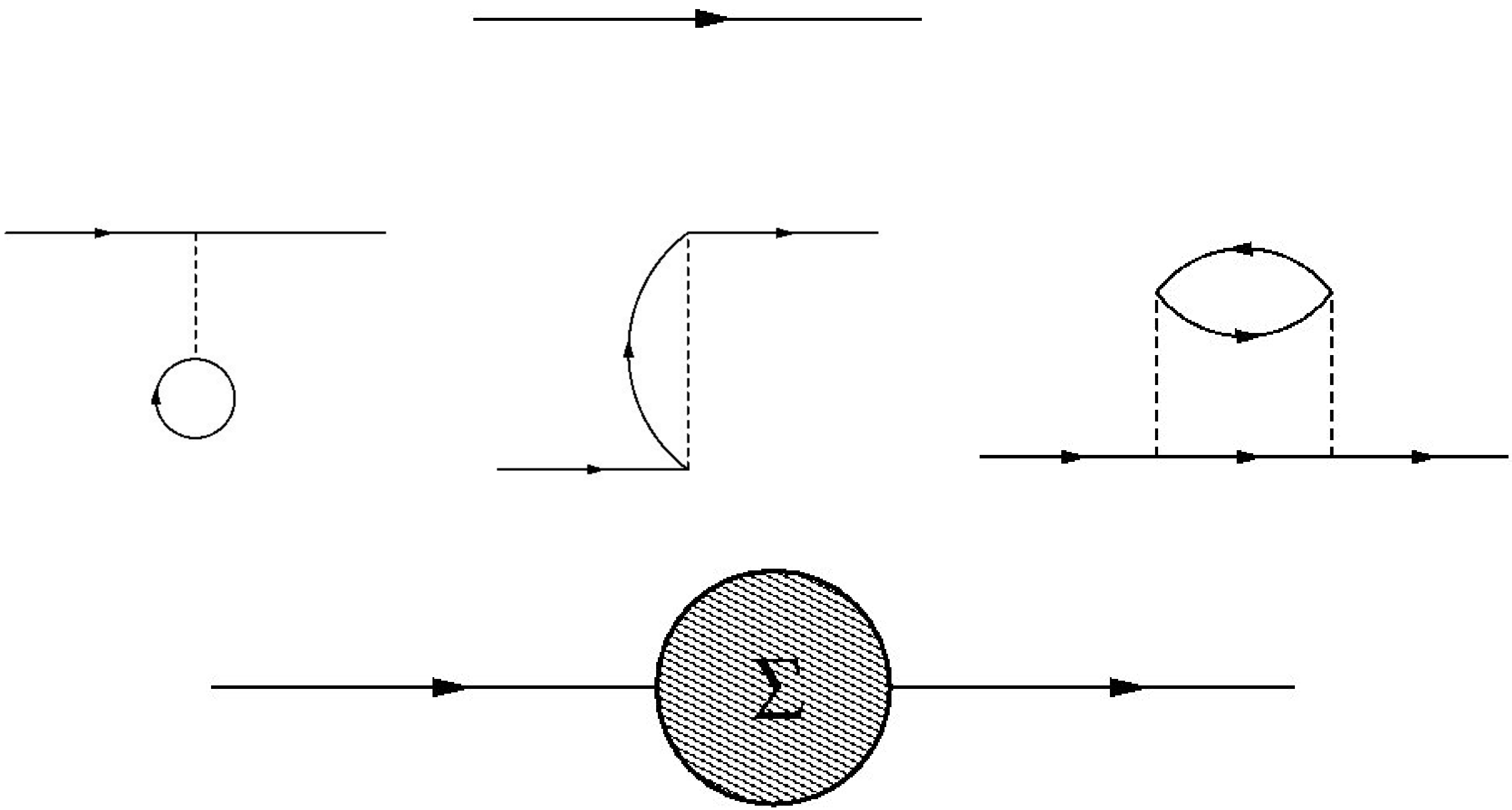






→ Propagators

$\mathcal{G}(1,2) = -i \langle T[\psi(1)\psi^{\dagger}(2)]\rangle \qquad 1=(r_1,\sigma_1,t_1)$



Dyson equation: $\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0\, \Sigma\, \mathcal{G}$

→ The effective world:

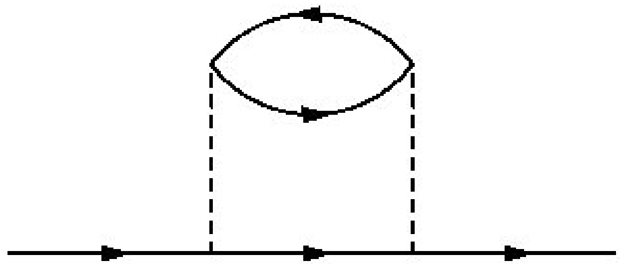
$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$v_{\mathrm{eff}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{H}}([n],\mathbf{r}) + v_{\mathrm{xc}}([n],\mathbf{r})$$

$$\Sigma(r,r',\varepsilon_i)$$

Designed for electron addition and removal spectra (bandstructure, lifetimes, satellites,....,density,...)

Other: DMFT $\Sigma_{ll}(\omega)$

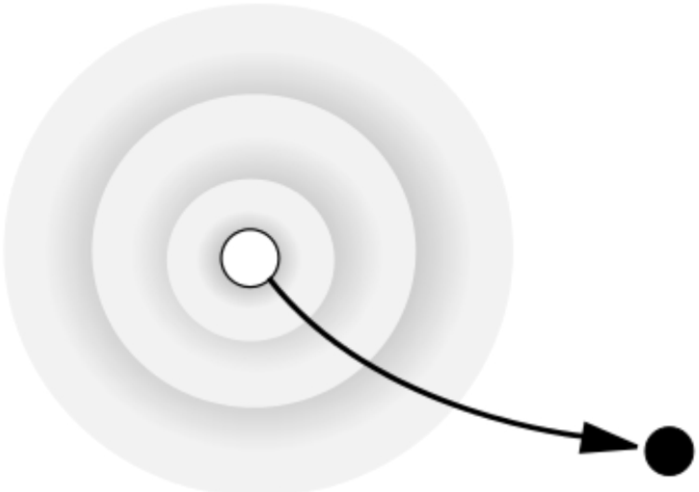


$+ \ldots\ldots\ldots$

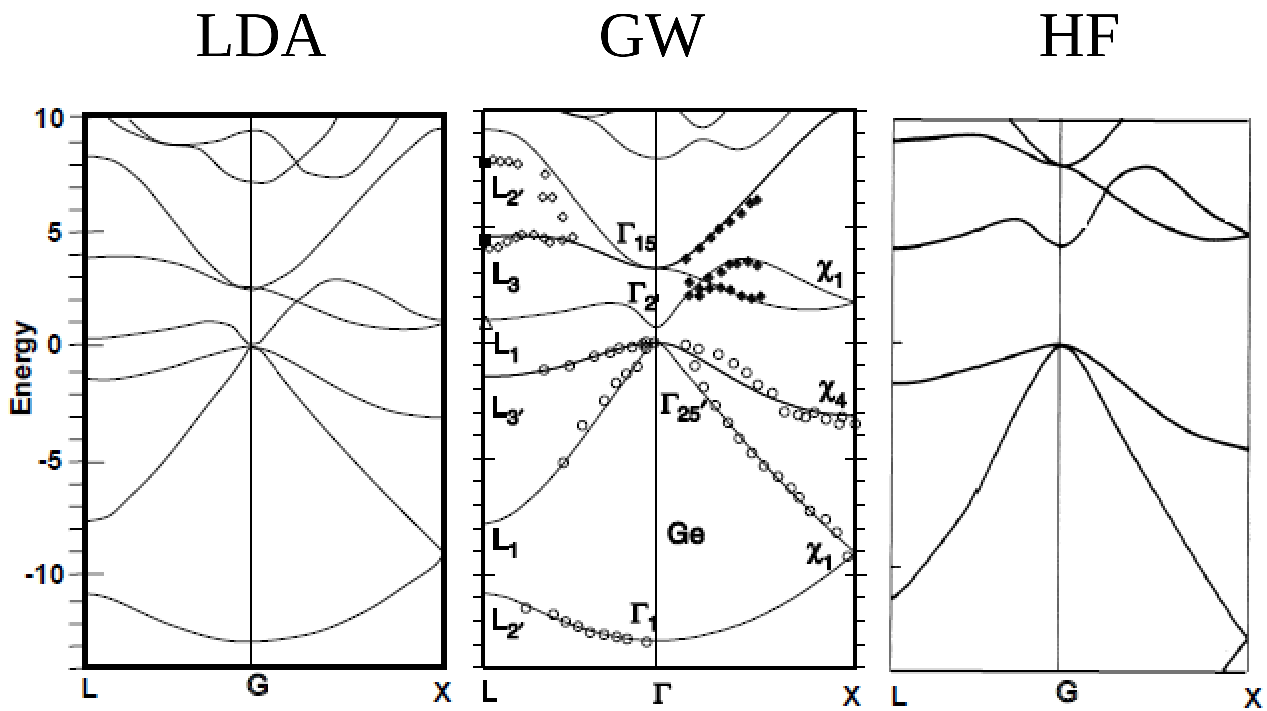
$\rightarrow \Sigma \sim i\,\mathcal{W}\mathcal{G}$ “GW”

L. Hedin (1965)

$$W = \varepsilon^{-1}(\omega)\, v$$



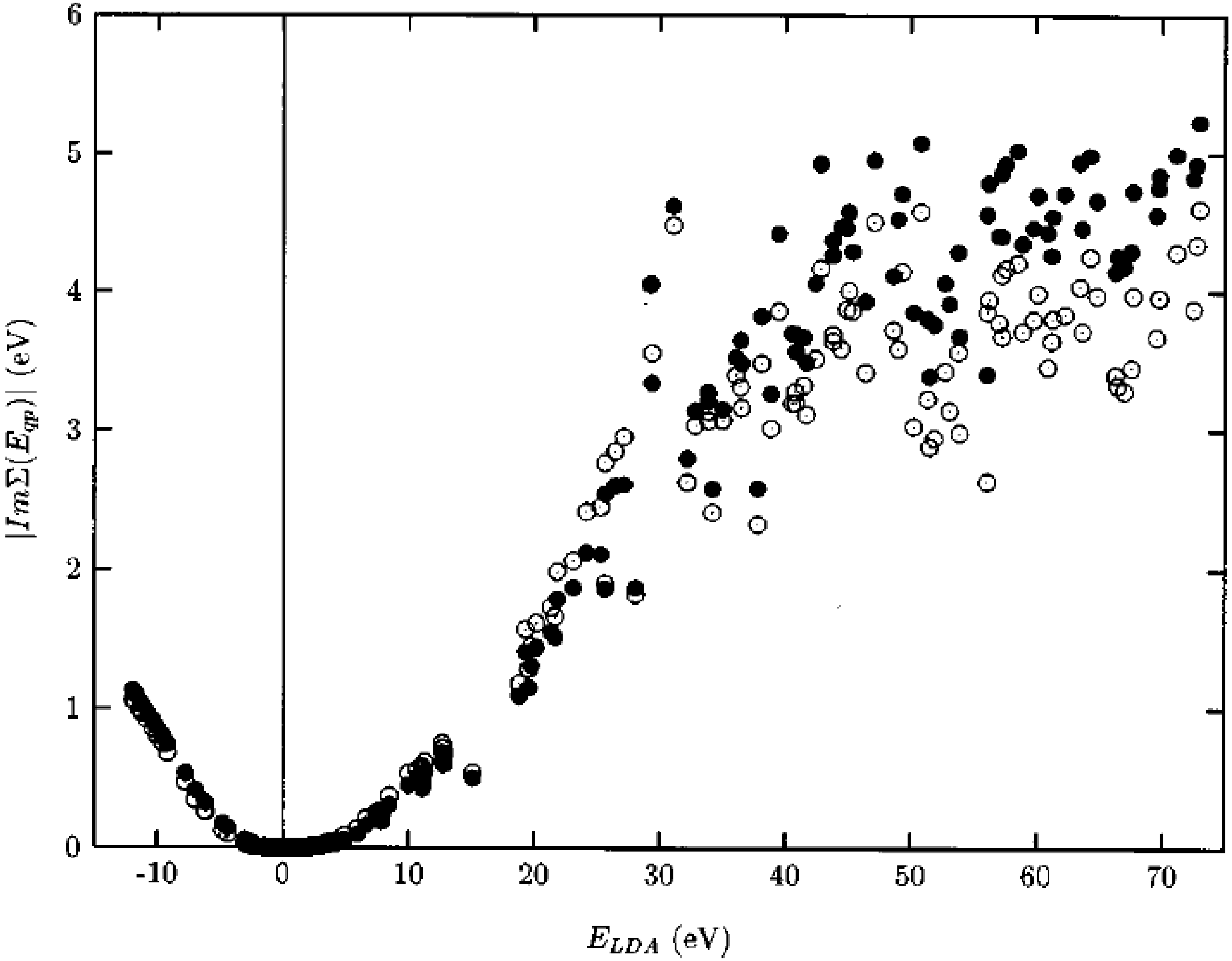
GW today: standard for bandstructures



Bandstructure of germanium, theory versus experiment

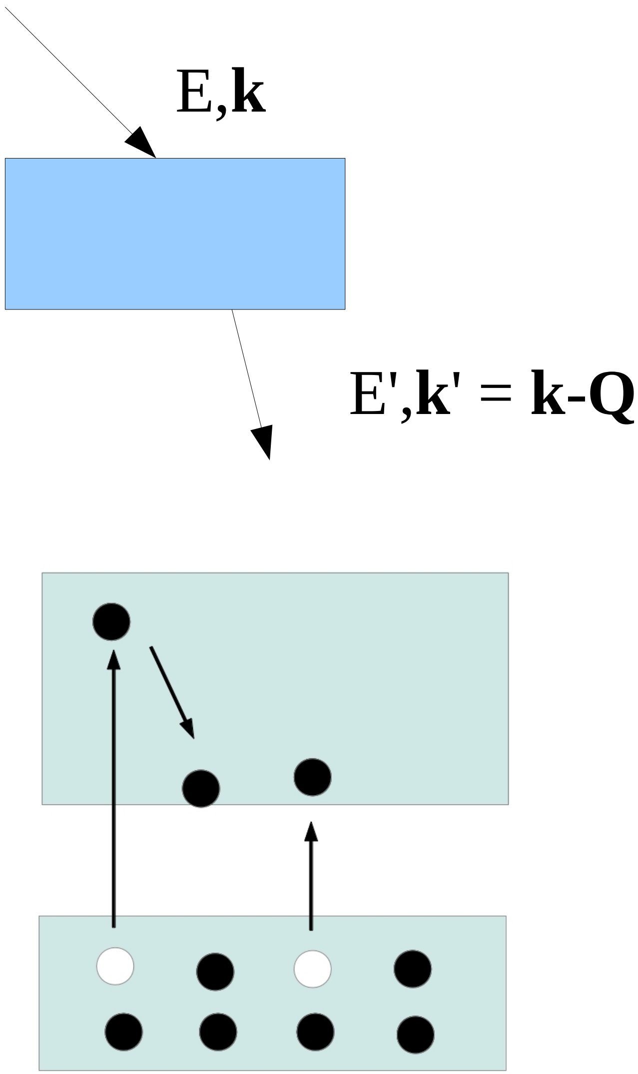
GW calculations, Rohlfing et al., PRB 48, 17791 (1993)

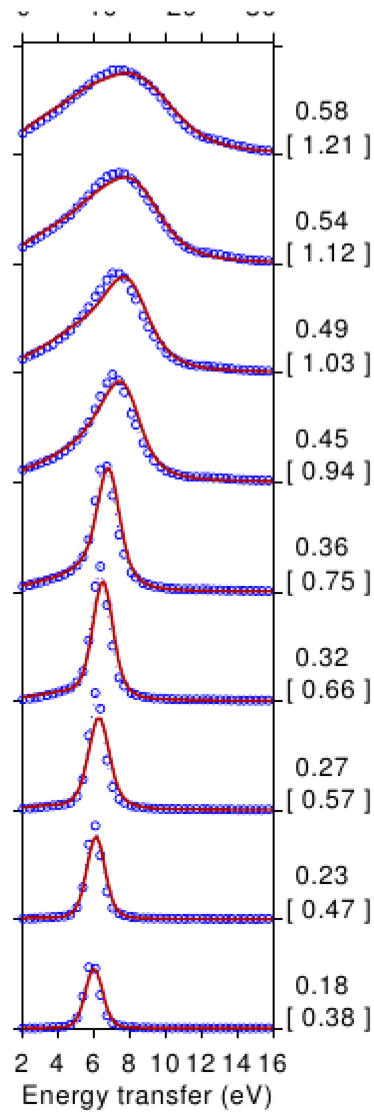
Inverse electron and hole lifetime in silicon



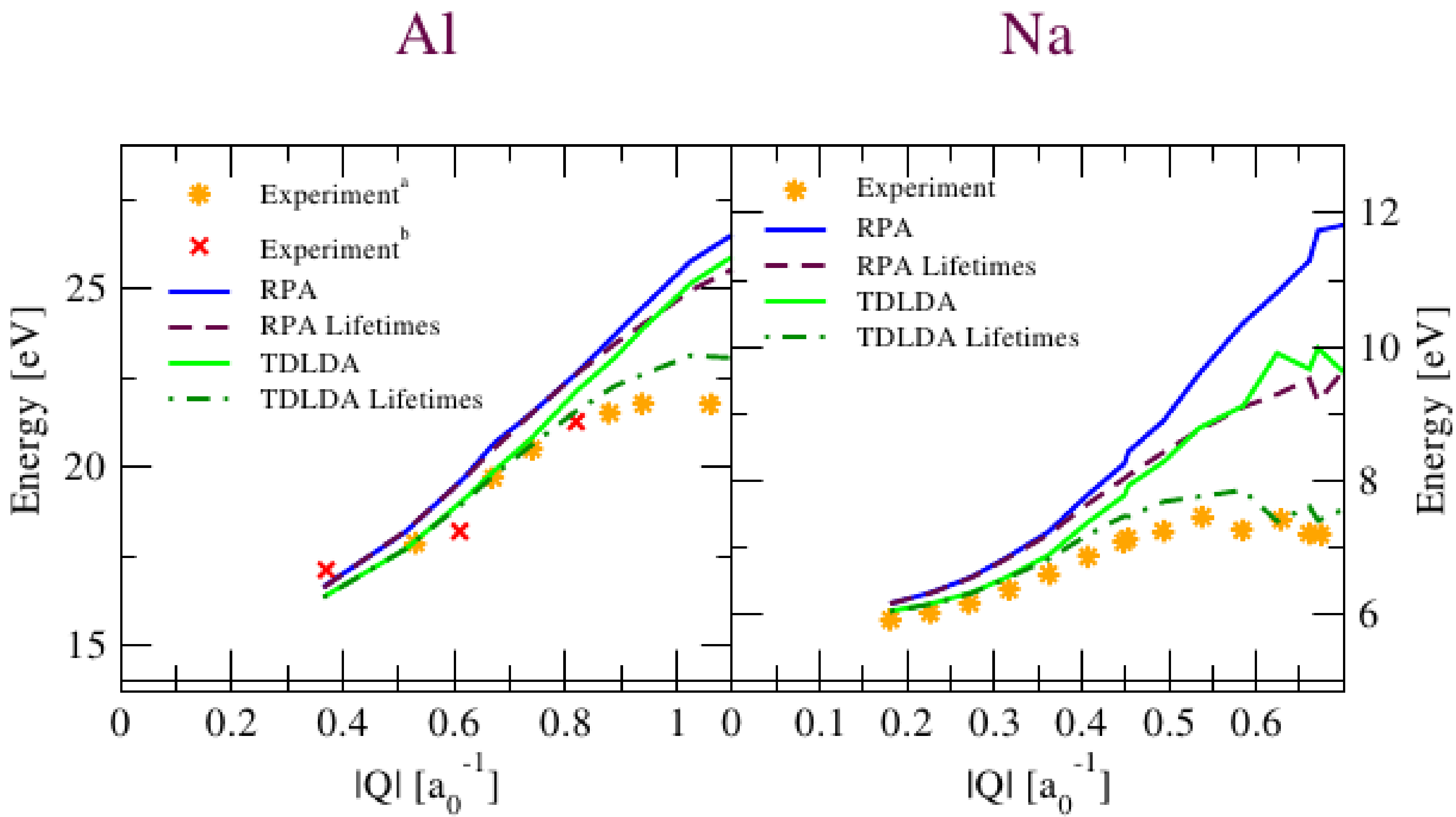
A. Fleszar and W. Hanke, PRB 56, 10228 (1997)

Effect of electron and hole decay on plasmon spectra





Effect of electron and hole decay on plasmon spectra

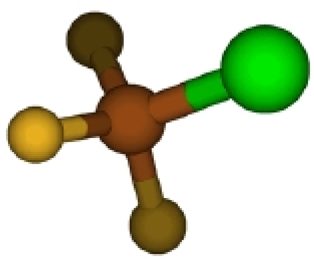


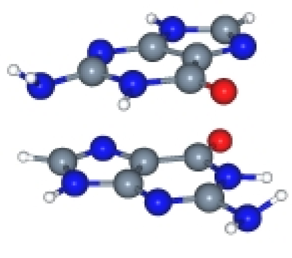
Cazzaniga et al;, Huotari et al.; PRB 84, 075108 and 075109 (2011)

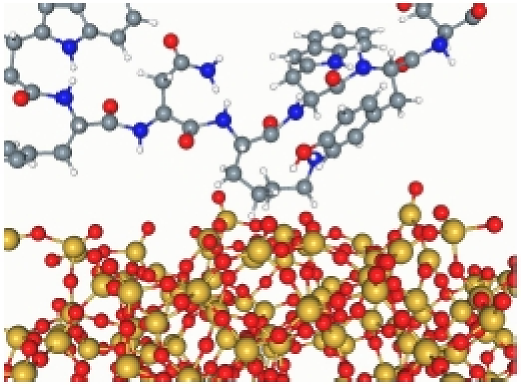
→ The effective quantities:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N, t) \longrightarrow G(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2) \longrightarrow \rho(\mathbf{r}, t)$$

CI, QMC — GF methods (GW, BSE) — DF

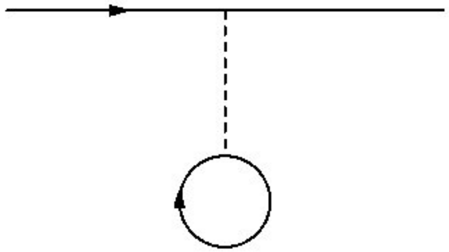


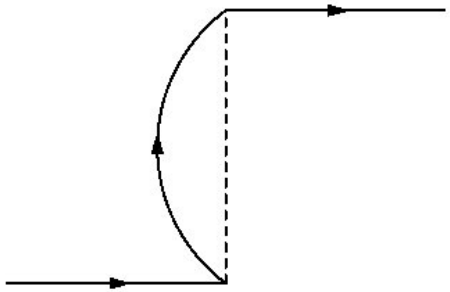


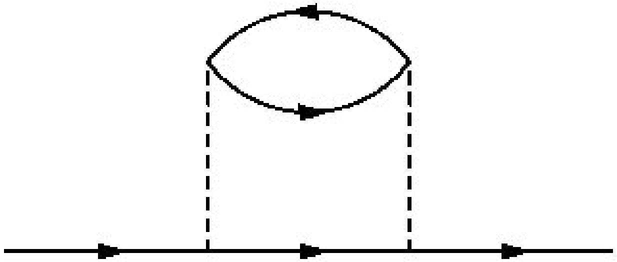


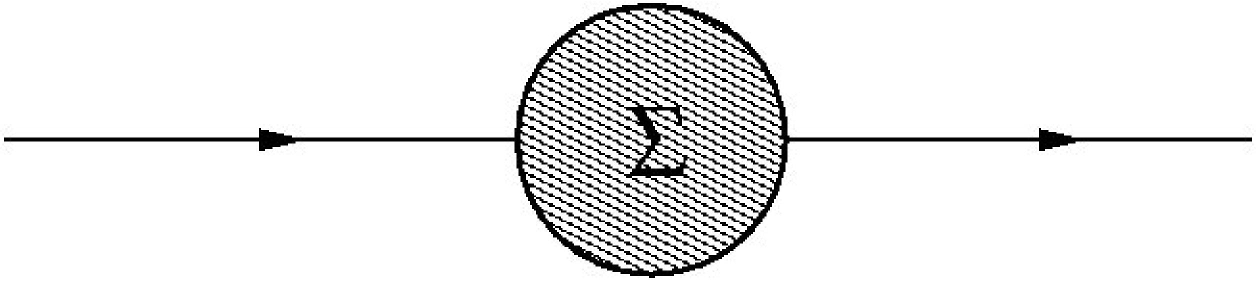
→ Propagators

$\mathcal{G}(1,2) = -i \langle T[\psi(1)\psi^{\dagger}(2)] \rangle \qquad 1=(r_1,\sigma_1,t_1)$









Dyson equation: $\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 \, \Sigma \, \mathcal{G}$

→ The effective world:

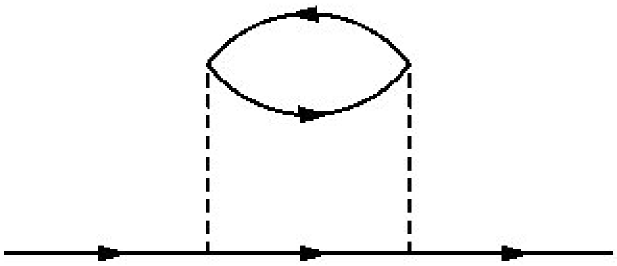
$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}([n],\mathbf{r}) + v_{\text{xc}}([n],\mathbf{r})$$

$$\Sigma(r,r',\varepsilon_i)$$

Designed for electron addition and removal spectra (bandstructure, lifetimes, satellites,....,density,...)

Other: DMFT $\Sigma_{ll}(\omega)$

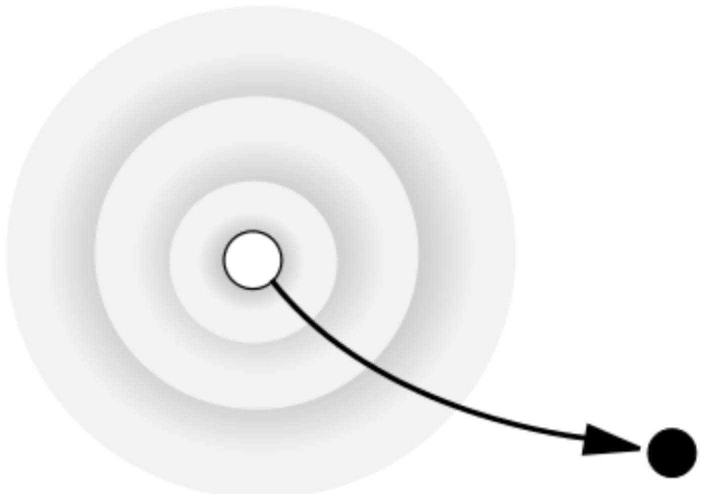


+ ....

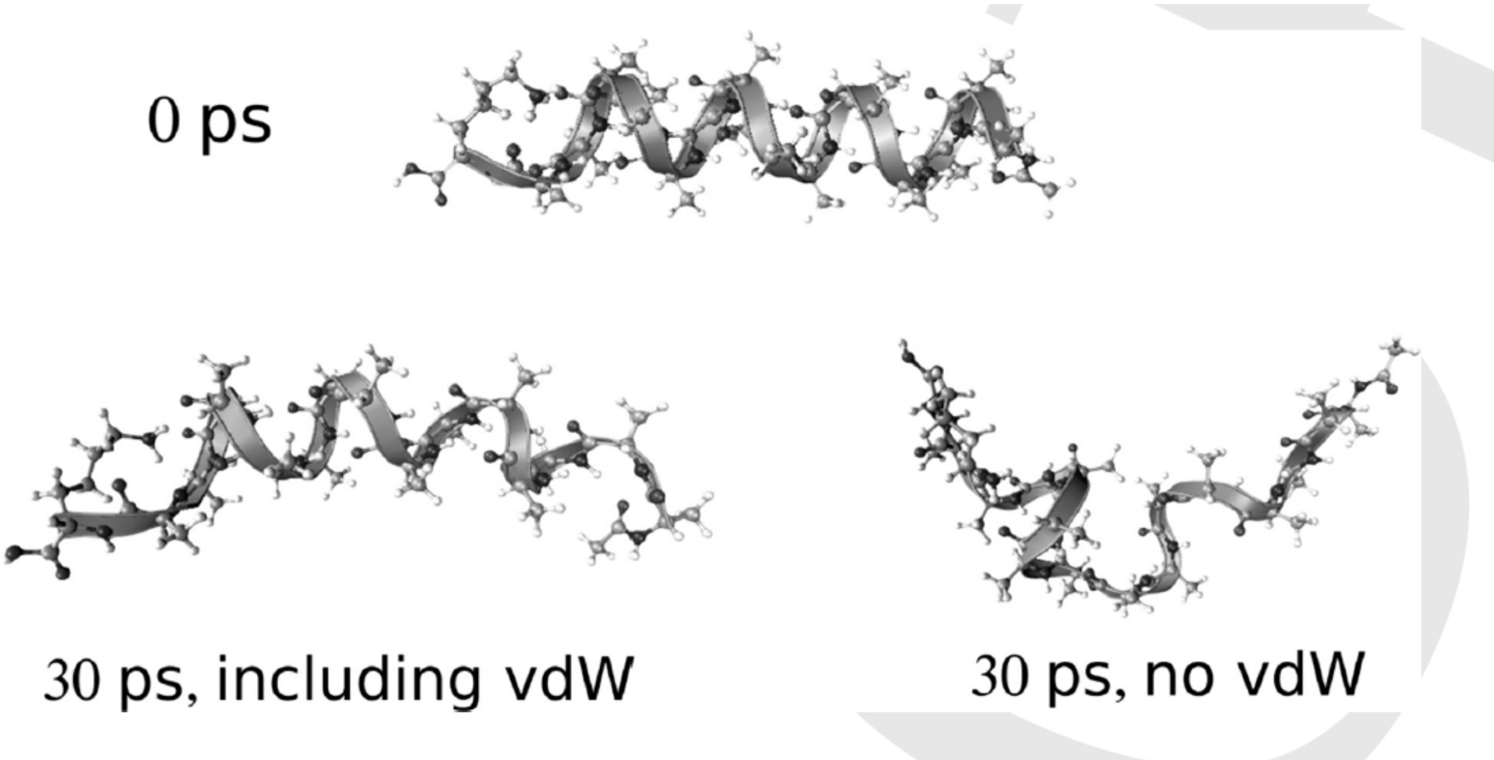
$\rightarrow \Sigma \sim i\,\mathcal{W}\mathcal{G}$ "GW"

L. Hedin (1965)

$$W = \varepsilon^{-1}(\omega)\ v$$



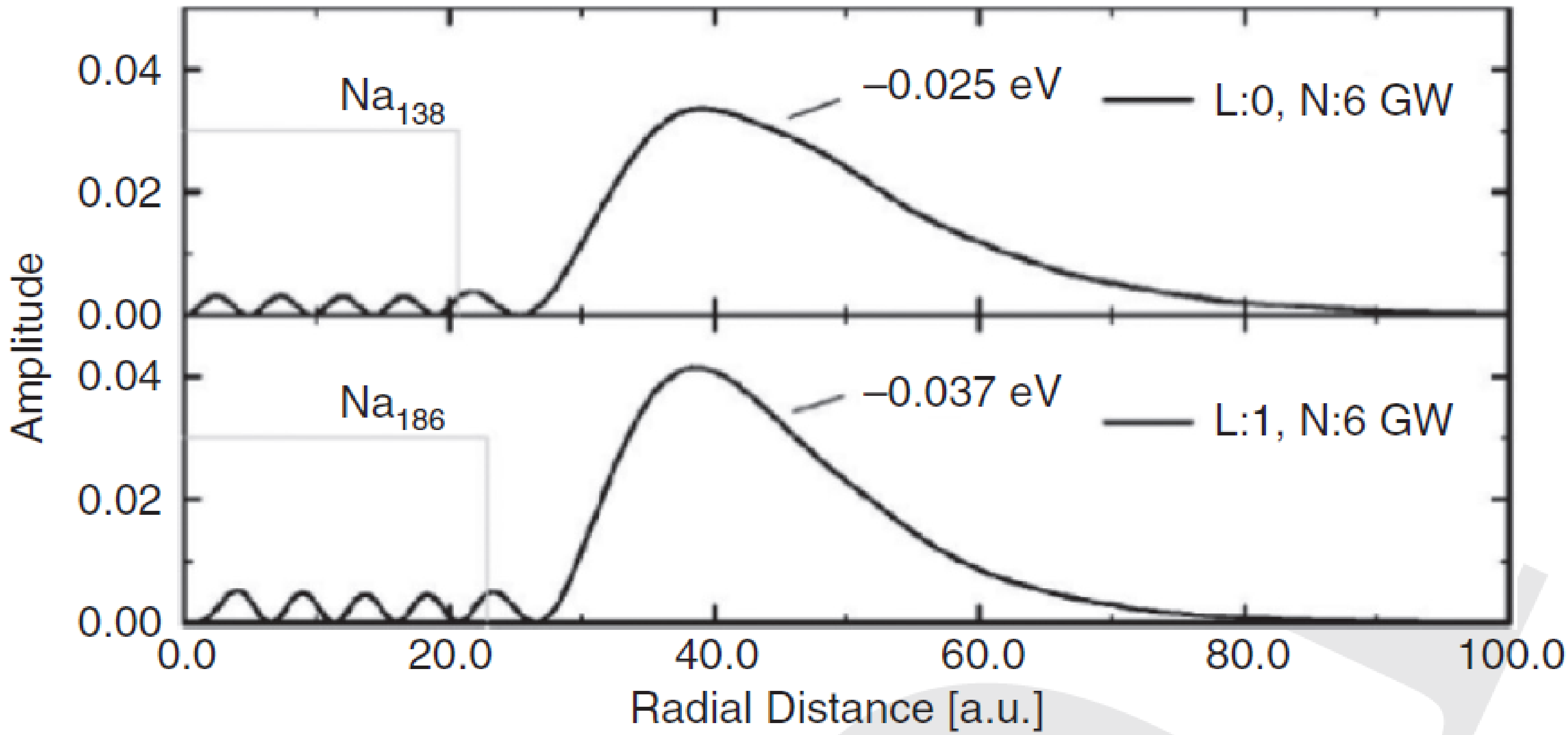
Van der Waals



alanine polypeptide

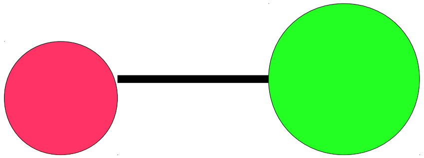
A. Tkatchenko et al., Phys. Rev. Lett. 106:118102, 2011

Image states

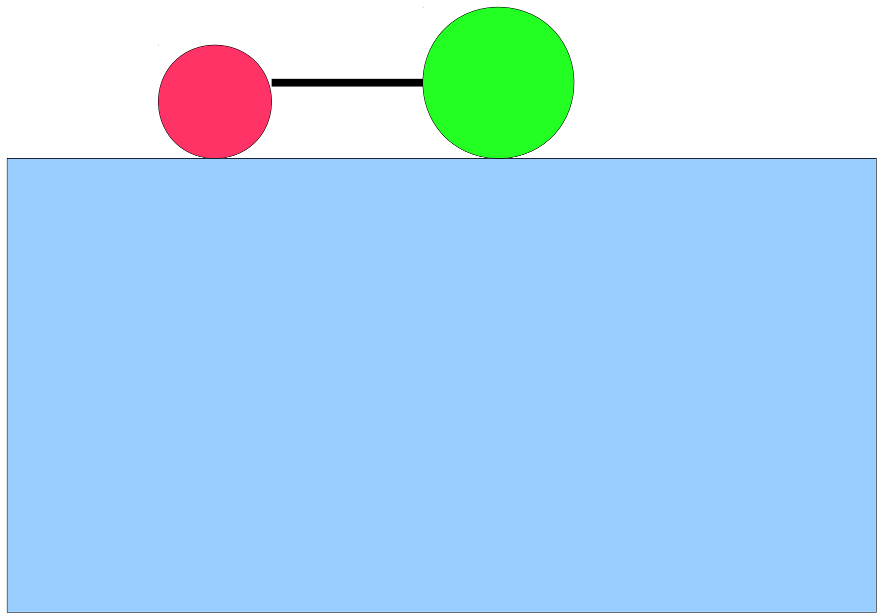


P. Rinke, et al., Phys. Rev. A 70:063201, 2004.

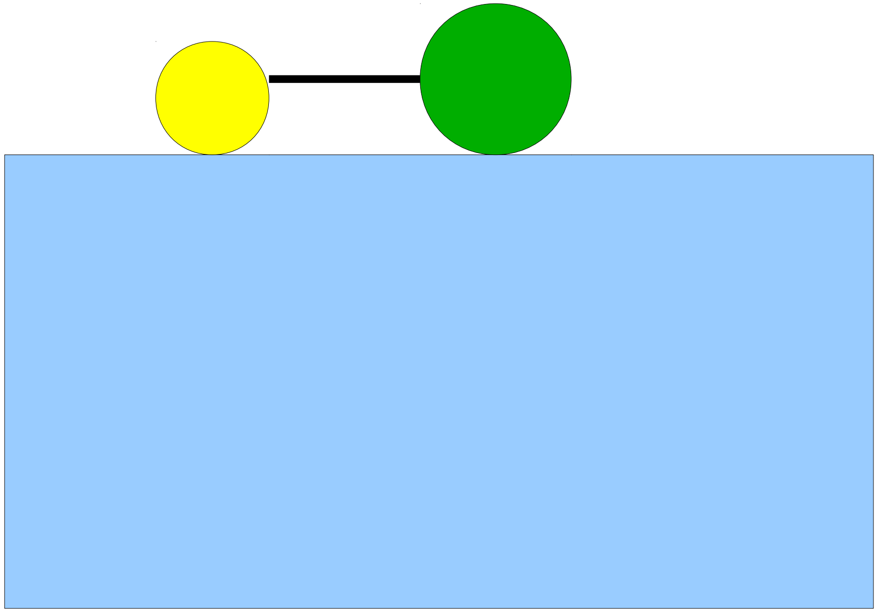
Molecules on surfaces



Molecules on surfaces

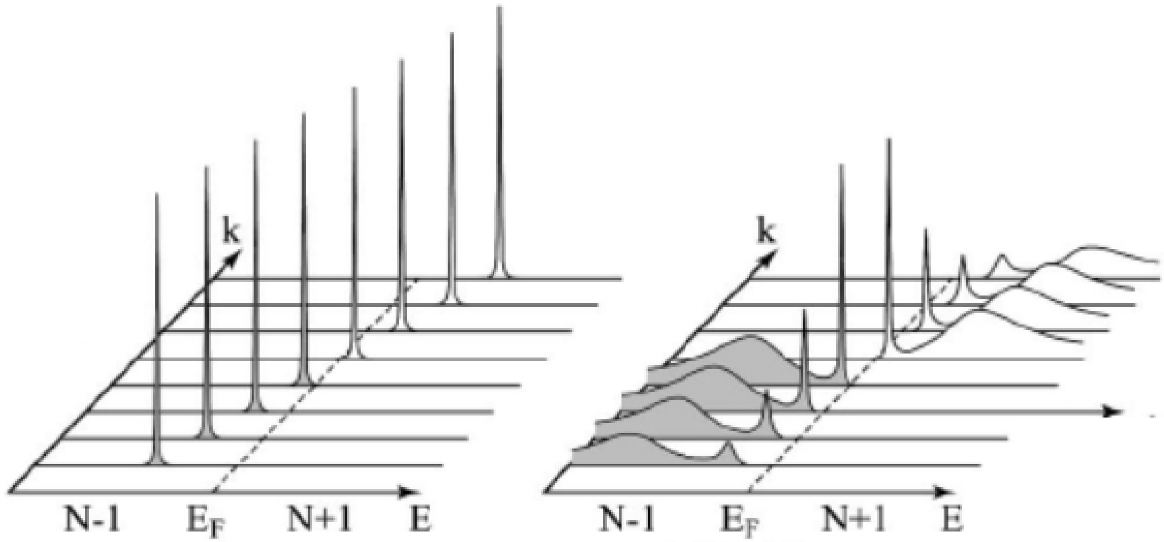


Molecules on surfaces



C. Freysoldt, et al., Phys. Rev. Lett. 103:056803, 2009.
J. M. Garcia-Lastra, et al, Phys. Rev. B 80:245427, 2009.

→ Interaction leads to........... additional excitations

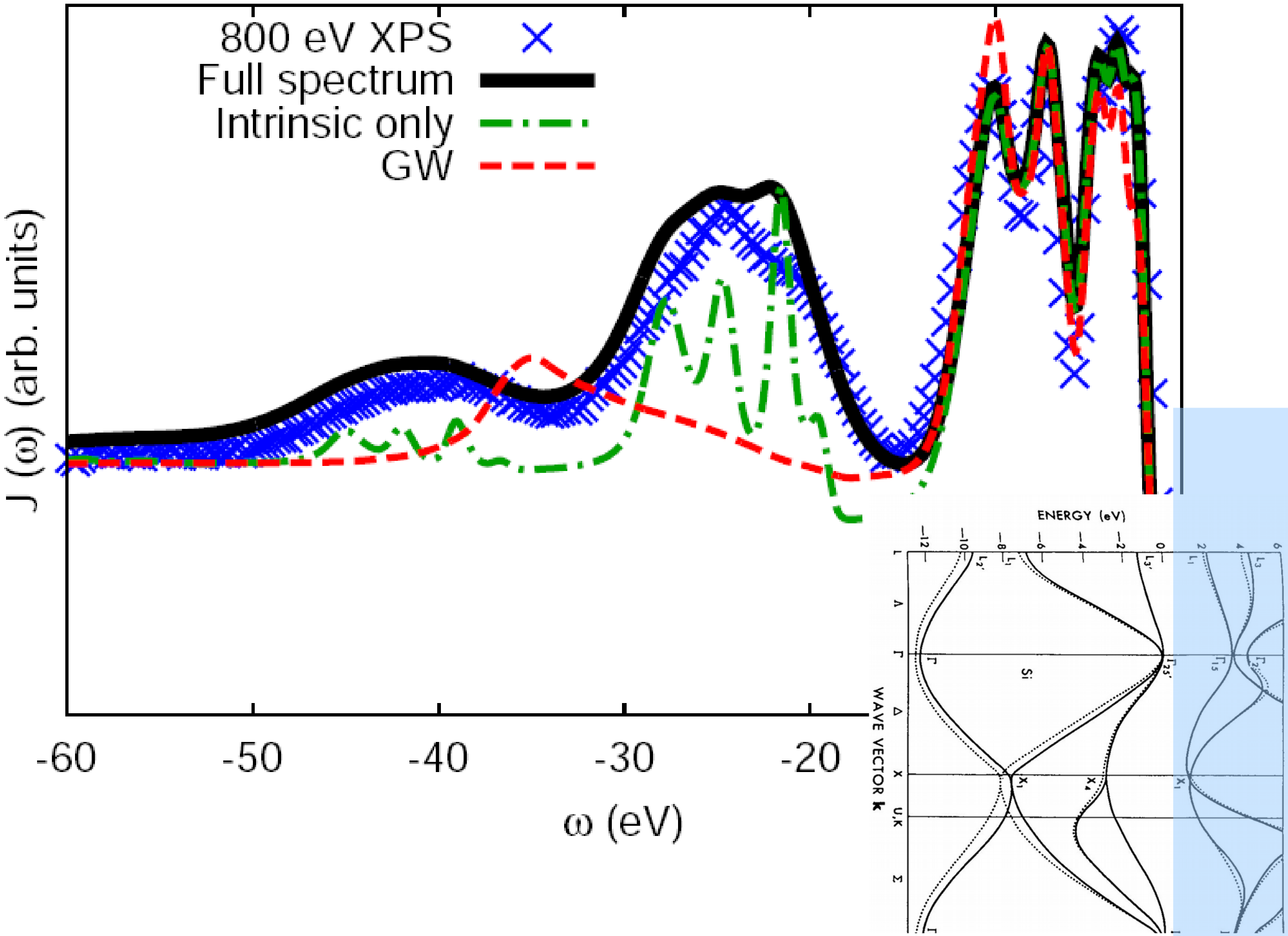


From Damascelli et al., RMP 75, 473 (2003)

Why study this? * More added value
* Example multiple exciton generation

+......

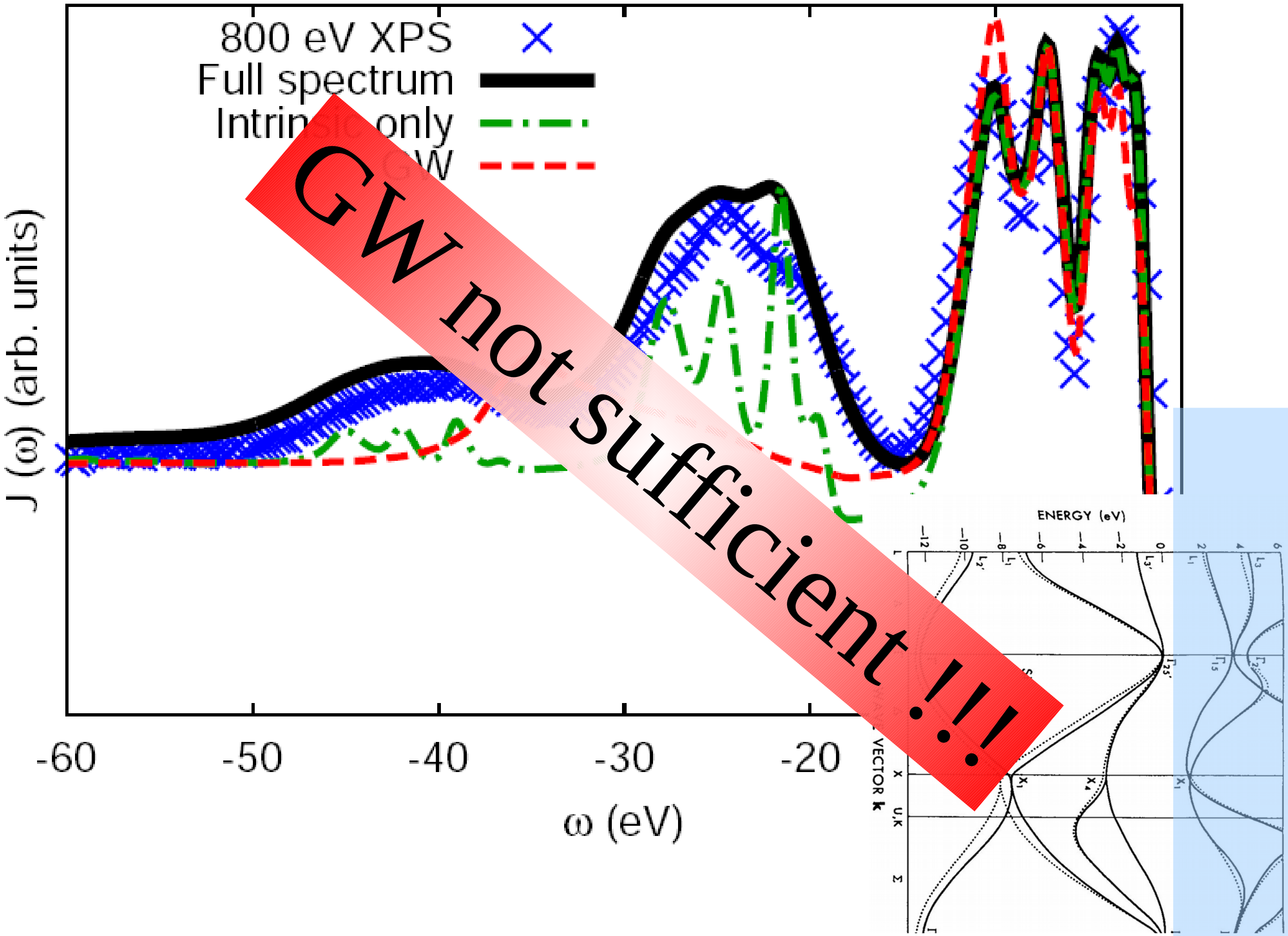
→ Interaction leads to.......... additional excitations



Cohen and Chelikowsky: “Electronic Structure and Optical Properties of Semiconductors” Solid-State Sciences 75, Springer-Verlag 1988)

M. Guzzo et al., PRL 107, 166401 (2011)

→ Interaction leads to.......... additional excitations



Cohen and Chelikowsky: “Electronic Structure and Optical Properties of Semiconductors” Solid-State Sciences 75, Springer-Verlag 1988)

M. Guzzo et al., PRL 107, 166401 (2011)

GW:

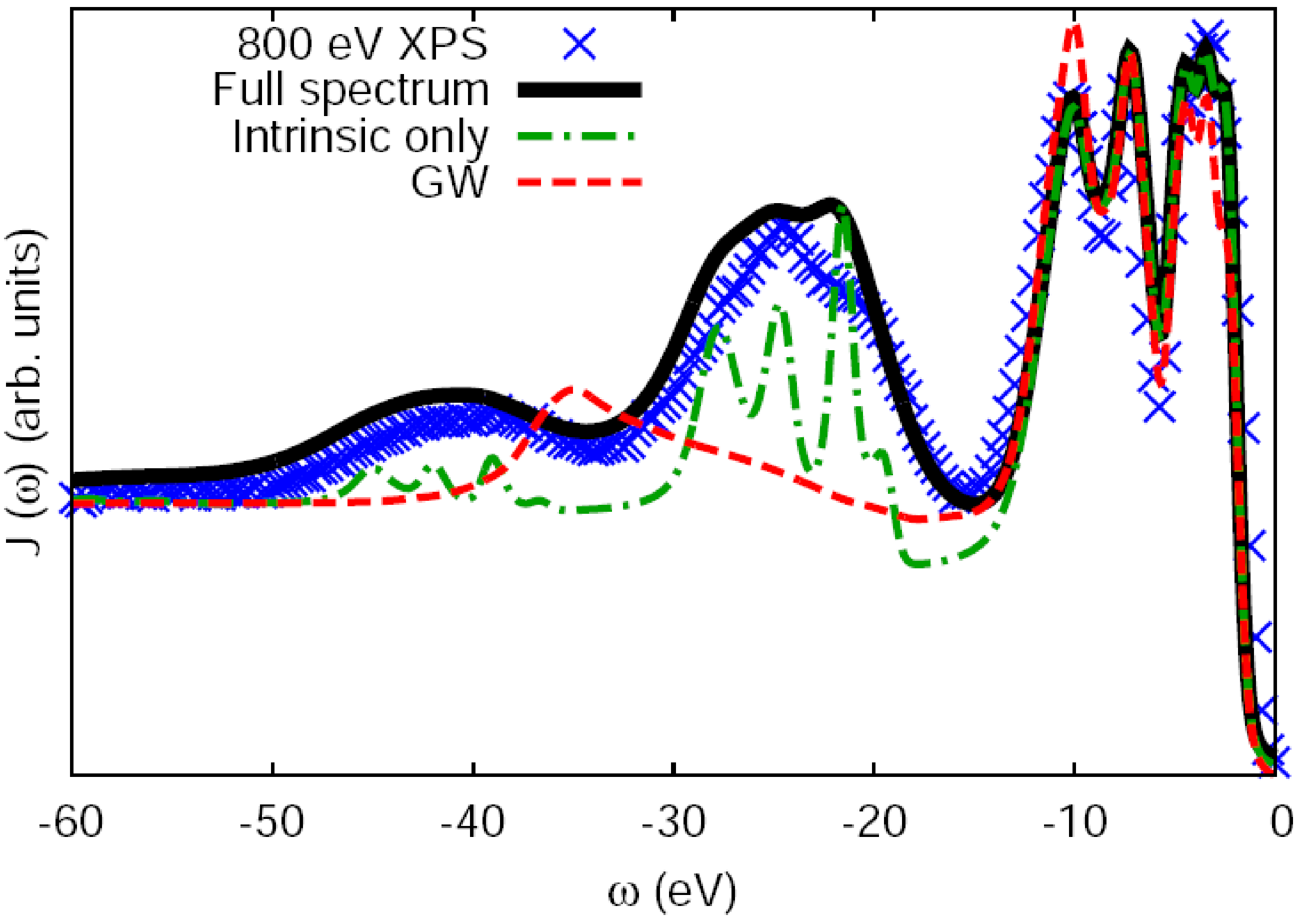
W(r,r',ω) → one efficient plasmon

$$A(\omega) = \frac{\Gamma}{\pi} e^{-\frac{\lambda}{\omega_p^2}} \Bigg[\frac{1}{(\omega - \varepsilon^{QP})^2 + \Gamma^2} + \\ + \frac{\lambda}{\omega_p^2} \frac{1}{(\omega - \varepsilon^{QP} + \omega_p)^2 + \Gamma^2} + \\ + \frac{1}{2} \left(\frac{\lambda}{\omega_p^2} \right)^2 \frac{1}{(\omega - \varepsilon^{QP} + 2\omega_p)^2 + \Gamma^2} + \\ + \frac{1}{6} \left(\frac{\lambda}{\omega_p^2} \right)^3 \frac{1}{(\omega - \varepsilon^{QP} + 3\omega_p)^2 + \Gamma^2} + \ldots \Bigg]$$

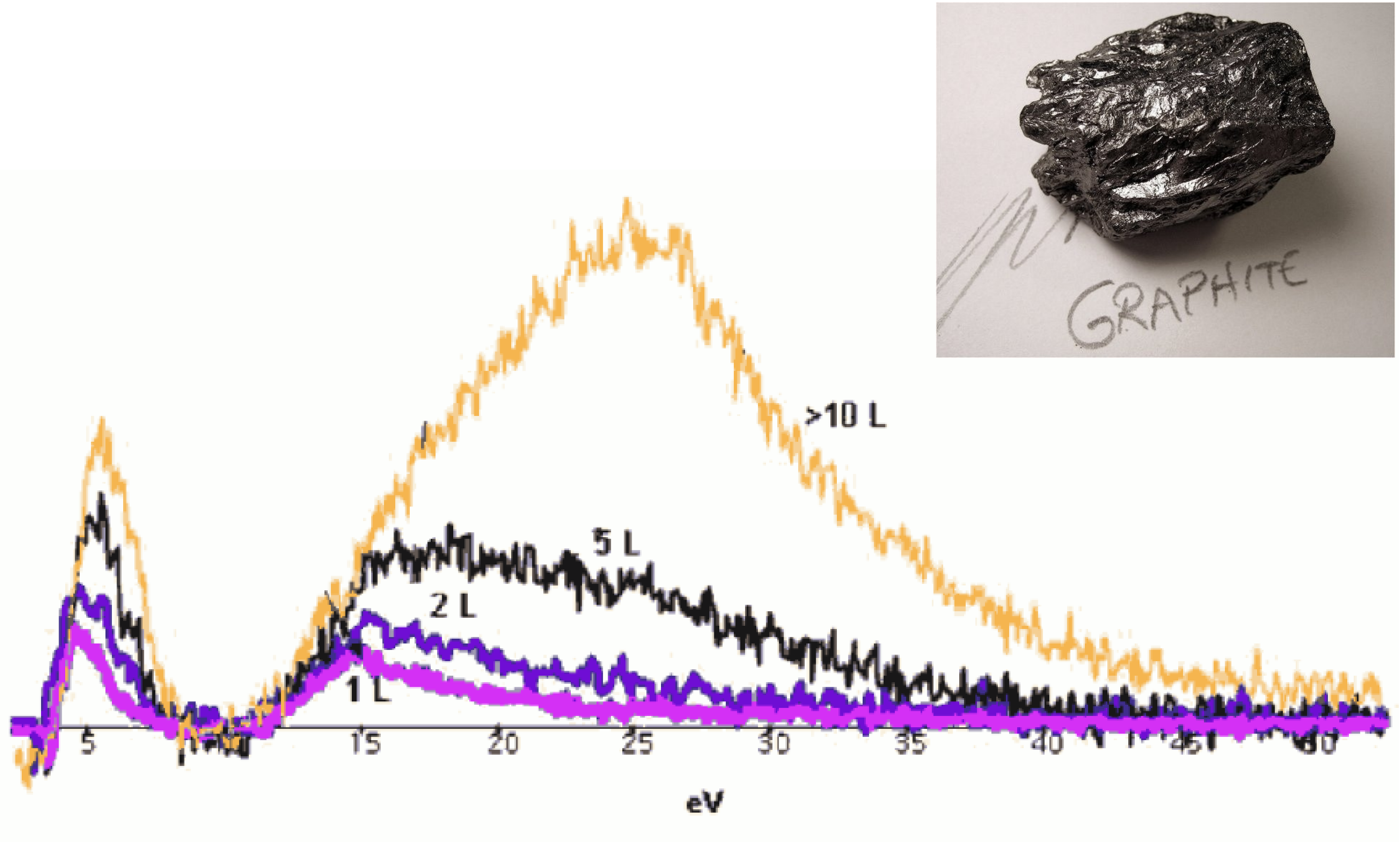
Cumulant:

W(r,r',ω) → series of plasmons

→ Interaction leads to many additional excitations

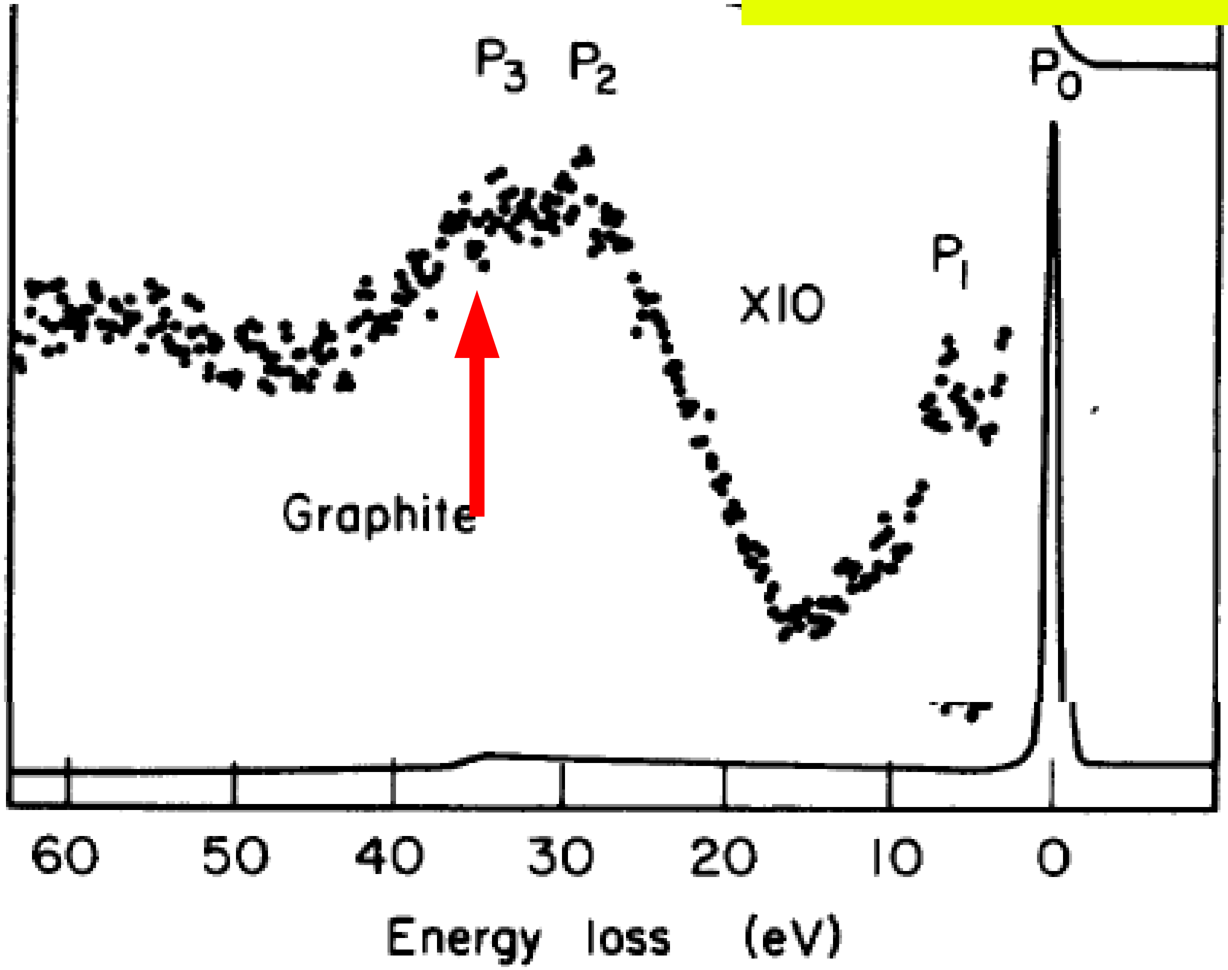


M. Guzzo et al., PRL 107, 166401 (2011)



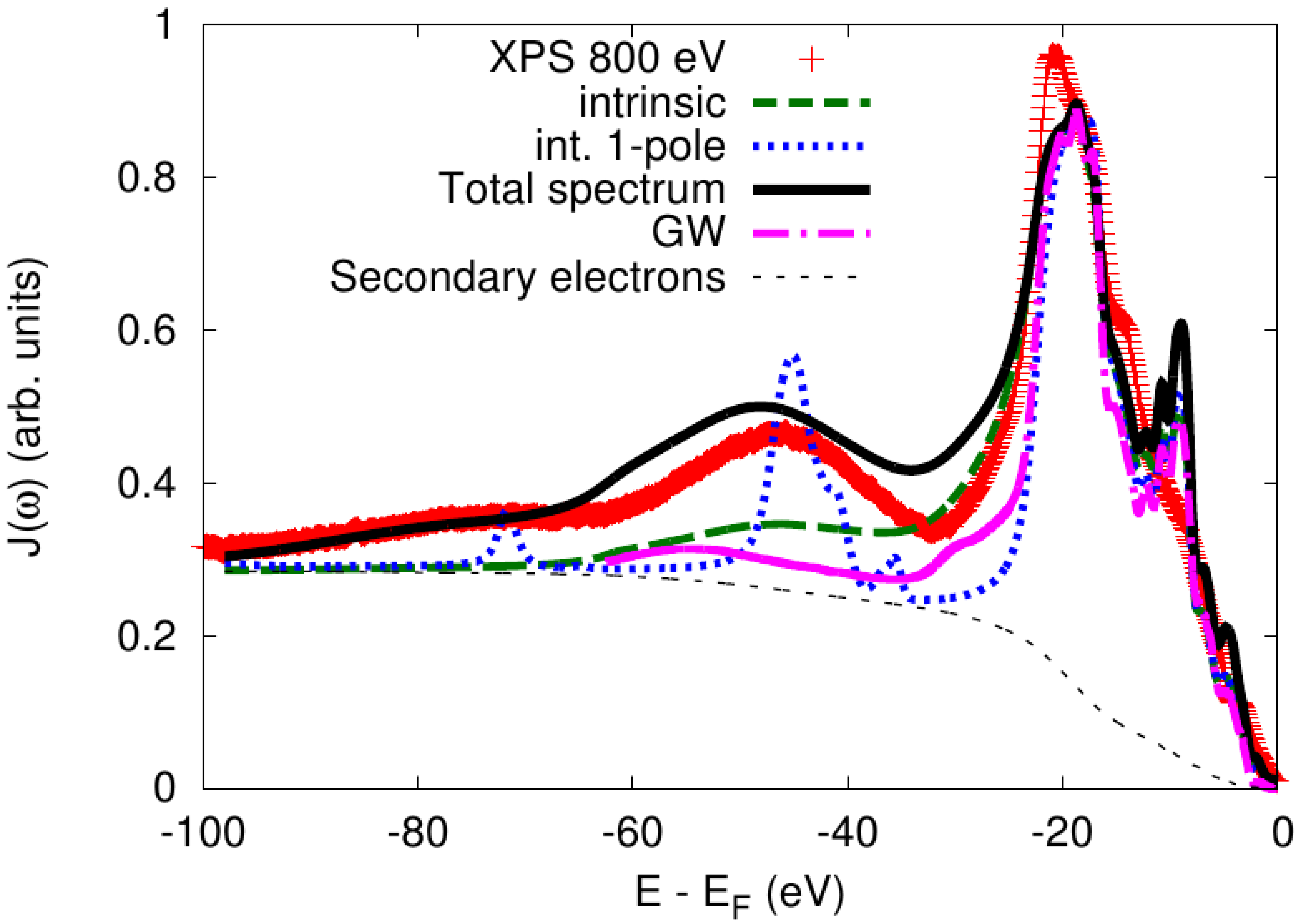
Exp: Eberlein et al., Phys. Rev. B 77, 233406 (2008)

XPS carbon 1s



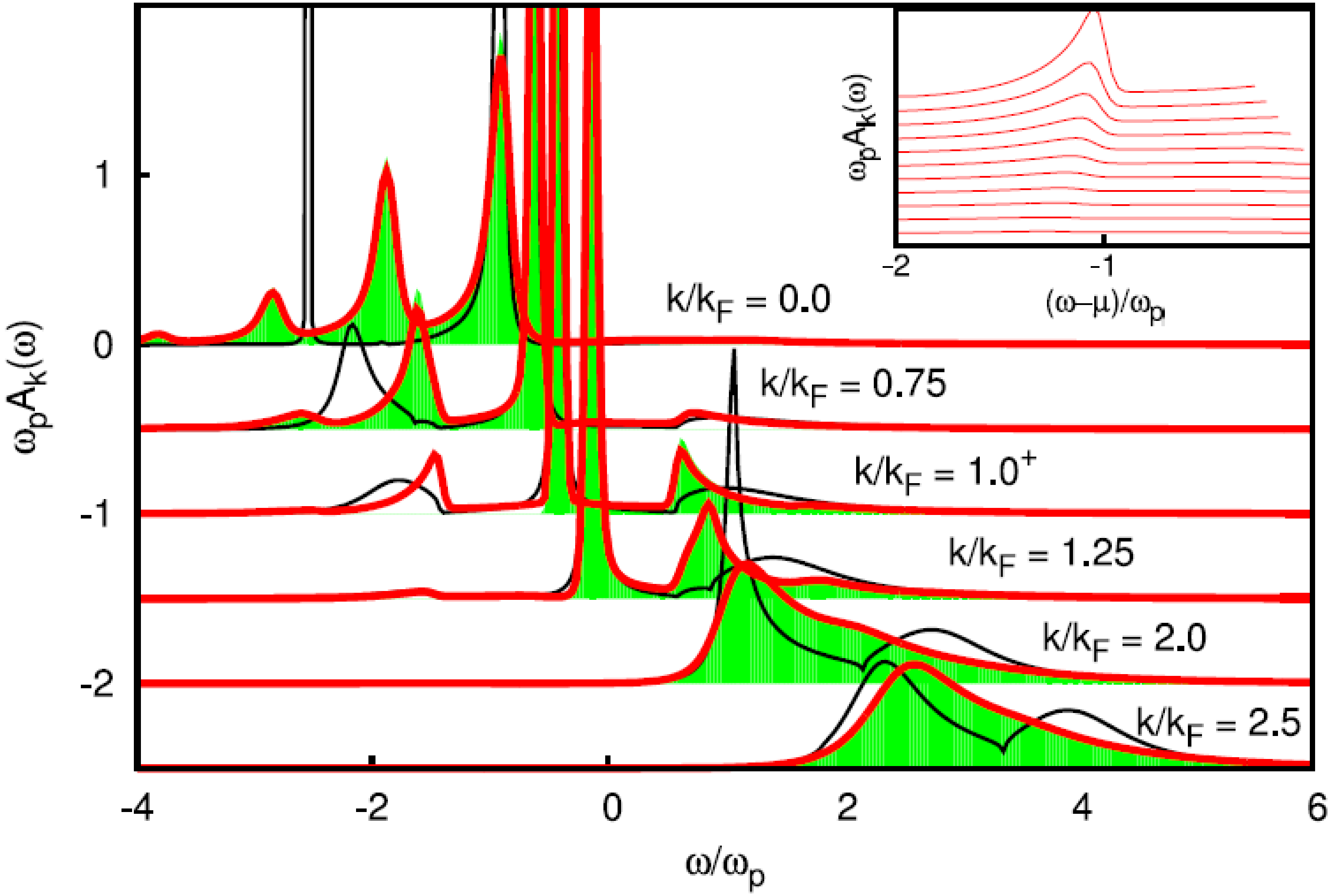
McFeely et al., PRB 9, 5268 (1974)

Graphite valence double plasmon: shift + broadening



M. Guzzo et al., Phys. Rev. B 89, 085425 (2014)

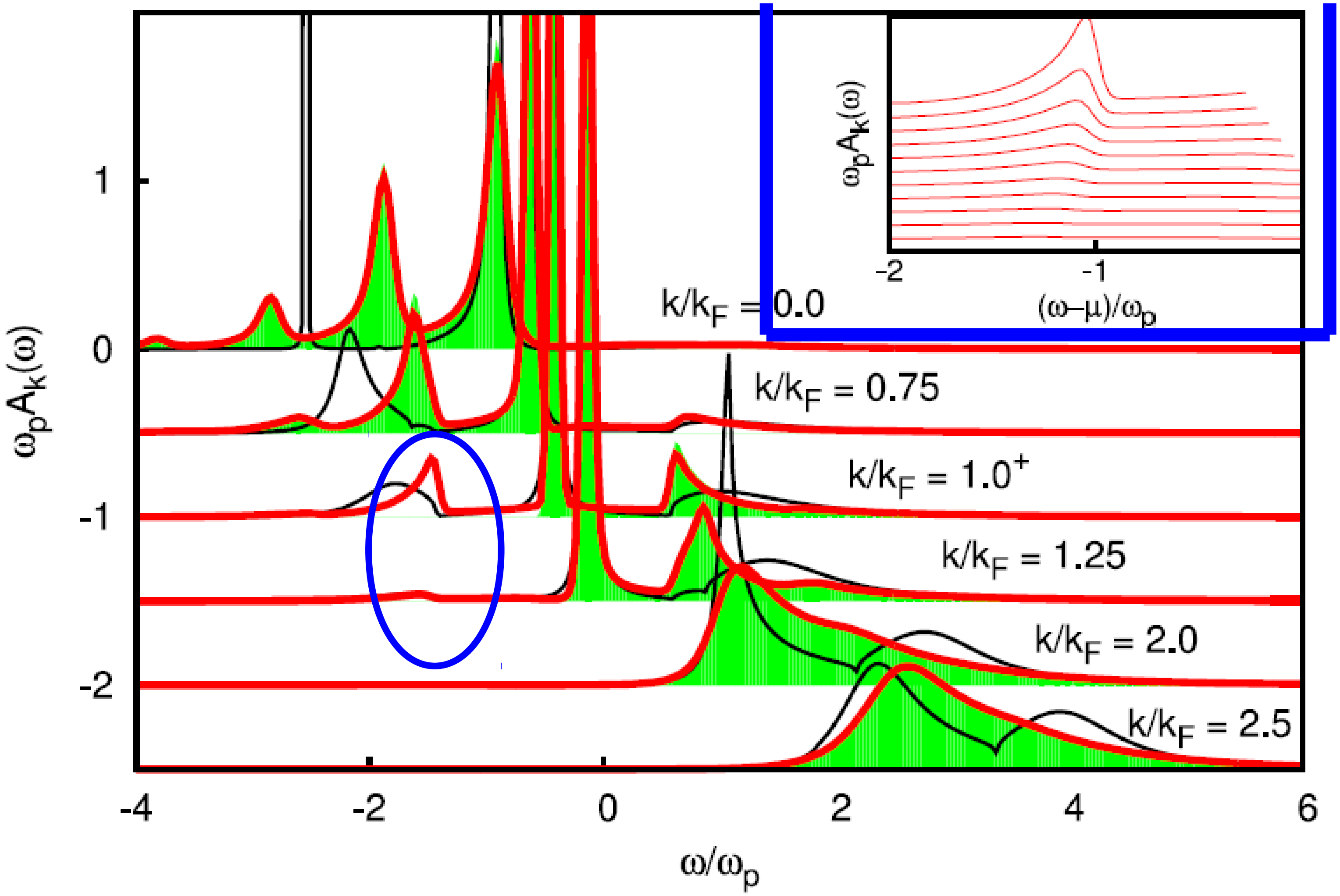
Coupling occupied and empty states: more correlation



Homogeneous Electron Gas

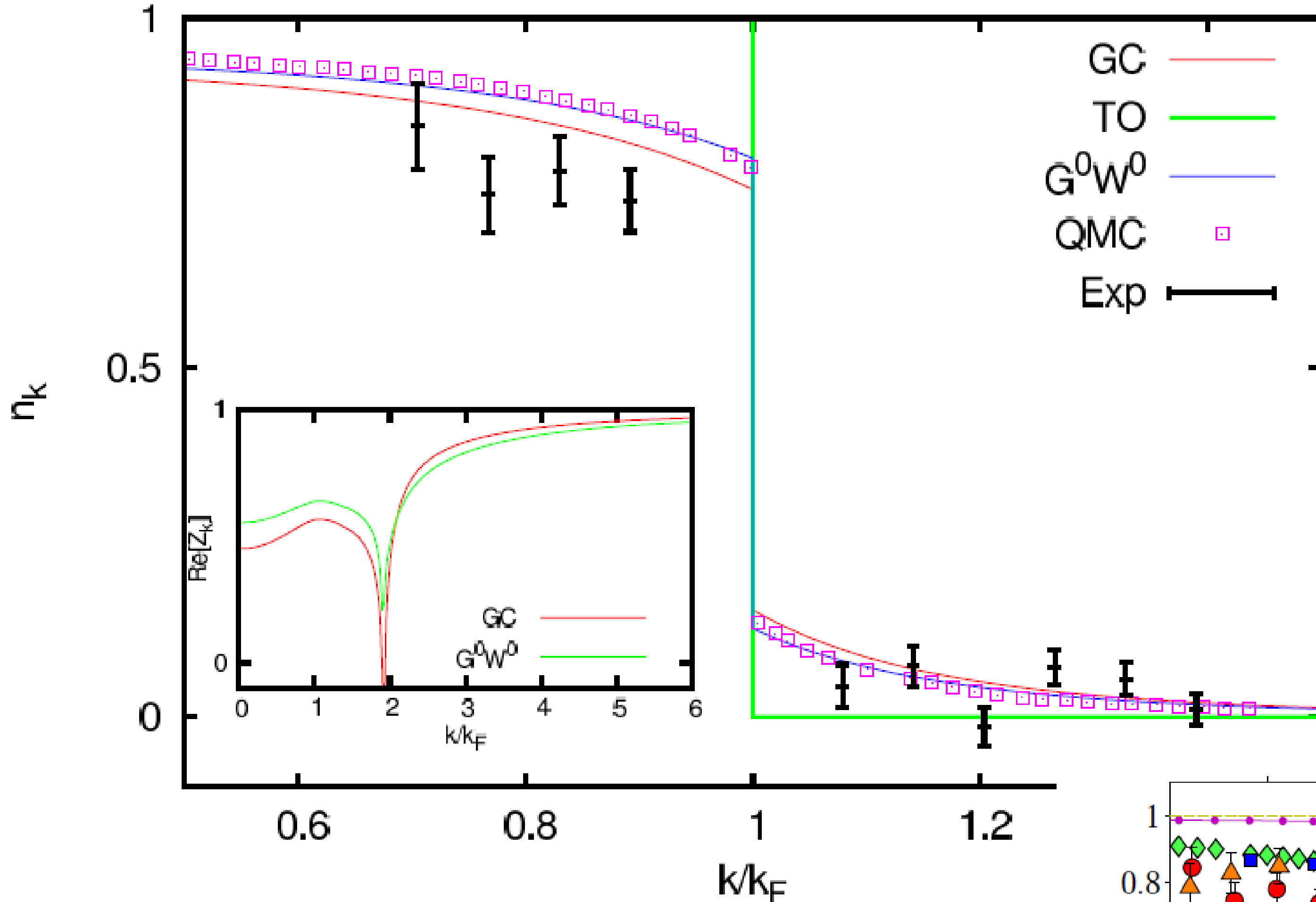
Kas, Rehr, Reining (2014) http://arxiv.org/abs/1402.0022

Coupling occupied and empty states: more correlation

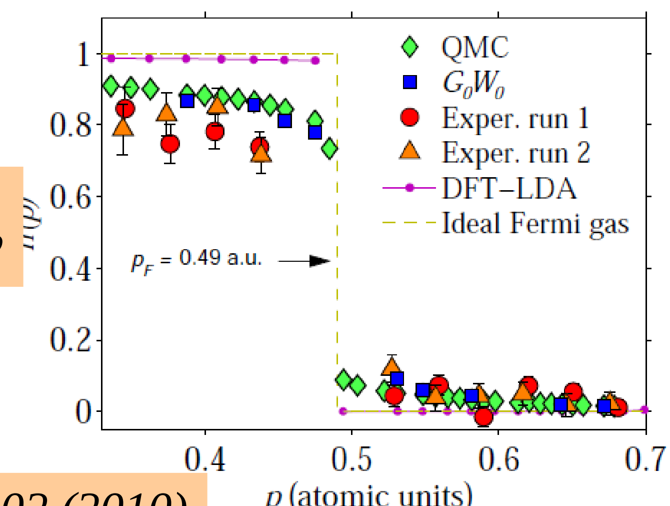


Homogeneous Electron Gas

Kas, Rehr, Reining (2014) http://arxiv.org/abs/1402.0022



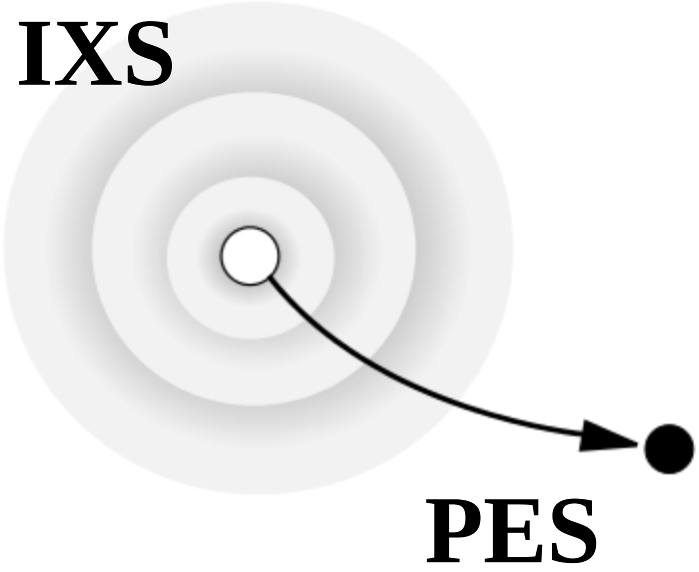
Homogeneous Electron Gas
Kas, Rehr, Reining (2014) http://arxiv.org/abs/1402.0022



Exp. Na, S. Huotari et al, PRL 105, 086402 (2010)

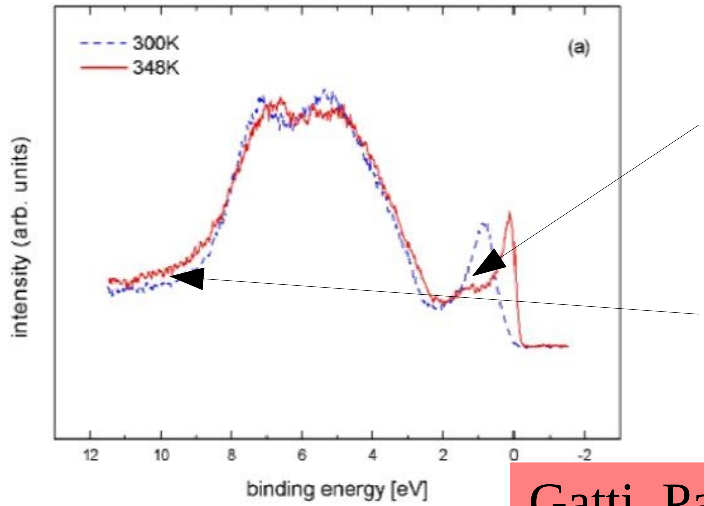
→ Understanding?

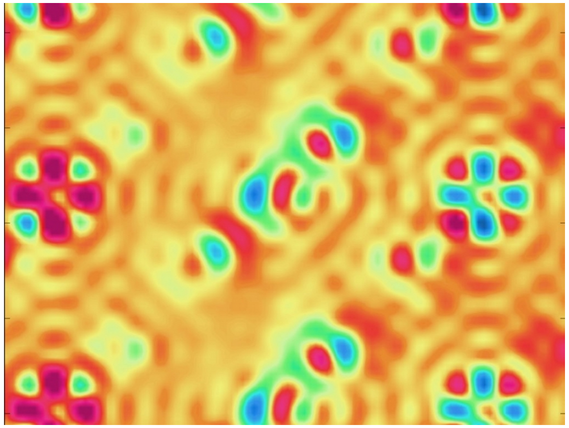
Our theory is:
decomposition into different experiments!



“Plasmon” contributions also interesting and accessible in TMOs:

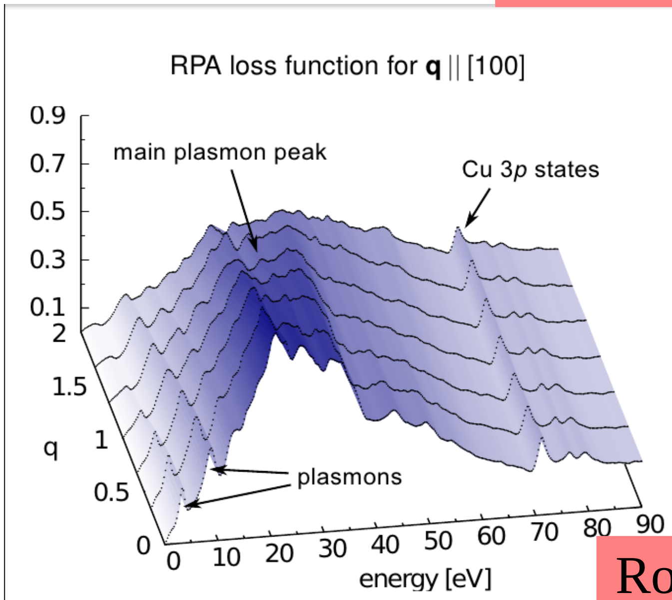
VO_2





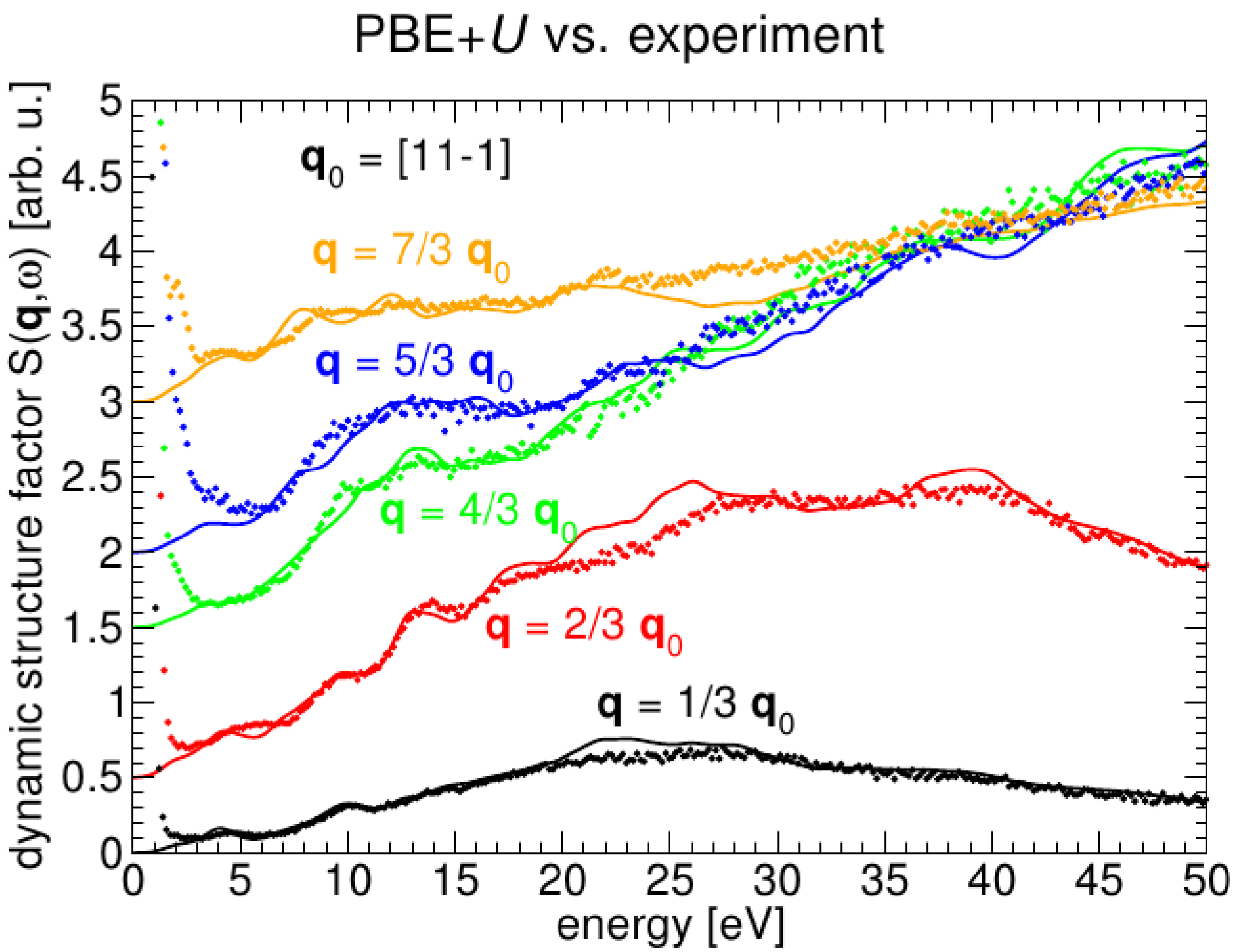
Gatti, Panaccione, Reining (PRL 2015)

CuO



GW gap 1.7 – 4.2 eV
Exp. 1.3 +/- 0.3 eV

Roedl, Sottile, Reining (PRB 2015)



ESRF

IXS experiment at ESRF:

K. Ruotsalainen,

A.-P. Honkanen, R. Verbeni,

S. Huotari

→ Gap theo. < ~ 2 eV;   exp. 1.4 +/- 0.3 eV

C. Roedl et al., 2016

→ Theory and Experiment

$$+ i \int_{t_1}^{\infty} dt_3 \int dt_4 W(t_3, t_4) g(t_3, t_2; [\varphi]) \theta(t_2 - t_4) \theta(t_4 - t_3)$$

$$= -i \int_{t_1}^{\infty} dt_3 g(t_3, t_2; [\varphi]) \varphi(t_3) \theta(t_3 - t_1) + \int_{t_1}^{\infty} dt_3 \int dt_{\bar{1}} g(t_{\bar{1}}, t_2; [\varphi])$$

$$+ i \int_{t_1}^{\infty} dt_3 \int dt_4 W(t_3, t_4) g(t_3, t_2; [\varphi]) \theta(t_2 - t_4) \theta(t_4 - t_3) \theta(t_3 - t_1)$$

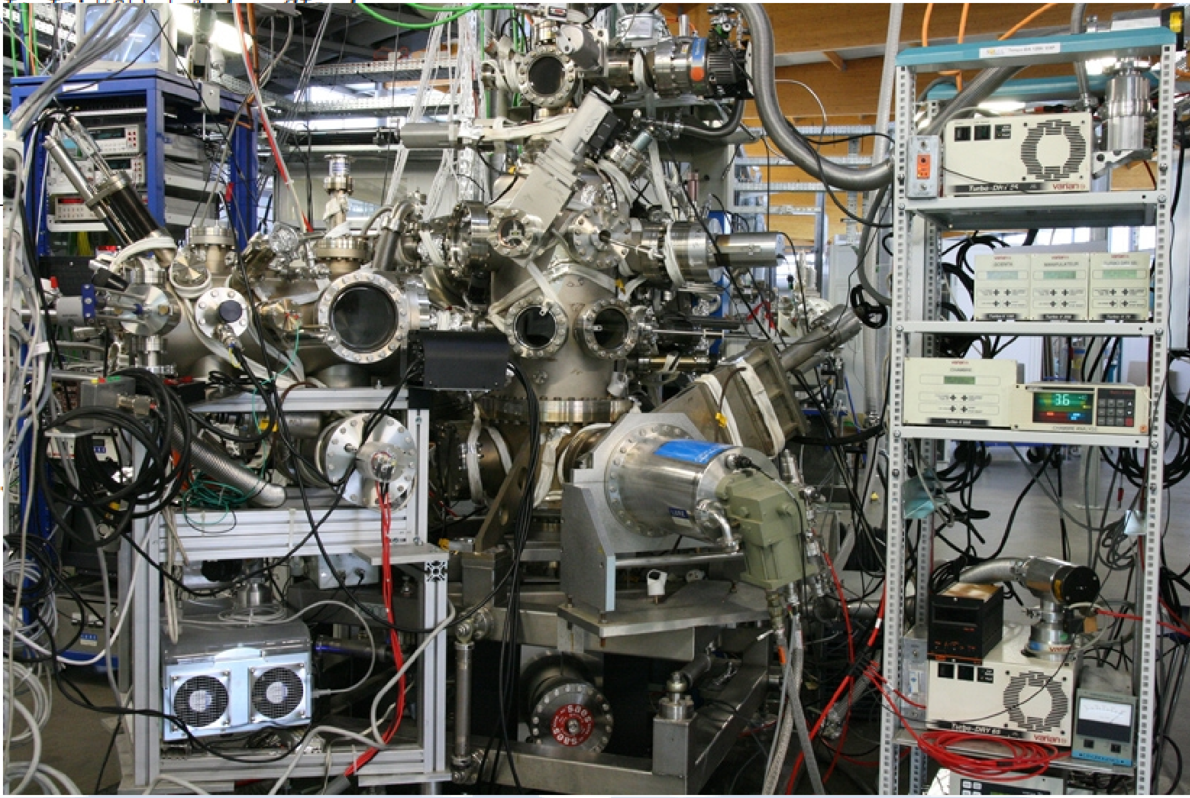
$$= -i \int_{t_1}^{\infty} dt_3 g(t_3, t_2; [\varphi]) \varphi(t_3) \theta(t_3 - t_1) + g(t$$

obtain a more compact expression:

$$\theta(t_2 - t_1) = i \int dt_3 g(t_3, t_2; [\varphi]) \Big\{ - \varphi(t_3) \theta(t_3 -$$

nipulate Eq. 1, with the change of variable y

$$= i\theta(t_2 - t_1) + i \int_{t_1}^{\infty} dt_3 \varphi(t_3) g(t_3, t_2; [\varphi]) + i^2$$



→ Theory and Experiment

$$+ i \int_{t_1}^{\infty} dt_3 \int dt_4 W(t_3, t_4) g(t_3, t_2; [\varphi]) \theta(t_2 - t_4) \theta(t_4 - t_3)$$

$$= -i \int_{t_1}^{\infty} dt_3 g(t_3, t_2; [\varphi]) \varphi(t_3) \theta(t_3 - t_1) + \int_{t_1}^{\infty} dt_3 \int dt_{\bar{1}} g(t_{\bar{1}}, t_2; [\varphi])$$

$$+ i \int_{t_1}^{\infty} dt_3 \int dt_4 W(t_3, t_4) g(t_3, t_2; [\varphi]) \theta(t_2 - t_4) \theta(t_4 - t_3) \theta(t_3 - t_1)$$

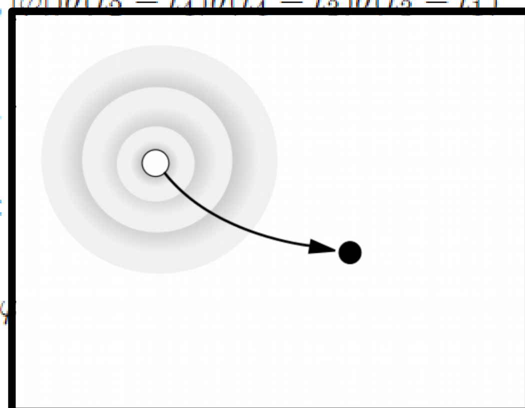
$$= -i \int_{t_1}^{\infty} dt_3 g(t_3, t_2; [\varphi]) \varphi(t_3) \theta(t_3$$

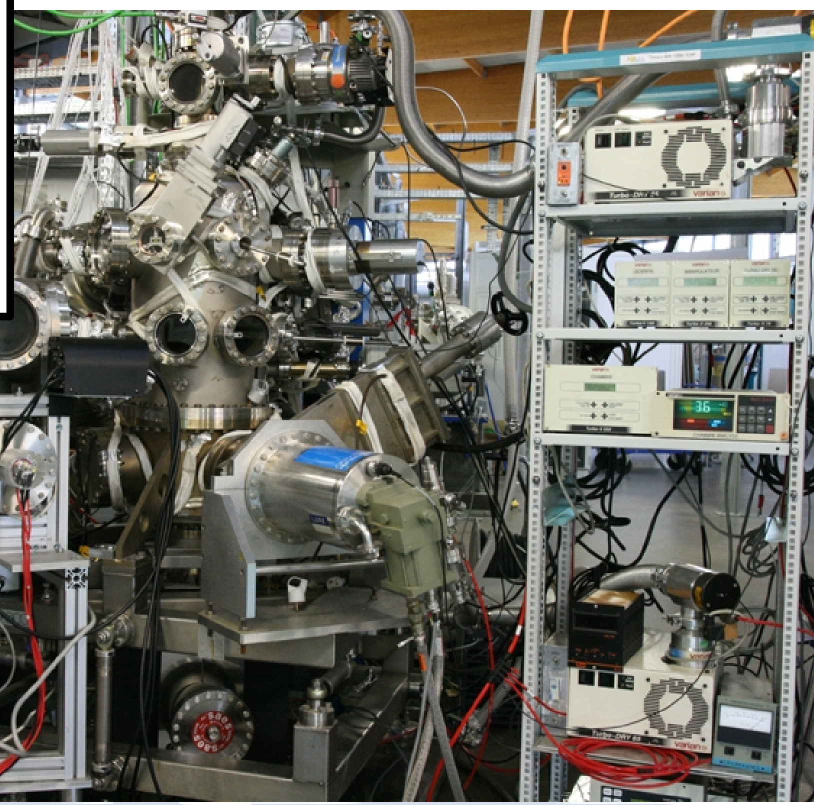
obtain a more compact expression:

$$\theta(t_2 - t_1) = i \int dt_3 g(t_3, t_2; [\varphi]) \Big\{ -$$

nipulate Eq. 1, with the change of variable y

$$= i\theta(t_2 - t_1) + i \int_{t_1}^{\infty} dt_3 \varphi(t_3) g(t_3, t_2; [\varphi]) + i^2$$





→ Theory and Experiment

$$+ i \int_{t_1}^{\infty} dt_3 \int dt_4 W(t_3, t_4) g(t_3, t_2; [\varphi]) \theta(t_2 - t_4) \theta(t_4 - t_3)$$

$$= -i \int_{t_1}^{\infty} dt_3 g(t_3, t_2; [\varphi]) \varphi(t_3) \theta(t_3 - t_1) + \int_{t_1}^{\infty} dt_3 \int dt_{\bar{1}} g(t_{\bar{1}}, t_2; [\varphi])$$

$$+ i \int_{t_1}^{\infty} dt_3 \int dt_4 W(t_3, t_4) g(t_3,$$

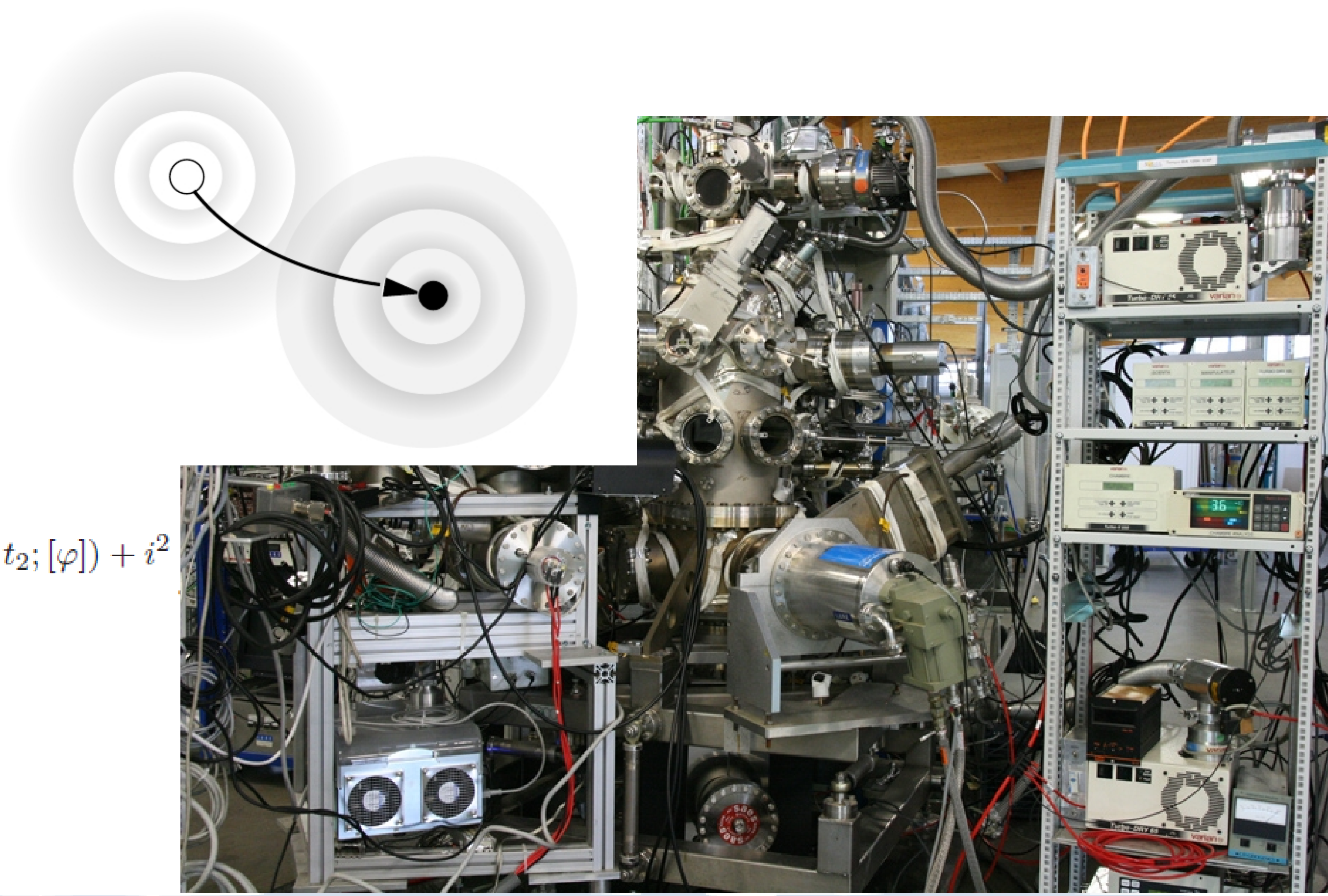
$$= -i \int_{t_1}^{\infty} dt_3 g(t_3, t_2; [\varphi]) \varphi(t_3) \theta$$

obtain a more compact expressi

$$(t_2 - t_1) = i \int dt_3 g(t_3, t_2; [\varphi]) \Big\{$$

nipulate Eq. 1, with the change

$$= i\theta(t_2 - t_1) + i \int_{t_1}^{\infty} dt_3 \varphi(t_3) g(t_3, t_2; [\varphi]) + i^2$$



→ Theory and Experiment

$$+ i\int_{t_1}^{\infty} dt_3 \int dt_4 W(t_3,t_4) g(t_3,t_2;[\varphi])\theta(t_2-t_4)\theta(t_4-t_3)$$

$$= -i\int_{t_1}^{\infty} dt_3 g(t_3,t_2;[\varphi])\varphi(t_3)\theta(t_3-t_1) + \int_{t_1}^{\infty} dt_3 \int dt_{\bar{1}} g(t_{\bar{1}},t_2;[\varphi])$$

$$+ i\int_{t_1}^{\infty} dt_3 \int dt_4 W(t_3,t_4) g(t_3,$$

$$= -i\int_{t_1}^{\infty} dt_3 g(t_3,t_2;[\varphi])\varphi(t_3)\theta$$

obtain a more compact expressi

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nipulate Eq. 1, with the change

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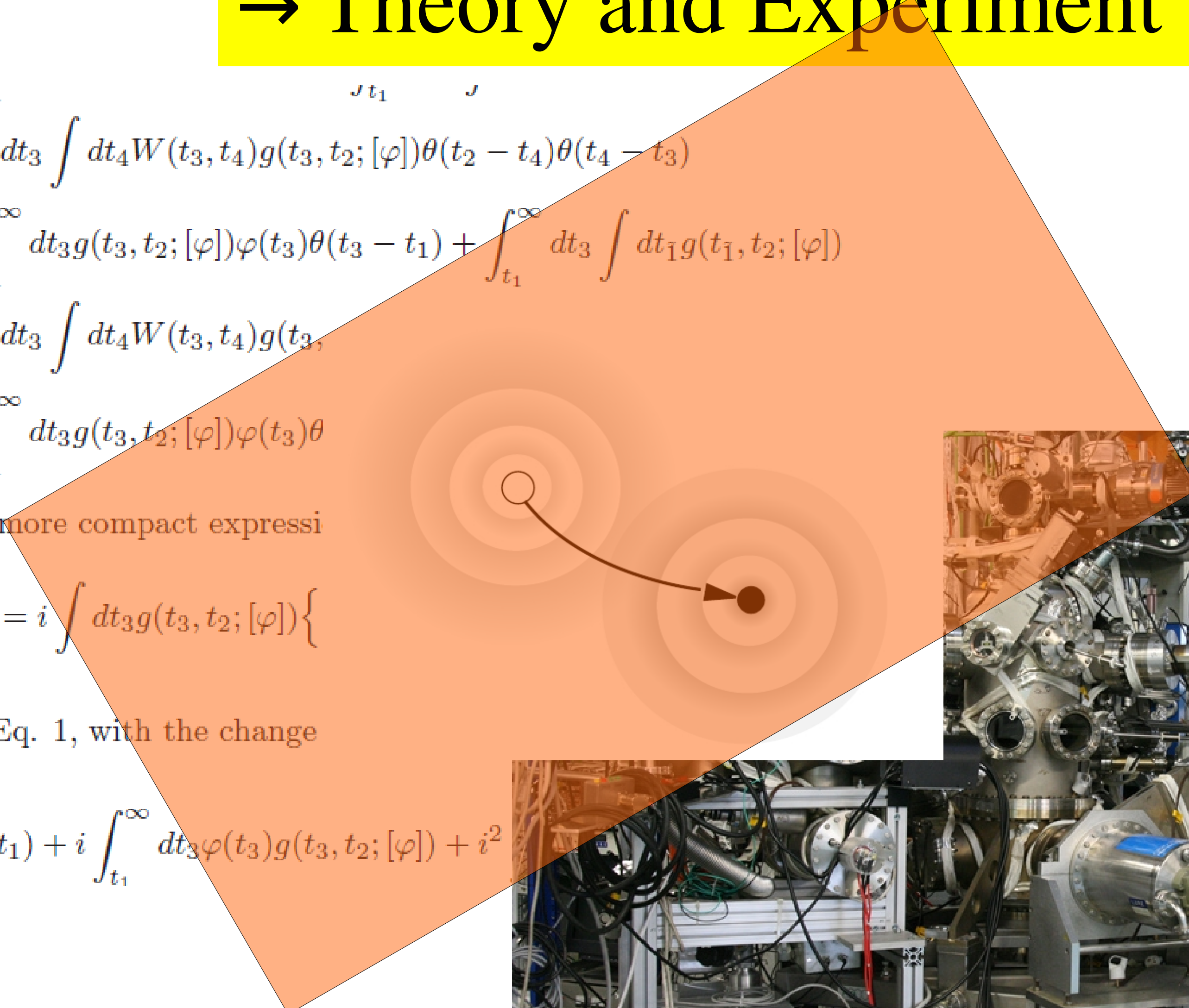
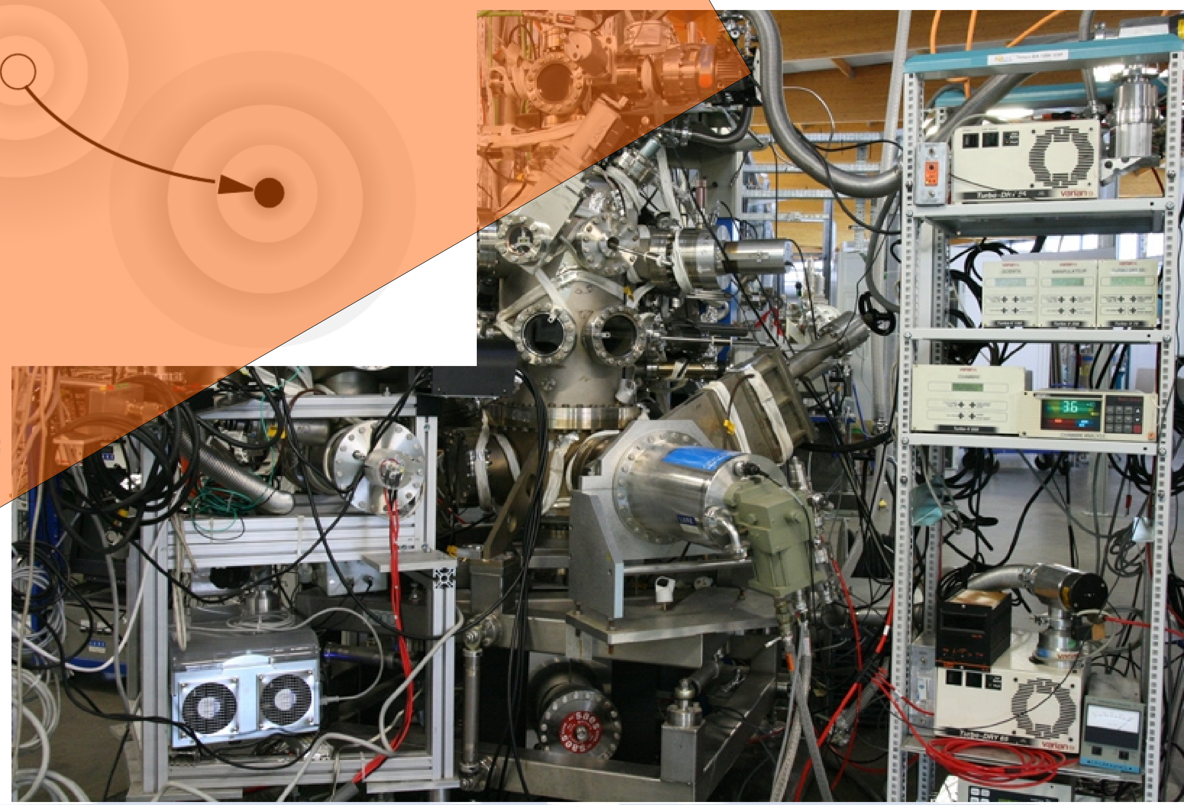
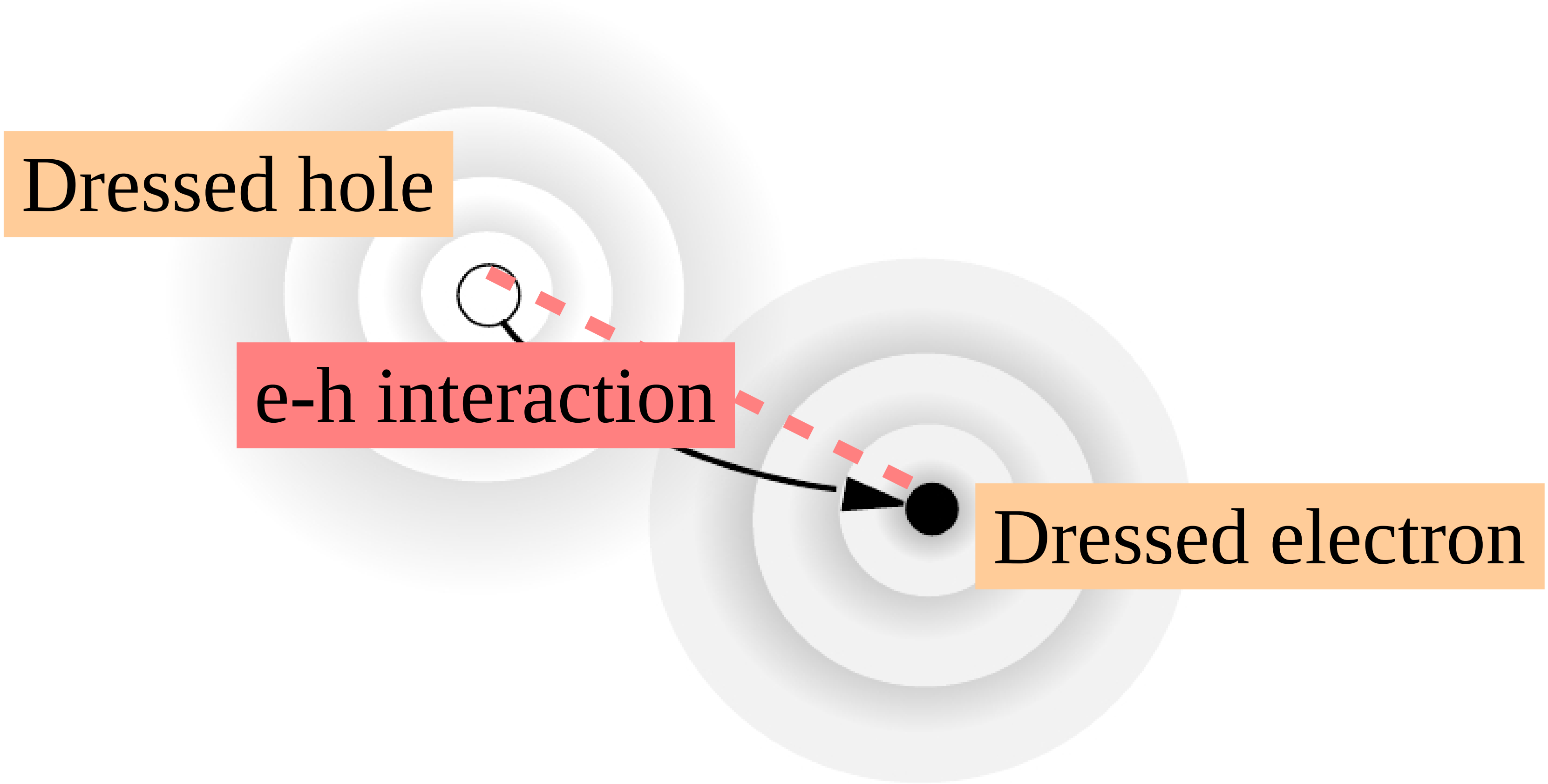
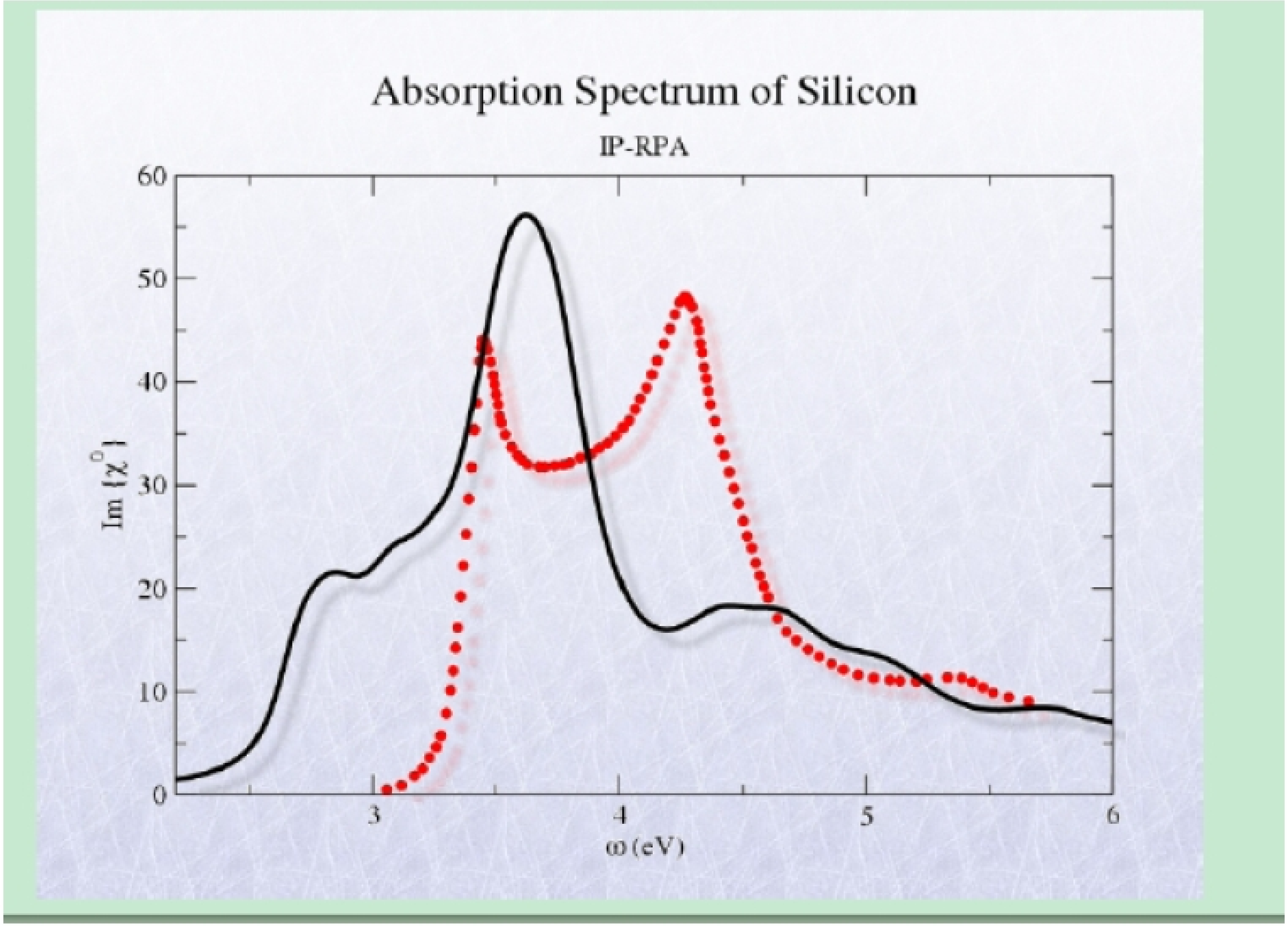




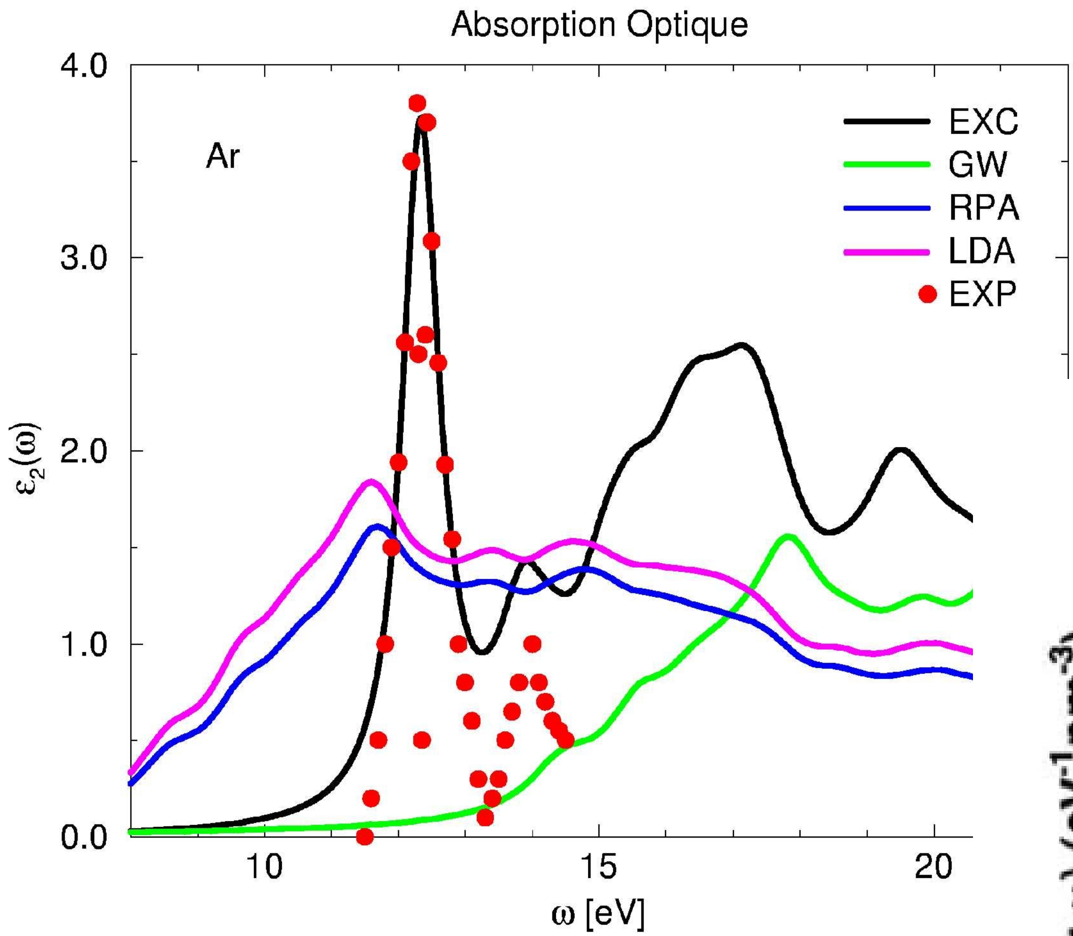
→ Electron-hole correlation

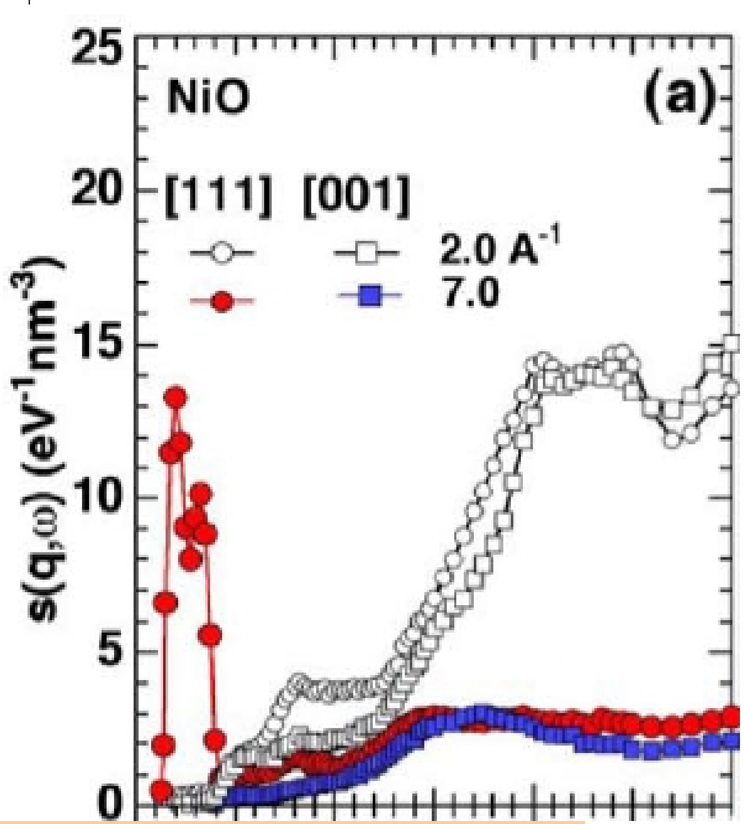


e-h problem: Bethe-Salpeter equation



Absorption Spectrum of Silicon
IP-RPA
Im {χ0}
ω (eV)
0
10
20
30
40
50
60
3
4
5
6





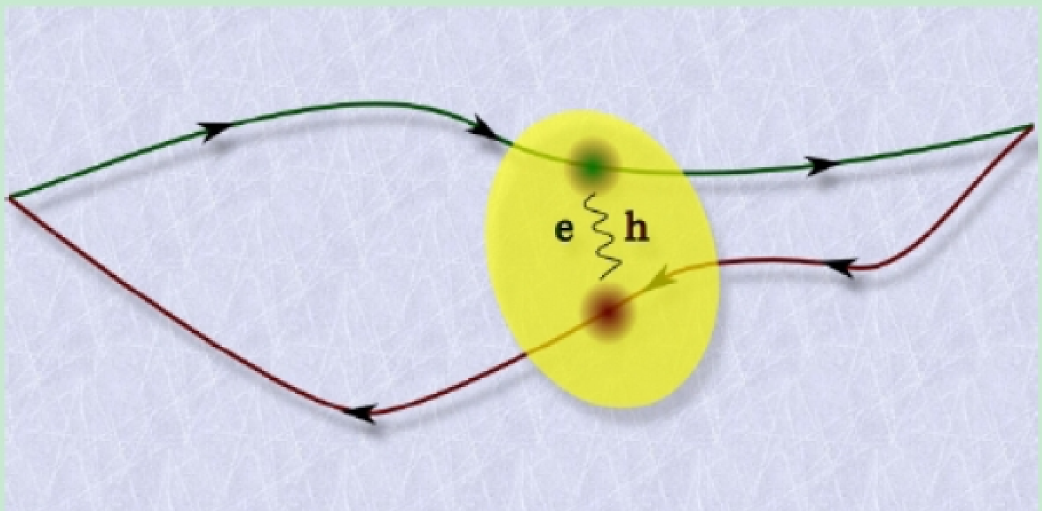
V. Olevano et al. (2000)
(bulk silicon 1998)

Larson et al., PRL 99, 026401 (2007)

Exciton: Lee, Hsueh, Ku, PRB 82, 081106 (2010)

GGΓ Polarizability

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



Comparison with Linear Response quantities

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

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

$$\frac{\delta V_H}{\delta V_{ext}} = \frac{\delta V_H}{\delta n}\frac{\delta n}{\delta V_{ext}} = v\chi$$

$$\frac{\delta V_{xc}}{\delta V_{ext}} = \frac{\delta V_{xc}}{\delta n}\frac{\delta n}{\delta V_{ext}} = f_{xc}\chi$$

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

with f_{xc} = exchange-correlation kernel

Bethe-Salpeter Equation

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

$$\sum_{n_3 n_4} H^{2p}{}_{n_1 n_2}^{n_3 n_4} A_\lambda^{n_3 n_4} = E_\lambda A_\lambda^{n_1 n_2}$$

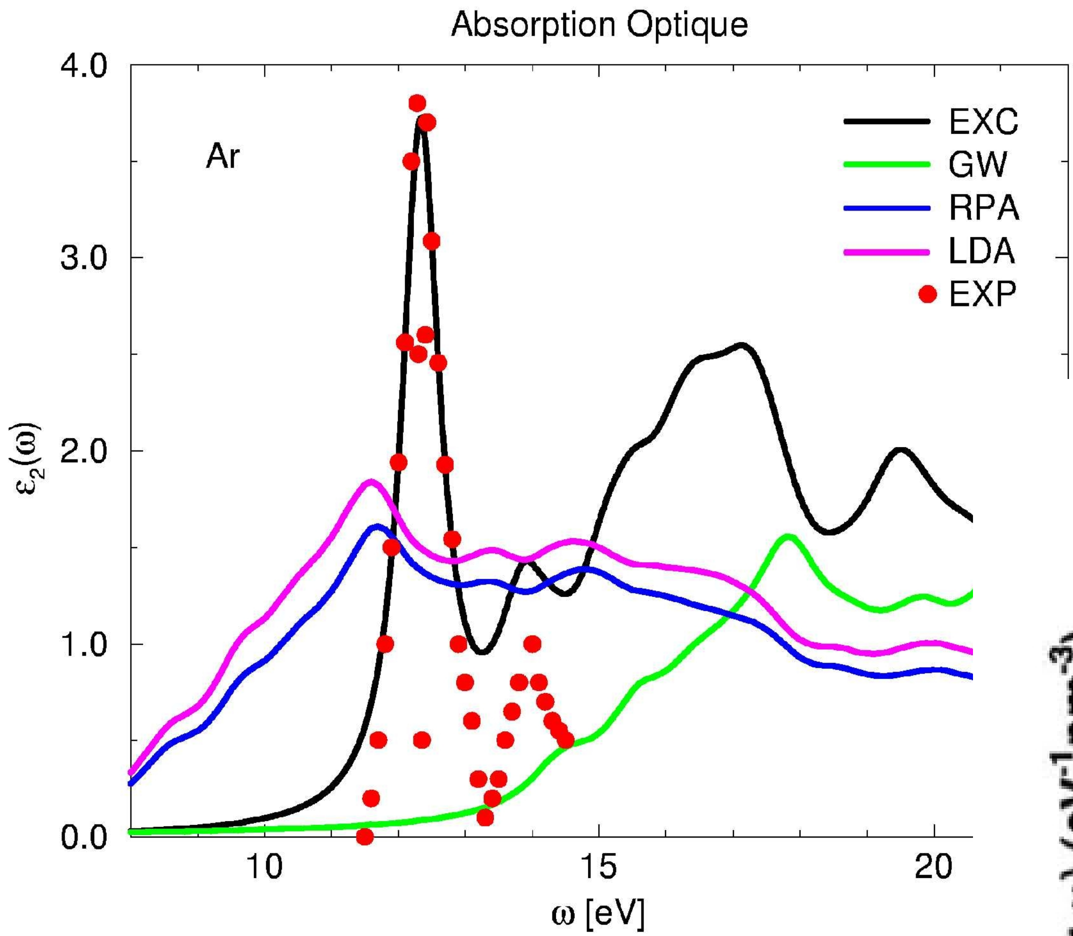
$$H^{2p}{}_{n_1 n_4 \sigma}^{n_3 n_2} \equiv \left(\varepsilon_{n_2\sigma} - \varepsilon_{n_1\sigma}\right) \delta_{n_1 n_3} \delta_{n_2 n_4} + \left(f_{n_1\sigma} - f_{n_4\sigma}\right) \Xi_{n_1 n_4 \sigma}^{n_3 n_2}$$

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

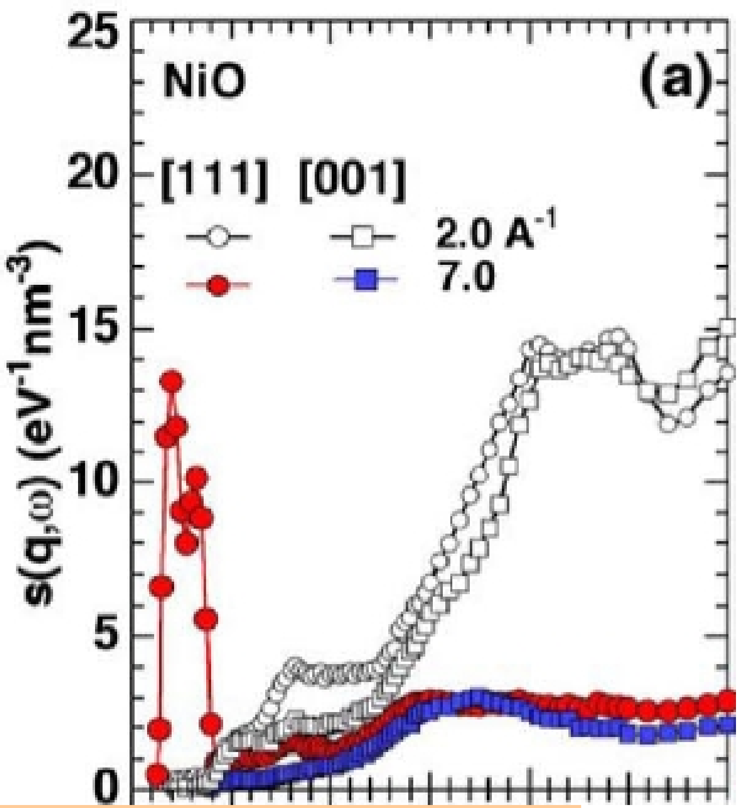
$$\Xi_{n_1 n_4 \sigma}^{n_3 n_2} = v_{n_1 n_4 \sigma}^{n_3 n_2} - W_{n_1 n_3 \sigma}^{n_4 n_2}$$

$$\chi^0_{00}(\mathbf{q},\omega) = \sum_{vc\mathbf{k}\sigma} \frac{|\tilde{\rho}_{v\mathbf{k}c\mathbf{k}+\mathbf{q}\sigma}|^2}{\omega - (\varepsilon_{c\mathbf{k}+\mathbf{q}\sigma} - \varepsilon_{v\mathbf{k}\sigma}) - i\eta}$$

$$\bar{\chi}_{00}(\mathbf{q},\omega) = \sum_{\lambda} \frac{|\sum_{vc\mathbf{k}\sigma} A_\lambda^{v\mathbf{k}c\mathbf{k}+\mathbf{q}\sigma}\,\tilde{\rho}_{v\mathbf{k}c\mathbf{k}+\mathbf{q}\sigma}|^2}{\omega - E_\lambda - i\eta}$$

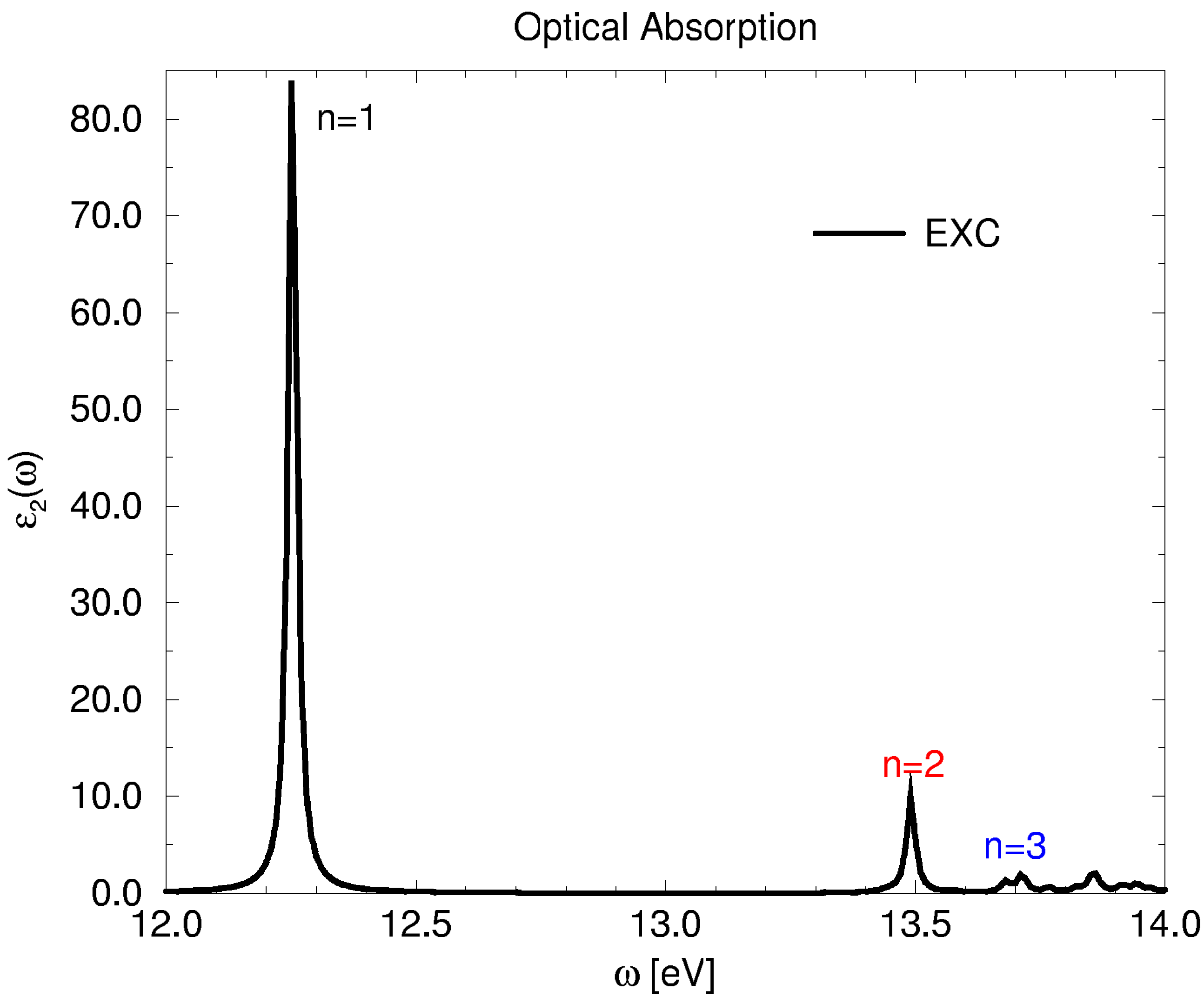


V. Olevano et al. (2000)
(bulk silicon 1998)

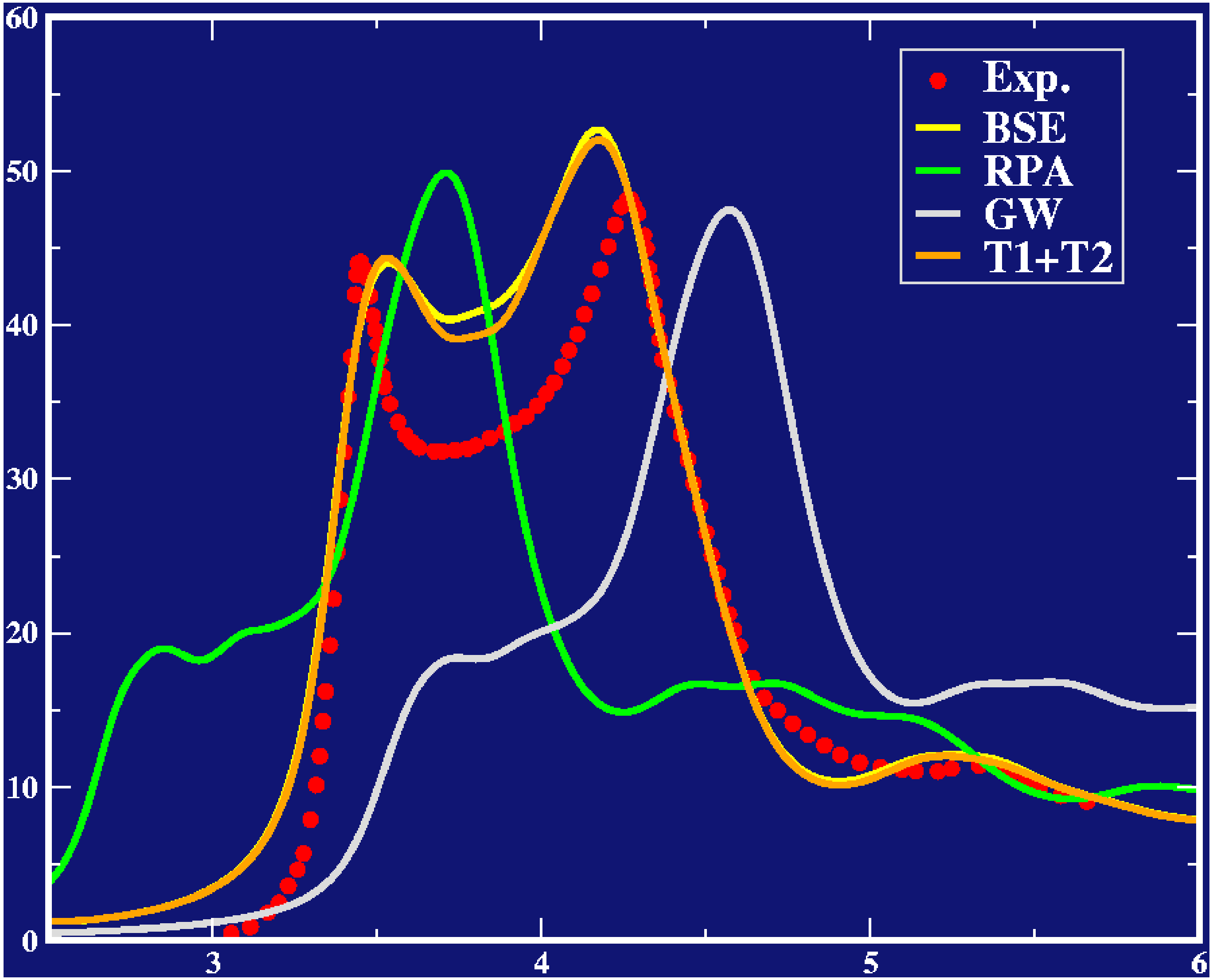


Larson et al., PRL 99, 026401 (2007)

Exciton: Lee, Hsueh, Ku, PRB 82, 081106 (2010)

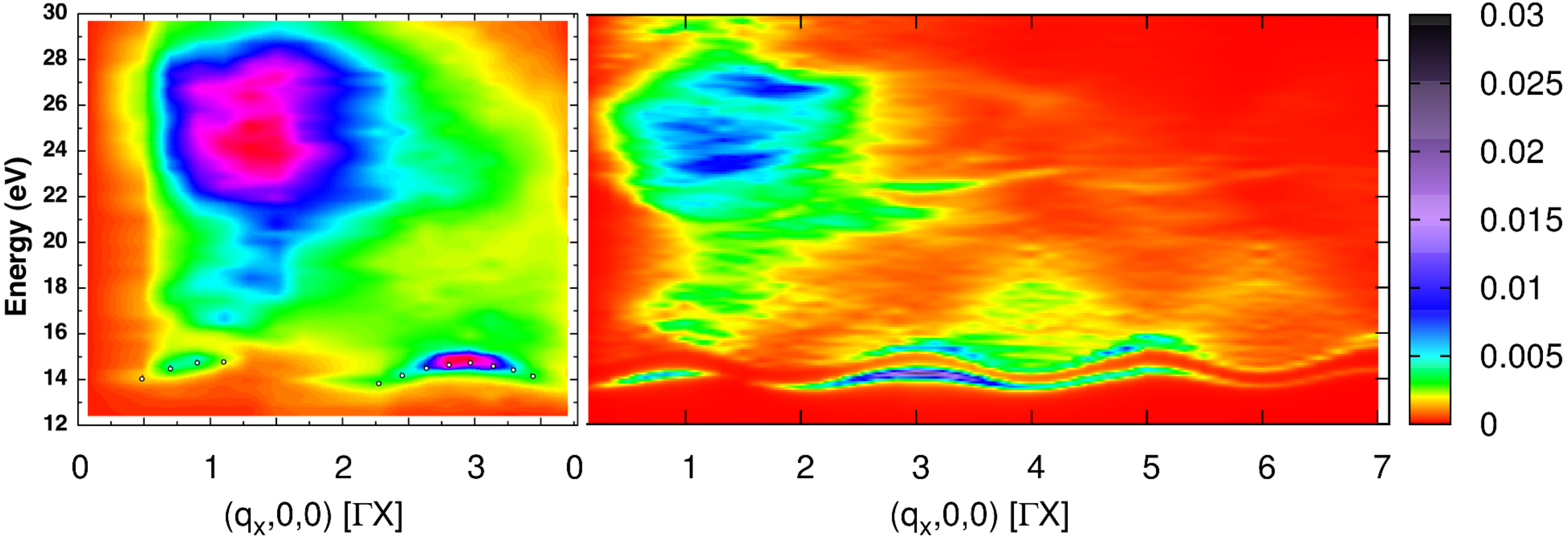


Hydrogen series in absorption spectrum of solid argon

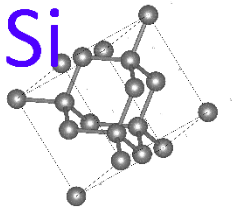


F. Sottile et al., Phys Rev. Lett **91**, 056402 (2003).

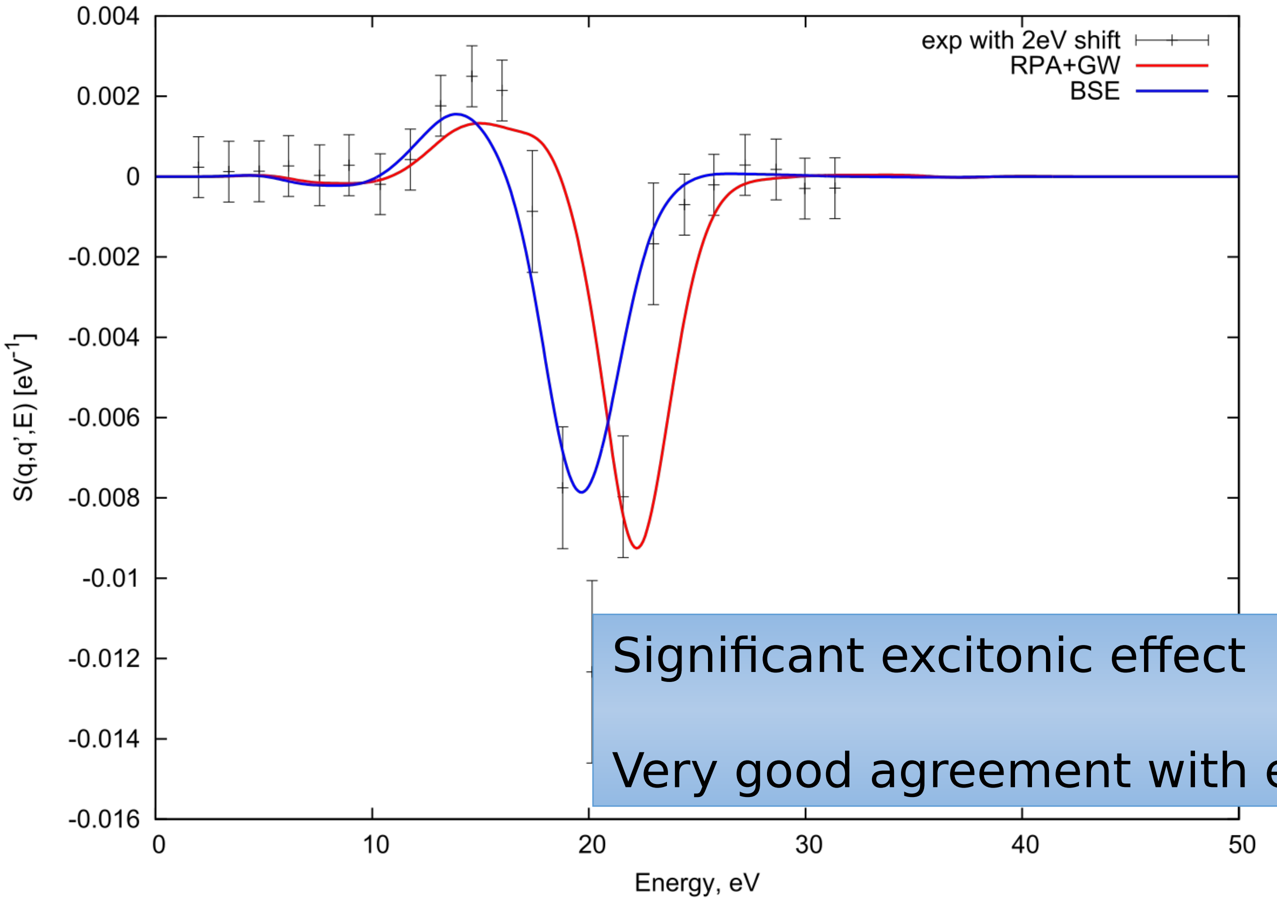
Exciton dispersion in LiF



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

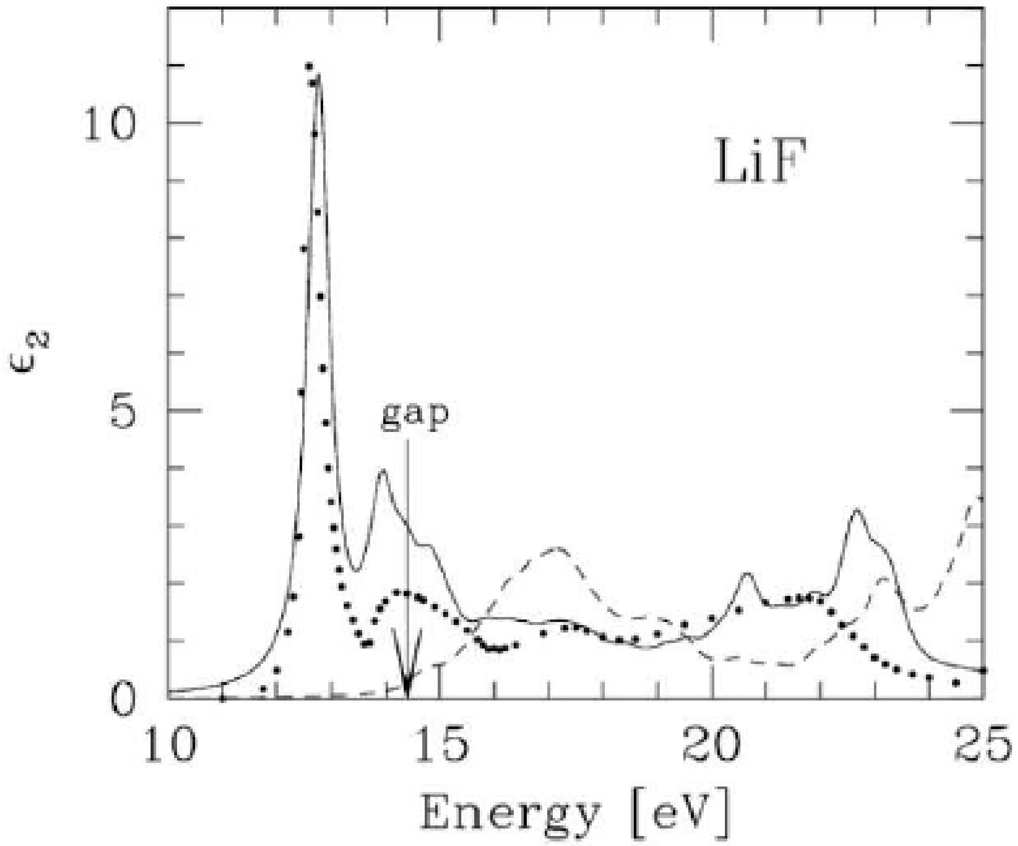


PhD thesis Igor Reshetnyak (23.9.2015)



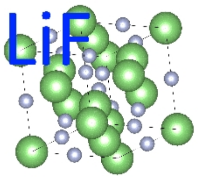
Significant excitonic effect

Very good agreement with experiment

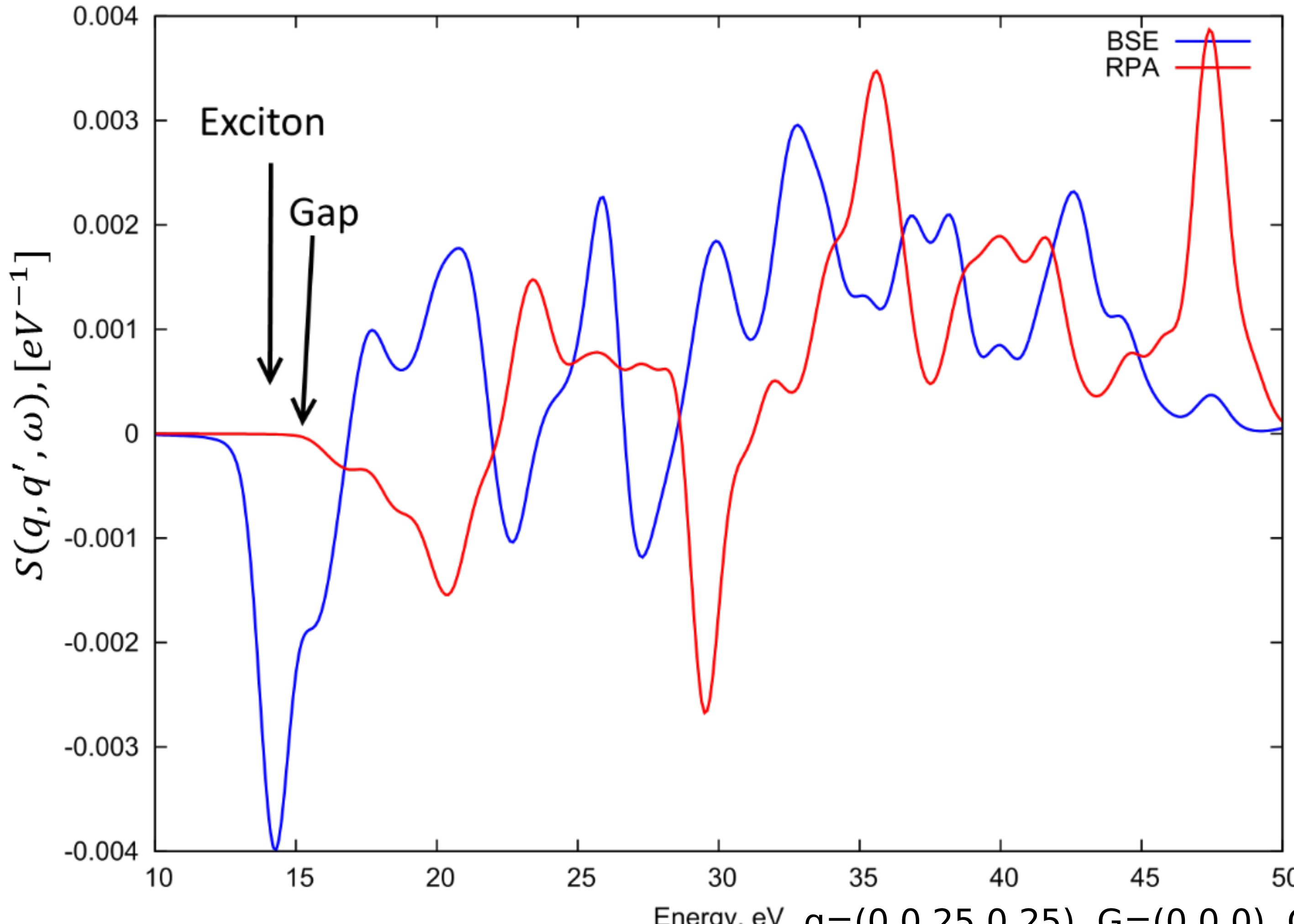


Rohlfing and Louie, PRL 81, 2312 (1998)

Mixed Dynamic Structure Factor



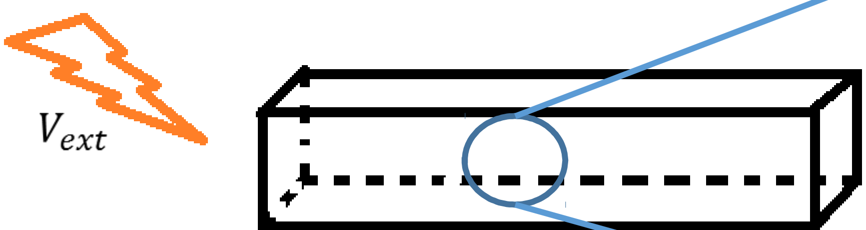
Strongly bound exciton visible

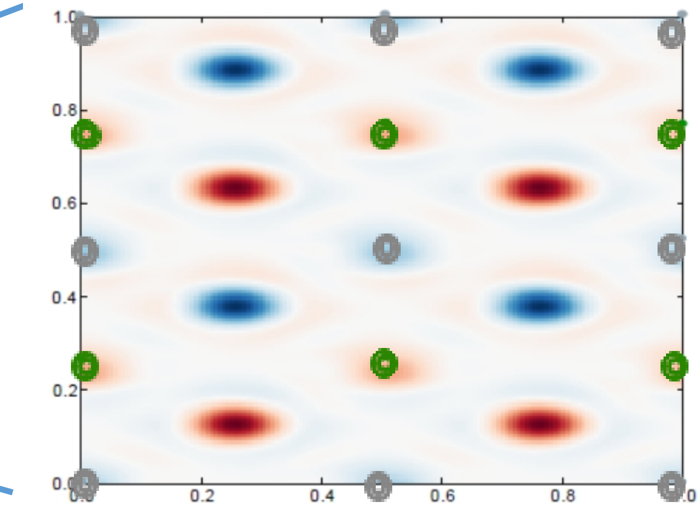


q=(0,0.25,0.25), G=(0,0,0), G'=(1,1,1)

PhD thesis Igor Reshetnyak (23.9.2015)

What can we do with it?
For example, induced charges





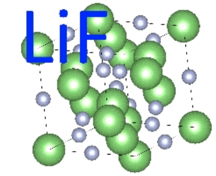
$$\hat{\mathbb{H}} = \hat{\mathbb{H}}_{electron} + \hat{\mathbb{H}}_{ext}(t)$$

(exchange)

In linear response:

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

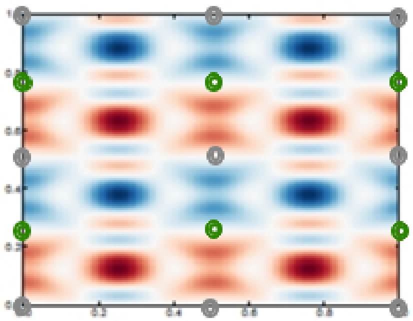
Ralf Hambach
Giulia Pegolotti
Claudia Roedl
Igor Reshetnyak



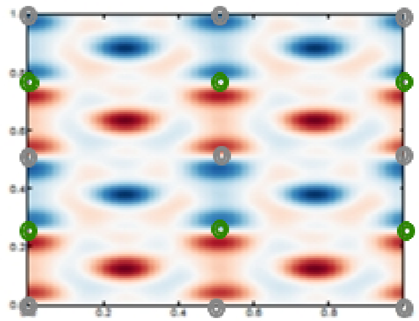
Induced Charges

$$\delta n(\boldsymbol{r},t) = \int d\omega \sum_{\boldsymbol{q},\boldsymbol{G},\boldsymbol{G}'} \chi_{\boldsymbol{G},\boldsymbol{G}'}(\boldsymbol{q},\omega) V_{ext}(\boldsymbol{q}+\boldsymbol{G}',\omega) e^{i(\boldsymbol{q}+\boldsymbol{G})\boldsymbol{r}} e^{-i\omega t}$$

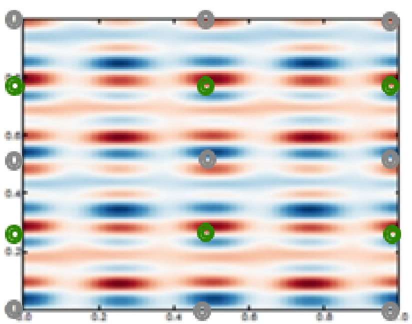
Plane-wave external potential



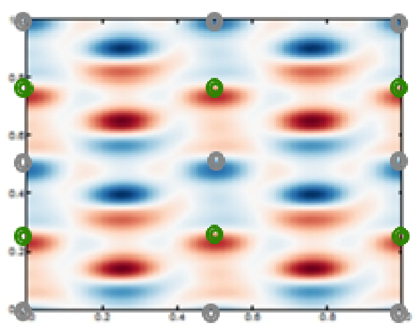
RPA susceptibility, $\omega = 14eV$



RPA susceptibility, $\omega = 25.6eV$



BSE susceptibility, $\omega = 14eV$

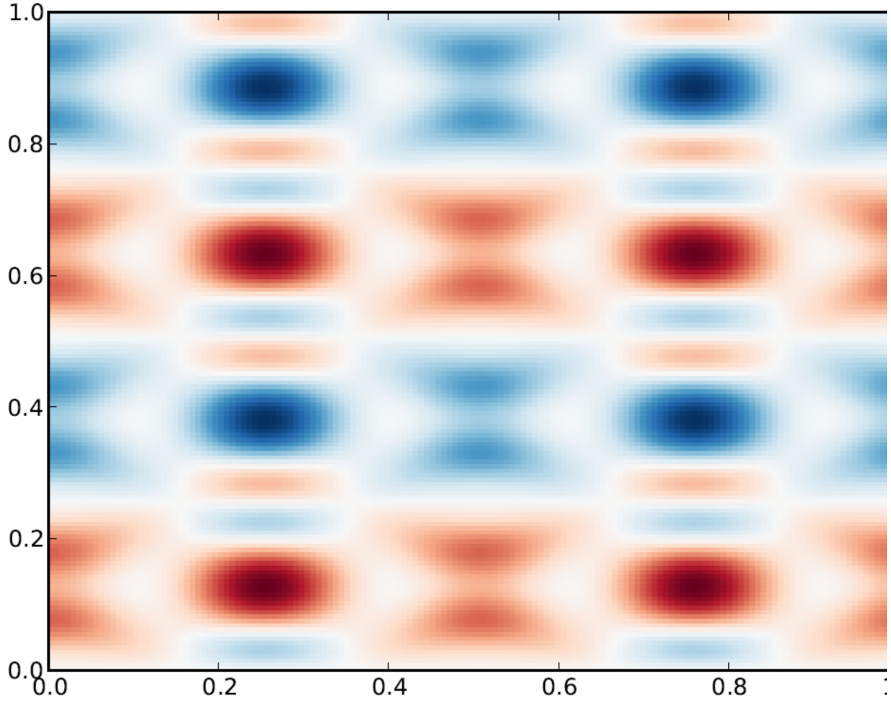


BSE susceptibility, $\omega = 25.6eV$

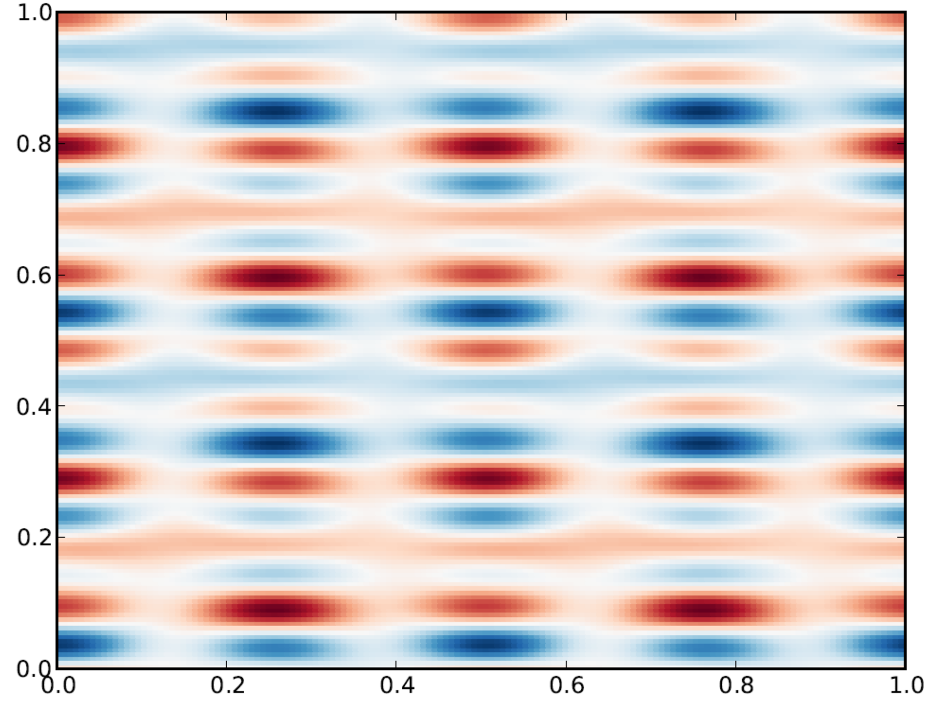
Excitonic effects visible

PhD thesis I. Reshetnyak

[1] P. Abbamonte et al. *Phys. Rev. Lett.* 2004. [2] P. Abbamonte et al. *Advanced Materials* 2010.



RPA



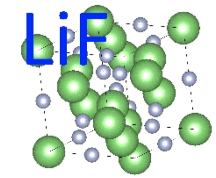
BSE

At 14.1 eV

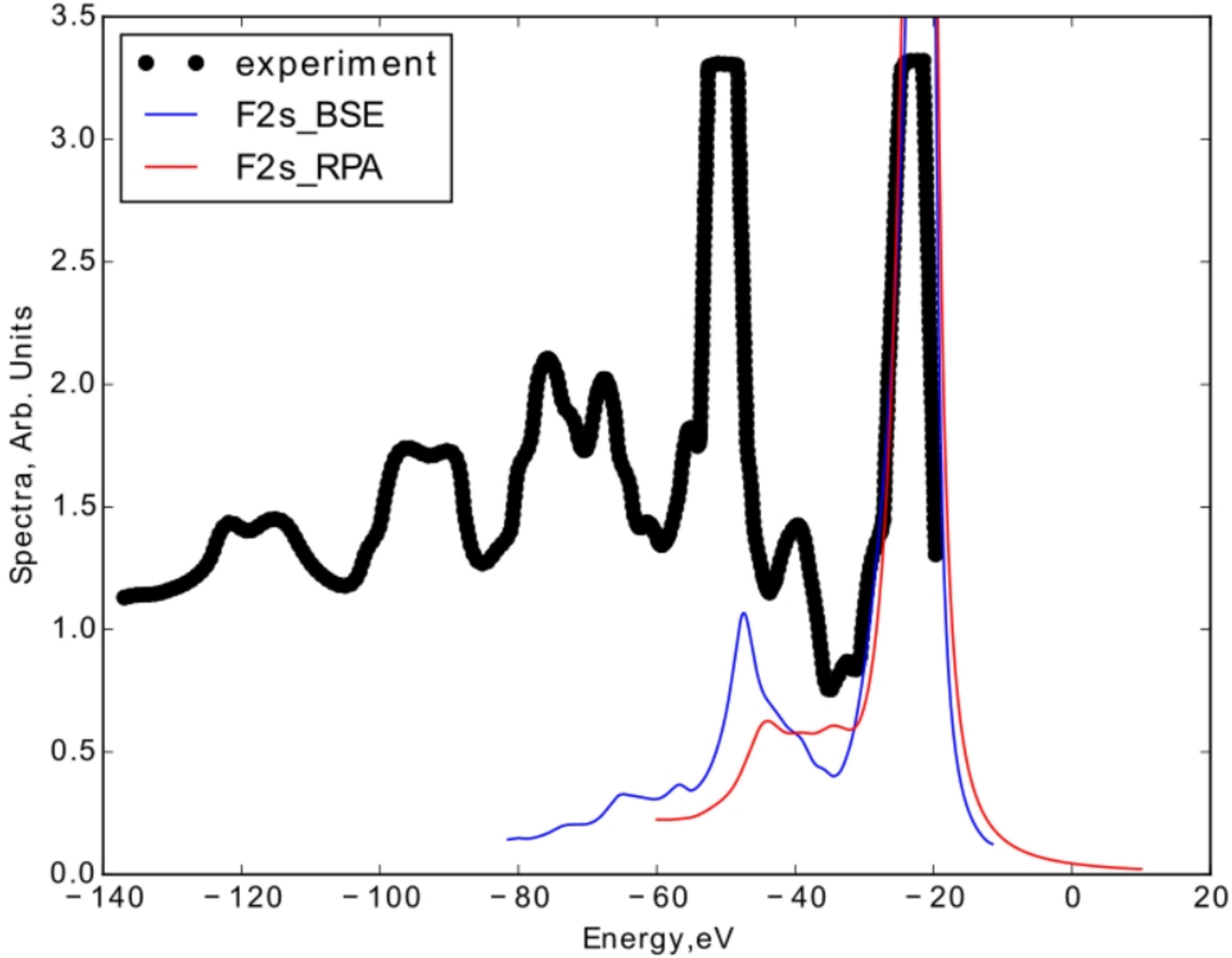
The whole matrix → follow excitations in real space and time

Consequences of excitons?

PhD thesis I. Reshetnyak



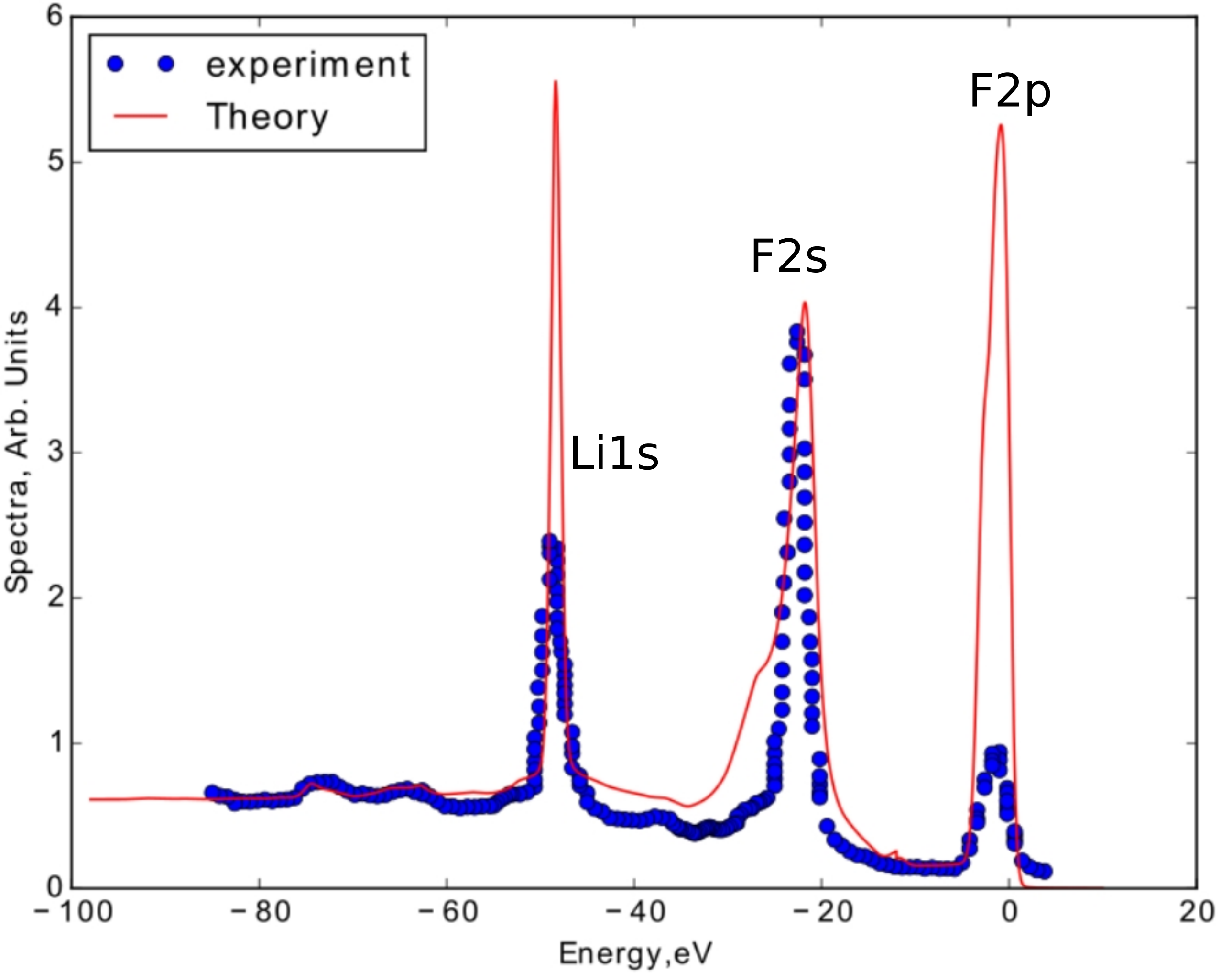
Excitonic effects in photoemission satellites



[1] Marisa Scrocco Phys. Rev. B, 1985.

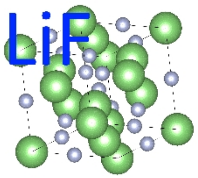
Overall comparison to experiments

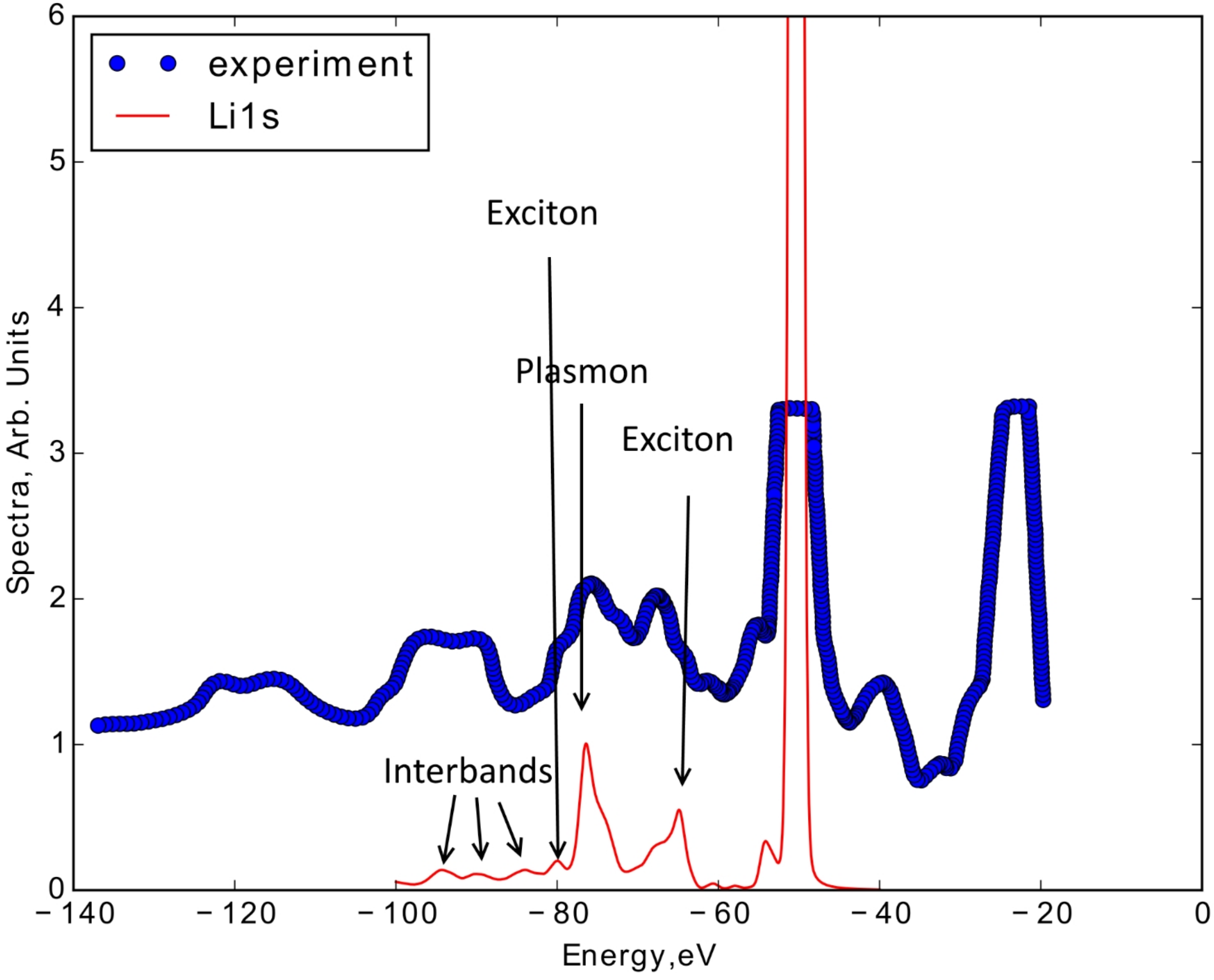
LiF



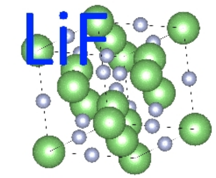
[1] S. P. Kowalczyk et al. *Phys. Rev. B*, 1974

Analysis

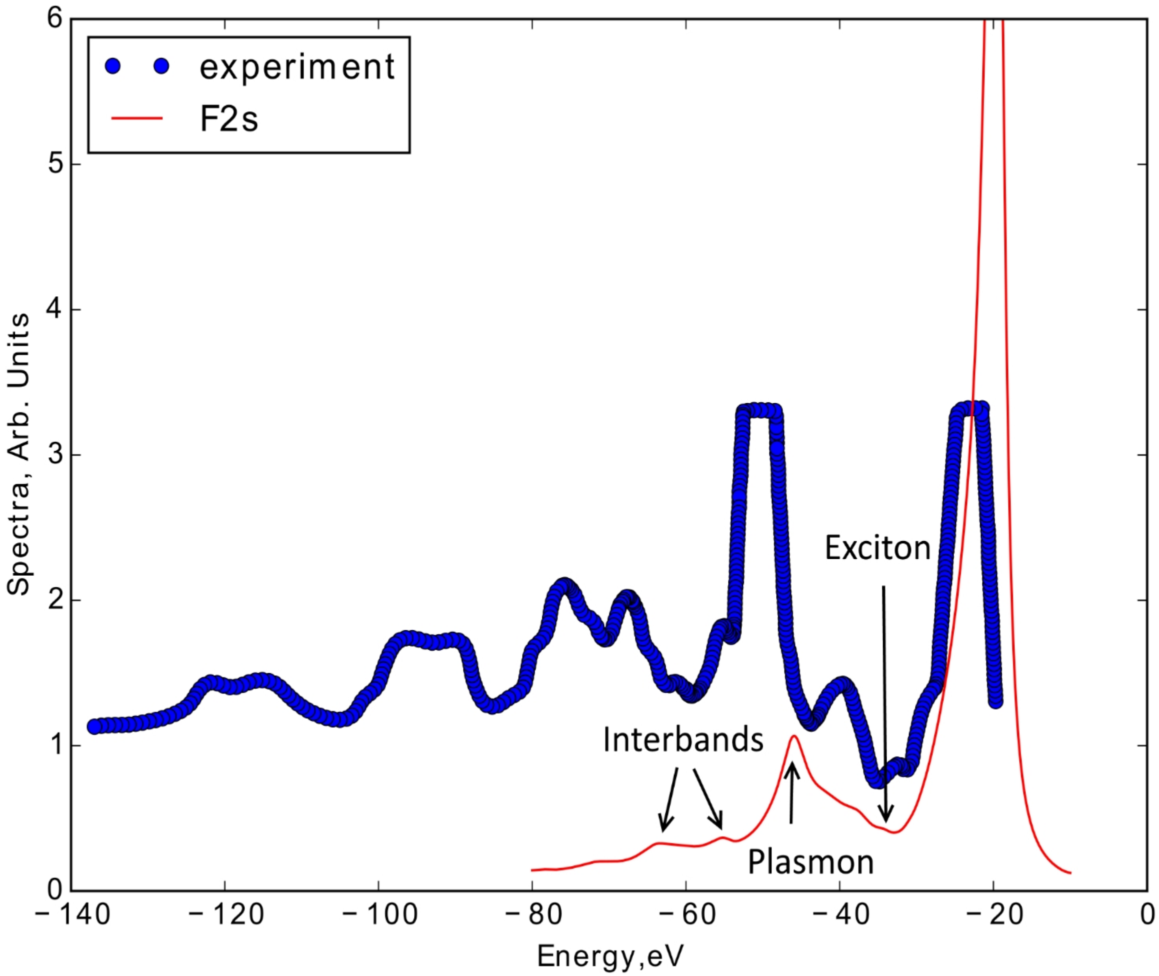




[1] Marisa Scrocco Phys. Rev. B, 1985.



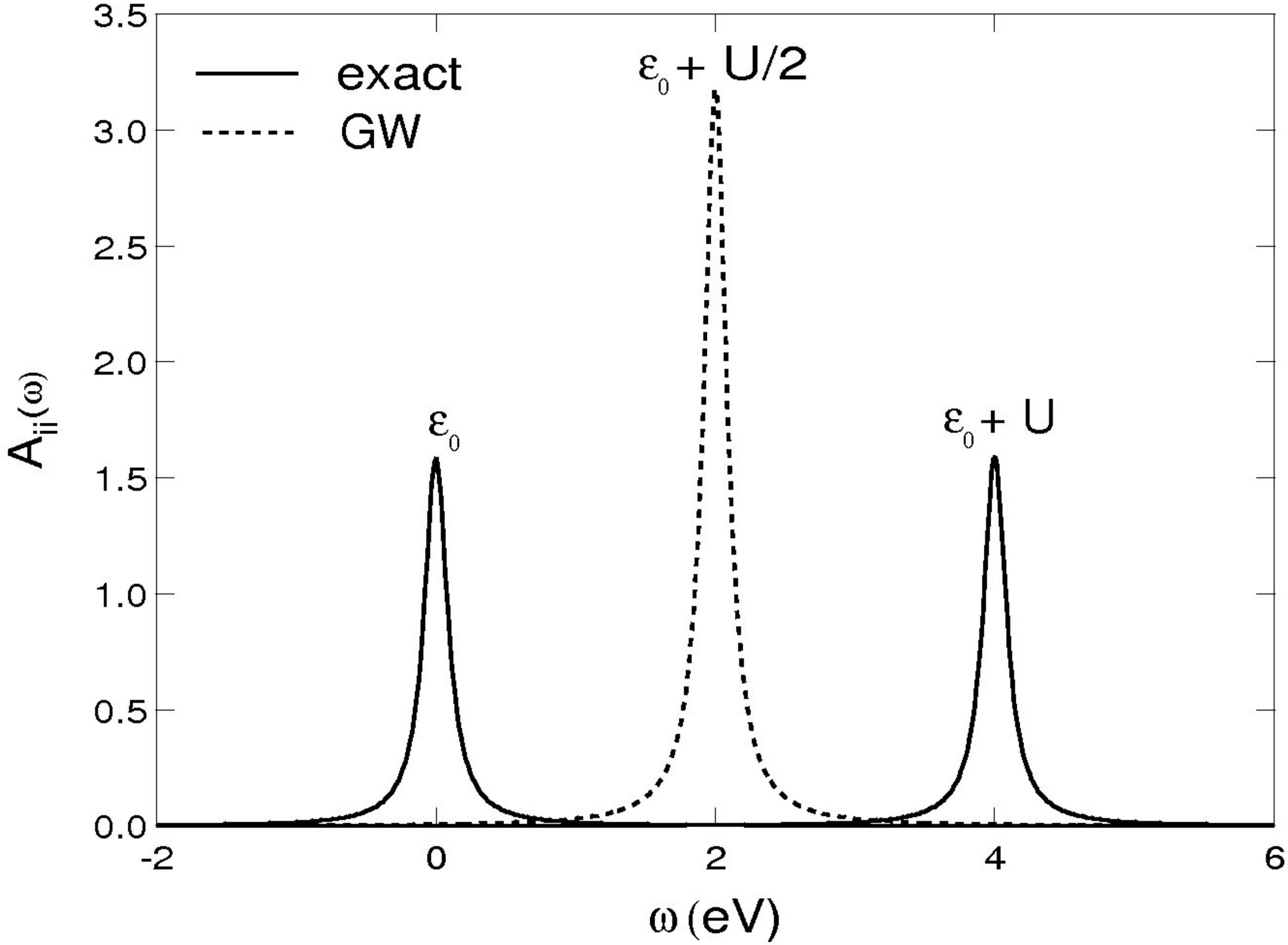
Analysis



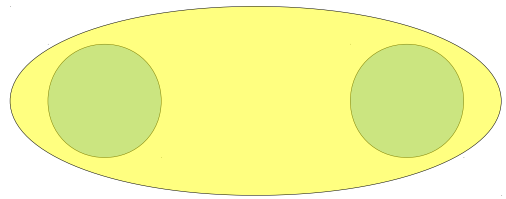
[1] Marisa Scrocco Phys. Rev. B, 1985.

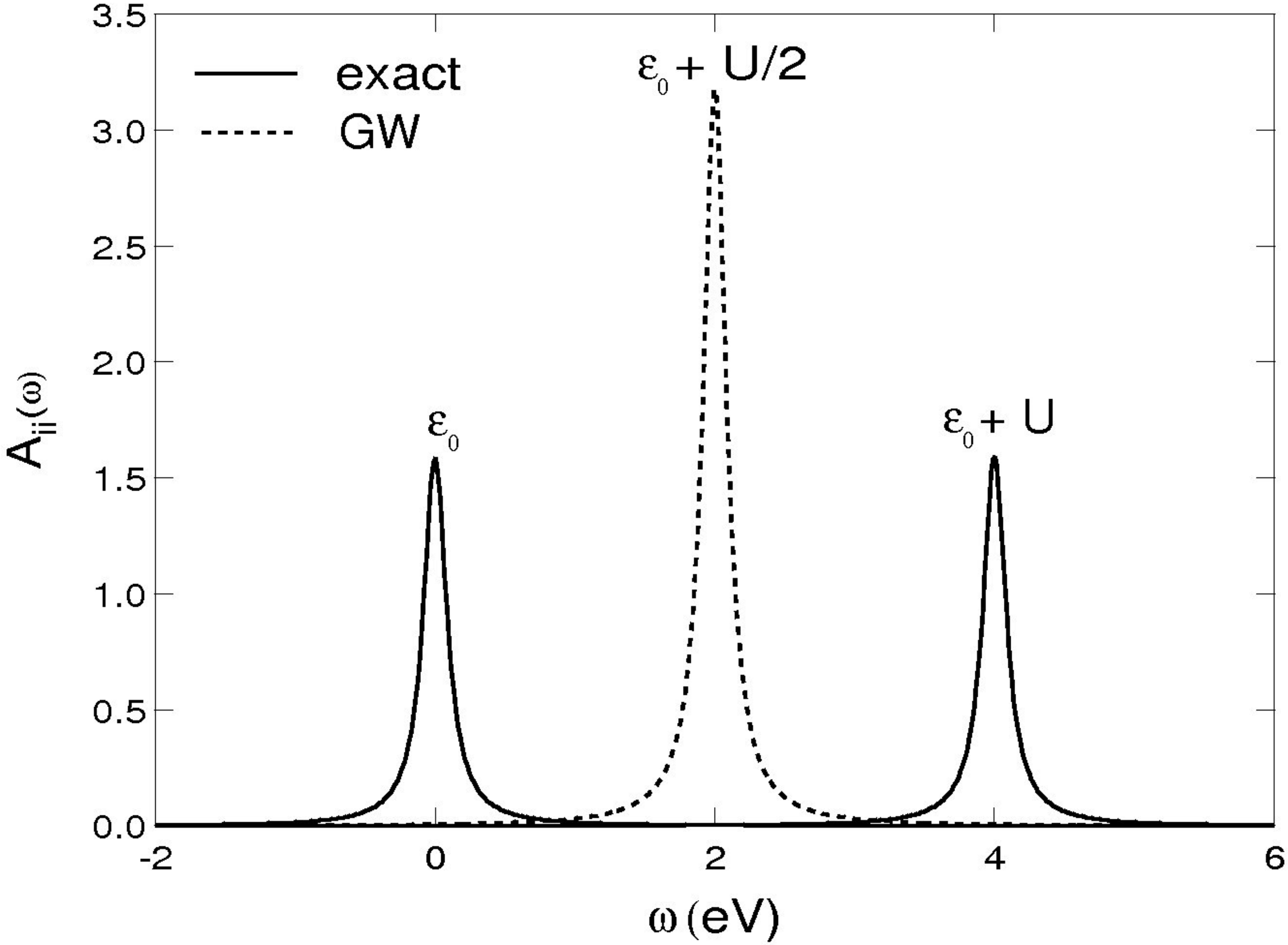
Is life that simple?

H_2^+



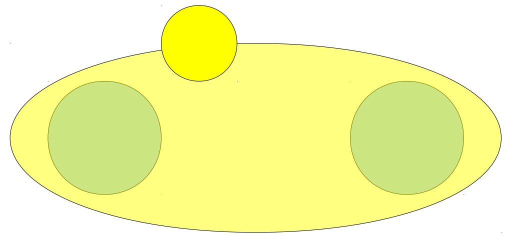
H_2^+

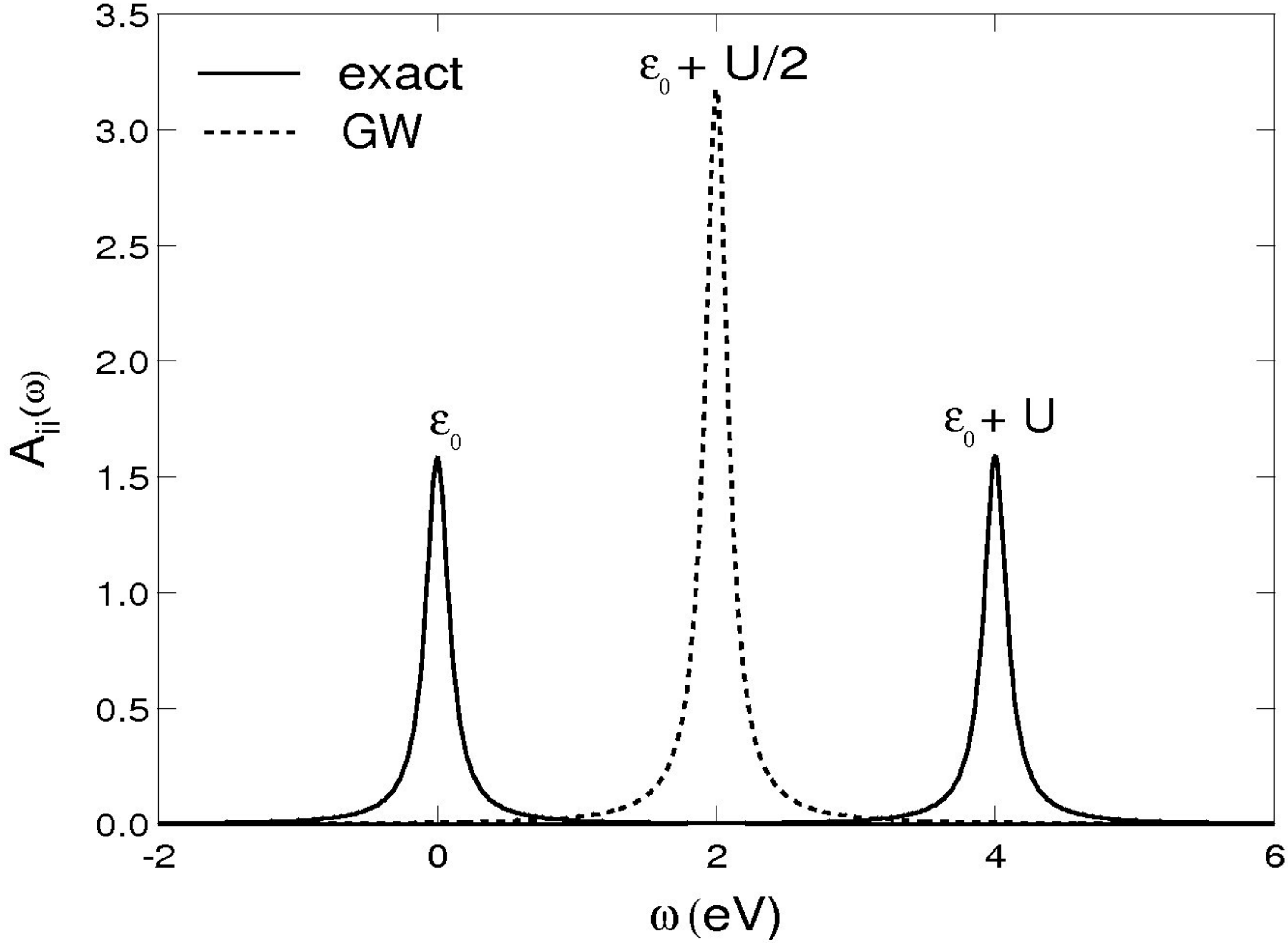




exact
GW
ε_0 + U/2
ε_0
ε_0 + U
$A_{ij}(\omega)$
ω (eV)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2
0
2
4
6

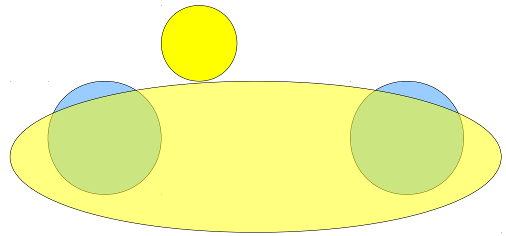
H_2^+

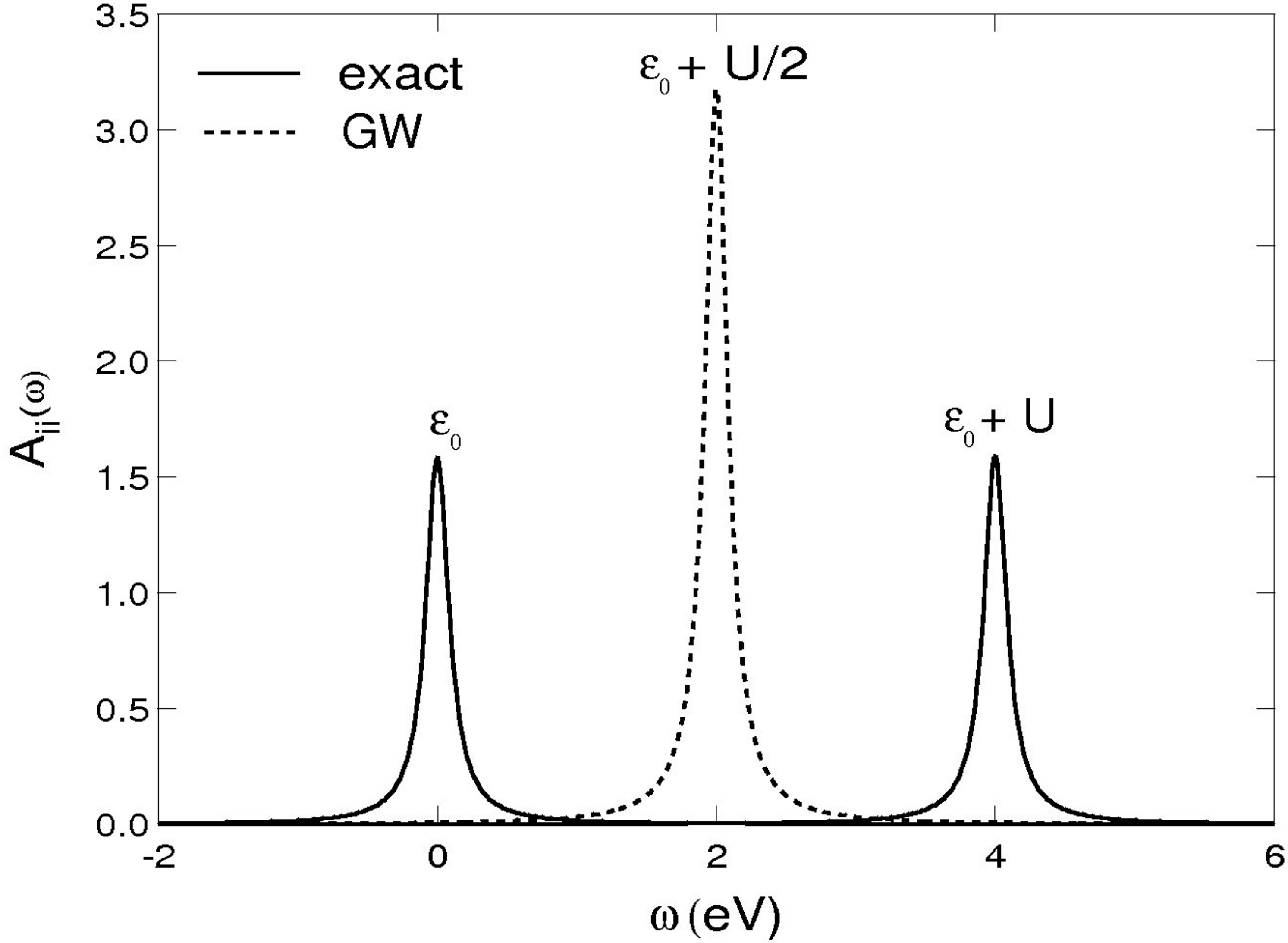




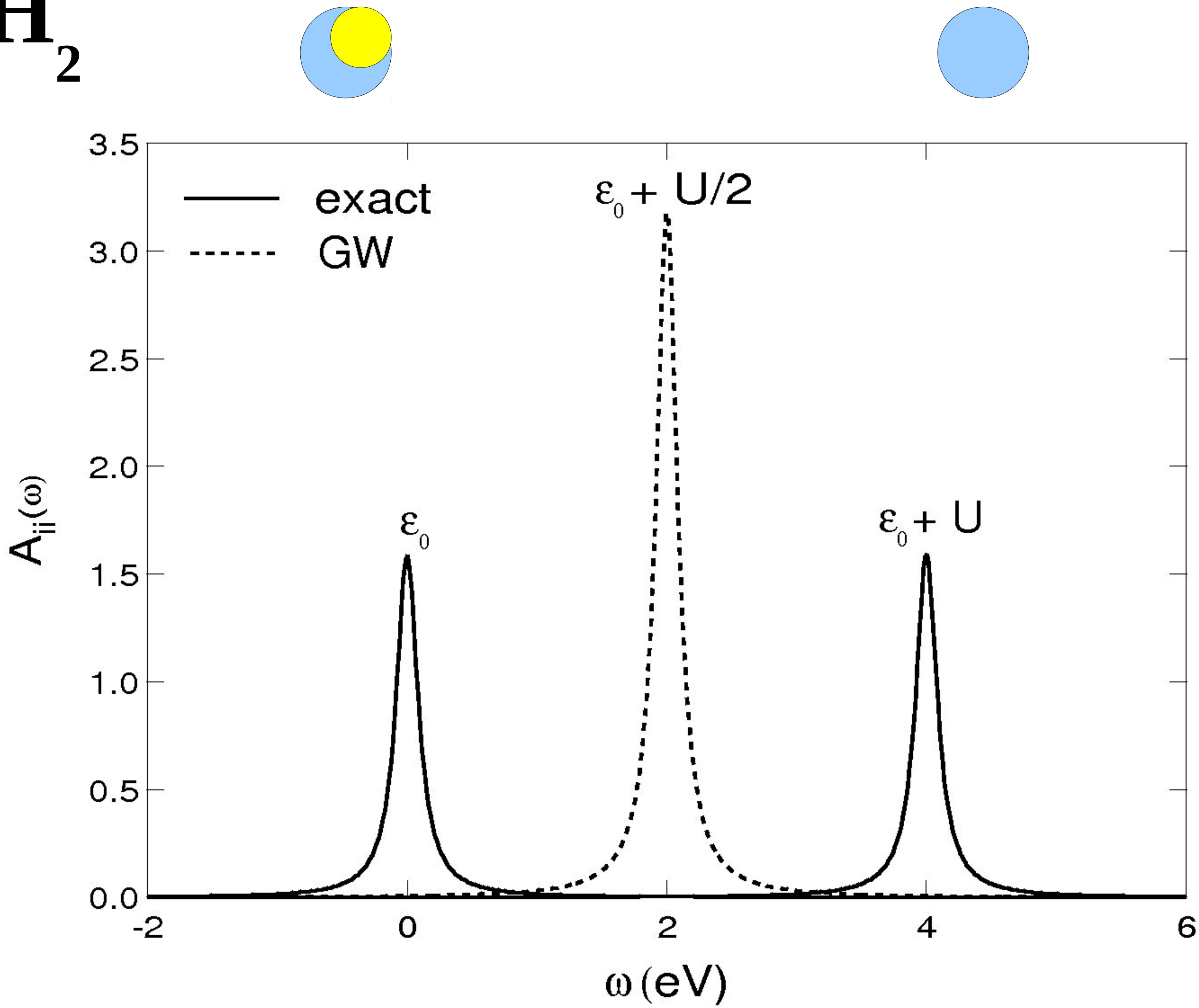
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
$A_{ii}(\omega)$
exact
GW
$\varepsilon_0 + U/2$
ε_0
$\varepsilon_0 + U$
-2
0
2
4
6
ω (eV)

H_2^+



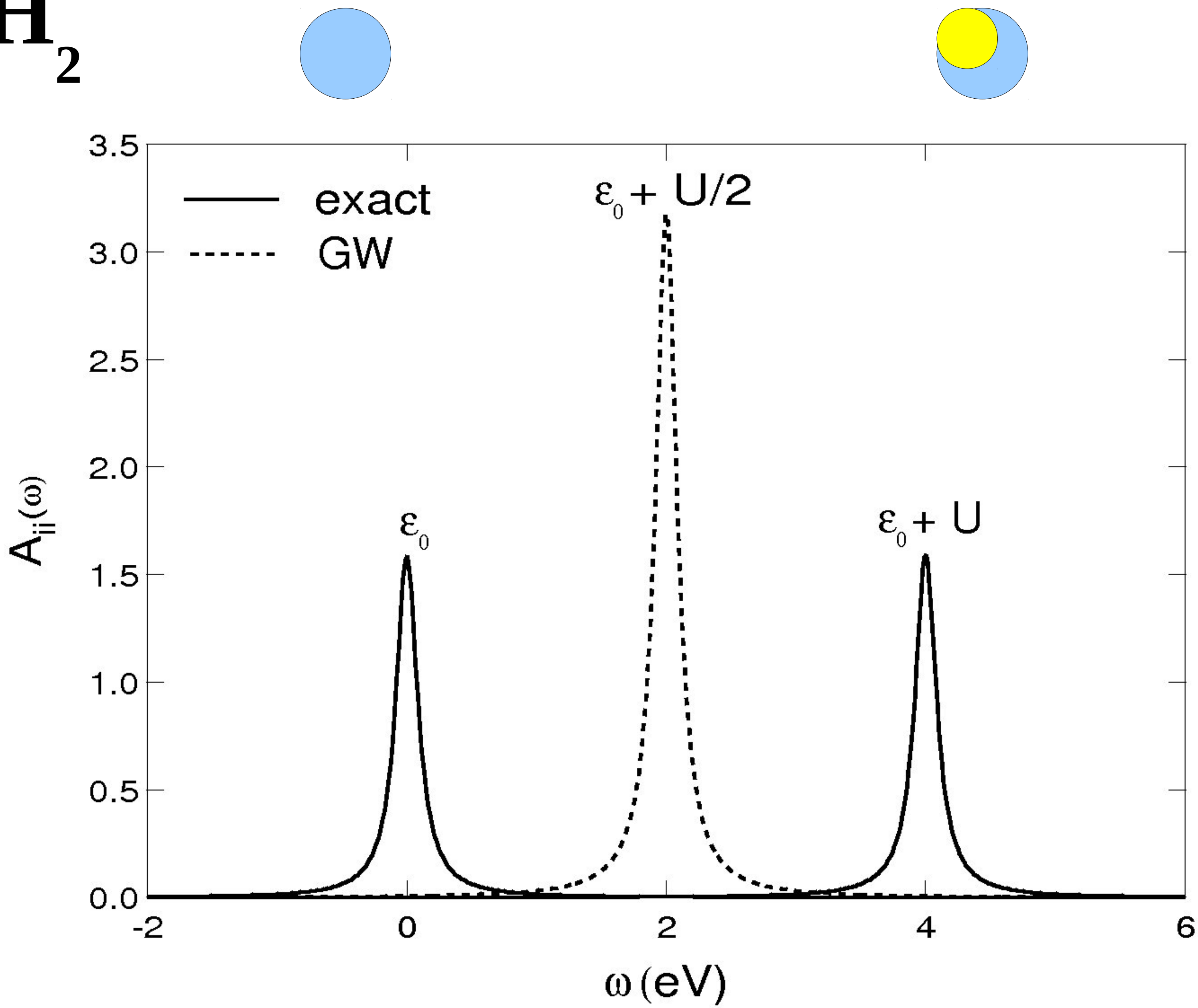


H_2^+



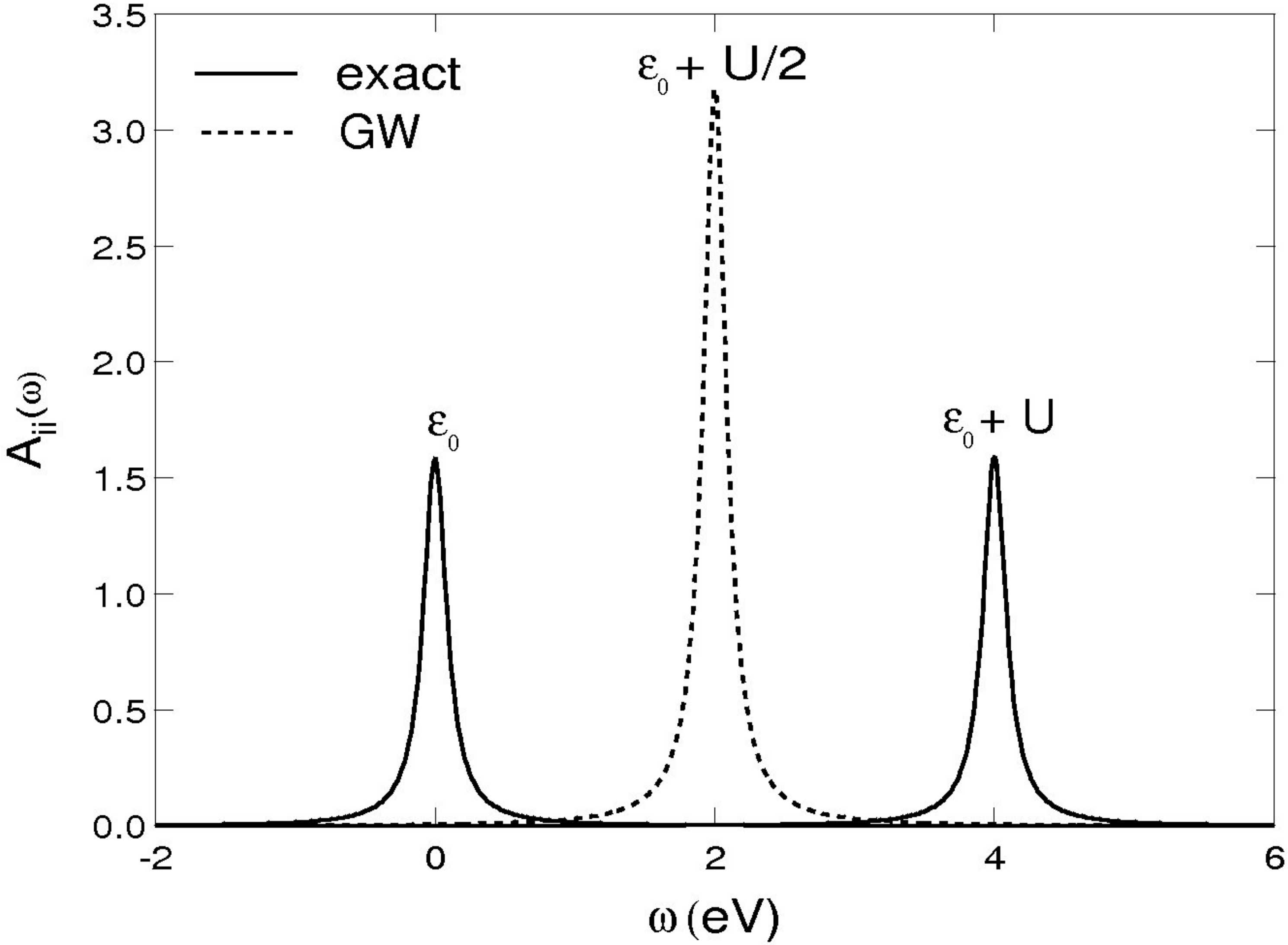
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
exact
GW
$\varepsilon_0 + U/2$
ε_0
$\varepsilon_0 + U$
$A_{ii}(\omega)$
-2
0
2
4
6
ω (eV)

H_2^+



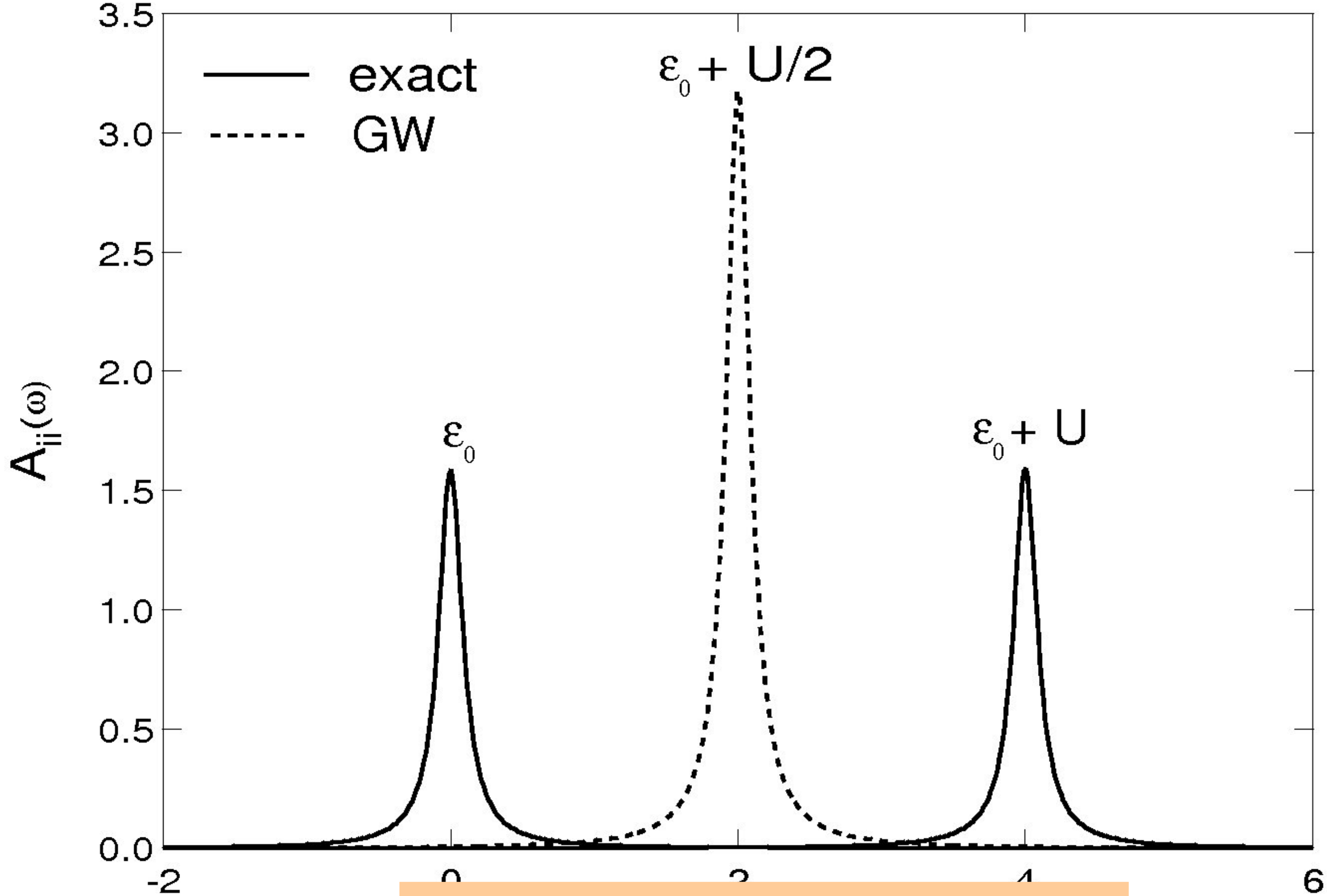
exact
GW
ε_0 + U/2
ε_0
ε_0 + U
$A_{ij}(\omega)$
ω (eV)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2
0
2
4
6

H_2^+



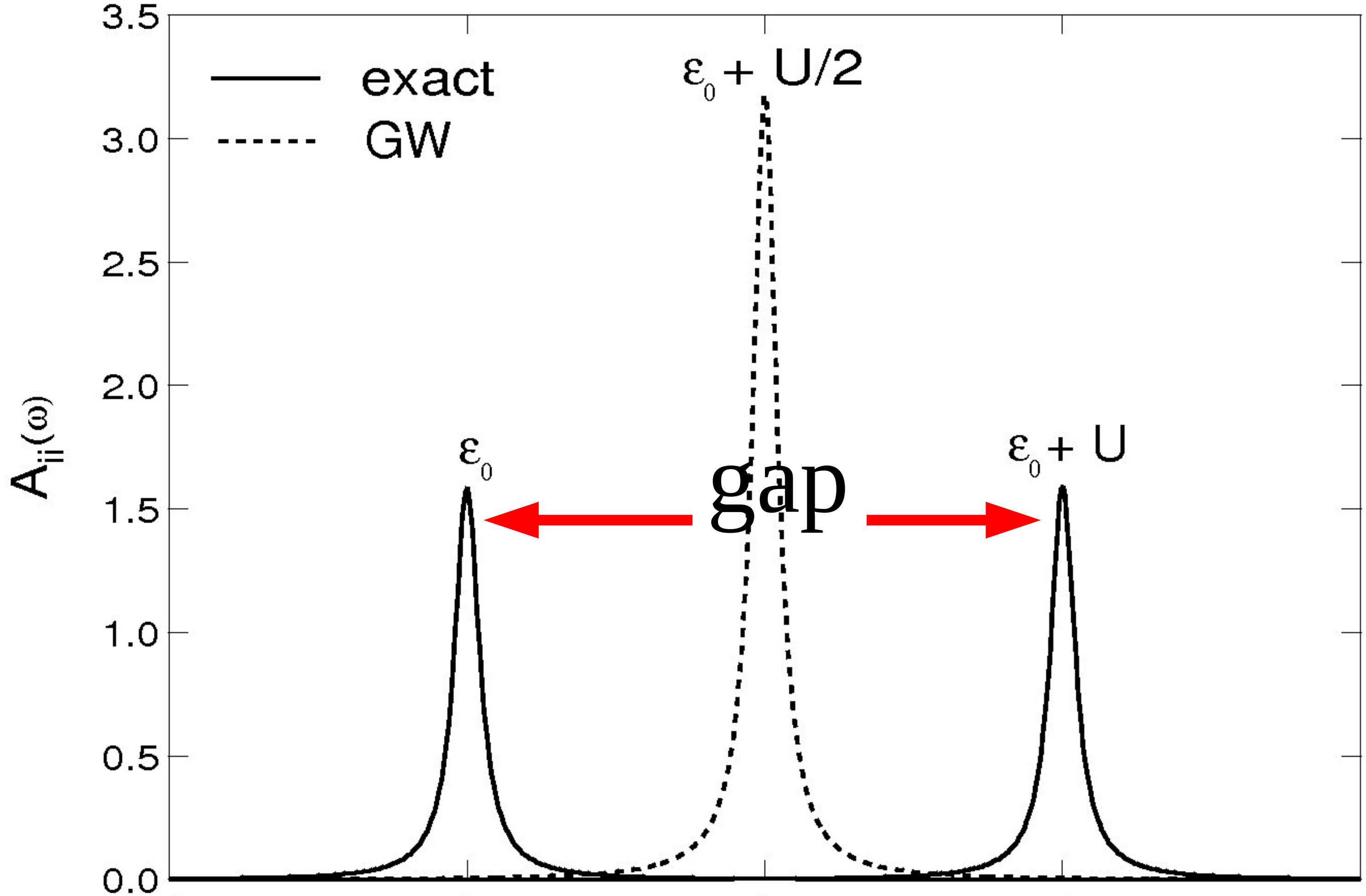
exact
GW
$\varepsilon_0 + U/2$
ε_0
$\varepsilon_0 + U$
$A_{ij}(\omega)$
ω (eV)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-2
0
2
4
6

H_2^+



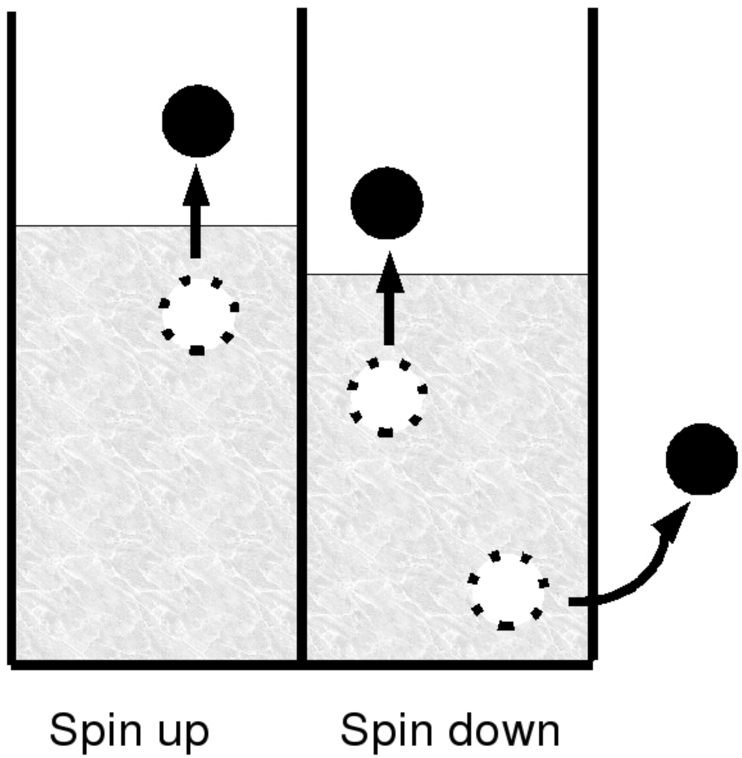
Romaniello, Guyot, Reining,
J Chem Phys 131, 154111 (2009)

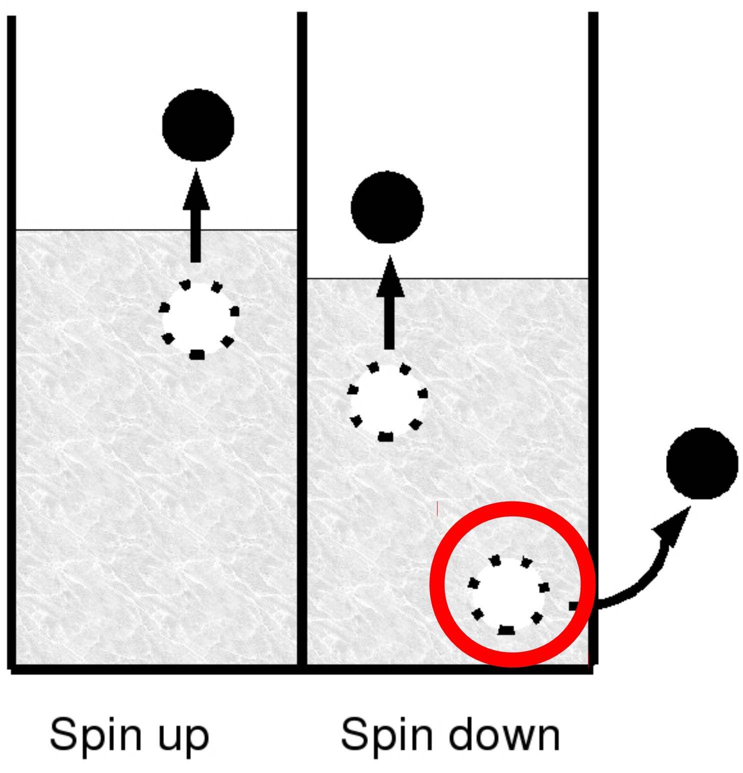
H_2^+



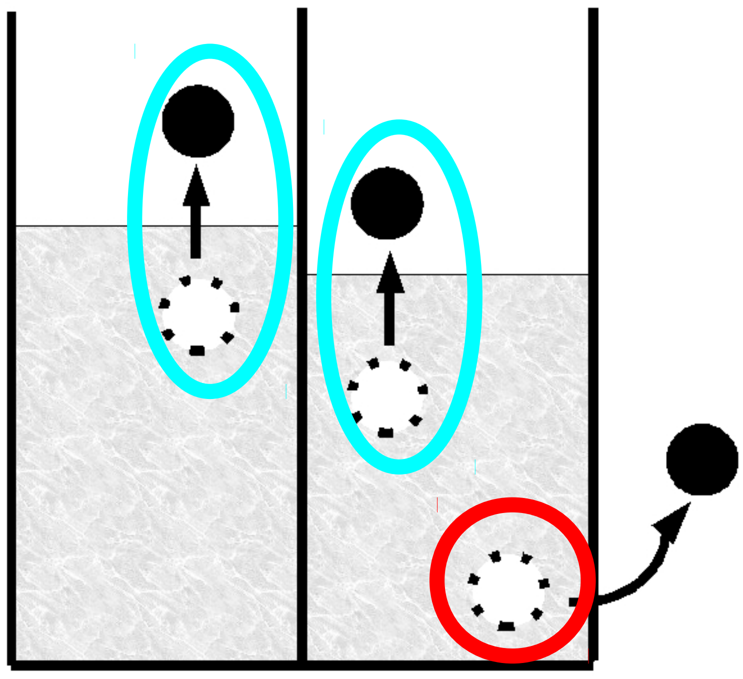
Correlation beyond mean field response

Is life that simple?



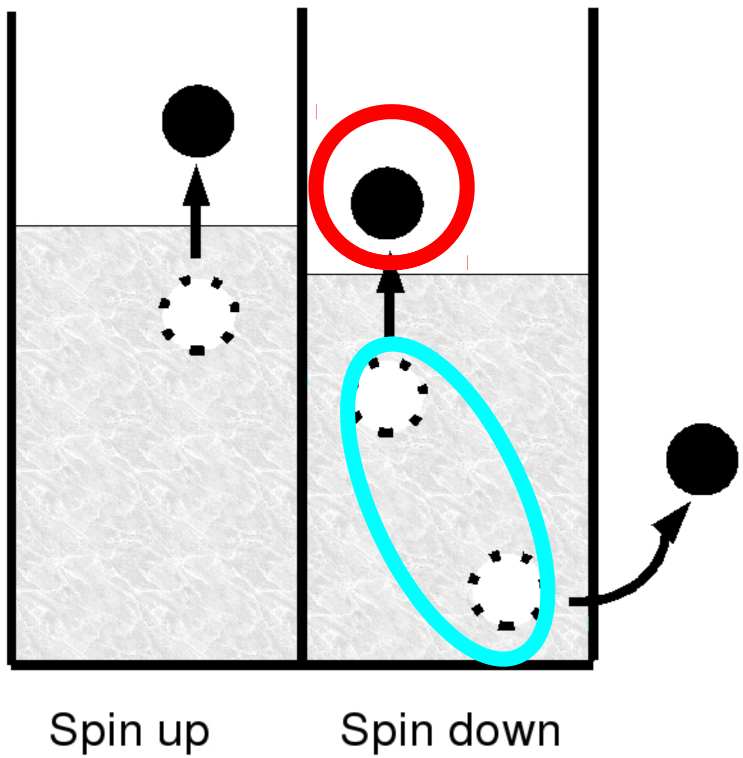


The GW image



The GW image

The T-matrix image



See also Romaniello, Guyot, Reining, J Chem Phys 131, 154111 (2009)
And
Romaniello, Bechstedt, Reining, PRB 85, 155131 (2012)

More than academic: 6 eV satellite in Ni = hole-hole

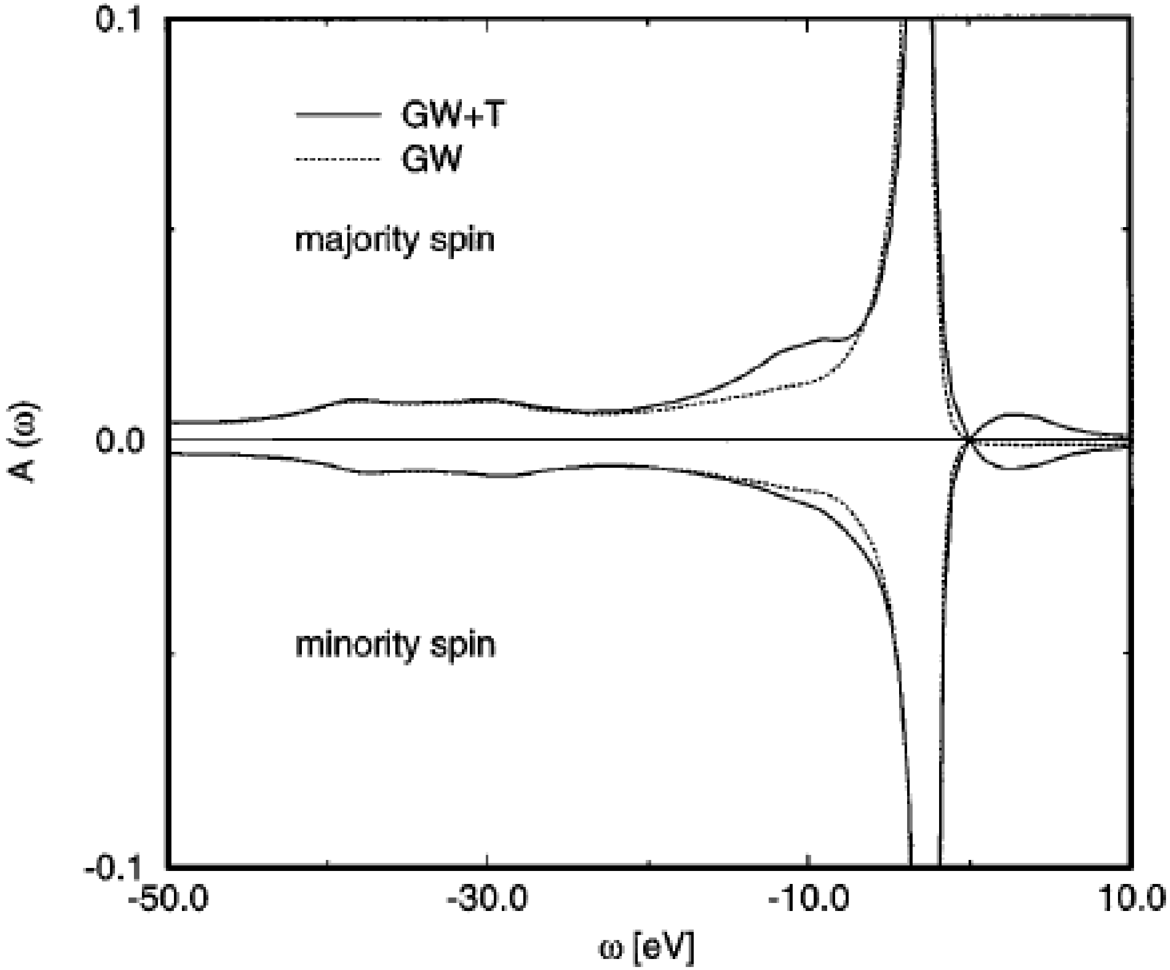


FIG. 4. Ni spectral function for the second occupied state (*d* band) at the *X* point.

Springer, Aryasetiawan, Karlsson, PRL 80, 2389 (1998)

→ Theoretical Spectroscopy: tools

Effective quantities in an effective world

A practical example, simulate zero gravity

Suggested Reading

L. Hedin, “On correlation effects in electron spectroscopies and the GW approximation,” J. Phys. C 11:R489–528, 1999. *Short review, very good for photoemission!*

F. Aryasetiawan and O. Gunnarsson, “The GW method,” Rep. Prog. Phys. 61:237–312, 1998; and:

W. G. Aulbur, L. Jonsson, and J. W. Wilkins, “Quasiparticle calculations in solids,” Solid State Phys. 54:1–218, 2000;
Two nice and quite complete reviews on GW

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.*

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
New book containing many-body perturbation theory, DMFT and QMC

Palaiseau Theoretical Spectroscopy Group & friends

Matteo Guzzo, Ralf Hambach, Igor Reshetnyak, Claudia Roedl, Lorenzo Sponza, Sky (Jianqiang) Zhou, Francesco Sottile, Matteo Gatti, Christine Giorgetti, Hansi Weissker, Lucia Reining

Toulouse: Pina Romaniello, Arjan Berger

U. Washington: John Rehr, Joshua Kas

Synchrotron SOLEIL: Fausto Sirotti, Matthieu Silly
Synchrotron ESRF: Simo Huotari, Giulio Monaco
Synchrotron ELETTRA: Giancarlo Panaccione

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