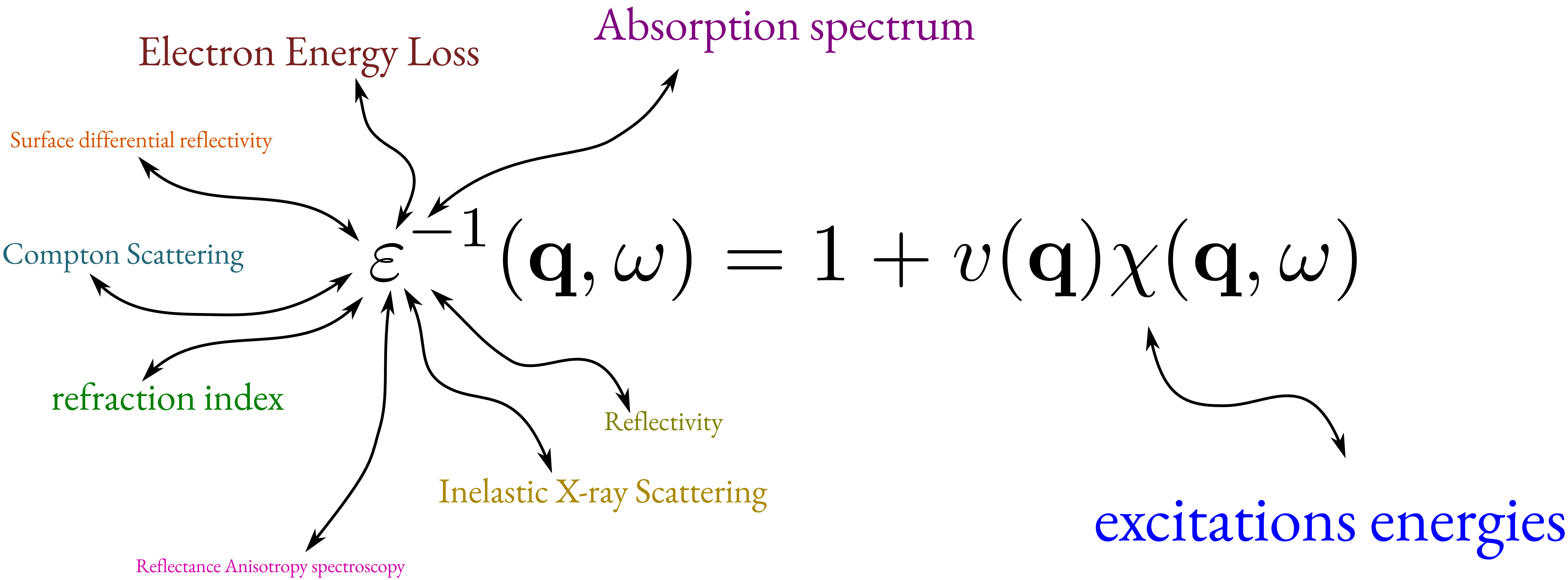
The Bethe-Salpeter Equation

Francesco Sottile

ETSF and LSI, École Polytechnique (France)

FAIRmat Hackathon

4 September 2024

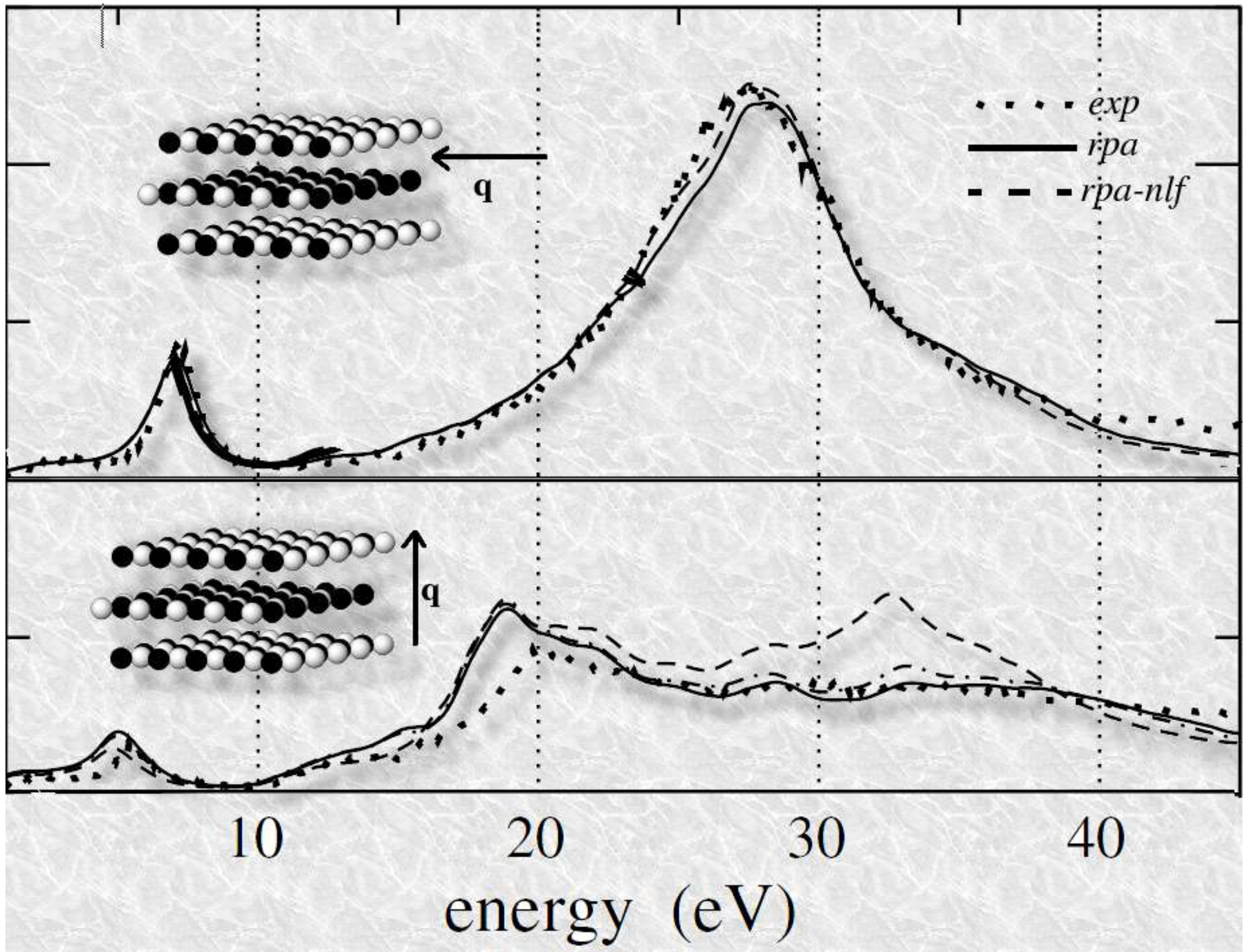

Absorption spectrum
Electron Energy Loss
Surface differential reflectivity
Compton Scattering
refraction index
Reflectivity
Inelastic X-ray Scattering
Reflectance Anisotropy spectroscopy
excitations energies
$\varepsilon^{-1}(\mathbf{q},\omega) = 1 + v(\mathbf{q})\chi(\mathbf{q},\omega)$

Independent particle polarisability

$$\chi^0 = \sum_{ij} (f_i - f_j) \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i\eta}$$

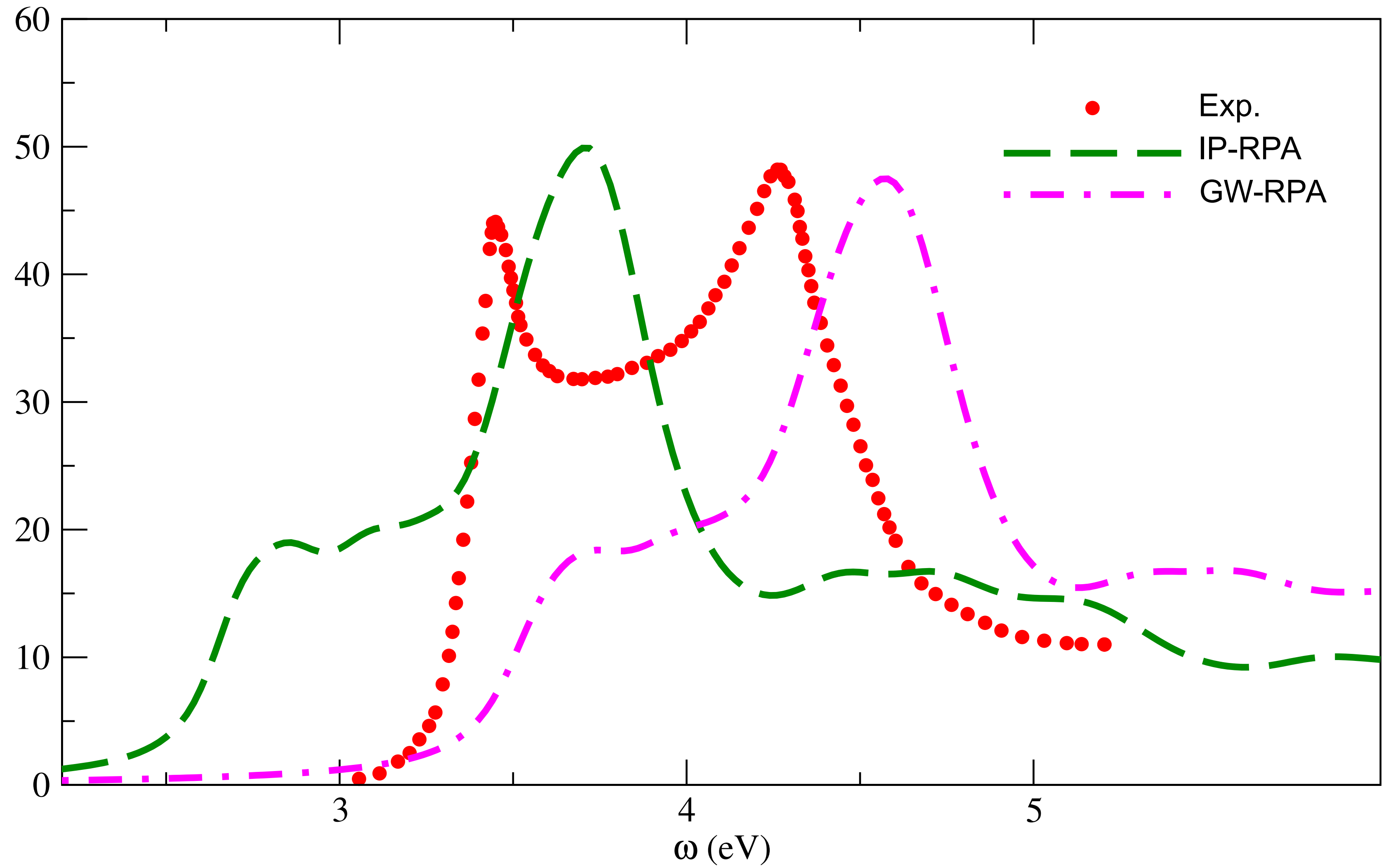
EELS of graphite

Marinopoulos *et al.* Phys. Rev. Lett. **89**, 076402 (2002)



$$\chi_0^{\mathrm{GW}}(\mathbf{r},\mathbf{r}',\omega) = \sum_{ij}(f_i - f_j)\frac{\tilde{\psi}_j^*(\mathbf{r}')\tilde{\psi}_i^*(\mathbf{r}')\tilde{\psi}_i(\mathbf{r})\tilde{\psi}_j(\mathbf{r})}{\omega - (\epsilon_j - \epsilon_i + \Delta_{ij}) + i\eta}$$

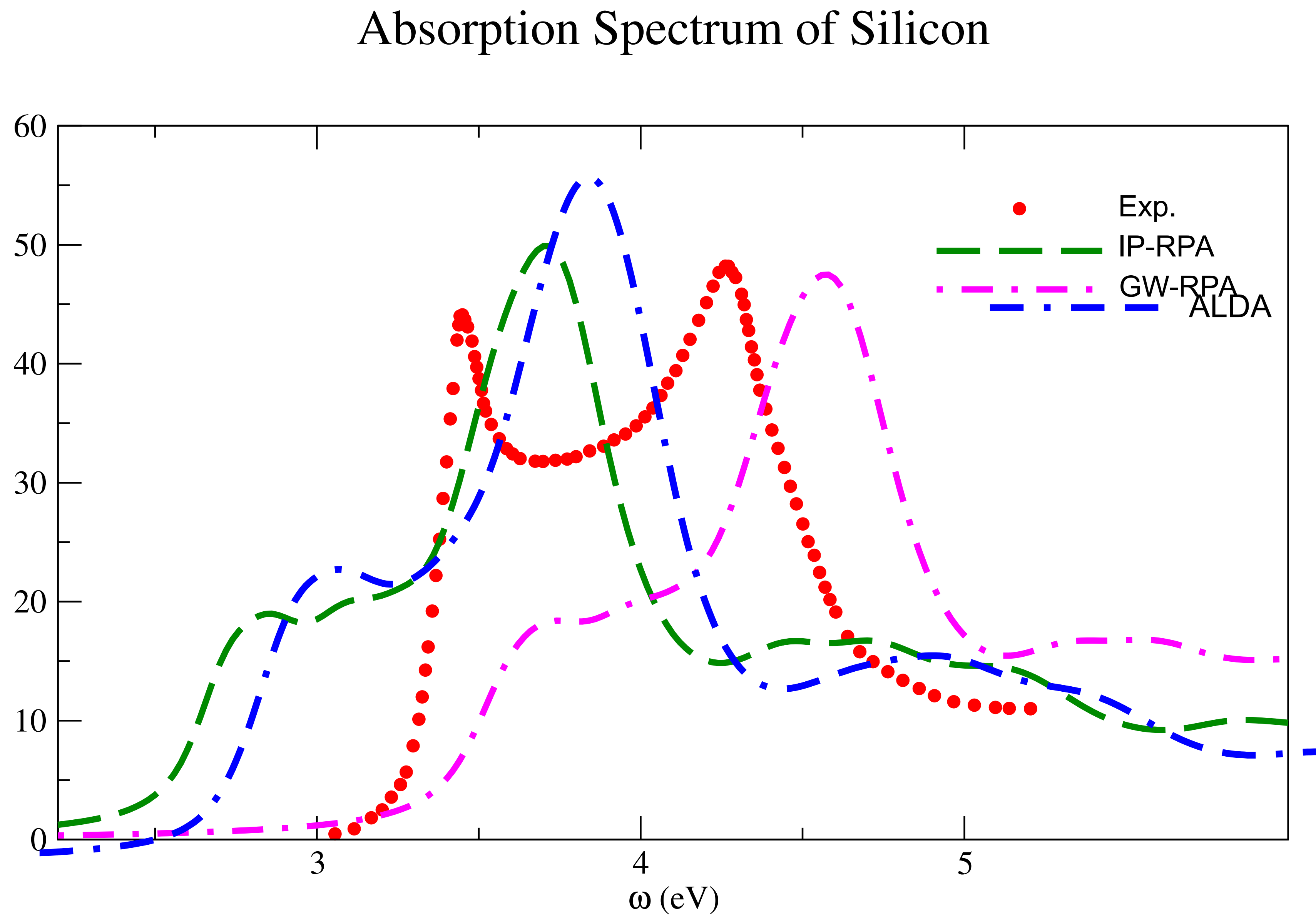
Absorption Spectrum of Silicon



$$\chi_0^{\mathrm{GW}}(\mathbf{r},\mathbf{r}',\omega)=\sum_{ij}(f_i-f_j)\frac{\tilde{\psi}_j^*(\mathbf{r}')\tilde{\psi}_i^*(\mathbf{r}')\tilde{\psi}_i(\mathbf{r})\tilde{\psi}_j(\mathbf{r})}{\omega-(\epsilon_j-\epsilon_i+\Delta_{ij})+i\eta}$$

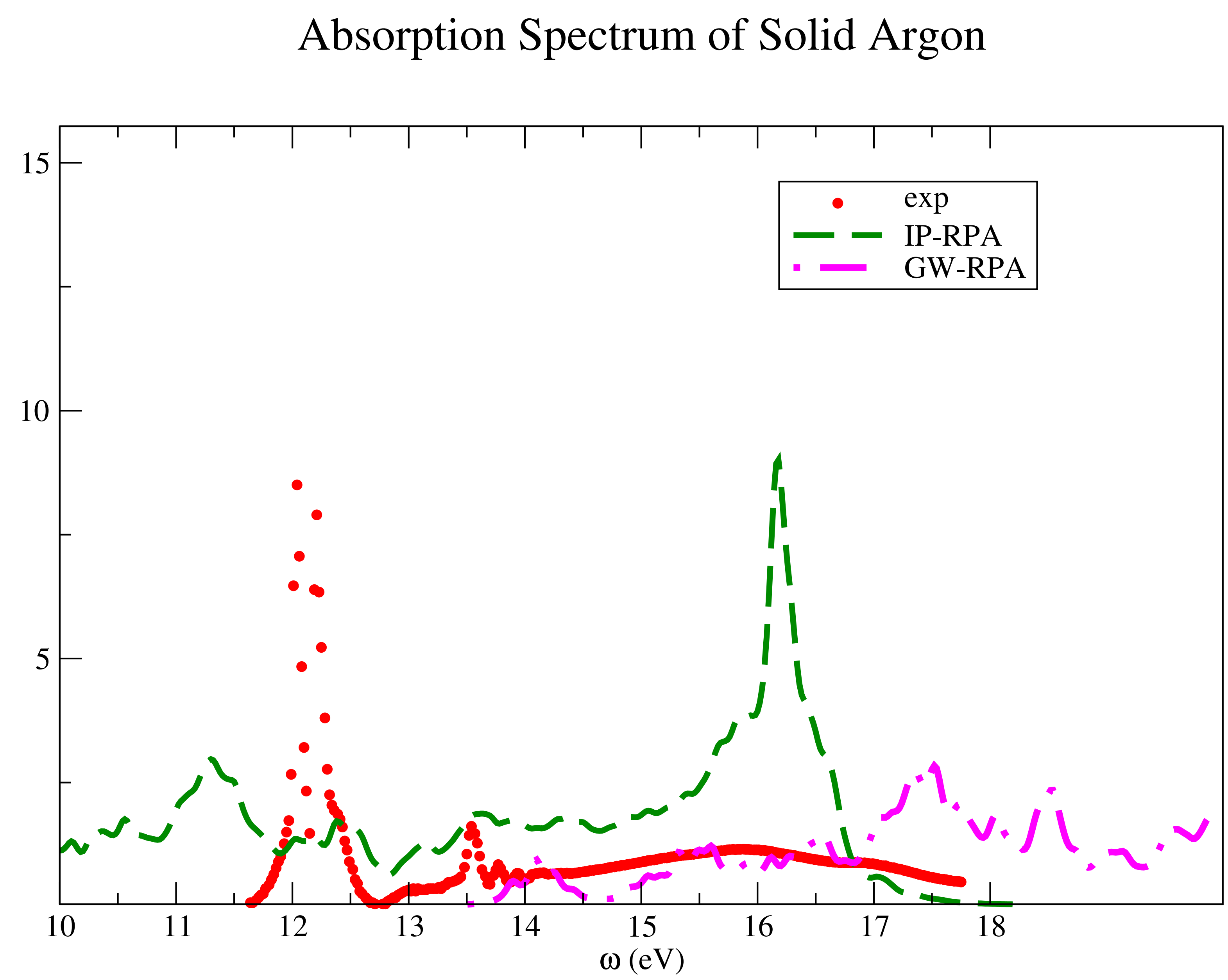
Polarisability within TDDFT

$$\chi = \chi^0 + \chi^0 \left[v + f_{xc} \right] \chi$$



~ ~ ~ ~

$$\chi = \chi_0 + \chi_0 \left(v + f_{xc}^{\mathrm{ALDA}}\right) \chi$$


Absorption Spectrum of Solid Argon
15
10
5
10
11
12
13
14
15
16
17
18
ω (eV)
exp
IP-RPA
GW-RPA

Alternative approach for χ or ε

Green's functions approach

$$\Sigma(1,2) = i\int d(34) W(1,3) G(1,4) \Gamma(4,2,3)$$

$$G(1,2) = G_0(1,2) + \int d(34)\, G_0(1,3) \left[V_H(3) + \Sigma(3,4)\right] G(4,2)$$

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int d(4567)\, \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)\Gamma(6,7,3) G(7,5)$$

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

$$W(1,2) = V(1,2) + \int d(45) V(1,4) P(4,5) W(5,2)$$

$$\chi(1,2) = \frac{\delta n(1)}{\delta V_{ext}(2)} = -i\frac{\delta G(1,1)}{\delta V_{ext}(2,2)}$$ Polarizability (2-point)

$$L(1,2,3,4) = -i\frac{\delta G(1,2)}{\delta V_{\text{ext}}(3,4)}$$ 4-point Polarizability

$$L(1,1,3,3) \rightarrow \chi(1,3)$$

$$L(1,2,3,4) = L_0(1,2,3,4) + \int d(5678) L_0(1,2,5,6) \left[v(5,7)\delta(5,6)\delta(7,8) + \Xi(5,6,7,8) \right] L(7,8,3,4)$$

$$L_0(1,2,3,4) = -iG(1,3)G(4,2) \qquad \Xi(5,6,7,8) = i\frac{\delta\Sigma(5,6)}{\delta G(7,8)}$$

$$L = L_0 + L_0(v + \Xi)L$$

BSE

$$L = L_0 + L_0(v + \Xi)L$$ BSE

$$\chi = \chi_0 + \chi_0\,(v + f_{xc})\,\chi$$ TDDFT

$$L(1,2,3,4) = L_0(1,2,3,4) + \int d(5678) L_0(1,2,5,6) \left[v(5,7)\delta(5,6)\delta(7,8) + \Xi(5,6,7,8) \right] L(7,8,3,4)$$

GW approximation

$$\begin{aligned} \Xi(5,6,7,8) &= i\frac{\delta\Sigma(5,6)}{\delta G(7,8)} = \\ &= -\frac{\delta[G(5,6)W(5,6)]}{\delta G(7,8)} = -W(5,6)\delta(5,7)\delta(6,8) - \underbrace{G(5,6)\frac{\delta W(5,6)}{\delta G(7,8)}}_{\text{second order in } W} \\ &\approx -W(5,6)\delta(5,7)\delta(6,8). \end{aligned}$$

$$L(1,2,3,4) = L_0(1,2,3,4) + \int d(5678) L_0(1,2,5,6) \left[v(5,7)\delta(5,6)\delta(7,8) - W(5,6)\delta(5,7)\delta(6,8) \right] L(7,8,3,4)$$

$$L(1,2,3,4) = L_0(1,2,3,4) + \int d(5678) L_0(1,2,5,6) \left[v(5,7)\delta(5,6)\delta(7,8) - W(5,6)\delta(5,7)\delta(6,8) \right] L(7,8,3,4)$$

static (W) approximation

$$W(1,2) \approx W(\mathbf{r}_1, \mathbf{r}_2, \omega = 0)\delta(t_1 - t_2),$$

$$\begin{aligned} L(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) = L_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) + \\ + \int d\mathbf{r}_5 d\mathbf{r}_6 d\mathbf{r}_7 d\mathbf{r}_8 L_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_5, \mathbf{r}_6, \omega) \big[v(\mathbf{r}_5 - \mathbf{r}_7)\delta(\mathbf{r}_5 - \mathbf{r}_6)\delta(\mathbf{r}_7 - \mathbf{r}_8) + \\ - W(\mathbf{r}_5, \mathbf{r}_6)\delta(\mathbf{r}_5 - \mathbf{r}_7)\delta(\mathbf{r}_7 - \mathbf{r}_8) \big] L(\mathbf{r}_7, \mathbf{r}_8, \mathbf{r}_3, \mathbf{r}_4, \omega) \end{aligned}$$

$$L(1,2,3,4;\omega) = L_0(1,2,3,4;\omega) + L_0(1,2,5,6;\omega) \left[v(5,7)\delta(5,6)\delta(7,8) - W(5,6)\delta(5,7)\delta(6,8) \right] L(7,8,3,4;\omega)$$

- GW approximation
- static (W) approximation
- independent propagation L_0

$$L_0 = -iG_0^{GW} G_0^{GW} = \chi_0^{\mathrm{GW}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) = \sum_{ij} (f_i - f_j) \frac{\psi_j^*(\mathbf{r}_3)\psi_i^*(\mathbf{r}_4)\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)}{\omega - (\epsilon_j - \epsilon_i + \Delta_{ij}) + i\eta}$$

and now ??

$$L(1,2,3,4;\omega) = L_0(1,2,3,4;\omega) + L_0(1,2,5,6;\omega)\left[v(5,7)\delta(5,6)\delta(7,8) - W(5,6)\delta(5,7)\delta(6,8)\right] L(7,8,3,4;\omega)$$

really invert 4-point function for each frequency ??

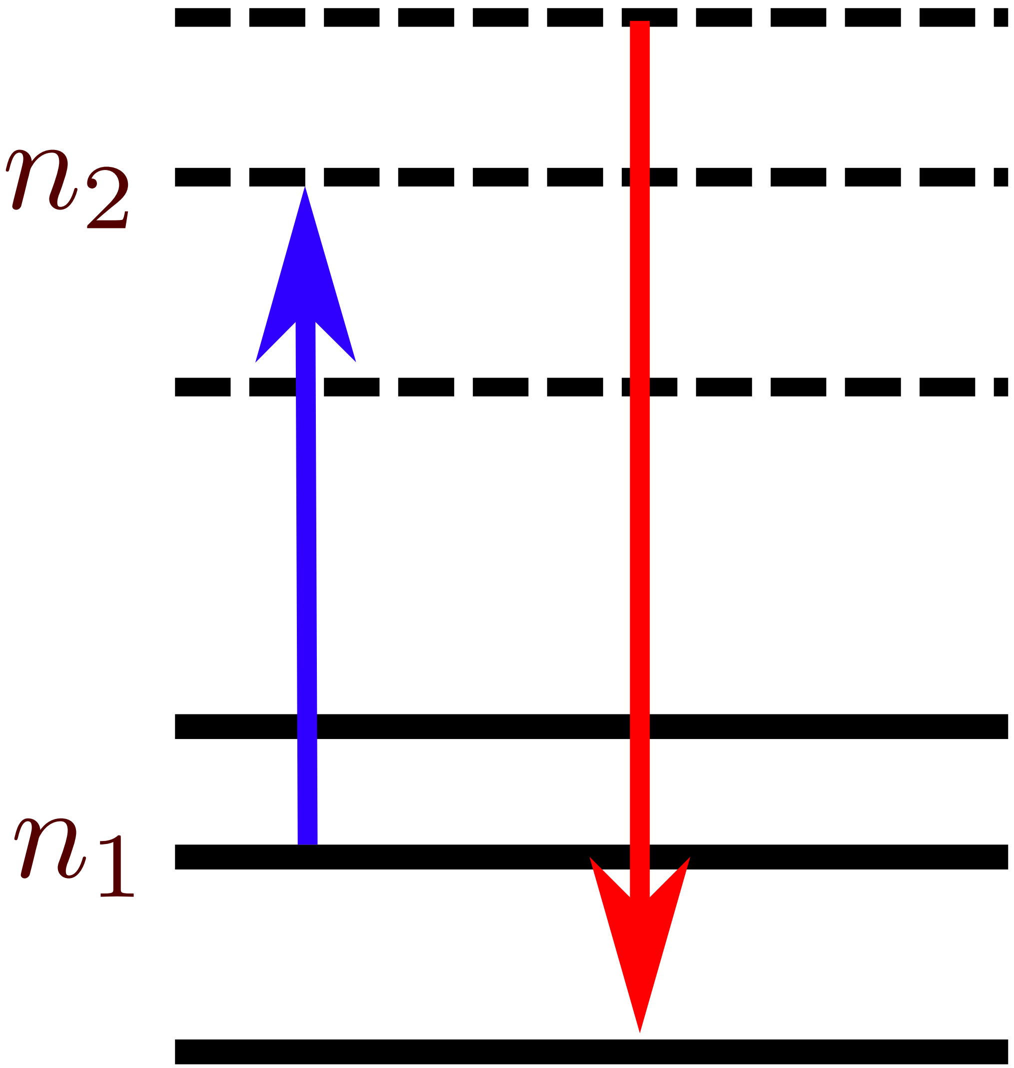
let's define a basis

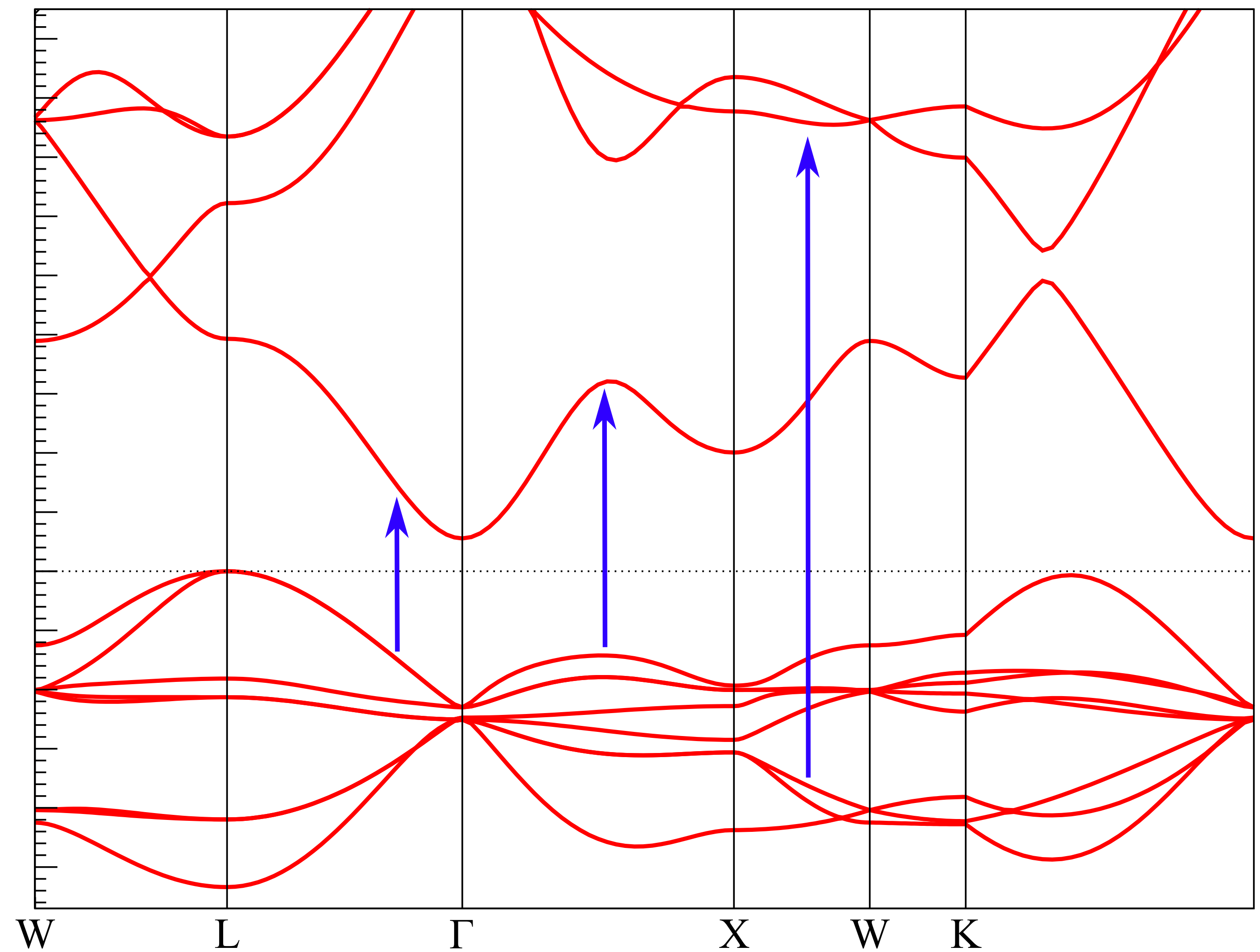
$\psi_{n_1}^*(\mathbf{r}_1)\psi_{n_2}(\mathbf{r}_2)$

orbital basis

transition basis

transition space $t = n_1 \to n_2$





$$L = \left[(L_0)^{-1} - (v - W) \right]^{-1}$$

$L^{n_3 n_4}_{n_2 n_2}$

$\omega - (E_{n_2} - E_{n_1})\delta_{n_1 n_4}\delta_{n_2 n_3}$

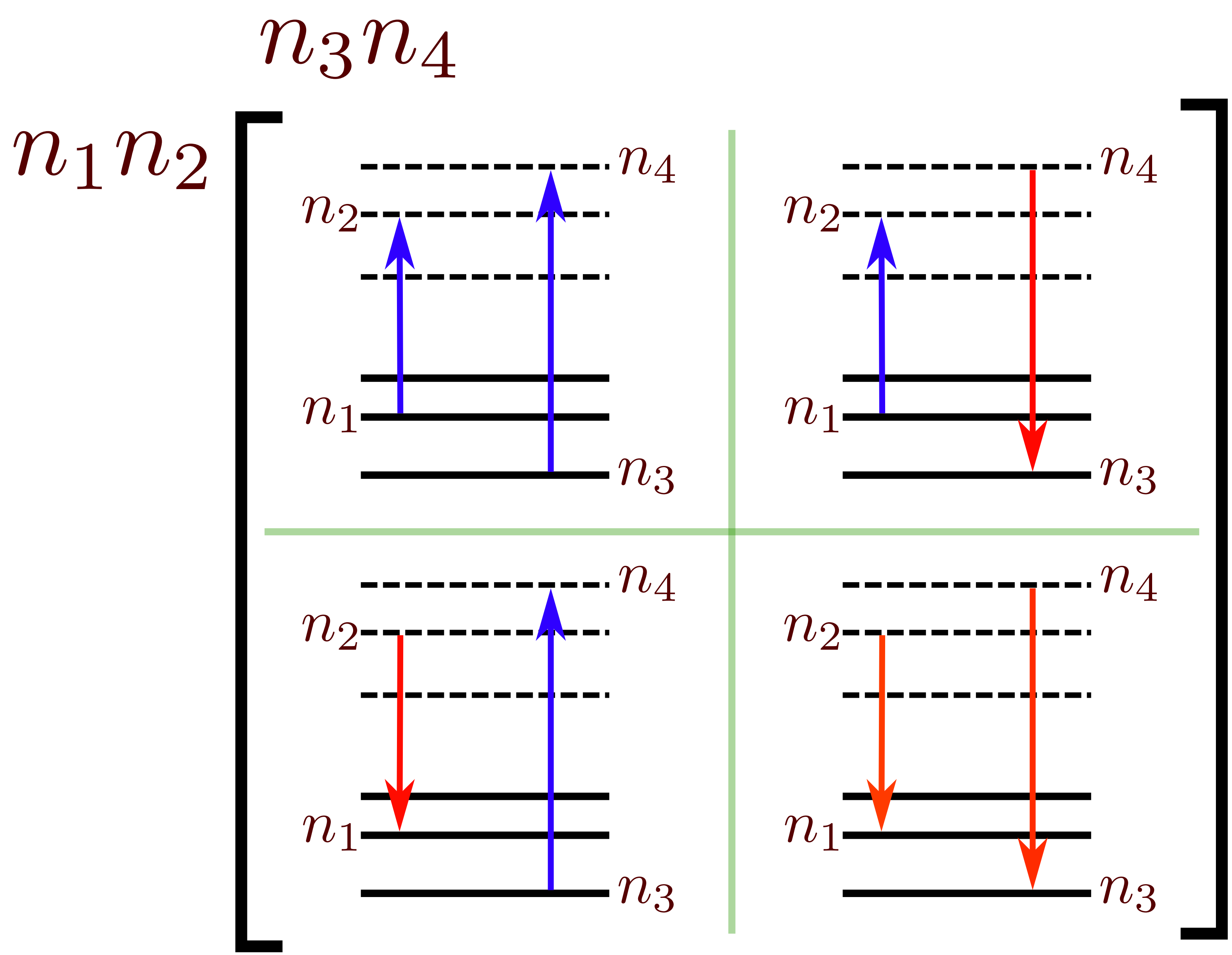
$v^{n_3 n_4}_{n_1 n_2} = \iint \psi^*_{n_1}(\mathbf{r})\psi^*_{n_2}(\mathbf{r}')v(\mathbf{r},\mathbf{r}')\,\psi_{n_3}(\mathbf{r})\psi_{n_4}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$

$W^{n_3 n_4}_{n_1 n_2} = \iint \psi^*_{n_1}(\mathbf{r})\psi^*_{n_2}(\mathbf{r})W(\mathbf{r},\mathbf{r}')\,\psi_{n_3}(\mathbf{r}')\psi_{n_4}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$

$$L = \frac{1}{\omega - H^{exc}}$$

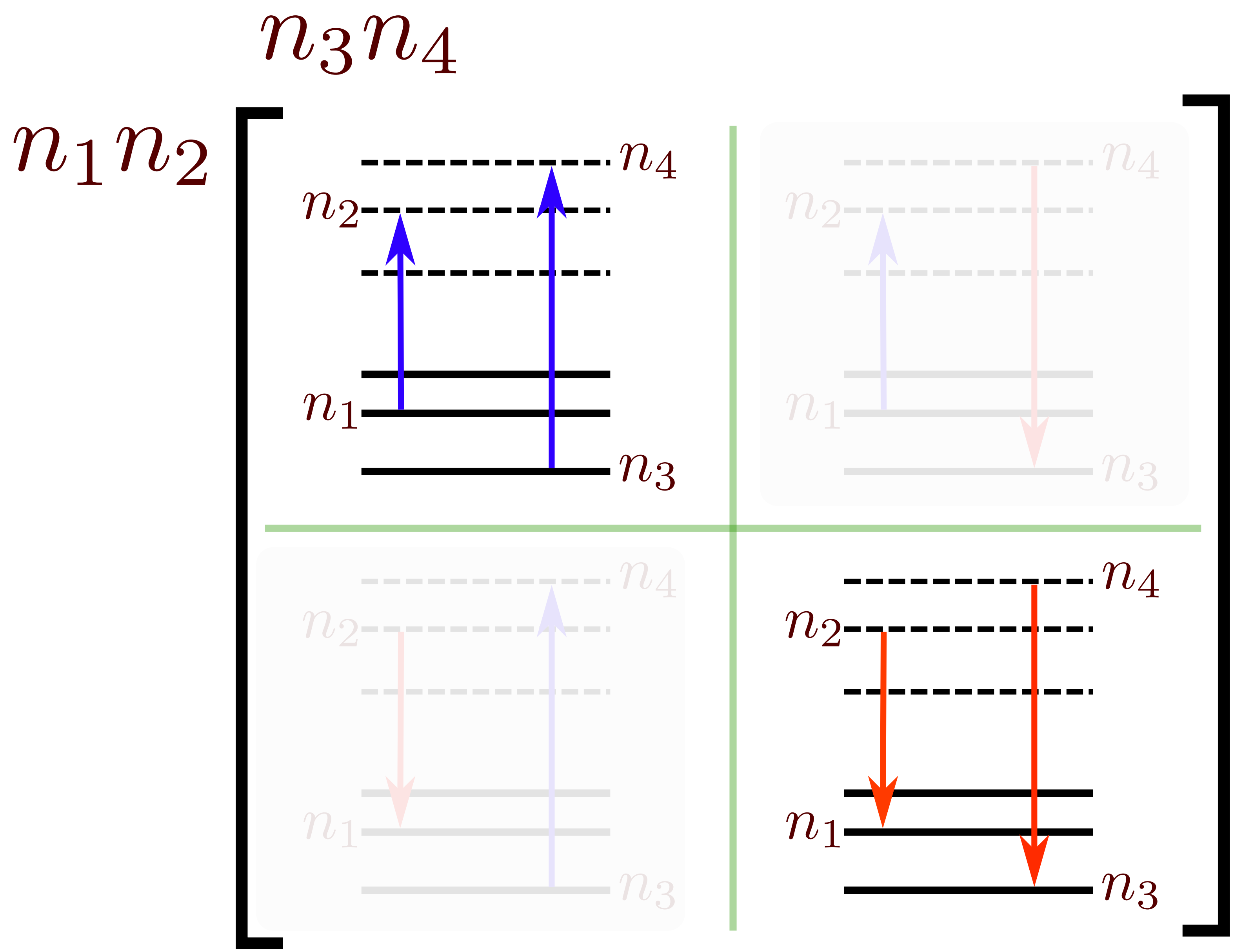
$$H^{exc} = (E_{n_2} - E_{n_1})\delta_{n_1 n_4}\delta_{n_2 n_3} + v^{n_3 n_4}_{n_1 n_2} - W^{n_3 n_4}_{n_1 n_2}$$

$$H^{exc} =$$



$$L = \frac{1}{\omega - H^{exc}} = \sum_{\lambda\lambda'} \frac{|\lambda\rangle \, S_{\lambda}^{\lambda'} \, \langle\lambda|}{\omega - E_{\lambda}}$$

$$H^{exc} =$$



Tamm-Dancoff approx

$$L = \frac{1}{\omega - H^{exc}} = \sum_{\lambda} \frac{|\lambda\rangle\langle\lambda|}{\omega - E_{\lambda}}$$

Tamm-Dancoff approx

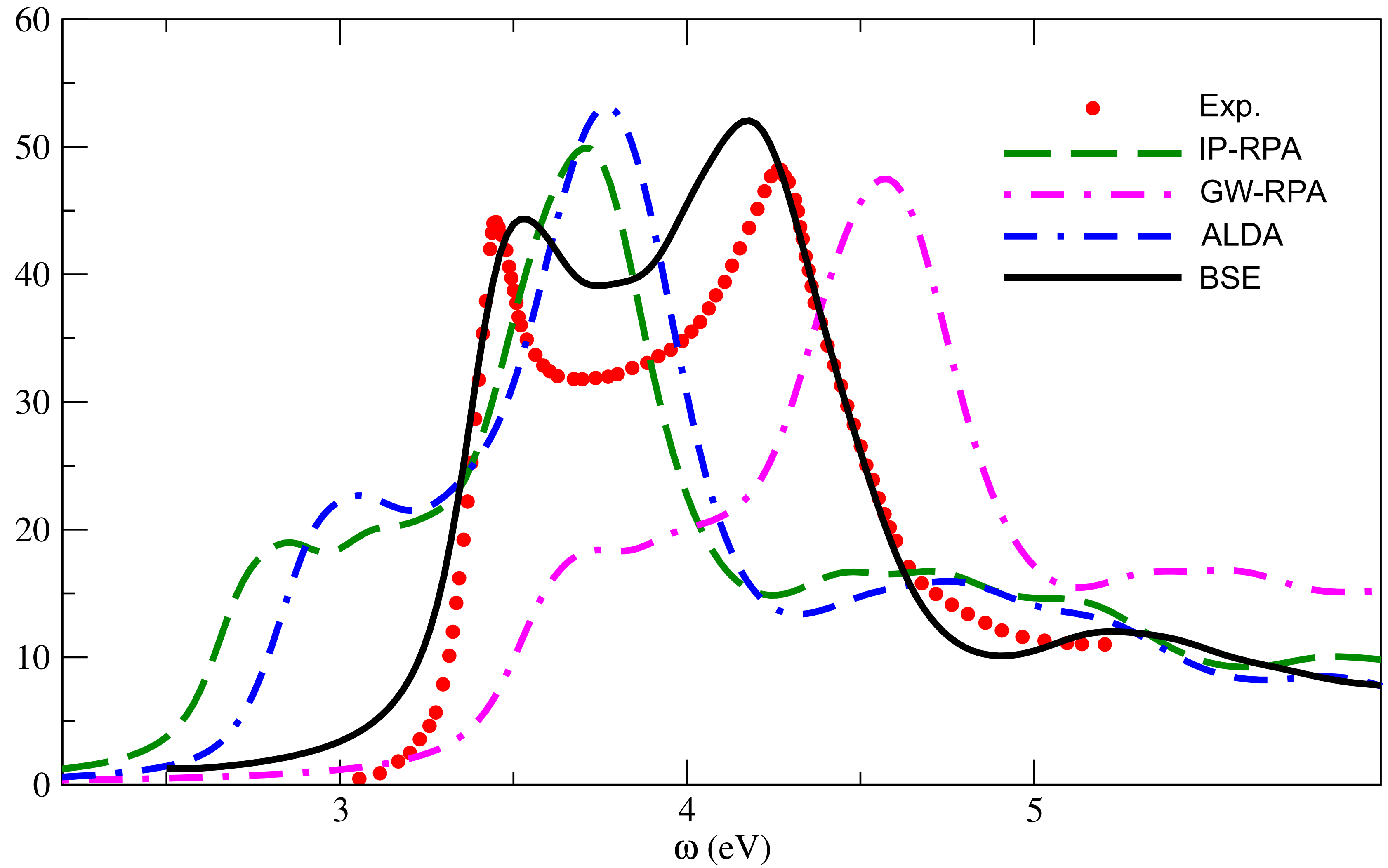
$$\varepsilon_{00}^{-1}(\mathbf{q},\omega) = 1 + v_0(\mathbf{q}) \sum_{\lambda} \frac{\left| \sum_{vc} \langle c | e^{-i\mathbf{q}\cdot\mathbf{r}} | v \rangle A_{\lambda}^{vc} \right|^2}{E_{\lambda}^{exc} - \omega - i\eta}$$

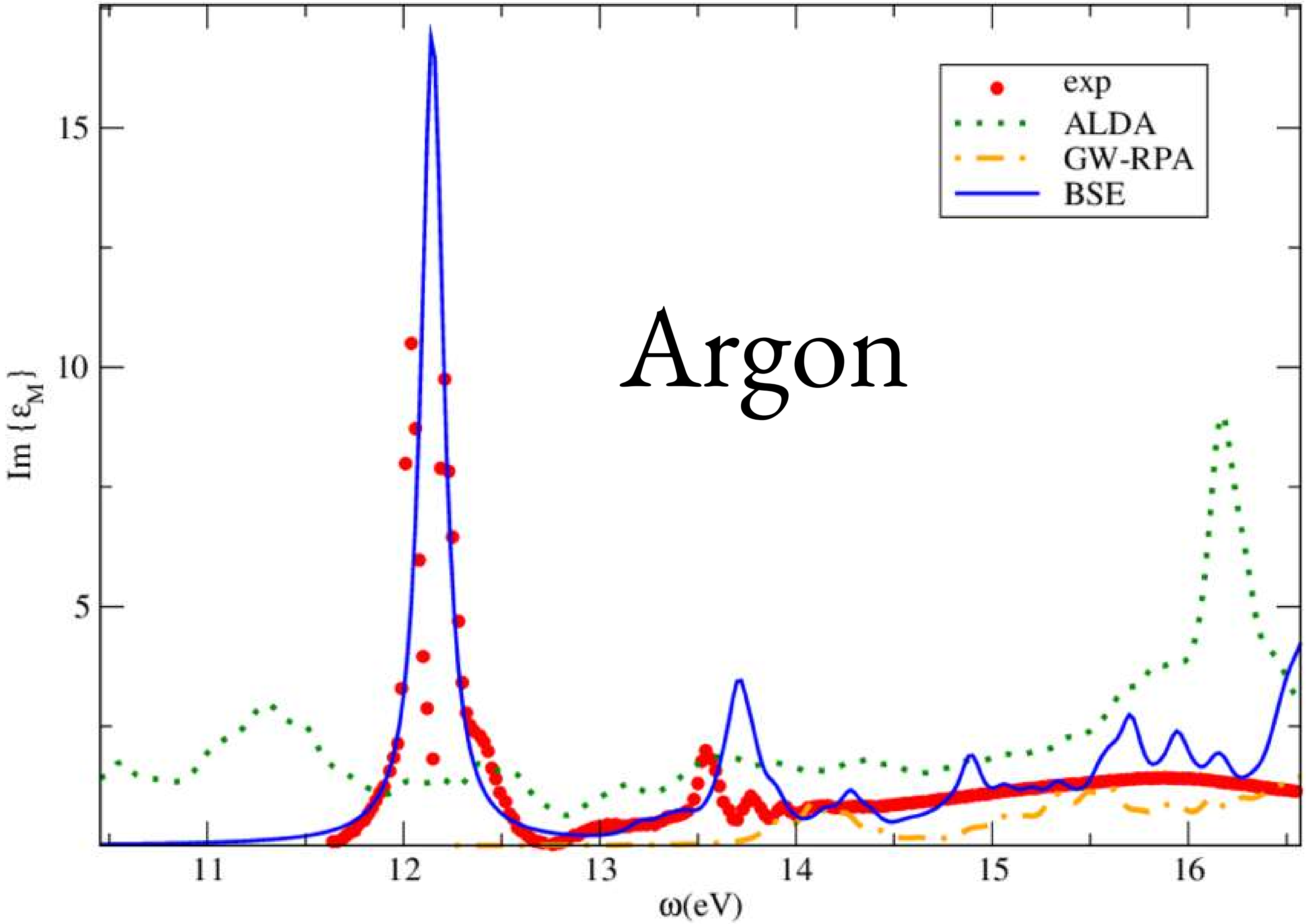
BSE

$$\varepsilon_{00}^{-1}(\mathbf{q},\omega) = 1 + v_0(\mathbf{q}) \sum_{vc} \frac{\left| \langle c | e^{-i\mathbf{q}\cdot\mathbf{r}} | v \rangle \right|^2}{(\epsilon_c - \epsilon_v) - \omega - i\eta}$$

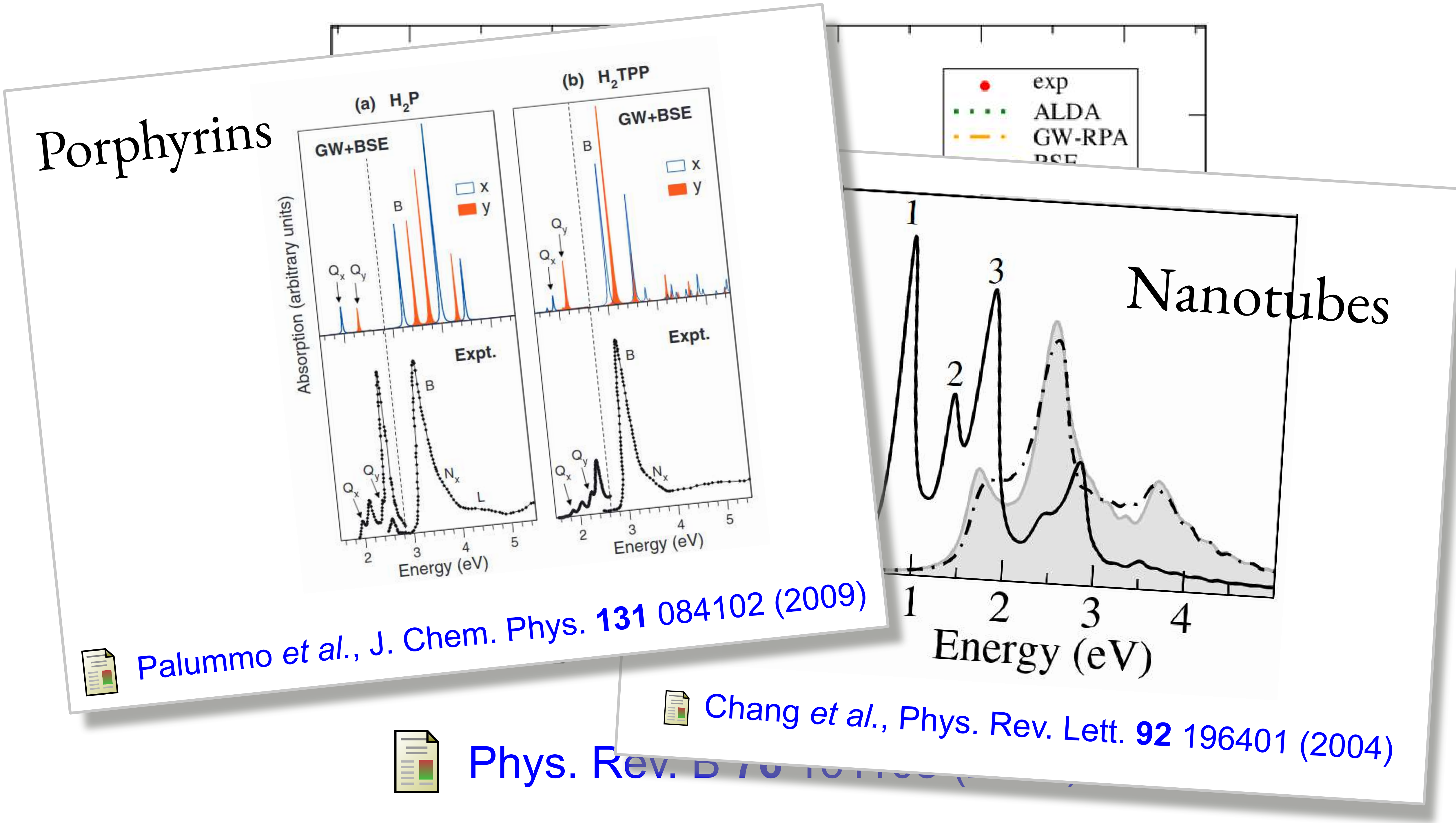
IP

Optical absorption of Silicon

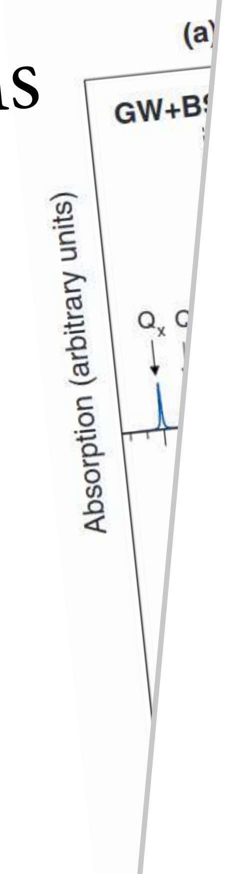




Phys. Rev. B **76** 161103 (2007)

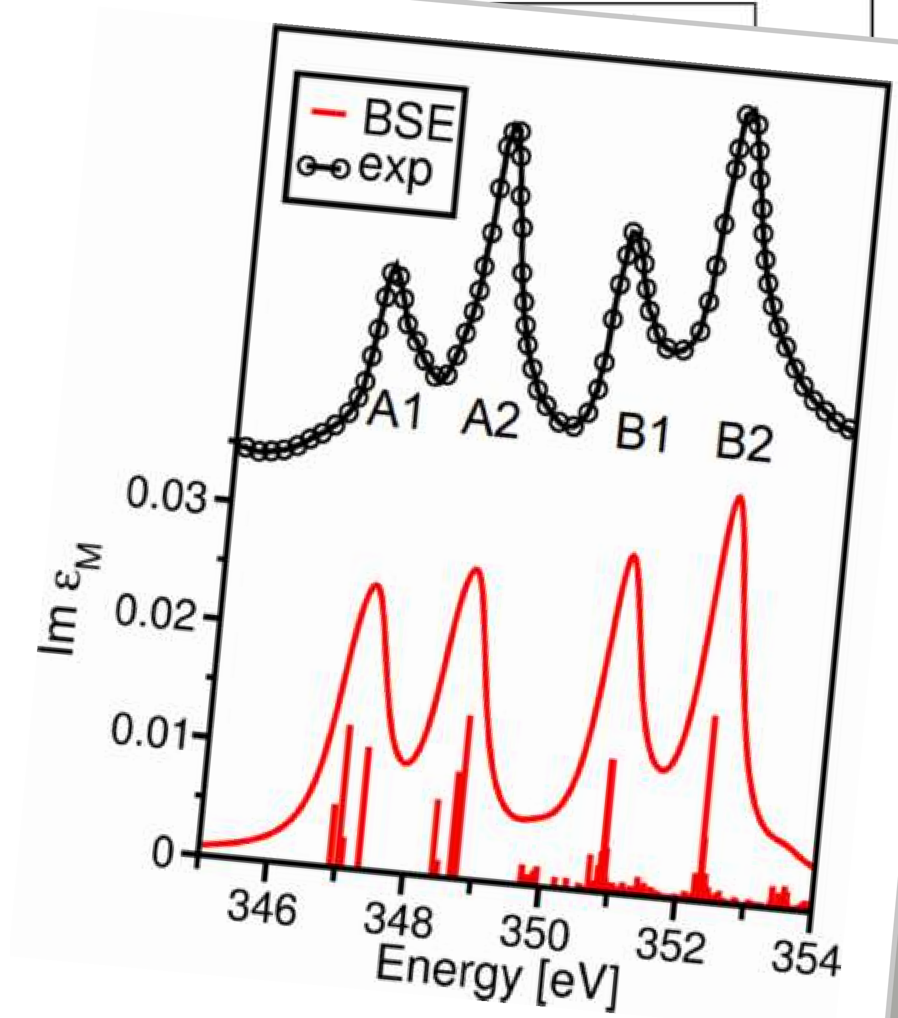

Porphyrins
(a) H2P
(b) H2TPP
GW+BSE
Expt.
Absorption (arbitrary units)
Energy (eV)
x
y
B
Qx
Qy
Nx
L
Palummo et al., J. Chem. Phys. 131 084102 (2009)
Nanotubes
exp
ALDA
GW-RPA
1
2
3
4
Energy (eV)
Chang et al., Phys. Rev. Lett. 92 196401 (2004)
Phys. Rev. B 70

Porphyrins



Palummo et a

CaO
Ca L-edge



Vorwerk *et al.*, Phys. Rev. B **95**, 155121 (2017)

otubes

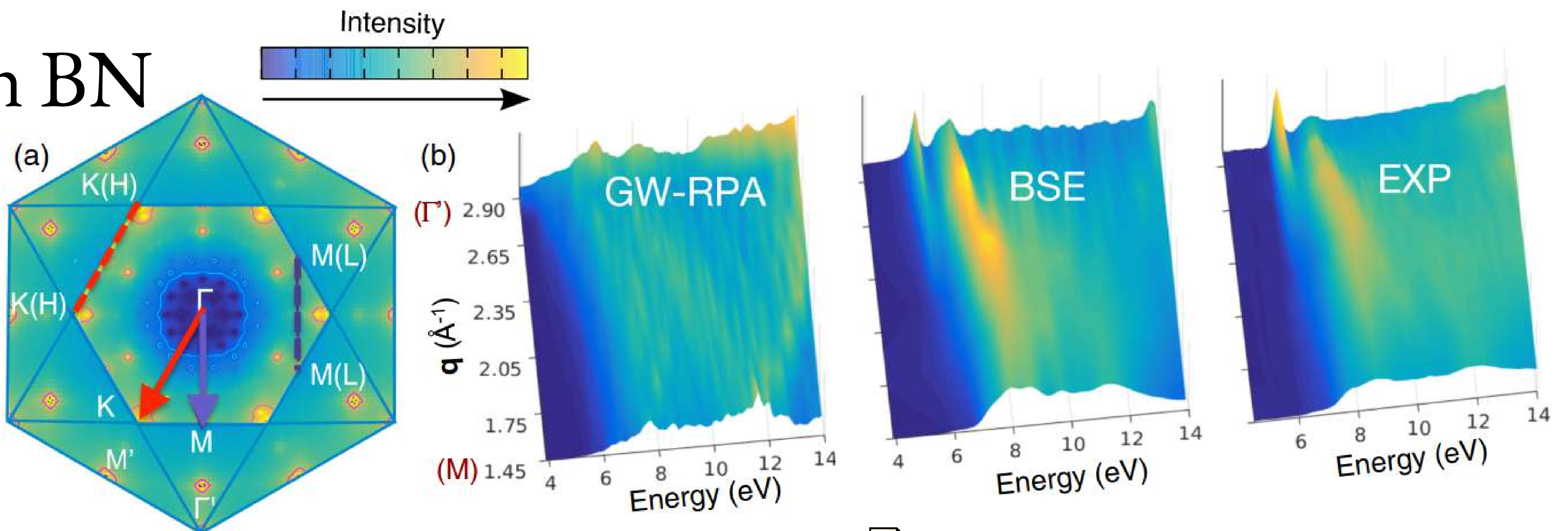
96401 (2004)

Phys. Rev. B 70

Bethe-Salpeter Equation - finite momentum transfer

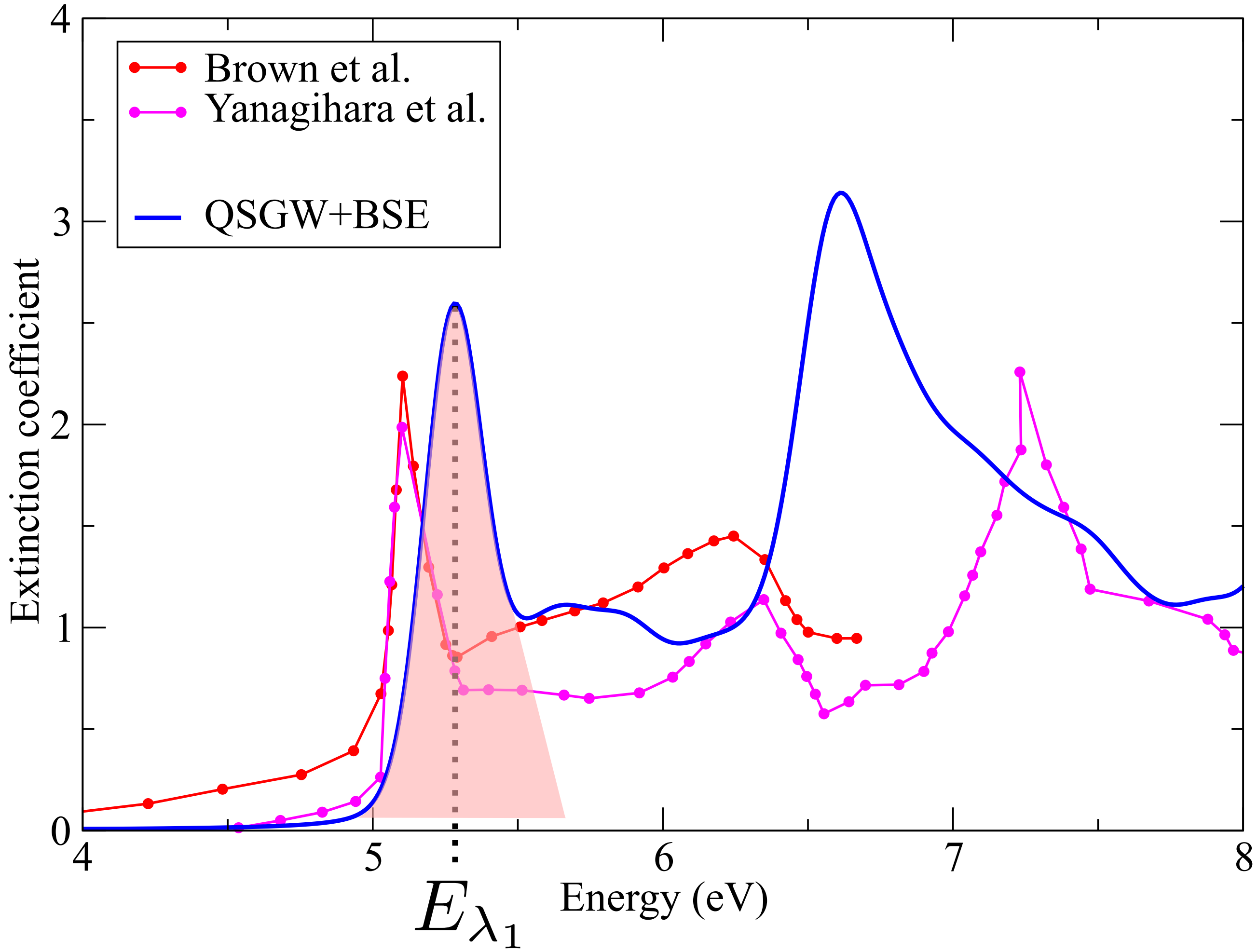
$$S(\mathbf{q},\omega) \propto \chi_M(\mathbf{q},\omega) = \sum_\lambda \frac{\left|\sum_{vc} A_\lambda^{vc,\mathbf{q}} \langle c|e^{i\mathbf{q}\cdot\mathbf{r}}|v\rangle\right|^2}{\omega - E_\lambda(\mathbf{q}) + i\eta}$$

h BN

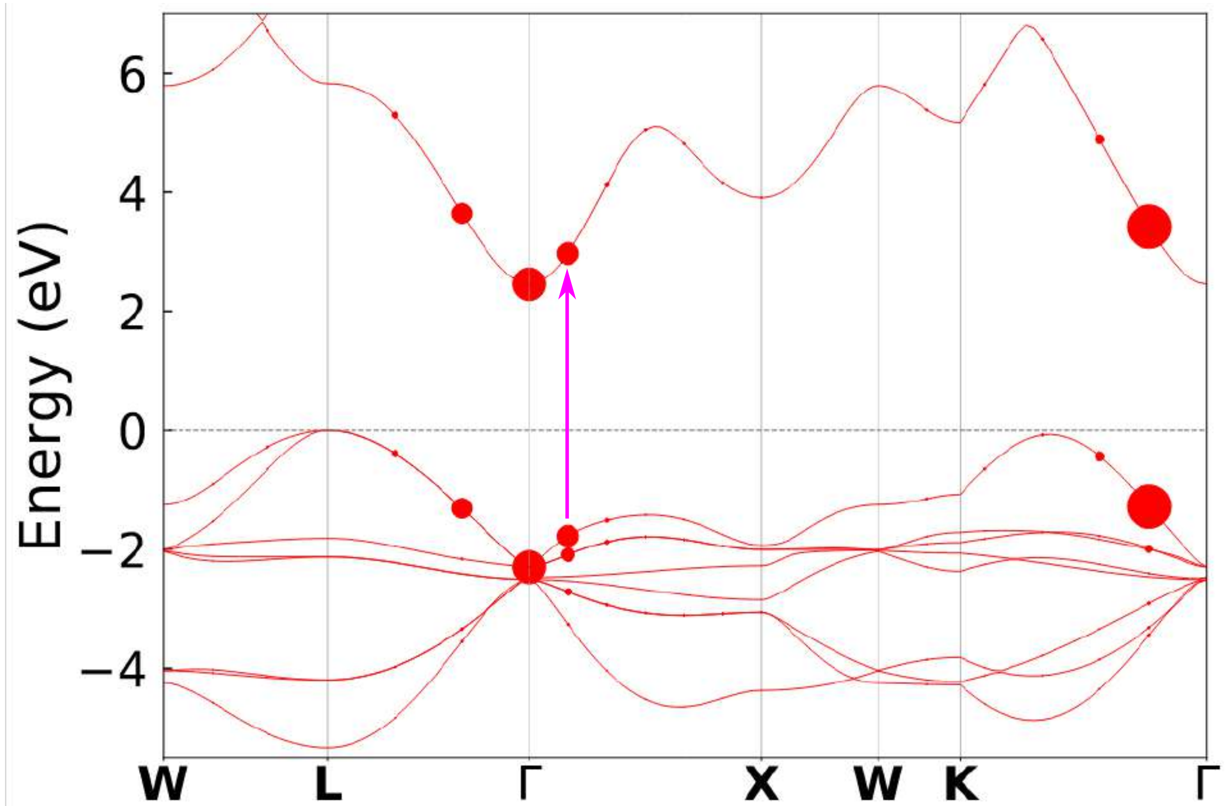


Fugallo *et al.* Phys. Rev. B **92**, 165122 (2015)

AgCl absorption



$$\chi_M = \sum_{\lambda} \frac{\left| \sum_{vc\mathbf{k}} A_{\lambda_1}^{vc\mathbf{k}} \langle c\mathbf{k}|\hat{\mathbf{d}}|v\mathbf{k}\rangle \right|^2}{\omega - E_\lambda + i\eta}$$

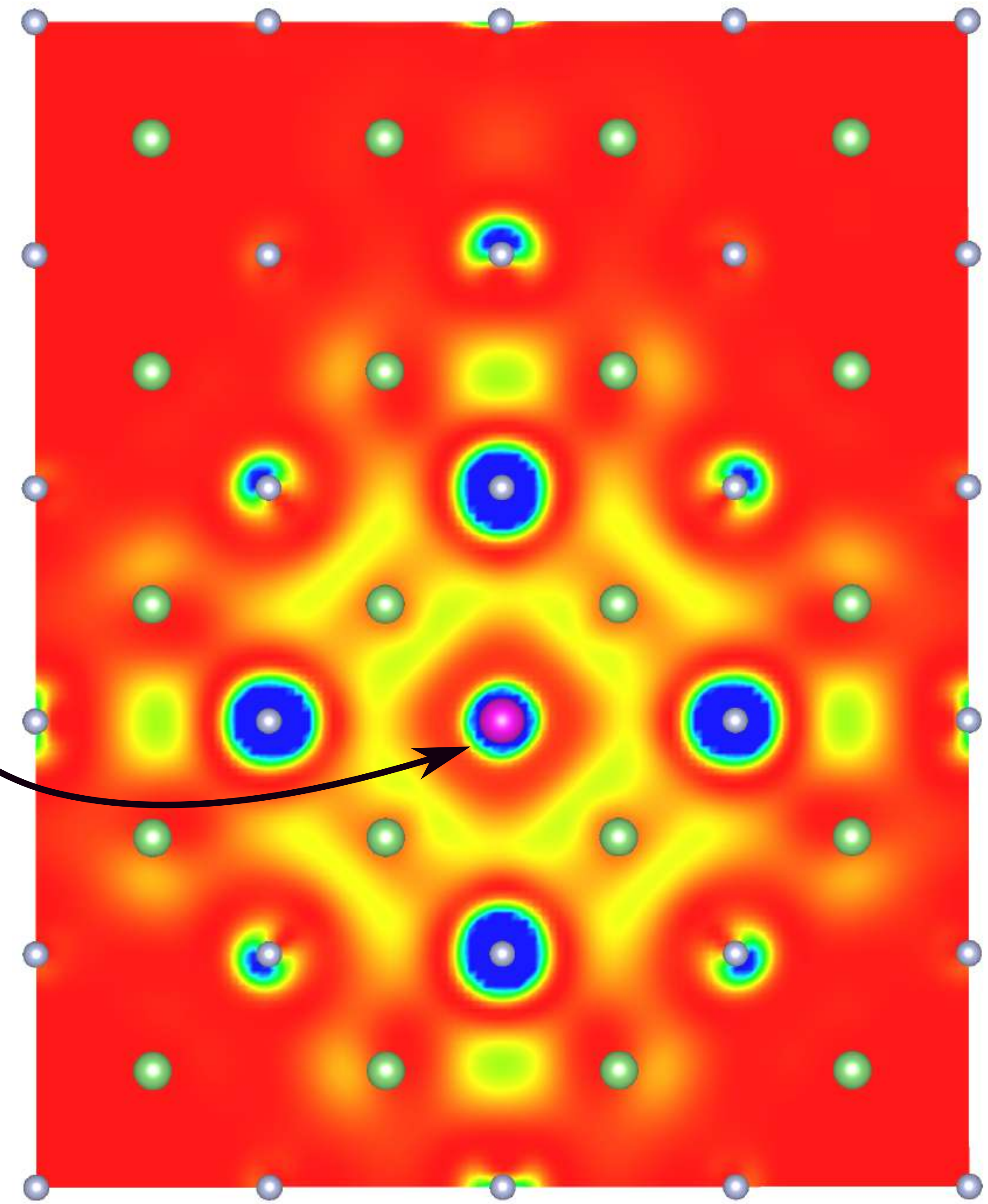


Lorin *et al.* Phys. Rev. B **104**, 235149 (2021)

Excitonic wavefunction of LiF

$$|\Psi_\lambda(\mathbf{r}_e,\mathbf{r}_h)|^2 = \left|\sum_{vc\mathbf{k}} A_\lambda^{vc\mathbf{k}} \psi^*_{c\mathbf{k}}(\mathbf{r}_e)\psi_{v\mathbf{k}}(\mathbf{r}_h)\right|^2$$

- where is the exciton localised ?
- how much ?



Gatti and Sottile, Phys. Rev. B **98**, 155113 (2013)

Workflow for a BSE calculation (for your hackathon)

- DFT-KS calculation $n(r)$ (approx :: v_{xc}, V_{ion}^{ps})
- DFT-KS calculation ψ_i, ϵ_i (approx :: v_{xc}, V_{ion}^{ps} k-sampling, empty bands)
- Screening calculation $W(\omega)$ (approx :: f_{xc})
- GW calculation $\Sigma(\omega)$ (approx :: ω-integration)
- BSE calculation for χ and spectra (approx :: tamm-dancoff, diago/iterative)

Absorption spectrum Inelastic X-ray Scattering refraction index Surface differential reflectivity
Compton Scattering Reflectivity Electron Energy Loss Reflectance Anisotropy spectroscopy

BSE in a code (like EXC, Yambo or Exciting)

$$\varepsilon^{-1}_{00}(\mathbf{q},\omega) = 1 + v_0(\mathbf{q}) \sum_{\lambda} \frac{\left| \sum_{vc\mathbf{k}} \langle c\mathbf{k} | e^{-i\mathbf{q}\cdot\mathbf{r}} | v\mathbf{k}-\mathbf{q} \rangle A_{\lambda}^{vc\mathbf{k}} \right|^2}{E_{\lambda}^{exc} - \omega - i\eta}$$

$|n\mathbf{k}\rangle = \psi_{n\mathbf{k}}(\mathbf{r})$ from DFT-KS calculations

$H^{exc} A_{\lambda}^{vc\mathbf{k}} = E_{\lambda}^{exc} A_{\lambda}^{vc\mathbf{k}}$ eigenvalues(vectors) of the EXC Hamiltonian

$$|n\mathbf{k}\rangle = \psi_{n\mathbf{k}}(\mathbf{r})$$ from DFT-KS calculations

$$H^{exc} A_{\lambda}^{vc\mathbf{k}} = E_{\lambda}^{exc} A_{\lambda}^{vc\mathbf{k}}$$ eigenvalues(vectors) of the EXC Hamiltonian

$$H^{exc} = (\epsilon_c + \Delta_c^{GW} - \epsilon_v - \Delta_v^{GW})\delta_{vv'}\delta_{cc'} + v_{vc}^{v'c'} - W_{vc}^{v'c'}$$

GW corrections (or scissor operator)

$$W_{vc}^{v'c'} = \int d\mathbf{r} d\mathbf{r}' \psi_c^*(\mathbf{r})\psi_{c'}(\mathbf{r}) W(\mathbf{r},\mathbf{r}')\psi_{v'}^*(\mathbf{r})\psi_v(\mathbf{r})$$

$$W(\mathbf{r},\mathbf{r}') = \int d\tilde{\mathbf{r}}\, \varepsilon^{-1}(\mathbf{r},\tilde{\mathbf{r}})\, v(\tilde{\mathbf{r}},\mathbf{r}')$$

screening (dielectric function)

from BSE in EXC and Exciting

$$\varepsilon^{-1}_{00}(\mathbf{q},\omega) = 1 + v_0(\mathbf{q}) \sum_{\lambda} \frac{\left| \sum_{vc\mathbf{k}} \langle c\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|v\mathbf{k}-\mathbf{q}\rangle\, A^{vc\mathbf{k}}_{\lambda} \right|^2}{E^{exc}_{\lambda} - \omega - i\eta}$$

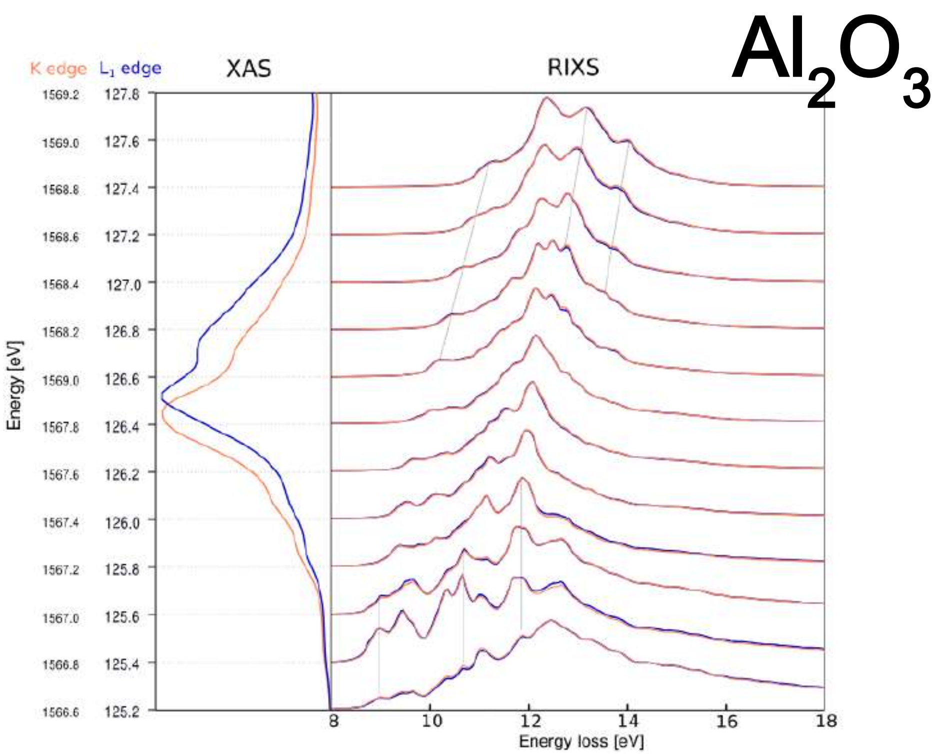
matelem.[h5/nc]

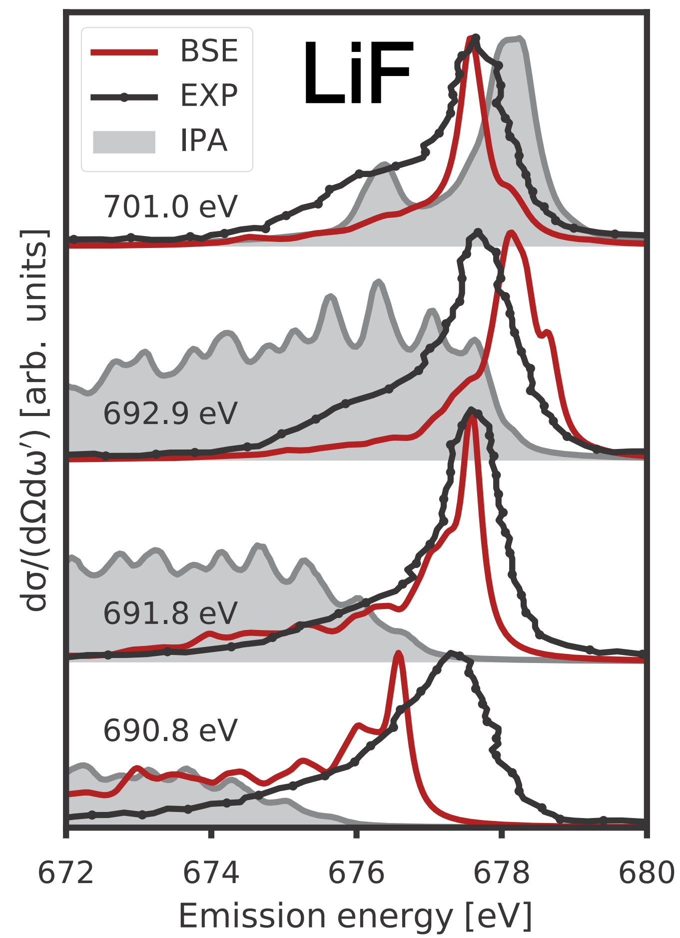
bse_out.[h5/nc]

to the description of RIXS

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \ \mathrm{Im} \sum_{\substack{\mu\mu'' \\ \lambda'_c\lambda_c\lambda}} \sum_{\substack{vv' \\ cc''}} \sum_{\substack{\mu'''\mu'''' \\ c'''c''''}} \left[\frac{A^{*\mu''''c''''}_{\lambda'_c} \tilde{\rho}_{c''''\mu''''} A^{\mu c}_{\lambda'_c} \tilde{\rho}^{*}_{\mu v}}{\omega_i - E_{\lambda'_c} + i\eta} \right]^* \frac{A^{vc}_{\lambda} A^{*v'c''}_{\lambda}}{\omega - E_{\lambda} + i\eta} \left[\frac{\tilde{\rho}^{*}_{\mu''v'} A^{\mu''c''}_{\lambda_c} A^{*\mu'''c'''}_{\lambda_c} \tilde{\rho}_{c'''\mu'''}}{\omega_i - E_{\lambda_c} + i\eta} \right]$$

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \mathrm{Im} \sum_{\substack{\mu\mu'' \\ \lambda'_c \lambda_c \lambda}} \sum_{\substack{vv' \\ cc''}} \sum_{\substack{\mu'''\mu'''' \\ c'''c''''}} \left[\frac{A^{*\mu''''c''''}_{\lambda'_c} \, \tilde{\rho}_{c''''\mu''''} \, A^{\mu c}_{\lambda'_c} \, \tilde{\rho}^*_{\mu v}}{\omega_i - E_{\lambda'_c} + i\eta} \right]^* \frac{A^{vc}_{\lambda} A^{*v'c''}_{\lambda}}{\omega - E_{\lambda} + i\eta} \left[\frac{\tilde{\rho}^*_{\mu''v'} \, A^{\mu''c''}_{\lambda_c} \, A^{*\mu'''c'''}_{\lambda_c} \, \tilde{\rho}_{c'''\mu'''}}{\omega_i - E_{\lambda_c} + i\eta} \right]$$





Urquiza *et al.* Phys. Rev. B **109**, 115157 (2024)

Vorwerk *et al.* Phys. Rev. Research **2**, 042003(R) (2020)

input file for EXC code

```
exciton                   # do a BSE calculation
tammdancoff               # use the approx
nbands 20                 # use 20 bands in total
matsh 10                  # use 10 shells of G's in W
wfncut 12.5               # use a cutoff energy (inHa) for wfns
omegae 10.0               # spectrum up to 10 eV
domega 0.1                # with step of 0.1 eV
broad 0.05                # eta is the Lorentzian broadening
                          #   (in eV)
q 0.125 0.0 0.250         # this is a finite momentum transfer
                          #   (in rl units)
```