Excitonic signatures in different spectroscopies

from optical to scattering experiments, via ab initio many-body approaches

Francesco Sottile
LSI, Ecole Polytechnique, Palaiseau and ETSF - France

UK- France Seed meeting Edinburgh 30-31 May 2024

Quantum Effects in Energy Harvesting

l'X ÉCOLE POLYTECHNIQUE
IP PARIS

ETSF

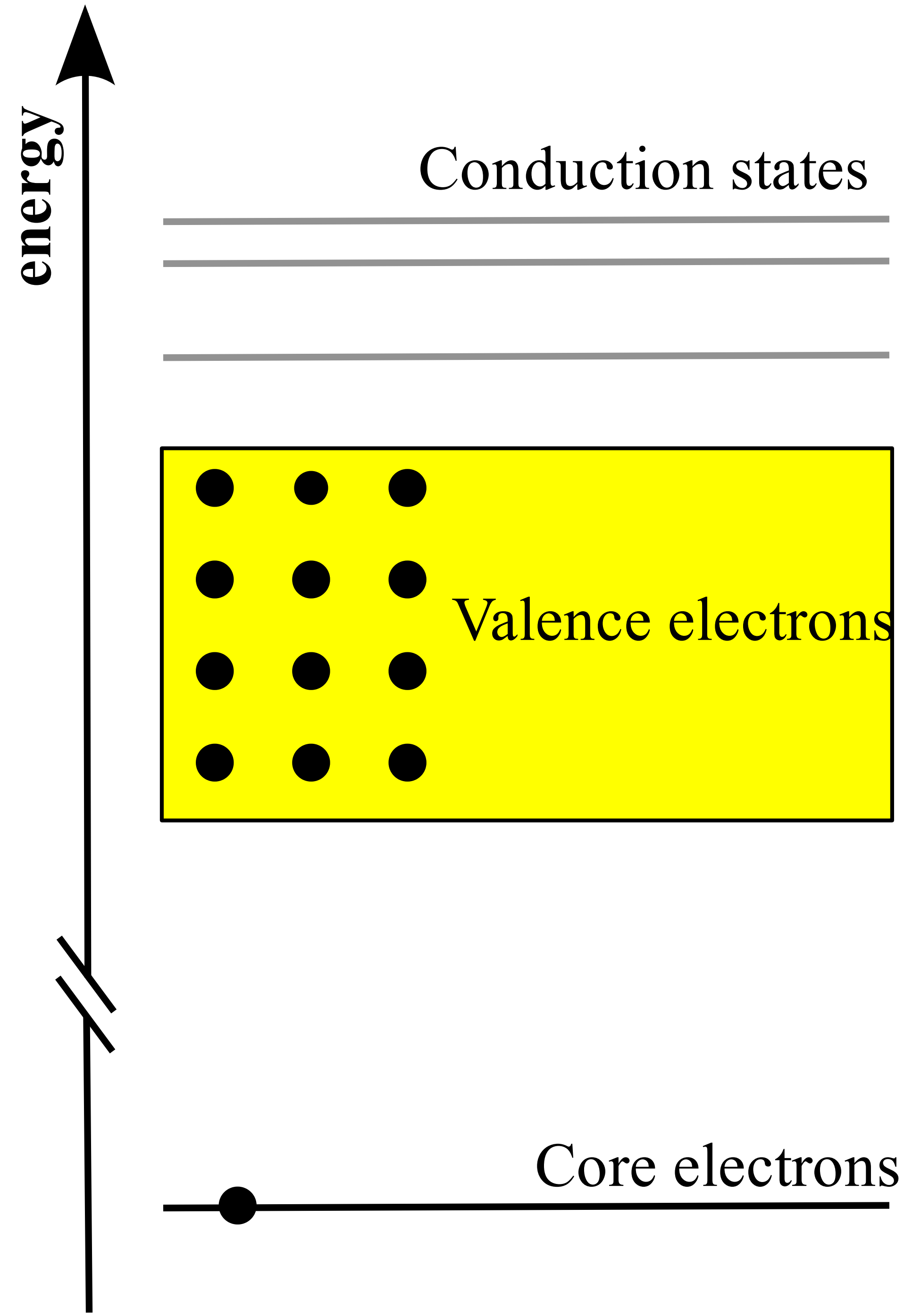
FRANCE 2030 Stratégie nationale PEPR Technologies Avancées des Systèmes Energétiques (TASE)

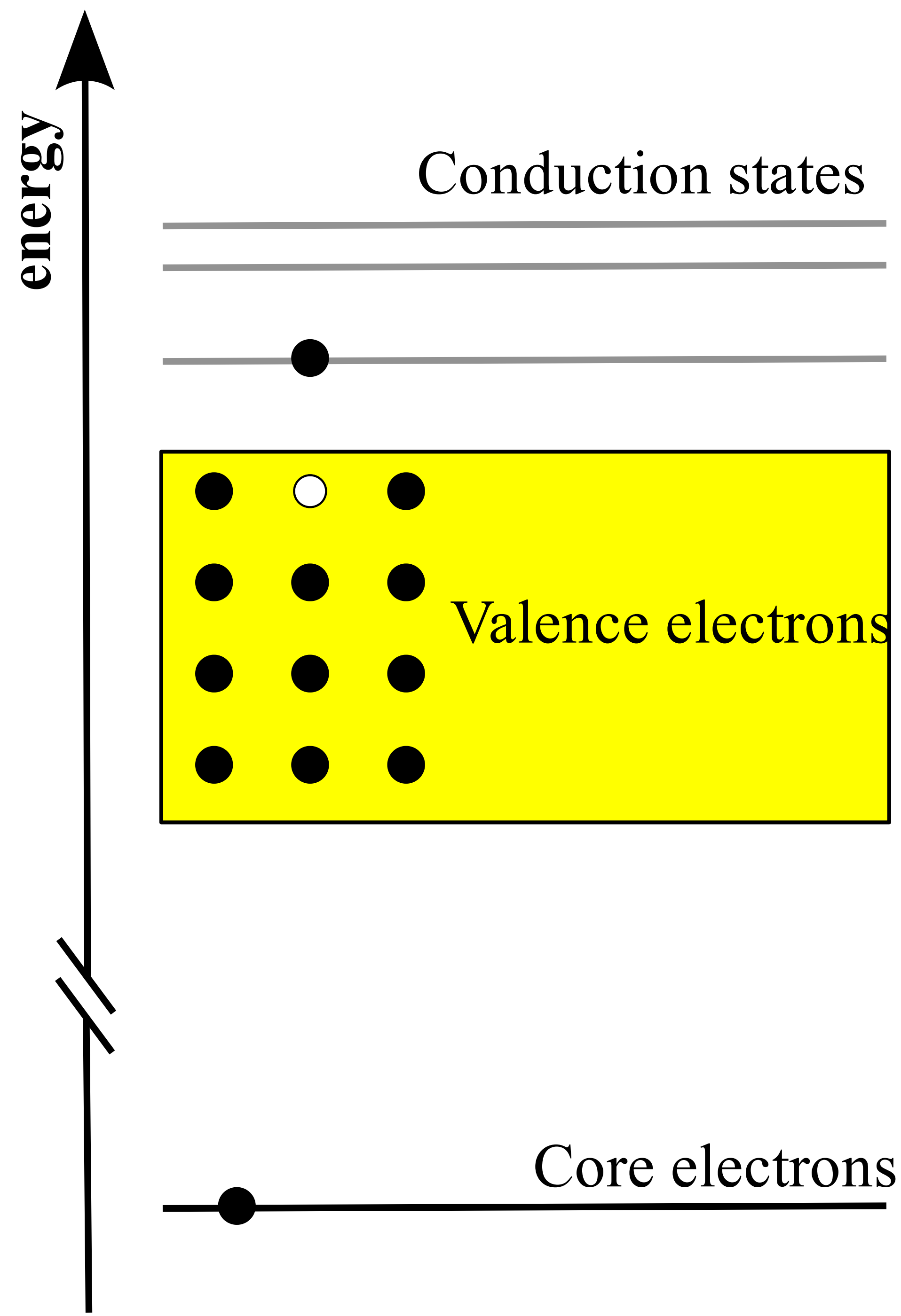
Multimodal approach combining IN-situ, ex-situ and Operando CharacTerizAtion with SimUlations for Highly REliable Next Generation Photovoltaics

MINOTAURE

GENERAL INFORMATIONS

Acronym: MINOTAURE
Reference Number: 22-PETA-0015
Project Region: Île-de-France
Discipline: 2 - SMI
PIA investment: 5,049,988 €
Start date: November 2023
End date: October 2028


energy
Conduction states
Valence electrons
Core electrons



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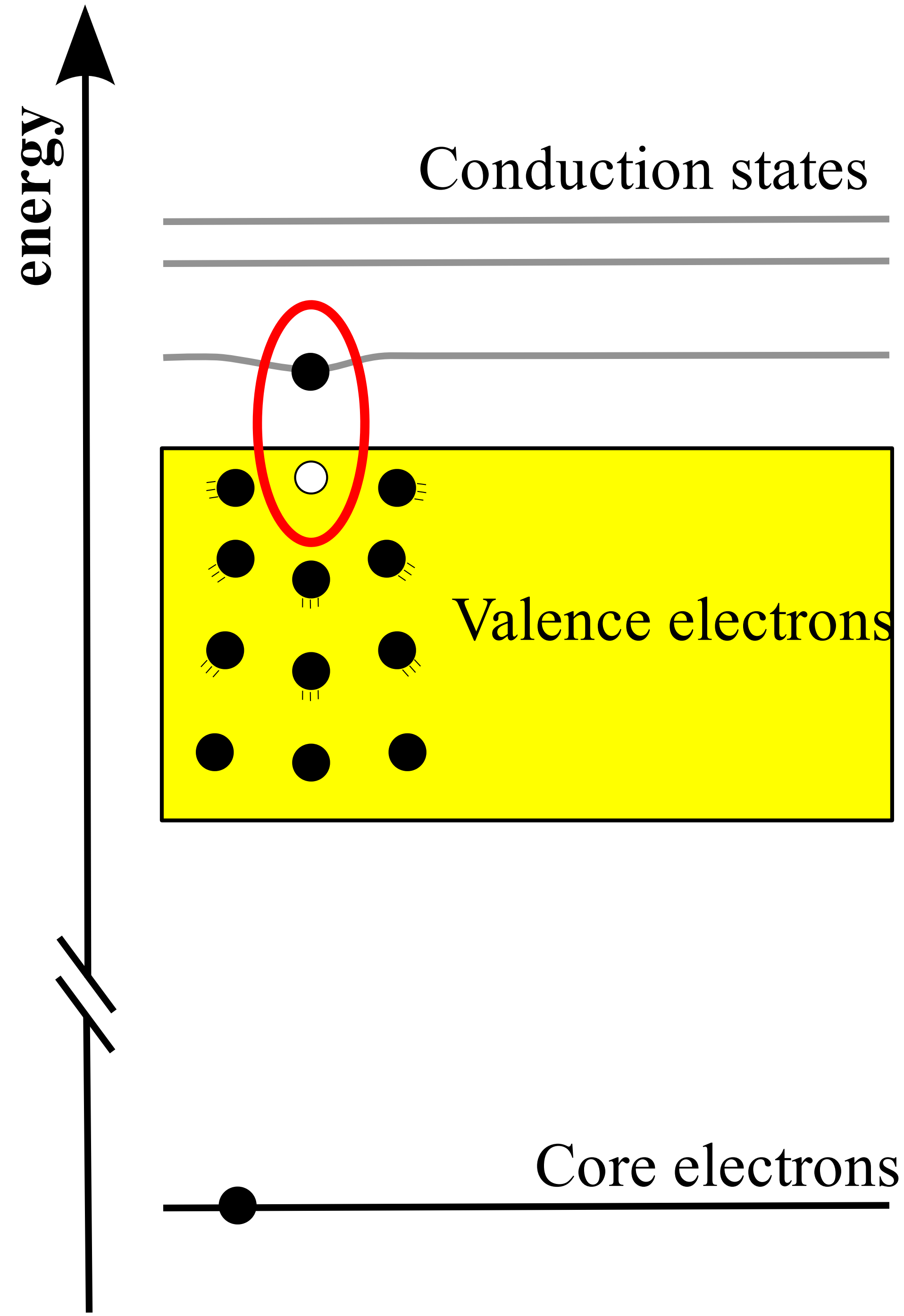
energy
Conduction states
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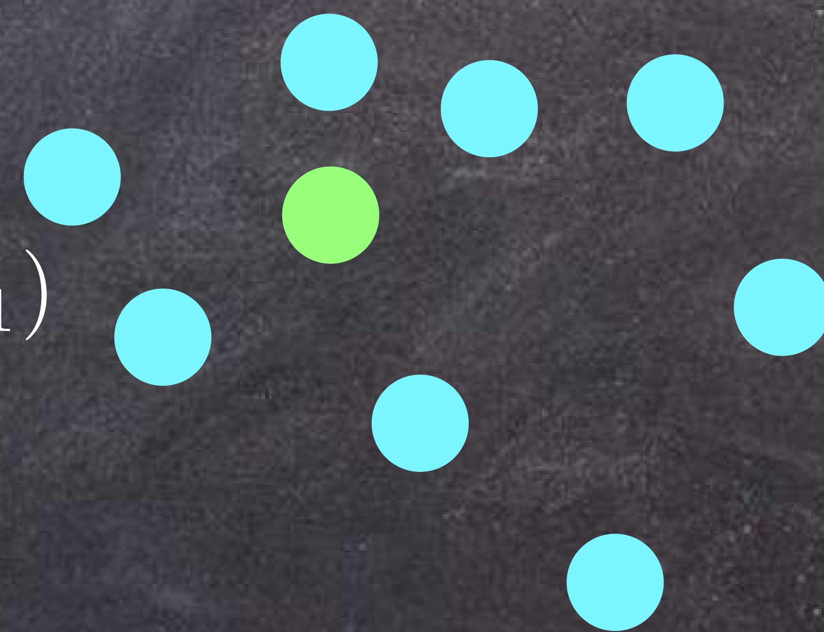
- Excitons via Green's functions many-body theory
- Challenges
- Results and accuracy

The Green's functions mb formalism

$$G(1,2)$$

$$1 = (\mathbf{r}_1, t_1, \sigma_1)$$



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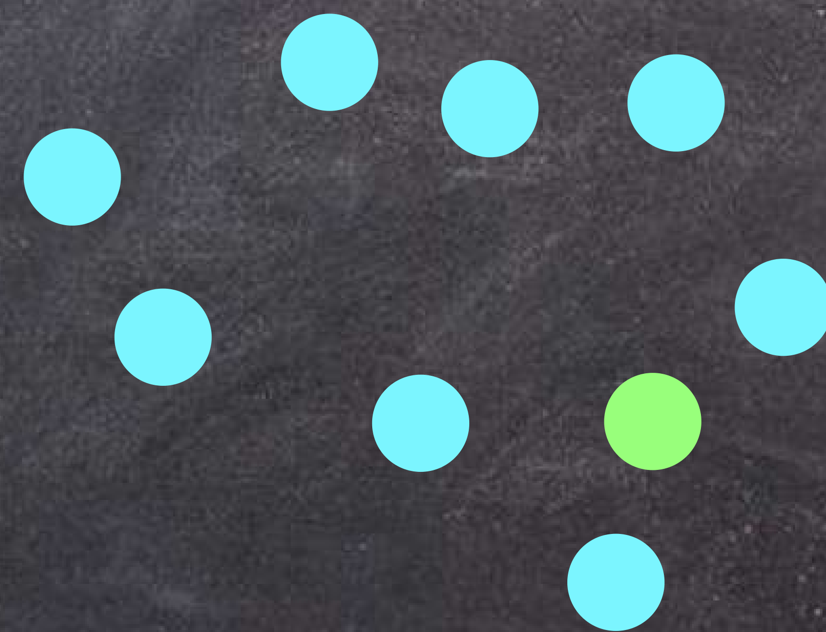
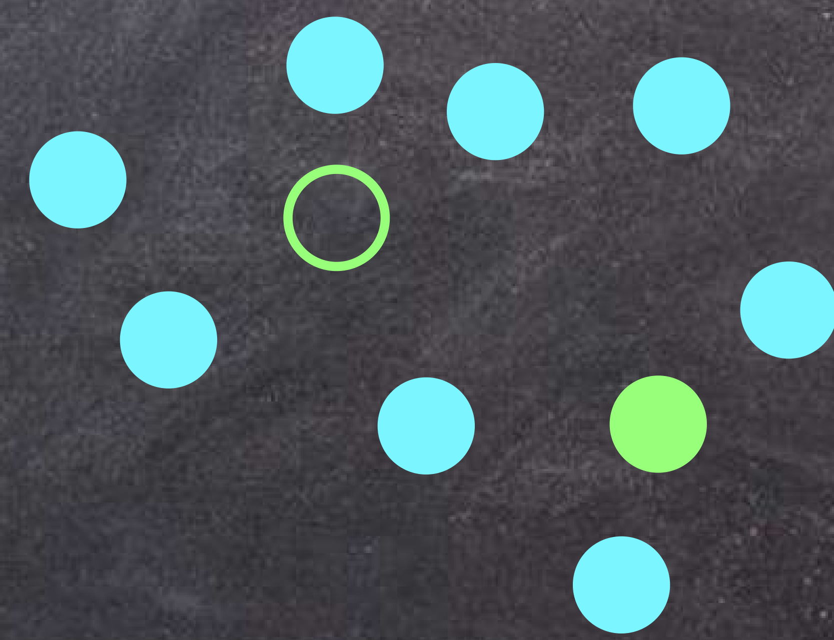


$$2 = (\mathbf{r}_2, t_2, \sigma_2)$$

The Green's functions mb formalism

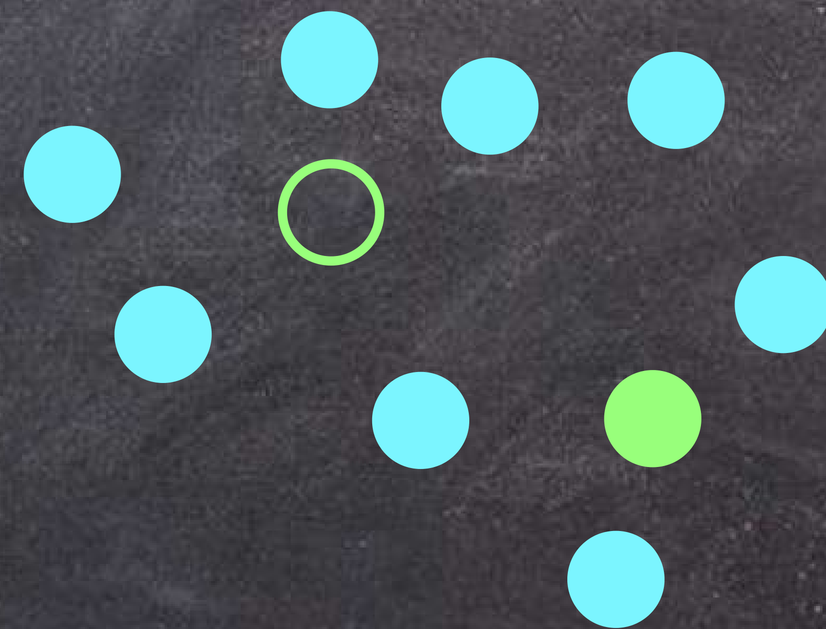
$$G(1,2)$$



$$G^{(2)}(1,2,3,4)$$

The Green's functions mb formalism

$$G(1,2)$$



$$G^{(2)}(1,2,3,4)-G(1,2)G(3,4) = -iL(1,2,3,4) = \frac{\delta G(1,3)}{\delta V_{ext}(2,4)}$$

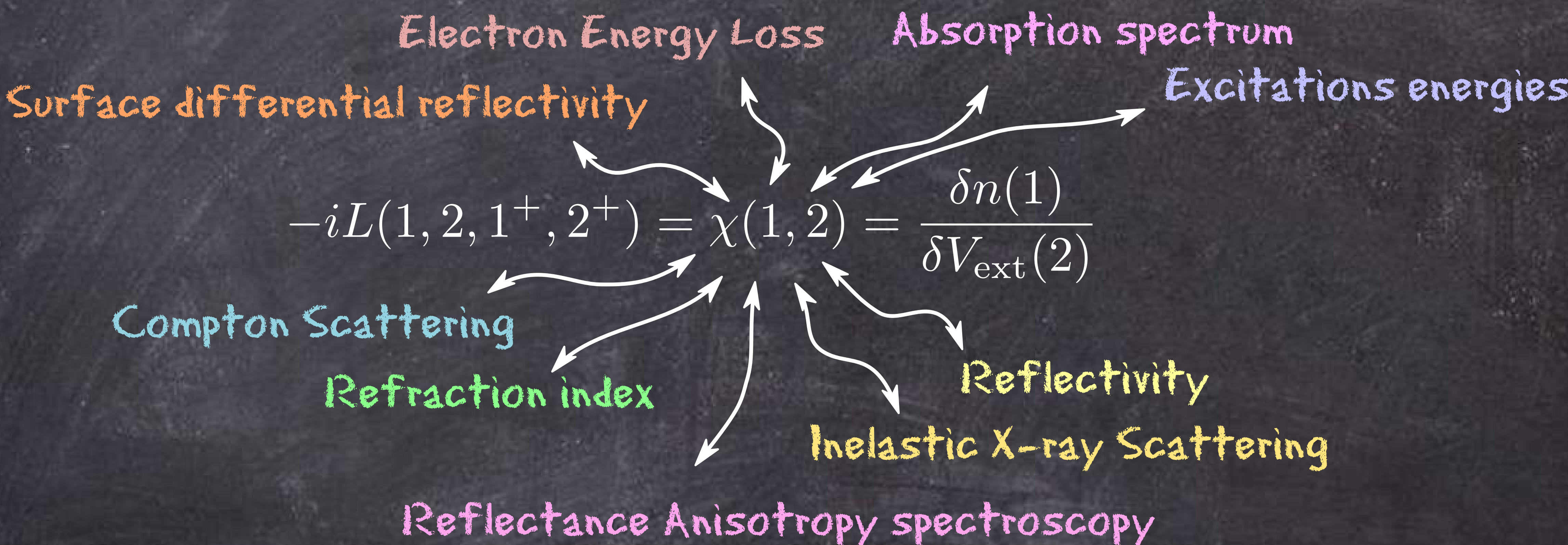
$$-iL(1,2,1^+,2^+) = \chi(1,2) = \frac{\delta n(1)}{\delta V_{\mathrm{ext}}(2)}$$

Electron Energy Loss

Excitations energies

$$-iL(1,2,1^+,2^+) = \chi(1,2) = \frac{\delta n(1)}{\delta V_{\text{ext}}(2)}$$

Inelastic X-ray Scattering



Electron Energy Loss
Absorption spectrum
Excitations energies
Surface differential reflectivity
$$-iL(1,2,1^+,2^+) = \chi(1,2) = \frac{\delta n(1)}{\delta V_{\text{ext}}(2)}$$
Compton Scattering
Refraction index
Reflectivity
Inelastic X-ray Scattering
Reflectance Anisotropy spectroscopy

The Bethe-Salpeter Equation

$$L(1,2,3,4) = L^0(1,2,3,4) + L^0(1,2,5,6)\left[v(5,7)\delta(5,6)\delta(7,8) + i\frac{\delta\Sigma(5,6)}{\delta G(7,8)}\right]L(7,8,3,4)$$

$$L^0(1,2,3,4) = G(1,2)G(3,4)$$

Electron Energy Loss

Absorption spectrum

Excitations energies

Surface differential reflectivity

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Reflectance Anisotropy spectroscopy

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- Results and accuracy

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starting G
LDA, GGA, HF

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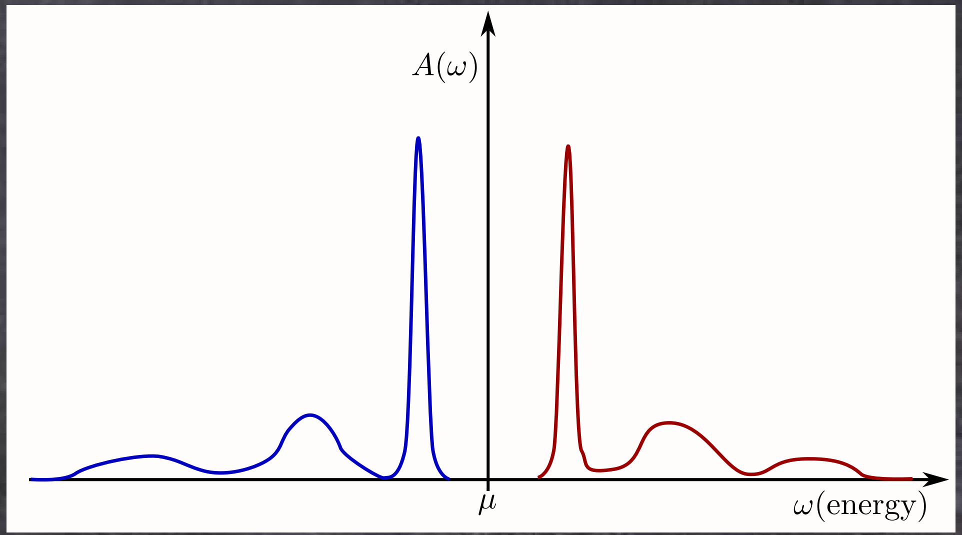

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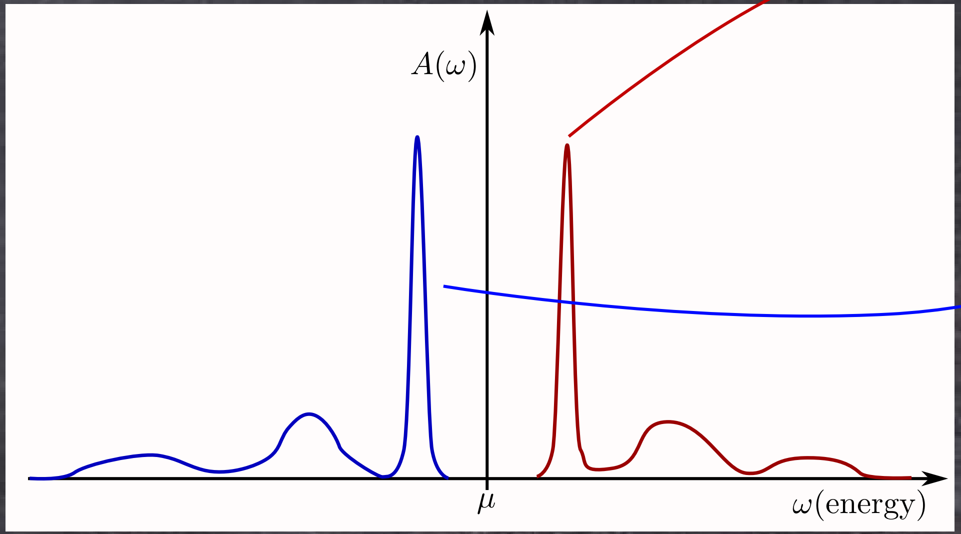

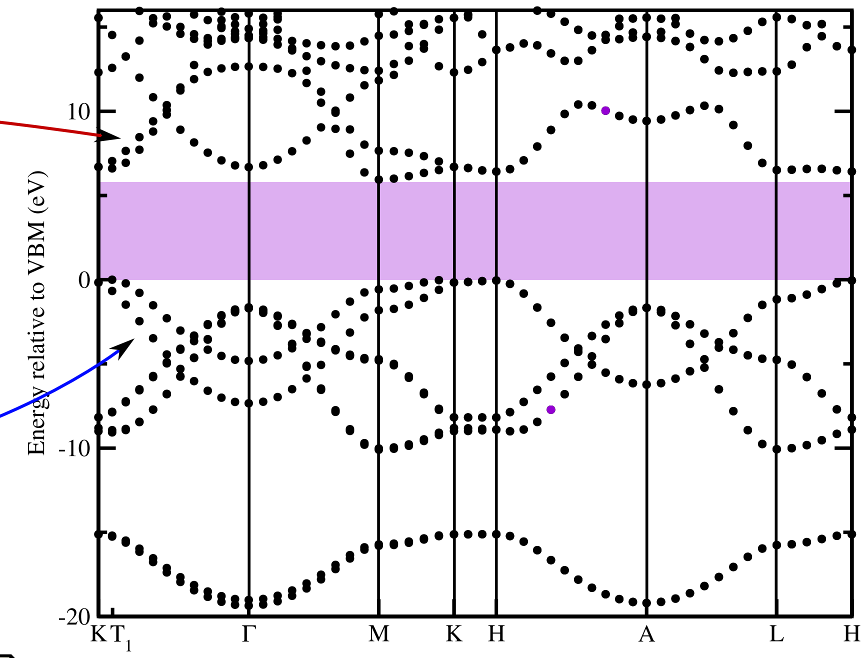

Arnaud *et al.*, PRL **96**, 026402 (2006)

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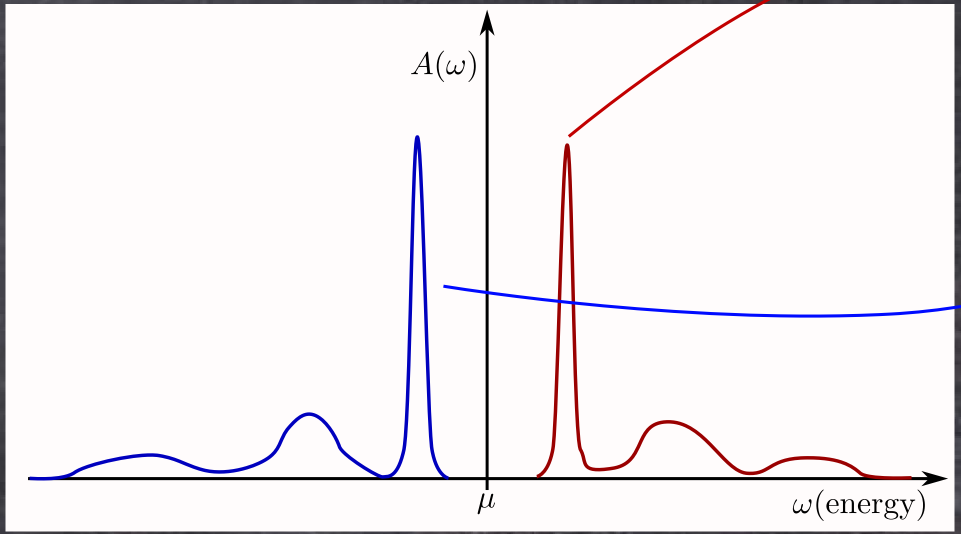

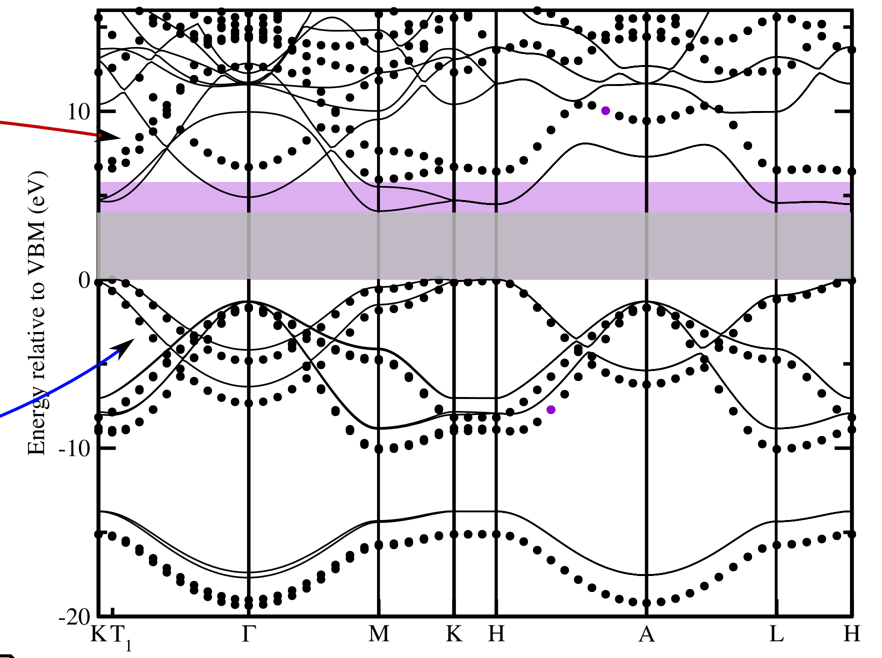

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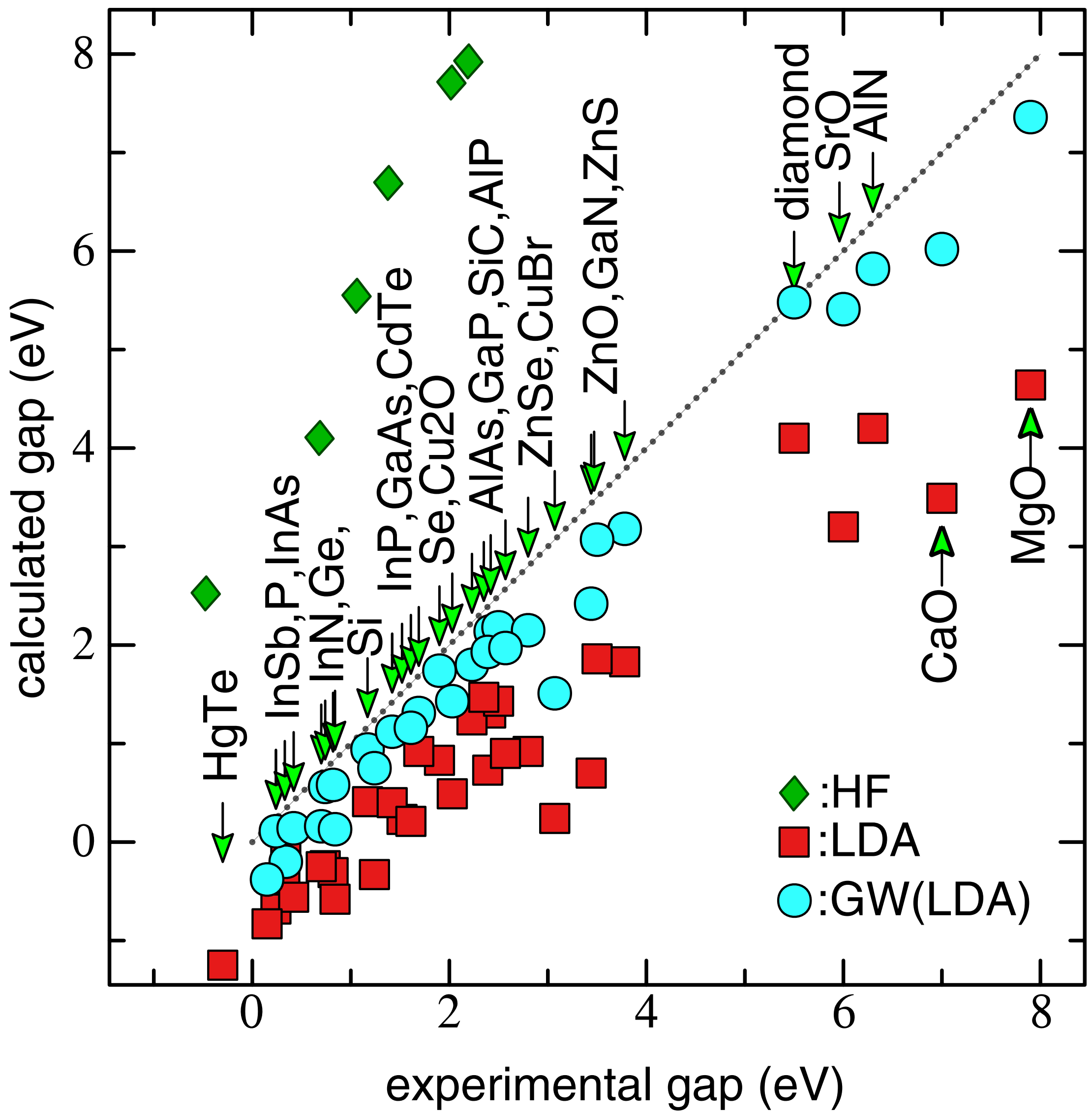
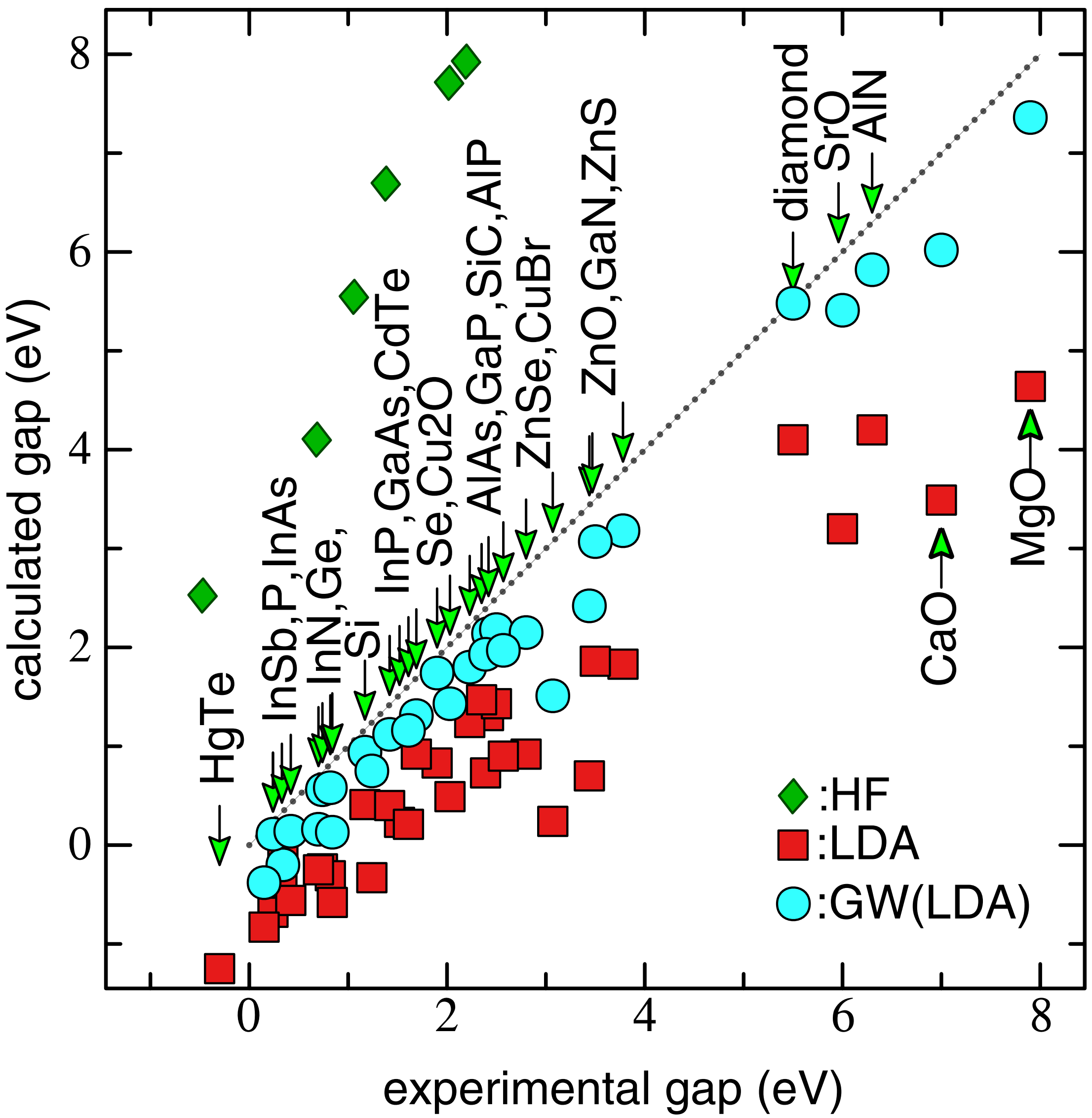
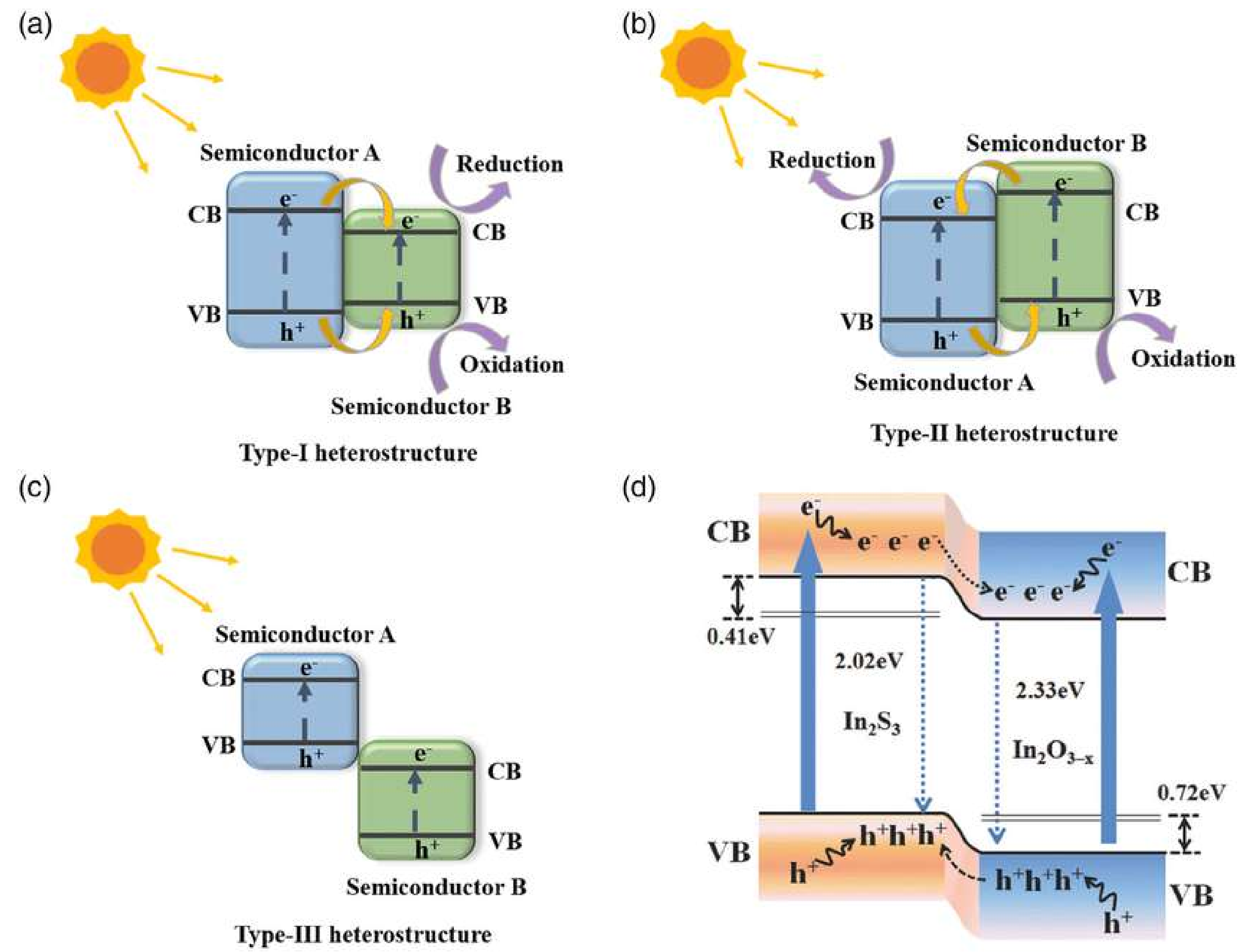


PRL **96**, 226402 (2006)





PRL **96**, 226402 (2006)

2nd challenge :: solving the BSE

$$L(1,2,3,4) = L^0(1,2,3,4) + L^0(1,2,5,6)\left[v(5,7)\delta(5,6)\delta(7,8) + i\frac{\delta\Sigma(5,6)}{\delta G(7,8)}\right] L(7,8,3,4)$$

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$$L(1,2,3,4) = GG + GG\left[v - W\right]L$$

$$L(r_1, r_2, r_3, r_4, \omega) \quad \Rightarrow \quad L_{vc}^{v'c'}(\omega)$$

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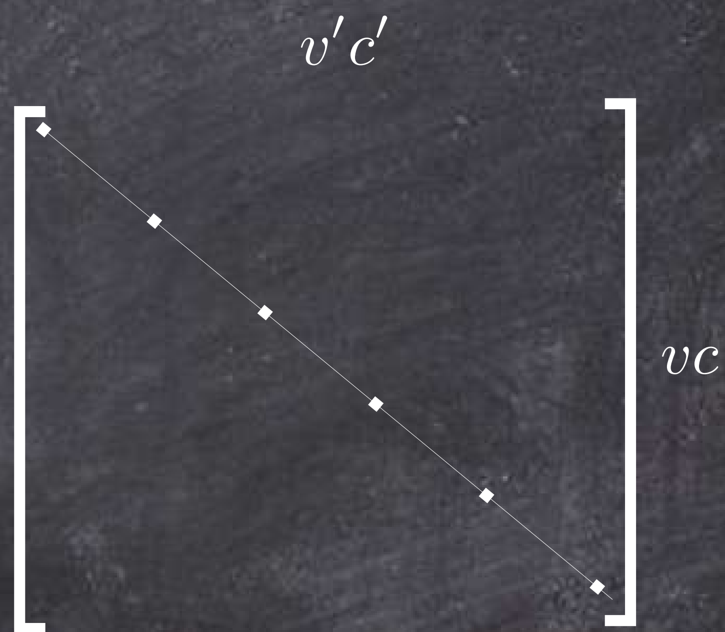

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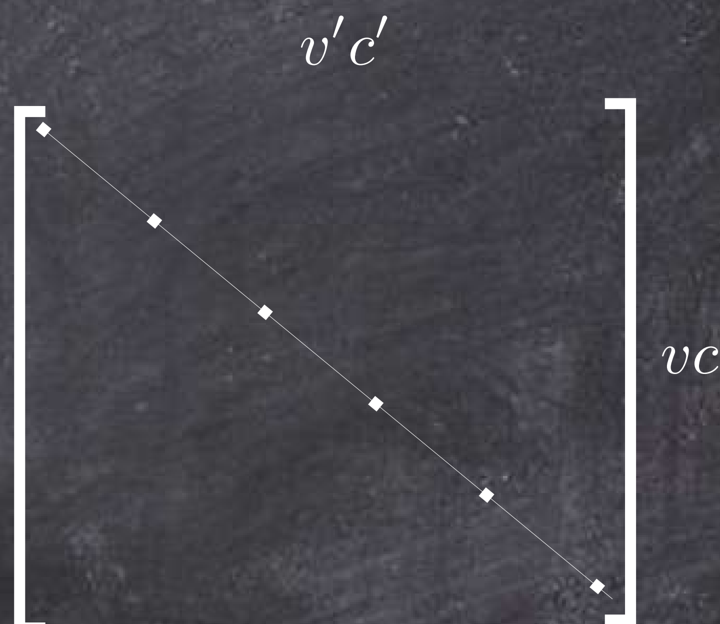
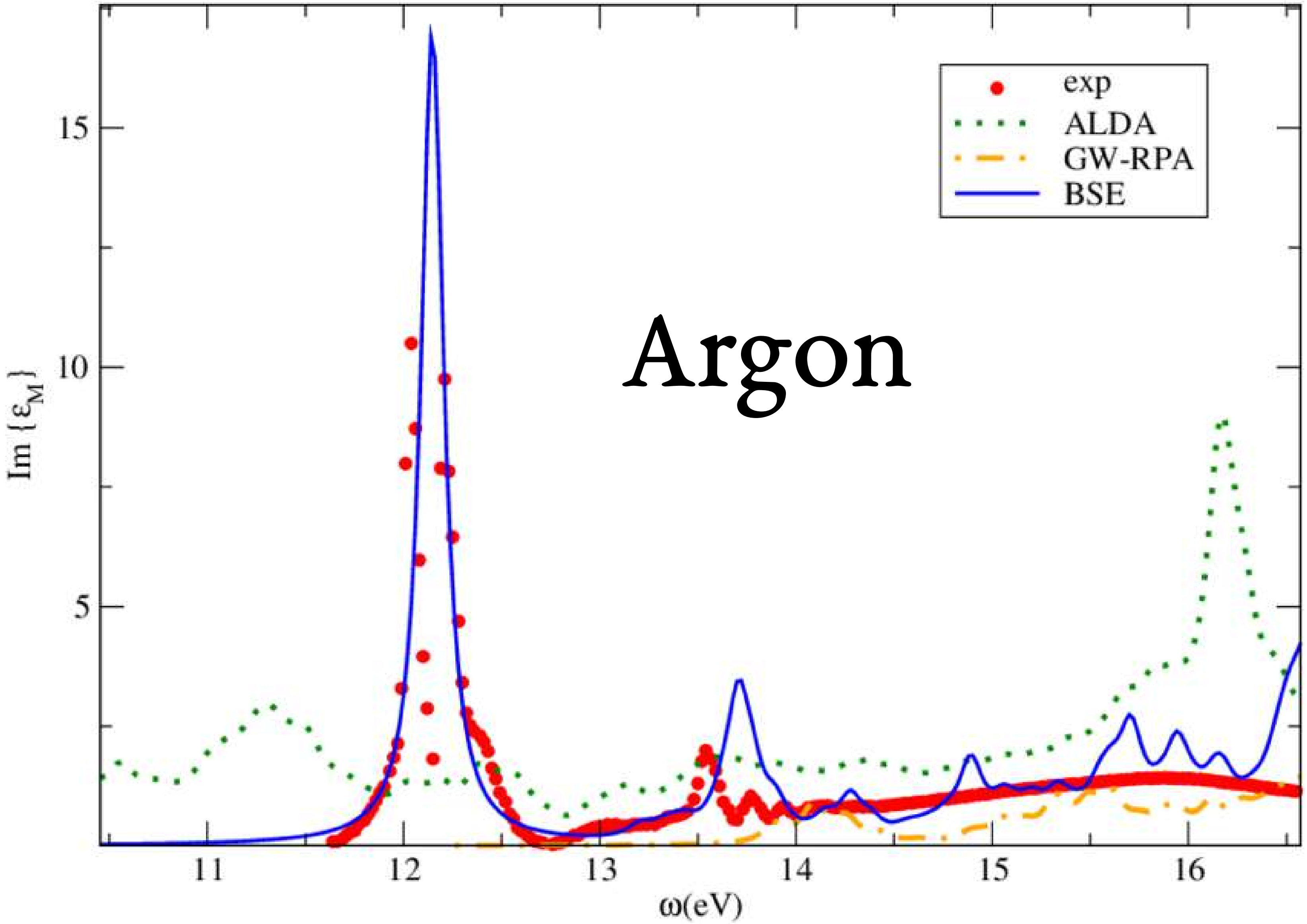
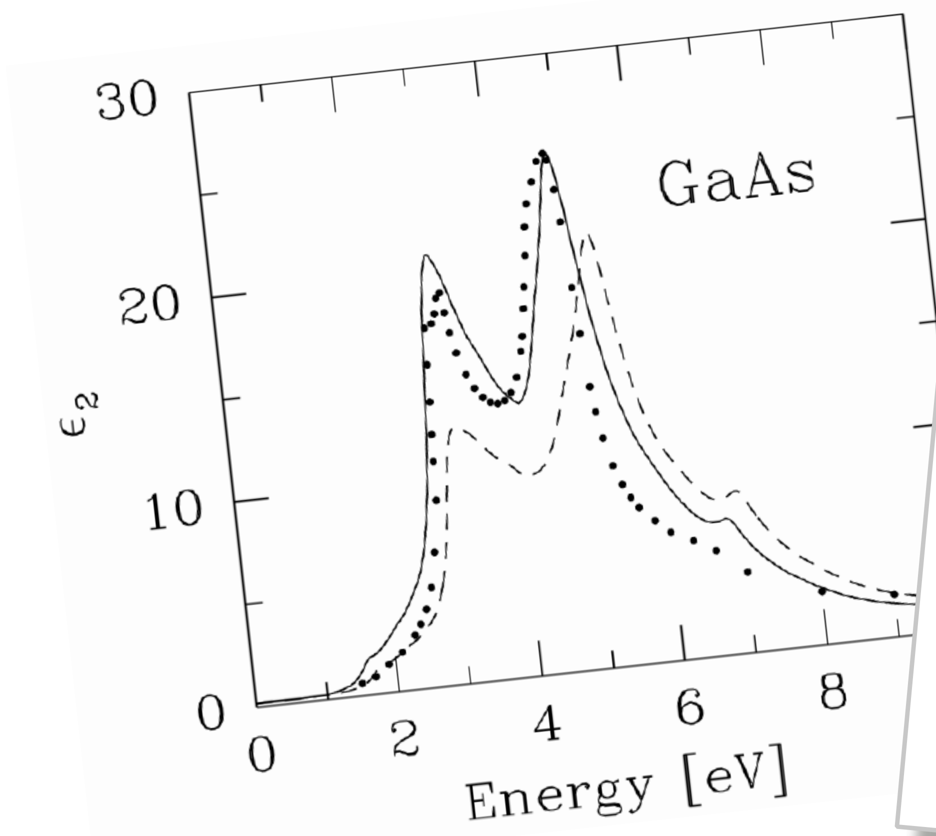


scaling N_{at}^{4-6}

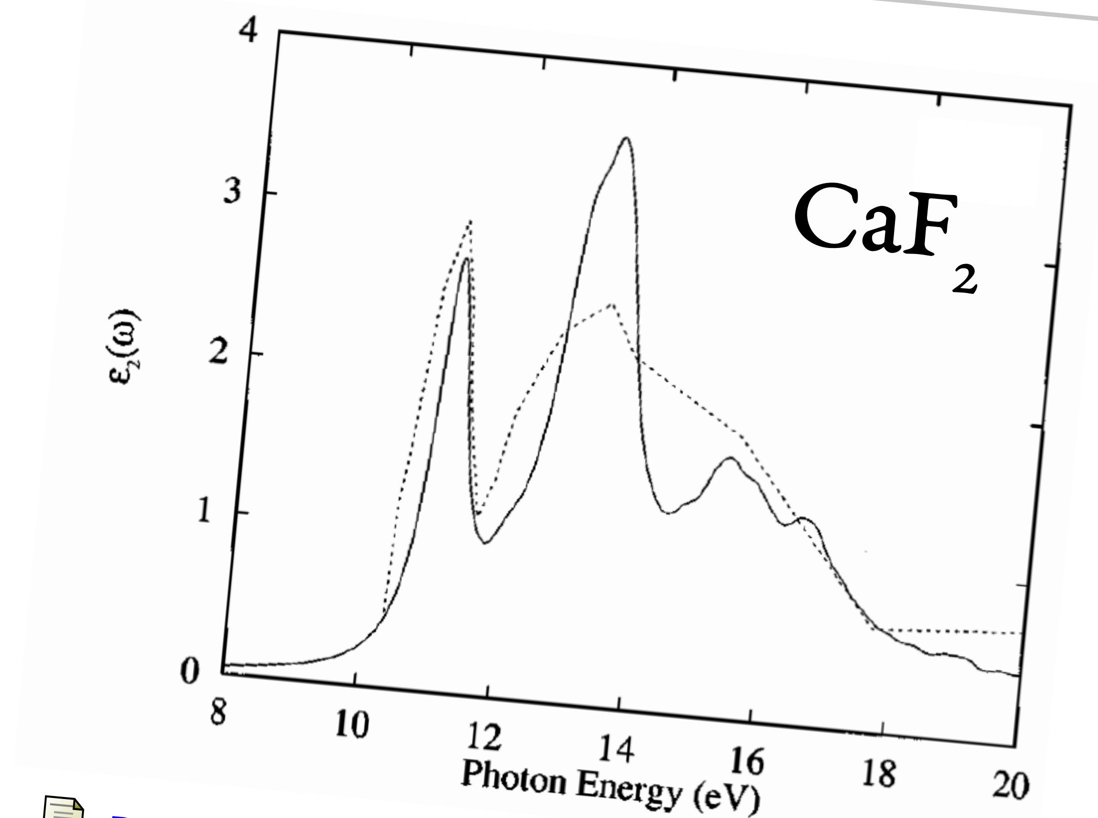
- Excitons via Green's functions many-body theory
- Challenges
- **Results and accuracy**



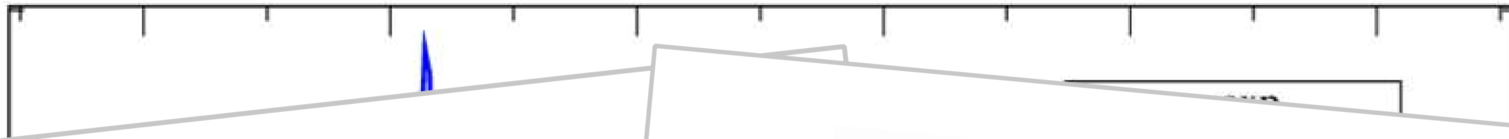
Phys. Rev. B **76** 161103 (2007)



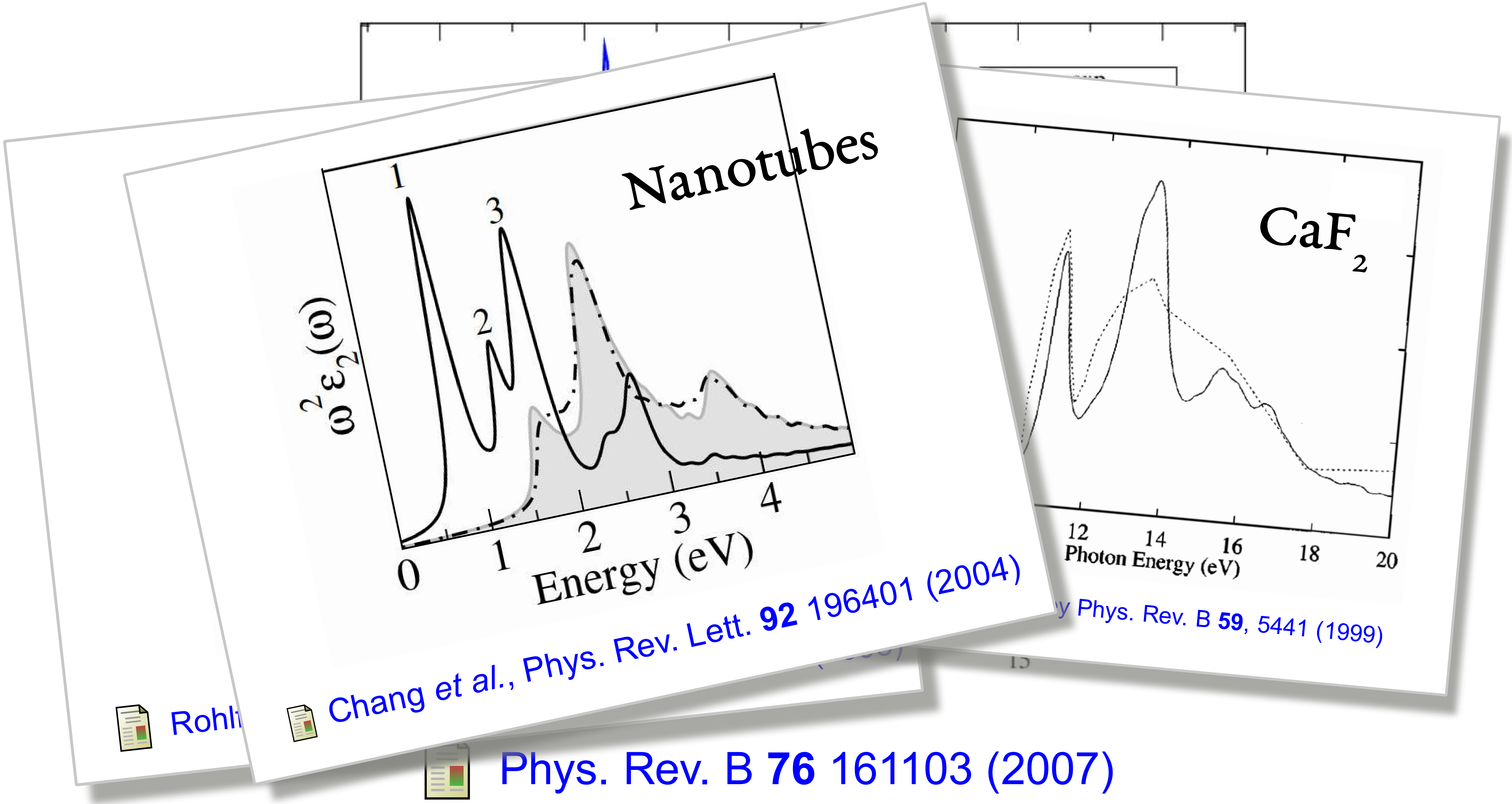
Rohlfing and Louie Phys. Rev. Lett. **81**, 2312 (1998)



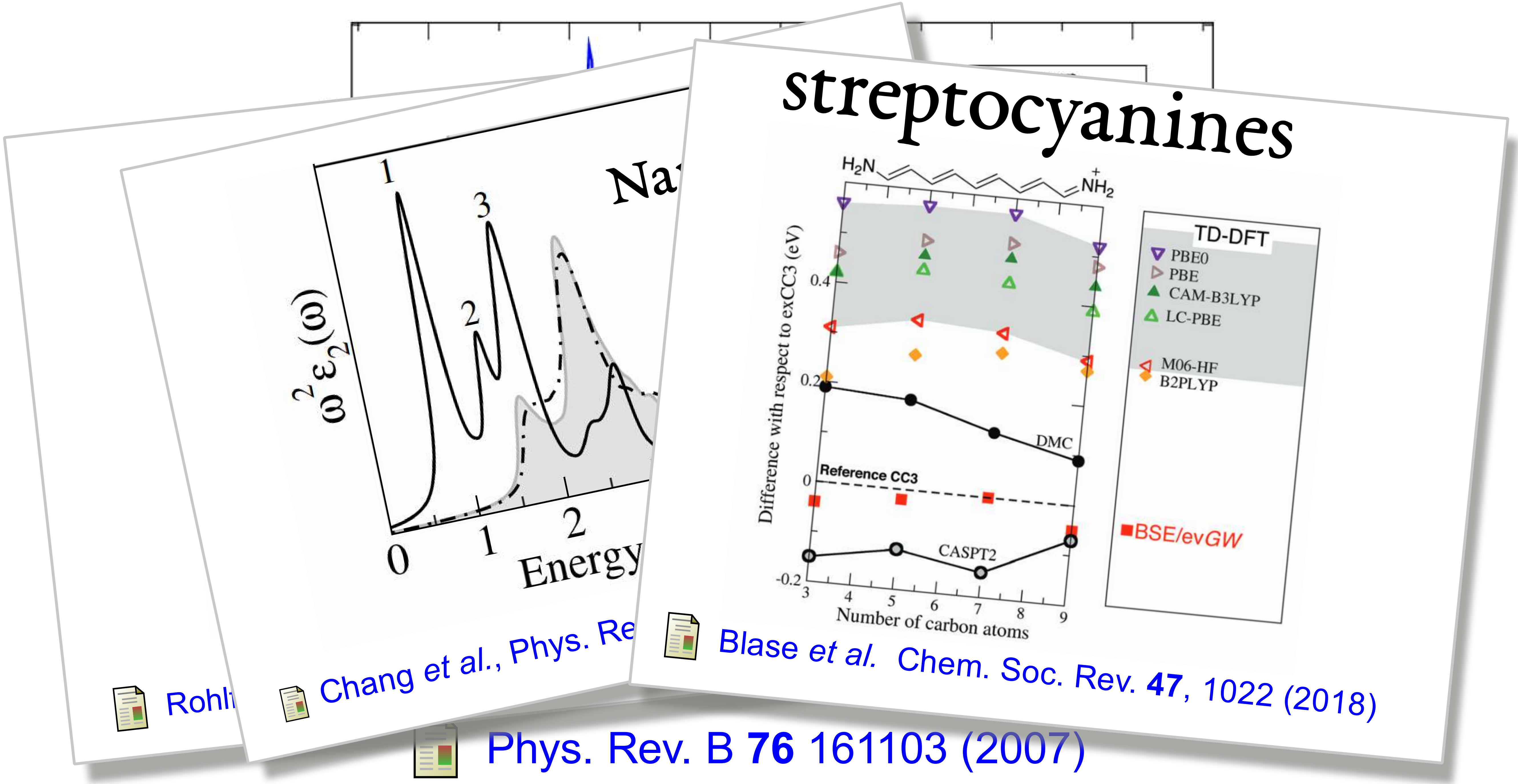
Benedict and Shirley Phys. Rev. B **59**, 5441 (1999)



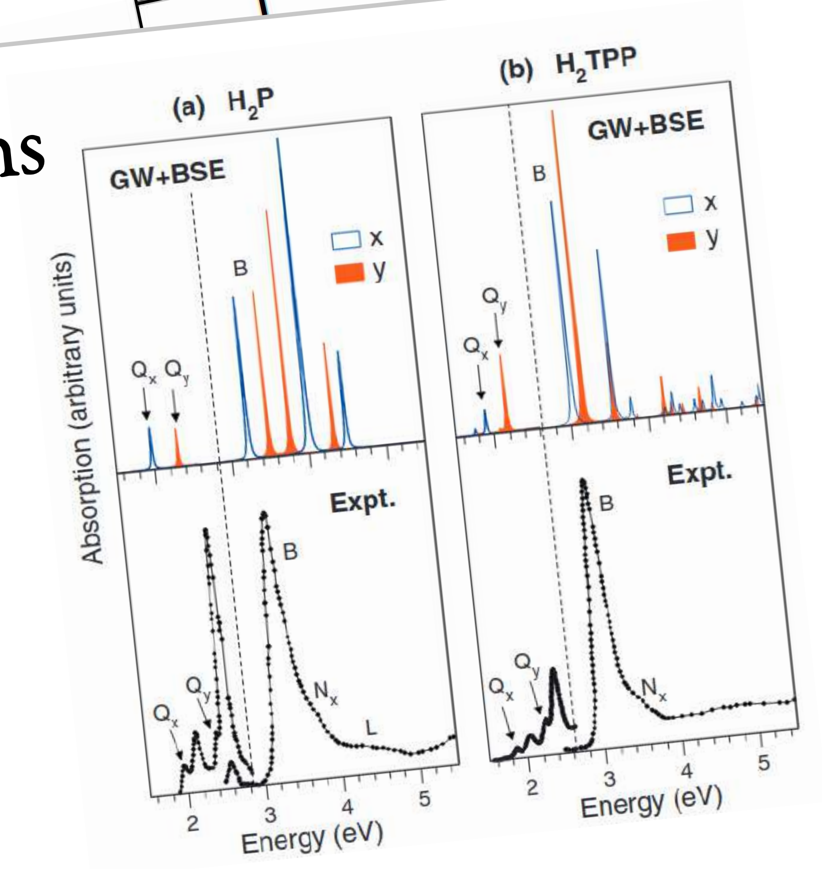
Phys. Rev. B **76** 161103 (2007)



Nanotubes
1
2
3
ω2ε2(ω)
0 1 2 3 4
Energy (eV)
Chang et al., Phys. Rev. Lett. 92 196401 (2004)
CaF2
12 14 16 18 20
Photon Energy (eV)
Phys. Rev. B 59, 5441 (1999)
Phys. Rev. B 76 161103 (2007)

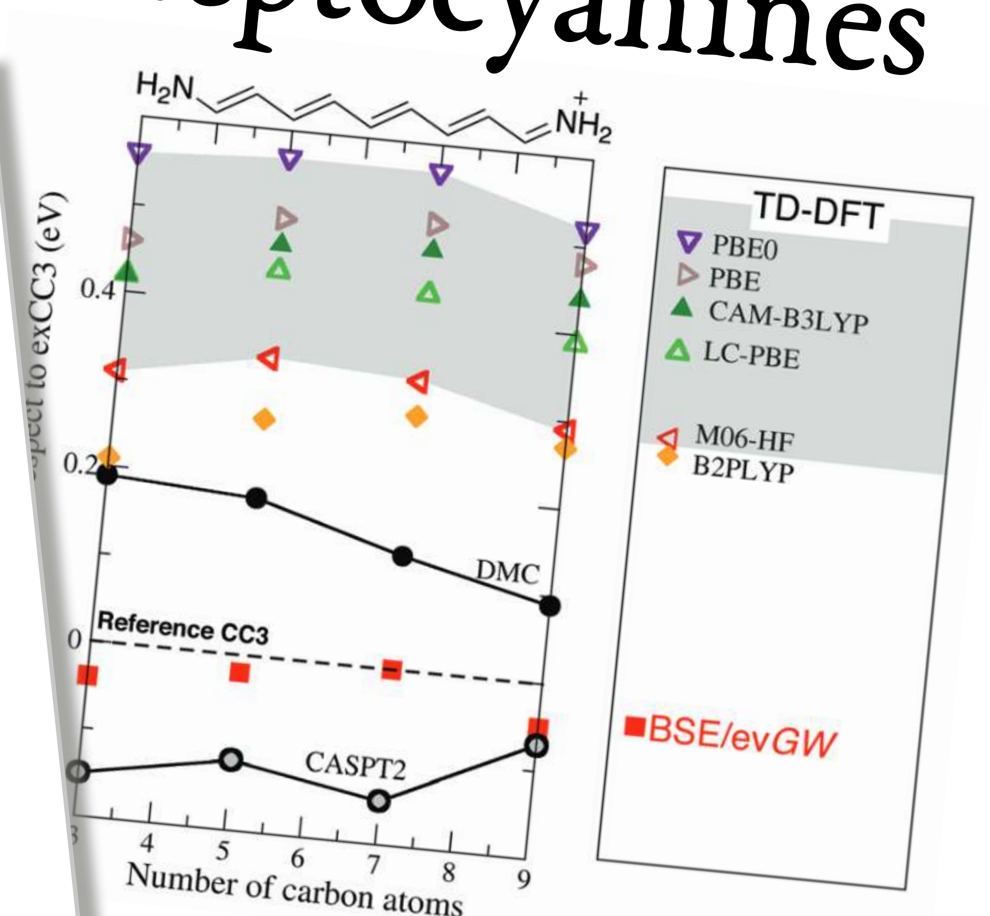

streptocyanines
H2N
NH2
Difference with respect to exCC3 (eV)
Number of carbon atoms
TD-DFT
PBE0
PBE
CAM-B3LYP
LC-PBE
M06-HF
B2PLYP
DMC
Reference CC3
CASPT2
BSE/evGW
Blase et al. Chem. Soc. Rev. 47, 1022 (2018)
Chang et al., Phys. Re
Energy
Rohl
Phys. Rev. B 76 161103 (2007)

Porphyrins



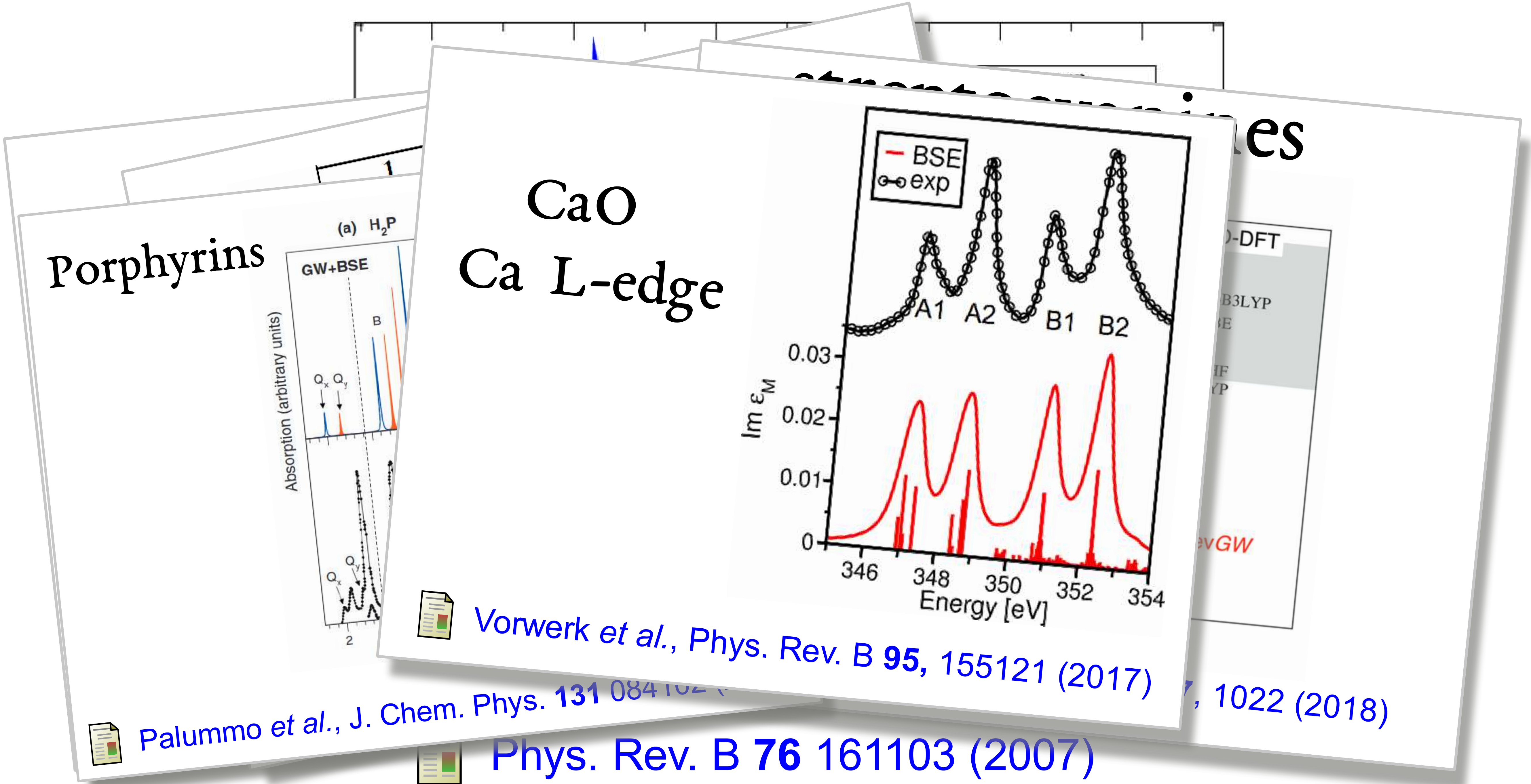
Palummo *et al.*, J. Chem. Phys. **131** 084102 (2009)

streptocyanines



et al. Chem. Soc. Rev. **47**, 1022 (2018)

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


Porphyrins
(a) H2P
GW+BSE
Absorption (arbitrary units)
Palummo et al., J. Chem. Phys. 131 084
CaO
Ca L-edge
BSE
exp
A1 A2 B1 B2
Im ε_M
0.03
0.02
0.01
0
346 348 350 352 354
Energy [eV]
Vorwerk et al., Phys. Rev. B 95, 155121 (2017)
, 1022 (2018)
Phys. Rev. B 76 161103 (2007)

BSE :: accurate for absorption spectra (and excitation energies)

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- it captures the physics of the electron-hole interaction

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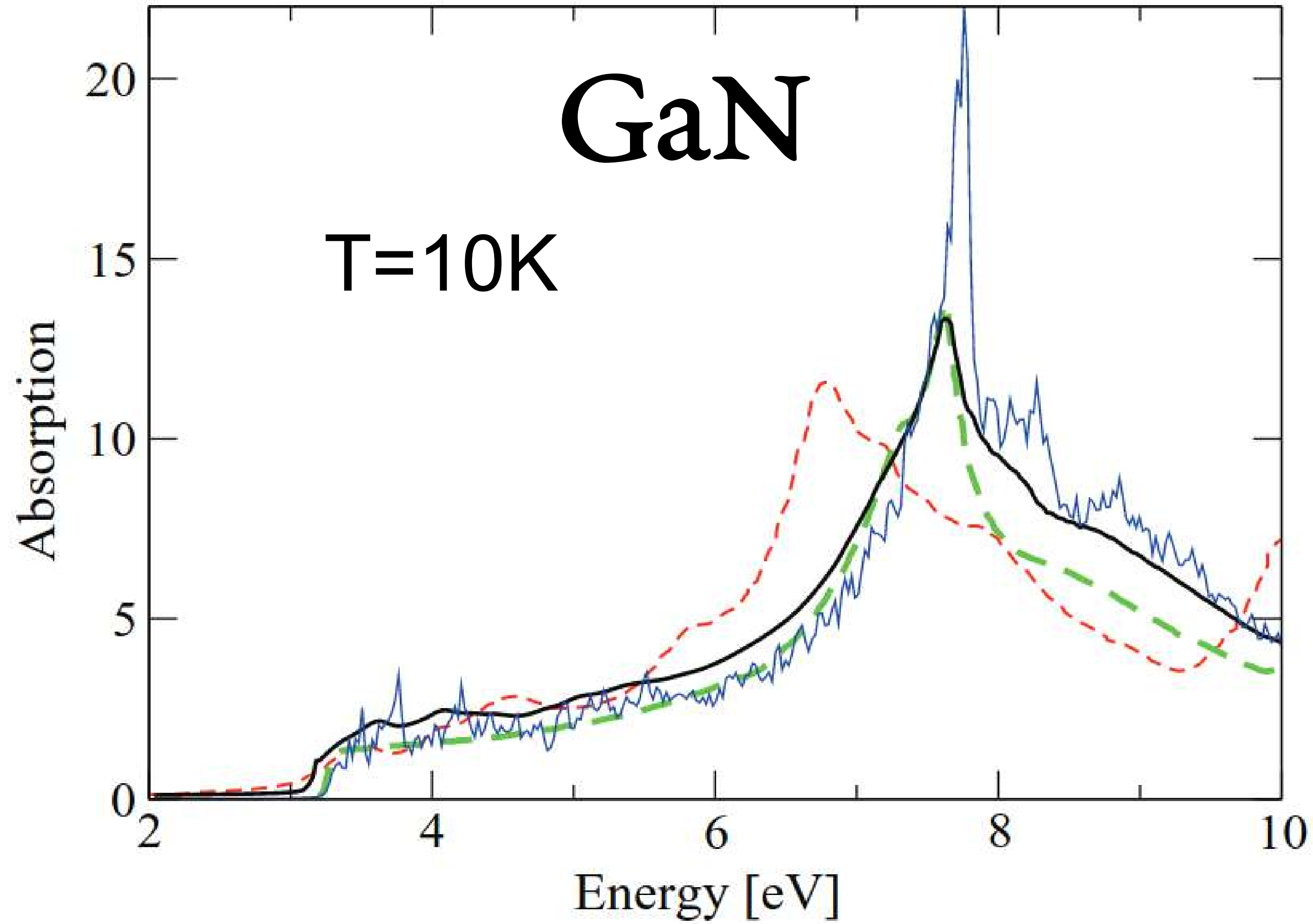
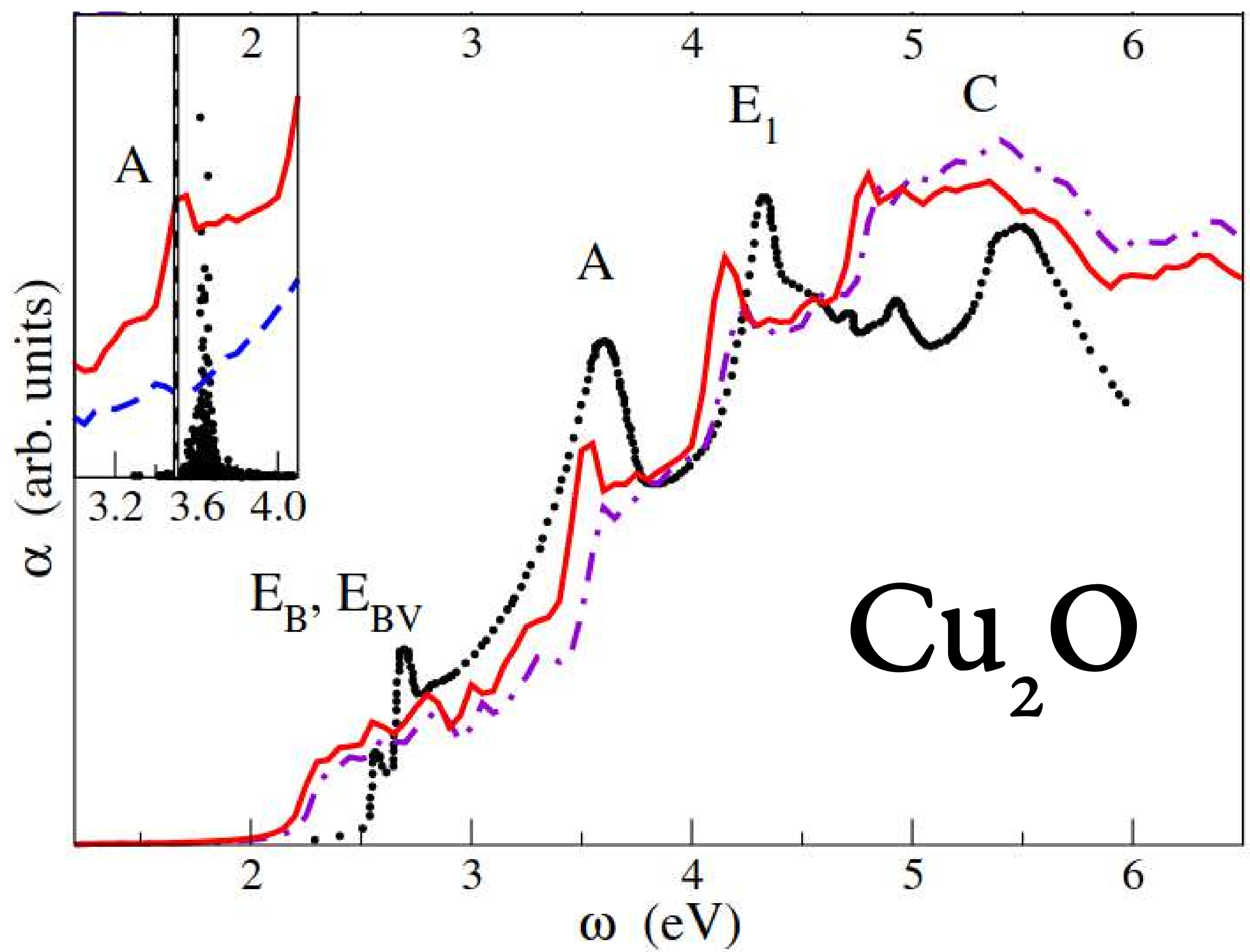
- it can (automatically) profit from extensions

Temperature
electron-phonon



Kawai *et al.* Phys. Rev. B **89**, 085202 (2014)

SC-GW band-structure



Bruneval *et al.* Phys. Rev. Lett. **97**, 267601 (2006)

Evidence of ideal excitonic insulator in bulk MoS_2 under pressure

S. Samaneh Ataei[a,1], Daniele Varsano[a,1], Elisa Molinari[a,b], and Massimo Rontani[a,2]

PNAS 2021 Vol. 118 No. 13 e2010110118 https://doi.org/10.1073/pnas.2010110118

PHYSICAL REVIEW B, VOLUME 65, 155332

Bethe-Salpeter equation for magnetoexcitons in quantum wells

Z. G. Koinov*
Department of Physics & Astronomy, University of Texas at San Antonio, San Antonio, Texas 78249

(Received 10 December 2001; published 11 April 2002)

PRL **116,** 196804 (2016) PHYSICAL REVIEW LETTERS week ending 13 MAY 2016

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Bethe-Salpeter Equation - finite momentum transfer

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

Caliebe *et al.* Phys. Rev. Lett. **84**, 3907 (2000)

Soininen and Shirley, Phys. Rev. B **61**, 16423 (2000)

Vinson *et al.* Phys. Rev. B **83**, 115106 (2011)

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

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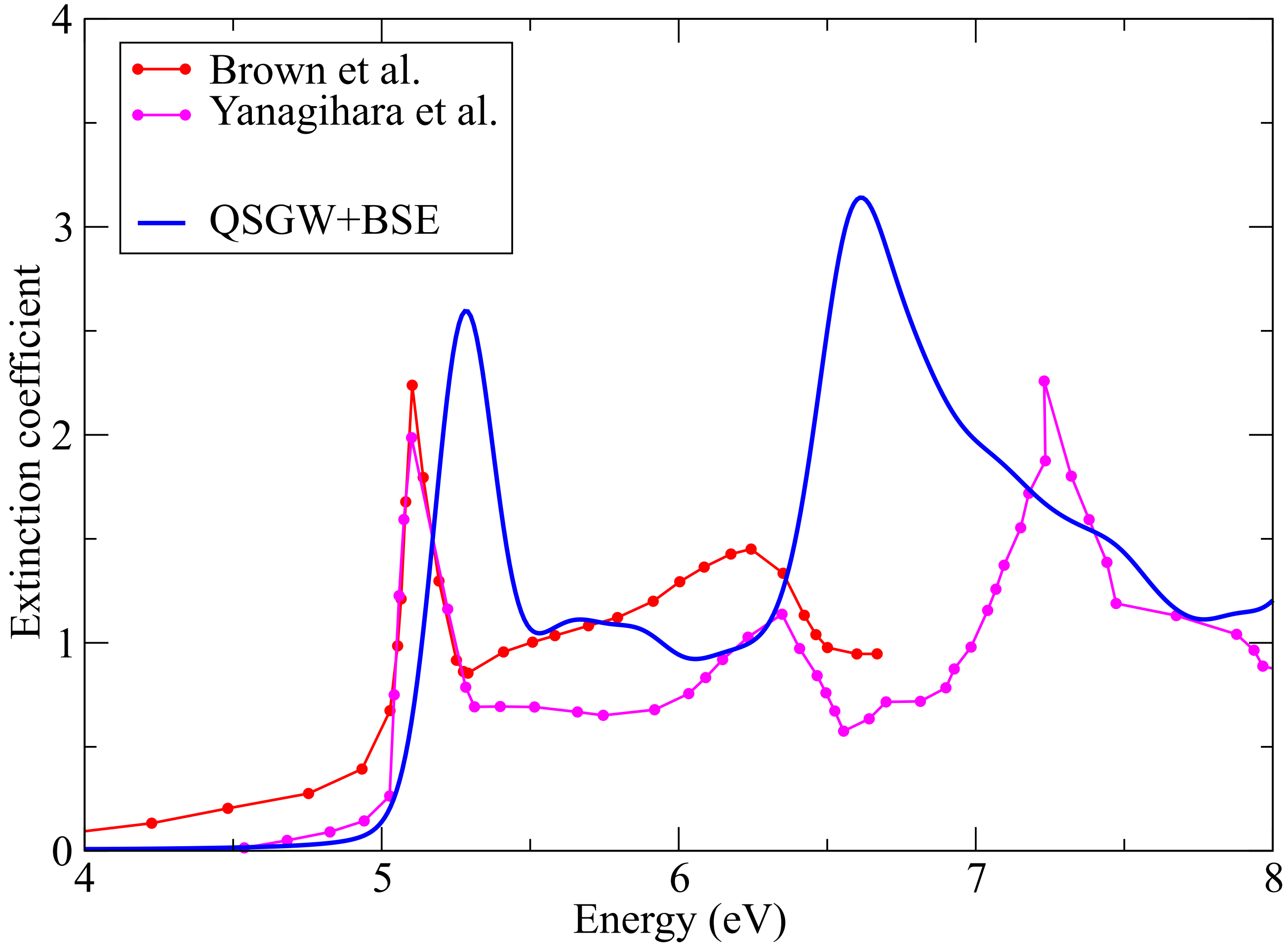
- *ab initio* → predictions
- analysis tools (why? how? who is responsable?)

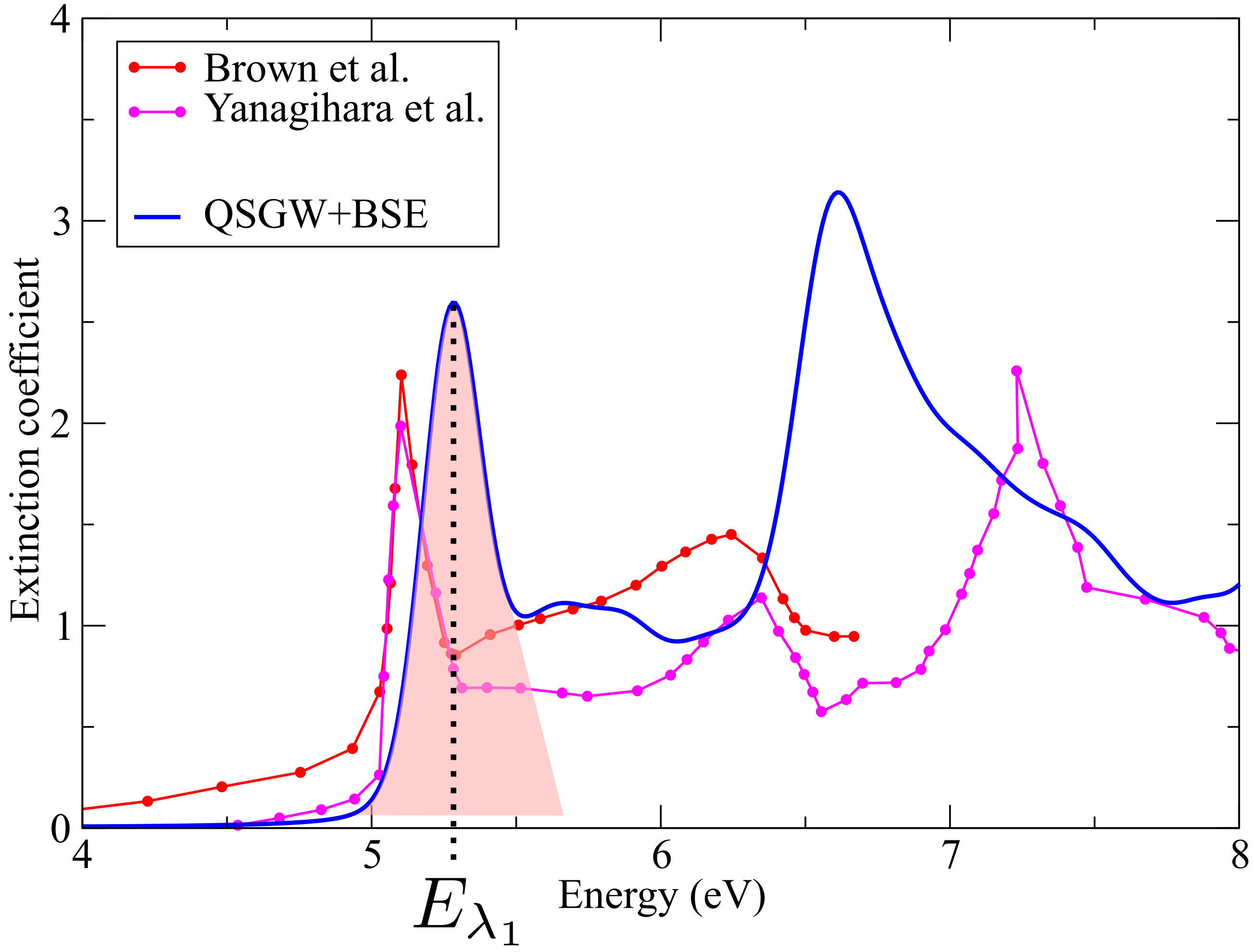


AgCl absorption

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

$$\kappa = \mathrm{Im}\sqrt{\frac{1}{1 + v_0\chi_M}}$$

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



AgCl absorption

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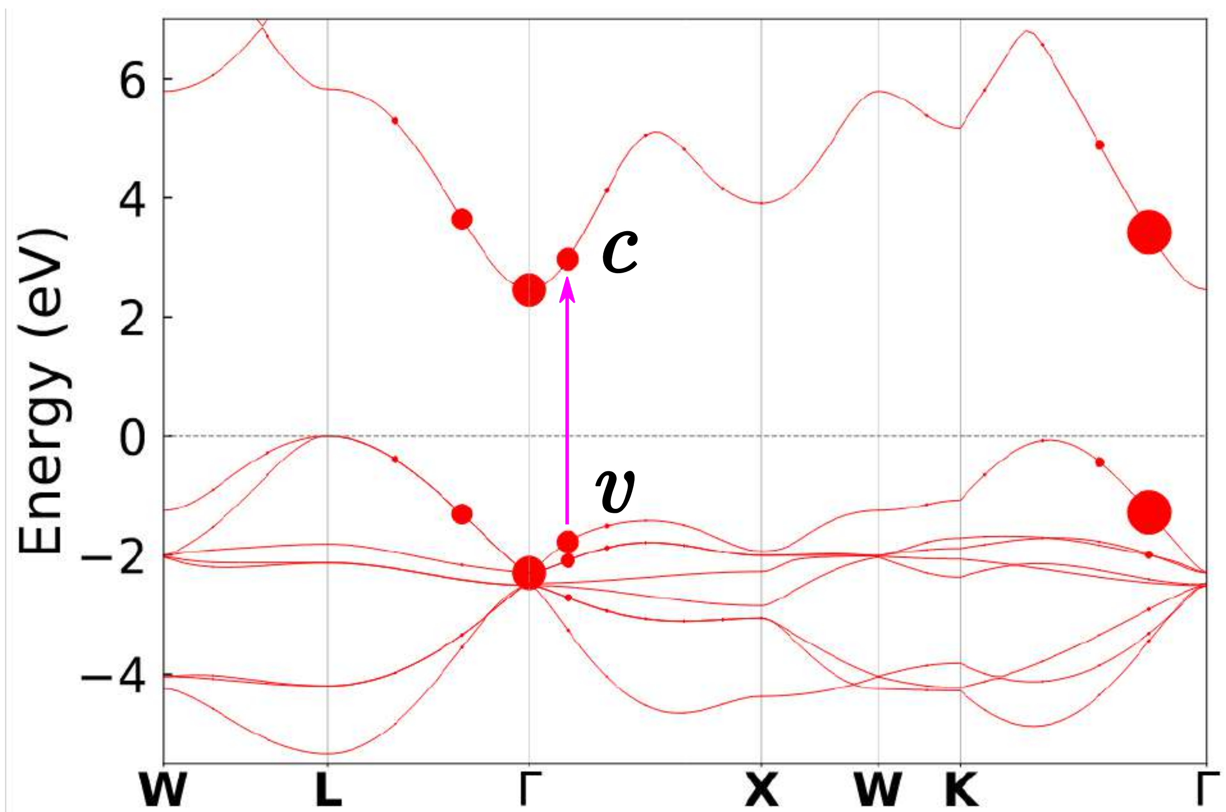


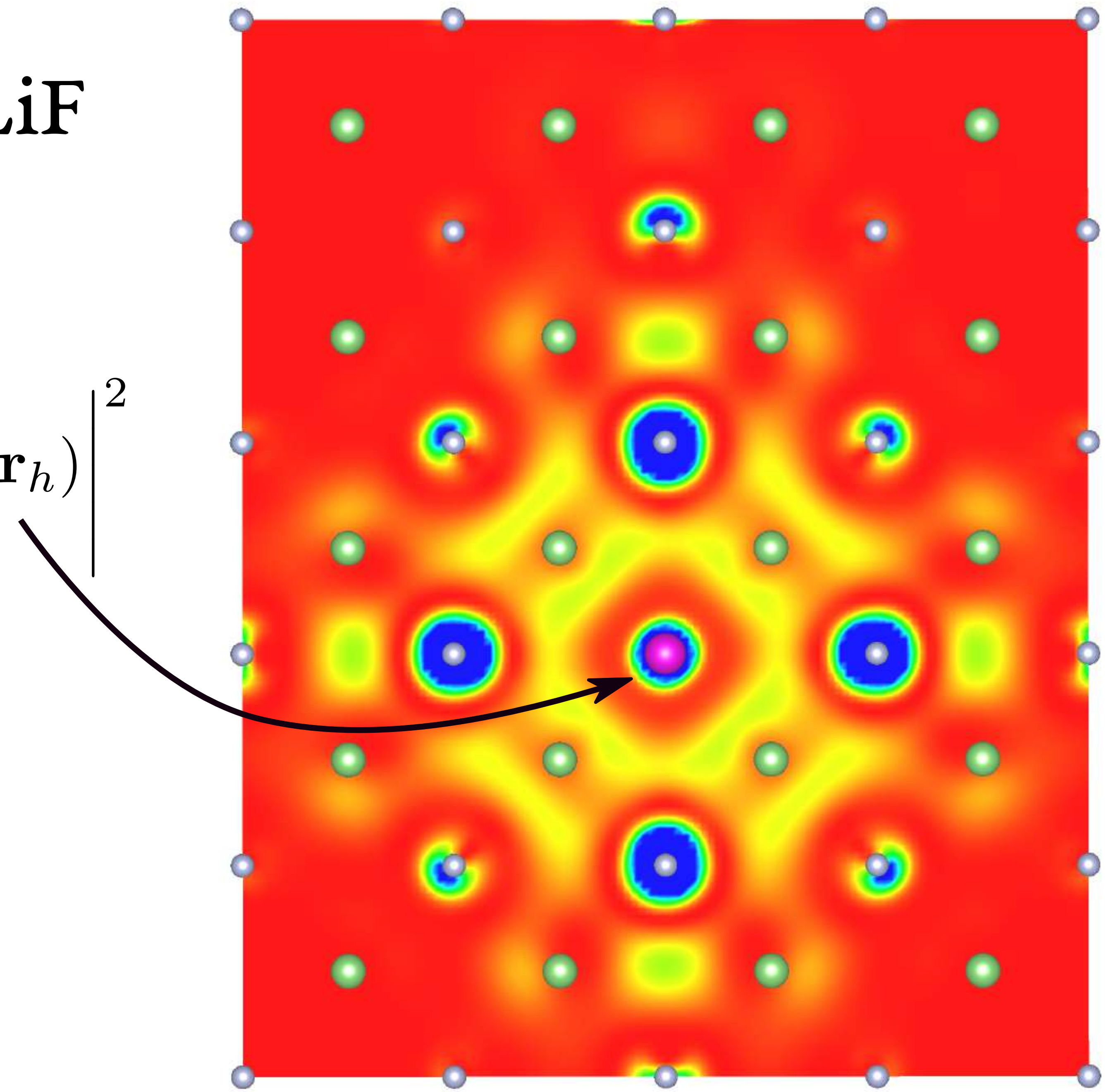
Lorin *et al.* Phys. Rev. B **104**, 235149 (2021)

Excitonic wavefunction of LiF

$$\Psi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{vc\mathbf{k}} A_\lambda^{vc\mathbf{k}} \psi_{c\mathbf{k}}^*(\mathbf{r}_e)\psi_{v\mathbf{k}}(\mathbf{r}_h)$$

Excitonic wavefunction of LiF

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

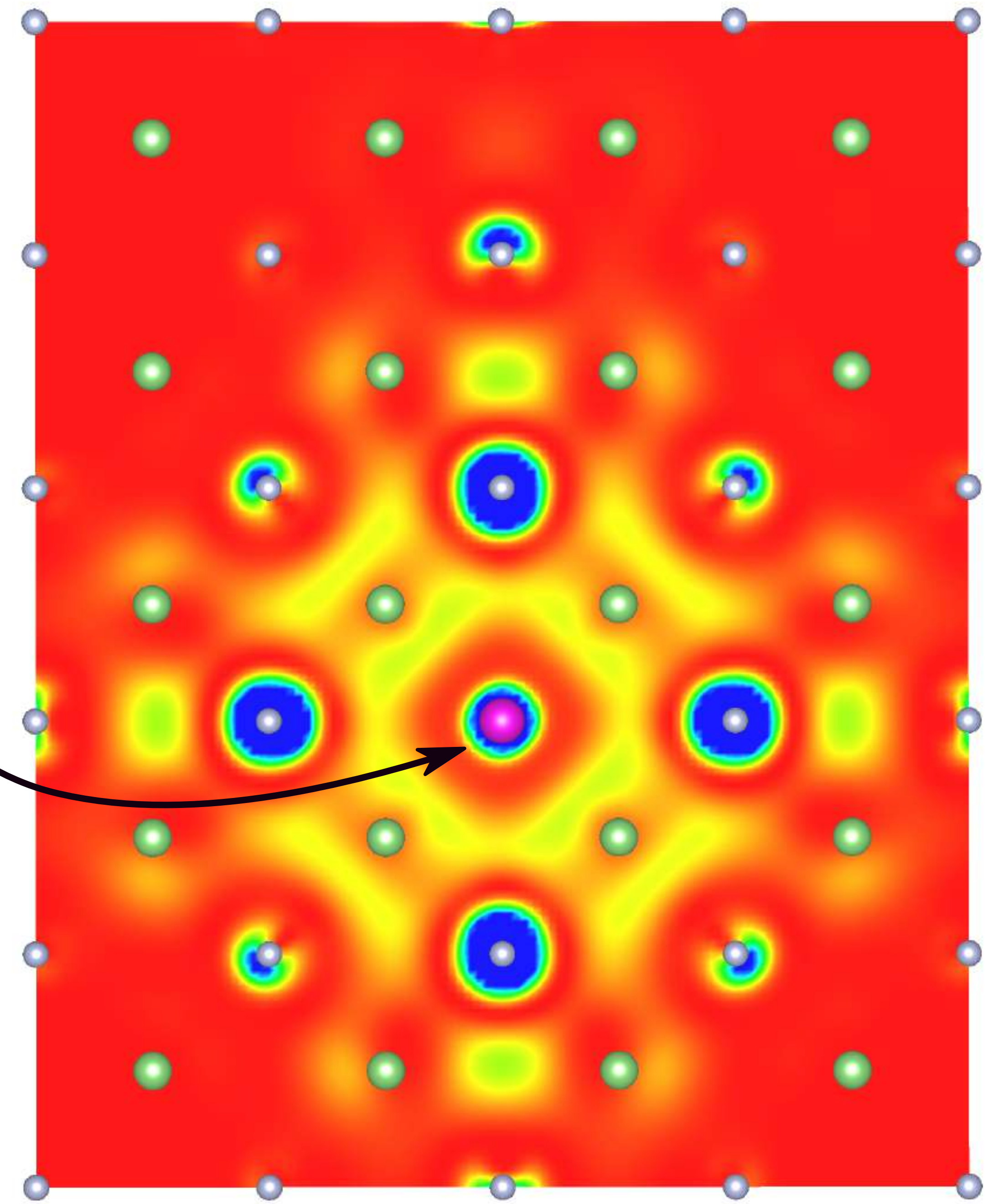


Gatti and Sottile, Phys. Rev. B **98**, 155113 (2013)

Excitonic wavefunction of LiF

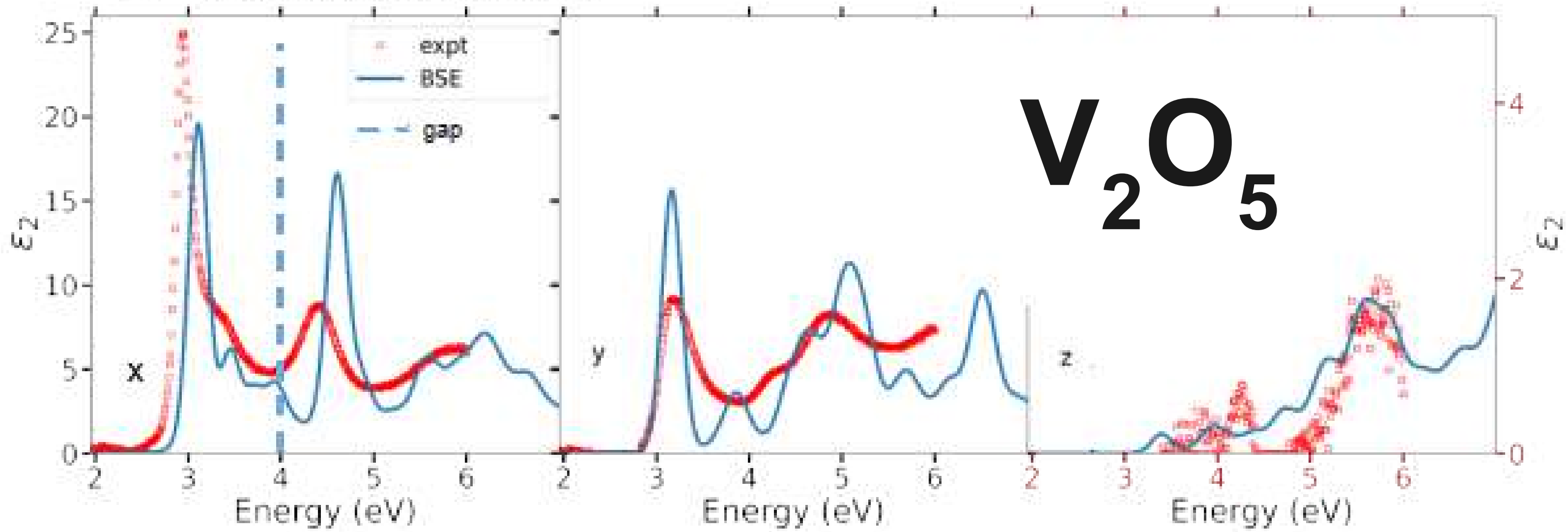
$$|\Psi_\lambda(\mathbf{r}_e, \mathbf{r}_h)|^2 = \left| \sum_{vc\mathbf{k}} A_\lambda^{vc\mathbf{k}} \psi^*_{c\mathbf{k}}(\mathbf{r}_e) \psi_{v\mathbf{k}}(\mathbf{r}_h) \right|^2$$

- where is the exciton localised ?
- how much ?



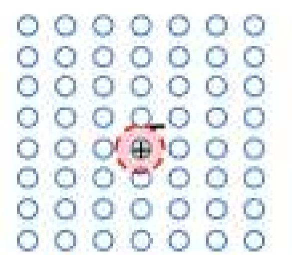
Gatti and Sottile, Phys. Rev. B **98**, 155113 (2013)

- Dielectric function

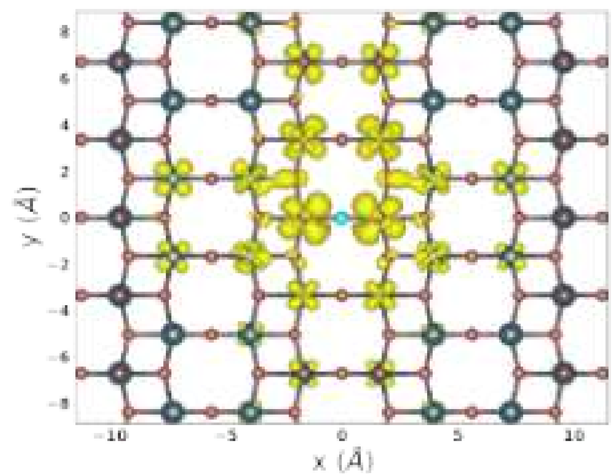


- Exciton wave function

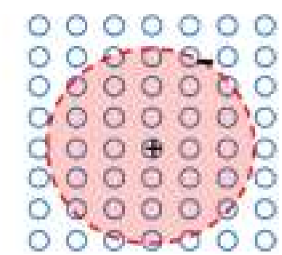
Textbook



Frenkel exciton
Binding energy ~1 eV



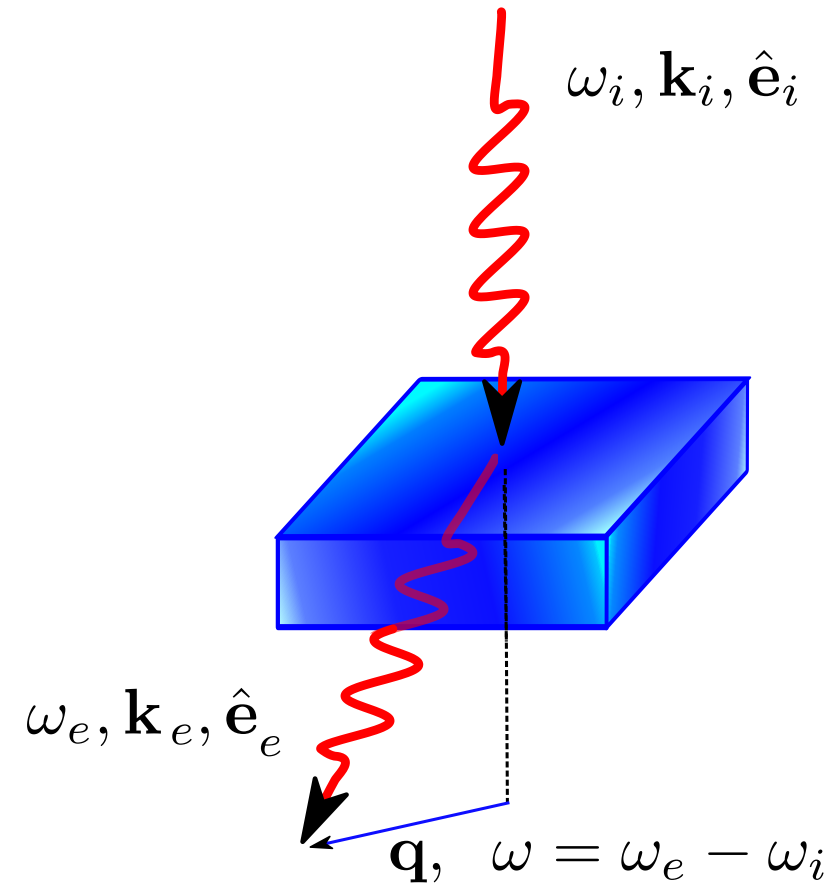
Textbook



Wannier-Mott exciton
Binding energy ~10 meV

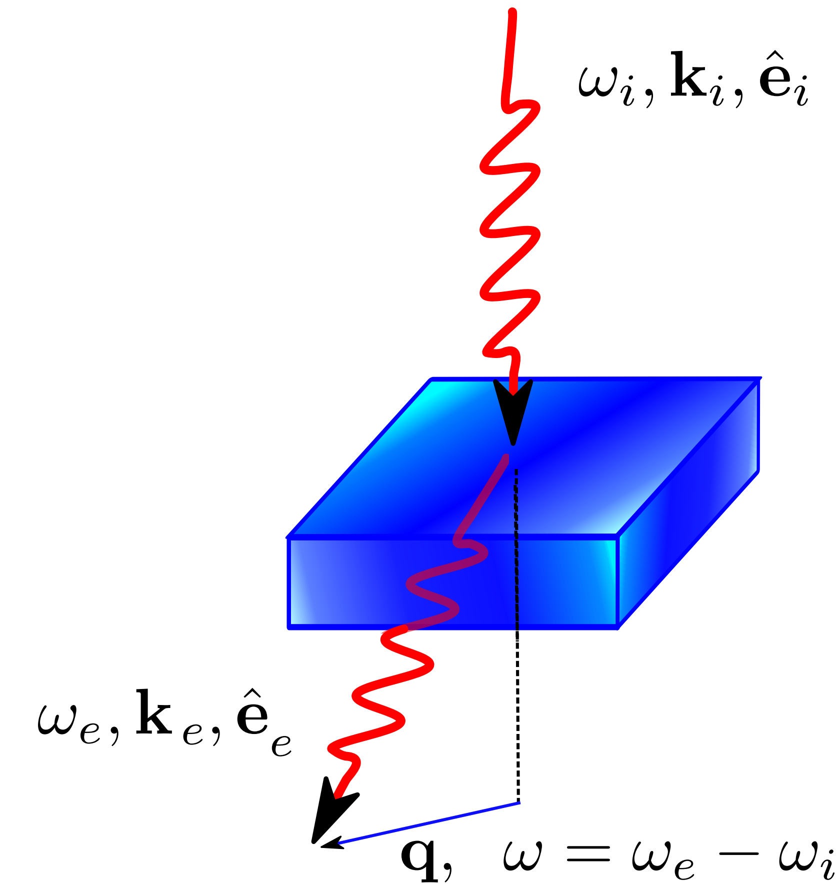
V. Gorelov *et al.*, npj Computational Materials **8** (2022)

X-ray scattering



$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \langle f | e^{i\mathbf{q}\cdot\mathbf{r}} | 0 \rangle - \frac{i\omega_{i/e}}{2mc^2} \sum_n \frac{\langle f | e^{-i\mathbf{k}_f\cdot\mathbf{r}} \nabla | n \rangle \; \langle n | e^{i\mathbf{k}_i\cdot\mathbf{r}} \nabla | 0 \rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

X-ray scattering



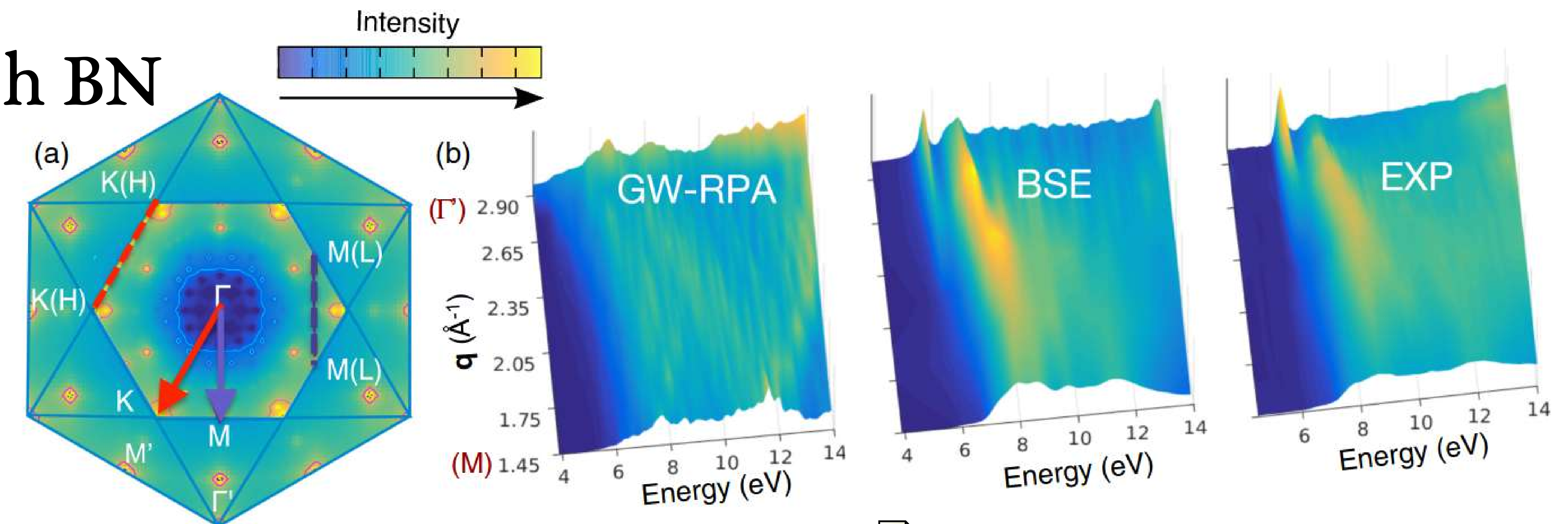
non-Resonant IXS

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \langle f | e^{i\mathbf{q}\cdot\mathbf{r}} | 0 \rangle - \frac{i\omega_{i/e}}{2mc^2} \sum_n \frac{\langle f | e^{-i\mathbf{k}_f\cdot\mathbf{r}} \nabla | n \rangle \ \langle n | e^{i\mathbf{k}_i\cdot\mathbf{r}} \nabla | 0 \rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

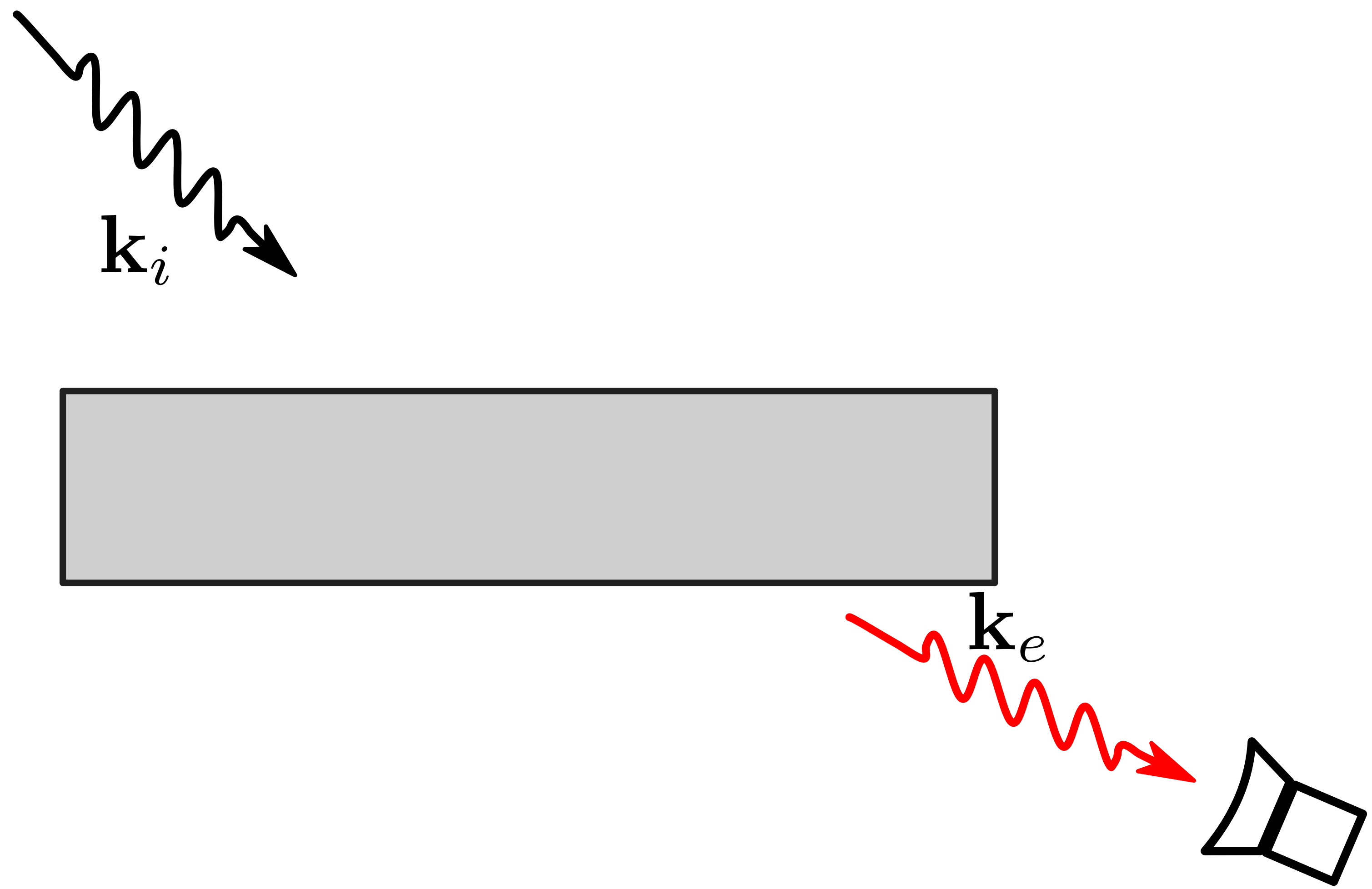
Bethe-Salpeter Equation - finite momentum transfer

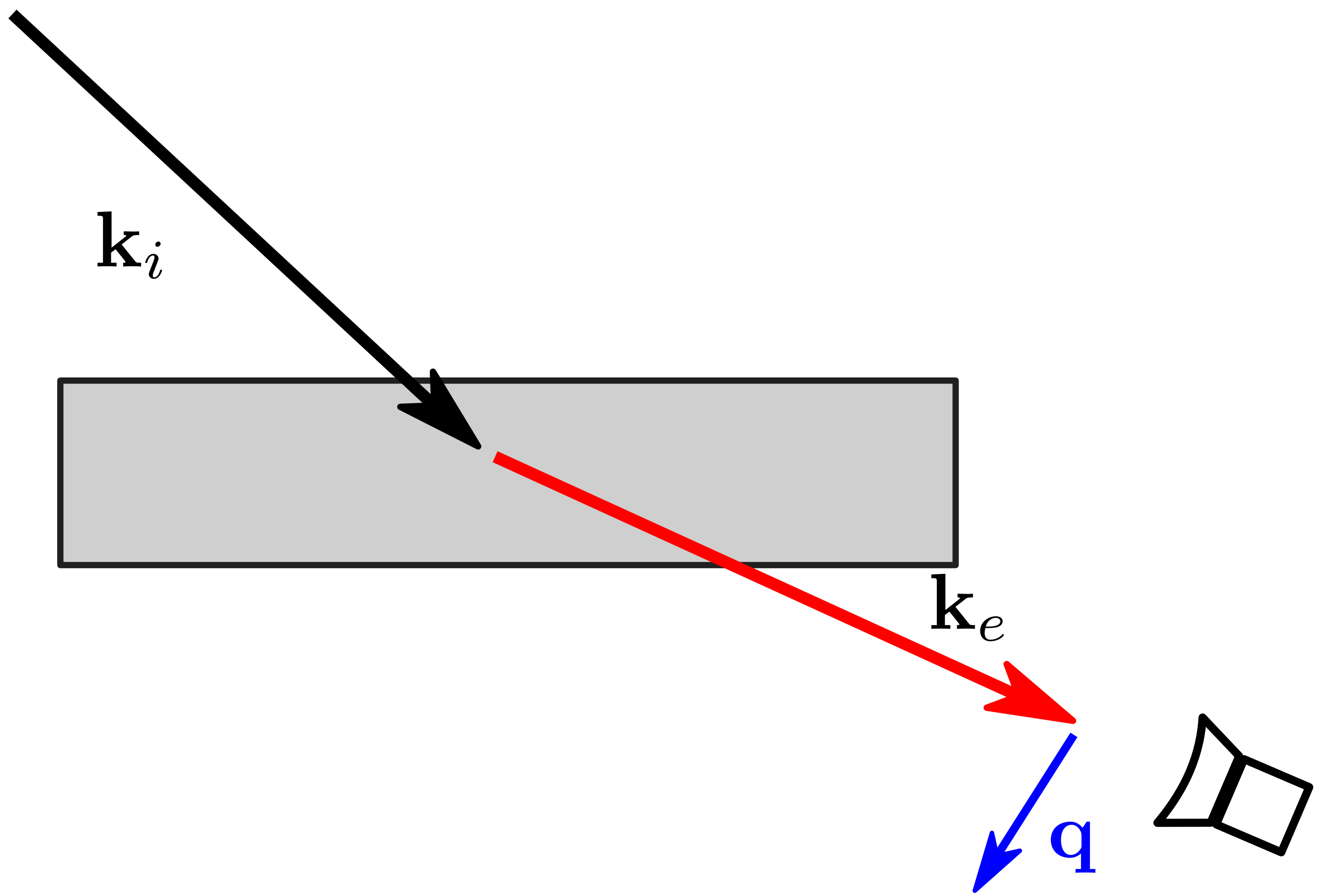
$$S(\mathbf{q},\omega) \propto \chi_M(\mathbf{q},\omega) = \sum_{\lambda} \frac{\left|\sum_{vc} A_{\lambda}^{vc,\mathbf{q}} \langle c|e^{i\mathbf{q}\cdot\mathbf{r}}|v\rangle\right|^2}{\omega - E_{\lambda}(\mathbf{q}) + i\eta}$$

h BN

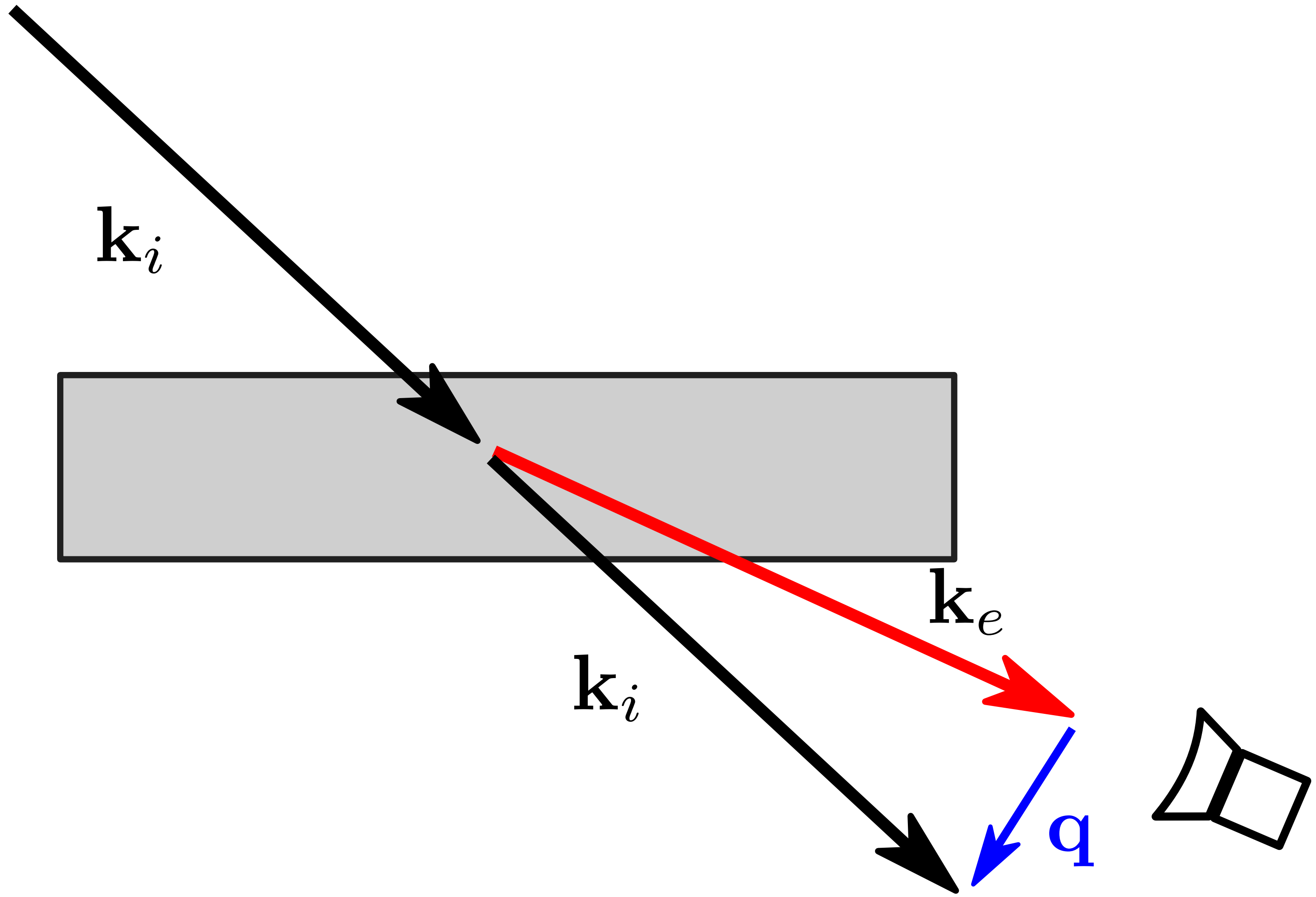


Fugallo *et al.* Phys. Rev. B **92**, 165122 (2015)

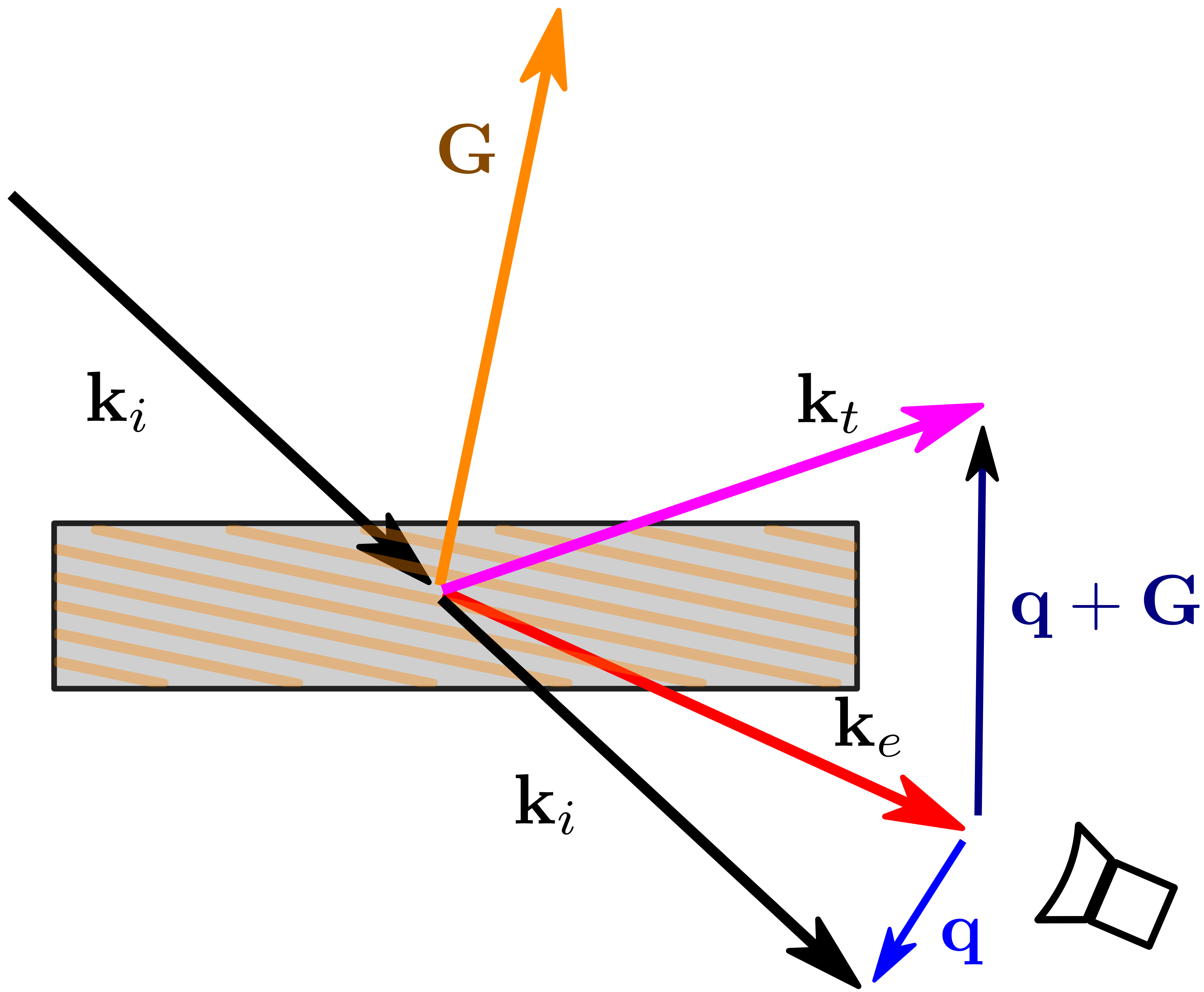

$\mathbf{k}_i$
$\mathbf{k}_e$



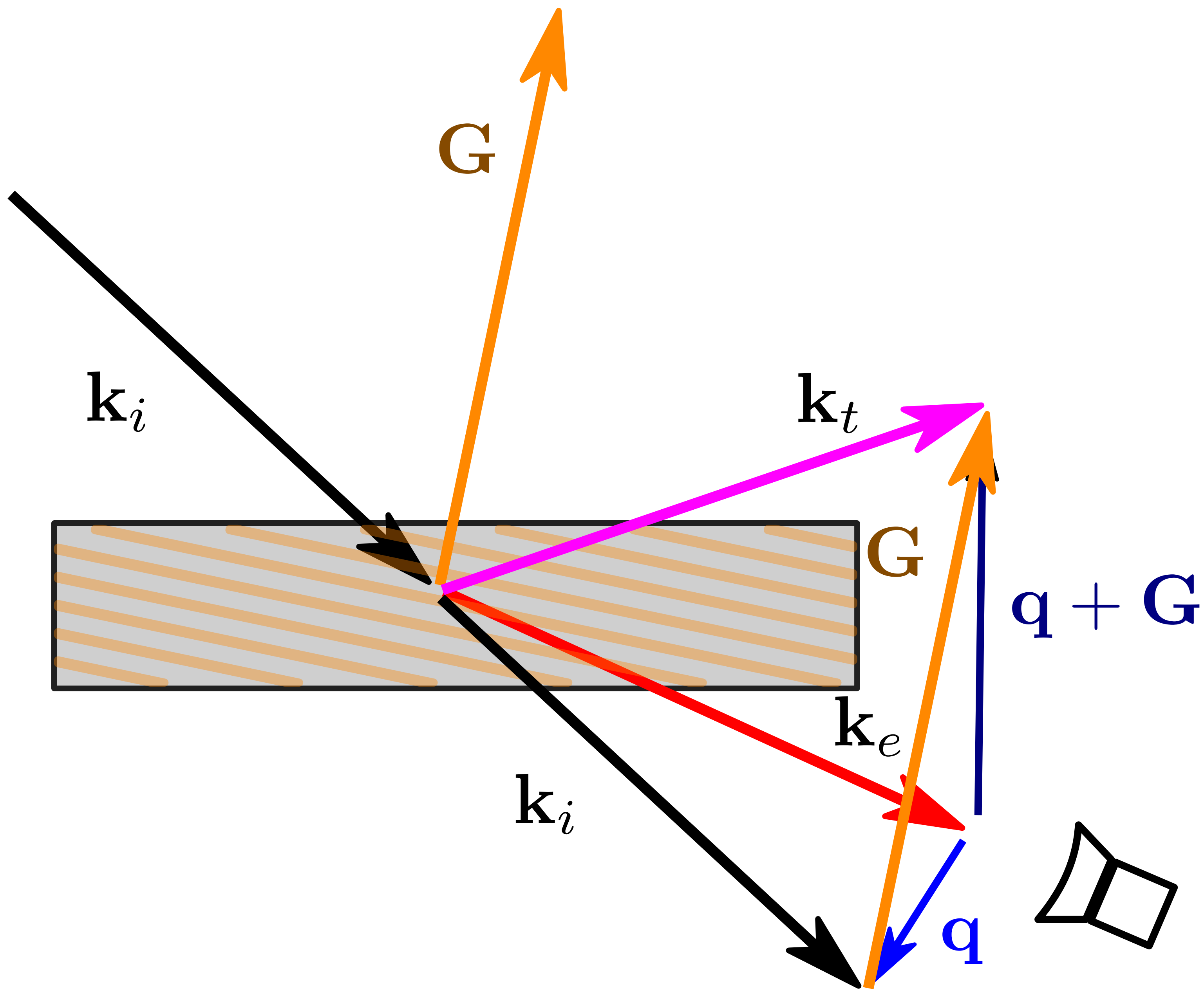
$\mathbf{k}_i$
$\mathbf{k}_e$
$\mathbf{q}$



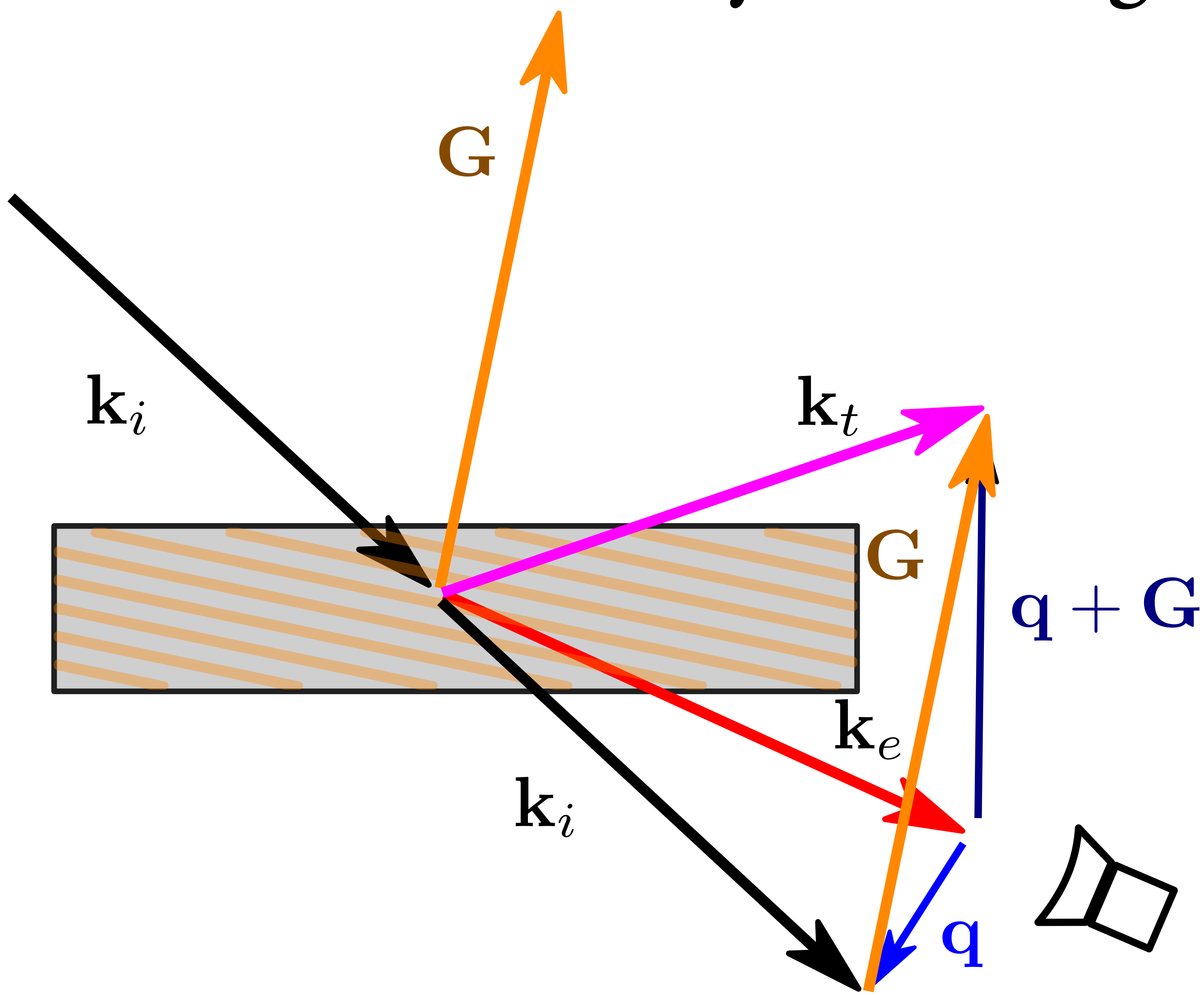
$\mathbf{k}_i$
$\mathbf{k}_e$
$\mathbf{k}_i$
$\mathbf{q}$



$\mathbf{G}$
$\mathbf{k}_i$
$\mathbf{k}_t$
$\mathbf{q} + \mathbf{G}$
$\mathbf{k}_e$
$\mathbf{k}_i$
$\mathbf{q}$


G
$\mathbf{k}_i$
$\mathbf{k}_t$
G
$\mathbf{q}+\mathbf{G}$
$\mathbf{k}_e$
$\mathbf{k}_i$
$\mathbf{q}$

Coherent Inelastic X-ray scattering



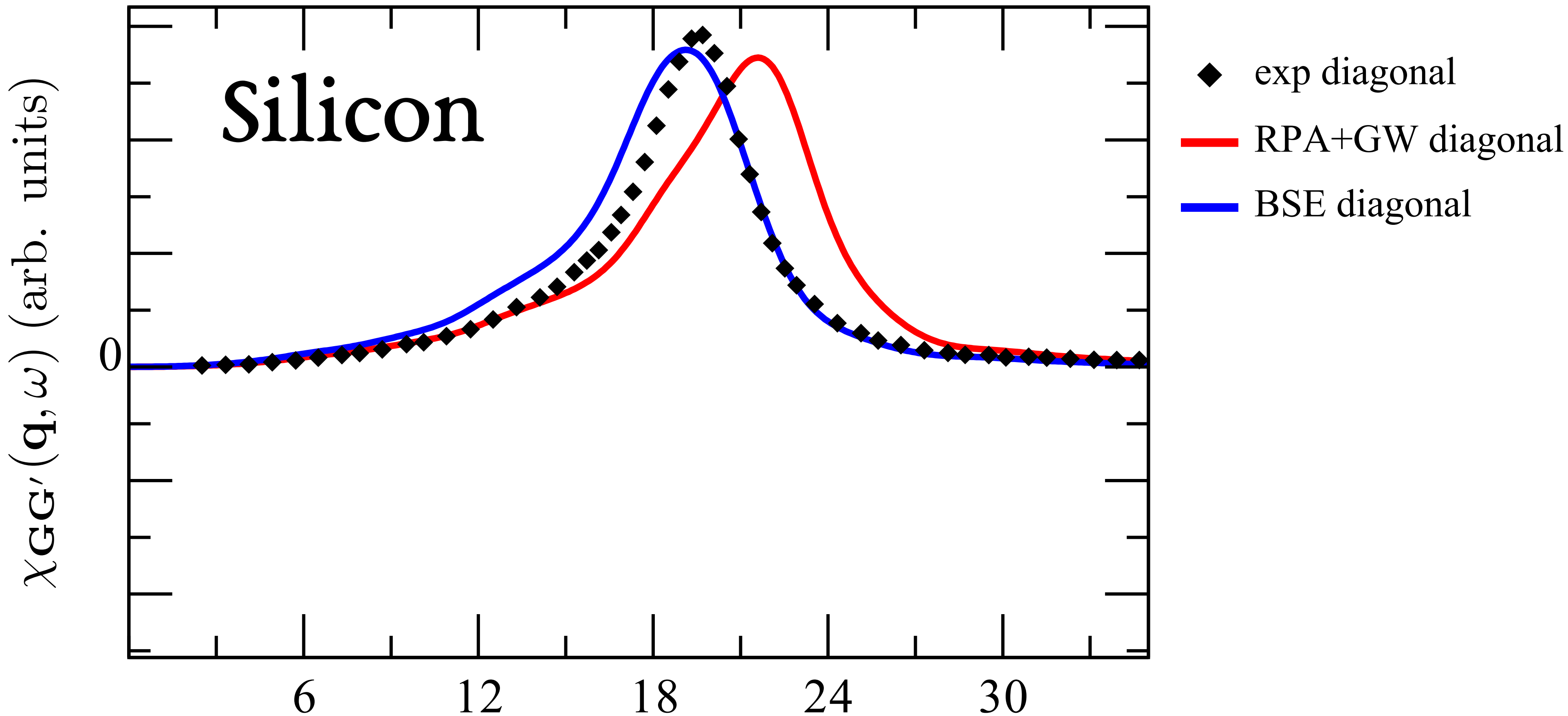
Coherent Inelastic X-ray scattering

$$\chi(\mathbf{q}, \mathbf{q}+\mathbf{G}, \omega) = \sum_{\lambda\lambda'} \frac{\sum_{vc} A_\lambda^{vc,\mathbf{q}} \langle c|e^{-i\mathbf{q}\cdot\mathbf{r}}|v\rangle \, S^{-1}_{\lambda\lambda'} \sum_{v'c'} A_\lambda^{*,v'c',\mathbf{q}} \langle v'|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c'\rangle}{\omega - E_\lambda(\mathbf{q}) + i\eta}$$

Coherent Inelastic X-ray scattering

$$\chi(\mathbf{q}, \mathbf{q}+\mathbf{G}, \omega) = \sum_{\lambda\lambda'} \frac{\sum_{vc} A_\lambda^{vc,\mathbf{q}} \langle c|e^{-i\mathbf{q}\cdot\mathbf{r}}|v\rangle S^{-1}_{\lambda\lambda'} \sum_{v'c'} A_\lambda^{*,v'c',\mathbf{q}} \langle v'|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c'\rangle}{\omega - E_\lambda(\mathbf{q}) + i\eta}$$

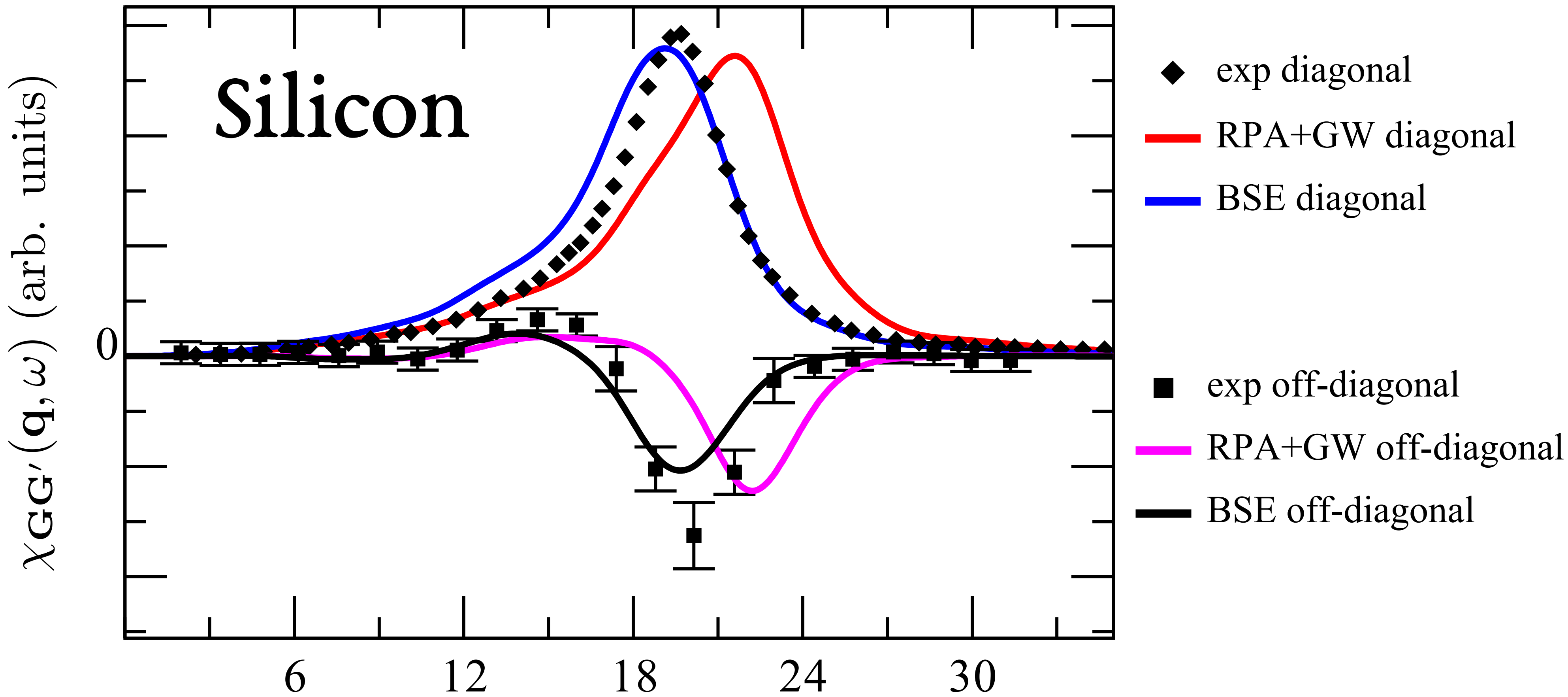
Igor Reshetnyak *et al.* Phys. Rev. Research **1**, 032010(R) (2019)



Weissker *et al.* Phys. Rev. B **81**, 085104 (2010).

Coherent Inelastic X-ray scattering

$$\chi(\mathbf{q},\mathbf{q}+\mathbf{G},\omega) = \sum_{\lambda\lambda'} \frac{\sum_{vc} A_{\lambda}^{vc,\mathbf{q}} \langle c|e^{-i\mathbf{q}\cdot\mathbf{r}}|v\rangle \, S^{-1}_{\lambda\lambda'} \sum_{v'c'} A_{\lambda}^{*,v'c',\mathbf{q}} \langle v'|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c'\rangle}{\omega - E_{\lambda}(\mathbf{q}) + i\eta}$$



Igor Reshetnyak *et al.* Phys. Rev. Research **1**, 032010(R) (2019)

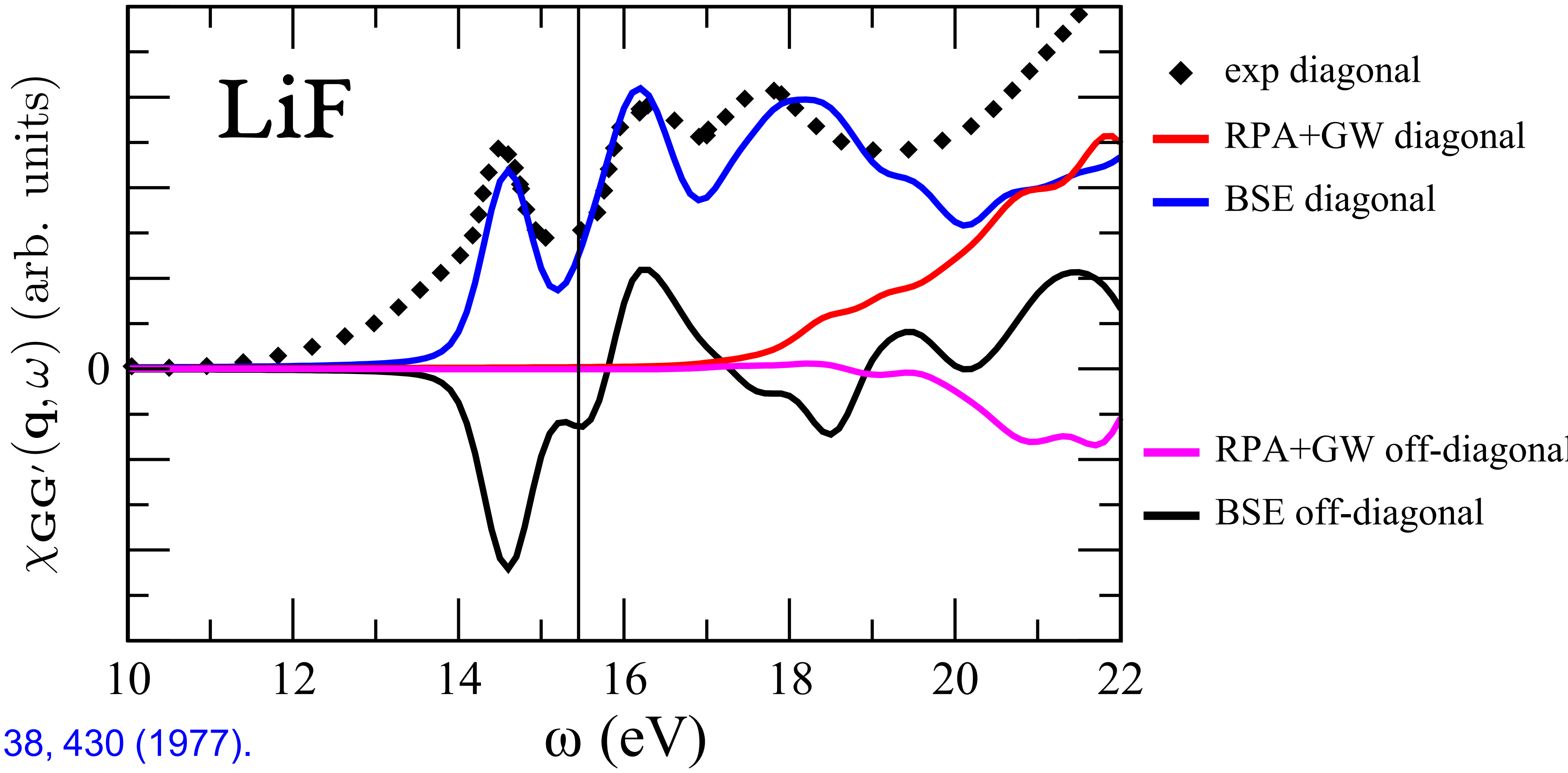
Schülke and Kaprolat, Phys. Rev. Lett. **67**, 879 (1991).

Weissker *et al.* Phys. Rev. B **81**, 085104 (2010).

Coherent Inelastic X-ray scattering

$$\chi(\mathbf{q},\mathbf{q}+\mathbf{G},\omega) = \sum_{\lambda\lambda'} \frac{\sum_{vc} A_\lambda^{vc,\mathbf{q}} \langle c|e^{-i\mathbf{q}\cdot\mathbf{r}}|v\rangle S^{-1}_{\lambda\lambda'} \sum_{v'c'} A_\lambda^{*,v'c',\mathbf{q}} \langle v'|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c'\rangle}{\omega - E_\lambda(\mathbf{q}) + i\eta}$$

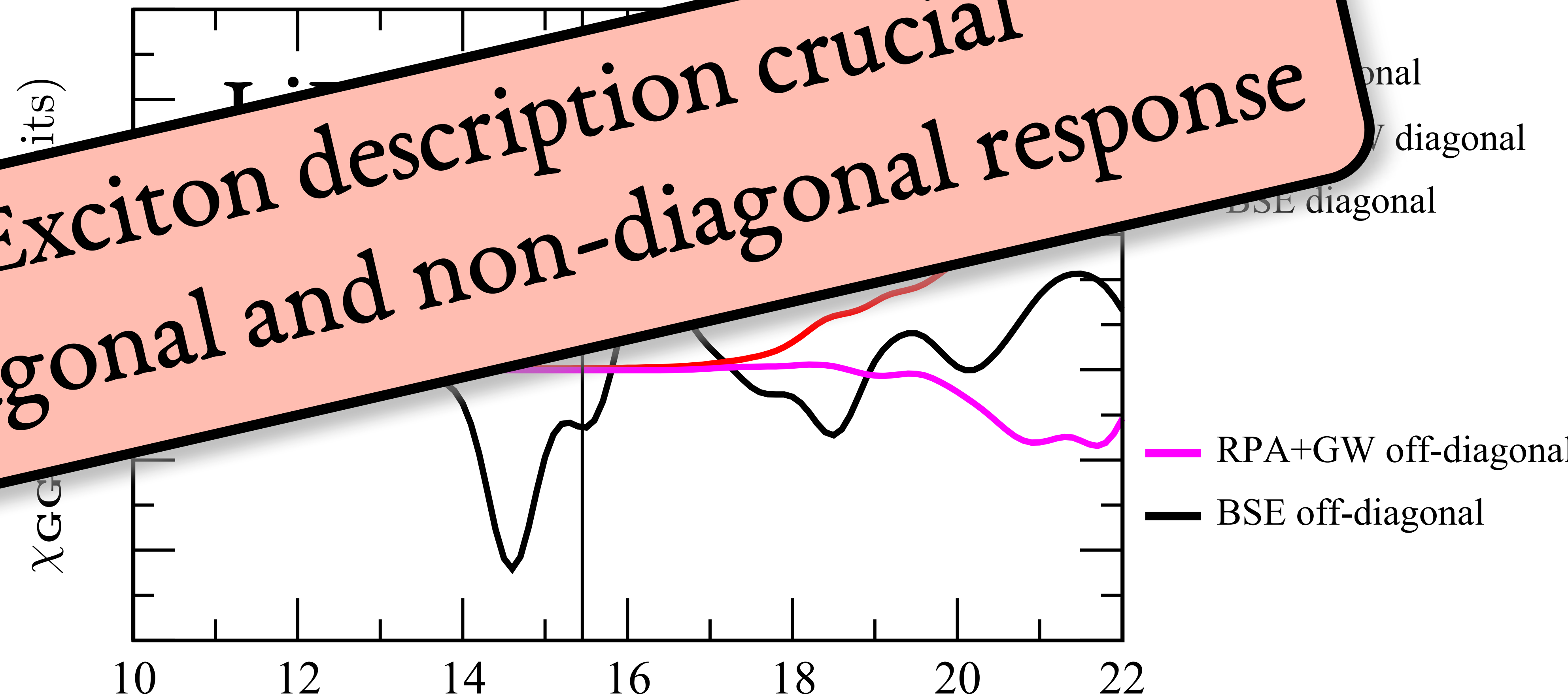
Igor Reshetnyak *et al.* Phys. Rev. Research **1**, 032010(R) (2019)



Fields *et al.* Phys. Rev. Lett. 38, 430 (1977).

Coherent Inelastic X-ray scattering

$$\chi(\mathbf{q},\mathbf{q}+\mathbf{G},\omega) = \sum_{\lambda\lambda'} \frac{\sum_{vc} A_\lambda^{vc,\mathbf{q}} \langle c|e^{-i\mathbf{q}\cdot\mathbf{r}}|v\rangle S^{-1}_{\lambda\lambda'} \sum_{v'c'} A_\lambda^{*,v'c',\mathbf{q}} \langle v'|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c'\rangle}{\omega - E_\lambda(\mathbf{q}) + i\eta}$$

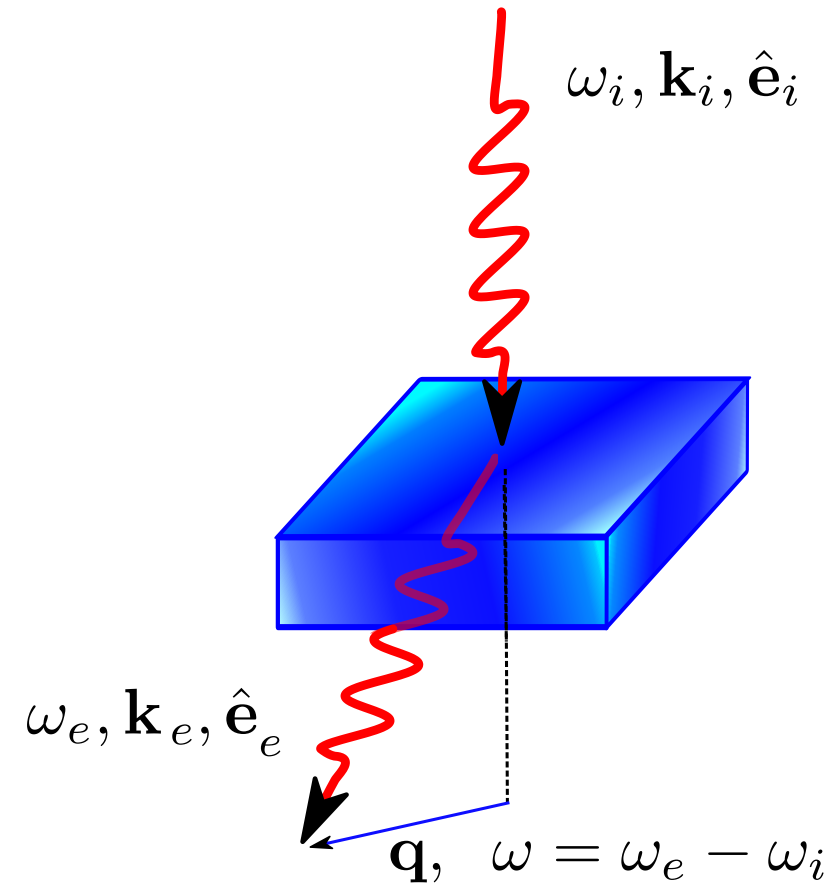


Exciton description crucial for diagonal and non-diagonal response

Igor Re... Phys. R... 032010(...)

Fields *et al.* Phys. Rev. Lett. 38, 430 (1977).

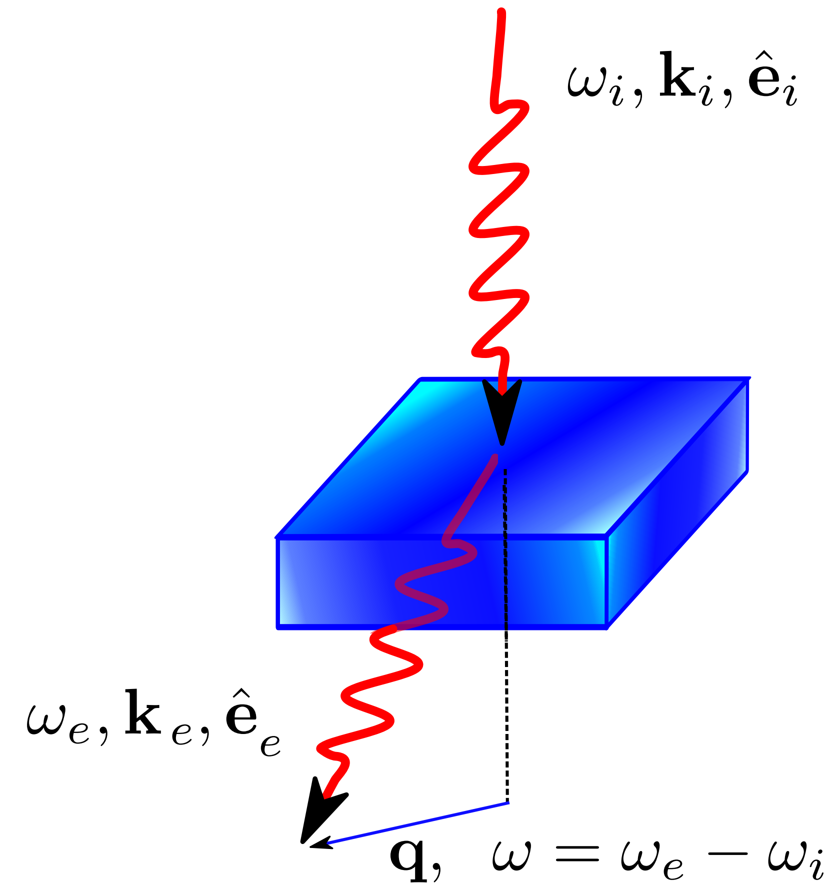
X-ray scattering



non-Resonant IXS

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \langle f | e^{i\mathbf{q}\cdot\mathbf{r}} | 0 \rangle - \frac{i\omega_{i/e}}{2mc^2} \sum_n \frac{\langle f | e^{-i\mathbf{k}_f\cdot\mathbf{r}} \nabla | n \rangle \ \langle n | e^{i\mathbf{k}_i\cdot\mathbf{r}} \nabla | 0 \rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

X-ray scattering



non-Resonant IXS

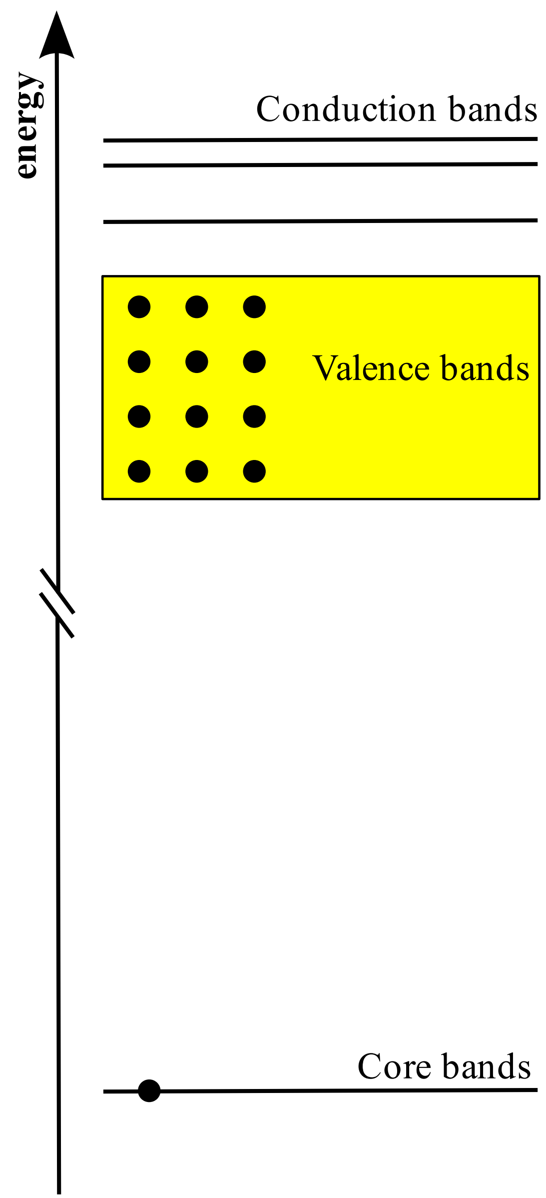
Resonant IXS

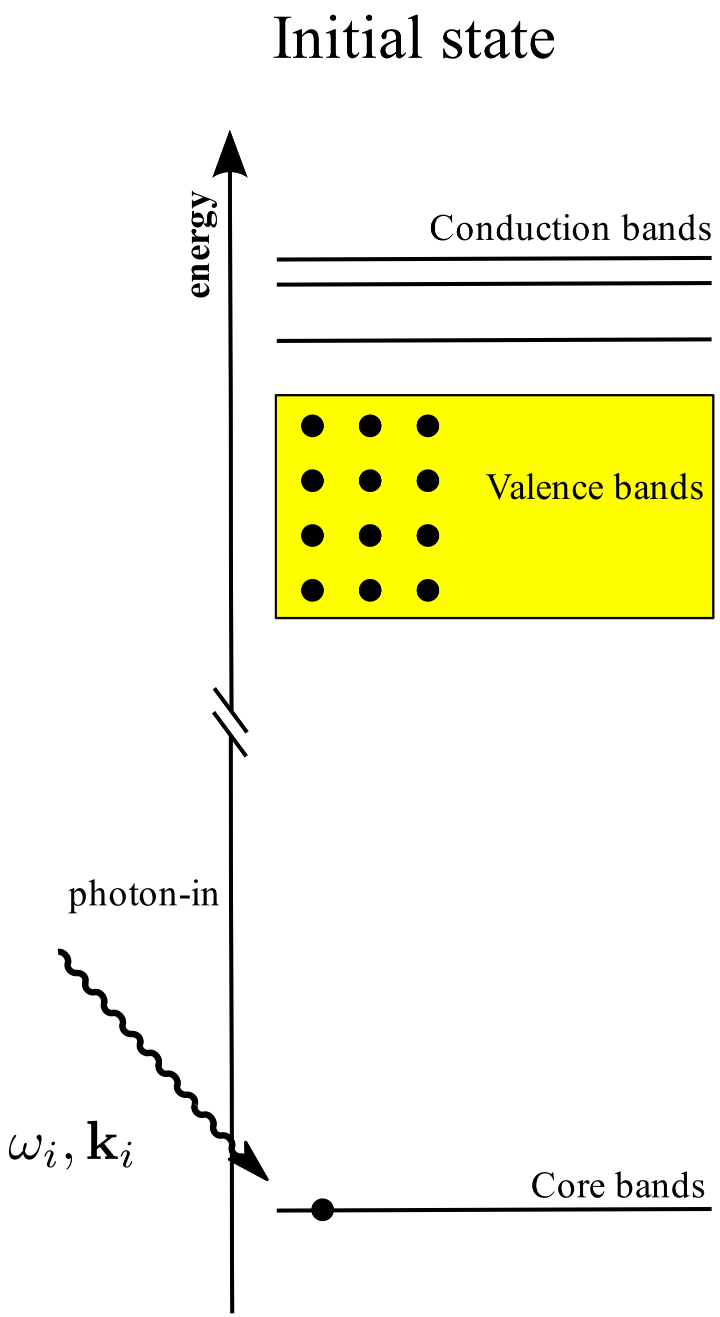
$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \langle f|e^{i\mathbf{q}\cdot\mathbf{r}}|0\rangle - \frac{i\omega_{i/e}}{2mc^2} \sum_n \frac{\langle f|e^{-i\mathbf{k}_f\cdot\mathbf{r}}\nabla|n\rangle \, \langle n|e^{i\mathbf{k}_i\cdot\mathbf{r}}\nabla|0\rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

Resonant IXS

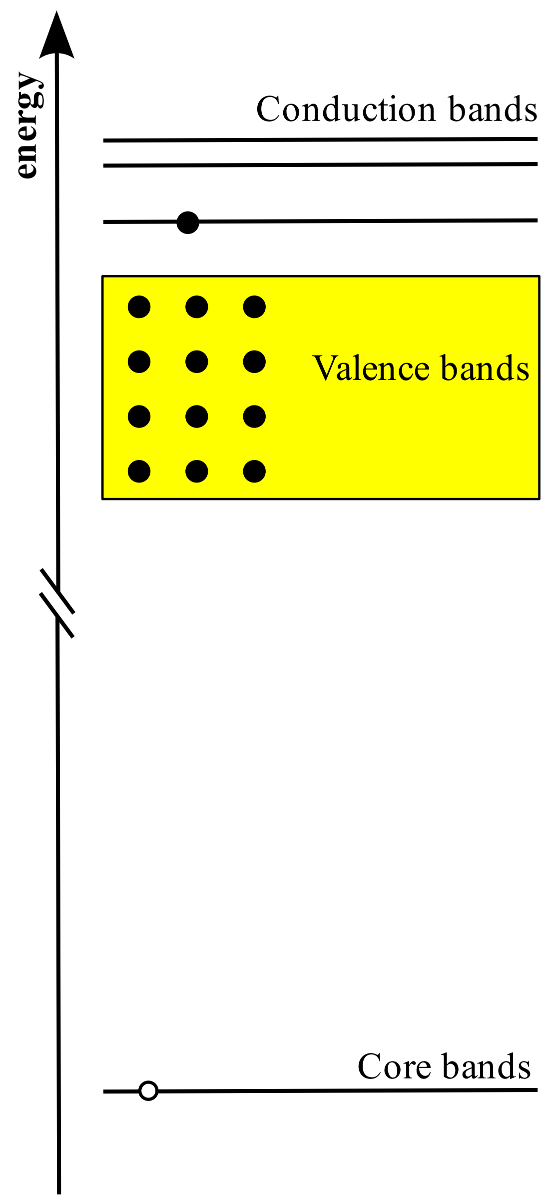
$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2\mathrm{d}\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f|e^{-i\mathbf{k}_f\cdot\mathbf{r}}\nabla|n\rangle\ \langle n|e^{i\mathbf{k}_i\cdot\mathbf{r}}\nabla|0\rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

Initial state

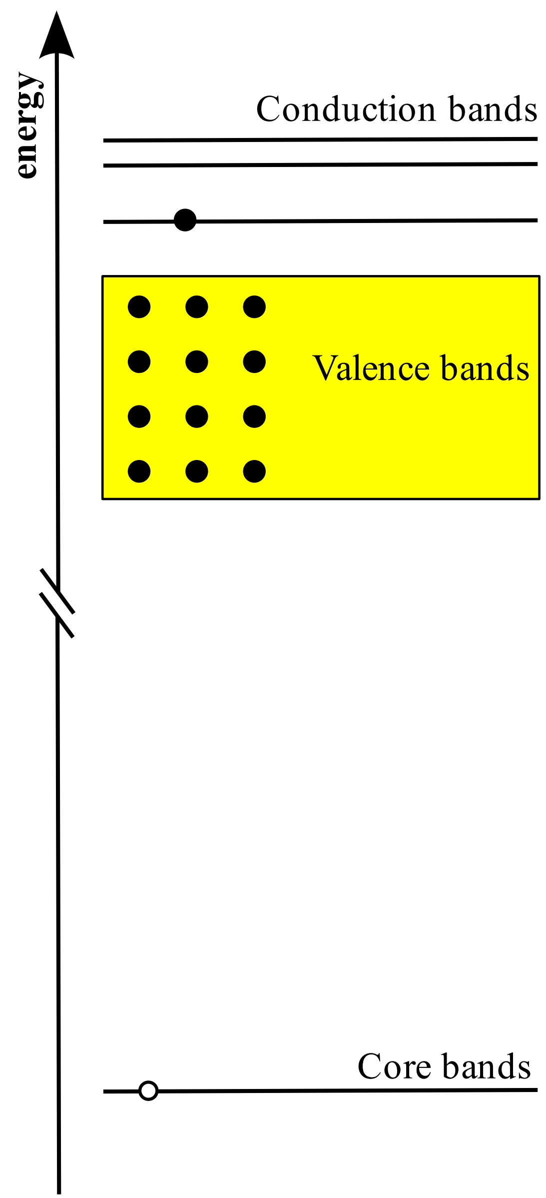



Initial state
energy
Conduction bands
Valence bands
photon-in
$\omega_i, \mathbf{k}_i$
Core bands

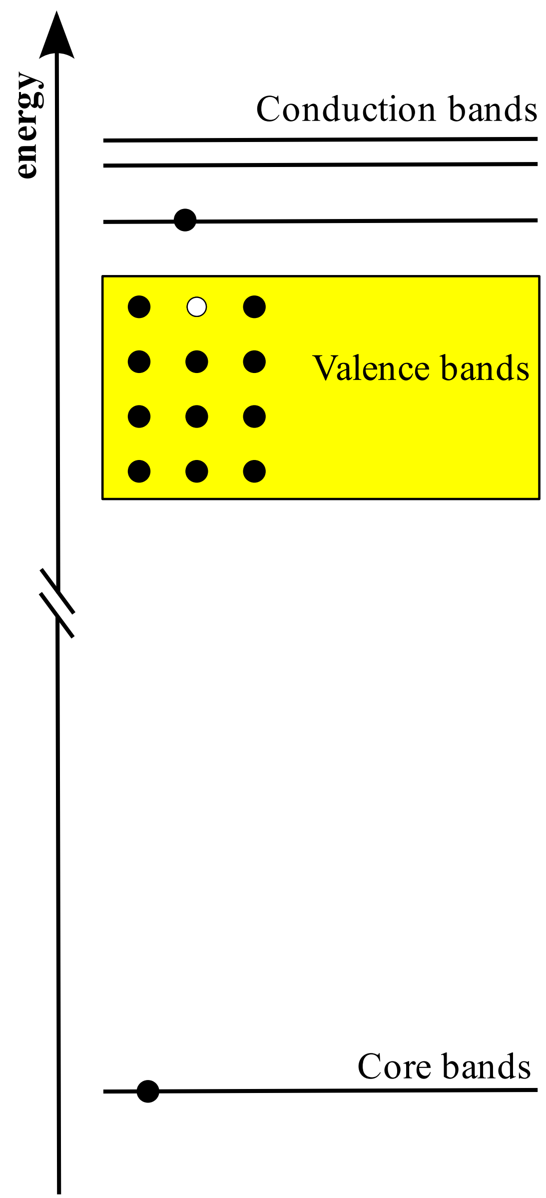
Intermediate state

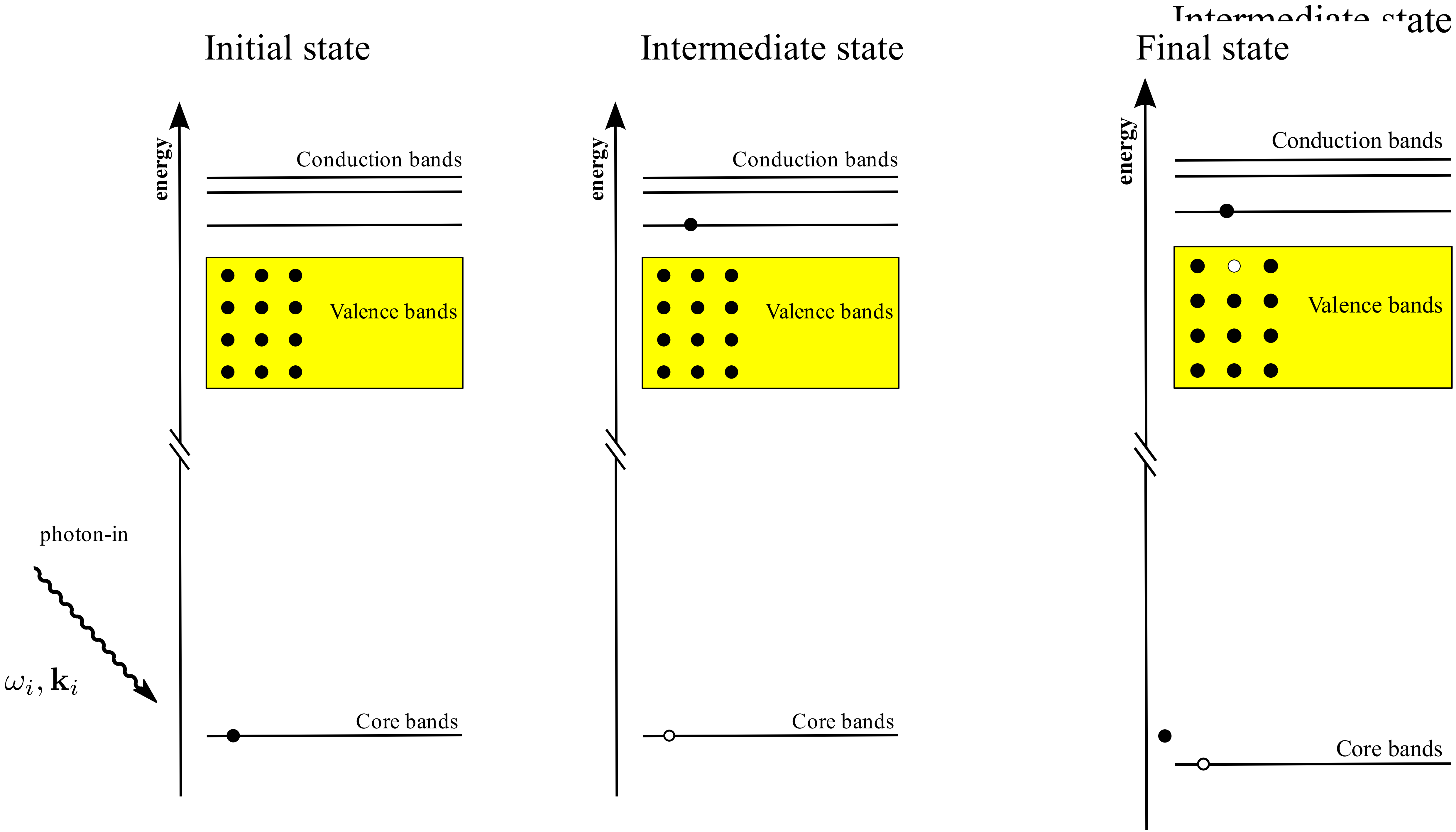


Intermediate state



Final state




Intermediate state
Initial state
Intermediate state
Final state
energy
Conduction bands
Valence bands
Core bands
photon-in
$\omega_i, \mathbf{k}_i$
energy
Conduction bands
Valence bands
Core bands
energy
Conduction bands
Valence bands
Core bands

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f | e^{-i\mathbf{k}_f \cdot \mathbf{r}} \nabla | n \rangle \ \langle n | e^{i\mathbf{k}_i \cdot \mathbf{r}} \nabla | 0 \rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

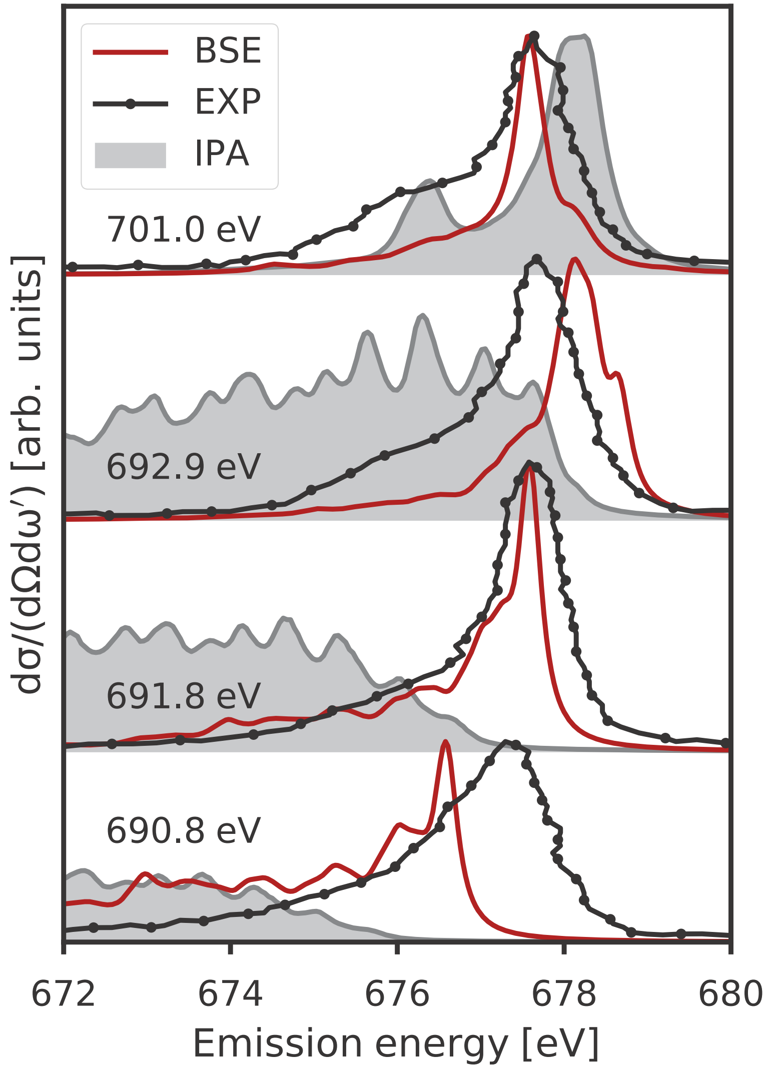
Shirley, Phys. Rev. Lett. **80**, 794 (1998)

Vinson *et al.*, Phys. Rev. B **94**, 035163 (2016)

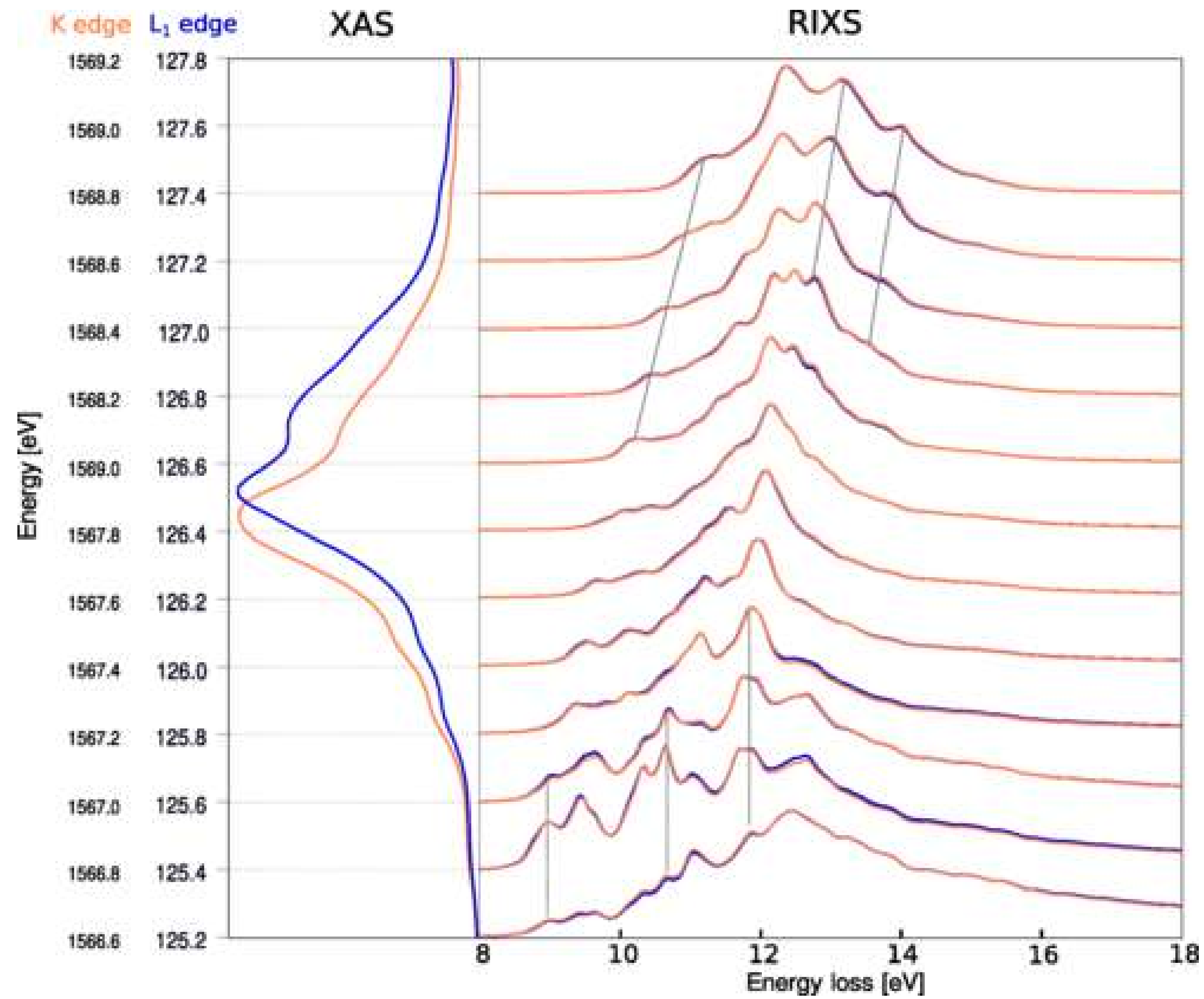
Geondzhian and Gilmore, Phys. Rev. B **98**, 214305 (2018)

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \mathrm{Im} \sum_{\substack{c, c', c'', c''' \\ \mu, \mu', \mu'', \mu'''}} \sum_{\substack{v, v' \\ \mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}} \left[\tilde{\rho}_{\mu v \mathbf{k}} \cdot \chi_{c\mu\mathbf{k}}^{c'\mu'\mathbf{k}'}(\omega_i) \cdot \tilde{\rho}_{c'\mu'\mathbf{k}'} \right]^* \chi_{cv\mathbf{k}}^{c''v'\mathbf{k}''}(\omega) \left[\tilde{\rho}_{\mu''v'\mathbf{k}''} \cdot \chi_{c''\mu''\mathbf{k}''}^{c'''\mu'''\mathbf{k}'''}(\omega_i) \cdot \tilde{\rho}_{c'''\mu'''\mathbf{k}'''} \right]$$

LiF



Al_2O_3



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

Vorwerk *et al.* Phys. Chem. Chem. Phys. **24**, 17439 (2022).

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

Urquiza *et al.*, Phys. Rev. B **107**, 205148 (2023)

Spectra and excitons via BSE

- Accurate and extendible
- Rely on the description of the initial (ground) state
- Ab initio and predictive
- Linear response (and beyond) spectroscopies
- Cumbersome calculations

Thanks to the Theoretical Spectroscopy Group

and to You