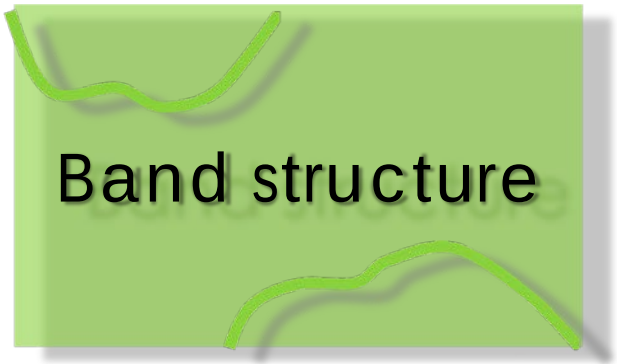
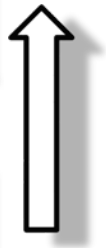
Neutral excitations

Claudia Draxl, HU and FHI Berlin

State of the art methodology



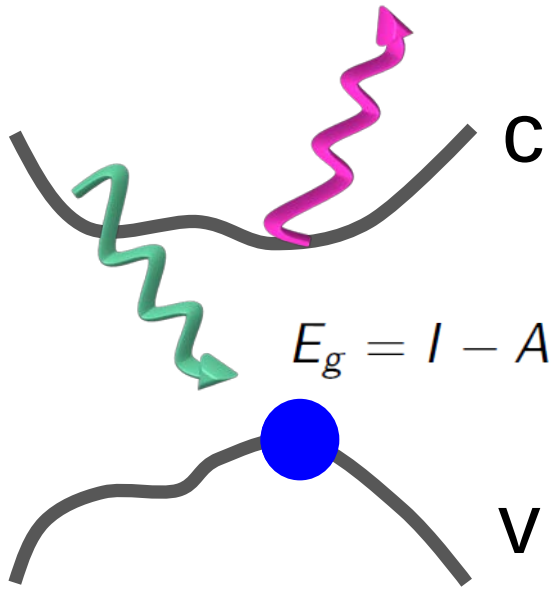


Density-functional theory

Kohn-Sham equation

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$$

State of the art methodology



Band structure

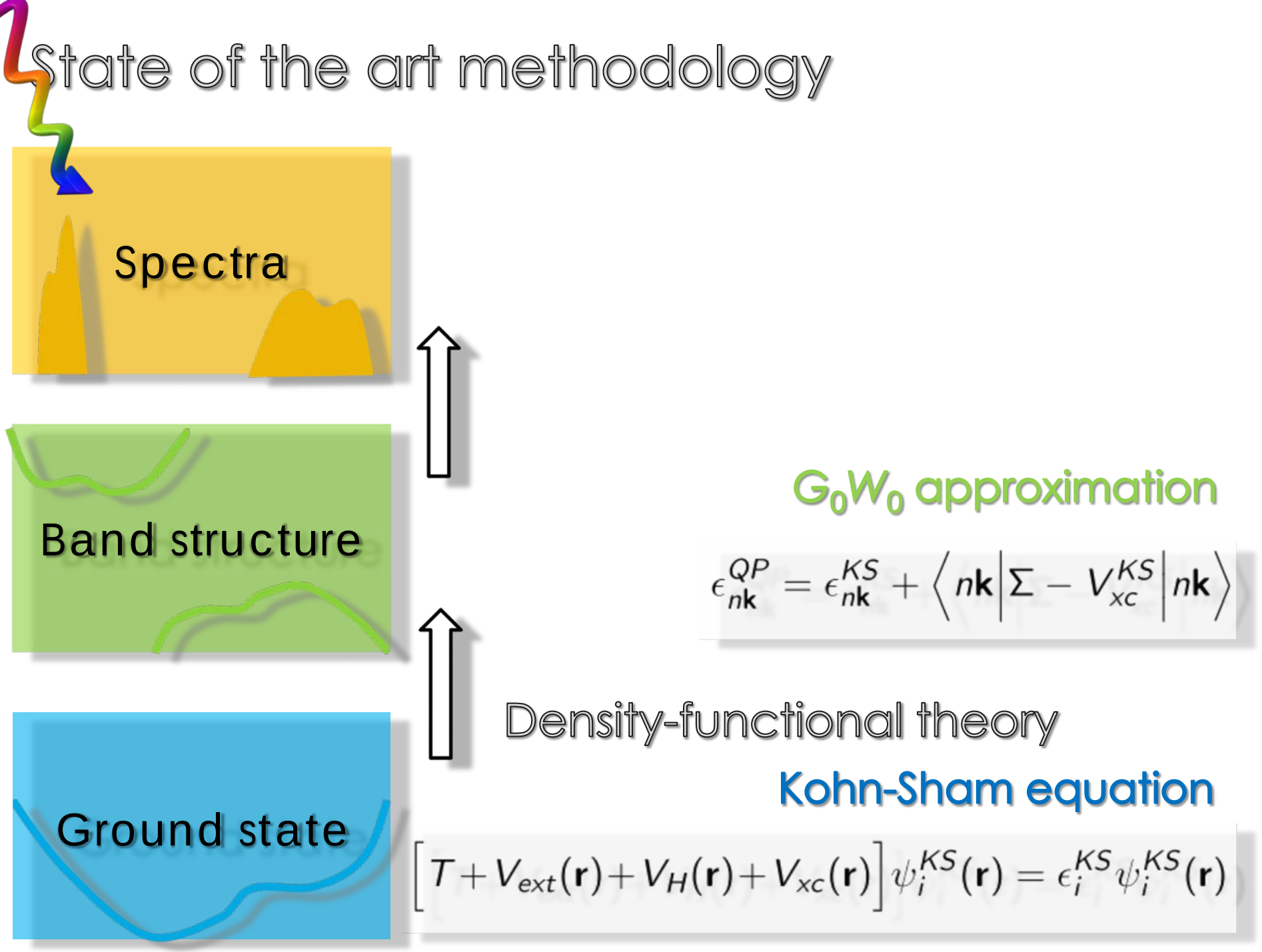
Ground state

Density-functional theory

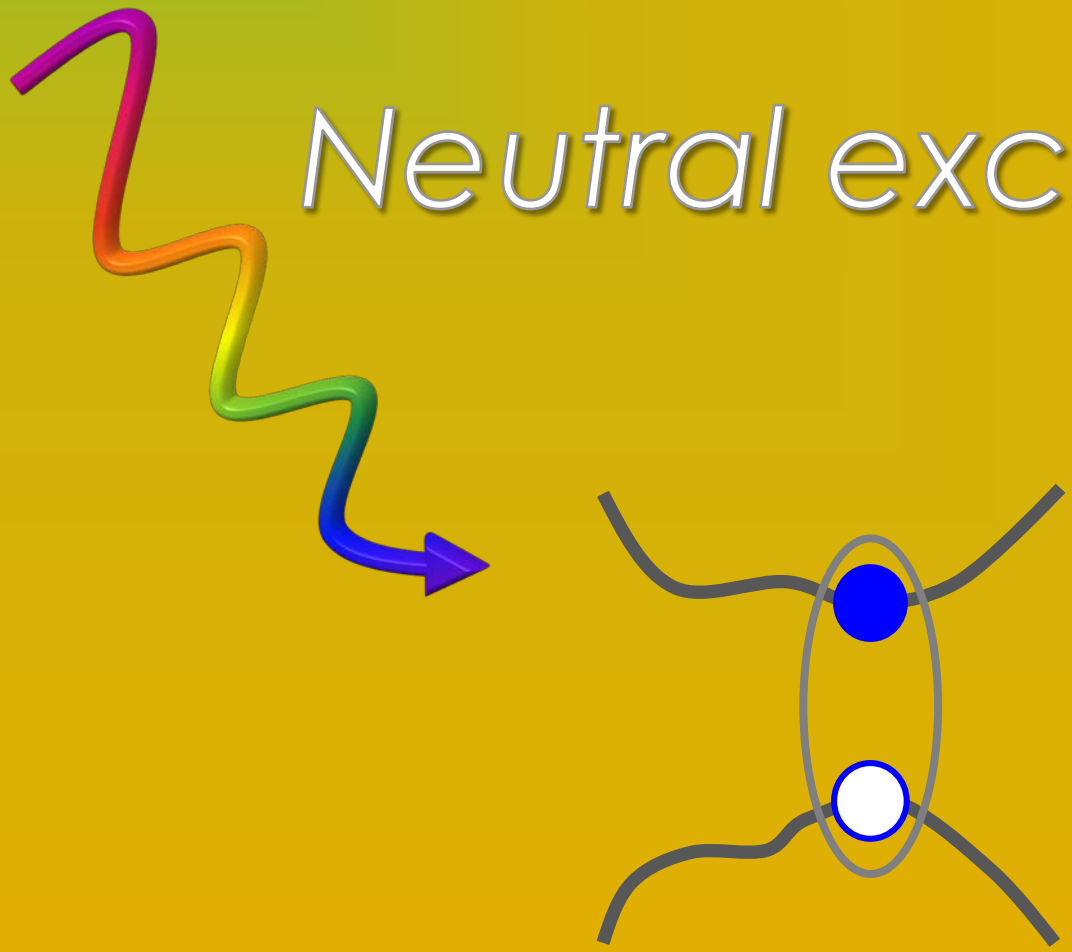
Kohn-Sham equation

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$$

State of the art methodology



Neutral excitations

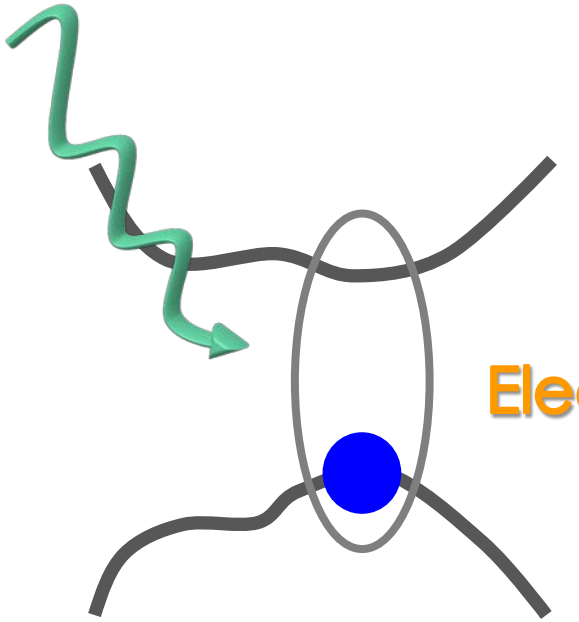


State of the art methodology

Spectra

Band structure

Ground state



Electron-hole pair

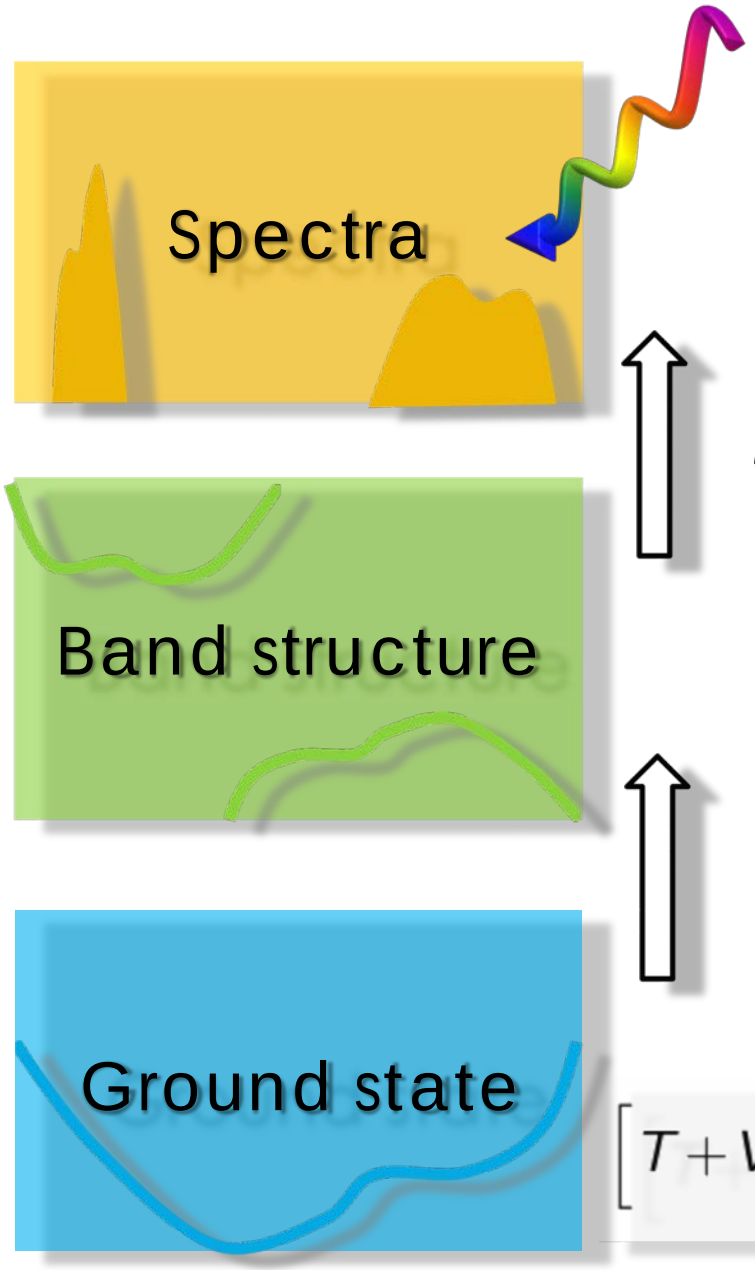
$$\epsilon_{n\mathbf{k}}^{QP} = \epsilon_{n\mathbf{k}}^{KS} + \left\langle n\mathbf{k} \middle| \Sigma - V_{xc}^{KS} \middle| n\mathbf{k} \right\rangle$$

Density-functional theory

Kohn-Sham equation

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS} \psi_i^{KS}(\mathbf{r})$$

State of the art methodology



$$\left[H_{el} + H_{hole} + H_{el-hole}\right] A_\lambda = E_\lambda A_\lambda$$

Bethe-Salpeter equation

Many-body perturbation theory

G_0W_0 approximation

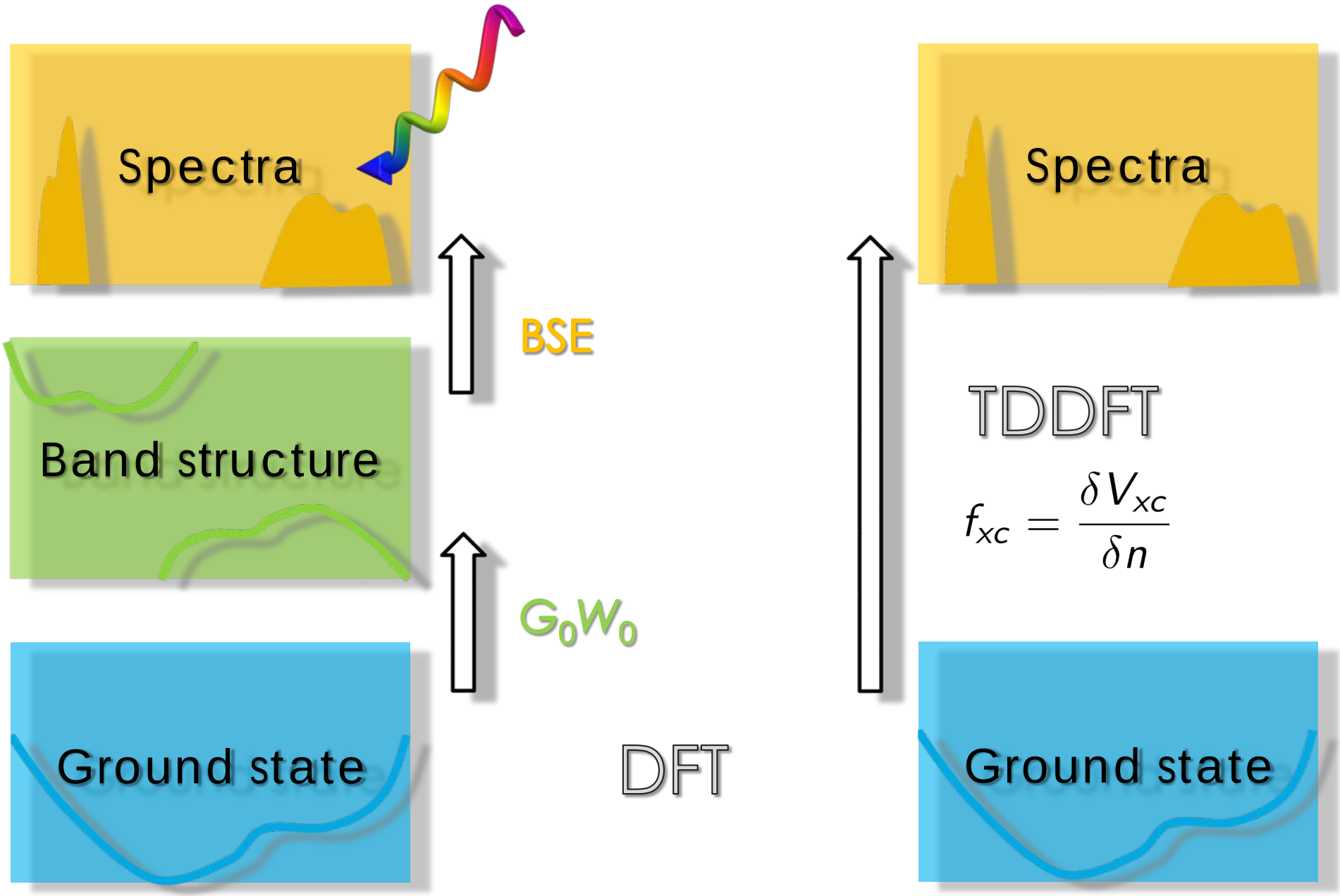
$$\epsilon_{n\mathbf{k}}^{QP} = \epsilon_{n\mathbf{k}}^{KS} + \left\langle n\mathbf{k} \middle| \Sigma - V_{xc}^{KS} \middle| n\mathbf{k} \right\rangle$$

Density-functional theory

Kohn-Sham equation

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right] \psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS} \psi_i^{KS}(\mathbf{r})$$

State of the art methodology



Light-matter interaction

Response to external electric field $\mathbf{E}$

Polarizability

$$P_\alpha = \sum_\beta \chi_{\alpha\beta} E_\beta + \sum_{\beta\gamma} \chi_{\alpha\beta\gamma} E_\beta E_\gamma + \cdots$$

Linear approximation

Susceptibility χ $\quad \mathbf{P} = \chi \mathbf{E}$

Conductivity σ $\quad \mathbf{J} = \sigma \mathbf{E}$

Dielectric tensor ε $\quad \mathbf{D} = \epsilon \mathbf{E}$

$$D_\alpha(\mathbf{r}, t) = \sum_\beta \int_{\mathbf{r}'} \int_{t'} \epsilon_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t - t') E_\beta(\mathbf{r}', t')$$

Fourier transform

$$D_\alpha(\mathbf{q} + \mathbf{G}, \omega) = \sum_\beta \sum_{\mathbf{G}'} \epsilon_{\alpha\beta}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) E_\beta(\mathbf{q} + \mathbf{G}', \omega)$$

Optical "constants"

Complex dielectric tensor

$$\xrightarrow{\text{KK}} \quad \mathrm{Re}\epsilon_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + \frac{2}{\pi} \mathrm{P} \int_0^\infty \frac{\omega' \,\mathrm{Im}\,\epsilon_{\alpha\beta}(\omega')}{\omega'^2 - \omega^2} d\omega'$$

Optical conductivity

$$\mathrm{Re}\,\sigma_{\alpha\beta}(\omega) = \frac{\omega}{4\pi} \mathrm{Im}\,\epsilon_{\alpha\beta}(\omega)$$

Complex refractive index

$$\mathrm{n}_{\alpha\alpha}(\omega) = \sqrt{\frac{|\epsilon_{\alpha\alpha}(\omega)| + \mathrm{Re}\,\epsilon_{\alpha\alpha}(\omega)}{2}} \quad \mathrm{k}_{\alpha\alpha}(\omega) = \sqrt{\frac{|\epsilon_{\alpha\alpha}(\omega)| - \mathrm{Re}\,\epsilon_{\alpha\alpha}(\omega)}{2}}$$

Reflectivity

$$\mathrm{R}_{\alpha\alpha}(\omega) = \frac{(\mathrm{n}_{\alpha\alpha} - 1)^2 + \mathrm{k}_{\alpha\alpha}^2}{(\mathrm{n}_{\alpha\alpha} + 1)^2 + \mathrm{k}_{\alpha\alpha}^2}$$

Absorption coefficient

$$\mathrm{A}_{\alpha\alpha}(\omega) = \frac{2\omega\, \mathrm{k}_{\alpha\alpha}(\omega)}{c}$$

Loss function

$$\mathrm{L}_{\alpha\alpha}(\omega) = -\mathrm{Im}\left(\frac{1}{\varepsilon_{\alpha\alpha}(\omega)}\right)$$

Symmetry of dielectric tensor

triclinic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{xz} \\ \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{yy} & \mathrm{Im}\,\epsilon_{yz} \\ \mathrm{Im}\,\epsilon_{xz} & \mathrm{Im}\,\epsilon_{yz} & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

monoclinic ($\alpha,\beta=90°$)

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & \mathrm{Im}\,\epsilon_{xy} & 0 \\ \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{yy} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

orthorhombic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{yy} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

tetragonal, hexagonal

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

cubic

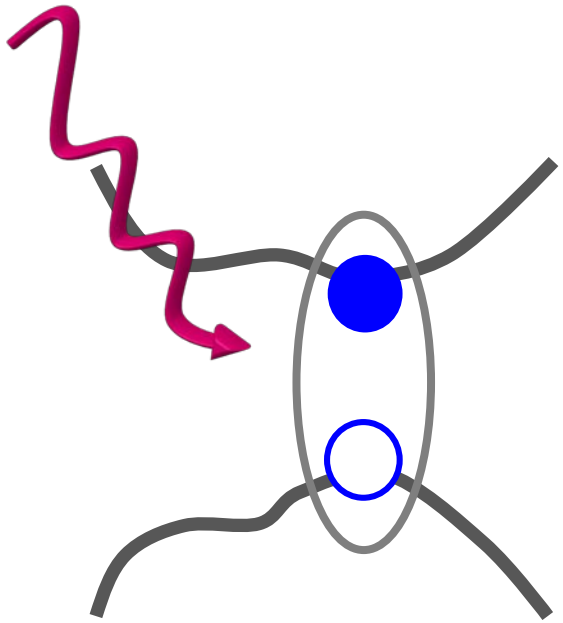
$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{xx} \end{pmatrix}$$

Absorption process

Quasi-particle formed by quasi-electron and quasi-hole

Exciton

Viewed as *effective hydrogen atom*



with binding energy

$$E_b\ [Ry] = \frac{\mu}{m}\frac{1}{\varepsilon^2}$$

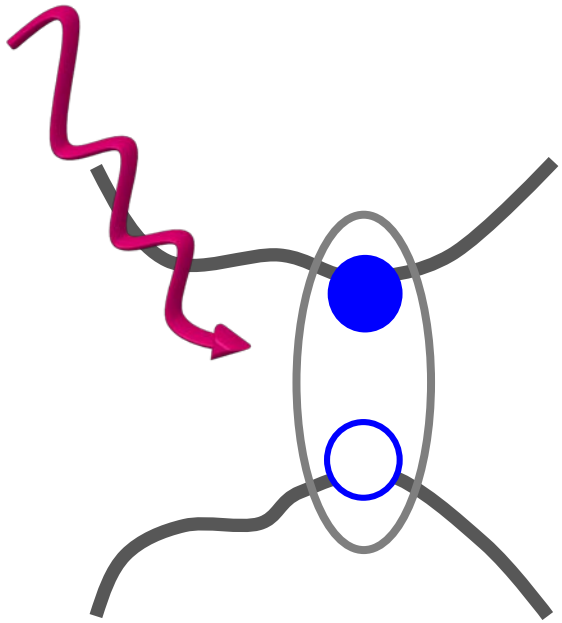
effective reduced mass μ

dielectric constant ε

Absorption process

Bethe-Salpeter equation (BSE)

$$\left[H_{el} + H_{hole} + H_{el-hole}\right] A_\lambda = E_\lambda A_\lambda$$



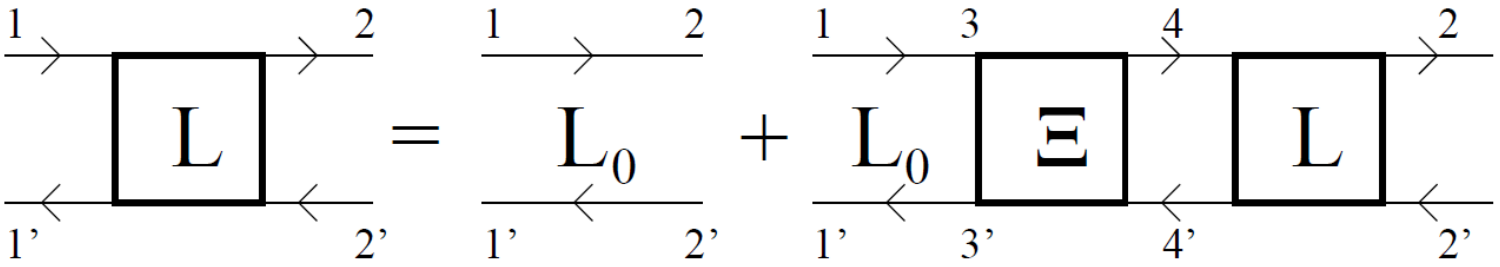
Two-body wavefunction

$$\Phi_\lambda(\mathbf{r}_{el}, \mathbf{r}_{hole}) = \sum_{cv} A_\lambda^{cv} \psi_c(\mathbf{r}_{el}) \psi_v(\mathbf{r}_{hole})$$

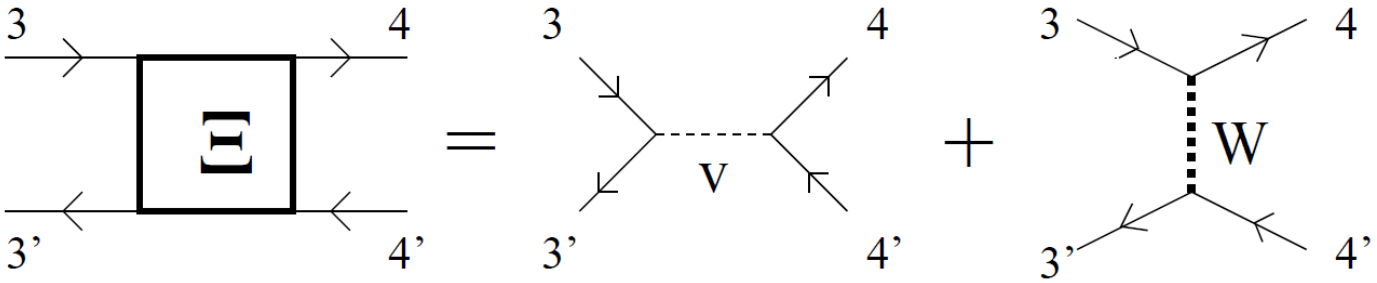
from groundstate

Diagrammatic representation of BSE

Dyson equation for two-particle correlation function



2 diagrams



Two-particle eigenvalue problem

$$\sum_{v'c'\mathbf{k}'} H^{e-h}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E_\lambda A^{\lambda}_{vc\mathbf{k}}$$

Scaling

Diagonal term

$$H^{\text{diag}}_{vc\mathbf{k},v'c'\mathbf{k}'} = (\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}})\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k}\mathbf{k}'}$$

Metals
Semiconductors
Insulators
Molecules

Direct term - attractive

$$H^{\text{dir}}_{cv\mathbf{k},c'v'\mathbf{k}'} = \int \mathrm{d}^3r\,\mathrm{d}^3r' \frac{\psi_{v\mathbf{k}}(\mathbf{r})\psi^*_{c\mathbf{k}}(\mathbf{r}')\epsilon^{-1}(\mathbf{r},\mathbf{r}')\psi^*_{v'\mathbf{k}'}(\mathbf{r})\psi_{c'\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Exchange term - repulsive

$$H^{\text{x}}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int \mathrm{d}^3r\,\mathrm{d}^3r'\,\psi_{v\mathbf{k}}(\mathbf{r})\psi^*_{c\mathbf{k}}(\mathbf{r})\,\bar{v}(\mathbf{r},\mathbf{r}')\,\psi^*_{v'\mathbf{k}'}(\mathbf{r}')\psi_{c'\mathbf{k}'}(\mathbf{r}')$$

Different scenarios

Spin singlets

$$H^{e-h} = H^{\text{diag}} + \gamma_c H^{\text{dir}} + 2\gamma_x H^{\text{x}}$$

Spin triplets

$$H^{e-h} = H^{\text{diag}} + \gamma_c H^{\text{dir}} + \cancel{2\gamma_x H^{\text{x}}}$$

Random-phase approximation

$$H^{e-h} = H^{\text{diag}} + \cancel{\gamma_c H^{\text{dir}}} + 2\gamma_x H^{\text{x}}$$

Independent-particle approximation

$$H^{e-h} = H^{\text{diag}} + \cancel{\gamma_c H^{\text{dir}}} + \cancel{2\gamma_x H^{\text{x}}}$$

Role of electron-hole interaction

in spectra

Dielectric function in IPA

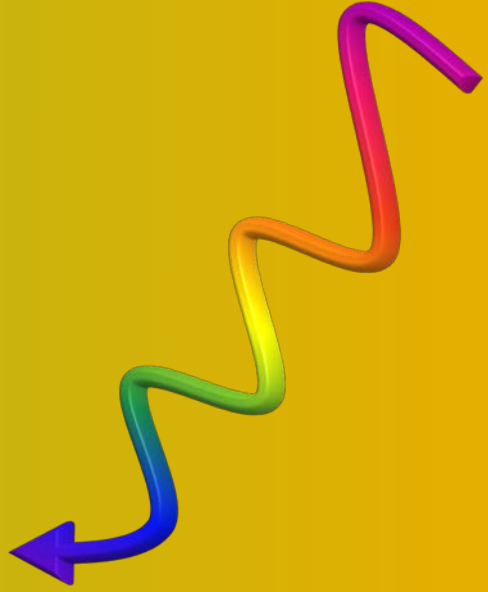
$$\mathrm{Im}\,\epsilon \sim \sum_{cv} \left| \frac{\langle c|\nabla|v\rangle}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(\varepsilon_c - \varepsilon_v - \omega)$$

Dielectric function from BSE

$$\mathrm{Im}\,\epsilon \sim \sum_{\lambda} \sum_{vc} \left| \frac{\langle c|\nabla|v\rangle A^{\lambda}_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E_{\lambda} - \omega)$$

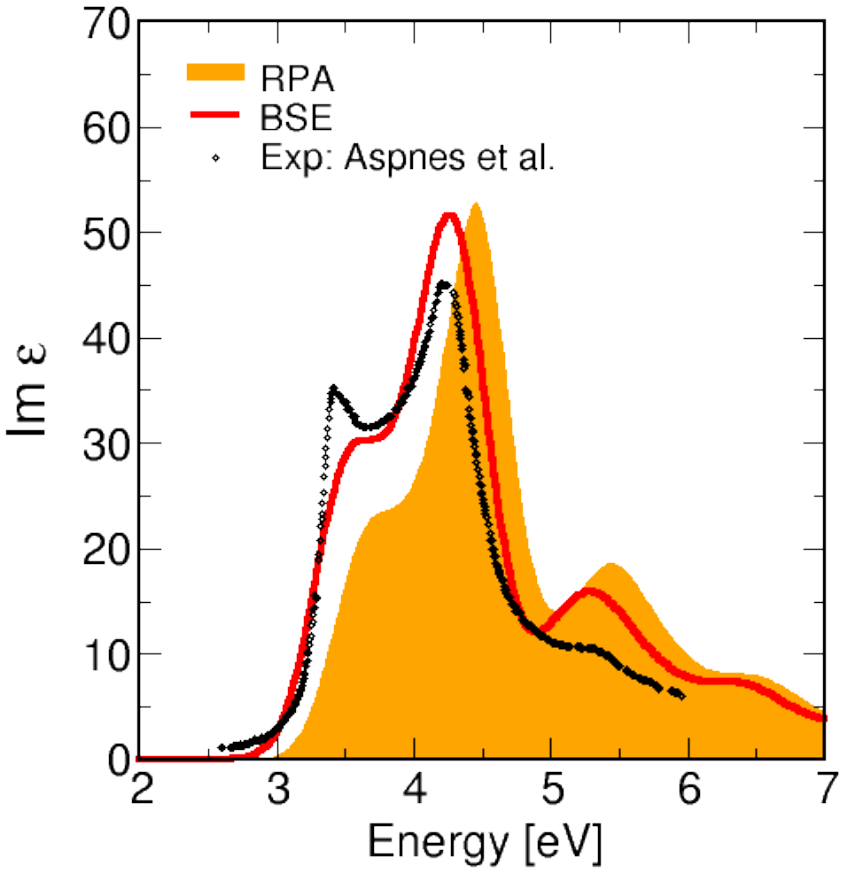
Peaks at electron-hole pair energies

Redistribution of oscillator strength

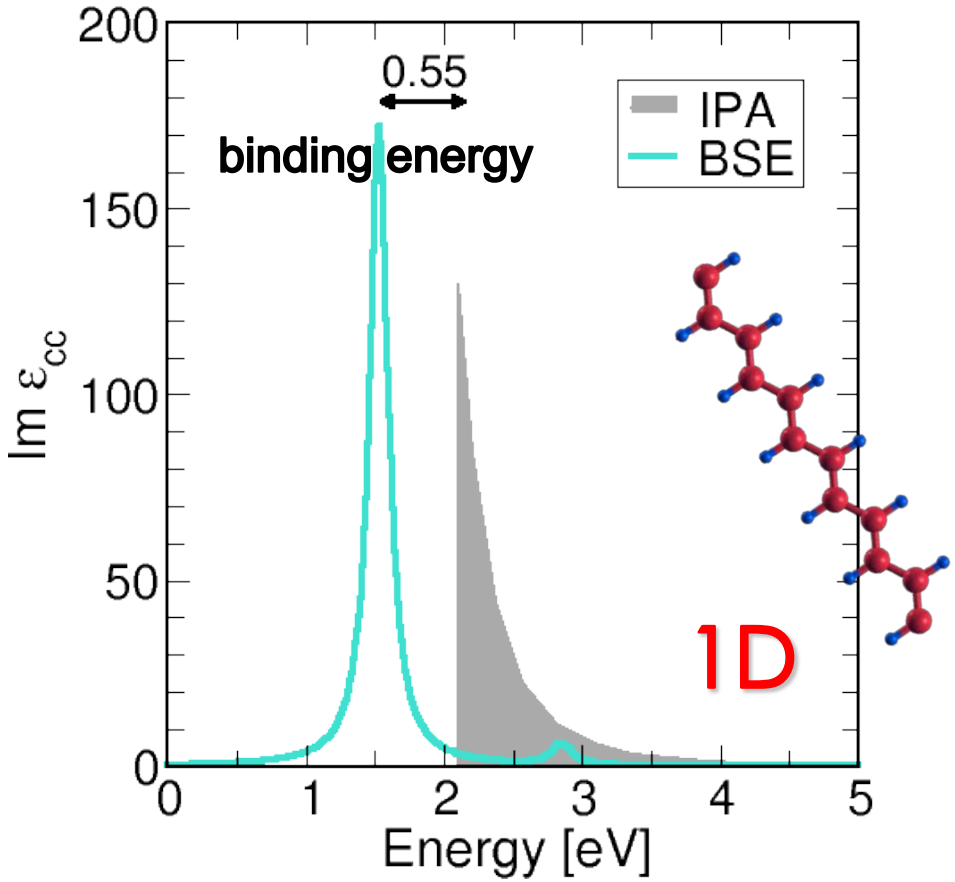


Examples

Examples



Silicon

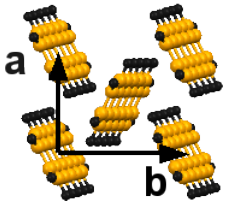


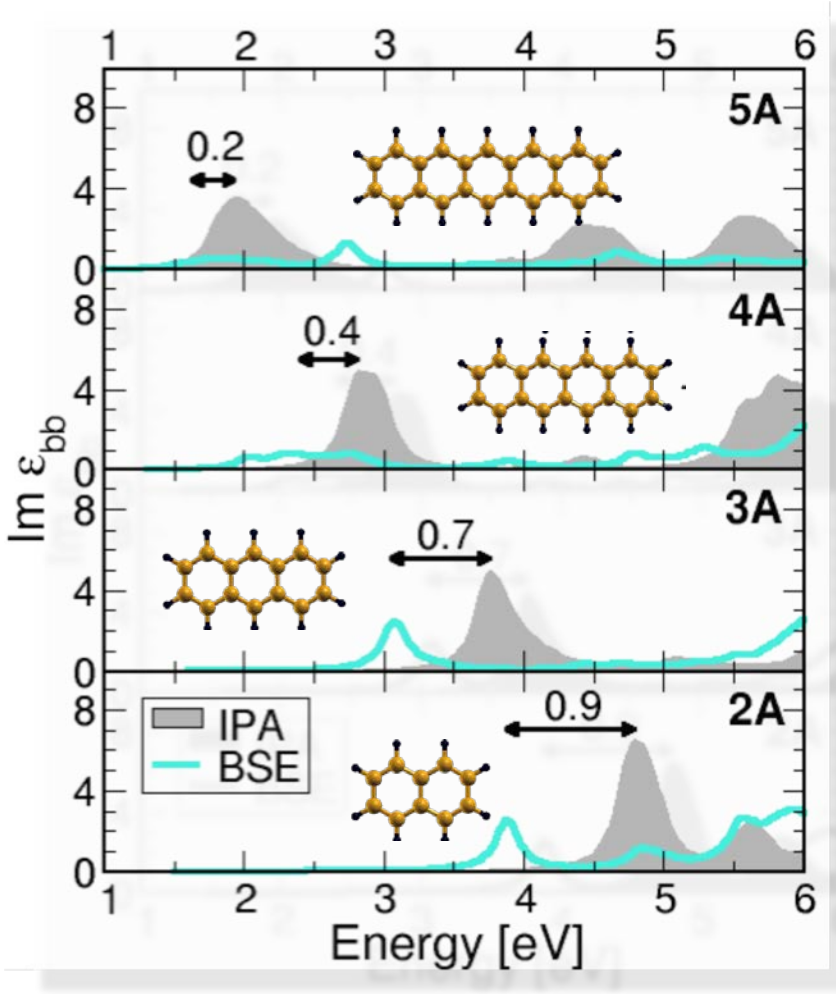
Poly-acetylene

Organic semiconductors: oligoacenes

Electron-hole binding energy depends on

- molecular size
- molecular packing
- polarization of light





Exciton binding energies

Singlet ~1 eV – 0.1 eV

Triplet ~2 eV – 1 eV

K. Hummer, P. Puschnig, & CD, PRL 92, 147402 (2004).

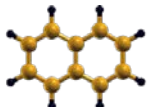
K. Hummer & CAD, PRB 71, 081202(R) (2005).

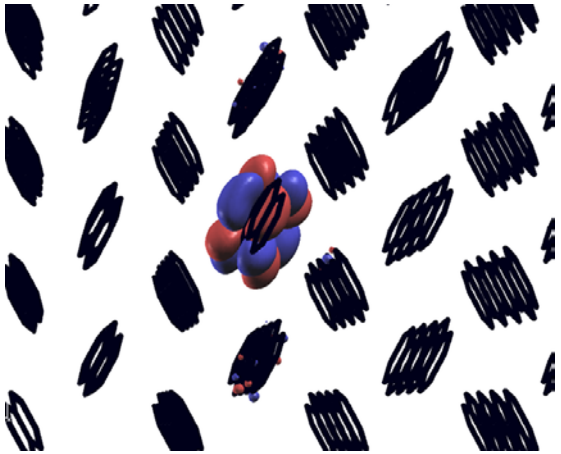
Organic semiconductors: oligoacenes

Size of electron-hole pairs depends on

- molecular size
- molecular packing
- polarization of light

$$\phi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cv} A_\lambda^{cv} \psi_c(\mathbf{r}_e)\ \psi_v(\mathbf{r}_h)$$





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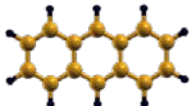
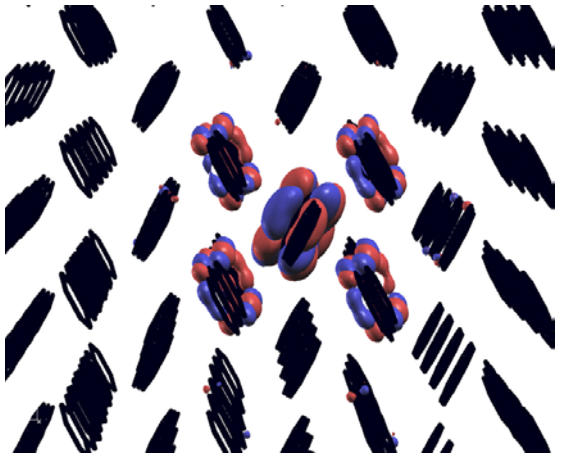


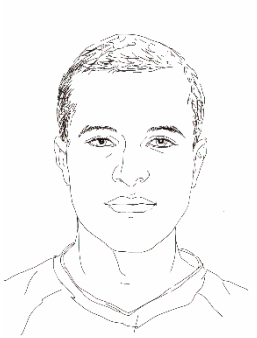


K. Hummer, P. Puschnig, & CD, PRL 92, 147402 (2004).
K. Hummer & CAD, PRB 71, 081202(R) (2005).

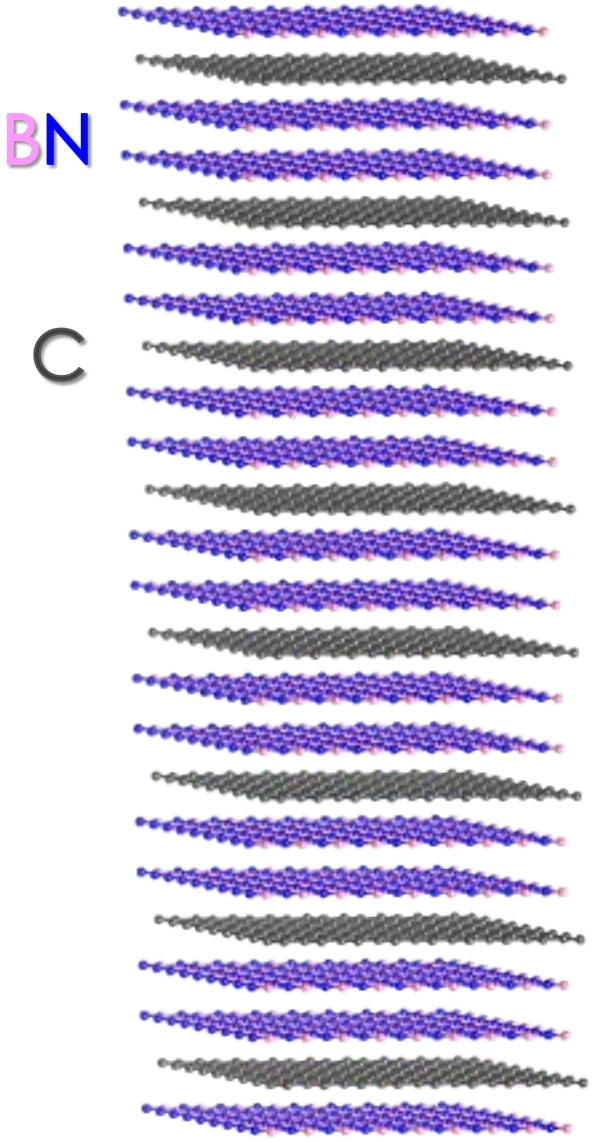
C / BN heterostructures

Several patterns open a gap in graphene

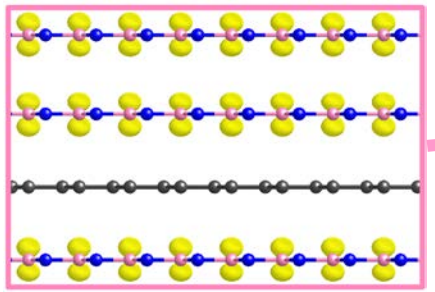
see also R. Quhe *et al.*,
NPG Asia Materials (2012)



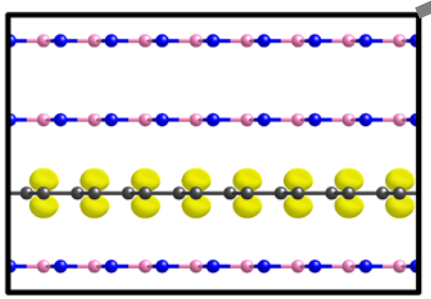
W. Aggoune, C. Cocchi, K. Rezouali, M. Belkhir, and CD,
J. Phys. Chem. Lett. 8, 1464 (2017).



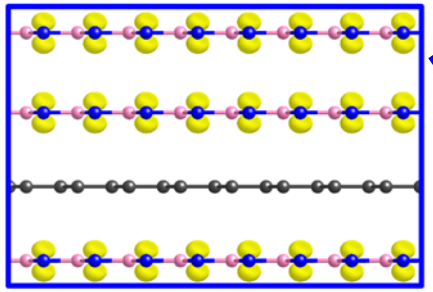
C / BN heterostructures



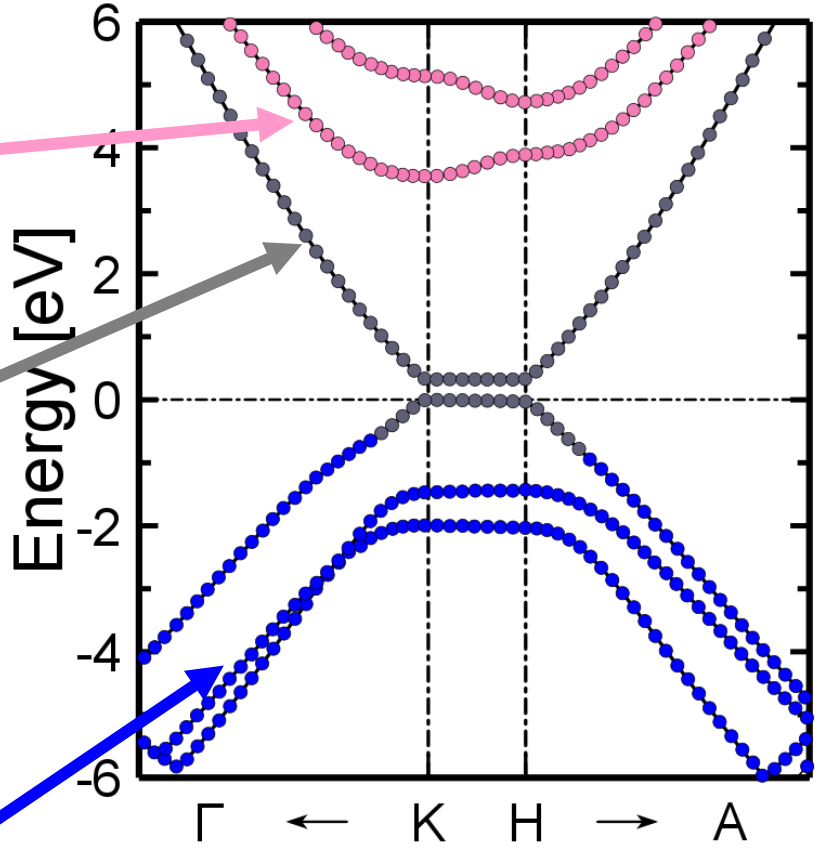
Boron

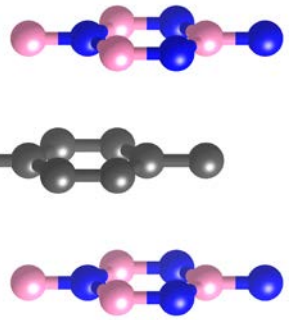


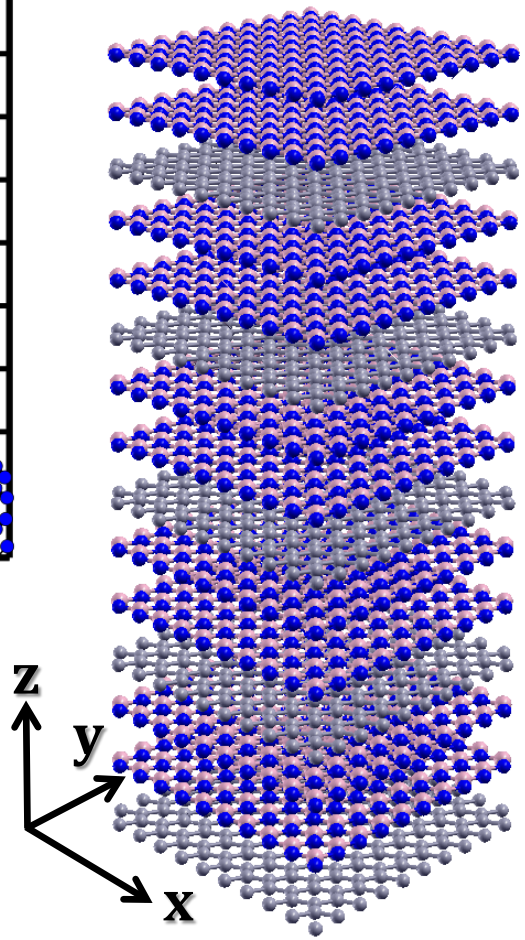
Carbon



Nitrogen





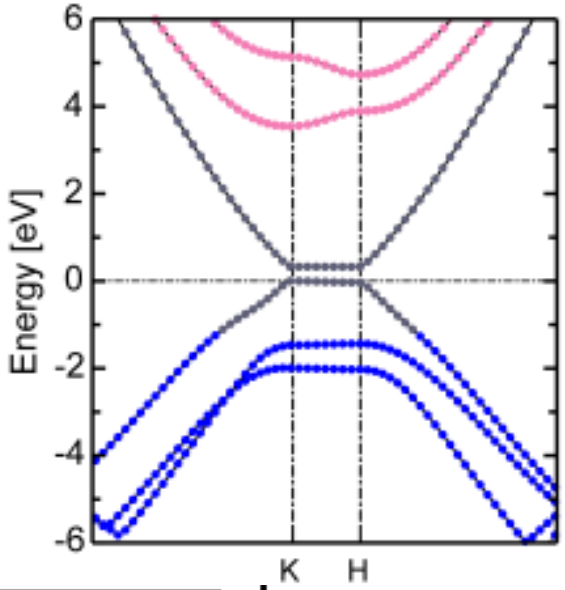


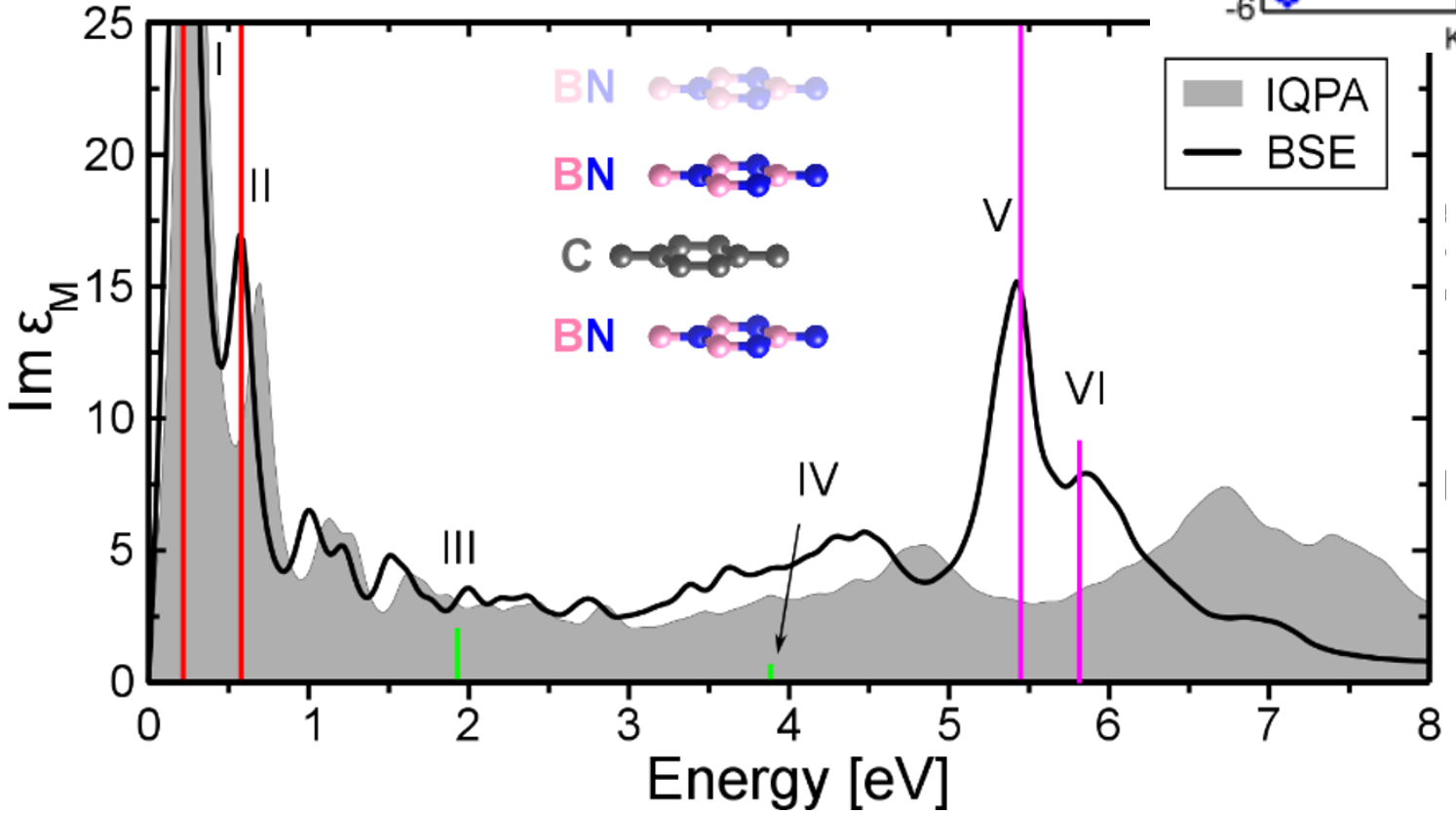
C / BN heterostructures

Intense peaks in the IR region

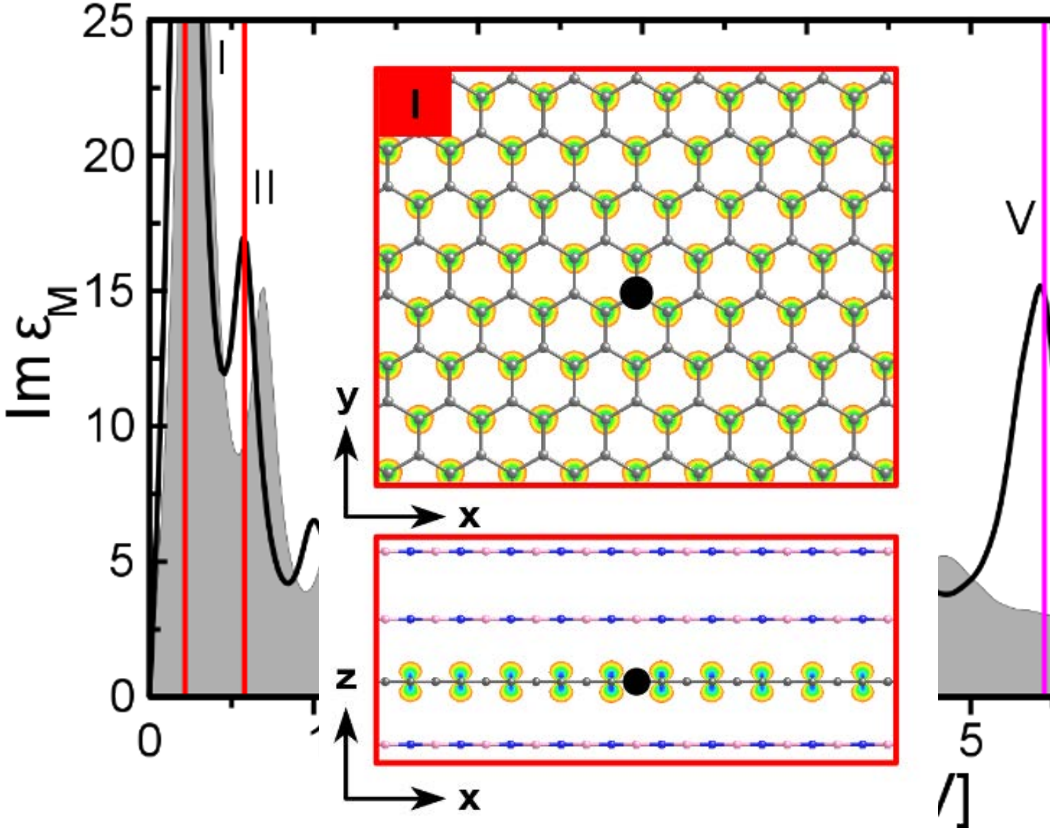
Finite absorption in the visible

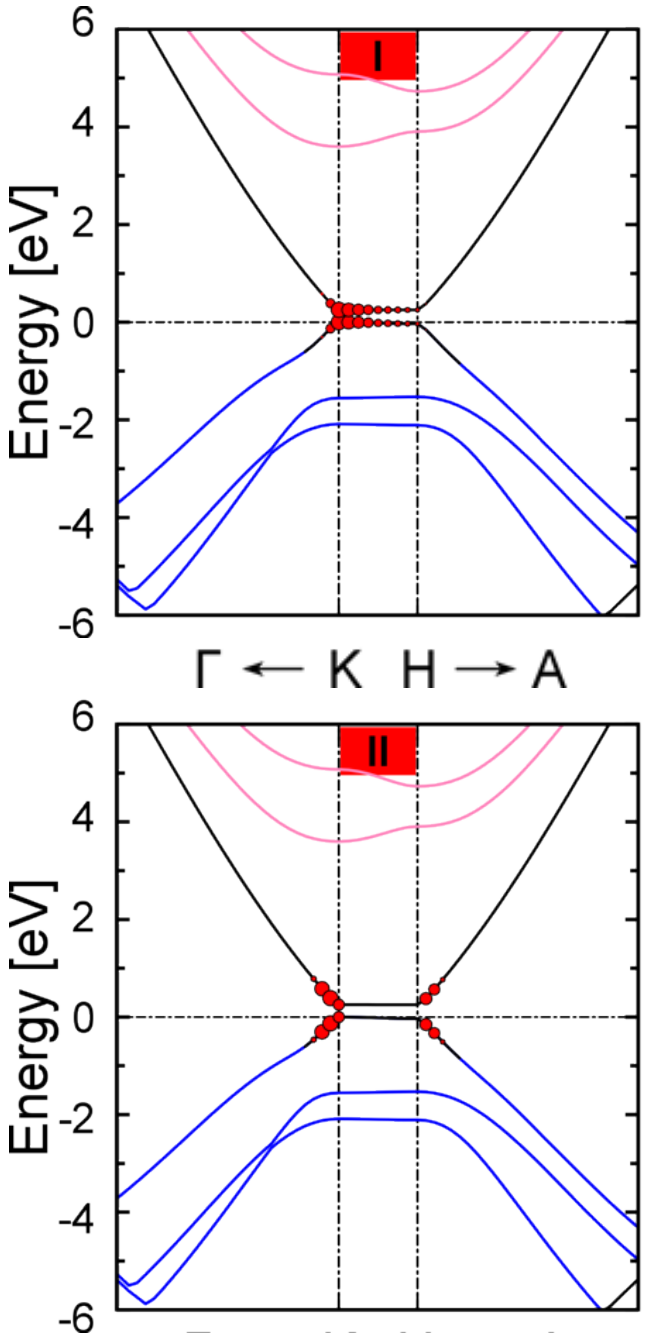
Excitons in the near-UV range





C / BN heterostructures



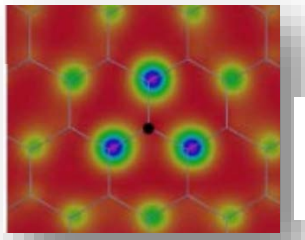


C / BN heterostructures

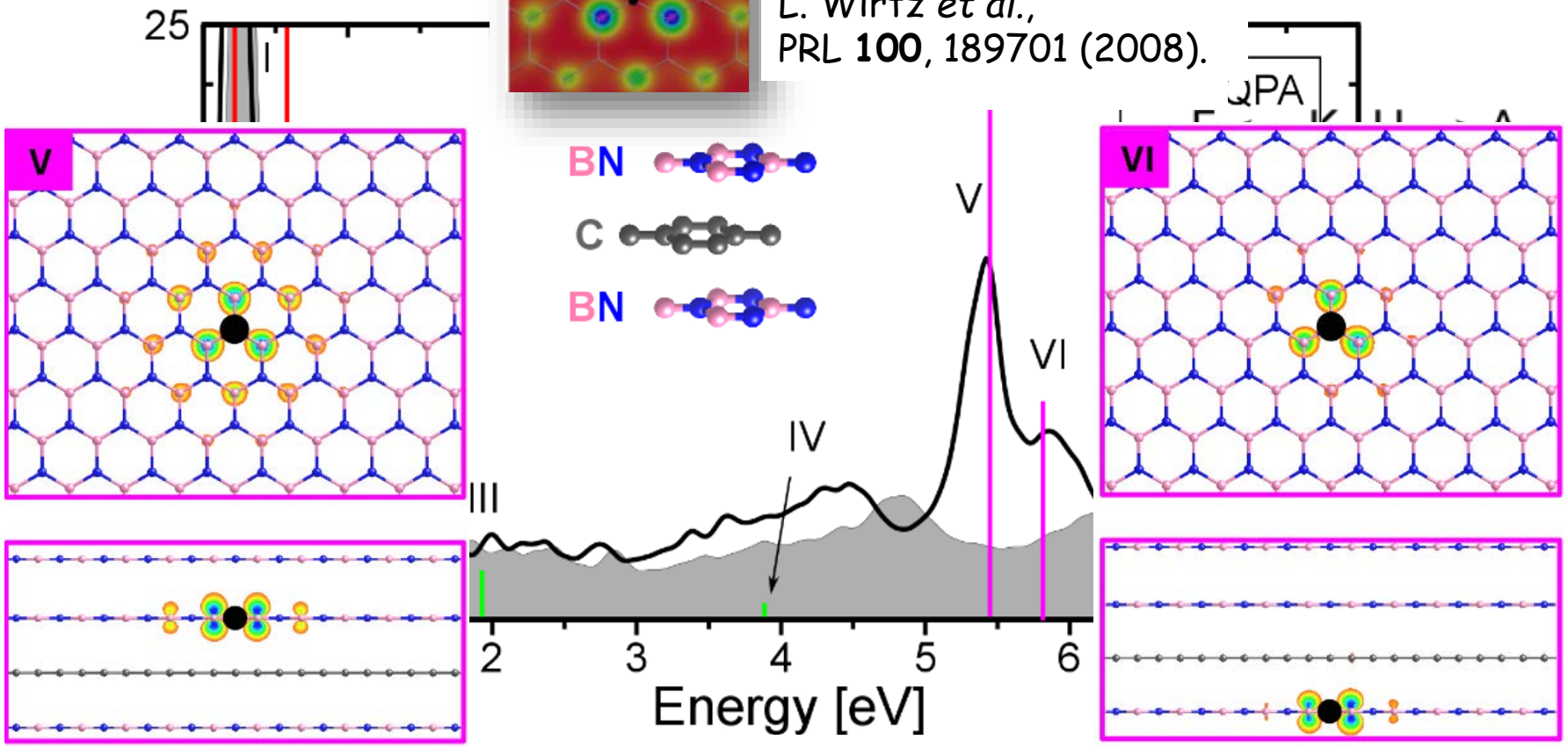
V, VI: BN ↔ BN

Strongly bound intralayer exciton

Like in h-BN bull



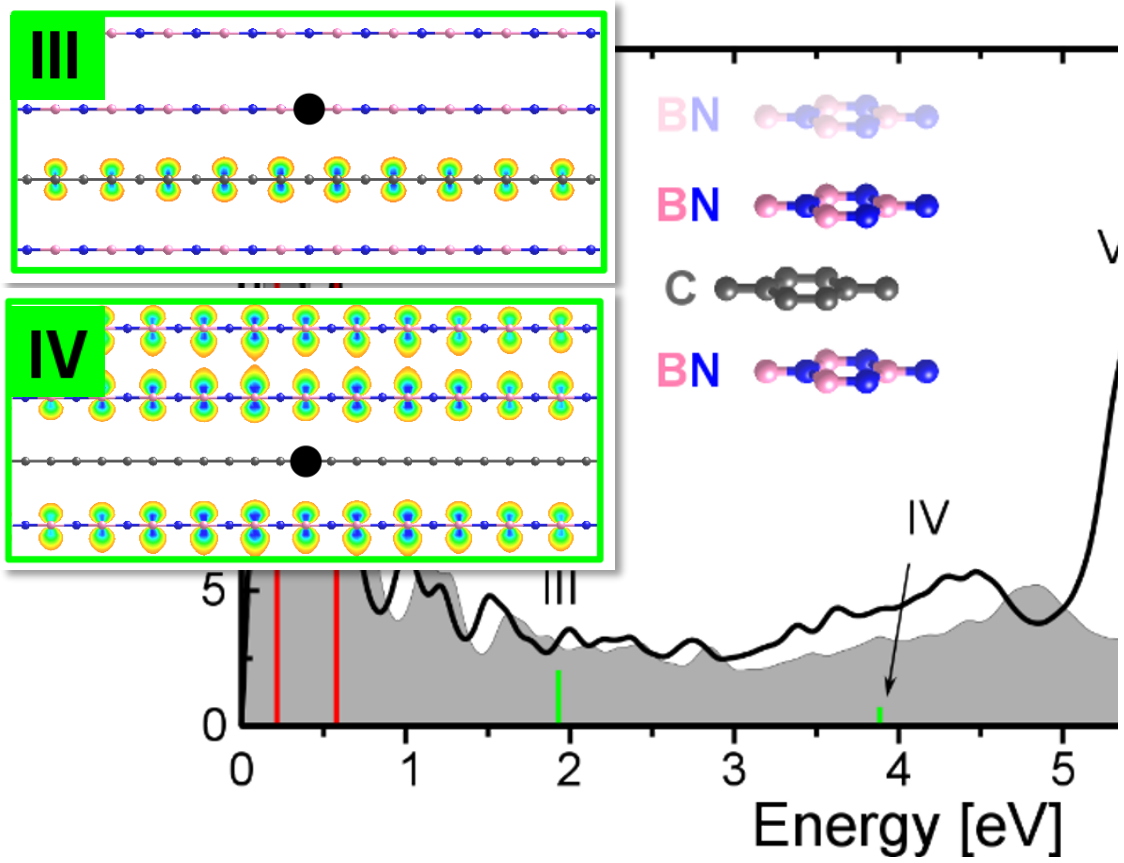
L. Wirtz *et al.*,
PRL **100**, 189701 (2008).

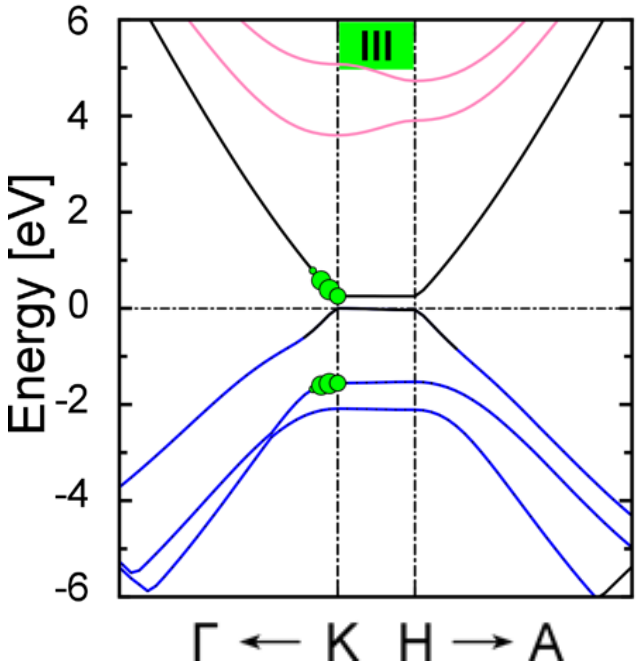


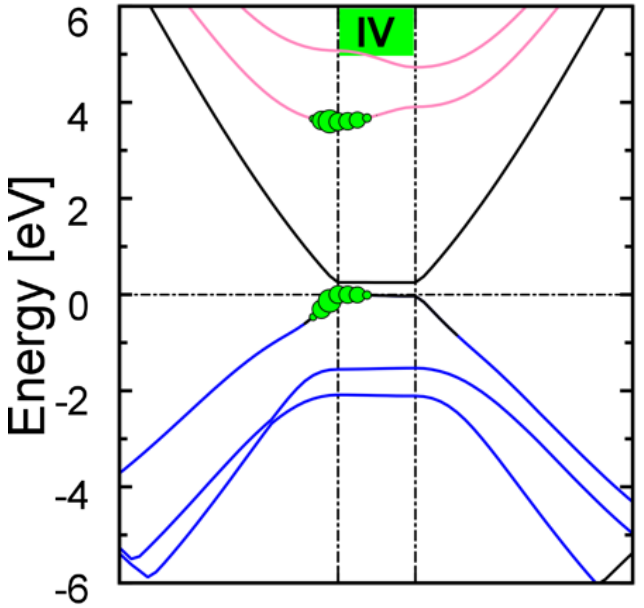
C / BN heterostructures

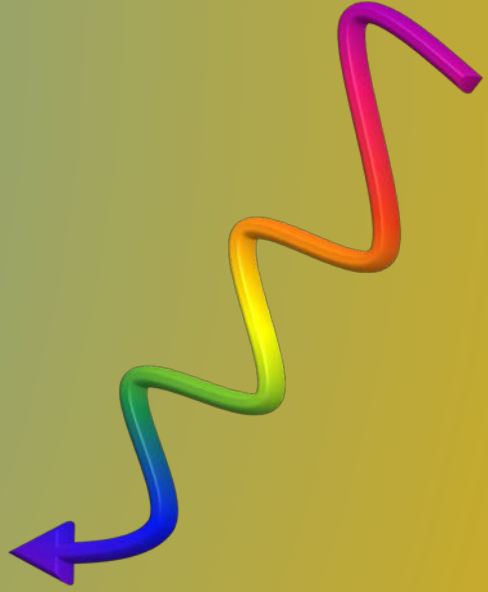
III, IV: graphene ↔ BN

Weakly bound CT excitations





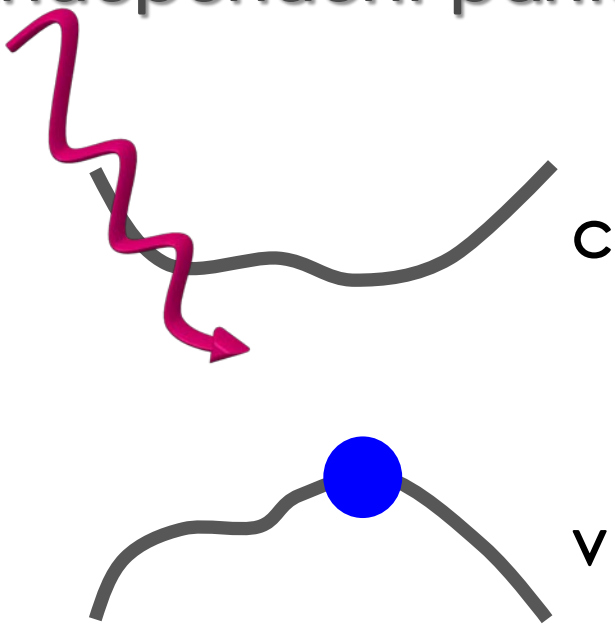




What about metals?

Absorption process

Independent-particle approximation



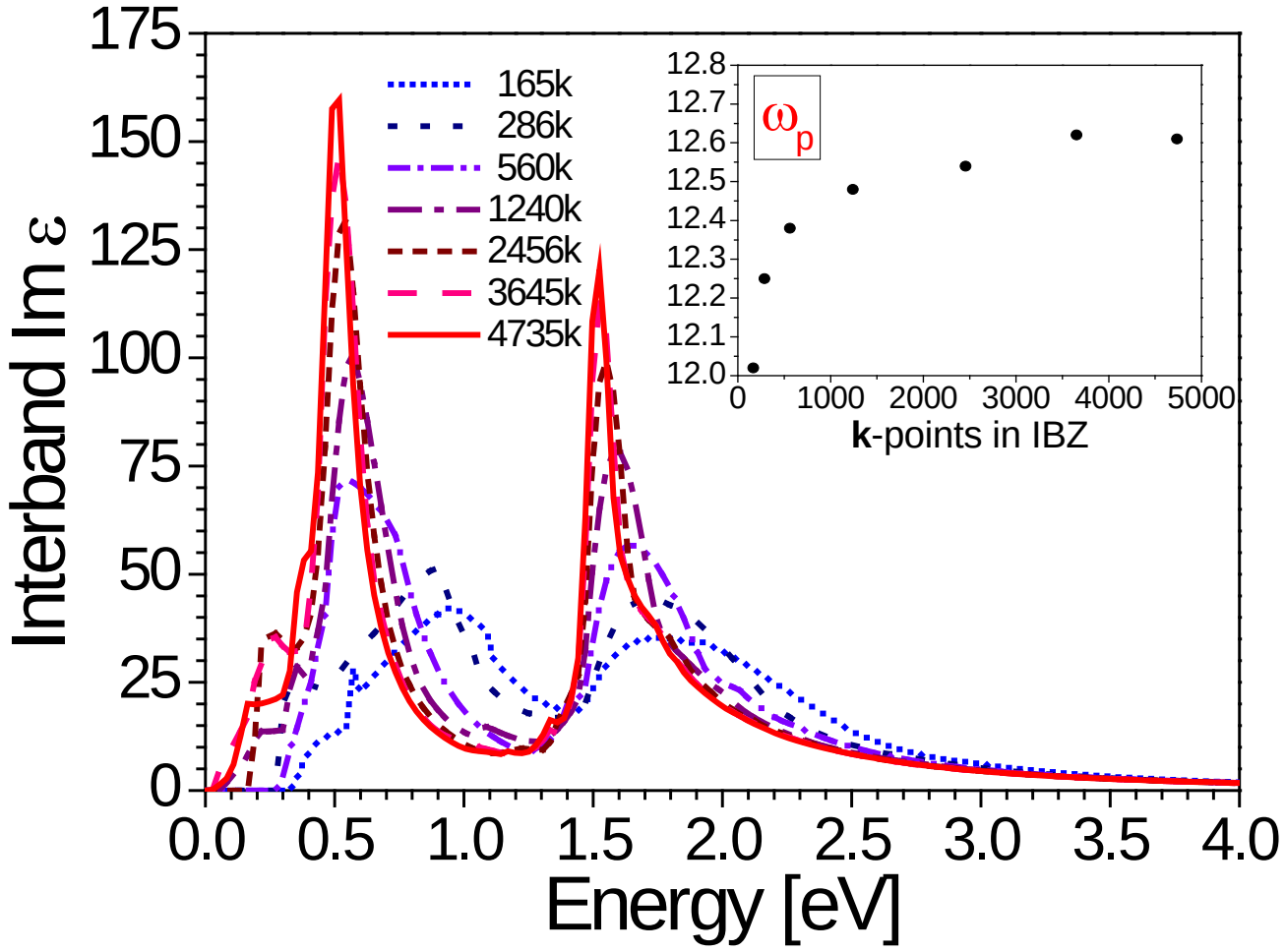
energy conservation

selection rules

$$\mathrm{Im}\,\epsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2}\sum_{c,v}\int d\mathbf{k}\ \langle c_\mathbf{k}|p^\alpha|v_\mathbf{k}\rangle\langle v_\mathbf{k}|p^\beta|c_\mathbf{k}\rangle\ \delta(\varepsilon_{c_\mathbf{k}} - \varepsilon_{v_\mathbf{k}} - \omega)$$

Example: Al

LDA eigenvalues

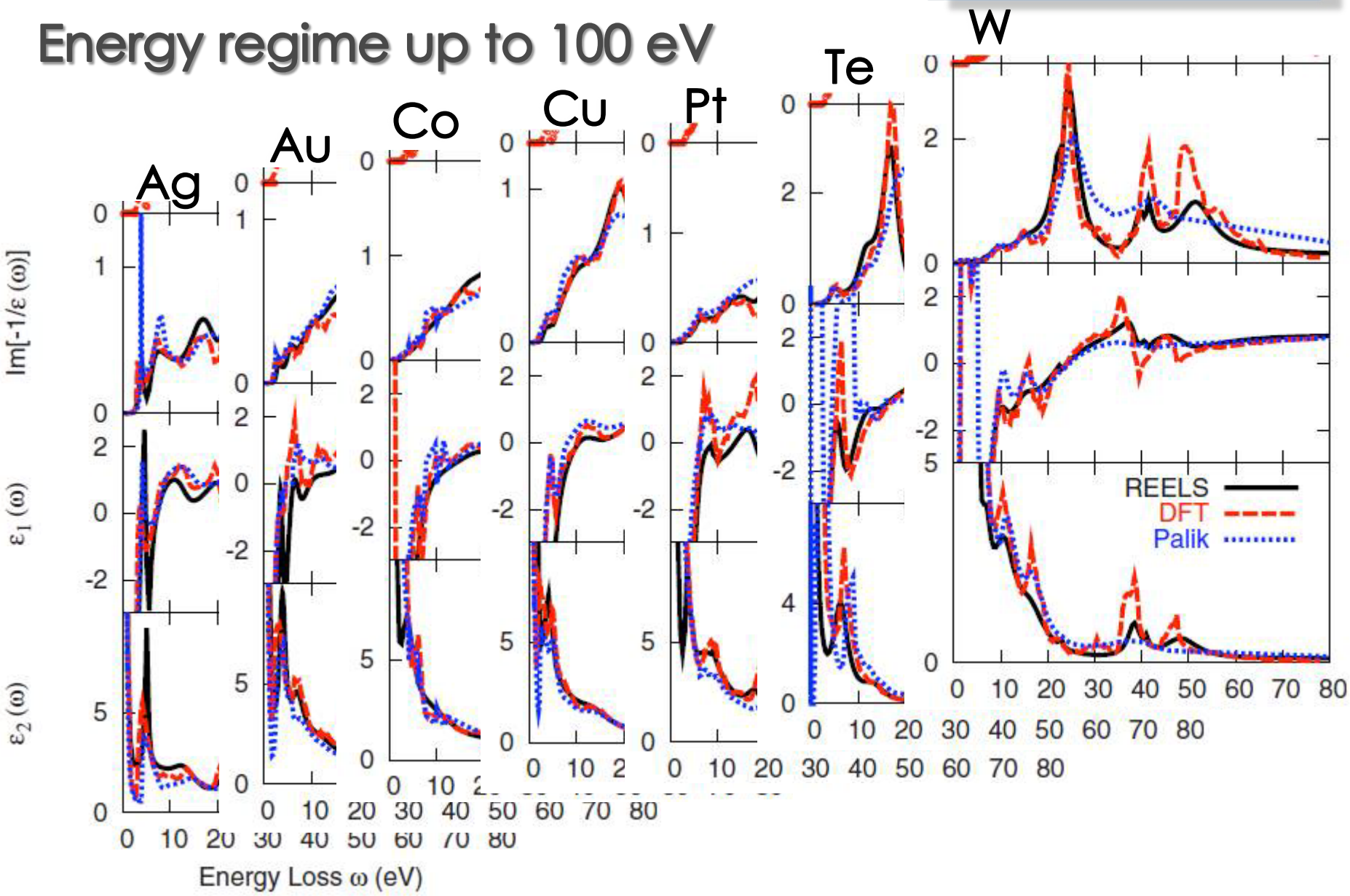


$$\mathrm{Im}\,\epsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2}\sum_{c,v}\int d\mathbf{k}\ \langle c_\mathbf{k}|p^\alpha|v_\mathbf{k}\rangle\langle v_\mathbf{k}|p^\beta|c_\mathbf{k}\rangle\ \delta(\varepsilon_{c_\mathbf{k}} - \varepsilon_{v_\mathbf{k}} - \omega)$$

Theory & experiment

LDA eigenvalues

Energy regime up to 100 eV



Theory & experiment

Overall very good agreement in the entire energy range (up to 100 eV)

New REELS data agree much better with DFT

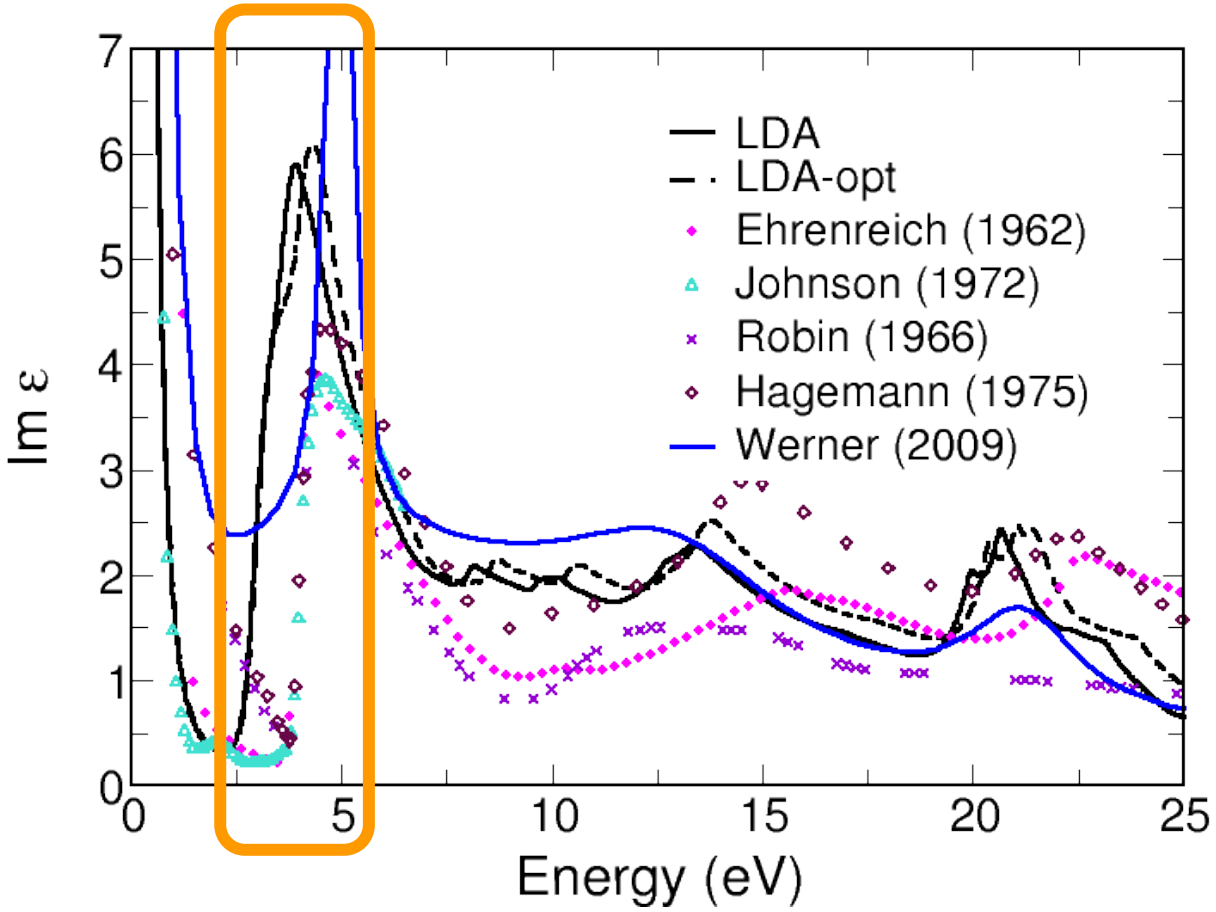
Details of the band structure matter ....

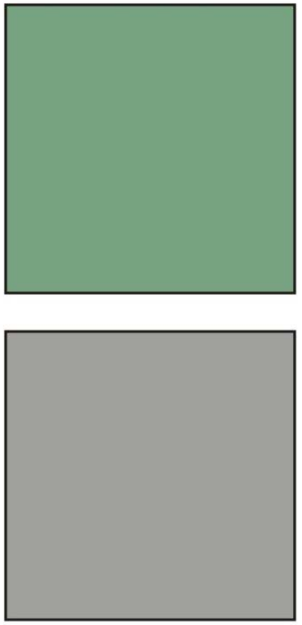
W. Werner, K. Glantschnig, and CAD
J. Phys. Chem. Ref. Data 38, 1013 (2009).

Details matter ...

Interband transition onset - *d* band position

Ab initio color





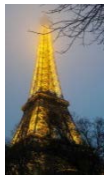
PBE

GW

A. Alkauskas, et al.
PRB 88, 195124 (2013).

Let's go to the core …

Electro-magnetic spectrum



wavelength
λ [m]

10^{4} 10^{2} 10^{0} 10^{-2} 10^{-4} 10^{-6} 10^{-8} 10^{-10} 10^{-12} 10^{-14}

radio waves microwaves IR UV X-rays Γ-rays

frequency
ν [Hz]

10^{4} 10^{6} 10^{8} 10^{10} 10^{12} 10^{14} 10^{16} 10^{18} 10^{20} 10^{22}

energy
E [eV]

10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4} 10^{6} 10^{8}

visible light

1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0

Dielectric function

$$\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$$

Macroscopic dielectric *constant*

$$\epsilon_M(\mathbf{q},\omega) = \frac{1}{\epsilon^{-1}_{00}(\mathbf{q},\omega)}$$

Momentum transfer by visible light very small

Wavelength much larger than interatomic distances

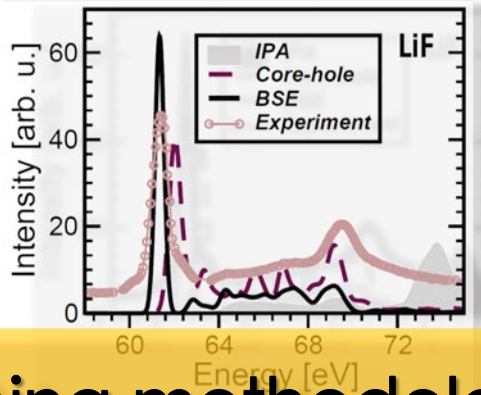
$a \sim 10^{-10}$ m

$\lambda \sim 10^{-6}$ m

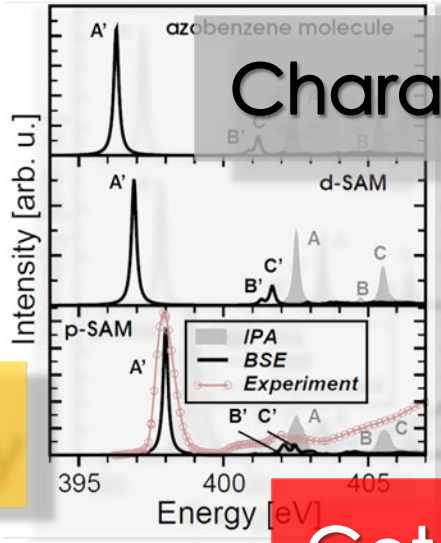
$$\mathbf{q} = \frac{2\pi}{\lambda} \approx 0$$

X-rays: not the case any more!

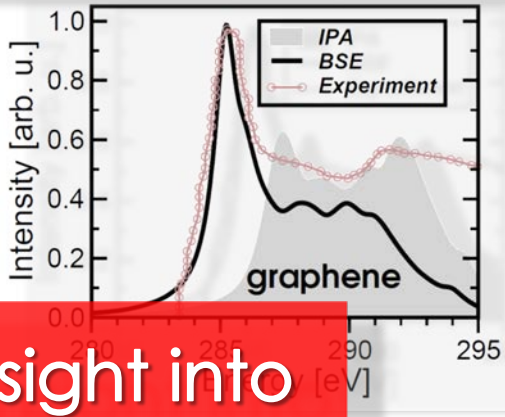
Why core spectroscopy?

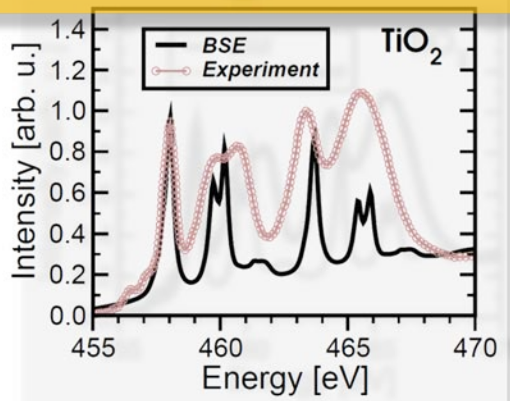


Probing methodology

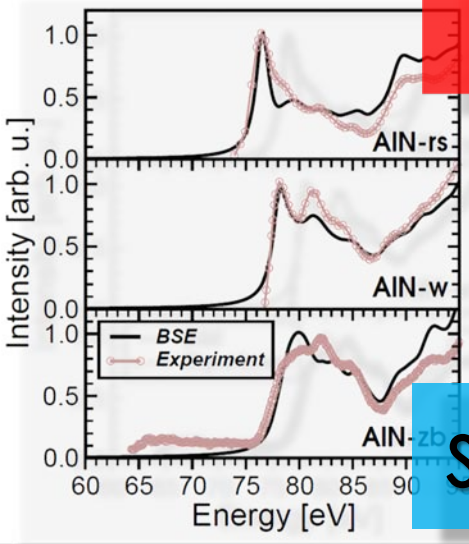


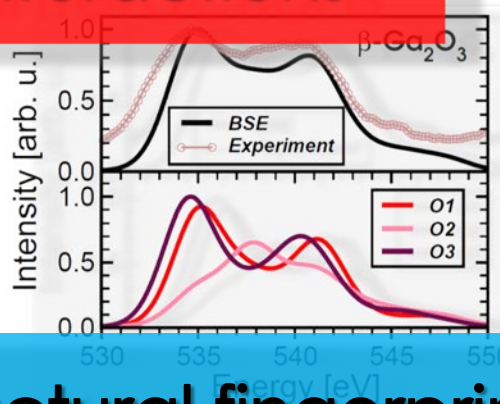
Characterize materials





Get insight into interactions



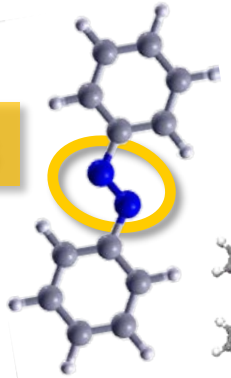


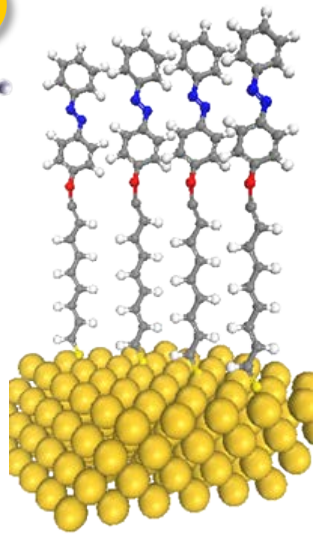
Structural fingerprints

XAS of molecuar materials

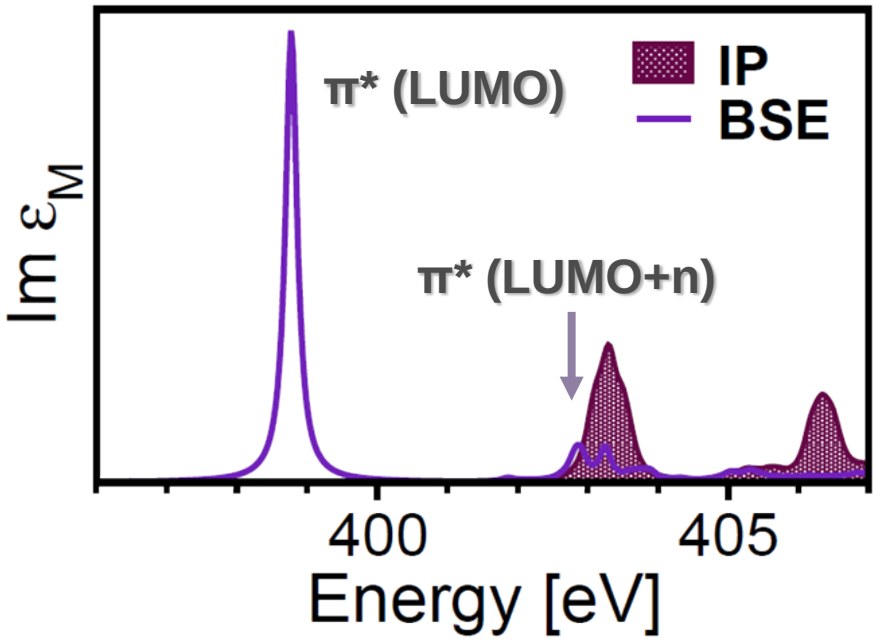
Azobenzene SAMs

Excellent agreement with experiment: exciton character and relative intensities

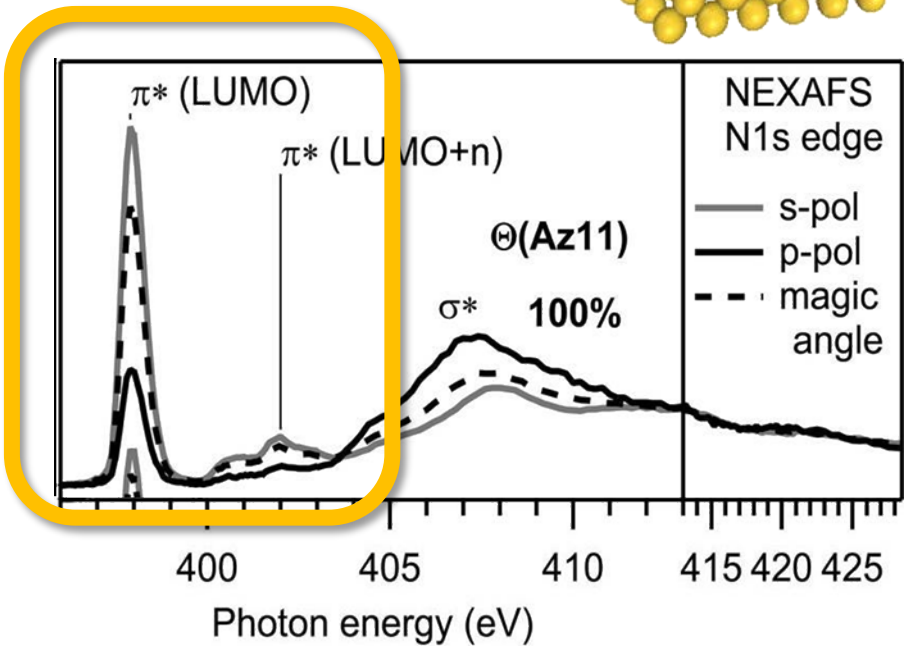




Theory



Experiment

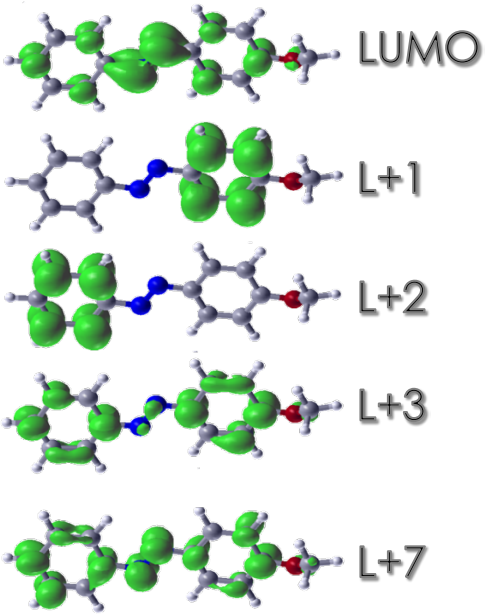


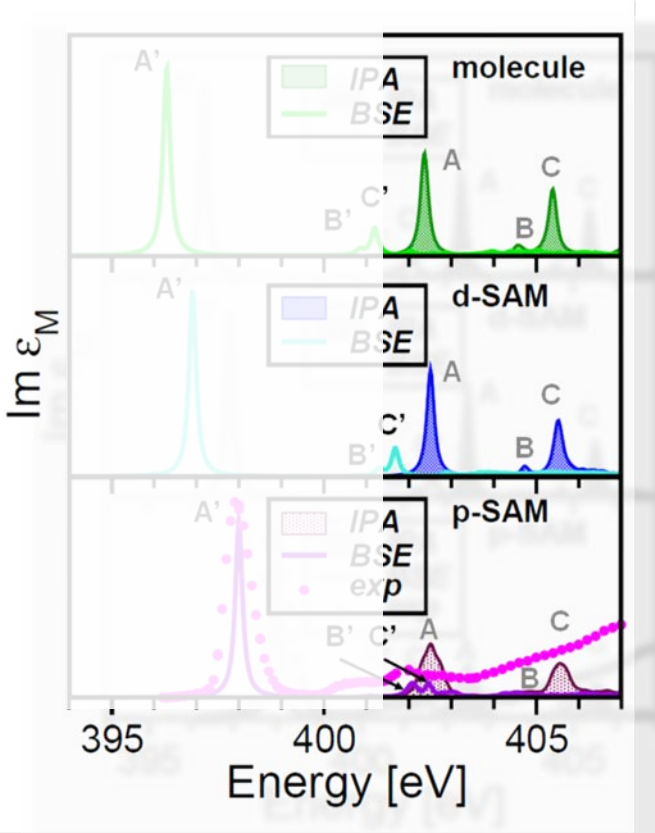
C. Cocchi & CD, PRB **92**, 205105 (2015).

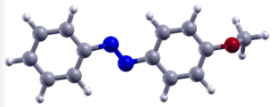
Moldt et al. Langmuir 31, 1048 (2015).

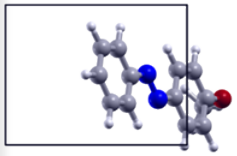
XAS of azobenzene SAMs

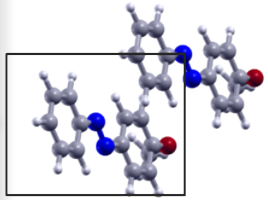
Impact of packing











Independent-particle picture

3 transitions

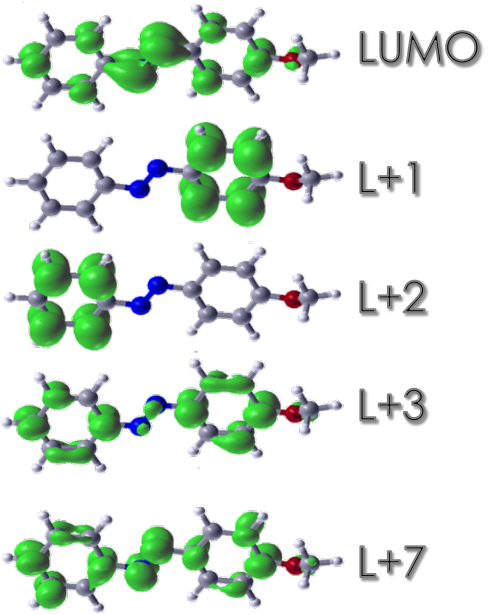
- A: 1s → LUMO (π*)
- B: 1s → LUMO+3 (π*)
- C: 1s → LUMO+7 (π*)

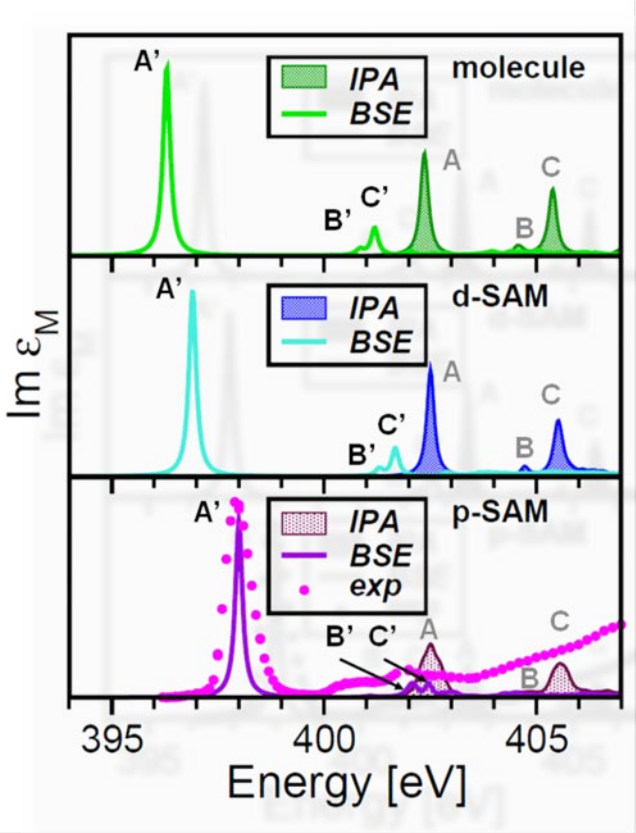
Peak positions unchanged

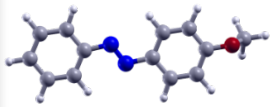
Similar intensities of A & C

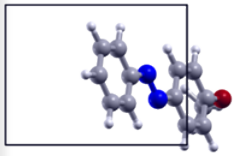
XAS of azobenzene SAMs

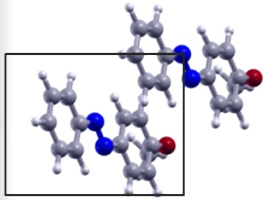
Impact of packing











Inclusion of excitonic effects

Mixing of transitions

Molecule

A': E_b ~ 6 eV

B' / C': E_b ~ 3.7 / 4.2 eV

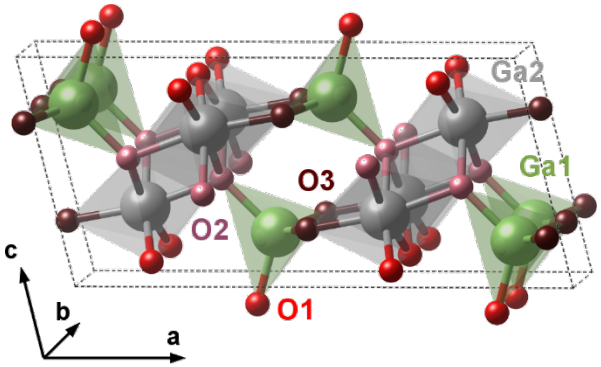
p-SAM

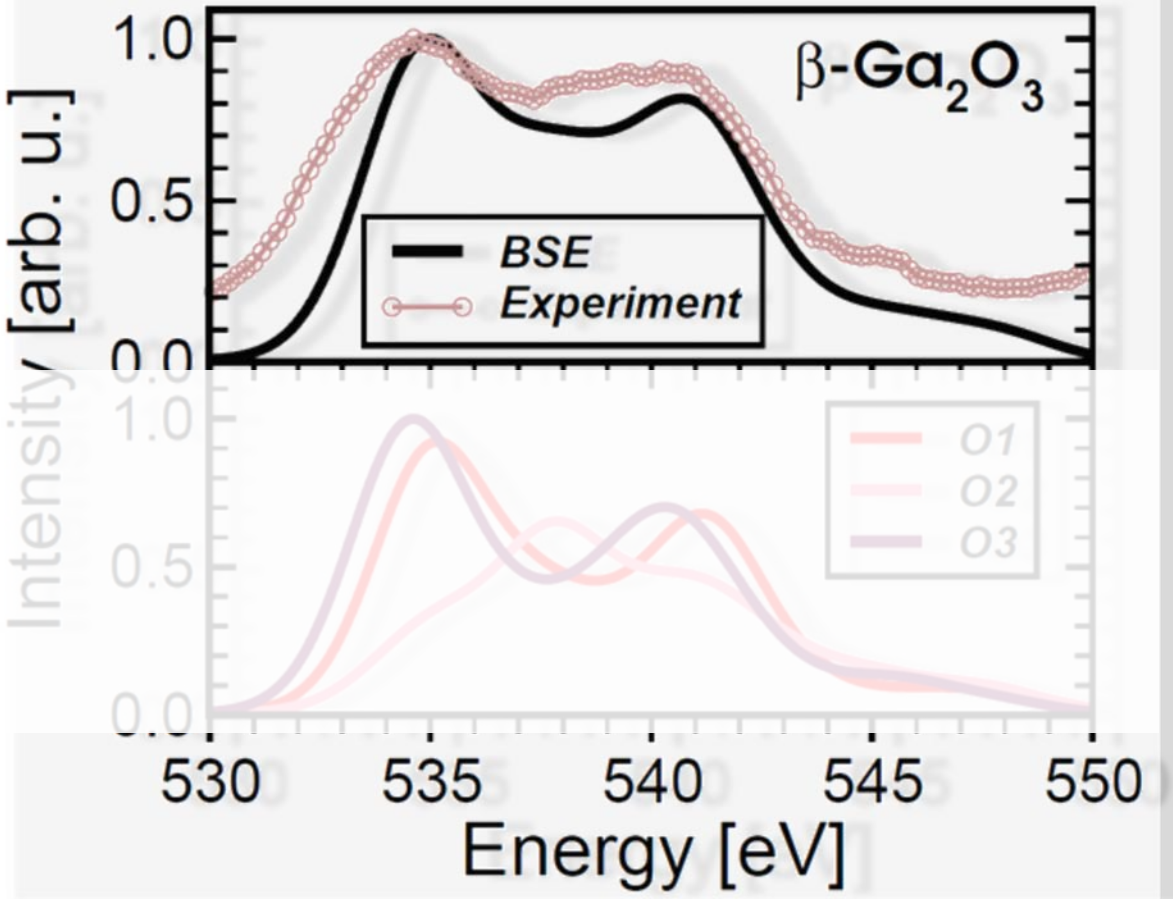
A': E_b ~ 4 eV

Structural fingerprints

Complementing ELNES experiments

O K edge in β-Ga_2O_3



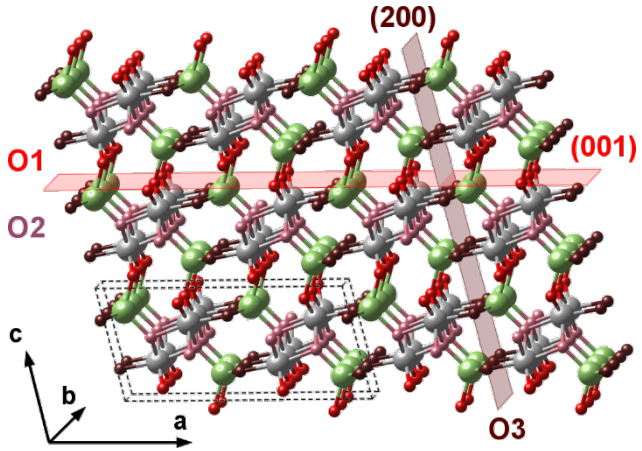


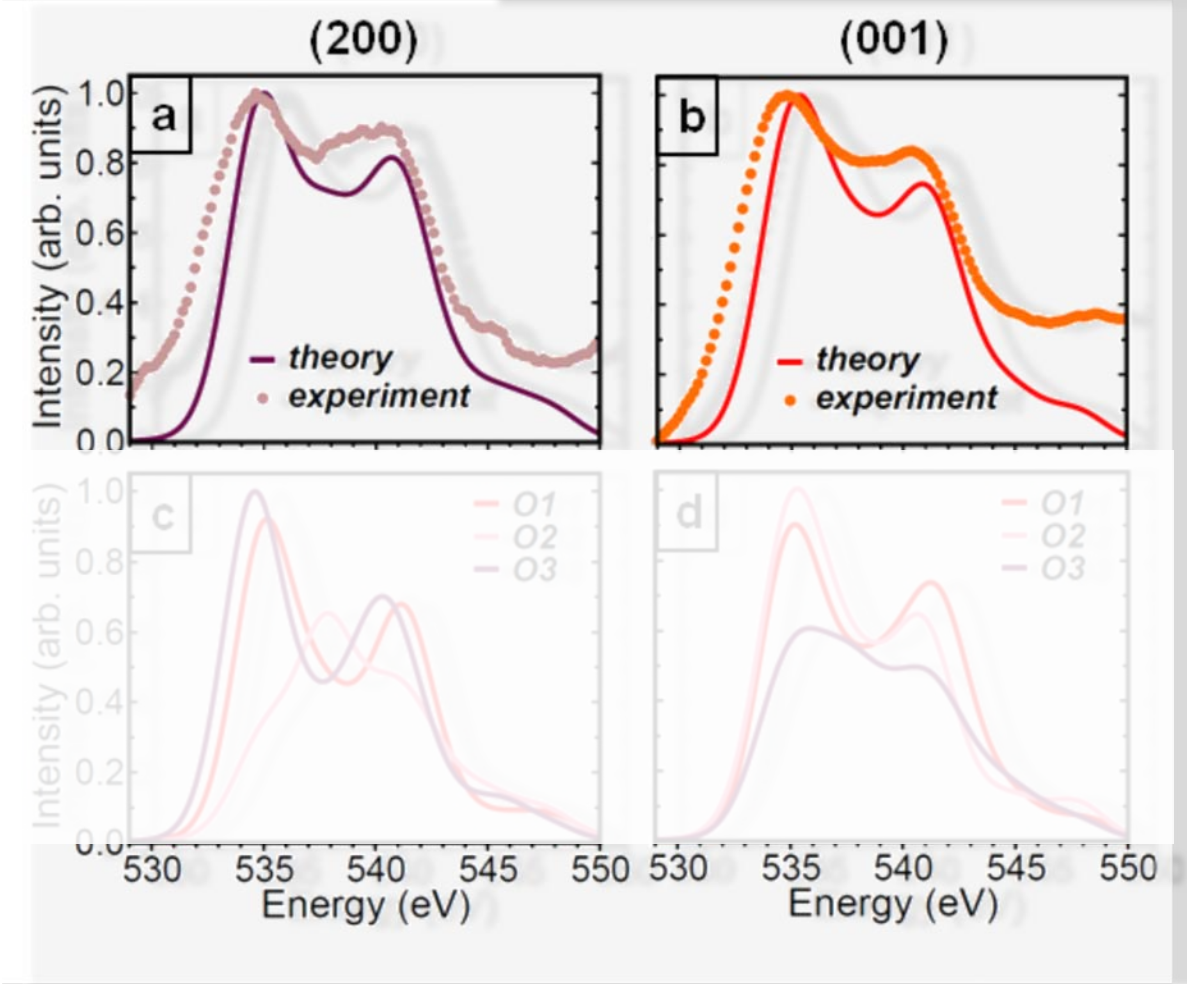
C. Cocchi et al., PRB (2016).

Structural fingerprints

Probing different index planes

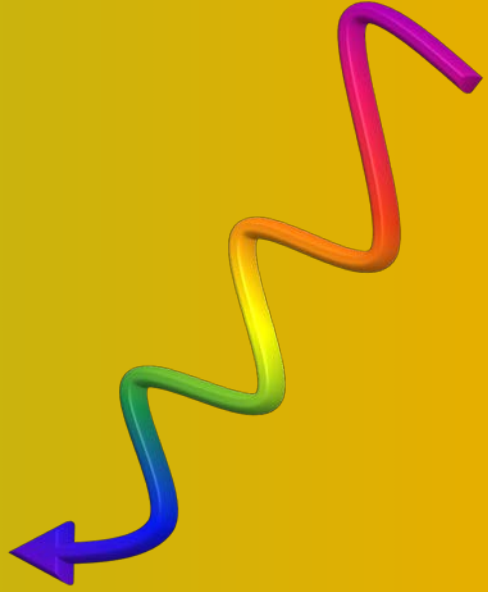
O K edge in β-Ga_2O_3





C. Vorwerk, C. Cocchi, and CD **Layer Optics**: Microscopic modeling of optical coeffcients in layered materials Comp. Phys. Commun. **201**, 119 (2016).

C. Cocchi et al., PRB (2016).



Tamm-Dancoff approximation

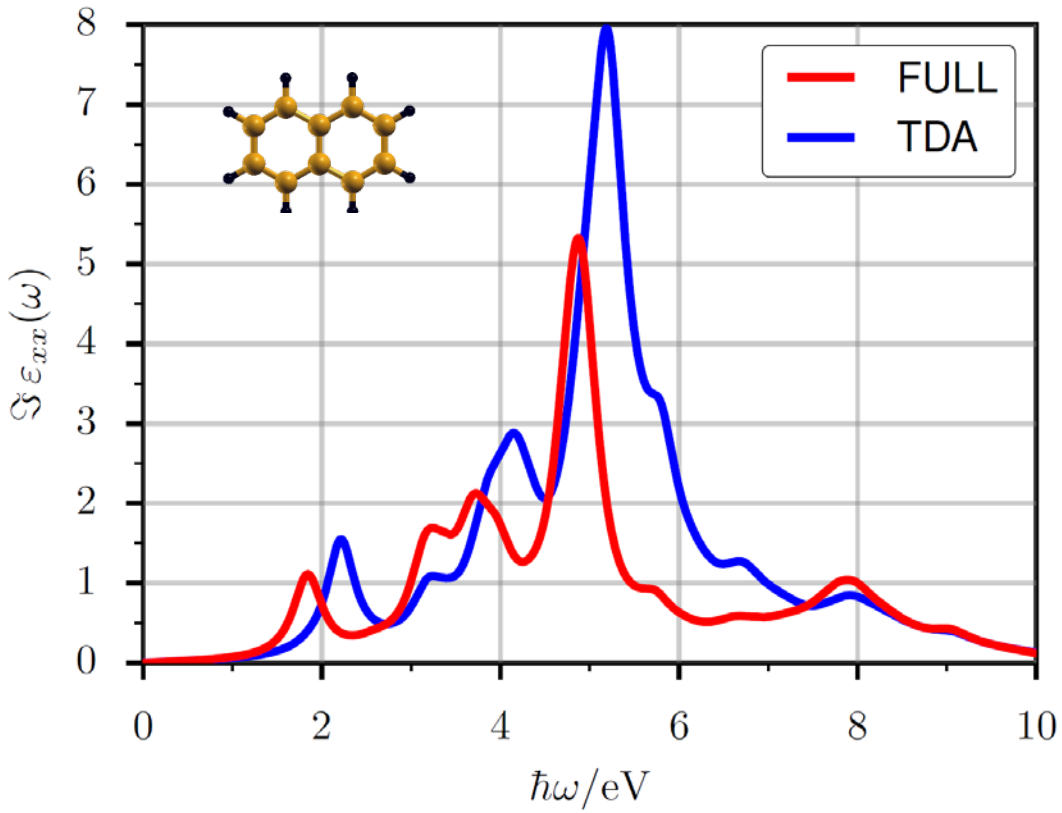
Beyond Tamm-Dancoff

resonant part, +ω

coupling term

$$H = \begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix}$$

anti-resonant part, - ω



C. Vorwerk, et al., Electronic Structure, **1**, 037001 (2019).

Our instrument ...

http://exciting-code.org

A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl

exciting: a full-potential all-electron package implementing density-functional theory and many-body perturbation theory
J. Phys: Condens. Matter 26, 363202 (2014).

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The exciting Code

exciting is a full-potential all-electron density-functional-theory package implementing the families of linearized augmented planewave methods. It can be applied to all kinds of materials, irrespective of the atomic species involved, and also allows for exploring the physics of core electrons. A particular focus are excited states within many-body perturbation theory.

A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl, "**exciting** — a full-potential all-electron package implementing density-functional theory and many-body perturbation theory", J. Phys.: Condens. Matter **26**, 363202 (2014)

Events

Download exciting

HoW exciting! Hands-on w

Developers Team

- exciting hub at the Humboldt Uni
- Current developers

Team work

Christian Vorwerk

Wahib Aggoune

Andris Gulans

Benjamin Aurich

Caterina Cocchi

Dmitrii Nabok

Data at NOMAD Repository - https://repository.nomad-coe.eu

NOMAD

THANKS !!