Revealing fingerprints of valence excitons in x-ray absorption spectra with Bethe-Salpeter equation

Nasrin Farahani, Daria Gorelova

I.Institute of theoretical Physics

August 8, 2023

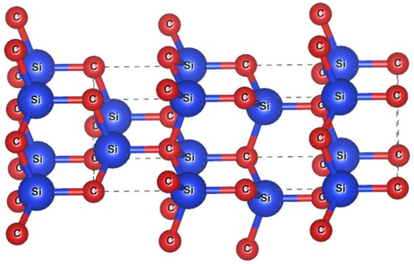
VolkswagenStiftung

Universität Hamburg

DER FORSCHUNG | DER LEHRE | DER BILDUNG

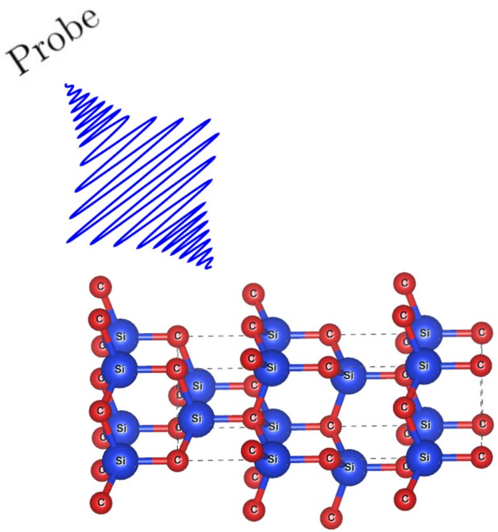
Motivation

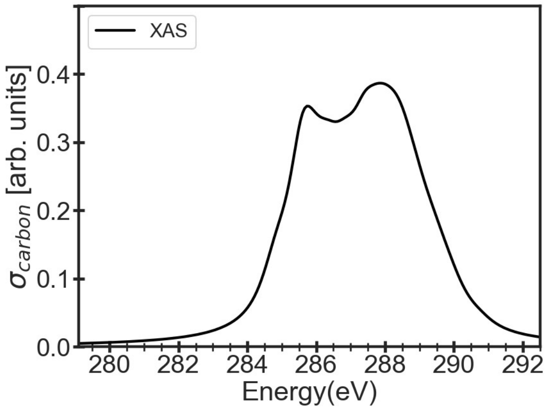
- Development an ab initio descrption of XAS experiment to probe valence-excitons in solids



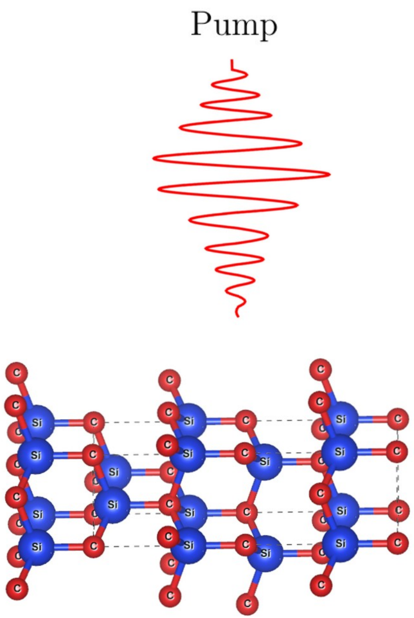
Motivation

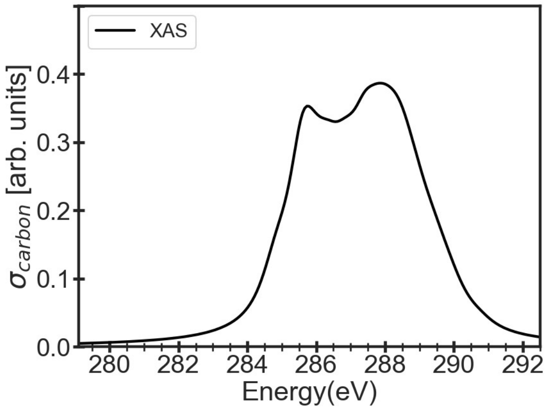
- Development an ab initio descrption of XAS experiment to probe valence-excitons in solids





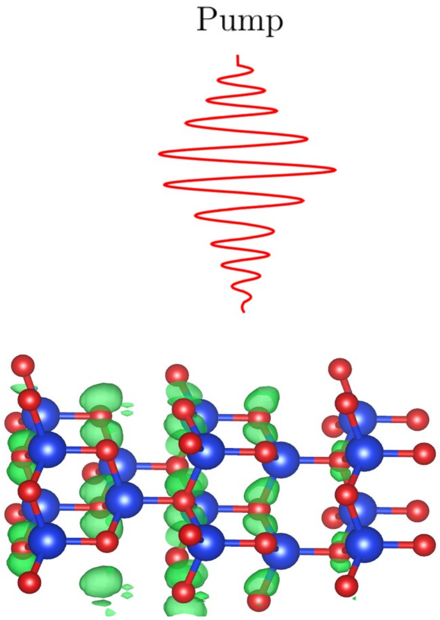
- Development an ab initio descrption of XAS experiment to probe valence-excitons in solids

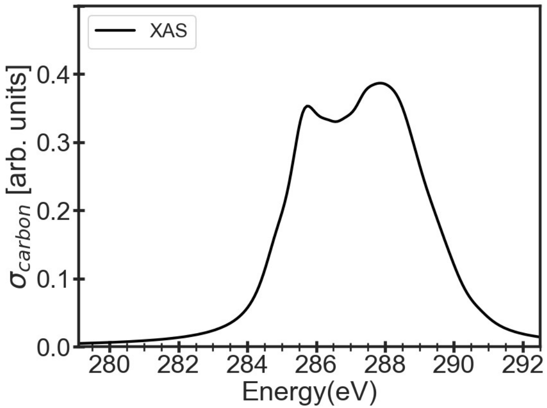




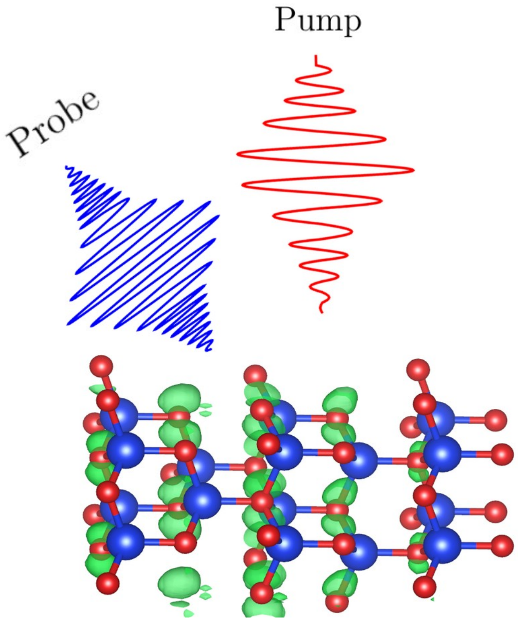
Motivation

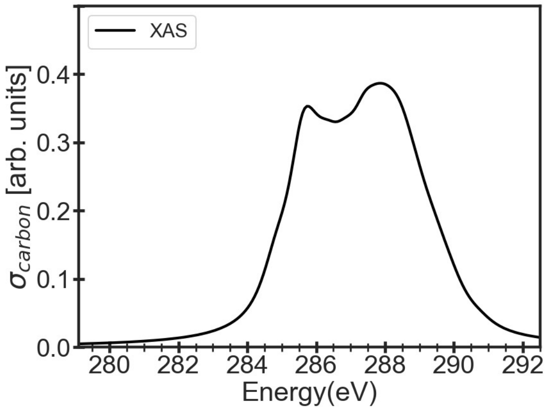
- Development an ab initio descrption of XAS experiment to probe valence-excitons in solids





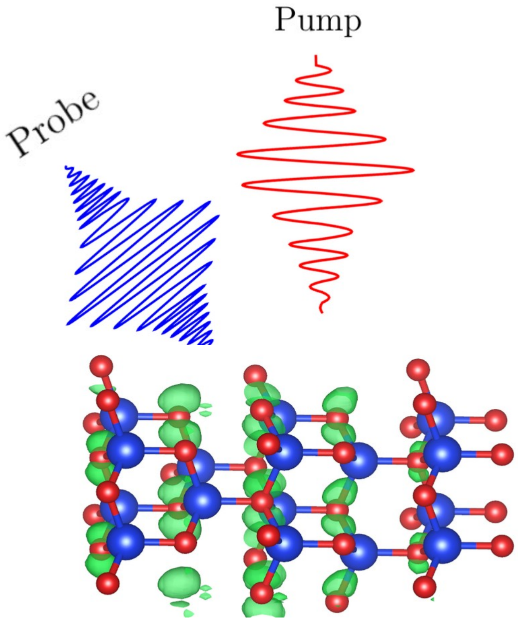
- Development an ab initio descrption of XAS experiment to probe valence-excitons in solids
- Strong need of theoretical modelling

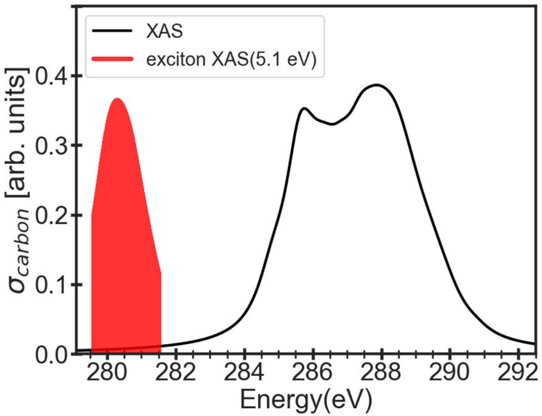




exciting

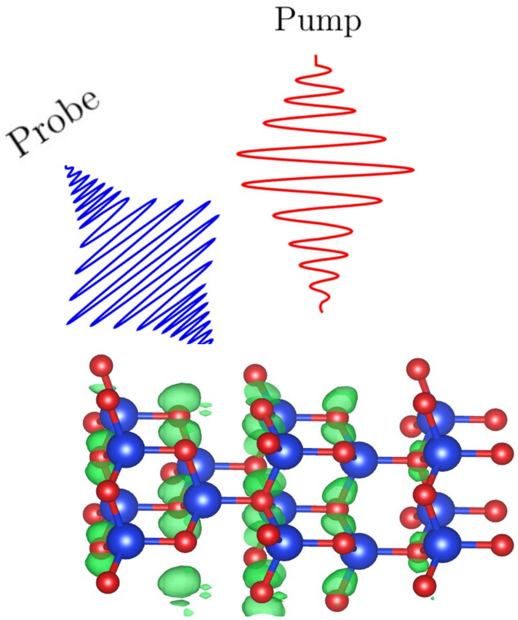
- Development an ab initio descrption of XAS experiment to probe valence-excitons in solids
- Strong need of theoretical modelling

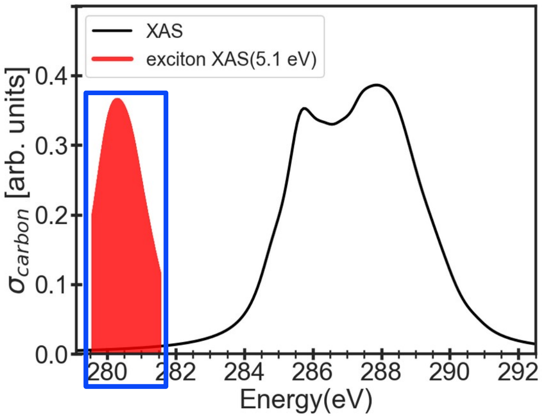




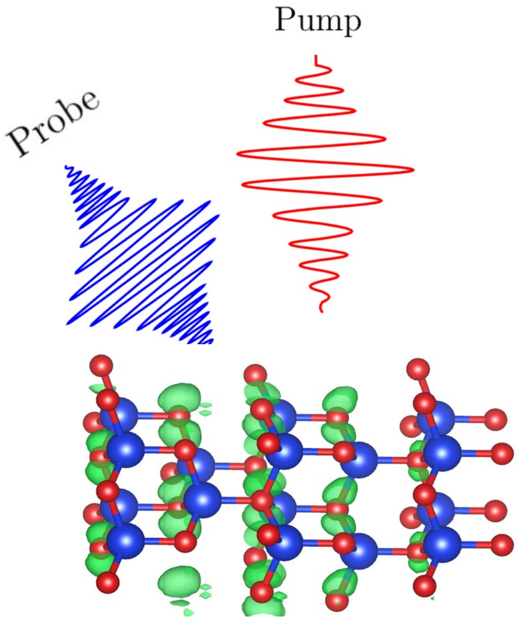
Motivation

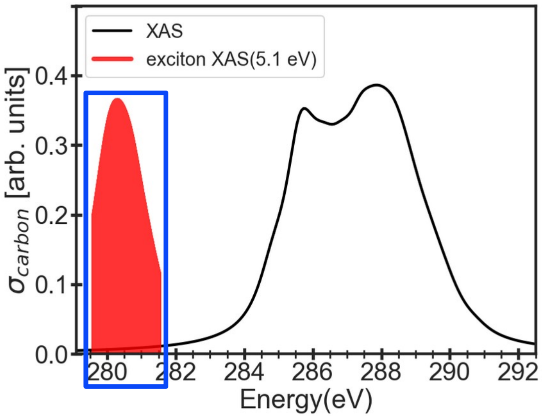
- Development an ab initio descrption of XAS experiment to probe valence-excitons in solids
- Strong need of theoretical modelling

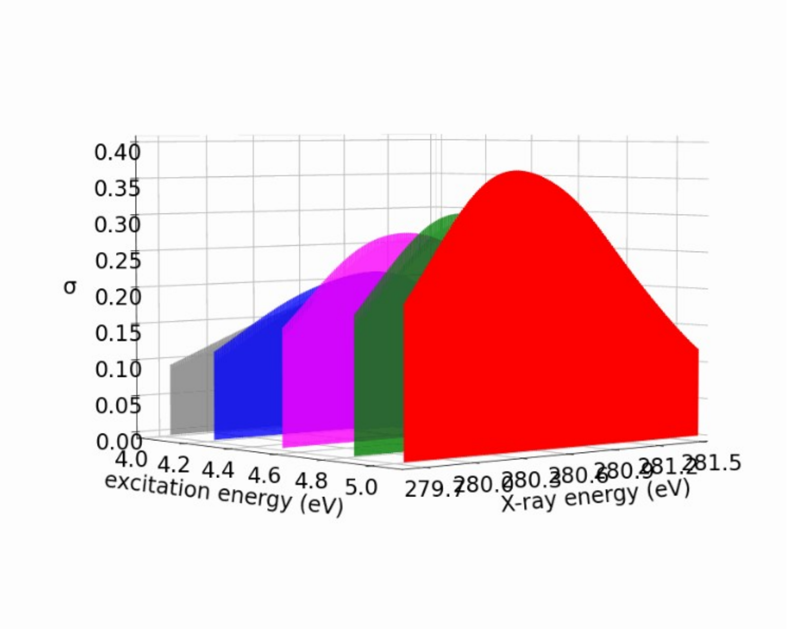




- Development an ab initio descrption of XAS experiment to probe valence-excitons in solids
- Strong need of theoretical modelling





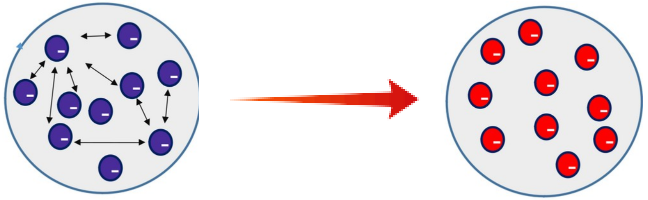


exciting

BSE+GW formalism

DFT

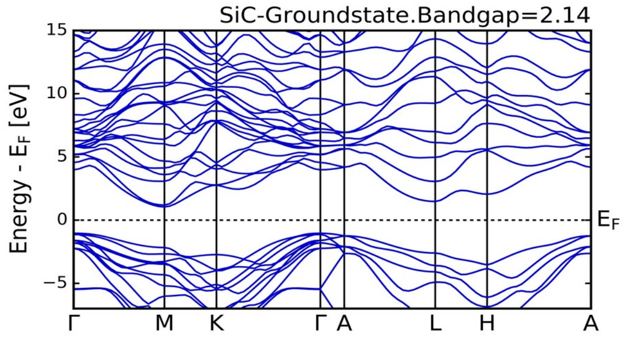
$$\{\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)\}\varphi_n^{KS}(r) = E_n^{KS}\varphi_n^{KS}(r)$$



BSE+GW formalism

DFT

$$\{\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)\}\varphi_n^{KS}(r) = E_n^{KS}\varphi_n^{KS}(r)$$

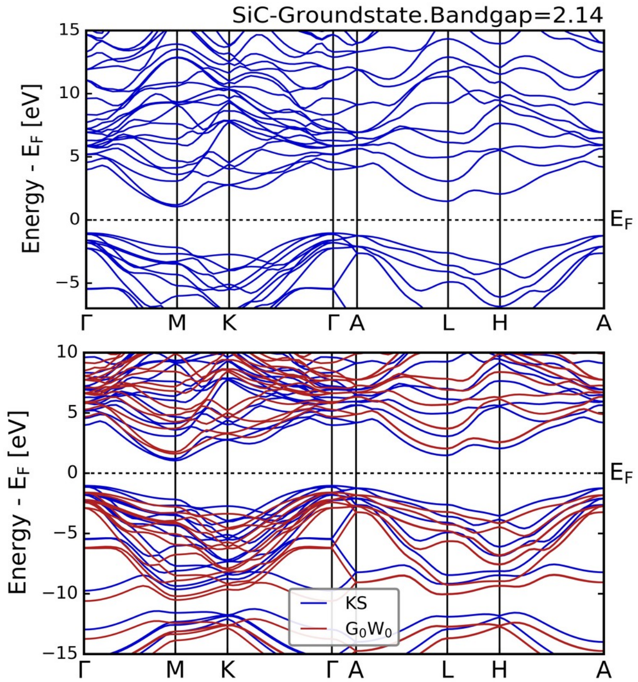


G_0W_0

$$\varepsilon^{QP} = \varepsilon^{KS} + \langle\varphi^{KS}|\Sigma - V_{xc}^{KS}|\varphi^{KS}\rangle$$

$$\{\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)\}\varphi_n^{KS}(r) = E_n^{KS}\varphi_n^{KS}(r)$$

$$\varepsilon^{QP} = \varepsilon^{KS} + \langle\varphi^{KS}|\Sigma - V_{xc}^{KS}|\varphi^{KS}\rangle$$



BSE+GW formalism

DFT

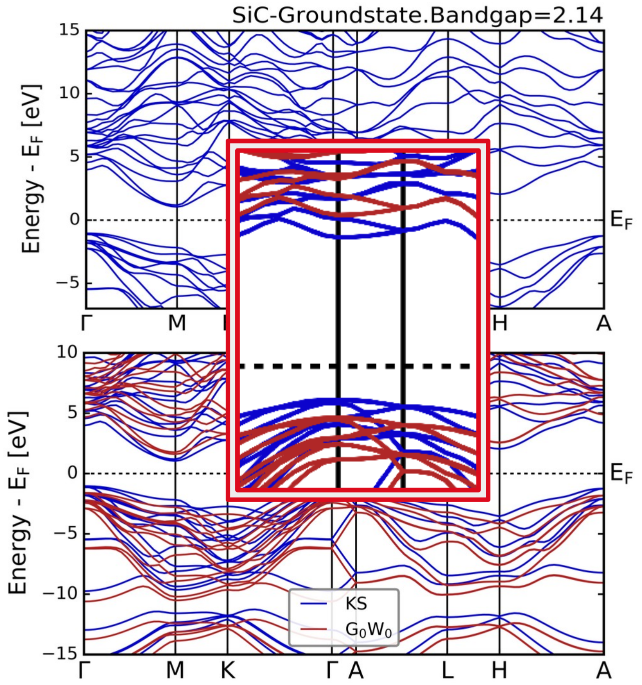
$$\{\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)\}\varphi_n^{KS}(r) = E_n^{KS}\varphi_n^{KS}(r)$$

G_0W_0

$$\varepsilon^{QP} = \varepsilon^{KS} + \langle\varphi^{KS}|\Sigma - V_{xc}^{KS}|\varphi^{KS}\rangle$$

BSE

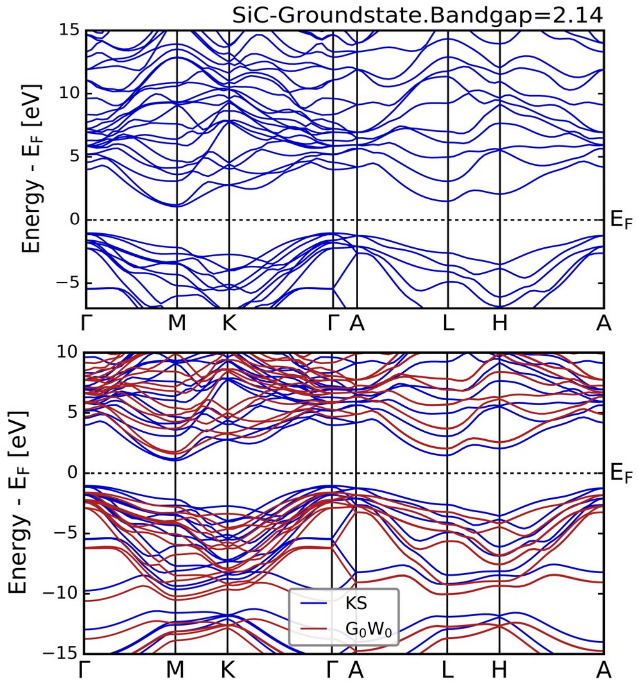
$$\{H_e + H_h + H_{e-h}\}A^\lambda = E^\lambda A^\lambda$$



$$\{\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)\}\varphi_n^{KS}(r) = E_n^{KS}\varphi_n^{KS}(r)$$

$$\varepsilon^{QP} = \varepsilon^{KS} + \langle\varphi^{KS}|\Sigma - V_{xc}^{KS}|\varphi^{KS}\rangle$$

$$\{H_e + H_h + H_{e-h}\}A^\lambda = E^\lambda A^\lambda$$



$$Im\varepsilon \sim \sum_{cv}\left|\frac{\langle c|\nabla|v\rangle}{\varepsilon_c - \varepsilon_v}\right|^2 \delta(\varepsilon_c - \varepsilon_v - \omega) \rightarrow Im\varepsilon \sim \sum_{\lambda}\sum_{cv}\left|\frac{\langle c|\nabla|v\rangle A_{cv}^\lambda}{\varepsilon_c - \varepsilon_v}\right|^2 \delta(E^\lambda - \omega)$$

BSE+GW formalism

DFT

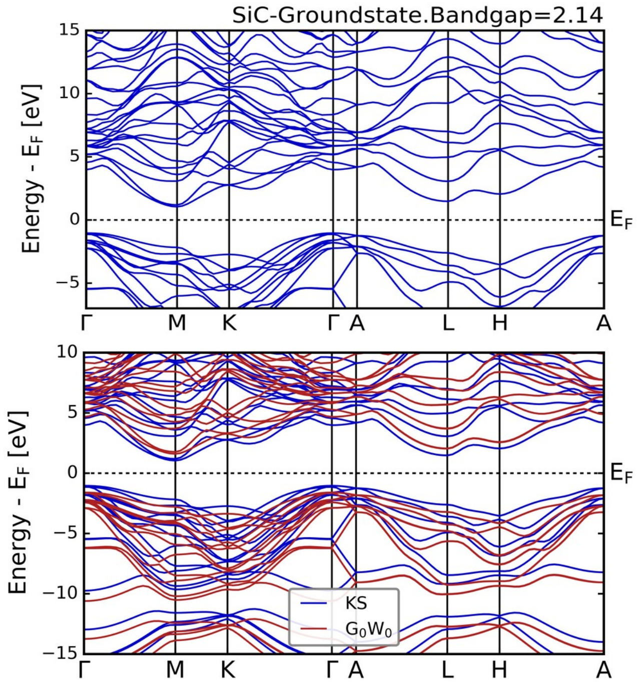
$$\{\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(r) + V_H(r) + V_{xc}(r)\}\varphi_n^{KS}(r) = E_n^{KS}\varphi_n^{KS}(r)$$

G_0W_0

$$\varepsilon^{QP} = \varepsilon^{KS} + \langle\varphi^{KS}|\Sigma - V_{xc}^{KS}|\varphi^{KS}\rangle$$

BSE

$$\{H_e + H_h + H_{e-h}\}A^\lambda = E^\lambda A^\lambda$$

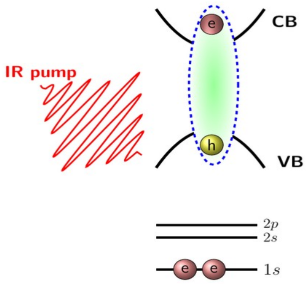


$$Im\varepsilon \sim \sum_{cv}\left|\frac{\langle c|\nabla|v\rangle}{\varepsilon_c - \varepsilon_v}\right|^2\delta(\varepsilon_c - \varepsilon_v - \omega) \rightarrow Im\varepsilon \sim \sum_{\lambda}\sum_{cv}\left|\frac{\langle c|\nabla|v\rangle A_{cv}^\lambda}{\varepsilon_c - \varepsilon_v}\right|^2\delta(E^\lambda - \omega)$$

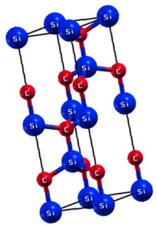
Step 1: **pump-pulse process**

exciting

- Imaging positive part of excitonic wave function



$$\phi_\lambda(r_e, r_h) = \sum_{cv} A^\lambda_{cv} \psi_{c(r_e)} \psi_v(r_h)$$

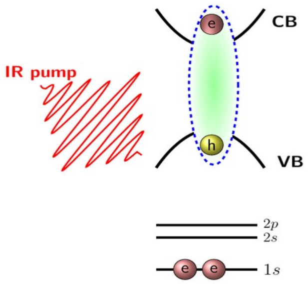


Why do we need to do BSE twice?

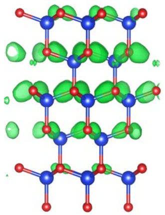
<u>*Step* 1</u>: **pump-pulse process**

exciting

- Imaging positive part of excitonic wave function



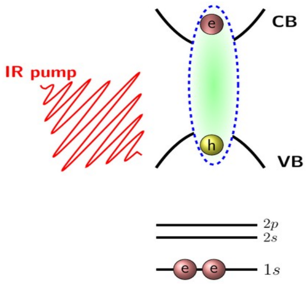
$$\phi_\lambda(r_e, r_h) = \sum_{cv} A^\lambda_{cv} \psi_{c(r_e)} \psi_v(r_h)$$



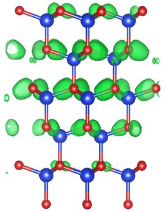
Why do we need to do BSE twice?

Step 1: **pump-pulse process**

- Imaging positive part of excitonic wave function

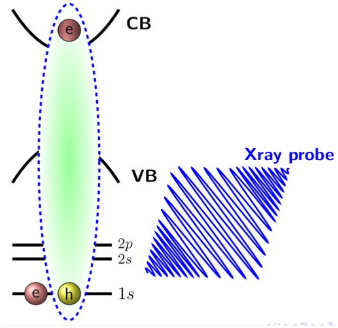


$$\phi_\lambda(r_e, r_h) = \sum_{cv} A^\lambda_{cv} \psi_{c(r_e)} \psi_v(r_h)$$



Step 2: **probe-pulse process**

- To describe core-excited states in carbon and silicon

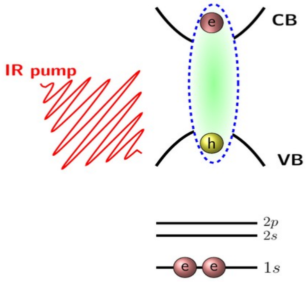


$$Im\varepsilon \sim \sum_\lambda \sum_{cv} \left| \frac{\langle c|\nabla|v\rangle A^\lambda_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E^\lambda - \omega)$$

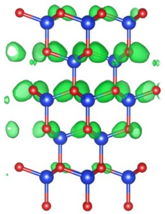
Why do we need to do BSE twice?

Step 1: **pump-pulse process**

- Imaging positive part of excitonic wave function

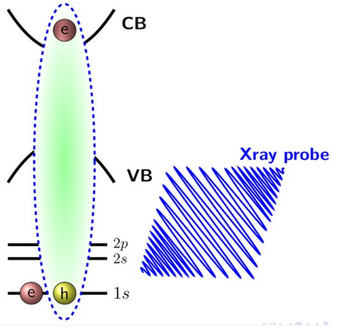


$$\phi_\lambda(r_e, r_h) = \sum_{cv} A^\lambda_{cv} \psi_{c(r_e)} \psi_v(r_h)$$

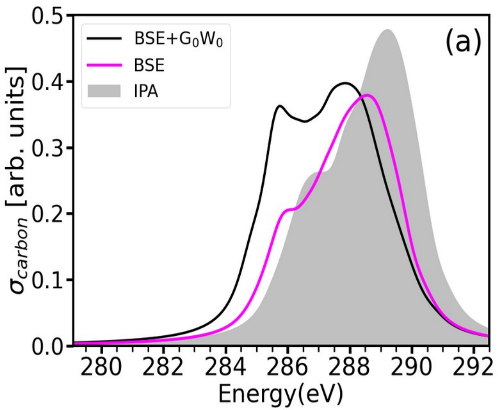


Step 2: **probe-pulse process**

- To describe core-excited states in carbon and silicon



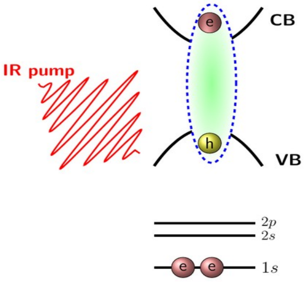
$$Im\varepsilon \sim \sum_\lambda \sum_{cv} \left| \frac{\langle c|\nabla|v\rangle A^\lambda_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E^\lambda - \omega)$$



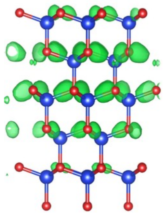
Why do we need to do BSE twice?

Step 1: **pump-pulse process**

- Imaging positive part of excitonic wave function

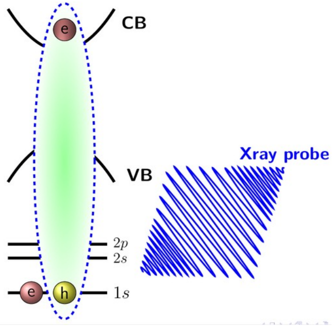


$$\phi_\lambda(r_e, r_h) = \sum_{cv} A^\lambda_{cv} \psi_{c(r_e)} \psi_v(r_h)$$

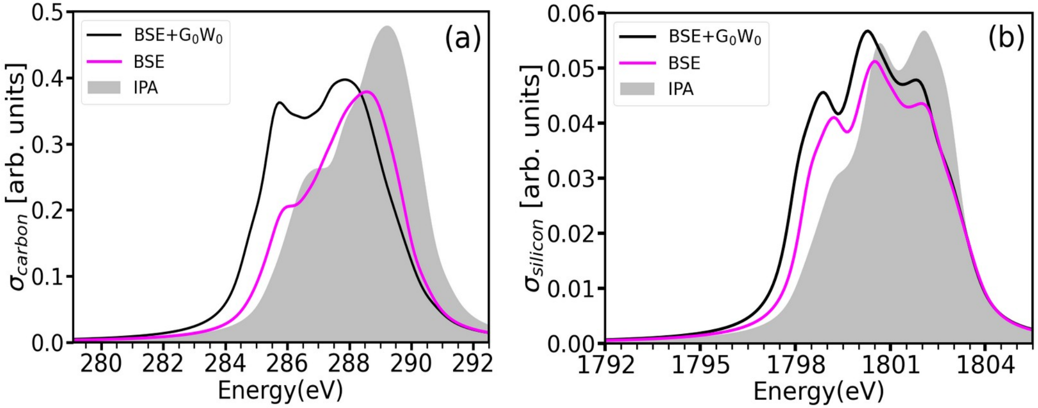


Step 2: **probe-pulse process**

- To describe core-excited states in carbon and silicon



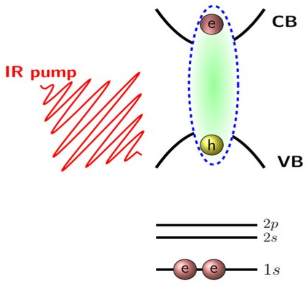
$$Im\varepsilon \sim \sum_\lambda \sum_{cv} \left| \frac{\langle c|\nabla|v\rangle A^\lambda_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E^\lambda - \omega)$$



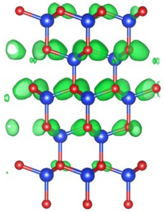
Why do we need to do BSE twice?

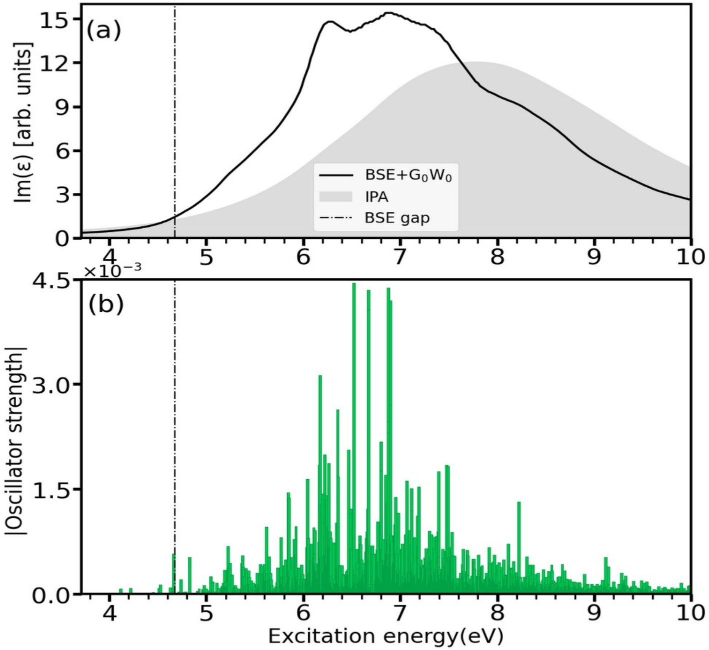
Step 1: **pump-pulse process**

- Imaging positive part of excitonic wave function



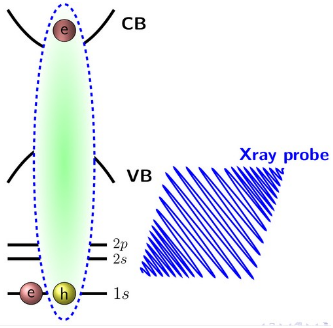
$$\phi_\lambda(r_e, r_h) = \sum_{cv} A^\lambda_{cv} \psi_{c(r_e)} \psi_v(r_h)$$



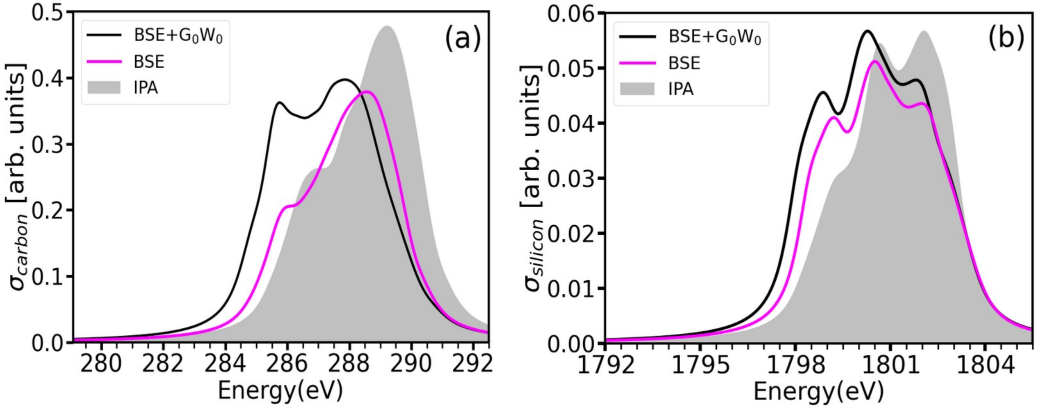


Step 2: **probe-pulse process**

- To describe core-excited states in carbon and silicon



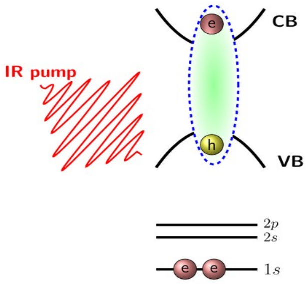
$$Im\varepsilon \sim \sum_\lambda \sum_{cv} \left| \frac{\langle c|\nabla|v\rangle A^\lambda_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E^\lambda - \omega)$$



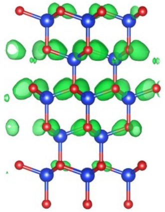
Why do we need to do BSE twice?

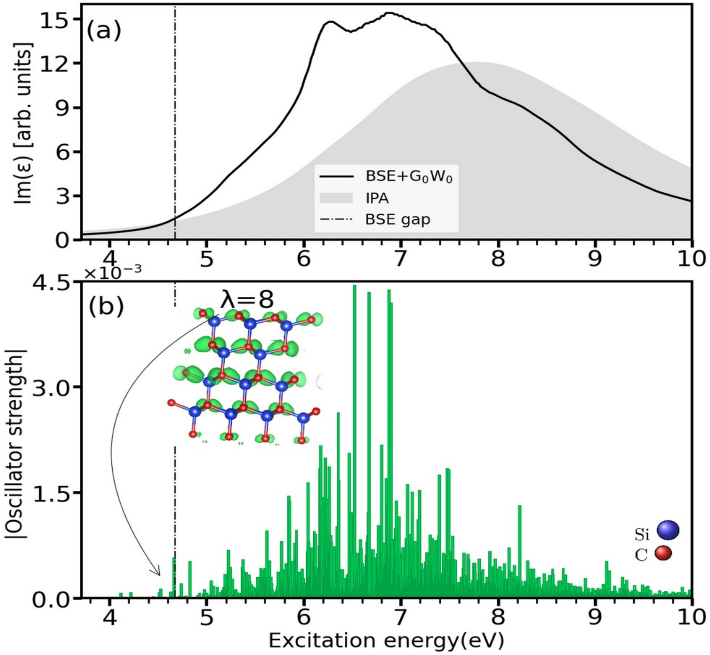
Step 1: pump-pulse process

- Imaging positive part of excitonic wave function



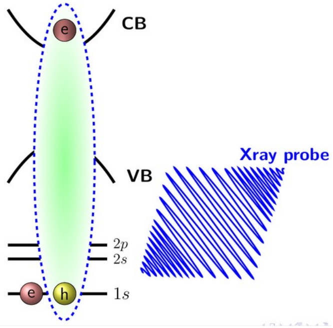
$$\phi_\lambda(r_e, r_h) = \sum_{cv} A^\lambda_{cv} \psi_{c(r_e)} \psi_v(r_h)$$



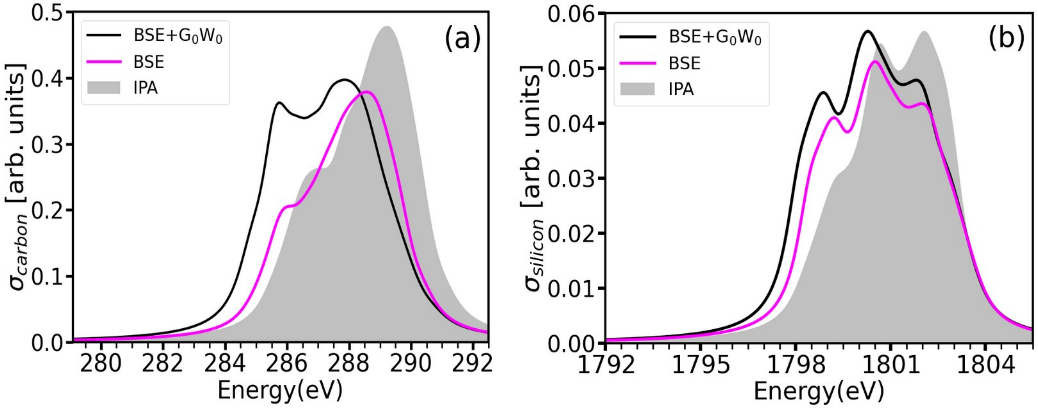


Step 2: probe-pulse process

- To describe core-excited states in carbon and silicon



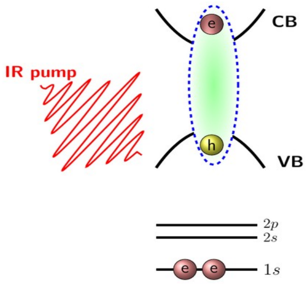
$$Im\varepsilon \sim \sum_\lambda \sum_{cv} \left| \frac{\langle c|\nabla|v\rangle A^\lambda_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E^\lambda - \omega)$$



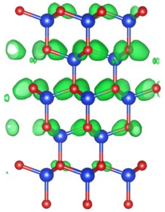
Why do we need to do BSE twice?

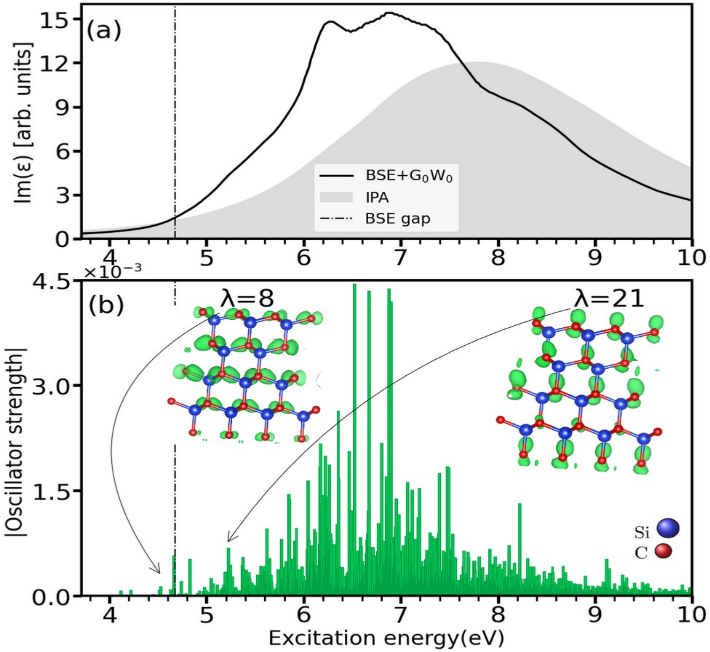
Step 1**: pump-pulse process**

- Imaging positive part of excitonic wave function



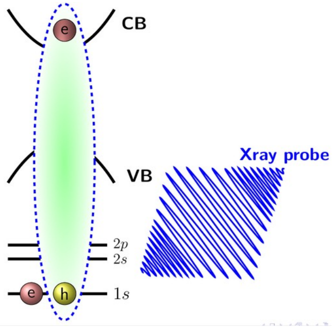
$$\phi_\lambda(r_e, r_h) = \sum_{cv} A^\lambda_{cv} \psi_{c(r_e)} \psi_v(r_h)$$



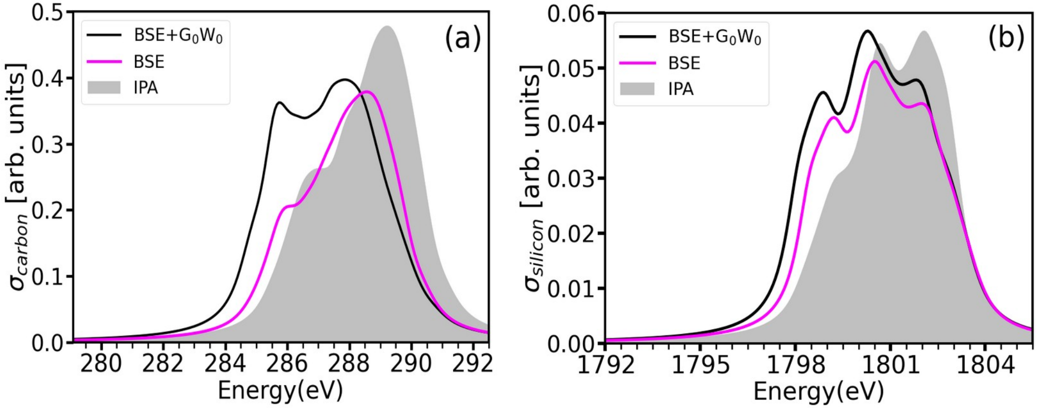


Step 2**: probe-pulse process**

- To describe core-excited states in carbon and silicon



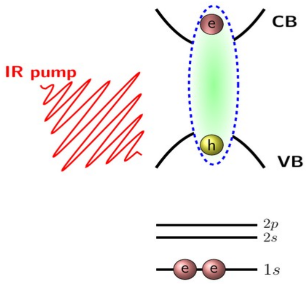
$$Im\varepsilon \sim \sum_\lambda \sum_{cv} \left| \frac{\langle c|\nabla|v\rangle A^\lambda_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E^\lambda - \omega)$$



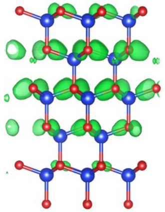
Why do we need to do BSE twice?

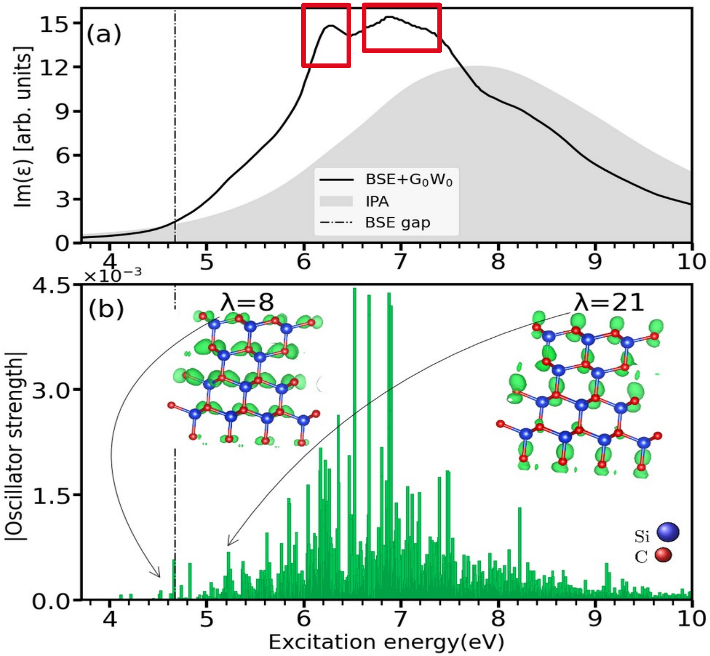
Step 1: **pump-pulse process**

- Imaging positive part of excitonic wave function



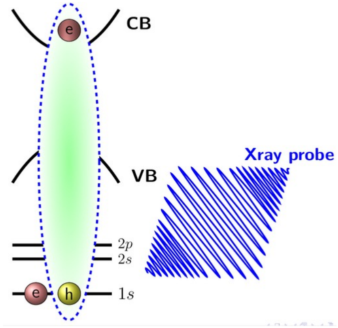
$$\phi_\lambda(r_e, r_h) = \sum_{cv} A^\lambda_{cv} \psi_{c(r_e)} \psi_v(r_h)$$



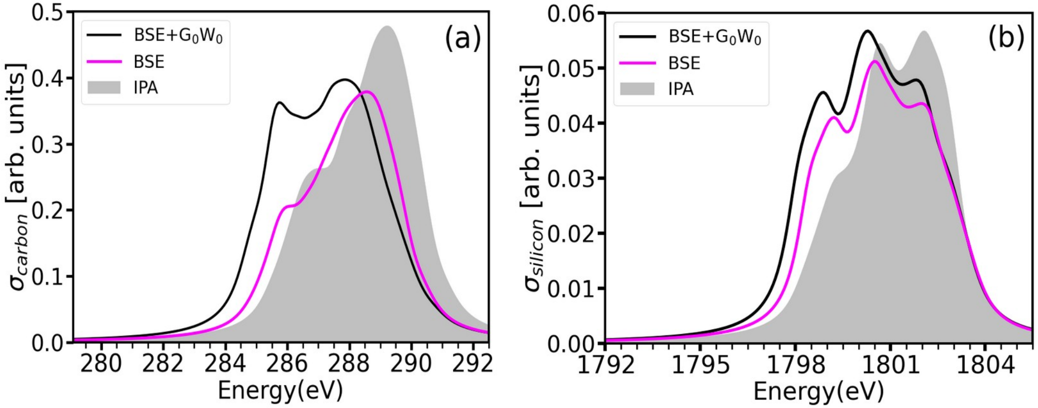


Step 2: **probe-pulse process**

- To describe core-excited states in carbon and silicon



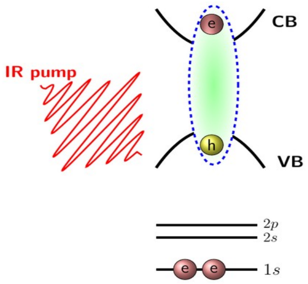
$$Im\varepsilon \sim \sum_\lambda \sum_{cv} \left| \frac{\langle c|\nabla|v\rangle A^\lambda_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E^\lambda - \omega)$$



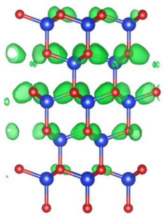
Why do we need to do BSE twice?

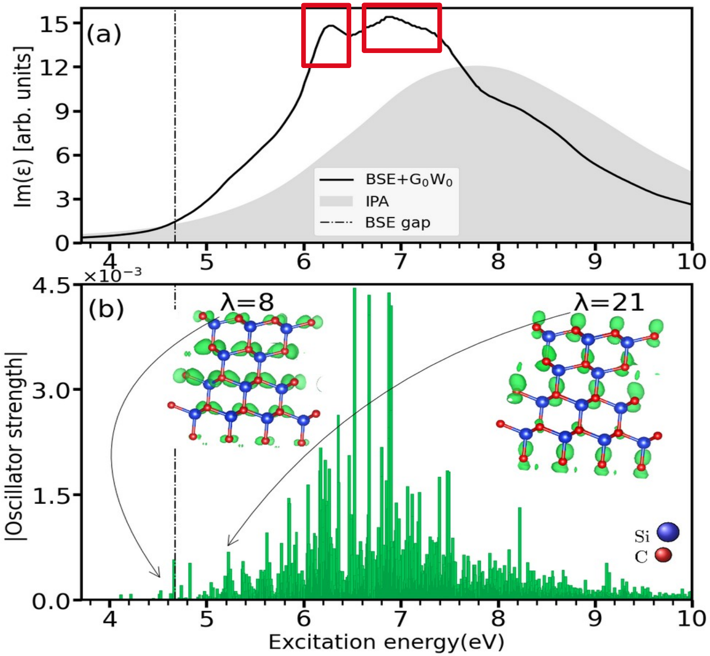
Step 1: **pump-pulse process**

- Imaging positive part of excitonic wave function



$$\phi_\lambda(r_e, r_h) = \sum_{cv} A^\lambda_{cv}\psi_{c(r_e)}\psi_v(r_h)$$

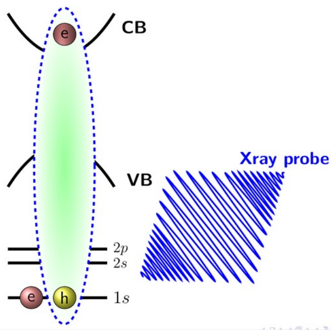




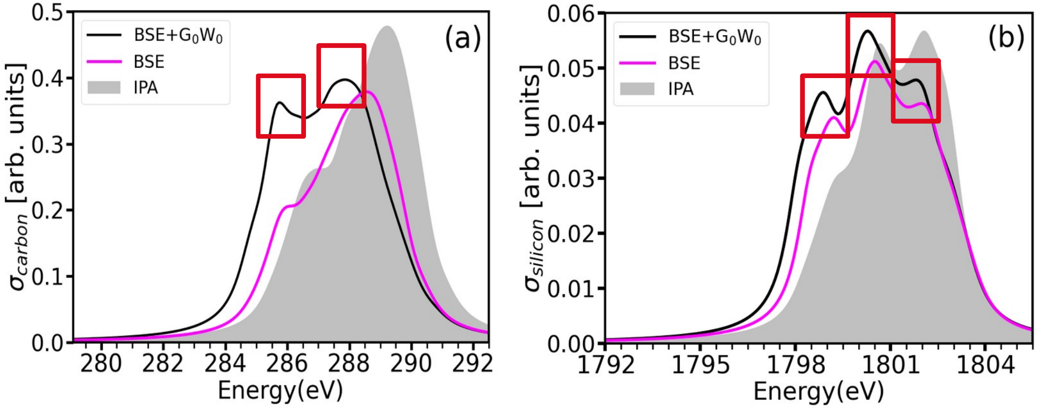
exciting

Step 2: **probe-pulse process**

- To describe core-excited states in carbon and silicon



$$Im\varepsilon \sim \sum_\lambda \sum_{cv} \left| \frac{\langle c|\nabla|v\rangle A^\lambda_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E^\lambda - \omega)$$



Pump+Probe process

Theoretical approach

- Valence exciton BSE calculations
- Core exciton BSE calculations
- Combination in our code

$$\sigma_F(\omega_I,\omega_F) = \frac{4\pi^2}{\omega_F-\omega_I}\alpha \times \left|\sum_{\mathbf{p},\mathbf{q}} \langle\varphi_{\mathbf{p}}|\mathbf{e}^{\mathbf{ik.x}}\epsilon_{\mathbf{k},\lambda_{\mathbf{in}}}.\frac{\nabla}{\mathbf{i}}|\varphi_{\mathbf{q}}\rangle\langle\Psi_F^{N_{el}}|\hat{c}_p^\dagger\hat{c}_q|\Psi_0^{N_{el}}\rangle\right|^2 \delta(\omega_F-(E_F^{\lambda_F}-E_0^{\lambda_I}))$$

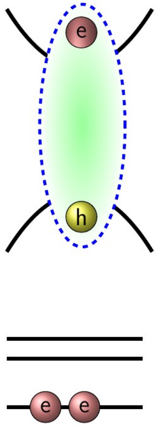
Robin Santra 2009 J. Phys. B: At. Mol. Opt. Phys. 42 023001

Pump+Probe process

Theoretical approach

- ✔ Valence exciton BSE calculations
- ☐ Core exciton BSE calculations
- ☐ Combination in our code

initial state

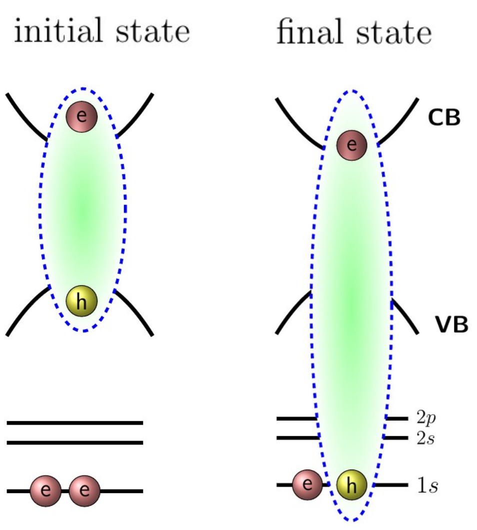


$$\Psi_0^{N_{el}} = A^{\lambda_I}_{c,v}|\hat{c}_c^\dagger\, \hat{c}_v\rangle$$

$$\sigma_F(\omega_I,\omega_F) = \frac{4\pi^2}{\omega_F-\omega_I}\alpha \times \left| \sum_{\mathbf{p},\mathbf{q}} \langle \varphi_{\mathbf{p}}| \mathbf{e}^{\mathbf{ik.x}} \epsilon_{\mathbf{k},\lambda_{\mathbf{in}}} \cdot \frac{\nabla}{\mathbf{i}} |\varphi_{\mathbf{q}}\rangle \langle \Psi_F^{N_{el}}|\hat{c}_p^\dagger \hat{c}_q|\Psi_0^{N_{el}}\rangle \right|^2 \delta(\omega_F - (E_F^{\lambda_F}-E_0^{\lambda_I}))$$

Theoretical approach

- [x] Valence exciton BSE calculations
- [x] Core exciton BSE calculations
- [ ] Combination in our code

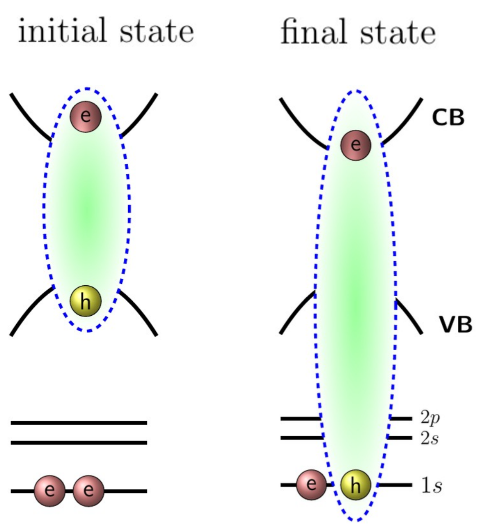


$$\Psi_0^{N_{el}} = A^{\lambda_I}_{c,v} |\hat{c}_c^\dagger \hat{c}_v\rangle \qquad \Psi_F^{N_{el}} = A^{*\lambda_F}_{c,\mu} |\hat{c}_c^\dagger \hat{c}_\mu\rangle$$

$$\sigma_F(\omega_I, \omega_F) = \frac{4\pi^2}{\omega_F - \omega_I}\alpha \times \left| \sum_{\mathbf{p},\mathbf{q}} \langle \varphi_{\mathbf{p}} | \mathbf{e}^{\mathbf{ik.x}} \epsilon_{\mathbf{k},\lambda_{\mathbf{in}}} \cdot \frac{\nabla}{\mathbf{i}} | \varphi_{\mathbf{q}} \rangle \langle \Psi_F^{N_{el}} | \hat{c}_p^\dagger \hat{c}_q | \Psi_0^{N_{el}} \rangle \right|^2 \delta(\omega_F - (E_F^{\lambda_F} - E_0^{\lambda_I}))$$

Theoretical approach

- Valence exciton BSE calculations
- Core exciton BSE calculations
- Combination in our code



$\Psi_0^{N_{el}} = A_{c,v}^{\lambda_I} |\hat{c_c^\dagger}\, \hat{c_v}\rangle$

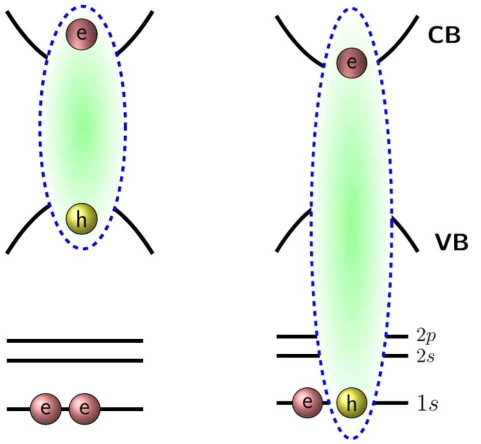
$\Psi_F^{N_{el}} = A_{c,\mu}^{*\lambda_F} |\hat{c_c^\dagger}\, \hat{c_\mu}\rangle$

$$\sigma_F(\omega_I, \omega_F) = \frac{4\pi^2}{\omega_F - \omega_I}\alpha \times \left| \sum_{\mathbf{p},\mathbf{q}} \langle \varphi_\mathbf{p} | \mathbf{e}^{\mathbf{ik}.\mathbf{x}} \epsilon_{\mathbf{k},\lambda_{\mathbf{in}}} . \frac{\nabla}{\mathbf{i}} | \varphi_\mathbf{q} \rangle \langle \Psi_F^{N_{el}} | \hat{c}_p^\dagger \hat{c}_q | \Psi_0^{N_{el}} \rangle \right|^2 \delta(\omega_F - (E_F^{\lambda_F} - E_0^{\lambda_I}))$$

Theoretical approach

- Valence exciton BSE calculations
- Core exciton BSE calculations
- Combination in our code

initial state | final state



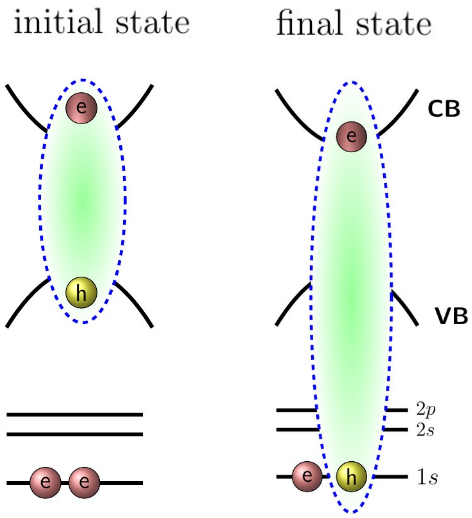
$\Psi_0^{N_{el}} = A^{\lambda_I}_{c,v}|\hat{c}_c^\dagger \; \hat{c}_v\rangle$ $\quad$ $\Psi_F^{N_{el}} = A^{*\lambda_F}_{c,\mu}|\hat{c}_c^\dagger \; \hat{c}_\mu\rangle$

$$\sigma_F(\omega_I,\omega_F) = \frac{4\pi^2}{\omega_F-\omega_I}\alpha \times \left|\sum_{\mathbf{p},\mathbf{q}} \langle\varphi_\mathbf{p}|\mathbf{e}^{\mathbf{ik.x}}\epsilon_{\mathbf{k},\lambda_{\mathbf{in}}}\cdot\frac{\nabla}{\mathbf{i}}|\varphi_\mathbf{q}\rangle\langle\Psi_F^{N_{el}}|\hat{c}_p^\dagger \hat{c}_q|\Psi_0^{N_{el}}\rangle\right|^2 \delta(\omega_F-(E_F^{\lambda_F}-E_0^{\lambda_I}))$$

$$\sigma(\omega_I,\omega_F)=\frac{4\pi^2}{\omega_F-\omega_I}\alpha\times Im\sum_{\lambda_I,\lambda_F}\frac{\left|\sum_{v\mu k}\langle\varphi_{vk}|e^{ik.x}\epsilon_{k,\lambda_{in}}\cdot\frac{\nabla}{i}|\varphi_{\mu k}\rangle\sum_c A^{*\lambda_F}_{c\mu k}\;A^{\lambda_I}_{cvk}\right|^2}{(\omega_F-(E_F^{\lambda_F}-E_0^{\lambda_I}))-i\Gamma}$$

Theoretical approach

- ☑ Valence exciton BSE calculations
- ☑ Core exciton BSE calculations
- ☑ Combination in our code



$$\Psi_0^{N_{el}} = A_{c,v}^{\lambda_I} | \hat{c}_c^\dagger \, \hat{c}_v \rangle \qquad \Psi_F^{N_{el}} = A_{c,\mu}^{*\lambda_F} | \hat{c}_c^\dagger \, \hat{c}_\mu \rangle$$

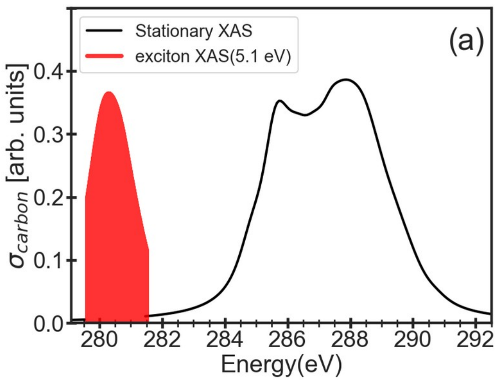
$$\sigma_F(\omega_I, \omega_F) = \frac{4\pi^2}{\omega_F - \omega_I} \alpha \times \left| \sum_{\mathbf{p},\mathbf{q}} \langle \varphi_\mathbf{p} | \mathbf{e}^{\mathbf{ik.x}} \epsilon_{\mathbf{k},\lambda_{\mathbf{in}}} \cdot \frac{\nabla}{\mathbf{i}} | \varphi_\mathbf{q} \rangle \langle \Psi_F^{N_{el}} | \hat{c}_p^\dagger \hat{c}_q | \Psi_0^{N_{el}} \rangle \right|^2 \delta(\omega_F - (E_F^{\lambda_F} - E_0^{\lambda_I}))$$

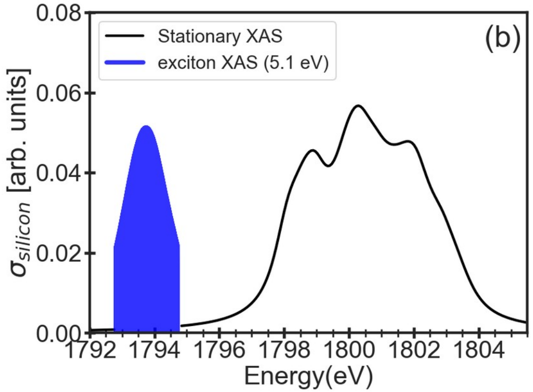
$$\sigma(\omega_I, \omega_F) = \frac{4\pi^2}{\omega_F - \omega_I} \alpha \times Im \sum_{\lambda_I, \lambda_F} \frac{\left| \sum_{v\mu k} \langle \varphi_{vk} | e^{ik.x} \epsilon_{k,\lambda_{in}} \cdot \frac{\nabla}{i} | \varphi_{\mu k} \rangle \sum_c A_{c\mu k}^{*\lambda_F} \; A_{cvk}^{\lambda_I} \right|^2}{(\omega_F - (E_F^{\lambda_F} - E_0^{\lambda_I})) - i\Gamma}$$

Robin Santra 2009 J. Phys. B: At. Mol. Opt. Phys. 42 023001

Developing code

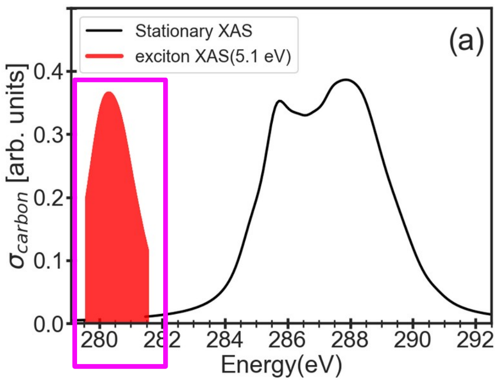
$$\sigma(\omega_I,\omega_F) = \frac{4\pi^2}{\omega_F-\omega_I}\,\alpha\times Im\sum_{\lambda_I,\lambda_F}\frac{\left|\sum_{v\mu k}\langle\varphi_{vk}|e^{ik.x}\epsilon_{k,\lambda_{in}}.\frac{\nabla}{i}|\varphi_{\mu k}\rangle\sum_c A^{*\lambda_F}_{c\mu k}\;\;A^{\lambda_I}_{cvk}\right|^2}{(\omega_F-(E_F^{\lambda_F}-E_0^{\lambda_I}))-i\Gamma}$$

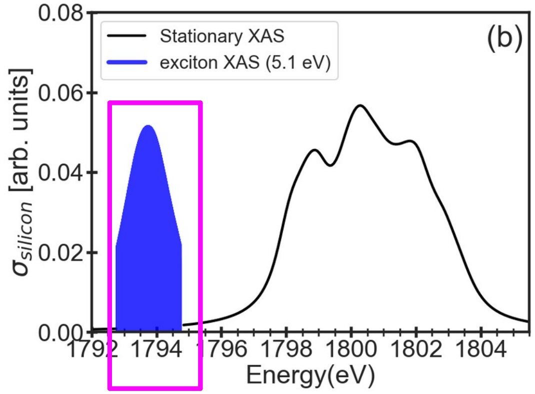




Developing code

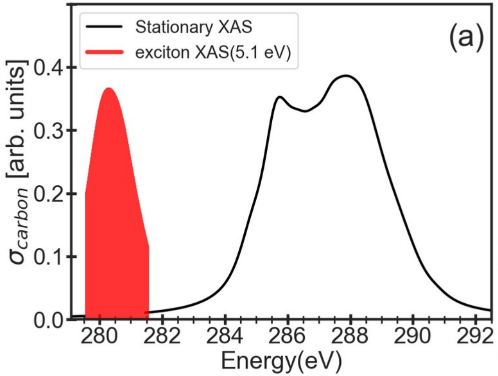
$$\sigma(\omega_I,\omega_F) = \frac{4\pi^2}{\omega_F-\omega_I}\,\alpha \times Im\sum_{\lambda_I,\lambda_F}\frac{\left|\sum_{v\mu k}\langle\varphi_{vk}|e^{ik.x}\epsilon_{k,\lambda_{in}}.\frac{\nabla}{i}|\varphi_{\mu k}\rangle\sum_c A^{*\lambda_F}_{c\mu k}\;\;A^{\lambda_I}_{cvk}\right|^2}{(\omega_F-(E_F^{\lambda_F}-E_0^{\lambda_I}))-i\Gamma}$$

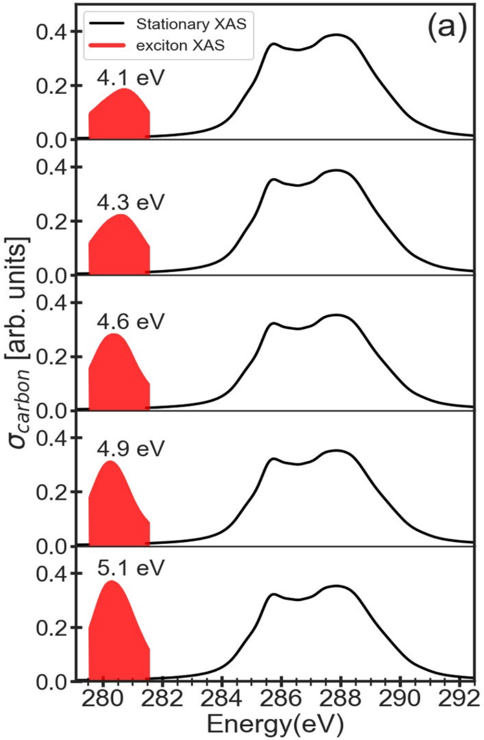


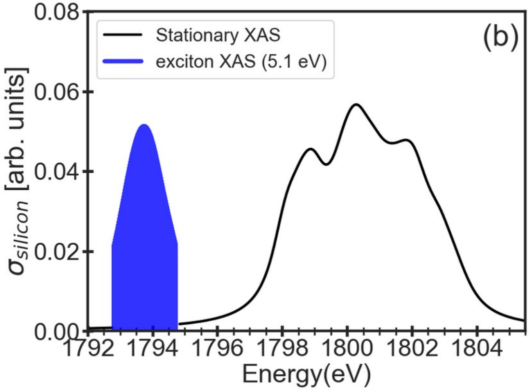


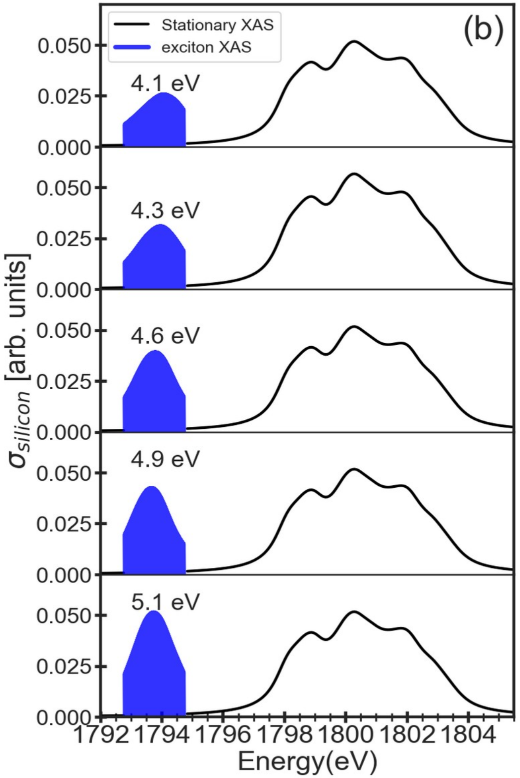
Developing code

$$\sigma(\omega_I,\omega_F) = \frac{4\pi^2}{\omega_F-\omega_I}\,\alpha \times Im \sum_{\lambda_I,\lambda_F} \frac{\left| \sum_{v\mu k} \langle \varphi_{vk} | e^{ik.x} \epsilon_{k,\lambda_{in}} . \frac{\nabla}{i} | \varphi_{\mu k} \rangle \sum_c A^{*\lambda_F}_{c\mu k} \;\; A^{\lambda_I}_{cvk} \right|^2}{(\omega_F - (E^{\lambda_F}_F - E^{\lambda_I}_0)) - i\Gamma}$$





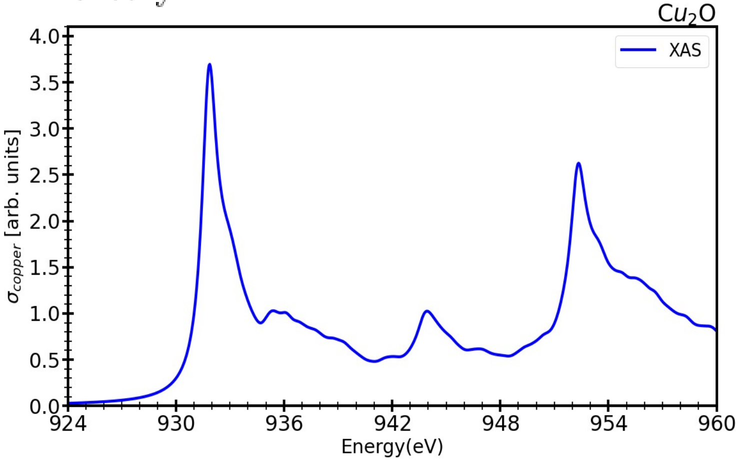




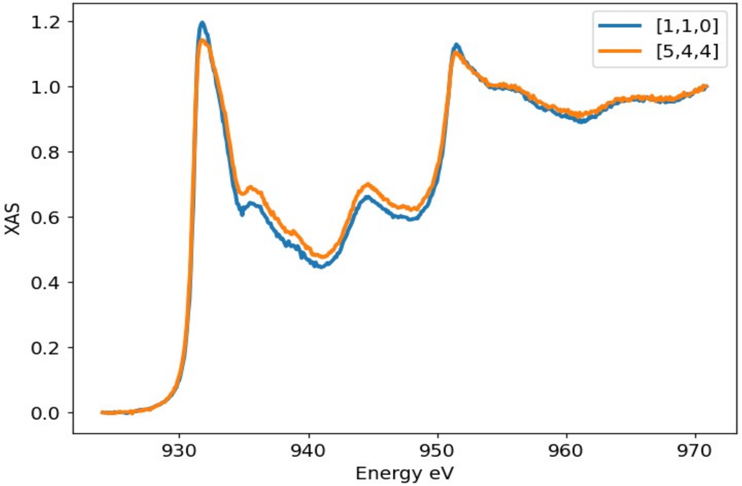
Are the simulations realistic?

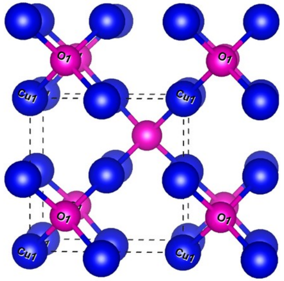
- experiment results
  - ✓ repreduce stationary XAS

theory



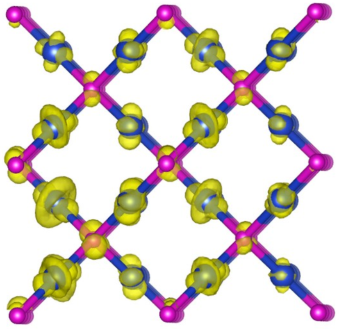
experiment



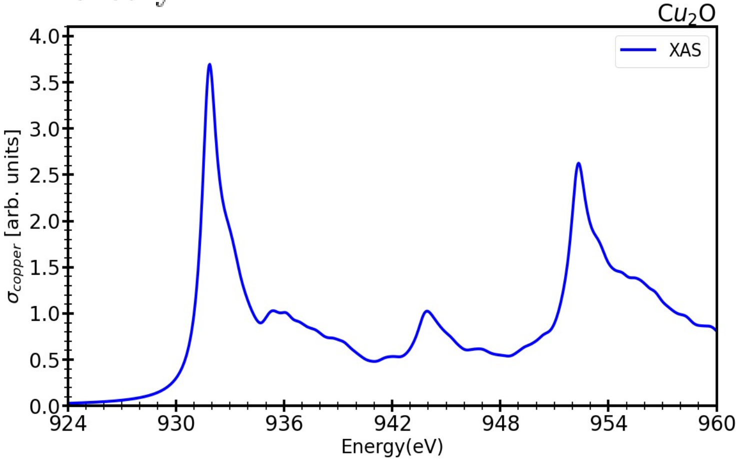


Are the simulations realistic?

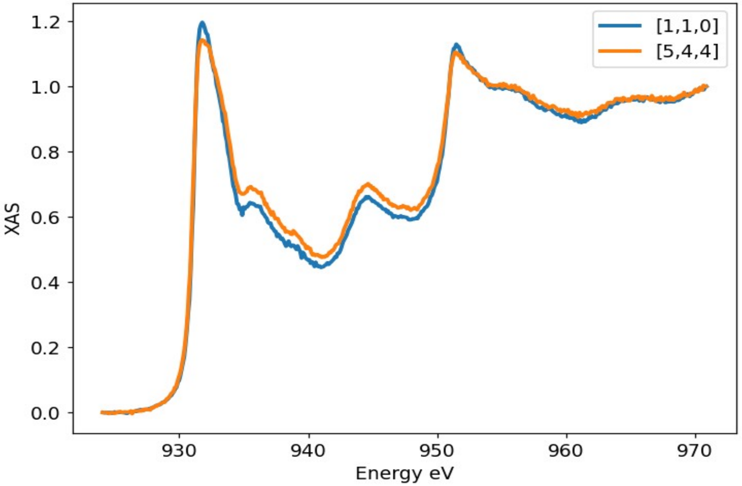
- experiment results
  - ✔ repreduce stationary XAS



theory



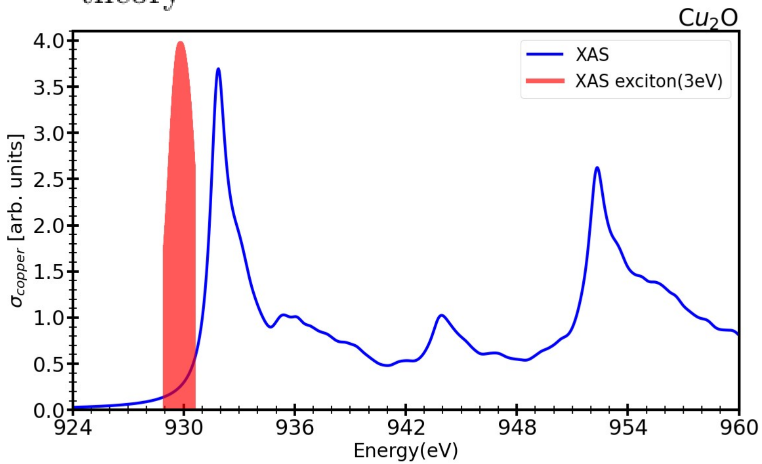
experiment



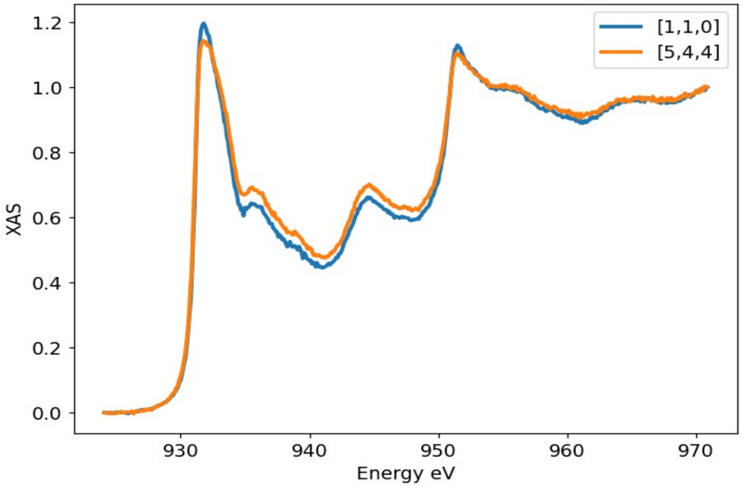
Are the simulations realistic?

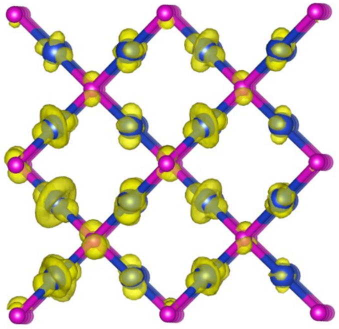
- experiment results
  - ✅ repreduce stationary XAS
  - ✅ probe valence exciton in 3 eV

theory



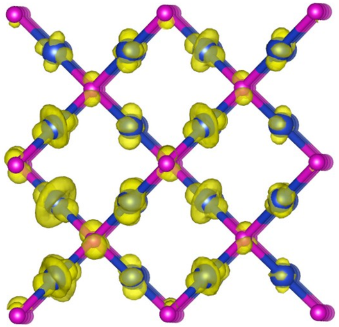
experiment



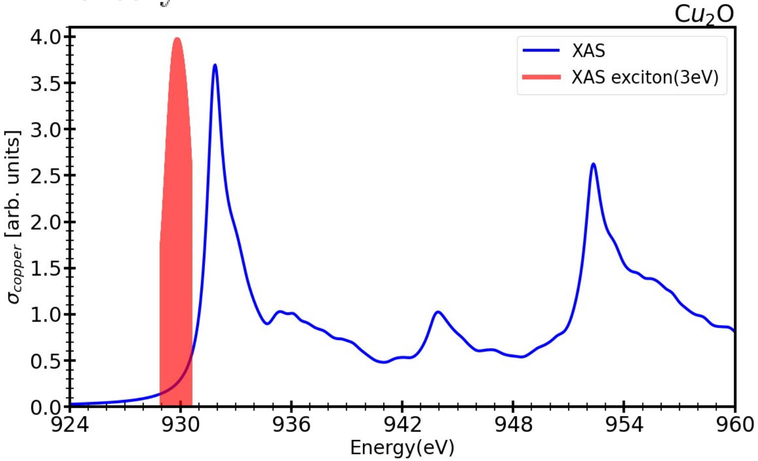


Are the simulations realistic?

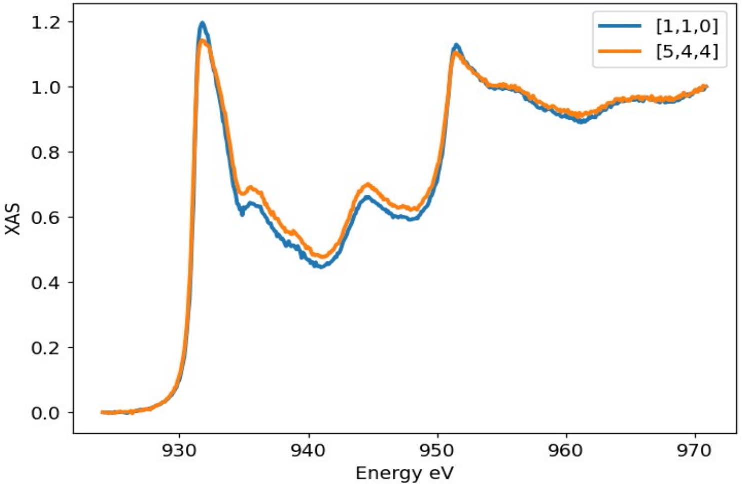
- experiment results
  - ✔ repreduce stationary XAS
  - ✔ probe valence exciton in 3 eV
  - ✔ well agreement with experiment

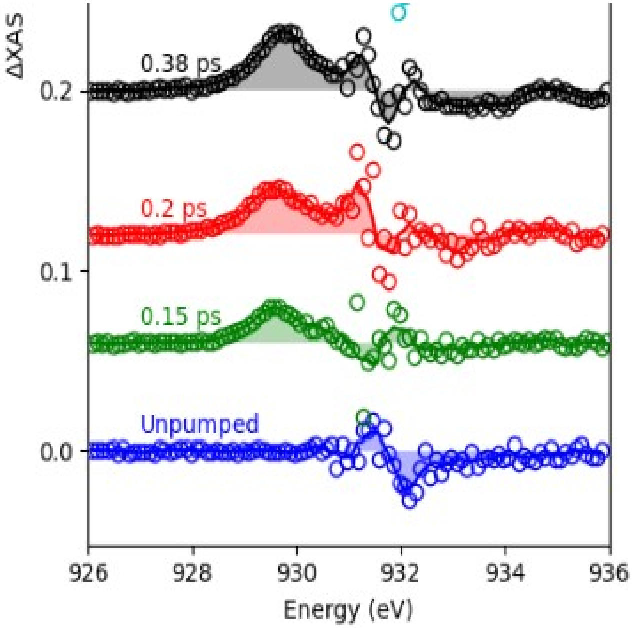


theory



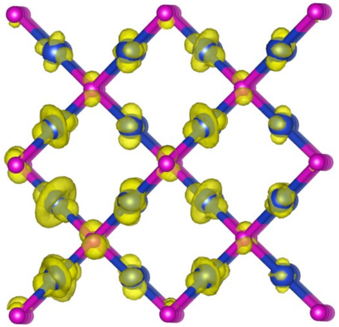
experiment



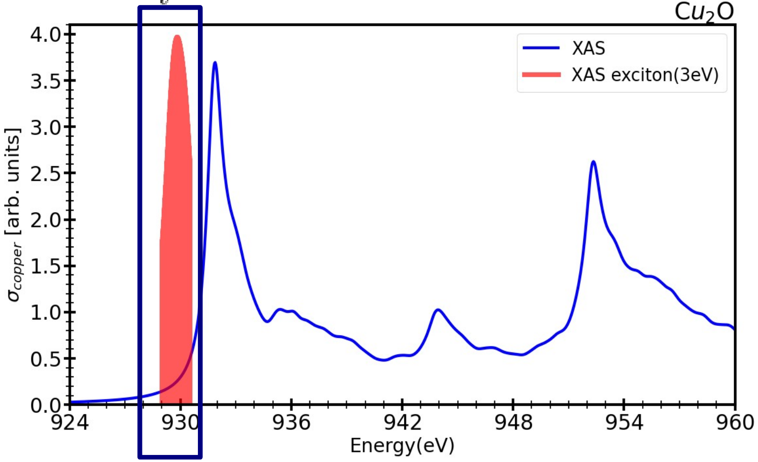


Are the simulations realistic?

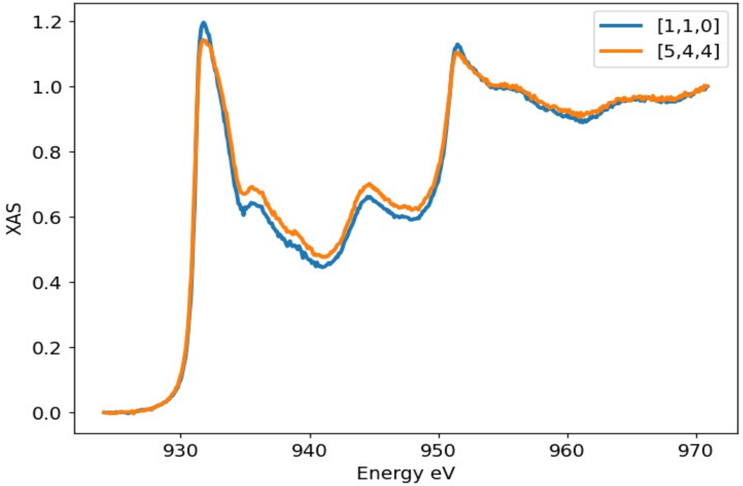
- experiment results
  - ✔ repreduce stationary XAS
  - ✔ probe valence exciton in 3 eV
  - ✔ well agreement with experiment

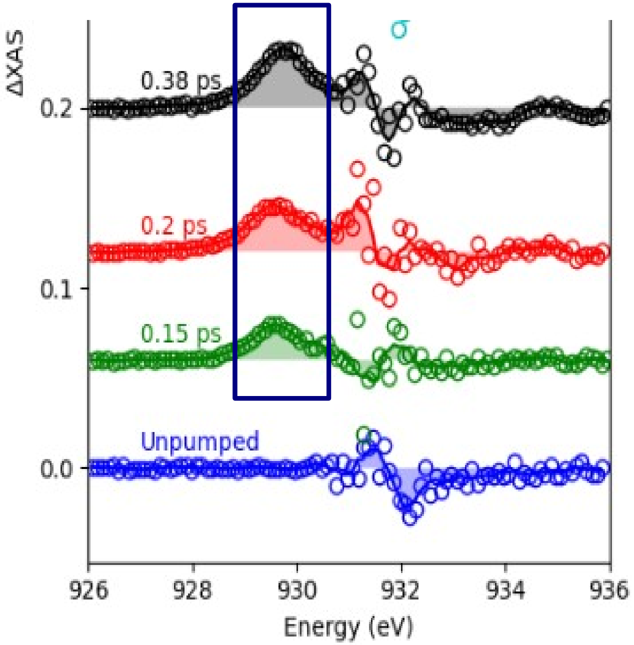


theory



experiment





Outlooks

Simulate the signal corresponds to excitons in real time

Develop these results for exciton dynamics

Daria Gorelova

Andreas Scherz

David Doblas-Jimenez

Loïc Le Guyader

Funding: VolkswagenStiftung

Manuel Izquierdo

Mano Raj

Thanks for your nice attention