Plasmons and the associated nonlinearities in phosphorene nanoribbons

Exploring extreme nonlinear optical response within a novel second principles scheme

HoW exciting! 2023, Berlin

Line Jelver[1]

[1] Center for Polariton–Driven Light–Matter Interactions, University of Southern Denmark, Odense

Outline

→ Method

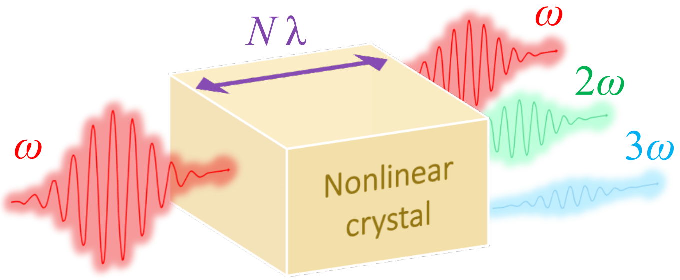
→ Plasmons and the associated nonlinearities in phosphorene nanoribbons

→ Electron-induced nonlinear response in atomic chains

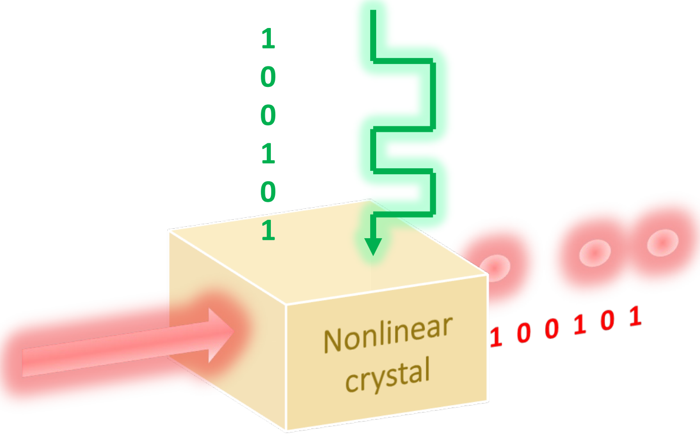
Nonlinear optics in nanostructures

POLIMA
Center for Polariton-driven Light-Matter Interactions

Traditional nonlinear optics

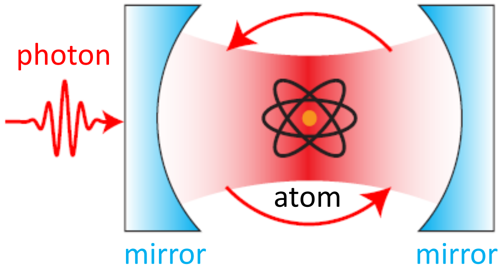


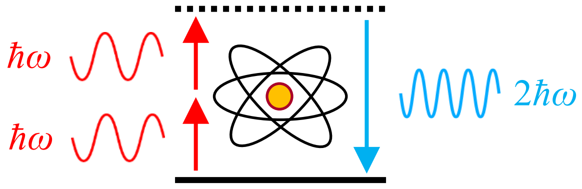
Frequency conversion



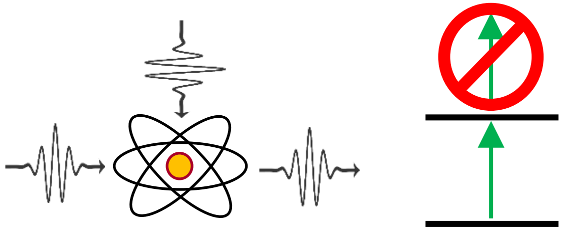
Ultrafast all-optical switching

Quantum nonlinear optics





Few-photon mixing



Single-photon blockade

Polaritons

- ✓ Hybridization of light and material excitations, such as excitons, phonons or plasmons.
- ✓ Beating the diffraction limit and enhances the field confinement which boost the light-matter interaction.

Solid-state HHG

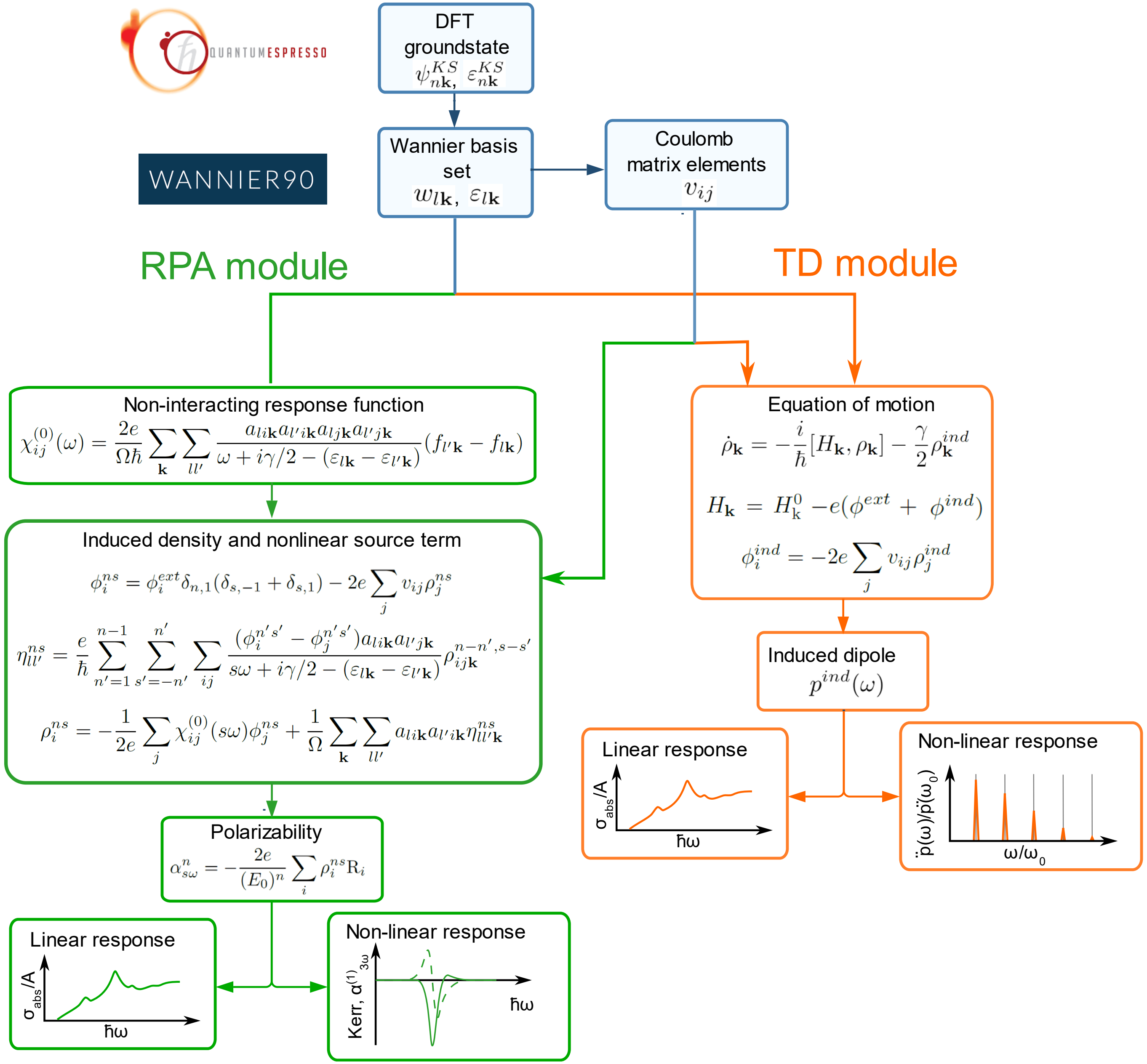
- ✓ Source of coherent high-frequency radiation which can be processed to produce **attosecond** optical pulses.

L. Jelver and J. D. Cox, arXiv:2305.09532

Method

Second principles optical response calculations

- ✓ Computationally feasible
- ✓ Offers chemical intuition
- ✓ Enables the exploration of system sizes around 10 nm's
  - ✓ The boundary between the quantum and classical regime
  - ✓ Structure sizes which enables the conversion of free light into polaritons



POLIMA
Center for Polariton-driven Light-Matter Interactions

Pertubative expansion of the density

- Monochromatic illumination
- Expanding the density in terms of **pertubative order n** and **harmonic order s**
- The induced density can be found from the response to the induced potential

$$\rho(t) = \sum_{n,s} \rho^{ns} \mathrm{e}^{-\mathrm{i}s\omega t}$$

Response from order (n,s) — Response from lower orders

$$\rho_l^{ns} = \sum_{l'} \chi_{ll'}^{(0)}(s\omega)\phi_{l'}^{ns} + \frac{b}{2\pi}\int_{-\pi/b}^{\pi/b} dk \sum_{jj'} a_{jl,k} a_{j'l,k}^* \eta_{jj',k}^{ns},$$

$$\alpha_{s\omega}^{n} = -\frac{2e}{(E_0)^n}\sum_i \rho_i^{ns}\mathrm{R}_i$$

$$\chi_{ll'}^{(0)}(s\omega) = \frac{2e^2}{\hbar}\frac{b}{2\pi}\int_{-\pi/b}^{\pi/b} dk \sum_{jj'} (f_{j',k} - f_{j,k}) \frac{a_{jl,k}a_{j'l,k}^* a_{jl',k}^* a_{j'l',k}}{s\omega + \mathrm{i}/2\tau - (\varepsilon_{j,k} - \varepsilon_{j',k})}$$

$$\phi_l^{ns} = \mathbf{r}_l \cdot \mathbf{E}^{\mathrm{ext}} \delta_{n,1}(\delta_{s,-1} + \delta_{s,1}) + \sum_{l'} v_{ll'}\rho_{l'}^{ns}$$

$$\eta_{jj',k}^{ns} = \frac{2e^2}{\hbar}\sum_{n'=1}^{n-1}\sum_{s'=-n'}^{n'}\sum_{ll'} \frac{\left(\phi_l^{n's'} - \phi_{l'}^{n's'}\right) a_{jl,k}^* a_{j'l',k}}{s\omega + \mathrm{i}/2\tau - (\varepsilon_{j,k} - \varepsilon_{j',k})} \rho_{ll',k}^{n-n',s-s'}$$

POLIMA Center for Polariton-driven Light-Matter Interactions

Single-particle density matrix formulation

- Time-dependent simulations solving the equation of motion

$$\frac{\partial \rho}{\partial t} = -\frac{\mathrm{i}}{\hbar}\left[\mathcal{H}^{\mathrm{TB}} - e\phi, \rho\right] - \frac{1}{2\tau}\left(\rho - \rho^{(0)}\right),$$

External potential Induced potential

$$\phi_l = \underbrace{\mathbf{r}_l \cdot \mathbf{E}}_{\text{External potential}} + \underbrace{\sum_{l'} v_{ll'} \rho_{l'}^{\mathrm{ind}}}_{\text{Induced potential}}$$

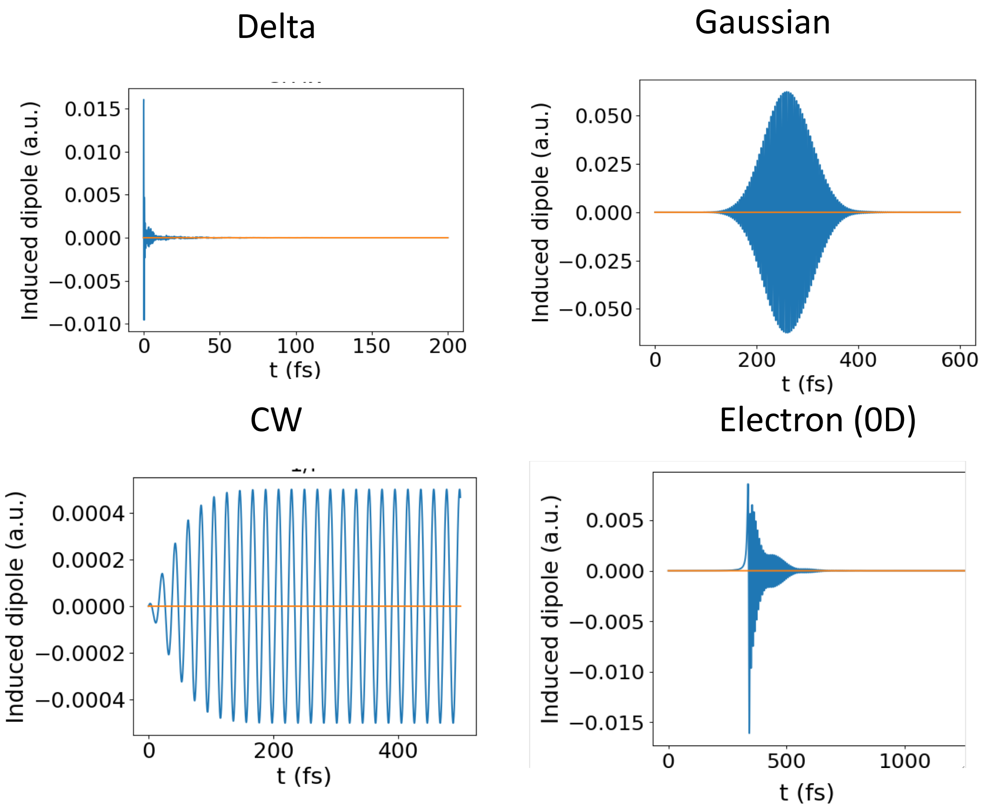
Induced density

$$\rho_l^{\mathrm{ind}} = -(eb/\pi) \int_{-\pi/b}^{\pi/b} dk \left(\rho_{ll,k} - \rho_{ll,k}^{(0)}\right)$$

Induced dipole

$$\mathbf{p}^{\mathrm{ind}}(t) = \sum_l \mathbf{r}_l \rho_l^{\mathrm{ind}}(t)$$

External potentials



POLIMA
Center for Polariton-driven Light-Matter Interactions

L. Jelver and J. D. Cox, arXiv:2305.09532

Plasmons and the associated nonlinearities in phosphorene nanoribbons

POLIMA
Center for Polariton-driven Light-Matter Interactions

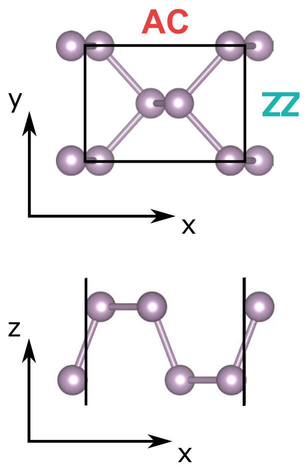
Phosphorene nanoribbons (PNRs)

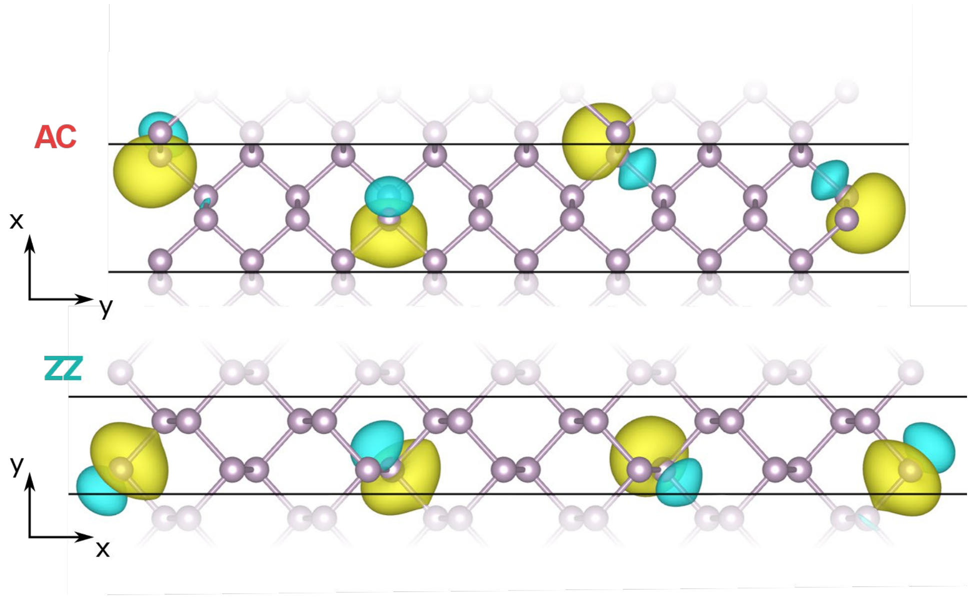
2D materials

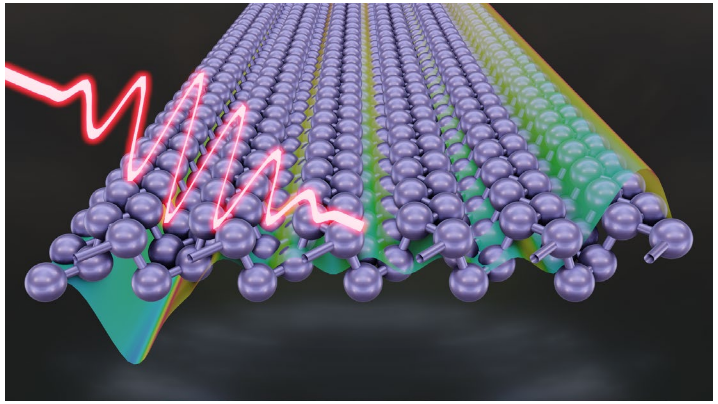
- ✓ Confinement in the out-of-plane direction
- ✓ Experience less screening which increases the probability of e-h recollisions.

Phosphorene

- ✓ Highly tunable anisotropic plasmonic resonances
- ✓ Strong light-matter interaction
- ✓ Extended system simulations show superior HHG compared to e.g. Graphene and MoS_2 [1]
- ✓ Can be nanostructured to break inversion symmetry allowing for even harmonics.





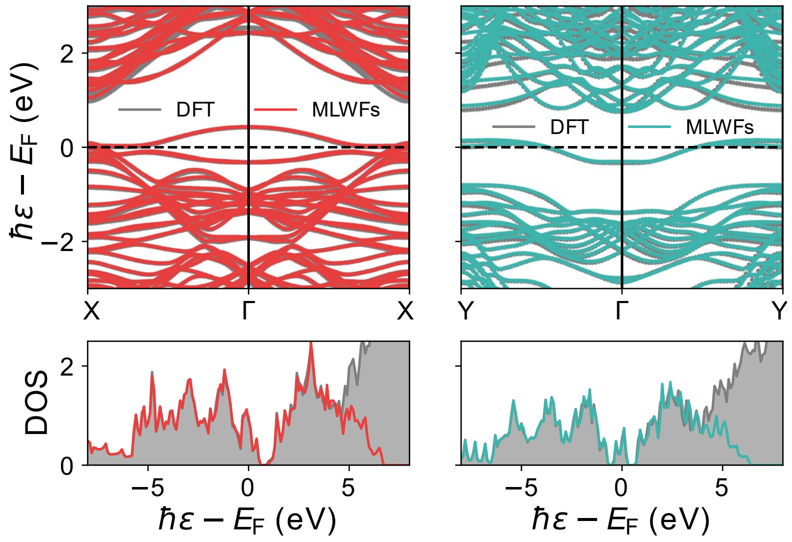


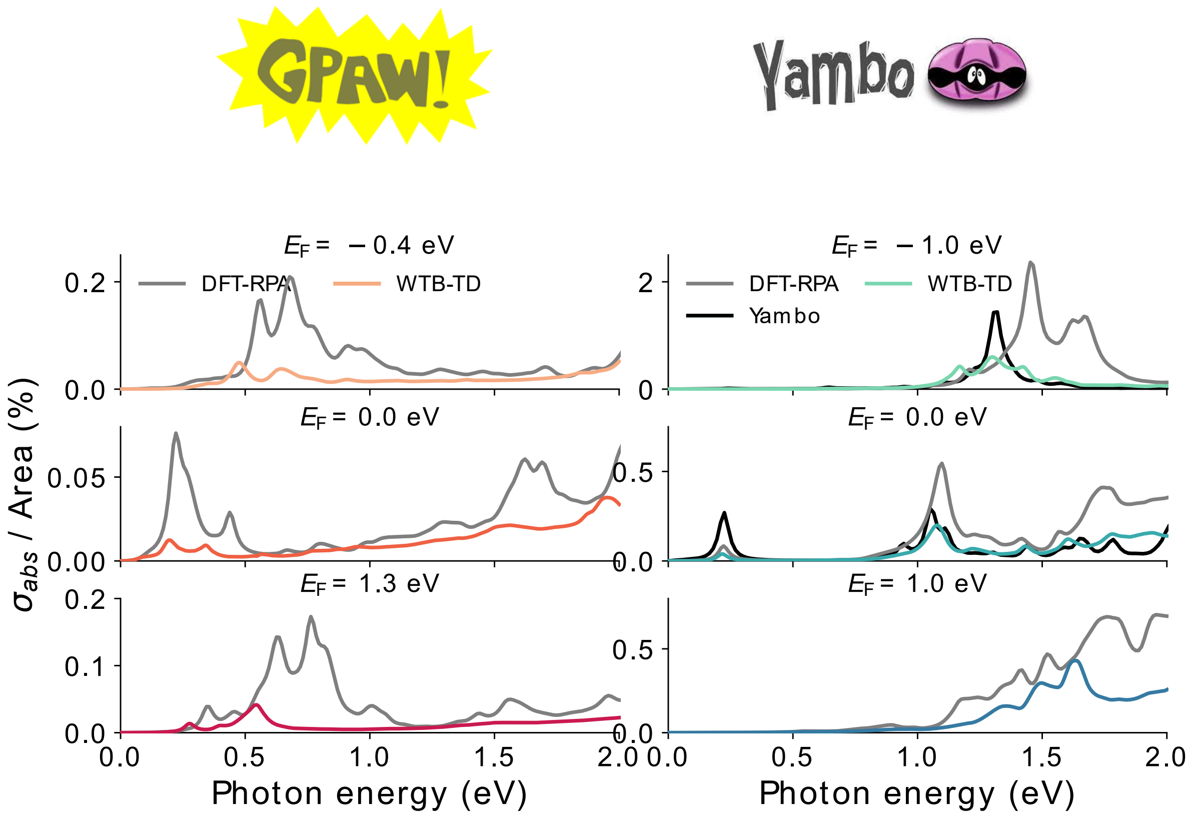
[1] Z.-Y. Chen and R. Qin, Nanoscale **11**, 16377 (2019).

POLIMA
Center for Polariton-driven Light-Matter Interactions

Comparison to ab-initio results

- ✓ The absorption cross section is obtained from the polarizability
- ✓ Agreement of single-particle bands 5 eV around the Fermi level.
- ✓ Qualitative features of the absorption as found from ab-initio calculations are reproduced.





Tunability of the plasmonic modes

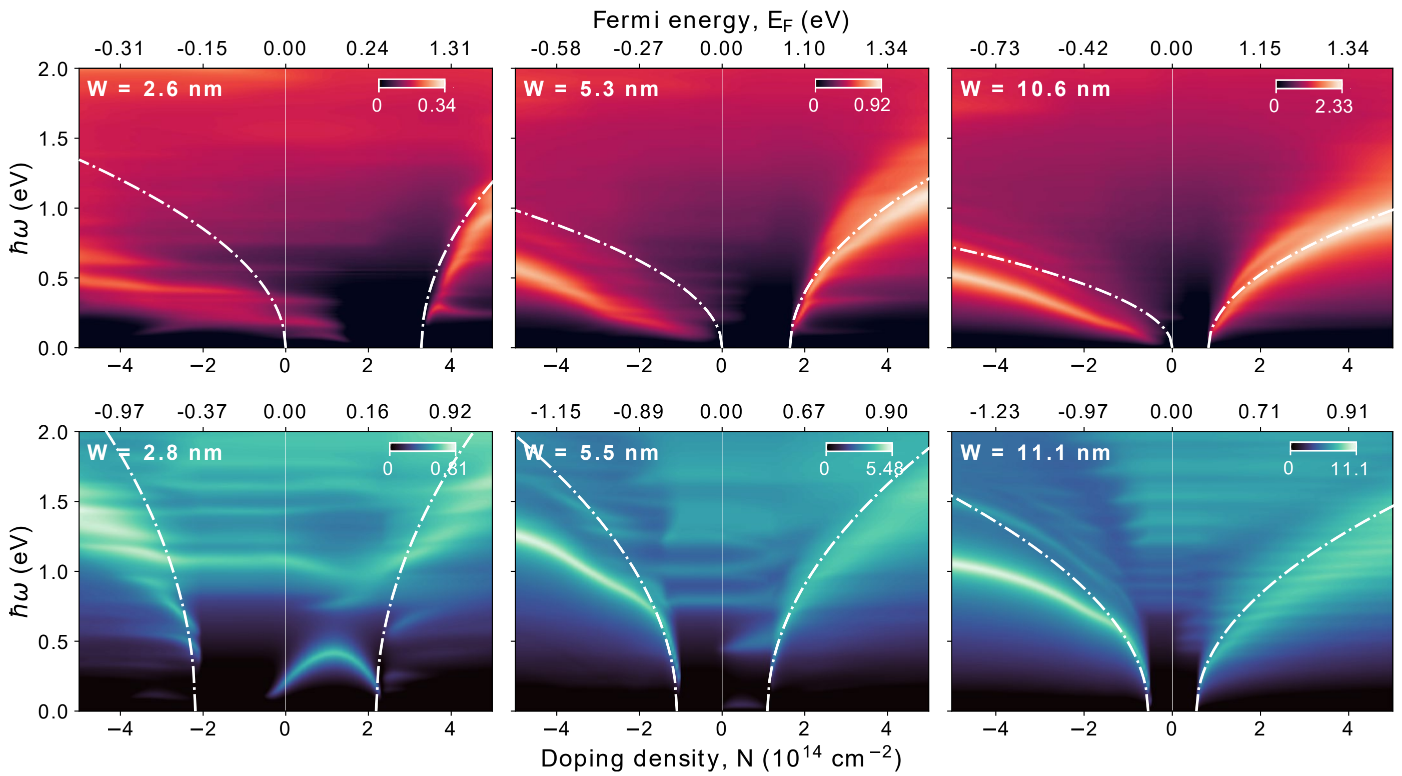
POLIMA
Center for Polariton-driven Light-Matter Interactions

- ✓ Plasmonic resonances in IR and MIR range with **tunability over ≈ 1 eV.**
- ✓ Landau damping especially pronounced in hole doped ribbons.
- ✓ Agreement with analytical model of plasmonic modes in nanostructures. [1,2]

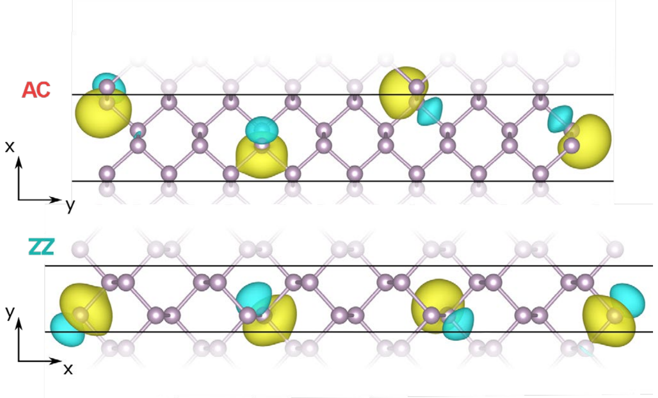
$$\omega_\alpha^{e/h} = \frac{1}{\sqrt{-\pi\eta_1\epsilon}}\sqrt{\frac{\mathcal{D}_\alpha^{e/h}}{W}},$$

$$\sigma_\alpha^{e/h}(\omega) = \frac{i\mathcal{D}_\alpha^{e/h}}{\pi(\omega + i\tau^{-1})},$$

$$\mathcal{D}_\alpha^{e/h} = \pi e^2|N|/m_{\alpha,c/v}$$



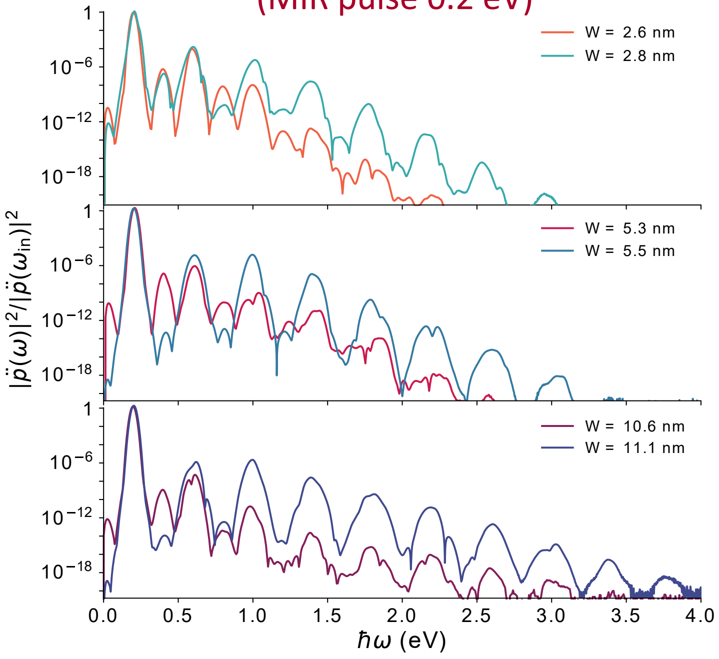
[1] R. Yu, J. D. Cox, J. R. M. Saavedra, and F. J. Garciá De Abajo, *Analytical Modeling of Graphene Plasmons*, ACS Photonics **4**, 3106 (2017).
[2] T. Low, R. Roldán, H. Wang, F. Xia, P. Avouris, L. M. Moreno, and F. Guinea, *Plasmons and Screening in Monolayer and Multilayer Black Phosphorus*, Phys. Rev. Lett. **113**, 5 (2014).

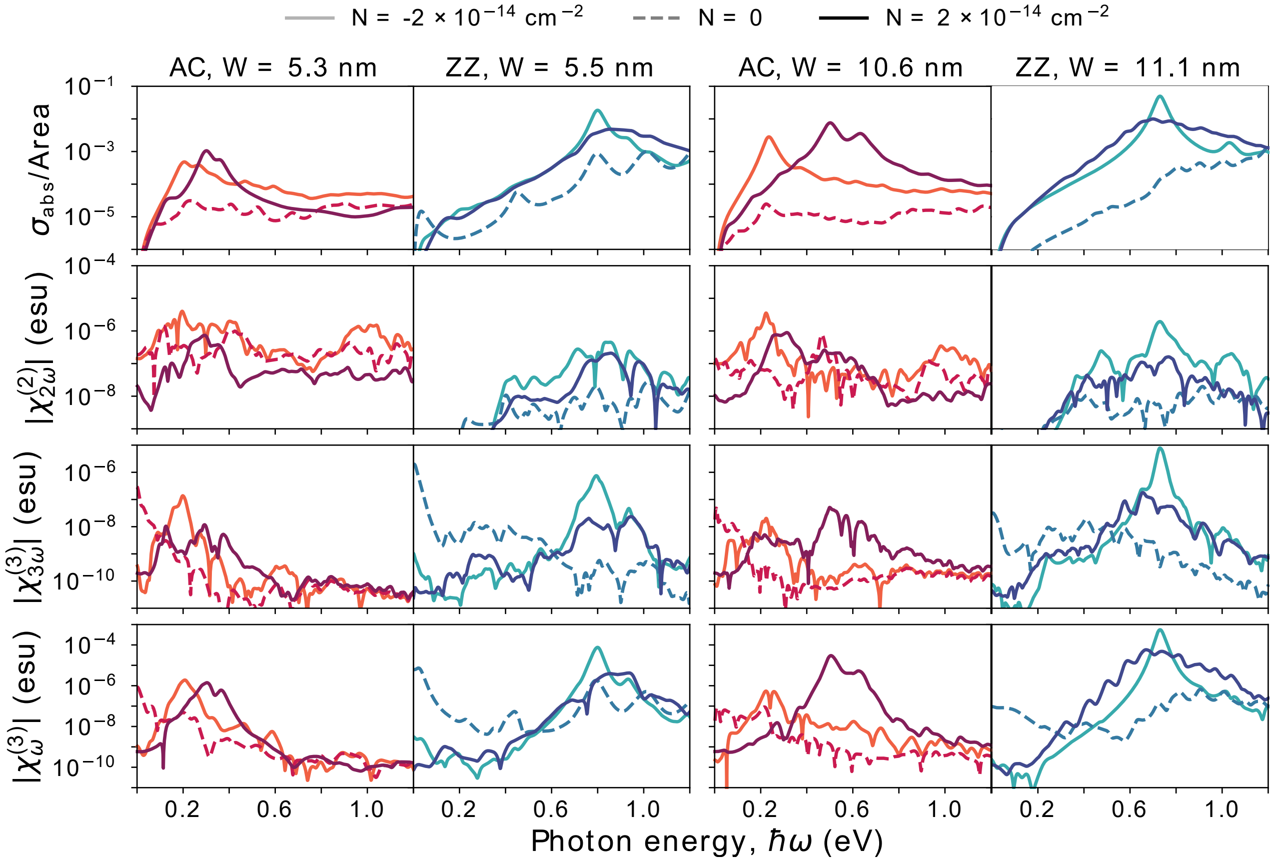


Nonlinear response in PNRs

- ✓ 2nd order susceptibilities up to the order of 10^{-5} esu.
- ✓ 3rd order susceptibilities in the order of of 10^{-5} esu.
- ✓ UV-range emission achieved for the two widest ribbons.

High-harmonic generation from pristine ribbons
(MIR pulse 0.2 eV)

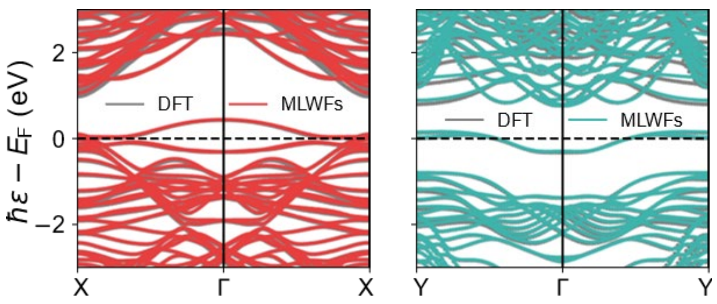


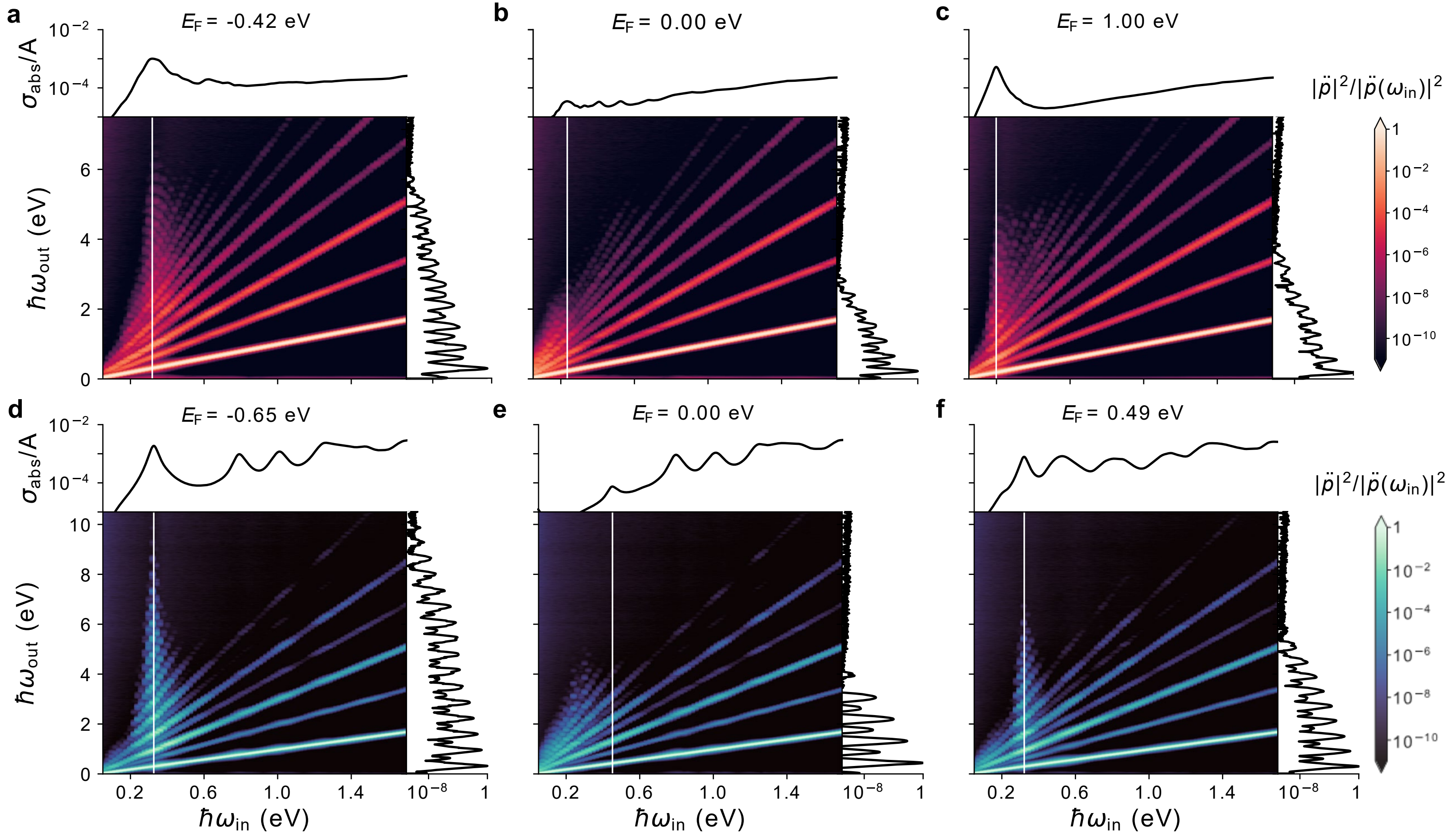


Plasmon enhanced HHG in 5 nm ribbons

POLIMA
Center for Polariton-driven Light-Matter Interactions

- ✓ Plasmon-assisted HHG is achieved.
- ✓ Pushes the emission towards the extreme-UV range (>10.3 eV)
- ✓ Large bandgap in hole-doped PNRs reduces quenching of the response by interband transitions.





Electron-induced nonlinearity in atomic chains

L. Jelver, *et. al.*, Phys. Rev. Research 5, L022015 (2023), DOI: 10.1103/PhysRevResearch.5.L022015

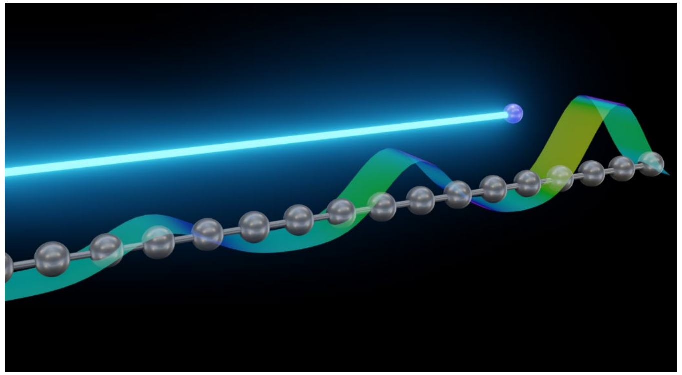
POLIMA
Center for Polariton-driven Light-Matter Interactions

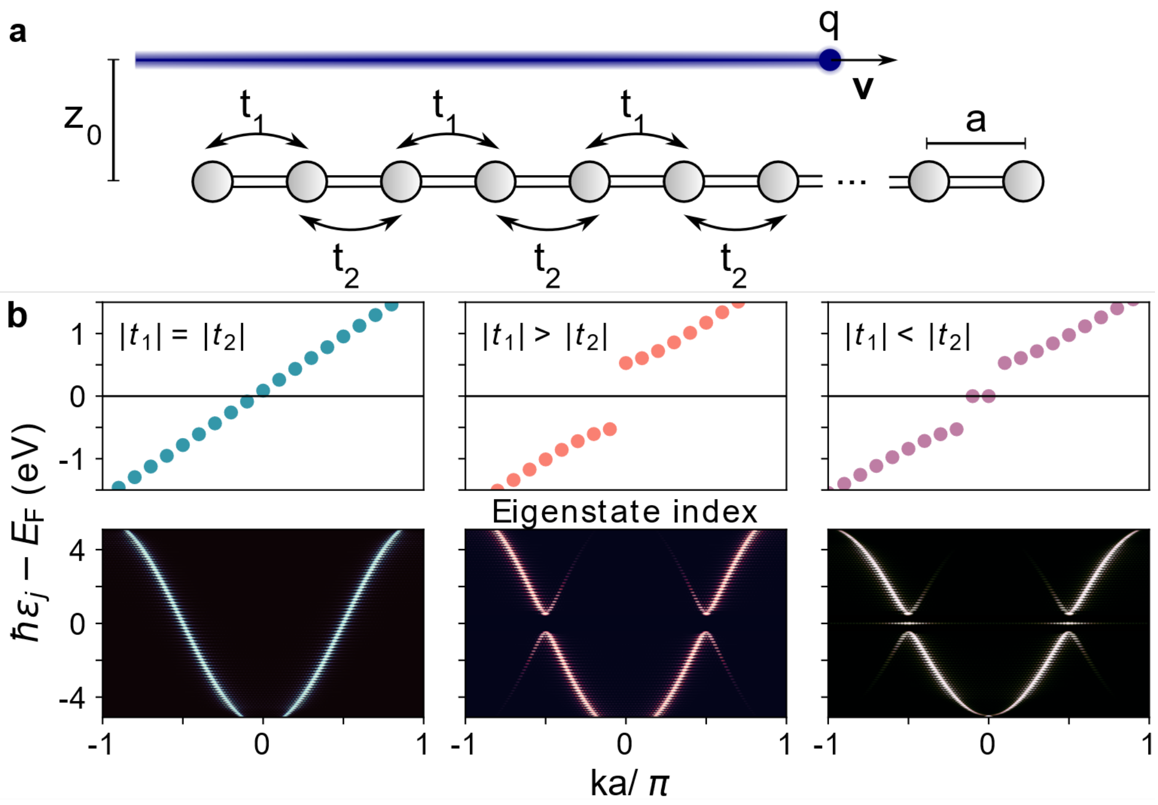
Electron-induced nonlinearity in SSH chains

- ✓ Relies on the overlap between the emanating electron field and the target.
- ✓ ~100 eV electrons can deliver optical fluences comparable to intense ultrashort optical pulses used for inducing nonlinear response.

$$\mathcal{H}^{\mathrm{TB}} = t_1 \sum_{l=1}^{N/2} |2l\rangle\langle 2l-1| + t_2 \sum_{l=1}^{N/2-1} |2l+1\rangle\langle 2l| + \mathrm{h.c.},$$

$$\phi_l^{\mathrm{ext}} = q\,|x_l\hat{\mathbf{x}} - \mathbf{r}_0 - \mathbf{v}t|^{-1}$$





POLIMA
Center for Polariton-driven Light-Matter Interactions

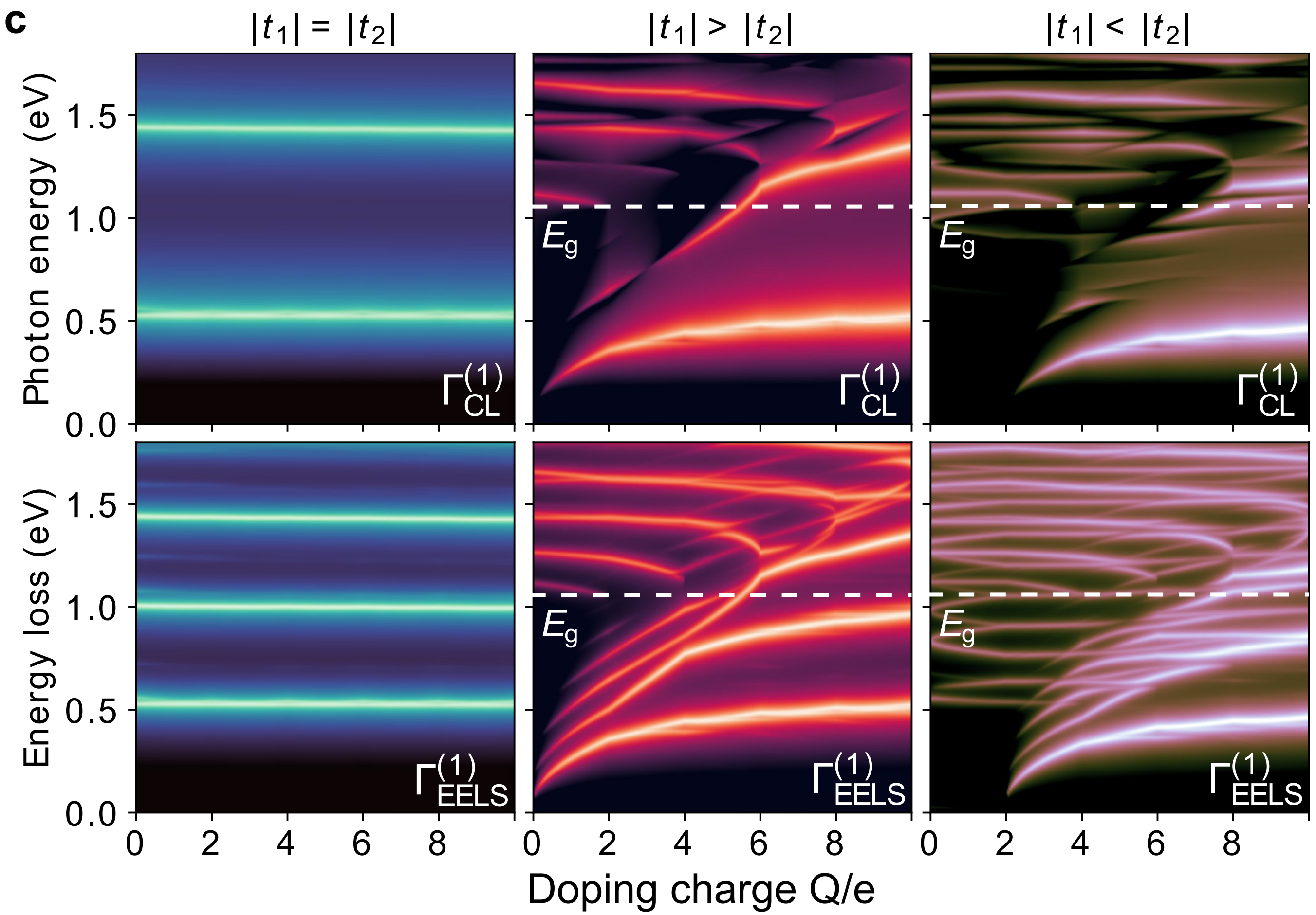
Plasmonic resonances in SSH chains

- ✓ Low-energy spectral features corresponding to plasmon resonances.
- ✓ EELS reveal the dark modes
- ✓ Tunability in the chains with electronic gaps.

$$\Gamma_{\rm CL} = 2\omega^3|\mathbf{p}_\omega|^2/3\pi\hbar c^3$$

$$\Gamma^{||}_{\rm EELS} = -\frac{2q}{\pi\hbar v}\sum_l K_0\left(\frac{\omega}{v}\sqrt{y_0^2+z_0^2}\right){\rm Im}\left\{\rho^{\rm ind}_{\omega,l}{\rm e}^{-{\rm i}\omega x_l/v}\right\},$$

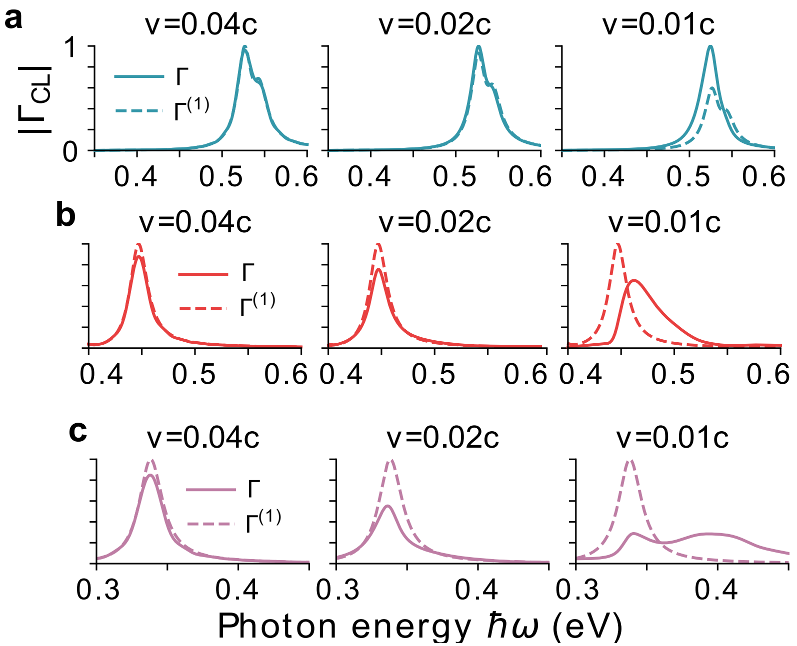
N = 100, v = 0.01c, z_0 = 0.5 nm



POLIMA
Center for Polariton-driven Light-Matter Interactions

Induced density fluctuations

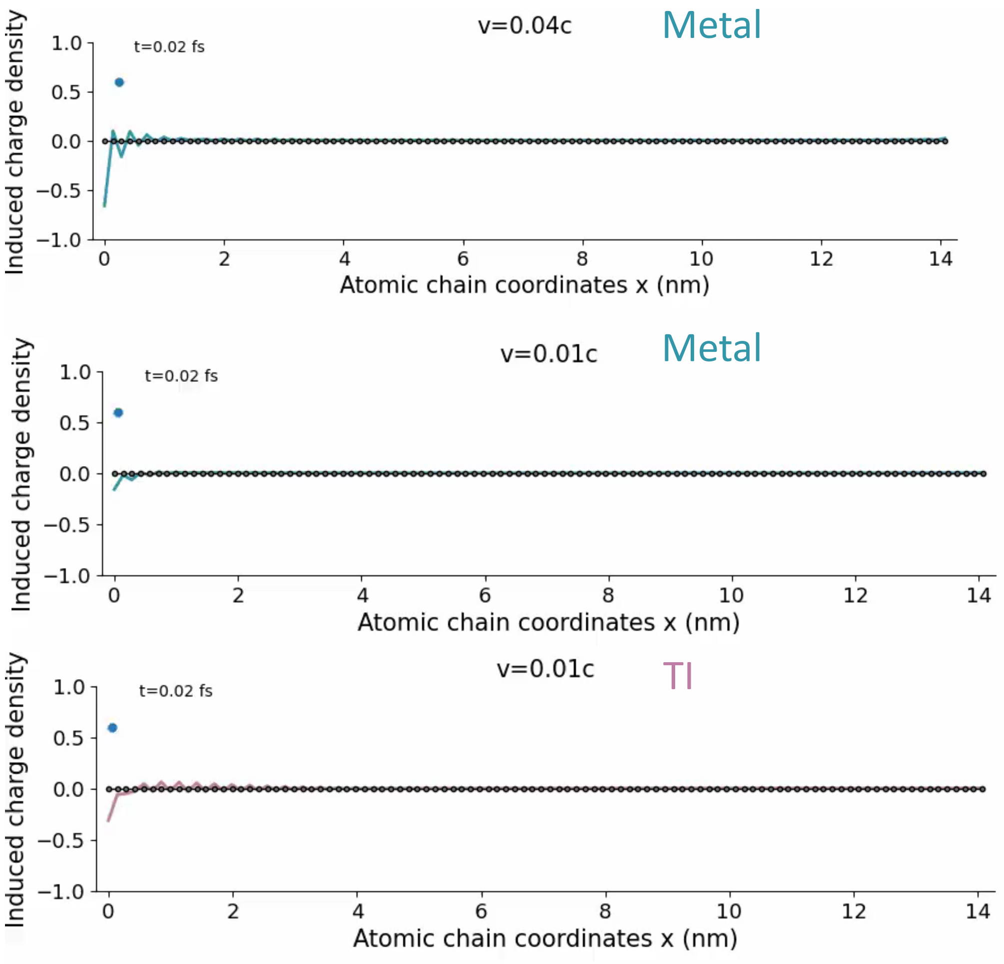
- ✓ Tuning the speed to the Fermi velocity creates the most prominent **non-linear** behaviour
- ✓ The gapped chains experience the largest effect presumably due to reduced screening



Metal

Semiconductor

TI



Conclusions

→ Novel second principles method which allows for simulating the nonlinear response of systems with up to ~500 atomic orbitals.

→ Prospects of phosphorene nanoribbons within nano-optics
- Excellent tunability of the plasmonic resonances
- Tuneable and high non-linear response
- Tuneable and large HHG yield.

→ Guidelines for inducing nonlinear response by e-beams
- Gapped systems are preferable
- The speed of the electrons should match the Fermi velocity

Acknowledgements

Joel D. Cox
Associate Professor
cox@mci.sdu.dk

POLIMA
Center for Polariton-driven Light-Matter Interactions

J. D. C. is a Sapere Aude research leader supported by VILLUM FONDEN (grant no. 16498) and Independent Research Fund Denmark (grant no. 0165-00051B)

POLIMA has received funding from the Danish National Research Foundation under grant agreement DNRF165.

THE VELUX FOUNDATIONS
VILLUM FONDEN ✕ VELUX FONDEN

INDEPENDENT RESEARCH FUND DENMARK

Danmarks Grundforskningsfond
Danish National Research Foundation