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Susceptibilidad óptica no lineal basada en primeros principios en semiconductores

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PAPER

Perturbative second-order optical susceptibility of bulk materials: a symmetry-enforced return to non-orthogonal localized basis sets

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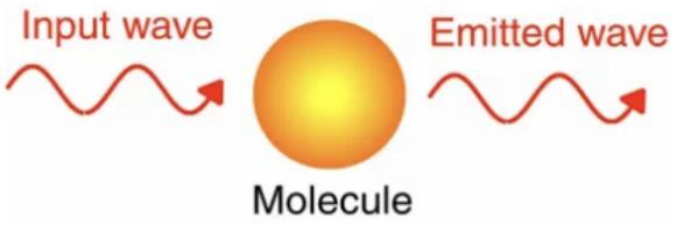
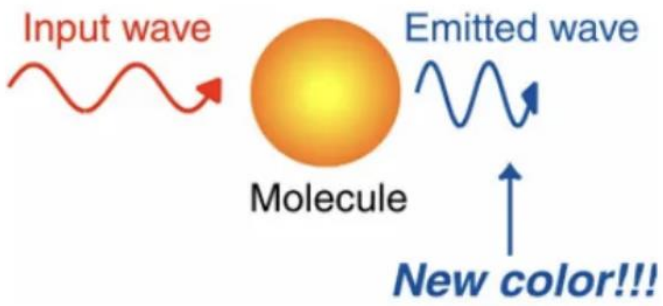
Linear and nonlinear optical responses:

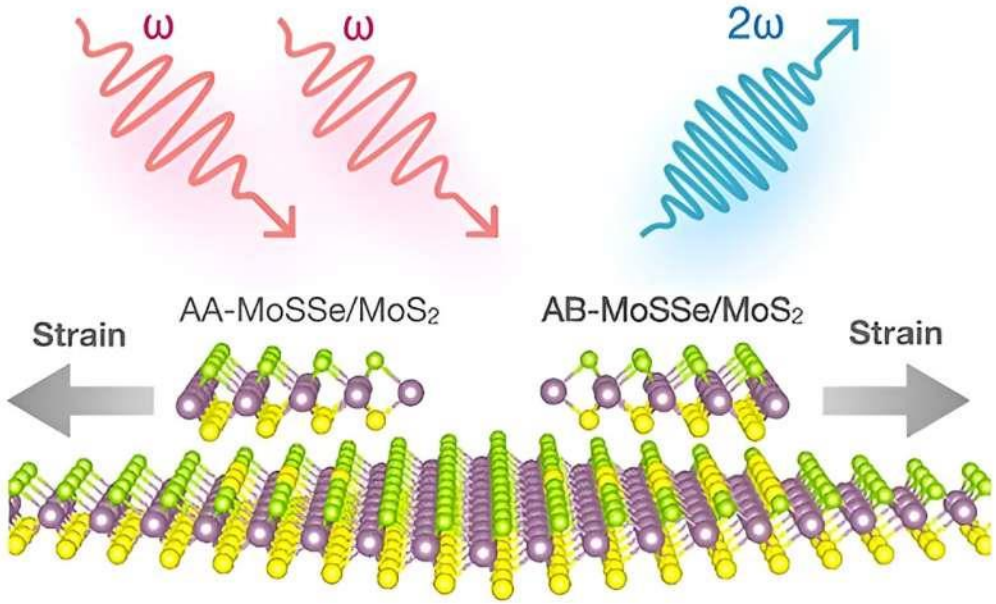


Linear material response



Nonlinear material response

Second harmonic generation



Typical of materials without an inversion center.

Nonlinear optical response: Phenomenology

Linear dependence between P and E.

$$\tilde{P}(t) = \epsilon_0 \chi^{(1)} \tilde{E}(t),$$

If *E* has a frequency ω, so does *P*.

General nonlinear case: The induced polarization can be written as a "Taylor" series on the electric field:

$$\begin{aligned}\tilde{P}(t) &= \epsilon_0 \left[\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \cdots \right] \\ &\equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \cdots .\end{aligned}$$

P can have frequencies $\omega, 2\omega, 3\omega, etc.$

The nonlinear (NL) polarization acts as a source of electromagnetic waves:

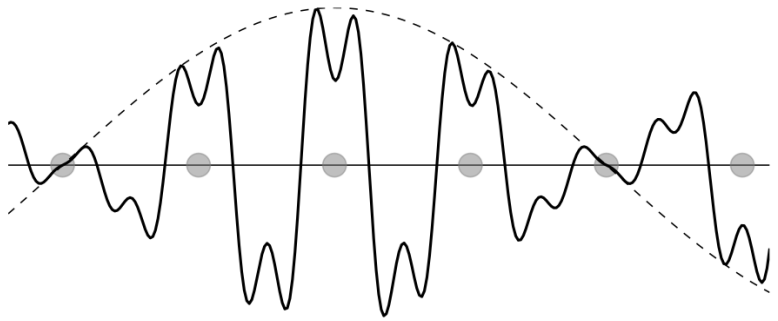
$$\nabla^2 \tilde{E} - \frac{n^2}{c^2} \frac{\partial^2 \tilde{E}}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 \tilde{P}^{\mathrm{NL}}}{\partial t^2},$$

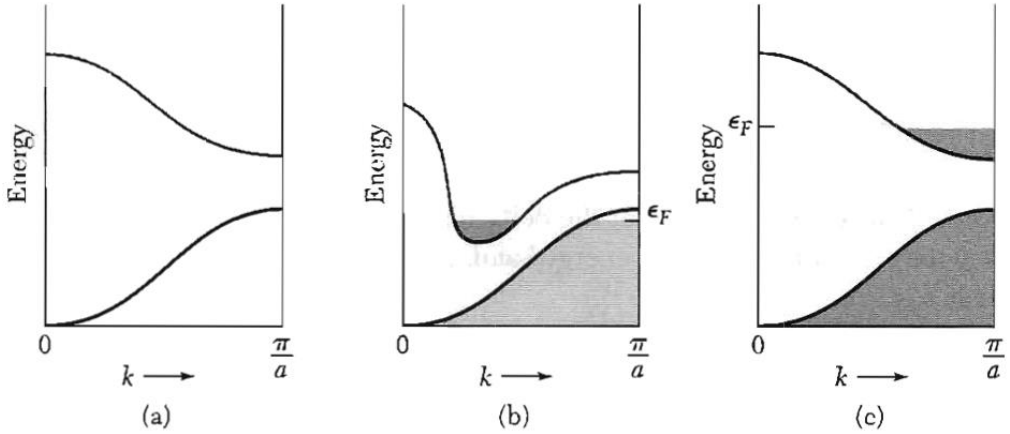
P^{NL}: nonlinear part of the induced polarization.

Microscopic (quantum mechanical) theory of the nonlinear optical susceptibility

- The key ingredients for a quantum mechanical description of the optical susceptibility of a semiconductor:
  - The wavefunctions or eigenstates: **Bloch waves.**
  - The eigenenergy: **Energy bands.**

  Both the eigenstates and eigenfunctions are indexed by a ***k-number*** and a ***band*** **index**.

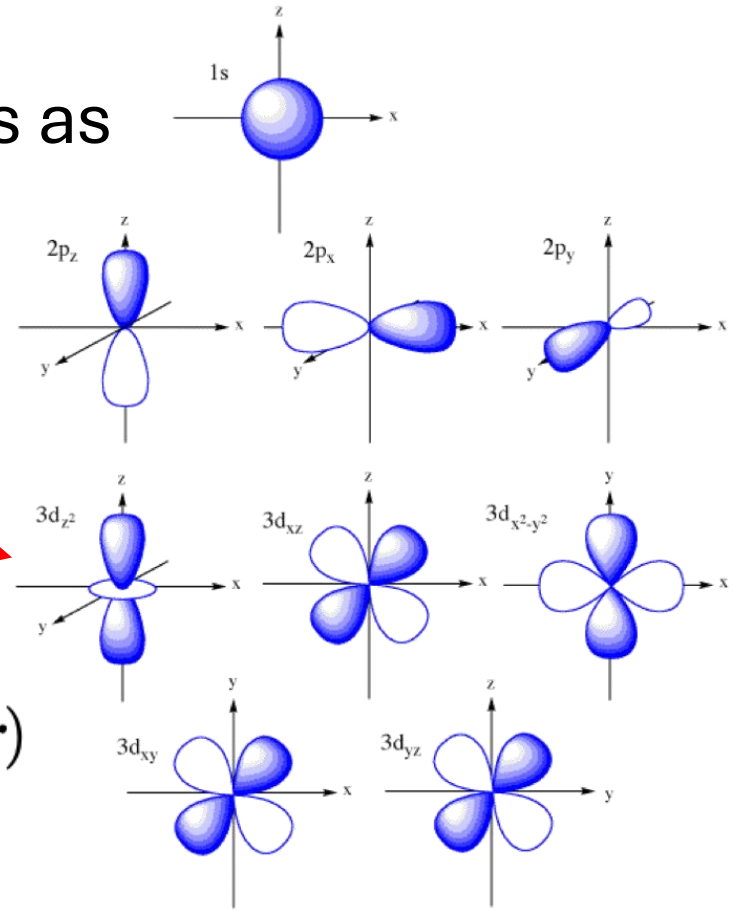




How to get Bloch eigenstates and energy bands: Density Functional Theory (DFT) !

- It allows to determine the Bloch eigenstates and energy bands in a material (semiconductor) self consistently.
- There are many DFT implementations (codes).
- We used *SIESTA*, which writes the Bloch eigenstates as combinations of **pseudo atomic orbitals** (PAOs):

$$\varphi_{\alpha \boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N_n}} \sum_{n_1=-n_1'}^{n_1'} \sum_{n_2=-n_2'}^{n_2'} \sum_{n_3=-n_3'}^{n_3'} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_{n_1,n_2,n_3}} \times \varphi_\alpha(\boldsymbol{r} - \boldsymbol{R}_{n_1,n_2,n_3} - \boldsymbol{\delta}_\alpha),$$



The final Bloch eigenstates come from a generalized eigenvalue problem:

$$H_0(\boldsymbol{k})\, C_n^0(\boldsymbol{k}) = \epsilon_n^0(\boldsymbol{k})\, S_0(\boldsymbol{k})\, C_n^0(\boldsymbol{k}), \quad \psi_{n\boldsymbol{k}}^0(\boldsymbol{r}) = \sum_{\alpha=1}^{\mathcal{N}} C_{\alpha n}^0(\boldsymbol{k})\, \varphi_{\alpha \boldsymbol{k}}(\boldsymbol{r})$$

Independent Particle Approximation (IPA):

Crystal Hamiltonian: $\hat{H}_0 = \hat{\boldsymbol{p}}^2/2m_e + V(\boldsymbol{r}),$

Light-matter coupling term (velocity gauge):

$$\hat{H}(t) = \frac{1}{2m_e}\left(\hat{\boldsymbol{p}} + e\boldsymbol{A}(t)\right)^2 + \hat{V}(\boldsymbol{r}) \simeq \hat{H}_0 + \hat{H}_1(t), \qquad \boxed{\hat{H}_1(t) = \frac{e}{m_e}\boldsymbol{A}(t)\cdot\hat{\boldsymbol{p}}.}$$

The induced polarization is obtained by calculating the **density matrix** in a perturbative way and from it the macroscopic current:

$$\hat{\rho} = \hat{\rho}^{(0)} + \hat{\rho}^{(1)} + \hat{\rho}^{(2)} + \cdots$$

$$\hat{\boldsymbol{j}} = \hat{\boldsymbol{j}}^{(0)} + \hat{\boldsymbol{j}}^{(1)} + \hat{\boldsymbol{j}}^{(1)} + \cdots.$$

$$\langle \boldsymbol{J} \rangle = \frac{1}{\Omega}\mathrm{Tr}\left(\hat{\rho}\hat{\boldsymbol{j}}\right), \qquad \boldsymbol{J} = \mathrm{d}\boldsymbol{P}/\mathrm{d}t$$

Expansions up to second order in H_1.

Linear and quadratic optical susceptibility:

$$P_i(\omega) = \varepsilon_0 \left(\chi_{ij}^{(1)} E^j(\omega) + \chi_{ijk}^{(2)} E^j(\omega) E^k(\omega) + \ldots \right)$$

Linear: symmetric tensor of rank 2

Quadratic: tensor of rank 3 symmetric in its last two indices

$$\mathrm{Im}\left[A_{ijk}(2\omega)\right] = \frac{e^3\hbar^3}{2\varepsilon_0 m_e^3}\int_{\mathrm{FBZ}}\frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3}\sum_{v=1}^{\mathrm{nvb}}\sum_{c=\mathrm{nvb}+1}^{\mathrm{nbands}}$$

$$\times\frac{16\pi}{\epsilon_{cv}^{0\,3}}\delta\left(\epsilon_{cv}^0-2\hbar\omega\right)\left(\sum_{v'=1}^{\mathrm{nvb}}\frac{\mathrm{Im}\left[p_{i;vc}\left\{p_{j;cv'},p_{k;v'v}\right\}\right]}{2\epsilon_{cv'}^0-\epsilon_{cv}^0}\right.$$

$$\left.-\sum_{c'=\mathrm{nvb}+1}^{\mathrm{nbands}}\frac{\mathrm{Im}\left[p_{i;vc}\left\{p_{j;cc'},p_{k;c'v}\right\}\right]}{2\epsilon_{c'v}^0-\epsilon_{cv}^0}\right),$$

The matrix elements of the momentum operators between Bloch eigenstates are calculated exploiting the symmetries of the PAOs. This reduces the computational effort.

The optical response (at the IPA level) is written in terms of the single body Bloch wavefunctions and energy bands.

$$\mathrm{Im}\left[B_{ijk}(\omega)\right] = \frac{e^3\hbar^3}{2\varepsilon_0 m_e^3}\int_{\mathrm{FBZ}}\frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3}\sum_{v=1}^{\mathrm{nvb}}\sum_{c=\mathrm{nvb}+1}^{\mathrm{nbands}}$$

$$\times\frac{\pi}{\epsilon_{cv}^{0\,3}}\delta(\epsilon_{cv}^0-\hbar\omega)\left(\sum_{n=1(n\neq c)}^{\mathrm{nbands}}\frac{\mathrm{Im}\left[p_{i;nc}\left\{p_{j;cv},p_{k;vn}\right\}\right]}{\epsilon_{cn}^0-2\epsilon_{cv}^0}\right.$$

$$\left.-\sum_{n=1(n\neq v)}^{\mathrm{nbands}}\frac{\mathrm{Im}\left[p_{i;vn}\left\{p_{j;nc},p_{k;cv}\right\}\right]}{\epsilon_{nv}^0-2\epsilon_{cv}^0}\right),$$

Application to cubic silicon carbide (3C-SiC):

Symmetry group T_d.
Independent tensor elements:

$$\chi^{(1)}_{xx} = \chi^{(1)}_{yy} = \chi^{(1)}_{zz}. \qquad \chi^{(2)}_{xyz} = \chi^{(2)}_{yzx} = \chi^{(2)}_{zxy},$$

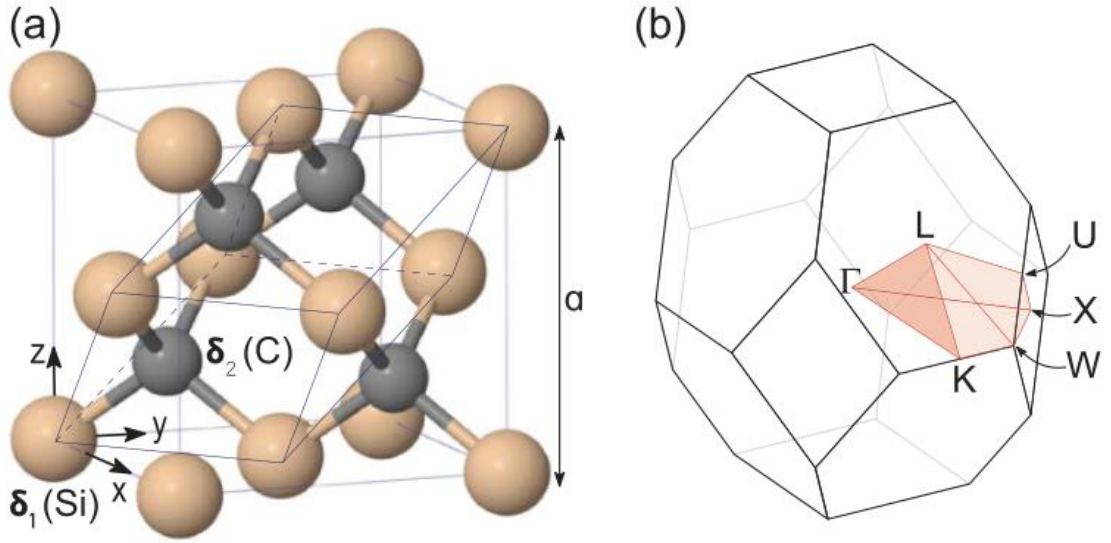
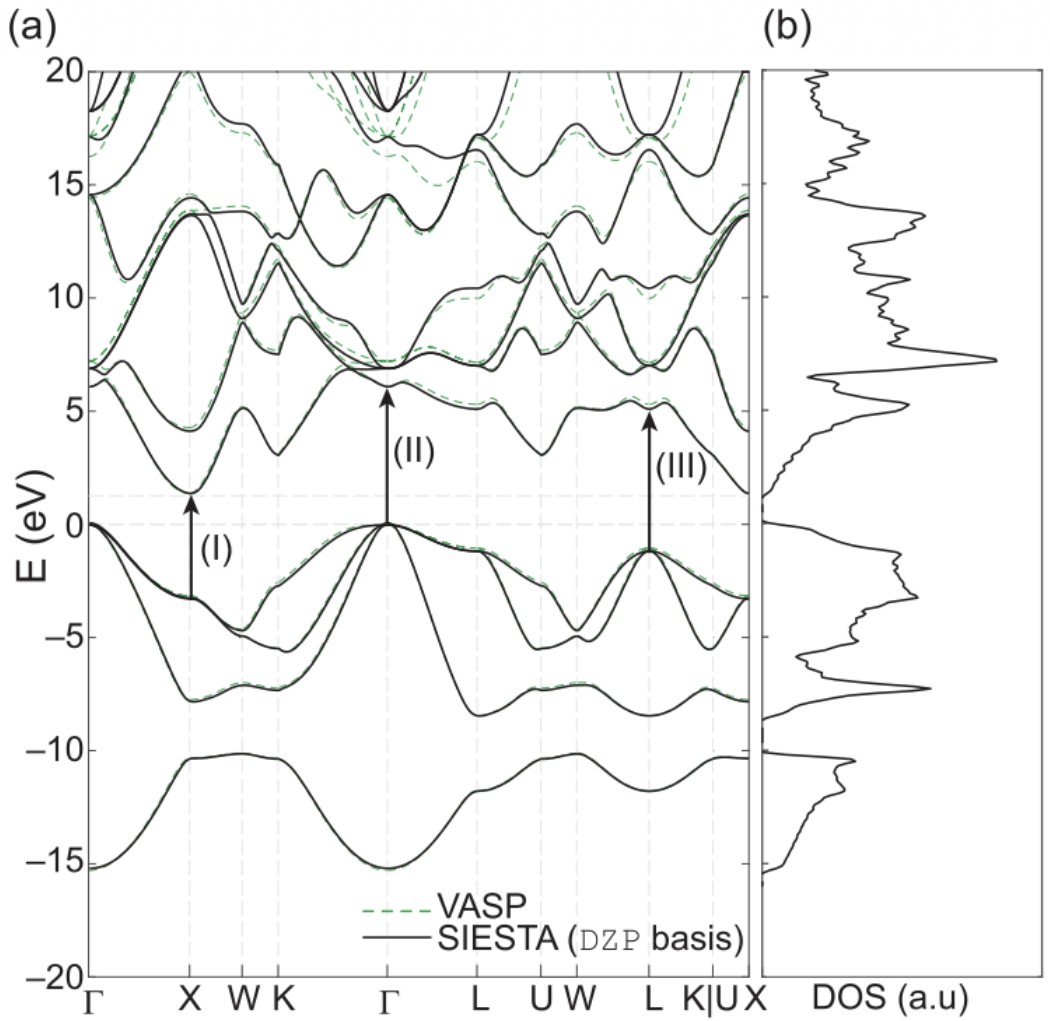
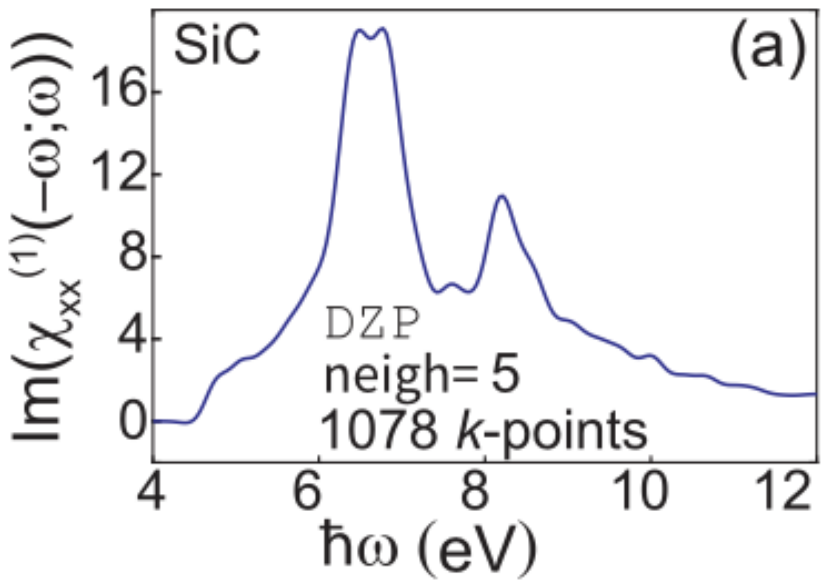


Figure 2. (a) 3C-SiC conventional cubic cell (with lattice parameter *a* shown) and primitive unit cell (parallelepiped). (b) FBZ with high-symmetry points indicated. The irreducible first Brillouin zone including time reversal symmetry is highlighted, too.



Energy bands along a high symmetry path in the FBZ.



Imaginary part of the linear optical susceptibility $\chi_{xx}^{(1)}$ as a function of the photon energy.

$$\chi_{xx}^{(1)} = \chi_{yy}^{(1)} = \chi_{zz}^{(1)}.$$

All other entries are zero.

$$\chi^{(2)}_{xyz} = \chi^{(2)}_{yzx} = \chi^{(2)}_{zxy},$$

Comparison with the literature

FBZ sampling

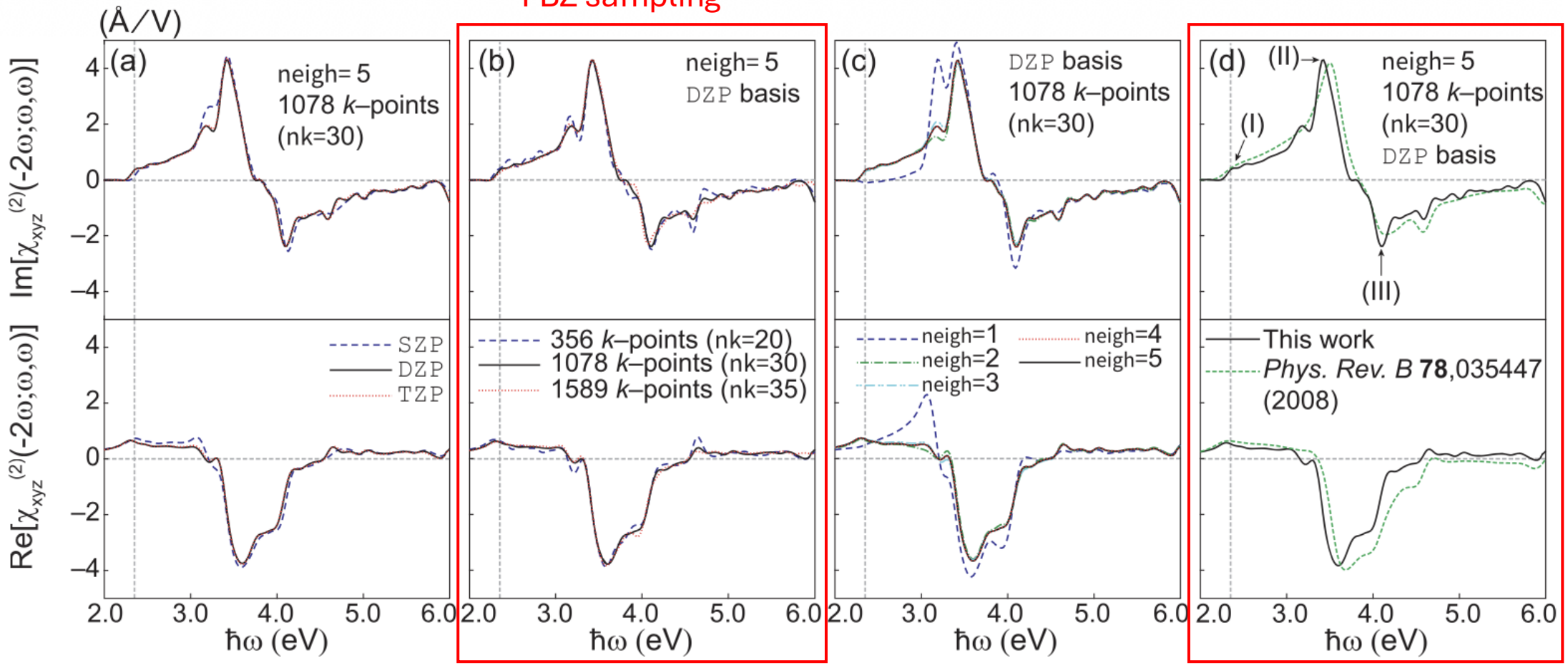


Figure 7. Im$[\chi^{(2)}_{xyz}]$ as a function of the photon energy $\hbar\omega$ for (a) three different basis sets, with a fixed number of neighbors and sampling of the trIFBZ; (b) three different samplings of the trIFBZ and a fixed number of neighbors and basis set (DZP); and (c) five different number of neighbors and fixed basis set (DZP) and sampling of the trIFBZ. (d) Comparison with previous literature. Vertical dashed lines indicating the onset of the susceptibility are shown in all panels. Reprinted (figure) with permission from [61], Copyright (2008) by the American Physical Society.

Thank you for listening !