Ultrafast Phonon Mediated Inter-valley Scattering with Tailored Light

Kevin Lively, Shunsuke Sato, Guillermo Albareda, Angel Rubio, Aaron Kelly

Max Planck Institute for the Structure and Dynamics of Matter
Deutsches Zentrum für Luft- und Raumfahrt

March 19th, 2025

PRR **6**, 013069 (2024)

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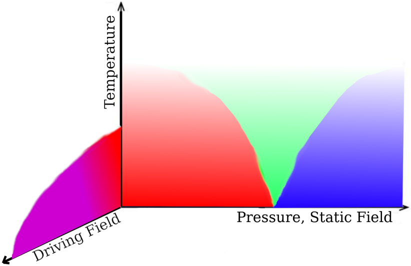
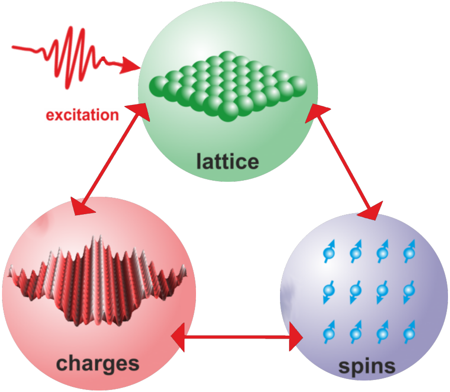
Non-Equilibrium Dynamics

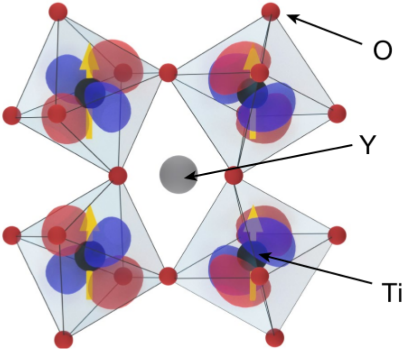




Adapted from Laurenz Rettig, Fritz Haber Institute

Non-Equilibrium Dynamics: Electron-Phonon Degrees of Freedom

$YTiO_3$: Ferromagnet under 27K



Nature **617**, 73–78 (2023)

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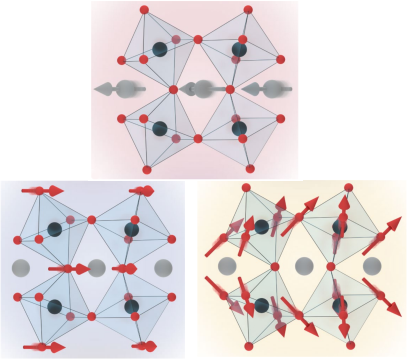

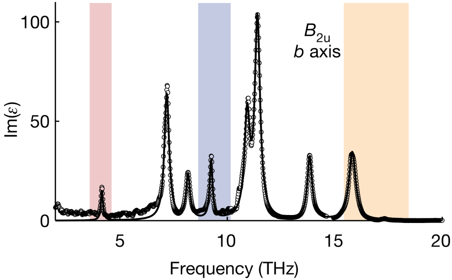

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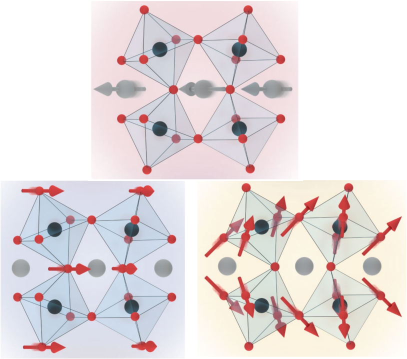

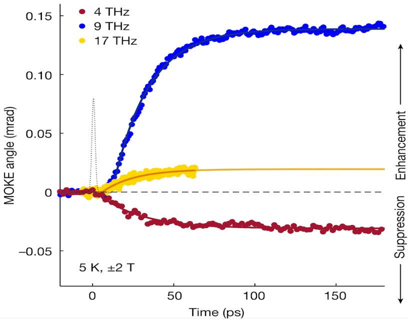

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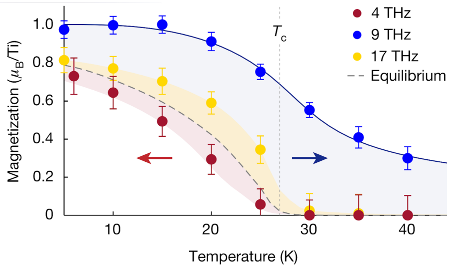

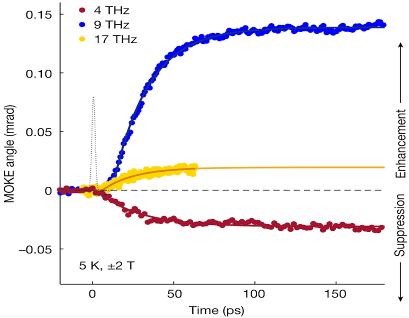

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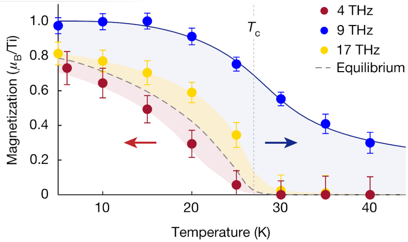
Non-Equilibrium Dynamics: Electron-Phonon Degrees of Freedom

Explanation?

- Crystal Distortion[a]
  $\sim 5 - 10\%$



[a]

[a]In similar experiments

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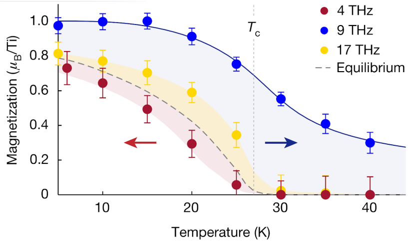

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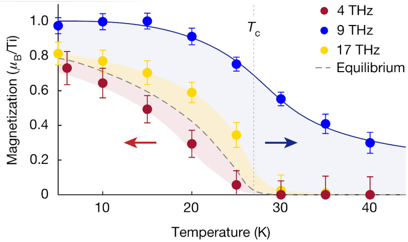
- $\sim 10 - 40\text{ps} \xrightarrow{\text{relax}} \sim 1\text{ns}$



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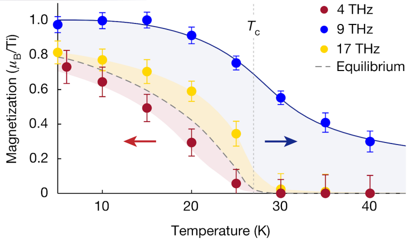
- Phenomenological Model



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Non-Equilibrium Dynamics: Electron-Phonon Degrees of Freedom

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- Crystal Distortion[a] $\sim 5 - 10\%$
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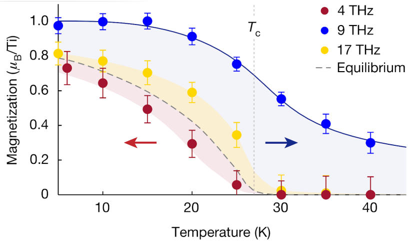
- Ab-Initio?

[a]In similar experiments



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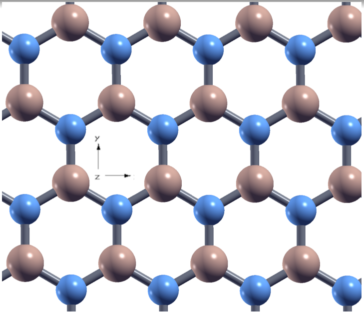
Ab-Initio Phonon Dynamics



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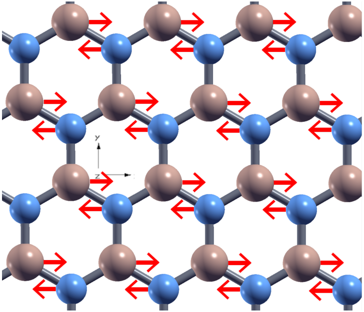
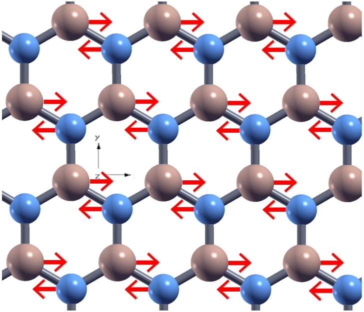


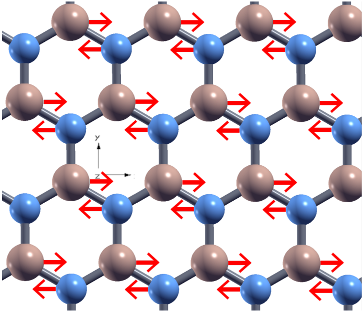
- Phonon Displacement: $\mathbf{e}_{\alpha\nu}(\mathbf{q}) \in \mathbb{C}^3$

Ab-Initio Phonon Dynamics



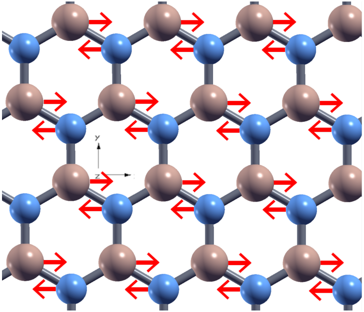
- Phonon Displacement: $\mathbf{e}_{\alpha\nu}(\mathbf{q}) \in \mathbb{C}^3$
- Atom α, primitive cell p

Ab-Initio Phonon Dynamics



- Phonon Displacement: $\mathbf{e}_{\alpha\nu}(\mathbf{q}) \in \mathbb{C}^3$
- Atom α, primitive cell p
- Phonon Momenta $\mathbf{q}$

Ab-Initio Phonon Dynamics



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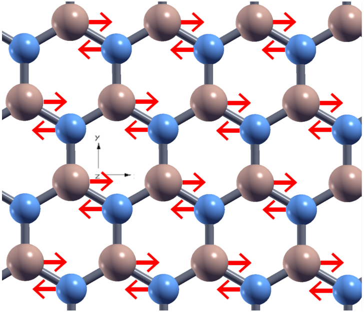
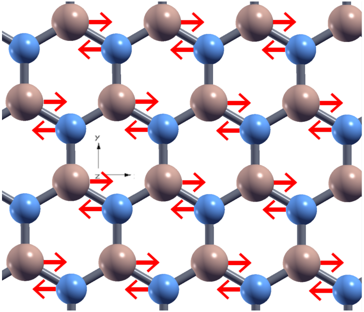
- Phonon Momenta $\mathbf{q}$
- Phonon Branch: ν

Ab-Initio Phonon Dynamics



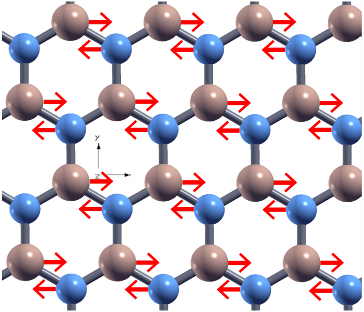
- Phonon Displacement: $\mathbf{e}_{\alpha\nu}(\mathbf{q}) \in \mathbb{C}^3$
- Atom α, primitive cell p
- Phonon Momenta $\mathbf{q}$
- Phonon Branch: ν
- Phonon Frequency: $\omega_{\mathbf{q}\nu}$

Ab-Initio Phonon Dynamics



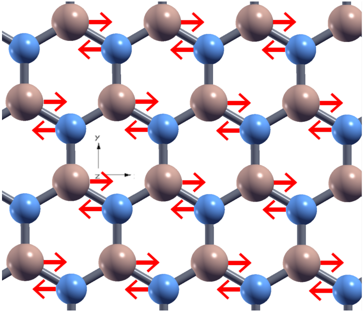
- Ionic displacement: $\delta \mathbf{R}_{\alpha p}$

Ab-Initio Phonon Dynamics



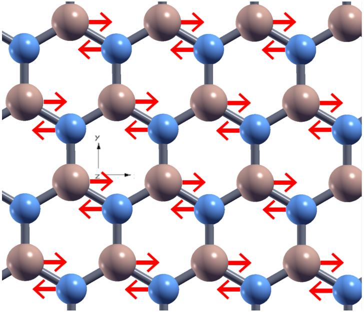
- Ionic displacement: $\delta\mathbf{R}_{\alpha p}$
- Phonon Coordinate: $z_{\mathbf{q}\nu}$

Ab-Initio Phonon Dynamics



- Ionic displacement: $\delta\mathbf{R}_{\alpha p}$
- Phonon Coordinate: $z_{\mathbf{q}\nu}$
- Phonon Momenta: $P_{\mathbf{q}\nu}$

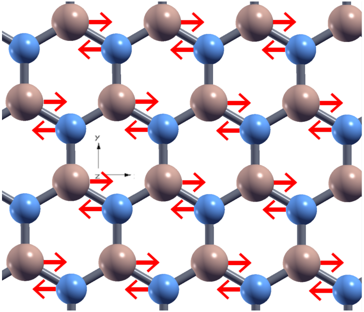
Ab-Initio Phonon Dynamics



- Ionic displacement: $\delta\mathbf{R}_{\alpha p}$
- Phonon Coordinate: $z_{\mathbf{q}\nu}$
- Phonon Momenta: $P_{\mathbf{q}\nu}$

  $\delta\mathbf{R}_{\alpha p} \propto \sum_{\mathbf{q}\nu} e^{i\mathbf{q}\cdot\mathbf{R}_p}\mathbf{e}_{\alpha\nu}(\mathbf{q}) z_{\mathbf{q}\nu}$

Ab-Initio Phonon Dynamics



- Ionic displacement: $\delta \mathbf{R}_{\alpha p}$
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$$\mathbf{P}_{\alpha p} \propto \sum_{\mathbf{q}\nu} e^{i\mathbf{q}\cdot\mathbf{R}_p} \mathbf{e}_{\alpha\nu}(\mathbf{q}) P_{\mathbf{q}\nu}$$

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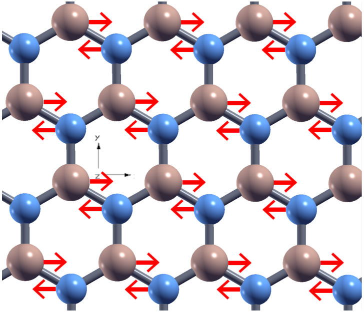

- Ionic displacement: $\delta\mathbf{R}_{\alpha p}$
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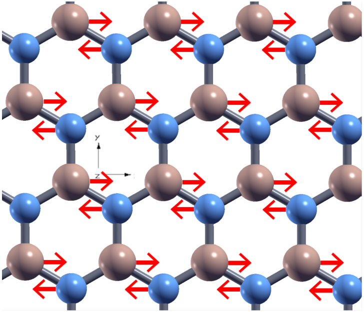
- Phonon Momenta: $P_{\mathbf{q}\nu}$

$$\delta\mathbf{R}_{\alpha p} \propto \sum_{\mathbf{q}\nu} e^{i\mathbf{q}\cdot\mathbf{R}_p}\mathbf{e}_{\alpha\nu}(\mathbf{q}) z_{\mathbf{q}\nu}$$
$$\mathbf{P}_{\alpha p} \propto \sum_{\mathbf{q}\nu} e^{i\mathbf{q}\cdot\mathbf{R}_p}\mathbf{e}_{\alpha\nu}(\mathbf{q}) P_{\mathbf{q}\nu}$$

$$\rho^W_{\mathrm{ph}} = \prod_{\nu,\mathbf{q}} \frac{\tanh(\omega_{\mathbf{q}\nu}/2k_BT)}{\pi} \exp\left[-\tanh(\omega_{\mathbf{q}\nu}/2k_BT)\left(\tilde{z}^2_{\mathbf{q}\nu} + \tilde{P}^2_{\mathbf{q}\nu}\right)\right]$$

Ab-Initio Phonon Dynamics



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- Phonon Momenta: $P_{\mathbf{q}\nu}$

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$$\mathbf{P}_{\alpha p} \propto \sum_{\mathbf{q}\nu} e^{i\mathbf{q}\cdot\mathbf{R}_p}\mathbf{e}_{\alpha\nu}(\mathbf{q}) P_{\mathbf{q}\nu}$$

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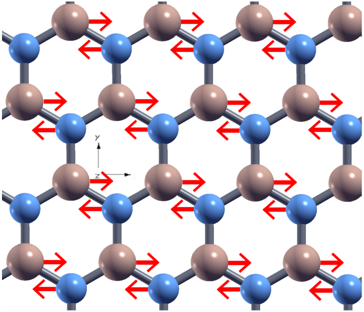
Position **Identical to Existing Static Methods**

Ab-Initio Phonon Dynamics



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Dynamics **Not Limited to Harmonic Motion**

$$\rho^W_{\mathrm{ph}} = \prod_{\nu,\mathbf{q}} \frac{\tanh(\omega_{\mathbf{q}\nu}/2k_BT)}{\pi} \exp\left[-\tanh(\omega_{\mathbf{q}\nu}/2k_BT)\left(\tilde{z}^2_{\mathbf{q}\nu} + \tilde{P}^2_{\mathbf{q}\nu}\right)\right]$$

Position **Identical to Existing Static Methods**

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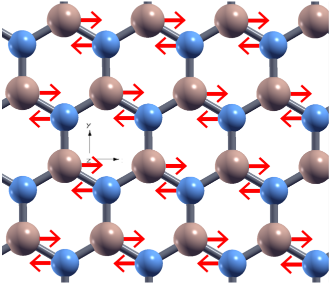
System

hexagonal Boron Nitride (hBN)



$\tilde{z}_{\mathbf{q}\nu}, \tilde{P}_{\mathbf{q}\nu} \sim \rho^{W}_{\text{ph}}$

Tight Binding (TB) Model:

$$\hat{H}_W(\mathbf{X}) = \frac{1}{2}\omega_{\mathbf{q}\nu}(\tilde{P}^2_{\mathbf{q}\nu} + \tilde{z}^2_{\mathbf{q}\nu})$$

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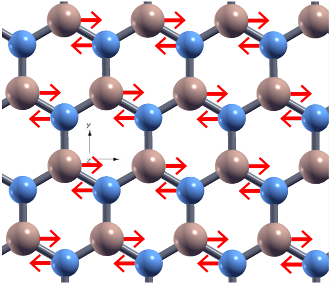

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$$+\Delta_\alpha \hat{\alpha}^\dagger_{\mathbf{k}}\hat{\alpha}_{\mathbf{k}} - t_0\left(\hat{a}^\dagger_{\mathbf{k}}\hat{b}_{\mathbf{k}}e^{i\mathbf{k}\cdot\boldsymbol{\delta}} + c.c.\right)$$

System

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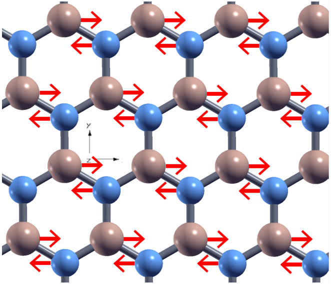

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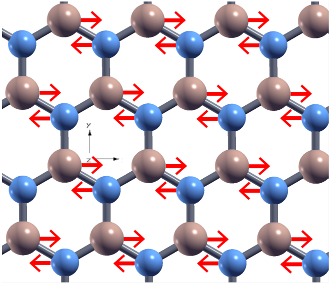

$$\tilde{z}_{\mathbf{q}\nu}, \tilde{P}_{\mathbf{q}\nu} \sim \rho^{W}_{\mathrm{ph}}$$
$$\delta \mathbf{R}_{\alpha p}, \mathbf{P}_{\alpha p} \sim \tilde{z}_{\mathbf{q}\nu}, \tilde{P}_{\mathbf{q}\nu}$$

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TDDFT Real Space Supercells

Real Time

LDA xc-functional

System

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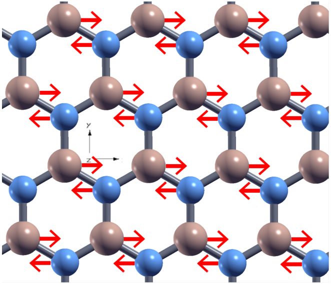

$$\tilde{z}_{\mathbf{q}\nu}, \tilde{P}_{\mathbf{q}\nu} \sim \rho^{W}_{\mathrm{ph}}$$
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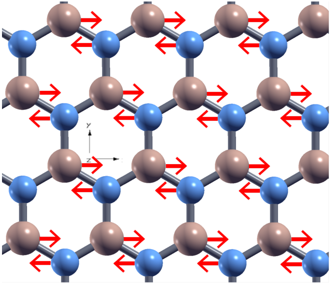


Density Functional Perturbation Theory Input:

$\omega_{\mathbf{q}\nu},\ \mathbf{e}_{\alpha\nu}(\mathbf{q})$

Tight Binding (TB) Model:

$$\hat{H}_W(\mathbf{X}) = \frac{1}{2}\omega_{\mathbf{q}\nu}(\tilde{P}^2_{\mathbf{q}\nu} + \tilde{z}^2_{\mathbf{q}\nu})$$
$$+ \Delta_\alpha \hat{\alpha}^\dagger_{\mathbf{k}}\hat{\alpha}_{\mathbf{k}} - t_0\left(\hat{a}^\dagger_{\mathbf{k}}\hat{b}_{\mathbf{k}}e^{i\mathbf{k}\cdot\boldsymbol{\delta}} + c.c.\right)$$
$$+ \tilde{z}_{\mathbf{q}\nu}\hat{M}(\mathbf{q},\nu,g^\nu(\mathbf{k},\mathbf{q}))$$

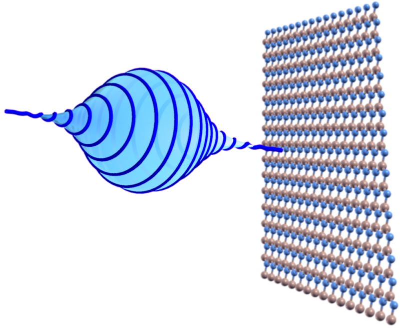
TDDFT Real Space Supercells

Real Time

LDA xc-functional

System Dynamics

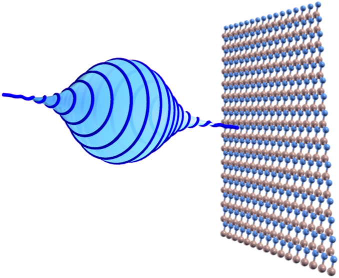
- Circularly Polarized Pump
- Ultrafast: FWHM 4.15 fs
- Intense: $7.9 \times 10^{11} \frac{\mathrm{W}}{\mathrm{cm}^2}$

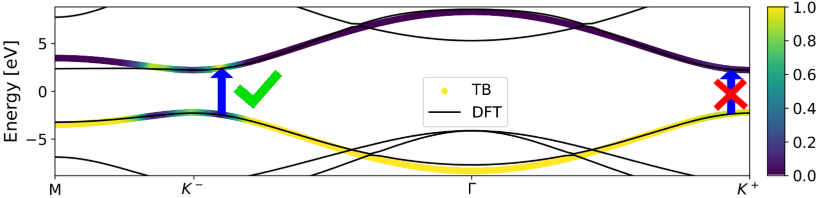


System Dynamics

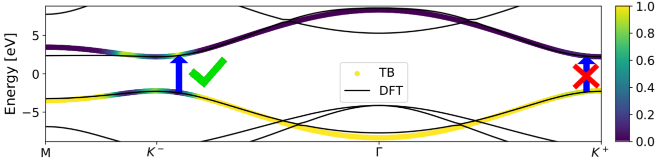
- Circularly Polarized Pump
- FWHM 4.15 fs
- Only Populates one Valley

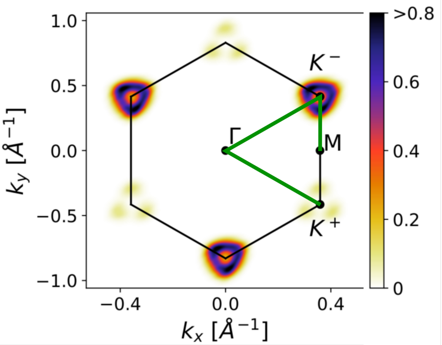
$$|c_{\mathbf{k}}|^2(t) = |\mathrm{Tr}\left[\hat{\rho}(t)\,|n\mathbf{k}\rangle\,\langle n\mathbf{k}|\right]|^2$$





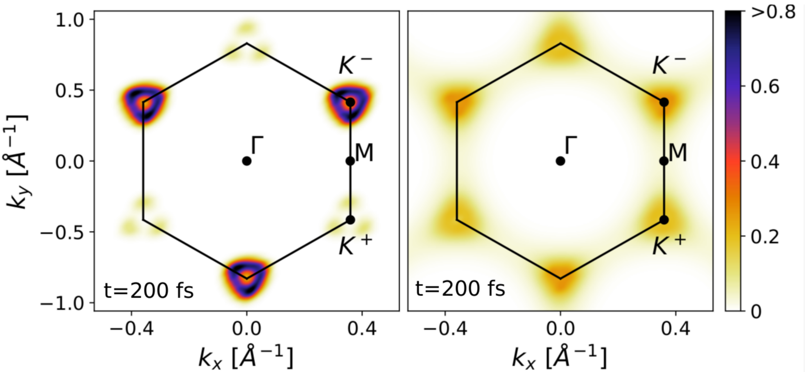
Valley Asymmetry – Theory Measure



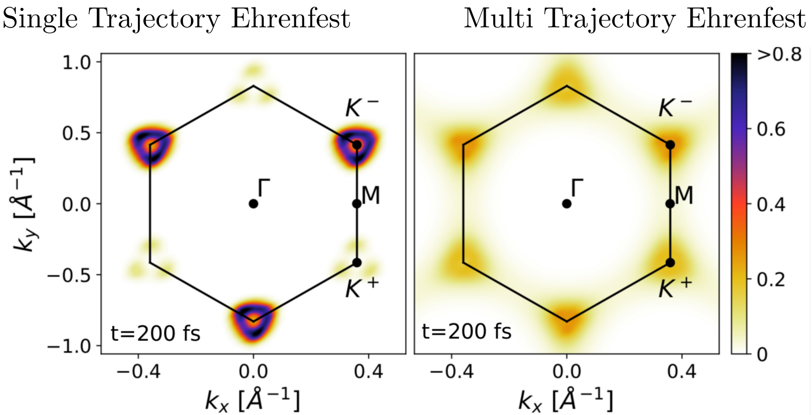


Valley Asymmetry – Theory Measure

Single Trajectory Ehrenfest — Multi Trajectory Ehrenfest



Valley Asymmetry – Theory Measure



Measuring VA: Transient Circular Dichroism

Transient Absorption Spectroscopy

- Pump with Circularly Polarized Light

Measuring VA: Transient Circular Dichroism

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- Pump with Circularly Polarized Light
  - $\mathbf{j}_{\text{pump}}(t)$

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  - $\mathbf{j}_{\text{pump-probe}}(t, \tau)$

Measuring VA: Transient Circular Dichroism

Transient Absorption Spectroscopy

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  - $\mathbf{j}_{\text{pump}}(t)$
- Probe, $\mathbf{E}_{\text{probe}}$, with Circularly Polarized Light at delay τ
  - $\mathbf{j}_{\text{pump-probe}}(t,\tau)$

$$\mathbf{j}_{\text{TAS}}(t,\tau) = \mathbf{j}_{\text{pump-probe}}(t,\tau) - \mathbf{j}_{\text{pump}}(t)$$

Measuring VA: Transient Circular Dichroism

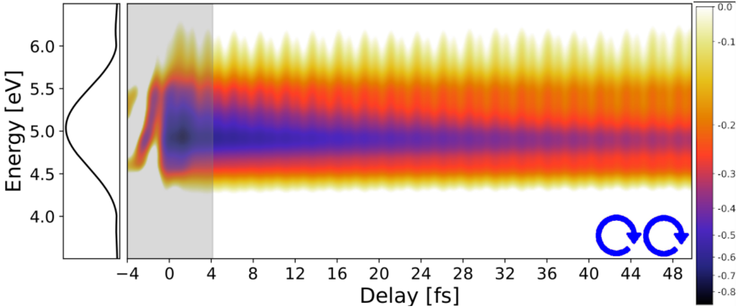
Transient Absorption Spectroscopy

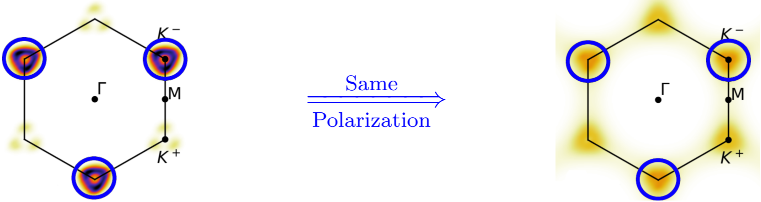
- Pump with Circularly Polarized Light
  - $\mathbf{j}_{\text{pump}}(t)$
- Probe, $\mathbf{E}_{\text{probe}}$, with Circularly Polarized Light at delay τ
  - $\mathbf{j}_{\text{pump-probe}}(t,\tau)$

$$\mathbf{j}_{\text{TAS}}(t,\tau) = \mathbf{j}_{\text{pump-probe}}(t,\tau) - \mathbf{j}_{\text{pump}}(t)$$

$$\sigma^{\text{TAS}}(\omega,\tau) = \frac{\int dt\ j_{\text{TAS}}(t,\tau)e^{i\omega t}}{\int dt\ E_{\text{probe}}(t)e^{i\omega t}} - \sigma_{\text{equil}}(\omega)$$

Measuring VA: Transient Circular Dichroism





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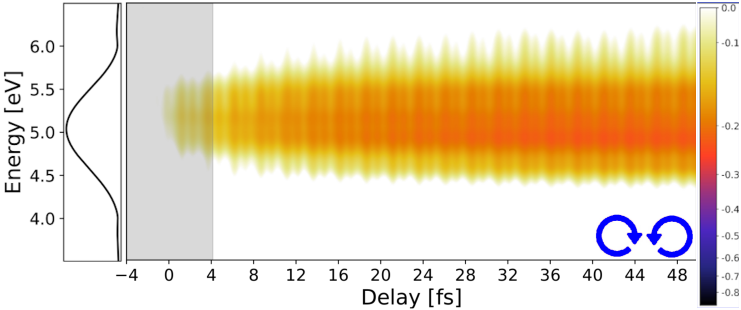
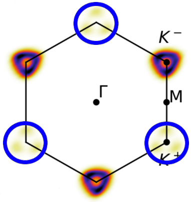
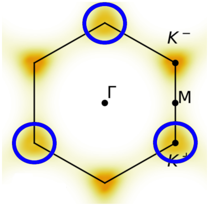




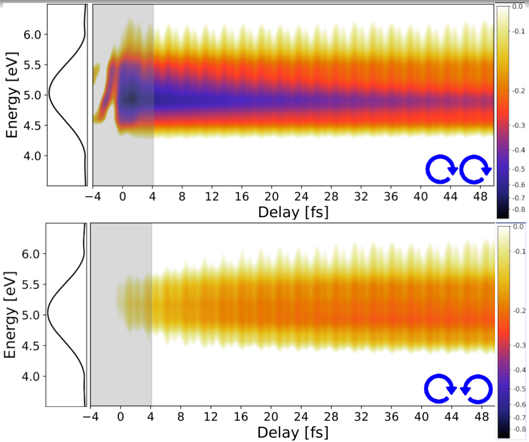
Cross ⟹ Polarization



Measuring VA: Transient Circular Dichroism

$\sigma_{\mathrm{TAS}}^{\mathrm{same}}(\omega, \tau)$

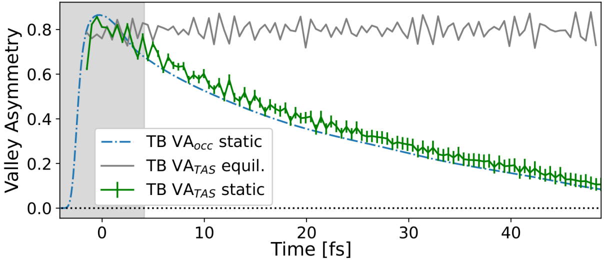
$\sigma_{\mathrm{TAS}}^{\mathrm{cross}}(\omega, \tau)$



$$\mathrm{VA}_{\mathrm{TAS}}(\tau) = \left| \frac{\int d\omega \ \mathrm{Re}\left[\sigma_{\mathrm{TAS}}^{\mathrm{cross}}(\omega, \tau) - \sigma_{\mathrm{TAS}}^{\mathrm{same}}(\omega, \tau)\right]}{\int d\omega \ \mathrm{Re}\left[\sigma_{\mathrm{TAS}}^{\mathrm{cross}} + \sigma_{\mathrm{TAS}}^{\mathrm{same}}(\omega, \tau)\right]} \right|, \qquad (1)$$

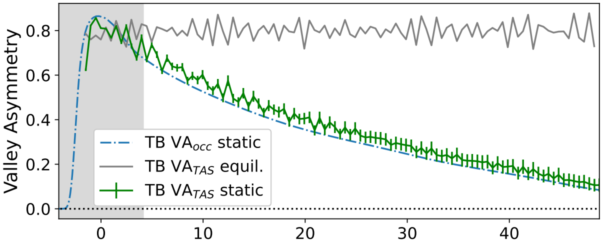
Measuring VA: Transient Circular Dichroism

TB Model

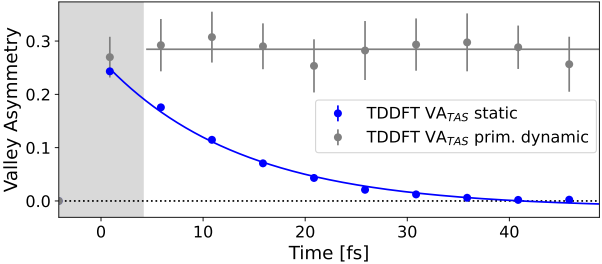


Measuring VA: Transient Circular Dichroism

TB Model



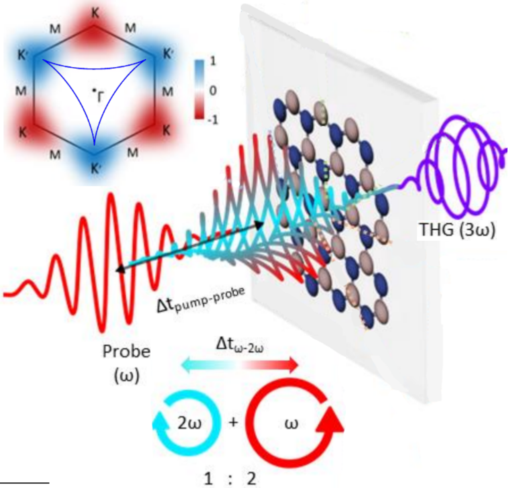
TDDFT
1800 atoms!



Measuring VA: Harmonic Ellipticity

Highly Intense (8 TW/cm^2), *off-resonant* pumping $\omega \sim 0.1E_{gap}$

- Trefoil Pump



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Measuring VA: Harmonic Ellipticity

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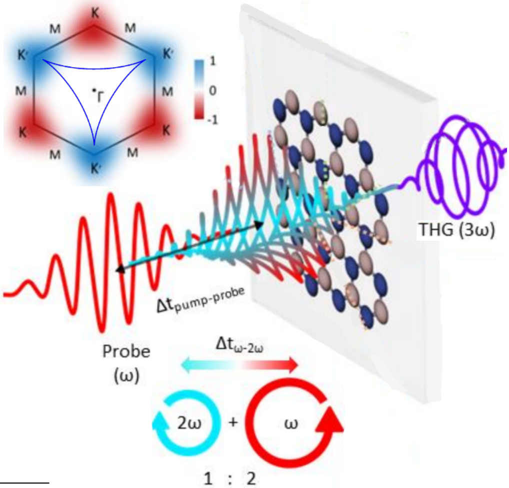

- Trefoil Pump
- Linear Probe

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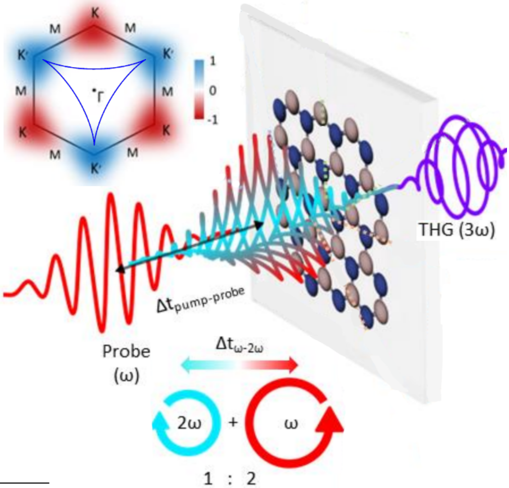
Signal from Third Harmonic Ellipticity



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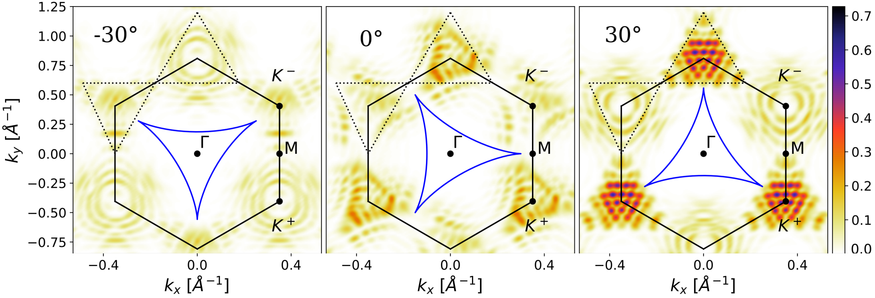
Measuring VA: Harmonic Ellipticity

TB Model: STEF



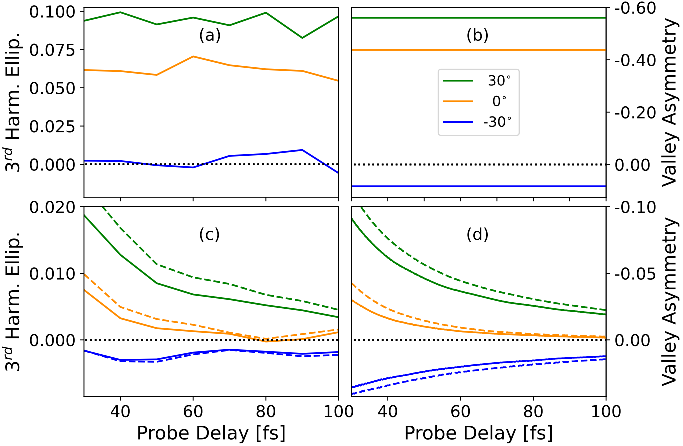
50fs after the pulse

Measuring VA: Harmonic Ellipticity

THG Ellipticity Vs. Valley Asymmetry

STEF

MTEF



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  - T_d-WTe_2: Weyl Semimetal $\rightarrow$ Manipulate Weyl nodes

Acknowledgements - Collaborators

Angel Rubio[1,2]

Aaron Kelly[1,3]

Guillermo Albareda[1,4]

Shunsuke A. Sato[1,5]

1. MPSD, Hamburg, Germany
2. Center for Computational Quantum Physics, Flatiron Institute, New York
3. Center for Ultrafast Imaging, Universität Hamburg
4. IDEADED Research, Barcelona, Spain
5. University of Tsukuba, Japan

Wigner Transform

$$\hat{O}_W(\mathbf{R},\mathbf{P}) = (2\pi)^{-dN}\int d\mathbf{Q}e^{-i\mathbf{P}\cdot\mathbf{Q}}\left\langle \mathbf{R}+\mathbf{Q}/2|\hat{O}|\mathbf{R}-\mathbf{Q}/2\right\rangle$$

Ab-Initio Phonon Dynamics

Initial electron-nuclear state

- $|\chi\rangle \xrightarrow[\text{Transform}]{\text{Wigner}} \rho_W(\mathbf{R}, \mathbf{P})$

Mean Field dynamics

Kelly, A. et al, Energy Transport in Biomaterial Systems, Springer Series in Chemical Physics, 93 pp. 383-413, 2009

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- $\partial_t |\phi_i(t)\rangle = -i\hat{H}_W(\mathbf{R}_i(t)) |\phi_i(t)\rangle$

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$$\langle O(t)\rangle = \frac{1}{N} \sum_i \langle \phi_i(t)|\hat{O}_W(\mathbf{R}_i(t), \mathbf{P}_i(t))|\phi_i(t)\rangle$$

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- Same evolution as Single Trajectory Ehrenfest (STEF)

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- Same evolution as Single Trajectory Ehrenfest (STEF)
- Approximate dynamic correlation→ Systematic Improvements

Kelly, A. et al, Energy Transport in Biomaterial Systems, Springer Series in Chemical Physics, 93 pp. 383-413, 2009

Phonon Basics

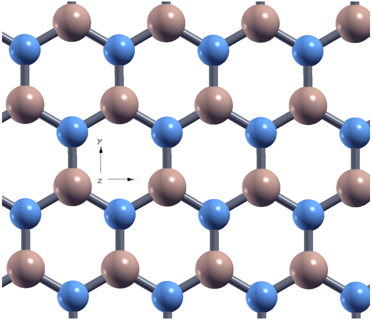
$$U = U_0 + \frac{1}{2} \sum_{\alpha p, \alpha' p'} \frac{\partial^2 E_0}{\partial \mathbf{R}_{\alpha p} \partial \mathbf{R}_{\alpha' p'}} \bigg|_{\mathbf{R}^0_{\alpha,p}, \mathbf{R}^0_{\alpha',p'}} \delta \mathbf{R}_{\alpha p} \delta \mathbf{R}_{\alpha' p'}$$

$$= U_0 + \frac{1}{2} C_{\alpha p, \alpha' p'} \delta \mathbf{R}_{\alpha p} \delta \mathbf{R}_{\alpha' p'},$$

$$D_{\alpha,\alpha'}(\mathbf{q}) = (M_\alpha M_{\alpha'})^{-1/2} \sum_p C_{\alpha 0, \alpha' p} \exp(i \mathbf{q} \cdot \mathbf{R}_p),$$

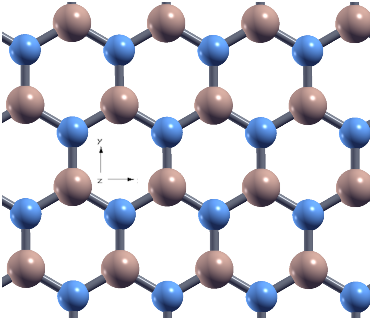
$$\sum_{\alpha'} D_{\alpha,\alpha'}(\mathbf{q}) \mathbf{e}_{\alpha' \nu}(\mathbf{q}) = \omega^2_{\mathbf{q}\nu} \mathbf{e}_{\alpha \nu}(\mathbf{q}).$$

Electron-Phonon Dynamics



“Non-interacting” limit:

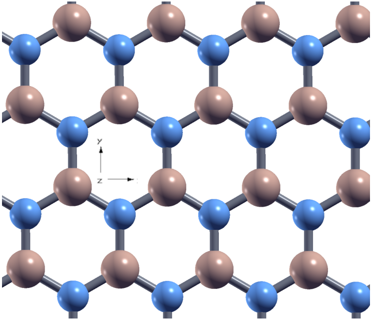
Electron-Phonon Dynamics



"Non-interacting" limit:
Equilibrium Geometry $\mathbf{R}_0$

$$\hat{H}(\mathbf{R}_0)\,|n\mathbf{k}\rangle = \epsilon_{n\mathbf{k}}\,|n\mathbf{k}\rangle$$

Electron-Phonon Dynamics

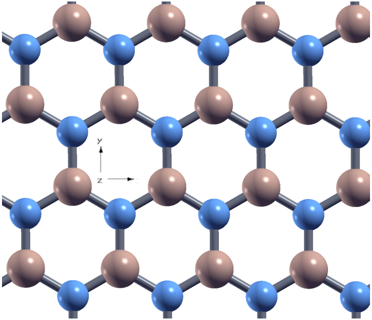


"Non-interacting" limit:
Equilibrium Geometry $\mathbf{R}_0$

$$\hat{H}(\mathbf{R}_0)\left|n\mathbf{k}\right\rangle = \epsilon_{n\mathbf{k}}\left|n\mathbf{k}\right\rangle$$

$$\left(-\frac{\partial^2}{\partial^2_{\mathbf{R}}} + \frac{\partial^2 E_0(\mathbf{R})}{\partial\mathbf{R}\partial\mathbf{R}}\Big|_{\mathbf{R}_0}\right)\left|n_{\mathbf{q}\nu}\right\rangle \rightarrow \omega_{\mathbf{q}\nu}\left|n_{\mathbf{q}\nu}\right\rangle$$

Electron-Phonon Dynamics

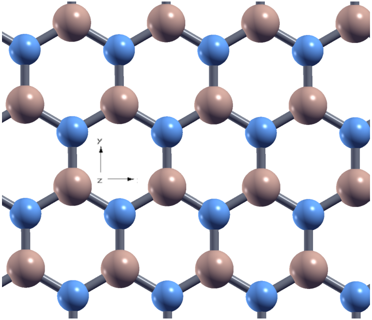


$|n\mathbf{k}\rangle$, $\epsilon_{n\mathbf{k}}$, $|n_{\mathbf{q}\nu}\rangle$, $\omega_{\mathbf{q}\nu}$

Time Dependent Boltzmann Equation (TDBE):

$$\partial_t |c_{n\mathbf{k}}|^2 \sim \sum_{\mathbf{q}m\nu} |g^{\nu}_{mn}(\mathbf{k},\mathbf{q})|^2 f(|c_{m\mathbf{k}}|^2, n_{\mathbf{q}\nu})$$
$$\partial_t n_{\mathbf{q}\nu} \sim \sum_{\mathbf{k}mn} |g^{\nu}_{mn}(\mathbf{k},\mathbf{q})|^2 h(|c_{m\mathbf{k}}|^2, n_{\mathbf{q}\nu})$$

Electron-Phonon Dynamics



$|n\mathbf{k}\rangle\,,\ \epsilon_{n\mathbf{k}},\ |n_{\mathbf{q}\nu}\rangle\,,\ \omega_{\mathbf{q}\nu}$

Supercell Static Displacement:

Phonon Coordinates $z_{\mathbf{q}\nu} \sim \mathbf{R}$

$$O(T) = \int \frac{dz_{\mathbf{q}\nu}}{\pi\sigma^2_{\mathbf{q}\nu}(T)} e^{z^2_{\mathbf{q}\nu}/\sigma^2_{\mathbf{q}\nu}(T)} \langle \hat{O}(z_{\mathbf{q}\nu}, T)\rangle$$

Time Dependent Boltzmann Equation

$$
\begin{aligned}
\partial_t f_{n\mathbf{k}} = 2\pi \sum_{m\nu\mathbf{q}} |g^{\nu}_{mn}(\mathbf{k},\mathbf{q})|^2 \\
\times\{(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\delta(\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}+\mathbf{q}}+\omega_{\mathbf{q}\nu})(n_{\mathbf{q}\nu}+1) \\
+(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\delta(\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}-\mathbf{q}}-\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu} \\
+f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}-\mathbf{q}}-\omega_{\mathbf{q}\nu})(n_{\mathbf{q}\nu}+1) \\
+f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}-\mathbf{q}}+\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu}\},
\end{aligned}
$$

$$
\begin{aligned}
\partial_t n_{\mathbf{q}\nu} = 4\pi \sum_{mn\mathbf{k}} |g^{\nu}_{mn}(\mathbf{k},\mathbf{q})|^2 f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}}) \\
\times\{\delta(\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}+\mathbf{q}}-\omega_{\mathbf{q}\nu})(n_{\mathbf{q}\nu}+1) \\
-\delta(\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}+\mathbf{q}}+\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu}\}.
\end{aligned}
$$

MTEF Initialization

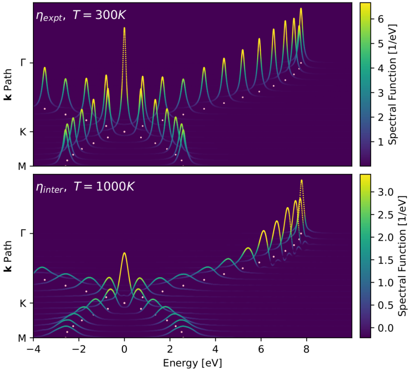
$$(\mathbf{R}_0, \mathbf{P}_0) = \mathbf{X_0} \sim \rho_{\text{ph}}^W$$
$$\rho_{\text{ph}}^W = \prod_{\nu,\mathbf{q}} \frac{\tanh(\omega_{\mathbf{q}\nu}/2k_BT)}{\pi} \exp\left[-\tanh(\omega_{\mathbf{q}\nu}/2k_BT)\left(\tilde{z}_{\mathbf{q}\nu}^2 + \tilde{P}_{\mathbf{q}\nu}^2\right)\right]$$

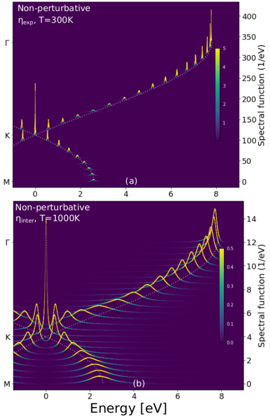
$$\hat{H}_W(\mathbf{X}^0)\left|\psi_l(\mathbf{X}^0)\right\rangle = \epsilon_l(\mathbf{X}^0)\left|\psi_l(\mathbf{X}^0)\right\rangle$$

$$\hat{\rho}_{\text{e}} = \sum_l f(\epsilon_l^0, T)\left|\psi_l\right\rangle\left\langle\psi_l\right|$$

Phonon Dressed Electronic Spectral Functions

$$A_{\mathbf{k}}(\omega) = \mathrm{Im}\left[G_{W,n\mathbf{k}}(\omega)\right]$$
$$G_{W,n\mathbf{k}}(t) = \frac{i}{N_t}\sum_{il} \langle n\mathbf{k}|\psi_l^i(t)\rangle \langle \psi_l^i(t=0)|n\mathbf{k}\rangle$$





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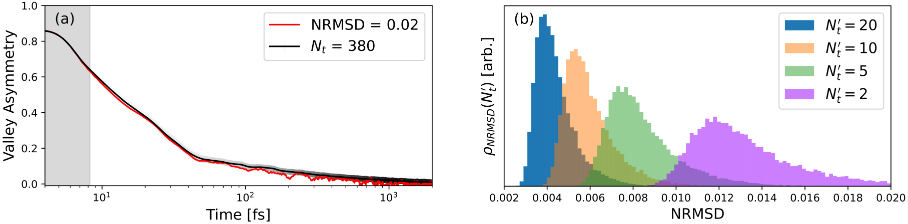
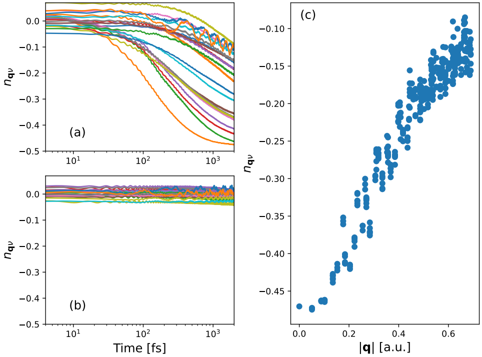
Rapidly Convergent

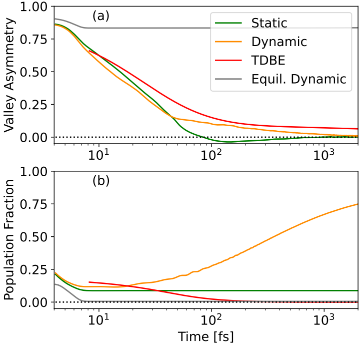
Distanced to Converged answer: NRMSD



$$\mathrm{NRMSD} = \sqrt{\int_{t_i}^{t_f} dt (f(t) - g(t))^2/(t_f - t_i)}/(\max(f) - \min(f))$$

ZPE Loss


(a)
(b)
(c)
Time [fs]
|q| [a.u.]


(a)
(b)
Static
Dynamic
TDBE
Equil. Dynamic
Valley Asymmetry
Population Fraction
Time [fs]

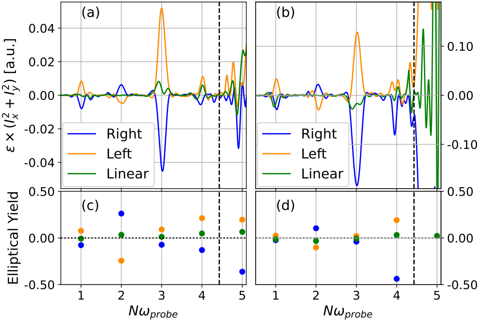
HHG Ellipticity

HHG Ellipticity Signal Picks up Valley Asymmetry

Resonant Circularly Polarized Pump

$$I_{x,y}(\omega) \propto \int dt\ e^{i\omega t} \partial_t j_{x,y}(t)$$

$$\epsilon\left[I_{x,y}(\omega)\right] \in [-1, 1]$$



(a): Tight Binding, (b): TDDFT