

Theoretical investigation of light-matter coupling on nuclear dynamics

Author: Elia Stocco

Supervisors: Mariana Rossi, Christian Carbogno

Coffee Talk: June 6th, 2023

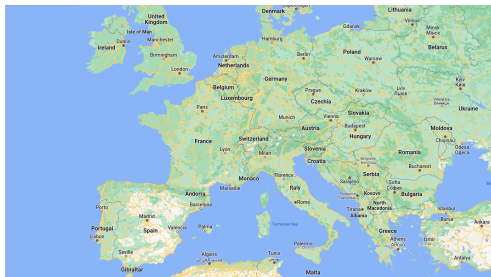


Something about myself

Education

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- ▶ European, Italian: lived in Cantalupo (really small town close to Milan)

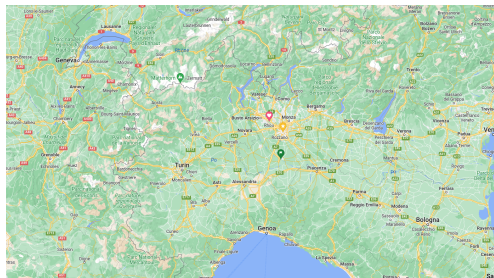


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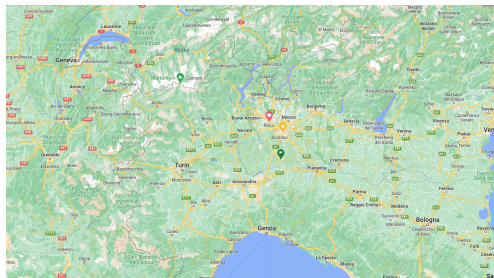


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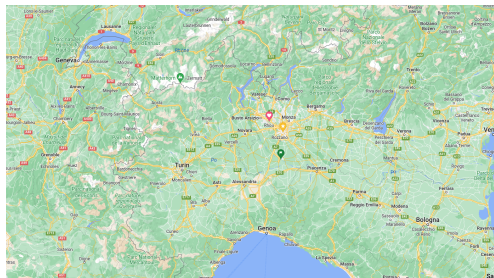


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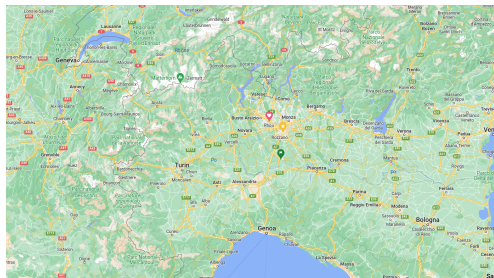


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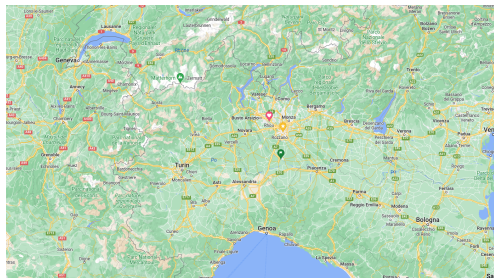


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- ▶ temporary position in FHI since October 1th 2022
- ▶ PhD in MPSD in Hamburg (Mariana Rossi's group) from July 1th 2023



Something about myself

Where I come from



(a) Milan Cathedral



(b) "Palio" of Legnano



(c) Risotto e ossobuco



(d) Cassoeula



(e) Trippa

Something about myself

Where I come from



(a) Bresaola



(b) Pizzoccheri



(c) Gorgonzola

Something about myself

Where I come from



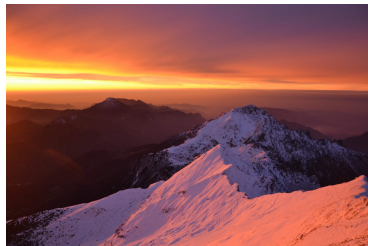
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(b) Pizzoccheri



(c) Gorgonzola



Something about myself

Where I come from



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(b) Pizzoccheri



(c) Gorgonzola



Introduction

Experimental results

Experimental results, by using a coherent laser pulse in the THz region:

- ▶ light-induced superconductivity in cuprates¹
- ▶ state manipulation/control in gas² and liquid³ phase systems
- ▶ polarization reversal in ferroelectric solids⁴

Light-Induced Superconductivity in a Stripe-Ordered Cuprate

D. Fausti,^{1,2,*}† R. I. Tobey,²†§ N. Dean,^{1,2} S. Kaiser,¹ A. Dienst,² M. C. Hoffmann,¹ S. Pyon,³ T. Takayama,² H. Takagi,^{1,2} A. Cavalleri^{1,2,*}

Metastable ferroelectricity in optically strained SrTiO₃

T. F. Nova^{1,2,*}, A. S. Disa¹, M. Fechner¹, A. Cavalleri^{1,2,3,*}

Nonlinear lattice dynamics as a basis for enhanced superconductivity in YBa₂Cu₃O_{6.5}

R. Mankowsky^{1,2,3,*}, A. Subedi⁴, M. Fries^{1,3}, S. O. Mariagar¹, M. Chellai¹, H. T. Lemko¹, J. S. Robinson¹, J. M. Glowinski¹, M. P. Minitti¹, A. Frano¹, M. Fechner¹, N. A. Spaldin¹, T. Loew¹, B. Keimer¹, A. Georges^{1,3,5} & A. Cavalleri^{1,2,3,6}

Polarizing an antiferromagnet by optical engineering of the crystal field

Ankit S. Disa^{1,2,6}, Michael Fechner¹, Tobia F. Nova¹, Bialong Liu¹, Michael Först¹, Dharmalingam Prabhakaran¹, Paolo G. Radaelli¹ and Andrea Cavalleri^{1,2,3,6}

Ultrafast Reversal of the Ferroelectric Polarization

R. Mankowsky,¹ A. von Hoegen,¹ M. Först,¹ and A. Cavalleri^{1,2}

¹Max Planck Institute for the Structure and Dynamics of Matter, 22761 Hamburg, Germany

²Department of Physics, University of Oxford, Clarendon Laboratory, Oxford OX1 3PU, United Kingdom

(Received 21 January 2017; published 10 May 2017)

¹Science, 331(6014), 189–191.

²Phys. Rev. Lett., 107, 163603.

³Nature Communications, 8(1), 14963.

⁴Phys. Rev. Lett., 118, 197601.

Introduction

Ab initio approach

Previous approaches:

- ▶ nuclear motion modeled as driven harmonic oscillators^{5,6}
- ▶ no nuclear quantum effect nor lattice distortion
- ▶ lowest-order anharmonicities only

Aim: develop an *ab initio* to study light-driven nuclear dynamics:

- ▶ method based on Molecular Dynamics
- ▶ Machine-Learning methods: speed-up and larger systems

Focus on:

- ▶ response of the system at varying **E** intensities and frequencies
- ▶ light-induced (structural) phase transitions
- ▶ light-driven control of the system state (out-of-equilibrium)

⁵Nature Physics 7, 854–856 (2011)

⁶Phys. Rev. B 89, 220301(R)

Theory

Electric Dipole Approximation

The Hamiltonian $\hat{\mathcal{H}}_{tot}$ of the system of electrons and nuclei is:

$$\hat{\mathcal{H}}_{tot} = \hat{\mathcal{T}}_e + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{en} + \hat{\mathcal{T}}_n + \hat{\mathcal{V}}_{nn}$$

Light-matter coupling using the Electric Dipole Approximation (EDA)⁷

$$\hat{\mathcal{H}}_{tot}^E = \hat{\mathcal{H}}_{tot} - \Omega \mathbf{P} \cdot \mathbf{E}(t) \quad (\Omega = \text{unit cell volume})$$

In the previous equations:

- ▶ \mathbf{P} is the polarization (dipole per unit volume)
- ▶ \mathbf{E} is the external electric field (with wavelength λ)
- ▶ the approximation is valid as long as $|\lambda| \gg$ lattice parameter (long-wavelength limit $\rightarrow \mathbf{E}$ is homogeneous over the system)

⁷ John Wiley & Sons, Photons and Atoms

Theory

Polarization in periodic systems

\mathbf{P} has an electronic and a nuclear contribution, i.e. $\mathbf{P} = \mathbf{P}^n + \mathbf{P}^e$:

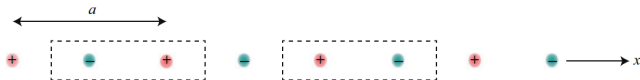
- ▶ \mathbf{P}^n is expressed through the classical formula:

$$\mathbf{P}^n = \frac{q_e}{\Omega} \sum_I^{N_n} Z^I \mathbf{R}^I \quad (\text{where } \mathbf{R}^I \text{ is the } I^{\text{th}} \text{ nucleus position})$$

- ▶ (the derivative of) \mathbf{P}^e is expressed using the **Modern Theory of Polarization**^{8,9}:

$$\partial_\lambda \mathbf{P}^e = \frac{q_e}{(2\pi)^3} \sum_n^{\text{occ}} \int_{\text{BZ}} d^3\mathbf{k} 2\text{Im} \langle \partial_\lambda u_{n\mathbf{k}} | \partial_{\mathbf{k}} u_{n\mathbf{k}} \rangle$$

\mathbf{P} is defined up to a quantum $|\mathbf{a}_i| q_e / \Omega$ along the lattice vector \mathbf{a}_i direction.



⁸ Phys. Rev. B 47, 1651(R)

⁹ Journal of Solid State Chemistry, 195, 2-10

Theory

Born-Oppenheimer approximation

Classical nuclei and Born-Oppenheimer/adiabatic approximation:

- ▶ with $\mathbf{E} = \mathbf{0}$

$$\text{electrons: } \hat{\mathcal{H}}_e(\mathbf{R}) |\psi_{\mathbf{R}}(\mathbf{r})\rangle = E_{\mathbf{R}}^{\text{KS}} |\psi_{\mathbf{R}}(\mathbf{r})\rangle \quad \xrightarrow{\text{DFT}} \quad 0 = \frac{\delta E_{\mathbf{R}}^{\text{KS}}[n]}{\delta n}$$

$$\text{nuclei: } \mathcal{H}_n^0 = T_n + V_{nn} + E_{\mathbf{R}}^{\text{KS}} \quad \xrightarrow{\text{MD}} \quad \mathbf{F}' = -\frac{\partial \mathcal{H}_n^0}{\partial \mathbf{R}'}$$

- ▶ with $\mathbf{E} \neq \mathbf{0}$ ¹⁰

$$\text{electrons: } 0 = \frac{\delta \mathcal{F}_{\mathbf{R}}(\mathbf{E})}{\delta n} = \frac{\delta}{\delta n} \left(E_{\mathbf{R}}^{\text{KS}} - \Omega \mathbf{P} \cdot \mathbf{E} \right)$$

$$\text{nuclei: } \mathcal{H}_n^{\mathbf{E}} = T_n + V_{nn} + \mathcal{F}_{\mathbf{R}}(\mathbf{E})$$

where $\mathcal{F}_{\mathbf{R}}(\mathbf{E})$, $E_{\mathbf{R}}^{\text{KS}}$, and \mathbf{P} depend *parametrically* on \mathbf{R}

¹⁰Phys. Rev. Lett. 89, 117602

Theory

Weak field approximation

Assumption: \mathbf{E} is small enough s.t. we can discard any induced change in the electronic structure.¹¹

We can then safely rely on the following approximated approach:

▶ **electrons:**

- ▶ KS equations are solved for $\mathbf{E} = \mathbf{0}$
- ▶ \mathbf{P} is computed only at the end of the scf procedure
- ▶ the *enthalpy* is approximate with a linear expression in \mathbf{E} :

$$\mathcal{F}_R(\mathbf{E}) \simeq E_R^{\text{KS}}|_0 - \mathbf{E} \cdot \mathbf{P}|_0$$

- ▶ **nuclei:** the nuclear Hamiltonian is then approximated with a linear expression in \mathbf{E} :

$$\begin{aligned} \mathcal{H}_n^{\mathbf{E}} &\simeq T_n + V_{nn} + E_R^{\text{KS}} - \Omega \mathbf{P} \cdot \mathbf{E} \\ &= \mathcal{H}_n^0 - \Omega \mathbf{P} \cdot \mathbf{E} \end{aligned}$$

¹¹Phys. Rev. B 107, 054102

Theory

Born Effective Charge tensors

Within these approximations, the **forces** gain just a simple term:

$$\mathbf{F}^I = - \frac{\partial \mathcal{H}_n^E}{\partial \mathbf{R}^I} \simeq \mathbf{F}^{0I} + \Omega \frac{\partial \mathbf{P}}{\partial \mathbf{R}^I} \cdot \mathbf{E}$$

We need to know the **Born Effective Charge** (BEC) tensors Z_{ij}^{*I} of each ion I :

$$Z_{ij}^{*I} = \frac{\Omega}{q_e} \frac{\partial P_i}{\partial R_j^I} \quad (q_e \text{ elementary charge, } \Omega \text{ u.c. volume})$$

The BEC tensors can be computed using:

- ▶ **finite differences** : $Z_{ij}^{*I} \propto \Delta P_i / \Delta R_j^I$
- ▶ **DFPT**¹²:

$$Z_{ij}^{*I} = \frac{\Omega}{(2\pi)^3} \sum_n^{\text{occ}} \int_{\text{BZ}} d^3\mathbf{k} 2\text{Im} \left\langle \frac{\partial u_{n\mathbf{k}}}{\partial R_j^I} \middle| \frac{\partial u_{n\mathbf{k}}}{\partial k_i} \right\rangle + Z^I$$

¹²Rev. Mod. Phys. 73, 515

Implementation

i-PI protocol

How to sample NVE and NVT ensembles:

- ▶ the potential is now **time-dependent** due to the term $\Omega \mathbf{P} \cdot \mathbf{E}(t)$
- ▶ we need a new *protocol* to perform driven-MD within i-PI:

$$p(t + \Delta t/2) = p(t) + \left[F(q(t)) + \mathbf{eZ}^* \cdot \mathbf{E}(t) \right] \Delta t/2$$

$$q(t + \Delta t) = q(t) + p(t + \Delta t/2) \Delta t/m$$

$$p(t + \Delta t) = p(t + \Delta t/2) + \left[F(q(t + \Delta t)) + \mathbf{eZ}^* \cdot \mathbf{E}(t + \Delta t) \right] \Delta t/2$$

- ▶ implemented sinusoidal \mathbf{E} fields (with a gaussian envelope function too)
- ▶ \mathbf{P} is *not strictly needed* for the dynamics, but the BEC tensors are
- ▶ ... but the BEC could **depend on the positions \mathbf{R}** :

$$Z_{ij}^{*l}(\mathbf{R}) = \frac{\Omega}{q_e} \frac{\partial P_i(\mathbf{R})}{\partial R_j^l}$$

Implementation

Driver

Quantum Espresso^{13,14,15}:

- ▶ plane-waves basis set
- ▶ Pseudo-Potentials
- ▶ different kind of functionals



Some modifications have been done:

- ▶ \mathbf{P} is computed using the Resta formalism¹⁶ at each MD step
- ▶ DFPT calculations are performed “on-the-fly” (merged `pw.x` with `ph.x`)
- ▶ the BEC are computed at each MD step
- ▶ implemented communication with `i-PI` for \mathbf{P} and Z_{ij}^{*l}

¹³ J. Phys.:Condens. Matter 21 395502 (2009)

¹⁴ J. Phys.:Condens. Matter 29 465901 (2017)

¹⁵ J. Chem. Phys. 152 154105 (2020)

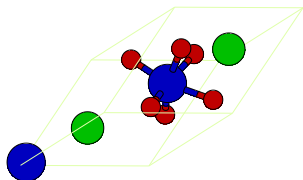
¹⁶ Phys. Rev. Lett. 80, 1800

Results

LiNbO₃: crystal structure

Properties:

- ▶ lattice: rhombohedral
- ▶ space group: 161
- ▶ u.c. volume: $\simeq 695 \text{ a.u.}^3$
- ▶ spontaneous polarization at 0 K: $\mathbf{P} \simeq 1.17 (\hat{\mathbf{v}}_1 + \hat{\mathbf{v}}_2 + \hat{\mathbf{v}}_3) \text{ a.u.}$



Nb (blue), Li (green), O (red)

$$\begin{pmatrix} \mathbf{v}_1 & \mathbf{v}_2 & \mathbf{v}_3 \\ 5.55 & 3.29 & 3.29 \\ 0.00 & 4.47 & 1.66 \\ 0.00 & 0.00 & 4.15 \end{pmatrix} \begin{matrix} x \\ y \\ z \end{matrix}$$

cell parameters (angstrom).

Results

LiNbO₃: BEC tensors

The BEC tensors have been computed as **E**-induced forces:

$$Z_{ij}^{*I} \propto \frac{\partial P_i}{\partial R_j^I} = -\frac{\partial^2 U}{\partial R_j^I \partial E_i} = \frac{\partial F_j^I}{\partial E_i}$$

Some examples of the computed BEC tensors:

$$Z^{*Li} = \begin{pmatrix} P_x & P_y & P_z \\ 1.21 & 0.09 & 0.18 \\ 0.20 & 1.00 & -0.11 \\ 0.01 & 0.21 & 0.97 \end{pmatrix} \begin{matrix} E_x \\ E_y \\ E_z \end{matrix} \quad Z^{*Nb} = \begin{pmatrix} P_x & P_y & P_z \\ 4.57 & -0.97 & 0.04 \\ -0.32 & 5.52 & -1.17 \\ -0.92 & 0.72 & 5.70 \end{pmatrix} \begin{matrix} E_x \\ E_y \\ E_z \end{matrix}$$
$$Z^{*O} = \begin{pmatrix} P_x & P_y & P_z \\ -1.45 & -0.27 & -0.02 \\ -0.33 & -2.79 & -1.16 \\ 0.28 & -0.91 & -2.49 \end{pmatrix} \begin{matrix} E_x \\ E_y \\ E_z \end{matrix}$$

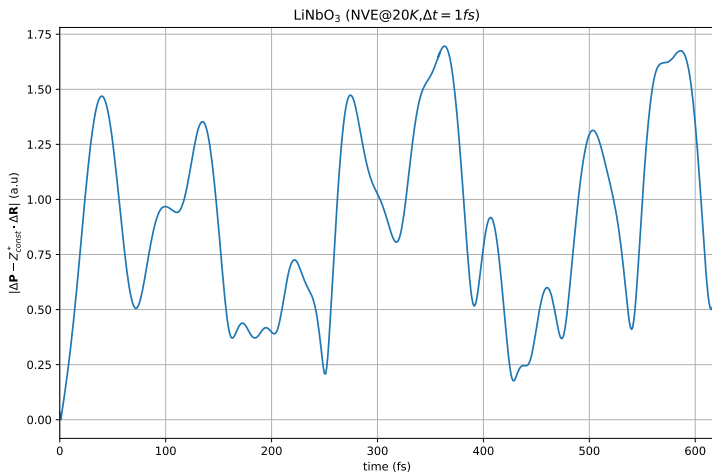
Different atoms (of the same species too) could have really different BEC tensors.

Results

LiNbO₃: BEC tensors

Why do we need to compute the BEC tensors at each MD step?

- ▶ \mathbf{P} can not be assumed linear w.r.t. the displacements: $\Delta\mathbf{P} \neq \mathbf{Z}_{const}^* \cdot \Delta\mathbf{R}$

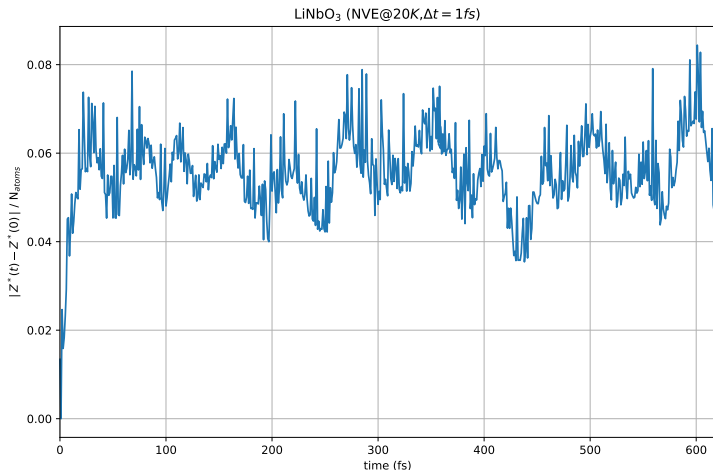


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LiNbO₃: BEC tensors

Why do we need to compute the BEC tensors at each MD step?

- ▶ \mathbf{P} can not be assumed linear w.r.t. the displacements: $\Delta \mathbf{P} \neq \mathbf{Z}_{const}^* \cdot \Delta \mathbf{R}$
- ▶ \mathbf{Z}^* can not be assumed constant w.r.t. \mathbf{R} .



Results

LiNbO₃: BEC tensors convergence

The BEC tensors need to be converged w.r.t. \mathbf{k} -points in DFPT calculatons.

Here are the results for Nb in the 1x1x1 primitive cell:

$$n_k = 1: \quad Z^{*\text{Nb}} = \begin{pmatrix} P_x & P_y & P_z \\ 4.6 & -1.0 & 0.0 \\ -0.3 & 5.5 & -1.2 \\ -0.9 & 0.7 & 5.7 \end{pmatrix} \begin{matrix} E_x \\ E_y \\ E_z \end{matrix} \quad \frac{-1}{N_n} \sum_l Z^{*l} = \begin{pmatrix} P_x & P_y & P_z \\ 1.75 & 0.88 & 0.50 \\ 0.88 & 0.46 & 0.30 \\ 0.59 & 0.30 & 0.21 \end{pmatrix} \begin{matrix} E_x \\ E_y \\ E_z \end{matrix}$$

$$n_k = 2^3: \quad Z^{*\text{Nb}} = \begin{pmatrix} P_x & P_y & P_z \\ 5.2 & -0.9 & 0.2 \\ -0.2 & 6.0 & -1.2 \\ -0.9 & 0.9 & 6.2 \end{pmatrix} \begin{matrix} E_x \\ E_y \\ E_z \end{matrix} \quad \frac{1}{N_n} \sum_l Z^{*l} = \begin{pmatrix} P_x & P_y & P_z \\ 0.07 & 0.00 & 0.00 \\ 0.00 & 0.07 & 0.00 \\ 0.00 & 0.00 & 0.07 \end{pmatrix} \begin{matrix} E_x \\ E_y \\ E_z \end{matrix}$$

$$n_k = 4^3: \quad Z^{*\text{Nb}} = \begin{pmatrix} P_x & P_y & P_z \\ 5.2 & -0.9 & 0.1 \\ -0.2 & 6.0 & -1.2 \\ -0.9 & 0.8 & 6.1 \end{pmatrix} \begin{matrix} E_x \\ E_y \\ E_z \end{matrix} \quad \frac{1}{N_n} \sum_l Z^{*l} = \begin{pmatrix} P_x & P_y & P_z \\ 0.01 & 0.00 & 0.00 \\ 0.00 & 0.01 & 0.00 \\ 0.00 & 0.00 & 0.01 \end{pmatrix} \begin{matrix} E_x \\ E_y \\ E_z \end{matrix}$$

pw.x + ph.x = eda.x does not work (yet) with $n_k > 1$: **debugging!**

Results

LiNbO₃: BEC tensors convergence

Observation: the sum rule $\sum_l Z^{*l} = 0$ “does not improve” if we increase the cell size and keeping n_k fixed.

Explanation: the BEC tensors are expressed using a \mathbf{k} -points derivative:

$$Z_{ij}^{*l} = \frac{\Omega}{(2\pi)^3} \sum_n^{\text{occ}} \int_{\text{BZ}} d^3\mathbf{k} 2\text{Im} \left\langle \frac{\partial u_{nk}}{\partial R_j^l} \middle| \frac{\partial u_{nk}}{\partial \mathbf{k}_i} \right\rangle + Z^l$$

To get more accurate results we need a denser \mathbf{k} -grid.

Problem: for large cells DFPT calculations are really expensive!

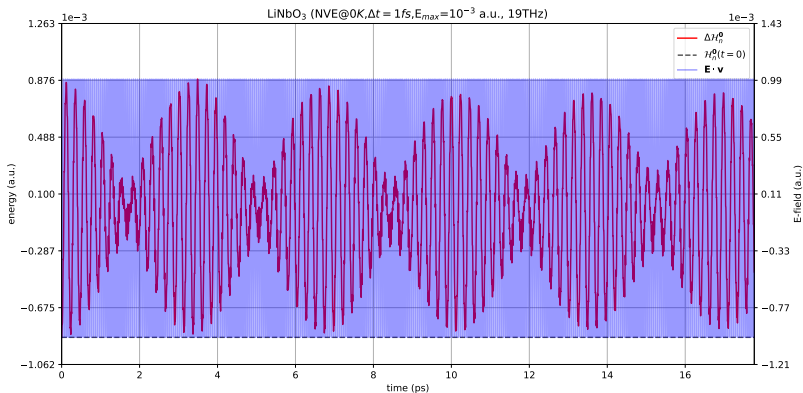
time	$n_k = 1^3$	$n_k = 2^3$	$n_k = 4^3$
$N_a = 10$	1m	5m	33m
$N_a = 30$	6m	38m	4h45m
$N_a = 80$	1h20m	15h	/

Possible solution: Machine-Learn the BEC tensors and/or polarization.

Results

LiNbO₃: EDA-NVE

Applied **E**-field with $E_{max} = 10^{-3} a.u.$ and $\omega = 19\text{THz}$.

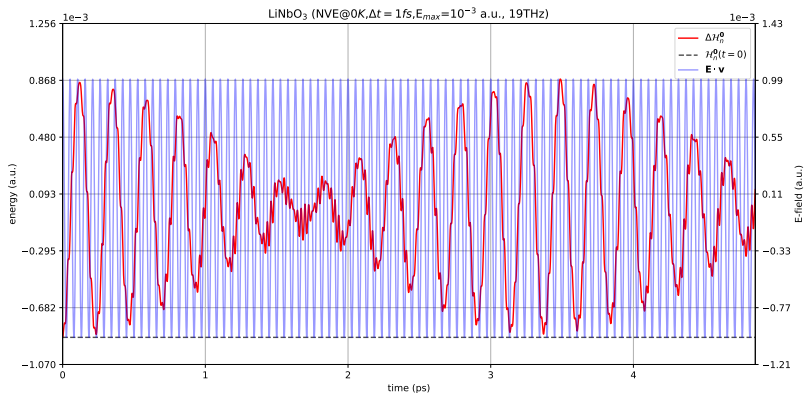


Question/outlook: how the system respond to an external perturbation?

Results

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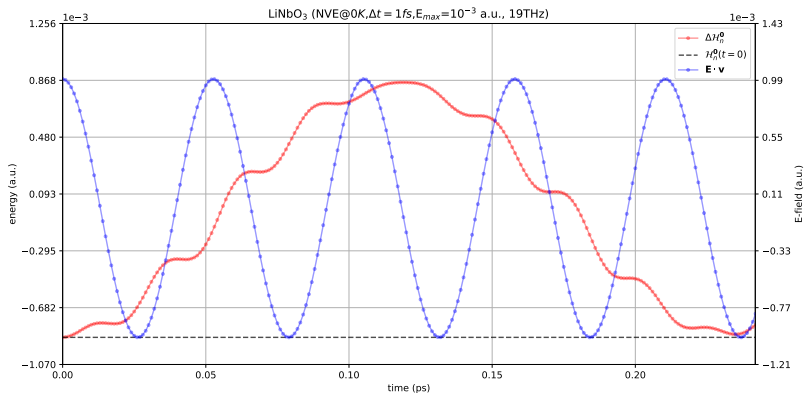


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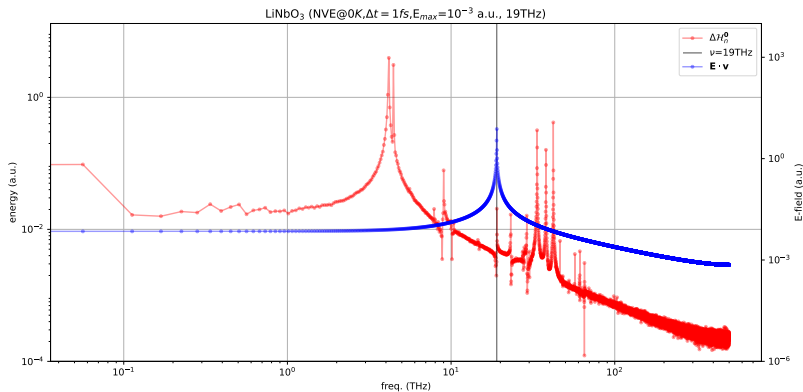


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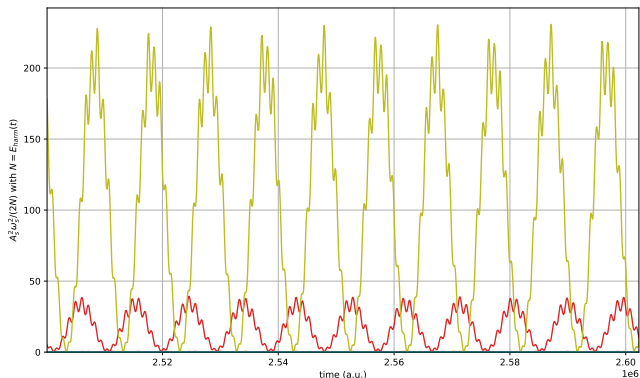


Question/outlook: how the system respond to an external perturbation?

Results

LiNbO₃: Projection on vibrational modes

Vibrational modes energy of LiNbO₃.



The 2 highly populated modes have frequencies 14.5 and 23 THz.

Further analysis to validate the **two coupled phonons model**.

Results

LiNbO₃: Two coupled phonons model

Simple mechanism for polarization reversal^{17,18}:

- ▶ there exists a **low frequency** phonon mode Q_P in the ferroelectric phase whose excitation induces changes in **P**
- ▶ the Q_P mode potential is a **double well**
- ▶ the Q_P mode is anharmonically coupled to a **high frequency** infrared-active phonon mode Q_{IR}

The potential of the two-phonons model is¹⁹:

$$V(Q_P, Q_{IR}) = \frac{1}{2}\omega_{IR}^2 Q_{IR}^2 - \frac{1}{4}\omega_P^2 Q_P^2 + \frac{1}{4}c_P^2 Q_P^4 - aQ_P Q_{IR}^2$$

We can obtain the EOM to perform a qualitative and intuitive study of the phonon populations (when an external driving is applied).

¹⁷ Phys. Rev. B 92, 214303

¹⁸ Phys. Rev. Lett., 118, 197601.

¹⁹ Phys. Rev. Lett. 118, 197601

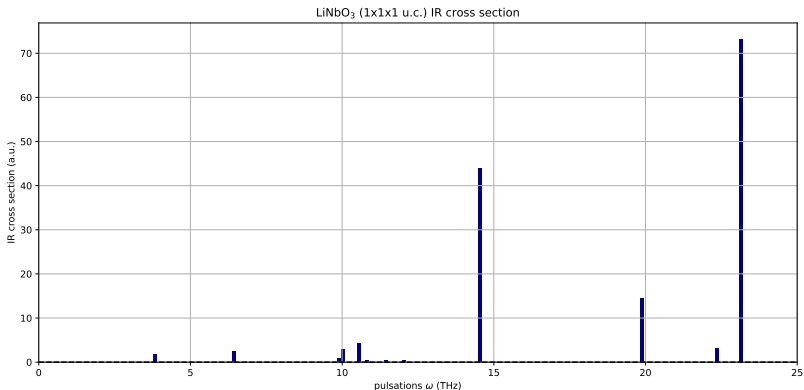
LiNbO₃

IR Raman activity

The IR activity \mathcal{I}_n of the vibrational mode \mathbf{Q}_n is defined as:

$$\mathcal{I}_n \stackrel{\text{def}}{=} \sum_{\alpha=x,y,z} \left| \frac{\partial P^\alpha}{\partial \mathbf{Q}_n} \right|^2 = \sum_{\alpha=x,y,z} \left| \sum_i^{3N} \frac{\partial P^\alpha}{\partial \mathbf{R}_i} \frac{\partial \mathbf{R}_i}{\partial \mathbf{Q}_n} \right|^2 = \sum_{\alpha=x,y,z} |\mathbf{Z}^* \cdot \mathbf{N}_n|^2$$

where \mathbf{N} is the matrix whose columns are the vibrational modes.



Conclusions

What has been done insofar:

- ▶ set up a theoretical framework to perform light-driven MD
- ▶ computation of Z^* “on-the-fly” using DFPT
- ▶ implemented communication of \mathbf{P} and Z^* between i-PI and QE
- ▶ preliminary study on LiNbO_3 (small cells)

What has to be done:

- ▶ machine-learn \mathbf{P} and Z^* to speed up MD simulations
- ▶ systematic study of LiNbO_3 with an external \mathbf{E} field:
 - ▶ validate the two coupled phonons model
 - ▶ study the \mathbf{E} -frequency/intensity response of the system
- ▶ implement NPT ensemble (improper piezoelectric tensor is needed)
- ▶ study other materials

Supplementary material

Further order terms

Let's go beyond the two approximations that have been adopted, i.e. slowly varying and weak fields.

High intensity fields: the **E**-induced changes on the electronic structure are

- ▶ no longer negligible → solve KS equation with external **E** field
- ▶ still negligible, but results are not accurate → consider the derivative w.r.t. **E** of the:
 - ▶ energy (i.e. polarizability) to properly defined a conserved quantity
 - ▶ BEC tensors, to get better values for the forces

Rapidly oscillating fields (high frequency/spatial inhomogeneity):

- ▶ consider quadrupole terms (computation could not be trivial at all)
- ▶ consider magnetic dipoles

Time to compute Z^* and \mathbf{P}

Time to compute the BEC tensors using DFPT:

time	$n_k = 1^3$	$n_k = 2^3$	$n_k = 4^3$
$N_a = 10$	1m	5m	33m
$N_a = 30$	6m	38m	4h45m
$N_a = 80$	1h20m	15h	/

Time to perform a DFT calculation + polarization calculation:

time	$n_k = 1^3$	$n_k = 2^3$	$n_k = 4^3$
$N_a = 10$	10s	20s	2m
$N_a = 30$	34s	3m	17m
$N_a = 80$	6m	43m	4h

Electric polarization

Electronic polarization \mathbf{P}^e , classical expression for a continuous charge distribution:

$$\mathbf{P}^e = \frac{1}{\Omega} \int_{\Omega} d^3\mathbf{r} n(\mathbf{r}) \mathbf{r}$$

Electronic polarization \mathbf{P}^e , classical expression for a continuous charge distribution:

~~$$\mathbf{P}^e = \frac{1}{\Omega} \int_{\Omega} d^3\mathbf{r} n(\mathbf{r}) \mathbf{r}$$~~ **ill-defined with pbc**

The Modern Theory of Polarization relies on a single-particle formalism (KS orbitals in Bloch-like form):

$$\partial_{\lambda} \mathbf{P}^e = \frac{q_e}{(2\pi)^3} \sum_n^{\text{occ}} \int_{\text{BZ}} d^3\mathbf{k} 2\text{Im} \langle \partial_{\lambda} u_{n\mathbf{k}} | \partial_{\mathbf{k}} u_{n\mathbf{k}} \rangle$$

In FHI-aims the integral is performed along the direction of a reciprocal lattice vector $\mathbf{n}_i = \mathbf{b}_i / |\mathbf{b}_i|$:

$$P_i^e(1) - P_i^e(0) = \int_0^1 d\lambda \frac{\partial P_i^e}{\partial \lambda} \xrightarrow[\substack{\text{assume that} \\ P_i^e(0)=0}]{} P_i^e = \oint_{\mathbb{T}^1} d\mathbf{n}_i \frac{\partial P_i^e}{\partial \mathbf{n}_i}$$

Theory

Projection on vibrational modes

The **vibrational modes** \mathbf{n}_l are the normalized mass-weighted eigenvectors of the **dynamical matrix**:

$$\underline{\underline{D}} \cdot \underline{\underline{\epsilon}} = \underline{\underline{\epsilon}} \cdot \underline{\underline{\Lambda}} \quad \text{with} \quad \Lambda_{ls} \stackrel{\text{def}}{=} \delta_{ls} \omega_s^2 \quad \rightarrow \quad \mathbf{n}_l \stackrel{\text{def}}{=} \frac{\underline{\underline{M}} \cdot \underline{\underline{\epsilon}}_l}{\left| \underline{\underline{M}} \cdot \underline{\underline{\epsilon}}_l \right|}$$

$\Delta \mathbf{R}(t)$ and $\mathbf{v}(t)$ are expressed as a superpositions of vibrational modes:

$$\Delta \mathbf{R}(t) = \sum_s^{N_n} A_s \frac{\underline{\underline{\epsilon}}_s}{\sqrt{\underline{\underline{M}}}} \cos(\omega_s t + \phi_s) \quad \rightarrow \quad \sqrt{\underline{\underline{M}}} \cdot \underline{\underline{\epsilon}}_l \cdot \Delta \mathbf{R}(t) = A_l \cos(\omega_l t + \phi_l)$$

$$\mathbf{v}(t) = \sum_s^{N_n} -A_s \omega_s \frac{\underline{\underline{\epsilon}}_s}{\sqrt{\underline{\underline{M}}}} \sin(\omega_s t + \phi_s) \quad \rightarrow \quad \omega_l^{-1} \sqrt{\underline{\underline{M}}} \cdot \underline{\underline{\epsilon}}_l \cdot \mathbf{v}(t) = -A_l \sin(\omega_l t + \phi_l)$$

We then get

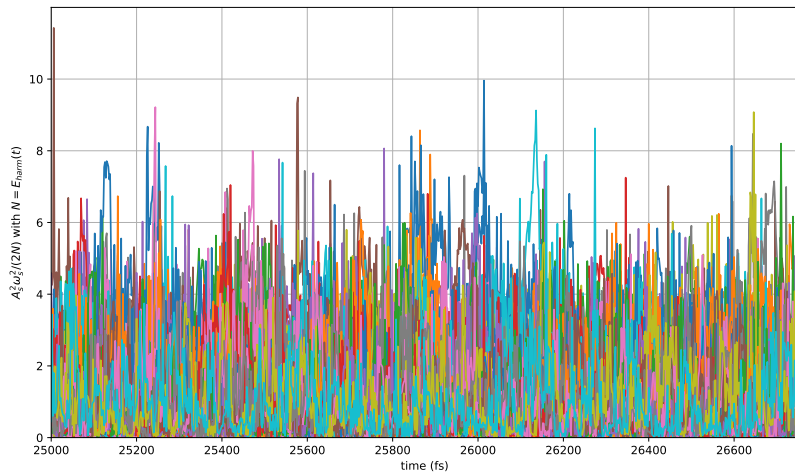
$$\mathcal{H}_{\text{harm}} = \sum_s^{3N} \frac{\omega_s^2 A_s^2}{2} = \sum_s^{3N} E_s \quad \rightarrow \quad A_s^2 = \frac{2E_s}{\omega_s^2}$$

(A_s has the dimension of length \times mass^{1/2})

LiNbO₃

Projection on vibrational modes

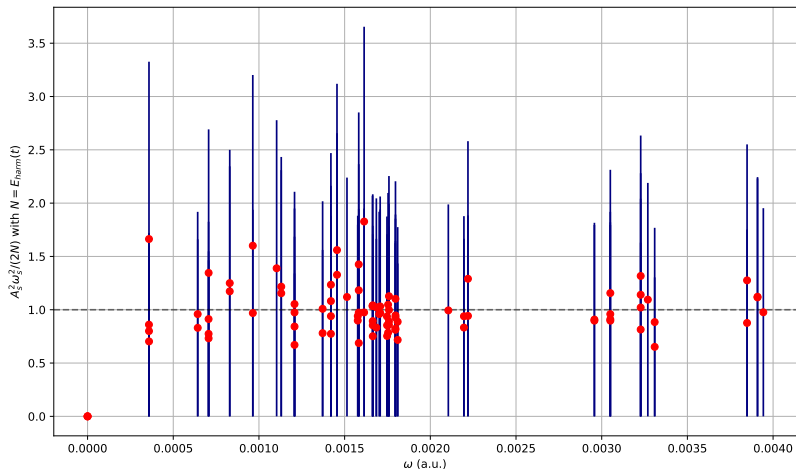
Thermalization using the GLE thermostat at 300K with $\omega_0 = 20\text{cm}^{-1}$



LiNbO₃

Projection on vibrational modes

Thermalization using the GLE thermostat at 300K with $\omega_0 = 20\text{cm}^{-1}$



The **equipartition theorem** is satisfied: $E_n = k_B T$.

Variable lattice parameters

A time-dependent **E**-field can induce **structural distortions**.
Promote the lattice parameters \mathbf{a}_i to dynamical variables:

$$\mathcal{H}_{n,\mathbf{a}_i}^{\mathbf{E}}(\mathbf{R}^l, \mathbf{p}^l) \longrightarrow \mathcal{H}_n^{\mathbf{E}}(\boldsymbol{\theta}^l, \boldsymbol{\omega}^l, \mathbf{a}_i, \boldsymbol{\kappa}_i)$$

where $\boldsymbol{\theta}^l$ are the fractional coordinates, $\boldsymbol{\omega}^l$ the corresponding conjugate variables, and $\boldsymbol{\kappa}_i$ the conjugate variables to the lattice parameters \mathbf{a}_i :

$$\mathbf{A} \stackrel{\text{def}}{=} [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3] = \begin{bmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{bmatrix} \longrightarrow \begin{aligned} \mathbf{R}^l &= \mathbf{A} \cdot \boldsymbol{\theta}^l \\ \mathbf{p}^l &= \mathbf{B} \cdot \boldsymbol{\omega}^l \end{aligned}$$

with $\mathbf{B} = (\mathbf{A}^{-1})^t$

References:

J. Phys. Chem. Solids Vol. 56, No. 3/4. pp. 501-505. 1995

Equations of motion

From the Hamilton equations of motion of \mathcal{H}_n^E we obtain:

$$\frac{d\mathbf{R}^I}{dt} = \frac{\mathbf{p}^I}{M^I} + \frac{d\mathbf{A}}{dt} \cdot \boldsymbol{\theta}^I$$

$$\frac{d\mathbf{p}^I}{dt} = \mathbf{F}^{0I} + \mathbf{F}^{EI} - \mathbf{B} \cdot \frac{d\mathbf{A}}{dt} \cdot \mathbf{p}^I$$

with

$$\mathbf{F}^{0I} = -\frac{\partial \mathcal{H}_n^0}{\partial \mathbf{R}^I} \quad \text{and} \quad \mathbf{F}^{EI} = -\Omega \mathbf{E} \cdot \frac{\partial \mathbf{P}}{\partial \mathbf{R}^I}$$

Attention! We need to know the following term:

$$\frac{d\kappa_i}{dt} = -\frac{\partial \mathcal{H}_n^E}{\partial \mathbf{a}_i} = -\frac{\partial \mathcal{H}_n^0}{\partial \mathbf{a}_i} - \frac{\partial}{\partial \mathbf{a}_i} (\Omega \mathbf{P} \cdot \mathbf{E})$$

Theory

Conserved quantity in time-dependent systems

Time-dependent Hamiltonian:

$$\mathcal{H}(p, q, t) \stackrel{\text{def}}{=} \mathcal{H}_0(p, q) + V(q, t)$$

Extended phase-space Hamiltonian:

$$\begin{aligned} \tilde{\mathcal{H}}(p, q, \tilde{q}, \tilde{p}) &\stackrel{\text{def}}{=} \mathcal{H}(p, q, \tilde{q}) + \tilde{p} \\ \dot{\tilde{p}} = -\frac{\partial \tilde{\mathcal{H}}}{\partial \tilde{q}} = -\frac{\partial \mathcal{H}}{\partial t} &\quad \dot{\tilde{q}} = \frac{\partial \tilde{\mathcal{H}}}{\partial \tilde{p}} = 1 \quad \rightarrow \quad \tilde{q} = t \end{aligned}$$

Solving the equations of motion for \tilde{p} we get the following conserved quantity:

$$A_{\text{cons}}(p, q, t) \stackrel{\text{def}}{=} \mathcal{H}(p, q, t) - \int_0^t \frac{\partial \mathcal{H}}{\partial \tau} d\tau = \mathcal{H}(p, q, t) - \int_0^t \frac{\partial V(q(\tau), \tau)}{\partial \tau} d\tau$$

Let's explicitly show that this is a conserved quantity:

$$\begin{aligned} \frac{dA_{\text{cons}}}{dt} &= \frac{\partial A_{\text{cons}}}{\partial t} + \frac{\partial A_{\text{cons}}}{\partial q} \frac{dq}{dt} + \frac{\partial A_{\text{cons}}}{\partial p} \frac{dp}{dt} \\ &= \cancel{\frac{\partial V(q, t)}{\partial t}} - \cancel{\frac{\partial V(q, t)}{\partial t}} + \frac{\partial A_{\text{cons}}}{\partial q} \frac{\partial \mathcal{H}}{\partial p} - \frac{\partial A_{\text{cons}}}{\partial p} \frac{\partial \mathcal{H}}{\partial q} \\ &= \frac{\partial \mathcal{H}}{\partial q} \frac{\partial \mathcal{H}_0}{\partial p} - \frac{\partial \mathcal{H}_0}{\partial p} \frac{\partial \mathcal{H}}{\partial q} = 0 \end{aligned}$$

LiNbO₃

Conserved quantity in time-dependent systems

