

Visualization of the nonlinear response for arbitrary crystal systems

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Abstract

Based on Dietrich Krebs and Nina Rohringer's theoretical framework for parametric x-ray optical wavemixing, this summer project concerns the 3D visualization of the nonlinear electronic response function, calculated in an *ab initio* framework, ABINIT. The visualization framework revolves around parallelepipeds (conventional unit cells), atom positions, and nonlinear response functions. In addition, this visualization framework focuses on three compounds: Diamond (C), Lithium Fluorine (LiF), and Silicon Dioxide (SiO₂). Concerning the *ab initio* framework, DFT calculations for a rhombohedral perovskite structure, BaTiO3, are conducted.

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1 Introduction

Having Wilhelm Röntgen discovered such a new type of radiation (x-rays) in 1895, several fields of science and technology have been broadening their horizons, such as agriculture [1], medicine [2], and archaeometry [3]. Particularly, x-ray scattering has long played a key role in structure determination of matter; for instance, x-ray crystallography is a prevalent method for protein structure determination [4]. In general, a standard x-ray diffraction study employs wavelengths ranging between 0.05 nm and 0.25 nm, which are suitable for typical interatomic spacings in crystals [5].

Besides structure determination of matter, there has been a long-standing interest in direct experimental measurement of the valence electron charge distribution. Isaac Freund [6] stated that such a direct measurement would sharpen the understanding of chemical bonding within crystals, however, regular x-ray diffraction methods were solely capable of gauging the total electron charge density. As far as Freund was concerned, tackling this problem entailed the incorporation of a nonlinear process, spontaneous X-ray parametric down-conversion, into the theoretical and experimental framework [6]. In contrast with Freund's ideas about x-ray diffraction experiments, Lovesey et al. suggested that valuable observations of valence electrons were feasible as long as x-rays were supplied by a synchrotron source [7]. In addition, they propounded an atomic model to analyze the data on Bragg's diffraction.

These aforementioned x-ray diffraction approaches aim at making strides in the microscopic resolution of valence electron distributions, overcoming the valence electrons' delocalized character in crystals. Purposely, the valance electrons play a relevant role in material properties, such as magnetoresistance, structural phase transitions, and magnetic phenomena [8]. Being a nonlinear process in which x-ray and optical fields mix within a medium, parametric x-ray and optical wave mixing promises to probe the microscopic details of light-matter interactions [9], hence valence electron distributions. Purposely, "parametric" means that the material system remains unchanged after the lightmatter interaction, i.e. $|\psi_{\text{initial}}^{\text{matter}}\rangle = |\psi_{\text{final}}^{\text{matter}}\rangle$. The x-ray optical wavemixing (XOWM) processes provide imaging capabilities similar to x-ray diffraction, while the optical field offers spectroscopic selectivity. Both features lead to specific probing of valence electrons' response, hence visualizing valence electron dynamics in the atomic-scale regime. From a experimental view, x-ray parametric down-conversion (XPDC) and sum- and difference-frequency generation (SFG/DFG) are XOWM processes [9]. Based on the theoretical framework developed by Dietrich Krebs and Nina Rohringer [10], there is a common theoretical description of such three XOWM processes.

Primarily, the goal of this summer project is the implementation of 3D visualization of the nonlinear response function for various crystal structures based on the D. Krebs and N. Rohringer XOWM framework. For the sake of code testing, additional Density Functional Theory (DFT) calculations for a non-cubic perovskite (BaTiO₃) were carried out because of the limited available data. The following section revolves around theoretical background and computational details. Subsequently, 3D visualization of the nonlinear response function for various crystal structures and DFT calculations are depicted from Sec. 3. Finally in Sec.4, there is an outlook on improvements and future steps.

2 Theory & Methods

2.1 Road to visualization

The subsequent aspects, extracted from the paper [10], are essential for building a visualization computer program for the nonlinear electronic response function. Adopting a scattering perspective in non-relativistic Quantum Electrodynamics (QED), D. Krebs and N. Rohringer associated an expression with the observable pattern of scattered x-rays, i.e. the expectation value of the x-ray-optical scattering observable:

$$\left\langle \hat{O}_{\mathbf{k}_{f},\lambda_{f}} \right\rangle = \frac{2\pi\alpha^{4}}{V\omega_{f}} \int_{-\infty}^{+\infty} \int_{-\infty}^{0} d^{3}x \int d^{3}y \int d^{3}y' e^{i\omega_{f}(t_{1}-t_{1}')} e^{-i\mathbf{k}_{f}(\mathbf{x}-\mathbf{x}')}$$

$$(\boldsymbol{\epsilon}_{f})_{\sigma} (\boldsymbol{\epsilon}_{f}^{*})_{\rho} (G_{\mathrm{X,IN}}^{(1)}(\mathbf{x}',t_{1}',\mathbf{x},t_{1}))_{\sigma\rho} \left((\overline{G}_{\mathrm{OPT}}^{(1)}(\mathbf{y}',t_{2}',\mathbf{y},t_{2}))_{\nu\mu} + (\overline{S}_{\mathrm{OPT}}^{(1)}(\mathbf{y}',t_{2}',\mathbf{y},t_{2}))_{\nu\mu} \right) \quad (1)$$

$$\sum_{I} p_{I} (\mathbf{P}_{I}(\mathbf{y},t_{2},\mathbf{x},t_{1}))_{\mu} (\mathbf{P}_{I}(\mathbf{y}',t_{2}',\mathbf{x}',t_{1}'))_{\nu}^{*}$$

Through a series of simplifications, such as time-dependent perturbation theory and weak light-matter coupling, Eq. 1 factorizes in terms of incoming x-ray pulse $(G_{X,IN}^{(1)})_{\sigma\rho}$, material's response to explicit x-ray perturbations $(\mathbf{P}_{I}(\mathbf{y}, t_{2}, \mathbf{x}, t_{1}))_{\mu}$, and material's response to explicit optical perturbations $((\overline{G}_{OPT}^{(1)})_{\nu\mu} + (\overline{S}_{OPT}^{(1)})_{\nu\mu})$. Purposely, \mathbf{k}_{f} and λ_{f} stand for a final plane wave mode throughout the scattering process. For the sake of crystalline matter, Eq.1 undergoes a transformation into reciprocal coordinates, yielding:

$$\left\langle \hat{O}_{\mathbf{k}_{f},\lambda_{f}} \right\rangle = \frac{\alpha^{4}}{V\omega_{f}(2\pi)^{13}} \int_{-\infty}^{+\infty} \int_{-\infty}^$$

Similar to Eq. 1, the result above entails contributions from matter (gray), x-ray field (brown) and optical field (blue) in a factorized form.

Given that the goal of this summer project revolves around the visualization of electronic response, such quantity is essentially captured by:

$$(\mathbf{P}_{I}(\mathbf{y}, t_{2}, \mathbf{x}, t_{1}))_{\mu} = \langle I | \hat{T}[(\hat{\mathbf{p}}(\mathbf{y}, t_{2}))_{\mu} \hat{n}(\mathbf{x}, t_{1})] | I \rangle$$
(3)

Eq. 3 represents the time-ordered correlation function of the electronic system's density $\hat{n}(\mathbf{x}, t_1)$ with its current density $\hat{\mathbf{p}}(\mathbf{y}, t_2) = \hat{\psi}^{\dagger}(\mathbf{y}, t_2)(-i\nabla)\hat{\psi}(\mathbf{y}, t_2)$, measured in the state

 $|I\rangle$; generally, $|I\rangle = |GS\rangle$, where GS stands for the Ground State.

Having separated Eq. 3 from the radiative aspects of the XOWM process, this scenario is under the scope of general electronic structure theory. Specifically, on the basis of DFT, Eq. 3 has a representation in terms Kohn-Sham orbitals:

$$\mathbf{P}_{I}(\mathbf{y}, 0, \mathbf{x}, t) = 2\sum_{i}^{\text{occ. unocc.}} \left(\Theta(t)e^{\mathrm{i}(\epsilon_{i}-\epsilon_{a})t}\mathbf{M}_{i.a}(\mathbf{x}, \mathbf{y})\Theta(-t)e^{-\mathrm{i}(\epsilon_{i}-\epsilon_{a})t}\mathbf{M}_{i.a}(\mathbf{x}, \mathbf{y})\right) \quad (4)$$

where the matrix elements $\mathbf{M}_{i,a}$ are given by:

$$\mathbf{M}_{i,a}(\mathbf{x}, \mathbf{y}) = \phi_i^*(\mathbf{x})\varphi_a(\mathbf{x})\varphi_a^*(\mathbf{y})(-\mathrm{i}\nabla)\varphi_i(\mathbf{y})$$
(5)

When numerical evaluation comes to, \mathbf{P}_I must be evaluated within a finite volume V_{\diamond} with periodic boundary conditions:

$$\mathbf{P}_{I}(\mathbf{y}, 0, \mathbf{x}, t) \approx w(\mathbf{y})w(\mathbf{x})\mathbf{P}_{I\diamondsuit}(\mathbf{y}, 0, \mathbf{x}, t)$$
(6)

where $w(\mathbf{x}) = 1$ inside the material, and $w(\mathbf{x}) = 0$ otherwise. Taking the Fourier transform of $\mathbf{P}_{I\Diamond}$ yields:

$$\mathbf{K}_{I\Diamond}(\mathbf{q} + \mathbf{G}_{1}, -\mathbf{q} + \mathbf{G}_{2}, \omega) = \lim_{\epsilon \to +0} 2\mathbf{i} \sum_{i}^{\text{occ. unocc.}} \sum_{a}^{\text{unocc.}} \left(\frac{\langle \varphi_{i} | e^{-\mathbf{i}(-\mathbf{q} + \mathbf{G}_{2}) \cdot \hat{\mathbf{x}}} | \varphi_{a} \rangle \langle \varphi_{a} | e^{-\mathbf{i}(\mathbf{q} + \mathbf{G}_{1}) \cdot \hat{\mathbf{x}}} \hat{\mathbf{p}} | \varphi_{i} \rangle}{\omega - (\varepsilon_{a} - \varepsilon_{o}) + \mathbf{i}\epsilon} + \frac{\langle \varphi_{i} | e^{-\mathbf{i}(\mathbf{q} + \mathbf{G}_{1}) \cdot \hat{\mathbf{x}}} \hat{\mathbf{p}} | \varphi_{a} \rangle \langle \varphi_{a} | e^{-\mathbf{i}(-\mathbf{q} + \mathbf{G}_{2}) \cdot \hat{\mathbf{x}}} | \varphi_{i} \rangle}{-\omega - (\varepsilon_{a} - \varepsilon_{o}) + \mathbf{i}\epsilon} \right)$$
(7)

Setting $\mathbf{G}_1 = 0$ and $\mathbf{q} = 0$ leads to:

$$\mathbf{K}_{I\Diamond}(0, \mathbf{G}, \omega) = \lim_{\epsilon \to +0} 2\mathbf{i} \sum_{i}^{\text{occ. unocc.}} \sum_{a}^{\text{unocc.}} \left(\frac{\langle \varphi_{i} | e^{-\mathbf{i}\mathbf{G} \cdot \hat{\mathbf{x}}} | \varphi_{a} \rangle \langle \varphi_{a} | \hat{\mathbf{p}} | \varphi_{i} \rangle}{\omega - (\varepsilon_{a} - \varepsilon_{o}) + \mathbf{i}\epsilon} + \frac{\langle \varphi_{i} | \hat{\mathbf{p}} | \varphi_{a} \rangle \langle \varphi_{a} | e^{-\mathbf{i}\mathbf{G} \cdot \hat{\mathbf{x}}} | \varphi_{i} \rangle}{-\omega - (\varepsilon_{a} - \varepsilon_{o}) + \mathbf{i}\epsilon} \right)$$

$$(8)$$

where **G** is a reciprocal lattice vector and ω is the photon's energy. Finally, through the Fourier-Synthesis, a nonlinear response density is reconstructed from $\mathbf{K}_{I\diamond}$:

$$\mathbf{R}_{I\diamondsuit}(\mathbf{x},\omega) = \frac{1}{V} \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\hat{\mathbf{x}}} \mathbf{K}_{I\diamondsuit}(0,\mathbf{G},\omega)$$
(9)

However, the visualization of the nonlinear electronic response does not concerns $\mathbf{R}_{I\diamond}(\mathbf{x},\omega)$ but $|\mathbf{R}_{I\diamond}(\mathbf{x},\omega)|^2$. In addition, different crystal structures lead to different **G** and space constraints.

2.2 Crystal Structure

Conventionally, a description of crystals begins with introducing the mathematical definition of the (direct) lattice. A lattice is a set of regularly spaced points defined by integer combinations of a set of linearly independent primitive lattice vectors [11]. For instance, the spatial distribution of such regularly spaced points in 3D is given by:

$$\mathbf{R} = n_1 \mathbf{a_1} + n_2 \mathbf{a_2} + n_3 \mathbf{a_3} \qquad n_1, n_2, n_3 \in \mathbb{Z}$$

$$(10)$$

where $\mathbf{a_1}, \mathbf{a_2}$ and $\mathbf{a_3}$ are the primitive lattice vectors. Another key element in crystals structure is the unit cell, which is a region in space that enables to reconstruct a periodic structure when repeated through space [11]. The last definition to fully characterize an ideal pure crystal is that of a basis. Once the unit cell has been chosen (see Fig.1), the basis of the crystal structure is defined with respect to the reference lattice point in such unit cell. The basis revolves around atoms and their positions[11][12].



Figure 1: A 2D representation of a periodic structure. There is a unit cell marked with dotted lines while black dots stand for lattice points. Extracted from [11].

Figure 2: Coordinates of the atoms in the unit cell with respect to the lower lefthanded corner point. Extracted from [11].

In general, the position of the center of an atom j of the basis relative to the unit cell is given by:

$$\mathbf{r}_j = x_j \mathbf{a_1} + y_j \mathbf{a_2} + z_j \mathbf{a_3} \tag{11}$$

where $0 \le x_j, y_j, z_j \le 1$ (fractional coordinate system [12]). Finally, when reconstructing the crystalline material, the positions of the atoms in the crystal are the lattice points, generated by Eq. 10, plus the basis, generated by Eq.11. In connection with unit cells, there are mainly two type of unit cells: primitive cells and conventional cells. A primitive unit cell for a periodic crystal is a unit cell that revolves around a unique lattice point. On the other hand, a conventional unit cell, which could be either primitive or non-primitive, displays the full symmetry of the lattice [12]. Purposely, there are six parameters that characterize a conventional unit cell: sides (a,b,c) and angles between such sides (α is the angle between sides a and c, β is the angle between sides b and c, γ is the angle between sides a and b). In the three-dimensional space, conventional unit cells are depicted through parallelepipeds (see Fig. 3).

The collection of lattice points is also called Bravais lattice. In the case of threedimensional crystalline material, there 14 different Bravais lattices. They are categorized into six crystal systems called triclinic, monoclinic, orthorhombic, tetragonal, hexagonal and cubic. In addition, the hexagonal system is often divided into two subsystems: hexagonal and trigonal. The definition of these systems in terms of unit cell parameters are given in Table.1. With regard to Table.1, the lattices associated with each



Figure 3: The conventional unit cells of the 14 Bravais lattices in 3D. The small grey circles stand for lattice points. Extracted from [13].

crystal systems are labeled P = primitive, I = body-centered, C = side-centered, F = face-centered, and R = rhombohedral. These lattices differs from one another in the set of linearly independent generating vectors. Unfortunately, the choice of these lattice vectors is not unique [11] which may lead to an issue when visualization of nonlinear response function for different crystal systems comes to; equivalently, the crystal systems and nonlinear response function should be generated through a common set of primitive lattice vectors and reciprocal lattice vectors to avoid inaccurate visualizations.

Essentially, the reciprocal lattice vectors are a set of three linearly independent vectors that allows to build the reciprocal lattice space through integer-only linear combinations of these vectors. The reciprocal lattice vectors are defined as follows:

$$\mathbf{b_1} = 2\pi \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}$$
$$\mathbf{b_2} = 2\pi \frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}$$
$$\mathbf{b_3} = 2\pi \frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}$$
(12)

while an arbitrary point in reciprocal space is defined as follows:

$$\mathbf{G} = m_1 \mathbf{b_1} + m_2 \mathbf{b_2} + m_3 \mathbf{b_3} \qquad m_1, m_2, m_3 \in \mathbb{Z}$$

$$(13)$$

Besides this previous reciprocal space conception, one could regard the reciprocal space as either a Fourier transform or families of lattice planes. D. Krebs and N. Rohringer regards the reciprocal space as families of lattice planes. Basically, the family of lattice planes are connected with the direction of reciprocal lattice vectors, being orthogonal to lattice planes, as long as the spacing between these lattice planes is $d = \frac{2\pi}{|\mathbf{G}_{\min}|}$ where \mathbf{G}_{\min} is the minimum length reciprocal lattice vector in this normal direction [11].

System	Cell sides	Cell angles	Lattices
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	Р
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = \frac{\pi}{2} \neq \gamma$	Р, С
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \bar{\gamma} = \frac{\pi}{2}$	P, I, C, F
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = \frac{\overline{\pi}}{2}$	Р, І
Trigonal	$a = b \neq c$	$\alpha = \beta = \frac{\pi}{2}, \gamma = \frac{2\pi}{3}$	Р
Hexagonal	$a = b \neq c$	$\alpha = \beta = \frac{\pi}{2}, \gamma = \frac{2\pi}{3}$	R
Cubic	a = b = c	$\alpha = \beta = \gamma = \frac{\pi}{2}$	P, I, F

Table 1: Crystal system for crystals in 3D [13].

2.3 Density Functional Theory (DFT)

Studying quantum many-particle systems under a time-independent framework is a highly complex task. Solving the many-particle Schrödinger equation for large systems leads to unsolvable matrix operations [14][15]. Fortunately, DFT circumvents this problem, carrying out calculations using either the electronic density $n(\mathbf{r})$ in the Hohenberg-Kohn formulation, or $n(\mathbf{r})$ and the single-particle wavefunctions $\psi_j(\mathbf{r})$ in the Kohn-Sham formulation [15]. Dietrich Krebs and Nina Rohringer numerically evaluate their theoretical framework on the basis of DFT to supply the electronic structure input for Eq.8. Currently, the numerical calculations are carried out through ABINIT, using the following exchange functionals: Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA).

2.3.1 Constant scissor operator

To overcome the well-known DFT-LDA (DFT-GGA) band gap problem [15], the simplest approximation revolves around a constant shift of the LDA (GGA) conduction bands upwards in energy, as follows:

$$E_n^{qp} \approx \begin{cases} E_n^{\text{LDA/GGA}}, & \text{if } E_n^{\text{LDA/GGA}} < E_{\text{Fermi}}.\\ E_n^{\text{LDA/GGA}} + \Delta, & \text{otherwise.} \end{cases}$$
(14)

where Δ is known as the "scissor operator"; Δ is the difference between the DFT-LDA(GGA) band gap and quasiparticle band gap $(G_0W_n, n \ge 0)$ [16].

2.4 Computational details

ABINIT is a software suite to calculate a variety of electronic-structure-related properties in materials, such as magnetic, and mechanical properties. Moreover, Green's functions and many-body perturbation theory methods are implemented in ABINIT. This software suite uses norm-conserving pseudopotentials to carry out plane-wave basis calculations under periodic boundary conditions [17][18]. Finally, in connection with the study of perovskite, the criteria for convergence were set to $1 \times 10^{-3} \frac{E_{\rm h}}{\text{atom}}$ for energy, and $5 \times 10^{-5} \frac{E_{\rm h}}{a_0}$ for force.



Figure 4: BaTiO3, rhombohedral phase : (a) Primitive unit cell. (b) Conventional unit cell. Barium atoms are in green, Ti atoms are in sky blue, and O atoms are in red [19][20].

2.5 Perovskite: BaTiO₃

Barium titanate (BT) is a polymorphic compound, ranging over cubic, tetragonal, orthorhombic, and rhombohedral crystal structures. It is noteworthy that, apart from the cubic phase, these phases exhibit the ferroelectric effect [21]. This feature enables BaTiO₃ to be used in electronics, nonlinear optics, and data storage [22]. In connection with the summer project, carrying out DFT calculations for perovskite crystal structure compounds provides additional data to benchmark the theoretical framework [10] and the visualization code.

Previously, D. Krebs and N. Rohringer succeeded in visualizing the nonlinear response function for cubic crystal structures, such as diamond [10]. Visualization for tetragonal and orthorhombic crystal structures is a trivial extension of such previous success. Hence, to accomplish the goal of this summer project, DFT calculations for the rhombohedral crystal structure were made. Purposely, to decrease the computation time, the primitive unit cell was employed throughout DFT calculations. It is noteworthy that the visualization of the nonlinear response concerns the conventional unit cell (see Fig.4).

3 Results & Discussion

3.1 Visualization code

With regard to the main goal of this summer project, the visualization framework, which was written in Python, is divided into 3 mains programs as well as some minors programs. The first program "Grid_properties.py" mainly performs space discretization across the crystal structure. The second program "_K_Fourier_synthesis.py" is constructed to load in the reciprocal primitive vectors and the Fourier transform of the time-ordered correlation function ($\mathbf{K}_{I\diamond}$ function). This program yields four numpy files: "x-grid.npy", "y-grid.npy", "z-grid.npy" and "Rdens.npy". The latter file is the absolute square of nonlinear response density while the rest of numpy files concerns space discretization. Finally, the third program "Visualization_general_conditions.py" loads in the data from the second program as well as data on the position of the atoms in the conventional unit cell; this program yields an extended rendering of $|\mathbf{R}_{GS\diamond}(\mathbf{x},\omega)|^2$ across the conventional unit cell. The response function dependence on space (see Eq. 9) motivates the development of a non-rectangular grid generator, which takes into account crystal structure geometries.

Moreover, this Python implementation prevents atoms from being displayed when they lie outside the conventional unit cell; regardless of the crystal system, users only provide the basis and primitive lattice vectors. This feature will potentially accelerate the benchmarking of the XOWM theoretical framework. In connection with validating this Python implementation, visualization of the nonlinear response for C (diamond) and SiO₂ (α -quartz) were performed. Although DFT-GGA calculations for BaTiO₃ (rhombohedral phase) were made, the $\mathbf{K}_{I\diamond}$ computation time for this perovskite crystal structure turned out to be long; at the time of writing, the $\mathbf{K}_{I\diamond}$ -related code is still running.

3.2 ABINIT: BaTiO₃

In connection with the DFT calculations for $BaTiO_3$, before computing band structures, ABINIT users should carry out several convergence tests on cut-off energy and **k**-points grid. Having set optimal values of such parameters, users should perform structural relaxations to find the optimal lattice parameters and ideal atomic/ionic positions. In connection with this system, the optical cut-off energy value is 33 Ha (see Fig.5, and building a $4 \times 4 \times 4$ Monkhorst-Pack grid secures energy convergence (see Fig.6).



Figure 5: Cut-off energy convergence test. There is no change in energy larger than 1×10^{-3} Ha per atom for cut-off energy values greater or equal than 33 Ha.



Figure 6: **k**-points grid convergence test. There is no change in energy larger than 1×10^{-3} Ha per atom for **k**-points grid values greater or equal than 4 (Grid: $4 \times 4 \times 4$).

Properties		Before computations	
Space group		R3m	
a = b = c(Å)		4.08113	
$\alpha=\beta=\gamma(^\circ)$		89.6646	
sites	u	v	w
$\operatorname{Ba}(1)$	0.00207	0.00207	0.00207
Ti(1)	0.51644	0.51644	0.51644
O(1)	0.48462	0.48462	0.97375
O(2)	0.97375	0.48462	0.48462
O(3)	0.48462	0.97375	0.48462

The initial crystallographic properties, extracted from the Materials project database, are displayed below:

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Table 2: Crystallographic data for ${\rm BaTiO_3}$ rhombohedral crystal structure before DFT-GGA.

The experimental lattice parameters of rhombohedral phase of BaTiO₃ are: a(Å) = 4.004 and $\alpha(\circ) = 89.8$ [23]. Generally, the exchange-correlation functional GGA-PBE overestimates bulk properties [15]. However, the crystallographic data obtained from ABINIT is moderately in agreement with the theoretical crystallographic data reported by Zhang and his collaborators [24].

Properties		After computations	
Space group		R3m	
a = b = c(Å)		4.06391	
$\alpha = \beta = \gamma(^{\circ})$		89.6574	
sites	u	v	w
$\operatorname{Ba}(1)$	0.00159	0.00158	0.00158
$\mathrm{Ti}(1)$	0.51654	0.51654	0.51654
O(1)	0.48489	0.48489	0.97358
O(2)	0.97358	0.48489	0.8489
O(3)	0.8489	0.97358	0.48489

Table 3: Crystallographic data for $BaTiO_3$ rhombohedral crystal structure after DFT-GGA.

Subsequently, in connection with the band structure, ABINIT predicted a band gap $E_{\rm gap} = 2.665$ eV on the basis of DFT-GGA, which is in agreement with previous reported DFT-GGA band gaps of rhombohedral BaTiO₃ [25]. In addition, the computed band structure (see Fig.7) displays an important feature: an indirect band gap [23][24][25]. Given that ABINIT outputs are not opposed to current literature, they are suitable for



Figure 7: DFT-GGA band structure for the rhombohedral phase of BaTiO₃.

computing the nonlinear response function. Purposely, the constant scissor operator was set to zero because nobody has reported either quasiparticle (GW) or experimental band gap of $BaTiO_3$.

3.3 Diamond, α -Quartz & LiF

The only available data to test the Python visualization code revolved around diamond, SiO_2 and LiF. Given that D. Krebs and N. Rohringer had previously provided an extended rendering of $|\mathbf{R}_{GS\diamondsuit}(\mathbf{x},\omega)|^2$ for diamond [10], assessing the code's outcome for diamond scenario reduced to a comparison of both visualizations. In this case, the visualization code yielded an extended rendering of the nonlinear response function in accordance with the one reported by D. Krebs and N. Rohringer [10]. In Fig.8, it is noteworthy that the nonlinear response correlates with the localization of valence charges along the valence bonds.

Concerning LiF, the code for arbitrary crystal systems yielded a 3D rendering that agreed with the visualization of LiF's $|\mathbf{R}_I|^2$ generated by the code exclusive for cubic crystal systems (see Fig.10).

Finally, there were no antecedent attempts to visualize hexagonal crystal structures, such as SiO_2 . In this case, the density of valence electrons and the nonlinear response were solely correlated around oxygen atoms (see Fig.9).



Figure 8: Diamond : (a) The nonlinear response is shown in terms of $|\mathbf{R}_{GS\diamondsuit}(\mathbf{x}, 0.057)|^2$ across the conventional unit cell. (b) The electronic density is shown across the conventional unit cell. Black: carbon atoms.

Purposely, SiO_2 is a covalent-ionic compound, and its valence band consists of two subbands separated by an ionic band gap. The uppermost section of its valence band is



(a)



(b)

Figure 9: SiO₂ : (a) The nonlinear response is shown in terms of $|\mathbf{R}_{GS\diamondsuit}(\mathbf{x}, 0.0569)|^2$ across the conventional unit cell. (b) The electronic density is shown across the conventional unit cell. Yellow: Si atoms, red: Oxygen atoms



Figure 10: Visualization of the nonlinear response for LiF ($|\mathbf{R}_{GS\diamondsuit}(\mathbf{x}, 0.4961)|^2$) across the conventional unit cell. Green: Li ions, purple: F ions.

formed by a narrow band of O $2p_{\pi}$ non-bonding orbitals while the lower narrow band revolves around O 2s states with an admixture of Si 3s and Si 3p states. It is noteworthy that the electron density distribution for the lowest sub-band mainly revolves around oxygen atoms due to their high electronegativity. On the other hand, for the upper sub-band, the electron density is localized in the direction orthogonal to the plane of the O–Si–O bonds [26]. The density of valence electrons illustrated in Fig.9(b) seemingly displays such features.

4 Conclusion & Recommendations

The current version of the Python code only requires users to input ABINIT output files and $\mathbf{K}_{I\diamond}$ -data file to display the boundary of the conventional unit cell in dark grey, the nonlinear response across the conventional unit cell, and atoms. In a sense, users should henceforth focus on DFT and $\mathbf{K}_{I\diamond}$ calculations without thinking of a manner of visualizing such data. The code worked properly for cubic crystal structures, as well. Concerning BaTiO₃, when the computations terminate, the visualization of the nonlinear function for such structure will contribute towards benchmarking the XOWM theoretical framework.

Worth mentioning is that there are two databases, Materials Project and The Open Quantum Materials Database (OQMD), that provide primitive lattice vectors and atom positions for several materials. Such parameters are vital for carrying out ABINIT calculations, hence $\mathbf{R}_{I\diamond}$. Finally, having managed to visualize a non-cubic crystal structure, the formulated and implemented Python visualization framework achieved the principal

goal of this summer project.

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