Vibrational Properties of FAPbBr₃

Summer Internship Report by

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Abstract

Hybrid organic-inorganic perovskites have recently gained attention as potential materials for optoelectronic applications. One such material FAPbBr₃ is the interest of this study. As a part of a summer internship at the TheoFEM lab, we have simulated the dispersion curves of cubic and orthorhombic $FAPbBr_3$ and the IR and Raman spectra of cubic FAPbBr₃. We find that FA ion in the perovskite undergoes interesting reorientations to attain a stable configuration. We encounter imaginary modes at Γ while simulating the cubic phase indicating instabilities in the unitcell itself. These modes, when visualized, revealed its origin from the titlting and rotating motion of the FA ion. VASP is unable to reorient the FA for which, we map out the potential energy landscape of the FA ion. We manually reorient the FA ion and also use the software Gadget (which is based on VASP, but it optimizes with respect to internal coordinates like dihedral angles, bond lengths, etc). After these exercises, we get rid of the imaginary modes. In case of orthorhombic, the unitcell contains 4 FA ions, and post a few relaxations with Gadget, we find that the FA ions are all in different orientations. Preliminary dispersions revealed an imaginary mode at Γ which arose from FA ion rotations coupled with the PbBr₃ octahedra tilting. This was different than imaginary modes encountered earlier as the former were purely due to FA motion. To address the imagniary mode, we use a PhonoPy functionality which displaces atoms in the unitcell along the direction of an eigenvector which we can specify. This helps us get rid of the imaginary modes, and in principle, this method can be applied for any system which is difficult to relax using VASP or other softwares. We also compute the IR and Raman spectra of cubic FAPbBr₃ and find that

1 Introduction

The need for renewable energy sources is increasing day-by-day with problems like pollution and climate change becoming more and more adverse. Solar energy has shown great potential in realizing the clean energy goal. Consequently, research has been focusing on ways to harness solar power via optoelectronic devices which directly convert sunlight to electricity (also termed as photovoltaic or photoelectric). Traditionally silicon had been widely used in solar cells but it has some problems for eg. sub-par energy conversion efficiency and high manufacturing cost. Recently, perovskites, with their excellent power conversion efficiency, have proved to be a promising candidates for optoelectronic applications.

Perovskites are named after their founder, Lev Perovski, who found the mineral $CaTiO_3$ which was named it perovskite. The name has stuck since then and any crystalline material with a formula ABX₃ and structure same as that of $CaTiO_3$ is classified as a perovskite. A typical perovskite figure is shown in Fig.[1].



Figure 1: Perovskite Crystal Structure

The central 'A' is sorrounded by the BX_3 octahedra occupying the corners of the unitcell. The 'A' cation can be a single atom like Cs,Ca or can be an organic cation like MA⁺ or FA⁺ in which case, the resulting perovskite is a hybrid perovskite. These materials have shown excellent optical absorption, long charge carrier lifetimes and a great photovoltaic device efficiency[1]. Solution processing capability of these materials is what makes them an exciting option for replacing inorganic perovskites. In this work, focus is on the hybrid perovskite FAPbBr₃, particularly its vibrational properties like phonon dispersions, density of states, IR and Raman spectra.From previous experimental works on FAPbBr₃ have revealed that it is known to change its phase from cubic (at room temperature) to tetragonal at around 240K and then finally to orthorhombic[2] at low temperatures. In this work, we focus on the cubic and orthorhombic structures.

Previous studies computational studies on $FAPbBr_3$ using density functional theory and non-equilibrium green's function formalism[3] suggested interesting behavior of the FA ion in the perovskite environment. Infact, in our study, we also find some interesting orientations of the FA ion which was motivated from the phonon mode visualizations discussed in detail in chapter 5.

An image of the unit-cell of cubic FAPbBr₃ is shown below



Figure 2: Cubic FAPbBr₃

After structure relaxation the FA ions reorient so that forces are negligible and the total energy is a minimum. We then proceed to compute the phonon dispersions and the IR and Raman spectra. The rest of the report is divided as follows: Chap 2 contains a brief introduction to Density Functional Theory and VASP, the DFT software used in this study. Chap 3 introduces some of the relevant lattice dynamical quantities and methods to evaluate them as well the software PhonoPy which is used in conjunction with VASP to obtain the lattice dynamical properties. Chap 4 gives a short introduction to Raman spectroscopy and how it is computed. Chap 5 is the main and final chapter which explores the work done on FAPbBr₃.

2 DFT and VASP

Density functional theory (DFT) is one of the most prominent tools used by computational materials scientists to model materials using first-principles. DFT reduces the problem of finding the many-body Schrodinger equation to finding the ground state density. The main teaching of DFT is that any property of a system of interaction particles can be expressed as functional of the ground state density[4]. Here, we first provide a short introduction to DFT and then proceed to introduce the DFT-software VASP.

2.1 Density Functional Theory

1. Problem with many body Hamiltonian

In order to find the energy levels for electrons crystal, we will need to solve the time independent Schrodinger Equation for the energy eigenvalues. The equation is given by

$$\left(-\frac{\hbar^2}{2m}\sum_i \nabla^2_{\vec{r}_i} + V(r,R)\right)\Psi(r|R) = E(R)\Psi(r|R)$$
(1)

 $\Psi(r|R)$ is the many electron wave function, R is Here, we have already applied the Born Oppenheimer approximation or the adiabatic approximation by keeping the nuclei fixed. In other words, R is just a parameter in the equation. The potential energy V(r, R) is the contribution of the following terms.

$$V(r,R) = \sum_{I \neq J} \frac{e^2}{2} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \sum_{i \neq J} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$
(2)

The first term is the nuclei potential energy, which is a constant as far as our electron wave function is concerned (Born Oppenheimer approximation). The second term is the potential energy of electrons due to the nuclei. The third term is the self interaction energy of the electrons. This term is the one which creates computational problems, as the number of electrons in a crystal are of the order of 10^{23} .

To tackle this problem, the many electron wave function is reduced to a hypothetical single electron wave function using Density Functional Theory [5].

2. Hohenberg Kohn Theorem[6]

Here, we state the theorem without proof. It states the ground state of any interacting many particle system with a given fixed inter-particle interaction is a unique functional of the electron density $\rho(r)$. In quantum mechanical terms, we have the density operator, $\hat{\rho}(\vec{r}) = \delta(\vec{r'} - \vec{r})$. Electron density for one electron is given by $\langle \psi^* | \hat{\rho(r)} | \psi \rangle = \int \psi^*(\vec{r'})\psi(\vec{r'})\delta(\vec{r'} - \vec{r})d\vec{r'} = |\psi(\vec{r})|^2$ For many body electrons, the electron density is simply the sum of individual single electron wavefunctions. Essentially, the many n body 3n variable problem is reduced to find $\rho(r)$ which is a 3 variable problem. We now turn to understand the Kohn Sham equations in which, we make use of the Hohenberg Kohn theorem.

3. Kohn Sham Method[7]

Although the original form of the Schrodinger equation is retained, the meaning of each

terms, changes in the new approach. The modified Kohn Sham Hamiltonian of (fictitious) non interacting electrons is given by

$$H\psi_i = \left(-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + V_R(\vec{r})\right)\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r})$$
(3)

The effective potential is a functional of charge density $\rho(\vec{r})$.

$$V_R(\vec{r}) = -\sum_I \frac{Z_I e^2}{|\vec{r} - \vec{R}_I|} + v[\rho(\vec{r})], \ \rho(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2$$
(4)

The form of the effective potential is unknown but approximate forms are known. DFT, in principle is valid only for ground state properties.

The total energy is also a functional of electron density, $E \implies E[\psi, R]$

$$E[\psi, R] = -\frac{\hbar^2}{2m} \sum_{i} \int \psi_i^*(r) \nabla^2 \psi_i(r) d\vec{r} + \int V_R(\vec{r}) \rho(\vec{r}) d\vec{r} + \frac{e^2}{2} \int \frac{n(\vec{r})n(\vec{r'})}{|\vec{r} - \vec{r'}|} + E_{xc}[n(\vec{r})] + \sum_{I \neq J} \frac{e^2}{2} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}$$
(5)

The Kohn Sham equations from the minimization of energy functional

$$E(R) = minE[\psi, R], \quad \int \psi_i^*(r)\psi_i(r)d\vec{r} = \delta_{ij}$$

Hellman-Feynman theorem is used to get the forces on atoms which are used to get the phonon frequencies.

$$\vec{F}_I = -\nabla_{\vec{R}_I} E(R) = -\int n(\vec{r}) \nabla_{\vec{R}_I} V_R(r) d\vec{r}$$

2.2 DFT using VASP

Vienna Ab-inito Simulation Package or VASP, originally based on code developed by Mike Payne and later brought to University of Vienna and developed by Jürgen Futhermüller and Georg Kresse in 1989, is a widely used DFT simulation software used by around 1400 researchers all over the world. VASP has several functioanlities allowing one to calculate DFT energies, forces, bandstructures, density of states, phonon frequencies at Γ , molecular dynamics simulations and much more.

The code is based on plane wave basis set as it is easier to implement, computationally friendly using FFTs. Even with this technique, however, we require a large number of plane waves to describe tightly bound states or rapid oscillations in the orbitals near the nucleus in the system. To overcome this issue, VASP uses Projector Augmented Wave (or PAW) method in which the core electrons are precalculated in the atomic environment and kept frozen in the course of remaining calculations. There are several types of exchange correlation functionals available, for eg. LDA, PBE, GGA, as well as hybrid functionals like PBE0, HSE, B3LYP.

The usual self-consistency cycle proceeds with an initial guess of the electronic density, constructing the potential, solving the Kohn Sham equations and then obtaining the density back and correcting the guess until there is little change in the density in two consecutive iterations.

For SCF calculations, to obtain energies and forces, VASP requires 4 input files- INCAR, KPOINTS, POSCAR and POTCAR.

- 1. **INCAR**: This is the file which decides how the calculations 'run'. This file specifies the cutoffs used for the SCF iterations, plane wave energy cutoffs, structure relaxation scheme and related parameters like step-size, force threshold as well. Besides these, there are other parameters which we can specify for eg. type of smearing used while integrating over the k-points, type of Van-der-Waals corrections, what all files needs to be written, etc.
- 2. **POSCAR**: This contains information about the unitcell and the positions which the atoms occupy in it. We can either explicitly mention which atoms occupy a particular position or just mention the number of atoms of each type and the pseudopotential ordering in POTCAR will decide which kind of atom is occupying a particular position. For molecular dynamics simulations, we can fix some atoms if required or even restrict the motion in a particular dimension. This is achieved with the use of 'Selective Dynamics' flag.
- 3. **KPOINTS**: This file mentions the k points in the Brilloiun zone (Wigner-Seitz cell in reciprocal space) over which the wavefunctions are calculated and summed over. We can either explicitly mention which k-points to be included or just mention the number of k-points to used in each dimension and VASP automatically selects a uniformly spaced grid around Γ (origin of reciprocal space) or some other k-point if we have mentioned a shift. This selection is based on the Monkhorst-Pack scheme[8].
- 4. **POTCAR**: This file contains the pseudopotentials used during the simulations. Since VASP is a proprietary software, these pseudopotentials are not publicly available and one needs to purchase a licensed copy to avail them. The pseudopotentials contains the information about the kind of atom as well the exchange correlation functional used.

The main output of VASP is written in the OUTCAR file and the vasprun.xml files which can be analysed either manually or through several other freely available softwares (eg. p4vasp).

In this study, we have used VASP to obtain DFT energies and forces as well the effective born charges (later used for Raman spectra) while incorporating van-der-waals forces with the Tkatchenko-Scheffler method.

3 Lattice Dynamics & Phonopy

All the computations of vibrational properties need interatomic force constants as their precursor. As seen in the previous section, DFT can aid us compute the forces and energies. In terms of the equilibrium crystal potential energy Φ_0 , the energy when the atoms are displaced can be written as[9]

$$\Phi = \Phi_0 + \sum_{l\kappa} \sum_{\alpha} \Phi_{\alpha}(l\kappa) u_{\alpha}(l\kappa) + \frac{1}{2!} \sum_{ll'\kappa\kappa'} \sum_{\alpha\beta} \Phi_{\alpha\beta}(l'\kappa') u_{\alpha}(l\kappa) u_{\beta}(l'\kappa') + \frac{1}{3!} \sum_{ll'l''\kappa\kappa'\kappa''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(l\kappa l'\kappa' l''\kappa'') \times u_{\alpha}(l\kappa) u_{\beta}(l'\kappa') u_{\gamma}(l''\kappa'') + \dots$$
(6)

Here, α, β run over the Cartesian indices and $\Phi_0, \Phi_\alpha(l\kappa), \Phi_{\alpha,\beta}(l'\kappa'), \Phi_{\alpha\beta\gamma}(l\kappa l'\kappa' l''\kappa'')$ are the zeroth, first, second and third order force constants respectively and $u_\alpha(l\kappa)$ denotes the displacement of l^{th} atom in κ^{th} unitcell in the α direction. It is necessary to construct a supercell before calculating the energies and forces since in a real system, the unitcell atoms experience a force theoretically from all other atoms in the crystal. However, the forces decay with distance, yet a supercell ensures that interactions within a certain cutoff are being accounted for. The supercell size can vary from system to system and generally for computational purposes, we set it so that there are around 100 atoms in the supercell. This is just a rule of thumb and in reality, one should vary it depending on the system.

Forces are obtained using $F_{\alpha}(l,\kappa) = -\frac{\partial \Phi}{\partial u_{\alpha}(l\kappa)}$ and the second order force constants are obtained using

$$\Phi_{\alpha\beta}(l\kappa l'\kappa') = -\frac{\partial F_{\beta}(l'\kappa')}{\partial u_{\alpha}(l\kappa)} = \frac{\partial^2 \Phi}{\partial u_{\alpha}(l\kappa)\partial u_{\beta}(l'\kappa')}$$
(7)

Hence, all we need is a set of displacements and DFT computed forces. We can then proceed via the method of finite displacement to obtain the force constants. DFT softwares like VASP can also get us forces using the Hellman-Feynman theorem can then again using Eqn[2], we can obtain the second order force constants.

Next, to obtain the phonon frequencies from the second order force constants, we compute the dynamical matrix which is a $3n_{atom} \times 3n_{atom}$ sized 2D matrix whose elements are

$$D^{\alpha\beta}_{\kappa\kappa'}(\mathbf{q}) = \sum_{l'} \frac{\Phi_{\alpha\beta}(0\kappa, l'\kappa')}{\sqrt{m_{\kappa}m_{\kappa'}}} e^{i\mathbf{q}[\mathbf{r}(l'\kappa') - \mathbf{r}(0\kappa)]}$$
(8)

Now to obtain the phonon frequencies and polarizations, we find eigenvalues and eigenvectors of this matrix. It is easy to see that $D(\mathbf{q})$ is hermitian and hence, will have real eigenvalues. The eigenvalues are related to the phonon frequencies by

$$D(\mathbf{q})\mathbf{e}_{\mathbf{q}_{j}} = \omega_{\mathbf{q}_{j}}^{2}\mathbf{e}_{\mathbf{q}_{j}} \text{ or } \sum_{\beta\kappa'} D_{\kappa\kappa'}^{\alpha\beta}(\mathbf{q})e_{\mathbf{q}_{j}}^{\beta\kappa'} = \omega_{\mathbf{q}_{j}}^{2}e_{\mathbf{q}_{j}}^{\alpha\kappa}$$
(9)

Once we obtain the phonon dispersion curves, we can obtain several lattice dynamical properties like sound velocity, heat capacity, atomic displacement parameters, etc. The phonon dispersion also gives us an idea about the stability of the material. Notice that in eqn[9], if the eigenvalues of the dynamical matrix are negative (but still real), the phonon frequencies will be imaginary. If we encounter such imaginary frequencies in our calculations, we can infer either numerical convergence issues (which can be easily taken care of for eg. by applying the acoustic sum rule) or it can indicate a real dynamical instability (for eg: a phase transition). To better understand this, let us take a look at the equation written for the displacements of atoms in terms of the phonon frequencies.

$$[\mathbf{u}(l1),\ldots,\mathbf{u}(l\kappa)] = \left[\frac{A}{\sqrt{m_1}}\mathbf{e}^{1}_{\mathbf{q}j}e^{i\mathbf{q}\cdot\mathbf{r}(l1)},\ldots,\frac{A}{\sqrt{m_{n_a}}}\mathbf{e}^{n_a}_{\mathbf{q}j}e^{i\mathbf{q}\cdot\mathbf{r}(l\kappa)}\right]$$
(10)

Where A is some complex constant. The thing to notice here, is the complex power of e which indicates oscillatory motion around some equilibrium position. Incase we obtain imaginary frequencies, there won't be any oscillation. Rather, the atoms will simply keep on moving until the system attains a new, stable configuration.

We will discuss this point in depth later when we encounter imaginary phonon modes in $FAPbBr_3$.

The software used to perform these calculations in conjunction with VASP is PhonoPy, developed by Atsushi Togo in 2015. PhonoPy is compatible with several DFT software like Espresso, Abinit, Siesta, etc. It offers to compute a wide range of properties building on the phonon dispersions like heat capacity, Gruneisen parameters (under the Quasi Harmonic Approximation), group velocity, density of states, atomic displacements, etc.

In this study, we have used phonopy to obtain the phonon dispersion curves of FAPbBr₃ in the cubic and orthorhombic phases. We use phonopy to generate the supercells with the displaced structures. Once, VASP obtains the energies and forces, we generate a force_sets file and later provide the q-path for the dispersion.

4 IR and Raman Spectra and SpectroscoPy

4.1 Fundamental Principles of IR and Raman spectra

When light is incident on a material, some of it will be absorbed and the rest scattered. We can we absorption of light as a form of an external excitation for the atomic vibrations. Long wavelength infrared photons will cause local dielectric polarization in the crystal which will oscillate in time as a photon is an oscillating electric and magnetic field. For a given wavelength, not all crystals will be able to oscillate at the photon's frequency and the absorption will be strong when the frequency of the photon matches that of a phonon. The phonon frequency corresponds to a resonance frequency and the absorption is markedly high for this particular frequency. However, it is required that the eigenvector of the excited phonon gives rise to a formation or a change in the local dipole moment. Without it, the photon cannot interact with the phonon. The absorption $A(\omega)$ will be proportional to the power spectrum of the fluctuations of the dipole moment M.

Absorption is given as [10]

$$A(\omega) \propto \left|\sum_{j} m^{-1/2}(j)q_{j}\mathbf{e}(j,\mathbf{q},\nu)\right|^{2} \times \frac{\hbar}{2\omega(\mathbf{q},\nu)}[n(\omega)+1]\delta(\omega-\omega(\mathbf{q},\nu))$$
(11)

Where, **e** is the phonon eigenvector, $\omega(\mathbf{q}, \nu)$ is the phonon frequency corresponding to phonon wavevector **q** and band-index ν . ω is the photon frequency. The above equation corresponds only to harmonic phonon modes and hence we can see the Dirac-delta function which will be 1 only if the external photon frequency matches the harmonic phonon frequency. Thus in the IR spectrum, under the harmonic approximation, we should see spikes only at some phonon frequencies whose eigenvectors can cause a change in local polarization. In reality, however, due to anharmonic effects, we don't observe spikes, rather, the peaks will be broadened corresponding to three or more phonon processes.

As for the scattered radiation, some of the radiation is scattered elastically, without any change in frequency, and some photons will either gain or loose energy. Here, we qualitatively try to understand Raman and Rayleigh scattering Elastic scattering's (or Rayleigh scattering) amplitude is proportional to the polarisability of the material α . The amplitude depends on polarizability as the scattered radiation originates from the dipole oscillations induced by the radiation. The amplitude of the scattered light will be proportional to the induced moment \mathbf{M} , $\mathbf{M} = \alpha \mathbf{E}$, where \mathbf{E} is vector amplitude of the electric field of incident radiation. The polarisability will depend on the bonding and bond-lengths in the crystal and hence will fluctuate as the atoms vibrate in the crystal. A simple model of polarizability where the crystal vibrates with a phonon frequency ω' is

$$\alpha(t) = \alpha_0 + \alpha'(\exp(i\omega't) + \exp(-i\omega't))Q \tag{12}$$

Where α_0 is the static polarisability, α' is a constant and Q is the amplitude of lattice vibration. With this simplistic model, we can understand the origin of Rayleigh and Raman scattering. Due to the incident radiation of with frequency ω , the electric field can be written as $E\exp(i\omega t)$, $M(t) = E\exp(i\omega t)\alpha(t)$

$$M(t) = E\alpha_0 \exp(i\omega t) + E\alpha'(\exp(i(\omega + \omega')t) + \exp(i(\omega - \omega')t))$$
(13)

In this equation, first term corresponds to the elastic Rayleigh scattering and the latter two correspond to Raman scattering, where the radiation either creates or absorbs a phonon of frequency ω' . The case where the radiation creates a phonon and lowers its energy is called a Stokes process and when the radiation absorps a phonon, the phenomenon is called an Anti-Stokes process. Not all phonon modes at Γ give rise to Raman scattering. The requirement is that the polarisability tensor should be non-zero. This is dependent on crystal symmetry and group theory analysis is required to understand which modes can participate in Raman scattering- these modes are called Raman active.

We would reiterate that this model helps us understand the qualitative picture of Raman scattering. In conventional experiments, the visible and infrared radiation used for IR and Raman spectroscopy interacts only with the zone-center phonons where wavelength approaches ∞ . Therefore, the IR and Raman spectra is resemble the phonon density of states (DoS) for **q** points close to Γ where the peaks are weighted by the spectroscopic activities and the linewidths by the mode lifetimes.

4.2 SpectroscoPy Module

SpectroscoPy module was developed by J. M. Skelton et. al.[11] in 2017 to enable computations of vibrational spectra. This package is to be used in conjuction with PhonoPy and VASP.

To get the Raman intensities, we need to get the change in polarisability due to a particular phonon mode,

$$\mathbf{I}_{\text{Raman}} \propto \frac{\partial \alpha}{\partial Q(\nu)} \equiv \frac{\partial \epsilon^{\infty}}{\partial Q(\nu)} \approx \frac{\Delta \epsilon^{\infty}}{\Delta Q(\nu)}$$
(14)

Where e^{∞} is macroscopic high frequency dielectric constant. Since e^{∞} is a tensor quantity, the Raman activity will also be a tensor. To get the scalar Raman intensities, we average the tensor for the measurement geometries. We get the following equation

$$I_{\text{Raman}} = 45 \left[\frac{1}{3} (I_{11} + I_{22} + I_{33}) \right]^2 + \frac{7}{2} \left[(I_{11} - I_{22})^2 + (I_{11} - I_{33})^2 + (I_{22} - I_{33})^2 + 6(I_{12}^2 + I_{13}^2 + I_{23}^2) \right]$$
(15)

The spectroscopy module help us produce the displacements along the normal modes as well as evaluate the Raman tensors using the method of finite difference. To obtain the polarizability, we need the Born-Effective charges on each atoms and in general this is a heavy computation for VASP (we need to set the LEPSILON flag to be TRUE to obtain the born effective charges). The displacements are made in pairs (+ and - s) and if the software does not detect any symmetry, it will displace all the atoms unit cell in all three possible directions creating a set of $3 \times n_{\text{atom}} \times 2$ displacements. Then, using the equations above, the module computes the Raman spectra.

5 $FAPbBr_3$

To begin with DFT computations, we first start with convergence study on the cubic phase of $FAPbBr_3$. In principle, the DFT computed energy is an observable (directly related to the formation energy based on what pseudopotentials we are using) and thus, we perform convergences on the total energy which can be seen in the OUTCAR file.

5.1 Computational Details

Via the convergence tests, for cubic, we select a plane wave energy cutoff of 700 eV and use a Γ centered $8 \times 8 \times 8$ kgrid for electronic structural relaxation. The convergence threshold for SCF calculations is set to 10^{-8} eV. The structure is relaxed so that the forces on all atoms are less than 0.001 eV/Å. We have used Tkatchenko-Scheffler method^[12] to account for long range Van-der-Waals interactions. Previous studies [13, 14] have highlighted the importance of incorporating vdW corrections while working with halide perovskites. PAW-PBE pseudopotentials^[15] have been used for all atoms. For the Pb atom, the d-orbitals electrons are also included in the pseudopotentials. The symmetry flag in VASP (ISYM) needs to be set to FALSE as due to introduction of the FA, the symmetry is reduced. For the orthorhombic structure, the plane wave energy cutoff is set to 800 eV and the SCF iterations are performed till the energies are converged up to 10^{-6} eV and a Γ centered kgrid of $6 \times 6 \times 6$ is used. Same vdW is used for orthorhombic as well and the structure is relaxed until the forces on atoms are less than 0.01 eV/A. For the dispersion calculations, a $2 \times 2 \times 2$ supercell was used for the cubic phase and the unitcell with 48 atoms was used for the orthorhombic phase. The atoms were displaced by 0.01Å and finite-difference method was used to obtain the force constants followed by the dynamical matrix and phonon frequencies and eigenvectors

5.2 Structure Relaxation and PES of FA in Cubic FAPbBr₃

Preliminary dispersion calculations revealed several imaginary modes at Γ . The cubic structure file for VASP contains one unit of FA and $1/8^{th}$ of the PbBr₃ octahedra. Hence, any motion involving the octahedra will not be revealed only by the unitcell. For the dispersion, we create a $2 \times 2 \times 2$ supercell and observe some imaginary modes at q-points other than Γ which were arising due to the octahedra tilting. The ones at Γ originated from the motion of FA ion alone in the unitcell indicating an unstable unitcell. This motivated the investigation of potential energy landscape of FA when rotated or tilted. Fig[3] below shows the initial orientation of FA.

This structure when relaxed with VASP using the conjugate gradient algorithm results in almost no reorientation of FA and some tilting of the octahedra. This structure however resulted in two imaginary modes at Γ as shown below.

The motion of atoms corresponding to a particular phonon mode can be visualized using the band.yaml output file of PhonoPy and with the following software: http://henriquemiranda.github.io/phononwebsite/phonon.html

This software revealed that the imaginary mode at -3.4 THz originated from tilting motion of FA ion. To investigate this, we rotate the FA ion in the xy plane around an axis passing through the carbon atom and map the DFT energies to get an idea of the PES. We



Figure 3: Initial Orientation of FA







Figure 5: Phonon Mode Visualization Software

rotate with a step size of 1° from 0° to 45°, as rotating beyond that will give us an equivalent structure due to cubic symmetry. The plot of the PES is shown below:

From fig[6], it is clear that the initial configuration is a saddle point. Although the forces



Figure 6: PES when rotating in XY Plane

are 0, the planar orientation is not a stable minima and hence resulted in imaginary modes. When the phonon dispersion calculations are rerun, we observe another imaginary mode as shown below, this time resulting from the rotation in the YZ plane.



Figure 7: Intermediate Dispersion

We use similar procedure to map the PES, this time in the YZ plane. Note that the FA ion is already rotated 45° in the XY plane and then in the YZ plane. We obtain the following PES

We see that although the energy difference in two configurations is around xx meV (much



Figure 8: PES when rotating in YZ Plane

less compared to yy meV in the former case), nevertheless, the structure is at an unstable equilibrium. Thus, after reorienting it again, and relaxing, this time using the software Gadget, we arrive at a fully relaxed unitcell.

After the relaxations, we find the lattice constant of the cubic structure to be around 6.02 Å in close agreement with the measured values as well as from previous computational studies[16]. The value is somewhat larger than experimental, and this underbinding is a known consequence of using PBE functionals[17].

For the orthorhombic, the unitcell contains 4 units of FA and a complete $PbBr_3$ octahedra. Initially all octahedra are planar and post few relaxations, all four units are in different orientations as shown below



Figure 9: Orthorhombic FAPbBr₃ before and after relaxations

In fig[9] the relaxed structure has lesser symmetry and hence VESTA[18] doens't show the images of the central octahedra like the former image. The orthorhombic structure is relaxed so that the forces are less than 0.01 eV/Å. Even in this scenario we encountered an imaginary mode at Γ and simple reorientation of FA will not work in this case as the unit-cell contains an entire octahedra whose motion coupled with the reorientation of FA. To address this issue, we used PhonoPy's modulation functionalit which can generate structures displaced along an eigenvector which we can specify. With this technique, we got rid of the imaginary modes.

5.3 **Phonon Dispersions**

After the structures were properly relaxed, we obtained the dispersion curves for the cubic and orthorhombic phases. The dispersion curve and density of states for the cubic structure is shown below:



Figure 10: Cubic FAPbBr₃ Dispersion

In the figure, we can see that there are no imaginary modes at Γ indicating a stable unitcell. However, there is one imaginary mode along M- Γ , Γ -K and K-X directions. When this mode is visualized, it originated from the rotating motion of the octahedra and thus cannot be solved by simply relaxing the unitcell further. As for the Raman spectra, we are only concerned with the phonon frequencies at Γ and thus we are okay. The imaginary frequencies can also indicate a phase transition which is known for FAPbBr₃.

In the dispersion curve, we can see some high frequency modes at around 100 THz which we generally don't see in any other 'purely' inorganic crystal. These modes correspond to the internal high frequency motion of the FA ions and such high frequencies are common among them. At lower frequencies, the mode correspond to the motion of the octahedra. A zoomed-in plot of the cubic dispersion is shown below



Figure 11: Zoomed-In version of cubic phase dispersion

What is peculiar in fig[11] is that the imaginary modes are in-between M and Γ unlike few other examples, where researchers computed imaginary modes at M (zone boundary). Fig below shows the dispersion computed for the orthorhombic structure. The orthorhombic structure shows few imaginary modes and it is much more difficult to relax than cubic.



Figure 12: Orthorhombic FAPbBr₃ dispersion

The structure used in fig[12] is relaxed with a force convergence threshold of 20 meV/Å.

Beyond this, neither VASP nor Gadget could relax as steps in the optimization started fluctuating.

There are few imaginary modes in fig[12] and these are difficult to get rid of as they don't represent only the motion of FA. Their motion is coupled with the distortions of the octahedra and hence a simple PES mapping won't work in this case. We use PhonoPy functionality called Modulation, which can help us get structures where the atoms are displaced along the directions of some eigenvector which we can specify. With this technique, we are able to relax the structures where the forces are less than 10 meV/Å. However, there is little change in the dispersion curves.

A possible way to alleviate this issue is to keep a much more tighter convergence factor, or simply map out the PES for the 4 FA ions and manually adjust the structure although this would be computationally heavy.

5.4 IR and Raman Spectra of Cubic FAPbBr₃

We start with the IR spectra shown below



Figure 13: IR Spectra of Cubic FAPbBr₃

Note that we require the born-effective charges on the relaxed structure only for computing the IR spectra. Next, using the spectroscoPy package, we plot the Raman spectra. To plot the Raman spectra, we need to calculate change in the dielectric tensor when the atoms vibrate in a particular phonon mode. The mode will be Raman active only if the change in the dielectric tensor is non-zero.



Figure 14: Peaks in the Raman Spectra

The peaks closely match the ones computed in Ref[16]. However, they do not exactly match as the authors have used a different opt-B88 vdW corrections whereas we have opted for the Tkatchenko-Scheffler method. We now plot the final Raman spectra where the peaks are broadened at 300K



Figure 15: Raman Spectra

SpectroscoPy uses Phono3Py package which uses the many body perturbative approach to calculate phonon life times. Due to these anharmonic effects, we find that the peaks are broadened and this broadning will depend on temperature.

5.5 Conclusions and Further Research

To summarize, we have performed structure relaxation calculations on cubic and orthorhombic $FAPbBr_3$ and computed their dispersion curves. In case of cubic phase, we find that the planar orientation of FA is not the most stable configuration and some manual reorientation is required to attain a stable structure. A software like Gadget which optimizes energy with respect to internal coordinates and some initial random orientation of FA is the best starting combination to achieve the most stable configuration. This method can however be time-consuming. For the orthorhombic case, post-relaxation, all 4 FA ions are oriented randomly yet giving a stable structure. This might indicate that in reality, for cubic phase of FAPbBr₃, where the crystals contain supercells, the FA ions could be randomly oriented and on an average the overall crystal symmetry could still be maintained.

In the dispersion curves, we observe some imaginary modes in the cubic phase at some q-points other than Γ which correspond to the tilting of the octahedra. We can see some high frequency modes in the dispersion curves of both phases corresponding to internal motion of FA ions. Few imaginary modes in the orthorhombic structure are less than 2THz and can be taken care of by using a tighter convergence threshold (0.001 eV/Å, although it may be computationally heavy) We also compute the IR and Raman spectra of the cubic phase and find it closely resembles the one computed in Ref.[16].

Further research in this direction could involve examining the effect of using different vander-waals corrections, using supercells for the cubic phase and simultaneously exploring the PES of all FA ions. IR and Raman spectra of orthorhombic FAPbBr₃ could offer interesting insights into the motion of FA ions inside the perovskite system.

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