Applying DFT to the Study of HHG in Crystals

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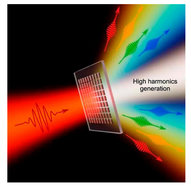
Introduction:

High-order harmonic generation (HHG) is a phenomenon where a material reemits harmonics of the incident laser light. HHG has been studied for around three decades. It was first observed in atomic gases starting in the late 80's. Since 2011, physicists have been observing HHG experimentally in bulk crystals: first with ZnO and later with many other materials including GaSe and SiO_2.



Motivation:

Research in SHG or second harmonic generation has been important in developing technologies like night vision. In that case, near-infrared light is absorbed, and light is emitted with double the frequency, producing a green image in the visible spectrum. In general, high harmonic generation can be used as the basis for sources of radiation for experiments in solid state physics and optics or for applications within technology. Fundamental understanding of HHG can improve these applications further.

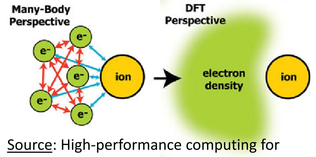
Building upon this work, we study HHG first with Mn_2RuGa applying DFT to run *ab initio* calculations of the phenomenon. Our goal is to use our ground state DFT calculation with Wien2k to understand the produced harmonic signals.

Density Functional Theory (DFT):

We use the program Wien2k to run our *ab initio* (or from-first-principles) calculation, and Wien2k uses density functional theory underneath. DFT is a method of addressing the computational complexity of such calculations. We use a system size of 48x48x48 for our primary data set, corresponding to 110592 cells. Each face-centered cubic (fcc) cell contains 4 atomic nuclei and 65 valence electrons, and each of these bodies interact. This is an impossible task. Building off the work of Kohn and his postdoc Sham, DFT replaces the many electron wavefunctions in the Kohn-Sham equations with the electron density.

Kohn-Sham Equations:

$$[-\nabla^2 + V_{\mathrm{NE}} + V_{\mathrm{EE}} + V_{\mathrm{XC}}]\psi_{\mathrm{ik}}(\mathbf{r}) = \mathrm{E}_{\mathrm{ik}}\psi_{\mathrm{ik}}(\mathbf{r})$$



Source: High-performance computing for materials design to advance energy science

Additionally, our calculations assume the nuclei are fixed within the lattice (though that is not generally true of DFT). DFT allows us to calculate the ground state of our system. We later produce the laser-induced ultrafast dynamics and HHG using the Liouville equation.

Liouville Equation:

$$ih\left\langle i\mathbf{k}\left|\frac{\partial\rho}{\partial t}\right|j\mathbf{k}\right\rangle = \langle i\mathbf{k}|[\mathbf{H_0}+\mathbf{H_1},\rho]|j\mathbf{k}\rangle$$

Reciprocal Space:

Figure 1 shows the first Brillouin zone for an fcc lattice like the one we use for Mn_2RuGa. This is a cell in reciprocal space, and it shows the Bragg planes of our material (important for how light interacts with it). We sample k-points from within this zone, and then we look at the data produced for highly-symmetric points. In particular, on this figure there are the important points Γ, x, x', and L. Γ point is the origin at the center. X and x' points are at the centers of the square Bragg planes. L point is at the center of the hexagonal Bragg planes. We chose k-points along the paths from Γ-x, Γ-x', and Γ-L. See the dotted lines.

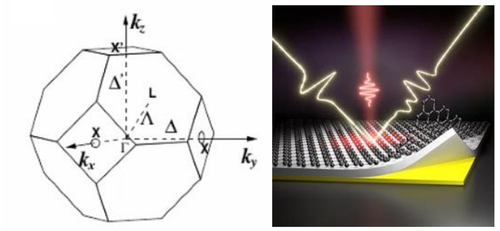


Figure 1.

Harmonic Signals and Band Structure:

From the DFT (ground state) calculation, we get the possible energies for each k-point. This allows us to plot the band energy dispersion along the three chosen directions in Figure 2. From the Liouville equation, we produce the momentum expectation vs. time. A Fourier transform of that data produces the harmonic signals. See figure 3.

Figure 2.

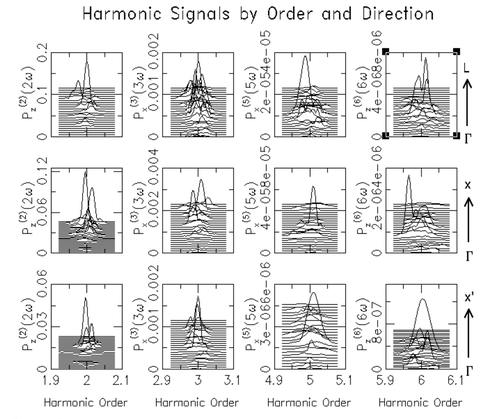


Figure 3.

Optical Eigenvalues:

First, we use the harmonic signals data to identify ranges of bands that are relevant for HHG. We take the large momentum matrix of the form

$$\begin{pmatrix} \mathrm{k}_1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & \mathrm{k}_n \end{pmatrix}$$

where the k's are smaller matrices corresponding to the contributions from each k-point. We then take the matrix for each k-point we include and include only the important rows/columns. We diagonalized these matrices to get what we call the optical eigenvalues. We plotted the maximum optical eigenvalues for different k-points and different included bands (based on the harmonic order we wanted to target). See figures 4-11.

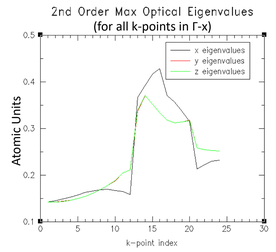


Figure 4.

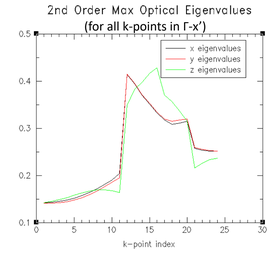


Figure 5.

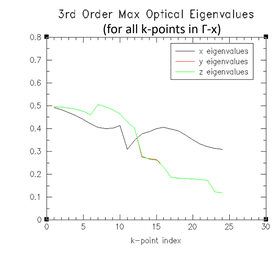


Figure 6.

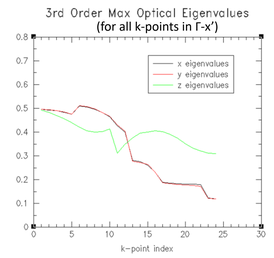


Figure 7.

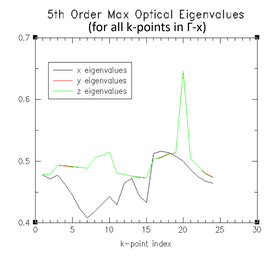


Figure 8.

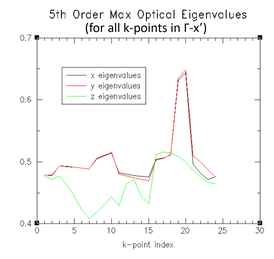


Figure 9.

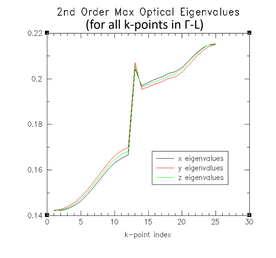


Figure 10.

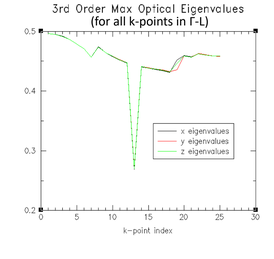


Figure 11.

While not our original purpose, we found the reflection of the symmetry of the Brillouin zone that is present in these figures interesting.

Conclusions:

We found that the optical eigenvalues have the following features:

- The y- and z-eigenvalues of k-points in Γ-x are coupled while the x-eigenvalue is independent.
- The x- and y-eigenvalues of k-points in Γ-x' are coupled while the z-eigenvalue is independent.
- If certain energy bands are not included, the coupling breaks down.
- Optical eigenvalues of the same order in Γ-x and Γ-x' are comparable if the independent and coupled eigenvalues are interchanged.

Key Insights:

Noting that certain choices of included energy bands broke this symmetry has given us a useful method for gauging whether we are including the right bands. Thus, we have refined our method of obtaining the optical eigenvalues. For Mn_2RuGa:

- We found that for the second order maximum optical eigenvalues follow the general trend of the harmonic signal.
- For higher orders, this explanation does not work.
- For this material, it is also still clear that this explanation is not perfect for the second order either.

Future Plans:

Our initial compound Mn_2RuGa does not have a simple structure. Therefore, when we try to use our optical eigenvalue results to draw conclusions, it is hard to be definitive.

- We have begun repeating our methods with fcc Ni which has a simpler structure.
- We expect to see some correlation between the k-points with large optical eigenvalues and large harmonic signals, especially for low orders.

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References:

Zhang G. P., *et al*. Generating high-order and spin harmonics from ferromagnetic monolayers. Nature Communications. (2018)

Ghimire S., *et al.* Observation of high-order harmonic generation in a bulk crystal. Nature Physics, **7**. 138-141 (2011)

Hohenleutner M., *et al.* Real-time observation of interfering crystal electrons in high-harmonic generation. Nature, **523**. 572-575 (2015)

Garg M., *et al.* Multi-petahertz electronic metrology. Nature, **538**. 359-363 (2016)