Ultrafast spectroscopy and control of correlated quantum materials

By

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Abstract

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Acknowledgements

Preface

The physics of solids is, to me, one of the most important and fundamental fields of modern science. This might seem, to some, a bit of a hot take. After all, by studying condensed matter physics, one learns next to nothing about, say, the formation of the stars and planets, or the origin of the universe. Nor does one learn about life, death, consciousness, disease, ethics, God, or any other question that perhaps puzzled humanity prior to about five hundred years ago. Certainly no one would argue that condensed matter physics is quite *useless*, given that nearly every device we interact with in modern life required some condensed matter physicist somewhere along the way to make one brilliant discovery or another – yet when the human mind starts to wander, and our thoughts turn to the metaphysical, we tend to look up, not down.

In my work I have taken a quite different view. Condensed matter physics, to me, is ultimately the study of how *truly boring* objects, when brought together in large quantites, *become* interesting, seemingly in spite of themselves. When electrons are put together in a lattice and allowed to interact slightly with the massive nuclei, at low enough temperatures they pair, the low-energy excitations become gapped, and current can flow for infinite times and with absolutely zero energy loss. Those same electrons, with some other set of interactions, may instead ionize (the opposite of pairing!) to create an electrically insulating state, whose low-energy excitation spectrum is nevertheless gapless and consisting of charge-neutral spin-$1/2$ particles. In all such cases, these systems exist in otherwise ordinary-looking rocks, fit in the palm of a hand[1], and are more or less indistinguishable from something you might find sticking into the bottom of your shoe.

While such systems may not tell us a lot[2] about the early universe, considering these and related problems lets us ask deep, fundamental questions about the world we live in – like, why is this thing a metal, but this thing is an insulator? What do those terms even mean? – that I don't think we would try to ask otherwise. To me, focusing our attention on

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[1]Hopefully, gloved.

[2] This discussion is obviously intentionally reductive. In truth there is still quite a bit one can learn about, e.g. the early universe by studying condensed matter physics, see the review by Kibble *et al.*, Ref. **?**.

these problems, despite their obviously terrestrial nature, is not a waste of time; rather, I think they remind us that even the most mundane aspects of the human experience involve a level of complexity far beyond what we are capable of understanding absent the pursuit of science.

Throughout the seven years of my Ph.D., I hope to have made a few contributions to this pursuit. As the title of this work implies, I have mainly focused on the application of ultrafast techniques to the study of correlated quantum materials, which I loosely define as those materials in which the interaction between particles is large enough so as to compete with the kinetic energy of those particles. It is in these materials that I think lies the true frontier of condensed matter physics; here, much of our basic intuition about non- or weakly-interacting theory fails, and more complicated notions of phase competition, phase separation, disorder, pairing, coherence, etc. are needed to property describe the relevant physics.

In my own view, and in the view of many scientists in this field [?], the main question for strongly correlated physics amounts to: "Given a correlated system with some defined combination of different interaction strengths, is there a general theory which allows us to predict the phase diagram of this system *a priori*?" Related of course are questions about the origins of high-T_c superconductivity, strange metallicity, quantum spin liquids, and other exotic phases that we find emerging from strongly interacting systems. Since such a theory does not currently exist, at least with the level of predictive power that I think most would find satisfactory, new advances in this field typically come directly from experiment. Ultrafast optics plays a special role in this regard, for reasons that I will explain in chapter 1.

Progress thus happens in this field somewhat unsystematically, with small pieces of the puzzle added at random, but not infrequent, intervals. Usually it is either new techniques or new materials that are the driving force here. To this end, I have tried to pursue both directions in my Ph.D. Appearing also in chapter 1 is thus a description of the materials I studied the most during my thesis, two of them, $CuBr_2$ and $CaMn_2Bi_2$ I consider criminally understudied. On the technique side, almost all of the work presented in this thesis was done using time resolved second harmonic generation (tr-SHG), a relatively new, nonlinear optical technique which, at the most basic level, probes the point group assumed by the charge distribution function $\rho(\boldsymbol{x})$ at any given point in time. Sec-

ond harmonic generation (SHG) and tr-SHG are tricky techniques, with many pitfalls both practically and theoretically; chapter 2 and **??** are thus devoted to what I hope is a useful, if not fully compehensive, description of the technique. My hope is that these sections are useful not only for the new student trying to build their own setup or analyze their own SHG data, but also for people for whom SHG is not a focus but nevertheless want to learn about it in slightly more detail than one would get from a typical paper or review article. Some aspects of **??** are devoted to work that we did developing a new way to control the polarization of the light in a tr-SHG experiment using stepper motors.

What follows, then, is a description of the three main research works I contributed during my Ph.D.. The first, which I describe in **??**, involves work that I did during my second and third years on $1T$-TaS$_2$, a very interesting charge density wave (CDW) material that, among other things, undergoes a mirror symmetry breaking CDW transition at 350 K that shows up in the SHG as a sudden distortion of the flower pattern at that temperature. Since this transition breaks mirror symmetry, two energetically degenerate domains should be present, corresponding to two opposite planar chiralities; in this work, we showed that SHG could differentiate between these two domains (i.e. the flower pattern in either domain looks different).

The second and third works, which I describe in **????**, in contrast to the $1T$-TaS$_2$work, both involve taking the system out of equilibrium to study the dynamics. In CaMn$_2$Bi$_2$ (**??**), we discovered that photoexcitation causes the antiferromagnetic (AFM) order in that compound to reorient (relative to equilibrium) to a metastable state which is impossible to reach from the equilibrium state thermodynamically. Light is thus used to *control* the magnetic order in this material.

In CuBr$_2$ (**??**), light is not used to control the order parameter like in CaMn$_2$Bi$_2$, but it does excite coherent oscillations of the collective modes of the multiferroic order (electromagnons), whose frequency, amplitude, damping, etc. may be probed in tr-SHG as a function of temperature – a methodology referred to as ultrafast *spectroscopy*. In doing so, we found that one of these collective modes is actually quite special, as it is in fact the analogue of the Higgs mode of particle physics in the context of a multiferroic material.

I conclude with various remarks in **??**, as well as an appendix, in which I enumerate briefly all of the null-result experiments I performed

during my Ph.D., in the hopes that future scientists don't have to waste time on what we already know are fruitless pursuits. If you have any questions about this or any other section of this thesis, please do not hesitate to reach out via email.

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2.1 Space groups, point groups, and Neumann's principle

The utility of SHG in studying condensed matter systems is derived from the following simple statement, attributed to Franz Neumann [**?**] and later Pierre Curie [**?**]:

Theorem 2.1.1 (Neumann's principle) *Let P_G be the symmetry group of a crystal structure and P_H the symmetry group of some physical property of that crystal. Then, P_G is a subgroup of P_H.*

There are a few things to digest here. Let us start by understanding the meaning of the phrase "symmetry group". For any given crystal, there exists some infinitely large set of operations G under which the crystal structure is symmetric. Each of these operations may be decomposed into two parts: a "point-preserving operation" R, corresponding to either the identity, rotation, inversion, mirror, or the product of mirror and rotation, followed by a translation by some vector $\boldsymbol{\tau}$:

$$G = \{(R|\boldsymbol{\tau})\} \tag{2.1}$$

where $(R|\boldsymbol{\tau})$ means "Perform R, then translate by $\boldsymbol{\tau}$". Clearly, the set G forms a group, since if both g_1 and $g_2 \in G$ leave the crystal structure

invariant, so does the product $g_1 g_2$, and so $g_1 g_2 \in G$. Thus, G is called the *space group* of the crystal. In three dimensions, there are 230 crystallographic space groups, which are tabulated in a number of places, most usefully Wikipedia [**?**].

For 73 of these groups, the translation parts of the τs in eq. (2.1) are only ever linear combinations of integer multiples of the lattice vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$; these are called *symmorphic* space groups. The remaining 157 groups involve translations that are not integer multiples of the lattice vectors; these are one's screw axes and glide planes, and so these groups are called *asymmorphic*.

Importantly, the "physical properties" of theorem 2.1.1 refer to the truly macroscopic properties of the crystal, like its conductivity, dielectric, or pyroelectric tensors. Consider, for example, that in SHG, we are typically studying the sample at optical wavelengths, where the wavelength of light is three or four orders of magnitude larger than the lattice spacing. Clearly, then, these properties do not care whether the correct symmetry is $(R|\tau)$ or $(R|\tau + {}^{\boldsymbol{a}}/_2)$. A more useful group, then, is the *point group* of the crystal

$$P_G = \{R \text{ s.t. } \exists\, \boldsymbol{\tau} \text{ s.t. } (R|\boldsymbol{\tau}) \in G\} \tag{2.2}$$

i.e., the point group is the set of point-preserving operations R for which R appears in G, regardless of whether you need to perform a translation with it. Once can show that P_G is also a group, and thus it is P_G which is involved in Neumann's principle for all intents and purposes[1].

The last ingredient that we need to understand theorem 2.1.1 is the concept of what is meant by "physical propery". The idea is that the response of the crystal $J_{i_1 i_2 \cdots i_n}$ (i.e., the current J_i, or the quadrupole moment Q_{ij}) is proportional to some field $F_{i'_1 i'_2 \cdots i'_m}$ via some tensor χ:

$$J_{i_1 i_2 \cdots i_n} = \chi_{i_1 i_2 \cdots i_n i'_1 i'_2 \cdots i'_m} F_{i'_1 i'_2 \cdots i'_m}. \tag{2.3}$$

For example, the conductivity σ_{ij} relates a current density J_i to an applied electric field E_j:

$$J_i = \sigma_{ij} E_j. \tag{2.4}$$

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[1]Of course this breaks down when the wavelength of light is comparable to the lattice spacing; in that case you need to consider the full space group.

Likewise, the polarization P_i due to the pyroelectric effect is related to the a temperature difference ΔT by a tensor p_i:

$$P_i = p_i \Delta T. \tag{2.5}$$

The tensors σ_{ij}, p_i, and generally, $\chi_{i_1 i_2 \cdots 1n i'_1 i'_2 \cdots i'_m}$ are commonly referred to as *matter tensors* [?], to emphasize the fact that they are the only part of the response equations that depend on the material. It should be noted that matter tensors generically come in two types: those that transform like a vector under inversion and those that transform like a pseudovector under inversion. You can tell which is which by applying inversion to either side of the response equation. For example, the tensor ϵ_{ij} relating the displacement field to the electric field

$$D_i = \epsilon_{ij} E_j \tag{2.6}$$

is a polar tensor, whereas the tensor χ_{ij}^{me} describing the magnetoelectric effect

$$M_i = \chi_{ij}^{me} E_j \tag{2.7}$$

is an axial tensor.

We are now ready to restate theorem 2.1.1 in a slightly more useful form, using the terminology we have developed about point groups and matter tensors:

Theorem 2.1.2 (Neumann's principle, restated) *Let P_G be the point group of a given crystal, and let χ be a matter tensor describing some response function of that crystal. Then, for all $g \in P_G$, we have*

$$g(\chi) = \chi. \tag{2.8}$$

Equation (2.8) can be more usefully expressed if we know the matrix R_{ij}^g corresponding to g. For example, if g is "threefold rotation about the z axis", we have

$$R_{ij}^g = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{2.9}$$

in which case one can show that eq. (2.8) reads

$$(\det R^g)^t R_{i_1 i'_1}^g R_{i_2 i'_2}^g \cdots R_{i_n i'_n}^g \chi_{i'_1 i'_2 \cdots i'_n} = \chi_{i_1 i_2 \cdots i_n}, \tag{2.10}$$

where t is 0 if χ is a polar tensor and 1 if χ is an axial tensor. Theorem 2.1.2 tells us that there is one copy of eq. (2.10) for each $g \in P_G$.

Apparently, each element $g \in P_G$ gives us a *constraint* on the numbers $\chi_{i_1 i_2 \cdots i_n}$, in that they have to satisfy eq. (2.10). This is a remarkably useful fact. Since different point groups enforce different constraints on χ, that means the *form* of χ (e.g. when written as a list of numbers) depends quite sensitively on the point group of the crystal we are studying. As an example, here is the dielectric permittivity tensor for crystals with the point group (in Schoenflies notation) C_2:

$$\epsilon_{ij} = \begin{pmatrix} a & 0 & e \\ 0 & b & 0 \\ e & 0 & c \end{pmatrix}_{ij} \tag{2.11}$$

versus in the point group D_{3d}:

$$\epsilon_{ij} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{pmatrix}_{ij}. \tag{2.12}$$

Clearly, any *measurement* of ϵ_{ij} will be able to easily differentiate a crystal with point group C_2 from one with point group D_{3d}. This is the fundamental basis, then, for SHG. In SHG, we measure the tensor χ_{ijk} corresponding to the response equation[2]

$$P_i(2\omega) = \chi_{ijk} E_j(\omega) E_k(\omega); \tag{2.13}$$

the numbers χ_{ijk} thus tell us about the crystallographic point group we are measuring from.

There are a couple of advantages to measuring χ_{ijk} over any other matter tensor in a given system. For one thing, χ_{ijk} is a third rank tensor, which means it has a few more degrees of freedom to work with compared to ϵ_{ij}, and thus does a better job at uniquely specifying each point group. It also doesn't have *too many* degrees of freedom, so that most of the time your experiment will be able to tell you all of your tensor elements[3]. In addition, since we are typically doing SHG at optical

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[2]This discussion is a bit simplified in the sense that there are actually *many* response functions which will give you light at 2ω; for a more detailed discussion, see **??**.

[3]Quadrupole SHG has this problem, see **??**.

wavelengths, the form of χ_{ijk} reflects the symmetry of the *charge distribution* $\rho(\boldsymbol{x})$, in contrast to e.g. x-ray diffraction, where the relevant tensors will tell instead you about the electron distribution, $n(\boldsymbol{x})$. This can be advantageous in cases where the long range order you are trying to study involves an ordering of the valence electrons but not the electrons in the cores of atoms. This is entirely the result of the fact that Neumann's principle, as expressed both in theorem 2.1.1 and theorem 2.1.2, tells us that the point group of our crystal is a *subgroup* of the point group we get from our measurement – the measurement can always be more symmetric than the crystal!

As another example of this fact, let us note that the response equation given by eq. (2.13) clearly has an additional symmetry $j \leftrightarrow k$, since the two copies of the electric field on the right hand side are equivalent. Obviously this is not a result of the material we are studying, it is simply a fact of doing SHG. Thus, in addition to the constraints given by Neumann's principle and eq. (2.10), we have the additional constraint

$$\chi_{ijk} = \chi_{ikj} \forall i, j, k. \tag{2.14}$$

This is known as *particularization* [**?**].

2.2 A classical understanding of SHG

In the last section we considered the SHG response function given by eq. (2.13). Where does this relationship come from, and how is $P(2\omega)$ eventually measured? Our starting point in the classical treatment will be the inhomogenous electromagnetic wave equation

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) E_i(\boldsymbol{x}, t) = S_i(\boldsymbol{x}, t), \tag{2.15}$$

which we understand as defining the field $E_i(\boldsymbol{x}, t)$ radiated by the source term $S_i(\boldsymbol{x}, t)$, which is induced by the incident field. To lowest order in a multipole expansion, $S_i(\boldsymbol{x}, t)$ is given by [**?**,**?**]

$$\mu_0 \frac{\partial^2 P_i(\boldsymbol{x}, t)}{\partial t^2} + \mu_0 \left(\epsilon_{ijk} \nabla_j \frac{\partial M_k(\boldsymbol{x}, t)}{\partial t} \right) - \mu_0 \left(\nabla_j \frac{\partial^2 Q_{ij}(\boldsymbol{x}, t)}{\partial t^2} \right) \tag{2.16}$$

where $P_i(\boldsymbol{x}, t)$, $M_i(\boldsymbol{x}, t)$, and $Q_{ij}(\boldsymbol{x}, t)$ are the induced electric dipole, magnetic dipole, and electric quadrupole densities, and ϵ_{ijk} is the Levi-Civita tensor.

If the incident electric field is small, then the terms $P_i(\boldsymbol{x}, t)$, $M_i(\boldsymbol{x}, t)$, and $Q_{ij}(\boldsymbol{x}, t)$ are linear functions of that electric field. However, for larger incident fields (such as those generated by pulsed lasers), they may be more generally written as a taylor series:

$$P_i = \chi_{ij}^{ee} E_j + \chi_{ij}^{em} H_j + \chi_{ijk}^{eee} E_j E_k + \chi_{ijk}^{eem} E_j H_k + \cdots \tag{2.17}$$

$$M_i = \chi_{ij}^{me} E_j + \chi_{ij}^{mm} H_j + \chi_{ijk}^{mee} E_j E_k + \chi_{ijk}^{mem} E_j H_k + \cdots \tag{2.18}$$

$$Q_{ij} = \chi_{ijk}^{qe} E_k + \chi_{ijk}^{qm} H_k + \chi_{ijkl}^{qee} E_k E_l + \chi_{ijkl}^{qem} E_k H_l + \cdots \tag{2.19}$$

where we have suppressed the arguments $\boldsymbol{x}$ and t for brevity.

Assuming the incident field is monochromatic,

$$E_i(\boldsymbol{x}, t) = E_i(\omega) e^{i(\boldsymbol{k} \cdot \boldsymbol{x} - \omega t)} + \text{c.c.} \tag{2.20}$$

$$H_i(\boldsymbol{x}, t) = H_i(\omega) e^{i(\boldsymbol{k} \cdot \boldsymbol{x} - \omega t)} + \text{c.c.} \tag{2.21}$$

the induced sources are also monochromatic, and (keeping only terms proportional to $e^{i2\omega t}$) we thus get

$$P_i(2\omega) = \chi_{ijk}^{eee} E_j(\omega) E_k(\omega) + \chi_{ijk}^{eem} E_j(\omega) H_k(\omega) \tag{2.22}$$

$$M_i(2\omega) = \chi_{ijk}^{mee} E_j(\omega) E_k(\omega) + \chi_{ijk}^{mem} E_j(\omega) H_k(\omega) \tag{2.23}$$

$$Q_{ij}(2\omega) = \chi_{ijkl}^{qee} E_k(\omega) E_l(\omega) + \chi_{ijkl}^{qem} E_k(\omega) H_l(\omega). \tag{2.24}$$

Since eq. (2.15) is linear, the electric field radiated by $S_i(\boldsymbol{x}, t)$ is simply proportional to it. In the limit where the first term of eq. (2.22) dominates, the intensity measured at our detector thus satisfies

$$I(2\omega) \propto |\hat{e}_i^{\text{out}} \chi_{ijk}^{eee} \hat{e}_j^{\text{in}} \hat{e}_k^{\text{in}}|^2, \tag{2.25}$$

where $\hat{e}^{\text{in}}$ and $\hat{e}^{\text{out}}$ are unit vectors in the direction of the incoming and measured electric fields[4]. χ_{ijk}^{eee} does typically dominate when inversion symmetry is broken, but if not, you have to consider all of the terms in eqs. (2.22) to (2.24). Actually, each of these terms needs to be considered twice, since there is both a surface contribution and a bulk contribution[5]. In my experience, the heirarchy of contributions (from most to least important, and assuming everything is allowed by symmetry) is typically:

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[4]Usually there are polarizers in the experiment which define these directions.

[5]The space group which constrains the surface contributions is the bulk space group less the operations which involve some change in the z coordinate.

1. Bulk electric dipole

2. Surface electric dipole, bulk electric quadrupole, and bulk magnetic dipole, at the same order[6]

3. Everything else

I've never seen anything outside of items 1 and 2, but in rare cases an electronic resonance may cause an enhancement in one of the other contributions [**?**].

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[6]Somehow the bulk electric quadrupole and magnetic dipole contributions have been labelled "exotic" by some in the community, but that has not been my experience. If I had to guess, almost half of the materials I have measured with inversion symmetry show electric quadrupole SHG.

Chapter Three

Second harmonic generation: practical

Chapter Four

Second harmonic generation as a probe of broken mirror symmetry in 1T-TaS$_2$

Chapter Five

Light-induced reorientation transition in the antiferromagnetic semiconductor $CaMn_2Bi_2$

Chapter Six

Amplitude-mode electromagnon in the XXZ chain CuBr$_2$

Chapter Seven

Concluding remarks

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