Theory and Design of Nonlinear Metamaterials

by

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Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Electrical and Computer Engineering in the Graduate School of Duke University

2013
Abstract

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Abstract

If electronics are ever to be completely replaced by optics, a significant possibility in the wake of the fiber revolution, it is likely that nonlinear materials will play a central and enabling role. Indeed, nonlinear optics is the study of the mechanisms through which light can change the nature and properties of matter and, as a corollary, how one beam or color of light can manipulate another or even itself within such a material. However, of the many barriers preventing such a lofty goal, the narrow and limited range of properties supported by nonlinear materials, and natural materials in general, stands at the forefront. Many industries have turned instead to artificial and composite materials, with homogenizable metamaterials representing a recent extension of such composites into the electromagnetic domain. In particular, the inclusion of nonlinear elements has caused metamaterials research to spill over into the field of nonlinear optics. Through careful design of their constituent elements, nonlinear metamaterials are capable of supporting an unprecedented range of interactions, promising nonlinear devices of novel design and scale. In this context, I cast the basic properties of nonlinear metamaterials in the conventional formalism of nonlinear optics. Using alternately transfer matrices and coupled mode theory, I develop two complementary methods for characterizing and designing metamaterials with arbitrary nonlinear properties. Subsequently, I apply these methods in numerical studies of several canonical metamaterials, demonstrating enhanced electric and magnetic nonlinearities, as well as predicting the existence of nonlinear magne-
toelectric and off-diagonal nonlinear tensors. I then introduce simultaneous design of the linear and nonlinear properties in the context of phase matching, outlining five different metamaterial phase matching methods, with special emphasis on the phase matching of counter propagating waves in mirrorless parametric amplifiers and oscillators. By applying this set of tools and knowledge to microwave metamaterials, I experimentally confirm several novel nonlinear phenomena. Most notably, I construct a backward wave nonlinear medium from varactor-loaded split ring resonators loaded in a rectangular waveguide, capable of generating second-harmonic opposite to conventional nonlinear materials with a conversion efficiency as high as 1.5%. In addition, I confirm nonlinear magnetoelectric coupling in two dual gap varactor-loaded split ring resonator metamaterials through measurement of the amplitude and phase of the second-harmonic generated in the forward and backward directions from a thin slab. I then use the presence of simultaneous nonlinearities in such metamaterials to observe nonlinear interference, manifest as unidirectional difference frequency generation with contrasts of 6 and 12 dB in the forward and backward directions, respectively. Finally, I apply these principles and intuition to several plasmonic platforms with the goal of achieving similar enhancements and configurations at optical frequencies. Using the example of fluorescence enhancement in optical patch antennas, I develop a semi-classical numerical model for the calculation of field-induced enhancements to both excitation and spontaneous emission rates of an embedded fluorophore, showing qualitative agreement with experimental results, with enhancement factors of more than 30,000. Throughout these series of works, I emphasize the indispensability of effective design and retrieval tools in understanding and optimizing both metamaterials and plasmonic systems. Ultimately, when weighed against the disadvantages in fabrication and optical losses, the results presented here provide a context for the application of nonlinear metamaterials within three distinct areas where a competitive advantage over conventional materials might
be obtained: fundamental science demonstrations, linear and nonlinear anisotropy engineering, and extremely compact resonant all-optical devices.
To my family, with whom I share all my accomplishments, and to whom I owe my character.
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8.9 (Reproduced with permission from Ref. [208].) Nanopatch scattering and fluorescence enhancement. (a) Dark-field microscope image of the nanopatches under white-light illumination. The dominant color of each nanopatch corresponds to the resonant wavelength ($\lambda_0$) of its cavity mode. (b) Normalized scattering spectrum for two nanopatches. (c) Fluorescence enhancement factor for individual nanopatches as a function of nanopatch resonance. The inset shows a typical fluorescence spectra from a nanopatch. Laser excitation ($\lambda_{ex}$, vertical line) and Cy5 in-solution emission spectra (shaded region) are shown for comparison.

8.10 Plot of the averaged fluorescence enhancement factor versus resonant wavelength in log-scale. The data is fit with a piece-wise linear function to determine a rough estimate of the variance in the measured data. This variance in turn is used in analyzing the goodness-of-fit of the simulations with the measured data, as shown in Fig. 8.9.

8.11 The simulated excitation, radiative, and non-radiative rates as a function of nanopatch resonant wavelength. The internal decay rate of Cy5, $\gamma_{nr}^0 \approx 5\gamma_r^0$, is shown to be negligible by comparison.
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1

Introduction to passive, tunable, and nonlinear metamaterials

Despite the seemingly diverse forms that natural materials take, whether texture, color, or room-temperature phase, their physical properties tend to occupy only a very narrow segment in a much wider spectrum. This is true whether we consider electromagnetic, mechanical, or thermal properties. There is no better testament to this lack of diversity in natural materials than the steadily increasing market for composite materials. Once reserved for spacecraft, composites make up roughly 50% of the Boeing 787 by weight. Composites have allowed bike frames to weigh less than 1 kg while retaining their stiffness. They show up in next generation prosthetics and vehicle armor.

Metamaterials represent a natural extension of composite materials engineering to electromagnetics. For example, fundamentally speaking, there is only one key difference in whether magnetic flux is carried in the orbit of a single electron about a nucleus, or by a sea of electrons following a closed conductive loop: the latter effect can be far, far stronger. Simply put, there is much greater freedom in patterning materials to form meta-atoms, and arranging these meta-atoms into metamaterials,
than exists in the natural world. In the early stages, the novel properties displayed by metamaterials spurred research into a wide range of newly-achievable phenomena. The resulting demonstrations attracted a large amount of excitement and attention, but were ultimately fundamental, rather than application-oriented. As the field has matured, however, researchers have started to revisit well-known problems in industry, using the tools of metamaterial engineering to try and improve on existing solutions in communications, imaging, and energy harvesting, to name a few.

1.1 Introduction to metamaterials

In the context of electromagnetics, a material’s response to an incident set of electric and magnetic fields is a composition of the discrete charges and currents that are carried by its basic atoms and molecules. For an exact solution of the fields, one would need to take into account the contribution from each individual particle. However, under the right conditions, certain approximations can be used to homogenize the material response, neglecting the microscopic details in favor of locally averaged, macroscopic fields. In this way, the numerous discrete charges and currents can be simply replaced by effective parameters. This is essentially the approximation inherent in the macroscopic version of Maxwell’s equations. The errors incurred are negligible as long as the length scale of the averaging is much larger than the length scale of the material’s inhomogeneity. In practice, this translates to the constraint that a material’s internal structure is much smaller than the particular wavelength of radiation. Nearly all natural materials satisfy this constraint well into the visible spectrum, as the length scales of their internal structure are on the order of atomic and molecular interactions. But at no point is it assumed that atoms and molecules are the only constituents that can be described in this way.

As opposed to natural materials, the charges and currents that constitute the electromagnetic response of a metamaterial are carried by the patterns and particles
of their internal structure. Thus, in exact analogy to natural materials, metamaterials can be described by homogeneous, constitutive parameters. But these patterns and particles can behave very differently from their atomic counterparts. This allows metamaterials to achieve properties that are either limited or entirely unachievable in naturally occurring materials. A medium composed of split ring resonators like that shown in Fig. 1.2, for example, can couple to incident magnetic fields to produce a region of negative permeability: a property not typically found in natural materials [1].

Several different phenomena have been demonstrated for the first time in metamaterials. In general, these involve the ability of metamaterials to achieve a wide range of simultaneous values for their electric permittivity, magnetic permeability, and magnetoelectric susceptibility tensors [2, 1, 3], as defined by the macroscopic polarization and magnetization

$$\vec{P}(\omega) = \epsilon_0 \chi^{(1)}_e(\omega) \vec{E}(\omega) + i \kappa^{(1)}(\omega) \vec{H}(\omega),$$

(1.1)

$$\mu_0 \vec{M}(\omega) = \mu_0 \chi^{(1)}_m(\omega) \vec{H}(\omega) - i \left[ \kappa^{(1)}(\omega) \right]^* \vec{E}(\omega),$$

(1.2)

respectively, where $\epsilon_0$ and $\mu_0$ are the permittivity and permeability of free-space, $\omega$ is an angular frequency, $\bar{\chi}^{(1)}$ are the rank-2 linear susceptibility tensors, and $\bar{\kappa}$ is the rank-2 linear magnetoelectric coupling tensor. Through the combination of these responses, metamaterials have led to the demonstration of a variety of novel and
anomalous properties, including negative refraction [4, 5] and cloaking [6, 7, 8].

Figure 1.2: The split ring resonator as a meta-atom, showing the current (black arrow) induced by an incident light wave.

Alongside the numerous demonstrations and fast paced research, new tools of analysis and characterization have been developed specifically for metamaterials. In particular, there exist several methods of homogenization for assigning appropriate effective parameters to a particular engineered structure. In essence, the retrieval process equates the unit cell of the metamaterial to a congruently sized homogeneous material with an unknown set of electromagnetic properties. In the linear case, the system is commonly solved by finding the equivalent permittivity, permeability, and magneto-electric coefficient that replicate the scattering parameters of the metamaterial [9, 10, 11]. This retrieval method has the added advantage of being easily applicable in practice through transmission and reflection experiments. Alternatively, constitutive parameters can be determined through the process of field averaging, but this technique is limited to cases where the local fields are known over the whole of a unit cell [12]. Another tool often associated with metamaterials is the material design methodology of transformation optics, wherein coordinate transformations are implemented in Maxwell’s equations to prescribe the material parameters necessary for a particular manipulation of the fields [13, 3].
1.2 Competing routes to active and tunable metamaterials

In addition, there exists a particular trait singular to resonant metamaterials, or metamaterials whose electromagnetic response is based around a resonant component or geometry. It was observed early on that these metamaterials, when operated near resonance, displayed highly non-uniform field distributions over a unit cell [2]. The extreme variation in the field density implies that these structures exhibit significant confinement of electromagnetic energy in small, critical volumes. This property of resonant metamaterials has spurred the hybridization of metamaterials with various functional materials, such as gain media, ferromagnets, piezoelectrics, and numerous other candidates, imbuing the metamaterial as a whole with the properties of the constituent material. This has led to the exciting demonstration of tunable metamaterials, that is, metamaterials whose properties can be dynamically and reversibly controlled as a part of an active device. In what follows, we discuss several potential routes towards tunable metamaterials (see, for example, Fig. 1.3). In particular, we develop this context for the introduction of metamaterials hybridized with nonlinear materials, which are shown to occupy an important niche within tunable metamaterials as a whole.

![Figure 1.3: Illustrative sketch of (a) mechanical, (b) phase change, and (c) nonlinear field-induced mechanisms for metamaterial tuning.](image)
1.2.1 Mechanical tuning

Perhaps the most obvious form of metamaterial tuning is mechanical. Metamaterial elements are highly sensitive to their microscopic structure, such that any small deformation to the geometry will be amplified in the metamaterial’s ability to reflect, absorb, or refract radiation [14, 15, 16].

Often, mechanical tuning exploits the freedom in positioning the lattice substrate itself. Lapine textslet. al., for example, demonstrated continuous tuning of the metamaterial resonance for lateral shifts between successive planes of microwave resonators [17]. Similar designs have been tested at THz frequencies, relying on the near-field coupling between successive elements [18]. However, these designs are not suitable for dynamic tuning. Instead, it is preferential to have a mechanism by which the substrate or housing can be deformed post-fabrication.

To this end, Li et. al. tuned the resonance of embedded metamaterial resonators by more than 8% by applying strain directly to a highly elastic substrate [19]. Alternatively, planar metamaterial elements have been divided across two mechanically separate but interlocked substrates, such that the internal unit-cell spacings can be controlled by an externally applied voltage [20, 21, 22], or by local heating [23]. Microactuators have also proven useful components for changing the most sensitive inter-element spacings (see, for example, Ref. [24] and Refs. within).

Clearly, the ability to reconfigure the geometry of metamaterial elements on the order of the interparticle spacings grants immense control over the metamaterial properties. However, such designs can be difficult to scale to the spacings necessary for near-infrared and visible wavelengths. Instead, the rearrangement supported by liquid crystals has been used to change the local electromagnetic environment in the near-field of metamaterial elements [25, 26, 27, 28]. However, mechanical reconfiguration is inherently a slow process, limited to switching on the order of
microseconds.

1.2.2 Phase transitions

Alternatively, certain materials are known to exhibit phase transitions in their optical properties for different arrangements of their constituent atoms and molecules. Hybridization of such phase transition materials with metamaterials can both localize external stimuli, such as heat or light, within the phase transition material, and enhance the effect of the phase transition on the overall optical properties. As before, the presence of a small amount of phase transition material can imbue the entire metamaterial structure with similar but enhanced properties.

For example, vanadium dioxide has proven a popular choice as a phase transition substrate, transitioning from an insulator to a conductor at a critical temperature. When coupled to metamaterial resonators, the resonance can be extinguished by vanadium dioxide’s conducting state, induced through heating of the entire structure [29, 30], application of an electrical pulse [31], or even through interaction with a high-field terahertz pulse [32].

Semiconductor chalcogenide glasses, on the other hand, are widely used in phase change rewriteable applications [33], owing to the large change in band-gap and conductivity associated with its easily accessible amorphous-crystalline transition. Plasmonics and metamaterial switches based around this phase transition have recently been demonstrated [34, 35, 36], with the potential for switching speeds on the order of 10s of nanoseconds.

Phase transition metamaterials like those listed above combine large, reversible, optically induced tuning with modulation speeds that are much faster than their mechanically tuned counterparts. However, the speeds are still too slow for applications in all-optical communication networks.
1.2.3 Nonlinearity

A nonlinear material is one whose electromagnetic response, i.e. the material’s polarization and magnetization in the presence of electric and magnetic fields, cannot be satisfactorily described by a linear proportionality with the incident fields. In fact, all materials have a nonlinear response for sufficiently strong incident fields. However, the important characteristic is that the nonlinear response is fast, such that the material responds at frequencies of the same order as the applied light. This kind of ultrafast response is unique to the nonlinear mechanism, and allows not only ultrafast switching times by using pump and probe light pulses, but can even induce changes in the frequency of an incident wave.

A defining feature of linear systems is the principle of superposition, or the fact that the output of a linear system from multiple inputs is equivalent to a sum of the outputs from each input individually. Nonlinear responses, or equivalently the higher-order terms in Eqs. (2.1) and (2.2), break this property, meaning that the output of a nonlinear system for a particular input can be changed by adding additional inputs. The violation of superposition is a driving force in many applications of nonlinear materials, and can allow for frequency generators and amplifiers in those frequency ranges that currently lack lasers [37], high-speed switches in communication networks [38, 39], and even sub-diffraction-limit imaging [40, 41].

Most importantly, however, nonlinear processes like difference frequency generation and amplification are phase sensitive, coherent processes, in which the output photons maintain a fixed phase relationship to the input photons. As such, nonlinear materials are the main source of squeezed and entangled light [42, 43, 44, 45], and a critical part of quantum information science [46].

Some of the most popular natural nonlinear materials for current nonlinear optics technologies include ferroelectrics, semiconductors, organic polymers, and cer-
tain glasses [47, 48]. However, the nonlinear responses of such materials are so weak that the subsequent devices typically require pulsed laser operation over long interaction lengths, further limiting the materials of choice to those that can be phase matched over long distances with small loss tangents and high damage thresholds [49]. Metal films offer an interesting alternative due to the much larger nonlinear responses that they possess [50, 51, 52, 53], but do not support bulk propagating waves and suffer from large ohmic losses. Thus, much of the nonlinear metamaterial research has focused on nanostructuring metals in such a way to enhance their already large nonlinearities while allowing the incident fields to couple in and out of the structure [54, 55, 56]. For example, second-harmonic generation (SHG) has been demonstrated from gold split-ring resonators, carefully controlling the polarization of the incident fields and induced dipoles to ensure efficient re-radiation of the second-harmonic [57, 58]. The third-order process of phase-conjugation has likewise been measured from metal nanostructures [41]. On the other hand, the nonlinearities of a substrate can themselves be enhanced by simple dielectric composites [59, 60] and by metal patterning [38, 61]. By relying on light localization in the substrate rather than the metal, such composites can potentially limit the effects of metallic losses while still achieving large nonlinearities.

Due to its ultrafast response and phase coherency, the nonlinear mechanism for tunable metamaterials deserves unique attention, with exciting applications as ultrafast optical switches, frequency generators, amplifiers, and sources of entangled photons for quantum information science [15]. To address the complexity of nonlinear metamaterials, with the hope of facilitating their design and application, the contents of this thesis are as follows: I introduce the formalism for describing nonlinear metamaterials in the context of conventional nonlinear optics in chapter 2. I develop the primary experimental and analytic tools for the design and characterization of nonlinear metamaterials in chapters 3 and 4. Next, I summarize and demonstrate
the two primary design strategies for nonlinear metamaterials: nonlinear susceptibility engineering, and phase matching, in chapters 5 and 6, respectively. In chapter 7, I present the experimental observation of several novel nonlinear phenomena in microwave metamaterials. Finally, in chapter 8, I extend the principles of nonlinear metamaterial engineering to the related field of plasmonics. Chapter 9 summarizes the presented material, offering my outlook for nonlinear metamaterials, their advantages and potential problems, and which applications are most likely to have a major impact.
The nonlinear susceptibilities

We focus here on materials that are linear in the limit of weak incident fields. For such materials, the polarization and magnetization can be expanded in a power-series, such that

\[
\vec{P}(t) = \vec{P}^{(1)}(t) + \vec{P}^{(2)}(t) + \vec{P}^{(3)}(t) + \ldots \tag{2.1}
\]

and

\[
\vec{M}(t) = \vec{M}^{(1)}(t) + \vec{M}^{(2)}(t) + \vec{M}^{(3)}(t) + \ldots \tag{2.2}
\]

where the superscript denotes the dependence on the fields, i.e. linear, quadratic, cubic, etc. We will divide our attention between two categories of nonlinear responses, namely second- and third-order, and the phenomena associated with each. Bulk second-order responses, mediated by \(\vec{P}^{(2)}(t)\) and \(\vec{M}^{(2)}(t)\), are associated with non-centrosymmetric materials, or materials that possess no inversion symmetry. Third-order responses, mediated by \(\vec{P}^{(3)}(t)\) and \(\vec{M}^{(3)}(t)\), can occur in both centrosymmetric and non-centrosymmetric media. Furthermore, it is convenient to investigate the related phenomena in the frequency domain, for which we use the expansion

\[
\vec{E}(t) = \sum_n \vec{E}(\omega_n)e^{-i\omega_n t}, \tag{2.3}
\]
and likewise for the other field quantities, where the summation is over both positive and negative frequencies. To satisfy the reality of the total fields, it follows that 
\[ \vec{E}(\omega_n) = \left[ \vec{E}(-\omega_n) \right]^* . \]

2.1 Coupled-wave theory

Nonlinear parametric processes, to which the majority of this thesis is devoted, are best understood intuitively within the context of coupled-wave theory [62, 63, 64]. It is typically the case that the nonlinear response—even for most metamaterials—is relatively small compared with the material’s linear response. The nonlinearity can then be treated as a perturbation, so that we can at least retain the intuition and language that we associate with linear wave propagation in a particular medium.

In particular, in source-free media, Maxwell’s macroscopic curl equations for the fields at frequency \( \omega \) in the presence of perturbations to both the polarization and magnetization are

\[ \nabla \times \vec{E} = i\omega \left[ \vec{B} + \mu_0 \vec{M}^{(n)} \right], \]
\[ \nabla \times \vec{H} = -i\omega \left[ \vec{D} + \vec{P}^{(n)} \right], \]

with the constitutive relations

\[ \vec{D} = \vec{\epsilon} \vec{E} + i\kappa \vec{H}, \]
\[ \vec{B} = \vec{\mu} \vec{H} - i\kappa^* \vec{E}. \]

Meanwhile, we know that, in the absence of the perturbation, the fields satisfy

\[ \nabla \times \vec{E}_\mu = i\omega \vec{B}_\mu, \]
\[ \nabla \times \vec{H}_\mu = -i\omega \vec{D}_\mu, \]

where we take \( \vec{E}_\mu \) and \( \vec{H}_\mu \) to represent the fields of some unperturbed mode \( \mu \) with unitary amplitude. Assuming purely real material properties, we follow the path
outlined in Ref. [64], combining Eqs. (2.4) through (2.9) to give

\[ \vec{H}^{*} \cdot \left[ \nabla \times \vec{E} \right] - \vec{E} \cdot \left[ \nabla \times \vec{H}^{*} \right] = i\omega \vec{H}^{*} \cdot \left[ \vec{B} + \mu_{0}\vec{M}^{(n)} \right] - i\omega \vec{E} \cdot \vec{D}^{*} \]  

(2.10)

and

\[ \vec{H} \cdot \left[ \nabla \times \vec{E}^{*} \right] - \vec{E}^{*} \cdot \left[ \nabla \times \vec{H} \right] = -i\omega \vec{H} \cdot \vec{B}^{*} + i\omega \vec{E}^{*} \cdot \left[ \vec{D} + \vec{P}^{(n)} \right] . \]  

(2.11)

Adding Eqs. (2.10) and (2.11), we can apply some vector calculus identities to obtain

\[ \nabla \cdot \left[ \vec{E} \times \vec{H}^{*} + \vec{E}^{*} \times \vec{H} \right] = i\omega \left[ \vec{P}^{(n)} \cdot \vec{E}^{*} + \mu_{0}\vec{M}^{(n)} \cdot \vec{h}^{*} \right] . \]  

(2.12)

From here, the coupled-mode equations can be found by choosing an explicit form for the fields \( \vec{E} \) and \( \vec{H} \) and the perturbations \( \vec{P}^{(n)} \) and \( \vec{M}^{(n)} \).

In particular, for a linear homogeneous medium, we typically discuss propagation in terms of a set of transverse electromagnetic (TEM) plane waves. Using the wave label \( \mu \) to denote frequency, polarization, and direction, we can write these waves through the electric field

\[ \vec{E}_{\mu} = A_{\mu}\vec{e}_{\mu}e^{i\vec{k}_{\mu} \cdot \vec{r}} \]  

(2.13)

and magnetic field

\[ \vec{H}_{\mu} = A_{\mu}\vec{h}_{\mu}e^{i\vec{k}_{\mu} \cdot \vec{r}} \]  

(2.14)

where \( A_{\mu} \) is the wave amplitude, and \( \vec{e}_{\mu} \) and \( \vec{h}_{\mu} \) are the corresponding polarization vectors. We can normalize the polarization vectors according to

\[ \frac{1}{2} \left( \vec{e}_{\mu} \times \vec{h}_{\mu}^{*} + \vec{e}_{\mu}^{*} \times \vec{h}_{\mu} \right) = \hat{s}_{\mu} , \]  

(2.15)

where \( \hat{s}_{\mu} \) is the unit-normal in the direction of the Poynting vector. For this normalization, the wave intensity is given simply by \( I_{\mu} = 2\text{Re} \left( \vec{E}_{\mu} \times \vec{H}_{\mu}^{*} \right) = 2|A_{\mu}|^{2} \). Using this form for wave \( \mu \), we can reduce Eq. (2.12) to

\[ \nabla A_{\mu}(\vec{r}) \cdot \hat{s}_{\mu} = i\omega_{\mu} \left[ \vec{P}^{(n)} \cdot \vec{e}_{\mu}^{*} + \mu_{0}\vec{M}^{(n)} \cdot \vec{h}_{\mu}^{*} \right] e^{-i\vec{k}_{\mu} \cdot \vec{r}} . \]  

(2.16)
Thus, wave propagation can still be described through the medium’s linear modes and waves, while the various amplitudes evolve in space according to a forcing term proportional to the nonlinear perturbations. This expression can be extended to include pulse dynamics [65], but is sufficient for illustrating the various nonlinear processes, both in homogeneous media and metamaterials.

2.2 Second-order response

Expanding the fields in the frequency domain allows us to write the second-order response of a medium in terms of eight independent second-order susceptibility tensors of rank-3, as given by the following definitions of the second-order polarization,

\[
\bar{\mathcal{P}}^{(2)}(t) = \sum_{qr} \left[ \bar{\chi}_{eee}^{(2)}(\omega_s; \omega_q, \omega_r) : \vec{E}(\omega_q) \vec{E}(\omega_r) + \bar{\chi}_{emn}^{(2)}(\omega_s; \omega_q, \omega_r) : \vec{H}(\omega_q) \vec{H}(\omega_r) + \bar{\chi}_{emm}^{(2)}(\omega_s; \omega_q, \omega_r) : \vec{H}(\omega_q) \vec{E}(\omega_r) + \bar{\chi}_{eem}^{(2)}(\omega_s; \omega_q, \omega_r) : \vec{E}(\omega_q) \vec{H}(\omega_r) \right] \exp(-i\omega_s t),
\]

\[(2.17)\]

and second-order magnetization,

\[
\mu_0 \bar{M}^{(2)}(t) = \sum_{qr} \left[ \bar{\chi}_{mmm}^{(2)}(\omega_s; \omega_q, \omega_r) : \vec{H}(\omega_q) \vec{H}(\omega_r) + \bar{\chi}_{mem}^{(2)}(\omega_s; \omega_q, \omega_r) : \vec{E}(\omega_q) \vec{E}(\omega_r) + \bar{\chi}_{mme}^{(2)}(\omega_s; \omega_q, \omega_r) : \vec{H}(\omega_q) \vec{E}(\omega_r) + \bar{\chi}_{mem}^{(2)}(\omega_s; \omega_q, \omega_r) : \vec{E}(\omega_q) \vec{H}(\omega_r) \right] \exp(-i\omega_s t).
\]

\[(2.18)\]

It is evident that, in such a medium, the fields at one frequency will drive responses at other frequencies, constituting what is known as three-wave mixing. In this way, energy in the medium can be transferred between different frequencies, subject to the constraint

\[
\omega_q + \omega_r = \omega_s.
\]

\[(2.19)\]

If we consider the wave-mixing in terms of photons, we see that this is a statement of energy conservation, as a photon’s energy is just \(\hbar \omega\), where \(\hbar\) is the reduced Planck constant.
As an example, using coupled-wave theory, we can consider the effect of waves 1 and 2, with frequencies $\omega_1$ and $\omega_2$, respectively, on wave 3 at the sum frequency

$\omega_3 = \omega_1 + \omega_2$, according to

$$\nabla \cdot \left[ A_3 \left( \vec{e}_3 \times \vec{h}_3^* + \vec{e}_3^* \times \vec{h}_3 \right) \right] = i \omega_3 \left[ \vec{P}^{(2)} \cdot \vec{e}_3 + \vec{M}^{(2)} \cdot \vec{h}_3^* \right] e^{-i \vec{k}_3 \cdot \vec{r}}. \quad (2.20)$$

If we assume a purely electric nonlinearity, such that

$$\vec{P}^{(2)} = 2 \chi^{(2)}_{eee} : \vec{E}_1 \vec{E}_2 = 2 A_1 A_2 \chi^{(2)}_{eee} : \vec{e}_1 \vec{e}_2 e^{i(\vec{k}_1 + \vec{k}_2) \cdot \vec{r}}, \quad (2.21)$$

and neglect $\vec{M}^{(2)}$, the coupled-wave equation takes the familiar form [64]

$$\nabla A_3(\vec{r}) \cdot \vec{s}_3 = i \omega_3 \chi^{(2)}_{eee} : \vec{e}_1 \vec{e}_2 \cdot \vec{e}_3 A_1(\vec{r}) A_2(\vec{r}) e^{i(\vec{k}_1 + \vec{k}_2 - \vec{k}_3) \cdot \vec{r}}. \quad (2.22)$$

For self-consistency, these equations can be derived for all three interacting waves, and solved for various configurations [66].

Thus, the second-order susceptibilities are responsible for sum frequency generation, second-harmonic generation ($\omega_1 = \omega_2$), difference frequency generation ($\omega_1$ or $\omega_2 < 0$), optical parametric amplification (a particular case of difference frequency generation in which a weak signal wave 3 is provided at the input), and the Pockels effect ($\omega_1 = 0$, corresponding to a static electric field, and $\omega_2 = \omega_3$, such that the static field changes the propagation of wave 3). But in any case, the key features influencing energy transfer and wave manipulation, such as the polarization of the various interacting waves, and phase matching, are evident in Eq. (2.22).
2.3 Third-order response

Analogous to the second-order material responses of Eqs. (2.17) and (2.18), let us consider third-order polarization and magnetization of the forms

\[
\tilde{P}^{(3)}(t) = \sum_{pqr} \tilde{\chi}_{eeee}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{E}(\omega_r) \\
+ \tilde{\chi}_{eemm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{E}(\omega_p) \tilde{H}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{eemq}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{emeq}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{E}(\omega_p) \tilde{H}(\omega_q) \tilde{E}(\omega_r) \\
+ \tilde{\chi}_{emee}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{H}(\omega_p) \tilde{E}(\omega_q) \tilde{E}(\omega_r) \\
+ \tilde{\chi}_{emmm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{emme}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{H}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{memm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{E}(\omega_r) \\
+ \tilde{\chi}_{meme}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{E}(\omega_r) \\
+ \tilde{\chi}_{meem}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{meee}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) \tilde{E}(\omega_r) \] e^{-i\omega_s t}, 

(2.23)

and

\[
\mu_0 \tilde{M}^{(3)}(t) = \sum_{pqr} \tilde{\chi}_{mmmm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{mmee}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{H}(\omega_p) \tilde{E}(\omega_q) \tilde{E}(\omega_r) \\
+ \tilde{\chi}_{mmme}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{E}(\omega_r) \\
+ \tilde{\chi}_{mmem}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{H}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{meme}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{E}(\omega_r) \\
+ \tilde{\chi}_{meem}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{meee}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) : \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) \tilde{E}(\omega_r) \] e^{-i\omega_s t}, 

(2.24)
thus defining 16 third-order susceptibility tensors of rank 4. As before, a third-order response allows for four-wave mixing, subject to the energy conservation constraint

$$\omega_p + \omega_q + \omega_r = \omega_s.$$  \hfill (2.25)

Again, the dynamics can be visualized through the coupled wave equations. Considering now four waves, we find

$$\nabla \cdot \left[ A_4 \left( \vec{e}_4 \times \vec{h}_4^* + \vec{e}_4^* \times \vec{h}_4 \right) \right] = i\omega_4 \left[ \vec{P}^{(3)} \cdot \vec{e}_4 + \vec{M}^{(3)} \cdot \vec{h}_4^* \right] e^{-i\vec{k}_4 \cdot \vec{r}}. \hfill (2.26)$$

If we assume a purely electric nonlinearity, such that

$$\vec{P}^{(3)} = 6\tilde{\chi}^{(3)}_{eeee} \tilde{\vec{E}}_1 \tilde{\vec{E}}_2 \tilde{\vec{E}}_3 = 6A_1 A_2 A_3 \tilde{\chi}^{(3)}_{eeee} : \vec{e}_1 \vec{e}_2 \vec{e}_3 e^{i(\vec{k}_1 + \vec{k}_2 + \vec{k}_3 - \vec{k}_4) \cdot \vec{r}}, \hfill (2.27)$$

and neglect $$\vec{M}^{(3)},$$

$$\nabla A_4(\vec{r}) \cdot \hat{s}_4 = i3\omega_4 \tilde{\chi}^{(3)}_{eeee} : \vec{e}_1 \vec{e}_2 \vec{e}_3 \cdot \vec{e}_4 A_1(\vec{r}) A_2(\vec{r}) A_3(\vec{r}) e^{i(\vec{k}_1 + \vec{k}_2 + \vec{k}_3 - \vec{k}_4) \cdot \vec{r}}. \hfill (2.28)$$

Similar to second-order susceptibilities, the third-order susceptibilities are responsible for sum and difference frequency generation, as well as third-harmonic generation ($\omega_1 = \omega_2 = \omega_3$), although the total number of combinations becomes larger since now four waves can be mixed. In addition, the third-order susceptibilities allow for special degenerate cases known as self- and cross-phase modulation, in which a wave’s propagation can be influenced by itself or the presence of another wave, respectively.
Nonlinear susceptibility retrieval: transfer matrix method

As mentioned earlier, one of the most powerful metamaterial tools is the homogenization process, consisting of a method for retrieval of effective permittivity and permeability. The applicability and accuracy of the linear retrievals has been essential in metamaterial research. However, additional parameters are needed to describe the rich and varied dynamics that follow from the inclusion of nonlinear materials and components. NLMMs cannot hope to achieve the same success as linear metamaterials without an analogous process for the retrieval of nonlinear susceptibilities. The following chapter is reproduced with permission from Alec Rose, Stéphane Larouche, Da Huang, Ekaterina Poutrina, and David R. Smith, Physical Review E, 82, 036608, 2010. Copyright (2010) by the American Physical Society.

For the vast majority of metamaterials, a method of homogenization is necessary to describe the effective response of their engineered structure. This process of effective parameter retrieval is vital for the characterization of fabricated metamaterials, as well as for the design of potential metamaterials relevant to specific applications. In essence, the retrieval process consists of equating the unit cell of
the metamaterial to a congruently sized homogeneous material with an unknown set of parameters. In the linear case, the system is commonly solved by finding the equivalent permittivity and permeability that replicate the scattering parameters of the metamaterial [9, 10, 11]. This retrieval method has the added advantage of being easily applicable in practice by implementing transmission and reflection experiments on a metamaterial sample. In order to effectively describe and design nonlinear metamaterials, a similar process is needed.

To this end, Larouche and Smith have recently proposed the use of a modified transfer matrix method for the retrieval of effective nonlinear susceptibilities in metamaterials [67]. The transfer matrix method for nonlinear media is described by Bethune for the calculation of third harmonic generation (THG) [68]. Larouche and Smith adapt the transfer matrix approach to the particular case of second harmonic generation (SHG), demonstrating that, for a layered system with known properties, the output harmonics can be accurately and efficiently computed from the incident fields in the non-depleted pump approximation—that is, under the assumption that higher order harmonics do not perturb the field pattern of the fundamental mode. The transfer matrix method can then be reversed to perform the opposite operation, in which the output harmonics, determined from simulation or experiment, are used to retrieve an effective nonlinear susceptibility. The usefulness of this method has been recently demonstrated at microwave frequencies using a VLSRR medium [69], where excellent agreement between the measured and theoretically predicted properties of a VLSRR medium was found.

The characterization of harmonics such as SHG or THG for nonlinear metamaterials represents only a subset of the applicability of nonlinear retrieval methods to metamaterials. In this paper, we extend the transfer matrix method formalism to incorporate an arbitrary-order nonlinearity and arbitrary input waves. We then explicitly apply the method to three- and four-wave mixing processes, validating the
determined field distributions of the sum and difference modes via finite element time-domain simulations. The extended transfer matrix method is then reversed, and the generalized nonlinear retrieval operation is demonstrated in the analysis of a three-wave mixing transmission experiment performed on a VLSRR sample.

3.1 Theory

The configuration of numerous recent nonlinear metamaterial experimental and theoretical studies has been a one dimensional system composed of layered slabs, in which at least one layer possesses a significant nonlinear susceptibility. A reasonable goal, given such a system, is to determine the steady-state complex field amplitudes at all positions for a given set of incident waves. The presence of the nonlinearity precludes the use of most conventional methods of solution, including transfer matrices, as these methods rely on the linear properties of a system. However, in many such experiments the nonlinear processes are weak enough that their effect on the incident waves is negligible, leaving the fields at these frequencies nearly identical with those expected in a linear system. This is known as the non-depleted pump (NDP) approximation, and, in this limit, an exact method of evaluation can be formulated. Hence, the NDP approximation is assumed in the following analysis. In this section, we outline a general formalism for the modified transfer matrix method, apply it to three- and four-wave mixing, and present the resulting nonlinear retrieval equations. The following analysis assumes an electric nonlinearity, but can be carried through identically for a magnetic nonlinearity, replacing references to the electric field with the magnetizing field, the polarization with the magnetization, and swapping all occurrences of the permittivity and the permeability.
3.1.1 Overview of the transfer matrix method

In essence, the transfer matrix method for nonlinear processes involves three steps [68]. First, the incident waves are linearly propagated by the usual transfer matrix operations, giving the electric fields at the fundamental frequency(ies) everywhere in the system. Second, the fields are used to calculate the material’s nonlinear polarization, which in turn can be treated as a field-generating source term. Finally, the fields thus created are propagated via transfer matrices to both boundaries of the system, yielding the reflected and transmitted field amplitudes at the generated frequencies. The system under consideration in this paper is presented in Fig. 3.1.

For linear materials

To demonstrate the transfer matrix approach, we consider a uniform slab of thickness \( d \), permittivity \( \varepsilon_2(\omega) \), and permeability \( \mu_2(\omega) \), bounded on the left by a semi-infinite layer with permittivity \( \varepsilon_1(\omega) \) and permeability \( \mu_1(\omega) \), and on the right by another semi-infinite layer with permittivity \( \varepsilon_3(\omega) \) and permeability \( \mu_3(\omega) \), where \( \omega = 2\pi f \) is the angular frequency corresponding to frequency \( f \). For now, all three layers are assumed to be linear and isotropic, but are free to exhibit loss in the form of complex material parameters. The system is excited by a plane wave at normal incidence, traveling in the positive \( \hat{z} \) direction with angular frequency \( \omega_q \), and originating from a source at \( z = -\infty \). Without loss of generality, the polarization of the wave can be neglected. The one-dimensional wave equation in layer \( i \) has the solution

\[
\mathcal{E}_i(z, t) = \text{Re}\{E_i^+ \exp(-i\omega_q t) + E_i^- \exp(-i\omega_q t)\},
\]

where \( \mathcal{E}_i(z, t) \) is the real electric field and \( E_i^\pm = A_i^\pm \exp(\pm iK_i z) \) is the complex amplitude of the electric field traveling in the \( \pm \hat{z} \) directions. \( K_i \) is the wavevector given by

\[
K_i = n_i \frac{\omega_q}{c},
\]
The system considered in this paper is composed of a central slab possessing an arbitrary electric nonlinearity of order \( \alpha \), bounded by two semi-infinite linear media. Incident on this slab is an arbitrary number of normally-propagating plane waves. The boundary conditions at the fundamental frequencies (\( \omega_q \)) are presented on top (blue), while the boundary conditions at the nonlinear-generated frequency (\( \omega_{nl} \)) are shown below (red).

\[
n_i = \pm \sqrt{\varepsilon_i \mu_i} \sqrt{\varepsilon_0 \mu_0} \tag{3.3}
\]

is the index of refraction, \( c \) is the speed of light in vacuum, and \( \varepsilon_0 \) and \( \mu_0 \) are the permittivity and permeability of free-space, respectively. Note that the ± in Eq. (6.12) allows for the possibility of negative refractive materials in the case where both \( \varepsilon_i \) and \( \mu_i \) are negative [71]. Thus, the three layers and two interfaces form a boundary value problem that can be solved by finding relations between the fields in
the different regions. Writing the complex amplitudes in vector notation as

$$\vec{E}_i(z) = \begin{bmatrix} E_i^+(z) \\ E_i^-(z) \end{bmatrix},$$

(3.4)

the fields on either side of the interface between the layers $i$ and $j$ at position $z_{i\leftrightarrow j}$ are related by

$$\vec{E}_j(z_{i\leftrightarrow j}) = M_{i\rightarrow j} \vec{E}_i(z_{i\leftrightarrow j}).$$

(3.5)

In this last equation we have introduced the interface transfer matrix

$$M_{i\rightarrow j} = \frac{1}{t_{j\rightarrow i}} \begin{bmatrix} 1 & r_{j\rightarrow i} \\ r_{j\rightarrow i} & 1 \end{bmatrix},$$

(3.6)

with the amplitude transmission and reflection coefficients of the interface given by

$$t_{j\rightarrow i} = \frac{2y_j}{y_i + y_j} \quad \text{and} \quad r_{j\rightarrow i} = \frac{y_j - y_i}{y_i + y_j},$$

(3.7)

where $y_i = \sqrt{\varepsilon_i/\mu_i}$ is the admittance of medium $i$. Note that the interface transfer matrix, defined here in the positive direction, depends on the amplitude coefficients in the opposite direction. Similarly, the electric field at opposite ends of the same layer follow the relation

$$\vec{E}_j(z_{i\leftrightarrow j}) = \Phi_j \vec{E}_j(z_{j\leftrightarrow k})$$

(3.8)

where $i$, $j$, and $k$ refer to consecutive layers,

$$\Phi_j = \begin{bmatrix} \phi_j & 0 \\ 0 & \phi_j^{-1} \end{bmatrix},$$

(3.9)

is the propagation transfer matrix for layer $j$, $\phi_j = \exp(+iK_jd_j)$ is the phase shift and attenuation factor from positive $\hat{z}$ propagation across layer $j$, and $d_j$ is the layer thickness.
The transfer matrix of a composite system is found by multiplying its individual transfer matrices in the appropriate order. Returning to the three-media example, we see that the composite matrix is

\[
M = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} = M_{2 \rightarrow 3} \Phi_2 M_{1 \rightarrow 2}. \tag{3.10}
\]

Given that there is no negatively propagating field in the third layer, the fields incident on and exiting from the composite system are related by

\[
\begin{bmatrix} E_3^+ (z_{2\rightarrow 3}) \\ 0 \end{bmatrix} = M \begin{bmatrix} E_1^+ (z_{1\rightarrow 2}) \\ E_1^- (z_{1\rightarrow 2}) \end{bmatrix}, \tag{3.11}
\]

yielding amplitude reflection and transmission coefficients

\[
r = -\frac{M_{21}}{M_{22}} \quad \text{and} \quad t = \frac{\det[M]}{M_{22}}, \tag{3.12}
\]

respectively. Assuming that the incoming wave amplitude \( E_1^+ \) is known, the fields in layer 2 at its interface with layer 1 are given by

\[
\vec{E}_2(z_{1\rightarrow 2}) = M_{1 \rightarrow 2} \begin{bmatrix} 1 \\ r \end{bmatrix} E_1^+ (z_{1\rightarrow 2}). \tag{3.13}
\]

If a total of \( N \) waves at different frequencies are incident on the system, this procedure can be carried out independently for each frequency \( \omega_q \) corresponding to \( q = 1, 2, \ldots, N \), taking care to evaluate the transfer matrices appropriately.

For an arbitrary nonlinear polarization

As stated above, in the NDP limit, the presence of a nonlinearity in one or more layers is assumed to have a negligible effect on the incident waves, but will give rise to radiation at other frequencies. In this subsection, we derive the transmitted and reflected fields generated by an arbitrary higher-order polarization.
Let us consider an arbitrary higher-order polarization of order $\alpha$, generated by the medium in layer 2, at the angular frequency $\omega_{nl}$. The presence of interfaces and reflections in the system leads to polarizations with multiple wavevectors at a single frequency. Thus, we introduce the decomposition by wavevector $Q$,

$$P_{2}^{(\alpha)}(z, \omega_{nl}) = \sum_{Q} P_{2}^{(\alpha,Q)}(z, \omega_{nl}), \quad (3.14)$$

such that the summation is over all existing wavevectors of the polarization at $\omega_{nl}$ in layer 2. In examining an individual term of this summation, we note that while the phase distribution of the polarization and thus the electric field source is determined by the wavevector $Q$, the subsequent linear propagation of the fields generated by that source follow the appropriate wavevector $K_2 = n_2 \omega_{nl} c$. For clarity, we denote all terms involving the source distribution in layer 2 by the subscript $s$, while referring to the forward and backward propagating fields in the usual notation $\vec{E}_2(\omega_{nl})$. As shown in the appendix, the electric field source produced by a higher-order polarization is given by

$$E_s^{(Q)}(z, \omega_{nl}) = \frac{P_{2}^{(\alpha,Q)}(z, \omega_{nl})}{\varepsilon_s^{(Q)}(\omega_{nl}) - \varepsilon_2(\omega_{nl})}, \quad (3.15)$$

where

$$\varepsilon_s^{(Q)}(\omega_{nl}) = \frac{Q^2}{\omega_{nl}^2 \mu_2(\omega_{nl})}. \quad (3.16)$$

It is important to emphasize the dependence of this electric field source on the specific wavevector of the nonlinear polarization, as this equation is, in part, a statement of the phase-matching condition. The interface transfer matrix for the electric field source is evaluated as

$$M_{s+2}^{(Q)} = \frac{1}{t_{2-s}^{(Q)}} \begin{bmatrix} 1 & r_{2-s}^{(Q)} \\ r_{2-s}^{(Q)} & 1 \end{bmatrix} \quad (3.17).$$
with reflection and transmission coefficients

\[ r_{2\to s}^{(Q)} = \sqrt{\varepsilon_2 - \varepsilon_s^{(Q)}} \quad \text{and} \quad t_{2\to s}^{(Q)} = \frac{2\sqrt{\varepsilon_2}}{\sqrt{\varepsilon_s^{(Q)}} + \sqrt{\varepsilon_2}}. \]  

(3.18)

Likewise, the propagation transfer matrix is given by

\[ \Phi_s^{(Q)} = \begin{bmatrix} \exp(+iQd) & 0 \\ 0 & \exp(-iQd) \end{bmatrix}. \]  

(3.19)

Taking into account both the source and the propagating fields, the constraint of continuity across each interface leads to

\[ \vec{E}_1(\zeta_{1\leftrightarrow 2}, \omega_{nl}) = M_{2\to 1} \vec{E}_2(\zeta_{1\leftrightarrow 2}, \omega_{nl}) \]
\[ + \sum_Q M_s^{(Q)} \vec{E}_s^{(Q)}(\zeta_{1\leftrightarrow 2}, \omega_{nl}) \]  

(3.20)

and

\[ \vec{E}_3(\zeta_{2\leftrightarrow 3}, \omega_{nl}) = M_{2\to 3} \Phi_2 \vec{E}_2(\zeta_{1\leftrightarrow 2}, \omega_{nl}) \]
\[ + \sum_Q M_s^{(Q)} \Phi_s^{(Q)} \vec{E}_s^{(Q)}(\zeta_{1\leftrightarrow 2}, \omega_{nl}), \]  

(3.21)

where all transfer matrices must be evaluated at \( \omega_{nl} \), and we have used \( M_s^{(Q)} = M_{s\to 2}^{(Q)} M_{2\to 1} \) and \( M_s^{(Q)} = M_{s\to 2}^{(Q)} M_{2\to 3} \). Eliminating \( \vec{E}_2 \) from these equations and dropping the explicit \( z \) and \( \omega_{nl} \) dependence gives

\[ \vec{E}_3 = M_{2\to 3} \Phi_2 (M_{1\to 2} \vec{E}_1 + \vec{S}_2), \]

(3.22)

where we have introduced the source term vector,

\[ \vec{S}_2 = \sum_Q (\Phi_2^{-1} M_{s\to 2}^{(Q)} \Phi_s^{(Q)} - M_{s\to 2}^{(Q)}) \vec{E}_s^{(Q)}. \]

(3.23)

Since there are no incident fields at \( \omega_{nl} \), we can rewrite this as

\[ R \begin{bmatrix} E_3^+ \\ 0 \end{bmatrix} - L \begin{bmatrix} 0 \\ E_1^- \end{bmatrix} = \begin{bmatrix} R_{11} & -L_{12} \\ R_{21} & -L_{22} \end{bmatrix} \begin{bmatrix} E_3^+ \\ E_1^- \end{bmatrix} = \vec{S}_2, \]

(3.24)
\[ R = \Phi^{-1}_2 M^{-1}_2 \] and \( L = M_{1 \rightarrow 2} \) are the transfer matrices on the right and left of the source term, respectively.

Thus, the total output fields at \( \omega_{nl} \) resulting from a nonlinearity of order \( \alpha \) are given by the equation

\[
\begin{bmatrix}
E^+_3(\omega_{nl}) \\
E^-_1(\omega_{nl})
\end{bmatrix} = \begin{bmatrix} R_{11} & -L_{12} \\ R_{21} & -L_{22} \end{bmatrix}^{-1} \hat{S}_2(\omega_{nl}). \tag{3.25}
\]

It should be noted that in the limit of perfect phase matching, the magnitudes of the components of Eq. (3.23) inside and outside of the parentheses approach zero and infinity, respectively. However, their product has a finite value in this limit [68]. In a numerical realization of these equations, this singularity can be avoided by imposing a small mismatch in the relevant material parameters.

### 3.1.2 Three- and four-wave mixing

A host of nonlinear electromagnetic phenomena are understood in relation to a material’s second and third-order nonlinear susceptibilities and, thus, the material’s second and third-order polarizations [49]. The second-order interaction is carried out by the process of three-wave mixing of three waves satisfying the frequency-matching relation

\[
\omega_q + \omega_r = \omega_{q,r}, \tag{3.26}
\]

where the subscripts \( q \) and \( r \) denote the contributing fundamental frequencies, and \( \omega_{q,r} \) is the frequency of the generated wave. Note that the fundamental frequencies are free to be negative, as in the case of difference frequency generation (DFG), and degenerate, as in SHG. Similarly, the third-order process consists of four-wave mixing satisfying the relation

\[
\omega_q + \omega_r + \omega_l = \omega_{q,r,l}. \tag{3.27}
\]

All second- and third-order nonlinear phenomena can be described through these two processes. Furthermore, a given set of fundamental frequencies inside a second- or
third-order nonlinear material will generate radiation at all frequency combinations satisfying the respective matching relation. In this section, we explicitly derive the nonlinear polarizations involved in the three- and four-wave mixing processes.

Since the formalism of nonlinear polarization is invariably messy, with multiple existing conventions, we will begin by defining some notation and relations. We consider a real electric field $\mathcal{E}(z,t)$ and polarization $\mathcal{P}(z,t)$, both of which can be transformed to the frequency domain with angular frequency $\omega_q$ and complex amplitudes $E(z,\omega_q)$ and $P(z,\omega_q)$, respectively. Dropping the explicit $z$ dependence, we define $E(-\omega_q) \equiv E(\omega_q)^*$, $P(-\omega_q) \equiv P^*(\omega_q)$, $\omega_{-q} \equiv -\omega_q$, and $K_{-q} \equiv -K_q^*$, which leads to the relations

$$\mathcal{E}(t) = \mathcal{E}_0 + \sum_q \frac{1}{2} E(\omega_q) \exp(-i\omega_q t), \text{ and}$$

$$\mathcal{P}(t) = \mathcal{P}_0 + \sum_q \frac{1}{2} P(\omega_q) \exp(-i\omega_q t),$$

where $\mathcal{E}_0$ and $\mathcal{P}_0$ are the zero-frequency (DC) amplitudes for the electric field and polarization, respectively. Both summations are over all values of $q \in \{-N, \ldots, N\}$, excluding zero, where the magnitudes of $\mathcal{E}(t)$ and $\mathcal{P}(t)$ are split evenly between the positive and negative frequencies, resulting in the $\frac{1}{2}$ coefficient before each element. To make the DC terms compatible, the zero-frequency wave amplitudes in the following equations should be interpreted as $E(0) = 2\mathcal{E}_0$ and $P^{(\alpha)}(0) = 2\mathcal{P}_0$.

Starting from the formal definition of the second-order polarization and utilizing the permutation symmetry of the second-order nonlinear electric susceptibility $\chi^{(2)}_{e}(\omega_q,r;\omega_q,\omega_r)$, we have

$$P^{(2)}(\omega_{q,r}) = \frac{1}{2} \varepsilon_0 \frac{1}{(q,r)} \chi^{(2)}_{e}(\omega_q,r;\omega_q,\omega_r) E(\omega_q) E(\omega_r)$$

$$= \frac{D}{2} \varepsilon_0 \chi^{(2)}_{e}(\omega_q,r;\omega_q,\omega_r) E(\omega_q) E(\omega_r), \quad (3.28)$$
where the parentheses denote that the summation is over all possible permutations of the subscripts for a given value of \( \omega_{q,r} \), and \( D \) is the total number of permutations. With this last statement is the implicit assumption that only one nonlinear process contributes to a specific frequency of polarization. In the case of degeneracy, and in the NDP approximation, the contribution from each process can be calculated individually, and then summed, giving the total polarization at the degenerate frequency. Similarly, it can be shown that the third-order polarization term at \( \omega_{q,r,l} \) is given by

\[
P^{(3)}(\omega_{q,r,l}) = \frac{D}{4} \varepsilon_0 \chi^{(3)}(\omega_{q,r,l}; \omega_q, \omega_r, \omega_l) E(\omega_q)E(\omega_r)E(\omega_l).
\]

(3.29)

For convenience, the nonlinear susceptibilities will be referred to without explicit indication of their frequency dependence, but should not be assumed dispersionless.

The electric fields in each layer can be written in terms of both forward and backward propagating waves, which produce nonlinear polarizations that propagate with multiple wavevectors and corresponding amplitudes. For compatibility with the transfer matrix method, the polarizations must be separated by wavevector and represented in a vector form. Thus, we substitute into these last two expressions

\[
E(\omega_q) = A^+_q \exp(iK_qz) + A^-_q \exp(-iK_qz),
\]

where \( A^\pm_q \) is the complex amplitude of the wave propagating in the \( \pm \hat{z} \)-direction at frequency \( \omega_q \). Note that here we are making an exception and using the subscript of the wave amplitude and wavevector to denote frequency and not layer. This results in a second-order polarization given by

\[
\vec{P}^{(2)}(\omega_{q,r}) = \vec{P}^{(2,K_q+K_r)}(\omega_{q,r}) + \vec{P}^{(2,K_q-K_r)}(\omega_{q,r}),
\]

(3.30)
where, in vector notation,
\[
\vec{P}^{(2,K_q+K_r)}(\omega_{q,r}) = \\
\varepsilon_0 \chi_e^{(2)} \frac{D}{2} \left[ A_q^+ A_r^+ \exp[+i(K_q + K_r)z] - A_q^- A_r^- \exp[-i(K_q + K_r)z] \right], \tag{3.31}
\]
\[
\vec{P}^{(2,K_q-K_r)}(\omega_{q,r}) = \\
\varepsilon_0 \chi_e^{(2)} \frac{D}{2} \left[ A_q^+ A_r^- \exp[+i(K_q - K_r)z] - A_q^- A_r^+ \exp[-i(K_q - K_r)z] \right]. \tag{3.32}
\]

Similarly, the third-order polarization is found to be
\[
\vec{P}^{(3)}(\omega_{q,r,l}) = \vec{P}^{(3,K_q+K_r+K_l)}(\omega_{q,r,l}) + \vec{P}^{(3,-K_q+K_r+K_l)}(\omega_{q,r,l}) + \vec{P}^{(3,K_q-K_r+K_l)}(\omega_{q,r,l}) + \vec{P}^{(3,K_q+K_r-K_l)}(\omega_{q,r,l}), \tag{3.33}
\]
where
\[
\vec{P}^{(3,K_q+K_r+K_l)}(\omega_{q,r,l}) = \\
\varepsilon_0 \chi_e^{(3)} \frac{D}{4} \left[ A_q^+ A_r^+ A_l^+ \exp[+i(K_q + K_r + K_l)z] - A_q^- A_r^- A_l^- \exp[-i(K_q + K_r + K_l)z] \right], \tag{3.34}
\]
\[
\vec{P}^{(3,-K_q+K_r+K_l)}(\omega_{q,r,l}) = \\
\varepsilon_0 \chi_e^{(3)} \frac{D}{4} \left[ A_q^- A_r^+ A_l^+ \exp[+i(-K_q + K_r + K_l)z] - A_q^+ A_r^- A_l^- \exp[-i(-K_q + K_r + K_l)z] \right], \tag{3.35}
\]
\[
\vec{P}^{(3,K_q-K_r+K_l)}(\omega_{q,r,l}) = \\
\varepsilon_0 \chi_e^{(3)} \frac{D}{4} \left[ A_q^+ A_r^- A_l^+ \exp[+i(K_q - K_r + K_l)z] - A_q^- A_r^+ A_l^- \exp[-i(K_q - K_r + K_l)z] \right], \tag{3.36}
\]
\[
\vec{P}^{(3,K_q+K_r-K_l)}(\omega_{q,r,l}) = \\
\varepsilon_0 \chi_e^{(3)} \frac{D}{4} \left[ A_q^+ A_r^+ A_l^- \exp[+i(K_q + K_r - K_l)z] - A_q^- A_r^- A_l^+ \exp[-i(K_q + K_r - K_l)z] \right]. \tag{3.37}
\]

It should be noted that this matrix form is imprecise, in that the ordering of the terms in each individual matrix is not fixed but rather determined by the direction.
of energy propagation, such that, in each layer, the wave carrying energy in the $+\hat{z}$ ($-\hat{z}$) direction is always on top (bottom). This can be handled by checking the sign of the quantity

$$\beta^{(\alpha,Q)} = \frac{Q}{n(Q)},$$

where

$$n(Q) = \pm \sqrt{\frac{\varepsilon_s}{\mu_2} \frac{\mu_2}{\mu_0}}$$

is a pseudo-index of refraction describing the phase distribution of the nonlinear polarization. Correct propagation is ensured by reordering the vector elements such that $\beta^{(\alpha,Q)}$ is positive (negative) for the top (bottom) element. For example, if $\beta^{(3, K_q + K_r - K_l)}$ is negative, then the two terms in Eq. (3.37) must be flipped to ensure appropriate propagation. Mathematically, this can be accomplished by multiplying each vector term by the corrective matrix

$$\frac{1}{2} \begin{bmatrix} 1 + \text{sgn}(\beta^{(\alpha,Q)}) & 1 - \text{sgn}(\beta^{(\alpha,Q)}) \\ 1 - \text{sgn}(\beta^{(\alpha,Q)}) & 1 + \text{sgn}(\beta^{(\alpha,Q)}) \end{bmatrix},$$

(3.38)

where sgn($x$) is the signum function.

We are now able to fully solve the forward problem of calculating the output fields generated by an arbitrary set of waves incident on a slab with a second- or third-order nonlinearity, in the NDP limit. In the context of our three-layer system, the decomposed polarizations in Eqs. (3.30) and (3.33) are evaluated from the fields given by Eq. (3.13). These, in turn, are used in Eqs. (3.15)-(3.25) to find the reflected and transmitted field amplitudes at each of the generated frequencies.

### 3.1.3 Nonlinear parameter retrieval

As stated in the introduction, our goal is to formulate a method for the homogenization of nonlinear metamaterials, extracting an effective nonlinear susceptibility from
the results of simulation or experiment. However, the nonlinear susceptibility is only one of many factors determining the magnitude and phase of the generated fields. A homogenization method must normalize for these extraneous factors, isolating the value of the effective nonlinear susceptibility.

Let us return to our three-layer system, but under the assumption that the nonlinear susceptibility of the middle slab, \( \chi^{(\alpha)}_{nl}(\omega_{nl}; \ldots) \), is unknown, where \((\omega_{nl}; \ldots)\) represents the dependence of the nonlinear susceptibility on the generated and fundamental frequencies. On the other hand, we assume that the transmitted field at \( \omega_{nl} \) has been measured by experiment or simulation. For clarity, this field will be denoted by \( E^{+}_{3,exp}(\omega_{nl}) \), where the subscript exp has been included to signify that this is a measured quantity.

From the equations of the previous section, we see that the nonlinear polarizations are directly proportional to the appropriate nonlinear susceptibility. This implies that the field sources, source terms, and generated fields are all directly proportional to the nonlinear susceptibility, as well. As such, the ratio of any of these quantities to the nonlinear susceptibility is, in fact, independent of the nonlinear susceptibility, and can be readily determined from the system’s linear and dimensional properties. In particular, the ratio of the transmitted field to the nonlinear susceptibility, given by \( E^{+}_{3}(\omega_{nl})/\chi^{(\alpha)}_{nl}(\omega_{nl}; \ldots) \), can be calculated by another set of equations similar to those presented in sections 2.A and 2.B for the generated fields, but with the nonlinear susceptibility factored out in each case. Thus, we arrive at a procedure for determining the field-to-susceptibility ratio.

First, the linear and dimensional parameters of the system under consideration are determined by conventional methods. These are used in the equations of section 2.A.1 to find the fundamental fields in the nonlinear layer. Then, the ratios of the nonlinear polarization terms to the nonlinear susceptibility, \( \vec{P}^{(\alpha,Q)}_{2}/\chi^{(\alpha)}_{nl} \), are calculated simply by factoring the nonlinear susceptibility out of Eqs. (3.30) - (3.37).
Similarly, we modify Eq. (3.15) to

\[ \vec{E}_s^{(Q)}/\chi^{(\alpha)} = \vec{F}_2^{(\alpha,Q)}/\chi^{(\alpha)}_{s(Q)} - \vec{E}, \]  

(3.39)

and, in turn,

\[ \vec{S}_2^{(\alpha)} = \sum_Q (\Phi_2^{-1} M_{s+2}^{(Q)} \Phi_s^{(Q)} - M_{s+2}^{(Q)}) \vec{E}_s^{(Q)}/\chi^{(\alpha)}_{s(Q)}, \]  

(3.40)

where we have dropped the explicit frequency dependence for convenience. This, at last, is used to calculate the field-to-susceptibility ratios,

\[ \left[ \begin{array}{c} E_s^{+}/\chi^{(\alpha)}_{e
\end{array} 
\right] = \left[ \begin{array}{cc} R_{11} & -L_{12} \\ R_{21} & -L_{22} \end{array} \right]^{-1} \vec{S}_2^{(\alpha)}/\chi^{(\alpha)}_{e}. \]  

(3.41)

It is worth restating that these ratios are independent of the nonlinear susceptibility, but are otherwise calculated by the same procedure outlined at the end of section 2.B.

We are now in a position to determine the nonlinear susceptibility of our sample. For consistency between our experimental and analytical results, we must have

\[ E_{3,\text{exp}}^{+}(\omega_{nl}) = \chi^{(\alpha)}_{e}(\omega_{nl}; \ldots) E_3^{+}(\omega_{nl})/\chi^{(\alpha)}_{e}(\omega_{nl}; \ldots). \]  

(3.42)

Rearranging this statement, we arrive at our final retrieval equation,

\[ \chi^{(\alpha)}_{e}(\omega_{nl}; \ldots) = \frac{E_{3,\text{exp}}^{+}(\omega_{nl})}{E_3^{+}(\omega_{nl})/\chi^{(\alpha)}_{e}(\omega_{nl}; \ldots)}. \]  

(3.43)

The numerator of Eq. (3.43) is determined directly from a nonlinear transmission experiment or simulation performed on the system, while the denominator is analytically derived from the system’s linear and dimensional properties. Thus, Eqs. (3.39) - (3.43) constitute the generalized nonlinear susceptibility retrieval equations.

Numerically, the situation is even simpler, as a little thought reveals that computing the ratios of the various quantities to the nonlinear susceptibility is equivalent
to calculating those same quantities with the substitution $\chi_\epsilon^{(\alpha)} = \text{unity}$. This gives the alternative retrieval equation,

$$\chi_\epsilon^{(\alpha)}(\omega_{\text{nl}}; \ldots) = \frac{E_{3,\text{exp}}^+(\omega_{\text{nl}})}{E_3^+(\omega_{\text{nl}})|_{\chi_\epsilon^{(\alpha)} = 1}},$$  \hspace{1cm} (3.44)$$

where the denominator can be calculated from the forward nonlinear transfer matrix equations, but with the aforementioned substitution for the nonlinear susceptibility. In addition, it is clear that Eqs. (3.43) and (3.44) can be written in terms of the reflected amplitude $E_{1,\text{exp}}^-(\omega_{\text{nl}})$ and its corresponding field-to-susceptibility ratio, if, alternatively, a reflection experiment is implemented.

### 3.2 Numerical Validation

The validity of the previous equations can be confirmed through comparison with an independent method of calculation. To this end, we have implemented time-domain finite element simulations using the COMSOL 3.5a software package.

To test the second-order equations, we return to the three-layer system. We let $\varepsilon_1 = \varepsilon_3 = \varepsilon_0$ and $\mu_1 = \mu_3 = \mu_0$, so that the nonlinear slab is sandwiched by semi-infinite regions of vacuum. The nonlinear material is assigned a permittivity $\varepsilon_2 = 7\varepsilon_0$, permeability $\mu_2 = 3\mu_0$, and constant nonlinear susceptibility $\chi_\epsilon^{(2)} = 10^{-12}$ m/V. The thickness of this material is varied over multiple simulations from 1 mm to 10 mm. The input port generates a plane wave excitation according to $\mathcal{E}(t) = \mathcal{E}_1 \cos(\omega_1 t) + \mathcal{E}_2 \cos(\omega_2 t)$, using the values $\mathcal{E}_1 = 10 \text{ GV/m}$, $\mathcal{E}_2 = 7 \text{ GV/m}$, $\omega_1 = 2\pi \times 10$ GHz, and $\omega_2 = 2\pi \times 6$ GHz. In order to avoid the transient effects and achieve an approximate steady-state solution, the sources are turned on for 1 ns before data is collected. This time-domain data is then Fourier transformed to obtain its spectrum amplitudes and phases.

The resulting field magnitudes for sum frequency (SFG), DFG, and SHG are
Figure 3.2: (Reproduced with permission from Ref. [70]. Copyright (2010) by the American Physical Society.) Comparison of the amplitudes of transmitted (a) and reflected (b) waves generated by three-wave mixing as calculated by the transfer matrix approach (lines) and finite element simulations (circles).

compared in Fig. 3.2 for both approaches. The agreement between these two methods is excellent. Equally high agreement is also found between the computed phases (not shown).

The same procedure as above is implemented for a third-order nonlinear material, using a nonlinear susceptibility of $\chi^{(3)} = 10^{-22}$ m$^2$/V$^2$. The incident radiation takes the form of $E(t) = E_1 \cos(\omega_1 t) + E_2 \cos(\omega_2 t) + E_3 \cos(\omega_3 t)$, with $E_1 = 10$ GV/m, $E_2 = 7$ GV/m, $E_3 = 5$ GV/m, $\omega_1 = 2\pi \times 10$ GHz, $\omega_2 = 2\pi \times 6$ GHz, and $\omega_3 = 2\pi \times 9$ GHz.

The results for four different frequency combinations are displayed in Fig. 3.3, once again showing excellent agreement between the two approaches despite considerable sensitivity to the thickness of the nonlinear slab. The transfer matrix method for nonlinear media is thus shown to be highly accurate in the NDP limit, especially with respect to the complicated contributions from the multiple reflections occurring
Figure 3.3: (Reproduced with permission from Ref. [70]. Copyright (2010) by the American Physical Society.) Comparison of the amplitudes of transmitted (a) and reflected (b) waves generated by four-wave mixing as calculated by the transfer matrix approach (solid lines) and finite element simulations (circles).

at both the fundamental and the generated frequencies.

3.3 Application to Experiment

It is highly desirable for a retrieval method to be experimentally practicable. In this section, we demonstrate the applicability of the transfer matrix retrieval by analyzing wave mixing measurements taken on a fabricated VLSRR medium.

We consider the same VLSRR metamaterial sample used by Huang et al. to study the power-dependent resonance frequency shift proportional to the third-order magnetic nonlinear susceptibility [72]. The unit cell is composed of a singly-split copper ring on a 0.2 mm thick FR4 PCB substrate. The ring is 17 µm thick and 0.5 mm wide, with an inner radius of 4 mm. The ring’s gap is 1 mm across and loaded
with a Skyworks SMV1231 varactor [73]. The varactor’s capacitance is given by

\[ C(V_D) = C_0(1 - V_D/V_P)^M, \]  

(3.45)

where \( V_D \) is the bias voltage, \( C_0 \) is the zero bias capacitance, \( V_P = 1.5 \) V is the intrinsic potential, and \( M = 0.8 \) is the gradient coefficient.

A metamaterial slab is created by arranging multiple VLSRR cubic unit cells, 10 mm on a side, into a \( 3 \times 15 \times 1 \) periodic structure. The rings are all oriented in the same direction so that the incident magnetic field will be along the SRR axes, while the direction of propagation is parallel to the sample’s third dimension. This structure is placed in a transmission line optimized for TEM propagation below 2 GHz, and shown via numerical simulations in CST Microwave Studio to exhibit a near-uniform concentration of 49% of the incident power between the top and bottom plates [69]. The system is excited by Agilent N9310A and N5181A PSG vector signal generators operating at variable angular frequencies \( \omega_1 \) and \( \omega_2 \), respectively, each with an output power of 15 dBm. The harmonics created by the generators are eliminated by a Mini Circuits VLF-800+ filter. The transmission line and the connecting cables are calibrated with standard techniques. In accordance with these measurements, we find that the pump signal attenuates by 7.5 ± 0.5 dB before the sample, and the sum frequency wave attenuates by 1.3 ± 0.2 dB after the sample. The transmitted signals are measured using an Agilent E4404B PSA spectrum analyzer.

The linear response of the sample is measured and fitted using a Lorentz oscillator model, sufficiently described by permittivity

\[ \varepsilon(\omega) = 1.63\varepsilon_0, \]  

(3.46)

and permeability

\[ \mu(\omega) = \mu_0\left(1 + \frac{F\omega^2}{\omega_0^2 - \gamma\omega - \omega^2}\right), \]  

(3.47)
where $F = 0.142$ is the oscillator strength, $\omega_0 = 2\pi \times 813$ MHz is the angular resonance frequency, and $\gamma = 2\pi \times 36$ MHz is the damping coefficient.

The frequency of the first signal generator is swept from 540 MHz to 1000 MHz at intervals of approximately 2 MHz, while the second signal generator operates at a constant frequency of $f_2 = 780$ MHz. The sum frequency transmission data is shown in Fig. 3.4. The oscillations are a Fabry-Perot-like resonance induced by reflections of the backward generated sum frequency wave off of the VLF-800+ filter. These are removed via Fourier processing, resulting in the smoothed transmission spectrum shown against the raw data in Fig. 3.4.

![Figure 3.4](image)

**Figure 3.4:** (Reproduced with permission from Ref. [70]. Copyright (2010) by the American Physical Society.) Plot of the transmitted SFG magnetic field spectrum. The red (solid) line is the raw data from experiment, while the black (dashed) line is the corresponding Fourier processed signal used in the retrieval.

For compatibility with our method, we can approximate the experimental setup as a $d = 1$ cm slab of homogeneous material, bounded by semi-infinite regions of vacuum, with linear properties given by Eqs. (3.46) and (3.47), and an unknown nonlinear susceptibility $\chi_m^{(2)}(\omega_1, \omega_2, \omega_3)$. The magnitudes of the incident fields are
given by

\[ |H_1^+(\omega_1)| = |H_2^+(\omega_2)| = \sqrt{\frac{2I}{z_0S}}, \]  

(3.48)

where \( z_0 = 377\Omega \) is the impedance of vacuum, \( S = 18 \text{ cm}^2 \) is the cross-sectional area of the waveguide, and \( I \) is the input power of each signal generator corrected for the cable and waveguide losses. The nonlinearity in the VLSRR is magnetic in nature, originating from the relation between the inductive coupling of the copper ring and the nonlinear capacitance of the varactor-loaded gap. As stated earlier, the retrieval equations can be applied to a magnetic nonlinearity by replacing references to the electric field with the magnetizing field, the polarization with the magnetization, and swapping all occurrences of the permittivity and the permeability. Thus, we perform the nonlinear retrieval by evaluating the magnetic equivalent of Eq. (3.43), using the Fourier processed spectrum, corrected for cable losses, as an approximate measurement of \( H_{3,\text{exp}}^+(\omega_{1,2}) \). On the other hand, we calculate \( H_s^+(\omega_{1,2})/\chi_m^{(2)}(\omega_{1,2}; \omega_1, \omega_2) \) according to Eqs. (3.39)-(3.41), using the second-order polarizations given by Eqs. (3.30) - (3.32). Despite the anisotropy of the sample, the method is still valid because only a single term of the permittivity, permeability, and susceptibility tensors is probed significantly. The experimental constraint of detecting the magnitude and not the phase of the outgoing wave means that, likewise, only the magnitude of the nonlinear susceptibility is retrieved. In addition, the uncertainty in the incident power results in an error of \( \pm 15\% \) in the retrieved susceptibility.

For comparison, we refer to the analytical expression recently presented by Poutrina et al. [74]. In this paper, the authors implement a perturbative solution of the nonlinear oscillator model to describe the effective RLC circuit of the VLSRR medium. The resulting form of the nonlinear susceptibility is given in terms of the unit cell geometry and the varactor’s intrinsic properties. This model was shown previously to quantitatively predict the second-order nonlinear susceptibility involved
in SHG from this same VLSRR medium with high accuracy [69]. Poutrina et al.’s expression for the three-wave mixing nonlinear susceptibility is given by

$$\chi^{(2)}_{m}(\omega_1,\omega_2;\omega_1,\omega_2) = -i a \frac{\omega_0^4 \mu_0 F A \omega_1 \omega_2}{D(\omega_1) D(\omega_2) D(\omega_1,\omega_2)}, \tag{3.49}$$

where $A$ is the area of the ring, $a = -M/2V_p$ is the second-order coefficient in the perturbative expansion, $D(\omega) = \omega_0^2 - i\gamma\omega - \omega^2$ is the denominator of the Lorentz oscillator at angular frequency $\omega$, and $F$ is the oscillator strength extracted from the previous linear retrieval. The magnitudes of the nonlinear susceptibility obtained by experimental retrieval and by Eq. (7.15) are both displayed in Fig. 3.5, showing excellent agreement.

![Figure 3.5](image)

**Figure 3.5:** (Reproduced with permission from Ref. [70]. Copyright (2010) by the American Physical Society.) Comparison of the experimentally retrieved (black diamonds) and the theoretical (red line) second-order nonlinear susceptibility of the VLSRR medium.

### 3.4 Conclusion

We have demonstrated a generalized, transfer matrix-based nonlinear retrieval method that is exact in the limit of the NDP approximation. Furthermore, this method is
proven highly applicable to metamaterial characterization, requiring only a trans-
mission or reflection wave-mixing experiment to extract the effective nonlinear sus-
ceptibilities.

However, as with all metamaterial homogenization methods, the effective param-
eters are only valid when the wavelengths considered are much larger than the unit
cell of the metamaterial. This can be a stricter limit for nonlinear phenomena, as the
generated wavelengths may be several times smaller than those of the fundamental
waves, as is the case in SFG and harmonic generation.

Due to the NDP approximation, this method is only valid for nonlinear phenom-
ena in which the fundamental input waves are negligibly affected by the presence
of the nonlinearity. As such, phenomena like the electro-optic effect and hysteresis,
wherein the input wave is obviously and significantly altered, cannot be directly an-
alyzed with this method. On the other hand, it should be possible to retrieve any
nonlinear susceptibility whose generated frequency is not equal to one of its funda-
mentals by adjusting the input power to a level that satisfies the NDP approximation,
notwithstanding the availability of appropriate power sources and detectors. A quick
comparison of the magnitudes of the generated and fundamental waves imply that
this approximation is reasonable for the presented experiment. Ideally, the validity
of the retrieved nonlinear susceptibility can be rigorously confirmed by repeating
the experiment over a wide range of input intensities. The results from this series
of experiments should provide an NDP power threshold, below which the retrieved
parameter is intensity-independent and reliable.

In this retrieval, we assume that the second-order process is the only significant
contributor to the SFG signal. However, all even higher-order terms also contribute.
For high enough intensities of the fundamental waves, this retrieval method will re-
turn a second-order susceptibility that is intensity-dependent, violating the usual
power-series interpretation of susceptibility. This problem imposes a stricter con-
straint on the incident power than the NDP limit, but is also easily avoided by repeating the experiment for varying intensities of the fundamental waves.

In addition, we assumed an isotropic medium at the start of the analysis. However, careful control of the polarizations at the input and output allow this method to be used for anisotropic materials as long as only one term of the susceptibility tensor is being probed at a time. In this way, the entire tensor can be determined methodically, including the cross terms. It is often the case with metamaterials that only a small number of these terms are ultimately important. For non-normal incidence, on the other hand, a more complete formalism is necessary [75].

The original suspicion of nonlinear enhancement in metamaterials is confirmed by the remarkably large value of the nonlinear susceptibility retrieved from the VLSRR medium. Even when operated off resonance to avoid the large inherent losses, the nonlinear susceptibility is shown to be many orders of magnitude larger than that of naturally occurring materials. This opens the door for exciting applications, especially when considering the possibility of analogous metamaterials tuned to operate in the infrared and optical regimes.

3.5 Appendix: Derivation of the source fields

Here, we derive Eqs. (3.15) and (3.16). In the absence of free charge and current, and assuming a steady-state solution proportional to \( \exp(-i\omega t) \), Maxwell’s equations in layer \( i \) are

\[
\nabla \times \vec{E}_i = i\omega \vec{B}_i, \quad (3.50)
\]

\[
\nabla \times \vec{H}_i = -i\omega \vec{D}_i, \quad (3.51)
\]

\[
\nabla \cdot \vec{D}_i = 0, \quad (3.52)
\]

\[
\nabla \cdot \vec{B}_i = 0, \quad (3.53)
\]
while the material equations are

\[
\vec{D}_i = \varepsilon_i(\omega)\vec{E}_i + \vec{P}_i^{(\alpha)}, \tag{3.54}
\]

\[
\vec{B}_i = \mu_i(\omega)\vec{H}_i, \tag{3.55}
\]

where \(E, D, B,\) and \(H\) are the complex electric, displacement, magnetic, and magnetizing fields, respectively, and \(\vec{P}_i^{(\alpha)}\) is a polarization of order \(\alpha > 1\). We assume that the material parameters \(\varepsilon_i\) and \(\mu_i\) are time and space invariant so that they can be factored out of the curl and divergence operators.

Inserting Eq. (3.55) in Eq. (5.34) gives

\[
\nabla \times \vec{E}_i = i\omega\mu_i(\omega)\vec{H}_i. \tag{3.56}
\]

Taking the curl of this equation and inserting Eqs. (5.33) and (3.54) results in

\[
\nabla \times \nabla \times \vec{E}_i = \omega^2\varepsilon_i(\omega)\mu_i(\omega)\vec{E}_i + \omega^2\mu_i(\omega)\vec{P}_i^{(\alpha)}. \tag{3.57}
\]

Using the identity

\[
\nabla \times \nabla \times \vec{E}_i = \nabla(\nabla \cdot \vec{E}_i) - \nabla^2 \vec{E}_i \tag{3.58}
\]

and the fact that \(\nabla \cdot \vec{E}_i = 0\), this can be rearranged to yield a wave equation according to

\[
\left[\nabla^2 + \omega^2\varepsilon_i(\omega)\mu_i(\omega)\right]\vec{E}_i = -\omega^2\mu_i(\omega)\vec{P}_i^{(\alpha)}. \tag{3.59}
\]

Let us consider a polarization of the form \(\vec{P}_i^{(\alpha)} = |\vec{P}_i^{(\alpha)}|\hat{p}\exp[i(Qz - \omega t)]\) and, similarly, an electric field \(\vec{E}_i = |\vec{E}_i|\hat{e}\exp[i(Qz - \omega t)]\). Substituting these into (7.15) gives

\[
\left[\nabla^2 + \omega^2\varepsilon_i(\omega)\mu_i(\omega)\right]\vec{E}_i = -\omega^2\mu_i(\omega)\vec{P}_i^{(\alpha)}, \tag{3.60}
\]

or equivalently

\[
\vec{E}_i = \frac{\vec{P}_i^{(\alpha)}}{\varepsilon_s - \varepsilon_i(\omega)}, \tag{3.61}
\]
where we have defined

\[ \varepsilon_s = \frac{Q^2}{\omega^2 \mu_s(\omega)}. \]  \hspace{1cm} (3.62)

Note that, due to the dependence of \( \varepsilon_s \) on \( Q \), polarizations that propagate with multiple wavevectors at a single frequency, within the same layer, must be separated and handled individually.
Extrapolating from the recent research in linear metamaterials, it is likely that a wealth of phenomena not previously possible will follow from tailoring the eight nonlinear susceptibilities in Eqs. (2.17) and (2.18), as well as their higher-order counterparts. However, as one quickly learns during the process of designing a metamaterial, the parameter space is virtually boundless, often probing effects and phenomena that are conventionally neglected. Design and application of metamaterials in nonlinear optics requires an intuitive understanding of the macroscopic properties and their origins.

Our purpose in this chapter is to derive a homogeneous description of three-wave mixing in a NLMM with a periodic but otherwise arbitrary microstructure of electrically polarizable materials. In other words, we seek the set of effective nonlinear properties that can exactly reproduce the metamaterial’s macroscopic nonlinear behavior. As in other metamaterial applications, we expect the sub-wavelength structure to give rise to macroscopic behavior of a wholly different nature than the
constituent materials. The final set of effective nonlinear properties not only simplifies the subsequent analysis of the NLMM, but can provide invaluable intuition into their design. The following chapter is reprinted with permission from Alec Rose, Stéphane Larouche, Ekaterina Poutrina, and David R. Smith, Physical Review A, 86, 033816, 2012. Copyright (2012) by the American Physical Society.

For a lossless medium composed of a cubic lattice of MM inclusions formed from electrically-polarizable materials, we make use of a coupled-mode theory formalism to derive simple, quasi-analytic expressions for the eight effective magnetoelectric nonlinearities. For example, the effective second-order susceptibility relating an electric polarization at frequency $\omega_3$ to the product of an electric field at $\omega_1$ and a magnetic field at $\omega_2$ is shown to be

\[ \chi_{eem}^{(2)}(\omega_3; \omega_1, \omega_2) = \frac{i}{a^3} \iiint \left[ \bar{\chi}_{loc}^{(2)}(\vec{r}) : \vec{\theta}_1(\vec{r}) \vec{\phi}_2(\vec{r}) \cdot \vec{\theta}_3(\vec{r}) \right] dV, \quad (4.1) \]

where $\bar{\chi}_{loc}^{(2)}(\vec{r})$ is the MM’s local electric nonlinear susceptibility tensor and $a$ is the lattice constant. $\vec{\theta}_n(\vec{r})$ and $\vec{\phi}_n(\vec{r})$ are, roughly speaking, the microscopic electric fields produced in response to a macroscopic electric or magnetic field, respectively, at frequency $\omega_n$, and can be found analytically and/or numerically from a Bloch analysis of a particular MM geometry. These expressions for the second-order susceptibilities are verified against existing nonlinear parameter retrieval methods [69, 70], finding excellent agreement. We extend the same procedure to the case of four-wave mixing in MMs, finding analogous relations for the sixteen effective third-order magnetoelectric nonlinearities. Further study of these expressions gives insight into the fundamental nature and construction of the various magnetoelectric nonlinearities. In particular, the formalism is demonstrated in the analysis of two prototypical nonlinear magnetoelectric MMs, predicting the dominant nonlinearities and wave-mixing processes supported in each, in agreement with recent experiments [76]. Finally, we give some consideration to possible applications of nonlinear magnetoelectric coupling, using
the examples of nonlinear interference and electro-optic-like effects.

4.1 Derivation of the effective nonlinear susceptibilities

Our purpose in this section is to derive a homogeneous description of three-wave mixing in a nonlinear MM with a periodic microstructure of electrically polarizable materials. In other words, we seek the set of effective nonlinear properties that can exactly reproduce the MM’s macroscopic nonlinear behavior. Conceptually, we correlate the nonlinear scattering observed or computed for a MM to what would be obtained from a homogeneous medium with defined linear and nonlinear constitutive parameters. This approach to MM effective medium theory has been used with great success to characterize linear MMs [9, 11, 12, 77, 78, 79, 80]; for example, a popular MM retrieval procedure involves computing the scattered (reflected and transmitted) waves from a thin slab of MM, and inverting the Fresnel formulas to ascribe homogenized values of the electric permittivity and magnetic permeability to the otherwise inhomogeneous medium [11]. The approach works extremely well to describe MMs formed with inclusions of nearly any shape or material composition, under a restricted set of assumptions. Alternatively, one can appeal to the basic nature of effective medium theory and apply averages over the computed microscopic fields associated with a given repeated MM cell to arrive at the homogenized, macroscopic fields. From these macroscopic fields, the effective constitutive parameters can be derived. Both methods have been shown to be in agreement with each other and with conventional effective medium approaches [12]. Regardless of the method, the final set of effective properties not only simplifies the subsequent analysis of MMs, but provides invaluable intuition into their design.

While a nonlinear medium can be exceedingly complex, coupling potentially an infinite set of harmonics or mix components with varying polarization and propagation directions, it is typically the case that the nonlinear response—even for most
MMs—is relatively small compared with the linear response. Thus, the nonlinearity can be treated as a perturbation, coupling together a restricted number of fundamental and harmonic or mix waves. Under this assumption of a perturbative nonlinear response, only a small subset of scattered waves need to be considered, making the problem far more tractable. For a homogeneous nonlinear medium under continuous wave excitation, coupled-wave theory [62, 63, 64] yields relatively straightforward expressions for the spatially varying wave amplitudes in terms of the underlying parameters of the medium. When applied in integral form, coupled-mode theory can provide similar expressions for an inhomogeneous medium in terms of integrals over the local variations. In this way, coupled-mode theory offers an approach—in the same spirit as field averaging—for the identification of effective nonlinear susceptibility parameters in a MM comprising periodically positioned inclusions of arbitrary shape and composition.

If we now replace the continuous nonlinear medium with a MM, we expect to obtain an expression similar to the above, with coupling proportional to an effective or averaged nonlinear susceptibility, rather than the intrinsic susceptibility. In fact, given the various responses available in MM inclusions, Eq. (2.16) will in general include both a magnetic and an electric response, in addition to magneto-electric terms. These other terms are usually not significant in conventional materials, but can be dominant in structured MMs. Continuing with the homogeneous perspective, the above coupled-wave analysis can be straightforwardly extended to consider the full contributions from Eqs. (2.17) and (2.18), yielding

\[
\nabla A_3(\vec{r}) \cdot \hat{s}_3 = i \Gamma_{3,1,2} A_1(\vec{r}) A_2(\vec{r}) e^{i(\vec{k}_1 + \vec{k}_2 - \vec{k}_3) \cdot \vec{r}}.
\]  

with coupling coefficient

\[
\Gamma_{3,1,2} = \omega_3 \left[ \tilde{\chi}_{\text{eee}}^{(2)} : \vec{e}_1 \vec{e}_2 \cdot \vec{e}_3^* + \tilde{\chi}_{\text{eme}}^{(2)} : \vec{h}_1 \vec{e}_2 \cdot \vec{e}_3 + \tilde{\chi}_{\text{emem}}^{(2)} : \vec{h}_1 \vec{h}_2 \cdot \vec{e}_3^* \\
+ \tilde{\chi}_{\text{mee}}^{(2)} : \vec{e}_1 \vec{e}_2 \cdot \vec{h}_3^* + \tilde{\chi}_{\text{mem}}^{(2)} : \vec{h}_1 \vec{e}_2 \cdot \vec{h}_3 + \tilde{\chi}_{\text{mmem}}^{(2)} : \vec{h}_1 \vec{h}_2 \cdot \vec{h}_3^* \right].
\]

(4.3)

4.1.1 Coupled-mode equations for wave mixing processes in a periodic medium

We consider a MM as being formed from an inclusion that is infinitely repeated in three dimensions. For such a periodic medium, the wave equation admits solutions in the form of Bloch modes indexed by the Bloch wavevector \( \vec{k} \). When the wavelength is much larger than the inclusion size and lattice constant, it becomes useful to average over the local fields and parameters associated with the inclusions, arriving at a set of macroscopic fields that are defined only at the edges and faces of the unit cells. These fields thus naturally satisfy a set of finite-difference equations, which, in the limit of weak nonlinearity, can be extended using coupled-mode theory to describe the fields resulting from wave mixing processes, such as second-harmonic generation (SHG), sum-frequency generation (SFG), and difference-frequency generation (DFG).

We can model our MM as an infinite medium described by a periodic relative permittivity, \( \epsilon(\vec{r}) \), and second-order electric nonlinearity, \( \chi_{\text{loc}}^{(2)}(\vec{r}) \), with implicit frequency dependencies. For simplicity, we will assume the unit cell is cubic with lattice constant \( a \) and primitive lattice vectors oriented along the three Cartesian axes, such that \( \epsilon(\vec{r}) = \epsilon(\vec{r} + \vec{R}) \) for lattice vector \( \vec{R} = (n_1 \hat{x} + n_2 \hat{y} + n_3 \hat{z})a \), where \( n_1, n_2, \) and \( n_3 \) are integers. Thus, the electric and magnetic fields corresponding to a particular Bloch mode \( \mu \) can be written as

\[
\vec{E}_\mu(\vec{r}) = A_\mu \vec{e}_\mu(\vec{r}) \exp(i\vec{k}_\mu \cdot \vec{r}),
\]

\[
\vec{H}_\mu(\vec{r}) = A_\mu \vec{h}_\mu(\vec{r}) \exp(i\vec{k}_\mu \cdot \vec{r}),
\]

(4.4)
where $A_\mu$ is the mode amplitude, $k_\mu$ is the Bloch wavevector, and $\vec{e}_\mu(\vec{r})$ and $\vec{h}_\mu(\vec{r})$ are periodic electric and magnetic Bloch functions, respectively, with the same periodicity as the MM lattice. The Bloch solutions form an orthogonal set of functions [81], allowing us to treat the Bloch modes in analogy to guided modes in coupled-mode theory [63, 64]. Moreover, we assume that only the fundamental or lowest Bloch modes play a significant role in wave propagation and scattering, as is usual for MMs.

At this point, it is appropriate to apply several constraints to the total fields in the presence of the perturbation. Since our goal is characterization of the effective nonlinear tensors, it is desirable to probe the elements of these tensors independently. Thus, at any time, we will consider only the subset of modes necessary to probe a single tensor element of each susceptibility, that is, just three modes with specified frequencies, polarizations, and propagation directions. This is very similar to what is done in linear retrieval methods [12], and is often enforced in simulations by appropriate boundary conditions. Thus, we derive the rate equations for a particular Bloch mode with frequency $\omega_3$, driven by Bloch modes at $\omega_1$ and $\omega_2$, such that $\omega_1 + \omega_2 = \omega_3$. Finally, we assume a sufficiently weak nonlinearity so that the mode amplitudes are slowly varying over a unit cell, allowing us to expand the fields within a unit cell in terms of the Bloch modes of the periodic, linear medium.

As before, we start by considering propagating modes at three distinct frequencies, whose coupling in the presence of a weak perturbation can be described by Eq. (2.12). Using the relations in (4.4), this gives

$$\nabla \cdot \left[ A_\mu \left( \vec{e}_3(\vec{r}) \times \vec{h}_3(\vec{r})^* + \vec{e}_3(\vec{r})^* \times \vec{h}_3(\vec{r}) \right) \right] =$$

$$i\omega_3 \left[ \vec{P}^{(2)}(\vec{r}) \cdot \vec{e}_3(\vec{r})^* + \vec{M}^{(2)}(\vec{r}) \cdot \vec{h}_3(\vec{r})^* \right] e^{-i\vec{k}_3 \cdot \vec{r}}. \quad (4.5)$$

Since we are considering MMs composed of purely electrically polarizable materials,
\( \vec{M}^{(2)}(\vec{r}) \) can be neglected, while the second-order polarization is given by

\[
\vec{P}^{(2)}(\vec{r}) = 2A_1 A_2 \tilde{\chi}^{(2)}_{loc}(\vec{r}) : \vec{e}_1(\vec{r})\vec{e}_2(\vec{r})e^{i(\vec{k}_1 + \vec{k}_2) \cdot \vec{r}}.
\]

(4.6)

However, a similar procedure can be employed for MMs composed of intrinsically magnetic materials.

Due to the inhomogeneous nature of the MM, the Bloch modes may contain rapidly varying fields that are generally unimportant in terms of predicting wave scattering behavior. It is thus convenient to average these rapidly varying field components over a unit cell, and instead follow the behavior of slowly varying (or macroscopic) fields at a discrete number of points that form a lattice with dimension \( a \). So long as \( a << \lambda \), the discreteness of the lattice is not of significance, though effects due to spatial dispersion may enter, especially near material resonances (see Section 4.4).

The integral formulation of coupled-mode theory lends itself naturally to this type of averaging. Moreover, for the Bloch modes defined in (4.4), it is natural to consider the mode amplitudes \( A_\mu \) as slowly varying envelopes in the presence of the nonlinear perturbation, while the rapid variations in field induced by local inhomogeneity are completely contained within the Bloch functions \( \vec{e}_\mu(\vec{r}) \) and \( \vec{h}_\mu(\vec{r}) \). Thus, we switch to the integral form of Eq. (2.12) and allow the mode amplitudes to vary explicitly with the spatial coordinates \( \vec{r} \), yielding

\[
\iint_{V_0} \nabla \cdot \left[ A_3(\vec{r}) \left( \vec{e}_3(\vec{r}) \times \vec{h}_3(\vec{r})^* + \vec{e}_3(\vec{r})^* \times \vec{h}_3(\vec{r}) \right) \right] dV = 0
\]

(4.7)

\[
2i\omega_3 \iint_{V_0} \left[ A_1(\vec{r}) A_2(\vec{r}) \tilde{\chi}^{(2)}_{loc}(\vec{r}) : \vec{e}_1(\vec{r})\vec{e}_2(\vec{r}) \cdot \vec{e}_3(\vec{r})^* \right] e^{i(\vec{k}_1 + \vec{k}_2 - \vec{k}_3) \cdot \vec{r}} dV,
\]

(4.8)

where the volume \( V_0 \) is taken to be a single unit cell, centered about the origin, 0.
We can distribute the divergence operator on the left-hand side, yielding

$$\int \int \int _{V_0} \nabla \cdot \left[ A_3(\vec{r}) \left( \vec{e}_3(\vec{r}) \times \vec{h}_3(\vec{r})^* + \vec{e}_3(\vec{r})^* \times \vec{h}_3(\vec{r}) \right) \right] dV =$$

$$\int \int \int _{V_0} \nabla A_3(\vec{r}) \cdot \left[ \left( \vec{e}_3(\vec{r}) \times \vec{h}_3(\vec{r})^* + \vec{e}_3(\vec{r})^* \times \vec{h}_3(\vec{r}) \right) \right] dV$$

$$+ \int \int \int _{V_0} A_3(\vec{r}) \nabla \cdot \left[ \left( \vec{e}_3(\vec{r}) \times \vec{h}_3(\vec{r})^* + \vec{e}_3(\vec{r})^* \times \vec{h}_3(\vec{r}) \right) \right] dV. \quad (4.9)$$

The integrand of the second term on the left-hand side vanishes identically, since it is proportional to the divergence of the Poynting vector of an unperturbed mode, leaving only the term proportional to $\nabla A_3(\vec{r})$. Invoking the slowly varying amplitude approximation, we can expand $\nabla A_3(\vec{r})$ about the origin in a Taylor series. Keeping only the lowest order term, we thus replace (4.8) with the approximate equation

$$\nabla A_3(0) \cdot \int \int \int _{V_0} \left[ \left( \vec{e}_3(\vec{r}) \times \vec{h}_3(\vec{r})^* + \vec{e}_3(\vec{r})^* \times \vec{h}_3(\vec{r}) \right) \right] dV \approx$$

$$2i\omega_3 \int \int \int _{V_0} \left[ A_1(\vec{r})A_2(\vec{r}) \chi^{(2)}_{loc}(\vec{r}) : \vec{e}_1(\vec{r})\vec{e}_2(\vec{r}) \cdot \vec{e}_3(\vec{r})^* \right] e^{i(\vec{k}_1+\vec{k}_2-\vec{k}_3) \cdot \vec{r}} dV. \quad (4.10)$$

Written this way, the integral on the left-hand side resembles the volume averaged Poynting vector for the unperturbed mode. Consistent with the homogeneous coupled-wave formalism, we introduce the normalization condition

$$\frac{1}{2a^3} \int \int \int _{V_0} \left[ \left( \vec{e}_\mu(\vec{r}) \times \vec{h}_\mu(\vec{r})^* + \vec{e}_\mu(\vec{r})^* \times \vec{h}_\mu(\vec{r}) \right) \right] dV = \hat{s}_\mu, \quad (4.11)$$

such that $\hat{s}_\mu$ represents the unit-normal in the direction of the averaged Poynting vector for the unperturbed mode $\mu$.

In order to reduce the right-hand side of Eq. (4.10), we similarly expand the fundamental mode amplitudes in a Taylor series, and again, invoking the slowly varying amplitude approximation, keep only the lowest order terms. Thus, we arrive at the following relation,

$$\nabla A_3(0) \cdot \hat{s}_3 = i\Gamma_{3,1,2} A_1(0) A_2(0), \quad (4.12)$$
with coupling coefficients

$$\Gamma_{3,1,2} = \frac{\omega_3}{a^3} \int \int \int_{V_0} \left( \chi^{(2)}_{\text{loc}}(\vec{r}) : \vec{e}_1(\vec{r}) \vec{e}_2(\vec{r}) \cdot \vec{e}_3(\vec{r}) e^{i(\vec{k}_1 + \vec{k}_2 - \vec{k}_3) \cdot \vec{r}} \right) dV. \quad (4.13)$$

We can then describe the coupling at any unit cell in the infinite lattice by translating Eq. (4.12) by lattice vector $\vec{R}$, yielding

$$\nabla A_3(\vec{R}) \cdot \hat{s}_3 = i\Gamma_{3,1,2} A_1(\vec{R}) A_2(\vec{R}) e^{i(\vec{k}_1 + \vec{k}_2 - \vec{k}_3) \cdot \vec{R}}. \quad (4.14)$$

Due to the periodicity of the Bloch functions and local material properties, the coupling coefficient $\Gamma_{3,1,2}$ is invariant to the unit cell at which it is defined, and effectively replaces the homogeneous nonlinear susceptibility of the previous subsection. In words, Eq. (4.15) gives an approximate relation for the rate of change of wave 3 in the direction of energy flow, proportional to the product of the fundamental wave amplitudes, the momenta mismatch, and an averaged coupling coefficient, on a discrete lattice that is defined by the MM's own structural periodicity.

The form of Eq. (4.14) is easily converted to a finite-difference system of equations by replacing the gradient with an appropriate finite-difference approximation. Alternatively, in the limit that $a \to 0$, we can take $\vec{R} \to \vec{r}$ and thus Eq. (4.14) approaches the continuous form,

$$\nabla A_3(\vec{r}) \cdot \hat{s}_3 = i\Gamma_{3,1,2} A_1(\vec{r}) A_2(\vec{r}) e^{i(\vec{k}_1 + \vec{k}_2 - \vec{k}_3) \cdot \vec{r}}, \quad (4.15)$$

as expected. It is clear that, from such a perspective, the detailed MM structure can be largely ignored once $\Gamma_{3,1,2}$ is obtained. Thus, the coupled-mode equations for a nonlinear MM, within the limits discussed above, are largely indistinguishable from the coupled-wave equations for a homogeneous nonlinear medium.

### 4.1.2 The effective second-order susceptibilities

In this subsection, we combine the results of the previous two subsections to arrive at expressions for the eight constitutive second-order susceptibilities describing the
nonlinear MM as a homogeneous medium. As is the usual case for homogenization of MMs, we require that the behavior of a single unit cell be perfectly replicated by an equivalent slab of homogeneous material. To simplify the analysis, we will use the continuous forms of the nonlinear coupling in both cases, thus implying the limit \( a \to 0 \) on the resulting equations. The more general form will be handled in Section 4.4. Moreover, we will consider the special case where the three Bloch modes propagate along the \( z \)-axis, with macroscopic electric fields polarized along the \( x \)-axis, and macroscopic magnetic fields polarized along the \( y \)-axis, so that, from the homogeneous perspective, the equations become scalar.

From inspection of the terms in Eqs. (4.2) and (4.15), homogenization requires two steps. First, we must establish equivalence in the linear wave propagation between the homogeneous and MM systems, consisting of the particular wavevectors and associated fields. Thus, we invoke standard eigenfrequency analyses to establish the wavevectors and Bloch functions in the periodic medium. Consistent with Smith and Pendry’s field-averaging method [12], the macroscopic electric and magnetic fields of our homogeneous system, then, are given by line integrals along the borders of the unit cell. This gives us the following relation between macroscopic and local electric fields,

\[
\tilde{e}_\mu = \frac{1}{a} \int_{-\frac{a}{2}}^{a/2} \left[ \vec{e}_\mu(x, \pm\frac{a}{2}, \pm\frac{a}{2}) \cdot \hat{x} \right] dx,
\]

where the tilde is used to denote a macroscopic quantity. The macroscopic magnetic field is likewise defined by

\[
\tilde{h}_\mu = \frac{1}{a} \int_{-\frac{a}{2}}^{a/2} \left[ \vec{h}_\mu(\pm\frac{a}{2}, y, \pm\frac{a}{2}) \cdot \hat{y} \right] dy.
\]
From here, we can define the wave impedance for mode $\mu$ as

$$Z_\mu = \frac{\hat{e}_\mu}{\hat{h}_\mu}. \quad (4.18)$$

Second, we must establish equivalence in the nonlinear behavior between the MM and homogeneous mediums. In the limit that $\alpha \to 0$, the nonlinear behavior is completely embodied by the coupling coefficients given in (4.3) and (8.5). Thus, substituting the macroscopic fields defined above into (4.3), we equate (4.3) and (8.5) and cancel like-terms to find

$$\frac{1}{a^3} \int \int \int_{V_0} \left( \chi_{loc}^{(2)}(\vec{r}) : \vec{e}_1(\vec{r}) \vec{e}_2(\vec{r}) \cdot \vec{e}_3^*(\vec{r}) e^{i(k_1 + k_2 + k_3)z} \right) dV =$$

$$\left[ \chi_{eee}^{(2)} \hat{e}_1 \hat{e}_2 \hat{e}_3^* + \chi_{eme}^{(2)} \hat{h}_1 \hat{e}_2 \hat{e}_3^* + \chi_{eem}^{(2)} \hat{e}_1 \hat{h}_2 \hat{e}_3^* + \chi_{emm}^{(2)} \hat{h}_1 \hat{h}_2 \hat{e}_3^* 
$$

$$+ \chi_{mee}^{(2)} \hat{e}_1 \hat{e}_2 \hat{h}_3^* + \chi_{mme}^{(2)} \hat{h}_1 \hat{e}_2 \hat{h}_3^* + \chi_{mem}^{(2)} \hat{e}_1 \hat{h}_2 \hat{h}_3^* + \chi_{mmm}^{(2)} \hat{h}_1 \hat{h}_2 \hat{h}_3^* \right]. \quad (4.19)$$

However, this single equation is not enough to solve for the eight as-yet-undetermined second-order susceptibilities. To introduce additional equations while still probing the same effective tensor elements, we note that all the forward propagating modes considered up to now must have a conjugate mode that propagates in the opposite direction. The above expressions, moreover, are easily extended to allow for modes propagating in either the positive or negative $z$ directions. Enforcing equality for each combination of modes independently, eight in total, we obtain a system of eight equations that can be written in compact form as

$$\frac{1}{a^3} \int \int \int_{V_0} \left( \chi_{loc}^{(2)}(\vec{r}) : \vec{e}_\rho(\vec{r}) \vec{e}_\psi(\vec{r}) \cdot \vec{e}_\nu^*(\vec{r}) e^{i(k_\rho + k_\psi - k_\nu)z} \right) dV =$$

$$\left[ \chi_{ccc}^{(2)} \hat{e}_\rho \hat{e}_\psi \hat{e}_\nu^* + \chi_{cem}^{(2)} \hat{h}_\rho \hat{e}_\psi \hat{e}_\nu^* + \chi_{ecm}^{(2)} \hat{e}_\rho \hat{h}_\psi \hat{e}_\nu^* + \chi_{emm}^{(2)} \hat{h}_\rho \hat{h}_\psi \hat{e}_\nu^* 
$$

$$+ \chi_{mce}^{(2)} \hat{e}_\rho \hat{e}_\psi \hat{h}_\nu^* + \chi_{mce}^{(2)} \hat{h}_\rho \hat{e}_\psi \hat{h}_\nu^* + \chi_{mme}^{(2)} \hat{e}_\rho \hat{h}_\psi \hat{h}_\nu^* + \chi_{mmm}^{(2)} \hat{h}_\rho \hat{h}_\psi \hat{h}_\nu^* \right], \quad (4.20)$$
for all combinations of $\nu = \pm 3, \rho = \pm 1$ and $\psi = \pm 2$, where a negative sign denotes a mode with identical frequency and polarization but propagating in the negative $z$ direction. The eight equations represented by (4.20) contain the eight undetermined effective nonlinearities and, in the most general case, can be solved by linear algebra.

This set of equations can be further simplified if we assume the unit cell’s linear local material properties are purely real, that is, there is no loss or gain in the system. In this case, the symmetry in the Bloch wave equation allows us to write the backward Bloch modes directly from the forward Bloch modes at the same frequency, such that

\[
\vec{e}_{-n}(\vec{r}) = \vec{e}^*_{n}(\vec{r}) \quad \text{and} \quad \vec{h}_{-n}(\vec{r}) = -\vec{h}^*_{n}(\vec{r}),
\]

(4.21)

for $n = 1, 2, 3$. Together with Eq. (4.18) and normalization condition (4.11), this implies $\tilde{e}_{\pm n} = \sqrt{Z_n}$ and $\tilde{h}_{\pm n} = \pm 1/\sqrt{Z_n}$.

Using these relations in (4.20), the equations can be rearranged to solve for the effective second-order susceptibilities in closed form, finally yielding the following expressions for the effective electric, magnetic, and magnetoelectric nonlinear sus-
ceptibilities:

\[ \chi^{(2)}_{\text{ее}}(\omega_3; \omega_1, \omega_2) = \frac{1}{a^3} \iiint_{V_0} dV \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \tilde{\theta}_1(\vec{r}) \tilde{\theta}_2(\vec{r}) \cdot \tilde{\theta}_3(\vec{r}) \right], \]  

\[ (4.22) \]

\[ \chi^{(2)}_{\text{emm}}(\omega_3; \omega_1, \omega_2) = -\frac{1}{a^3} \iiint_{V_0} dV \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \tilde{\phi}_1(\vec{r}) \tilde{\phi}_2(\vec{r}) \cdot \tilde{\theta}_3(\vec{r}) \right], \]  

\[ (4.23) \]

\[ \chi^{(2)}_{\text{em}}(\omega_3; \omega_1, \omega_2) = \frac{i}{a^3} \iiint_{V_0} dV \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \tilde{\phi}_1(\vec{r}) \tilde{\phi}_2(\vec{r}) \cdot \tilde{\theta}_3(\vec{r}) \right], \]  

\[ (4.24) \]

\[ \chi^{(2)}_{\text{me}}(\omega_3; \omega_1, \omega_2) = \frac{i}{a^3} \iiint_{V_0} dV \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \tilde{\phi}_1(\vec{r}) \tilde{\phi}_2(\vec{r}) \cdot \tilde{\phi}_3(\vec{r}) \right], \]  

\[ (4.25) \]

\[ \chi^{(2)}_{\text{mme}}(\omega_3; \omega_1, \omega_2) = \frac{i}{a^3} \iiint_{V_0} dV \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \tilde{\phi}_1(\vec{r}) \tilde{\phi}_2(\vec{r}) \cdot \tilde{\phi}_3(\vec{r}) \right], \]  

\[ (4.26) \]

\[ \chi^{(2)}_{\text{mem}}(\omega_3; \omega_1, \omega_2) = \frac{1}{a^3} \iiint_{V_0} dV \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \tilde{\phi}_1(\vec{r}) \tilde{\phi}_2(\vec{r}) \cdot \tilde{\phi}_3(\vec{r}) \right], \]  

\[ (4.27) \]

\[ \chi^{(2)}_{\text{mm}}(\omega_3; \omega_1, \omega_2) = \frac{1}{a^3} \iiint_{V_0} dV \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \tilde{\phi}_1(\vec{r}) \tilde{\phi}_2(\vec{r}) \cdot \tilde{\phi}_3(\vec{r}) \right], \]  

\[ (4.28) \]

\[ \chi^{(2)}_{\text{m}}(\omega_3; \omega_1, \omega_2) = \frac{1}{a^3} \iiint_{V_0} dV \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \tilde{\phi}_1(\vec{r}) \tilde{\phi}_2(\vec{r}) \cdot \tilde{\phi}_3(\vec{r}) \right], \]  

\[ (4.29) \]

where we have introduced the quantities

\[ \tilde{\theta}_n(\vec{r}) = \frac{1}{2} \left[ \frac{\bar{e}_n(\vec{r})}{\bar{e}_n} e^{ik_nz} + \frac{\bar{e}_{-n}(\vec{r})}{\bar{e}_{-n}} e^{-ik_nz} \right] = \text{Re} \left[ \frac{\bar{e}_n(\vec{r})}{\bar{e}_n} e^{ik_nz} \right] \text{ and} \]  

\[ (4.30) \]

\[ \tilde{\phi}_n(\vec{r}) = \frac{1}{2i} \left[ \frac{\bar{e}_n(\vec{r})}{h_n} e^{ik_nz} + \frac{\bar{e}_{-n}(\vec{r})}{h_{-n}} e^{-ik_nz} \right] = \text{Im} \left[ \frac{\bar{e}_n(\vec{r})}{h_n} e^{ik_nz} \right]. \]  

\[ (4.31) \]

These final forms for the second-order susceptibility can be understood from an intuitive, if informal, perspective, by considering \( \tilde{\theta}_n(\vec{r}) \) and \( \tilde{\phi}_n(\vec{r}) \) as standing wave patterns. From a macroscopic perspective, \( \tilde{\theta}_n(\vec{r}) \) corresponds to a standing wave distribution with an electric field anti-node at the unit cell center. \( \tilde{\phi}_n(\vec{r}) \) is then the electric field distribution corresponding to a macroscopic magnetic field anti-node at the unit cell center. Thus, by specifying the dominant \textit{macroscopic} fields, the appropriate nonlinearity can be related quite naturally to the corresponding

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microscopic fields. In this way, the macroscopic field symmetries are enforced in the local response, such that the homogenized nonlinearities are unambiguous. As an example, typical plots of $\vec{\theta}(\vec{r})$ and $\vec{\phi}(\vec{r})$ are shown in Fig. 4.1 for a MM consisting of high-dielectric spheres, obtained from eigenfrequency simulations.

This final result for the effective second-order magnetoelectric susceptibilities is very satisfying and highly intuitive. By rearranging the Bloch modes, we are able to describe the local electric fields that are, from a macroscopic perspective, either electrically or magnetically induced. The effective response is completely characterized by the overlap of these local field distributions within the nonlinear component of the unit cell. In short, Eqs. (4.22) through (4.29) reveal that, as expected, clever structuring of MM inclusions can give rise to complex macroscopic nonlinear behaviors of a fundamentally different nature than the constituents.

The above analysis assumed propagation along the $z$-axis for simplicity, as well as a homogenized medium whose normal modes, in the linear regime, are linearly polarized plane waves. Thus, while the effective nonlinear susceptibilities are themselves
tensors, the above procedure only probes a single element of each tensor, determined by the polarizations of the macroscopic waves, i.e. the $\chi^{(2)}_{eee}$ in the above formalism is actually $\chi^{(2)}_{eee,xxx}$, $\chi^{(2)}_{mmm}$ is $\chi^{(2)}_{mmm,yyy}$, etc. However, even if the local nonlinearity is diagonal, the subwavelength structure of the MM can give rise to overlap between the different polarizations and thus non-zero cross-terms in the effective tensors [59, 83]. To recover the other elements of the susceptibility tensors, the polarization and direction of each wave can be manipulated successively, and the above procedure repeated independently for each tensor element. Additionally, if the normal modes of the linear homogenized medium cannot be decomposed into linearly polarized plane waves, as is the case, for example, in chiral MMs, an appropriate basis for homogenization, with well-defined wave impedances and wavevectors, should be used instead.

We note here that the decision to write the equations of motion for the fields at $\omega_3$ is an arbitrary one. However, certain permutation symmetries and self-consistencies are readily found in the above expressions. Assuming $\omega_3 > \omega_2 > \omega_1 > 0$, permutation of the fundamental waves gives the same effective nonlinearity, i.e. $\chi^{(2)}_{eme}(\omega_3; \omega_1, \omega_2) = \chi^{(2)}_{eem}(\omega_3; \omega_2, \omega_1)$. Additionally, the complimentary nonlinearities, by which we mean the nonlinearities describing the three-wave mixing process at the fundamental frequencies, are the conjugate of the first, i.e. $\chi^{(2)}_{eme}(\omega_3; \omega_1, \omega_2) = [\chi^{(2)}_{mee}(\omega_1; \omega_3, -\omega_2)]^* = [\chi^{(2)}_{eem}(\omega_2; \omega_3, -\omega_1)]^*$, where we have used the constraint of real total fields to relate the negative and positive frequency components. These properties of the nonlinear susceptibilities can be shown to ensure the proper photon and energy conservation requirements, as in the Manley-Rowe relations [49].

Finally, it is also worth noting that the units of the second-order susceptibilities are not all the same, but have been chosen to ensure the permutation symmetries discussed above. As seen in Eq. (4.3), each nonlinear susceptibility enters the equation for the coupling coefficient with a different leading coefficient, related to the
wave impedances at the involved frequencies. Using Eq. (4.18), it is convenient to define individual coupling coefficients,

$$\gamma_{g_3 g_1 g_2} = \omega_3 \sqrt{G_1 G_2 G_3 \chi^{(2)}_{g_3 g_1 g_2}}$$

(4.32)

where $G_n = Z_n$ for $g_n = e$, and $G_n = Y_n = 1/Z_n$ for $g_n = m$, such that

$$\Gamma_{\nu,\rho,\psi} = \gamma_{eee}^{(2)} + \text{sgn}(\rho)\gamma_{eme}^{(2)} + \text{sgn}(\psi)\gamma_{eem}^{(2)} + \text{sgn}(\rho\psi)\gamma_{emm}^{(2)}$$

$$+ \text{sgn}(\nu)\gamma_{imee}^{(2)} + \text{sgn}(\rho\nu)\gamma_{imee}^{(2)} + \text{sgn}(\psi\nu)\gamma_{imee}^{(2)} + \text{sgn}(\rho\psi\nu)\gamma_{imee}^{(2)}.$$  (4.33)

where sgn() is the signum function. The eight individual coupling coefficients have units of $\text{m}^{-1}(\text{W/m}^2)^{-1/2}$, and provide a means for direct comparison of the relative magnitudes and phases of the various second-order susceptibilities. Also, it is worth noting that the contributions from each nonlinearity to $\Gamma_{\nu,\rho,\psi}$ are uniquely dependent on the propagation directions of the three waves, denoted in our convention by the sign of the subscripts: a fact responsible for interesting interference effects in the presence of multiple nonlinearities, as discussed in Section 4.3.1.
4.1.3 The effective third-order susceptibilities

Analogous to the second-order material responses of Eqs. (2.17) and (2.18), let us consider a third-order polarization and magnetization of the form

\[
P^{(3)}(t) = \sum_{pqr} \left[ \tilde{\chi}_{eeee}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{E}(\omega_r) \right. \\
+ \tilde{\chi}_{eemm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{H}(\omega_r) + \tilde{\chi}_{emem}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{eeme}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{E}(\omega_p) \tilde{H}(\omega_q) \tilde{E}(\omega_r) + \tilde{\chi}_{emee}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{E}(\omega_r) \\
+ \tilde{\chi}_{emem}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{H}(\omega_r) + \tilde{\chi}_{memm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{memm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{E}(\omega_r) \right] \exp(-i\omega_s t), \tag{4.34}
\]

\[
\mu_0 \tilde{M}^{(3)}(t) = \sum_{pqr} \left[ \tilde{\chi}_{mmmm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{H}(\omega_r) \right. \\
+ \tilde{\chi}_{memm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{H}(\omega_p) \tilde{E}(\omega_q) \tilde{E}(\omega_r) + \tilde{\chi}_{mmem}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{H}(\omega_p) \tilde{H}(\omega_q) \tilde{E}(\omega_r) \\
+ \tilde{\chi}_{meme}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{H}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) + \tilde{\chi}_{memm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{E}(\omega_p) \tilde{H}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{meme}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{E}(\omega_p) \tilde{H}(\omega_q) \tilde{E}(\omega_r) + \tilde{\chi}_{memm}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{E}(\omega_p) \tilde{H}(\omega_q) \tilde{H}(\omega_r) \\
+ \tilde{\chi}_{meme}^{(3)}(\omega_s; \omega_p, \omega_q, \omega_r) \tilde{E}(\omega_p) \tilde{E}(\omega_q) \tilde{H}(\omega_r) \right] \exp(-i\omega_s t), \tag{4.35}
\]

where \( \sum_{pqr} \) denotes a triple sum and \( \omega_s = \omega_p + \omega_q + \omega_r \), thus defining 16 third-order susceptibility tensors of rank 4. The same procedure as in the previous section can be carried out for four-wave mixing in a MM composed of a periodic electric third-order susceptibility, \( \tilde{\chi}^{(3)}(\mathbf{r}) \). This gives a system of 16 equations relating the microscopic
Bloch field distributions to the 16 macroscopic susceptibilities, represented by

$$\frac{1}{a^3} \iiint_{V_0} dV \left( \tilde{\chi}_{loc}(\vec{r}) \cdot \tilde{e}_p(\vec{r}) \tilde{e}_\psi(\vec{r}) \tilde{e}_\zeta(\vec{r}) \cdot \tilde{e}_\nu(\vec{r}) \right) =$$

$$\chi_{eeee} \tilde{e}_p \tilde{e}_\psi \tilde{e}_\zeta \tilde{e}_\nu + \chi_{eeme} \tilde{e}_p \tilde{h}_\psi \tilde{e}_\zeta \tilde{e}_\nu + \chi_{eeem} \tilde{e}_p \tilde{e}_\psi \tilde{h}_\zeta \tilde{e}_\nu + \chi_{eemm} \tilde{e}_p \tilde{h}_\psi \tilde{h}_\zeta \tilde{e}_\nu$$

$$+ \chi_{meee} \tilde{h}_p \tilde{e}_\psi \tilde{e}_\zeta \tilde{e}_\nu + \chi_{memm} \tilde{h}_p \tilde{h}_\psi \tilde{e}_\zeta \tilde{e}_\nu + \chi_{meme} \tilde{h}_p \tilde{e}_\psi \tilde{h}_\zeta \tilde{e}_\nu + \chi_{memm} \tilde{h}_p \tilde{h}_\psi \tilde{h}_\zeta \tilde{e}_\nu$$

$$+ \chi_{memm} \tilde{h}_p \tilde{h}_\psi \tilde{e}_\zeta \tilde{e}_\nu + \chi_{meme} \tilde{h}_p \tilde{e}_\psi \tilde{h}_\zeta \tilde{e}_\nu + \chi_{meme} \tilde{h}_p \tilde{h}_\psi \tilde{h}_\zeta \tilde{e}_\nu,$$  

(4.36)

for \( \rho = \pm 1, \psi = \pm 2, \zeta = \pm 3, \nu = \pm 4 \). As before, assuming lossless materials, 16 closed form expressions can be derived for the effective third-order susceptibilities of the form

$$\chi_{eeme}(\omega_4; \omega_1, \omega_2, \omega_3) = \frac{i}{a^3} \iiint_{V_0} dV \left[ \tilde{\chi}_{loc}(\vec{r}) \cdot \tilde{\theta}_1(\vec{r}) \tilde{\phi}_2(\vec{r}) \tilde{\theta}_3(\vec{r}) \cdot \tilde{\theta}_4(\vec{r}) \right].$$  

(4.37)

For brevity, and due to similarities with the second-order expressions, we will omit the equations for the 15 other third-order susceptibilities.

### 4.2 Numerical examples

According to (4.22) through (4.29), the eight homogenized nonlinear magnetostrictive susceptibilities can be evaluated directly from the Bloch modes at the three frequencies, found either analytically or numerically. Moreover, since the quantities in the denominators of (4.30) and (4.31) are explicitly derived from the numerators, the phases and amplitudes of \( \tilde{\theta}_n(\vec{r}) \) and \( \tilde{\phi}_n(\vec{r}) \) are automatically normalized, precluding the usual problems associated with ill-defined Bloch modes. When calculating the effective nonlinearities from numerical simulations, the computed Bloch modes can be used directly in (4.30) and (4.31), facilitating the homogenization process. Thus, the effective linear and nonlinear properties describing three-wave mixing in a MM
can be characterized from the results of just three eigenfrequency simulations. In this section, we apply this procedure to several example MMs, demonstrating the ability of these structures to support electric, magnetic, and magnetoelectric second-order responses.

### 4.2.1 The split ring resonator

In order to validate the above expressions for the second-order susceptibilities, we first apply the analysis to a well-researched nonlinear MM: the split-ring resonator (SRR). For simplicity, we assume the local second-order response of the SRR is zero everywhere except for a small dielectric slab loaded into the structure’s capacitive gap, modeled by $\epsilon/\epsilon_0 = 25$ and $\chi^{(2)}_{\text{loc,zzz}}/\epsilon_0 = 1\text{pm/V}$. The background dielectric is taken to be that of free-space. To allow extrapolation over a wide range of frequencies, the SRR’s dimensions, given in Fig. 4.2 (a), are related to the lattice constant $a$, and the results are given as a function of normalized frequencies, $\omega_n a/2\pi c$. To validate the use of Eq. (4.21), dielectric losses are neglected, and the metal ring is modeled by a perfect electric conductor with thickness $a/100$. Using COMSOL Multiphysics, we employ eigenfrequency simulations on the unit cell to determine the lowest forward propagating Bloch modes and eigenfrequencies over a range of wavevectors, assuming the incident fields are polarized according to Fig. 4.2 (a). In this way, we first determine the wavevectors and wave impedances as a function of frequency, according to Ref. [12]. From previous theoretical investigations [74], we know that, when excited by a fundamental frequency (FF) close to the magnetic resonance, SHG is mediated by the purely magnetic nonlinearity, $\chi^{(2)}_{\text{mmm}}$. Moreover, due to the small size and high permittivity of the nonlinear dielectric, the $\hat{z}$ component of the electric field within the gap is nearly constant, allowing the integral in Eq. (4.26) to be approximated by the product of the average values of $\vec{\phi}_n$ within the gap and the nonlinear dielectric’s volume. Thus, we record the eigenfrequency and $\vec{\phi}_n \cdot \hat{z}$
in the gap for a wide range of wavevectors, interpolating the results to determine \( \chi_{mmm}^{(2)}(2\omega; \omega, \omega) \) as a function of the normalized FF \( \omega a/2\pi c \), according to Eq. (4.26).

**Figure 4.2:** (Reproduced with permission from Ref. [82]. Copyright (2012) by the American Physical Society.) (a) Nonlinear SRR used in validating Eq. (4.26). Plots of the SRR’s retrieved linear (b) and nonlinear (c) properties via both scattering and eigenfrequency simulations. The effective \( \chi_{mmm}^{(2)}(2\omega; \omega, \omega) \) is retrieved by both the nonlinear transfer matrix method and Eq. (4.26), showing excellent agreement. The grayed frequency bands where no data is plotted correspond to either the FF or second-harmonic falling in the SRR’s stop band that extends over a narrow range of frequencies above the magnetic resonance.

For comparison, we perform full-wave numerical simulations, using the existing nonlinear parameter retrieval method based on transfer matrices [67, 70]. This method has been previously established for the retrieval of purely magnetic nonlinearities [69, 84]. Thus, we retrieve the effective magnetic nonlinearity, \( \chi_{mmm}^{(2)}(2\omega; \omega, \omega) \), from nonlinear scattering simulations for a single unit cell with appropriate periodic boundary conditions. The linear properties are likewise determined from the linear scattering parameters [11]. The results of both retrieval techniques are presented in Fig. 4.2 (b) and (c). The excellent agreement between the two methods lends validity to the procedure employed here. Small discrepancies between the two approaches can be attributed to the coupling between neighboring unit cells in the direction of propagation, neglected in the scattering simulations.
4.2.2 Prototypical nonlinear magnetoelectric metamaterial

Recently, nonlinear magnetoelectric coupling was demonstrated in a MM at microwave frequencies [76]. The MMs were varactor loaded split-ring resonators (VL-SRRs), consisting of copper ring resonators with two capacitive gaps on either side. The varactor diodes provided the second-order response. Unlike the previous SRR, the gaps were oriented such that both electric and magnetic fields could excite voltages across the varactors, allowing nonlinear magnetoelectric coupling to take place.

Here, we analyze the analogous doubly-split ring resonator depicted in Fig. 4.3 (a), in which the capacitive gaps are loaded with small nonlinear dielectric films, as in the previous example. The effective linear properties are obtained via field averaging and plotted in Fig. 4.3 (b), showing the expected magnetic resonance. In terms of the nonlinear properties, we consider two structures, corresponding to orientation of the nonlinear dielectrics in the same direction (symmetric SRR), or in opposite directions (anti-symmetric SRR). These configurations imply even and odd symmetries in the nonlinear properties with respect to the z-coordinate, i.e. \( \bar{\chi}^{(2)}_{loc}(x, y, z) = \bar{\chi}^{(2)}_{loc}(x, y, -z) \) and \( \bar{\chi}^{(2)}_{loc}(x, y, z) = -\bar{\chi}^{(2)}_{loc}(x, y, -z) \), respectively. We follow the same procedure as before, but evaluating all of the second-order susceptibilities for both configurations. The magnitudes of the strongest four \( \gamma \) are plotted in Fig. 4.3 (c) and (d), normalized by the value for a solid block of the nonlinear dielectric, \( \gamma_{loc} \).

At the resonance frequency, we see the dominant nonlinear process to be \( \chi^{(2)}_{mmm}(2\omega; \omega, \omega) \) in the anti-symmetric SRR, and \( \chi^{(2)}_{emm}(2\omega; \omega, \omega) \) in the symmetric SRR, in agreement with experiments on analogous VLSRRs [76]. The nature of these differing nonlinearities is further illustrated in Fig. 4.3 (e) and (f), which give a cross-section of the SHG electric fields outside of the MM. These SHG field maps are generated from an infinite column of SRRs resonantly excited by a FF plane wave with the indicated polarization and direction. The electric- and magnetic-dipole-like
patterns are clearly evident in the SHG radiation patterns.

These plots display a number of other prominent features. In particular, the contrasting symmetries in the nonlinear properties of the two unit cells result in two distinct sets of nonlinear susceptibilities. The susceptibilities are highly dispersive, with different nonlinearities dominant at different frequencies. On the one hand, since the magnetic induction of the SRR must go to zero as the frequencies go to DC, we see that all of the nonlinearities vanish in this limit, with the exception of $\chi_{ee e}^{(2)}$, which flattens out to a constant value nearly equal to the nonlinear dielectric alone. This non-resonant enhancement of the electric nonlinearity is impressive when considering that the nonlinear dielectric makes up less than 1 part in 50,000 of the MM’s volume. On the other hand, when one of the involved frequencies is tuned
near the magnetic resonance frequency, we see that the overall nonlinear activity of the MM exceeds that of the nonlinear dielectric by orders of magnitude.

4.3 Examples of nonlinear magnetoelectric phenomena

Up until now, we have focused on the problem of constructing and characterizing nonlinear magnetoelectric MMs, but avoided discussing how the full set of nonlinear susceptibilities can be used to achieve unique and interesting phenomena. Indeed, the parameter space that Eqs. (4.22) through (4.29) encompass is gigantic, especially when the tensorial nature of the nonlinear susceptibilities is considered. While it is beyond the scope of this paper to search out and categorize the range of phenomena nonlinear magnetoelectric MMs can give rise to, this section is devoted to two demonstrative examples. First, we consider interference effects in MMs possessing two nonlinear susceptibilities of comparable magnitude. Having direct analogues in natural materials, nonlinear interference effectively tailors the harmonic and mix wave generation by suppressing and/or enhancing generation along certain directions, especially in optically thin slabs. Second, we analyze electro-optic effects in such MMs under the application of a static electric field. We show that, depending on geometry, the linear permittivity, permeability, and/or magnetoelectric coupling coefficient can be tuned by applying a voltage to the bulk MM. These examples are further illustrated through the prototypical SRRs of Section 4.2.2.

4.3.1 Nonlinear interference

From Fig. 4.3, it is clear certain MM designs can support nonlinear processes with contributions from several effective nonlinear susceptibilities. The fields generated by the different nonlinearities can potentially interfere with each other, either enhancing or suppressing harmonic and mix wave generation. Nonlinear interference has been demonstrated in certain antiferromagnetic compounds [85, 86, 87], for example, in
which $\chi_{eoe}^{(2)}$ and $\chi_{mee}^{(2)}$ are found to have similar magnitudes. The process, however, is generally very weak and has been used mostly in probing the antiferromagnetic domains in such materials, using the fact that $\chi_{eoe}^{(2)}$ reverses sign when going from one domain to another [88].

To offer a concrete example of nonlinear interference, let us consider collinear DFG in a homogeneous (or homogenized) medium, wherein forward propagating waves at $\omega_3$ and $\omega_2$ generate forward and backward waves at the frequency $\omega_1 = \omega_3 - \omega_2$. If we assume a sufficiently weak nonlinearity, we can take $A_3$ and $A_2$ to be constant, known as the non-depleted pump approximation. Assuming a slab of length $L$ and no initial input at $\omega_1$, Eq. (4.2) can be solved to give the intensities of the forward and backward DFG waves,

$$I_1(z) = \frac{1}{2} I_3 I_2 |\Gamma_{1,3,2}|^2 \text{sinc}^2 \left( (k_3 - k_2 - k_1) \frac{z}{2} \right) z^2,$$  \hspace{1cm} (4.38)

$$I_{-1}(z) = \frac{1}{2} I_3 I_2 |\Gamma_{-1,3,2}|^2 \text{sinc}^2 \left( (k_3 - k_2 + k_1) \frac{L - z}{2} \right) (L - z)^2,$$  \hspace{1cm} (4.39)

where, since we are considering DFG, the notation $2^*$ is used to indicate a negative frequency in calculating the coupling coefficient. Nonlinear interference, then, refers to the fact that the coupling coefficients in Eqs. (4.38) and (4.39) are superpositions of the eight second-order susceptibilities, which can add constructively or destructively in the generation of the forward and backward waves, $A_{\pm 1}$, depending on the relative phases and magnitudes of the susceptibilities, as well as the directionality of the involved waves. That is to say, $|\Gamma_{1,3,2}|$ is not necessarily equal to $|\Gamma_{-1,3,2}|$. Alternatively, if only one nonlinearity is dominant, it is easy to verify that the magnitudes of the coupling coefficients are independent of inversion of any of the involved waves, or inversion of the medium itself.

While it may seem difficult and coincidental to find a MM supporting two second-order susceptibilities with similar enough magnitudes to make this effect noticeable,
the permutation symmetries detailed above can lead to this behavior quite naturally. For example, let us consider DFG in the symmetric doubly-split ring resonator MM, or \( \chi^{(2)}(\omega_1;\omega_3,-\omega_2) \) for \( \omega_3 > \omega_{1,2} \). In particular, we take \( \omega_3 a/2\pi c = 0.087 \), close to the resonance frequency, while sweeping the other frequencies and calculate the associated nonlinearities, shown in Fig. 4.4. Permutation symmetry implies that \( \chi^{(2)}_{mme}(\omega_1;\omega_3,-\omega_2) \rightarrow \chi^{(2)}_{mme}(\omega_1;\omega_3,-\omega_2) \) in the limit that \( \omega_1 \approx \omega_2 \approx \omega_3/2 \), resulting in the crossing point in Fig. 4.4 (a). Since these are the dominant nonlinearities contributing to DFG, we see from Eq. (4.33) that \( \Gamma_{1,3,2} \approx 2\gamma_{mme} \) and \( \Gamma_{-1,3,2} \approx 0 \) in the limit \( \omega_1 \to \omega_2 \to \omega_3/2 \), leading to unidirectional DFG in the forward direction.

![DFG nonlinearity diagram](image)

**Figure 4.4:** (Reproduced with permission from Ref. [82]. Copyright (2012) by the American Physical Society.) The second-order susceptibilities of the symmetric (a) and anti-symmetric (b) SRRs for DFG, calculated via (4.22) through (4.29), for \( \omega_3 a/2\pi c = 0.087 \). (c) and (d) show field maps of DFG from infinite columns of symmetric and anti-symmetric SRRs, respectively, in the nearly degenerate case. The comparable magnitudes in the two dominant nonlinear susceptibilities leads to unidirectional DFG, favoring forward generation in the symmetric SRR, and backward generation in the anti-symmetric SRR.

For the same configuration, DFG in the anti-symmetric SRR is dominated by
both $\chi^{(2)}_{mnm}$ and $\chi^{(2)}_{eme}$, owing to a rough balance of the electric and magnetic coupling strengths at these frequencies, as shown in Fig. 4.4 (b). However, these nonlinear susceptibilities are out of phase, in contrast to the previous example. The result is that forward DFG is suppressed, in favor of backward DFG. Such unidirectional behavior is fundamentally different from that associated with phase matching, and is in fact most noticeable in subwavelength slabs where phase matching effects are negligible. Indeed, interference between nonlinear magnetoelectric susceptibilities offers an alternate route towards realizing unidirectional devices such as the nonlinear optical mirror [89]. The unidirectional behavior is further illustrated in the field maps shown in Fig. 4.4 (c) and (d). Similar to Fig. 4.3, the field maps show a cross-section of the DFG emanating from an infinite column of SRRs. The SRRs are excited by plane waves at the resonance frequency and half the resonance frequency, so that the DFG processes depicted in Fig. 4.4 (c) and (d) correspond to the mid-points of plots (a) and (b), respectively, where the nonlinear interference is maximized.

4.3.2 Electro-optic effects

The tuning of optical properties is a highly desirable feature for many applications, and no less so in magnetoelectric media [90]. Since the metamaterials considered here have constituents that are susceptible to the electro-optic effect, it is natural to consider what effect a static electric field can have on all of the metamaterial’s effective properties, as described by the effective second-order susceptibilities. Thus, let us consider the propagation of a monochromatic wave, labeled ‘s’, under the application of a static electric field, labeled ‘0’. Under these conditions, we can show
that the corresponding second-order susceptibilities are given by
\[
\chi^{(2)}_{ee}(\omega_s; 0, \omega_s) = \frac{1}{a^3} \int_0 \int_0 \int_0 dV \left[ \bar{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \vec{\theta}_0(\vec{r}) \vec{\theta}_s(\vec{r}) \cdot \vec{\theta}_s(\vec{r}) \right],
\] (4.40)
\[
\chi^{(2)}_{mem}(\omega_s; 0, \omega_s) = \frac{1}{a^3} \int_0 \int_0 \int_0 dV \left[ \bar{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \vec{\theta}_0(\vec{r}) \vec{\phi}_s(\vec{r}) \cdot \vec{\phi}_s(\vec{r}) \right],
\] (4.41)
\[
\chi^{(2)}_{eem}(\omega_s; 0, \omega_s) = \frac{i}{a^3} \int_0 \int_0 \int_0 dV \left[ \bar{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \vec{\theta}_0(\vec{r}) \vec{\phi}_s(\vec{r}) \cdot \vec{\phi}_s(\vec{r}) \right],
\] (4.42)
\[
\chi^{(2)}_{mee}(\omega_s; 0, \omega_s) = -\frac{i}{a^3} \int_0 \int_0 \int_0 dV \left[ \bar{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \vec{\theta}_0(\vec{r}) \vec{\phi}_s(\vec{r}) \cdot \vec{\phi}_s(\vec{r}) \right],
\] (4.43)

while all other nonlinearities must be identically zero. If we define the material relations according to
\[
\vec{D}(\omega) = \bar{\epsilon}_0 \vec{E}(\omega) + i \bar{\kappa} \vec{H}(\omega),
\] (4.44)
\[
\vec{B}(\omega) = \bar{\mu}_0 \vec{H}(\omega) - i \bar{\kappa}^* \vec{E}(\omega),
\] (4.45)

it follows that the effective material properties are given by
\[
\bar{\epsilon}(\omega, \vec{E}_0) = \epsilon_0 \left[ 1 + \bar{\chi}^{(1)}_{ee}(\omega) + \frac{1}{\epsilon_0} \bar{\chi}^{(2)}_{ee}(\omega; 0, \omega) : \vec{E}_0 \right],
\] (4.46)
\[
\bar{\mu}(\omega, \vec{E}_0) = \mu_0 \left[ 1 + \bar{\chi}^{(1)}_{mem}(\omega) + \frac{1}{\mu_0} \bar{\chi}^{(2)}_{mem}(\omega; 0, \omega) : \vec{E}_0 \right],
\] (4.47)
\[
\bar{\kappa}(\omega, \vec{E}_0) = \frac{1}{c} \left[ \bar{\chi}^{(1)}_{em}(\omega) + \frac{c}{i} \bar{\chi}^{(2)}_{eem}(\omega; 0, \omega) : \vec{E}_0 \right].
\] (4.48)

In this context, it appears quite natural that \( \chi^{(2)}_{eem} \) and \( \chi^{(2)}_{mee} \) are purely imaginary for transparent media, such that the effective linear magnetoelectric coupling coefficients are real-valued.

In essence, Eqs. (4.46) through (4.48) constitute the electro-optic effect for the linear electric, magnetic, and magnetoelectric properties, respectively. The corresponding second-order susceptibilities for the two MMs are shown in Fig. 4.5, approximating \( \vec{\theta}_0(\vec{r}) \) by a Bloch mode calculated at very low frequency. Thus, the
The effective second-order susceptibilities of the symmetric (b) and anti-symmetric (c) SRRs under a static electric field, calculated via (4.40) through (4.43).

Figure 4.5: (Reproduced with permission from Ref. [82]. Copyright (2012) by the American Physical Society.) The effective second-order susceptibilities of the symmetric (b) and anti-symmetric (c) SRRs under a static electric field, calculated via (4.40) through (4.43).

symmetric SRR supports field-induced contributions to the permittivity and permeability. The anti-symmetric SRR, on the other-hand, supports field-induced magneto-electric coupling. This is made particularly more interesting since magneto-electric coupling in this SRR vanishes in the absence of an electric field. Similar control of optical activity has been realized in a chiral metamaterial through a third-order nonlinear process [91]. In this way, the linear magneto-electric properties of a medium can be tuned dynamically.

4.4 Spatial dispersion in the nonlinear susceptibilities

As stated earlier, the expressions for the second-order nonlinearities in (4.22)-(4.29) are only valid in the limit that $a \rightarrow 0$. In other words, they neglect the spatial
dispersion effects in the material properties that accompany a finite unit cell extent. In this section, we derive the leading order effect of spatial dispersion in the nonlinear susceptibilities. In doing so, we find that the magnetoelectric nonlinearities naturally fall into two subsets depending on their tensorial nature (polar or axial), yielding two independent systems of equations. Using the simple case of a MM formed from a thin nonlinear slab periodically embedded in a dielectric matrix, we demonstrate that spatial dispersion tends to distribute a fundamental nonlinearity across the other three effective nonlinear susceptibilities of the same tensor type, analogous to spatial dispersion in the linear properties of MMs.

To obtain a more general set of expressions for the nonlinear susceptibilities that encompass spatial dispersion, homogenization can be achieved by direct comparison of Eq. (4.14) and the equivalent expression for a homogeneous material. Thus, casting the coupled-wave equations for a homogeneous medium, described by Eqs. (2.17) and (2.18), into the same integral form as Eq. (4.14) yields

\[
\nabla A_\mu(\vec{R}) \cdot \hat{s}_\mu = iA_\rho(\vec{R})A_\psi(\vec{R})\tilde{\Gamma}_{\mu,\rho,\psi} \frac{1}{a^3} \iiint_{V_0} e^{i(k_\rho + k_\psi - k_\mu)z} dV. \tag{4.49}
\]

Applying the same restrictions to wave propagation and polarization as described in Section 4.1.2, we can equate like-terms in (4.49) and (4.14), implying that homogenization is achieved for

\[
\frac{1}{a^3} \iiint_{V_0} \left( \tilde{\chi}^{(2)}_{loc}(\vec{r}) : \tilde{e}_\rho(\vec{r})\tilde{e}_\psi(\vec{r}) \cdot \tilde{e}_\nu(\vec{r}) e^{i(k_\nu + k_\psi - k_\rho)z} \right) dV = \]

\[
\left[ \tilde{\chi}^{(2)}_{eeee} \tilde{e}_\rho \tilde{e}_\psi \tilde{e}_\nu^* + \tilde{\chi}^{(2)}_{eeme} \tilde{h}_\rho \tilde{e}_\psi \tilde{e}_\nu^* + \tilde{\chi}^{(2)}_{eeem} \tilde{e}_\rho \tilde{h}_\psi \tilde{e}_\nu^* + \tilde{\chi}^{(2)}_{emmm} \tilde{h}_\rho \tilde{h}_\psi \tilde{e}_\nu^* 
\]

\[
+ \tilde{\chi}^{(2)}_{meee} \tilde{e}_\rho \tilde{e}_\psi \tilde{h}_\nu^* + \tilde{\chi}^{(2)}_{meme} \tilde{h}_\rho \tilde{e}_\psi \tilde{h}_\nu^* + \tilde{\chi}^{(2)}_{meem} \tilde{e}_\rho \tilde{h}_\psi \tilde{h}_\nu^* + \tilde{\chi}^{(2)}_{mmmm} \tilde{h}_\rho \tilde{h}_\psi \tilde{h}_\nu^* \right] \int_{-a/2}^{a/2} \frac{1}{a} e^{i(k_\rho + k_\psi - k_\mu)z} dz. \tag{4.50}
\]

This again represents eight equations containing eight effective second-order susceptibilities.
By comparing Eq. (4.50) to (4.20), we see that the approximation inherent in Section 4.1.2 is equivalent to
\[ \int_{-a/2}^{a/2} \frac{1}{a} e^{i(k_\nu k_\psi - k_\varsigma)z'} dz' \approx 1, \]
i.e., the phase mismatch accumulated over a single unit cell is small. This is not always valid, as many MM unit cells have lattice constants that are not entirely negligible in comparison to the wavelength. As such, the previous steps cannot be repeated to yield a closed form expression for each nonlinear susceptibility. For example, if we attempt to derive an expression analogous to (4.22), we find
\[
\frac{1}{a^2} \iiint_{V_0} \left[ \tilde{\chi}^{(2)}_{loc}(\vec{r}) : \vec{\phi}_1(\vec{r}) \vec{\phi}_2(\vec{r}) \cdot \vec{\phi}_3(\vec{r}) \right] dV = \\
\chi^{(2)}_{eee} \int_{-a/2}^{a/2} \cos(k_1z) \cos(k_2z) \cos(k_3z) dz \\
+ i\chi^{(2)}_{eme} \frac{\tilde{h}_1}{\bar{e}_1} \int_{-a/2}^{a/2} \sin(k_1z) \cos(k_2z) \cos(k_3z) dz \\
+ i\chi^{(2)}_{eem} \frac{\tilde{h}_2}{\bar{e}_2} \int_{-a/2}^{a/2} \cos(k_1z) \sin(k_2z) \cos(k_3z) dz \\
- \chi^{(2)}_{emm} \frac{\tilde{h}_1 \tilde{h}_2}{\bar{e}_1 \bar{e}_2} \int_{-a/2}^{a/2} \sin(k_1z) \sin(k_2z) \cos(k_3z) dz \\
- i\chi^{(2)}_{mee} \frac{\tilde{h}_3}{\bar{e}_3} \int_{-a/2}^{a/2} \cos(k_1z) \cos(k_2z) \sin(k_3z) dz \\
+ \chi^{(2)}_{mme} \frac{\tilde{h}_1 \tilde{h}_3}{\bar{e}_1 \bar{e}_3} \int_{-a/2}^{a/2} \sin(k_1z) \cos(k_2z) \sin(k_3z) dz \\
+ \chi^{(2)}_{mem} \frac{\tilde{h}_2 \tilde{h}_3}{\bar{e}_2 \bar{e}_3} \int_{-a/2}^{a/2} \cos(k_1z) \sin(k_2z) \sin(k_3z) dz \\
+ i\chi^{(2)}_{mmm} \frac{\tilde{h}_1 \tilde{h}_2 \tilde{h}_3}{\bar{e}_1 \bar{e}_2 \bar{e}_3} \int_{-a/2}^{a/2} \sin(k_1z) \sin(k_2z) \sin(k_3z) dz.
\] (4.51)
Rather than a single effective nonlinear susceptibility, the right-hand side appears to contain contributions from all eight. However, since the limits of the integrals
on the right-hand side of Eq. (4.51) are symmetric, all of the terms containing odd
integrands, or equivalently an odd number of sine terms, must vanish, leaving just
four non-zero terms. This procedure can be repeated to find all eight analogous
equations (see Appendix 4.7). In doing so, the nonlinear susceptibilities naturally
fall into two subsets, such that all of the terms from one subset or the other vanish
in any given matrix element, leading to two independent systems of equations. The
reason for this separation can be understood by considering the effective nonlinear
tensor types. Specifically, for the construction considered here, the effective nonlinear-
properties $\bar{\chi}^{(2)}_{eee}$, $\bar{\chi}^{(2)}_{mme}$, $\bar{\chi}^{(2)}_{mem}$, and $\bar{\chi}^{(2)}_{emm}$ are polar tensors, while $\bar{\chi}^{(2)}_{mmm}$, $\bar{\chi}^{(2)}_{eem}$, $\bar{\chi}^{(2)}_{eme}$, and
$\bar{\chi}^{(2)}_{mee}$ are axial tensors. This follows naturally from the polar and axial vector nature
of the electric and magnetic fields themselves, and the assumption that the local
nonlinearity is a polar tensor [92]. Since spatial dispersion in this context should
not depend on the handed-ness of the coordinate system, it follows that the affected
susceptibilities must be of the same tensor type.

Figure 4.6: (Reproduced with permission from Ref. [82]. Copyright (2012) by the
American Physical Society.) (a) Illustration of the unit cell for investigating spatial
dispersion in the nonlinear properties, consisting of a thin nonlinear slab of thickness
d embedded in a dielectric matrix with periodicity $a$. (b) The effective nonlinear
susceptibilities, assuming $\epsilon_r = 2$, $d/a = 0.01$, $\chi^{(2)}_{loc}/\epsilon_0 = 100$ pm/V, $\omega_2 = 1.5\omega_1$, and
$\omega_3 = \omega_1 + \omega_2$, as a function of $\omega_3a/2\pi c$. 

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To see how a non-negligible unit cell extent changes the effective nonlinear properties of a MM, let us use the example of a 1-dimensional MM consisting of a thin nonlinear dielectric slab of extent $d$, periodically loaded in a dielectric spacer with period $a$, shown in Fig. 4.6. For propagation normal to the slab, the field and polarization vectors become scalar. Moreover, to remove the effects of linear spatial dispersion, let us assume the slab and dielectric spacer have the same relative permittivity, $\epsilon_r$. Thus, the Bloch modes are simple plane waves with $k_n = \sqrt{\epsilon_r \omega_n / c}$. In the long-wavelength limit, Eqs. (4.22) through (4.29) reveal that all of the effective nonlinear susceptibilities vanish except for the electric nonlinearity, which reduces to a simple volume average of the local nonlinearity,

$$\chi^{(2)}_{ee} (\omega_3; \omega_1, \omega_2) = \frac{d}{a} \chi^{(2)}_{loc} \quad \text{long wavelength limit,} \quad (4.52)$$

in agreement with previous studies of composite nonlinear media [59]. Since the nonlinear susceptibilities naturally separate into two subsets, the four c-type nonlinear susceptibilities are identically zero for all wavelengths. This leaves us with a system of four equations and four unknown i-type nonlinear susceptibilities. If $d = a$, i.e. the medium is simply a homogeneous slab of nonlinear dielectric, then (4.57)-(4.64) can be solved to give $\chi^{(2)}_{ee} = \chi^{(2)}_{loc}$ for all frequencies, as expected. On the other hand, in the limit $d << a$, the left-hand sides of (4.58)-(4.64) vanish. Solving this system to leading order in $k_i a$, we find

$$\chi^{(2)}_{ee} = \left[ 1 - \frac{1}{8} a^2 (k_1^2 + k_2^2 + k_3^2) \right] \frac{d}{a} \chi^{(2)}_{loc} \quad (4.53)$$

$$\chi^{(2)}_{emm} = +Z_1 Z_2 \left( \frac{1}{12} a^2 k_1 k_2 \right) \frac{d}{a} \chi^{(2)}_{loc} = +Z_0^2 \left( \frac{\pi^2}{3} \frac{a^2}{\lambda_1 \lambda_2} \right) \frac{d}{a} \chi^{(2)}_{loc} \quad (4.54)$$

$$\chi^{(2)}_{mme} = -Z_1 Z_3 \left( \frac{1}{12} a^2 k_1 k_3 \right) \frac{d}{a} \chi^{(2)}_{loc} = -Z_0^2 \left( \frac{\pi^2}{3} \frac{a^2}{\lambda_1 \lambda_3} \right) \frac{d}{a} \chi^{(2)}_{loc} \quad (4.55)$$

$$\chi^{(2)}_{mem} = -Z_2 Z_3 \left( \frac{1}{12} a^2 k_2 k_3 \right) \frac{d}{a} \chi^{(2)}_{loc} = -Z_0^2 \left( \frac{\pi^2}{3} \frac{a^2}{\lambda_2 \lambda_3} \right) \frac{d}{a} \chi^{(2)}_{loc} \quad (4.56)$$

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where $\lambda_n = 2\pi c/\omega_n$ is the wavelength in free-space. Thus, spatial dispersion manifests itself in the susceptibilities of the same inversion symmetry, proportional to the square of the lattice constant-to-wavelength ratio. The second-order susceptibilities are plotted in Fig. 4.6 (b) for typical values. While the above equations are specific to this example, the qualitative behavior and consequences of spatial dispersion in the nonlinear properties can be considered representative of MMs in general.

4.5 Symmetry considerations

At this point, it is useful to consider the effective nonlinear properties from a symmetry standpoint. Given that the eight nonlinear tensors naturally separate into polar and axial tensors, we would expect that the internal symmetries of a given metamaterial would favor one group of tensors over another. For example, let us consider a metamaterial whose linear properties are centrosymmetric, that is, for some choice of origin $\bar{e}(\bar{r}) = \bar{e}(\bar{r})$ for all $\bar{r}$ within the unit-cell. Such symmetry is a good approximation for regular arrangements of nanoparticles and many circuit-based metamaterials like dual-split SRRs and ELCs. It is worth noting that we are not referring to the crystal symmetry of the local materials, at least some of which must be non-centrosymmetric to support a $\chi^{(2)}_{loc}$, but rather the structural symmetry of the metamaterial unit-cell, which depends on the relative arrangement of the constituent materials and inclusions. As such, even though the anisotropy of the nonlinear elements, as well as the presence of substrates, will, strictly speaking, break the inversion symmetry, it is instructive to consider the structural symmetry of the inclusion as the dominant force influencing the effective properties. In any case, for a centrosymmetric unit-cell, we know from Bloch theory that a similar symmetry is enforced in the local fields, or $\bar{e}_n(\bar{r}) = \bar{e}_n(-\bar{r})^*$. From their definitions, we see that this in turn implies that $\bar{\theta}(\bar{r})$ is an even function of $\bar{r}$, while $\bar{\phi}(\bar{r})$ is odd.
Figure 4.7: Illustration of symmetries in nonlinear metamaterials. (a) A centrosymmetric inclusion, the double-gap SRR, placed over a uniform nonlinear substrate for maximizing the polar second-order susceptibility tensors. (b) A centrosymmetric inclusion placed over an anti-symmetric nonlinear substrate for maximizing the axial second-order susceptibility tensors. (c) A non-centrosymmetric inclusion placed over a uniform substrate excludes neither polar nor axial second-order susceptibility tensors.

Clearly, these symmetry properties will have a strong impact on which effective nonlinearities are dominant. If the nonlinear properties are similarly centrosymmetric, i.e. $\chi^{(2)}_{\text{loc}}(\vec{r}) = \chi^{(2)}_{\text{loc}}(-\vec{r})$, then the integrands of the axial nonlinear tensors are odd functions of $\vec{r}$ and therefore the axial nonlinear tensors vanish identically. If, on the other hand, the material is poled in such a way that the local nonlinear properties are anti-symmetric, $\chi^{(2)}_{\text{loc}}(\vec{r}) = -\chi^{(2)}_{\text{loc}}(-\vec{r})$, then the polar nonlinear tensors vanish. These cases are illustrated in Fig. 4.7 (a) and (b), respectively.

At microwave frequencies, where circuit elements such as varactor diodes are often used as the nonlinear inclusions, it is simple to choose the symmetries in the nonlinear properties, giving access to any of the eight nonlinear susceptibilities. At optical frequencies, however, local electric nonlinearities are often introduced by using a nonlinear crystal as a substrates or embedding matrix. While a nonlinear crystal as a whole can be aligned along a particular axis, enforcing local directionality in a bulk medium or substrate can be very difficult, especially on the length scales that would be required in a metamaterial. This implies that, at optical frequencies, the
class of nonlinear metamaterials composed of centrosymmetric inclusions will tend to support nonlinear processes through effectively polar nonlinear tensors. Accessing the axial tensors requires non-centrosymmetric inclusions, such as the single-gap SRR shown in Fig. 4.7 (c), which is known to support nonlinearities of the type $\chi^{(2)}_{mmm}$ [69].

4.6 Conclusion

Through a coupled-mode analysis, we have developed a method for describing the nonlinear behavior of MMs in terms of well-known nonlinear susceptibilities. These effective nonlinear susceptibilities are derived directly from the microscopic fields supported by the MM, giving a physically intuitive perspective of the nonlinear properties. By investigating these relations analytically and numerically, we have shown that the macroscopic nonlinear behavior of MMs can differ from its constituent materials not only in magnitude but in kind. In a simple dual-gap SRR medium, we were able to demonstrate a configuration and frequency combination at which each of the eight second-order susceptibilities, defined in Eqs. (2.17) and (2.18), was the dominant nonlinearity. However, it is likely that more interesting and beneficial structures can maximize the usefulness of nonlinear mangetoelectric coupling, particularly chiral MMs, owing to the prominent role magnetoelectric coupling plays in such mediums.

To give context to this work, we note that certain magnetic materials are known to support wave-mixing processes, such as SHG, mediated through naturally occurring magnetoelectric nonlinearities [93, 94, 90, 95, 96]. These materials, however, are rare, and the strengths of such processes are limited by the weak optical magnetic responses of natural materials in general. In this context, the simple expressions in (4.22)-(4.29) show that MMs can potentially support similar processes, but at far higher efficiencies.

Perhaps most significantly, nonlinearities of different types can be brought to-
together in a single medium in a controllable way that is simply impossible in naturally occurring materials. This implies a virtually boundless design space for the nonlinear properties of MMs. In particular, by combining nonlinear susceptibilities of roughly equal magnitudes in a single medium, one can access the phenomena of nonlinear interference, whereby unidirectional generation of harmonics and mix frequencies can be achieved. Through clever design of the MM unit cell, nonlinear processes can be suppressed to avoid parasitic losses, or enhanced by orders of magnitude to form the core of compact, efficient nonlinear devices.

While we believe this work represents a fundamental step in understanding the nonlinear magnetoelectric properties of MMs, it is by no means intended to be an exhaustive description of the phenomena resulting from nonlinear magnetoelectric coupling. Indeed, inspired by the wide range of potential applications that have been found for various combinations of the linear electric, magnetic, and magnetoelectric properties of MMs, we hope that this work will spark similar creativity and ingenuity for combining the electric, magnetic, and magnetoelectric nonlinear properties of MMs in new and unforeseen ways, while laying the foundations for the design, characterization, and physics thereof.
4.7 Appendix: Derivation of the nonlinear susceptibilities in the presence of spatial dispersion

Using the short-hand notation \( S_n = \sin(k_n z) \) and \( C_n = \cos(k_n z) \) and dropping the explicit integral limits, we can rearrange (4.20) into the following eight equations:

\[
\frac{1}{a^2} \iiint \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \vec{\theta}_1(\vec{r}) \vec{\theta}_2(\vec{r}) \cdot \vec{\theta}_3(\vec{r}) \right] dV = \\
\chi^{(2)}_{\text{eee}} C_1 C_2 C_3 dz - \chi^{(2)}_{\text{emm}} \frac{\tilde{h}_1 \tilde{h}_2}{\epsilon_1 \epsilon_2} \int S_1 S_2 C_3 dz \\
+ \chi^{(2)}_{\text{mem}} \frac{\tilde{h}_2 \tilde{h}_3}{\epsilon_2 \epsilon_3} \int C_1 S_2 S_3 dz + \chi^{(2)}_{\text{mme}} \frac{\tilde{h}_1 \tilde{h}_3}{\epsilon_1 \epsilon_3} \int S_1 C_2 S_3 dz, \tag{4.57}
\]

\[
-\frac{1}{a^2} \iiint \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \vec{\phi}_1(\vec{r}) \vec{\phi}_2(\vec{r}) \cdot \vec{\phi}_3(\vec{r}) \right] dV = \\
\chi^{(2)}_{\text{eee}} \frac{\tilde{e}_1 \tilde{e}_2}{\h_1 \h_2} \int S_1 S_2 C_3 dz + \chi^{(2)}_{\text{emm}} \int C_1 C_2 C_3 dz \\
+ \chi^{(2)}_{\text{mem}} \frac{\tilde{e}_1 \tilde{h}_3}{\h_1} \int S_1 C_2 S_3 dz + \chi^{(2)}_{\text{mme}} \frac{\tilde{e}_2 \tilde{h}_3}{\h_2} \int C_1 S_2 S_3 dz, \tag{4.58}
\]

\[
\frac{1}{a^2} \iiint \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \vec{\theta}_1(\vec{r}) \vec{\phi}_2(\vec{r}) \cdot \vec{\phi}_3(\vec{r}) \right] dV = \\
\chi^{(2)}_{\text{eee}} \frac{\tilde{e}_2 \tilde{e}_3}{\h_2 \h_3} \int C_1 S_2 S_3 dz + \chi^{(2)}_{\text{emm}} \frac{\tilde{h}_1 \tilde{e}_3}{\epsilon_1 \h_3} \int S_1 C_2 S_3 dz \\
+ \chi^{(2)}_{\text{mem}} \int C_1 C_2 C_3 dz - \chi^{(2)}_{\text{mme}} \frac{\tilde{h}_1 \tilde{e}_2}{\epsilon_1 \h_2} \int S_1 S_2 C_3 dz, \tag{4.59}
\]

\[
\frac{1}{a^2} \iiint \left[ \tilde{\chi}^{(2)}_{\text{loc}}(\vec{r}) : \vec{\phi}_1(\vec{r}) \vec{\theta}_2(\vec{r}) \cdot \vec{\phi}_3(\vec{r}) \right] dV = \\
\chi^{(2)}_{\text{eee}} \frac{\tilde{e}_1 \tilde{e}_3}{\h_1 \h_3} \int S_1 C_2 S_3 dz + \chi^{(2)}_{\text{emm}} \frac{\tilde{h}_2 \tilde{e}_3}{\epsilon_2 \h_3} \int C_1 S_2 S_3 dz \\
- \chi^{(2)}_{\text{mem}} \frac{\tilde{e}_1 \tilde{h}_2}{\h_1} \int S_1 S_2 C_3 dz + \chi^{(2)}_{\text{mme}} \int C_1 C_2 C_3 dz, \tag{4.60}
\]
Eqs. (4.57) through (4.60) represent a system of four equations for the four polar second-order susceptibility tensors, while Eqs. (4.61) through (4.64) represent an independent system of four equations for the four axial second-order susceptibility tensors. Both systems can be solved using linear algebra.
Engineering the effective nonlinear susceptibilities

Enhancing the otherwise weak optical nonlinearities associated with natural materials is one of the most enticing capabilities of NLMMs. Metamaterials naturally support highly inhomogeneous field distributions, where electromagnetic energy can be concentrated into small, critical volumes [2]. Any nonlinear element placed in these volumes experiences a local field strength much greater than the average field. Enhancement of nonlinearities through light localization is well known, and has been exploited in plasmonic media [97, 98, 99, 100, 101], photonic crystals [102, 103], and resonant cavities [104, 105]. However, there is a fundamental difference between the field localization in these structures and that associated with NLMMs: cavities and electromagnetic ‘hot spots’ localize fields to tiny spatial volumes, restricting configurations to surfaces or similarly small fractions of the whole medium. Wave behavior in such systems is typically described in terms of scattering rather than propagation, since the density and distribution of the enhancement regions are so sparse. In contrast, the field localization in NLMMs is distributed periodically throughout a volume with no fundamental constraint on wave propagation; in other words, the enhancement associated with NLMMs is inherently a bulk effect, imbuing the meta-
material composite with an effective, continuous nonlinear susceptibility many times
greater than that of any of the constituent materials. This important distinction
renders NLMMs an approach to the design of a new generation of materials with
the potential for unprecedented bulk nonlinearities. Indeed, once designed, artificial
materials of this type can subsequently be used in many of these same advantageous
setups that are currently employed for natural materials, allowing for cumulative
mechanisms of enhancement. The following sections are reproduced with permission
from Alec Rose, Stéphane Larouche, David R. Smith, Physical Review A, 84, 053805,

5.1 The nonlinear retrieval method for media with nonlinear polar-
ization and magnetization

The enhancement of nonlinear properties in NLMMs relates directly to the magni-
tude of the local field enhancement within the metamaterial elements. Full wave
simulations can offer direct measurements of the field enhancement factor by sim-
ulating the excitation of either metamaterial or plasmonic structures; however, the
results are specific to the setup employed, and do not constitute a general descrip-
tion of an effective medium comprising such structures. The ‘enhancement factors’
quoted in such studies are, at best, indirect measures of the resulting nonlinear prop-
erties [97, 98, 101]. Since it is our goal to demonstrate the enhancement of nonlinear
optical processes in a bulk NLMM medium, we require a tool for the accurate com-
putation of the NLMM’s effective nonlinear properties, using the results of nonlinear
scattering simulations on a single unit cell.

To apply the nonlinear retrieval method for the structures studied here, however,
some modifications are required. The retrieval method, as first introduced, is con-
strained by the assumption that only a nonlinear electric polarization or magnetization—
but not both simultaneously—is present. This assumption fails explicitly for many
mixed media NLMMs, such as the magnetic split-ring resonator embedded in a nonlinear dielectric. Furthermore, even for unit cells containing polarizable elements of only one type, a single nonlinear polarizability can still fail to characterize the structure in the presence of significant spatial dispersion \[78\]. In order to completely characterize a generic nonlinear medium, nonlinear dependences on the incident fields in the material’s electric polarization and magnetization must be taken into account. In this section, a brief extension to the nonlinear retrieval method is outlined, allowing for the simultaneous retrieval of the nonlinear magnetic and electric susceptibilities contributing to any given wave-mixing process.

It is well known that, for sufficiently weak excitations, the higher-order terms in the power series expansion of a medium’s polarization,

\[
P = \epsilon_0 \left( \chi_e^{(1)} E + \chi_e^{(2)} E^2 + \chi_e^{(3)} E^3 + \ldots \right),
\]

(5.1)
can be modeled simply as a radiating source, and likewise for the magnetization,

\[
M = \chi_m^{(1)} H + \chi_m^{(2)} H^2 + \chi_m^{(3)} H^3 + \ldots,
\]

(5.2)
invoking what is known as the first Born approximation \[49\]. A medium with a nonlinearity present in either its polarization or its magnetization can thus be modeled as having a distributed electric or magnetic source, respectively, whose magnitude and phase depend on the distribution of the exciting, or ‘fundamental’ fields, along with the corresponding higher-order susceptibility. For convenience, we will consider explicitly the electric fields scattered by an electric nonlinearity (denoted by subscript \(e\)) and the magnetic fields scattered by a magnetic nonlinearity (denoted by subscript \(m\)). Furthermore, because we are assuming weak excitations and neglecting cascaded interactions, it follows that we can neglect coupling between the electric and magnetic nonlinearities, i.e. the scattering associated with each nonlinearity is assumed to have no effect on the other.
As an example, we consider a one-dimensional three layered structure in which an arbitrary nonlinear slab is sandwiched between semi-infinite regions of vacuum, as shown in Fig. 5.1 (b). Under excitation by a set of linearly polarized monochromatic plane waves (the fundamental fields), and in the first Born approximation, the medium’s nonlinear polarization and magnetization will produce radiating fields in the output and input vacuum regions. Assuming knowledge of the linear properties at the fundamental frequencies, the distribution of the fundamental fields can be
completely solved for by transfer matrices. As such, the solution for the fundamental fields is omitted here, and the rest of the analysis will only involve the nonlinear scattered fields. We assume that the nonlinear slab, at the scattered frequency of interest, can be completely characterized by permittivity $\varepsilon_2$, permeability $\mu_2$, and $\alpha$-order electric and magnetic nonlinear susceptibilities $\chi_{e}^{(\alpha)}$ and $\chi_{m}^{(\alpha)}$. In keeping with the notation of the existing nonlinear retrieval method, we split the fields into their forward (+) and backward (-) propagating parts, keeping track of the complex field amplitudes at the medium interfaces. Thus, the transmitted electric field, produced by a nonlinear electric polarization, and located in the output medium at its interface with the nonlinear slab, is denoted by $E_{3e}^{+}$, while the reflected electric field, located in the input medium at its interface with the nonlinear slab, is denoted by $E_{1e}^{-}$. Similarly, the nonlinear magnetization generates $H_{3m}^{+}$ and $H_{1m}^{-}$. If the nonlinear slab’s higher-order susceptibilities are known, these fields can be analytically calculated according to the nonlinear transfer matrix method. If, alternatively, the nonlinear susceptibilities involved are unknown and instead the scattered fields have been measured, as in the typical homogenization problem, the existing nonlinear retrieval method can be used to determine the effective nonlinearity if only one nonlinearity is non-negligible. If nonlinearities in both the magnetization and polarization simultaneously contribute to the scattered fields, then the problem must be reduced to a superposition of two, independent homogenization problems: one considering only an electric nonlinearity with the associated scattered fields $E_{3e}^{+}$ and $E_{1e}^{-}$, and one considering only a magnetic nonlinearity with the scattered fields $H_{3m}^{+}$ and $H_{1m}^{-}$. Once the sub-problems have been properly defined, as in Fig. 5.1 (c), the retrieval operation can be performed in each case, yielding effective values for both the electric and magnetic higher-order susceptibilities.

Obviously, we cannot probe the field contributions from the electric and magnetic
nonlinearities individually, since it is the total scattered fields, $E_3^+$ and $E_1^-$, given by

$$E_3^+ = E_{3e}^+ + Z_0 H_{3m}^+,$$  \hspace{1cm} (5.3)

$$E_1^- = E_{1e}^- - Z_0 H_{1m}^-,$$  \hspace{1cm} (5.4)

that will be measured in any experiment or simulation, as in Fig. 5.1 (a). Thus, our goal is to isolate the fields according to the nonlinear source that produced them (electric or magnetic) so that we can run each set of scattered fields through an independent retrieval procedure. In the transfer matrix retrieval method the field-to-susceptibility ratios $E_{3e}^+/\chi_e^{(\alpha)}$ and $E_{1e}^-/\chi_e^{(\alpha)}$, and likewise for the magnetic terms, are needed, where $\alpha$ denotes the order of the nonlinearity. The method for calculation of these quantities is given elsewhere [70], and requires only the thickness of the sample and its effective linear properties as inputs. Taking the ratio of these two quantities, we can compute the ratios of the reflected to the transmitted scattered fields for each process, which we denote as

$$R_e = E_{1e}^-/E_{3e}^+,$$ \hspace{1cm} (5.5)

$$R_m = H_{1m}^-/H_{3m}^+.$$ \hspace{1cm} (5.6)

We reiterate that these ratios can be calculated analytically, employing slightly modified equations from the nonlinear transfer matrix method, and without any knowledge of the nonlinear susceptibility involved. We thus arrive at four equations and four unknowns, which can be rearranged to give

$$E_{3e}^+ = \frac{R_m E_3^+ + E_1^-}{R_e + R_m},$$ \hspace{1cm} (5.7)

$$H_{3m}^+ = \frac{1}{Z_0} \frac{R_e E_3^+ - E_1^-}{R_e + R_m},$$ \hspace{1cm} (5.8)

and similarly for the reflected fields. Finally, we are able to merge the above analysis with the pre-existing nonlinear retrieval method, yielding the following retrieval
These represent slight modifications to the former nonlinear retrieval equations. In contrast to the previous method, these equations make use of both the transmitted and reflected spectrums, but still require measurements from only a single experiment or simulation. However, Eqs. (5.9) and (5.10) now retrieve both electric and magnetic contributions in a given nonlinear process, allowing for the complete characterization of more general NLMMs. While the presence of both electric and magnetic nonlinear susceptibilities is rare for naturally occurring materials, the situation is very common for NLMMs, thus motivating the modifications considered here.

The modified retrieval procedure described above is sufficient to analyze the structures in the following sections. We note, however, that we ignore any effects due to magnetoelastic coupling between unit cells either in the fundamental or the harmonics. Because magnetoelastic coupling appears to be of concern only when both the electric and magnetic responses are simultaneously resonant, its neglect here is reasonable for the configurations we consider. [106, 107, 77, 78]

5.2 Simulations and retrievals

In this section, we analyze the nonlinearity enhancement effect in the context of four distinct types of NLMM structures: the electric-field-coupled resonator (ELC), the split-ring resonator (SRR), the cut-wire medium, and the I-beam medium. The nonlinearity in each case comes from a generic nonlinear dielectric matrix in which the metallic structure is embedded. Full-wave, frequency domain simulations, using the
COMSOL multi-physics suite, are performed on a single unit cell of each NLMM, with the appropriate nonlinear equations evaluated in the dielectric matrix. Periodic boundary conditions are used to simulate a metamaterial slab with infinite extent in the transverse directions. The metal structures are assumed to be silver, which is modeled with a Drude dispersion using a plasma frequency of \( 2.179 \times 10^{15} \text{ Hz} \) and a relaxation rate of \( 4.352 \times 10^{12} \text{ Hz} \) [108]. The dielectric medium is modeled with a permittivity of \( 2.40\epsilon_0 \). Two nonlinear processes, corresponding to two distinct NLMMs, are considered for each metamaterial: SHG in the case of embedding in a second-order nonlinear dielectric, and SPM in the case of a third-order nonlinear, or Kerr, dielectric. The simulations consist of two distinct domains for the fundamental and nonlinear scattered fields. The fundamental fields are solved for first, neglecting the nonlinearity, consistent with the non-depleted pump approximation. The distribution of the fundamental fields is then used in the calculation of the nonlinear polarization in the dielectric, which operates as a distributed source in the second, nonlinear scattering domain. This two-part design strictly enforces the first Born approximation, prohibiting all cascaded and cyclic nonlinear effects. This is true even in the case of SPM, where, despite the degeneracy in frequency, the nonlinear scattered fields are kept separate from the fundamental fields. The validity and self-consistency of these simulations have been verified on simple, homogeneous slabs of nonlinear dielectric.

For each simulation, the unit cell is excited by a plane wave travelling in the positive \( z \)-direction, with the electric field polarized along the \( x \)-axis. The linear properties are retrieved using the standard scattering-parameter retrieval techniques [9, 10, 11], while the fields scattered by the presence of the appropriate nonlinearity are measured at the output and input ports and fed into the above nonlinear retrieval equations. For the simulations of SHG, the retrieval equations yield the effective electric and magnetic second-order susceptibilities \( \chi^{(2)}_{e,xxx}(2\omega; \omega, \omega) \) and \( \chi^{(2)}_{m,yyy}(2\omega; \omega, \omega) \), re-
spectively. For SPM, the retrieved parameters are the effective electric and magnetic third-order susceptibilities $\chi^{(3)}_{e,xxxx}(\omega; \omega, -\omega, \omega)$ and $\chi^{(3)}_{m,yyyy}(\omega; \omega, -\omega, \omega)$, respectively.

Though the local fields will inevitably contain multiple field components, the boundary conditions at the ports enforce the scattered waves to be the same polarization as the incident wave. Thus, even though the local fields will probe all elements of the local nonlinear tensor in the dielectric, the simulations will ultimately investigate just a single element of each of the NLMM’s effective nonlinear tensors. The polarization and orientation used in the following simulations were chosen to ensure maximum coupling between the incident wave and the structure. Though it is not presented here, the full effective linear and nonlinear tensors can be retrieved by the same procedure, provided that the appropriate polarizations of the various contributing waves are enforced. In the following subsections, the tensorial notation in the material properties is omitted for brevity.

The higher-order susceptibility alone, however, is not an adequate measure of the enhancement over the bulk embedding medium, due to the simultaneous effect of the periodic inclusions on the medium’s impedance. Instead, we define the material figure of merit (see Appendix),

$$\kappa^{(2)} = \frac{Z(\omega)\sqrt{Z(2\omega)}}{Z_0} \chi^{(2)}_e + \frac{Z_0}{Z(\omega)\sqrt{Z(2\omega)}} \chi^{(2)}_m,$$

where $Z(\omega) = \sqrt{\frac{\mu(\omega)}{\epsilon(\omega)}}$ is the effective impedance of the NLMM and $Z_0$ is the impedance of free-space. This is a slight modification to the usual definition in a purely electric medium [109] (p. 445). With this definition, the corresponding material figure of merit of the nonlinear dielectric alone is

$$\kappa^{(2)}_d = \frac{Z_d^{3/2}}{Z_0} \chi^{(2)}_d,$$

where the subscript $d$ refers to the properties of the dielectric. For consistency, we
Figure 5.2: (Reproduced with permission from Ref. [84]. Copyright (2011) by the American Physical Society.) (a) An ELC embedded in a nonlinear dielectric. (b) The electric field norm at the resonance frequency. (c) The retrieved linear properties. (d) Log-scale plot of the second- and third-order electric field localization factors (Eq. (5.15)). (e-j) The retrieved electric and magnetic higher-order susceptibilities and corresponding material figures of merit, normalized by the nonlinear bulk dielectric: (e-g) are the second-order properties corresponding to SHG and (h-j) are the third-order properties corresponding to SPM. The real (solid blue curve) and imaginary (dashed green curve) parts are shown for the higher-order susceptibilities.

define an analogous material figure of merit for SPM,

$$\kappa^{(3)} = \frac{Z(\omega)^2}{Z_0} \chi_e^{(3)} + \frac{Z_0}{Z(\omega)^2} \chi_m^{(3)},$$

(5.13)

with units of m$^2$/W. It can be shown that the first-order correction in the power-dependent refractive index is directly related to this figure and given by $\Delta n = \frac{3}{4} \kappa^{(3)} I$, where $I$ is the field intensity. The material figure of merit in the third-order nonlinear dielectric alone is given by

$$\kappa_d^{(3)} = \frac{Z_d^2}{Z_0} \chi_d^{(3)}.$$

(5.14)

We reiterate here that the deviations of the NLMM’s effective nonlinearities from
that of the embedding medium are not due to the addition of nonlinearities, as we neglect the nonlinearity of the metal structures themselves, but rather come from the induced localization of the fundamental fields within the embedding dielectric. Additionally, since the retrieved properties are necessarily a sort of average over the whole unit cell, it may seem that the small volumes in which the majority of the field localization occurs will have the effect of counterbalancing the enhancement. Indeed, the additional nonlinear activity in the areas of high field concentration will be accompanied by reduced nonlinear activity in the areas of low field concentration. However, since the local nonlinear effects scale as higher-order powers of the local fields, the field localization is in effect weighted more strongly than the effective reduction in contributing volume, and, consequently, the bulk nonlinear susceptibility must take on a larger value than the background medium alone. To measure the degree of field localization, we introduce the localization factor, analogous to the enhancement factors employed in previous plasmonic studies [97, 98],

\[
L(|E|^\alpha) = \frac{\int_V |E_{\text{MM}}(\vec{r})|^\alpha d\vec{r}^3}{\int_V |E_{\text{hom}}(\vec{r})|^\alpha d\vec{r}^3},
\]

(5.15)

where the numerator is a volume integral of the fundamental electric field norm raised to the \(\alpha\) power, integrated over the metamaterial unit cell. The denominator is the same integral but for a homogeneous slab with equivalent linear properties. Thus, \(L(|E|^\alpha)\) is a direct measure of the degree of inhomogeneity in the fields within the metamaterial, normalized by an otherwise equivalent homogeneous medium. As we show in the following subsections, the deviations of the NLMM’s effective nonlinearities from that of the embedding medium can be quite dramatic, especially when the structures are operated near resonance, where the second- and third-order localization factors reach their maximums.
5.2.1 The nonlinear electric-field-coupled resonator (ELC)

The ELC is a resonant metamaterial structure designed to exhibit an electric resonance [110]. The dominant coupling of the incident fields into and out of this structure is capacitive, and thus it is classified as an electric resonator. At resonance, the incident electric fields become highly confined in the capacitive gaps, as shown in Fig. 5.2 (b), making this an ideal structure for the resonant enhancement of the nonlinearities of any medium placed in these gaps.

The ELC employed here, displayed in Fig. 5.2 (a), is composed of 50 nm thick, 100 nm wide silver with two 100 nm gaps. The outer dimensions of the silver pattern are 1.6 µm, while the ELC itself is arranged in a cubic lattice with a lattice constant of 2 µm. For the SHG simulation, the nonlinear dielectric is given a non-zero second-order electric susceptibility for both fundamental and harmonic fields polarized in the x-direction. All other elements of the nonlinear tensors, both second- and third-order, are zero. For SPM, the dielectric’s nonlinearity takes the form of a non-zero third-order electric susceptibility for fields polarized in the x-direction. The retrieved linear properties are shown in Fig. 5.2 (c). The retrieved values of the second-order and third-order susceptibilities and material figures of merit, normalized by the nonlinear dielectric, are displayed in Fig. 5.2 (e-j). The higher-order magnetic susceptibilities are normalized by the impedance of free-space where appropriate.

As expected, the retrieved nonlinearities of the ELC show massive enhancements near the ELC’s resonance. The second-order and third-order figures of merit show peak values that are two orders and four orders of magnitude larger than the embedding nonlinear dielectric, respectively. The retrieved nonlinear susceptibilities themselves also show the expected Lorentzian features in their real and imaginary parts. It is noteworthy that the second-order properties show weaker (one order of magnitude) enhancements when the fundamental frequency corresponds to half the
resonance frequency. This behavior has been predicted before in several analytical studies [49, 74]. The nonlinear ELC also seems to support a non-negligible magnetic nonlinearity in both the SHG and SPM retrievals. However, the excitation of a magnetic moment in this structure for this particular polarization is impossible, and so these nonlinearities must be attributed to spatial dispersion. While spatial dispersion in the nonlinear properties of metamaterials will be treated elsewhere [111], we content ourselves here by noting that the magnetic properties have roughly a $\pi$ phase relation with the corresponding electric properties, akin to the ‘anti-resonance’ features common to linear metamaterial retrievals [112].
5.2.2 The nonlinear split-ring resonator (SRR)

The second structure we consider is the SRR, displayed in Fig. 5.3 (a), which also exhibits an LC-type resonance. In contrast to the ELC, however, the dominant coupling in this structure is inductive, coming from magnetic flux passing through the interior of the metallic ring. As such, the SRR is a magnetic resonator, and on resonance the electric fields, shown in Fig. 5.3 (b), become highly confined in the capacitive gap. Though the only nonlinearity present is the electric nonlinearity of the dielectric medium, the coupling of the generated electric fields to the magnetic resonance of the SRR makes the dominant effective nonlinearity magnetic in nature.

Like the ELC, the SRR is composed of 50 nm thick, 100nm wide silver, but with a single 100 nm gap. The outer dimensions and lattice constant are identical to the ELC. However, since the capacitive gap is rotated compared to the ELC, the highly localized electric fields of the SRR are dominantly in the $z$-direction. Thus, the dielectric’s nonlinearities considered in these simulations only involve fields polarized in the $z$-direction and, again, all other elements of the dielectric’s nonlinear tensors are set to zero. The retrieved linear, second-order, and third-order properties are displayed in Fig. 5.3 (c-j).

Again, for excitation near the resonance frequency of the SRR, the retrieved nonlinearities are highly enhanced compared to the bulk nonlinear dielectric. Many of the same features in the retrieval of the ELC are present, but with the difference that the effective nonlinearities are mostly magnetic in nature. The spatial dispersion effects are also slightly mitigated due to the lower resonance frequency of the SRR. Furthermore, while the SPM material figure of merit is slightly larger for the SRR, the ELC shows roughly double the enhancement in SHG. This can be explained in terms of the necessary overlap of the field distributions at the fundamental and second-harmonic frequencies required for efficient conversion in a bulk material, sim-
Figure 5.4: (Reproduced with permission from Ref. [84]. Copyright (2011) by the American Physical Society.) (a) A cut-wire medium embedded in a nonlinear dielectric. (b) The electric field norm at 10 THz. (c) The retrieved linear properties. (d) Log-scale plot of the second- and third-order electric field localization factors (Eq. (5.15)). (e-j) The retrieved electric and magnetic higher-order susceptibilities and corresponding material figures of merit, normalized by the nonlinear bulk dielectric: (e-g) are the second-order properties corresponding to SHG and (h-j) are the third-order properties corresponding to SPM. The real (solid blue curve) and imaginary (dashed green curve) parts are shown for the higher-order susceptibilities.

ilar to the nonlinear coupling between different modes in a waveguide. Because the $x$-component of the local electric field is dominant at all frequencies in the ELC, the coupling between the field distributions at different frequencies is more efficient than in the SRR, where the $z$-component of the local electric field is only strong for frequencies sufficiently close to the resonance. For SPM, where all involved frequencies are degenerate, the mode overlap is identically unity in both structures.

5.2.3 The nonlinear cut-wire medium

The cut-wire medium, on the other hand, can be employed as a non-resonant metamaterial, often to provide a relatively broadband electric response. Though this
medium will lack the dramatic resonance-induced enhancements of the SRR and ELC, it supports an inhomogeneous field distribution, as seen in Fig. 5.4 (b), with electric fields weakly confined to the capacitive gap between neighboring cut-wires. Like the ELC, coupling between this structure and the incident fields is capacitive in nature.

The cut-wire structure, shown in Fig. 5.4 (a), is composed of a silver rectangular rod, 100 nm thick, 200 nm wide, with a gap of 100 nm between neighboring cut-wires. These dimensions are thicker than the previous structures in order to reduce the cut-wire’s effective inductance, ensuring operation well below the structure’s resonance. The lattice constant is 2 \( \mu \)m in all directions. For the SHG simulation, the embedding dielectric is given a non-zero second-order electric susceptibility for both fundamental and harmonic fields polarized in the \( x \)-direction. For SPM, the dielectric’s nonlinearity takes the form of a non-zero third-order electric susceptibility for fields polarized in the \( x \)-direction. The retrieved linear, second-order, and third-order properties are displayed in Fig. 5.4 (c-j).

The retrieved nonlinearities of the cut-wire medium are very different from the previous two resonant structures. For a fundamental frequency of 10 THz, roughly the frequency of interest for this analysis, the enhancement in SHG is 5-fold, while the nonlinearity for SPM is 56 times greater than the nonlinear dielectric alone. While these enhancements are much less dramatic than the resonant SRR and ELC, they deserve some discussion. Unlike its resonant counterparts, the cut-wire medium shows fairly broadband enhancements of the material figures of merit, asymptoting at low frequencies to values greater than unity. Moreover, these enhancements are not accompanied by significant losses. In fact, the effective loss tangents at 10 and 20 THz in the cut-wire medium are just \( 1.1 \times 10^{-3} \) and \( 2.8 \times 10^{-3} \), respectively. Spatial dispersion effects are also much less prominent. Thus, there exists a significant trade-off between resonant and non-resonant metamaterial structures in terms of enhancing
5.2.4 The nonlinear I-beam structure

The I-beam structure belongs to the same category of non-resonant electric metamaterials as the previous cut-wire medium, but with the extended arms providing additional capacitance. Due to the increased capacitance, the I-beam supports a stronger electric response and confines a greater fraction of the incident field to the gaps between neighboring structures than the cut-wire medium, as seen in Fig. 5.5 (b) and (d). Thus, this medium can be expected to show a strong, broadband enhancement of the embedding medium’s nonlinearities.
The I-beam, displayed in Fig. 5.5 (a), consists of 100 nm thick, 200 nm wide silver in the shape of an ‘I’, with arms that extend 1.6 µm from tip-to-tip. The lattice constant and gap between neighboring I-beams are 2 µm and 100 nm, respectively. The embedding dielectric used is the same as the nonlinear cut-wire and ELC mediums. The retrieved linear, second-order, and third-order properties are displayed in Fig. 5.5 (c-j).

As expected, the I-beam structure shows similar features to the cut-wire medium, but with much larger overall enhancements. For a fundamental frequency of 10 THz, the SHG and SPM material figures of merit are enhanced by a factor of 55 and 400, respectively, both roughly an order of magnitude larger than the cut-wire medium. However, the useable frequency range of the I-beam structure is significantly reduced: the capacitance is so large that the resonance frequency of this structure is brought into view. The massive spatial dispersion in both the linear and nonlinear properties call into question the validity of the SHG retrieval at 10 THz, as the second-harmonic frequency passes through the resonance frequency well below the 10 THz target frequency for the fundamental. However, the low frequency asymptotic value for SHG is still valid, as well as the SPM results, which do not suffer from involving a frequency at twice the fundamental frequency. Additionally, at 10 THz, the effective loss tangent is $1.1 \times 10^{-2}$, more than small enough to consider the nearly three orders of magnitude enhancement in the SPM material figure of merit a low-loss, non-resonant effect. Thus, there exists a trade-off between the cut-wire and I-beam structures, where the operational frequencies, the loss tangent, and the magnitude of the enhancement can be weighed against one another for a given application.

5.3 Calculation of the nonlinear conversion efficiencies

The retrieved parameters of the previous section fully characterize the four nonlinear metamaterials, allowing for the metamaterials to be analyzed as if they were per-
fectly homogeneous materials. Thus, we are in a position to give a more thorough analysis of the NLMMs in terms of their applicability in realistic nonlinear devices. In particular, the NLMMs presented here offer competing effects in the enhancement of nonlinear phenomena: on the one hand, they show nonlinearities that are orders of magnitude larger than the embedding medium alone; on the other hand, the periodic metallic inclusions are a major source of ohmic losses, constraining the maximum lengths of any resulting devices. Before NLMMs can be endorsed as an avenue to improving on existing nonlinear devices, the NLMM enhancement effect must be weighed against the accompanying losses in the context of realistic device specifications. In this section, using a coupled mode theory derived for homogeneous materials, we calculate the figures of merit and conversion efficiencies for nonlinear devices based on slabs of the four NLMMs, analyzing both the second- and third-order processes. We show that, despite the severe constraints imposed by material losses, the NLMMs are able to support reasonable conversion efficiencies in the form of compact, even subwavelength, devices.

5.3.1 Second-harmonic generation

SHG from a monochromatic, planar wave, travelling in a homogeneous second-order nonlinear medium, can be described by a coupled mode analysis. Using the simplifying assumptions of non-depleted pump and slowly varying amplitude, the following expression can be derived for the output second-harmonic intensity [109]:

\[
I_{\text{out}}(2\omega) = \frac{\omega^2}{2c^2} |\kappa(2) [I_{\text{in}}(\omega)]^2 L^2 h(L),
\]

(5.16)

where \(L\) is the total interaction length, \(I_{\text{in}}(\omega)\) is the input intensity of the fundamental wave, and

\[
h(L) = \exp \left[ - \left( \frac{\alpha(2\omega)}{2} + \alpha(\omega) \right) L \right] \frac{[\sinh(\Delta\alpha L/2)]^2}{(\Delta\alpha L/2)^2}
\]

(5.17)
contains the contributions from the absorption coefficients \(\alpha(\omega)\) at both frequencies, and \(\Delta \alpha\) is given by

\[
\Delta \alpha = \frac{\alpha(2\omega)}{2} - \alpha(\omega).
\]  

(5.18)

Note that, for the sake of narrowing the focus of the analysis, the terms dependent on the phase mismatch between the interacting waves have been removed.

From the above, we can define the system’s conversion efficiency as

\[
\eta(2) = \frac{I_{\text{out}}(2\omega)}{I_{\text{in}}(\omega)} = \frac{\omega^2}{2c^2} |\kappa^{(2)}|^2 L^2 h(L) I_{\text{in}}(\omega).
\]

(5.19)

In determining the maximum efficiency and the corresponding device length for SHG, we find the quantity \(L^2 h(L)\) to be maximized by an optimum interaction length

\[
L_{\text{opt}} = \frac{2}{\Delta \alpha} \tanh^{-1}\left(\frac{\Delta \alpha}{\alpha(2\omega)/2 + \alpha(\omega)}\right).
\]

(5.20)

For interaction lengths longer than \(L_{\text{opt}}\), linear absorption begins to dominate, and the conversion efficiency declines.

We use Eqs. (5.19) and (5.20), together with the retrieved parameters of the four NLMMs, to calculate realistic device sizes and efficiencies. For the ELC and SRR, we choose optimum fundamental frequencies close to the respective resonance frequencies to maximize the resonant enhancement. A fundamental frequency of 10 THz is used for the cut-wire medium, while the I-beam structure, to avoid significant spatial dispersion, is operated at 5 THz, noting that the efficiencies of these non-resonant structures are characteristic of broad frequency bands. The ratio of the efficiencies of the NLMMs to the nonlinear dielectric alone is given by

\[
F(\eta^{(2)}) = \frac{\eta^{(2)}}{\eta_d^{(2)}} = h(L) \left| \frac{\kappa^{(2)}}{\kappa_d^{(2)}} \right|^2.
\]

(5.21)
This quantity directly compares devices of the same lengths, operating frequencies, and input powers, while taking into account both the enhancement effect and the additional losses introduced by the periodic metallic inclusions. Thus, $F(\eta^{(2)})$ represents a complete, albeit simplistic, measure of the relative performances of NLMMs and natural materials as frequency doublers. The optimum lengths and efficiencies for all four NLMMs are displayed in Table 5.1, assuming a value of $\chi_d^{(2)} = 20 \text{ pm/V}$ for the embedding nonlinear dielectric, and an input intensity of $I_{in}(\omega) = 40 \text{ MW/cm}^2$.

Table 5.1: (Reproduced with permission from Ref. [84]. Copyright (2011) by the American Physical Society.) Optimal lengths, efficiencies, and normalized efficiencies for SHG in each NLMM. The conversion efficiencies are calculated using the value $\chi_d^{(2)} = 20 \text{ pm/V}$ for the nonlinear dielectric, and assuming an input intensity of $40 \text{ MW/cm}^2$.

<table>
<thead>
<tr>
<th>NLMM</th>
<th>$\omega (2\pi \times \text{THz})$</th>
<th>$L_{opt}$ ($\mu$m)</th>
<th>$\eta^{(2)} (\times 10^{-6})$</th>
<th>$F(\eta^{(2)})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELC</td>
<td>11.4</td>
<td>4</td>
<td>8.65</td>
<td>1170</td>
</tr>
<tr>
<td>SRR</td>
<td>8.6</td>
<td>4</td>
<td>1.07</td>
<td>253</td>
</tr>
<tr>
<td>cut-wire</td>
<td>10</td>
<td>650</td>
<td>456.12</td>
<td>3.03</td>
</tr>
<tr>
<td>I-beam</td>
<td>5</td>
<td>216</td>
<td>132.32</td>
<td>31.9</td>
</tr>
</tbody>
</table>

Though the above analysis ignores the role of phase matching, this interesting and crucial factor deserves a few words. In principal, conventional approaches to phase matching [49] should be largely applicable to NLMMs based on periodic inclusions in a nonlinear dielectric by applying the same techniques to the embedding medium itself. However, due to the range and configurability in their linear properties, NLMMs may offer unique advantages in overcoming phase mismatch. For example, a number of recent studies have revealed novel configurations for phase matching and quasi-phase matching (QPM) that are singular to NLMMs [113, 114, 89, 115]. Furthermore, the relatively small interaction lengths proposed in Table 5.1 have the added effect of relaxing the constraints imposed by phase mismatch. As a numerical example, the coherence length in the nonlinear ELC for a fundamental frequency of
11.4 THz is \( L_{\text{coh}} = 2\pi / \Delta k = 14.9\ \mu m \), which is actually larger than the optimum interaction length, making phase mismatch essentially a non-factor in this structure. Thus, phase matching should not pose a significant challenge to the implementation of NLMMs in nonlinear devices, and could ultimately prove to be an advantage. A detailed analysis of phase matching in NLMMs will be treated in the next chapter.

5.3.2 Self-phase modulation

Among third-order nonlinear processes, SPM has unique applications with its own set of definitions and figures of merit. However, since it is our intention to investigate the enhancement properties of NLMMs on third-order processes in general, we omit a discussion of the particulars of SPM and instead describe the process through a coupled mode analysis, analogous to SHG. Specifically, we continue to invoke the non-depleted pump approximation, and calculate the intensity of the nonlinear scattered fields. Though the non-depleted pump is inappropriate for describing most devices involving SPM, such as directional couplers, the following analysis and figures of merit have the advantage of being readily applicable to third-order processes in general, such as non-degenerate four-wave mixing. For a more detailed analysis of metamaterials for optical switching and related applications, the reader is referred to Ref. [38].

Let us consider a monochromatic, planar wave, travelling in a homogeneous third-order nonlinear medium. In the non-depleted pump limit and taking the slowly varying amplitude approximation, we can describe the SPM process in terms of the intensity of the nonlinear scattered fields, given by

\[
I_{\text{out}}^{\text{NL}}(\omega) = \frac{9}{16} \frac{\omega^2}{c^2} |\kappa^{(3)}|^2 L^2 g(L) \left[ I_{\text{in}}^{\text{FF}}(\omega) \right]^3, \tag{5.22}
\]

where

\[
g(L) = \exp \left[ -2\alpha(\omega)L \right] \tag{5.23}
\]
contains the effect of propagation losses on efficiency. It follows that the conversion efficiency is given by the ratio of the nonlinear scattered intensity to the input intensity,
\[
\eta^{(3)} = \frac{I_{\text{NL}}^{\text{out}}(\omega)}{I_{\text{FF}}^{\text{in}}(\omega)} = \frac{9}{16} \frac{\omega^2}{c^2} |\kappa^{(3)}|^2 L^2 g(L) \left[ \frac{I_{\text{FF}}^{\text{in}}(\omega)}{\alpha(\omega)} \right]^2
\]  
(5.24)

As before, we find an optimum interaction length by maximizing the quantity \(L^2 g(L)\), so that maximum efficiency is obtained for a slab of length
\[
L_{\text{opt}} = \frac{1}{\alpha(\omega)}.
\]  
(5.25)

Normalizing Eq. (5.24) by the efficiency of the dielectric alone, we arrive at the figure of merit describing the enhancement of third-order nonlinear process in the four NLMMs:
\[
F(\eta^{(3)}) = \eta^{(3)} \eta_d^{(3)} g(L) \left| \frac{\kappa^{(3)}}{\kappa_d^{(3)}} \right|^2.
\]  
(5.26)

The optimum lengths and conversion efficiencies for SPM in the four NLMMs are displayed in Table 5.2, assuming a value of \(\chi_d^{(3)} = 10^{-20} \text{ m}^2/\text{V}^2\) for the embedding nonlinear dielectric, and an input intensity of \(I_{\text{FF}}^{\text{in}}(\omega) = 40 \text{ MW/cm}^2\).

Table 5.2: (Reproduced with permission from Ref. [84]. Copyright (2011) by the American Physical Society.) Optimal lengths and conversion efficiencies for SPM in each NLMM. The conversion rates are calculated using the value \(\chi_d^{(3)} = 10^{-20} \text{ m}^2/\text{V}^2\) for the nonlinear dielectric.

<table>
<thead>
<tr>
<th>NLMM</th>
<th>(\omega \times (2\pi \times \text{THz}))</th>
<th>(L_{\text{opt}} \times (\mu\text{m}))</th>
<th>(\eta^{(3)} \times 10^{-7})</th>
<th>(F(\eta^{(3)}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELC</td>
<td>11.5</td>
<td>2</td>
<td>4.25</td>
<td>8.25 \times 10^6</td>
</tr>
<tr>
<td>SRR</td>
<td>8.7</td>
<td>2</td>
<td>8.70</td>
<td>2.95 \times 10^7</td>
</tr>
<tr>
<td>cut-wire</td>
<td>10</td>
<td>1124</td>
<td>51.28</td>
<td>417</td>
</tr>
<tr>
<td>I-beam</td>
<td>10</td>
<td>66</td>
<td>9.39</td>
<td>2.21 \times 10^4</td>
</tr>
</tbody>
</table>

In the resonant structures for both the second-order and third-order nonlinear processes, however, the linear absorption in the metamaterials is strong enough to potentially invalidate the slowly varying amplitude approximation. In order to verify
the above results, the conversion efficiencies of the ELC and SRR were calculated directly using the nonlinear transfer matrix method [68], finding the error to be less than 25% in all cases.

5.4 Anisotropy and poling in the effective nonlinear tensors

Within an *inhomogeneous* medium, the local fields can vary quite dramatically from the macroscopic and applied fields, both in magnitude and direction [59, 116, 117]. While field concentration has been a driving force in the search for metamaterials and plasmonic media with enhanced nonlinear coefficients [2, 118, 102, 84, 54, 56], control over field orientation has received less attention. However, it is this control of the directionality of the local fields that allows access to effective properties of fundamentally different natures than the constitutive materials. Not only can metamaterials lead to effective magnetic and magneto-electric behavior, but they can also control the anisotropy of optical properties. In effect, manipulating the directionality of the local fields in metamaterials can supplement the overall enhanced coefficients, while offering additional degrees of functionality and flexibility. The following section is reproduced with permission from Alec Rose, Ryan Latterman, David R. Smith, and Philip Sullivan, Applied Physics Letters 103, 031102, 2013. Copyright (2013) by the American Institute of Physics.

If we assume a metamaterial with negligible magnetism and losses, we can employ the coupled-mode theory of chapter 4 to relate the effective $\chi^{(2)}$ to overlap integrals in the limit that the lattice constant is much smaller than a wavelength, [82]

$$\chi^{(2)}_{ijk} = \frac{1}{V_0} \int \int \int_{V_0} dV \vec{\chi}^{(2)}(\vec{r}) : \vec{e}_j(\vec{r}) \vec{e}_k(\vec{r}) \cdot \vec{e}_i(\vec{r}), \quad (5.27)$$

where $\vec{e}_n(\vec{r})$ is the electric field of the Bloch mode with macroscopic polarization and frequency indexed by $n$, and the integral is performed over a single unit-cell with
Figure 5.6: (Reproduced with permission from Ref. [119]. Copyright (2013) by the American Institute of Physics.) Sketch of a Pockels cell composed from a nanoparticle-ONLO composite, with variable dimensions indicated (a). The gap size is controlled by the extent of the ONLO around the nanorod, while we define the overlap as the percentage of the nanorod that coincides transversely with its nearest neighbors. Illustration of polymer ordering before (b) and after (c) a poling field is applied to the medium.

If the Bloch modes were nothing more than simple plane waves, as in a homogeneous medium, then it is clear that the effective susceptibility would be a simple volume average of the local one, and only the (typically) weaker off-diagonal tensor elements could couple waves with orthogonal polarizations. However, due to the inhomogeneous nature of the metamaterial, the local electric fields can overlap despite the orthogonality of the macroscopic fields, leading to great flexibility in the effective nonlinear tensors. The consequences of Eq. (5.27) are most evident in electrooptics, indicating that a simple poling voltage in an inhomogeneous metamaterial can lead to strong coupling of originally orthogonal polarizations. When one of these polarizations is associated with the metamaterial’s internal resonance, the overall
effect can be quite dramatic. Moreover, an applied poling field or voltage can likewise induce local fields that are much stronger, or even differently oriented, than the applied field, leading to poling thresholds and configurations that are distinct from a simple bulk medium.

Figure 5.7: (a) Illustration of the nanorod-polymer array, with the basic rectangular unit-cell indicated by the dashed red box. Plot of the real (b and c) and imaginary (d and e) parts of the effective indices for both polarizations.

As a demonstrative example, consider the simple idealized nanoparticle array shown in Fig. 5.7 (a), consisting of gold nanorods 65 nm in length and 8 nm in diameter, and coated in an organic nonlinear optical dielectric (ONLO) ($\varepsilon = 2.19$). These nematic-like (alternating) gold nanorods are loosely based on those in Refs. [120, 121], and are known to support a polarization sensitive plasmonic resonance [122]. Using a transfer-matrix based nonlinear retrieval method, we show that this class of metamaterial supports a set of non-zero Pockels coefficients at telecommunication wavelengths that are both distinct in orientation and enhanced in magnitude compared to the ONLO alone. By changing the interstitial spacing (gap) and overlap between nearest neighbors, along with the choice of poling orientation,
we demonstrate a continuum of nonlinear tensor configurations and strengths. Ultimately, metamaterials with this degree of control over the effective nonlinear tensor can lead to Pockels cells with reduced dimensions and poling thresholds.

In the linear regime, fields normally incident on the surface of such a structure can be decomposed into two orthogonal polarizations, corresponding to the electric field parallel (\(\hat{z}\)) and transverse (\(\hat{x}\)) to the rod axis. For light with wavelength \(\lambda = 1530\) nm, as in typical telecommunications systems, we can describe the anisotropic interaction through effective complex indices of refraction, \(n_j = n_j' + i n_j''\), applying the well-known set of retrieval equations [11] to the results of finite-element simulations (COMSOL multiphysics). We simulate a single unit-cell, defined by the dashed red box in Fig. 5.7 (a), using periodic boundary conditions along the transverse boundaries and assuming a lattice constant of 100 nm in the direction of propagation (\(\hat{y}\)). The resulting effective indices are displayed in Fig. 5.7 (b). As expected, for certain combinations of gap and overlap, the \(\hat{z}\) polarization excites the dominant plasmonic resonance at \(\lambda = 1530\) nm, as evidenced by the strong peak in absorption (\(n_z''\)). At the same time, the \(\hat{x}\) polarization exhibits near transparency (\(n_x \approx 1\)). However, it is interesting to note that despite such large anisotropy, both polarizations will tend to excite significant electric fields in the gaps between adjacent nanorods, dominantly oriented transverse to the rod surfaces. This is illustrated in Fig. 5.8 for DC fields: while the macroscopic fields drive charge buildup in the individual nanorods, the overlap between nearest neighbor nanorods focuses the energy into these gaps, regardless of polarization.

In addition, this analysis immediately reveals the potential for lowering the effective poling thresholds in such a structure. Confinement of energy in small gaps must be accompanied by local field enhancement, and so macroscopic poling fields can be reduced while still achieving the required field strengths to pole the ONLO located within the gaps. As a rough measure of this factor in poling threshold reduction, we
plot the local electric field at the center-point between two nanorods, normalized by the applied field, as a function of gap and overlap in Fig. 5.8 (b) for both transverse poling configurations. Both configurations display poling threshold reductions, while the local directionality of the second-order material is now a function of the applied field and the local structure.

In calculating the effective nonlinear coefficients of the nanorod metamaterial, we turn to the recently developed transfer-matrix based retrieval method [67, 70], which has shown success in determining the susceptibilities related to second-harmonic generation and self-phase modulation in similar structures [83, 84]. In particular, we investigate the Pockels effect, in which a propagating field is modified by the presence
of a strong DC or slowly varying electric field. However, a similar method could be applied to determine effective wave-mixing coefficients.

Again using finite-element simulations via COMSOL multiphysics, we first simulate the poling field by applying a voltage in either of the transverse poling configurations. To simplify and generalize our results, we assume the ONLO will orient itself completely in the direction of the local poling field, and only consider the local nonlinear susceptibility along this axis. Next, we use the product of propagating and DC fields to excite the ONLO according to its local nonlinear tensor, collecting the re-radiated fields at the entrance and exit planes of the simulation, as in Ref. [84]. The nonlinear retrieval method is applied to this result to give the effective nonlinear susceptibility, and the process is repeated for all possible permutations of poling and propagating polarizations. From the nonlinear susceptibilities, we can calculate the Pockels coefficients according to

$$r_{ij} = \frac{\epsilon_0^2}{\epsilon_r} \chi_{ijk}^{(2)}.$$  

For comparison, we consider electrooptic modulation of the refractive indices, proportional to the material figure of merit, $(n_in_j)^{3/2}r_{ijk}$ [49]. The magnitudes of these figures of merit are normalized by $n^3r_{33}$ of the ONLO alone and plotted in Fig. 5.9, according to the usual contracted index notation, for all non-zero elements in the two transverse poling configurations.

As expected, the coefficients $r_{33}$ and $r_{31}$ are largest in magnitude, enhanced by more than an order of magnitude for the geometries that support plasmonic resonances close to the operational wavelength, $\lambda = 1530$ nm. The coefficients $r_{51}$ and $r_{53}$, though weaker, are interesting from an additional perspective: $r_{51}$ and $r_{53}$ represent the ability of a DC field to induce coupling between the two originally orthogonal polarizations. In this way, the transparency of the $\hat{x}$ polarized wave can be switched off by forcing it to couple to the inherently lossy plasmonic resonance of the nanorods. This differs drastically from a homogeneous medium, which would need to employ an ONLO that itself had large off-diagonal tensor elements, limiting
Figure 5.9: Magnitude of the Pockels coefficient figures of merit for the gold nanorod-ONLO array, \((n_i n_j)^{3/2} r_{ijk}\), normalized by the figure of merit for the ONLO itself, in dB. The plots are separated by row, corresponding to the two transverse poling configurations, shown schematically: poling field along \(\hat{z}\) (top row) and poling field along \(\hat{x}\) (bottom row).

5.5 Appendix: Second-harmonic generation in a doubly nonlinear medium

We present here a derivation of the second-harmonic intensity in a medium with second-order nonlinear dependencies on the incident fields in both the electric polarization and magnetization. This analysis assumes plane waves with a single polarization, no losses, and real material parameters, but can be extended to these more complex regimes by standard perturbations [66]. A similar development can be employed for other three- and four-wave mixing processes in a doubly nonlinear medium.

Let us consider a linearly polarized plane wave travelling with angular frequency
through a homogeneous, isotropic medium. We orient our axes such that the
electric field is along the $x$-axis, magnetic field along the $y$-axis, and propagation is
in the positive $z$-direction. Using the convention that $\vec{E}(z,t) = \sum_n \frac{1}{2} \vec{E}(\omega_n) e^{-i\omega_n t}$, and
likewise for the other field variables, the $x$-component of the second-order electric
polarization at frequency $2\omega$ is given by [49]

$$P^{(2)}(2\omega) = \frac{1}{2} \epsilon_0 \chi^{(2)}(2\omega; \omega, \omega) [E(\omega)]^2,$$

where, owing to the linear polarization of the involved fields, we have substituted
scalars for the usual vectors and tensors. The magnetization is defined in an analo-
gous way:

$$M^{(2)}(2\omega) = \frac{1}{2} \chi_m^{(2)}(2\omega; \omega, \omega) [H(\omega)]^2,$$

Thus, the material equations can be written as

$$D(2\omega) = \epsilon(2\omega) E(2\omega) + P^{(2)}(2\omega),$$

$$B(2\omega) = \mu(2\omega) H(2\omega) + \mu_0 M^{(2)}(2\omega),$$

where $\epsilon(\omega)$ and $\mu(\omega)$ are the absolute, frequency-dependent permittivity and perme-
ability. For brevity, the frequency dependence of the field quantities will be denoted
through subscripts.

We start from Maxwell’s equations for time-harmonic fields, considering a second-
order polarization and magnetization,

$$\nabla \times \vec{H}_2 = -i2\omega \left( \epsilon_2 \vec{E}_2 + \vec{P}^{(2)} \right),$$

$$\nabla \times \vec{E}_2 = i2\omega \left( \mu_2 \vec{H}_2 + \mu_0 \vec{M}^{(2)} \right),$$

$$\nabla \cdot \vec{D}_2 = 0,$$

$$\nabla \cdot \vec{B}_2 = 0.$$
In the absence of the nonlinear terms, and with the above assumptions, Eqs. (5.33) - (5.36) have solutions of the form

\[ \vec{E}_2 = (e^+_2 \exp(ik_2 z) + e^-_2 \exp(-ik_2 z)) \hat{x}, \]  
\[ \vec{H}_2 = (h^+_2 \exp(ik_2 z) + h^-_2 \exp(-ik_2 z)) \hat{y}, \]

where \( k_2 = 2\omega \sqrt{\epsilon_2 \mu_2} \). We take the ansatz that the solutions in the presence of the nonlinearities are simply a perturbation of the solutions to the linear problem, where \( e^\pm_2 \) and \( h^\pm_2 \) are taken to be spatially varying in \( z \). Furthermore, we assume the slowly varying amplitude approximation, such that the forward and backward propagating terms can be considered decoupled from each other and thus solved independently.

Focusing solely on the forward propagating terms, we substitute our trial solutions into Eqs. (5.33) and (5.34), giving

\[ -ik_2 H_2 - \frac{dh_2}{dz} \exp(ik_2 z) = -i2\omega (e_2 E_2 + P^{(2)}), \]  
\[ ik_2 E_2 + \frac{de_2}{dz} \exp(ik_2 z) = i2\omega (\mu_2 H_2 + \mu_0 M^{(2)}), \]

We solve Eq. (5.39) for \( H_2 \) and substitute this into Eq. (5.40),

\[ ik_2 E_2 + \frac{de_2}{dz} \exp(ik_2 z) = \]  
\[ i2\omega \left( Z_2 \left( e_2 E_2 + P^{(2)} + \frac{i}{2\omega} \frac{dh_2}{dz} \exp(ik_2 z) \right) + \mu_0 M^{(2)} \right), \]

where \( Z_2 = \sqrt{\frac{\mu_2}{\epsilon_2}} \) is the impedance of the medium. Rearranging and cancelling terms, we arrive at the following expression:

\[ \left( \frac{de_2}{dz} + Z_2 \frac{dh_2}{dz} \right) \exp(ik_2 z) = i2\omega \left( Z_2 P^{(2)} + \mu_0 M^{(2)} \right), \]

Next, we introduce the quantity \( \gamma = e_2 + Z_2 h_2 \) and use Eqs. (5.28) and (5.29) to give

\[ \frac{d\gamma}{dz} = i\omega \left( Z_2 \epsilon_0 \chi_{e}^{(2)} e_1^2 + \mu_0 \chi_{m}^{(2)} h_1^2 \right) \exp(i\Delta k z), \]
where \( \Delta k = 2k_1 - k_2 \) is the phase mismatch.

For simplicity, we assume the non-depleted pump approximation, such that \( e_1 \) and \( h_1 \) are constants that satisfy the linear form of Maxwell’s equations with \( e_1 = Z_1 h_1 \). Thus, the above equation can be integrated over an interaction length \( L \) with the boundary condition \( \gamma(0) = 0 \), giving

\[
\gamma(L) = i\omega \sqrt{\frac{Z_2}{Z_1}} \frac{e_1^2 \exp(i\Delta k L)}{i\Delta k} \left( \epsilon_0 Z_1 \sqrt{Z_2 \chi_e^{(2)}} + \mu_0 \frac{1}{Z_1 \sqrt{Z_2}} \chi_m^{(2)} \right).
\]  

(5.44)

If at the point \( z = L \) a significant amount of second-harmonic field has built up, we can take the approximation that \( |\frac{de_2}{dz}(L)| \) and \( |\mu_0 \omega \chi_m^{(2)} h_1^2| \) are small compared to the other terms in Eq. (5.40), implying that \( i k_2 E_2(L) = i2\omega \mu_2 H_2(L) \), or equivalently \( e_2(L) = Z_2 h_2(L) \). Thus, in this limit, \( \gamma(L) = 2e_2(L) \), and we find that

\[
e_2(L) = \frac{\omega}{2c} \frac{\sqrt{Z_2}}{Z_1} e_1^2 \kappa^{(2)} \exp(i\Delta k L) - 1 \left( \epsilon_0 Z_1 \sqrt{Z_2 \chi_e^{(2)}} + \mu_0 \frac{1}{Z_1 \sqrt{Z_2}} \chi_m^{(2)} \right),
\]

(5.45)

where we have introduced the material figure of merit

\[
\kappa^{(2)} = \frac{Z_1 \sqrt{Z_2}}{Z_0} \chi_e^{(2)} + \frac{Z_0}{Z_1 \sqrt{Z_2}} \chi_m^{(2)},
\]

(5.46)

and \( Z_0 \) is the impedance of free space. Looking at this equation, it is clear that the electric field at the second-harmonic is a phase-sensitive superposition of the contributions from the electric and magnetic nonlinearities alone. Subsequently, we define the fundamental and second-harmonic intensities according to

\[
I_1 = \frac{1}{2Z_1} |e_1|^2 \quad \text{and} \quad I_2(L) = \frac{1}{2Z_2} |e_2(L)|^2,
\]

(5.47)

and finally obtain

\[
I_2(L) = \frac{\omega^2}{2c^2} |\kappa^{(2)}|^2 I_1^2 L^2 \sin^2 \left( \frac{\Delta k L}{2} \right) \left( \frac{\Delta k L}{2} \right)^2.
\]

(5.48)
In the presence of dispersion, the phase matching conditions are not automatically satisfied and a wavevector mismatch will exist. The effect of this mismatch can be visualized more clearly by considering the nonlinear material as an infinite collection of radiation sources. The distribution and phase of each source is determined by the polarization of the material, which in turn is dependent on both the material’s properties and the incident radiation. As with an antennae array, the direction and magnitude of the produced radiation is determined by the strength and relative phases of the many sources. Dispersion tends to induce phase misalignment in these radiation sources, and thus is often a prominent factor limiting the efficiency of natural nonlinear materials. The advantage of metamaterials then, in this context, is that they vastly extend the achievable range of linear and nonlinear properties. These novel and often extreme properties, such as negative refraction, can offer a variety of solutions to phase matching in wave-mixing processes. The following chapter is reprinted with permission from Alec Rose, David R. Smith, Optical Materials Express, 1, 1232, 2011. Copyright (2011) by The Optical Society.

We begin the analysis with the general expressions for phase matching, discussing
the conventional techniques and their usages and limitations. Next, we define five broad categories of phase matching techniques in metamaterials: anomalous dispersion phase matching, birefringence phase matching, quasi-phase matching, negative-index phase matching, and index-near-zero phase matching, which make up Sections 3 through 7. While Sections 3 through 5 discuss the application of conventional techniques to metamaterials, Sections 6 and 7 outline unique phase matching configurations that have only been achieved in metamaterials. In each case, numerical and/or experimental examples are given to demonstrate the various forms of phase matching. Finally, we conclude our paper in Section 8, summarizing our results and offering an outlook for the potential applications of nonlinear metamaterials.

6.1 Wave-mixing and phase mismatch: an overview

Wave-mixing refers broadly to processes involving the interaction between multiple photons, mediated by a nonlinear medium. As such, these processes are subject to two major constraints: conservation of photon energy and conservation of photon momentum. For simplicity, we will focus on three-wave mixing in a medium with a bulk second-order nonlinear susceptibility, noting that the conclusions of this paper can be extended to higher-order wave-mixing processes. For three-wave mixing of plane waves in a homogeneous medium, energy and momentum conservation can be written as

\[ \omega_1 + \omega_2 = \omega_3 \]  

(6.1)

and

\[ \vec{k}_1 + \vec{k}_2 = \vec{k}_3, \]  

(6.2)

following the convention \( \omega_1 \leq \omega_2 \leq \omega_3 \). These equations apply to all three-wave mixing processes, such as difference frequency generation, sum frequency generation, and optical parametric amplification and oscillation. For the wave-mixing process
to be efficient, both Eqs. (6.1) and (6.2) must be satisfied to within the uncertainties given by the system’s finite spatial and temporal extents [123]. Moreover, it is convenient to define the phase mismatch \( \Delta k = |\vec{k}_1 + \vec{k}_2 - \vec{k}_3| \). The physical meaning of the phase mismatch can be understood by considering the coherence length \( L_{\text{coh}} = \frac{2\pi}{\Delta k} \), which is the propagation length required for the lower-frequency and high-frequency waves to complete a full phase cycle relative to each other. When the phase matching condition is met, the coherence length becomes infinite.

Since the wave-mixing interaction requires spatio-temporal overlap between the interacting waves, most systems are restricted to the case where the wavevectors are co-linear. Taking propagation to be along the \( z \)-axis, we can write \( \vec{k}_i = \pm \frac{n_i \omega_i}{c} \hat{z} \), where the \( \pm \) corresponds to propagation in the positive/negative \( z \)-direction. We summarize the four possible co-linear phase matching configurations in Table 6.1. In labeling these configurations, we borrow the conventional notation of birefringent phase matching, such that Type I refers to like-propagating lower-frequency waves, and Type II refers to unlike-propagating lower-frequency waves. While most nonlinear devices to date are based on the parallel-I configuration, the anti-parallel configurations are crucial to several highly intriguing and advantageous devices, such as the mirror-less optical parametric oscillator (MOPO) [124, 125, 126, 127] and the nonlinear optical mirror [113]. However, since all natural materials are constrained by \( n > 0 \), the anti-parallel configurations require rather extreme techniques to overcome phase mismatch [66].

Among artificial materials, metamaterials retain the advantage of being described by homogenized, constitutive parameters. Moreover, the characterization and language of nonlinear metamaterials has recently been extended to the standard formalism of nonlinear optics [74]. As such, the general equations and physics of wave mixing processes and phase matching used in the analysis of natural nonlinear mate-
Table 6.1: (Reproduced with permission from Ref. [83]. Copyright (2011) by The Optical Society.) Directions of Propagation and Corresponding Phase Matching Condition for the Four Co-linear Three-Wave Mixing Configurations

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$\omega_1$</th>
<th>$\omega_2$</th>
<th>$\omega_3$</th>
<th>Phase matching condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>parallel-I</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>$n_1\omega_1 + n_2\omega_2 = n_3\omega_3$</td>
</tr>
<tr>
<td>anti-parallel-I</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>$n_1\omega_1 + n_2\omega_2 = -n_3\omega_3$</td>
</tr>
<tr>
<td>anti-parallel-IIa</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>$-n_1\omega_1 + n_2\omega_2 = n_3\omega_3$</td>
</tr>
<tr>
<td>anti-parallel-IIb</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>$n_1\omega_1 - n_2\omega_2 = n_3\omega_3$</td>
</tr>
</tbody>
</table>

rials are equally applicable to metamaterials. The advantage of metamaterials then, in this context, is that they vastly extend the achievable range of linear and nonlinear properties. These novel and often extreme properties, such as negative refraction, can offer a variety of solutions to phase matching in wave-mixing processes.

6.2 Anomalous dispersion phase matching

The parallel-I configuration is the simplest and most common wave-mixing setup, in which all three waves propagate in the same direction. It is easily shown that, considering waves of the same polarization and frequencies far from any absorption features, the refractive index of a medium increases monotonically with frequency and thus satisfaction of the phase matching condition given in Table 6.1 is impossible [49]. However, by carefully choosing these frequencies to be around a medium’s absorption feature, the anomalous dispersion in this frequency range can, in principle, exactly counteract the normal dispersion. This technique is known as anomalous dispersion phase matching, and has been achieved, for example, in polymer waveguides through the incorporation of nonlinear chromophores with an absorption maximum between the lower-frequency and high-frequency waves [128].

Many metamaterials are purposefully designed around an analogous absorption feature, originating from a resonance in its constituent elements. As an example, consider the split-ring resonator (SRR) medium, composed of a periodic array of
planar metallic rings with a capacitive gap [2]. The SRR displays an LC circuit resonance, and has been shown to be characterized, in a range of frequencies around its resonance, by a permeability [74]

$$\mu(\omega) = \mu_0 \left(1 + \frac{F \omega^2}{\omega_0^2 - \omega^2 - i\gamma \omega}\right)$$

(6.3)

where $F$ is the oscillator strength, $\omega_0$ is the resonance frequency, and $\gamma$ is the damping coefficient. If we assume the nearly degenerate case $\omega_1 \approx \omega_2$ and take the limit as $\gamma \to 0$, the phase matching condition can be simplified to

$$\sqrt{1 + \frac{F \omega_1^2}{\omega_0^2 - \omega_1^2}} = \sqrt{\frac{\epsilon_3}{\epsilon_1}}.$$  

(6.4)

where we have taken $n_i = \sqrt{\epsilon_i \mu_i/\epsilon_0 \mu_0}$, and $\epsilon_i$ is the permittivity seen by the $i^{th}$ wave. Assuming the metamaterial contains no electrically resonant elements at these frequencies and neglecting the effects of spatial dispersion, it follows that the permittivity must display normal dispersion and thus the right hand side will be greater than 1. To meet the phase matching condition, the frequencies must therefore satisfy $\omega_1 < \omega_0 < \omega_3$. Furthermore, if, to avoid losses, the frequencies are equally detuned from resonance such that $\omega_0^2 - \omega_1^2 = \omega_3^2 - \omega_0^2 = \frac{1}{3} \omega_0^2$, then phase matching is achieved with an oscillator strength of

$$F = \frac{\delta\epsilon}{10 + 8\delta\epsilon},$$

(6.5)

where $\delta\epsilon = \frac{\epsilon_3 - \epsilon_1}{\epsilon_1}$. For $\delta\epsilon \sim 0.1$, phase matching would require $F \sim 0.01$. While anomalous dispersion phase matching applies naturally to resonant metamaterials, residual absorption in the transparency windows will tend to limit its applicability.
6.3 Birefringence phase matching

Alternatively, one can consider mixing between waves of differing polarizations, mediated by the appropriate off-diagonal elements of the nonlinear susceptibility tensor. Thus, in an anisotropic medium, where the refractive index is dependent on a wave’s direction of propagation and polarization, the phase matching conditions in Table 6.1 can potentially be satisfied by selecting the polarizations of the interacting waves.

The principal configurations for this technique, known as birefringent phase matching, are generally divided into Types I and II, where Type-I involves lower-frequency waves of the same polarization, and Type-II involves lower-frequency waves with orthogonal polarizations. In a uniaxial crystal, propagation of ordinary and extraordinary polarized waves is governed by the ordinary index $n_o^i$ and the extraordinary index $n_e^i(\theta)$ in the material, where

$$\frac{1}{(n_e^i(\theta))^2} = \frac{\sin(\theta)^2}{(\bar{n}_e^i)^2} + \frac{\cos(\theta)^2}{(n_o^i)^2}, \quad (6.6)$$

$\bar{n}_e^i$ is the principal value of the extraordinary index, and $\theta$ is the angle between the optical axis and the direction of propagation. Thus, provided the birefringence is large enough, the phase matching condition can be met by selecting the polarizations of each wave and tuning $\theta$ through rotation of the crystal. As an example, let us consider Type I-$(eeo)$ phase matching in the nearly degenerate case, $\omega_1 \approx \omega_2$.

For this configuration, phase matching can be achieved in a nonlinear crystal if the maximum birefringence, $\bar{n}_3^e - n_3^o$, is greater than the material dispersion, $\bar{n}_3^e - \bar{n}_1^e$. This condition is true of many anisotropic nonlinear crystals in the visible and infrared spectral regions. However, for $\theta \neq 0^\circ, 180^\circ, \pm 90^\circ$, walk-off between the ordinary and extraordinary beams imposes a limit on the maximum interaction length [48].

The anti-parallel configurations, on the other hand, require more extreme material properties. For example, let us consider Type II-$(eoo)$ birefringent phase matching
in the anti-parallel-IIa configuration for the nearly degenerate case, $\omega_1 \approx \omega_2$, where wave 1 is anti-parallel to waves 2 and 3. Invoking (eoo) polarizations in the refractive indices of Table 6.1, phase matching in this case requires a birefringence of $n_1^e - n_1^o \geq 2n_3^o$. Taking $n_3^o \approx n_1^o$, this constraint implies an extraordinary index that is roughly three times the ordinary index, something no natural material has been found to support. If instead $\omega_1 << \omega_2$, this constraint is relaxed, leading to speculation that birefringent phase matching for backward wave oscillation will likely only be achievable with a signal frequency in the mid- or far-infrared spectrum, while the idler and pump are near-infrared or higher frequency waves [124].

In addition, birefringent phase matching requires a sufficiently strong cross-term in the nonlinear tensor, corresponding to the direction of propagation and polarizations required by phase matching considerations. The strength of the various cross-term nonlinear coefficients vary by material and are often identically zero due to crystal symmetries [48]. These constraints on both the linear and nonlinear tensors limit the desirable wave-mixing configurations, as well as the useable nonlinear materials.

Metamaterials, meanwhile, have greatly extended the achievable types and magnitudes of material anisotropy, introducing, for example, indefinite media [129]. Anisotropic metamaterials with extraordinary indices of refraction in excess of five times the ordinary indices of refraction have been demonstrated at terahertz frequencies [130]. Such large and configurable anisotropies can lift many of the conventional limitations in applying birefringence phase matching to natural materials. In addition, engineering of the nonlinear tensor in metamaterials can ensure that the particular cross-term involved is both non-zero and sufficiently large.

As a simple and demonstrative example, we consider a metamaterial composed of overlapping silver bars arranged in a cubic lattice with a lattice constant of $1 \mu$m, immersed in a hypothetical nonlinear dielectric with $\epsilon_d = 2\epsilon_0$ and $d_{11} = 10$ pm/V.
Figure 6.1: (Reproduced with permission from Ref. [83]. Copyright (2011) by The Optical Society.) A nonlinear metamaterial consisting of overlapping silver bars embedded in a nonlinear dielectric, designed to operate as a birefringence phase matched MOPO. (a) Schematic of a single layer of the metamaterial, showing the propagation direction and angle relative to the crystal axes. (b) The basic unit-cell of the metamaterial. (c) The retrieved extraordinary and ordinary indices of refraction. (d) Plot of the phase matched signal and idler frequencies as a function of angle. (e) Real and imaginary parts of the retrieved nonlinear coefficient.

Such a structure is easily fabricated by existing techniques, with a frequency range of operation that includes the far-infrared wavelength of 10.6 µm, corresponding to the output of a CO₂ laser. Labeling the crystal axes as in Fig. 6.1(b), this metamaterial supports coupling between the structure and the incident fields only for electric fields polarized in the Z-direction. Furthermore, the fields coupled into the structure naturally localize in the capactive gaps between overlapping bars, with a dominant electric field component in the X-direction. The symmetry of the metamaterial prevents linear coupling between these polarizations, and thus the metamaterial is strongly biaxial with effective linear susceptibility tensors that are diagonal in the XYZ basis. The resulting nonlinear tensors, however, are not diagonal. Consider-
ing Type-I(eeo) and propagation in the $YZ$-plane, there is significant overlap of the $X$-components of the electric fields of the three modes in the capacitive gaps, and the metamaterial thus supports a non-zero $d_{35}$ nonlinear coefficient. This artificially engineered nonlinearity, combined with the massive anisotropy, can support birefringence phase matched oscillations without a mirror, with distinct benefits compared to alternate implementations.

To verify the linear and nonlinear properties, we implement full-wave, finite element simulations on a single unit-cell of the nonlinear metamaterial using COMSOL Multiphysics. We employ periodic conditions in the transverse directions and implement a Drude model for the dielectric function of silver [108], using a plasma frequency of 2179 THz and a collision frequency of 4.35 THz. We then retrieve the linear properties via standard effective parameter retrieval techniques [11]. Constraining propagation to the $YZ$ plane, the metamaterial is positive uniaxial to within simulation error, with extraordinary and ordinary waves corresponding to TM and TE polarizations, respectively. The principal values of the extraordinary and ordinary indices are shown in Fig. 6.1(c), displaying anomalously large birefringence, as expected. Furthermore, we perform Type-I(eeo) difference frequency generation simulations using the techniques outlined in Ref. [84], using an ordinary-polarized 10.6 $\mu$m pump wave as wave 3, and sweeping the frequencies of waves 1 and 2. We use the results of these simulations in the transfer matrix-based nonlinear retrieval method to determine the $d_{35}$ nonlinear coefficient [70], plotted in Fig. 6.1(e). Although the cross-terms of the local nonlinear tensor in the dielectric are zero everywhere, the metamaterial supports an effective $d_{35}$ coefficient that is both non-zero and several times larger than the $d_{11}$ in the background dielectric, owing to the field localization enhancement effect [84]. Renaming waves 1, 2 and 3 to signal, idler, and pump, these results are immediately applicable to the nonlinear process of optical parametric oscillation. Indeed, the anisotropy is large enough to support birefringent phase
matching of a counter-propagating signal wave, corresponding to the anti-parallel-IIa configuration. By rotating the direction of propagation $z$ relative to the optical axis $Z$, depicted in Fig. 6.1(a), the anti-parallel-IIa phase matching condition can be satisfied for signal and idler frequency pairs over a wide frequency range, as shown in Fig. 6.1(d). Thus, for pumping with a CO$_2$ laser, this metamaterial can be expected to support mirror-less oscillations, generating a tunable signal wave with a frequency ranging from 1 to 8 THz. Moreover, the natural material chosen as the embedding dielectric does not require significant birefringence nor nonlinear cross-terms, allowing for high flexibility in the choice of embedding material, and, consequently, the potential achievement of competitively-low oscillation thresholds. We note that the large anisotropy, however, is accompanied by proportionately large walk-off, except near $\theta = 90^\circ$, corresponding to $\omega_1 \approx 2\pi \times 8.18$ THz and $\omega_2 \approx 2\pi \times 20.10$ THz. Similarly, walk-off can be eliminated at any single signal-idler frequency pair by redesigning the anisotropy of this metamaterial to ensure that the principal values of the refractive indices satisfy the phase matching condition.

6.4 Quasi-phase matching

If instead we allow for an inhomogeneous medium, a third phase matching technique becomes available. This technique, known as quasi-phase matching (QPM), relies on the introduction of some sort of periodicity in the direction of propagation [131, 132]. Thus, the wavevectors can be conserved up to a multiple of the reciprocal lattice vector $\vec{G} = \frac{2\pi}{\Lambda} \hat{z}$, where $\Lambda$ is the length of one period. Typically, the inhomogeneity employed is a periodic modulation of the sign of the nonlinear susceptibility, called periodic poling, but it can be much more general [133]. Including the contribution from the periodicity in the above phase relations, QPM is achieved for $\Delta k = m\vec{G}$, or equivalently $\Lambda = mL_{coh}$, where $m$ is any integer. As such, the possible frequencies
for phase matching are strictly limited by the choice of poling period, with small associated tuning bandwidths [133]. The effective nonlinear coefficient of the wave-mixing process, however, is necessarily reduced compared to the bulk value, with a reduction factor of $2/\pi$ in the case of first-order QPM [49].

QPM in natural nonlinear crystals has been achieved for second-harmonic generation in the anti-parallel-I configuration [134] and for MOPO in the anti-parallel-IIa configuration [135]. Due to the massive phase mismatch introduced by the backward-propagating signal, the poling period required in the MOPO was a remarkable 800 nm. In principle, the other anti-parallel configurations presented in Table 6.1 can be achieved in a similar fashion, though the fabrication constraints of such small poling periods will invariably limit the useable materials, frequencies, and interaction lengths.

QPM extends naturally to metamaterials, which have proven viable options in various laminar and gradient-style devices [136, 6]. At microwave frequencies, periodically poled QPM has been demonstrated by the precise orientation of the nonlinear inclusion itself (see Fig. 6.2(a)) [89]. At infrared and visible frequencies, however, the application of periodically poled QPM will depend on the metamaterial design. In nonlinear metamaterials composed of periodic metallic structures embedded in a nonlinear dielectric [84], for example, the conventional techniques of ferroelectric domain engineering can be applied directly to the embedding dielectric. Assuming it represents the dominant source of nonlinear activity, the reversal of the phase of the embedding dielectric’s nonlinear susceptibility will necessarily cause an inversion of the sign of the effective bulk nonlinearity. In any case, precise control of the metamaterial unit-cell can allow for complex spatial distributions of the nonlinear parameters for the purpose of QPM.

The generalized form of QPM, which utilizes a periodic variation in any of the electromagnetic material properties, is particularly attractive in the special class of
active metamaterials. This stems from the fact that active metamaterials have been shown to support dynamically tunable linear properties, using active mechanisms such as photoconductivity, electrical bias, and temperature tuning [137, 138, 139, 30]. In such a system, one can envision introducing a periodic grating with a tunable periodicity, analogous to an acoustically-induced Bragg cell but with a modulation depth several orders of magnitude larger, depicted in Fig. 6.2(b) (see Appendix). Thus, it was demonstrated theoretically that a wave-mixing process taking place in an active metamaterial Bragg cell can support QPM over a widely tunable frequency range [115]. However, active metamaterials of this kind can be difficult to realize for frequencies above the THz regime. Furthermore, this form of tunable QPM comes at the price of a largely reduced effective nonlinear coefficient.

**Figure 6.2:** (Reproduced with permission from Ref. [83]. Copyright (2011) by The Optical Society.) (a) Diagram of the periodic poling technique employed in Ref. [89] for the varactor-loaded split-ring resonator medium, whereby the phase of the nonlinear coefficient is periodically flipped by reversing the orientation of the nonlinear element in each individual unit-cell. (b) Schematic of tunable parallel-I QPM difference frequency generation in an active metamaterial Bragg cell. An external stimulus is used to produce a periodic variation in the linear properties of the metamaterial with a tunable period \( \Lambda \).
6.5 Negative-index phase matching

One of the first and most exciting applications of metamaterials was the achievement of a negative index of refraction through the engineering of a composite with both \( \text{Re}[\varepsilon] < 0 \) and \( \text{Re}[\mu] < 0 \) in a certain frequency band \([1, 4]\). This, in turn, spurred several theoretical studies of the nonlinear phenomena supported by nonlinear negative-index mediums \([140, 113, 114]\). These studies showed that the phase matching conditions of the anti-parallel wave-mixing configurations could be satisfied if the backward-propagating wave was in a negative-index band. This arises from the fact that the wavevector and Poynting vector are oppositely directed in a negative-index medium, such that a wave propagating in the negative \( z \)-direction supports a positively-directed wavevector. In particular, there were two processes that proved highly intriguing from a theoretical viewpoint: mirror-less optical parametric amplification and oscillation, and the nonlinear optical mirror effect.

The so-called nonlinear optical mirror effect is the name given to a device that both converts the frequency of an incoming wave and redirects it backwards. As originally conceived, the device operates via the degenerate case of the anti-parallel-I configuration, in which the system is excited by a forward-propagating fundamental wave, generating a backward-propagating, or ‘reflected’, second-harmonic \([113]\). Thus, in a homogeneous medium, the phase matching condition is given by \( n_1 = -n_3 \) and requires either the fundamental or second-harmonic wave to propagate in a negative-index band and the other in a positive-index band. Such a device has been demonstrated at microwave frequencies, shown schematically in Fig. 7.5(b) \([89]\). The dispersion relation of the nonlinear metamaterial was found to be

\[
k(\omega) = \omega \sqrt{\mu \left( \varepsilon_b \left( 1 - \frac{\omega_p^2}{\omega^2} \right) \right)}, \tag{6.7}
\]
where
\[ \mu = \mu_0 \left( 1 + \frac{F \omega^2}{\omega_0^2 - i\gamma \omega - \omega^2} \right). \] (6.8)

The various parameters were experimentally characterized, yielding \( F = 0.22, \omega_0 = 2\pi \times 608 \text{ MHz}, \gamma = 2\pi \times 14 \text{ MHz}, \epsilon_b = 2.2\epsilon_0, \) and \( \omega_c = 2\pi \times 674 \text{ MHz}. \) The corresponding index of refraction and coherence lengths are plotted in Fig. 7.5(a), showing a dramatic rise in the coherence length of the anti-parallel-I configuration as the fundamental wave is tuned through the negative-index band. Thus, owing to negative-index phase matching, second-harmonic generation in the anti-parallel-I configuration was shown to be far more efficient than in the parallel-I configuration [89].

The mirror-less parametric processes could be achieved through either of the anti-parallel-II configurations, employing wave 3 as a pump. The backward-propagating wave provides an automatic feedback mechanism, removing the need for a mirror and the associated calibrations and complexities. While the dynamics of a negative-index MOPO are analogous to the previously discussed quasi-phase matched MOPO, the materials involved and the nature of the phase matching are entirely different. However, the losses associated with negative-index mediums will likely limit the overall efficiencies of wave-mixing processes. Negative-index phase matching should thus have its most meaningful applications in those devices specifically based on negative refraction [141, 142].

6.6 Index-near-zero phase matching

Furthermore, there exists an interesting class of both natural materials and metamaterials whose real parts of the refractive index vanish at some frequency, with a number of intriguing characteristics as a consequence [143, 144]. In general, this material property can be found near the plasma frequencies of various metals, or in
any material with a sufficiently strong Lorentzian contribution to its material properties [? ]. If any of the waves involved in a wave-mixing process should propagate in such an index-near-zero band, it can be seen from Table 6.1 that the phase matching conditions of multiple unique configurations become degenerate. For example, if $n_3 = 0$, the anti-parallel-IIa and anti-parallel-IIb configurations are both satisfied by $n_1 \omega_1 = n_2 \omega_2$. This characteristic of index-near-zero materials can be used to achieve simultaneous phase or QPM of two or more configurations, opening avenues to a wide range of simultaneous and/or cascaded nonlinear processes.

Indeed, simultaneous QPM of degenerate ($\omega_1 = \omega_2$) parallel-I and anti-parallel-I configurations has been achieved at microwave frequencies, using the same metamaterial described above by Eqs. (6.7) and (7.9), but in the region where $n_1 \approx 0$ [89]. Figure 7.5(a) demonstrates that, at the index-near-zero frequency given by the sec-
ond dashed vertical line, the coherence lengths of the parallel-I and anti-parallel-I processes are equal. Thus, periodic poling was employed with a poling period of \( \Lambda \approx \frac{2\pi}{\Delta k} \), where \( \Delta k \approx |k_3| \) for both configurations, so that an incident fundamental wave was able to simultaneously generate second-harmonic waves in the positive and negative \( z \)-directions, shown schematically in Fig. 7.5(c).

6.7 Conclusion

We have studied the potential phase matching solutions for nonlinear metamaterials in the context of co-linear three-wave-mixing. We find that metamaterials support multiple paths to overcoming phase mismatch, including alternate and even novel methods compared to those used in natural materials. These results validate the potential application of metamaterials to nonlinear devices by demonstrating the feasibility of phase matching in such structures. Moreover, we have shown that the novel phase matching configurations provide advantages of their own, especially with regard to exotic devices such as MOPOs and nonlinear optical mirrors, in which one of the interacting waves propagates opposite to the others. Birefringence phase matching in metamaterials deserves particular attention due to the unprecedented level of engineering that metamaterials offer in both the linear and nonlinear tensors. Through this engineering, we have demonstrated numerically a relatively simple and flexible metamaterial design for a MOPO that can produce widely tunable THz radiation from the output of a CO\(_2\) laser.

However, there remain several important limitations to the application of metamaterial-based nonlinear devices. First, fabrication considerations will inevitably limit the complexity and scale of the desired bulk metamaterial mediums. One potential solution is the implementation of thin films or channels of metamaterials, effectively changing the problem to that of wave-mixing in a dielectric waveguide. Though not considered here, a similar analysis could be carried out to include waveg-
uide dispersion with analogous conclusions. More fundamental is the subject of losses, which are invariably introduced by the inclusion of metal structures. While it has been shown that non-resonant nonlinear metamaterials can potentially support only modest absorption [84], metamaterials based on metallic components will tend to be limited to operation in the THz and far- and mid-infrared frequency ranges, where metals are less lossy. Otherwise, the bulk metamaterial must be sufficiently compact compared to an absorption length, with a consequent reduction in total efficiency. These constraints are partially responsible for the fact that current experimental demonstrations of phase matching in metamaterials are limited to microwave frequencies. However, the potentialities of metamaterials, both in terms of enhanced nonlinearities and phase matching, are great enough that these limitations should not be considered insurmountable. We expect this work to provide a crucial step in connecting current research in the design of metamaterials with outstanding linear and nonlinear properties, to the functional goal of highly efficient and intriguing nonlinear devices.

6.8 Appendix: Quasi-phase matching in a continuous medium

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Consider a homogeneous medium with a second-order nonlinear electric response and linear magnetic response. Though QPM is applicable to wave mixing in general, we choose to analyze SHG as a demonstrative case. Assuming time-harmonic fields in one dimension, the total polarization of the medium is given by $P(z,\omega) = \epsilon(\omega)E(z,\omega) + P^{(2)}(z,\omega)$, where $E(z,\omega)$ and $P^{(2)}(z,\omega)$ are the complex amplitudes of the electric field and second-order polarization, respectively, and $\epsilon(\omega)$ is the linear permittivity of the medium. We allow for a magnetic permeability $\mu(\omega)$, such that the medium has impedance $\eta(\omega) = \sqrt{\mu(\omega)/\epsilon(\omega)}$ and index of refraction
\( n(\omega) = \sqrt{\epsilon(\omega)\mu(\omega)/\epsilon_0\mu_0}, \) where \( \epsilon_0 \) and \( \mu_0 \) are the permittivity and permeability of free space, respectively. We assume a plane wave, propagating at fundamental frequency (FF) \( \omega_1 \), of the form \( E_1(z) = A_1 \exp(ik_1z) \), where \( A_1 \) is the electric field amplitude and \( k_1 = n_1\omega_1/c \) is the wave vector in the medium, with the subscripts denoting the frequency dependence. For simplicity, we assume the non-depleted pump (NDP) approximation, such that \( A_1 \) is taken to be a constant. The second-order polarization at the second-harmonic (SH) frequency \( (\omega_2 = 2\omega_1) \) is

\[
P^{(2)}_2(z) = \epsilon_0\chi^{(2)}(\omega_2;\omega_1,\omega_1)E^2_1(z),
\]

where \( \chi^{(2)}(\omega_2;\omega_1,\omega_1) \) is the quadratic nonlinear susceptibility involved in SHG. The wave equation describing electric field propagation at \( \omega_2 \) is given by [49]

\[
\left[ \frac{d^2}{dz^2} + \omega_2^2\epsilon_2\mu_2 \right] E_2(z) = -\omega_2^2\mu_2P^{(2)}_2(z),
\]

with solutions of the form \( E_2(z) = A_2(z)\exp(ik_2z) \), where \( A_2(z) \) is the spatially varying amplitude. Thus, taking the slowly varying amplitude approximation and neglecting material losses, the rate of change of the amplitude of the SH wave can be expressed as

\[
\frac{dA_2}{dz} = iI_1\kappa \exp(i\Delta kz),
\]

where \( \kappa = \frac{1}{2}\epsilon_0\omega_1\eta_1\eta_2\chi^{(2)} \) is the coupling coefficient, \( I_1 = 2A_1^2/\eta_1 \) is the intensity of the FF wave, and \( \Delta k = 2k_1 - k_2 \) is the phase-mismatch. Clearly, a non-zero phase-mismatch causes the FF and SH waves to oscillate in and out of phase with each other, severely restricting the conversion efficiency.

In order to achieve a feasibly tunable QPM condition, we choose to subject the refractive index of a homogeneous system to a periodic perturbation with period \( \Lambda \), giving rise to an inhomogeneous index profile. We constrain the perturbation to be spatially continuous and sufficiently weak so that reflections are negligible.
It is convenient to write the index of refraction at \( \omega_l \) \((l = 1, 2)\) as a perturbation superposed on a homogeneous value,

\[
\eta_l(z) = \bar{\eta}_l + \beta_l(z),
\]

where \( \beta_l(z) \) represents the periodic spatial variation of the index, and we have introduced the averaged index

\[
\bar{\eta}_l = \frac{1}{\Lambda} \int_0^\Lambda \eta_l(z) dz.
\]

We represent the inhomogeneous impedance and nonlinear susceptibility, on the other hand, as

\[
\eta_l(z) = \bar{\eta}_l \xi_l(z) \quad \text{and} \quad \chi^{(2)}(z) = \bar{\chi}^{(2)} \theta(z),
\]

respectively, with the same convention for the barred terms. Thus, the phase advance of wave \( l \) at position \( z \) is given by

\[
\phi_l(z) = \int_0^z \frac{\omega_l}{c} n(z', \omega_l) dz'.
\]

Using Eqs. (6.12) and (6.15), we write the phase-mismatch as

\[
\Delta k = 2\phi_1(z) - \phi_2(z) = \Delta \bar{k} + u(z),
\]

where, for convenience, we have introduced the function

\[
u(z) = \int_0^z \left( \frac{2\omega_1}{c} \beta_1(z') - \frac{\omega_2}{c} \beta_2(z') \right) dz'.
\]

Since \( \beta_l(z) \) is defined as the perturbation away from a mean, it will necessarily average to zero over a whole period, implying that \( u(z) \) is a periodic function with period \( \Lambda \). With these definitions, Eq. (6.11) becomes

\[
\frac{dA_2}{dz} = i I_1 \bar{\kappa} \exp(i \Delta \bar{k} z) \xi_1(z) \xi_2(z) \theta(z) \exp (i u(z)).
\]
In this form, the contribution from all of the perturbative functions can be represented by a single function,

\[ v(z) = \xi_1(z)\xi_2(z)\theta(z)\exp(iu(z)), \]  

which is, consequently, also periodic with period \( \Lambda \). Integrating this with respect to \( z \) over an interaction length \( L \) composed of an integer \( N \) periods gives

\[ A_2 = \int_0^L i I_1 \tilde{\kappa} \exp(i\Delta \bar{k} z) v(z) \, dz \]

\[ = i I_1 \tilde{\kappa} \sum_{q=0}^{N-1} \exp(iq\Delta \bar{k} \Lambda) \int_0^\Lambda \exp(i\Delta \bar{k} z) v(z) \, dz. \]  

To achieve QPM, we impose the condition

\[ \Delta \bar{k} = \frac{2\pi m}{\Lambda}, \]  

where \( m \) is any integer. Meanwhile, the periodic function \( v(z) \) is expanded in a Fourier series,

\[ v(z) = \sum_{r=-\infty}^{\infty} G_r \exp(-i\frac{2\pi r}{\Lambda} z). \]  

Substituting Eqs. (6.21) and (6.22) into Eq. (6.20), we arrive at the following expression for the SH amplitude:

\[ A_2 = i I_1 \tilde{\kappa} N \int_0^\Lambda \sum_{r=-\infty}^{\infty} G_r \exp(i\frac{2\pi r}{\Lambda}(m-r)z) \, dz, \]  

which is integrated trivially to yield

\[ A_2 = i I_1 \tilde{\kappa} L G_m, \]  

showing linear growth of the SH with \( L \). The corresponding internal normalized efficiency is given by

\[ \eta_{\text{int}} = \frac{1}{L^2} \frac{I_2}{I_1} = \frac{2}{\eta_2} G_m^2 I_1 \tilde{\kappa}^2, \]  

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reduced from the perfect phase-matching case by the factor $G_m^2 < 1$. For first-order periodically poled QPM, for example, this factor is $G_1^2 = (2/\pi)^2 \approx 41\%$ [49].

Thus, QPM is achieved through periodic perturbation of one or more material properties, subject to the constraint of Eq. (6.21), and with field growth proportional to the $m^{th}$-order Fourier coefficient of $v(z)$. Within this framework, the particular properties of the medium can be chosen with considerable freedom. Most importantly, this form of QPM can be satisfied without permanent poling of the nonlinear sample. Even a spatially constant nonlinear susceptibility, i.e. $\theta(z) = 1$, can still achieve QPM provided that the linear properties are periodic. As such, it is worth noting that this technique is applicable to wave mixing in third and higher-order nonlinear mediums. By contrast, the domain engineering associated with periodically poled QPM cannot be employed on the odd-order nonlinear susceptibilities of a given medium.
Scale invariance is a fundamental property of Maxwell’s equations, such that the mathematics and associated phenomena are equivalent when both the spatial and temporal variables are scaled by the same factor. The implication is that conclusions drawn from experiments within a particular frequency spectrum are applicable, at least in theory, to ALL frequency spectra, provided the system can be similarly scaled. This is important for structured media such as metamaterials and photonic crystals: while many of the interesting and industrial applications of composite media lie in the terahertz, infrared, and optical frequency ranges, the costs in terms of time, equipment, and materials can be prohibitive for experimentation purposes. For this reason, the microwave frequency range, particularly between 500 MHz and 10 GHz, has served as a testing ground for metamaterial concepts and devices. Metamaterials can be fabricated for this frequency range by circuit board photolithography and tested by versatile network analyzers. In this chapter, I introduce the basic features and techniques involved in microwave nonlinear metamaterial experiments, and subsequently present three novel demonstrations.
7.1 Overview of microwave nonlinear metamaterials

For nonlinear metamaterials, the microwave frequency range has been crucial for initial demonstrations [145, 146, 147, 72, 148]. This is in large part to the use of variable capacitance diodes, or varactors. Often, the nonlinear response of the metamaterial at these frequencies is achieved by loading the capacitive gaps of planar metallic patterns with varactors. The planar metallic patterns serve to couple to the incident radiation into the varactor, while the dependence of the varactor’s properties, principally its capacitance, on the induced voltage imbues the entire structure with an effectively nonlinear electromagnetic response. In analogy with the polarizability in natural materials, the charge-voltage relationship of the varactor can be expanded about the bias point in a power series, as illustrated in Fig. 7.1.

![Figure 7.1: Typical Q(V) curve for a varactor diode, compared to a third-order power series expansion, with good agreement for low voltages. When loaded in the capacitive gap of a microwave metamaterial, the power series coefficients can be related to the metamaterial’s macroscopic second- and third-order polarization and magnetization [74].](image)

In this way, the resonance frequency of a varactor-loaded split-ring resonator (VLSRR) was shown to be intensity dependent [145, 146, 147], while phase conjugation was demonstrated through the direct application of a time-varying voltage [149]. Alternatively, wave-mixing and harmonic generation have been demonstrated in nu-
merous microwave metamaterial samples [150, 148]. Shadrivov et. al., for example, reported harmonic generation up to the seventh harmonic in a VLSRR wire composite [145].

7.1.1 Circuit model

Often, the properties of these metamaterials are related to standard inductance and capacitance parameters through a quasi-static circuit model [2, 110]. In their paper, Poutrina et. al. consider the usual RLC model of the single-gap SRR, a canonical metamaterial consisting of a planar metallic ring, patterned onto a PCB substrate, with a gap in the ring providing the capacitance of the resonant circuit. However, they consider the case where the capacitance, and thus the induced voltage across the gap, is a nonlinear function of the amplitude of the charge oscillations, such that [74]

\[ L \frac{d^2 Q}{dt^2} + R \frac{dQ}{dt} + V_D(Q) = -\frac{\partial \Phi_m}{\partial t}, \quad (7.1) \]

where \( L \) and \( R \) are, respectively, the circuit inductance and resistance, \( Q \) is the time-dependent charge on the capacitor, \( V_D \) is the induced voltage, and \( \Phi_m \) is the magnetic flux through the SRR. The induced voltage is then expanded as a Taylor series in \( Q \), whose coefficients are derived from the junction capacitance of the particular diode in use. In the case of a Skyworks varactor diode, the capacitance can be written as

\[ C(V_D) = C_0(1 - V_D/V_P)^{-K}, \quad (7.2) \]

where \( C_0 \) is the zero bias capacitance, \( V_P \) is the intrinsic potential, and \( K \) is the gradient coefficient, all of whose values can be found for the particular varactor [73]. From this expression, they derive the induced voltage as a function of reduced charge \( q = Q/C_0 \), yielding the Taylor expansion

\[ V_D(q) \approx q + aq^2 + bq^3, \quad (7.3) \]
with coefficients \( a = -\frac{K}{2V_P} \) and \( b = -\frac{K(2K-1)}{6V_P^2} \). From here, the nonlinear oscillator equation becomes [74]

\[
d\frac{q}{dt} + \gamma q + \omega_0^2(q + \omega_0^2q + b) = -A\omega_0^2B, \quad (7.4)
\]

with the usual definitions of \( \gamma = R/L \) and \( \omega_0^2 = 1/LC_0 \), \( A \) is the area of the ring, and \( B \) is the time-dependent magnetic field. Through frequency decomposition and a perturbative expansion of the reduced charge, they find the linear magnetic susceptibility of the VLSRR medium to be [74]

\[
\chi_m^{(1)}(\omega) = \frac{F\omega^2}{D(\omega)}, \quad (7.5)
\]

where \( F = N\omega_0^2\mu_0A^2C_0 \) is the oscillator strength and \( D(\omega) = \omega_0^2 - \omega^2 - i\gamma\omega \) is the resonant denominator, as expected. More importantly, they show the quadratic nonlinear susceptibility of the VLSRR medium to be [74]

\[
\chi_m^{(2)}(\omega_s; \omega_q, \omega_r) = -ia\omega_0^4\omega_s\omega_q\omega_r\mu_0AF
\]

\[
\times \frac{\omega_0^2A^2}{D(\omega_s)D(\omega_q)D(\omega_r)}\left[\frac{\omega_0^2a^2}{D(\omega_q + \omega_r)} + \frac{\omega_0^2a^2}{D(\omega_q + \omega_l)} + \frac{\omega_0^2a^2}{D(\omega_r + \omega_l)} - \frac{3}{2}b\right], \quad (7.6)
\]

The resonant nature of the nonlinearities is immediately apparent, as the denominator terms are minimized when their respective arguments pass through the resonance frequency. While a similar circuit analysis can reveal the precise expressions for the higher-order susceptibilities in other metamaterials, the general forms of Eqs. (7.6) and (7.7) can be considered representative of a large class of magnetically resonant metamaterials that share qualitative features with the VLSRR.
7.1.2 Simulation

In practice, metamaterial designs can quickly outpace the analytical formulas in terms of complexity. While the expressions presented above are often still valid qualitatively, some of the parameters are simply too approximate, and need to be determined through more precise methods. Fortunately, rather than putting the time and expense into numerous rounds of fabrication and experiment, numerical models can serve as a predictive design tool. In this section, I discuss typical simulations using a commercial finite element method software, COMSOL multiphysics. These simulations can be used to verify the previous expressions, perform fittings for the various free parameters, and design new and more complicated nonlinear metamaterials.

The building block of the nonlinear simulation is the three-dimensional, frequency domain boundary value problem. To limit the domain size and the problem complexity, it is often best to enforce periodic boundary conditions along the transverse boundaries, so that the domain effectively models a metamaterial ‘slab’ that is infinite in its transverse extent. Moreover, the problem is far more tractable by taking the non-depleted pump approximation, so that we can separate the nonlinear problem into two non-iterating steps: first, the fundamental fields are solved, and second, these fields are used to drive a source term at the harmonic or mix-wave frequency. Thus, before modeling the nonlinear properties, it is necessary to first determine the salient linear scattering features, such as transmission, reflection, and absorption for the desired interacting polarizations and frequencies. At the same time, these simulations determine the linear fields and voltages that will ultimately drive the system’s nonlinearity. Once this is done, a proper model of the local nonlinearity, in this case the varactor’s voltage-dependent capacitance, needs to be put into a suitable form for the simulation to handle, usually by introducing either a source term
in the weak expression, or by directly imposing a voltage source. The amplitude, phase, and distribution of the source is taken from the appropriate product of the nonlinear coefficient and the fundamental fields, and the resulting boundary value problem is solved to give the output harmonic and mix-wave amplitudes.

As an example, consider second-harmonic generation from a varactor-loaded split-ring resonator. Using lumped element capacitors and resistors, we can model the varactor’s linear (or weak-excitation) properties and determine the voltage across the diode for a range of input frequencies. We expand Eq. (7.3) in the frequency domain to find the second-harmonic voltage term, given by

\[ V_D(2\omega) = \frac{1}{2} aV_D(\omega)^2. \]  

Thus, together with the previous solutions for \( V_D(\omega) \), we have the driving voltage at the second-harmonic, which we can solve to find the output harmonics in both the entrance and exit media.

7.1.3 Measurement

The greatest advantage to working with microwave metamaterials is in the fabrication. Since most metamaterial designs are based around metallic patterns that are roughly an order of magnitude smaller than the wavelength of operation, working in the 1-10 GHz range requires patterns on the order of 3-30 mm. This level of detail is easily achieved via standard circuit board photolithography, using transparency masks written by conventional printers. For the samples that will be discussed in the following chapters, the fabrication process consisted of ultraviolet exposure through a mask, application of developer chemicals, agitation in a ferrochloric acid bath, and finally milling and by-hand assembly. When necessary, varactor diodes were soldered in place using solder paste and a reflow oven. In this way, the entire fabrication and assembly of a hundred element nonlinear metamaterial medium could be done in a
single day by one person for minimal training and cost.

Sample characterization at microwave frequencies is typically done in one of three ways. First, free-space measurements can be made by placing a metamaterial slab between two horn antennas and measuring the complex transmission and reflection as a function of frequency. However, this requires a sample that is large enough to at least large encompasses the beam waist, in addition to careful calibration of the horns. Alternatively measurements can be made in a metallic waveguide, such as a rectangular or circular waveguide. The waveguide provides lateral confinement, and can easily impose particular polarizations on the interacting waves. The waveguide’s dispersive features, however, will necessarily influence the measurement, and can be difficult to account for in practice. Instead, the transmission line, as shown in Fig. 7.2, can often provide the best of both worlds. On the one hand, transmission lines provide subwavelength lateral confinement, such that metamaterial can be characterized from just a small sample. In addition, the fundamental mode supported by the transmission line is quasi-TEM without cut-off, such that a very wide frequency range can be studied in a transmission line without having to take into account dispersion introduced by the waveguiding apparatus. For nonlinear metamaterials, in which multiple frequencies can interact simultaneously, the lack of dispersion is ideal. For these reasons, we utilized the transmission line as the primary tool for sample characterization in the microwave frequency range.

**Figure 7.2:** Schematic of the transmission line used to characterize the microwave metamaterial samples.
The characterization of nonlinear metamaterial samples requires systems capable of supplying and measuring multiple frequencies simultaneously. While this can be accomplished through the use of separate devices for input and measurement, such as a vector network analyzer and a spectrum analyzer, phase information is often lost in this setup, not to mention the difficulty in performing and calibrating multi-frequency sweeps. To avoid these issues, we employed a nonlinear vector network analyzer (Agilent PNA-X N5245A), such that all facets of excitation and detection can be performed simultaneously.

7.2 Phase matching in a nonlinear negative-index medium

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While a wide range of nonlinear processes have already been demonstrated in NLMMs, including frequency generation [57, 151, 148], parametric amplification [113, 152], and bistability [153, 146], the setups have been constrained to sub-wavelength interaction lengths for fear of the destructive effects of phase mismatch. As such, the conversion efficiencies achieved are only a fraction of their potential. However, phase matching (PM) is an exciting subject that involves the entire set of linear and nonlinear properties, bringing to bear the full capabilities of NLMMs to manipulate light at will. This claim has been supported by several theoretical studies on NLMMs, most notably the prediction of a nonlinear-optical mirror that generates second-harmonic (SH) back towards the fundamental frequency (FF) source [140, 114, 113], but experimental verification of the remarkable PM effects achievable in bulk NLMMs has been lacking.

Here, we experimentally demonstrate three unique PM configurations for second-harmonic generation (SHG) in a metallic waveguide loaded with a magnetic NLMM
at microwave frequencies. The three configurations are reflected SH PM in a negative-index band, transmitted SH quasi-phase matching (QPM), and simultaneous QPM of both the reflected and transmitted SHs near a zero-index band. The resulting SH spectrums, showing strong PM-induced enhancements, are supported qualitatively by nonlinear transfer matrix method (TMM) calculations on a homogeneous slab with equivalent effective properties.

The NLMM under investigation is the varactor-loaded split-ring resonator (VL-SRR), the canonical subject of numerous recent studies. The constituent unit-cell of this NLMM is composed of a 17 µm thick, 0.75 mm wide copper ring printed on a 0.2 mm FR4 PCB substrate. The 1 mm gap is loaded with a Skyworks SMV1231 varactor diode, whose capacitance varies with applied voltage according to $C(V_D) = C_0(1 - V_D/V_p)^M$, where $V_D$ is the voltage across the diode, $C_0 = 2.35$ pF is the zero-voltage capacitance, $V_p = 1.5$ V is the intrinsic potential, and $M = 0.8$ is the gradient coefficient [73]. Our bulk material, displayed in Fig. 7.3, consists of 16 layers (24 cm in length) of VLSRRs placed in an aluminum waveguide with cross-section 15 cm × 1.5 cm, completely filling the waveguide in the transverse direction, and arranged in a square lattice with 1.5 cm spacings. For the purpose of periodic poling, the VLSRR sample is divided into four identical sections that can be reoriented independently. These dimensions ensure that the resonance frequency of the VLSRR is below the cutoff frequency of the waveguide’s lowest-order mode. As such, the NLMM loaded waveguide is expected to support a backward mode at frequencies where the VLSRR’s permeability is negative, that is, a mode whose phase velocity is opposite to the direction of power flow [71, 1, 154]. In addition, near the cutoff frequency, the wavevector of this mode vanishes, yielding a second region of interest for PM.

The linear properties of the VLSRRs were characterized in a transmission line setup by measuring the transmittance ($|S_{21}|$) of a single layer and fitting to known
Figure 7.3: (Reproduced with permission from Ref. [89]. Copyright (2011) by the American Physical Society.) Photograph of the waveguide with the top removed, loaded with four identical sections of VLSRRs. The inset shows an enlarged view of the NLMM unit-cell.

property models [69], shown in Fig. 7.4 (a). We find our VLSRR medium to be well-described by a constant permittivity $\epsilon_y(\omega) = 2\epsilon_0$, and a permeability given by the Lorentz oscillator-like formula

$$\mu_x(\omega) = \mu_0 \left( 1 + \frac{F\omega^2}{\omega_0^2 - i\gamma\omega - \omega^2} \right),$$  \hspace{1cm} (7.9)

where $F = 0.22$ is the oscillator strength, $\omega_0 = 2\pi \times 608$ MHz is the resonance frequency, and $\gamma = 2\pi \times 14$ MHz is the damping coefficient. The permeability is assumed to be that of free-space along the other axes.

Subsequently, we measured the SHG output from this setup. Using the nonlinear TMM retrieval method [67, 70, 69], we extracted the second-order magnetic nonlinear susceptibility from the SH spectrum (shown in Fig. 7.4 (b)). The result was then fitted to an effective medium model obtained via a perturbative circuit analysis, [74]

$$\chi_m^{(2)}(2\omega; \omega) = \frac{-(2i)a F \omega_0^4 A \mu_0 \omega^3}{(\omega_0^2 - i\gamma\omega - \omega^2)^2 (\omega_0^2 - 2i\gamma\omega - 4\omega^2)},$$  \hspace{1cm} (7.10)

where $a = \pm 0.198$ V$^{-1}$ is the fitted strength of the nonlinearity, and $A = 113$ mm$^2$ is the ring’s area. The sign of $a$ is determined by the orientation of the varactor diode.
Figure 7.4: (Reproduced with permission from Ref. [89]. Copyright (2011) by the American Physical Society.) Plot of the magnitude of the retrieved (solid blue) and fitted (dashed green) transmittance (a) and second-order susceptibility (b) for a single-layer VLSRR slab.

in the VLSRR, reflecting the fact that reversing the diode direction is analogous to reversing the orientation of the nonlinear metacryystal, and thus is expected, by symmetry arguments, to induce a $\pi$ phase shift in the even-order nonlinearities. Note that the magnitude of $a$ is close to the predicted value of $\frac{M^2}{2V^p} = 0.267 \text{ V}^{-1}$ [74].

The longitudinal wavevector of the TE$_{10}$ mode of the metallic waveguide is modeled by

$$k_z(\omega) = \pm \omega \sqrt{\mu_x \left( \varepsilon_y \left( 1 - \frac{\omega_c^2}{\omega^2} \right) \right)},$$

(7.11)

where $\omega_c = \frac{\pi}{k_0\sqrt{\varepsilon_y \mu_0}} = 2\pi \times 674 \text{ MHz}$ is the cutoff frequency and $b = 15 \text{ cm}$ is the waveguide width. As in typical negative-index media, the negative sign is chosen when both terms in the square root are negative, i.e., when $\mu_x < 0$ and $\varepsilon_y \left( 1 - \frac{\omega_c^2}{\omega^2} \right) < 0$. The former occurs just above the resonance frequency of the VLSRR, while the latter requires operation of the waveguide below cutoff, so that we can expect a backward-wave to exist for frequencies of roughly $615 \text{ MHz} < \omega/2\pi < 674 \text{ MHz}$. Furthermore, for a FF below cutoff, it can be shown that only the TE$_{10}$ mode will
propagate at the SH, simplifying our analysis. For coupling between the TE\textsubscript{10} modes at the FF and SH, we obtain an overlap integral of $\Gamma \approx 1.2$.

The PM effects in our VLSRR loaded waveguide can be examined by employing the above experimentally fitted models to calculate the SHG phase mismatch and coherence lengths. For example, the phase mismatch for SHG in a homogeneous medium is given by

$$\Delta k = \pm k_z(2\omega) - 2k_z(\omega), \quad (7.12)$$

where it is assumed that the energy of the FF wave propagates in the positive $z$ direction, and the $\pm$ refers to a positively (transmitted) or negatively (reflected) propagating SH wave. Thus, assuming the SH is far from resonance, it is clear that a forward-wave ($k_z(\omega) > 0$) at the FF will tend to phase match with a transmitted SH wave, as is seen in conventional nonlinear optics. A backward-wave ($k_z(\omega) < 0$) at the FF, on the other hand, will tend to phase match with a reflected SH wave, as predicted earlier [140, 114, 113]. This odd behavior can be seen more clearly by computing the coherence lengths, $L_{coh} = \frac{2\pi}{\Delta k}$, shown in Fig. 7.5 using Eqs. (7.11) and (7.12). As expected, the coherence length for the transmitted SH is small (less than the interaction length), while the coherence length for the reflected SH is much larger throughout the negative-index band. The reflected PM region, shown in gray in Fig. 7.5, represents the frequency range in which our NLMM acts as the nonlinear-optical mirror of Refs. [113] and [114], with the vast majority of the SH power traveling opposite to the FF.

In an inhomogeneous medium with some spatial periodicity, however, the PM condition is rewritten to include the corresponding reciprocal lattice vector. In periodically poled QPM, for example, the sign of the nonlinear susceptibility is reversed in neighboring layers with a period of $\Lambda$. QPM then requires

$$\pm k_z(2\omega) = 2k_z(\omega) + 2m\pi/\Lambda, \quad (7.13)$$
or, equivalently, $\Lambda = mL_{\text{coh}}$, where $m$ is any integer. As mentioned earlier, poling in our system can be achieved by simple reorientation of appropriate sections of VLSSRs, analogous to domain engineering. Thus, taking $m = 1$ in Fig. 7.5, the intersection of the dashed lines (representing poling periods of 12 and 24 cm) with the coherence length curves indicate the frequencies at which Eq. (7.13) is expected to be satisfied, resulting in enhanced SHG output for the respective configuration.

Furthermore, we see that something interesting happens as the FF approaches the waveguide cutoff. Near this frequency, $k_z(\omega)$ vanishes. Thus, Eq. (7.13) can be satisfied for both the reflected and transmitted modes by the same poling period. This is indicated in Fig. 7.5 as the point where the reflected and transmitted modes cross, corresponding to where the FF passes through the cutoff frequency. Thus, for poling periods in the proximity of this coherence length, we expect to see QPM enhancement of both the reflected and transmitted SH waves.

In order to inject and measure the FF and SH waves, respectively, the inner conductors (probes) of two coaxial cables are inserted into the waveguide on either
side of the VLSRR sample. The probes are positioned 1.5 cm from the sample and covered with an alumina shell to reduce the impedance mismatch between the coaxial cable and the waveguide. Rectangular aluminum slabs with cross-section exactly equal to the waveguide are placed at a variable distance from the probes. By manually optimizing the distance between these back walls and the probes, we are able to reduce reflections at the coaxial-waveguide interface to less than 0.75 dB at the SH frequencies of interest, preserving the directionality of the generated SH wave. The FF, however, does not need to be matched because the much larger material losses in the FF range prevent significant back-reflection inside the sample. In other words, the vast majority of the incident FF power that is able to enter the sample travels in the forward direction and is absorbed by the NLMM before reaching the second interface, preserving the directionality of the FF wave. Thus, by pumping through one probe at the FF and measuring the SH power at both probes, we are able to simultaneously investigate the reflected and transmitted SHG in the VLSRR loaded waveguide. For clarity, a diagram of the experimental apparatus is shown in Fig. 7.6. An Agilent PNA-X N5245A network analyzer is used as both the source and receiver.

![Diagram of the experimental setup](image)

**Figure 7.6:** (Reproduced with permission from Ref. [89]. Copyright (2011) by the American Physical Society.) Diagram of the experimental setup employed to measure the SH spectrums, depicting a cross-section of the VLSRR loaded aluminum waveguide.

In order to validate our experimental results and interpretations, we employ non-
linear TMM calculations on a homogeneous slab with equivalent effective properties to the VLSRR loaded waveguide, sandwiched between semi-infinite slabs of vacuum, assuming the non-depleted pump approximation [67, 70]. The power incident on the sample at the FF is approximated by $P_i = P_0 - P_r$, where $P_r$ is the reflected power measured in the experiment and $P_0$ is the source’s output power. The losses before and after the sample are assumed to be 0.75 dB at all frequencies. Although this system is clearly a rough approximation of the actual experimental setup, qualitative agreement is still expected, especially regarding the location and shape of the PM enhancements.

First, we investigate PM of the reflected SHG in a negative-index band. All four sections are aligned to simulate a homogeneous nonlinear medium. The source is swept from 600 to 650 MHz with an output power of -5 dBm. The resulting transmitted and reflected SH spectrums are plotted in Fig. 7.7. The plot shows significant enhancement in the SHG of the reflected wave over the transmitted, and is supported qualitatively by the inset showing the TMM result. Furthermore, the peak

\[ \text{Figure 7.7: (Reproduced with permission from Ref. [89]. Copyright (2011) by the American Physical Society.) Comparison of the transmitted (solid blue) and reflected (dashed green) SHG powers when all sections are aligned. The right inset depicts the experimental configuration, and the left inset shows the TMM calculation.} \]
frequency of 1255 MHz lies well within the range predicted by the coherence length calculation of Fig. 7.5. These results confirm the referenced theoretical studies, and in this configuration our NLMM can be considered a nonlinear-optical mirror. For the network analyzer’s maximum output, we were able to display a conversion efficiency as high as 1.5%.

In the next experiment, the previous configuration is retained in all ways except that sections 2 and 4 are physically rotated by 180 degrees, effectively producing a periodically poled nonlinear crystal with $\Lambda = 12$ cm. The transmitted SH spectrum of this QPM setup is compared to that of the original in Fig. 7.8. The transmitted SH power is greatly increased due to QPM, with the peak frequency of 1253 MHz in excellent agreement with Fig. 7.5. Once again, qualitative agreement is found between the experimental data and the TMM calculations.

![Figure 7.8](image)

**Figure 7.8:** (Reproduced with permission from Ref. [89]. Copyright (2011) by the American Physical Society.) Comparison of the transmitted SHG power when the varactors are aligned (solid blue) and when they are periodically poled with $\Lambda = 12$ cm (dotted red).

In the final configuration, sections 1 and 2 are aligned and oriented opposite to sections 3 and 4, simulating a poling period of 24 cm. Since this poling period is close to the $k_z(\omega) = 0$ crossing point in Fig. 7.5, we can expect a strong enhancement of
the reflected wave near a SH frequency of 1330 MHz, with a simultaneous (though weaker) enhancement of the transmitted wave. This is precisely what is shown in Fig. 7.9, with the SHG powers for the un-poled case plotted for comparison. While the inset again shows good qualitative agreement between the TMM and the experimental results, it should be noted that the peak emitted powers are off by an order of magnitude, whereas much better agreement is found in the previous two configurations. This is most likely due to the inherent sensitivity when approaching the near-zero frequency band, and it was confirmed in TMM calculations (not shown) that small changes in the linear properties produce large changes in the magnitude of the emitted radiation, but with similar qualitative behavior. Moreover, it has been shown that spatial dispersion, neglected here, can play an important role as the wavevector vanishes [155].

**Figure 7.9:** (Reproduced with permission from Ref. [89]. Copyright (2011) by the American Physical Society.) Comparison of the transmitted (solid blue and dotted red) and reflected (dashed green and dotted black) SHG power when the varactors are aligned and when they are periodically poled with Λ = 24 cm, respectively.

The exotic PM effects shown here are made possible due to the unique linear properties accessible in NLMMs, in particular negative- and zero-index behavior. In addition, the use of varying periods to achieve periodic poling to switch between the
various SHG schemes demonstrates the compatibility between NLMMs and QPM—a key result. We expect these results to be a necessary and vital step towards the realization of high efficiency nonlinear mirrors and other NLMM-based devices at microwave and terahertz frequencies.

7.3 Prototypical nonlinear magnetoelectric metamaterial

While nonlinear magnetoelectric responses exist in natural materials [96], their applications are largely limited to material studies [86]. Most device-oriented applications of nonlinear optics, such as wave-mixing and parametric processes, utilize just $\chi^{(2)}_{\text{ee}}$-type nonlinearities [49]. This stems from the fact that, at optical frequencies, the magnetic responses of natural materials tend to be exceedingly weak. However, the subwavelength structuring in metamaterials can lead to effective responses fundamentally different from the constituent materials. Metamaterials are not only able to support the full set of second-order responses, but can do so simultaneously and in a variety of combinations, while retaining or even enhancing the superior strengths of $\chi^{(2)}_{\text{ee}}$-type materials. Nonlinear magnetoelectric coupling, in particular can lead to a number of interesting and unique phenomena. The following chapter is reproduced with permission from Alec Rose, Da Huang, and David R. Smith, Applied Physics Letters, 101, 051103, 2012. Copyright (2012) by the American Institute of Physics.

To demonstrate nonlinear magnetoelectric coupling, we propose the doubly-split ring resonator depicted in Fig. 7.14, known to possess a fundamental magnetic-dipole resonance [2]. Each gap is loaded with a varactor diode, as in Ref. [69, 148], but with the gaps oriented parallel to the incident electric fields. We analyze the unit-cell via standard numerical procedures [11], modeling each varactor as a 2.35 pF capacitor in series with a 2.5 Ω resistor [73]. When excited by a magnetic field normal to the ring, circulating currents are induced in the structure, as shown in
Fig. 7.10 (b). Conversely, electric fields polarized parallel to the gaps couple to a symmetric current mode. Thus, for the polarization indicated, the incident electric and magnetic fields will couple to distinct current modes in the structure. Since the response of each varactor is invariably orientation-dependent, we are able to design two VLSRRs with identical linear properties (see Fig. 7.10 (a)) but differentiable nonlinear responses, which we label symmetric (both varactors oriented together) and anti-symmetric (varactors oriented oppositely).

The nonlinear processes supported by such structures can be inferred from the internal symmetries of the VLSRR itself and the induced currents it supports. For the case of SHG, excitation by a fundamental frequency (FF) wave induces voltages across both varactors. These FF voltages are mixed in each diode to produce voltages at the second-harmonic frequency (SH). For sufficiently weak excitation powers, the SHG in each varactor is given by [74]

$$V(2\omega) = \pm \frac{K}{2V_p} [V(\omega)]^2$$  \hspace{1cm} (7.14)

where $V(\omega)$ is the voltage across the varactor at frequency $\omega$, $K = 0.8$ is the gradient coefficient, $V_p = 1.5$ V is the varactor’s intrinsic potential, and the ‘±’ accounts for the orientation of the varactor. These SH voltages then drive the VLSRR’s current modes, such that the VLSRR supports an effective electric and/or magnetic polarization at the SH. As depicted in Fig. 7.10 (c), a simple analysis of the induced voltages across the varactors implies that, when driven by FF fields near the magnetic resonance, the anti-symmetric VLSRR will support an effective second-order magnetization proportional to $\chi^{(2)}_{mmm}(2\omega; \omega, \omega)$, while the symmetric VLSRR will support an effective second-order polarization proportional to $\chi^{(2)}_{emm}(2\omega; \omega, \omega)$.

For experimental verification, both VLSRR samples are fabricated from 17 μm-thick copper patterned on FR4 and loaded with Skyworks SMV1231 varactor diodes,
differing only in the orientation of the varactor diodes. These samples are placed, one at a time, into the impedance-matched transmission line appartus of Ref. [69], depicted in Fig. 7.11 (a). The VLSRRs are excited by 1 mW waves launched from port 1 of an Agilent PNA-X N5245A network analyzer. The frequency of these waves is swept in a range around the magnetic resonance frequency of 0.97 GHz. Second-harmonic (SH) signals are generated by the VLSRR samples and propagate in both directions. The SH electric fields reaching the network analyzer at ports 1 and 2, labeled $E_{2\omega}^{\pm}$, respectively, are measured. Due to the highly-subwavelength size of the samples, the reflected and transmitted SH signals have nearly identical magnitudes, and so just the reflected spectrum is shown in Fig. 7.12. Moreover, the spectrums
from both samples show the same characteristic peak when the FF is tuned to the VLSRR’s magnetic resonance, indicating that both SHG processes are dominated by the magnetic response at the FF.

We supplement the experimental results with frequency domain scattering simulations in COMSOL Multiphysics. FF plane waves are launched from air at a single unit-cell with appropriate periodic boundary conditions, simulating an infinite slab. Using Eq. (7.14) for the second-order response of the varactors, the solution for the FF fields is used to drive the system at the SH, from which the transmitted and reflected SH signals are collected. For direct comparison with experiment, we take into account the attenuation in the experimental setup, as well as the inhomogeneous mode profile within the transmission line. We calculate numerically the overlap integrals in the empty transmission line, giving power correction factors of 0.14 and 0.20 for the magnetic and mangetoelectric SHG processes, respectively. The resulting SH spectrums are plotted in Fig. 7.12, in good agreement with the measured data.

We note that the particular design of the VLSRRs was chosen so that the coupling of the structure with incident magnetic and electric fields is roughly equal in the second-harmonic frequency range, resulting in SHG of roughly equal magnitudes in

**Figure 7.11:** (Reproduced with permission from Ref. [76]. Copyright (2012) by the American Institute of Physics.) (a) Schematic of the experimental setup used in measuring the SH signals from the VLSRR samples. (b) Photograph of the single-layer VLSRR samples.
both samples.

Figure 7.12: (Reproduced with permission from Ref. [76]. Copyright (2012) by the American Institute of Physics.) Measured (blue markers) and simulated (dashed lines) SHG from the two VLSRR samples. The reflected SH spectrums are plotted in the upper diagrams, while the phase differences between the transmitted and reflected SH signals are plotted below. For comparison, the insets illustrate SHG from thin homogeneous sheets with the indicated nonlinearity. As expected, the symmetric VLSRR shows behavior consistent with an effective second-order polarization, proportional to the square of the FF magnetic field.

In order to classify the nature of the macroscopic SHG process, we use the fact that a nonlinear polarization, like an electric dipole, radiates symmetrically, while a nonlinear magnetization radiates anti-symmetrically, with respect to the electric field (see insets in Fig. 7.12). Thus, the phase difference between the generated transmitted and reflected signals, $\phi = \angle \left( E_{2\omega \rightarrow 2\omega}^+ / E_{2\omega \rightarrow 2\omega}^- \right)$, should indicate the dominant nonlinear process: $\phi = 0$ for a nonlinear polarization, and $\phi = \pi$ for a nonlinear magnetization.
However, asymmetries in the paths traveled by the transmitted and reflected signals before being measured, either in the transmission line or in the network analyzer itself, will tend to skew their phases relative to one another. Over a narrow frequency band, the effect of this asymmetry on the phase difference can be approximated by a constant phase shift, $\delta \phi$. We find a reasonable value of $\delta \phi = -0.8$ radians by comparing the anti-symmetric VLSRR measured phase data to simulations, justifying this fitting by noting that metamaterials of this type have been previously shown to support second-order magnetizations [74]. Using this phase calibration, we plot $\phi$ for the symmetric VLSRR in Fig. 7.12, in excellent agreement with simulations. As expected, the symmetric VLSRR’s transmitted and reflected SH signals are nearly in-phase, indicating that the dominant SHG process is $\chi^{(2)}_{emm}(2\omega; \omega, \omega)$. It should be noted, however, that the SH signals collected from both samples will contain contributions from processes other than the dominant one. These SHG processes will influence the phase and magnitudes of the SH signals according to their relative strengths, as evidenced by the slight dispersion in $\phi$ in both simulation and experiment.

The doubly-split ring resonator employed in this work by no means represents the only means of achieving nonlinear magnetoelectric coupling, but rather provides a simple and easily verified realization of the phenomena. In fact, the coupled split-ring resonators (CSRRs) of Ref. [156] are shown to support similar nonlinear coupling between electrically- and magnetically-driven current modes, and we believe that, under similar experimental conditions to those used here, the SHG process of the CSRRs could be classified as a form of nonlinear magnetoelectric coupling.

In short, we have confirmed experimentally nonlinear magnetoelectric coupling in a VLSRR metamaterial, demonstrating second-harmonic generation via $\chi^{(2)}_{emm}(2\omega; \omega, \omega)$ at microwave frequencies. We achieved this phenomena by leveraging the ability of metamaterials to couple strongly to both electric and magnetic fields, utilizing both
analytical and numerical techniques to achieve the desired effective properties. These results represent an important step towards probing the vast parameter space available to nonlinear metamaterials. We expect this metamaterial design to serve as a prototype for future investigations into nonlinear magnetoelectric coupling and related phenomena.

7.4 Nonlinear interference

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Nonlinear optical effects with magnetic origin can have very different properties compared to those with electric origin. When mechanisms of both electric and magnetic natures are present, a particular nonlinear process, such as second-harmonic generation (SHG), can contain multiple contributions with varied strengths and phases, giving rise to constructive and destructive interference. In natural materials, this so-called nonlinear interference has provided a pathway for observing antiferromagnetic (AF) domains [86, 157, 87, 88], since the AF’s magnetic properties, and in turn the nonlinear interference effects, reverse themselves in neighboring domains. For example, Fiebig et. al. exploited the similar magnitudes of $\chi^{(2)}_{eee}$ and $\chi^{(2)}_{mee}$ in Cr$_2$O$_3$ to experimentally observe nonlinear interference via SHG [85, 158]. However, natural materials suffer from (typically) weak magnetic contributions, limiting the overall efficiency of nonlinear interference and nonlinear magnetoelectric coupling in general.

Alternatively, certain plasmonic nanoparticles have shown promise in supporting strong effective magnetic and quadrupolar contributions [160, 161, 57, 61, 162], which has lead to the observation of nonlinear interference in the generation of optical harmonics [163, 164, 165]. In particular, Zdanowicz et. al. attributed asymmetric SHG
Figure 7.13: (Reproduced with permission from Ref. [159]. Copyright (2013) by the American Physical Society.) Graphical illustration of the nonlinear parameter space. Insets depict nonlinear generation (arrows indicate electric fields) from a thin nonlinear slab for four limiting cases, corresponding to the areas under the colored cones. When the second-order polarization (magnetization) is dominant, as in the vertical (horizontal) cones, the nonlinear generation resembles an electric (magnetic) dipole. When a second-order polarization and magnetization are present, however, the interference can favor nonlinear generation in a particular direction, illustrated by the insets next to the diagonal cones. This is an oversimplification, however, as both the polarization and magnetization are, in general, complex valued.

from L-shaped gold nanoparticles to the nonlinear interference between second-order electric, magnetoelectric, and quadrupolar tensors [166]. This recent progress suggests that artificial media, or metamaterials, constructed from arrays of nanoparticles might provide a means to tailor the effective nonlinear susceptibilities.

Indeed, clever structuring of metamaterials can lead to effective magnetic and magnetoelectric behavior, even when composed of non-magnetic materials [2]. This flexibility in the linear behavior of metamaterials has lead to such exciting phenomena as negative refraction [4] and electromagnetic cloaking [6]. The split-ring resonator (SRR), for example, is the canonical magnetic metamaterial [2], wherein an intrinsic resonance is formed by inserting a capacitive gap into a conducting loop. The SRR’s resonance is typically excited by incident magnetic fields, which couple inductively
to the structure. When these same metamaterials are hybridized with nonlinear components, the degrees of freedom grow exponentially. This sort of control and balance of nonlinear properties is paramount to a whole host of phenomena. In this context, nonlinear interference is seen to occupy a region in the more general nonlinear parameter space, depicted in Fig. 7.13, in which careful balance of the nonlinear polarization and magnetization leads to unidirectional harmonic and microwave generation. Nonlinear magnetoelectric coupling, in turn, offers a platform for accessing the full range of nonlinear properties and phenomena [82].

**Figure 7.14**: (Reproduced with permission from Ref. [159]. Copyright (2013) by the American Physical Society.) (a) The nonlinear SRR proposed in Ref. [82] for observation of nonlinear interference. Both electric (left) and magnetic (right) incident fields interact with the nonlinear dielectric, resulting in nonlinear magnetoelectric coupling. (b) Photograph of the analogous VLSRRs from Ref. [76].

Quasi-analytic expressions for the effective magnetoelectric nonlinear properties of metamaterials have been derived generally via a Bloch mode analysis, assuming only electric nonlinearities [82]. Qualitatively, a general requirement for nonlinear
magnetolectric coupling is for the fields locally induced by incident electric and magnetic fields to overlap within the nonlinear element. A SRR design, consisting of a metallic ring with two nonlinear dielectric-loaded gaps, was proposed for the observation of nonlinear interference, as shown in Fig. 7.14 (a). Though ultimately intended for operation at terahertz or infrared frequencies, microwave metamaterials offer a convenient platform for proof-of-concept demonstrations. When placed in the capacitive gaps, the field-dependent properties of varactor diodes have allowed the varactor-loaded (VL) SRR to be used as a microwave nonlinear metamaterial [167, 168, 114, 146], leading to proof-of-concept demonstrations of resonance tuning [145, 146], solitons [169], and negative-index SHG [89], to name a few.

In this letter, we employ a microwave nonlinear magnetolectric SRR, consisting of dual-gap copper rings on FR4 substrate, loading both capacitive gaps with Skyworks SMV1231 varactor diodes [76] (see Fig. 7.14 (b)). These VLSRRs are then divided into two groups, differing only in the relative orientation of the varactor diodes: symmetric (varactors oriented together) and anti-symmetric (varactors oriented oppositely), as shown in Fig. 7.15. The relative orientation of the varactors plays a key role in the VLSRR’s nonlinear properties and, thus, nonlinear interference effects. The qualitative features of the second-order susceptibilities in both VLSRR samples are obtained from a Bloch mode analysis [82], which are used together with a simple 1-dimensional model to predict the nonlinear behavior of a thin slab. We then study DFG in these VLSRRs, confirming the presence of nonlinear interference in a single layer by experiment and simulation.

To describe nonlinear interference in the VLSRRs, we consider the interaction between two waves, termed signal ($s$) and pump ($p$), in producing idler ($i$) waves via DFG, such that $\omega_i = \omega_p - \omega_s$, where $\omega$ is an angular frequency. For a simple 1-dimensional system, the forward (+) and backward (−) idler waves satisfy the scalar
wave equation [82]

\[ \frac{\partial A_\pm}{\partial z} = S_\pm e^{\pm ik_i z} \quad (7.15) \]

where we have defined the wave amplitudes \( A_\pm \) such that the wave intensity is \( I_\pm = 2|A_\pm|^2 \). The pump and signal waves mix in the nonlinear medium to produce source terms at the difference frequency, given by

\[ S_\pm = \pm i \omega_i \left[ \sqrt{Z_i} P^{(2)}(\omega_i) \pm \frac{1}{\sqrt{Z_i}} \mu_0 M^{(2)}(\omega_i) \right], \quad (7.16) \]

where \( Z_i \) is the wave impedance at \( \omega_i \), and \( P^{(2)}(\omega_i) \) and \( M^{(2)}(\omega_i) \) are given by Eqs. (2.17) and (2.18).

To simplify the analysis, we fix the pump wave at the magnetic resonance. Since the electric field of the pump wave cannot excite the VLSRR’s magnetic resonance, we can neglect all non-resonant nonlinearities. Moreover, the internal symmetry of the symmetric VLSRR suppresses all axial second-order tensors [82], such that \( \chi^{(2)}_{mmm} = \chi^{(2)}_{mee} = \chi^{(2)}_{eme} = \chi^{(2)}_{cem} = 0 \). Thus, the source term for the symmetric VLSRR reduces to just

\[ S_\pm = \pm i \omega_i \left[ \sqrt{Z_i} \chi^{(2)}_{emm}(\omega_i; \omega_p, -\omega_s) H(\omega_p) H(\omega_s)^* \right. \\
\left. \pm \frac{1}{\sqrt{Z_i}} \chi^{(2)}_{mme}(\omega_i; \omega_p, -\omega_s) H(\omega_p) E(\omega_s)^* \right]. \quad (7.17) \]

For an optically thin slab of extent \( a \), we can neglect phase matching and pump depletion, so that Eq. (7.15) has the simple solution

\[ I_\pm = \frac{1}{2} a^2 I_p I_s |\gamma_{emm} \pm \gamma_{mme}|^2. \quad (7.18) \]

where the coupling coefficients \( \gamma \) are just renormalizations of the nonlinear susceptibilities,

\[ \gamma_{g_s g_p g_s} = \omega_i \sqrt{G_s G_p G_s} \chi^{(2)}_{g_s g_p g_s}. \quad (7.19) \]
where \( G_i = Z_i \) for \( g_i = e \), \( G_i = 1/Z_i \) for \( g_i = m \), and likewise for the pump and signal. For compactness, we have dropped the explicit frequency dependence. Thus, we expect to observe maximum nonlinear interference, i.e. maximum asymmetry between the forward and backward idler intensities, when the magnitudes of \( \gamma_{mme}(\omega_i; \omega_p, -\omega_s) \) and \( \gamma_{mem}(\omega_i; \omega_p, -\omega_s) \) are roughly equal. We can infer the frequency range for maximum nonlinear interference from the permutation symmetries, noting that simultaneously interchanging the first and last frequencies and field components should leave the nonlinearity unchanged, such that \( \gamma_{mme}(\omega_i; \omega_p, -\omega_s) = \gamma_{emm}(\omega_s; \omega_p, -\omega_i) \) [82]. It follows that \( \gamma_{mem}(\omega_i; \omega_p, -\omega_s) \) and \( \gamma_{mme}(\omega_i; \omega_p, -\omega_s) \) are equal at the degeneracy point, \( \omega_s = \omega_i \), denoted by the black circle in Fig. 7.15. Thus, for \( \omega_s \approx \omega_i \approx \omega_p/2 \), Eq. (7.18) implies constructive (destructive) interference for the forward (backward) propagating idler.

We can follow the same procedure for the anti-symmetric VLSRR, noting that the internal symmetries suppress all polar second-order tensors, such that \( \chi^{(2)}_{eee} = \chi^{(2)}_{mme} = \chi^{(2)}_{mem} = \chi^{(2)}_{emm} = 0 \). Thus, the idler waves emitted by a thin slab are given by

\[
I_i^\pm = \frac{1}{2} a^2 I_p I_s |\gamma_{eme} \pm \gamma_{mmm}|^2. \tag{7.20}
\]

The dominant nonlinearities contributing to DFG in the anti-symmetric VLSRR are \( \gamma_{eme}(\omega_i; \omega_p, -\omega_s) \) and \( \gamma_{mmm}(\omega_i; \omega_p, -\omega_s) \), and so we cannot rely on permutation symmetry. Instead, we use the fact that, in the frequency range of interest, the VLSRR couples non-resonantly to the electric field and resonantly to the magnetic field. Since induction vanishes at sufficiently low frequencies, this implies a frequency range where the VLSRR’s coupling to electric and magnetic fields are comparable. We have purposefully designed this VLSRR to support roughly balanced electric and magnetic coupling for \( \omega_s \approx \omega_i \approx \omega_p/2 \), so that nonlinear interference in the two samples can be directly compared. However, in contrast to the symmetric VL-
Figure 7.15: (Reproduced with permission from Ref. [159]. Copyright (2013) by the American Physical Society.) Second-order susceptibilities calculated for symmetric and anti-symmetric nonlinear SRRs in Ref. [82] as a function of $\omega_i/\omega_p = 1 - \omega_s/\omega_p$, for $\omega_p$ fixed at the SRR resonance. The resonant susceptibilities (involving the magnetic component of the pump field) are dominant over most of the spectrum in each VLSRR, so that DFG is dominated by their interference, as in Eqs. (7.18) and (7.20). The insets graphically illustrate the resulting nonlinear interference in each sample, with the optimum occurring in the neighborhood of $\omega_s \approx \omega_i \approx \omega_p/2$.

SRR, Fig. 7.15 shows that the anti-symmetric VLSRR’s dominant nonlinearities are out-of-phase, i.e. $\gamma_{eme}(\omega_i; \omega_p, -\omega_s) \approx -\gamma_{mmm}(\omega_i; \omega_p, -\omega_s)$ for $\omega_s \approx \omega_i \approx \omega_p/2$, so that, according to Eq. (7.20), the anti-symmetric VLSRR is expected to favor idler emission in the backward direction.

To observe nonlinear interference, the VLSRRs are arranged into square lattices with separation $a = 1$ cm, as in Fig. 7.14 (b), forming a thin 1-dimensional layer. The samples are then placed into the impedance-matched transmission line apparatus of Ref. [69], shown schematically in Fig. 7.16 (a). Pump and signal waves are launched from Agilent PNA E8364B and PNA-X N5245A network analyzers, respectively. The pump power is 0 dBm at fixed frequency $\omega_p/2\pi = 970$ MHz, corresponding
to the magnetic resonance frequency of the VLSRRs, while the 10 dBm signal has its frequency swept from 400 MHz to 570 MHz. The VLSRRs generate idler waves in both directions via DFG, which are measured at ports 1 and 2 of the network analyzer. The low-pass and band-pass filters block the pump and signal, respectively, minimizing the DFG noise generated by the network analyzers themselves. A 6 dB splitter is used to draw a portion of the forward idler signal for measurement at port 2. Assuming perfect matching at the interconnects, the splitter and attenuator ensure that reflections from the band-pass filter incur at least 26 dB of attenuation before reaching the VLSRRs and/or measurement ports throughout the signal/idler frequency band. Ultimately, this ensures that the directionality of the idler and signal waves is preserved throughout. The forward and backward idler spectra are corrected for attenuation along the paths to their respective ports and displayed in Fig. 7.16 (b). The idler spectra show considerable unidirectionality, with the symmetric VLSRR favoring forward generation by more than 6 times, and the anti-symmetric VLSRR favoring backward generation by an order of magnitude. As such,
the results are fully consistent with the predicted nonlinear interference, mediated by nonlinear magnetoelastic coupling in the VLSRR samples.

To support the experimental data, we also include frequency domain scattering simulations in COMSOL Multiphysics, as in Ref. [76]. Pump and signal plane waves are launched from air at a single unit-cell with appropriate periodic boundary conditions, simulating an infinite slab, from which the forward and backward DFG signals are collected, using a Taylor expansion of the varactor’s SPICE model to simulate DFG in the varactors [74]. For direct comparison with experiment, we take into account the attenuation in the experimental setup, as well as the inhomogeneous mode profile within the transmission line. The resulting SH spectra are plotted in Fig. 7.16 (b), in quantitative agreement with measured data. While contributions from the non-resonant nonlinearities are expected to prohibit perfect unidirectional-ity, it is likely that some amount of the weak measured spectra are attributable to unwanted reflections in the experimental setup, implying that the unidirectionality of the fabricated VLSRRs may approach the ideal values achieved in simulation for improved setups.

Both the analysis provided here and the general SRR designs and properties are scalable to terahertz and infrared frequencies, simply by replacing the varactors with nonlinear crystals, or placing the entire structure on a nonlinear substrate. While the configuration of the anti-symmetric SRR represents a difficult fabrication challenge, it is easy to envision implementing the symmetric SRR via lithography over gallium arsenide (GaAs), for example, as in Ref. [61] for near-infrared frequencies, and Ref. [170] for terahertz. Moreover, there exist a number of metamaterial structures capable of supporting a similar overlap of the electrically and magnetically driven local fields, such as paired nanorods and fishnet structures [171]. By proper inclusion of nonlinear dielectrics in these metamaterials, effective properties throughout the nonlinear parameter space should be possible at terahertz, infrared, and even visible
frequencies.
Plasmonic platforms for the visible spectrum

The realization of the strict definition of metamaterials, that is, homogenizable arrays of subwavelength elements, at near-infrared and optical frequencies remains a difficult challenge, both in terms of fabrication and material constraints [171]. As an alternative, metamaterials are often merged with the larger field of plasmonics, which revolves around the exploitation of surface and local plasmon oscillations in metallic structures to manipulate and enhance the interacting electric fields. Indeed, nonlinear metamaterials and plasmonics share many of the same design principles, particularly in that both often utilize subwavelength resonating elements to navigate the competition between linear losses and nonlinear enhancement [172]. On the one hand, the already substantial nonlinear coefficients of metals [56] can be further boosted by the irresistibly large plasmonic enhancements of local fields near metallic surfaces. On the other hand, bulk metals do not support propagating waves by themselves and showcase significant optical losses. In short, the wave propagation characteristics of metals make long interaction lengths impossible at optical frequencies, but their plasmonic and nonlinear properties are promising for achieving high-efficiencies at sub-wavelength scales [57, 58, 54, 55]. Thus, there exists the po-
tential to apply many of the principles discussed throughout this thesis to plasmonic systems.

In this chapter, I consider two plasmonic platforms in detail. First, I discuss four-wave mixing in metal films, since the simplicity of the structure allows for analytic solutions, demonstrating the basic principles of wave mixing with surface plasmons. Second, I present the film-coupled nanoparticle. This system supports features representative of plasmonic dimers in general, but is simpler to fabricate than typical electron-beam etched samples. In lieu of investigating nonlinearity directly in such a structure, I study its properties for fluorescence enhancement due to the availability of experimental results for comparison and verification. Fluorescence and nonlinear enhancements share many common features, particularly a strong sensitivity to the local field enhancement, and so these results can be considered a first-step towards achieving drastically enhanced nonlinear plasmonic activity in the same film-coupled nanoparticles.

8.1 Metal films for nonlinear enhancement

Owing to the centrosymmetry of many metals, the introduction of surfaces and microstructure are not only beneficial, but necessary, to demonstrate significant second-order nonlinear processes. Indeed, second-harmonic generation has been demonstrated in a variety of metal films [173, 174] and nanostructures [175, 176, 163, 177, 178]. Although the third-order nonlinear response of metals does not require such symmetry breaking, the inhibition of propagation in metals requires studying third-order nonlinearities in metal films [179, 179, 180], nanoparticles [181, 182, 183], and gratings [184]. While the metal nanoparticles are theoretically capable of larger enhancements and flexibility than metal films, many of the same principles are shared between these systems. Thus, surface plasmon-enhanced nonlinear processes offer an intuitive and analytically approachable introduction to the broader field of nonlinear
plasmonics.

In particular, the condition for a surface plasmon existing at the interface between two semi-infinite, non-magnetic media can be derived by considering the reflection coefficient,

$$R = \frac{\epsilon_1 k_{2z} - \epsilon_2 k_{1z}}{\epsilon_1 k_{2z} + \epsilon_2 k_{1z}},$$

(8.1)

where $\hat{z}$ is taken to be the direction normal to the interface, and the subscripts ‘1’ and ‘2’ denote the medium. The surface plasmon condition is equivalent to the pole in $R$, which is given by

$$\epsilon_1 k_{2z} + \epsilon_2 k_{1z} = 0.$$  

(8.2)

Clearly, satisfaction of such a relation requires permittivities of opposite values. If we take medium 2 to be a metal with $\text{Re}[\epsilon_2] < 0$, then this is equivalent to

$$k_x = \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_0 (\epsilon_1 + \epsilon_2)}} \frac{\omega}{c},$$

(8.3)

which is ultimately a condition on the angle of incidence required to couple to the surface plasmon. However, since $\epsilon_2$ is negative, then it is clear that the lower bound on $k_x$ is given by $k_x > \sqrt{\epsilon_1/\epsilon_0} \frac{\omega}{c} = |k_1|$. Hence, given a single interface, a propagating wave simply cannot carry enough transverse momentum to directly excite the surface plasmon.

As a product of nonlinear wave-mixing, however, the generated waves have transverse momentum, which we can call $Q_x$, equal to the sum of the interacting waves. As such, three- and four-wave mixing can directly generate surface plasmons [185, 186, 187]. In fact, this can be demonstrated in the analytical expression for the generated electric field at the film [188, 189]

$$E_{1x} = \frac{k_{1z}}{(\epsilon_1 k_{2z} + \epsilon_2 k_{1z})(|Q|^2 - |k_2|^2)} \left[ P_x^{(3)}(|k_2|^2 - Q_x^2 - Q_z k_{2z}) + P_z^{(3)} Q_x(k_{2z} - Q_z) \right].$$

(8.4)
Indeed, the pole in Eq. (8.4) is identical to the surface plasmon condition for the generated wave, implying massive enhancement of the four-wave mixed field when it is coupled to a surface plasmon.

![Image]

**Figure 8.1**: (Reproduced with permission from Ref. [189]. Copyright (2013) by The Optical Society.) Norms of the reflected (a) and transmitted (b) fields generated from a silver film in the Kretschmann configuration as a function of the incident angles of the two fundamental waves. Dashed lines denote the surface plasmon excitation conditions derived from Eq. (8.3). (c, d) Generated field patterns at points I (c) and II (d).

However, it is a far more interesting problem to consider the case when surface plasmons exist for all of the interacting waves. To this end, Liu et. al. extended the transfer matrix method of Chapter 3 to include waves with off-normal incidence [189]. With the transfer matrix method, we were able to extend the above analytic expression to consider multiple interfaces. In particular, in the Kretschmann configuration, in which the fundamental fields are incident on a thin film from a high dielectric, allows for sufficient transverse momentum that the fundamental fields can excite surface plasmons on the far, low dielectric side. As an example, we consider a 40
nm silver film, sandwiched by two semi-infinite regions with $\epsilon_1 = 3\epsilon_0$ and $\epsilon_3 = \epsilon_0$. By launching waves with wavelength 628 nm and 780 nm and calculating the field magnitude at the four-wave mixed wavelength 525.6 nm, we can see the important features in Fig. 8.1 (a, b) as a function of incident angles. Eq. (8.3) predicts that the fundamental fields will couple to surface plasmons at angles of $\pm36.32^\circ$ and $\pm35.93^\circ$, respectively. Furthermore, since the silver film is sandwiched by two different materials (dielectric and air), the generated fields can alternatively couple to surface plasmons or propagating waves at either interface. Thus, the generated spectrum naturally divides into three regions: propagating fields on both sides of the metal film, propagating fields on the substrate side and evanescent fields on the air side, and evanescent fields on both sides, as shown in Fig. 8.1 (c, d). In summary, the nonlinear transfer matrix analysis of the Kretschmann metal film configuration illustrates the most desirable features of a nonlinear plasmonic system: that is, the coupling of highly localized field modes, namely surface and local plasmons, with radiative modes in a highly compact structure, so that energy can be successfully coupled into and out of the system’s nonlinear elements [189].

8.2 Film-coupled nanoparticles for fluorescence enhancement

Metal films, however, can at best confine light in only one dimension. Clearly, the flexibility of plasmonic nanostructures to confine light in two or three dimensions can support even greater enhancements to nonlinear conversion efficiencies. For example, the plasmonic dimer, consisting of two closely spaced metallic nanoparticles, in theory can provide field enhancements that push the very limits of classical assumptions. In practice, however, precise and reliable fabrication of the nanoscale gaps poses an exceedingly difficult obstacle.

Alternatively, advances in layer-by-layer techniques have allowed for very precise control of the spacing between uniform metal films and nanoparticles adsorbed over
Figure 8.2: Diagram of the simulation domain used in exploring fluorescence within the film-coupled nanocube. Inset shows a cross-section, with dimensions and variables indicated.

the surface of a nanoscale insulating layer [190, 191]. Such film-coupled nanoparticles, shown in Fig. 8.2, can display many of the same enhancement features as their plasmonic dimer cousins through the interaction of the nanoparticle and its image, but can be cheaply and quickly manufactured over large areas. In this way, Ciraci et al. were able to probe the limits placed on plasmonic enhancement by the nonlocality of electrons in metals [192].

While the properties of film-coupled nanoparticles suggest them as excellent candidates for nonlinear enhancement, such experiments are quite involved and difficult. Instead, fluorescence can be used as a much easier route to verifying the enhancements achievable in such systems. Indeed, as predicted in 1946 by Purcell, a quantum emitter immersed in a resonant cavity experiences an acceleration in spontaneous emission proportional to $Q/V$, where $Q$ is the mode quality factor and $V$
is the mode volume [193]. Purcell’s pioneering work has been verified in a variety of experimental settings, such as flat interfaces [194], Fabry-Pérot resonators [195], photonic crystals [196], and the near-field of probes [197, 198] and plasmonic nanoantennas [199, 200].

More to the point, fluorescence engineering is generally described through the rates of various atomic transitions. For a quasi-two level system, these channels are conventionally grouped into three rates: the excitation rate, describing transition to a higher energy state often by external pumping; the radiative emission rate ($\gamma_r$), stemming from the emission of free photons; and the non-radiative rate ($\gamma_{nr}$), which includes the generation of bound photons, energy dissipation in the environment, and relaxation into various phononic or trapped modes, such that $\gamma_{sp} = \gamma_r + \gamma_{nr}$. Competition between radiative and nonradiative decay in emissive materials is an active area of research with direct implications in the efficiency of LEDs, lasers, and photovoltaics [201, 202, 203]. The environment of the quantum dot or molecule is known to play a decisive role in its emissive properties, in particular when the environment includes metallic components [195, 194]. While metallic films are known to exhibit massive enhancements in the non-radiative decay rates, inducing fluorescence quenching [204], certain plasmonic nanostructures can offer equally large enhancements to the radiaton rates, leading to a rich and complex engineering space [205, 206].

Here, I computationally investigate a disperse population of film-coupled nanoparticles, correlating changes in the decay rates, quantum yield, and excitation rates with the local plasmonic resonances. I study the film-coupled nanodisk in particular detail, due to its high symmetry and similarity to the plasmonic nanopatch antenna [207]. Furthermore, by varying the particle dimensions and the particle-film gap, I demonstrate fluorescence enhancements of more than four orders of magnitude. Finally, I use the same procedure to predict the enhancement from nanopatches hybridized with fluorophores, and compare these results to experimentally measured
enhancement factors, showing excellent agreement.

8.2.1 Calculating rates and enhancements

In what follows, I employ a simple model for point-dipole emitters in an arbitrary environment, similar to the approach outlined in Ref. [199]. Considering an emitter described by a quasi-two level system and located at position $\vec{r}_m$ within a complex environment, we can write the rate of spontaneous emission as

$$\gamma_{sp} = \frac{2\omega_{sp}}{3\hbar}\vec{p}^2 \rho(\vec{r}_m, \omega_{sp}) + \gamma_{int}^0, \quad (8.5)$$

where $\omega_{sp}$ is the emission frequency, $\vec{p}$ is the transition dipole moment, and $\rho(\vec{r}, \omega)$ is the electromagnetic density of states (LDOS). We have introduced $\gamma_{int}^0$ to represent the non-radiative decay internal to the emitter itself. This can include decay into various phononic or trapped modes of the emitter, such that our model can account for realistic molecules that exhibit non-radiative decay even in the absence of loss. Furthermore, we assume that this internal rate is unaffected by the environment. It is useful to decompose the spontaneous radiation rate according to

$$\gamma_{sp} = \gamma_r + \gamma_{nr} + \gamma_{int}^0, \quad (8.6)$$

where $\gamma_r$ and $\gamma_{nr}$ are traditionally the rate of energy transfer into the radiating and non-radiating modes of the environment, respectively. However, from an experimental perspective, it is often more convenient to consider $\gamma_r$ as the rate of energy transfer to a detector, often positioned in the far-field, and thus lump all other radiative and non-radiative decay into the environment within the parameter $\gamma_{nr}$. In any case, from the emission perspective, the important parameter is the probability of a dipole transition resulting in a radiated photon, given by the quantum yield,

$$QY = \frac{\gamma_r}{\gamma_{sp}}. \quad (8.7)$$
In free-space, by comparison, the only non-radiative channels are internal, or
\[ \gamma_{sp}^0 = \gamma_r^0 + \gamma_{int}^0 = \frac{\gamma_r^0}{QY^0}, \]
where \(QY^0\) is the quantum yield of the fluorophore in free-space. Written this way, it is evident that when the LDOS is very large, the internal channel of decay becomes completely negligible, and the quantum yield of the emitter is nearly independent of its free-space value. As we will show, this holds true for all of the plasmonic systems we consider.

We can express the LDOS using the system’s dyadic Green’s function, \(\bar{G}\), such that
\[ \rho(\vec{r},\omega) = \frac{6\omega}{\pi c^2} [\vec{n}_p \cdot \Im\{\bar{G}(\vec{r},\vec{r})\} \cdot \vec{n}_p], \tag{8.8} \]
where \(\vec{n}_p\) is the dipole moment unit-vector. The radiative and non-radiative rates thus give
\[ \gamma_r + \gamma_{nr} = \frac{2\omega_{sp}}{3\hbar \epsilon_0} [\vec{n}_p \cdot \Im\{\bar{G}(\vec{r},\vec{r})\} \cdot \vec{n}_p]|\vec{p}|^2. \tag{8.9} \]

There are multiple paths to distinguishing between the radiative and non-radiative decay rates in a lossy environment. In Ref. [199], they directly calculate the ohmic losses to find \(\gamma_{nr}/\gamma_{sp}^0\), and use this together with the total rate \(\gamma_{sp}\) to derive \(\gamma_r\) and the quantum yield. However, it is common that for comparison with an experiment, the desired quantity is the power incident on a detector in the far-field. In either case, the results should be self-consistent, although they can differ in their ease of calculation. In what follows, we approximate the total absorption by integrating the absorbed power over the entire simulation domain, \(P_{nr}\). Thus, we can define the non-radiative rate through
\[ \gamma_{nr}/\gamma_r^0 = \frac{P_{nr}}{P_r^0}, \tag{8.10} \]
where \(P_r^0 = \omega^4|\vec{p}|^2/(12\pi \epsilon_0 c^3)\) is the total power radiated by a dipole in free-space.
The quantum yield, in turn, can be written as

\[
QY = \frac{\gamma_r/\gamma_r^0}{\gamma_{sp}/\gamma_r^0} = 1 - \frac{P_{nr}/P_r^0 + \gamma_{int}^0/\gamma_r^0}{\left[\vert \vec{n}_p \cdot \Im \{\bar{G}(\vec{r},\vec{r}) \cdot \vec{n}_p \} \right] + \gamma_{int}^0/\gamma_r^0}
\] (8.11)

The excitation enhancement, on the other hand, is much easier to calculate, stemming only from local enhancements to the exciting fields. For continuous wave excitation at frequency \( \omega_{ex} \), for example, the excitation rate is given by

\[
\gamma_{ex}/\gamma_{ex}^0 = \frac{\left| \vec{E}(\vec{r}_m, \omega_{ex}) \cdot \vec{n}_p \right|^2}{\left| \vec{E}^0(\vec{r}_m, \omega_{ex}) \cdot \vec{n}_p \right|^2}.
\] (8.12)

Furthermore, at equilibrium, the rates of change in the populations of the involved atomic levels must be equal. For a quasi-two level system, depicted in Fig. 8.3, this implies \( N_1 \gamma_{ex} = N_2 \gamma_{sp} \), where \( N_1 \) and \( N_2 \) are the level populations. If we assume weak excitation such that \( N_1 \) is negligibly depleted, we can define a total enhancement
factor by comparing the power radiated by the emitter to that in free-space, giving

\[
\text{EF} = \frac{N_2\gamma_r}{N_1^0\gamma_r^0} = \frac{N_1\gamma_{ex}/\gamma_{sp} \gamma_r}{N_1^0\gamma_{ex}^0/\gamma_{sp}^0 \gamma_r^0} = \frac{\gamma_{ex}}{\gamma_{ex}^0} \frac{\text{QY}}{\text{QY}^0}.
\]  

(8.13)

Written this way, it is clear that the overall enhancement of fluorescence is controlled by two key factors: the local electric field exciting the emitter, which can be enhanced by orders of magnitude; and the quantum yield, which can be no greater than 1, and is often much lower for realistic systems and molecules. Both of these quantities are expected to be highly sensitive to the emitter’s position relative to nearby plasmonic nanostructures. For example, Ref. [199] demonstrates a transition between quenching and enhancement as a quantum emitter is brought within \(\sim 5\) nm of a gold nanoparticle.

8.2.2 Fluorescence enhancement in film-coupled nanoparticles

In the context of plasmonic enhancement, then, the goal is to access the large local fields in exciting the fluorophore, while avoiding quenching of the quantum yield by the unavoidable ohmic losses and bound modes that accompany metals. In what follows, we computationally investigate a disperse population of film-coupled nanoparticles, correlating changes in the decay rates, quantum yield, and excitation rates with the local plasmonic resonances. We study the film-coupled nanodisk in particular detail, due to its high symmetry and similarity to the nanopatch. Furthermore, by varying the particle dimensions and the particle-film gap we predict spontaneous decay rates accelerated by more than four orders of magnitude, while simultaneously achieving near unity quantum yields.

Using a finite-element method software package (COMSOL multiphysics), we first simulate the scattering of a plane wave at \(\lambda_{ex}\) from the film-coupled nanoparticle (Fig. 8.2) to determine the local field strength exciting the fluorophore from the laser. For film-coupled nanoparticles with resonances close to \(\lambda_{ex}\), the tightly confined
Figure 8.4: Simulated emissive properties of a 100 nm diameter silver nanosphere located 5 nm over a silver film as a function of fluorophore position.

cavity mode induces a local field under the nanodisk many times greater than the exciting field. Next, we investigate the effect of the film-coupled nanoparticles on fluorophore emission by placing a unitary point-dipole at various positions under the nanoparticle. We model the emitter as a monochromatic point-dipole source. While the fluorophore under the cube can be randomly oriented, the \( \hat{z} \)-component of the electric field is dominant in the nanoparticle-film gaps, such that we can neglect the transverse orientations. While the results are intended to be applicable to a wide class of quantum emitters, for the sake of a realistic model, we select parameters to fit with the experiments recently performed in Ref. [208], which used the fluorophore sulfo-cy5 carboxylic acid (Cy5) with an emission peak at \( \lambda_{sp} = 665 \text{ nm} \), a free-space quantum yield of \( QY^0 = 0.2 \), and excited by a HeNe laser (\( \lambda_{ex} = 632.8 \text{ nm} \)). For normalization, the same simulations are carried out for a point-dipole in free-space. As an example, the rate enhancements are calculated in this way for a typical film-
coupled nanosphere and plotted in Fig. 8.5.

Silver nanocubes have provided a similar plasmonic platform, but with several important advantages. In such film-coupled structures, termed nanopatch antennas, the fundamental resonance can be described as a Fabry-Perot effect in the guided gap-plasmon mode. As a consequence, the plasmonic resonance scales easily and predictably with the nanocube dimension, and can be tuned throughout the visible and near-infrared spectra. For example, Moreau et al. used nanopatches to construct a surface with controlled optical reflectance [207]. Furthermore, the nanopatch antenna naturally couples to a high density of radiative modes, making it an excellent candidate for the enhancement of fluorescence and spontaneous emission. For comparison to the film-coupled sphere, the rate enhancements are calculated for a typical nanopatch antenna and plotted in Fig. 8.5. Not only does the nanocube support higher fluorescence enhancements, but it does so over a much greater surface area.
In most experimental setups, however, the fluorophores are spatially distributed under the nanocubes. Thus, it is useful to consider the mean values of the various emission and excitation quantities, denoted by $< x >$. We find approximate values for $< \text{QY} >$, $< \gamma / \gamma^0 >$, and $< \gamma_{ex} / \gamma^0_{ex} >$ by averaging over the computed fluorophore grid directly beneath the nanocubes. For a constant gap thickness of 5 nm, we perform this calculation for a variety of nanocube sizes, and display the resulting rates and enhancements as a function of nanocube resonance in Fig. 8.6.

Clearly, the largest enhancements are achieved by matching the nanopatch reso-
Figure 8.7: Averaged enhancements in the emissive properties of a silver nanodisk over a silver film for various disk diameters and gap thicknesses, constrained such that the resonant wavelength is fixed at 632.8 nm, plotted as a function of gap thickness.

Resonance to the excitation wavelength. However, since both the gap size and nanocube dimension can tune the resonance, there are a continuum of nanopatch geometries that can resonate at the same frequency. To explore this parameter space, we find the combination of disk diameter and gap that resonate at $\lambda_{ex}$, and plot the enhancement as a function of gap size in Fig. 8.7. Both the excitation enhancement and quantum yield improve for smaller gap sizes and nanocubes, in agreement with the conclusions of Ref. [205] for film-coupled nanowires. It is worth noting, however, that this scaling is ultimately limited by many competing effects that become non-negligible at sub-nanoscale gaps, including electron nonlocality and exciton generation, which are ignored in the presented calculations [209, 210, 204].
For comparison to the above theory, nanopatches were synthesized and hybridized with fluorophores, demonstrating spontaneous emission from a large population of variously sized nanopatches. As predicted, the fluorescence shows a strong and robust correlation with the nanopatch resonance, with averaged fluorescence enhancements of more than 30,000 for nanopatches resonating at the fluorophore’s wavelength of excitation. The following subsection is reproduced with permission from Ref. [208].

**Figure 8.8:** (a) Schematic of the plasmonic nanopatch antenna platform, consisting of colloidally synthesized nanocubes dispersed over a silver film and separated by a fluorophore-coated spacer layer. (b) Comparison of typical plasmonic enhancement systems. The top row shows the geometry and resonant electric field distribution, while the bottom rows describe the plasmonic systems qualitatively through effective and image dipoles and radiation patterns.
The nanopatch antennas consist of colloidally synthesized silver nanocubes deposited over a 50 nm silver film. The cubes and film are separated by a $\sim 5$ nm self-assembled polyelectrolyte (PE) spacer layer, coated with a dilute layer of fluorophores (sulfo-cy5 carboxylic acid (Cy5), inset in Fig. 8.8 (a)). Like its namesake, the nanopatch naturally couples to a high density of radiative modes, concentrating incident light to the gap between the nanocube and the metal film (Fig. 8.8 (b)).

It is important to note that while field localization has been exploited in bowtie nanoantennas [200] and nanosphere dimers [211], the plasmonic resonance in the nanopatch is fundamentally distinct, arising from Fabry-Perot-like oscillations in the gap-plasmon mode supported between the nanocube and the silver film [207]. As a consequence, for a given silver film and spacer layer, simply increasing the size of the nanocube can red-shift the resonance throughout the visible and near-infrared spectra. Indeed, our nanopatch population was observed, via dark-field imaging, to elastically scatter white light with varying colors, indicative of the resonant wavelength of each nanopatch. Moreover, the nanopatch gap covers a surface area equal to its own physical cross-section. Thus, while the singular-like ‘hot spots’ in bowtie and nanosphere dimers can offer large single-molecule enhancements, the nanopatch is far better suited for both large-area and tunable applications.

With this in mind, we define for each nanopatch an averaged fluorescence enhancement factor, $<EF> = \frac{P_{np} A_{roi}}{P_c A_{np}}$, where $P_{np}$ is the emitted intensity collected through a far-field aperture and integrated over a region of interest containing a single nanopatch; $P_c$ is the same quantity from a control sample consisting of glass, PE, and Cy5; $A_{roi}$ is the area of the region of interest; and $A_{np}$ is the physical cross-section of the nanopatch, as measured by scanning electron microscope (SEM).

Averaged enhancement factors were measured for 48 isolated nanopatches, with side-lengths ranging from 50 to 100 nm, under excitation by a continuous wave HeNe laser.
(λ_{ex} = 632.8 nm). Additionally, the resonance wavelength (λ₀) of each nanopatch was obtained from its elastic scattering spectra.

Though all 48 nanopatches had the same gap thicknesses, the measured fluorescence ranged from near background levels, indicative of quenching, to enhancements of more than four orders of magnitude. The fluorescence enhancement factors are given as a function of resonance wavelength in Fig. 8.9. As expected, the enhancement factors correlate strongly with nanopatch resonance, such that the nanopatches with the largest \( < \text{EF} > \) are those that resonate close to the excitation wavelength. The statistical variation in the measured enhancement factors can be attributed to the random distribution of Cy5 over the spacer layer, leading to non-uniform numbers of fluorophores in the relatively large gaps of each nanopatch. These results are in contrast to Ref. [212], which reports fluorescence quenching when the plasmon resonance matches the emission wavelength, as well as Ref. [199], in which a transition from fluorescence enhancement to quenching occurs for fluorophore-nanoparticle distances below 5 nm.

Using Eq. (8.13), normalized by the glass configuration instead of free-space, and finite-element simulations (COMSOL multiphysics), we found quantitative agreement - in both trend and magnitude - with the measured enhancement factors as a function of nanopatch resonance. The resonances and excitation enhancement of the individual nanopatches were obtained in a manner similar to Ref. [207], using a spherical domain with absorbing boundaries to model the scattering from a nanocube over a silver film. Since losses in silver films can be hard to know a priori due to surface roughness and oxidation, we include a multiplicative factor to the imaginary part of the permittivity and find that a value of 1.75 gives good agreement between the full-width half maxima of the simulated and measured scattering resonances. To calculate the emissive properties, additional simulations were performed following the procedure outlined in Ref. [199], modeling the Cy5 molecules
as monochromatic point-dipoles ($\lambda_{sp} = 665$ nm) located all along a grid in the gap between the nanocube and the spacer layer. The local fields in the nanopatch are up to two orders of magnitude larger than the incident fields, such that the largest single-molecule enhancement factors occur in fluorophores located at the corners and edges. Finally, following the usual assumption that the fluorophores are randomly distributed over the surface, the fluorescence enhancement factors were averaged over all orientations and locations beneath the cube, and normalized by the same quantities obtained from simulations of the control sample.

In order to understand the worth of the model as a predictive tool, we employ a simple goodness of fit analysis. Since it appears from the data that the standard deviation in the measured $< EF >$ is not uniform but rather scales with $< EF >$, 
a fact consistent with a random distribution of fluorophores, it is more useful to consider the data in log-scale, as in Fig. 8.2.3. To get a rough estimate of the variance in the measured EF, we perform a least-squares fit of a piece-wise linear function to the measured data. Using this value for the variance of the measured $\langle EF \rangle$, we perform a standard reduced chi-squared analysis between the measured EF and the simulation results from Fig. 8.9 (c), again in log-scale, and find $\chi^2_{\text{red}} = 1.21$. Such a value corresponds to a p-value of 0.15, indicative of a reasonable fit between the simulation and experimental results [213].

![Figure 8.10](image.png)

**Figure 8.10:** Plot of the averaged fluorescence enhancement factor versus resonant wavelength in log-scale. The data is fit with a piece-wise linear function to determine a rough estimate of the variance in the measured data. This variance in turn is used in analyzing the goodness-of-fit of the simulations with the measured data, as shown in Fig. 8.9.

The average simulated excitation, radiative, and non-radiative rates are shown in Fig. 8.2.3 as a function of nanopatch resonance. In a lossless environment, $\gamma_{nr}$, and thus the quantum yield, is determined by internal channels of decay. Extrapolating the internal decay rate of Cy5 from its in-solution quantum yield ($\sim 20\%$), however, it becomes clear that the internal decay channel is simply too slow to significantly contribute in the proximity of the plasmonic resonance [200]. Instead, spontaneous
decay in the nanopatch can be visualized as a two-step process. First, the excited fluorophore experiences an accelerated decay into one of the gap-plasmon modes of the nanopatch, such that the spontaneous decay rate is maximized in nanopatches resonating at the peak emission wavelength, $\lambda_{sp}$. From here, the gap-plasmons couple to radiative modes, are absorbed within the metal, or couple to surface modes and are eventually absorbed, as well. This second step is defined by the nanopatch geometry, and is key in avoiding quenching. By comparison, fluorophores sufficiently close to a bare silver film experience accelerated decay into surface-plasmon modes, enhancing the spontaneous decay rate at resonance [214]. In the absence of nanostructures and defects, however, these surface modes do not radiate, and contribute only to the non-radiative rate. This difference in the nanopatch, namely the subsequent coupling of gap-plasmons to radiative modes, explains why the quantum yield is not quenched at resonance, but instead stays in the range of 20 - 30%. On the other hand, the largest field localization occurs at the nanopatch resonance, such that the rate of excitation, and thus $\langle EF \rangle$, is markedly enhanced for nanopatches resonating at $\lambda_{ex}$.

While the fluorescence enhancement experiments purposefully used a non-uniform population of nanopatches, a surface of properly tuned nanopatch antennas can function as an ideal, uniform, large-area emitter. In fact, after correcting for the intrinsic quantum yield of Cy5 compared to the fluorophores used in other studies [215, 216], the area-averaged fluorescence enhancement factors of the excitation-correlated nanopatch are the highest to-date when extrapolated for a surface coverage of only $\sim 1\%$. This is remarkable when considering that the nanopatch is colloidally fabricated, potentially enabling inexpensive single-photon sources for quantum information applications [46]. Furthermore, the control over the spontaneous emission demonstrated herein, nearly independent of the fluorophore’s in-solution quantum yield, is especially promising for biosensing and fluorescence imaging [217, 218], with
Figure 8.11: The simulated excitation, radiative, and non-radiative rates as a function of nanopatch resonant wavelength. The internal decay rate of Cy5, $\gamma_{nr}^0 \approx 5\gamma_r^0$, is shown to be negligible by comparison.

the potential to enhance the performance of conventionally poor labels.
The benefits metamaterials bring to the field of nonlinear optics can be broken into three categories. The first is simply in terms of flexibility, in that nonlinear metamaterials are capable of supporting combinations of linear and nonlinear properties that are simply unavailable, or exceedingly weak, in conventional nonlinear materials. For example, the realization of a nonlinear response in a negative-index medium lead to the first demonstration of direct phase matching of a second-harmonic wave in the opposite direction to the fundamental wave, shown in chapter 7. Nonlinear magnetoelectric coupling also deserves mention here. By simple tweaks to well-established metallic patterns, nonlinear metamaterials can support a massive spectrum of possible property combinations. However, these demonstrations fall into the category of fundamental science, and are more interesting for their novelty than their application to real-world problems. Indeed, such exotic properties almost always require operation within narrow frequency bands of resonant elements, which introduces loss, spatial dispersion, and a host of fabrication problems when considering the scaling of such designs to terahertz and optical frequencies. Nevertheless, a broad range of novel phenomena remain to be demonstrated. The work in section 1 of chapter 7,
for example, can be extended to the parametric amplification of a negative index wave as a potential solution to the problem of losses in negative index materials. In addition, microwave metamaterials lend themselves to experimental field mapping, which should be extendable to nonlinear processes. This is especially interesting for investigating the nonlinear mixing of surface plasmons, a problem with many implications in the optical domain, as described in chapter 8, but can be more easily investigated and understood in the microwave regime with suitable metamaterial ‘plasmonic’ surfaces.

The second advantage of metamaterial engineering for nonlinear optics comes in the form of more modest adjustments to existing nonlinear materials. By this, I mean the use of non-resonant metallic components, or even all-dielectric composites, to moderately enhance and reconfigure the effective linear and nonlinear properties of the constituents. The cut-wire and I-beam structures studied in chapter 5 are canonical examples. Such composites can, for example, adjust the linear anisotropy in order to extend the bandwidth of birefringence phase matching, or even allow for birefringence phase matching of counter propagating waves, as shown in chapter 6, while mitigating the optical losses. Devices based on this sort of moderate metamaterial engineering would indeed resemble conventional nonlinear devices, operating over optically large distances, while introducing additional loss and/or fabrication complexity in exchange for optimization of some important property, such as poling voltage, operating intensity, or bandwidth. In particular, such designs hold the greatest promise in the terahertz range, where metals are less lossy but the applications still significant. By engineering metamaterials simultaneously in the infrared and terahertz regimes, it should be possible to improve on existing infrared-pumped terahertz amplifiers and oscillators. The birefringence phase matched counter-propagating terahertz oscillator, in particular, is exciting both from a fundamental science viewpoint and in terms of its advantages over standard cavity-based oscillators.
Finally, the third and potentially most exciting application of nonlinear metamaterials comes in the form of extremely compact all-optical devices. Indeed, the losses associated with nonlinear metamaterials, especially those operating near resonance, ensure that they can never compete with the efficiencies of the much larger conventional devices based on ferroelectrics and glasses. However, as demonstrated by the ELC and SRR in chapter 5, a slab of resonant nonlinear metamaterial can achieve significant efficiencies in a device that is in fact smaller than the wavelength of operation. While this trade-off of total conversion efficiency for dramatic miniaturization implies that the nonlinear metamaterial cannot compete in many industrial applications where efficiency is most important, it is not hard to envision niche markets where device footprint is the limiting factor, especially when considering the recent trend towards photonic integrated circuits [219]. In this area, optical nonlinear metamaterials, and the broader field of nonlinear plasmonics, have the potential to achieve certain operating constraints in devices that are orders of magnitude more compact than conventional materials. The experimental results for fluorescence in the nanopatch, specifically the enhancement of more than four orders of magnitude presented in chapter 8, pave the way for demonstrations of even greater enhancements in a plethora of nonlinear processes, which of course scale nonlinearly with local field enhancements. As an example, one can envision a next-generation quantum information platform, sitting on a silicon chip, and housing an unobtrusive and inexpensive 1 µm² panel of film-coupled nanoparticles as its source of down-converted entangled photons, exploiting the nonlinearity of the metal itself.

Indeed, nonlinear metamaterials will continue to be an exciting and attractive field. Metamaterials can surmount many of the barriers in nonlinear optics within a variety of fundamental and niche applications, due to the unprecedented configurability and enhancements that these composites offer. As the field inevitably moves towards real world applications, the ability to accurately design and characterize non-
linear metamaterials will prove essential. With this goal in mind, I have presented a very general set of tools for understanding, designing, and optimizing parametric processes in metamaterials. The demonstrations that have followed are merely the lowest hanging fruit made accessible by this framework, and will hopefully generate greater intuition in achieving, and excitement for realizing, novel nonlinear metamaterials as the core of a new generation of compact, all-optical devices.
Appendix A

Clarification of contributions

All of the text here, even that reproduced from published articles, is my own. Smith advised and counseled throughout all of the presented work.

The derivation and formalism in chapter 2 is my own adaptation of the well-established framework within nonlinear optics.

The transfer matrix method retrieval was conceived and developed by Larouche and Smith for second-harmonic generation [67]. I carried out the derivation of chapter 3 extending this framework to arbitrary three- and four-wave mixing. The VLSRR medium used to verify the transfer matrix retrieval method was fabricated by Huang, and measured by both Huang and myself. I carried out the numerical verification in COMSOL, as well as the experimental retrieval and comparison to analytic formula.

I conceived and derived the coupled mode theory for nonlinear metamaterials presented in chapter 4, with input from Larouche, Smith, and Poutrina for the final form of the equations. I performed all of the numerical comparisons used in verifying its accuracy. In the process of its derivation, I discovered the applications to nonlinear magnetoelectric coupling and nonlinear interference, and both designed and
investigated the prototypical nonlinear magnetoelectric metamaterial. I subsequently derived the symmetry and spatial dispersion characteristics.

I performed the simulations for all four canonical nonlinear metamaterials of chapter 5, as well as the subsequent analysis of the optimal lengths and efficiencies. The concept of anisotropy and poling engineering in section 4 was developed by myself and Sullivan, while I performed the simulations and analysis of the gold nanorod array. I also carried out the derivation in the appendix for finding two simultaneous nonlinearities with the transfer matrix method, while Larouche has since extended this to include all eight nonlinearities.

I derived all of the metamaterial phase matching conditions presented in chapter 6, including that of quasi-phase matching in a continuous medium. I proposed and analyzed the birefringence phase matched MOPO using overlapped silver bars.

The circuit model presented in chapter 7 was developed by Poutrina et al. [74]. I conceived, designed, and analyzed the experiments for negative-index phase matching, index-near-zero phase matching, quasi-phase matching, nonlinear magnetoelectric coupling, and nonlinear interference. The fabrication and measurement for each sample was performed by both myself and Huang.

The transfer matrix method for off-normal incidence was derived by Liu and Poutrina [189]. I advised its application to the Kretschmann and multi-layer configurations and contributed to the analysis and interpretation. The fluorescence experiments were conceived, designed, and implemented by McGuire, Mock, Hoang, Mikkelsen, and Smith [208]. I derived the effective analysis of the fluorescence rates, loosely following that of Ref. [199]. I designed and implemented all fluorescence simulations, performed the comparison between experiment and simulation, and wrote the subsequent analysis. Figure 8.8 contains contributions from Ciraci.
Bibliography


[73] SMV123x series: hyperabrupt junction tuning varactors (Data sheet), 2009.


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[215] For sufficiently strong enhancements, the fluorescence enhancement factor is inversely proportional to the intrinsic quantum yield of the fluorophore, such that a system’s figure of merit is best described by ‘$<EF> \propto QY^0$’.


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