

A quantum chemical approach to the design of chiral negative index materials

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Abstract: This paper presents methodology developed for the computational modeling and design of negative refractive index materials (NIMs) based on molecular chirality. An application of the methodology is illustrated by *ab initio* computations on two organometallic molecules which constitute the monomer units of a chiral polymer. Comparisons with experimental data for the polymer are made. Even though the resulting chirality parameter for the pristine material is small, it is shown that negative index can be achieved by introducing sharp plasmonic resonances with metal nanoparticle inclusions.

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References and links

1. A. N. Grigorenko, "Negative refractive index in artificial metamaterials," *Opt. Lett.* **31**, 2483-2485 (2006).
2. J. B. Pendry, "Negative refraction makes a perfect lens," *Phys. Rev. Lett.* **85**, 3966-3969 (2000).
3. S. Tretyakov, I. Nefedov, A. Sihvola, S. Maslovski, and C. Simovski, "Waves and energy in chiral nihility," *J. Electromagn. Waves Appl.* **17**, 695-706 (2003).
4. J. B. Pendry, "A chiral route to negative refraction," *Science* **306**, 1353-1355 (2004).
5. Y. Jin and S. He, "Focusing by a slab of chiral medium," *Opt. Express* **13**, 4974-4979 (2005).
6. J. Q. Shen and S. He, "Backward waves and negative refractive indices in gyrotropic chiral media," *J. Phys. A: Math. Gen.* **39**, 457-466 (2006).
7. J. Q. Shen, M. Norgren, and S. He, "Negative refraction and quantum vacuum effects in gyroelectric chiral medium and anisotropic magnetoelectric material," *Ann. Phys. (Leipzig)* **15**, 894-910 (2006).
8. V. M. Agranovich, Yu. N. Gartstein, and A. A. Zakhidov, "Negative refraction in gyrotropic media," *Phys. Rev. B* **73**, 045114 (2006).
9. Q. Cheng and T. J. Cui, "Negative refractions in uniaxially anisotropic chiral media," *Phys. Rev. B* **73**, 113104 (2006).
10. V. Yannopapas, "Negative index of refraction in artificial chiral materials," *J. Phys.: Condens. Matter* **18**, 6883-6890 (2006).
11. E. U. Condon, "Theories of optical rotatory power," *Rev. Mod. Phys.* **9**, 432-457 (1937).
12. K. Ruud and T. Helgaker, "Optical rotation studied by density-functional and coupled-cluster methods," *Chem. Phys. Lett.* **352**, 533-539 (2002).
13. J. J. Maki and A. Persoons, "One-electron second-order optical activity of a helix," *J. Chem. Phys.* **104**, 9340 (1996).
14. S. A. Tretyakov, F. Mariotte, C. R. Simovski, T. G. Kharina, and J.-P. Heliot, "Analytical antenna model for chiral scatterers: Comparison with numerical and experimental data," *IEEE Trans. Antennas Propag.* **44**, 1006 (1996).
15. V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyonovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H. W. Spiess, S. D. Hudson, and H. Duan, "Self-organization of supramolecular helical dendrimers into complex electronic materials," *Nature* **419**, 384-387 (2002).

16. M. Krykunov, M. D. Kundrat, and J. Autschbach, "Calculation of circular dichroism spectra from optical rotatory dispersion, and vice versa, as complementary tools for theoretical studies of optical activity using time-dependent density functional theory," *J. Chem. Phys.* **125**, 194110-13 (2006).
17. C. R. Jeggo, "Nonlinear optics and optical activity," *J. Phys. C: Solid State Physics* **5**, 330-337 (1972).
18. A. D. Buckingham and M. B. Dunn, "Optical activity of oriented molecules," *J. Chem. Soc. A* **1988** (1971).
19. M. Krykunov and J. Autschbach, "Calculation of origin independent optical rotation tensor components for chiral oriented systems in approximate time-dependent density functional theory," *J. Chem. Phys.* **125**, 034102-10 (2006).
20. J. Autschbach and T. Ziegler, "Calculating electric and magnetic properties from time dependent density functional perturbation theory," *J. Chem. Phys.* **116**, 891-896 (2002).
21. J. Autschbach, T. Ziegler, S. Patchkovskii, S. J. A. van Gisbergen, and E. J. Baerends, "Chiroptical properties from time-dependent density functional theory. II. Optical rotations of small to medium sized organic molecules," *J. Chem. Phys.* **117**, 581-592 (2002).
22. E. J. Baerends et al., Amsterdam density functional, Theoretical Chemistry, Vrije Universiteit, Amsterdam (URL <http://www.scm.com>).
23. M. Krykunov and J. Autschbach, "Calculation of optical rotation with time-periodic magnetic field-dependent basis functions in approximate time-dependent density functional theory," *J. Chem. Phys.* **123**, 114103-10 (2005).
24. J. Autschbach, L. Jensen, G. C. Schatz, Y. C. E. Tse, and M. Krykunov, "Time-dependent density functional calculations of optical rotatory dispersion including resonance wavelengths as a potentially useful tool for determining absolute configurations of chiral molecules," *J. Phys. Chem. A* **110**, 2461-2473 (2006).
25. W. T. Doyle, "Optical properties of a suspension of metal spheres," *Phys. Rev. B* **39**, 9852-9858 (1989).
26. S. Tretyakov, A. Sihvola, and L. Jylhä, "Backward-wave regime and negative refraction in chiral composites," *arXiv:cond-mat/0509287*, **1** (2005).
27. J. Autschbach, "Density Functional Theory applied to calculating optical and spectroscopic properties of metal complexes: NMR and Optical Activity," *Coord. Chem. Rev.*, in press.

1. Introduction

There is a tremendous interest in the possibility of development of materials and structures (metamaterials) with the ability to exhibit a negative index of refraction [1]. Various approaches have been proposed to achieve the negative index within an electromagnetic wavelength range of interest, with the highest interest in the materials for the visible-infrared range. There are a number of technological challenges that are difficult to meet with typical metamaterial approaches. The optical losses of the medium have to be manageable to provide for effects such as focusing by plane-parallel negative index material (NIM) slabs [2]. It would also be advantageous if the negative index could be obtained over a range of directions for propagation of light. One of the proposed routes towards negative refractive indices is based on the use of strongly chiral media [3-10]. This may potentially lead to materials for which some of the problems encountered with metamaterials are alleviated. In particular, neither permittivity nor permeability needs to be negative to achieve NIM in this approach. Moreover, the difficulty of the NIM paradigm is avoided of extending the concept of a magnetic resonance to the frequency region corresponding to the visible range. Electrical and magnetic properties in the resonant region are treated within the same framework of quantum chemical simulations. The new paradigm calls for the use of chiral molecules or chiral supramolecular and polymeric structures. By using such a "chemical" approach, it is possible to reduce the need for including metamaterial components with dimensions comparable to the wavelength of light, and to use smaller active elements than in the typical metamaterial approach, which would help to reduce scattering losses. In this paper we investigate a quantum chemical protocol for the design and optimization of molecular structures suitable as building blocks for negative refractive index (meta) materials.

2. Methodology

In a chiral medium, i.e. in a medium exhibiting electromagnetic handedness, an electric or magnetic excitation simultaneously produces both electric and magnetic polarization. The

background of our approach stems from the so-called bi-isotropic formulation of the constitutive relations proposed by Condon in his early 1937 paper [11]. This formulation of the constitutive relations assumes a reciprocally bi-isotropic chiral medium. The sought-after material is indeed isotropic because we assume a non-ordered random distribution of chiral structures inside, for example, a host matrix, with $\lambda \gg a$, where λ is the wavelength of the incident light and a is a characteristic size of the material's constituents. It is also reciprocal because it is assumed linear and non-magnetic (i.e. a magneto-electric effect does not occur). Finally, the bulk material is chiral as consisting of chiral molecules. The bi-isotropic constitutive relations are given as

$$\begin{aligned}\bar{D} &= \epsilon \bar{E} + (\chi - i\kappa) \sqrt{\epsilon_0 \mu_0} \bar{H}, \\ \bar{B} &= \mu \bar{H} + (\chi + i\kappa) \sqrt{\epsilon_0 \mu_0} \bar{E}\end{aligned}\quad (1)$$

in SI units, where χ is the non-reciprocity parameter and κ is the chirality parameter. Evidently, $\chi = 0$ for a reciprocal material. Negative refraction (or backward waves) will occur at one of the eigen (circular) polarizations of the incident light, if the chirality parameter, κ , is larger than the square root of the product of permittivity and permeability [3]:

$$k_{\pm} = k_0 (\sqrt{\epsilon \mu} \pm \kappa). \quad (2)$$

Here, $k_{\pm}$ is the propagation constant of two eigen-waves in the isotropic chiral medium, κ is the chirality parameter, ϵ denotes the scalar macroscopic dielectric permittivity (for an isotropic material), and μ denotes the macroscopic magnetic permeability.

Development of methods for the *ab initio* theoretical modeling of chiral NIMs is of great significance as it can provide a basis to understand the structure-property relations necessary for a rational design of the material's building blocks. In turn, this can lead to an optimization of structures for producing molecular materials with large chiral parameters. It is worthwhile to note that in the area of computational nanophotonics density functional theory (DFT) is usually preferred to wavefunction based *ab initio* calculations. This is because DFT combines affordable computational costs and reasonably high accuracy due to effects from electron correlation. We present in this paper a framework to study NIMs which utilizes first principles quantum chemical computations of the mixed electric-magnetic polarizabilities that are responsible for chiral properties of molecules. In this quantum-theoretical approach we start out by building the basic building blocks of the material from atomic nuclei and electrons and express the whole system in terms of the Schrödinger or Dirac equations. These equations can only be solved after using a series of approximations based on the underlying physics and mathematics. The property of interest is then obtained by applying time-dependent variational density-functional response theory to calculate the linear response functions with respect to electric and magnetic dipole fields [12, 19-21]. These have now been coded for the calculation of most electromagnetic properties, resonant or non-resonant, representing low or high orders in the matter-field interaction, including the electromagnetic linear or nonlinear chirality properties of interest. Theoretical modeling can fulfill two important tasks: to predict the chirality of a given material on the molecular level and to establish structure-property relations that can assist the chemical synthesis of new materials with the desired functionality. To find a molecule with the highest possible value of molecular chirality, it would be desirable to preliminarily analyze the possible outcome before starting time-consuming *ab initio* calculations. Such an analysis may be based on analytical models [13, 14] of electric dipole-magnetic dipole polarizability of a small particle. Though classical in nature, for a helical molecule these models might yield the same scaling law with pitch and radius of the helix as in the quantum mechanical calculations. This would allow for identifying promising candidates for refined *ab initio* computations simply by inspecting an optimized geometry

(which can be obtained with fast semi-empirical methods, such as AM1 or PM3). A higher value of the ratio of radius to pitch should be expected to indicate an increase in the value of the optical rotatory parameter, in particular when comparing systems that have similar chromophores (meant here as highly polarizable moieties). Other criteria are also of importance. For molecules with chains containing delocalized π -electrons such a criterion is the conjugation length, which influences the magnitude of the molecular polarizability. This and other issues have to be addressed in the design process. We envision that simple models may be used for a fast screening of a large set of potential compounds. However, follow-up *ab initio* computations need to confirm if the system has a large chirality parameter since the relation between structure and optical activity is complex and influenced by many factors such as functional groups, the exact nature of the chromophore and so on.

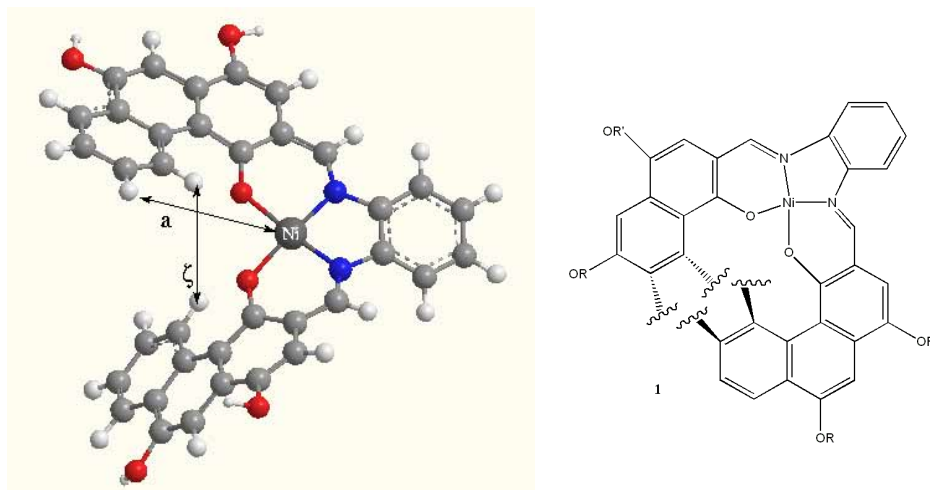


Fig. 1. Monomeric Ni complex 1. Right: monomer unit of the polymer. Left: model complex used in the *ab-initio* computations to represent the monomer.

Once a promising structure is chosen, the quantum chemical *ab initio* computations can be applied to determine the microscopic molecular chirality as well as the polarizability. Various approaches can then be used to assess the macroscopic dielectric properties of a medium composed of chiral molecules. In the simplest case one can assume an oriented gas without interactions between the molecules that constitute the components of the material. Composite materials can be dealt with through an effective medium (EM) approach, for instance the Maxwell-Garnett mixing formula. Within this approach one can also assess the influence of modifications in the local fields encountered by the chiral molecule on the macroscopic chirality parameter. One possible way of obtaining very large chirality parameters is the so-called supramolecular approach where self-assembling helical structures of chiral molecules boost the chirality [15]. Such an approach may, however, require a more refined theoretical methodology for computation of the chirality since *ab initio* computations of the optical activity of supramolecular assemblies are far from being straightforward. However, we envision that *ab initio* computations may be instrumental even for macromolecules in this framework. For instance they may be utilized to determine the transition dipole moments of the electronic excitations for the monomer structures and the influence of coupling between a few oligomer units. Based on this and some basic structural information, a coupling model should be able to yield a reliable estimate of the chirality parameter near a resonance. For wavelengths far away from resonances direct computations of the optical rotatory strength for the monomer and small oligomer units might yield useful insight.

In the following we illustrate how quantum chemistry derived data can be used to predict properties of a model chiral material. We employ here computations carried out on two chiral organometallic complexes. The complexes are not yet optimized for high chirality but are representative of relatively small chiral molecules with comparatively strong optical activity. The computed values can be compared to a set of preliminary experimental data that we have obtained from circular dichroism studies. The complexes are shown in Figs. 1 and 2.

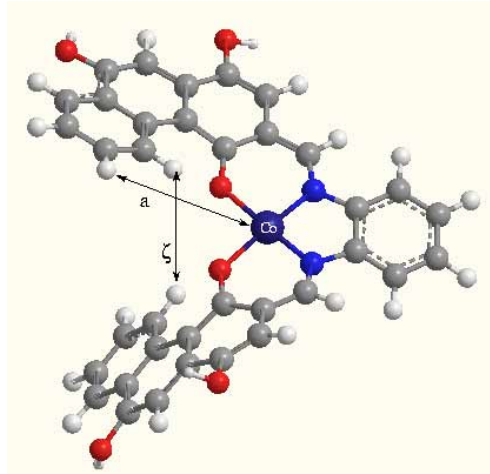


Fig. 2. Monomeric Co complex 2

3. Estimation of the chirality parameter from an experimental CD spectrum

To compare the computational results to experiment we propose the use of circular dichroism (CD) data. The chirality parameter of a material is directly related to the optical rotation strength and thus can be measured via the optical rotatory dispersion (ORD). This is not always practical for a large range of wavelengths, and thus an alternative way of estimating the chirality parameter is to employ the Kramers-Kronig (KK) transform of the circular dichroism spectrum of a material. We have measured the CD spectrum of the Ni complex (Fig. 1) in polymeric form in solution at a concentration of 4.4×10^{-6} M. A numerical KK transformation (see Ref. 16 for details) yielded the ORD from which the value of the optical rotatory parameter, β , at each wavelength can be extracted. Based there upon we estimate the chirality parameter (in SI units) of the Ni complex from [17]:

$$\kappa = N\mu_0\beta\omega c, \quad (3)$$

where N is the concentration of the chiral molecules, μ_0 is the permeability of free space, ω is the light's frequency, c is the speed of light in vacuum. Further, β is the optical rotatory parameter of a molecule that is equal to the difference between the orientationally averaged polarizabilities for the left-handed and right-handed polarization of light. The optical rotatory parameter β in units of $[C^2 m^3 / J]$ is related to the macroscopically observed optical rotation angle φ of a medium as:

$$\varphi = \frac{1}{3} \omega^2 (n^2 + 2) N \mu_0 \beta, \quad (4)$$

where φ is in [rad/m] and n is the refractive index of the medium. The $(n^2 + 2)/3$ factor in the last equation may be determined in the *ab initio* (see below) computations by considering medium effects on β directly, for instance by employing a continuum model. For the purpose of this initial study we have neglected medium effects in the computations.

In Fig. 3 we show the measured molar ellipticity in conventional units of [deg cm²/dmol] and the ORD obtained from a numerical Kramers-Kronig transformation of the CD spectrum. Further, we show the corresponding dispersion of the chirality parameter, κ , for the dilute solution used for the measurements. As one can see, the chirality parameter is extremely small, even in the resonant region. The magnitude of κ can readily be increased by about 5 orders of magnitude by using a bulk solid of the chiral polymer instead of a dilute solution. In the solid the concentration of the chiral molecules would be on the order of 1 – 10 M. However, even in the case of a medium composed entirely of the chiral Ni complex polymer the chirality parameter would still be on the order of 10⁻³ which is significantly lower than what is needed to achieve a negative refractive index in the off-resonant frequency range. This prompts for a modeling and design of molecular structures with significantly higher chirality.

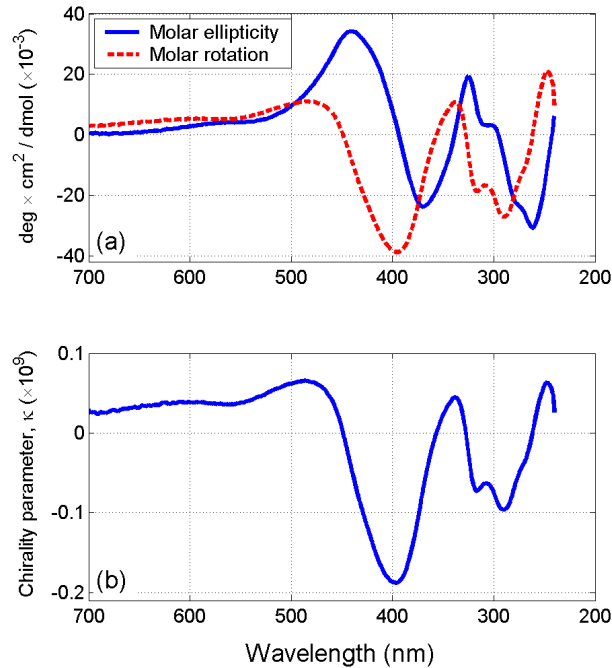


Fig. 3. (a). Dispersion of molar ellipticity (experimental data) and molar rotation (KK transform of CD spectrum), and (b) chirality parameter of the Ni complex 1

4. Estimation of the chirality parameter by means of *ab initio* calculations

Having an experimental estimate for the magnitude of the chirality parameter, we now embark on theoretical modeling of the chiroptical properties to assess the fidelity of the quantum chemical approach. The chirality parameter can be estimated through Eq. (3), taking the values of β computed *ab initio* according to

$$\beta = -\frac{1}{\omega} (G'_{xx} + G'_{yy} + G'_{zz})/3, \quad (5)$$

where G_{ii}' are the diagonal elements of the gyration tensor (mixed electric-magnetic dipole polarizability) which is formally defined as

$$G_{\alpha\beta}'(-\omega, \omega) = -\frac{2}{\hbar} \sum_{n \neq 0} \frac{\omega}{\omega_{n0}^2 - \omega^2} \Im m \langle 0 | \hat{\mu}_\alpha | n \rangle \langle n | \hat{m}_\beta | 0 \rangle. \quad (6)$$

Here $\hat{\mu}$ and $\hat{m}$ are electric dipole and magnetic dipole moment operators, respectively. It is worthwhile to note here that the trace of gyration tensor is gauge origin independent which makes it the only observable quantity for a chiral isotropic medium (solution of chiral molecules). In order to obtain origin-independent optical rotation tensor elements it is necessary to include an electric quadrupole term in addition to G' [18,19]. We point out that the optical rotatory parameter is not calculated explicitly from a summation as in Eq. (6) but from a linear response function derived specifically for the time-dependent density-functional theory (TDDFT) approach that was used for this study [20, 21]. In this approach all excitations possible within the given finite basis set are implicitly included in the calculation of β .

We have performed TDDFT linear response calculations in a wide range of frequencies for the Ni and Co complexes shown in Figs. 1 and 2 (see Tables I and II for the results). The value of interest is the electric dipole-magnetic dipole polarizability (gyration tensor). All computations were performed with a developer's version of the Amsterdam Density Functional (ADF) program package [22] using the code described in Ref. 23. Optimized geometries were obtained using the revised Perdew-Burke-Ernzerhof (revPBE) functional and a polarized triple-zeta (TZP) Slater-type atom-centered basis set for Ni and Co, a double-zeta (DZ) basis set for H, and a polarized double-zeta (DZP) basis set for C, N, O. The basis sets were taken from the ADF [22] standard basis set library. The linear-response calculations for the Ni complex were performed at the TZP/revPBE level of theory. In order to obtain reliable optical rotations at or near resonance wavelengths we have employed a global damping parameter, γ [24], which was set to 0.19 eV based on previous experience with similar computations [16]. This damping parameter roughly corresponds to the half-width at half peak height of the CD bands in the UV-Vis region of the spectrum (the full width at half peak height of the 450 nm band in Fig. 3(a) is ca. 0.4 eV) and therefore represents a physically meaningful quantity in the linear response computations near this resonance. For the exchange-correlation kernel the adiabatic local density approximation has been used.

Table I Dispersion of electric polarizability, magnetizability, and optical rotatory parameter for Ni complex 1

Wavelength (nm)	$\Re(\alpha)$ (a.u.)	$\Im(\alpha)$ (a.u.)	$\Re(\xi)$ (a.u.)	$\Re(\beta)$ (a.u.)
734.9	773.90	97.902	-490.14	264.13
650.9	803.88	166.05	-480.71	221.65
584.1	757.01	252.68	-528.54	-239.07
548.9	714.01	266.24	-528.88	-306.84
529.8	705.67	253.79	-520.52	-288.55
474.6	701.66	332.79	-503.27	-72.22
451.1	655.35	357.66	-499.67	23.06
438.1	613.51	363.79	-498.23	21.04
421.9	575.99	324.70	-498.64	11.83
387.8	591.93	303.09	-504.49	-97.39

Table II Dispersion of optical rotatory parameter for Co complex 2

Wavelength (nm)	$\Re(\beta)$ (a.u.)
734.9	98.121
650.9	95.268
584.1	-265.68
548.9	-294.61
529.8	-258.15
474.6	-143.98
451.1	-130.10
438.1	-78.077
421.9	-49.968
387.8	-131.33

The results of our *ab initio* calculations are depicted in Fig. 4. The concentration of chiral molecules was set to 4.4×10^{-6} M in order to compare directly with the experiment. The comparison is obviously somewhat limited in scope because the experimental data have been obtained for a polymer whereas the computation was performed on the monomer unit. Nonetheless, the theoretical data should give a rough estimate of the chirality parameter to be expected as long as the monomer units in the polymer do not couple too strongly. This does not seem to be the case since the theoretically computed κ is of the same order of magnitude as the one computed from the experimental CD spectrum (see Figs. 3 and 4). As already mentioned, the low absolute value of the chirality parameter is in part due to the low concentration of chiral species in solution.

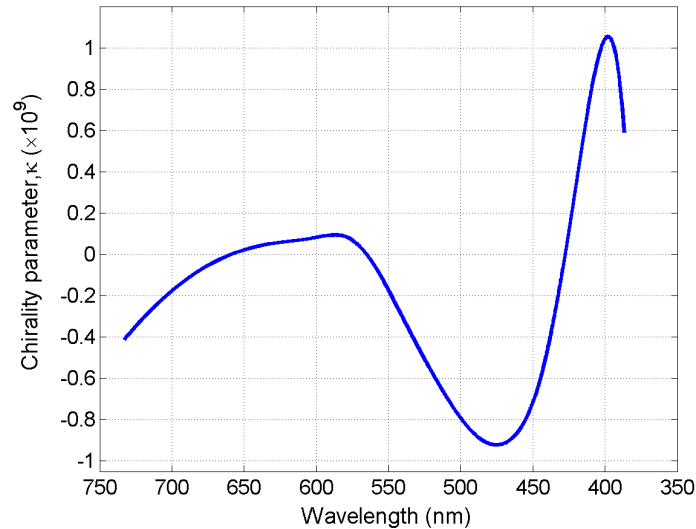


Fig. 4. Theoretical chirality parameter for Ni complex 1

One needs to mention here that in case of the bulk material with a very high number density of the constituent entities, the effective chirality parameter of the medium may need to be computed with a more realistic model for the local field effects. However, the increase of concentration alone will not yield a chirality parameter that is large enough to achieve negative refraction in a system built of relatively simple molecules like those considered here. As mentioned before, one scheme to achieve amplification of chirality is through supramolecular assembly of chiral units in helical form.

Alternately, or in addition to that, one might be able to make use of a narrow resonance to lower the value of the real part of the dielectric constant locally. This may provide a chance to obtain a negative refractive index in a narrow frequency range. This latter approach is considered in the next section.

5. Tuning the effective refractive index of the chiral medium by applying plasmonic inclusions

One can envisage a situation where the dielectric function of a material is modified by adding to the chiral matrix another component which provides for a local suppression of the dielectric constant. One such possibility is through introducing plasmonic inclusions, such as metal nanoparticles. This can lower the real part of dielectric permittivity of the composite material, thereby providing the so-called “chiral nihility”, and even help in suppressing the imaginary part of the permittivity, thus overcoming resonant loss. We should note here that “chiral nihility” condition can in principle be realized in general bi-isotropic non-reciprocal (Tellegen) media or gyrotropic chiral media without any additional inclusions. However, this would only arise when the non-reciprocity parameter is large or when diagonal and off-diagonal components of the permittivity tensor cancel each other. These situations are analysed in much detail in Refs. 6 and 7 and will therefore not be discussed further in this work. According to [25], the effective dielectric permittivity of a medium composed of spherical particles embedded into a host matrix can be computed as follows:

$$\epsilon_{\text{eff}} = \epsilon_{\text{host}} \frac{x^3 - 3ifT_1^E}{x^3 + 3ifT_1^E/2}, \quad (7)$$

where $x = 2\pi a / \lambda$ is the sphere size parameter, a is the radius of the sphere, λ is the wave length in the host medium, f is the volume fraction of nanoparticles, and T_1^E is the electric-dipole component of the scattering T -matrix in Mie approximation.

We modeled such an effective medium, consisting of the chiral Ni complex molecules discussed in the previous sections, and gold nanoparticles. We made use of Eq. (7) and our computed electric polarizabilities and gyration tensor. The concentration of chiral molecules was set to 2 M, and the volume fraction of 20 nm diameter nanoparticles was optimized to 0.132. Electromagnetic (EM) coupling between chiral molecules of the host matrix and the nanoparticles was neglected which means that the effective contribution of the chiral molecules to the chirality of the composite material is essentially the same as that of the oriented gas. It is worthwhile to note here that the dielectric permittivity of the chiral medium, ϵ_{host} , and the chirality parameter were obtained by taking into account the local field effects (in the framework of Clausius-Mossotti model corresponding to quasistatic dipolar limit) which are of importance for such a high number density of constituent particles. The results of our modeling are presented in Fig. 5. As one can see, inclusion of gold nanoparticles results in the expected lowering of the real part of the effective dielectric permittivity of the composite material. This, in turn, leads to the negative real part of the effective refractive index in a very narrow band around 676.5 nm. The imaginary part of the effective permittivity is nevertheless large. As the chirality parameter changes sign and reaches a maximum negative value at 550 nm, we could in principle get negative refractivity for the opposite sense of polarization [a positive sign in Eq. (2)] provided that the real part of permittivity is modified to reach zero at this particular wavelength. It is also worthwhile to note here that magnetic permeability of the composite was set to 1. As one can see from Table I the values of the magnetizability are of the same order of magnitude as those of the polarizability. Therefore, the relative macroscopic magnetic susceptibility is at least two orders of magnitude less than relative macroscopic electric susceptibility according to the general electrodynamics relations. We confirmed this numerically and found that relative changes of magnetic permeability in the wavelength range

of interest are less than 0.01 % (the relative susceptibility is of the order of 10^{-4}). This is not surprising because the molecule has no unpaired electrons.

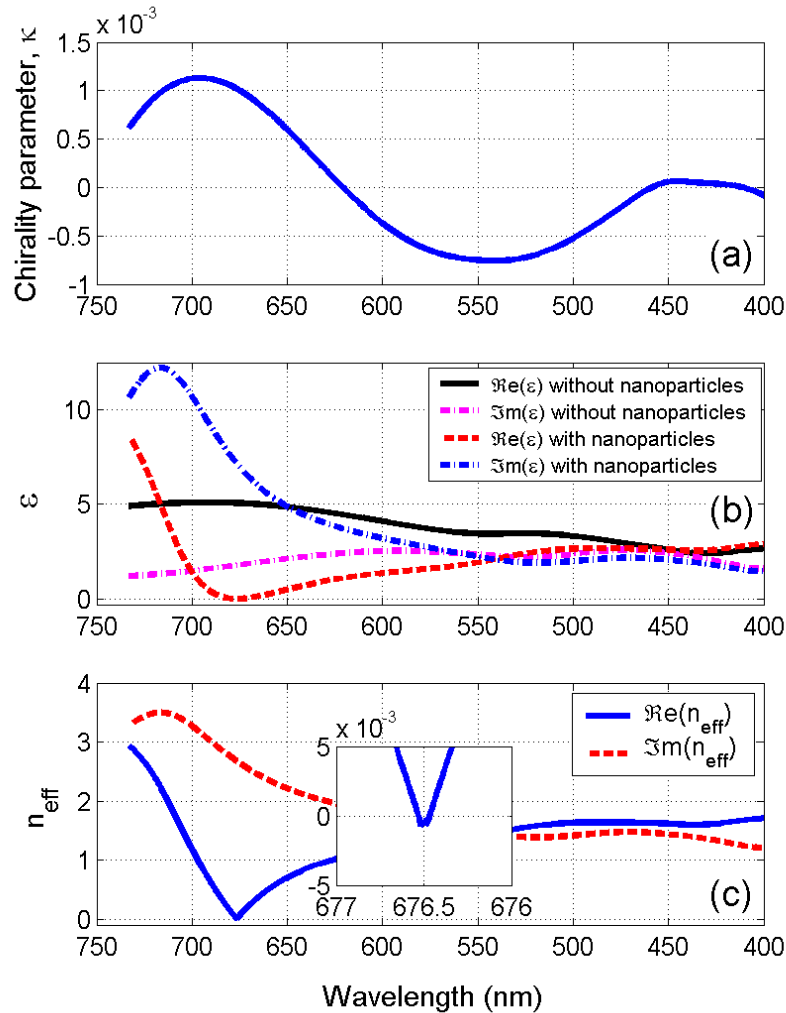


Fig. 5. Material parameters of composite medium when electromagnetic coupling between chiral molecules and nanospheres is neglected: (a) Chirality parameter, (b) Effective dielectric permittivity, (c) Effective index of refraction.

If electromagnetic coupling between chiral species and plasmonic nanoinclusions is accounted for in a manner described in Ref. [26], the effective chirality parameter of the composite material acquires an additional resonance at 533 nm (Fig. 6). The resonance of the effective permittivity is also blue-shifted. A negative refractive index is obtained for a different sense of the circular polarization compared to the case without coupling, because now the effective chirality parameter is negative. The absorption loss is lower in this case because of the lower imaginary part of the effective permittivity (Fig. 6). The optimum volume fraction of nanoparticles in this case equals 0.027. It is worthwhile to note here that introducing EM coupling results not only in the blue shift of the resonant effective material

parameters, but also in a much lower volume fraction of nanoparticles needed to obtain the NIM behavior.

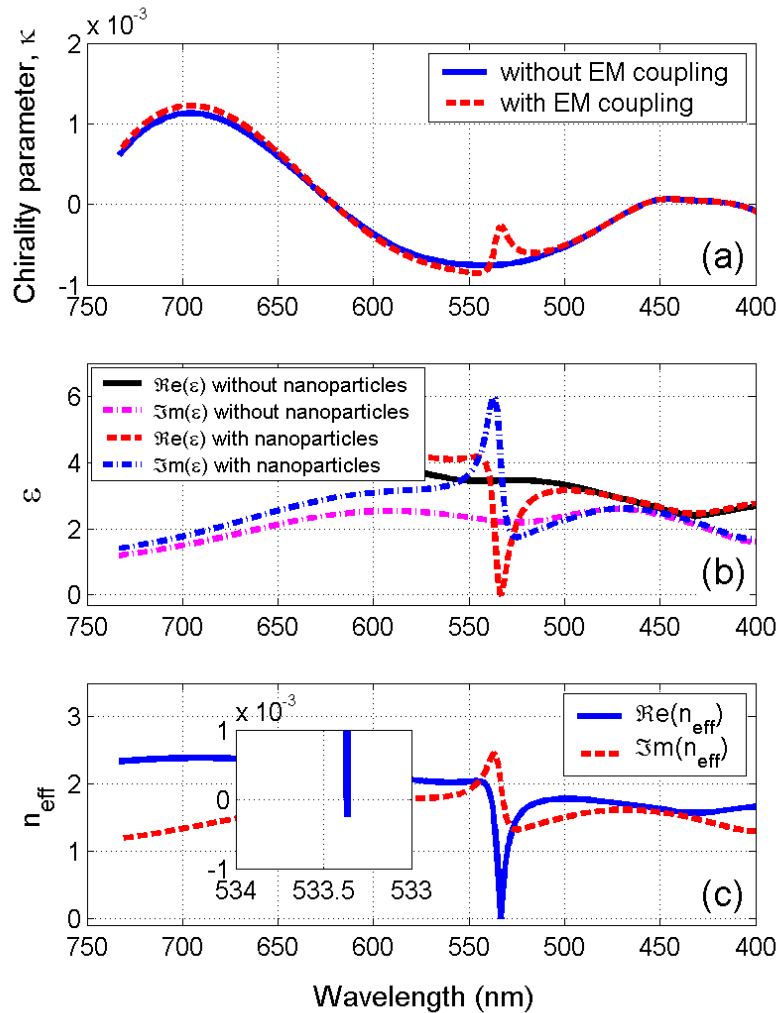


Fig. 6. Material parameters of composite medium when electromagnetic coupling between chiral molecules and nanospheres is accounted for: (a) Chirality parameter, (b) Effective dielectric permittivity, (c) Effective index of refraction.

6. Discussion

In order to be consistent with the proposed methodology of the quest for the prospective NIMs, we analyzed the optimized geometries of both organo-metallic complexes with respect to the radius-to-pitch ratio, a/ζ (see Figs. 1 and 2). The value of this useful estimative quantity is 0.809 for Co complex and 0.821 for Ni complex. Such a simple estimate does indeed carry some information about the strength of optical rotation and may cautiously be used if rigorous quantum chemical calculations of polarizabilities are not feasible for some reasons. If one is interested in absolute value of the optical rotatory strength, the

proportionality factor for a family of compounds must be computed along with the radius-to-pitch ratio [14].

The central part of the problem pertaining to realization of NIMs is obviously the loss. Introducing plasmonic nanoinclusions with concentration much lower, than that of the chiral molecules, allows for shifting the resonance of the composite material to a frequency range, where the loss of the chiral constituent is lower. On the other hand there is also the additional loss due to plasmonic resonance. Consequently the latter needs to be smaller in magnitude, than the resonant loss of the chiral host matrix which is presumably achievable with the low concentration of nanoparticles. Making use of core-shell nanoparticles can give additional flexibility when it comes to tuning plasmonic resonances. It is worthwhile to mention at this point the sharpness of the plasmonic resonances (see Figs. 5 and 6). One may argue that such sharp resonances are not likely to be encountered in practice because of several factors e.g. the dispersion in sizes of the plasmonic nanoparticles. However, the need for sharpness of a resonance will be alleviated as stronger molecular chirality is achieved.

As regarding the *ab initio* modeling, there are a number of potential shortcomings arising from the approximations that need to be applied in order to keep the computational effort manageable. For instance, the TDDFT modeling of excitation spectra, CD spectra, and optical rotation is influenced by truncation of the basis set, by approximations in the density functionals, by neglecting or an approximate treatment of the molecule's chemical environment, or the neglect of vibrational corrections [27]. In principle, these obstacles can be overcome at the expense of computational resources (CPU time and memory). From the comparison of the chirality parameter calculated for a monomer solution with the experimentally derived data we see that the agreement is reasonable for wavelengths below about 600 nm. It appears that the computed excitation energies are somewhat red shifted which, by virtue of the KK relations, rationalizes to some degree the overestimation of κ in the computations. In the long-wavelength regime perfect agreement between the computed chirality parameter and the data derived from experiment should not be expected. The reason lies in the fact that the experimental chirality parameter has been obtained from a numerical KK transformation of the CD spectrum, with the concomitant truncation errors from the finite range of integration. Two of us have shown previously [16] that such truncation errors can be significant in the long-wavelength limit whereas a good quality resonant ORD can be obtained by using KK transformations over a finite wavelength range.

7. Conclusions

A methodology allowing for rational design of chiral materials possessing negative index of refraction and based on quantum chemical *ab initio* calculations of corresponding microscopic polarizabilities is presented. Realization of such a negative refractive index material is shown to be feasible provided molecular entity with high optical activity is synthesized. Plasmonic inclusions are demonstrated to be able to locally lower the real part of dielectric permittivity of a composite material thereby ensuring conditions of chiral nihility within a very narrow frequency range. The need for a three orders of magnitude increase in the value of the macroscopic chirality parameter to obtain a material in which a negative refractive index might be obtainable may be alleviated by the use of inclusions providing sharp resonances. Concomitant use of supramolecular self-assemblies and metal nanoparticles may be a viable pathway to obtaining isotropic negative refractive index materials.

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