Research article

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Importance of higher-order multipole transitions on chiral nearfield interactions

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Abstract: Surface-enhanced circular dichroism (SECD) of chiral molecules adsorbed on plasmonic nanostructures can substantially enhance chiroptical molecular signals by several orders, which is otherwise very weak to be directly measured. Several mechanisms were proposed to explain this extreme enhancement, but the exact mechanism is still controversial. We investigate strong higher-order multipole contribution to SECD near plasmonic nanostructures using the superposition T-matrix method and discuss how 3-dimensional full-field simulations implementing a homogeneous chiral medium have succeeded in the reconstruction of the extreme enhancement. We also discuss how theoretical studies modeling chiral molecules based on dipole approximation have failed to reconstruct the extreme enhancement and show that SECD enhancement of such chiral dipoles is directly governed by optical chirality enhancement. In addition, strong multipolar transitions in subwavelength chiral plasmonic nanoparticles are discussed based on the T-matrix. This work reviews theoretical frameworks describing chiral molecules, demonstrates significant contribution of a multipolar transition on the extreme SECD enhancement near plasmonic nanostructures, and emphasizes the importance of a multipolar transition in chiral nearfield interaction.

Keywords: surface-enhanced spectroscopy; plasmonics; chiroptical spectroscopy; circular dichroism (CD); superposition T-matrix method.

1 Introduction

Surface-enhanced spectroscopic techniques utilizing plasmonic nanostructures have succeeded in the sensitive measurement of molecular signatures, and practical applications include surface-enhanced Raman spectroscopy where extreme enhancement up to single or few molecule levels has been demonstrated [1]. This surface enhancement scheme has also been applied to increase very weak intrinsic chiroptical signals of chiral molecules (CMs), which allows us to access extra information about handedness of CMs and structural conformation of biomolecules. This handedness information is particularly important in pharmaceuticals, as well as synthetic chemistry, because drugs can act as medicine or poison depending on the handedness. Therefore, enantioselective sensing and sorting of CMs using light is actively researched for the nondestructive and rapid optical measurement and manipulation. Ultrasensitive chiral sensing of a minute amount of biomolecules using plasmonics was demonstrated [2–4] with enhancement up to 10^6 [5] and zeptomole-level sensitivity [6]. The mechanism of this extreme enhancement factor exceeding 10^3 is still controversial, because theoretical models could not explain such large enhancement [7]. In our opinion, one of the reasons why the theoretical study of surface-enhanced circular dichroism (SECD) and other chiral nearfield interactions has been difficult is that description of electromagnetic (EM)-chiral object itself (i.e. CM) is often too simplified. Higher-order multipole contribution cannot be ignored in nearfield interaction [8, 9] and has been suggested to explain SECD [2, 5]. However, theoretical studies have often neglected this contribution from field gradient possibly due to the complexity and calculation effort, which multipolar generalization requires [8, 9], and EM-chiral effects have usually been treated as interplay between electric dipole (E1) and magnetic dipole (M1) [10].

In this paper, we emphasize the role of higher-order multipole transitions in SECD and chiral nearfield interactions specifically near plasmonic nanostructures. First, we briefly review theoretical frameworks describing EM-chiral objects, and we use these methods to reconstruct

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SECD and understand its mechanism. We suggest dipole approximation as one possible reason for this discrepancy between theory and experiment. Finally, we demonstrate strong multipolarity of chiral plasmonic nanostructures. We believe this work will be helpful for theoretical analysis of chiral scattering processes near plasmonic nanostructures, which can be applied to optical forces and spectroscopy, enantiomeric separation using optical and enantiomeric spectroscopic sensing.

2 Theoretical frameworks describing chiral scatterers

First, we review theoretical frameworks describing CMs and small scatterers. EM chirality has been known to originate from the transition between E1 and M1 (E1–M1) and E1 and electric quadrupole (E2) modes (E1–E2), but E1–E2 contribution is often ignored because it disappears through orientation averaging [10]. At dipole regime, polarizability tensors are expressed as $\mathbf{p}/\varepsilon = \alpha_e \mathbf{E} + i\eta\alpha_c \mathbf{H}$ and $\mathbf{m} = \alpha_m \mathbf{H} - i\alpha_c \mathbf{E}/\eta$, where $\mathbf{p}$ and $\mathbf{m}$ are induced electric and magnetic dipole moments, $\mathbf{E}$ and $\mathbf{H}$ are incident (external) electric and magnetic fields, and η and ε are wave impedance and permittivity of host medium. The EM-chiral property of a dipolar chiral polarizable element is expressed by the cross-polarizability term α_c . Another popular description of the EM-chiral scattering system is a finite volume of the chiral medium with its constitutive relations [11] given as $\mathbf{D} = \varepsilon \mathbf{E} + i\kappa \mathbf{H}/c$ and $\mathbf{B} = \mu \mathbf{H} - i\kappa \mathbf{E}/c$, where κ , ε , and μ are the chirality parameter, permittivity, and permeability of the chiral medium, respectively, $\mathbf{D}$ is the electric displacement field, and $\mathbf{B}$ is the magnetic flux density. Such a system is equivalent to a random collection of CMs, so we will refer to this method as the effective medium approach (EMA).

The polarizability formalism has widely been used to describe small EM-chiral objects to conveniently express chiral scattering [12–14] and even chiral opto-mechanical processes, such as force and torque for optical trapping application [15–19], but we will show that this method fails to reconstruct a strong SECD enhancement factor because of the dipole approximation. On the other hand, EMA is not susceptible to the dipole approximation, but such a system may not be appropriate to describe one or few CMs, and we cannot distinguish contributions from different multipolar transitions. This description contains higher-order transition terms, which may or may not be relevant to the problem of interest depending on physical situation; that is, a random collection of CMs confined

in a finite volume may be described using EMA, but this approach may not be appropriate to describe a coupling between a single CM and a nanoparticle (NP). Therefore, in this paper, we use the superposition T-matrix method to account for multiple scattering between NP and CM in a numerically exact manner; see Section S2 in Supplementary Material for more details.

3 Mechanisms of SECD

Several mechanisms have been proposed to explain the extreme enhancement of chiral signals from CMs adsorbed on plasmonic nanostructures; the proposed mechanisms include superchiral field [12], Coulomb interaction through nearfield enhancement [13], and radiative coupling [20, 21]. The optical chirality density (C) was recognized to be proportional to the excitation rate difference of CMs at opposite circularly polarized lights (CPLs) [12], where the time-averaged optical chirality density is $C = (\varepsilon\mu\omega/2)\text{Im}(\mathbf{E} \cdot \mathbf{H}^*)$ and $*$ represents complex conjugate. This local field quantity of chirality density has brought many following works on superchiral field near nanostructures and possible enhancement of chiral interaction [21–24], which assumed that the SECD enhancement factor (E_{SECD}) is related to the optical chirality enhancement factor $E_c \equiv C/|C_{\text{CPL}}| = \eta \text{Im}(\mathbf{E} \cdot \mathbf{H}^*)/|\mathbf{E}_{\text{CPL}}|^2$. However, $\langle E_c \rangle$ near plasmonic nanostructures is quite limited due to the quasistatic nature of small plasmonic nanostructures [25], where $\langle \cdot \rangle$ is volume-averaged quantity. Large chiral plasmonic structures exhibited strong $\langle E_c \rangle$ of $\sim 10^2$ [22, 26], but an intense chiral signal from the structures would overshadow a much weaker signal from CMs. Achiral high-index nanostructures have theoretically supported large $\langle E_c \rangle$ up to $\sim 10^2$ [24, 27, 28]. However, to the best of our knowledge, ultrasensitive chiral sensing utilizing such high-index nanostructures has not been experimentally reported.

Radiative coupling occurs through the coherent exchange of photon between scattering objects, which act as a nanoantenna that can both receive and re-emit EM energy, and a CM placed near a nanoantenna can form a strongly coupled state [29]. Explanation based on the superchiral field focuses on dissipation in the CM only, whereas one based on coupling additionally considers perturbation to the nanoantenna. Recent reports suggest that backaction of CM on the NP may be a major factor of SECD effects [23], whose microscopic origin has been analyzed by decomposing the observed CD as induced CD of NP and inherent CD of CM. To distinguish and study the origin of SECD, we use two different E_{SECD} definitions:

$E_{\text{SECD}}^{\text{CM}} = \text{CD}_{\text{abs}}^{\text{CM}} / \text{CD}_0$ represents enhancement of inherent CD, and $E_{\text{SECD}} = \text{CD}^* / \text{CD}_0$ represents enhancement of the total observed CD, where $\text{CD}_{\text{abs}}^{\text{CM}}$ is absorption part of intrinsic CD originating from CM, CD_0 is CD of CM in the absence of NP, and CD^* is observed SECD from the NP-CM complex (see Section S1 in Supplementary Material for more details and explicit expressions).

4 Higher-order multipole contribution to SECD

In this paper, we use isotropic dipole CM with its property originating from the E1–M1 transition ($\text{CM}_{\text{E1-M1}}$) with Lorentzian spectral lineshape (see Section S3 in Supplementary Material). Note that throughout this work, we do not consider the properties of a real molecule, but simplified artificial one, and achiral NP to discard CD from NP and effectively capture and describe the SECD effect only [23, 27, 30]; the host medium has $n=1.33$ for all configurations. The simplest configuration of a $\text{CM}_{\text{E1-M1}}$ near the Ag sphere successfully reconstructs SECD effects near plasmon resonance (Figure 1). $E_{\text{SECD}}^{\text{CM}}$ (Figure 1B) is identical to E_c (Figure 1A), because Tang and Cohen derived their equations on absorption dissymmetry assuming dipolar CM [12], where their experimental configuration of counter-propagating CPLs is valid [32]. In the case of SECD, however, E_{SECD} is around 10 times larger than $E_{\text{SECD}}^{\text{CM}}$ (Figure 1B); that is, the observed CD signal is much larger

than the CD signal originating from the absorption to the CM [21, 23]. $E_{\text{SECD}}^{\text{CM}}$ of $\text{CM}_{\text{E1-M1}}$ directly relates to E_c , whereas induced CD does not. The sign of induced CD is known to depend on the multipolar modes of the NP and CM parameters [23].

The simulated E_{SECD} of $\sim 10^2$ (Figure 1B) is still far weaker than the experimentally observed enhancement of three to six orders [5, 20]. In the next section, we study SECD near a nanoantenna with strong field gradient to study multipolar contribution to SECD. We used dimer configurations that are designed to exhibit strong E_c using M1 resonance from the E1 loop (Figure 2A) [21] and using hybridization of M1 (Figure 2D) [24]. The gap sizes were determined so that the maximum E_c becomes ~ 10 . $\text{CM}_{\text{E1-M1}}$ implemented inside Ag and Si dimer gap exhibited E_{SECD} of $\sim 10^2$, and $E_{\text{SECD}}^{\text{CM}}$ is identical to E_c (Figure 2B and E).

We used isotropic CM with the chiral property from the E2–M2 transition ($\text{CM}_{\text{E2-M2}}$) such that it has extinction and CD identical to $\text{CM}_{\text{E1-M1}}$ under planewave incidence. This property can be easily implemented using the T-matrix (see Section S2 in Supplementary Material). $\text{CM}_{\text{E2-M2}}$ embedded inside Ag dimer exhibited maximum E_{SECD} of 5×10^5 (Figure 2C), which is $\sim 10^3$ times stronger than the one observed using $\text{CM}_{\text{E1-M1}}$ (Figure 2B). For the Si dimer case, E_{SECD} also increased, but only up to ~ 600 (Figure 2F). This large enhancement difference between Ag and Si dimer cases may explain why SECD effects have been observed using plasmonic substrates.

E_{SECD} of $\sim 10^3$ has been observed in EMA using numerical methods [34]. Such strong enhancement is possible,

Figure 1: SECD of $\text{CM}_{\text{E1-M1}}$ from a single Ag sphere. (A) Electric ($E_E = |\mathbf{E}|^2/|\mathbf{E}_0|^2$, black solid) and magnetic field enhancement ($E_H = |\mathbf{H}|^2/|\mathbf{H}_0|^2$, black dotted) and optical chirality enhancement E_c (red solid) in the absence of CM. (B) CD enhancement factor of the NP-CM complex (E_{SECD}) and CM alone ($E_{\text{SECD}}^{\text{CM}}$). The Ag sphere has a radius of 20 nm, and CM is located 5 nm away from the surface. Optical parameters of Ag were taken from [31].

Figure 2: SECD of (B, E) CM_{E1-M1} and (C, F) CM_{E2-M2} from (A–C) Ag dimer and (D–F) Si dimer. (A, D) Electric ($E_E = |\mathbf{E}|^2 / |\mathbf{E}_0|^2$, black solid) and magnetic field enhancement ($E_H = |\mathbf{H}|^2 / |\mathbf{H}_0|^2$, black dotted) and optical chirality enhancement E_C (red solid) in the center of the dimer gap in the absence of CM. E_{SECD} (black) and $10 \times E_{SECD}^{CM}$ (red) of (B, E) CM_{E1-M1} and (C, F) CM_{E2-M2} . Ag dimer has a radius of 30 nm and a gap distance of 6 nm, and Si dimer has a radius of 30 nm and a gap distance of 2 nm. Optical parameters of Si were taken from [33].

because EMA is not susceptible to dipole approximation. This approach can also be implemented using the T-matrix method to describe a chiral sphere or spherical chiral core shell (see Section S5 in Supplementary Material), and the higher-order transition can be treated to possibly take a non-negligible part in nearfield interaction. A spherical

chiral core shell exhibits higher E_{SECD}^{CM} (Figure 3A) than CM_{E1-M1} near the Ag sphere (Figure 1B). Also, a small chiral sphere would have negligible higher-order contribution to extinction and CD under farfield interaction (i.e. planewave excitation), but exhibited strong E_{SECD} over 10^4 embedded inside the Ag dimer (Figure 3B). This result

Figure 3: SECD of a chiral medium near plasmonic nanostructure. E_{SECD} (black) and $E_{\text{SECD}}^{\text{CM}}$ (red) of (A) a spherical chiral shell enclosing an Ag sphere and (B) a chiral sphere in Ag dimer. Geometric parameters are: (A) chiral shell with 30-nm outer radius and 20-nm inner radius; (B) chiral sphere with 8-nm radius, Ag dimer with 30-nm radius and 20-nm gap distance. Chiral medium has $n = 1.4 + 0.02i$ and $\kappa = 1 + 0.01i$.

shows that a higher-order transition, which may not be visible in farfield interaction, could strongly contribute in nearfield interaction.

Recently, Wu et al. recognized that strong field gradient may also take part in SECD; only the field amplitude where the point dipole exists matters at dipole regime, but generally, scatterers can be excited by field gradient and even higher-order modes [14]. Previous analytic theories that relied on this dipole approximation to describe CMs [12, 13] could not capture large field gradient near plasmonic nanostructures. Therefore, we think that this higher-order transition may be a major factor in the SECD effects, and C is not a reliable field quantity to represent SECD, and the radiative coupling mechanism better describes the SECD effects. This perturbation to the nanoantenna should be critical for SECD to be practical, because achiral absorption of CM increases more dramatically near plasmonic NP compared to CD of CM due to larger field enhancement [35]. In addition, we relied on spherical dimers, but even stronger field gradient is expected from bowtie configuration due to its sharp tips and lightning-rod effect, which would allow even a stronger higher-order transition to be excited. Our finding is contrary to the recent finding that multipolar contribution in chiral nearfield is negligible and can be explained by local description using EMA [7], but their experimental condition was far from plasmonic resonance, where field gradient may have been negligible. In addition, E2 contribution was adopted to construct anisotropic constitutive relations for oriented CMs [36, 37]. It is also worth noting that chiroptical response originating from the interaction between optical angular momentum of twisted light and CM is cancelled out for CM with only

the E1–M1 transition [38], but can survive for CM with the E1–E2 transition [39].

5 Plasmonic chiral scatterers

Strong chiral effects have been demonstrated from subwavelength plasmonic chiral NPs [40–42], which are possible candidates for chiral metamaterial-based optical devices [42], sensors [5, 6], and trapping and separation of CMs [17, 19]. In this section, we use the T-matrix to show that many plasmonic chiral systems involve a higher-order transition for their chiral properties. Twisted nanorods [41] and helical assembly [40] are two experimentally demonstrated plasmonic chiral systems. Although their sizes are subwavelength, their properties are not dipolar and contain higher-order transitions in a complicated manner (Figure 4A and B). Such systems are difficult to be described using polarizability tensor formalism, which is specialized in describing a dipolar system. Twisted nanorods exhibit chiral effects at $\mathbf{k} \parallel \hat{\mathbf{z}}$, but this feature cannot be reconstructed using dipole approximation. These higher-order transitions are usually not expected for subwavelength particles, but a scattering system composed of coupled plasmonic particles has non-negligible higher-order contribution [43, 44]. Even a single, continuous plasmonic particle with gaps exhibits a strong higher-order transition (Figure 4C) [42]. Considering that dominantly dipolar systems (i.e. a small chiral sphere, Figure 3B) can exhibit strong higher-order contribution to SECD in nearfield, plasmonic chiral scatterers with non-negligible multipolar response even in farfield

Figure 4: Subwavelength plasmonic chiral scatterers with a higher-order transition. (A–C) Geometrical representation (inset), extinction ($\Sigma\sigma$) and CD (left) of (A) twisted nanorods, (B) helical assembly, and (C) cNP, and their T-matrix (right) at (A) 790 nm, (B) 540 nm, and (C) 640 nm. $\Sigma\sigma$ (black) and CD (red) at $k \parallel \hat{x}$ (dashed), $k \parallel \hat{y}$ (dot-dashed), and $k \parallel \hat{z}$ (solid). Geometric parameters are: (A) twisted-nanorods with 5-nm radius, 25-nm gap, 38-nm length, and 50° twist angle; (B) helical assembly with 17-nm major radius, 5-nm minor radius, 56-nm pitch, and 1.5-turn; (C) cNP with 50-nm edge length, 5-nm gap width, 20-nm gap depth, and 60° gap angle. The optical parameters of the Au particles are taken from [31].

would experience enormous higher-order contribution in nearfield interaction. Therefore, one should be cautious when studying nearfield interaction involving plasmonic nanostructures.

6 Conclusion

In this paper, we emphasize the possible importance of a higher-order transition in SECD effects and chiral nearfield interaction. First, we reviewed and clarified description of EM-chiral objects. We confirmed that the optical chirality enhancement E_c only directly governs the enhancement of inherent CD of chiral dipoles, and that inherent CD

seems to take only a portion of total observed CD; therefore, E_c may not be the standard to estimate SECD effects. We showed that a higher-order transition is critical for extreme SECD enhancement, which cannot be reproduced under dipole approximation. Due to the small size of CMs, it may be difficult to experimentally verify the results, but large biomolecules, such as protein and DNA, may have a non-negligible higher-order transition especially in nearfield. We only discussed particle systems due to the limitation in the methods, but we believe that important insights can be extended to different systems including periodic or particles on a substrate. We believe that enantiomeric sorting and sensing are actively researched areas, which may especially benefit from this work. Also,

the general concept of this work to describe the EM properties of coupled scatterers using the coupled multipole method and T-matrix may be extended to non-reciprocal or active systems.

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