Surface plasmon amplification by stimulated emission in nanolenses

Kuiru Li,[1,*] Xiangting Li,[2,3,†] Mark I. Stockman,[1,‡] and David J. Bergman[2,§]
[1]*Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303, USA*
[2]*School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv, 69978, Israel*
[3]*Institute of Theoretical Physics, Shanghai Jiaotong University, Shanghai 200240, China*
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We propose surface plasmon amplification by stimulated emission of radiation (spaser) in nanolenses: Linear center-symmetric chains of metal nanospheres, embedded in an active medium of quantum dots. Predominantly amplified are the dark, odd-parity eigenmodes, which do not suffer dipole-radiative losses and produce coherent local optical fields comparable in strength to atomic fields, with minimal far-field radiation. There are many prospective applications for such spasers.

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I. INTRODUCTION

There have recently been tremendous advances in nanoscience and nanotechnology. Among those, we mention the detection and spectroscopy of single molecules by surface-enhanced Raman scattering (SERS)[1,2] and laser-induced fluorescence.[3] In aqueous solutions, the Raman scattering cross section is smaller by a factor $\sim 10^{-13}$ than that for the excitation of molecular fluorescence. However, the single-molecule SERS gives enhancements by a factor $K_{\mathrm{SERS}} \sim 10^{12}-10^{13}$, making the Raman scattering as intense as fluorescence.[1,2,4] This giant enhancement is due to surface plasmon (SP) resonances; in electromagnetic theory, $K_{\mathrm{SERS}} \sim Q^4$, where Q is the quality factor of the SP resonance,[5] which for individual silver nanospheres ($Q \lesssim 30$) yields $K_{\mathrm{SERS}} \lesssim 10^6$. To explain the much larger enhancements in the single-molecule SERS, it has been suggested that they originate from molecules situated in nanogaps between metallic nanocrystals,[6] where much stronger local fields are expected. This explanation is in line with the direct observation of enhanced local fields ("squeezed" SP's) between metal nanoparticles[7,8] and with the correlation between the SERS enhancement and fractal aggregation of silver nanoparticles.[4] Recently, an efficient nanolens has been proposed,[9] which is a self-similar chain of a few metal nanospheres, that can enhance local fields in the gaps between the smallest nanospheres by a factor of $\gtrsim 10^3$, thus yielding $K_{\mathrm{SERS}} \gtrsim 10^{12}$. This nanolens provides a simple, solvable, and reproducible model where a giant enhancement of SERS can be realized.

These phenomena and applications are based on the resonant excitation of local fields in a nanostructure by an external laser source. Significant inherent limitations are imposed by this method of excitation: (i) Only a very small fraction of the incident energy is transferred to the local field, while the rest only creates a stray background. (ii) It is impossible to excite a single desired SP mode. (iii) Only bright (luminous) SP modes of a nanosystem can be excited, while a significant fraction of the SP's may be dark.[10] A fundamentally different way of exciting giant local fields on the nanoscale has been recently proposed by the introduction of surface plasmon amplification by stimulated emission of radiation (spaser).[11] A spaser is a metal nanosystem that supports SP eigenmodes, surrounded by an active medium of the population-inverted two-level emitters that we will take to be semiconductor quantum dots (QDs) for definiteness. The metal nanosystem is a counterpart of the laser cavity, while the SPs are analogous to photons: They are uncharged spin-one bosons, which are extremely harmonic. The QDs undergo radiationless transitions that are much more probable than the emission of free photons, transferring their energy to SPs of the metal nanosystem. This process is stimulated by the SPs already in the system, leading to an avalanching accumulation of coherent SPs in a single mode. The spaser does not generate propagating electromagnetic fields, therefore the dark SP eigenmodes can be excited. Strong, almost atomic strength, local optical fields can be produced.

In this paper, we propose a spaser whose metal nanosystem is a center-symmetric nanolens made of a few nanospheres. We show that such a nanolens spaser will generate predominantly the dark SP modes, because these modes do not emit electric dipole radiation. This exclusive dark-mode quantum generation has not been earlier proposed theoretically or observed experimentally. The dark modes possess a principal advantage for nano-optics and nanotechnology, because they produce strong local fields suitable for various applications (nanospectroscopy, nanoprobing, nanomodification, etc.) *without a background of emitted stray radiation*. We show that the simplest such a spaser is based on a symmetric metal nanosphere dimer and will generate mostly transverse (to the symmetry axis) modes. More complicated center-symmetric self-similar nanolenses turn out to be highly efficient as local field generators where both longitudinal and transverse dark modes can be excited.

II. THEORY

Consider a spaser as an aggregate of metal nanospheres with dielectric permittivity $\varepsilon_m(\omega)$, depending on frequency ω, embedded in an active host medium with dielectric constant ε_h. The eigenmodes (SPs) satisfy the following partial differential equation:[10,12] $\nabla \cdot [\theta(\mathbf{r}) \nabla \phi_n(\mathbf{r})] = s_n \nabla^2 \phi_n(\mathbf{r})$, where $\phi_n(\mathbf{r})$ and s_n are the eigenfunctions and eigenvalues, and $\theta(\mathbf{r})$

is the characteristic function that is equal to 1 inside the nanospheres and 0 in the host. For the system under consideration, the eigenfunctions can be expanded in spherical harmonics centered around each sphere.[13,14] The resulting eigenproblem can be solved numerically with high accuracy.[9]

For an eigenmode n, complex SP frequency $\Omega_n \equiv \omega_n + i\gamma_n^j$ satisfies $s(\Omega_n)=s_n$, where $s(\omega)=[1-\varepsilon_m(\omega)/\varepsilon_h]^{-1}$ is the spectral parameter. The real SP frequency ω_n is determined by the equation $\mathrm{Re}[s(\omega_n)]=s_n$, while the nonradiative spectral width γ_n^j (due to internal losses in the metal) is given by $\gamma_n^j=\mathrm{Im}[s(\omega_n)]/s_n'$, $s_n'=d\mathrm{Re}[s(\omega)]/d\omega|_{\omega=\omega_n}$. For silver, which has the smallest losses of any natural metal in the visible and infrared spectrum,[15] the internal lifetime $\tau_n^j=1/\gamma_n^j$ is relatively long (50–120 fs for $1.7>\hbar\omega_n>0.8$ eV).[11]

The bright SPs also exhibit radiative decay with rate

$$\gamma_n^r = \omega_n^3 \varepsilon_h^{5/2} V f_n/(4\pi c^3 s_n'), \tag{1}$$

where V is the total metal volume, c is the speed of light, and f_n is the dipole strength of the mode, normalized so that the f-sum rule is $\Sigma_n f_n=1$.[10] The total decay rate is $\gamma_n=\gamma_n^j+\gamma_n^r$. Because $\gamma_n^r \propto V$, the radiative decay is not important for the previously considered thin V-shaped nanoantenna,[11] but can be crucial in the case of the more "massive" nanolens made of nanospheres. The existence of many well-controlled dark modes can be ensured by using a system whose structure is invariant under space inversion $\mathbf{r}\to-\mathbf{r}$. In that case, all eigenmodes have definite parity (even or odd), and the odd modes $\mathbf{E}_n(-\mathbf{r})=-\mathbf{E}_n(\mathbf{r})$ will all be dark. For axially symmetric systems, all the eigenmodes with magnetic quantum number $|m|\geqslant 2$ are also dark.

Quantization of the SPs is standard, as described in Ref. 11. The emitters, denoted by index a, interact with the SP system by means of their dipole moment $\mathbf{d}_a$, with matrix element $\mathbf{d}$ for the relevant transition, via the Hamiltonian $H'=\Sigma_a \mathbf{d}_a\cdot\nabla\phi(\mathbf{r}_a)$. Perturbation theory leads to the following expression for the dimensionless gain $\alpha_n \equiv (A_n-\gamma_n)/\gamma_n$, where A_n is Einstein's coefficient of stimulated emission:

$$\alpha_n = \frac{4\pi}{3\hbar}\frac{|\mathbf{d}|^2 s_n p_n q_n}{\varepsilon_h s_n' \gamma_n^2} - 1. \tag{2}$$

If γ_n is replaced by γ_n^j, this reduces to a similar result of Ref. 11, where p_n is the spatial overlap factor of the population inversion and eigenmode intensity, and q_n is the spectral overlap factor. In the limit of maximal population inversion and thick active medium, where emitters occupy all of the host volume, we get $p_n=(1-s_n)\rho$, where ρ is the density of the emitters. The spectral overlap factor depends on the transition width of the emitters and can realistically be close to 1.[11] Quantum generation and amplification of SPs require $\alpha_n>0$.

III. NUMERICAL RESULTS

In all of our numerical computations, we choose silver as the metal. For QDs, the transition dipole moment can be estimated from Kane's theory; for PbS and PbSe QDs, $|\mathbf{d}| \approx 1.9\times10^{-17}$ esu. We assume the realistic value R_D

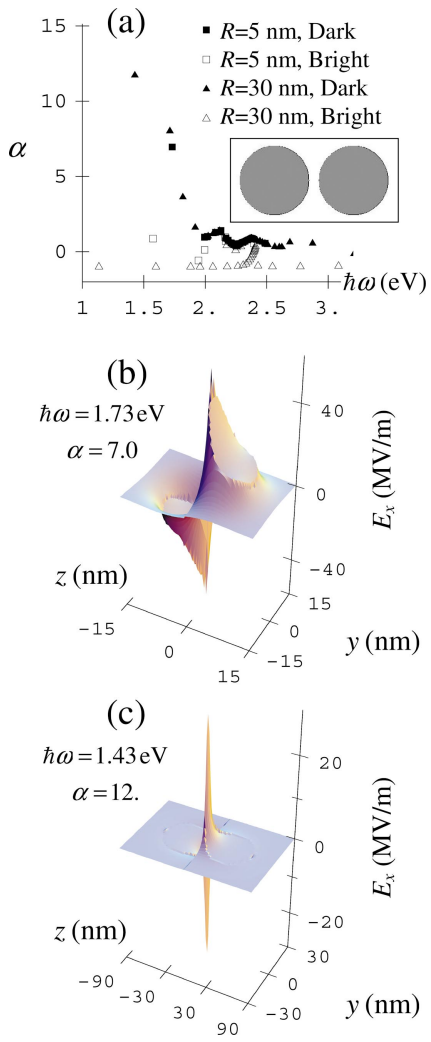

FIG. 1. (Color) Results for system of two identical silver spheres with radius R and fixed surface-to-surface distance $d=1.5$ nm, embedded in an active medium with dielectric constant 10—see inset drawing in panel (a). (a) Gain α_n of different SP eigenmodes plotted vs the real eigenfrequency ω_n. Squares correspond to $R=5$ nm, triangles to $R=30$ nm. Open symbols correspond to the bright eigenmodes, filled symbols to the dark eigenmodes. Inset: Geometry of the system. (b) Local electric-field component E_x per one quantum, for the highest-gain x-polarized eigenmode ($\hbar\omega_n=1.73$ eV and $\alpha_n=7.0$) of the smaller dimer ($R=5$ nm) in the yz plane, which contains the system symmetry axis z. (c) Similar to (b), but for $R=30$ nm, where the highest-gain mode has $\hbar\omega_n=1.42$ eV and $\alpha_n=12$.

≈ 2.3 nm for the QD radii. The effective dielectric constant of the active medium is estimated using the Maxwell Garnett formula. Assuming a dense packing of QDs in a dielectric host medium with permittivity 2 and adopting the known value ≈ 23 for the dielectric permittivity of bulk PbS and PbSe, we estimate $\varepsilon_h \approx 10$. In all computations, we consider linear coaxial aggregates of spheres, aligned along the z axis.

Consider first the simplest nanolens, namely a dimer of two identical nanospheres [see inset of Fig. 1(a)]. The calculated gains α_n for such symmetric dimers with radii $R=5$ nm and $R=30$ nm, separated by the same surface-to-surface distance $d=1.5$ nm, are shown in Fig. 1(a). The most

dramatic feature of this figure is that most of the bright eigenmodes have negative gains, i.e., they cannot spase. This is certainly due to the radiative losses. A few of the bright eigenmodes do have small positive gains—these belong to small ($R=5$ nm) spheres that have lower radiative losses [$\gamma_n^r \propto R^3$, cf. Eq. (1)]. The highest gain ($\alpha_n \approx 12$) is exhibited by the *lowest frequency dark eigenmode* of the larger spheres dimer. The frequency of this mode is also close to where the SP lifetime is maximal in silver (cf. Ref. 11). All other eigenmodes with high gains also appear in the frequency range (1.2–1.8 eV) where the SP lifetime is relatively long.

In Fig. 1(b), we show the E_x field (per one quantum)[11] for the highest-gain ($\alpha_n \approx 7$) eigenmode of the $R=5$ nm dimer. Evidently, $\mathbf{E}_n(-\mathbf{r})=-\mathbf{E}_n(\mathbf{r})$, which is the odd-parity characteristic of the dark eigenmodes, and the field is mostly concentrated within the gap, (a squeezed SP) where it is very strong: $E_x \approx 50$ MV/m—just a few orders of magnitude less than atomic-scale fields. This is a transverse twice-degenerate mode with $\hbar\omega_n=1.73$ eV, whose magnetic quantum number is $m=\pm 1$. A similar mode for the larger dimer ($R=30$ nm) is shown in Fig. 1(c). Its frequency is significantly lower ($\hbar\omega_n=1.43$ eV) and its gain is significantly larger ($\alpha_n \approx 12$), because this mode is very close in frequency to the maximal SP lifetime. The concentration of this SP in the gap, seen in Fig. 1(c), is much more pronounced than in panel Fig. 1(b), because the gap itself is relatively much narrower.

For dimers, all of the high yield eigenmodes are dark and have magnetic quantum numbers $m=\pm 1$, being twice degenerate. Their electric-field polarization in the gap between the nanospheres is mostly transverse [either x polarization, as in Figs. 1(b) and 1(c), or y polarization]. These transverse modes have dominant gains because their frequencies are shifted to the red, toward the spectral area of low losses, with respect to the SPs of the individual nanospheres. This shift is due to the fact that the oscillating surface charges on one nanosphere closely face opposite charges on the other nanosphere. By contrast, for the longitudinal (mostly z polarized in the gap) dark eigenmodes, the oscillating surface charges on one side of the small intersphere gap face like charges on the other side of that gap. This causes a blueshift to a higher loss spectral region and thus lower gains.

More complicated nanolenses, containing a greater number of nanospheres, are very efficient enhancers of local fields, concentrating energy of external optical excitation in the narrow gap between the smallest nanospheres.[9] Here, we investigate the properties of such nanolenses as spasers. As the number of nanospheres increases, so does the system size, and the radiative losses become even more important than in the case of the two-sphere nanolens. In an asymmetric nanolens, the lack of definite parity of $\mathbf{E}_n(\mathbf{r})$ makes the dark eigenmodes less common, therefore such a system will not make an efficient spaser.

We consider, as an example, the symmetric six-nanosphere nanolens shown in the inset of Fig. 2(a). Panel Fig. 2(a) shows more high-gain ($\alpha_n \gtrsim 5$) eigenmodes than either the $R=5$ nm or $R=30$ nm dimer. Again, the bright eigenmodes exhibit negative or very low positive gains, which means that spasing is impossible, or inefficient. Panel

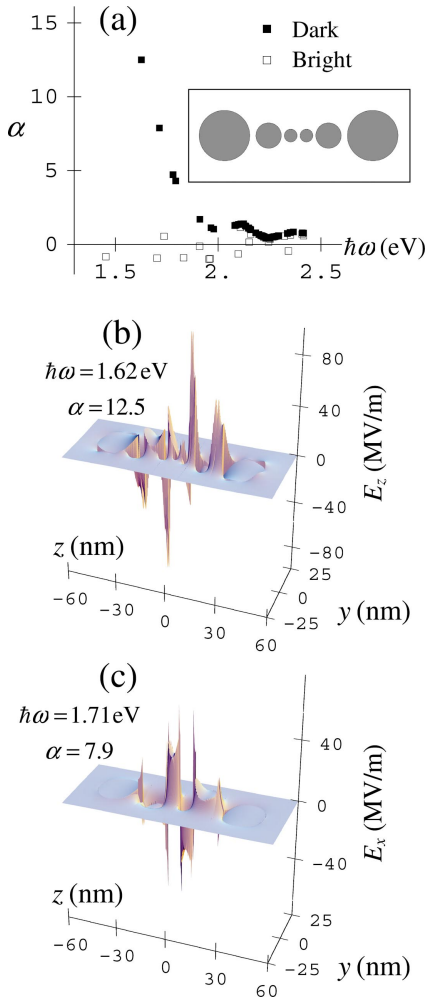

FIG. 2. (Color) Symmetric nanolens of six silver nanospheres with radii $R=12:6:3:3:6:12$ nm. The surface-to-surface distance between the two smallest nanospheres is 1.5 nm and increases self-similarly (in proportion to R) for the larger nanospheres. (a) Gains for bright (open squares) and dark (filled squares) eigenmodes. Inset: Geometry of the system in a cross section through the symmetry axis z. (b) Local field distribution E_z per one quantum for high-gain longitudinal (z-polarized) SP mode in the yz plane. (c) Similar to (b), but for E_x of x-polarized transverse mode.

Fig. 2(b) shows E_z for the highest gain mode ($\hbar\omega_n=1.62$ eV, $\alpha_n=12.5$) which is dark longitudinal (i.e., $m=0$ and E_z is the dominant field component), and has odd parity. An important feature of this mode is that it is *nondegenerate*. This proves to be a great advantage compared to the strong spasing modes of the dimer, all of which are transverse and have $m=\pm 1$: In spaser, such twice-degenerate modes compete for the relevant inverted population, i.e., the limited amount of QDs which spatially overlap the eigenmodes. The very high gain of the mode of Fig. 2(b) also derives from the fact that its frequency lies in the very low-loss spectral region of metallic silver. The local field (per one SP) is also highest for this mode, reaching ~ 100 MV/m, which is $\sim 10^{-3}$ of atomic-scale fields. The maximum field strength is achieved inside the gap between the smallest and the next-to-smallest nanospheres, unlike the external excitation of the

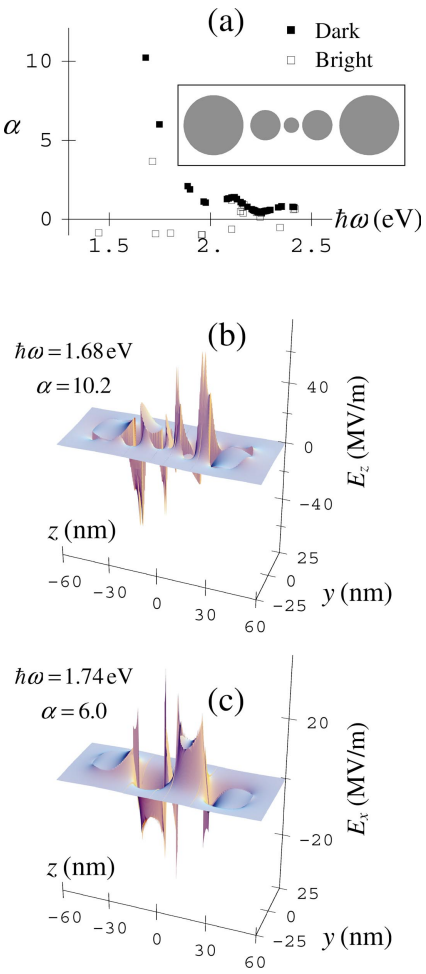

FIG. 3. (Color) Symmetric nanolens of five silver nanospheres with radii $R=12:6:3:6:12$ nm. The surface-to-surface distance between the smallest and neighboring nanospheres is 1.5 nm and increases self-similarly (in proportion to R) for the larger nanospheres. The rest is the same as for Fig. 2.

nanolens where the nanofocus appears in the gap between the two smallest nanospheres.[9]

The SP eigenmode with the next-to-highest gain ($\hbar\omega_n=1.71$ eV, $\alpha_n=7.9$) is the transverse mode shown in Fig. 2(c). It is twice degenerate, which is unfavorable for spasing, as already explained. Its gain and local field are smaller than in Fig. 2(b). The maximum field appears between the two smallest nanospheres, in contrast with Fig. 2(b). Due to the mode competition, the spaser is most likely to generate in the highest-gain, $\hbar\omega_n=1.62$ eV nondegenerate mode of Fig. 2(b).

We have also studied a symmetric five-nanosphere nanolens where the results are shown in Fig. 3. Generally, these results are similar to those for the six-nanosphere system. The bright eigenmodes are mostly nonspasing due to the radiative losses. Both longitudinal [see Fig. 3(b)] and transverse dark SP [panel (c)] modes can have high gains. The intense fields of these eigenmodes are likewise concentrated in the gaps betweeen the nanospheres.

IV. CONCLUDING DISCUSSION

In summary, we have proposed spaser in linear center-symmetric chains of silver nanospheres embedded in an active host medium made of QDs. For the nanospheres, in contrast with planar nanostructures, the radiative losses are important, and we take them into account. Consequently, only the dark odd-field SPs are efficient for spasing. The gains are especially high for SP eigenmodes with frequencies in the range 1.2–1.8 eV: α_n can then be larger than 12. This means that SPs can be created by stimulated emission at rates that are more than an order of magnitude greater than their decay rates. Because the SP lifetimes in this region are on the order of tens of femtoseconds, it follows that such a spaser can generate ultrashort pulses. The simplest nanolens, a symmetric dimer (such dimers of gold nanospheres were synthesized and spectroscopically studied recently)[16] can support a spaser which generates transverse dark eigenmodes. A more complicated nanolens, namely a self-similar linear center-symmetric chain of silver nanospheres, can support an even more efficient spaser with a larger number of high-gain SP eigenmodes. It also generates dark eigenmodes, but in contrast to the dimer case, these eigenmodes can be longitudinal, i.e., nondegenerate, which makes them advantageous for spasing. These nanolens spasers generate the strongest local fields, which can be comparable to atomic-scale fields, in the gaps between the nanospheres.

The very intense, spatially coherent, radiative background-free, highly localized optical fields generated by the nanolens spasers could have many applications. The most obvious application is in ultrasensitive detection of molecules (including single molecules) and biological nano-objects (viruses, DNA, RNA, proteins, etc.) using SERS. Nonlinear response to the ultrastrong and ultrashort local fields between the nanospheres will produce ultrashort nanolocalized field pulses at the second and third harmonic frequencies which can be used in nanospectroscopy. These fields can also cause ionization and emission of ultrashort pulses of electrons and ions from the gap regions between the nanospheres.

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*Electronic address: phykxl@panther.gsu.edu
†Electronic address: xiangtingli@yahoo.com
‡Electronic address: mstockman@gsu.edu; URL: http://www.phy-astr.gsu.edu/stockman
§Electronic address: bergman@post.tau.ac.il

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