Ultrafast processes in metal-insulator and metal-semiconductor nanocomposites

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ABSTRACT
We discuss theoretical predictions for ultrafast (mostly femtosecond) linear and nonlinear optical phenomena in metal/insulator and metal/semiconductor nanocomposites. In metal/insulator nanocomposites, we consider spontaneous and coherently-controlled energy concentration. We show that very strong (many orders of magnitude in local-field intensity) ultrafast concentration of energy on nanoscale is possible. In metal/semiconductor quantum dot nanocomposites, we consider a fascinating possibility of quantum generator due to spaser (surface plasmon amplification by stimulated emission of radiation). Various applications are discussed.

Keywords: Nanosystems, local fields, ultrafast excitation, coherent, localization, energy concentration, spaser

1. INTRODUCTION
We will overview recent ideas and results in the field of ultrafast optical responses of nanosystems. There are compelling reasons to consider phenomena that are simultaneously ultrafast and localized on nanoscale from both the fundamental and applied points of view. Interaction between different parts of a nanostructured system is very strong due to small, nanoscale distances separating them. At optical frequencies, a universal part of such an interaction at the intermediate scale is the dipole-dipole interaction, while at the minimum scale all multipoles should be taken into account. Such interactions on the nanoscale lead to femtosecond times of energy and polarization transfer and relaxation within the nanosystem. And vice versa, ultrashort external excitation creates non-equilibrium distribution of excitation energy and carriers on the nanoscale. Additionally, nanosize eliminates effects of electromagnetic retardation and thus facilitates coherent ultrafast kinetics.

From the point of view of applications, there is a great interest in phenomena occurring simultaneously on nanometer spatial scale and femtosecond temporal scale. Those applications include, but not limited to, time resolved nanoscale probing and detection, including nano-Raman spectroscopies, nanomodification of nanosystems where ultrafast excitation and relaxation of the processes helps preserving nanoscale spatial resolution, and computing with the nanoscale devices where femtosecond cycle time is a goal for ultrafast computations.

There recently has been a tremendous and ever growing interest in both ultrafast (femtosecond and attosecond) laser-induced kinetics and in nanoscale properties of matter. Within the scope of this paper, particular attention has been attracted by phenomena that are simultaneously nanoscale and ultrafast, see, e.g., Refs. 1–16.

We will concentrate on metal-dielectric and metal-semiconductor nanosystems. In metal-dielectric systems, the dominating processes induced by ultrafast optical radiation are concentration (localization) and delocalization of excitation in space and time. The first phenomenon that we will consider is the “Ninth Wave” effect. Namely, in the course of evolution of the system induced by a femtosecond laser pulse, excitation initially spread over the whole system spontaneously concentrates in a narrow region, where a local field develops that can exceed the average and exciting fields by orders of magnitude. The spatio-temporal behavior of the local fields is deterministically chaotic, i.e., random, but fully reproducible for the given system and the exciting pulse.

This effect is a dynamic counterpart of the chaoticity of the eigenmodes, their inhomogeneous localization, and giant spatial fluctuations of the local fields in random systems predicted earlier for steady-state excitation. These predictions were confirmed by experimental observations that found chaotic distributions of local field intensities, dramatically enhanced in small regions (“hot spots”) where the local intensity exceeds the average.

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intensity by orders of magnitude.\cite{21,22} The femtosecond dynamics of the local field at the site of a hot spot is very different from that of the averaged field. The spatial distribution of the femtosecond local fields near the maximum-field time is very singular and localized, and dramatically different from the steady-state distribution.

The concentration of energy in the “Ninth Wave” effect occurs at random sites due to the giant fluctuations\cite{20} of local fields for the excitation pulses that are much shorter that the dissipation times in the system. Then energy is conserved, and when the giant fluctuations of the local fields develop, they increase the local energy at a random hot spot to such a degree that there is not much energy left for the other sites of the system. This implies that there will be a site with a giant local field (the “ninth wave”\footnote{There had been a superstitious belief among old sailors that each ninth wave in a stormy sea is especially huge and devastating.  (It was called the “ninth wave” in the Russian tradition; in the English language tradition, it was the “seventh wave”.)}) while the other parts of the system will be left without much excitation energy. This concentration of energy occurs at random sites for different systems and the parameters of the excitation pulses. Nevertheless, it is a completely deterministic chaotic process: for a given system and given excitation pulse it is reproducible and the corresponding computations are stable.

The next fundamental problem to be considered is to control the process of the energy localization in space and time.\cite{15,23} The general challenge in optically controlling the spatial distribution of optical excitation of a nanosystem is that optical radiation loses its spatial degrees of freedom on the nanoscale: within a nano-object, any electromagnetic wave looks like a \textit{spatially uniform} electric field oscillating in time at optical frequencies. The only remaining functional degrees of freedom are the temporal ones: the frequency spectrum and phase modulation of the exciting electric field. Posing an additional problem, the universal, long-range dipole interaction induces ultrafast transfer of excitation in nanostructures,\cite{13} which causes a redistribution of the excitation energy across a nanosystem and may lead to delocalization. For instance, consider a local excitation of the system using a near-field scanning optical microscope (NSOM) or a nano-aperture. In this case, the source of the excitation is indeed well localized, but this initially localized excitation will spread over the nanosystem on the atto- to nanosecond scale due to the dipolar interaction between different parts of the nanosystem. Note that additionally, the NSOM’s or nano-aperture spectral bandwidth may be insufficient to conduct the \textit{ultrafast} localized excitation.

To solve this problem, we have proposed to use phase modulation of an exciting femtosecond pulse as a functional degree of freedom to coherently control spatial distribution of the excitation energy. This possibility exists due to the fact that polar excitations (surface plasmons) in inhomogeneous nanosystems tend to be localized with their oscillation frequency (and, consequently, phase) correlated with position.\cite{17,18,19,24} The pulse phase modulation will cause the exciting field to take energy away from surface plasmons localized in those parts of the system where the oscillations are out of phase with the driving pulse and move it, with time, to the surface plasmon excitations in other parts where such oscillations occur in phase with the driving pulse. Alternatively, one may think that the “instantaneous frequency” of the exciting pulse is changing, adiabatically passing through the resonance with a localized mode. As a result, this mode will initially be excited and later, as the pulse progresses, de-excited and its excitation energy moved to the next group of modes and further in the frequency domain in the same manner. Because the frequency and localization in space for the eigenmodes of a nanosystem are correlated, it will lead to the flow of the excitation energy in space allowing for the directed localization of the entire excitation energy at a given site of the nanosystem.

Coherent control has been successfully used earlier to spectrally concentrate the energy of an ultrashort nonlinearly-generated pulse in a given high harmonic.\cite{25} Impressive results have been obtained by using coherent control to affect spatial movement of particles and polarization using continuous-wave (CW) fields (see, e.g., Refs. 26, 27 and references cited therein). The possibility has been shown to concentrate the energy of acoustic waves at a given time and site inside a region when these waves are generated by a laser-induced excitation of the surface of that region.\cite{28} A possibility of coherent control of sideband THz generation in quantum well–optical microcavity systems has been demonstrated.\cite{29} Later, coherent control has been used to control the vibrational excitations of molecules under non-resonant conditions.\cite{30} Our effect is based on the same general idea of interference between different components of the resonant exciting radiation, governed by the phase modulation. However, it is different, because it requires ultrashort pulses to preserve the coherence in time in contrast to Refs. 26, 27, but it is a linear effect unlike Refs. 25, 27, and it results in the concentration of energy in the space on the nanoscale and not on the micro- to macroscale as in Ref. 28.
The general feature of the effects introduced above is that the optical radiation is generated in the far, wave zone. This radiation interacts with a nanosystems creating enhanced local fields on the nanoscale. These local fields have numerous applications for optical probing and modification of nano-objects. Due to the existence of the hot spots, the optical responses are gigantically enhanced and can be strong enough to allow, in particular, observation of Raman scattering from a single molecule attached to a metal colloidal particle. A promising area is local optical nanosize probing by a metal tip that creates enhanced fields in its vicinity. This was demonstrated for near-field fluorescence microscopy based on two-photon excitation. A theory of manipulation of particles by enhanced optical fields at a metal tip (optical nano-tweezers) was developed. It was suggested, quite early, to use local fields for linear and nonlinear optical nanoprobing and nanomodification.

Reiterating, the above phenomena and applications are based on the excitation of local fields in a nanostructure by a resonant external optical field. Significant limitations are imposed by this mode of excitation. In particular, only a very small fraction of the excitation field energy can be concentrated in the local field. It is almost impossible to select a single mode or a few modes to excite. Also, there exist a large number of dark eigenmodes that have attractive localization properties, but cannot be excited by an external wave.

In Ref. 16, we have proposed a new way to excite localized fields directly in the nanosystem using surface plasmon amplification by stimulated emission of radiation (spaser). The spaser radiation consists of SPs that are bosons and undergo stimulated emission, but in contrast to photons can be localized on the nanoscale. Spaser as a system incorporates an active medium formed by two-level emitters, excited in the same way as a laser active medium: optically, or electrically, or chemically, etc. One promising type of such emitters are quantum dots (QDs). These emitters transfer their excitation energy by radiationless transitions to a resonant nanosystem that plays the same role as a laser cavity. These transitions are stimulated by the SPs already in the nanosystem, causing buildup of a macroscopic number of SPs in a single mode.

Though spaser, similar to laser, is based on the phenomenon of stimulated emission, spaser is not a laser: Its two-level emitters (QDs, in particular) do not emit light waves, but rather generate quasi-electrostatic fields of SPs. It is possible to generate dark SPs that do not couple to far-zone fields. Spaser is designed to generate intense, nanoscale-localized, optical-frequency fields with many possibilities for prospective applications in nanoscience and nanotechnology, in particular for near-field nonlinear-optical probing and nanomodification.

2. SPONTANEOUS FEMTOSECOND CONCENTRATION OF OPTICAL EXCITATION ENERGY IN NANOSYSTEMS (THE “NINTH WAVE” EFFECT)

In this Section following Ref. 13, we consider ultrafast optical responses of strongly disordered systems (fractal clusters, rough surfaces, and random composites) whose size is on the nanoscale: much larger than the atomic size but much smaller than the light wavelength. Such random systems, as we have shown earlier, show chaos of eigenmodes and giant fluctuations of the local fields. These fluctuations in the femtosecond regime are the cause of the “Ninth Wave” effect.

2.1. Theory

We consider a system consisting of N nanoparticles (monomers) positioned at coordinates \( r_i, \ i = 1, \ldots, N \). The electric field of the exciting pulse at an \( i \)th monomer at time \( t \), denoted \( E_i^{(0)}(t) \), is assumed to be non-saturating and known. Its duration is supposed to be short enough, so the dissipation of energy does not have time to take place. Here, we will use the model with dipole interaction between monomers (the rest of this paper is based on a more general method of Green’s functions for the original quasi-electrostatic equations). We define the local field at the \( i \)th monomer \( E_i \) in terms of the corresponding induced dipole moment \( \mathbf{d}_i(\omega) = \alpha_0(\omega)E_i(\omega) \), where \( \alpha_0(\omega) \) is the dipole polarizability of an isolated monomer at a frequency \( \omega \). Throughout the paper, we imply the Fourier (frequency) domain by simply indicating frequency arguments \( \omega, \ldots \), as opposed to time variables \( t, t', \ldots \) for the real time domain. In specific computations, we consider the monomers as spheres of radius \( R_m \), for which \( \alpha_0(\omega) = R_m^3(\varepsilon(\omega) - 1)/(\varepsilon(\omega) + 2) \), where \( \varepsilon(\omega) \) is the relative dielectric function of the monomer material.

The local field \( E_i(t) \) at a time \( t \) at an \( i \)th monomer is given by a retarded tensor Green’s function \( G^r \),

\[
E_{ij}(t) = \sum_{j=1}^{N} \int_{-\infty}^{t} G_{i,j}^{r}(t-t')E_{j}^{(0)}(t')dt'.
\]

Here and below, Greek subscripts denote Cartesian components with summation over recurring indices implied. To find \( G^r \), we use two well-tested approximations, already
mentioned above. First, the quasistatic approximation implies that the size of the system is much smaller than the light wavelength and absorption depth. It preserves the rich femtosecond dynamics that is due to motion of surface plasmons on sub-wavelength scale. The second is the dipole approximation that is applicable because the effects predicted are collective, formed by interactions of many monomers at distances $\gg R_m$. We use the dipolar spectral theory\cite{38,39} that is an approximation of the more general quasistatic spectral theory.\cite{24,40}

In the dipole approximation, the local field problem reduces to a well-known set of coupled-dipole equations, $Z(\omega)d_{i\beta}(\omega) = E_{i\beta}^{(0)}(\omega) - \sum_{\gamma=1}^{N} W_{i\gamma}(\mathbf{r}_i, \mathbf{r}_j)d_{j\gamma}(\omega)$, where $Z(\omega) = \alpha_0^{-1}(\omega)$, and the dipole-interaction tensor is $W_{i\gamma}(\mathbf{r}, \mathbf{r}') = -\frac{\partial}{\partial \mathbf{r}_i} \frac{\partial}{\partial \mathbf{r}'_\gamma} \frac{1}{\lVert \mathbf{r} - \mathbf{r}' \lVert}$. We introduce 3N-dimensional vectors $\lvert d \rangle$, $\lvert E^{(0)} \rangle$, ... with the components $(i\beta \lvert d) = d_{i\beta}$, $(i\beta \lvert E^{(0)} \rangle) = E_{i\beta}^{(0)}$ (and similarly for other vectors) and obtain a single equation in a 3N-dimensional space, $(Z(\omega) + W) \langle d(\omega) \rangle = \langle E^{(0)}(\omega) \rangle$, where $(i\beta \lvert W \lvert j\gamma) = W_{i\gamma}(\mathbf{r}_i, \mathbf{r}_j)$.\cite{39} The solution of these coupled-dipole equation is determined by the eigenvalues $\omega_n$ and eigenvectors (eigenmodes) $\lvert n \rangle$ of the stationary $W$ operator, $(W - \omega_n \lvert n \rangle) = 0$, where $n = 1, \ldots, 3N$ is the eigenmode’s number. These eigenmodes are the surface plasmons of the whole system. Finally, the retarded Green’s function is: $G_{i\beta,j\gamma}(\omega) = Z(\omega) \sum_n (i\beta \lvert n \rangle \langle j\gamma \lvert n) (Z(\omega) + \omega_n)^{-1}$, where $(i\beta \lvert n)$ is an amplitude of an $n$th eigenmode at an $i$th monomer with polarization $\beta$.

2.2. The “Ninth Wave” Effect: Numerical Results

We have carried out numerical computations for three types of random systems generated by the Monte Carlo method. Two of them are fractal clusters, namely cluster-cluster aggregates (CCA) in two and three dimensions,\cite{36,37} and the third is represented by random composites of spheres with fill factor $f = 0.12$. For definiteness, we assume that the monomers are silver nanospheres whose dielectric function is that of bulk silver.\cite{41} For 3d CCA and for composites, we take the ambient medium to have a dielectric constant of 2.0, while for 2d CCA it is vacuum. The number of monomers in a cluster or in the composite’s unit cell is set $N = 1500$. For composites, we impose periodic boundary conditions on the unit cell. We use a Gaussian shape with linear polarization for the exciting pulse with unit amplitude, carrier frequency $\omega_0$, and pulse length $T$, $E^{(0)}(t) = \cos(\omega_0 t) \exp(-t^2/T^2)$. For each system, $\omega_0$ has been chosen near the absorption maximum.

We show in Fig. 1 the predicted femtosecond dynamics of induced local optical (electric) fields for a three-dimensional (3d) CCA cluster (a fractal with Hausdorff dimension $D \approx 1.75$). The local field $E_{mz}$ at the site of its maximum (hot spot) is enhanced by more than two orders of magnitude with respect to both the exciting field $E^{(0)}$ and the averaged local field $\langle E_{iz} \rangle$. The hot-spot field $E_{mz}(t)$ reaches its maximum by the end of the exciting pulse, which implies that the excitation process is coherent, occurring before relaxation runs its course. The mean-field dynamics exhibits pronounced coherent beats due to interference between different eigenmodes.

The dynamics of the spatial distribution of local fields is shown in Fig. 2. At all times, the distributions are very chaotic and singular. After just a few oscillations of the driving pulse [$t = 6.4$ fs, see panel (a)], the fields are excited non-selectively at most of the monomers, because such short an excitation acts as an instantaneous perturbation. In contrast, the development of a self-consistent polarization requires certain time. In other terms, the initially-excited surface plasmons have to move through the system to establish true eigenmodes, and there has not been enough time for that. In contrast, at the moment of the “ninth wave” $t = 40$ fs [panel (b)], there
Figure 2. Local fields $E_{12}(t)$ for a 3D CCA cluster as functions of the spatial coordinates $(x,y)$ for the moments of time indicated in the figure for an exciting pulse of $T = 25$ fs length, carrier frequency $\omega_0 = 1$ eV, and linear $z$ polarization. The fields are summed over $z$ for all monomers with the same $(x,y)$ but different $z$ to display the required 3d distribution on a plane figure.

is a dominating hot spot with the electric field enhanced by a factor of $\sim 250$, while the rest of the system is weakly excited. This “ninth wave” persists long into the free-induction stage [$t = 92$ fs, panel (c)] where the exciting pulse is long gone. At a long time, $t = 196$ fs [panel (d)], the relaxation takes its course, the fields decay and yet again change their spatial distribution.

Similar results have been obtained for 2D CCA clusters (Hausdorff dimension $D \approx 1.4$) that can serve as a model for surface roughness. Certain concentration of energy at “hot spots” have also been found for non-fractal random composites. This supports the universality of the “Ninth Wave” effect, which is related to the universality of the giant fluctuations of local fields.20

3. COHERENT CONTROL OF SPATIO-TEMPORAL ENERGY CONCENTRATION IN NANOSYSTEMS

Above in Sect. 2, we have discussed spontaneous concentration of energy in complex nanosystems, which occurs on the femtosecond-nanometer spatio-temporal scale due to ultrafast giant fluctuations of the local fields, related to the chaoticity of the system’s eigenmodes. In this Section, we turn our attention to active, coherent control of the spatio-temporal dynamics of the energy concentration, following Refs. 15, 23. Additionally, we will drop the dipole approximation, invoking the full set of eigenmodes that is obtained in the quasistatic approximation (assuming the size of the system to be much less than the excitation wavelength) and otherwise exact.24

3.1. Quasistatic Eigenmodes of Nanosystems24

The polar eigenmodes of nanosystems are traditionally called surface plasmons (SPs). Such eigenmodes mediate interaction of optical fields with nanosystems. Our nanosystem is assumed to consists of two constituents, characterized by dielectric permittivities $\varepsilon_1(\omega)$ (inclusion) and $\varepsilon_2(\omega)$ (host). Assuming the nanosystem heterogeneity scale is much less than the wavelength of light, the quasistatic approximation is applicable. This does not imply that processes are slow, but rather the opposite: the small size prevents retardation effects even for ultrafast processes. The local system response is described by a space- and frequency-dependent dielectric function $\varepsilon(r,\omega)$. The electric potential $\varphi(r)$ satisfies the equation $\nabla \cdot [\varepsilon(r,\omega) \nabla \varphi(r)] = 0$ in the rectangular-prism-shaped volume $0 \leq x \leq L_x$, $0 \leq y \leq L_y$, $0 \leq z \leq L_z$. Conventional Dirichlet-Neumann boundary conditions are imposed

$$\varphi(r) = \varphi_0(r)|_{z=0,L_z}; \frac{\partial \varphi(r)}{\partial x}|_{x=0,L_x} = \frac{\partial \varphi(r)}{\partial y}|_{y=0,L_y} = 0,$$

where $\varphi_0(r) = -E_0 z$ is the potential of the uniform external or volume-average electric field. We also make use of the spectral parameter $s(\omega) \equiv [1 - \varepsilon_1(\omega)/\varepsilon_2(\omega)]^{-1}$.

The material-independent eigenmodes (SPs) of this problem are characterized by eigenvalues $s_i$ and eigenfunctions $\varphi_i(r)$, which satisfy a generalized eigenproblem

$$s_i \nabla^2 \varphi_i(r) = \nabla \cdot [\theta(r) \nabla \varphi_i(r)],$$
Figure 3. For a planar random continuum composite (in the $y z$-plane), the density of the inclusion component (left panel) and all eigenmodes plotted as oscillator strength $f_i$ vs. localization radius $L_i$ (right panel). The size of the embedding space is $8 \times 32 \times 32$ in grid units.

along with the homogeneous variant of the boundary conditions of Eq. (1), i.e., for $\varphi_0(\mathbf{r}) \rightarrow 0$. Here $\theta(\mathbf{r})$ is the characteristic function of the $\varepsilon_1$ constituent, equal to 1 inside that constituent and equal to 0 everywhere else, so that $\varepsilon(\mathbf{r}, \omega) = \varepsilon_1(\omega)\theta(\mathbf{r}) + \varepsilon_2 \left[1 - \theta(\mathbf{r})\right]$. We set $\theta(\mathbf{r}) = 0$ near the system boundaries.

For any functions, say $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$, we introduce a binary operation $(\psi_1 \mid \psi_2) = -\int \psi_1^* (\mathbf{r}) \nabla^2 \psi_1 (\mathbf{r}) \, d^3 r$, where the integral is extended over the volume of the problem $V = L_x L_y L_z$. If these functions, $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$, satisfy the homogeneous version of the boundary conditions of Eq. (1), then form $(\psi_1 \mid \psi_2)$ possesses the necessary and sufficient properties of a scalar product: it is a binary, symmetric, and positive-defined operation. With this scalar product, the eigenfunctions of Eq. (2) are orthogonal and can be normalized as $(\varphi_n \mid \varphi_m) = \delta_{nm}$.

Using $\varphi_i(\mathbf{r})$ and $s_i$, spectral representations are exploited to compute the local potential $\varphi(\mathbf{r})$ and the macroscopic (bulk) effective dielectric permittivity $\varepsilon$:

$$
\varphi = \varphi_0 + \sum_i \frac{m_i^s \varphi_i}{s(\omega) - s_i} , \quad \varepsilon(\omega) = 1 - p \sum_i \frac{f_i}{s(\omega) - s_i} ; \quad m_i = s_i \left(\varphi_0 \mid \varphi_m\right) , \quad f_i = \frac{s_i}{p \varepsilon^0} |(\varphi_0 \mid \varphi_m)|^2 . \quad (3)
$$

Here $p$ is the fill factor (volume fraction) of the inclusion constituent $\varepsilon_1(\omega)$, and $f_i$ is the oscillator strength (weight) of the eigenmode $i$. The localization radius $L_i$ of an eigenmode is defined as the gyration radius of its electric field intensity $|E_i(\mathbf{r})|^2$, namely, $L_i^2 = \int r^2 |E_i|^2 d^3 r - \left(\int r |E_i|^2 d^3 r\right)^2$, where $E_i \equiv -\nabla \varphi_i$.

There are two exact sum rules of the problem:

$$
\frac{1}{\pi} \int_{-\infty}^{\infty} ds \, \text{Im} \left(\frac{\varepsilon(s + i\delta)}{\varepsilon_2}\right) = p , \quad \text{or} \quad \sum_i f_i = 1 ; \quad \Phi_i(z) \equiv \int D_{ix}(x, y, z) \, dx dy \equiv \text{const} , \quad (4)
$$

where $D_i = (1 - \theta s_i^{-1}) E_i$ is the electric displacement field of the eigenmode $i$, and $\Phi_i(z)$ is its normal flux through the $xy$ planes, which is independent of $z$. The constancy (conservation) of $\Phi_i(z)$ follows from the Gauss theorem and constitutes an additional integral of motion specific for this problem due to the electroneutrality of SPs; the sum rule for $f_i$ expresses the well-known Thomas-Reiche-Kuhn (TRK) dipole sum rule (or, $f$-sum rule).

All numerical calculations have been performed on a discrete version of Eqs. (2)-(3) for a random planar composite (RPC). We have generated an RPC on a cubic lattice by randomly positioning cubes of size $2 \times 2 \times 2$ (all sizes are in units of the grid step) with some probability $p_0$. In the examples discussed below, we limit ourselves to a thin monolayer of width 2 around the central $yz$ plane, with $p_0 = 0.5$ as the filling probability in that layer. The system obtained is a thin film composite in three-dimensional space. Such systems have recently been studied extensively (see, e.g., Ref. 42 and references therein). The eigenmodes of the finite matrix eigenvalue problem, obtained by the above described spatial discretization, were found using LAPACK. The error is expected to be $\propto 1/L_i^4$. Because the step function $\theta(\mathbf{r})$ has a singular derivative, we decided to smooth its discontinuities using Gaussian smoothing with an RMS width equal to the grid step size. Such smoothing does not affect the properties of the system at intermediate or large scales, and it actually makes the small scale structure more realistic by eliminating sharp edges.
In Fig. 3 we show the smooth, discretized nanostructure of one particular composite sample, as well as all of its eigenmodes (surface plasmons) in a plot of oscillator strength \( f_i \) vs. localization length \( L_i \). These eigenmodes are strikingly unusual. First, there is a large number of eigenmodes with negligible oscillator strengths \( f_i < 10^{-5} \). Such eigenmodes do not couple to propagating waves, and they can be neither observed nor excited from the far (wave) zone. We call them dark modes. They can, however, be excited and observed by NSOM (near-field scanning optical microscope) type probes in the near-field region. There are also many eigenmodes with relatively large weights, \( f_i > 1/V \sim 10^{-4} \), which we call luminous modes, that couple efficiently to the far-zone fields. Second, both the luminous and the dark modes have localization radii \( L_i \) with all possible values, from zero to one half of the diagonal system size, and with very little correlation between \( f_i \) and \( L_i \), except for the superlocalized (zero-size) eigenmodes which are all dark. This wide range of \( L_i \) shows that Anderson localization does not occur for most of the modes, including the luminous modes, in contradiction to what was found in Ref. 42. Supporting our findings and similar to them in certain respects, deviations from the simple Anderson localization have been seen in some studies of the spatial structure of vibrational modes\(^{44,45} \) and dephasing rates\(^{46} \) in disordered solids induced by long-range (dipole-type) interactions.

One can rigorously prove that all Anderson-localized eigenmodes are dark, and no system can exist whose all eigenmodes (SPs) are Anderson localized. This proof includes three steps. (i) The oscillator strength of Eq. (4) can be exactly expressed as \( f_i = L_i^2 |\Phi_i(z)|^2 / \rho \). (ii) If an eigenmode is Anderson-localized, then the electric field near at least one of the \( xy \) boundary planes must be exponentially small. Therefore the flux \( \Phi_i(z) \) will be exponentially small at all \( xy \) planes, and consequently also \( f_i \) will be exponentially small. Thus these localized modes cannot significantly couple to fields in the far zone and must be dark. (iii) If all eigenmodes of the system were Anderson localized, then all \( f_i \) would vanish, which is impossible because it would contradict the TRK (f-sum) rule of Eq. (4).

To gain more insight, we show in Fig. 4 the local electric field intensities \( |E_i(r)|^2 \) for particular eigenmodes of four extreme types, all with eigenvalues very close to \( s_i = 0.2 \). All the distributions in Fig. 4 are very singular, containing high fields concentrated at the minimum scale (hot spots). They qualitatively have the same properties as polar eigenmodes studied earlier in dipole approximation,\(^{17,18} \) which are responsible for the giant fluctuations of the local fields.\(^{20} \)

The data of Fig. 4 confirm the above-discussed absence of correlation between localization length and oscillator strength, and also show that there is no correlation between the topology of \( |E_i(r)|^2 \) and that strength—compare the pairs of eigenmodes: panel (a) with (d) and panel (b) with (c). Clearly, the hot spots seen in Fig. 4 cannot yield dominant contributions to the weight (oscillator strength) \( f_i \) or the amplitude \( m_i = s_i L_i \Phi_i(z) \), since we could have calculated the total flux \( \Phi_i(z) \) at a value of \( z \) where those hot spots are absent. This implies that a hot spot actually consists of regions where \( D_i(z) \) has large values but with opposite signs, which nearly cancel out in the evaluation of \( \Phi_i(z) \). The occurrence of “very dark” modes of the type shown in panels (c) and (d)

\(^1\)Anderson localization implies that the characteristic size of an eigenmode \( L_i \) is much smaller than the total size of the system, and that its fields decrease exponentially in space at distances greater than \( L_i \).
of Fig. 4] is due to the symmetry of the microstructure under reflection in the mid-plane of the composite. The odd-parity eigenmodes exhibit a strictly vanishing total flux \( \Phi_i(z) = 0 \) (see Ref. 24 for further discussion).

### 3.2. Green’s function of Nanosystem and Coherent Control

Apart from the fundamental interest of their own, the eigenmodes (SPs) are important as elementary excitations mediating the interactions of a nanosystem with light. Consider a nanosystem excited by an external field with potential \( \varphi_0(r, t) \). The local field potential \( \varphi(r, t) \), induced by this external potential, is determined by the retarded Green’s function \( G^r(\mathbf{r}, \mathbf{r}'; t) \) of the system

\[
\varphi(r, t) = \varphi_0(r, t) - \int \varphi_0(\mathbf{r}', t') \frac{\partial^2}{\partial \mathbf{r}^2} G^r(\mathbf{r}, \mathbf{r}'; t - t') \, d^3r' \, dt' .
\]

This retarded Green’s function is computed as a spectral expansion in the coordinate-frequency domain:

\[
G^r(\mathbf{r}, \mathbf{r}'; \omega) = \sum_i \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}') s_i / (\omega - s_i) .
\]

We have found the eigenfunctions \( \varphi_i(\mathbf{r}) \) and eigenvalues as discussed above in Sec. 3.1, and the retarded Green’s function is determined numerically from Eq. (6). After computing that Green’s function in the real-space and frequency domains, the convolution in Eq. (5) is effected using a fast Fourier transform. We use 4096 frequency or temporal points. The rank of the eigenproblem is 8192, corresponding to space dimensions in \( x, y \) and \( z \) of \( 32 \times 8 \times 32 \) (all sizes are in grid steps). We have verified, by testing, that this number of spatial and time-frequency points leads to acceptable computational precision. This have also been confirmed by later computations on a \( 32 \times 16 \times 32 \) lattice.

We study two planar systems, an “engineered” V-shape and a random planar composite (RPC) (see Sec. 3.1). The geometry of these systems after smoothing is shown in Fig. 5. We have computer-generated them by positioning cubes of size \( 2 \times 2 \times 2 \) on the central \( xz \) plane. The material dielectric function is set as that of silver \(^{41} \) in a host whose dielectric constant is \( \varepsilon_h = 2.0 \).

We consider four different exciting pulses shown in Fig. 6 (a)-(d). For the first three of them [(a)-(c)], the exciting field \( \varphi_0(\mathbf{r}, t) \) is a \( z \)-polarized chirped pulse with Gaussian envelope and duration \( T \),

\[
\varphi_0(\mathbf{r}, t) = -z \exp \left\{ -i \omega_0 (t - T/2) \left[ 1 + \alpha (t - T/2)/T \right] - (3/2) \left[ (t - T/2)/T \right]^2 \right\} + \text{c.c.} ,
\]

where \( \alpha \) is a dimensionless phase-modulation parameter equal to 0, -0.03, and 0.03 for the first, second, and third columns in Fig. 6, respectively. The fourth excitation pulse, panel (d), is a compressed one, computed for \( |\alpha| = 0.3 \) as \( \varphi_0(\mathbf{r}, t) = \int e^{-i \omega t} |\varphi_0(\mathbf{r}, \omega)| \, d\omega \), where \( \varphi_0(\mathbf{r}, \omega) \) is a Fourier transform of \( \varphi_0(\mathbf{r}, t) \) of Eq. (7). Note that pulses (b)-(d) possess identical power spectra and differ only by frequency-phase modulation; pulses (a)-(c) have identical temporal envelopes. Comparison of the responses to them enables one to isolate effects of spectral compositions and phase modulation.
Figure 6. Temporal dependence of the four excitation pulses studied [panels (a)-(d)]. Parameters of the pulses are: \( T = 50 \text{ fs} \), carrier frequency \( \omega_0 = 0.8 \text{ eV} \), and amplitude \( E_0 = 1 \), with zero chirp \( \alpha = 0 \), panel (a), negative chirp \( \alpha = -0.3 \), panel (b), positive chirp \( \alpha = 0.3 \), panel (c). Panel (d) displays a compressed pulse (see text). Panels (e)-(k) show the field at the “opening” of the V-shape \( x = 23, z = 32 \); panels (m)-(q) show the field at the apex of this nanosystem \( x = 17, z = 2 \). All fields are plotted using the same units, where the maximum value of the exciting field is set as 1.

In Fig. 6, panels (e)-(k) show the dynamics of the local field at the “opening” of the V-shape and panels (m)-(q) show that at the apex of this nanosystem. As one can conclude by comparing the four columns in Fig. 6, both the spectral composition and the phase modulation are important for the local field dynamics. First, we conclude that local fields at the apex are strongly enhanced, almost by two orders of magnitude in maximum with respect to the exciting field, and this enhancement is significantly greater for pulses with broad spectral composition [panels (n)-(q)]. The temporal structure of the response is preferable (more concentrated, with no tails of “ringing” at long times) for the pulses with spectral-phase modulation [panels (n) and (p)]. Note that tails of “ringing” in the free-induction decay stage [panels (m) and (q)] are similar to behavior of the known responses of noble-metal nanospheres.

Quite non-trivial, responses to phase-conjugated (time-reversed) pulses [panels (b) and (c)] are different. This shows that there is not the complete time-reversibility in the system, which is due to the non-zero dissipation whose effect is likely enhanced by the probable chaoticity of the SP modes.

Overall, the spatio-temporal concentration of energy is most pronounced for the negatively chirped pulse (b): in this case, the oscillations at the opening of the V-shape [panel (f)] and the apex (n) do not overlap in time; oscillations at the opening of the V-shape [panel (f)] first grow and then decay rapidly due to an unfavorable phase relation with the driving pulse. This is analogous to the phenomenon of adiabatic passage through a resonance. There is a pronounced concentration of energy at the apex at time \( t \approx 100 \text{ fs} \) [panel (n)]. This concentration occurs after the excitation pulse has ended, in the stage of the free-induction decay. From the aggregate of data, we can conclude that this concentration is an interference phenomenon, where the SP wave packets excited in the different parts of the system constructively interfere. The phase modulation is an effective controlling degree of freedom because it affects the relative phases of the excited SPs, influencing the interference.

The spatial distributions of the local fields at different instants for the case of negative chirp are shown in Fig. 7. The distribution in panel (a) for \( t = 57.3 \) fs (near the time of the excitation pulse maximum) is peaked at the V-shape “opening”. At the end of the driving pulse \( t = 80.3 \) fs, panel (b)], the excitation energy has sharply concentrated at the apex of this nanosystem, where the maximum field enhanced almost by two orders of magnitude (with respect to the driving field) develops [with the normal \( z \) polarization]. Within two oscillations \( t = 89.7 \) fs, panel (b), the maximum field is equally enhanced and concentrated at the apex, but
in the parallel (z) polarization. This energy concentration persists long after the excitation pulse is over [see panel (d) at \( t = 118 \text{ fs} \)]. To summarize, for a comparatively long period \((t \approx 80 - 120 \text{ fs})\), almost the entire excitation energy is concentrated at one point, at the apex of the V-shaped nanostructure, where the local fields are greatly enhanced and the oscillations persist in the form of free induction long after the driving pulse is over. This energy concentration is very similar to the “Ninth Wave” effect\(^{13}\) with one principal distinction: Here it is due to the phase modulation of the exciting pulse, while in Ref. 13 it is a result of the randomness of the system. Similar results we have found for RPC.

4. QUANTUM NANOPLASMONICS AND SURFACE PLASMON AMPLIFICATION BY STIMULATED EMISSION OF RADIATION (SPASER)

4.1. Quantum Nanoplasmonics\(^{16}\)

To develop theory of spaser (see the Introduction, Sec. 1) and for many other quantum theories, one has to quantize the SP field. Surface plasmons are bosons, like photons. However, they are related to the polarization of the medium, and are longitudinal waves describable by (quasi)electrostatic potential \(\phi(r)\) that becomes an operator in the quantum theory. To quantize SPs, one has to determine their physical frequencies \(\omega_n\) and decay rates \(\gamma_n\), or their complex frequencies \(\Omega_n = \omega_n + i\gamma_n\), from the found real eigenvalues \(s_n\) (Sec. 3.1). The quantization is straightforward when SPs are well-defined, i.e., their relaxation is small, \(\gamma_n \ll \omega_n\). As we see below, this is true in the red to infrared spectral region. In the actual quantization procedure, as usual, the decay of SPs is neglected, i.e., we set \(\gamma_n \to 0\).

The complex SP frequencies \(\Omega_n\) satisfy an equation \(s(\Omega_n) = s_n\), where \(s_n\) is the spectral parameter (Sec. 3.1). For weak relaxation, \(\gamma_n \ll \omega_n\), one finds that \(\omega_n\) satisfies an equation \(\text{Re}[s(\omega_n)] = s_n\) and that

\[
\gamma_n = \frac{\text{Im}[s(\omega_n)]}{s_n'}, \quad s_n' = \frac{d\text{Re}[s(\omega)]}{d\omega}\bigg|_{\omega=\omega_n}.
\]

Quantization of the SP system, valid in the quasi-static regime for times shorter than the SP lifetime \(\tau_n \equiv 1/\gamma_n\), is carried out by using the following approximate expression for the energy \(H\) of an electric field \(E(r, t)\), which is obtained for a dispersive system by following Ref. 47,

\[
H = \frac{1}{4\pi T} \int_{-\infty}^{\infty} \frac{d[\omega]E(r, \omega)}{d\omega} E(r, -\omega) \frac{d\omega}{2\pi} d^3r.
\]

Here \(T\) is an integration time used to calculate Fourier transforms, e.g., \(E(r, \omega) = \int_{-T/2}^{T/2} E(r, t)e^{i\omega t} dt\). This time should satisfy \(\tau_n \gg T \gg 1/\omega_n\), which is possible in the weak relaxation case, where the final results are independent of \(T\). We expand the field operator \(E(r, t) \equiv -\nabla \phi(r, t)\) in a series of the eigenstates \(\varphi_n(r)\):

\[
\phi(r, t) = \sum_n \sqrt{\frac{2\pi \hbar s_n}{\varepsilon_0 s_n'}} \varphi_n(r)e^{-\gamma_n t} \left[ a_n e^{-i\omega_n t} + a_n^* e^{i\omega_n t} \right],
\]
where \( a_n^\dagger \) and \( a_n \) are the creation and annihilation operators of a SP in the state \( \varphi_n(r) \). From Eq. (9), using Eq. (10), the quantized Hamiltonian takes on the standard harmonic oscillator form: \( H = \sum_n \hbar \omega_n (a_n^\dagger a_n + 1/2) \).

### 4.2. Theory of Spaser\(^{16}\)

A spaser consists of a metallic nanoparticle that plays the role of a laser’s resonator, whose eigenmodes are quantized in Sec. 4.1 and the active medium of two-level emitters. Here we consider theory of spaser, including interactions between the active medium and the kinetic equation of spasing (quantum generation of SPs).

Now assume an active host medium to be modeled as a collection of two-level dipolar emitters with population densities \( \rho_0(r) \) and \( \rho_1(r) \) in the ground and excited states, positioned at the points \( r_n, \alpha = 1, 2, \ldots \) and having dipole moments \( d^{(n)} \) with the transition matrix element \( d_{10} \). The interaction of this active medium with the SP field is described by the perturbation \( H' = \sum_n d^{(n)} \cdot \nabla \varphi(r_n) \) to the system Hamiltonian.

Applying Fermi’s golden rule to \( H' \), and taking into account Eqs. (8) and (10), we obtain a kinetic equation governing the number \( N_n \) of SPs in the \( n \)-th mode: \( \dot{N}_n = (A_n - \gamma_n) N_n + B_n \). Assuming an isotropic distribution of the transition dipoles, we calculate the Einstein coefficient \( A_n \), which describes the net stimulated emission of SPs, \( A_n = 4\pi \gamma_n s_n^2 \rho_n d_{10}^2 \sqrt{\hbar} \left( 6 \hbar \varepsilon_n \Im [\omega_n \rho_0] \right) \), where \( \rho_n \) is the spatial overlap factor of the population inversion and eigenmode intensity, \( \rho_n = 4 \int [\nabla \varphi_n(r)]^2 [\rho_1(r) - \rho_0(r)] d^3r \). The spectral overlap factor is \( q_n = \left( F(\omega) \right)^2 \left[ (\omega - \omega_n)^2 / \gamma_n^2 \right] \) d\( \omega \), where \( F(\omega) \) is the normalized-to-1 spectrum of dipole transitions in the active medium, close to its fluorescence peak. The Einstein spontaneous emission coefficient \( B_n \) is similar to \( A_n \), but the excited state population \( \rho_1 \) replaces the population inversion \( \rho_1 - \rho_0 \) in the expression for \( p_n \).

To discuss the behavior of this system, we introduce the dimensionless gain of the \( n \)-th eigenmode, \( \alpha_n = (A_n - \gamma_n) / \gamma_n \). Quantum amplification and generation of SPs exist if \( \alpha_n > 0 \). For \( \alpha_n > 1 \), the spontaneous emission is unimportant, coherent generation occurs, and the number of SP’s in a single eigenmode grows exponentially fast, \( N_n \propto \exp(\gamma_n \alpha_n t) \), eventually limited by the inversion depletion. Consider some limiting cases. For the maximum population inversion, \( \rho_1 \gg \rho_0 \), and a thick active medium, a universal upper limit is approached, \( p_n \approx \rho \), where \( \rho = \rho_1 + \rho_0 \) is the total density of the two-level energy donors. In this case, the gain does not depend on the field distribution of individual modes, but only on their frequencies. The factor \( q_n \) depends on the width \( \Gamma \) of the spectral function \( F(\omega) \) as compared to the SP linewidth \( \gamma_n \). For \( \Gamma \gg \gamma_n \), \( q_n \approx \gamma_n / \Gamma \). In the opposite case \( \Gamma \ll \gamma_n \), assuming that the donor transition is centered at the SP frequency, we have \( q_n \approx 1 \).

The specific geometry of a metal/dielectric nanosystem is a flat V-shaped metallic nano-inclusion described in Sec. 3.2, see Fig. 5 (left panel). We assume that the active host medium has a planar distribution of emitters parallel to this V-shaped inclusion and consider two cases: In a thin medium, the two-level emitters occupy the central grid plane (except for the volume occupied by the V-shape itself), as well as the two neighboring grid planes above and below that plane, resulting in a total thickness of three grid steps (from 3 to 15 nm). In the opposite case of a thick medium, the emitters occupy all the host volume. In all cases we assume \( \rho_1 = \rho \) and \( q_n = 1 \), as already discussed.

Emission in the nIR, where spasing is expected, imposes stringent requirements on the emitters. Infra-red dyes are inefficient and not very stable at room temperature. Two other possibilities are rare-earth ions and semiconductor quantum dots (QDs). The latter seem the most promising, since they are tunable in frequency due to quantum confinement, have relatively large transition dipoles \( d_{10} \) and narrow transition lines, and allow dense packing without compromising their optical properties.\(^{48}\) The well-studied CdSe QDs emit at visible frequencies, too high for the spaser medium. The novel PbS and PbSe QDs can be synthesized with radii \( R_D = 1 - 8 \) nm to have transition energies 0.7 – 1.8 eV (see, e.g., Refs. 49, 50), which are ideally suited for spasing.

The dipole element for the \( 1S_r \rightarrow 1S_h \) transition in QDs can be estimated from Kane’s theory, conventionally assuming strong overlap of the envelope states, as \( d_{10} = e^2 f K / (2 m_0 \omega_n^2) \), where \( f \) is the transition oscillator strength, \( K \approx 3 \) eV is Kane’s interband parameter, and \( m_0 \) is the bare electron mass. Setting \( f \approx 1 \), which somewhat underestimates \( d_{10} \) as well as the consequent gain, we obtain \( d_{10} = 1.9 \times 10^{-17} \) esu. To estimate \( \varepsilon_n \), we note that the highest-gain SPs have to be strongly localized at the metal surface and, consequently, also in the medium of the QDs. We estimate \( \varepsilon_n \) from the Maxwell Garnett formula assuming a dense packing of QDs in vacuum and adopting the known value of \( \approx 23 \) for the dielectric constant of PbS and PbSe, obtaining \( \varepsilon_n = 6.6 \).
The QD spectral width $\Gamma$ is mostly due to the inhomogeneous broadening. In chemically synthesized QDs, $\Gamma$ is small enough, $\Gamma \sim \gamma_n$, yielding $\alpha_n \sim 1$, which is sufficient for spasing. Because both $d_{10}$ and $\varepsilon_h$ are essentially independent of the QD size, Einstein’s stimulated emission coefficient $A_n$ and, consequently, the spaser gain $\alpha_n$, are higher for smaller QDs, $A_n \propto \rho \propto R_D^{-3}$. For our computations, we chose a moderately small $R_D = 2.3$ nm, to be on the conservative side in estimating the gain.

The spaser gain $\alpha_n$ is displayed in Fig. 8 vs. $\hbar\omega_n$ for both a thick and a thin medium. High values of $\alpha_n$, up to 12, are predicted for the latter [panel (b)]. The maximum value of $\alpha_n$ is even greater for the thick medium, and the amplification spectral band is wider [panel (a)]. The similarity in response of these two samples is due to the strong localization near the metal surface of the efficient spasing modes: only those QDs contribute that are positioned in the areas filled by these modes. The large gain for a thin (a few monolayers) QD active medium which surrounds the metal inclusion is advantageous: a spaser is possible whose total size is on the nanoscale.

In a thin active medium [Fig. 8(b)], the function $\alpha_n(\hbar\omega_n)$ exhibits some irregularities (“noise”). These come from fluctuations of the overlap factor $p_n$ from mode to mode, which reflect the chaotic nature of these modes. These fluctuations lead to random suppression of the gain. Fortunately, the gain is maximal for $\hbar\omega_n$ between 1.1 eV and 1.9 eV, where these fluctuations are small. When Au replaces Ag, computations indicate (data not shown) a positive gain $\alpha_n$ only if $R_D < 2$ nm, and $\alpha_n$ values that are significantly smaller. This is due to the higher losses in Au. When the spaser amplification condition $\alpha_n > 0$ is satisfied, a generating $n$-th eigenmode accumulates a macroscopic number $N_n$ of coherent SPs, which induces a local field of root-mean-square (RMS) magnitude $E(r) = \left(\langle |\nabla \phi(r)|^2 \rangle \right)^{1/2} = E_n(r) (N_n + 1/2)^{1/2}$, where $E_n(r) = \left(4\pi \hbar s_n (\nabla \phi_n(r))^2 / \varepsilon_h s_n \right)^{1/2}$.

As we found previously (see Sec. 3.1), there exist dark eigenmodes which cannot be excited or observed from the far field (wave) zone. Among them are all the Anderson-localized eigenmodes. As we show below, these dark eigenmodes can be generated by spaser. This is not only a principal fundamental question, but is also of significant importance for applications: Strongly localized dark eigenmodes excited in a spaser are promising for nanometer probing and high-field nanoscale photomodification.

In Fig. 9, we show the RMS amplitude $E_n(r)$ in the metal nanostructure plane for eigenmodes with the highest spaser gains at the two spectral maxima $\hbar\omega_n \approx 1.16$ eV [panels (a) and (b)], and $\hbar\omega_n \approx 1.6$ eV [panels (c) and (d)]. The highest gain occurs for a luminous eigenmode [panel (a)] with $\hbar\omega_n = 1.15$ eV [cf. Fig. 8]. This eigenmode is concentrated within a radius $a \approx 15$ nm around the tip of the V-shape. The spasing of this mode will be seen in the far zone as almost isotropic radiation with an anomalously narrow spectrum (high temporal coherence) and high spectral intensity. A dense enough ensemble of spasers may actually form a laser developing also spatial coherence, which is an interesting effect that we will discuss elsewhere.

Another high gain spaser eigenmode at $\hbar\omega_n = 1.18$ eV, displayed in Fig. 9(b), is a completely dark eigenmode that creates very high local fields of $\approx 7 \cdot 10^7 (N_n + \frac{1}{2})^{1/2}$ V/m, which are only a few orders of magnitude below atomic-strength fields. These fields are sharply localized at the tip of the nanostructure providing a unique tool for possible applications in nanoscale optical probing and modification where the undesirable, background far-zone radiation from the tip itself is absent.

In the second spectral maximum, the spaser eigenmodes at $\hbar\omega_n = 1.63$ eV [Fig. 9(c)] and 1.56 eV [Fig. 9(d)] are similar in some but not all respects to those in panels (a) and (b) discussed above: A dark eigenmode at
1.63 eV is now delocalized, while a luminous eigenmode at 1.56 eV is strongly localized at the tip. However, the gains of these eigenmodes are about half of those at \( \approx 1.16 \) eV. Note that the selection of this vs. the previous group of eigenmodes can be done by tuning the transition frequency of QDs by selecting their sizes. At a given frequency, an eigenmode can be selected by positioning QDs in the region where its local fields are maximal.

The present quantum-plasmonics theory may have applications other than spaser. One such application is based on the fact that the Hamiltonian is a functional of the system geometry on the nanoscale, through the dependence of the eigenfrequencies \( \omega_n \) on the characteristic function \( \theta(\mathbf{r}) \), namely, \( H = \sum_n \hbar \omega_n [\theta(\mathbf{r})](N_n + \frac{1}{2}) \).

This brings about mechanical stresses in the system which depend linearly on the local energy of excitation, but exist even for \( N_n = 0 \), i.e., in the vacuum state of SPs (Casimir effect).

To summarize, we proposed the spaser effect and prospective quantum-nanoplasmonic device. Spaser is not a laser: Its two-level emitters (QDs, in particular) do not emit light waves, but rather undergo radiationless transitions where their excitation energy is transformed into quasi-static electric field energy of SPs. The stimulated nature of this energy transfer causes buildup of macroscopic numbers of coherent SPs in individual eigenmodes of a nanosystem. It is possible to generate dark SPs that do not couple to far-zone fields. Spaser generates intense, nanoscale-localized optical-frequency fields with many possibilities for prospective applications in nanoscale and nanotechnology, in particular for near-field nonlinear-optical probing and nanomodification.

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