Control of the temporal profile of the local electromagnetic field near metallic nanostructures

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\textbf{Abstract.} We study control of the temporal profile of the local electric field in the vicinity of a small doped semiconductor or metal nanostructure. Unlike in the case of control in a gas or liquid phase, the collective response of electrons in the nanostructure may significantly enhance different frequency components of the external field. This enhancement strongly depends on the geometry of the nanostructure and can substantially modify the temporal profile of the local field. The changes in the amplitude and phase of the local field are studied using linear response theory within the random phase approximation. The inverse problem of finding the external electromagnetic field to generate an arbitrary target temporal profile of the local field, including the time-dependent polarization of the field, is considered and solved. We systematically study the pulse enhancement and shape distortion effects for a set of control pulses of various shapes.
1. Introduction

1.1. Control in gas or liquid phase

The last two decades have witnessed the birth and rapid progress in manipulation of quantum systems, such as atoms and molecules [1, 2], semiconductor quantum dots [3] or even complex biological systems [4] by means of optimally shaped ultrashort laser pulses. Coherent control is usually achieved in an homogeneous gas or liquid phase by the direct coupling of electronic or molecular vibrational degrees of freedom of the system being controlled to the external electromagnetic field [2].

Using ultrafast optical fields with duration of the order of the typical time of molecular bond breaking or shorter, one can create nonequilibrium electron populations and successfully interfere with important chemical reactions, controlling the outcome products, or induce reactions which cannot be activated through a conventional thermal mechanism [5].

Because atomic and molecular relaxation processes in a gas (and in some cases in liquid) phase are relatively slow on the timescale of control (tens or hundreds of femtoseconds), one can usually neglect the decoherence effects that suppress the possibility of coherent control [6]. For example, using a closed loop laboratory design [7] one can efficiently optimize the time-dependent shape of control fields with the help of genetic algorithms [5, 8, 9]. The polarization of the control field may be also controlled independently [10, 11].

One needs to emphasize that in a gas or liquid phase the controlled quantum systems are exposed to the same temporal profile of the control field scaled by the dielectric constant of the medium, as it is generated by the laser. For typical field intensities in experiments [5], one may neglect the quantum nature of the control field, and treat it as a classical object described by a time-dependent function $E(t)$.

1.2. Control near metal surfaces

However, it is known that most of the important chemical reactions in nature and technology take place at surfaces or interfaces. For example, at the surface of a catalyst (usually metal) an
efficient breaking and formation of new chemical bonds takes place on a femtosecond timescale, and observation of the dynamics can be performed, e.g., using a pump–probe technique [12, 13, 15].

Photo-irradiation at metal surfaces induces electronic excitations both in the metal and in molecules on the surface (adsorbates). This leads to various chemical processes, including charge transfer between adsorbates and metal, and chemical reactions of adsorbates. Therefore, the induction and control of chemical processes on a metal surface using ultrashort laser pulses is a very important subject from both scientific and technological points of view [12–14].

For coherent control of atoms or molecules near metallic surfaces, metallic clusters or other nanostructures, the situation becomes very different from the control in a homogeneous dielectric medium. The interaction of valence electrons in the metal nanostructure with the external field may lead to collective, geometry-dependent excitation modes and produce local fields, which are a few orders of magnitude larger than the external field itself [16]. In this case, the direct coupling of the control field to the controlled atom or molecule is much weaker than the indirect coupling via interaction with the excited plasmon modes. The enhancement of different frequency components of the external field strongly depends on the geometry of the nanostructure and may substantially modify the temporal profile of the local field.

Another complexity of the control problem is associated with a strong inhomogeneity of the local field near metal/dielectric interfaces. In the case of control in a gas or liquid phase the control field is relatively homogeneous and can be treated as a constant on the scale up to tens of nanometers that is still much smaller than a typical wavelength of the laser control field 500–1500 nm. However, the interaction of an electromagnetic pulse with a metallic nanostructure can create highly inhomogeneous local field distributions with the spatial variations as small as one nanometer [16]. Note that one has to distinguish between the static spatial localization of the induced field near sharp edges of the metallic nanostructure, and excitation of spatially localized plasmon–polariton modes [16].

The effect of the presence of a metallic nanostructure near a controlled atom or molecule is not limited to the local field enhancement and pulse shape distortion. It may also result in an effective broadening of a state linewidth of the molecule due to the enhanced radiative losses and due to the non-radiative energy losses into metal [17]. For example, recent measurements demonstrate [18] the reduction of fluorescence lifetime of dye molecules (from 2.8 ns to less than 1 ns) in the presence of a nanostructured metal surface.

Since the time-dependent ab initio simulations of both controlled quantum system and metal nanostructure may be computationally extremely expensive, most of the previous modeling of temporal characteristics of the local fields and associated electron dynamics was typically performed for significantly simplified models, which usually are more focused on the quantum dynamics of the controlled molecule.

For example, hybrid quantum control of photodesorption of a NO molecule from a Pt(111) metal surface was considered theoretically [21]. In this work, the authors studied the influence of strong dissipation due to coupling of the molecule to the metal surface on optimal control. However, the authors did not consider the collective response of electrons at the metal surface that would lead to the local field enhancement and distortion of the control.

In another study, a quantum mechanical treatment of the time-dependent screening and associated transient effects due to sudden creation of a charge in the close vicinity of a two-dimensional (2D) electron gas was considered in [22].
Many simulations, involving more realistic geometries than an idealized 2D electron gas, are usually performed using a phenomenological description of the material response. For example, one can mention coherent control of nanoscale localization of optical excitations in nanoscale systems [16], where Maxwell equations with a local phenomenological dielectric constant $\epsilon(r)$ were used.

A detailed study [10] was done on spatiotemporal and field polarization control using bulk response theory with local phenomenological dielectric constants. The authors in [10] used an expensive adaptive optimization technique to obtain optimal control solutions. However, a brute force optimization technique usually gives some locally optimal result, and does not guarantee the convergence to the optimal field for an arbitrary control.

The validity of local classical response theory is questionable for relatively small or highly inhomogeneous nanostructures, where quantum mechanical effects may play a critical role. Quantum corrections may be also significant for local field distributions in the close vicinity (on the order of the Fermi wavelength) near relatively large metallic nanostructures. In the quantum limit one needs to take into account the discreteness of the energy spectrum, nonlocal electron density response, dynamical screening effects and tunneling [23, 24]. As an illustration of this statement one can mention recent ab initio simulations of the response of small metal dipoles [19, 20], which predict a finite optimal size of the dipole to maximize the local field. That is qualitatively different from the classical picture using the local dielectric constant. The results [19, 20] confirm the earlier prediction [23] made with the help of a simple quantum mechanical description.

In the present study, we consider the problem of control over the time evolution of the local electric field in the presence of a small metal or doped semiconductor nanostructure, and propose to use the local field enhancement due to geometrical and resonant plasmon excitation for optimal control of atoms and molecules. We examine the inhomogeneous distribution of the induced field, and study how the control pulse intensity and phase are transformed due to the plasmon response of a small custom-engineered nanostructure.

2. Theory

2.1. Nonlocal linear response theory

As can be seen, control of local electric fields near metallic nanostructures becomes a much more complex task than in a gas or liquid phase. It is important for a theory to capture the fact that the incident electromagnetic field is coupled both to single particle and collective plasma excitations in the nanostructure, and the field in the nanostructure is neither completely screened, nor purely transverse. To develop a theory of the local field control at nano (i.e. subwavelength) scale, we need to map out spatiotemporal or spatiospectral amplitude as well as the phase of the local field in relation to the external spatially uniform, but temporally shaped excitation field.

More importantly, the inverse problem of finding the external field, corresponding to the required local control field for the best performance needs to be addressed. It may seem that the modification of the control field in the vicinity of a metal nanostructure makes coherent control very difficult or even impossible, and the only way to resolve it is to use a brute force optimization technique, as was done in [10]. However, we will show that one can successfully generate arbitrary local control fields with the prescribed temporal behavior and take advantage of the local field enhancement.

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The nonequilibrium dynamics of electrons in the nanostructure can be described in terms of the time-dependent density operator \( \rho(t) \), which can be expanded in a perturbation series with respect to the matter–field interaction:

\[
\rho(t) = \rho^0 + \rho^1(t) + \rho^2(t) + \cdots,
\]

where \( \rho^0 \) is the density operator for the system at thermal equilibrium (unperturbed). We assume that the external control field is relatively weak, so it can be treated within the linear response theory, keeping only the \( \rho^1(t) \) term. This term can be used to calculate the spatial distribution of the induced electron density in the system. In this case, the most general relationship between the external potential \( \phi_{\text{ext}}(\mathbf{r}) \) and the total potential \( \phi_{\text{tot}}(\mathbf{r}) \) in and near the nanostructure is:

\[
\phi_{\text{tot}}(\mathbf{r}, t) = \int_{-\infty}^{t} \int d\mathbf{r}' \epsilon^{-1}(\mathbf{r}, \mathbf{r}', t, t') \phi_{\text{ext}}(\mathbf{r}', t') \, d\mathbf{r}',
\]

where \( \epsilon^{-1}(\mathbf{r}, \mathbf{r}', t, t') \) is the inverse of the dielectric function of the nanostructure and the surrounding medium. Note that due to the causality principle the time integration in equation (2) is performed up to the time moment \( t \). It is convenient to extend the time integration to infinity, assuming \( \epsilon^{-1}(\mathbf{r}, \mathbf{r}', t, t') \equiv 0 \) for \( t' > t \). In order to simplify the transition into Fourier space, we assume that the inverse dielectric function is translation invariant in the time variables \( \epsilon^{-1}(\mathbf{r}, \mathbf{r}', t, t') \equiv \epsilon^{-1}(\mathbf{r}, \mathbf{r}', t - t') \), but not in the space variables. Thus, the nonconservation of the photon momentum due to the broken spatial symmetry is explicitly taken into account.

We assume that the incoming external field with an arbitrary time-dependent polarization

\[
\mathbf{E}_{\text{ext}}(t) = (E_{\text{ext}}^x(t), E_{\text{ext}}^y(t), E_{\text{ext}}^z(t))
\]

can be decomposed into a Fourier series, with each component independently:

\[
E_{\text{ext}}^a(t) = \sum_{i=1}^{N} E_{\text{ext}}^{a,i} e^{-i \omega_i t},
\]

where \( a = x, y, z \). The number of frequency components \( N \) may be either finite or infinite. The results derived below would not change if one considers the field spectrum represented by a continuum variable \( \omega \) instead of the discrete \( \omega_i \). In this case, the summation operation is just replaced by the integration.

In the linear response theory, the frequencies do mix, i.e. electrons in the nanostructure oscillate at the same frequency as the external field. In this case, the connection between the spectral components can be formulated independently for each frequency component:

\[
\phi_{\text{tot}}^i(\mathbf{r}) = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega_i) \phi_{\text{ext}}^i(\mathbf{r}') \, d\mathbf{r}'.
\]

where \( \epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega_i) \) is the Fourier transform of the inverse dielectric function. The total local field \( \phi_{\text{tot}}^i \) is represented as a sum of the external \( \phi_{\text{ext}}^i \) and the induced \( \phi_{\text{ind}}^i \) potentials:

\[
\phi_{\text{tot}}^i(\mathbf{r}) = \phi_{\text{ext}}^i(\mathbf{r}) + \phi_{\text{ind}}^i(\mathbf{r}),
\]

where \( \phi_{\text{ext}}^i(\mathbf{r}) \) is the external potential at a given frequency \( \omega_i \),

\[
\phi_{\text{ext}}^i(\mathbf{r}) = -x E_{\text{ext}}^{x,i} - y E_{\text{ext}}^{y,i} - z E_{\text{ext}}^{z,i}.
\]

Here, it is explicitly assumed that the nanostructure is much less than the field wavelength, and the external potential is a linear function of coordinates \( x, y, z \).
Applying the gradient operator $-\nabla$ to both sides of equation (5), and assuming a certain local observation point $r = r_0$, one obtains

$$E^{a,i}_{\text{ind}}(r_0, \omega_i) = \hat{Z}_{a,b}(r_0, \omega_i) E^{b,i}_{\text{ext}},$$

where we introduce the response kernel

$$\hat{Z}_{a,b}(r_0, \omega_i) = \nabla_a \left[ \int \epsilon^{-1}(r_0, r', \omega_i) r' n^b \, dr' \right].$$

(9)

Here, we denote indices $a, b = x, y, z$, and $n^b$ is a unit vector, parallel to the corresponding axis. Here, we also use the fact that the nanostructure is much smaller than the field wavelength, corresponding to the maximum frequency component $\omega_i$ of the external field, so one can neglect the retardation effects. In this case, the local field is simply related to the potential through the expression $E^{a,i}_{\text{tot}} = -\nabla \phi_{\text{tot}}$.

$\hat{Z}_{a,b}(r_0, \omega_i)$ has the structure of a three-by-three complex valued matrix. We assume this matrix is not singular for any values of $\omega_i$ and $r_0$. This assumption is equivalent to there being no complete field screening near the small nanostructure. If the matrix $\hat{Z}_{a,b}(r_0, \omega_i)$ is nonsingular, the expression (8) can be explicitly inverted just by calculating the inverse matrix at each frequency of interest $\hat{Z}^{-1}_{a,b}(r_0, \omega_i)$.

Thus, the external time-dependent field $E^{a,i}_{\text{ext}}(t)$ can be uniquely restored given the desired local control field $E^{a,i}_{\text{local}}(r_0, t)$ at a given observation point $r_0$. Note that our procedure works in the case of an arbitrary complex time-dependent polarization of the local field, and it is much simpler than the solution proposed in [10] using iterative optimization.

By calculating all the components of the total field $E^{a,i}_{\text{tot}}(r_0, \omega_i)$ at the observation point $r = r_0$, which result from the application of the external field of a fixed strength along the directions $x, y$ and $z$ at different frequencies $\omega_i$, one can compute all the elements of the matrix $\hat{Z}_{a,b}(r_0, \omega_i)$, which completely characterize the linear response of the nanostructure at a given point.

In practice, the explicit calculation and inversion of the nonlocal dielectric function $\epsilon^{-1}(r, r', \omega_i)$, which is necessary to determine $\hat{Z}_{a,b}(r_0, \omega_i)$ using equation (9), may be computationally too expensive. Instead of doing this, we use a much faster, but fully equivalent method of the solution of the integral equation with the density–density correlation function as the nonlocal kernel of the equation [23].

In this approach, one starts from the calculation of the induced charge density within the linear response theory. The induced charge density $\rho_{\text{ind}}(r, t)$ is assumed to be proportional to the total potential $\phi_{\text{tot}}(r, t) = \phi_{\text{ind}}(r, t) + \phi_{\text{ext}}(r, t)$, and is given by

$$\rho_{\text{ind}}(r, t) = \int_{-\infty}^{\infty} \int d\tau' \chi_0(r, r', t, \tau') \phi_{\text{tot}}(r', \tau') \, d\tau',$$

(10)

where

$$\chi_0(r, r', t, \tau') = -\theta(t - \tau') \langle \rho(r, t), \rho(r', \tau') \rangle_0$$

(11)

is the electron density–density correlation function. Note the factor $\theta(t - \tau')$ ensures the causality of the electron response. The statistical average is performed over the equilibrium state. It is natural to assume that the unperturbed system is charge neutral, $\langle \rho(r, t) \rangle_0 = 0$. Note that the density–density correlation function $\chi_0(r, r', \omega)$ is defined through the statistical average over the ground state of the electronic system and has no uncertainties related to quantum dynamics of electrons in the nanostructure.
As we did for the dielectric function $\epsilon$, here we also assume that the density–density correlation function is translation invariant in the time variables $\chi_0(\mathbf{r}, \mathbf{r}', t, t') \equiv \chi_0(\mathbf{r}, \mathbf{r}', t - t')$, but not in the space variables. By making Fourier transform in the time domain one arrives at the expression for the induced charge density oscillating at frequency $\omega_i$

$$\rho_i^{\text{ind}}(\mathbf{r}) = \int d\mathbf{r'} \chi_0(\mathbf{r}, \mathbf{r'}, \omega_i) \phi_i^{\text{tot}}(\mathbf{r'}).$$  \hfill (12)

One can express $\chi_0(\mathbf{r}, \mathbf{r'}, \omega)$ in terms of eigenenergies $E_i$ and eigenfunctions $\psi_i(\mathbf{r})$ of the unperturbed electronic Hamiltonian within the random phase approximation (RPA) [23, 24]:

$$\chi_0(\mathbf{r}, \mathbf{r'}, \omega) = \sum_{i,j} \frac{f(E_i) - f(E_j)}{E_i - E_j + \hbar \omega + i\gamma} \psi^*_i(\mathbf{r}) \psi_i(\mathbf{r'}) \psi^*_j(\mathbf{r'}) \psi_j(\mathbf{r}),$$  \hfill (13)

where $f$ is the Fermi distribution function, and the small parameter $\gamma$ accounts for a finite width of quantum levels in the nanostructure.

The eigenproblem for electrons confined in the nanostructure

$$H \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r}),$$  \hfill (14)

can be solved using numerical diagonalization. The full information about the geometry of the nanostructure is implicitly contained in the eigenspectrum of equation (14).

The induced potential $\phi_i^{\text{tot}}(\mathbf{r})$ is determined from the self-consistent integral equation [23]

$$\phi_i^{\text{tot}}(\mathbf{r}) = \int \int \chi_0(\mathbf{r}, \mathbf{r'}, \omega_i) \phi_i^{\text{tot}}(\mathbf{r'}) V_C(|\mathbf{r} - \mathbf{r'}|) \, d\mathbf{r'} \, d\mathbf{r''},$$  \hfill (15)

where $V_C(|\mathbf{r} - \mathbf{r'}|) = \frac{1}{|\mathbf{r} - \mathbf{r'}|}$ is the Coulomb potential. Here we again make use of the fact that the nanostructure is much smaller than the wavelength of the incoming field, so the retardation effects can be neglected and the induced charge density and the induced potential are related through the Coulomb integral:

$$\phi_i^{\text{tot}}(\mathbf{r}) = \int \rho_i^{\text{ind}}(\mathbf{r'}) V_C(|\mathbf{r} - \mathbf{r'}|) \, d\mathbf{r'}.$$  \hfill (16)

In order to find the induced potential $\phi_i^{\text{tot}}(\mathbf{r})$, we discretize the self-consistent integral equation (15) on a real space cubic mesh and solve it numerically. Equation (15) establishes one-to-one correspondence between the homogeneous external control field $E_{\text{ext}}$ and the total (local) field $E_{\text{tot}}^{\text{ind}}(\mathbf{r})$ at any given point $\mathbf{r}$, and within the RPA this is equivalent to more explicit formulation using equation (5) and the dielectric response function $\epsilon(\mathbf{r}, \mathbf{r'}, \omega)$.

Note that for a symmetric nanostructure and the external field applied along a symmetry axis, the vector relationship equation (8) may be reduced to a much simpler scalar expression.

3. Results

3.1. Geometry and resonance properties of the nanostructure

To illustrate our approach we consider a finite nanostructure made of a doped semiconductor with the dimensions $L \times L \times d$, $L = 33$ nm, $d = 10$ nm, with a bow-tie-shaped hole, 10 nm × 10 nm, see figure 1. Nanoholes of such shape are routinely manufactured for the local field enhancement [28]. We assume the carrier concentration $n = 9.5 \times 10^{19}$ cm$^{-3}$. For a given
geometry, size of the nanostructure and the carrier concentration there are a total of 1042 electrons confined in the system. For the considered carrier concentration the electron effective mass is taken to be $0.2m_e$, where $m_e$ is the bare electron mass [29].

The carrier concentration in the nanostructure is intentionally chosen to generate a plasmon resonance around the photon energy 0.8 eV, which corresponds to the wavelength $\lambda = 1550$ nm. The experimental techniques for generation, shaping and detection of ultrashort pulses at this wavelength are readily available. Also, this wavelength range is important for excitation and optimal control of molecular wave packet formation using, e.g., a two-color pump–probe scheme [26]. The electron Fermi wavelength $\lambda_F$ at this carrier concentration is $\lambda_F \approx 10$ nm, comparable to the size of the nanostructure (several tens of nanometers, which is within the capabilities of modern nanofabrication methods). A relatively small size of the nanostructure motivates us to use a quantum nonlocal linear response theory [23]. In our simulations, we set the phenomenological level broadening parameter to $\gamma = 3.8$ meV [25]. We performed simulations assuming room temperature $T = 300$ K $\approx 25.8$ meV and linearly polarized external field with the polarization direction parallel to the $y$-axis (see figure 1). We also assume that the observation point $\mathbf{r}_0$ is localized at the center of the hole, where the local field is maximum, which is our target region and the location of the controlled molecule (shown by the arrow in figure 1).

First, we performed calculations of the normalized local field intensity $|\mathbf{E}_{\text{tot}}(\mathbf{r})|^2/|\mathbf{E}_{\text{ext}}|^2$ and the local field phase in the target region of the nanostructure for different frequencies of the external harmonic field, see figure 2. The external field phase is set to zero. The phase of the local field differs from zero because the local field contains both real and imaginary parts, which is a manifestation of retardation effects. From figure 2, one can readily identify the main plasmon resonance peak that occurs at $\omega \approx 0.8$ eV, as the local field phase reaches

Figure 1. Nanostructure with a bow-tie hole (the third dimension of the nanostructure is not shown). The magenta circles correspond to the real space discretization points. In all our simulations we consider a linearly polarized control field with the polarization direction parallel to the $y$-axis.
Local field intensity, $|E_{\text{tot}}|^2/|E_{\text{ext}}|^2$

Figure 2. Normalized local field intensity $|E_{\text{tot}}(r_0)|^2/|E_{\text{ext}}|^2$ (solid line) and the phase (dashed line) in the center of the nanostructure as a function of the frequency $\hbar \omega$ of the external field. Many local extrema are present due to multiple geometric resonances in the nanostructure. The main plasmon resonance peak occurs at $\hbar \omega \approx 0.8 \text{ eV}$ as the local field phase reaches the value $\pi/2$. The enhancement of the local field intensity reaches $4 \times 10^5$ at the plasmon resonance. The frequency dependence has many local extrema due to multiple geometric resonances in the nanostructure and boundary effects. We have also performed calculations for slightly larger size of the nanostructure and found that increasing the size does not move significantly the position of the main plasmon resonance peak. Moreover, the boundary effects may be useful to engineer the response of the nanostructure.

After the identification of the main resonance properties of the nanostructure, we study the spatial local field intensity and the real part of the electron density distributions at different excitation frequencies. As we mentioned above, the local field may acquire an additional phase. This means that the local field is a complex valued function. Since the local and the external fields oscillate at the same frequency, what we plot is just an absolute value squared of the amplitude of the local field at different spatial points, or the real part of the induced electron density, which also oscillates at the frequency of the external field.

Figure 3 shows the spatial distribution of the normalized total field intensity $|E_{\text{tot}}(r)|^2/|E_{\text{ext}}|^2$ (left plot) and the spatial distribution of the real part of the induced electron density (right plot) at the quasi-static limit ($\hbar \omega = 10^{-3} \text{ eV}$). The field intensity and the induced charge distribution are taken at $z = 5 \text{ nm}$, i.e. the cross section is taken at the middle of the nanostructure. Note a relatively strong field enhancement in the vicinity of the bow-tie hole. Another interesting observation is that the induced charge density is present not only at the surface of the nanostructure, but also inside it. This is consistent with the fact that the field screening takes place on the scale of the Fermi wavelength $\lambda_F$, which for a given carrier concentration $\lambda_F \approx 10 \text{ nm}$ is comparable with the size of the nanostructure. However, the partial screening can be observed (the reduced local field intensity represented by the blue area on the left plot).

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Figure 3. Left plot: normalized local field intensity $|E_{\text{tot}}(r)|^2/|E_{\text{ext}}|^2$ in the nanostructure with a bow-tie-shaped hole, at the quasi-static limit ($\hbar \omega = 10^{-3} \text{ eV}$). Right plot: the real part of the induced electron density distribution (arbitrary units) at the same excitation frequency. The field intensity and the induced charge distribution are taken at $z = 5 \text{ nm}$.

Figure 4. Left plot: normalized local field intensity $|E_{\text{tot}}(r)|^2/|E_{\text{ext}}|^2$ in the nanostructure with a bow-tie-shaped hole, at the plasmon resonance frequency ($\hbar \omega = 0.8 \text{ eV}$). Note a strong field enhancement near the sharp edges. Right plot: the real part of the induced electron density distribution at the same excitation frequency. The field intensity and the induced charge distribution are taken at $z = 5 \text{ nm}$.

In figure 4, we plot the spatial distribution of the same physical quantities as in figure 3, but at the plasmon resonance frequency ($\hbar \omega = 0.8 \text{ eV}$). Note a very strong field localization and enhancement in the vicinity of the control area. The enhancement is achieved through a strong localization of the induced charge density in the bow-tie area (see left plot). Note the complex structure of the induced charge density distribution.

We also show in figure 5 the spatial distribution of the total field intensity together with the induced charge density at another geometric resonance frequency of the system, corresponding to the peak in figure 2 at frequency $\hbar \omega = 1.5 \text{ eV}$. Note the local field enhancement in and
Figure 5. Left plot: normalized local field intensity $|E_{\text{tot}}(r)|^2/|E_{\text{ext}}|^2$ in the nanostructure with a bow-tie-shaped hole, at frequency $\hbar \omega = 1.5$ eV. Note a strong field enhancement around the hole boundary. Right plot: the real part of the induced electron density distribution (arbitrary units) at the same excitation frequency. The field intensity and the induced charge distribution are taken at $z = 5$ nm.

3.2. Short pulse excitation

Now we are going to switch from the frequency to the real time domain and consider the effect of the resonant excitation of the nanostructure using various ultrashort control pulses. As we discussed in the Introduction, plasmon resonances may significantly alter the temporal profile of the local field.

Using the spectral response data of figure 2 and the superposition principle, the temporal structure of the local field induced by an arbitrary incident field can be uncovered, see equation (8), by Fourier transform of the product of the response of the nanostructure and the incident field complex spectrum. Similarly, the external control field in the frequency domain can be computed simply by the inverting of the system of linear equations (8).

Here, we would like to stress that the nanostructure acts as a linear amplitude and phase filter, which connects the external and local fields in a nonsingular fashion, making the solution to the inverse problem at a given observation point $r_0$ completely deterministic. The uncertainty in the determination of the local field given the external one, and vice versa, may arise only in an experimental realization of the scheme due to imperfections in nanostructure manufacturing or uncertainty in molecule positioning. To deal with these problems, one might need experimental iterative approaches [1], but it is not required by the theory.

A typical example of the control field is shown in figure 6(a): it is a 10 fs transform-limited Gaussian pulse, incident on the nanostructure, with the amplitude normalized to unity. The spectral intensity of the pulse, shown in figure 6(b), is also normalized to unity. The central frequency of the pulse is set to 0.8 eV.

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Figure 6. (a) Gaussian pulse (with the pulse amplitude normalized to unity) duration of 10 fs. (b) The spectral intensity (normalized to unity) shown by the solid line and the phase of the incoming pulse (dashed line). The phase of the incident pulse is set to zero.

Figure 7. (a) Temporal profile of the local field excited in the target region by the pulse shown in figure 6(a). (b) Normalized spectral intensity (solid line) and the phase (dashed line) of the local field.

If the laser pulse figure 6(a) is applied to the nanostructure, assuming the linear polarized pulse with the polarization vector along the y-axis, it will result in a time-dependent local field in the target area, shown in figure 7(a). As we expected, the amplitude of the local field is significantly enhanced due to the plasmon resonance in the nanostructure. Note a substantial difference in the shape of the local field as compared with the incident field, particularly the parasitic ‘ringing’ following the main pulse. This is not surprising if one takes a look at the spectral intensity and the phase of the local field shown in figure 7(b). The spectral structure of the local field is substantially modified, and the local field phase is identical to the phase shown in figure 2.

The solution to the ‘inverse’ control problem is displayed in figure 8(a). This pulse, being applied as an external field to the nanostructure, will result in the local field in the target area with the temporal profile shown in figure 6(a). The result can be interpreted by looking at the
Figure 8. (a) Temporal profile of the external control field that excites the local field in the target region, same as in figure 6(a). (b) Normalized spectral intensity (solid line) and the phase (dashed line) of the incoming pulse shown in (a).

spectral intensity and the phase of the local field shown in figure 8(b). It is easy to notice that the phase of the designed incident field is simply the inverted phase of the nanostructure’s response. Similarly, the spectral amplitude structure of the incident field compensates for the spectral variations of the nanostructure response, so it results in a smooth amplitude spectrum of the local field. As a consequence, the ‘ringing’ on the control pulse is exactly out of phase with the nanostructure’s ‘ringing’, so that the two contributions simply cancel each other.

To understand the interaction of electrons in the nanostructure with a short external control pulse, we may use a simplified model of a damped 1D oscillator. Let us assume \( x(t) \) is the collective coordinate of electrons in the nanostructure, assuming that they move as a whole with the resonance plasmon frequency \( \omega_{pl} \). We also introduce effective damping in the system \( \gamma_{eff} \). The equation of motion for the collective coordinate is

\[
\frac{d^2}{dt^2}x(t) + 2\gamma_{eff} \frac{dx(t)}{dt} + \omega_{pl}^2 x(t) = \frac{F(t)}{m_{tot}},
\]

where \( m_{tot} \) is the total mass of the electrons, and \( F(t) \) is the external driving field. The analytical solution of the equation of motion, assuming the initial conditions \( x(0) = 0, x'(0) = 0 \), is

\[
x(t) = \omega_1 \int_0^t dt' F(t') e^{-(t-t')\gamma_{eff}} \sin(\omega_1(t-t')) \tag{18}
\]

where \( \omega_1 = \sqrt{\omega_{pl}^2 - \gamma_{eff}^2} \). For an impulsive force \( F(t) = A\delta(t) \), the system undergoes an exponential decay with the oscillation frequency close to \( \omega_{pl} \approx \omega_1 \):

\[
x(t) \propto \sin(\omega_1 t) e^{-\gamma_{eff} t}. \tag{19}
\]

This simplified picture can be compared with the response of the nanostructure to an ultrashort Gaussian 1 fs pulse (figure 9(a)). Qualitatively the dynamics can be described using equation (19). First, there is a strong excitation of the system, and then there is an exponential decay of the local field oscillations with the frequency close to \( \hbar \omega_{pl} = 0.8 \text{ eV} \) (see figure 9(b)). Note a strong enhancement of the local field in the target region (by approximately a factor of 200).
In figure 9(c) we show a solution to the inverse control problem: with this pulse applied, a molecule localized in the target region will feel the local field, which is identical to figure 9(a). Note the pulse shown in figure 9(c) is significantly longer than 1 fs. Based on this observation, one may suggest to use the linear dielectric properties of the nanostructure to create more localized pulses in the time domain.

Note that in order to solve the inverse control problem within the simplified 1D classical oscillator model, the procedure is even simpler. One needs to substitute the target dynamics of the electron collective coordinate (which is proportional to the local field amplitude), represented by \( x_{\text{target}}(t) \) into the left-hand side of equation (17). After taking the time derivatives, the resulting expression will give the necessary driving field \( F(t) \). It is clear that within the simplified 1D classical oscillator model the inverse control problem can always be solved.

3.3. Pulse shape distortion

As we discussed in the Introduction, different frequency components of the incoming pulse may be enhanced (or suppressed) differently, depending on the geometry of the nanostructure and the point of observation. We have already seen in the previous section that for a given geometry and a fixed observation point the calculated or measured response kernel \( \hat{Z}_{a,b}(t, \omega_i) \) gives a ‘universal recipe’ to calculate the transformation for an arbitrary target local field.

In this section, we study the effect of pulse enhancement, its shape distortion due to the excitation of the spatially localized plasmon modes, and the inverse control problem for some standard pulse shapes.

In figure 10(a), we show a rectangular pulse duration of 100 fs and zero phase. The carrier frequency is set to 0.8 eV. In figure 10(b), we show the temporal profile of the local field in the target region. Note a considerable amplitude enhancement (by a factor of \( \approx 300 \)) and the pulse shape deformation. For a longer rectangular pulse, one may expect less distortion of the pulse shape, because its spectral density will converge to the Dirac delta function centered at the carrier frequency.

In figure 10(c), we show a solution to the inverse control problem. With this pulse applied, a molecule localized in the target region will feel the local field identical to figure 10(a). The field shown in figure 10(c) contains high harmonics with relatively larger amplitudes in order to construct through the interference the target square pulse at the given observation point. Here we
would like to reiterate our statement that the nanostructure works only as a linear filter, i.e. all harmonics in the local field are also contained in the external one, but with different amplitudes.

In figure 11(a), we show a triangular pulse duration of 65 fs, with the carrier frequency set to 0.8 eV, and in figure 11(b), we show the temporal profile of the local field in the target region. In figure 11(c), we also show a pulse, which results in the perfect triangular pulse at the target region. As in the example with the square pulse, the field in figure 11(c) contains higher harmonics with relatively large amplitudes.

As the last example in this section, we repeat our simulations considering a sequence of two Gaussian pulses duration of 10 fs each and separated by 40 fs delay (see figure 12(a)). The carrier frequency is again set to 0.8 eV. A similar pulse sequence is often used in various pump–probe techniques [5]. In figure 12(b), we plot the temporal profile of the local field in the target region for this sequence. Note the third ‘parasitic’ pulse, which is present due to the interference between different excited plasmon–polariton modes. In figure 12(c), we show a pulse, which results in a perfect pump–probe pulse sequence at the target region.

3.4. Sensitivity analysis

As we discussed in the Introduction, the local response of a nanostructure may strongly depend on the observation point (see equations (8) and (9)). In other words, the same external field...
Figure 12. (a) Sequence of two Gaussian pulses duration of 10 fs each, and separated by 40 fs delay. (b) Temporal profile of the local field excited in the target region by the pulse (a). (c) Temporal profile of the external field that excites the local field in the target region, same as (a).

Figure 13. Left plot: normalized local field intensity $|E_{\text{tot}}(r_0)|^2/|E_{\text{ext}}|^2$ in the center of the nanostructure (solid line), and at the point 1 nm shifted from the center along the $y$-axis (dashed line), as a function of the frequency $\hbar \omega$ of the external field. Right plot: the phase of the local field in the center of the nanostructure (solid line), and at the point 1 nm shifted from the center along the $y$-axis (dashed line), as a function of the frequency $\hbar \omega$ of the external field.

Pulse may generate local fields with different temporal and even polarization profiles, depending on the observation point. Therefore, it is significant to know how strongly is the local field sensitive to the variations of the observation points. In this section, we perform the sensitivity analysis of the local field with respect to various points within the nanostructure. It is valuable information, which gives a sense how strongly one needs to localize a controlled molecule in the vicinity of the nanostructure. In recent studies \[31\], it was shown that for some geometries of the nanostructure it is possible to trap molecules using the plasmon-enhanced local fields. However, small position fluctuations of the molecule are always present.

In figure 13 we plot the normalized local field intensity (left plot) and the local field phase (right plot) as a function of external field frequency for two different observation points. The first point belongs to the target region (see figure 1), and the second point is shifted with respect to the first one, by 1 nm along the $y$-axis.
Figure 14. Left plot: normalized local field intensity $|E_{\text{tot}}(r_0)|^2/|E_{\text{ext}}|^2$ in the center of the nanostructure (solid line), and at the point 1 nm shifted from the center along the $x$-axis (dashed line), as a function of the frequency $\hbar \omega$ of the external field. Right plot: the phase of the local field in the center of the nanostructure (solid line), and at the point 1 nm shifted from the center along the $x$-axis (dashed line), as a function of the frequency $\hbar \omega$ of the external field.

Figure 15. Left plot: normalized local field intensity $|E_{\text{tot}}(r_0)|^2/|E_{\text{ext}}|^2$ in the center of the nanostructure (solid line) and at the point 5 nm shifted from the center along the $y$-axis (dashed line), as a function of the frequency $\hbar \omega$ of the external field. Right plot: the phase of the local field in the center of the nanostructure (solid line), and at the point 5 nm shifted from the center along the $y$-axis (dashed line), as a function of the frequency $\hbar \omega$ of the external field.

In figure 14, we plot similar quantities as in figure 13, but the second point is shifted with respect to the first one (which is again in the target region), by 1 nm along the $x$-axis. From figures 13 and 14, it is clear that relatively large position fluctuations within 1 nm from the target region do not significantly modify the local response of the nanostructure.

If the second observation point is located at a relatively large distance from the target region, the field intensity and the field phase start to differ considerably. In figure 15, we plot the local field intensity and the local field phase at the target region and at the second
point, shifted by 5 nm along the y-axis. Note that most of the deviations become significant for relatively higher harmonics. An interesting observation is that while the local field amplitude may vary significantly from point to point, the phase of the local field is less sensitive to the spatial variations, see figure 15 (right plot). This effect provides an additional phase robustness to the position fluctuations of the controlled molecule.

4. Discussion

In conclusion, we have demonstrated theoretically the feasibility of the design of the temporal profile of the local electric field near small metallic and doped semiconductor nanostructures. Although the dielectric response of the nanostructures under consideration was in a quantum nonlocal regime ($\lambda_F \propto L$), we are able to use the resonant properties of the nanostructure to generate strongly enhanced, spatially and temporally localized local control fields. From equation (8), it follows that the present strategy may be applied to all three field components simultaneously, resulting in the design of the local field polarization. We have also shown that quantum dynamics of electrons, finite temperature and a finite electron level broadening in the nanostructure do not preclude local field control, and the local field shape deformation as well as the parasitic ‘ringing’ can be completely eliminated. This result can be applied to optimal coherent control of atoms and molecules near metallic nanostructures.

For relatively weak fields, one can readily find an external control field that for the particular geometry and a given carrier concentration in the nanostructure will generate the target local control field at a given observation point. The solution of the inverse problem equation (8) exists for an arbitrary shape and polarization of the target local field. One can conclude that under the discussed approximations, if optimal control is possible in vacuum or a homogeneous dielectric medium, it is also possible near metal nanostructures. As a matter of fact, the existence of an arbitrary control near a nanostructure is equivalent to the invertibility of the response matrix $\hat{Z}$, which allows us to write equation (8) as $E_{a,i}^{\text{ext}}(r_0, \omega_i) = \hat{Z}^{-1}_{a,b}(r_0, \omega_i) E_{b,i}^{\text{tot}}$. Therefore, if the response matrix is invertible, one can calculate the proper external field $E_{\text{ext}}^{a,i}$ for any local field $E_{\text{tot}}^{a,i}$. Moreover, one can use the dielectric properties of the nanostructure to enhance and localize the control field. In practice, the optimal control pulse can be found using standard closed loop techniques [1], because the exact response of each given nanostructure will be nearly impossible to measure.

In the present work, we also study the dependence of the local response of the nanostructure on the spatial variations of the observation point. We found that the inhomogeneous local field intensity may vary significantly from point to point. At the same time, we discovered that the phase of the local field is much less sensitive to the spatial variations. This effect provides additional phase robustness to the position fluctuations of the controlled molecule.

Now let us discuss some restrictions of the presented theory. In the present simulations, we used a simplified model of electrons interacting at the RPA level. Such simplifications will potentially lead to underestimation of the Landau damping [30], resulting in narrower resonance peaks. However, the position of the main resonance peaks obtained, for example, using the density functional theory, should be similar to our model [30]. The applicability of the linear response theory, used in this study, is limited to relatively weak fields, much less than the characteristic field created by an electron at the distance of the effective Bohr radius for a given material. For many optimal control applications this assumption holds. However, in some cases the field intensity may be high enough, resulting in a significant temperature rise and a
strongly nonequilibrium electron distribution \([12]\), which will require the use of the nonlinear response theory. Further, the breakdown of the linear response approximation will make the matrix \(\hat{Z}_{a,b}(\mathbf{r}_0, \omega)\) dependent on the amplitude of the external field. In this case, one cannot guarantee the inversion of equation (8) for an arbitrary optimal local field.

The electron–electron, electron–phonon scattering and other processes, having an unpredictable, stochastic nature, lead to the thermalization of the electron gas in the nanostructure and eventually to the loss of coherence in the controlled molecule \([25]\). However, if the controlled molecule is not in direct contact with the nanostructure, these processes would not limit the possibility of the optimal control. Because of the relatively large number of electrons in the nanostructure, the local electric field has no uncertainties related to the quantum dynamics of electrons, and the nanostructure effectively acts as a linear filter. In this case, the coherent control is limited by the intrinsic decoherence times of the controlled molecule. However, as we mentioned above, these times may be decreased due to the presence of a metal nanostructure \([18]\).

Since the temporal profile of the local control field may keenly depend on the position of the controlled molecule on the nanostructure, one needs to address possible mechanisms of the spatial localization of the molecule. It was theoretically demonstrated that the plasmon-generated spatially inhomogeneous field between metal nanoparticles can serve as a trap for molecules \([31]\) without a direct contact to the nanoparticles, which otherwise would lead to a strong decoherence. It was also shown \([23,31]\) that the field enhancement is maximum in the space between the nanoparticles. Thus, properly arranged arrays of metal nanoparticles (dimers) may offer both trapping and field enhancement capabilities.

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