Metallic nanostructures as electronic billiards

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Optical properties of the metallic nanoparticles are most often described in terms of plasmons, that is, coupled states of light and electrons. Here we show that many discrete resonances, resulting from the quantum confinement of electronic wavefunctions inside the metallic nanostructure, may lead to a single strong composite resonance, located typically in the low-frequency (mid-infrared and terahertz) range. They give rise to strong nonlinearities allowing efficient generation of terahertz and mid-infrared frequencies on the distances of just hundred nanometers. Especially effective are the processes which couple the quantum-confinement-induced resonances with Mie-type ones.

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Introduction. At it was first shown by Mie [1], optical properties of metallic nanostructures may demonstrate resonant behaviour because of light-induced movement of the electronic cloud close to the surface. Beyond the Mie resonances, several other types of resonances related to light-electron coupling in metallic and dielectric nanostructures exist, such as anapole modes [2], bound states in continuum [3] and some others [4,5]. These resonances are related to light and not to bound motion of electrons in metal. They are typically formulated in the terms of scattering of incident light rather than in terms of an intracavity trapping, although these formulations are in fact exchangeable.

Many electrons in metal, moving in the optical field, can be considered as an “electronic fluid”. Dynamics of such fluid can also be nonlinear [6,7], giving rise to the nonlinear optical response, including generation of harmonics. Other type of nonlinearity specific for metals is a nonlinear ultrafast electron heating [8,9]. This process, although important for picosecond-scale pulses and longer, is relatively slow and is negligible for pulse duration at the sub-100-fs level [9,10]. In contrast, the nonlinearities resulting due to transitions between different energy bands (interband) and inside the conduction band (intra band) [11] are nearly instantaneous and prevail for short pulses.

Another source of nonlinearity are the resonances, appearing due to quantum confinement of electrons in the finite volume of a nanoparticle. This type of resonances is very different from the photon-related resonances mentioned above, since not photons but electrons are confined. Such resonances were up to now observed in a semiconductor quantum dots (QDs) [12]. A QD can be considered as a “cavity” for a single free electron, or speaking in other terms, an electronic quantum billiard [13]. For instance, for a cube-shaped QD (of the size $L$) the corresponding electronic wavefunctions are standing waves $\psi(x, y, z) = \cos(2\pi n_x/L) \cos(2\pi n_y/L) \cos(2\pi n_z/L)$ (with $n_x, n_y, n_z$ being integer) with the energy levels given by $E \sim n_x^2 + n_y^2 + n_z^2$. When many of such levels are involved, the statistics of level spacings reveals a peak close to zero frequency. That is, many closely spaced resonances may, in certain sense, work as a single composite resonance located at low frequency. In the billiards of more complicated shape [14,15], demonstrating quantum chaos [13], this peak can be shifted to higher frequencies.

In contrast, in metallic nanostructures, neither discrete nor composite electronic resonances has been considered up to now. This sounds very logical, since in metals the width of resonances is huge and many of such broad resonances, closely spaced, compose quite a continuous band. Nevertheless, they certainly play a role in the optical response. For instance, in [11] the linear and nonlinear optical properties of metallic nanostructures were calculated taking into account the electronic quantum confinement - although still in approximation of the continuous density of states - with the result in agreement with experiment for short pulses [9,11].

Here we show that many resonances, arising due to quantum confinement of electrons inside metallic nanostructures and nanoclusters, form a single “super-resonance”. In contrast to Mie-type resonances, it typically lies at low, mid-infrared (MIR) or terahertz (THz) frequencies and, as we show, plays a critical role in the optical response at those frequencies. Because of their composite nature and very short relaxation times, such resonances are extremely broad, promising applications in ultrafast optics. In particular, as an application, we demonstrate a possibility of optical rectification and difference-frequency mixing, enabling an efficient broadband conversion from optical to MIR or THz ranges.
nanoscale distances. We also show that conversion efficiency can be strongly enhanced by an interplay with the usual Mie resonances.

**Billiard resonances.** To approach the problem analytically, we consider a spherical metallic particle of the radius $a$. Since we are interested in low frequencies, we neglect the interband transitions. We neglect the temperature effects assuming that $N$ electrons in conduction band occupy all levels below Fermi energy $\mathcal{E}_F$ (see Fig. 1). We also neglect the periodic potential created by the crystalline lattice. The energy structure is calculated assuming one-electron approximation and corresponds to that of a single free electron in an infinite-strength spherical potential of the radius $a$. To take into account finiteness of the potential, the levels above the work function $\mathcal{E}_W$ are disregarded. The corresponding single-particle eigenproblem can be then formulated as $H_0\psi = \mathcal{E}\psi$, with $H_0 = -\hbar^2/2m_e\Delta + V(r)$. $V(r) = 0$ for $r \leq a$ and $V(r) = \infty$ for $r > a$ ($m_e$ is the electron mass). With the approximations above, we neglect various effects of electron-electron and electron-ion interaction such as interband transitions, electron heating, the change of the eigenstates due to the finite height of the potential, and other effects, which play only minor role at low frequencies and ultrashort sub-100-fs pulse durations. Despite its extreme simplicity, this approximation was successful [16] in determining of nonlinearity in metallic nanostructures, at least away from resonances. The advantage of this approach is the possibility to determine the energy structure analytically. The corresponding eigenfunctions are combinations of spherical harmonics (see Supplementary). The energies are defined as $\mathcal{E}_{nl} = \mathcal{E}_0\alpha_{nl}^2$ where $n, l$ are quantum numbers, $\mathcal{E}_0 = \frac{\hbar^2}{2m_ea^2}$, $\alpha_{nl}$ is the $n$th zero of the Bessel function of order $l$. In contrast to the Coulomb potential, there is no degeneracy in $l$.

This allows to calculate the linear ($\chi^{(1)}$) as well as nonlinear ($\chi^{(3)}$) susceptibilities using a variation of the standard perturbative iterative approach [16] which takes into account selection rules following from the Fermi-Dirac statistics (see Supplementary for details). The linear susceptibility $\chi^{(1)}$ consists of the part corresponding to quasi-free electron motion (Drude-like dispersion), and the part describing quantum confinement of the electron inside the nanostructure [11]. For the Drude part, we used phenomenological coefficients for the bulk metal [17]. The confinement-based contribution can be interpreted as a sum over all virtual transitions between the levels below and above the Fermi level and back (see an exemplary transition in Fig. 1(b), as well as the Supplementary for explicit expressions). The resulting $\chi^{(1)}$ for a single gold nanoparticle (without the Drude part), assuming population decay time $T_1 = 50$ fs and dephasing time $T_2 = 5$ fs, is shown in Fig. 2 for different radii $a$. The important feature of the spectrum is the presence of a single resonance-like peak at a frequency which lies in MIR/THz range and decreases with the particle radius. This resonance is different from the Mie resonances which are at much higher frequencies.

We explain this resonance in the following way: the impact to the $\chi^{(1)}$ is made mostly by the transitions from the upper levels below Fermi energy to the lowest levels above Fermi energy. Although in general there are many such transitions even for smallest nanostructure diameters (see Fig. 1), the energy levels have a certain characteristic energy distance, so that many separate transitions have frequencies nearby. Because each of these transitions is very broadband with $T_2 = 5$ fs, they are “glued together” into one single “super-resonance”. This is visualized via level difference statistics in Fig. 2(c),(d), where normalized probability $P$ of the difference between levels $\delta\omega$ with $\mu \neq 0$ is plotted in dependence on $\delta\omega$ ($\mu \neq 0$ implies, in particular, $\Delta l = \pm 1$). As one can see, the maximum of the histogram corresponds very well to the resonances at the corresponding diameters. For large $n$ and $l$ and assuming in addition $n \gg l$, an analytical estimation is possible: in this case we have $\alpha_{nl} \approx (2n+1)\pi/2$, so that for a sufficiently large particle size $\delta\omega$ can be estimated as:

$$\delta\omega \approx \pi\sqrt{\mathcal{E}_F\mathcal{E}_0}/\hbar = \frac{\pi}{a} \sqrt{\frac{\mathcal{E}_F}{2m_e}},$$

and thus we expect the resonance around this value, which exhibits the decrease with radius $a$ as predicted numerically. Comparison to Fig. 2 shows that this rule works well even for the smallest particles.

Thus, the resonance we see here is different from typical atomic-like resonances in the sense that it consists of many transition with quite different $n, l$. In this respect it is becoming somewhat similar to the “super-resonances”, the peaks in the level statistics distribution in systems demonstrating quantum chaos [13].

**Nonlinearities.** Low frequency resonances described before are expected to lead also to strong nonlinearities; in our case, $\chi^{(3)} \neq 0$ as calculated using the approach described above (see Supplementary Material for details). We note that such approach to calculate Kerr nonlinearity was already utilized in [11], however, instead of discrete spectrum, approximation of continuous density of states were used in [11]. Nevertheless, we checked that our calculations give quantitative agreement with [11]; they are also in agreement with experimental measurements for short pulses (see [9] and references therein). An example of $\chi^{(3)}(\omega;\omega,\omega,-\omega)$ for the four wave mixing (FWM) process $\omega + \omega - \omega = \omega$ (corresponding to the Kerr nonlinearity) is shown in Fig. 3 for several radii. The low-frequency resonance we observed in $\chi^{(1)}$ is also well-visible here.

We now try to exploit the low-frequency resonance described above. Motivated by detection and spectroscopic
applications of THz and MIR radiation, we focus on the four wave mixing providing a signal in THz and MIR range, caused by sub-100 fs pump pulses. The FWM process can be described as a sum of contributions from virtual transitions from inside the Fermi see to outside and back, with every path containing 4 segments (see Fig. 1).

In Fig. 3b,c, the nonlinear susceptibilities $\chi^{(3)}(\delta; \omega_0, \omega_0, -2\omega_0 + \delta)$ and $\chi^{(3)}(\delta; \omega_0, \omega_0 + \delta, -2\omega_0)$, which lead to a signal at frequency $\delta$ as a result of a FWM process in a two-color pump at frequencies $\omega_0$ (fundamental) and $2\omega_0$ (second harmonics of the fundamental), are presented for $\omega_0 = 2.4$ eV (530 nm wavelength). In Fig. 3d $\chi^{(3)}(\delta; \omega, \omega, -2\omega + \delta_0)$ for fixed $\delta_0/2\pi = 1$ THz is shown in dependence on $\omega$. One can directly see that both Kerr nonlinearities and the FWM nonlinearities presented in Fig. 3 are several orders of magnitude higher than the Kerr nonlinearity for fused silica (around $10^{-21}$ m$^2$/V$^2$).

**Efficient frequency difference generation.** As an interesting application we consider the process of optical rectification and difference frequency generation, governed by nonlinearities $\chi^{(3)}(\delta; \omega_0, \omega_0, -2\omega_0 + \delta)$ and $\chi^{(3)}(\delta; \omega_0, \omega_0 + \delta, -2\omega_0)$, with a two-color optical pump at around $\omega_0$ and $2\omega_0$ and signal $\delta \ll \omega_0$ in THz and MIR. Assuming slowly varying envelope approximation and neglecting nonlinear effects for the pump waves, we have:

$$\frac{\partial A_0}{\partial z} = \frac{1}{2c\varepsilon_0} \frac{\partial P}{\partial t} = -\frac{i\delta\chi_{\text{eff}}^{(3)}(\delta)}{2c} A_2^*(z)A_2(z) - \alpha_0 A_0,$$

(2)

$$\partial_z A_n = ik_n A_n - \alpha_n A_n, \ n = 1, 2,$$

(3)

where $c$ is the speed of light in vacuum, $\varepsilon_0$ is vacuum permittivity, $A_i$, $\chi_{i}$, $k_i$, $i = 0, 1, 2$ are the slow (complex) amplitudes, linear losses, and wavevectors for $i$th harmonic (signal is assumed to be here the “0th harmonic”), $\chi_{\text{eff}}^{(3)}(\delta)$ is the effective nonlinear susceptibility for the corresponding process. The analytical solution of Eqs. (2)-(3) is

$$A_0 = -i A e^{-\alpha_0 L} (e^{\kappa L} - 1)/\kappa,$$

(4)

where $A = \delta\chi_{\text{eff}}^{(3)} A_2^2(0) A_2^* / 2c$, $L$ is the propagation distance, $\kappa = i(k_0 + 2k_1 - k_2) - 2\alpha_1 - \alpha_2 + \alpha_0$.

Both $\chi_{\text{eff}}^{(3)}$ and the linear susceptibility $\chi_{i}^{(1)}$ are calculated for given linear and nonlinear properties of the nanoparticles ($\chi_{NP}^{(1)}, \chi_{NP}^{(3)}$) and host ($\chi_{h}^{(1)}, \chi_{h}^{(3)}$) using the effective medium approach [18] (see also Supplementary). As a host material, we take fused silica which possesses strong losses in the range between 30 and 40 THz (see Fig. 1), but otherwise is quite transparent [19]. We consider the filling factor of $f = 0.01$ and neglect the nonlinearity of the host. Resulting effective linear quantities are shown in Fig. 4. One can see the Mie resonance at the wavelength around 530 nm (photon energy 2.4 eV), with the width of around 30 THz. We are interested

![FIG. 1. Electron in spherical potential of the nanostructure. (a) The potential $V(r)$ determines the energy structure of the electrons. In the absence of light, electrons fill all levels below the Fermi level $E_F$ (brown-shaded area). Electrons above $E_F + E_W$ are not confined anymore. (b) The energy structure in dependence on quantum numbers $n, l$ is shown for an exemplary size of $a = 2.75$ nm. The area below $E_F$ is also brown-shaded. Levels populated in the absence of the field are shown by black circles, unpopulated levels by blue circles. Linear and nonlinear optical response can be described as a sum over virtual transitions, examples of which contributing to $\chi^{(1)}$ (two virtual transitions) and to $\chi^{(3)}$ (four virtual transitions) are shown by red lines.](image-url)
FIG. 2. Linear susceptibility [imaginary part: (a), real part: (b) as a function of frequency for different nanostructure radii. In (c),(d), level-difference statistics (for the level pairs with nonzero dipole moments) for exemplary radii $a = 2.75$ nm (c) and $a = 7$ nm (d) are shown. Vertical lines in (a,c) and (b,d) indicate the central frequencies of the transitions for the corresponding radii. The other parameters are given in text.

In the shortest pulses which are still supported by this resonance, that is around 30 fs in duration.

For in THz range, that is, for $\delta/2\pi \leq 30$ THz, we assume the pump is located at $\omega_0$ and $2\omega_0$. For short pulses we consider the frequencies $j\omega_0$ and $j\omega_0 + \delta$ ($j = 1, 2$) which are both located within the spectrum of the pump. Therefore the nonlinearity is a sum of several possible processes:

$$\chi^{(3)}_{NP}(\delta) \approx \chi^{(3)}(\delta; \omega_0, \omega_0, -2\omega_0 + \delta) + \chi^{(3)}(\delta; \omega_0 + \delta, \omega_0, -2\omega_0) + \chi^{(3)}(\delta; \omega_0, \omega_0 + \delta, -2\omega_0).$$

In contrast, to obtain the signal in the MIR range $\delta/2\pi > 30$ THz, we consider the second harmonic to be shifted by $\delta$ to $2\omega_0 + \delta$. The only process contributing to the nonlinear conversion in this case is:

$$\chi^{(3)}_{NP}(\delta) = \chi^{(3)}(\delta; \omega_0, \omega_0, -2\omega_0 + \delta).$$

The resulting field amplitude at 0th harmonic $A_0$, calculated according to Eq. (5), is given in Fig. 3 for different parameters and for the pump amplitudes $A_1 = A_2 = 10^{10}$ V/m. This pump for 30-fs pulses corresponds to a fluence around $0.3$ J/cm$^2$, which is yet below the damage threshold of gold (around $0.5$ J/cm$^2$ [20]) and of fused silica (around $1$ J/cm$^2$ [21]). One can see that in THz range the field amplitude reaches $5 \times 10^8$ V/m corresponding to efficiency of around $10^{-3}$. In MIR range, the amplitude can exceed $10^9$ V/m, so that efficiencies above percent level are possible. Moreover, already after 100 nm of propagation the efficiency is at the maximum (in THz range) or close to it (in MIR rage); in MIR, the maximum is achieved at the propagation distances around 1 $\mu$m. These findings indicate a possibility to manufacture miniaturized frequency-conversion devices. From Fig. 4 it is also seen that the most efficient conversion is achieved for the pump frequency $\omega_0$ centered at the Mie resonance (solid lines in Fig. 4). In this case, the coupling of the pump to the signal is most efficient. For pump offset from the Mie resonance (dashed lines at Fig. 4) the resulting amplitude is around one order of magnitude lower. As a function of nanoparticle radius, the conversion efficiency increases up to $a \approx 7$ nm, after which it barely depends on the radius (at least up to $a = 15$ nm, the limit we could afford with the computational power at our disposal).

Conclusions. As a conclusion, we showed that, in spite of extremely high relaxation rates in metals and large number of states, the discrete nature of the energy landscape in the conduction band due to quantum confinement still plays an important role, especially in MIR and THz ranges. The global structure of levels reveals characteristic energy difference, which manifests itself in a
FIG. 3. Nonlinear susceptibility for the Kerr nonlinearity $\chi^{(3)}(\omega; \omega, \omega, -\omega)$ (a,b) and for the optical rectification $\chi^{(3)}(\omega; \omega_0, \omega_0, -2\omega_0 + \omega_0)$ (with $\omega_0$ corresponding to 800 nm wavelength) (c,d) in dependence on $\omega$ for nanostructures of different radii. Real part: (a,c), imaginary part: (b,d). The other parameters are given in text.

...single composite resonance, comprising many transitions. Nonlinear response resulting from such resonances can be used to effectively down-convert light to THz and MIR range with high efficiency already after 100-nm distances. The multi-level nature of the resulting resonance is similar to the level spacing peaks arising in the quantum chaos theory. It is therefore possible that these resonances can be controlled by modifying geometrical shape of the nanostructure.

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FIG. 4. Efficient generation of THz and MIR light in a composite of gold spheres with 2-color pump. (a) effective refractive index $n_{\text{eff}}$ and effective losses $\alpha_{\text{eff}}$ in dependence on frequency $\omega$ for a gold nanostructures with $a = 10$ nm immersed into fused silica with filling factor $f = 0.01$. Vertical lines show two variants of the 2-color pump at $\omega_0$ and $\omega_0$ with $\omega_0 = 2.4$ eV ($\lambda_0 = 530$ nm, solid line) and $\omega_0 = 1.55$ eV ($\lambda_0 = 800$ nm, dashed line). The components of two-color pump are connected by horizontal lines. (b) Generated amplitude $E_0$ according to Eq. (4) from 2-color excitation [see (a)], for different propagation distances $L$ and nanostructure radii $a$. In the legend, the quantities $\omega_0$, $L$, $a$ are given for every line. The peak pump fields are $A_1 = A_2 = 10^{10}$ V/m (corresponding intensity is around 10 TW/cm$^2$). Solid vertical line in (b) separates THz from MIR band; in THz range ($\delta < 30$ THz) nonlinearity is calculated according Eq. (5) whereas in MIR Eq. (6) is used.

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