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1

Introduction and Description of Contents

In this introductory chapter a description of the aims of the monograph and its contents is given. The main results are briefly stated in the context of previous publications and knowledge. The applications of nano-plasmonics presented in the book are outlined.

The publication of this book is intended to meet the considerable recent interest in subdiffraction light manipulation by plasmon excitations in nanoscale metallic components [1]. The related rapid development of the new field of nano-plasmonics overlaps with nanophotonics and new-generation optoelectronics [1–6]. From the quantum physics point of view, metallic nanoparticles are quite different from semiconductor quantum dots (QDs) [7] despite their similar spatial confinement sizes. In a nutshell: QDs are manufactured nanometre-sized quantum wells that are relatively shallow and do not possess the singularities present in Coulomb confinement. Quantum dots are typically located in semiconductor surroundings and are able to trap conduction-band electrons, valence-band holes, or excitons from the surrounding material. They localize electrons in discrete quantum states analogous to those of atoms, though without the limitation caused by the instability of the atomic nucleus. Quantum dots can thus be filled with several carriers, electrons or holes; however, this is limited in practice by the depth of the QD well. The analogy between QDs and ordinary atoms can be somewhat misleading owing to the strong dephasing of states in QDs by collective excitations in the surroundings (mostly phonons). This dephasing occurs because the energy scales of the trapped carriers in QDs and of the collective phonon excitations in the surrounding crystal are similar. Hence, the decoherence of QD states (hybridization with collective band excitations) is, by several orders of magnitude, larger than that in atoms [8]. Nevertheless, the concept of a QD is physically straightforward and allows for easy and efficient numerical modelling based upon an elementary quantum mechanics scheme for a small number of particles.

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For metallic nanoparticles the situation is different and is related to the much more complicated physics of metals. The typical situation for metals is a deep Fermi sea of nearly free electrons with a well-defined Fermi surface even at high temperatures; the Fermi energy in metals, of the order of 10^4 K, greatly exceeds the melting temperature. The theory of metals was developed for bulk metals in the 1960s by the application of advanced methods for multiparticle systems, mostly in terms of the Green function approach [9]. The quantum degeneracy of the dense Fermi liquid of electrons in metals (actually the degeneracy of the Landau quasiparticles, which are stable on the Fermi surface [9]) makes a finite metal sample confined at the nanoscale a quantum system very different from a QD low-populated with band carriers in semiconductors. In metals, the crystalline positive ion background that is essential for the definition of the related quantum states causes an additional complication. There have been many successful attempts to describe the excitations in metals using quantum statistical physics and many-body theory methods [9–11] or a quasiclassical phenomenological approach [12, 13].

Besides the low-energy excitations near the Fermi surface in metals (i.e., the electrons that can be expressed in terms of so-called Landau quasiparticles [9, 11]), there exist also collective high-energy excitations involving all the electrons simultaneously, not just those located close to the Fermi surface. For a bulk metal, an efficient theory for these high-energy collective excitations of electrons in metals was developed in 1952, within the random phase approximation (RPA) approach, by Pines and Bohm [14, 15]; these high-energy collective excitations were called plasmons. Owing to the large energy difference between plasmons and the Landau quasiparticles close to the Fermi surface, plasmons do not interact with the Landau quasiparticles, although all the electrons collectively create plasmons. Thus, plasmons cannot be excited just by low-energy electrons, as the plasmon energy in a bulk metal is typically of the order of 10 eV, exceeding even the Fermi energy, which is usually of the order of 7−8 eV. The plasmon energy is thus of a scale similar to that of ultraviolet (UV) photons, and so plasmons can be excited by sufficiently hard electromagnetic radiation.

However, in confined metallic nanoparticles the energies of plasmons are considerably lower [17–21], and in noble metals (Au, Ag, Cu) they fit with the visible photon energies. This observation sparked the nanotechnology revolution related to the modification and control of visible light by plasmons in metallic nanostructures [1–6] whose spatial size is much lower than the wavelength of light, referred to as subdiffraction light manipulation. It should be noted that plasmas and their excitations were the subject of interest early in the twentieth century [18] and since then have been investigated in relation to high-energy plasmas of charged particles (mostly protons) in stellar kernels, tokamaks, galaxy ion clouds, and the ionosphere. This interest has been stimulated also by the development of over-horizon radar and

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anti-radar technology, which has been accelerated in recent years by achievements in metamaterial construction (such as an 'invisibility cloak') allowing control over light in a manner different from ordinary reflection and refraction.

The main objective of this book is to present an effective theory of plasmons in metallic nanoparticles that is as analytical as possible, allowing universal applications that are not restricted to previously studied numerical models. The numerical methods developed in the 1980s for *ab initio* approaches to plasmons in metallic clusters were limited to approximately 300 electrons (owing to the high numerical complexity of the solution of the Kohn–Sham equations) [19, 20]. In view of these problems, insights into the plasmonics of metallic nanoparticles were confined to phenomenological approaches; these approaches used experimentally aided modelling [22] of the dielectric function in the solution of the classical Fresnel–Maxwell equations for the boundary problem of a metallic nanoparticle with spherical geometry and an incident planar wave. The analytical solution of this problem is known as the Mie approach [17, 18] and results in formulae for the scattering and extinction cross sections for light incident on a metallic sphere.

However, the Mie approach uses a phenomenological dielectric function for the metal as a prerequisite to model light absorption in the metallic nanoparticle (according to the conventional Drude–Lorentz model) [17]. The same approach is used for the numerical solution of the Maxwell equations with boundary conditions in the COMSOL system (which is not limited to spherical geometry); this utilizes the finite element method to solve the Maxwell equations. The COMSOL calculus includes the plasmon dynamics only phenomenologically, via a predefined dielectric function of the metallic compound. However, recognition of the plasmon properties of metallic nanoparticles is not available in either of the aforementioned approaches, which is a significant drawback. Therefore, progress in the description of plasmon excitations in metallic nanoparticles within a microscopic framework, preferably in an analytical form, may have considerable significance for improving upon the very popular Mie-type and COMSOL methods. Upgrading these classical methods may consist in a better declaration of the dielectric functions of the objects under study, since these functions are prerequisites for both the Mie and COMSOL calculus. The modelling of dielectric functions at the nanoscale is a source of certain discrepancies between the numerical solutions and experiments because a predefined dielectric function is usually supported by experimental data that come from bulk metals or thin films, rather than from nanoscale particles. Thus, theoretical insights into the properties of plasmons at the nanoscale that include quantum effects are necessary to improve the conventional numerical models. This can be done via the development of a microscopic quantum model for surface and volume plasmons in metallic nanoparticles using the RPA approach [16] for finite nanoscale geometries [23], in a generalization of the Pines–Bohm theory [14–16].

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We will demonstrate this approach in the present text and describe an analytical description of all the multipole modes (for spherical symmetry) for surface and volume plasmons within the RPA model that agrees well with experimental observations.

Surface plasmons in a metallic nanoparticle correspond to the translational collective oscillation modes of all the electrons in the nanoparticle when the charge fluctuations that are not compensated by the static positive ion jellium occur only on the nanoparticle surface. This condition is in contrast with volume plasmons, which are compressional-type modes with charge density varying along the nanoparticle radius. Remarkably, the surface plasmons in nanoparticles have resonance energies lower than the energy of the bulk plasmons, i.e., $\hbar\omega_p = \hbar\sqrt{ne^2/(m\varepsilon_0)}$ (n is the electron density in the metal, e and m are the electron charge and mass, and ε_0 is the dielectric constant); for the simplest case, that of dipole-type surface plasmon oscillations, $\hbar\omega_1 = \hbar\omega_p/\sqrt{3}$ (the Mie energy). However, the volume plasmons in nanoparticles have resonance energies higher than those in the bulk. Neither type of plasmon excitation – the surface or the volume plasmons – occurs in the bulk metal (although for a half-space geometry there are surface plasmons at the so-called Ritchie frequency, $\omega_p/\sqrt{2}$ [5]).

The essential difference between the RPA Pines–Bohm model for bulk metals [16] and the RPA theory for metallic nanoparticles consists in the explicit definition, in the latter theory, of the finite rigid jellium (defining the shape of the nanoparticle) [23]. In the RPA Pines–Bohm theory, the infinite jellium in the bulk is renormalized out via an ideal compensation with a uniform long-wavelength coherent electron fluctuation (i.e., a uniform plasmon mode with momentum $\mathbf{q} = 0$). For a finite nanoparticle, however, such a renormalization is impossible because of the absence of translational invariance and the presence of quantum numbers that are different from momentum quantum numbers for the plasmon excitations, owing to the explicit presence of the jellium rim.

The quantum dynamics equation in the Heisenberg representation determines the self-modes for collective local charge density fluctuations [16, 23]. The gradient operator in the kinetic energy term produces Dirac delta singularities on the rim of the jellium; these arise from the derivative of the Heaviside step functions defining the jellium border. Because these singularities are located on the edge of the nanoparticle, they allow separation of the surface and volume plasmon components in the dynamics equation [23]. However, a mutual dependence of the two types of excitation is visible within the RPA approach. Moreover, the problem of the so-called spill-out of the electron liquid beyond the rim of the jellium can also be considered in the RPA theory. Nevertheless, the spill-out appears to be on the scale of the Thomas–Fermi length [19] and is thus unimportant for nanoparticles with a radius larger than about 5 nm, though for smaller nanoparticles

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(of size 2−3 nm) the spill-out considerably dilutes the electron density inside the cluster and redshifts the resonance plasmon frequencies, which are proportional to the square root of the charge density [19–21]. Surface effects such as spill-out and Landau damping [20] (the latter corresponds to the decay of plasmons into a pair of quasiparticles distant from the Fermi surface and thus unstable) become less important for larger nanoparticle sizes, and for nanospheres with radii larger than 5 nm these surface effects are negligible [20]. The reduction in the role of spill-out (which makes the surface fuzzy and perturbs the surface modes) for particles larger than a few nanometres in radius supports the usability of the RPA approach in a quasiclassical way: it is a sufficiently accurate quantum approach at this nanoparticle size [23] as it allows the separation of volume and surface local electron density fluctuations. In ultrasmall nanoparticles [19], mixing of the surface and volume excitations occurs for up to approximately 60 electrons, when shell effects cease to contribute [19, 21]; for larger nanoparticles the separation between the surface and volume excitations improves for greater numbers of electrons [23] and is almost ideal for nanospheres with radii larger than approximately 5 nm. The quantum dynamics equation (the Heisenberg equation for the second-order time derivative of the local electron density operator [16, 23]) has a complicated form owing to the presence of the finite jellium. However, after making the RPA simplification, including a quasiclassical averaging of the kinetic energy according to the so-called five-thirds Thomas–Fermi formula [16]), this quantum dynamics equation describes a plethora of plasmon modes in the nanoparticle [16], many more than the single volume mode of the bulk metal [16].

An important advantage of the RPA model developed in this book is the possibility of including dissipation effects such as those due to electron scattering on other electrons, on phonons, on admixtures and defects or on the boundary of the nanoparticle. The resulting shift in the plasmon resonance caused by the scattering damping of plasmons scales as $1/a$, where a is the radius of a nanoparticle [24], which agrees with experimental observations for the radius range $5 < a < 10$ nm (for Au in a vacuum), where electron scattering energy dissipation dominates other damping channels [25].

Nevertheless, plasmon oscillations are also damped by radiation, an effect that increases with the electron number in a nanoparticle and leads to pronounced cross-over in the size dependence of the plasmon attenuation and the related resonance shift for nanosphere radii a of 10−12 nm (for Au in vacuum, in general the cross-over depends on the metal and the dielectric surroundings). At nanoparticle sizes corresponding to this cross-over, the decrease in the plasmon damping as $1/a$ changes to a strong increase proportional to a^3 [26], the a^3 dependence is related to the fact that all the electrons participate in plasmon oscillations and their radiation properties; this is true even for surface plasmons.

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Thus, the contribution of all the electrons in a nanoparticle is manifested by the volume factor a^3, which causes a similar scaling in the radiative damping of plasmons resulting from the so-called Lorentz friction [26], i.e., the energy loss of oscillating charged particles due to the radiation of electromagnetic waves. For a sufficiently large number of electrons inside the nanosphere, the Lorentz friction losses dominate other channels of plasmon damping. The large radiation energy loss expressed by the Lorentz friction damping initially grows with a^3, as mentioned above [27], but then saturates at approximately $a \sim 50$ nm (for Au in vacuum) and gradually decreases for larger nanoparticles. This behaviour is identified and described in this text.

Such behaviour reveals that the inclusion of Lorentz friction considerably changes the plasmon oscillation regime: the oscillations are not of the harmonic-oscillator type because the Lorentz friction is proportional to the third-order time derivative rather than the first-order time derivative as is the case for the ordinary friction of a harmonic oscillator. The harmonic oscillator model appears to be incorrect for plasmons in large metallic nanoparticles, and many simplified harmonic models of plasmons that are popular in the literature are misleading. In particular, the overdamped regime typical for harmonic damped oscillators, which would terminate plasmon oscillations within the harmonic model at approximately 57 nm, for Au in vacuum, does not reflect reality. The solution of the third-order dynamic differential equation is different from that for a harmonic oscillator, and the relationship between the frequency and damping of a harmonic oscillator, $\sqrt{\omega_0^2 - 1/\tau^2}$ (which defines the overdamped regime when the expression under the square root is negative), is not valid for plasmons. Beyond the harmonic model the relationship between frequency and damping also has an analytical form, which has been derived and which allows us to describe plasmon behaviour precisely.

The exact solution of the Lorentz friction problem for plasmons in metallic nanoparticles [26] gives very good agreement with experiment, with respect to the size dependence of plasmon resonances in metallic nanospheres. This result provides more precise modelling of metal dielectric functions, for specific sizes of nanostructure configurations, that includes plasmon damping and has also been applied to modify numerical studies using COMSOL and Mie-type calculation schemes [28, 22, 29], in both cases these schemes use predefined dielectric functions for the systems analysed. The results have been confirmed experimentally for Au and Ag nanoparticles.

The RPA theory of plasmons in metallic nanoparticles and their radiative properties is useful for modelling the so-called plasmon-aided photovoltaic (PV) effect. The damping of the plasmons changes radically when another electrical system is located near a metallic nanoparticle with plasmons; such a system could be a semiconductor substrate with a band electron system. In such a case, the

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semiconductor substrate receives an extremely strong flow of energy from the plasmons to the band electrons, which corresponds to plasmon damping greatly exceeding the Lorentz friction losses in the dielectric surroundings. This new and strong channel of energy transfer can be described by applying the Fermi golden rule to the quantum interband electron transitions induced by the near-field radiation of plasmons in a metallic nanoparticle deposited on a semiconductor substrate [30]. The mediation by plasmons in the energy harvesting of a photoactive semiconductor layer results in significant modification of the ordinary photoeffect.

This phenomenon is of high practical importance in view of the current rapid development of photovoltaics; in 2015, the total power of all PV solar cell installations worldwide was approximately 250 GW, whereas the total power produced by conventional coal or gas energy plants was approximately 29 GW in Poland. There could be an increase in the efficiency of solar cells (particularly thin-film solar cells and organic 'plastic' cells) by several per cent due to mediation by plasmons in metallic nanoparticles deposited on the cell surfaces (metallic coverings with low densities, $\sim 10^{8-10}/\mathrm{cm}^2$ and thus low costs and easy accessibility for industry technology) [31]. This could have a large economic impact in the field of renewable energy sources [32–36].

In Au, Ag, and Cu nanoparticles with radii $a \sim 10-50$ nm the photoeffect efficiency is enhanced, in laboratory setups of photodiodes, by a factor $2-10$ owing to energy transfer from the incident photons to the semiconductor substrate via plasmons in the deposited metallic components [31–36]. However, in solar cells the efficiency of the photoeffect is only one factor amongst many other factors that define the final total efficiency of a cell, and a large increase in photoeffect efficiency causes a more modest increase in the total efficiency of a solar cell.

Through the quantum calculus of the Fermi golden rule scheme, we can demonstrate [30] that the near-field coupling of the dipole mode of the surface plasmons in metallic nanoparticles deposited on top of a semiconductor is very efficient, i.e., this coupling effect causes a strong increase in the probability of interband transitions compared with the ordinary photoeffect, in which the plane-wave photons interact directly with the band electrons. The advantage of the result obtained via the Fermi golden rule approach is its analytical form (which is similar to the formula for the ordinary photoeffect in a semiconductor, though the calculus for plasmon mediation is much more complicated; however, it is analytically attainable [30]). The analytical form of this approach allows for the analysis of various competing mechanisms, and leads to an expression for the photoeffect efficiency increase due to plasmons in solar cells.

The related calculations explicitly demonstrate that the absence of translational invariance for a nanoparticle coupled in a near-field zone with a semiconductor substrate removes the constraints imposed by the momentum conservation rule.

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Thus, in addition to the vertical interband transitions (conserving the electron momentum plus the negligible photon momentum) found in the ordinary photoeffect, all indirect interband transitions between arbitrary electron momenta are available, which strongly enhances the probability of interband transition. The momenta of incident photons with energies beyond the forbidden energy gap are negligible compared with the momenta of the Bloch states of the band electrons in a semiconductor, which results in a constraint to 'vertical' interband transitions in the ordinary photoeffect. This constraint is removed when the translational symmetry is violated for a small metallic nanoparticle. The coupling of the plasmon dipole in the near-field regime allows all skew interband transitions, enhancing the total probability of interband excitations of carriers in the semiconductor substrate. This effect favours smaller metallic nanoparticles but, conversely, larger nanoparticles have larger dipoles (in proportion to the electron number), which also enhances the transition probability. The resulting trade-off of these opposing tendencies defines the optimal size for a metallic nanoparticle to increase the photoeffect efficiency. Moreover, the type of nanoparticle deposition used plays an important role. Though problematic from a technological perspective, a convenient deposition method is the complete embedding of the metallic nanoparticles into the semiconductor layer. The theory has been developed to allow analysis of the aforementioned size trade-off and of the role of the nanoparticle deposition method on the photodiode surface.

Energy transfer through the coupling of the subphoton near field (i.e., the near field on a length scale 10−100 times smaller than the photon wavelength) with the surface plasmon dipoles is very efficient. This high efficiency results in high damping of the plasmons, much higher than the radiative damping due to Lorentz friction and the damping due to electron scattering [23], and elucidates the very strong plasmonic PV effect that is observed experimentally. The prospects for large-scale utilization of this effect in industry and commercial photovoltaic devices depend on the practical deposition methods for nanoparticles on cell surfaces, which usually reduce the net effect as too high a density of metallic particles results in inconvenient interference reflection effects of the metallic nanocover. Nevertheless, at low surface concentrations of the metallic nanoparticles, the theoretically determined resonance curves agree very well with the experimental results [30, 31, 33]. Another experiment elucidated by the theory concerns a two-layer structure of Si–ZnO nanopillars, consisting of a thick layer of p-Si covered with n-ZnO vertical nano-rods with diameters ranging from 200 to 300 nm and heights of approximately 1000 nm [30]. When the top of the structure was covered with silver nanoparticles (with radii of 5, 20, or 50 nm), the photoresponse doubles. This increase is caused in part by ZnO subgap transitions but also by the Si substrate; this is revealed by the characteristic size dependence. This proves that the range of the

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plasmonic effect is at least 1 micrometre, which makes the effect convenient for thin-layer solar cell technology [34–36]. Multi-crystalline Si solar cells sparsely covered with nanoparticles have recently shown very good agreement with the predictions of the theory; the gains in efficiency have reached 5.6% for Au nanoparticles and 4.8% for Ag nanoparticles, whereas, for CIGS (copper indium gallium diselenide) cells, gains of 1.2% (Au) and 1.4% (Ag) have been achieved [31]. Many other, even greater, experimental results have been reported. However, as mentioned, an excessive concentration of metallic covering diminishes the efficiency of solar cells (owing to screening and reflection effects).

The successful theoretical RPA description of plasmons in a single metallic nanoparticle and the recognition of their radiative properties allows for the development of the RPA model for interacting systems (arrays) of metallic nanoparticles, in particular for metallic nano-chains that could serve as low-loss plasmon–polariton wave guides for the desired miniaturization of optoelectronics. Plasmon–polaritons are collective wave-type modes of surface plasmons hybridized with an electromagnetic wave propagating, with almost lossless kinetics, along a periodic chain of metallic nanoparticles. They are analogous to the surface mode of plasmon propagation along a metal–insulator interface, also called a plasmon–polariton [1, 5].

The change in the configuration of the electromagnetic field near the metal–insulator interface around a metallic wire is utilized in high-frequency microwave techniques (e.g., in single-wire Goubau transmission lines [37]). This effect raises an interesting issue for similar propagation along discrete metallic nano-chains [38–43] – experiments confirm the lossless propagation of dipole collective wave-type oscillations in the range of several micrometres [39, 40] with group velocity at least 10 times lower than c (the velocity of light). The latter property allows for a reduction in the diffraction constraints [38] that severely limit the miniaturization of the opto-nanoelectronics, where the wavelengths of photons with energies typical for the nanoelectronics scale (meV) greatly exceed the dimensions of the nanoscale electronic elements (because of the high value of c), precluding miniaturization. The transformation of the electromagnetic signal into a plasmon–polariton, which has the same frequency but a 10 times (at least) shorter wavelength, allows the avoidance of diffraction limits. This is promising for future nanoscale plasmon optoelectronics [5, 38, 42].

An analysis has been developed of the plasmon–polariton kinetics inhmkujkj metallic nano-chains using a far-reaching analytical formulation of the RPA theory [44–46] (which has made significant progress in comparison with numerical-only studies [41, 43]). This analytical formulation allows the precise identification of various factors that were previously resistant to insight within complex numerical approaches [42, 43]. These factors are related to detailed identification of how the damping and the group velocity of plasmon–polaritons depend on the material and geometry parameters.

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In particular, it has been demonstrated that the accurate inclusion of all terms in the dipole interaction in the near-, medium-, and far-field zones, together with retardation effects (frequently neglected in the literature), leads to ideal compensation of the Lorentz friction in each nanosphere in a chain by the radiation energy income from the remaining nanoparticles in the chain [46]: thus the propagation of plasmon–polaritons in the chain is radiatively lossless. Taking into account that the Lorentz friction in a large metallic nanosphere, with radius > 12 nm, for Au in vacuum, greatly exceeds the electron scattering energy losses (i.e., the irreversible dissipation of plasmon energy into Joule heating due to scattering from electrons, phonons, admixtures, defects, and boundaries), a metallic nano-chain behaves as an almost lossless ideal wave guide for plasmon–polaritons [46]; this agrees with experimental observations [39, 38] and indicates possible applications in sub-diffraction plasmon-optoelectronics due to the low group velocity (and wavelength) of plasmon–polaritons.

The RPA model developed for plasmon–polaritons [46] shows that this ideal compensation of the Lorentz friction occurs only inside the light cone (on which the plasmon–polariton phase velocity equals the velocity of light); outside the light cone the damping of plasmon–polaritons is strengthened to values above the Lorentz friction scale (this damping outside the light cone increases steadily with increasing plasmon–polariton wave number for longitudinal plasmon–polariton polarization, when the dipoles oscillate along the chain direction, and increases stepwise for transverse polarization [47, 45]).

On the light cone (in one dimension there are only two points in the Brillouin zone for a periodic chain – the light cone here is a triangle as a function of the chain separation), a logarithmic singularity of the dynamics equation occurs [45]. This singularity is caused by constructive interference of the radiation from the nanospheres in the chain in the far-field zone and occurs only for transverse polarizations of the plasmon–polaritons; it causes a similar divergence at all orders in the perturbation series for the dispersion [45]. The logarithmic perturbative divergence in the dispersion of the plasmon–polaritons in turn causes a hyperbolic singularity in the group velocity for transversely polarized plasmon–polaritons, which is observed in many numerical simulations presented in the literature (in a numerical solution of the dynamics, a certain kind of perturbative solution is linked with an unavoidable truncation of the exact infinite Green function series, which produces a numerical artefact that has been erroneously interpreted as superluminal propagation).

The aforementioned error has been explained in detail and is not present in an exact solution of the dynamic equation for plasmon–polaritons obtained using a special nonperturbative method (i.e., by separate solution of the nonlinear problem at approximately 20,000 points of the Brillouin zone by a Newton-type

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