Resonant interaction of optical pulses with plasmonic oscillations in metal nanoparticles

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We derive envelope equations which generate the Maxwell-Lorentz model and describe the interaction of optical pulses with plasmonic oscillations in metal nanoparticle composites. A family of solitary wave solutions is found which is analogous to self-induced transparency in Maxwell-Bloch. The evolution of incident optical pulses is studied numerically as are the collision dynamics of the solitary waves. These simulations reveal that the collision dynamics vary from near perfectly elastic to highly radiative depending on the relative phase of the initial pulses. © 2022 Optical Society of America

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Quantum effects in metal nanoparticles driven by a resonant optical field play an important role in inducing a strong nonlinear response, as was recently shown.\textsuperscript{1,2} In this Letter we consider the nonlinear resonant interaction of ultrashort optical pulses with metal nanoparticles distributed uniformly in a host medium. We restrict to the case of composite materials for which the resonance frequencies of the host medium are well separated from those of the nanoparticles. Examples include silver or gold spherical or spheroidal nanoparticles embedded in SiO\textsubscript{2}. In these cases, the plasmonic resonance frequencies are in the visible part of the spectrum while the resonance of the host is in the ultraviolet.

Light interaction with metal nanoparticles can be described by a system consisting of Maxwell’s equations for the electric field, and an oscillator equation describing the displacement of conduction electrons in the metal nanoparticles from equilibrium (plasmonic oscillations). The nanoparticles are much smaller than the optical carrier wavelength $\lambda_0$. This allows light scattering and spatial effects in the nanoparticles to be neglected. As shown by
Rautian\textsuperscript{1} and Drachev, et al.,\textsuperscript{2} who further developed the earlier work by Hache, et al.,\textsuperscript{3} the response of the conduction electrons in the metal nanoparticles to an external electric field induces a leading-order cubic nonlinearity. The interaction of the electric field with plasmonic oscillations in nanoparticles with resonance frequency $\omega_r$ in the presence of this cubic nonlinearity can be described by the forced Duffing equation

$$\ddot{Q} + \omega_r^2 \dot{Q} + \kappa \dot{Q}^3 = (e/m) \tilde{E}. \quad (1)$$

In this expression $\dot{Q}$ represents plasmon displacement from equilibrium, $T$ is time, $\kappa$ is the coefficient of nonlinearity, $e$ and $m$ are the electron charge and rest mass, respectively, and $\tilde{E}$ is the electric field. The tilde is used to denote rapidly-varying quantities. The nonlinear coefficient $\kappa$ can be estimated by comparing the off-resonance nonlinear response in Eq. (1) with the Drude nonlinearity for (non-resonant) conduction electrons in metal nanoparticles. That susceptibility is characterized by\textsuperscript{1} $\chi^{(3)} \simeq Ne^4a^2/(m\hbar^2\omega_0^4)$). Here $a$ and $N$ are the radius of the nanoparticle and the conduction electron density of the metal, respectively, and $\omega_0$ is the optical carrier frequency. This results in the estimate $\kappa \simeq (ma\omega_0^2/\hbar)^2$.

We are interested in pulse dynamics which vary on a much slower scale than the plasmonic, host atom, and carrier wave oscillations, and can be described using a slowly-varying envelope approximation. In this approximation, Eq. (1) becomes

$$i \dot{Q} + (\omega_r - \omega_0) Q + (3\kappa/2\omega_0)|Q|^2Q = -(e/2m\omega_0)\mathcal{E}, \quad (2)$$

where the slowly-varying envelopes of the electric field and plasmonic oscillations are represented by $\mathcal{E}$ and $Q$ respectively. Maxwell’s equation couples to the material polarization
induced by the plasmonic oscillations. The equation for the electric field envelope is

\[ i \left( E_Z + \frac{1}{v_g} E_T \right) = -\frac{2\pi \omega_0 N_pe}{cn_0} \langle Q \rangle - \frac{2\pi \omega_0 N_a |d|^2}{cn_0 \hbar \Delta_{\omega}} E - \frac{2\pi i \omega_0 N_a |d|^2}{cn_0 \hbar \Delta_{\omega}^2} E_T, \]  

(3)

where \( Z \) is the propagation coordinate, \( v_g \) is group velocity, \( c \) is the speed of light, \( n_0 \) is the refractive index evaluated at the carrier frequency \( \omega_0 \), \( N_p \) is the product of the conduction electron density \( N \) and the metal filling factor \( p \) (the fraction of the composite occupied by metal). \( N_a \) is the concentration of host atoms, \( d \) is the projection of the dipole matrix element in the direction of the electric field polarization, and \( \Delta_{\omega} = \omega_a - \omega_0 \) is detuning from the resonance frequency of host atoms. The last two terms in Eq. (3) represent corrections to the refractive index and group index due to the off-resonance interaction with the host medium, which, for illustration, is considered as an ensemble of two-level atoms. This equation is derived from the Maxwell-Bloch equations in the non-resonant case by considering \( \Delta_{\omega} \) as a large parameter and applying the adiabatic following approximation. Additional resonances would produce similar terms. We consider the case where optical pulse intensity and duration as well as composite material parameters are such that the characteristic length of resonant light interaction with plasmonic oscillations is much smaller than the characteristic lengths for both group velocity dispersion and nonlinearity induced by the host medium. Therefore the terms representing these effects are omitted from Eq. (3).

In a composite material, the sizes and shapes of metal nanoparticles vary due to limited fabrication tolerances. It is known that the plasmon resonance in spherical metal nanoparticles depends weakly on size in the range between 10 and 50nm, so that variations in size are not important. However, variations in the shape and orientation of the nanoparticles can significantly change plasmonic resonance frequencies. This results in a broadening of the
resonance line of the bulk composite. The angle brackets \( \langle Q(t, z, \omega) \rangle = \int_{-\infty}^{\infty} Q(t, z, \omega) g(\omega) \, d\omega \) denote averaging over the distribution \( g(\omega) \) of the resonance frequencies (line shape). Defining

\[
E = -E \frac{2m\omega_0^3}{e} \sqrt{\frac{2}{3\xi}} \exp(ik_s Z), \quad Q = Q\omega_0 \sqrt{\frac{2}{3\xi}} \exp(ik_s Z),
\]

where \( k_s = 2\pi\omega_0N_a|d|^2/cn_0\hbar \Delta_a \), and introducing the copropagating coordinate system \( z = (\omega_p^2/4cn_0\omega_0)Z, \quad t = \omega_0(T - Z/u) \), \( (ue\) here is shifted group velocity defined as \( u^{-1} = v_g^{-1} + (2\pi\omega_0N_a|d|^2/cn_0\hbar \Delta_a^2), \omega_p^2 = 4\pi N_p e^2/m, \omega = (\omega_q - \omega_0)/\omega_0 \), Eqs. (2) and (3) can be reduced to the simpler form

\[
iE_z = \langle Q \rangle, \quad iQ_t + \omega Q + |Q|^2 Q = E.
\]

These equations represent a generalization of the classical Maxwell-Lorentz model. In the case of identical nanoparticles, the averaging in (5) can be reduced to a single dimensionless frequency \( \bar{\omega} \) [i.e. detuning frequency distribution \( g(\omega) = \delta(\omega - \bar{\omega}) \)]. Under this condition the system has solitary wave solutions:

\[
E(t, z) = \frac{v^{3/4} \exp[i\varphi + i\Omega t - iK\xi - i\chi(\xi)]}{\xi_0[\cosh(\xi/\xi_0) + K]^{1/2}}, \quad Q(t, z) = E(t, z) \frac{\exp[-2i\chi(\xi)]}{\sqrt{v}},
\]

where \( \xi = [z - v(t - \tau)]/\sqrt{v}, \chi(\xi) = \arctan[\Gamma \tanh(\xi/2\xi_0)], \xi_0 = 1/2(1 - K^2)^{1/2}, \Gamma = [(1 - K)/(1 + K)]^{1/2}, \) and \( K = (\bar{\omega} - \Omega)/2\sqrt{v} \). These solutions are parameterized by velocity \( v \), frequency \( \Omega \), phase shift \( \varphi \), and position \( \tau \). The velocity \( v \) is the amount by which the wave is slowed from the copropagating frame velocity \( u \). Thus in the laboratory frame, the actual pulse velocity is \( u - v \). The quantity \( \xi_0 \) must be real, hence \( 1 - K^2 > 0 \). Thus the condition for existence of these solutions is \( |\bar{\omega} - \Omega| < 2\sqrt{v} \). This choice of parameters provides relatively simple mathematical expressions for the solitary waves. In practice it is easier to
both control and measure peak amplitude, $A = 2v^{3/4}(1 - K)^{1/2}$, than the pulse velocity, therefore $A$, $\Omega$, $\varphi$, $\tau$ form a more suitable set of parameters. Given the pulse amplitude $A$, the corresponding velocity parameter depends on the value of the quantity $\bar{\omega} - \Omega$. If $\bar{\omega} = \Omega$, then $v = (A/2)^{4/3}$ trivially. For the case when $\bar{\omega} \neq \Omega$, write the amplitude as $A = 2v^{3/4}(1 - |\bar{\omega} - \Omega|/2\sqrt{v})^{1/2}$, where the parameter $\sigma = \text{sgn}(\bar{\omega} - \Omega)$. Then defining $\bar{v} = (2\sqrt{v}/|\bar{\omega} - \Omega| - \sigma)^{1/2}$ and $\bar{A} = \sqrt{27/2}|\bar{\omega} - \Omega|^{-3/2}A$ leads to an expression for the rescaled velocity $\bar{v} = (y^{-1/3} - \sigma y^{1/3})/\sqrt{3}$, where $y = \sigma[(\bar{A}^2 + \sigma)^{1/2} - \bar{A}]^{1/2}$. In this calculation, the appropriate branches have been chosen so that the expressions are consistent with reality and positivity conditions on the parameters.

In optics it has become standard practice to refer to certain solutions of nonintegrable systems as solitons. These solutions are characterized as solitary waves which are robust to external perturbations including collisions with other solitary waves. In addition, arbitrary initial data for these “soliton” supporting systems tends to evolve into a sum of solitary waves and continuous radiation. The remainder of this Letter details our numerical investigation of these properties, in which Eqs. (5) are integrated in the case of delta-distributed resonance frequencies and zero detuning.

Numerical simulations of the evolution of Gaussian initial data are presented in Figs. 1a and b. In Fig. 1a the initial condition $E(t, 0) = \exp(-t^2/2)/2$ simply evolves into continuous radiation, while in Fig. 1b the initial condition $E(t, 0) = 2\exp(-t^2/2)$ emits some radiation but also achieves energy confinement and persists as a soliton. This behavior is similar to the self-induced transparency exhibited by the Maxwell-Bloch equations which describe optical pulse interaction with resonant two-level media. As the amplitude of the initial pulse is increased, the pulse splits into two [illustrated in Fig. 2a for the initial condition $E(t, 0) = \exp(-t^2/2)/2$].
or more solitons and emits continuous radiation. The inset shows a comparison between the numerics and the analytic form of the solitary waves of Eq. (6). The velocity and frequency of the solitary waves are obtained from measurements of their amplitudes and half widths in our simulation. The agreement of the analytic forms with the simulation results indicates that the system self-selects the solitary waves presented in Eq. (6). Fig. 2b shows the amplitude(s) of these solitons as a function of input pulse amplitude. As the input pulse amplitude increases, the output soliton amplitude also increases until a bifurcation occurs and a new soliton emerges. Increasing the input pulse amplitude further results in the production of more solitons, along with continuous radiation.

Two simulations illustrating collision dynamics are presented in Figs. 3a and 3b, where the sum of two well-separated solitary waves is used as the initial condition. Fig. 3a illustrates an in-phase collision, in which the relative phase \( \Delta \varphi = \varphi_1 - \varphi_2 = 0 \), where the subscripts identify the soliton. The other initial soliton parameters are \( v_1 = 1, \Omega_1 = 0, \tau_1 = -10 \), \( v_2 = 2, \Omega_2 = 0, \) and \( \tau_2 = 0 \). In Fig. 3b an out-of-phase \( \Delta \varphi = \pi \) collision is illustrated. The same parameters are used except for a shift in the relative phase. This results in a much faster collision. In both simulations the solitary waves persist after the interaction, although their characteristic parameters undergo shifts and radiation is emitted during the collision. A numerical study indicates that the collisions are quasielastic for values in the approximate interval \( \Delta \varphi \in (\pi, 2\pi) \). For some \( \Delta \varphi \) values away from this interval, simulations show that one of the solitons is completely destroyed while the other persists. A detailed analysis of the dependence on initial parameters will be presented elsewhere.

The soliton phenomena described above occurs at light intensities such that the dimensionless field amplitude \( E \) is at least of order one. The intensity at which \( E \) is order one
estimated as $I \simeq (c/x)(m\omega_0^3/e)^2 \simeq c(h\omega_0/ea)^2$. For the particle radius $a = 20\text{nm}$ and the carrier wavelength $\lambda_0 = 500\text{nm}$, this results in light intensity of $I \sim 10\text{GW/cm}^2$ which can be easily obtained with ultrashort laser pulses. The optical pulse durations for which this model is valid are limited by the condition $\Delta \omega \ll \omega_0$, (the spectral width of the pulse must be much smaller than the carrier frequency) required by the slowly varying envelope approximation. The pulse duration should also be much shorter than the characteristic plasmonic oscillation damping time, which is determined by the time required for electron thermalization in the metal nanoparticles ($\sim 400\text{fs}^{7,8}$). The envelope approximation is appropriate for pulses with width $\tau \gtrsim 20\text{fs}$.

In summary, a family of solitary wave solutions is derived in the envelope approximation for the Maxwell wave and Duffing oscillator equations, showing that energy confinement is possible for resonant optical pulse interaction with plasmonic oscillations in metal nanoparticles. The existence condition for these solutions is presented. Numerical simulations show that stable solitary waves evolve from arbitrarily-shaped initial pulses with sufficient amplitudes and exhibit behavior analogous to self-induced transparency in Maxwell-Bloch. Simulations also reveal that the collision dynamics are highly dependent on initial soliton parameters, behaving quasielastically in some regimes but having radically different behavior in others. The authors are grateful to V. P. Drachev for helpful discussions. In addition, we would like to acknowledge funding under Arizona Proposition 301, LANL, and NSF.

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2. Left: Evolution of electric field amplitude with initial condition \(5\exp(-t^2/2)\). The inset shows a comparison of the numerics (dashed line) with the analytic form of the solitary wave solutions (solid line). Right: output solitary wave amplitude(s) as a function of Gaussian input pulse amplitude \(A_0\), where the initial condition is given by \(A_0\exp(-t^2/2)\).

3. Electric field amplitude showing collision dynamics of solitons for different values of relative phase. Left: \(\Delta\varphi = 0\); right: \(\Delta\varphi = \pi\).
Fig. 1. Evolution of electric field amplitude with initial conditions $\exp(-t^2/2)/2$ (left) and $2\exp(-t^2/2)$ (right).
Fig. 2. Left: Evolution of electric field amplitude with initial condition $5 \exp(-t^2/2)$. The inset shows a comparison of the numerics (dashed line) with the analytic form of the solitary wave solutions (solid line). Right: output solitary wave amplitude(s) as a function of Gaussian input pulse amplitude $A_0$, where the initial condition is given by $A_0 \exp(-t^2/2)$. 
Fig. 3. Electric field amplitude showing collision dynamics of solitons for different values of relative phase. Left: $\Delta \varphi = 0$; right: $\Delta \varphi = \pi$. 