Plasmon electron energy-gain spectroscopy

A Asenjo-García1,2 and F J García de Abajo1,3,4

1 ICFO—Institut de Ciencies Fotoniques, Mediterranean Technology Park, 08860 Castelldefels (Barcelona) Spain
2 IQFR—CSIC, Serrano 119, 28006 Madrid, Spain
3 ICREA—Institució Catalana de Recerca i Estudis Avançats, Barcelona, Spain
E-mail: javier.garciaadeabajo@icfo.es

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Abstract. We explore multiple energy losses and gains undergone by swift electrons interacting with resonant evanescent light fields. We predict remarkably high gain probabilities in the range of a percentage when the electrons are passing near a resonant plasmonic structure under continuous-wave illumination conditions with moderate laser intensities \( \sim 10^8 \text{ W m}^{-2} \). Additionally, we observe fine structure in the dependence of the gain and loss probabilities on the light wavelength, which reveals a complex interplay between multiple plasmon–electron interactions. These results constitute a solid basis for the development of a new spectroscopy technique based upon the analysis of energy gains, capable of rendering information on the optical properties of the sampled resonant nanostructures. We illustrate this concept for plasmon-supporting noble metal nanoparticles.

4 Author to whom any correspondence should be addressed.

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1. Introduction

Since Feynman pointed out the suitability of electron microscopes to fulfill the need for better imaging down to the nanoscale [1], electron microscopy has undergone a tremendous 100-fold improvement in spatial resolution down to $\sim 1\,\text{Å}$ [2], just a factor of $\sim 40$ larger than the de Broglie wavelength at typical electron-beam energies $\sim 200\,\text{keV}$. The analysis of energy exchanges between the electrons and the sample adds further information on the chemical composition and electronic structure of the specimen with similar spatial resolution. In particular, electron energy-loss spectroscopy (EELS) [3, 4] has proved to be extremely useful to resolve chemical species by sampling differences in the electronic environment [5].

The spatial resolution of electron microscopes is well suited to study plasmons, the collective excitations of conduction electrons in metals [6]. Actually, plasmons were first revealed as energy loss features in the spectra of electrons reflected from metal surfaces [7]. Since then, electron beams have become an important tool to yield information on plasmons [8, 9]. More recently, EELS has been extensively used to map plasmons in metallic nanostructures [10, 11], and it is thus helping to develop new applications of these collective modes to biomedicine [12], photovoltaics [13] and quantum optics [14]. For example, plasmons have been recently mapped in silver nanowires with an impressive energy resolution $<0.1\,\text{eV}$ relying on a new generation of transmission electron microscopes (TEMs) that are equipped with electron monochromators [15], although they involve a compromise between signal intensity and energy resolution. However, the latter is still limited by the width of the zero-loss peak (i.e. the peak of electrons that have not undergone inelastic scattering). An alternative method that combines the spatial resolution of electron beams and the energy resolution of optical probes has been suggested based on the analysis of energy gains experienced by the electrons [16, 17]. In this so-called electron energy-gain spectroscopy (EEGS), electrons that have absorbed energy from an external light source appear on the negative side of the energy-loss spectrum, and the area under an energy-gain peak reflects the response of the sample at the illuminating frequency, thus increasing the energy resolution, which is no longer limited by the width of the electron zero-loss peak. In this context, the observation of multiple energy gains and losses in pulsed electrons in coincidence with pulsed laser irradiation constitutes an important step toward the experimental realization of EEGS [18, 19]. The multiple energy
transfers between the electrons and the samples are well understood [20–22], and in particular, the electrons have been shown to undergo a complex evolution involving multiple energy exchanges on the sub-femtosecond time scale [20]. The interesting possibility of interfering losses stimulated by external illumination and inelastic losses has been recently discussed [23].

In this paper, we extend our previous results and show that these multiphoton gains and losses can be useful not only for imaging but also for performing time- and space-resolved spectroscopy, particularly in plasmonic structures. This can be achieved by varying the external light frequency, and due to the field enhancement produced by the surface plasmons, it can be performed at low light intensities. Additionally, we develop a simple model to describe EELS, EEGS and cathodoluminescence (CL) in a unified quantum treatment that provides further intuition into the physical mechanisms underlying these processes.

2. Outline of the theory

In a TEM, the electrons can be described as a coherent superposition of plane waves [11]. The degrees of freedom associated with momentum components perpendicular to the beam direction \( \hat{z} \) can be neglected for a swift electron, which can then be accurately described as a plane wave moving along \( \hat{z} \). We intend to obtain the probability of gain and loss processes by solving the quantum-mechanical evolution of the electron wavefunction in the presence of a semi-classical coupling to the external laser field.

Following the method derived in a previous paper [20], the unperturbed electron wavefunction can be written as \( \psi_0(z, t) = \psi^G_k(z, t) \), where
\[
\psi^G_k(z, t) = N_k \exp \left[ i k z - i \epsilon_k t - \frac{(t - z/v_k)^2}{\Delta^2} \right]
\]
is a Gaussian electron pulse of temporal duration \( \sim 2\Delta_t \). Here, \( |N_k|^2 = \left( \frac{\pi}{2} \right)^{1/2} (\Delta_t v_k)^{-1} \) is a normalization constant, \( \hbar \epsilon_k = c(\hbar^2 k^2 + m^2 e^2 c^2)^{1/2} \) is the relativistic electron energy and \( v_k = \partial \epsilon_k / \partial k \) is the pulse group velocity (\( v \approx 0.7c \) for the 200 keV electrons here considered).

We describe multiphoton energy gains and losses undergone by the electron using a semiclassical model in which the quantum mechanical evolution of the electron is solved including its interaction with the evanescent light field. The electron–photon coupling Hamiltonian consists of two terms, one proportional to the absorption and the other to the emission of one photon:
\[
H_1(z, t) = -\frac{e\hbar}{m_e \omega} \left[ E_z(z, t) - E^*_z(z, t) \right] \frac{\partial}{\partial z},
\]
where \( \omega \) is the central light frequency and the electric field parallel to the electron beam is described by a temporal Gaussian wave-packet
\[
E_z(z, t) = E_z(z) \exp \left[ -i \omega t - \frac{(t + \tau)^2}{\Delta^2_p} \right],
\]
where \( \sim 2\Delta_p \) is the light pulse duration and \( \tau \) is the delay between the arrivals of the photon and the electron pulses at the position of the sample.
The self-consistent electron wavefunction is readily given by the Lippman–Schwinger equation [24]

$$\psi(z, t) = \psi_0(z, t) + \int dz' dt' G(z - z', t - t') H_I(z', t') \psi(z', t'),$$

where

$$G(z - z', t - t') \simeq -\frac{i}{2\pi\hbar} \int dk \exp[i k |z - z'| - i \epsilon_k (t - t')]$$

is the one-dimensional electron Green function corresponding to propagation along \( \hat{z} \). We solve this equation by writing the wavefunction as a sum over different perturbation orders [20]

$$\psi(z, t) = \sum_{N=0}^{\infty} (G \cdot H_I)^N \psi_0 \equiv \sum_{N=0}^{\infty} \psi_N(z, t),$$

where the dot expresses the convolution operator. In equation (1), \( N \) represents the order of scattering, which is also the number of emission and absorption events experienced by the electron. At an order of scattering \( N \), we find electrons that have gained or lost \( |L| \leq N \) photons.

Equation (1) can be solved by recursion. From the resulting self-consistent wavefunction, we can readily calculate the probability that the electron ends up with momentum around \( k_L = k_0 + L \omega/v \), so that it has emitted \( (L < 0) \) or gained \( (L > 0) \) an amount of energy corresponding to \( |L| \) photons. We find

$$P_L = \sum_{N=-|L|}^{\infty} \sum_{N'=-|L|}^{\infty} C_L^N (C_L^{N'})^* \frac{\exp \left[ -\frac{(N+N')(\tau/\Delta_p)^2}{1+[(N+N')/2](\Delta_e/\Delta_p)^2} \right]}{\sqrt{1 + \frac{(N+N')^2(\Delta_e/\Delta_p)^2}{2}}}$$

where \( C_L^N \) are constants.

Remarkably, we find that the multiphoton probabilities depend on the pulse durations and delay only through the ratios \( \tau/\Delta_p \) and \( \Delta_e/\Delta_p \). Clearly, a delay in the arrival of photon and electron pulses is translated into a decrease in the effective interaction strength and therefore, it acts as an eraser of the multiphoton probabilities.

3. Numerical results and discussion

We focus on the light-frequency dependence of the multiphoton exchange probabilities and discuss the interaction with a plasmonic sample, as we intend to analyze the suitability of EEGS to yield information on its optical response. In particular, we consider nanoshells consisting of a silica core \((\epsilon = 2)\) coated with either 5 nm of gold or 4 nm of silver. The full diameter of the particle is 100 nm in all cases. The choice of metal thickness is made to feature a spectrally isolated dipole plasmon around 700–800 nm light wavelength. Upon illumination with the laser external field \( E_{\text{ext}} \), we approximate the induced electric field in that spectral region by its dominant dipolar component \( E = [k^2 p + (p \cdot \nabla) \nabla] \exp(ikr)/r \), where \( k = \omega/c \) is the light wavevector and \( p = \alpha E_{\text{ext}} \) is the induced dipole moment. Here, we incorporate retardation effects in the polarizability \( \alpha \) by expressing it in terms of the dipolar Mie coefficient as \( \alpha = 3t_f^L/2k^3 \), where \( t_f^L \) finds a closed-form analytical expression for spherical shells [25]. We use a measured frequency-dependent dielectric function for silver and
gold [26] to represent the response of the metallic coating of the nanoshells. Figure 1 depicts a sketch of the system, for which we assume co-parallel electron and laser beams. Under this configuration, the electron is only sensitive to the induced field, as the incident field is normal to the electron velocity and losses/gains are mediated by the electric field along the beam direction. Similar results are obtained for other light incidence directions and polarization conditions, and although the particle-mediated light–electron coupling strength depends on these parameters, our qualitative conclusions remain unchanged. The coupling strength can be intuitively understood by examining the $z$ component of the electric field produced by the induced dipole. The extinction cross-section $\sigma^{\text{ext}}$ of the nanoshells (figure 1(b), solid curves, obtained from $\sigma^{\text{ext}} = 4\pi k \text{Im}(\alpha)$) shows a prominent near-infrared plasmon that is isolated from other modes of the system (cf solid and dashed curves, with the latter obtained with inclusion of all multipoles [25]; notice that both calculations are in excellent agreement, except for the $\sim 580$ nm quadrupolar plasmon of silver, which is obviously absent from the dipolar results). It is important to realize that only the component of the electric field along $z$ contributes to the photon–electron coupling (i.e. only the induced field contributes). Figure 1(c) shows the intensity of the induced field for illumination at the peak plasmon frequency, which exhibits a clear enhancement with respect to the incident field. Silver nanoshells have larger on-resonance extinction and induced field, which translate into higher multiphoton probabilities (see below).

Interestingly, the occupation probability of the electron states changes dramatically by varying the frequency of the incoming light. When the frequency approaches the dipole plasmon resonance of the particle, the near-field intensity is enhanced, and therefore, the interaction with the electron is stronger. We show in figure 2(a) that the electron is mostly in the elastic or zero-loss channel for low intensities. When the intensity increases, this channel is increasingly depleted and shows a dip at the plasmon frequency. This depletion is accompanied by a complex dynamics that results in a sizable population of electron inelastic channels, as shown in

Figure 1. (a) Scheme of the system under consideration: a 200 keV electron passes 10 nm away from the surface of a 100 nm nanoshell consisting of a silica core coated with a layer of either 5 nm gold or 4 nm silver. (b) Optical extinction cross-section of the nanoshells. (c) Induced electric field intensity along the $\hat{z}$ direction as a function of distance along the electron trajectory upon irradiation with light of wavelength $\lambda = 762$ nm for gold and 745 nm for silver. Solid curves: contribution of the dipole plasmon. Broken curves: full multipolar calculation (nearly indistinguishable from the dipolar contribution).
Figure 2. Occupation probability of different multiphoton exchange channels as a function of incoming light wavelength for the silver nanoshell considered in figure 1. (a) Depletion of the elastic channel for different intensities under continuous (dashed curves) and pulsed (solid curves) light irradiation. (b) Probabilities of the $L=0$–2 channels for a laser intensity of $10^{11}$ W m$^{-2}$. The electron energy is 200 keV and its impact parameter relative to the particle surface is 10 nm. The electron and laser pulse durations in the solid curves of both panels are $\Delta_e = \Delta_p = 200$ fs. The gray dashed lines show the resonance plasmon wavelength.

We must stress that the intensity of the external field needed to produce these effects is orders of magnitude lower than that reported in previous works [18, 20], thanks to the mediation of the particle plasmons, which act as optical amplifiers. In particular, figure 2(a) shows small depletion of the zero-loss channel even for peak laser intensities as low as $10^8$ W m$^{-2}$.

Incidentally, there is a small shift between near and far field resonance frequencies, as previously reported for light scattering from nanoparticles [27, 28]. This is clear from figure 2, where the gray dotted line, representing the plasmon frequency as obtained from the extinction cross-section (far-field), is blue-shifted a few nanometers with respect to the maximum depletion of the elastic electron component. This is a manifestation of the fact that the coupling between photons and electrons is mediated by the near field, which is dominated by evanescent components (i.e. the localized plasmons die away from the particle, and they are mainly consisting of non-propagating fields involving wavevectors outside the light cone, where coupling to the electromagnetic field of the electron is possible).

The occupation probability depends on the ratio between the photon and the electron pulse durations (see figure 3). In the limit of continuous-wave (cw) illumination (i.e. when the electron pulse is much shorter than the light pulse), the elastic signal is depleted at low intensities compared with the depletion for pulsed illumination, which can be intuitively understood from the stronger interaction associated with continuous plasmon excitation (cf e.g. the higher depopulation of the elastic channel for continuous and pulse illumination in figure 3).
Figure 3. Probability of multiphoton emission ($L < 0$) and absorption ($L > 0$) as a function of both incoming light wavelength and net number of exchanged photons $L$. Each column corresponds to a different level of external light intensity (see upper labels). We present results for (a) a gold nanoshell with $\Delta_e = \Delta_p = 200 \text{ fs}$, (b and c) a silver nanoshell with (b) $\Delta_e = \Delta_p = 200 \text{ fs}$ and (c) cw illumination. The electron energy is $200 \text{ keV}$ and its impact parameter relative to the particle surface is $10 \text{ nm}$. 

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Compared with gold, the silver nanoshell produces higher depletion of the elastic channel at lower intensities, compatible with cw illumination without damaging the samples. Multiphoton events can be observed for intensities as low as $\sim 10^9$ W m$^{-2}$. Although we have focused on nanoshells because of the tutorial character of the dipolar model with which they can be modeled, similar conclusions can be also drawn for metallic nanorods, the plasmons of which can be tuned by changing their aspect ratio. In particular, the lowest-order dipolar mode of a rod is expected to also produce significant field enhancement that can yield even stronger EEGS signals under cw illumination conditions.

4. Unified analytical quantum model for electron energy-loss spectroscopy (EELS), electron energy-gain spectroscopy (EEGS) and cathodoluminescence (CL)

In order to place the above EEGS probabilities in perspective, it is useful to compare them with those of more traditional electron spectroscopies –EELS and CL. We formulate a simple quantum model in this section that unifies the description of all these three spectroscopies and provides further insight into the mechanisms that underlie the exchanges between photons, plasmons and fast electrons. For simplicity, we consider a sample consisting of a plasmon-supporting small particle.

We describe photons and plasmons in terms of their annihilation (creation) operators $a_i$ and $b_l$ ($a_i^\dagger$ and $b_l^\dagger$), where $i$ and $l$ label different modes of frequencies $\omega_i$ and $\tilde{\omega}_{pl}$, respectively. We consider degenerate plasmons and include their inelastic decay rate $\Gamma_{pl}$ as an imaginary part in $\tilde{\omega}_{pl} = \omega_{pl} - i\frac{\Gamma_{pl}}{2}$. Likewise, $c_k$ ($c_k^\dagger$) creates (annihilates) a fast electron of energy $\hbar \epsilon_k$ and momentum $\hbar k \hat{z}$. We neglect the dynamics of the electron along directions perpendicular to $\hat{z}$, which is a safe assumption for typical electron beams with small divergence angles. The Hamiltonian of this system can then be written as

$$H = H_0 + H_{\text{int}},$$

where

$$H_0 = \hbar \sum_k \epsilon_k c_k^\dagger c_k + \hbar \sum_i \omega_i a_i^\dagger a_i + \hbar \sum_l \tilde{\omega}_{pl} b_l^\dagger b_l,$$

is the non-interacting part, whereas the interaction Hamiltonian consists of just two components, $H_{\text{int}} = H_{\text{ph–pl}} + H_{\text{e–pl}}$, because electrons and photons do not directly couple in free space. The photon–plasmon coupling Hamiltonian

$$H_{\text{ph–pl}} = -\mathbf{p} \cdot \mathbf{E}$$

is expressed in terms of the particle dipole operator

$$\mathbf{p} = \sum_l \mathbf{d}_l (b_l^\dagger + b_l) = \sum_l d_l \hat{x}_l (b_l^\dagger + b_l),$$

and the quantized electromagnetic field

$$\mathbf{E} = \mathbf{E}^+ + \mathbf{E}^- = i \sum_i \sqrt{\frac{2\pi \hbar \omega_i}{V}} \hat{\epsilon}_i (a_i - a_i^\dagger),$$

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where $V$ is the mode quantization volume, $\hat{\epsilon}_i$ is the polarization vector and the particle is assumed to be at $r = 0$. We adopt the rotating wave approximation, which allows us to write

$$H_{\text{ph-pl}} = -i \sum_{i,l} g_{il} (b_{\hat{i}} a_i - b_i a_{\hat{i}}^\dagger)$$  \hspace{1cm} (7)

with real coupling coefficients

$$g_{il} = \sqrt{\frac{2\pi \hbar \omega_i}{V}} d_i (\hat{x}_i \cdot \hat{\epsilon}_i).$$  \hspace{1cm} (8)

The electron–plasmon interaction Hamiltonian is

$$H_{e-pl} = \sum_{k,k',l} (g_{k'kl} c_{k'}^\dagger c_k b_{\hat{l}}^\dagger + g_{kkl}^* c_k^\dagger c_{k'} b_{\hat{l}}),$$  \hspace{1cm} (9)

where $g_{k'kl}$ are complex coupling constants given by (see appendix A)

$$g_{k'kl} = \frac{2e}{\gamma^2 L} d_i [\gamma' |k'-k| K_1 (|k'-k| R_0/\gamma) \hat{R}_0 + i (k' - k) K_0 (|k' - k| R_0/\gamma) \hat{z}].$$  \hspace{1cm} (10)

$\gamma = 1/\sqrt{1 - v^2/c^2}$ is the Lorentz factor, $L$ is the electron quantization length along the beam direction, $K_0$ and $K_1$ are modified Bessel functions and $R_0$ is the impact parameter of the beam relative to the particle (see figure 1(a)). The states of the system consist of the tensorial product of electron, photon and plasmon states. In the initial state, the electron has energy $\epsilon_{k_0}$, the light mode $i$ of the illuminating laser has a population of $N_i \gg 1$ photons, and no plasmons are excited: $|k_0, N_i, 0\rangle = |k_0\rangle \otimes |N_i\rangle \otimes |0\rangle$. For low irradiation intensities, the interactions can be treated as perturbations and we solve the evolution up to second order. In this picture, higher order processes involving multiple plasmon excitation produce stimulated emission effects, which are discussed later in this section. At first order in perturbation theory (see figure 4(a)),

**Figure 4.** (a) Diagrams for all processes involving the creation of one plasmon, up to second order. (b) Electron energy loss spectra for a 200 keV electron passing 10 nm away from a silver nanoshell, for different incoming light wavelengths under cw illumination. The light intensity is $10^8 \text{W m}^{-2}$. 

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two processes are possible: extinction of light by the nanoshell and electron energy loss. At second order, the processes that involve the creation of only one plasmon are CL and EEGS. For the system sketched in figure 1(a), the probability per unit of transferred energy for EELS, EEGS and CL is

$$\Gamma_{\text{EELS}}(\omega) = \frac{4 e^2 \omega^2}{\pi \hbar^2 v^4 \gamma^2} \left[ K_1^2 \left( \frac{\omega R_0}{v \gamma} \right) + \frac{1}{\gamma^2} K_0^2 \left( \frac{\omega R_0}{v \gamma} \right) \right] \text{Im}[\alpha(\omega)], \quad (11)$$

$$\Gamma_{\text{EEGS}}(\omega) = \frac{8\pi e^2 \omega^2}{\hbar^2 v^4 c \gamma^2} I_0 K_1^2 \left( \frac{\omega R_0}{v \gamma} \right) |\alpha(\omega_i)|^2 \delta(\omega - \omega_i), \quad (12)$$

$$\Gamma_{\text{CL}}(\omega) = \frac{8e^2 \omega^5}{3\pi \hbar^2 c^3 v^4 \gamma^2} \left[ K_1^2 \left( \frac{\omega R_0}{v \gamma} \right) + \frac{1}{\gamma^2} K_0^2 \left( \frac{\omega R_0}{v \gamma} \right) \right] |\alpha(\omega)|^2, \quad (13)$$

which agree with previous results obtained from dielectric theory [11, 17]. In the above equations, $\alpha(\omega) = \frac{e^2}{\hbar \omega} \frac{1}{\omega^2 - \omega^2}$ is the particle polarizability (see appendix B.1.1), $\omega_i$ is the incident light frequency and $I_0 = \left( \frac{c}{2\pi} \right) |E_{\text{ext}}|^2$ is the light intensity, which as expected, only appears in the photon-assisted processes (EEGS).

In the above, we discuss rather elementary processes in a diagramatic fashion. This basic academic approach can nonetheless be applied to actual experiments, as we can regard the particle and its plasmons as an intermediate coupler between the incident photons and the electron, so that a factor proportional to the large number of incident photons $N_i$ (i.e., $I_0$) pops up in equation (12). Alternatively, we could have described the laser by a coherent photon state, which excites a coherent plasmon state. In both of these approaches, the inverse process

\[\text{Figure 5.} \quad \text{Electron energy loss (a) and gain (b) spectra for a 200 keV electron passing 10 nm away from a silver nanoshell. The integral of the EELS probability over the dipole plasmon peak yields $P_{\text{EELS}} = 4.5 \times 10^{-3}$, which should be compared with the EEGS probability shown in (b) for different incoming light frequencies under cw illumination. The full solution of equation (2) (solid curves) is in excellent agreement with the integrated analytical expression of equation (12) (broken curves) in (b) (nearly indistinguishable).}\]
of stimulated photon emission into state $i$ (i.e., the electron loses energy $\hbar \omega_i$ and a photon is emitted in this mode), mediated by particle plasmons, has exactly the same probability, but now multiplied by $N_i + 1$ instead of $N_i$. For large $N_i$, the stimulated EELS (SEELS) probability is approximately given by equation (12) (i.e., $N_i + 1 \approx N_i$). Incidentally, EEGS, SEELS and CL are intimately related to the Einstein coefficients for absorption, stimulated emission and spontaneous emission, respectively. For the single plasmon mode under consideration, the absorption and stimulated emission coefficients are identical, and so are the EEGS and EELS matrix elements in the limit of large photon numbers.

Figure 4(b) shows calculated energy loss spectra for a silver nanoshell under the conditions of figure 1(a) based upon equations (11)–(13), taking into account the SEELS contribution just discussed. The $\delta$ function in the latter is slightly broadened for clarity (the actual width of this peak will be essentially limited by both the laser width and the resolution of the energy analyser). Several photon energies around the plasmon peak have been considered, giving rise to substantial contributions comparable to the regular EELS intensity when the light is tuned to the plasmon energy.

Finally, we compare in figure 5 calculated EEGS and EELS spectra for the same silver nanoshell as in figure 4. The probability of exciting one plasmon in EELS is comparable to the probability of gaining/losing one photon in EEGS when the nanoshell is illuminated with intensities as low as $10^8$ W m$^{-2}$, below the damage threshold of the materials involved, thus indicating that this effect is measurable using cw illumination. Incidentally, figure 5(b) shows excellent agreement between the full numerical results of equation (2) and the analytical expression resulting from considering only single-photon absorption (i.e. after integrating the delta function in equation (12)), with only small deviations at high energies originating in nonlinear multiphoton inelastic scattering.

5. Conclusions

In summary, the interaction between swift electrons and intense induced light fields mediated by plasmon-supporting nanostructures provides useful information on the sample, with great potential to combine unprecedented space-, energy- and time-resolutions in a single spectral microscopy technique. Remarkably, we find the plasmonic enhancement of the induced field to lead to large energy-gain (and stimulated losses) probabilities using moderate levels of incident light intensity compatible with cw illumination without damaging the samples. The electron undergoes a complex temporal evolution in its interaction with the particles, which takes place over a time scale in the sub-femtosecond domain, thus opening a window to ultrafast phenomena that could be eventually explored by resorting on laser pulse shaping.

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Appendix A. Electron–plasmon coupling

The electron–plasmon coupling constants are derived by using a model Hamiltonian consisting of a free part

\[ H_0 = \hbar \sum_l \omega_l b_l^\dagger b_l + \hbar \sum_k \epsilon_k |k\rangle \langle k|, \]

where \(|k\rangle\) represents an electron of momentum \(\hbar k \hat{z}\) and energy \(\hbar \epsilon_k\), and an electron–plasmon interaction term

\[ H_{e-pl} = -\mathbf{p} \cdot \mathbf{E}_c, \]

where \(\mathbf{p} = \sum_l d_l (b_l^\dagger + b_l) \hat{x}_l\) is the particle dipole operator and \(\mathbf{E}_c\) is the electron Coulomb field. Given that relativistic electron velocities are typically employed in electron microscopes (e.g. \(v \approx 0.7 c\) for 200 keV electrons), we include retardation corrections in what follows. In the electron rest frame (primed quantities), the Coulomb field reduces to

\[ \mathbf{E}_c'(\mathbf{r}') = e \frac{|\mathbf{r}'|}{r} \]

at the particle position \(\mathbf{r}'\). We now change to the laboratory frame through the customary transformation \(\mathbf{R}' = -\mathbf{R}, z' = -\gamma z, \mathbf{E}_\mathbf{R} = \gamma \mathbf{E}_\mathbf{R}'\) and \(E_z = E_z', \gamma\), which leads to

\[ \mathbf{E}_c = -e \left( \frac{\gamma \nabla - \frac{1}{\gamma} \frac{1}{|\mathbf{R}|}}{\gamma} \right), \]

In Fourier space, the Hamiltonian becomes

\[ H_{e-pl} = -\sum_{k,k',l} d_l (b_l^\dagger + b_l) \hat{x}_l \cdot \langle k' | \mathbf{E}_c | k \rangle |k'\rangle \langle k|, \]

where

\[ \langle k' | \mathbf{E}_c | k \rangle = \int d\mathbf{r} d\mathbf{r}' \langle k' | r' \rangle \langle r' | \mathbf{E}_c | r \rangle \langle r | k \rangle. \]

Using a suitable electron wavefunction \([11]\) \(|r|k\rangle = L^{-1/2} \varphi_0(\mathbf{R}) e^{i k z}, \) where \(L\) is the quantization length along \(\hat{z}\), approximating \(|\varphi_0(\mathbf{R})|^2 \approx \delta(\mathbf{R} - \mathbf{R}_0)\) for a well focused electron, and considering the momentum representation of the Coulomb interaction

\[ \frac{1}{r} = \frac{1}{\pi} \int dq z K_0(|q z| R) e^{i q z}, \]

we find

\[ \langle k' | \mathbf{E}_c | k \rangle = -\frac{2e}{\gamma^2 L} \left[ -\gamma |q z| K_1(|q z| R_0/\gamma) \hat{R}_0 + i q z K_0(|q z| R_0/\gamma) \hat{z} \right] \]

with \(q z = k' - k\), and from here,

\[ H_{e-pl} = \frac{2e}{\gamma^2 L} \sum_{k,k',l} d_l (b_l^\dagger + b_l) \hat{x}_l \cdot \left[ -\gamma |q z| K_1(|q z| R_0/\gamma) \hat{R}_0 + i q z K_0(|q z| R_0/\gamma) \hat{z} \right] |k'\rangle \langle k|. \quad (A.1) \]

Finally, comparing equations (9) and (A.1), and using the correspondence \(c^\dagger_\mathbf{k} |\phi\rangle \leftrightarrow |k\rangle\) and \(|\phi| c_k \leftrightarrow |k\rangle\), where \(|\phi\rangle\) is the electron vacuum state, we readily obtain equation (10).

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Appendix B. Derivation of EELS, EEGS and CL probabilities

Starting from the Hamiltonian model of equations (2)–(10), we provide here detailed derivations of the probabilities given by equations (11)–(13).

B.1. First order processes

B.1.1. Light extinction. This process is mediated by $H_{\text{ph}-\text{pl}}$ and the final state corresponds to one lost photon and one excited plasmon in mode $l$: $|k_0(N-1)l\rangle$. The transition rate from the initial state to all possible final states with an excited plasmon is given by

$$\Gamma_{\text{ext}} = \frac{2\pi}{\hbar^2} \sum_l |\langle k_0(N-1)l|H_{\text{ph}-\text{pl}}|k_0Nl\rangle|^2 \delta(\tilde{\omega}_{\text{pl}} - \omega_l)$$

$$= \frac{2\pi}{\hbar^2} N \sum_l |g_{li}|^2 \delta(\tilde{\omega}_{\text{pl}} - \omega_l)$$

$$= \frac{4\pi^2 N\omega_l}{\hbar V} \sum_l |d_l(\hat{x}_l \cdot \epsilon_i)|^2 \delta(\tilde{\omega}_{\text{pl}} - \omega_l)$$

$$= \frac{4d^2\pi N\omega_l}{\hbar V} \text{Im} \left\{ \frac{1}{\tilde{\omega}_{\text{pl}} - \omega_l} \right\},$$

where we have assumed a spherically symmetric particle ($d_l = d$ and $\sum_l(\hat{\epsilon}_l \cdot \hat{x}_l)^2 = 1$) and we have implicitly defined $\delta(\tilde{\omega}_{\text{pl}} - \omega_l) = (1/\pi)\text{Im} \left\{ \frac{1}{\tilde{\omega}_{\text{pl}} - \omega_l} \right\}$ and the imaginary part comes from $\tilde{\omega}_{\text{pl}}$ through the plasmon width $\Gamma_{\text{pl}}$. Now, computing the light intensity as $I_0 = (c/2\pi)\langle\mathbf{E}^* \mathbf{E}\rangle = \frac{c\omega_i N}{V}$, we find the extinction cross-section

$$\sigma_{\text{ext}}(\omega) = \frac{\hbar\omega_i \Gamma_{\text{ext}}}{I_0} = \frac{4\pi\omega_i}{c} \text{Im} \left\{ \frac{d^2}{\hbar \tilde{\omega}_{\text{pl}} - \omega_l} \right\},$$

which corresponds to an effective polarizability given by

$$\alpha(\omega_i) = \frac{d^2}{\hbar} \frac{1}{\tilde{\omega}_{\text{pl}} - \omega_l}.$$

This expression is used in the following sections.

B.1.2. Electron energy loss. This process is mediated by $H_{e-\text{pl}}$ and the final state corresponds to an electron that has lost energy $\epsilon_k - \epsilon_{k_0} > 0$ to excite the plasmon mode $l$: $|kN_l\rangle$. The probability of losing the energy of one plasmon is given by

$$p_{\text{EELS}} = \frac{2\pi L}{\hbar^2} \sum_l |\langle kN_l|H_{e-\text{pl}}|k_0N_0\rangle|^2 \delta(\epsilon_k - \epsilon_{k_0} + \tilde{\omega}_{\text{pl}})$$

$$= \frac{2\pi L}{\hbar^2} \sum_l |g_{kk_0}|^2 \delta(\epsilon_k - \epsilon_{k_0} + \tilde{\omega}_{\text{pl}})$$

$$= \frac{8e^2d^2}{\hbar^2 v L \gamma^2} |k - k_0|^2 \left[ K_0^2(|k - k_0|R_0/\gamma) + \frac{1}{\gamma} K_1^2(|k - k_0|R_0/\gamma) \right] \text{Im} \left\{ \frac{1}{\epsilon_k - \epsilon_{k_0} + \tilde{\omega}_{\text{pl}}} \right\}.$$
where the transition rate has been multiplied by the interaction time $L/v$ and we again consider a spherical particle. From here, we find the EELS probability per unit of energy loss $h$ as

$$\Gamma_{\text{EELS}}(\omega) = \frac{1}{\hbar} \sum_k p_{\text{EELS}} \delta(\epsilon_k - \epsilon_{k_0} + \omega).$$

Finally, using the prescription $\sum_k \rightarrow (L/2\pi) \int dk$ and working in the non-recoil approximation (i.e. $\epsilon_k - \epsilon_{k_0} \approx (k - k_0)v$), we obtain equation (11) for the EELS probability.

### B.2. Second order processes

#### B.2.1. Electron energy gain

This corresponds to the process (see figure 4(a)) $|k_0 N_i 0_i\rangle \xrightarrow{H_{\text{e-pl}}} |k_0(N - 1), 1_i\rangle \xrightarrow{H_{\text{e-pl}}} |k(N - 1), 0_i\rangle$, the probability of which is given by

$$p_{\text{EEGS}} = \frac{2\pi L}{\hbar^4 v} \left| \sum_k \frac{\langle k(N - 1), 0_i|H_{\text{e-pl}}|k_0(N - 1), 1_i\rangle \langle k_0(N - 1), 1_i|H_{\text{e-pl}}|k_0 N_i 0_i\rangle}{\omega_i - \omega_{\text{pl}}} \right|^2 \delta(\epsilon_k - \epsilon_{k_0} - \omega_i).$$

Noticing that $\langle k(N - 1), 0_i|H_{\text{e-pl}}|k_0(N - 1), 1_i\rangle = g_{kk_0 l}$ and $\langle k_0(N - 1), 1_i|H_{\text{e-pl}}|k_0 N_i 0_i\rangle = -i\sqrt{N} g_{il}$, and considering the light incidence and polarization conditions (see figure 1(a)), we find

$$p_{\text{EEGS}} = \frac{2\pi NL}{\hbar^4 v} \left| \sum_k g_{ii}g_{kk_0 l} \right|^2 \delta(\epsilon_k - \epsilon_{k_0} - \omega_i) = \frac{16\pi^2 \delta^2}{\hbar^4 v L C \gamma^2} \frac{I_0 |k - k_0|^2}{\omega_i - \omega_{\text{pl}}}^{2} \delta(\epsilon_k - \epsilon_{k_0} - \omega_i)$$

Finally, equation (12) directly follows from evaluating the EEGS probability per unit of transferred energy, $\Gamma_{\text{EEGS}}(\omega) = \hbar^{-1} \sum_k p_{\text{EEGS}} \delta(\epsilon_k - \epsilon_{k_0} - \omega)$. 

#### B.2.2. Cathodoluminescence

The electron loses energy and excites a plasmon that afterwards radiates to all possible light modes. The corresponding CL process (see figure 4(a)) $|k_0 N_i 0_i\rangle \xrightarrow{H_{\text{e-pl}}} |k N_i 1_i\rangle \xrightarrow{H_{\text{ph-pl}}} |k N_i 1_j 0_i\rangle$ has probability

$$p_{\text{CL}} = \frac{2\pi L}{\hbar^4 v} \sum_j \left| \sum_k \frac{\langle k N_i 1_j 0_i|H_{\text{ph-pl}}|k N_i 1_i|H_{\text{e-pl}}|k_0 N_i 0_i\rangle}{\epsilon_{k_0} - \epsilon_k - \omega_{\text{pl}}} \right|^2 \delta(\epsilon_k - \epsilon_{k_0} + \omega_j).$$

Proceeding as in section B.2.1, with $\langle k N_i 1_j 0_i|H_{\text{ph-pl}}|k N_i 1_i\rangle = ig_{ji}$ and $\langle k N_i 1_i|H_{\text{e-pl}}|k_0 N_i 0_i\rangle = g_{kk_0 l}$, we obtain

$$p_{\text{CL}} = \frac{2\pi L}{\hbar^4 v} \sum_j \left| \sum_k g_{ij} g_{kk_0 l} \right|^2 \delta(\epsilon_k - \epsilon_{k_0} + \omega_j).$$
The sum over all the possible radiated modes $j$ involves summing over both polarizations $\sigma_j$ and wavevectors $k_j = k_j (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$. Choosing the two independent linear polarization vectors as $\hat{\theta}$ and $\hat{\phi}$ and taking $\hat{R}_0 = \hat{x}$, we find

$$
\sum_{\sigma_j} \left| \sum_l g_{j,l} g_{kkl} l \right|^2 = \frac{8\pi d^4 e^2 \hbar \omega_j}{V L^2 \gamma^2} \left| k - k_0 \right|^2 \left[ K_1^2 \left( \left| k - k_0 \right| R_0 / \gamma \right) \left( \sin^2 \varphi + \cos^2 \theta \cos^2 \varphi \right) + \frac{1}{\gamma} K_0^2 \left( \left| k - k_0 \right| R_0 / \gamma \right) \sin^2 \theta \right],
$$

and from here, using the customary prescription $\sum_{k_j} \rightarrow (V/(2\pi)^3 c^3) \int d\Omega \int \omega_j^2 d\omega_j$, we obtain

$$
P^{\text{CL}} = \frac{16d^4 e^2}{3\hbar^3 V L^3 c^5 \gamma^2} \left| \frac{k - k_0}{\epsilon_{k_0} - \epsilon_k - \omega_{\text{pl}}} \right|^2 \left( \epsilon_{k_0} - \epsilon_k \right)^3 \left[ K_1^2 \left( \left| k - k_0 \right| R_0 / \gamma \right) + \frac{1}{\gamma} K_0^2 \left( \left| k - k_0 \right| R_0 / \gamma \right) \right].
$$

Finally, equation (13) is directly given by substituting this expression in the spectrally resolved CL probability, $\Gamma^{\text{CL}}(\omega) = \hbar^{-1} \sum_k P^{\text{CL}}(\epsilon_k - \epsilon_{k_0} + \omega)$.

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