Electron energy-gain spectroscopy

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\textit{New Journal of Physics} 10 (2008) 073035 (8pp)
Received 27 May 2008
Published 21 July 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/7/073035

\textbf{Abstract.} We introduce electron energy-gain spectroscopy as a tool to yield information on local optical excitations of nanostructured systems using transmission electron microscopes equipped with external optical illumination. The new spectroscopy combines the superb spatial resolution of electron microscopes with unprecedented energy resolution below the milli-electron-volt level, only limited by the bandwidth of the external light. The analysis of energy gain events should reveal hyperfine details in the optical response of individual nanostructures (e.g. plasmons in nanoparticles). Our conclusions rely on a general formalism capable of describing light absorption by fast electrons moving in vacuum near an illuminated nanostructure, thus paving the way towards new light-assisted electron- and ion-acceleration schemes. Energy gain probabilities are shown to be comparable to those observed in energy loss experiments for reasonable illumination intensity.

\textbf{Contents}

1. Introduction 2
2. Theoretical formalism 3
3. Feasibility of EEGS 6
4. Conclusions 8
Acknowledgments 8
References 8

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1. Introduction

The energy–momentum mismatch between freely propagating charges and photons prevents the linear coupling of fast electrons and light in vacuum. However, the presence of neighboring materials structured on subwavelength scales can produce evanescent optical fields that carry the necessary complex momentum to make this coupling possible. Electron energy losses due to this coupling are very familiar but energy gain can also occur. This has been already observed in the inverse Smith–Purcell effect [1], in which a grating supplies the momentum difference needed to produce electron acceleration. In a related development, the inverse Cherenkov effect has been observed through acceleration of electrons moving faster than light inside an illuminated dielectric [2]. Therefore, it is plausible that similar phenomena occur in situations where electrons traveling in vacuum, but close to a surface, interact with the evanescent tails of surface plasmons and scattered light (e.g. under total internal reflection), leading to a new spectroscopy technique, as already proposed by Howie [3]. Actually, evanescent light is inherent to surface plasmons, thus making electron acceleration a natural probe of plasmonic structures. However, an analysis of the interaction of fast charges with plasmons and other optical excitations is still missing, and so are the theoretical tools that allow exploration of the application of this phenomenon to new spatially resolved spectroscopy and electron acceleration schemes.

Electron energy-loss spectroscopy (EELS) performed in scanning transmission electron microscopes (STEMs) has produced many beautiful examples of optical characterization of nanostructures with exquisite spatial resolution [4, 5]. A demonstration of such capabilities has been recently reported, combining nanometre spatial resolution with 0.2 eV energy resolution to map the distribution of plasmon excitations in metallic nanoparticles [6, 7]. However, EELS is limited in the low-energy, visible region of the spectrum by the tail of the zero-loss peak (ZLP), which partially masks optical features. And more importantly, the energy resolution is currently limited to ∼0.1 eV, which makes it impossible to resolve finer details in the optical response. This resolution is already an impressive achievement, considering that it has to be separated out of the typical 100–300 keV kinetic energy of the microscope beam electrons, but it is still insufficient to compete with optical techniques.

Here, we develop a general formalism describing the interaction of fast charged particles with photons in the presence of nanostructured materials. We demonstrate that a charged particle traveling in vacuum, but close to a surface, can absorb photons and therefore be accelerated. Taking advantage of this phenomenon, we introduce electron energy-gain spectroscopy (EEGS) as a tool for dramatically improving energy resolution. We demonstrate that EEGS is capable of resolving optical response features with the same energy resolution as conventional optical techniques and with the nanometre spatial resolution characteristic of electron microscopes. The basic concept is illustrated in figure 1. The electrons pick up energy out of an external light beam illuminating the structure through scattered, evanescent components. Under low illumination intensity conditions, the full width of the energy-gain peak must correspond to electrons that have absorbed one photon, and therefore, the energy resolution of this spectroscopy is limited not by the width of the ZLP or the resolution of the electron analyzer but rather by the energy width of the external light, which can be brought down to the sub-meV domain using well-established tunable laser sources [8]. (Notice that low excitations (e.g. sub-meV excitation energies) will be difficult to resolve due to the ZLP background. Here, we refer instead to the ability to resolve higher-energy excitation features (e.g. 1 eV) separated by minute excitation energy differences (e.g. 1 eV versus 1.001 eV).)
Figure 1. Schematic description of EEGS. (a) An electron passes near a nanostructure (a nanoparticle in the illustration) that is being illuminated by light of frequency $\omega$. (b) A regular EELS spectrum acquired in a STEM shows a gain peak on the left-hand side with respect to the ZLP, corresponding to electrons that have absorbed one photon from the external light. (c) The electron energy-gain probability for light of frequency $\omega$ is proportional to the area of the energy-gain peak. The gain process is assisted by localized excitations of the nanostructure, which supplies the necessary momentum to couple evanescent, scattered light to the electron, so that the EEGS probability exhibits features as a function of photon frequency mimicking the excitation modes of the nanostructure.

Energy-gain spectroscopy should be compared to cathodoluminescence (CL), which is also capable of combining light spectroscopy with electron-beam focusing [9]. However, CL is limited by low emission efficiency, reducing the signal-to-noise ratio when probing localized optical excitations, and thus damaging the energy resolution. In contrast to this, and noticing that processes leading to energy loss and energy gain have equal probability (see below), EEGS benefits from large populations of photons supplied by the external illumination. And unlike EELS, EEGS offers unique possibilities for separately resolving the symmetry of degenerate photonic states by playing with the polarization and incidence direction of the external light.

2. Theoretical formalism

We now proceed to formulate a quantitative description of EEGS and EELS using a common fully quantum-mechanical formalism that allows us to make a fair comparison between the two techniques. We focus on an energetic electron described by

$$|k\rangle = \frac{1}{L^{1/2}} e^{i\mathbf{k} \cdot \mathbf{z}} \phi(x, y),$$

where $\hbar k$ is the momentum along the direction of motion (taken along the positive z-axis), $L$ is the electron quantization length along that direction, and $\phi(x, y)$ is a wave function in the perpendicular plane, focused within a narrow spot ($\lesssim 1$ nm) centered at $\mathbf{R}_e = (x_e, y_e)$. The slow motion in the $xy$-plane permits us to assume that $\phi(x, y)$ remains unchanged during the
interaction with the sample. The electron can transfer to the sample momentum $\hbar \mathbf{q} = \hbar (\mathbf{k}_i - \mathbf{k}_f)$ along $z$ and energy $\hbar \omega \approx \hbar \mathbf{q} \cdot \mathbf{v}$, where $\mathbf{k}_i$ and $\mathbf{k}_f$ are the wavevectors before and after the interaction, $\mathbf{v}$ is the electron velocity, and the non-recoil approximation ($q \ll k_i$) has been invoked.

Consider first a non-absorbing sample, for which the entire EELS signal turns into light emission (i.e. the EELS probability is identical to the full CL probability, unless there is coupling to bound photonic states). Working in the Coulomb gauge with vanishing scalar potential, the coupling between light and electron is described through the Hamiltonian [10]

$$H' = -\frac{ie\hbar}{mc} \hat{A} \cdot \nabla,$$

where the vector potential operator

$$\hat{A} = c \sum_j \sqrt{\frac{2\pi \hbar}{\omega_j}} [\hat{a}_j^+ \mathbf{f}_j^\ast (\mathbf{r}) + \hat{a}_j \mathbf{f}_j (\mathbf{r})]$$

can be chosen to be transverse in the absence of charges other than the fast electron and it is expressed as a sum over photon states of frequencies $\omega_j$, with creation and annihilation operators $\hat{a}_j^+$ and $\hat{a}_j$, respectively, and electric-field eigenfunctions $\mathbf{f}_j (\mathbf{r})$. The latter are solutions of [10]

$$\nabla \times \nabla \times \mathbf{f}_j (\mathbf{r}) - (\omega_j^2/c^2)\epsilon(\mathbf{r}, \omega) \mathbf{f}_j (\mathbf{r}) = 0,$$

satisfying the following orthonormality condition: $\int d^3 \mathbf{r} \epsilon(\mathbf{r}, \omega) \mathbf{f}_j (\mathbf{r}) \cdot \mathbf{f}_{j'} (\mathbf{r}) = \delta_{jj'}$. The probability that the electron creates a photon in state $j$ while loosing energy $\hbar \omega_j$ is given by Fermi’s golden rule as

$$P_j = \frac{2\pi L}{\hbar^2 v} \sum_{k_i} \left| \langle k_i | (j | H' | 0) | k_i \rangle \right|^2 \delta(\omega_j - q v),$$

where we have multiplied by the interaction time $L/v$, and $|0\rangle$ and $|j\rangle$ denote the ground state of the photon field and the state with one photon in state $j$, respectively. The evaluation of this matrix element is simplified by the relation $\nabla |k_i\rangle \approx \hat{z} (imv/\hbar) |k_i\rangle$, which is valid in the non-recoil approximation, and by transforming the sum into an integral using box quantization, $\sum_{k_i} \rightarrow (L/2\pi) \int dk_i$. We find

$$P_j = \frac{2\pi e^2}{\hbar \omega_j} \int dz \hat{z} \cdot \mathbf{f}_j (\mathbf{R}_e, z) e^{-i\omega_j z/v}.$$

Interestingly, this expression yields both the probability of single-photon emission at $\omega_j$ by the electron when the system is in the ground state (i.e. a state with no photons) and the probability of photon absorption by the electron when as stated the initial state contains a single photon at $\omega_j$. The gain and emission probabilities are obviously vanishing in infinite vacuum because of

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4 We use a photon quantization scheme valid for dispersionless, lossless inhomogeneous media [10]. However, there is no explicit dependence on the photon eigenfunctions $\mathbf{f}_j$ in equations (6) and (7), and therefore, these formulae are directly applicable to dispersive materials if one considers that they are derived for each frequency $\omega$ in a medium of dispersionless dielectric function corresponding to the actual permittivity at that frequency. The extension to lossy materials requires more sophisticated quantization techniques, as shown by R Matloob [11], but equations (6) and (7) can be easily derived for lossy materials using a classical description of the photon field.
the mismatch of momentum conservation in the integral of equation (3) when $f_j$ is a light plane wave. The presence of a material introduces higher momentum components in $f_j$ through $\epsilon$ in equation (2), giving rise to finite contributions to $P_j$.

Now, the EELS probability per unit of energy loss $\hbar \omega$ is readily obtained from equation (3) as

$$\Gamma_{\text{EELS}}(\omega) = \frac{1}{\hbar} \sum_j P_j \delta(\omega - \omega_j).$$

It is easy to show that this fully quantum-mechanical expression for EELS reduces to the well-known formula obtained from a classical formalism.

Thermal excitations constitute a potential source of electron energy gain that is worth discussing first. Similar to equation (4), we can write the probability for EEGS produced by thermal excitations as

$$\Gamma_{\text{EEGS}}(\omega) = \frac{1}{\hbar} \sum_j n(\omega_j) P_j \delta(\omega - \omega_j) = n(\omega) \Gamma_{\text{EELS}}(\omega),$$

where $n(\omega) = 1/(e^{\hbar \omega/k_B T} - 1)$ is the Bose–Einstein distribution function at temperature $T$. In a pioneering development, Boersch et al. [13] measured $\Gamma_{\text{EEGS}}$ through phonon absorption of electrons traversing LiF films using an electron accelerator. Analysis of their results (not shown) indicates good agreement with equation (5).

Unfortunately, thermal EEGS is limited to excitation energies of the order of $k_B T$ and it has the same energy resolution as conventional EELS. In contrast, our proposed EEGS scheme (figure 1) should work for a wide spectral range in the optical domain and with highly improved energy resolution. But we need to demonstrate that EEGS probabilities are sufficiently large for reasonable illumination intensities. We thus need an expression for the EEGS probability, which we can obtain directly from equation (1) upon substitution of $\hat{A}$ by the vector potential observable corresponding to the applied light field. We obtain

$$P_{\text{EEGS}}(\omega) = \left(\frac{\epsilon}{\hbar \omega}\right)^2 \left| \int dz E_z(R_e, z) e^{-i\omega z/v} \right|^2,$$

where $E_z$ is the electric field component along the trajectory (incident plus scattered). If the incident field is a plane wave and the electron moves in vacuum, only scattered components contribute to the EEGS probability, because the momentum gained by the electron ($\hbar \omega/v$) is always larger than the free-space momentum of light. Therefore, we can substitute the total field by the induced field in equation (6).

When the electron is moving inside a dielectric faster than light in the medium, electron acceleration can be achieved via the inverse Cherenkov effect [2, 14]. Similarly, light scattered from a grating contains evanescent components that can produce energy gain in a passing electron, a process that has been termed the inverse Smith–Purcell effect [1]. These forms of light-induced electron acceleration, and their conceivable extensions to surface-plasmon and
It should be noted that, in contrast to our quantum-mechanical derivation of EEGS, a classical approach based upon the work exerted by the scattered light field on the electron (similar to what is done in classical derivations of EELS) yields an incorrect linear relation between the gain probability and the light field amplitude rather than the intensity, together with a dependence on the absolute phase of the applied field.

So far we have considered lossless samples, but similar results are obtained in dissipative environments. In particular, equation (6) is still valid for lossy materials. Furthermore, the relation between EELS and thermal EEGS given by equation (5) is a plausible one in virtue of the reciprocity in the coupling of the fast electron with excitations in the complex system formed by the sample electronic state and the radiation field.

Useful analytical formulae can be derived for small particles in which the dipolar response is dominant, via their electric polarizability $\alpha$. The EEGS probability is given by integration of the dipole scattered field, $E_z = \alpha \{ (\omega^2/c^2) E_{\text{ext}}^0 + (E_{\text{ext}} \cdot \nabla) \delta_z \} \exp(i \omega t/c)/r$. Direct application of equation (6) yields

$$P_{\text{EELS}}(\omega) = \left| \frac{2e \omega \alpha}{\hbar v^2} \right|^2 \left[ |E_{\text{ext}} \cdot R_e|^2 K_1^2 + \frac{|E_{\text{ext}}|^2}{\gamma^2} K_0^2 \right],$$

where $\gamma = 1/\sqrt{1 - v^2/c^2}$ is the Lorentz contraction factor, $R_e$ is the electron impact parameter relative to the dipole origin, and $K_0$ and $K_1$ are the modified Bessel functions, the argument of which is $\omega R_e/v \gamma$. Interestingly, the field scattered out of an external field oriented perpendicularly with respect to the electron trajectory picks up $z$ components that couple to the electron, giving rise to the $K_1^2$ contribution in equation (7). Similarly, the EELS probability near the dipole particle reduces to

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

For a lossless particle, the optical theorem leads to $\text{Im} \{ \alpha \} = (2\omega^3/3c^3) |\alpha|^2$ [15], which allows us to write $\Gamma_{\text{EELS}} = (P_{\text{EELS}}) \rho^0 f$, where $\rho^0 = \omega^2/\pi^2 c^3$ is the free-space local density of photonic states, the factor $f = 2\pi \hbar \omega$ corrects for the number of photons contained in the normalized external field $E_{\text{ext}}$ (i.e. $|E_{\text{ext}}|^2 = 1$), and the average over orientations of this field has been performed. In other words, the EELS probability, or equivalently the CL probability ($\Gamma_{\text{CL}}$) in our lossless particle, coincides with the EEGS probability for an incoherent source containing one photon per photon state. For a dissipative particle, we have $\Gamma_{\text{EELS}} > \Gamma_{\text{CL}}$, but the relation $\Gamma_{\text{CL}} = (P_{\text{EELS}}) \rho^0 f$ still holds.

3. Feasibility of EEGS

We are now ready to make a quantitative comparison of EEGS and EELS. Incidentally, $\Gamma_{\text{EELS}}$ has units of inverse energy, whereas $P_j$ and $P_{\text{EELS}}$ are dimensionless, so that the comparison requires that we integrate $\Gamma_{\text{EELS}}$ over a finite energy-loss range $\hbar \Delta \omega$. We have $P_{\text{EELS}}/(\hbar \Delta \omega \Gamma_{\text{EELS}}) \sim \pi |E_{\text{ext}}|^2/(2\hbar \Delta \omega \text{Im} \{ -1/\alpha \})$. For instance, for a 100 nm gold nanoparticle illuminated with a laser of moderate intensity $\sim 10^6 \text{ W cm}^{-2}$ tuned at the

*New Journal of Physics* 10 (2008) 073035 (http://www.njp.org/)
particle plasmon energy $\hbar \omega = 2.5 \text{ eV}$, and taking $\hbar \Delta \omega = 0.1 \text{ eV}$ (the plasmon width), we find $P_{\text{EEGS}}/(\hbar \Delta \omega \Gamma_{\text{EELS}}) \approx 40$. This should be compared with $\Gamma_{\text{CL}}/\Gamma_{\text{EELS}} < 1$.

The dipole particle provides the general trend that we find in more realistic descriptions of actual nanoparticles. As an example, we compare in figure 2 calculations of EELS, CL and EEGS probabilities for electrons passing near a gold nanorod with acute tips, the synthesis and optical properties of which have been recently reported [16]. We consider an axially symmetric rod and calculate EELS and CL probabilities and the induced field using the boundary element method [17, 18]. The electron trajectory and particle shape are sketched in figure 2(a) and the calculated spectra are represented in figure 2(b). A dominant longitudinal plasmon mode is observed in all three spectra at $\sim 738 \text{ nm}$, with two additional shorter-wavelength modes showing up in the EELS spectrum. The latter do not efficiently couple to radiation. As anticipated, we find strong similarity between CL and EEGS spectra. The EELS probability integrated within the longitudinal plasmon peak is 0.003, to be compared with the peak EEGS probability $P_{\text{EEGS}} = 3.6$ for a reasonable light intensity of $10^6 \text{ W cm}^{-2}$. This should allow EEGS spectra to be obtained with excellent statistics. Further improvement in signal quality could be achieved using temporal correlations between gain probabilities and light intensities, including frequency modulated illumination and phase sensitive detection techniques, which might be important in reducing the damaging effect of the ZLP background.

The recently demonstrated power of EELS to resolve plasmon maps in nanoparticles [6] is matched by EEGS, as shown in figures 2(c) and (d). Besides the improvement in energy resolution, EEGS is advantageous in that it allows the plasmon symmetry to be explored by playing with the light polarization and direction of incidence (e.g. $P_{\text{EEGS}}$ is negligible for $\mathbf{E}^{\text{ext}}$ perpendicular to the rod axis).
4. Conclusions

In summary, we have developed a comprehensive theoretical framework for the simulation of energy gain spectra, which exhibits large probabilities for reasonable levels of the external illumination intensity, exceeding by orders of magnitude the yield of loss and emission events in EELS and CL. Our findings provide solid support for an unprecedented combination of space and energy resolution in EEGS, which should find wide application to investigate plasmons and other optical excitations in nanostructured environments. The ability of evanescent fields to couple to charges moving in vacuum opens the possibility to realize compact electron and ion accelerators based upon intense energy gain in purposely designed geometries. Finally, our fully quantum-mechanical formulation of the energy-gain phenomenon is well suited to study new effects triggered by non-classical photon statistics of the external light, as well as nonlinear gain processes expected to occur in optical hot spots (e.g. in the gap between nearly touching metal nanoparticles).

Acknowledgments

FJGA thanks Professor Archie Howie for helpful discussions and for having pointed out EEGS as an exciting possibility for a long time. This work was supported in part by the Spanish MEC (MAT2007-66050) and by the EU (STRP-016881-SPANS).

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