Far-Field Electron Spectroscopy of Nanoparticles

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A new excitation mechanism of nanoparticles by relativistic, highly focused electron beams, is predicted under nanoparticle recoil. The corresponding electron energy loss spectra, calculated for metallic (silver and gold) and insulating (SiO₂) nanoplatelets, reveal dramatic enhancements of radiative electromagnetic modes within the light cone, allowed by the breakdown of momentum conservation in the inelastic scattering event. These modes can be accessed with e-beams in the vacuum far-field zone, offering interesting capabilities for signal transmission across nano to meso length scales.

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A powerful approach to the study of nanoparticles is provided by very fast (relativistic) electron beams (e-beams), with typical lateral resolution on an atomic scale, available in scanning transmission electron microscopes (STEM)¹ ². As discussed previously¹ ², when the e-beam is restricted to the vacuum near a selected nanoparticle, its electromagnetic (EM) interaction with surface plasmons or surface plasmon-polaritons (SPPs) is reminiscent of the near-field interaction of subwavelength optical probes. Several works have recently studied realizations of Cherenkov radiation excitation within various dielectric media by e-beams moving in near-field vacuum zones.² ³ ⁴ ⁵ ⁶ ⁷.

In the present paper we show that by considering recoil effects of the nanoparticle during the scattering event one introduces far-field coupling between the electron and the nanoparticle, which dramatically enhances the radiative channels in the loss spectrum. To illustrate our main points we consider here a simple model where the e-beam is propagated in the vacuum along a wide face of a rectangular nanoplatelet (oriented, e.g., in the x–y plane), and a surface or guided wave induced by the electron is propagated with a wave number kₓ along the beam axis. The spatially sensitive nature of the corresponding electron energy loss process arises from the exponential dependence, e⁻²Kₗb, of the EM interaction between the e-beam and the platelet on the impact parameter b. The extinction coefficient, K* = √(k² – (ω/c)²), with k² = kₓ² + kᵧ², determines the tail of the evanescent field in the vacuum for values of k outside the light-cone, i.e. for k > ω/c. Inside the light-cone, i.e. for k < ω/c, K* is purely imaginary and the corresponding interaction becomes spatially oscillating, allowing the electron to exchange photons with the particle far away into the vacuum. This striking possibility has been overlooked in the recent literature of STEM-electron energy loss spectroscopy (EELS), since the excitation by an electron moving in the vacuum with a classical velocity v, has been restricted to a constant longitudinal wavenumber kₓ = ω/v > ω/c, implying EM coupling to the nanoparticle which is restricted to the evanescent tail near the surface.

Following Ref.¹, the focused e-beam is described here as a one-dimensional wave, propagating along the x-axis, while in the transverse (y–z) directions it is described by a wave-packet localized within a smoothly converging cross section along the beam axis, whose shape is assumed to be squared for the sake of simplicity. The nanoplatelet half-sides a* , b* , c* along the x, y, z axes respectively, are assumed to satisfy b* ≫ a* ≫ c* (see below for more details). Within the framework of this quantum-mechanical approach we use an effective beam-nanoparticle interaction Hamiltonian based on the retarded four-vector image potential of the e-beam and Born-Oppenheimer-like separation of coordinates (i.e. the ‘slow’ transverse coordinates from the ‘fast’ longitudinal one), justified by the small e-beam converging angle. The corresponding rate of change of inelastic scattering probability of the incident e-beam at an impact parameter b and for energy loss ∆E = ℏω, calculated to first order in the effective interaction Hamiltonian, H'EM ≈ −eΦ − EM brawl Aₓ, can be written in the form:

\[
R \propto \sum_{qₓ, qᵧ, q_z} e^{-\beta (\Delta qₓ, qᵧ, q_z)^{2}} \times \left\{ \begin{array}{l}
\frac{1}{2} \int_{-L}^{L} dx \left[ \int_{-L}^{L} dy \left[ \int_{-L}^{L} dz \chi_{qₓ}^{*}(x, y, z) \chi_{qᵧ}(x, y', z') \times \delta \left( \Delta qₓ - qₓ - \Delta qᵧ - qᵧ - \Delta q_z - q_z \right) \right] \right]
\end{array} \right\}
\]

where Φ and Aₓ are the scalar and x-component of the four-vector potential respectively, dominating the interaction with the e-beam, pₓ = ℏqx , v = ℏqx /m its initial longitudinal velocity and m is the relativistic electron mass: m = m₀ /√(1 – (v/c)²). In Eq. (11) ∆qₓ ≈ (ω/v) + ℏ \left[ (qₓ')² – (qₓ)² \right] / 2mv is the longitudinal momentum transfer of the e-beam, qₓ' = (qᵧ', q_z')
and $\frac{\gamma}{f}$ its transverse momenta, initial and final respectively, and $\epsilon^{q_x} \chi_{q_y}(y, z; x)$ is an unperturbed e-beam eigenfunction with a longitudinal wave number $q_x$ and asymptotic transverse wavevector $-\mathbf{q}_{t_r}$. Note that the width $\beta^{-1}$ of the Gaussian distribution function, introduced in Eq. (11) to account for the high transverse-energy cutoff caused to the e-beam by the objective aperture, determines a region around the beam focal plane whose length $L$ may be used as a normalization factor for the e-beam wave functions in our model.

The condition $a^* \gg e^*$ ensures that the interaction potential between the platelet and an external electron at a projected distance $|x|$ from the platelet center decays to zero at least as quickly as $1/x^2$ for $|x| > a^*$ (see, e.g., Ref. [12]). Under these circumstances the limits of integrations over $x$ in Eq. (11) may be set at $-a^*$ and $a^*$, rather than at $-L$ and $L$. The potential correlation function for $t > 0$ may be expressed in terms of the relevant components of the 4-tensor photon propagator $D_{\nu \mu}(\mathbf{q}_y', \mathbf{q}_y; t, \nu, \mu = 0, 1, 2, 3)$, by: $-i\left(B_{t_EM}^\nu(x', y', z'; t) B_{t_EM}^{\nu*}(x, y, z; 0)\right) = D_{0,0}(\mathbf{q}_y', \mathbf{q}_y; t) + \frac{\epsilon}{\mu c} D_{0,1}(\mathbf{q}_y', \mathbf{q}_y; t) + \frac{\epsilon}{\mu c} D_{1,0}(\mathbf{q}_y', \mathbf{q}_y; t) + \frac{\epsilon P}{\mu c} D_{1,1}(\mathbf{q}_y', \mathbf{q}_y; t)$. For the sake of simplicity we neglect the finite size effects parallel to the wide $(x-y)$ face of the platelet in the calculated photon propagator. Consequently the energy loss rate in Eq. (11) reduces to:

$$R \propto \int dk_x \int dk_y \text{Im} \left\{ \frac{r(k_x, k_y, \omega)}{K^*} \right\}$$

$$\sum_{\tilde{q}_{t_r}, \tilde{q}_{t_r}^*} e^{-\beta(hq_{t_r})^2/2m} \left| J \left( \tilde{q}_{t_r}^f, \tilde{q}_{t_r}^i; k_y, K^*; \Delta q_x - k_x \right) \right|^2,$$

where:

$$J \left( \tilde{q}_{t_r}^f, \tilde{q}_{t_r}^i; k_y, K^*; \Delta q_x - k_x \right) \equiv$$

$$\frac{1}{2L} \int_{-a^*}^{a^*} dx e^{(\Delta q_x - k_x)x} \int d\mathbf{q}_y \mathcal{J} \left( \tilde{q}_{t_r}^f, \tilde{q}_{t_r}^i; k_y, K^*; x \right),$$

and

$$\mathcal{J} \left( \tilde{q}_{t_r}^f, \tilde{q}_{t_r}^i; k_y, K^*; x \right) \equiv$$

$$\int d\mathbf{q}_x \chi_{K^*} \int d\mathbf{y} e^{-ik_y y} \chi_{K^*}(y, z; x) \chi_{q_y}(y, z; x).$$

The effective surface dielectric response function, appearing in Eq. (2), is given by:

$$r(k_x, k_y, \omega) \approx r_{0,0} + (hq_{t_r}/mc) r_{0,1} + (hq_{t_r}/mc) r_{1,0} + \left(\frac{h^2 q_{t_r}^2}{mc^2}\right) r_{1,1}$$

where $r_{\nu \mu}$ are the components of the EM reflection 4-tensor, which determine the dressed photon propagator in the vacuum outside the rectangular platelet [12]:

$$D_{\nu \mu}(\mathbf{k}, z, z'; \omega) = \frac{\eta_{\nu \mu}}{2\pi K^*} \left[ \delta_{\nu \mu} e^{-K^*|z - z'|} - r_{\nu \mu} e^{K^*(z+z')} \right],$$

with $\eta_{\nu \mu} = 1$, or $-1$ for $\nu = 0$, or $\nu = 1, 2, 3$ respectively. In the long wavelengths limit discussed in Ref. [12] we find that:

$$\text{Im} \left\{ \frac{r(k, \omega)}{K^*} \right\} \approx$$

$$\text{Im} \left\{ \left( (K^*/k^2) f_e + \left( (v/c)^2 - (\omega/cK^*)^2 \right) f_o/K^* \right) e^{-2K^*t} \right\},$$

where $f_e = \left( (\omega^2 K^2 - Q^2) / D^+_e D^-_e \right) / f_o = \left( (K^2 - Q^2) / D^+_o D^-_o \right) = \varepsilon K^* + Q \coth (Qc^*), D^+_e = \varepsilon K^* + Q \coth (Qc^*), D^-_e = \varepsilon K^* + Q \coth (Qc^*), Q = \sqrt{K^2 - (\omega/c)^2 \varepsilon (\omega)}$, and $\varepsilon (\omega)$ is the local bulk dielectric function of the platelet. In the limit of a semi-infinite medium the resulting expression reduces to the surface dielectric response function obtained in Ref. [14] by using Maxwell’s equations with macroscopic boundary conditions.

The standard classical approximation for the loss function [14] is obtained from Eq. (2) by making the following assumptions: (1) the e-beam transverse momentum distribution function $J \left( \tilde{q}_{t_r}^f, \tilde{q}_{t_r}^i; k_y, K^*; x \right)$ is a constant, that is equivalent to a $\delta$-function in the corresponding real-space transverse coordinates, (2) the contribution of the transverse energy to $\Delta q_x$ can be as large as $(\omega/v)$. Assumption (3), in conjunction with (1), yields the conservation of longitudinal momentum, i.e., $\Delta q_x - k_x = 0$, which together with assumption (2) imposes the fixed condition $k_x = (\omega/v)$. In the present paper we remove only the third assumption by allowing $a^*$ to be a finite length, which reflects an effective range of the beam-particle interaction along the beam axis. Consequently the longitudinal momentum distribution around $\Delta q_x - k_x = 0$, defined by the integral in Eq. (3), is smeared and many wavenumbers $k_x$ inside the light-cone start contributing to the loss rate, Eq. (2).

The condition for the smearing to be significant is $\pi/a^* \gtrsim (\omega/v)$, so that typically for frequencies $\omega$ in the visible range $a^*$ should be smaller than $200$ nm. Nanoplatelets of that lengths should dramatically enhance radiative excitations by the e-beam, previously overlooked in the literature. It should be stressed that, for the sake of simplicity, this is done by invoking the dielectric response function of an infinitely wide platelet. A consistent treatment of the breakdown of translation invariance is expected, however, to further enhance all radiative channels.
FIG. 1: EEL spectra (solid lines) of 100 nm long Ag and Au platelets calculated for a 100 keV external e-beam at various impact parameters between 10 and 40 nm. The experimental optical dielectric functions, $\varepsilon(\omega)$, for silver and gold have been exploited. Dashed lines represent spectra calculated by the classical theory. Inset: SPP dispersion curves, $\omega(\text{Re} k)$, $\omega(\text{Im} k)$ in the complex $k$-plane for silver. The indicated values of $k$ and $\omega$ are normalized by $k_n = \omega_n/c$, and $\omega_n = 10$ eV, respectively.

As a first example we calculate the EEL function of a 100 nm long silver and gold platelets for an external 100 keV e-beam at various impact parameters (see Fig.1). To analyze the various SPP resonances one may consider the zeros of the denominator of the extraordinary wave amplitude $f_e$ in Eq.(4) in the complex $k$-plane. With the experimental optical dielectric function, $\varepsilon(\omega)$, for silver the resulting dispersion relation (inset, Fig.(1)) exhibits a rather flat branch of $\omega(\text{Re} k)$ inside the light-cone, which can be attributed to radiative SPP, seen as a mirror image of the usual non-radiative SP dispersion curve with respect to the light-line. The sector of $\omega(\text{Re} k)$ connecting the two branches across the light line exhibits a negative slope, where $\text{Im} k(\omega) \propto \text{Im} \varepsilon(\omega)$ has a sharp peak. The sharp dip in the EEL spectrum just above the classical SP frequency (at 3.8 eV) reflects these closely related features. These peculiar features are missing in the loss spectrum of the gold platelet, Fig.1.

At slightly higher frequencies the EEL signals exhibit a pronounced rise due to the enhanced SPP density of states associated with the flat radiative SPP branch. The corresponding EEL peak intensity exhibits a remarkably weak attenuation, in marked contrast to the exponential attenuation of the main SP peak, calculated in the classical limit for increasing impact parameter. The radiative nature of the beam-particle coupling shown in Fig.(1) is even more pronounced in the low energy region below the main SP peak, where the classically calculated signal drops to zero. Here our calculated EEL function exhibits a pronounced broad band with linearly increasing intensity for increasing frequency and almost no attenuation with increasing impact parameter. These features are due to the fact that the loss signal well below the main SP frequency is dominated by the contribution from the ordinary wave amplitude $f_o$, appearing in Eq.(4), which is singularly enhanced near the light line (where $K^* \to 0$), and thus reflecting the nearly pure (transverse) photonic nature of the excitations by the e-beam in this ‘classically forbidden’ region.

A similar and even more dramatic situation arises in the forbidden energy gap of the electron-hole pair excitations in semiconductors and insulators, as shown, e.g. in Fig.(2) for a 100 nm long SiO$_2$ platelet. The EEL spectra of an external 100 keV e-beam, propagating parallel to the $x - y$ face of the platelet at various impact parameters $b$, reveal a pronounced broad peak within the forbidden gap region, which does not decay with increasing $b$ values. Similarly to the situation with the silver platelet well below the main SP peak, the strong radiative nature of this feature arises from the ordinary wave
amplitude $f_\omega$, corresponding to the excitation of purely transverse EM waves, polarized within the $x-y$ plane, which totally dominates the loss signal in the gap region.

The spectrum shown in Fig.(2) for an impact parameter $b = 10$ nm may be compared to the result reported in Ref.[10] for an electron moving parallel to a 90° SiO$_2$ wedge at a distance of 8.5 nm (see Inset to Fig.(2)). The pronounced radiative broad band within the gap region, obtained in our calculation, dramatically contrasts the vanishing loss signal shown there in Fig.(4) for an electron with the same velocity ($v = 0.54c$) and nearly the same impact parameter. The lack of far-field coupling in the latter theoretical approach restricted the fast external e-beam to excite EM waves propagating within the dielectric medium only $\parallel$, similar to ordinary waveguide modes which can develop within a thin SiO$_2$ slab in the forbidden gap region where $Re \varepsilon(\omega) \approx 2$, and $Im \varepsilon(\omega) \rightarrow 0$. For ideal planar geometry (as assumed in our calculation of the dielectric response function $r(\mathbf{k},\omega)$), the corresponding waveguide modes appear as extremely narrow resonances which can not be excited by an e-beam with $\Delta q_x$ values outside the light cone due to the vanishingly small dielectric damping, $Im \varepsilon(\omega)$.

Such radiation excitations become possible for the non-planar geometries studied in Refs.[3],[10] even under the recoilless scattering approximation exploited there (but only above a threshold beam energy considerably higher than 100 keV) due to the translational symmetry-broken dielectric media considered in their calculations. Yet, the corresponding Cherenkov channels remain fundamentally different from the ones we propose: The opening of scattering channels with wave numbers inside the light cone allows coupling of the e-beam to the continuum of EM modes which are extended into the vacuum, leading to dramatic enhancement of the loss signal at e-beam energies around 100 keV. The relative strength of the radiative effect calculated here may be further appreciated by noting the close proximity of the e-beam to the sharp SiO$_2$ wedge in [10], which strongly enhances the (evanescent) near-field coupling with the e-beam. In summary, applying a quantum-mechanical approach to the scattering problem, we have shown that Cherenkov radiation of highly focused relativistic e-beams in STEM, discussed recently in the literature[8],[9],[10], have a much broader scope than originally presented. The dramatic enhancement of radiative channels, imposed by the finite nanoparticle size, arises from the breakdown of momentum conservation in the inelastic scattering event along the e-beam axis. Further enhancement should be realized due to the extreme lateral confinement of the e-beam and its associated transverse momentum uncertainty, which were neglected here. The radiation predicted to be emitted from both conducting and insulating nanoplatelets can be generated at impact parameters much larger than the evanescent tail of the excited surface EM modes. Large deviations from the classical, nonradiative EEL signal are found to persist also at small impact parameters, which can be readily tested experimentally. The proposed spectroscopic experiments are closely related to recent developments in the field of SPP-based far-field optics.[17] Far field EELS can therefore become a useful complementary tool for an already recognized new emerging field.

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Ag, Au platelets:
c* = 10 nm
a* = 50 nm
v/c = 0.54
solid−quantum
dashed−classical

Au b = 10 nm
Ag b = 10 nm

20 nm
40 nm

\( \omega(\text{Re}k) \), \( \text{Im}(k/k_n) \)

light line
surface plasmon
