Probing the Photonic Local Density of States with Electron Energy Loss Spectroscopy

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Electron energy loss spectroscopy performed in transmission electron microscopes is shown to directly render the photonic local density of states with unprecedented spatial resolution, currently below the nanometer. Two special cases are discussed in detail: (i) 2D photonic structures with the electrons moving along the translational axis of symmetry and (ii) quasiplanar plasmonic structures under normal incidence. Nanophotonics in general and plasmonics, in particular, should benefit from these results connecting the unmatched spatial resolution of electron energy loss spectroscopy with its ability to probe basic optical properties such as the photonic local density of states.

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While a plethora of nanophotonic structures is currently being devised for diverse applications like achieving single molecule sensitivity in biosensing [1] or molding the flow of light over nanoscale distances for signal processing [2], no optical characterization technique exists that can render spectroscopic details with truly nanometer spatial resolution. The need for that kind of technique is particularly acute in nanometric plasmonic designs that benefit from sharp edges and metallic surfaces in close proximity to yield large enhancements of the electromagnetic field.

Scanning transmission electron microscopes (STEM) can plausibly cover this gap, as they perform electron energy loss spectroscopy (EELS) with increasingly improved energy resolution that is quickly approaching the width of plasmon excitations in noble metals [3] and with spatial resolution well below the nanometer [4]. The connection between EELS and photonics can be readily established when low-energy losses in the sub-eV to a few eV range are considered, compatible with typical photon energies in photonic devices. A formidable amount of information is available in the literature for this so-called valence EELS, including for instance studies of single nanoparticles of various shapes [3,5], interacting nanoparticles [6], thin films [7], composite metamaterials [8], and carbon nanostructures [9]. Many of these reports are relevant to current nanophotonics research, in which the optical response of nanoparticles, nanoparticle assemblies, and patterned nanostructures plays a central role. In this context, EELS has been recently demonstrated to image plasmon modes with spatial resolution better than a hundredth of the wavelength in triangular nanoprisms [3]. However, despite significant progress from the theoretical side [10], no synthetic and universal picture has emerged to explain the spatial modulation of EELS measurements on arbitrary nanostructures.

In this Letter, we show that EELS provides direct information on the photonic local density of states (LDOS), and thus it constitutes a suitable tool for truly nanometric characterization of photonic nanostructures. A rigorous derivation of this statement is offered, illustrated by numerical examples for both translationally invariant geometries and planar structures. Our results allow directly interpreting EELS data in terms of local photonic properties that encompass the full display of optical phenomena exhibited by nanostructures, ranging from localized and propagating plasmons in patterned metallic surfaces [6] to band gaps in dielectric photonic crystals [11].

Green tensor and LDOS.—The optical response of a nanostructure is fully captured in its electric Green tensor and its LDOS [12]. In particular, the electric field produced by an external current density $\mathbf{j}(\mathbf{r}, \omega)$ in an inhomogeneous medium of permittivity $\epsilon(\mathbf{r}, \omega)$ can be written in frequency space ω as

$$\mathbf{E}(\mathbf{r}, \omega) = -4\pi i\omega \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}', \omega)\mathbf{j}(\mathbf{r}', \omega) \quad (1)$$

in terms of G, the electric Green tensor of Maxwell's equations in Gaussian units, satisfying

$$\nabla \times \nabla \times G(\mathbf{r}, \mathbf{r}', \omega) - (\omega^2/c^2)\epsilon(\mathbf{r}, \omega)G(\mathbf{r}, \mathbf{r}', \omega) = \frac{-1}{c^2}\delta(\mathbf{r} - \mathbf{r}') \quad (2)$$

and vanishing far away from the sources.

We then define the LDOS projected along a unit vector $\hat{\mathbf{n}}$ as [13]

$$\rho_{\hat{\mathbf{n}}}(\mathbf{r}, \omega) = \frac{-2\omega}{\pi} \mathrm{Im}\{\hat{\mathbf{n}} \cdot G(\mathbf{r}, \mathbf{r}, \omega) \cdot \hat{\mathbf{n}}\}. \quad (3)$$

In free space, the uniform LDOS is known from blackbody theory (with a factor of $1/3$ arising from projection over a specific Cartesian direction $\hat{\mathbf{n}}$):

$$\rho^0_{\hat{\mathbf{n}}}(\mathbf{r}, \omega) = \omega^2/3\pi^2c^3. \quad (4)$$

Similar to its electron counterpart in solid state physics, the photonic LDOS equals the combined local intensity of all eigenmodes of the system under consideration, provided they are well defined (e.g., in the absence of lossy media)

[14]. An alternative interpretation, which holds even in the presence of lossy materials [15], comes from the realization that $(4\pi^2\omega D^2/\hbar)\rho$ is the decay rate for an excitation dipole strength D [16,17]. Finally, we point out that a complete definition of the LDOS should include a magnetic part [18], which is however uncoupled to our fast electrons.

Energy loss probability.—The energy loss suffered by a fast electron passing near an inhomogeneous sample and moving with constant velocity $\mathbf{v}$ along a straight line trajectory $\mathbf{r} = \mathbf{r}_e(t)$ can be related to the force exerted by the induced electric field $\mathbf{E}^{\text{ind}}$ acting back on the electron as [19]

$$\Delta E = e \int dt\, \mathbf{v} \cdot \mathbf{E}^{\text{ind}}[\mathbf{r}_e(t), t] = \int_0^\infty \hbar\omega\, d\omega\, \Gamma(\omega), \quad (5)$$

where the $-e$ electron charge has been included (i.e., $\Delta E > 0$) and

$$\Gamma(\omega) = \frac{e}{\pi\hbar\omega} \int dt\, \text{Re}\{e^{-i\omega t}\mathbf{v} \cdot \mathbf{E}^{\text{ind}}[\mathbf{r}_e(t), \omega]\} \quad (6)$$

is the loss probability. The Fourier transform

$$\mathbf{E}^{\text{ind}}(\mathbf{r}, t) = \int \frac{d\omega}{2\pi} e^{-i\omega t}\mathbf{E}^{\text{ind}}(\mathbf{r}, \omega) \quad (7)$$

has been introduced and the property $\mathbf{E}^{\text{ind}}(\mathbf{r}, \omega) = [\mathbf{E}^{\text{ind}}(\mathbf{r}, -\omega)]^*$ has been used.

The external current density corresponding to the moving electron is now given by

$$\mathbf{j}(\mathbf{r}, \omega) = -e\mathbf{v} \int dt\, e^{i\omega t}\delta[\mathbf{r} - \mathbf{r}_e(t)]. \quad (8)$$

Assuming without loss of generality that the velocity vector is directed along the positive z axis and using the notation $\mathbf{r} = (\mathbf{R}, z)$, with $\mathbf{R} = (x, y)$, the current density reduces to

$$\mathbf{j}(\mathbf{r}, \omega) = -e\delta(\mathbf{R} - \mathbf{R}_0)e^{i\omega z/v}\hat{\mathbf{z}}, \quad (9)$$

where $\mathbf{R}_0 = (x_0, y_0)$ is the 2D impact parameter of the electron trajectory relative to the z axis. Inserting Eq. (9) into Eq. (1), and this in turn into Eq. (6), we find

$$\Gamma(\mathbf{R}_0, \omega) = -\frac{4e^2v^2}{\hbar} \times \int dt dt'\, \text{Im}\{e^{i\omega(t'-t)}G^{\text{ind}}_{zz}[\mathbf{r}_e(t), \mathbf{r}_e(t'), \omega]\}, \quad (10)$$

where $G_{zz} = \hat{\mathbf{z}} \cdot G \cdot \hat{\mathbf{z}}$, the dependence of the loss probability Γ on $\mathbf{R}_0$ is shown explicitly, and G^{ind} denotes the induced Green tensor obtained from G by subtracting the free-space Green tensor.

Relation between EELS and LDOS.—Noticing that $z_e(t) = vt$, the time integrals of Eq. (10) yield the Fourier transform of the induced Green tensor with respect to z and z', $G^{\text{ind}}_{zz}(\mathbf{R}, \mathbf{R}', q, -q', \omega)$, in terms of which Γ becomes

$$\Gamma(\mathbf{R}_0, \omega) = -\frac{4e^2}{\hbar}\, \text{Im}\{G^{\text{ind}}_{zz}(\mathbf{R}_0, \mathbf{R}_0, q, -q, \omega)\} = \frac{2\pi e^2}{\hbar\omega}\rho_{\hat{\mathbf{z}}}(\mathbf{R}_0, q, \omega), \quad (11)$$

where $q = \omega/v$ and we have defined

$$\rho_{\hat{\mathbf{n}}}(\mathbf{R}, q, \omega) = \frac{-2\omega}{\pi}\, \text{Im}\{\hat{\mathbf{n}} \cdot G(\mathbf{R}, \mathbf{R}, q, -q, \omega) \cdot \hat{\mathbf{n}}\} \quad (12)$$

as a generalized density of states that is local in real space along the $\mathbf{R}$ directions and local in momentum space along the remaining z direction, parallel to the electron velocity vector.

The value of $q = \omega/v$ reflects conservation of energy and momentum in the transfer of excitations of frequency ω and momentum $\hbar q$ from the electron to the sample. It is interesting to note that for an electron moving in an infinite vacuum one has

$$\rho_{\hat{\mathbf{z}}}(\mathbf{R}, q, \omega) = L\frac{\omega}{2\pi c^2}(1 - q^2c^2/\omega^2)\theta(\omega/c - q), \quad (13)$$

which is always zero for subluminal electrons moving with velocity $v < c$. Here, L is the *quantization* length along z. As expected, the vacuum density of states does not contribute to the EELS signal, and this allows dropping the superscript *ind* from Eq. (11), as it has been implicitly assumed already when writing Eq. (12). Incidentally, the Cherenkov effect is deduced from $\rho_{\hat{\mathbf{z}}}(\mathbf{R}, q, \omega) = (L\omega/2\pi c^2)(1 - q^2c^2/\omega^2\epsilon)\theta(\epsilon\omega^2/c^2 - q^2)$, valid for a homogeneous dielectric of real permittivity ϵ.

The proposed formalism yields exactly the same results as any other local, retarded theory, but it provides a new paradigm for understanding EELS as connected to a local quantity: the LDOS. This is in contrast to the common view of EELS as a tool capable of retrieving local electronic properties hidden in the permittivity, which is in turn involved in the nonlocal response of inhomogeneous structures probed by the electrons and has resulted in endless discussions regarding how to eliminate delocalization.

2D systems possessing translational invariance.—If the sample under consideration is translationally invariant along z, the Green tensor $G(\mathbf{r}, \mathbf{r}', \omega)$ depends on z and z' only via $z - z'$, and thus one can write

$$G(\mathbf{r}, \mathbf{r}', \omega) = \int \frac{dq}{2\pi}\tilde{G}(\mathbf{R}, \mathbf{R}', q, \omega)e^{iq(z-z')}, \quad (14)$$

where $\tilde{G}(\mathbf{R}, \mathbf{R}', q, \omega) = (1/L)G(\mathbf{R}, \mathbf{R}', q, -q, \omega)$. Accordingly, the local density of states can be decomposed into momenta components $\hbar q$ along the z axis,

$$\rho_{\hat{\mathbf{n}}}(\mathbf{r}, \omega) = \int \frac{dq}{2\pi}\tilde{\rho}_{\hat{\mathbf{n}}}(\mathbf{R}, q, \omega), \quad (15)$$

where

$$\tilde{\rho}_{\hat{\mathbf{n}}}(\mathbf{R}, q, \omega) = \frac{-2\omega}{\pi} \mathrm{Im}\{\hat{\mathbf{n}} \cdot \tilde{G}(\mathbf{R}, \mathbf{R}, q, \omega) \cdot \hat{\mathbf{n}}\} = \frac{1}{L} \rho_{\hat{\mathbf{n}}}(\mathbf{R}, q, \omega). \quad (16)$$

Finally, combining Eqs. (11) and (16), one finds a relation between the loss probability per unit of path length and the LDOS,

$$\frac{\Gamma(\mathbf{R}_0, \omega)}{L} = \frac{2\pi e^2}{\hbar\omega} \tilde{\rho}_{\hat{\mathbf{z}}}(\mathbf{R}_0, q, \omega), \quad (17)$$

with $q = \omega/v$.

Equation (17) provides a solid link between LDOS and EELS in a wide class of geometries that includes aloof trajectories in semi-infinite surfaces and thin films. Interestingly, only $q > \omega/c$ values are probed, lying outside the light cone, and therefore difficult to study via optical techniques. Trapped modes such as surface-plasmon polaritons lie in that region and are a natural target for application of our results. Besides, the present study can be directly applied to cathodoluminescence (CL) in all-dielectric structures, in which energy loss and CL emission probabilities are identical.

A connection between the photonic density of states in momentum space and EELS has been previously reported for electrons moving parallel to pores in 2D self-assembled alumina photonic crystals [11]. However, the above derivation is the first proof to our knowledge that a formal relation exists between LDOS and EELS.

For illustration, we offer in Fig. 1 the EELS probability for electrons moving inside a finite hexagonal 2D crystal of aligned Si nanowires, calculated with the boundary element method (BEM) [20]. The photon wavelength range under consideration includes two Mie modes of the isolated wire (broken curve), and significant hybridization between neighboring wires takes place in the array. The loss probability varies relatively smoothly with impact parameter, a behavior which was expected in the LDOS for photon wavelengths relatively large compared to the diameter of the cylinders. Interestingly, the loss probability takes significant values in the interstitial regions, several tens of nanometers away from the Si. Finite structures like that considered in Fig. 1 present a colorful evolution of modes, the analysis of which can be useful for instance in the design of microlaser cavities. In infinite crystals, the loss probability exhibits van Hove singularities [21], which follow rigorously those of the LDOS in translationally invariant systems according to Eq. (17).

Planar geometries.—As microchip features continue to shrink, lithographically patterned metal structures are becoming natural candidates to replace current electronic microcircuits. The new structures will operate at frequencies above the terahertz rather than gigahertz, and will carry electric signals strongly mixed with the electromagnetic fields that they generate in what is known as surface plasmons. The optical properties of metallic planar structures are routinely obtained using scanning near-field optical microscopy, although the lateral resolution of this technique can hardly reach 50 nm. Here again EELS renders much higher lateral resolution (down to the nanometer) and permits obtaining information directly related to the LDOS. Besides the formal relation between EELS and the momentum-resolved LDOS expressed in Eq. (11), we offer in Fig. 2 a more detailed comparison between EELS and $\rho(\mathbf{r}, \omega)$ (local in all spatial directions) for an Ag disk calculated with BEM [20]. This figure proves how the EELS probability can mimic quite closely $\rho_z(\mathbf{r}, \omega)$, with z perpendicular to the planar structure and parallel to the electron velocity. This resemblance holds for different accelerating voltages, making the interpretation robust with respect to experimental details. Figure 2 provides a solid example supporting the use of EELS to measure

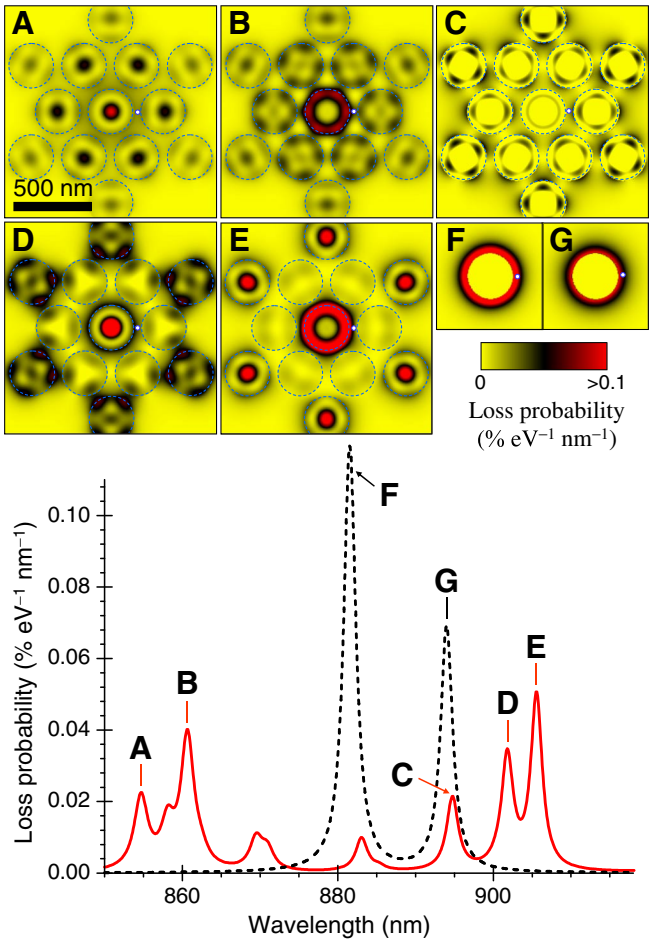

FIG. 1 (color online). EELS probability for 200-keV electrons moving parallel to an array of 13 Si nanowires of 300 nm in diameter (solid curve), as compared to an isolated nanowire (broken curve). The nanowires are arranged in a hexagonal lattice with a period of 350 nm. The contour-plot insets show the impact-parameter dependence of the EELS probability for selected energy losses (labeled A–G), with the position of the electron beam considered in the curves indicated by an open symbol and the cylinder contours shown by dashed curves.

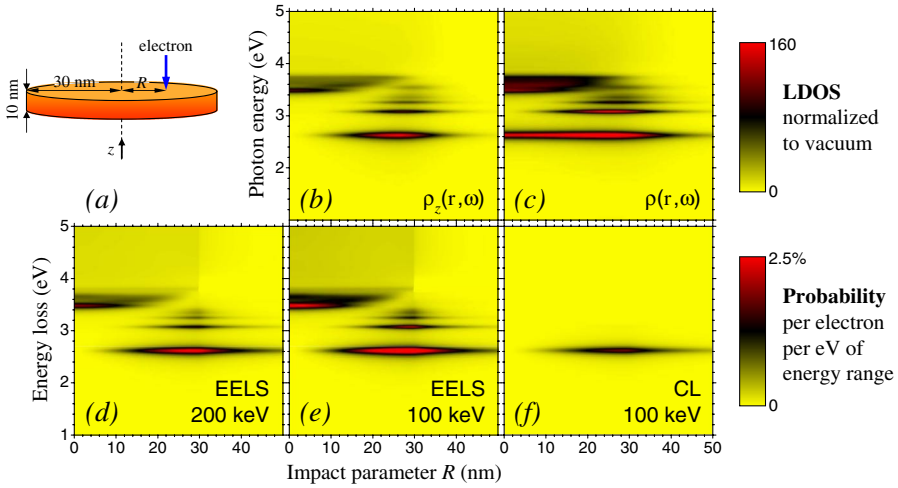

FIG. 2 (color online). Relation between EELS and LDOS in planar geometries. (a) We consider an Ag disk of height 10 nm and radius 30 nm. The electrons move along z, perpendicular to the disk. The EELS probability for 200-keV (d) and 100-keV (e) electrons mimics closely the z-projected LDOS in a plane 10 nm above the disk (b), and less closely the unprojected LDOS ($\rho = \rho_x + \rho_y + \rho_z$) (c). The CL emission only picks up part of the inelastic signal (f).

plasmon intensities with unprecedented lateral resolution. A first demonstration of such types of measurements has been recently reported [3].

We thus conclude that the energy loss probability is directly related to the local density of states in arbitrary systems, where we understand locality in real space for the directions perpendicular to the electron trajectory and in momentum space along the direction of the electron velocity vector. In 2D systems and for electrons moving along the direction of translational symmetry, the loss probability is exactly proportional to the photonic local density of states projected on the trajectory and decomposed into parallel momentum transfers $\hbar q$. Numerical examples have been presented showing a similar relation between LDOS outside planar metallic disks and EELS spectra for electrons traversing them perpendicularly. Our results provide a solid foundation for the use of EELS performed in STEMs to directly probe photonic properties of nanostructures.

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[1] C. Burda, X. Chen, R. Narayanan, and M. A. El-Sayed, Chem. Rev. **105**, 1025 (2005).
[2] W. L. Barnes, A. Dereux, and T. W. Ebbesen, Nature (London) **424**, 824 (2003).
[3] J. Nelayah *et al.*, Nature Phys. **3**, 348 (2007).
[4] P. E. Batson, N. Dellby, and O. L. Krivanek, Nature (London) **418**, 617 (2002).
[5] A. Howie and R. H. Milne, Ultramicroscopy **18**, 427 (1985).
[6] D. Ugarte, C. Colliex, and P. Trebbia, Phys. Rev. B **45**, 4332 (1992).
[7] C. H. Chen and J. Silcox, Phys. Rev. Lett. **35**, 390 (1975).
[8] D. W. McComb and A. Howie, Nucl. Instrum. Methods Phys. Res., Sect. B **96**, 569 (1995).
[9] O. Stéphan *et al.*, Phys. Rev. B **66**, 155422 (2002).
[10] A. Rivacoba, N. Zabala, and J. Aizpurua, Prog. Surf. Sci. **65**, 1 (2000).
[11] F. J. García de Abajo *et al.*, Phys. Rev. Lett. **91**, 143902 (2003).
[12] There is a univocal correspondence between the spatially dependent local dielectric function and the Green tensor that works frequency by frequency, as can be clearly deduced upon inspection of Eq. (2). Furthermore, the photonic LDOS is directly obtained from the Green tensor following Eq. (3). The inverse relation is less direct, although one can extend the equivalent of Hohenberg-Konh theorem [see P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)] to light, thus asserting that there is a univocal correspondence between dielectric functions and LDOS, with both quantities defined within a finite frequency range above $\omega = 0$ (i.e., the correspondence is not local in frequency).
[13] D. P. Fussell, R. C. McPhedran, and C. Martijn de Sterke, Phys. Rev. A **71**, 013815 (2005).
[14] G. Colas des Francs *et al.*, Phys. Rev. Lett. **86**, 4950 (2001).
[15] G. D'Aguanno *et al.*, Phys. Rev. E **69**, 057601 (2004).
[16] S. M. Barnett and R. Loudon, Phys. Rev. Lett. **77**, 2444 (1996).
[17] D. P. Fussell, R. C. McPhedran, and C. Martijn de Sterke, Phys. Rev. E **70**, 066608 (2004).
[18] K. Joulain, R. Carminati, J. P. Mulet, and J. J. Greffet, Phys. Rev. B **68**, 245405 (2003).
[19] R. H. Ritchie, Phys. Rev. **106**, 874 (1957).
[20] F. J. García de Abajo and A. Howie, Phys. Rev. B **65**, 115418 (2002); Phys. Rev. Lett. **80**, 5180 (1998).
[21] L. Van Hove, Phys. Rev. **89**, 1189 (1953).