Quantum correlations in electron microscopy: supplement

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Supplementary Material

Table of contents

S.1 Derivation of the electron's reduced density matrix when interacting with a general optical environment

In this section, we develop analytical expressions for the electron reduced density matrix after its interaction with a general electromagnetic environment. The derivation is based on the formalism of macroscopic quantum QED [4,8], linking the quantum properties of the electron to the classical properties of the electromagnetic fields. In subsection S.1.1 we derive the density matrix for the specific case when the initial electron state is a coherent plane wave, and in subsection S.1.2 we generalize our derivations to the case of a general initial density matrix.

S.1.1 Derivation in the case of an initial coherent plane wave

We describe the interaction as a perturbation of the minimal coupling Hamiltonian of quantum electrodynamics (QED) on a relativistic free electron. We use second quantization and the Coulomb gauge for the electromagnetic vector potential and write the Hamiltonian of the whole system

$$H = H_\text{e} + H_\text{em} + H_\text{int} \tag{S1}$$

where $H_\text{e} = \mathbf{p}^2/2m\gamma$ is the electron's Hamiltonian, $H_\text{em} = \int d\mathbf{r} \int d\omega \, \hbar\omega[\hat{\mathbf{f}}^\dagger(\mathbf{r}, \omega) \cdot \hat{\mathbf{f}}(\mathbf{r}, \omega)]$ describes the electromagnetic field (omitting the zero-point energy), and $H_\text{int} = \frac{e}{m\gamma}\mathbf{A}(\mathbf{r}) \cdot \mathbf{p}$ is the interaction Hamiltonian. Note that the Hamiltonians relevant for the electron (H_e and H_int) are valid only for paraxial electron beams [1], which is indeed the case analyzed in this paper. In these expressions, m denotes the electron mass, γ is the Lorentz factor, $\mathbf{p}$ is the electron momentum operator and $\mathbf{A}(\mathbf{r})$ is the electromagnetic vector potential operator. The appearance of γ constitutes the relativistic correction to the electron mass. According to macroscopic QED, the electromagnetic vector potential can be written as:

$$\mathbf{A}(\mathbf{r}) = \sqrt{\frac{\hbar}{\pi\epsilon_0}\frac{1}{c^2}} \int \omega d\omega \int d\mathbf{r}' \sqrt{\text{Im}\,\epsilon(\mathbf{r}',\omega)}\,\overline{\overline{\mathbf{G}}}(\mathbf{r},\mathbf{r}',\omega)\hat{\mathbf{f}}(\mathbf{r}',\omega) + \text{h.c.} \qquad (S2)$$

where $\hbar$ is the reduced Planck constant, ϵ_0 is the vacuum permittivity, and c is the speed of light. In equation (S2), the macroscopic optical properties of any general structure are described using the imaginary part of the relative permittivity, $\text{Im}\big(\epsilon(\mathbf{r}',\omega)\big)$, and the medium's dyadic Green's function, $\overline{\overline{\mathbf{G}}}(\mathbf{r},\mathbf{r}',\omega)$ that satisfies $\nabla \times \nabla \times \overline{\overline{\mathbf{G}}} - \epsilon(\mathbf{r},\omega)\frac{\omega^2}{c^2}\overline{\overline{\mathbf{G}}} = \delta(\mathbf{r}-\mathbf{r}')\overline{\overline{\mathbf{1}}}$. The optical excitation annihilation operator, $\hat{\mathbf{f}}(\mathbf{r}',\omega) = \big(\hat{f}_x(\mathbf{r}',\omega),\hat{f}_y(\mathbf{r}',\omega),\hat{f}_z(\mathbf{r}',\omega)\big)$, and creation operator, $\hat{\mathbf{f}}^\dagger(\mathbf{r}',\omega)$, satisfy the bosonic commutation relations $\big[\hat{f}_i(\mathbf{r},\omega),\hat{f}_j^\dagger(\mathbf{r}',\omega')\big] = \delta_{ij}\delta(\omega-\omega')\delta(\mathbf{r}-\mathbf{r}')$ [4,8].

We describe the effect of the interaction Hamiltonian within first-order time-dependent perturbation theory, such that the Hamiltonian itself acts at most once on the joint wavefunction of the electron and the excitations. In the bra-ket notation, the joint wavefunction is written as a tensor-product of the states of the electron and the excitations: $|\psi(\mathbf{x}\omega j)\rangle_{\text{e}}|1_{\mathbf{x}\omega j}\rangle_{\text{exc}}$, such that $|1_{\mathbf{x}\omega j}\rangle_{\text{exc}} = f_j^\dagger(\mathbf{x},\omega)|0\rangle_{\text{exc}}$. Meaning, $|\psi(\mathbf{x}\omega j)\rangle_{\text{e}}$ is the wavefunction of the electron after exciting a dipole at location $\mathbf{x}$, direction j and frequency ω. Using these definitions and the interaction Hamiltonian in Eqs. (S1,S2), we obtain the electron wavefunction in the momentum basis after interacting with a specific optical excitation $(\mathbf{x}\omega j)$. We expand the post-interaction electron state (which is now coupled to the optical excitation), to first-order in perturbation theory. The electron wavefunction due to the interaction is $|\psi(\mathbf{x}\omega j)\rangle_{\text{e}} = \frac{e}{m\gamma}\mathbf{A}_{\mathbf{x}\omega j}\cdot\mathbf{p}|\psi_0\rangle_{\text{e}}$, where

$\mathbf{A}_{\mathbf{x}\omega j}(\mathbf{r}) = \sqrt{\frac{\hbar}{\pi\epsilon_0}\frac{1}{c^2}}\omega\sqrt{\text{Im}\,\epsilon(\mathbf{x},\omega)}\big(\sum_m G_{mj}^\dagger(\mathbf{r},\mathbf{x},\omega)\big)$ captures the optical excitation and $\mathbf{p} = -i\hbar\overline{\nabla}$. Then, by assuming the initial electron state as a plane wave in the z direction, the momentum representation of the electron becomes

$$\langle \mathbf{k} | \psi(\mathbf{x}\omega j) \rangle_e = \frac{i}{\hbar} \frac{e}{\gamma m} \int dt \, \langle \mathbf{k} | \mathbf{A}(\mathbf{r}) \cdot \mathbf{p} | \psi_0 \rangle$$

$$= -i \frac{e v_0}{4\pi c^2} \sqrt{\frac{1}{2\hbar\epsilon_0}} \omega \sqrt{\mathrm{Im}\,\epsilon(\mathbf{x}, \omega)} \, \delta(\omega - v_0 |\mathbf{k}_0 - \mathbf{k}|_z) \int d\mathbf{r} \, e^{i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}} G_{zj}^\dagger(\mathbf{r}, \mathbf{x}, \omega) \qquad \text{(S3)}$$

where e is the electron charge, and v_0, $\mathbf{k}_0$ are the initial electron's velocity and wave vector, respectively.

After the interaction, the electron and the optical excitations are entangled. To find the reduced electron density matrix, we trace-over [3] the optical excitations' degrees of freedom in the joint density matrix,

$$\rho_e = \mathrm{Tr}_{\mathrm{exc}}\{\rho_{\mathrm{joint}}\} = \sum_j \int d\mathbf{x} \int d\omega \, |\psi(\mathbf{x}\omega j)\rangle_e \langle \psi(\mathbf{x}\omega j)|_e.$$

Expressing the last result in the three-dimensional electron momentum basis, the reduced electron density matrix becomes

$$\rho_e(\mathbf{k}, \mathbf{k}') = \left(\frac{e}{4\pi c} \sqrt{\frac{1}{2\hbar\epsilon_0}} \right)^2 \int d\omega \int d\mathbf{r}' d\mathbf{r}'' e^{i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}'} e^{-i(\mathbf{k}_0 - \mathbf{k}') \cdot \mathbf{r}''} \mathrm{Im}\, G_{zz}(\mathbf{r}', \mathbf{r}'', \omega) , \qquad \text{(S4)}$$

where we have used the identity $\frac{\omega^2}{c^2} \int d\mathbf{x} \, \mathrm{Im}\epsilon(\mathbf{x}, \omega) \overline{\overline{G}}(\mathbf{r}, \mathbf{x}, \omega) \overline{\overline{G}}^\dagger(\mathbf{r}', \mathbf{x}, \omega) = \mathrm{Im}\, \overline{\overline{G}}(\mathbf{r}, \mathbf{r}', \omega)$ [4]. Eq. (S4) emphasizes the important use of the macroscopic QED formalism, as it is completely general, for any optical excitation in any optical media. Moreover, the equation can be seen as a nonlocal generalization of the results in Ref. [9].

In a standard microscope, the electron spatial detector is a two-dimensional; therefore, we describe the wavefunction according to the electron's transverse coordinate, $\mathbf{r}_T$, immediately after

the interaction with the sample. Accordingly, we can express Eq. (S4) in the transverse position basis of the electron:

$$\rho_e(\mathbf{r}_T, \mathbf{r}_T', \omega) = \frac{\alpha}{\pi^2} \frac{1}{cS} \int dz\, dz'\, e^{i\frac{\omega}{v_0}(z-z')} \mathrm{Im}\, G_{zz}(\mathbf{r}_T, z;\, \mathbf{r}_T', z';\omega) \qquad (S5)$$

where S is the electron beam area and α is the fine-structure constant. Reaching Eq. (S5) concludes the derivation of this part, yielding Eq. (3) in the main text.

Notably, our treatment can be generalized to calculate the density matrix at finite times. This possibility can cause an interference between energy components and add noise to the system. To find the electron density matrix at time t, assuming that the density matrix in some initial time (e.g., $t = 0$) is known, we integrate the S-matrix element $\frac{i}{\hbar} \frac{e}{\gamma m} \int dt\, \langle \mathbf{k}|\mathbf{A}(\mathbf{r}) \cdot \mathbf{p}|\psi_0 \rangle$ over a finite time interval. This integration effectively replaces the delta function in energy by a sinc function. Then, the reduced density matrix, which follows from integrating over all EM field frequencies (and positions), is given by.

$$\rho_e(\mathbf{r}_T, \mathbf{r}_T'; \Delta E) \propto \int d\Omega\, \mathrm{sinc}^2\left[\frac{t}{2\pi}\left(\Omega - \frac{\Delta E}{\hbar}\right)\right] \int dz\, dz'\, e^{i\frac{\Omega}{v_0}(z-z')} \mathrm{Im}\, G_{zz}(\mathbf{r}_T, z;\, \mathbf{r}_T', z';\Omega).$$

Here, the fundamental energy-time uncertainty relation is manifested by the sinc function, and there are indeed multiple frequencies involved in the determination of the energy-resolved electron density matrix in short interaction times. This finite-time formula could have interesting consequences, for example, if measuring the electron at short distances after an interaction, because that could create additional uncertainty. We note that this usage of time-dependent perturbation theory might not be gauge invariant in the special case where the electron is measured while still being under the influence of the interaction. In the general case of electron microscopy,

the electron is measured a long time after the interaction has ended, yet we believe that this special case of measurement during interaction could be interesting for future work.

S.1.2 Electron-source imperfections

In this subsection, we discuss electron-source imperfections and their effects on the theoretical predictions. Furthermore, we generalize Eq. (S5) to the case of a general electron density matrix.

The situation of an initial plane-wave electron, which the derivation in S.1.1 assumes, could be altered in a number of ways. First, the electron state could be composed of a (pure) superposition of momentum components, both in the transverse direction or longitudinal direction. Second, the electron could be generated in a mixed state, for example in the energy basis, manifested in an initial energy spread.

One interesting mathematical difference between the cases of coherent and incoherent superposition of electron momenta lies in the partial trace stage. In this stage, the electron-excitation pure state is transformed to an electron-only mixed state in the following manner: for every final state of the excitations, the corresponding electron (pure) state is obtained. As a result, the final electron density matrix is an incoherent sum of the above pure states. In the initially plane-wave electron, the spontaneous emission process (due to momentum conservation) yields a single electron contribution for each excitation final state. However, when the electron is initially a (pure) wavepacket, each final excitation state has contributions from multiple electron momenta, which are summed coherently. However, in the mixed-state case all the contributions are summed incoherently.

In both cases, as seen in the derivation below, the inclusion of additional initial momentum-components means that the electron diffraction pattern (obtained by our derivation) is convolved with the initial momentum distribution. This convolution occurs coherently or incoherently,

depending on the coherence between the different initial momentum components. As a result, there would be different smearing effects of the diffraction pattern, and a decrease in the image resolution.

We now generalize Eq. (S5) to the case where the electron is initially described by a general density matrix in the momentum basis $\rho_i(\mathbf{k}_i, \mathbf{k}_i')$, with carrier velocity v_0 oriented in the z direction. Similarly to subsection S.1.1, we still assume the validity of the paraxial and no-recoil approximations, and that the electron momentum spread in the longitudinal direction is small. We use Eqs. (S1, S2) to write the following general relation between the initial (ρ_i) and final (ρ_f) electron density matrices:

$$\rho_f(\mathbf{k}_f, \mathbf{k}_f') = \sum_{\mathbf{k}_i, \mathbf{k}_i'} \rho_i(\mathbf{k}_i, \mathbf{k}_i') \sum_{\mathbf{r}\omega\alpha} M_{\mathbf{k}_i \rightarrow \mathbf{k}_f \mathbf{r}\omega\alpha} M^*_{\mathbf{k}_i' \rightarrow \mathbf{k}_f' \mathbf{r}\omega\alpha} \tag{S6}$$

where $M_{\mathbf{k}_i \rightarrow \mathbf{k}_f \mathbf{r}\omega\alpha}$ is the matrix element of the interaction, which is written in an explicit form in Eq. (S3). Using this explicit form of $M_{\mathbf{k}_i \rightarrow \mathbf{k}_f \mathbf{r}\omega\alpha}$, we arrive at this relation between the electron initial and final density matrices and the Green's function, all in their momentum basis:

$$\rho_f(\mathbf{k}_f, \mathbf{k}_f') = \frac{1}{S} \int d\mathbf{k}_i d\mathbf{k}_i' \rho_i(\mathbf{k}_i, \mathbf{k}_i') \delta(E_i' - E_f' - E_i + E_f) \left[\mathbf{v}_i \mathrm{Im}\, \mathbf{G}\left(\mathbf{k}_i' - \mathbf{k}_f', \mathbf{k}_i - \mathbf{k}_f, \frac{E_i - E_f}{\hbar} \right) \mathbf{v}_i' \right] \tag{S7}$$

Where $\mathbf{v}_i = \frac{\hbar \mathbf{k}_i}{\gamma m}$. It is evident that the final density matrix is given by the two-sided convolution with the response function $\mathrm{Im}\, \mathbf{G}(\mathbf{k}_i - \mathbf{k}_f, \mathbf{k}_i' - \mathbf{k}_f', \omega)$. For the next steps, we use the approximation for the electron initial velocity $v_0 \cong \frac{\hbar k_i}{m}\hat{\mathbf{z}} \cong \frac{\hbar k_i'}{m}\hat{\mathbf{z}}$, and the no-recoil approximation ($\frac{E_i - E_f}{\hbar} \cong (\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{v}_0$), as used in the plane-wave derivation. Using the transformation to the position basis of all quantities, we arrive at the final general result:

$$\rho_f(\mathbf{r}_T, \mathbf{r}'_T, \omega) = \rho_i(\mathbf{r}_T, \mathbf{r}'_T) \cdot \frac{\alpha}{\pi^2} \frac{1}{c} \int dz\, dz'\, e^{i\frac{\omega}{v_0}(z-z')} \operatorname{Im} G_{zz}(\mathbf{r}_T, z;\, \mathbf{r}'_T, z'; \omega)\,. \qquad \text{(S8)}$$

As seen in Eq. (S8), the final electron density matrix is a product of its initial density matrix and the effects of the optical excitations, identically to Eq. (S5). Meaning, the electron coherence still captures the coherence of the sample, but up to its initial coherence. In the momentum basis, by the convolution theorem, this statement corresponds to convolution of the initial electron's momentum distribution and the sample's momentum-response, as apparent in Eq. (S7).

S.2. The case of surface plasmon polaritons (SPPs)

In this section, we analyze the case of interaction with SPPs. In subsection S.2.1 we analyze the density matrix in terms of coherence, proving Eq. (5) from the main text. In subsection S.2.2 we provide information regarding our simulation and theoretical fitting done in Fig. 2(d) in the main text. In subsection S.2.3 we provide the simulation parameters used for obtaining Fig. 2 in the main text.

S.2.1 The coherence of the electron

In this subsection, we analyze the density matrix of the electron in terms of its coherence. In a similar manner to classical optics [6], we can define the coherence of the electron wave:

$$\gamma(\mathbf{r}_T, \mathbf{r}_T') = \frac{\rho_e(\mathbf{r}_T, \mathbf{r}_T')}{\sqrt{\rho_e(\mathbf{r}_T, \mathbf{r}_T)}\sqrt{\rho_e(\mathbf{r}_T', \mathbf{r}_T')}}$$

Intuitively, this quantity measures the phase-correlation between the points $\mathbf{r}_T, \mathbf{r}_T'$ on the electron density matrix. The electron's spatial coherence is 1 (in absolute value) when the phases at these two points are completely correlated, and 0 when they completely uncorrelated. The correlation of phases determines, for example, the result of a double-slit experiment done with the slits at $\mathbf{r}_T, \mathbf{r}_T'$; complete correlation implies maximal interference (with visibility that depends on the diagonal terms of ρ_e) and vanishing correlation implies no interference.

In our scenario, where the optical excitations lie in a translation-invariant sample, the electron coherence is a convenient metric to analyze the post-interaction electron, and accordingly the interaction itself. As the optical excitations, the coherence is translation-invariant and can be obtained directly from the diffraction image of the electron. Let us derive this result. For readability, we omit the ω argument of ρ_e, but the derivation applies in the energy-filtered case as

10

well. We start from the definition of $\gamma(\mathbf{r}_T, \mathbf{r}'_T)$,and write $\rho_e(\mathbf{r}_T, \mathbf{r}'_T)$ in the transverse momentum basis, using a Fourier relation. We exploit the fact that ρ_e is diagonal in the momentum basis, and derive Eq. (S9), which is identical to Eq. (6) from the main text:

$$\gamma(\mathbf{r}_T, \mathbf{r}'_T) = \gamma(\Delta\mathbf{r}_T) = \frac{\rho_e(\Delta\mathbf{r}_T)}{\rho_e(\mathbf{0})} = \frac{\int \rho_e(\mathbf{k}_T)e^{i\mathbf{k}_T \cdot \Delta\mathbf{r}_T}\,d\mathbf{k}_T}{\int \rho_e(\mathbf{k}_T)\,d\mathbf{k}_T} \tag{S9}$$

where we used $\Delta\mathbf{r}_T = \mathbf{r}_T - \mathbf{r}'_T$. This expression resembles the Van Cittert-Zernike theorem [2] from classical optics.

S.2.2 Fitting to experimental data

In order to validate our theory, we compare Eq. (S9) to previous experiments in the literature. The result of the comparison is depicted in Fig. 2(d) in the main text. For comparison, we used the experimental data from Fig. 3(c) in [7], presenting the electron spatial coherence after interacting with 15.5 eV plasmons in Aluminum (separating the spatial decoherence from the temporal decoherent due to the energy difference of inelastically-scattered electrons). The coherence values in the experiment are normalized to that in the zero-loss results [7], that is, we normalized the results to include electron preparation imperfections that can impair its coherence regardless of its interaction with the plasmons. Our derivations in subsection S.1.2, and specifically Eq. (S8), capture the limited electron coherence before the interaction, which also appears in [7].

Our theoretical curve, colored in red in Fig. 2(d) in the main text, is simulated based on the experimental data given in Ref. [7]. In order to have realistic parameters of the material itself, which are necessary for computing its Fresnel reflectance coefficient (see Eq. (4) in the main text), we use the Drude model for the frequency-dependent permittivity and conductivity. The

parameters for the Drude model for Aluminum are taken from Ref. [5]. Using the Fresnel coefficients, we have computed the Green's function (Eq. (4) in the main text), and eventually the electron's density matrix (Eq. (5) in the main text). The coherence was obtained from the density matrix using Eq. (S9), as would be done in an experimental implementation of this method.

S.2.3 SPP simulation Parameters

In the results presented in the paper, including Fig. 2(b-c), we have used a 10 nm thick metallic slab, with permittivity obeying the Drude model and the following parameters: plasma frequency $\hbar\omega_{\mathrm{p}} = 8.5$ eV and relaxation time of $\tau = 2$ fs. Additionally, the electron kinetic energy was 300 keV, and the width of EELS energy filter was 0.05 eV. For wider energy filters, the bandwidth will convolve with the numerical results, e.g., broaden Fig. 2(b) vertically, and decrease the spatial coherence in Fig. 2(c). The range of energies used for Fig. 2(b) is $0 - 6.5$ eV.

S.3. The case of nanoparticles

In this section, we analyze the case of interaction with a nanoparticle. In subsection S.3.1 we derive the density matrix of the electron after the interaction (Eq. (7) in the main text). In subsection S.3.2 we analyze the interaction in terms of the entanglement created between the electron and the optical excitations. In subsection S.3.3 we elaborate on the ability to extract and calculate the entanglement created in the interaction from standard experimental data. In subsection S.3.4 we provide the simulation parameters used for obtaining Fig. 3 in the main text.

S.3.1 Derivation of the electron density matrix

In this subsection, we derive the electron density matrix in case of interaction with a nanoparticle. We start from Eq. (S5) and set the electromagnetic Green's function to that of a single dipole located in the origin. This Green's function can be written as:

$$\overline{\overline{G}}(\mathbf{r},\mathbf{r}',\omega) = \omega^2 \mu_0 \overline{\overline{G}}_{\text{fs}}(\mathbf{r},\mathbf{0},\omega)\overline{\overline{\alpha}}(\omega)\overline{\overline{G}}_{\text{fs}}(\mathbf{0},\mathbf{r}',\omega) \qquad (S8)$$

where μ_0 is the magnetic permeability of the vacuum, $\overline{\overline{G}}_{\text{fs}}(\mathbf{x},\mathbf{y},\omega)$ is the Green's function of free space ($\epsilon(\mathbf{r},\omega) = 1$) and $\overline{\overline{\alpha}}(\omega)$ is the frequency-dependent polarizability tensor of the nanoparticle. This Green's function represents the process of the electron in $\mathbf{r}'$ that excites a dipole located in $\mathbf{x} = \mathbf{0}$, which itself creates an electric field in $\mathbf{r}$. The expression for $\overline{\overline{G}}_{\text{fs}}(\mathbf{r},\mathbf{r}',\omega)$ can be written as $\overline{\overline{G}}_{\text{fs}}(\mathbf{r},\mathbf{r}',\omega) = \left(\overline{\overline{I}} + \frac{1}{k^2}\overline{\nabla}\overline{\nabla}\right)g(R)$, where $\overline{\overline{I}}$ is the identity tensor, $k = \frac{\omega}{c}$, $\overline{\nabla}$ is the gradient operator, and $g(R) = \frac{e^{ikR}}{4\pi R}$, with $R = |\mathbf{r} - \mathbf{r}'|$. From these expressions, a straightforward calculation yields the different components of the Green's tensor that can be excited by a z-direction dipole, $G_{\text{fs}_{xz}} = -k\frac{k^2 xz}{4\pi k^5 R^5}e^{ikR}(k^2R^2 + 3ikR - 3)$ (and symmetrically for y), and $G_{\text{fs}_{zz}} = k\frac{1}{4\pi k^3 R^3}e^{ikR}\left[k^2R^2 + \right.$

13

$(ikR - 1) - \frac{z^2}{R^2}[(k^2 R^2 + 3ikR - 3)]\Big]$. Note that $G_{\mathrm{fs}_{xz}}, G_{\mathrm{fs}_{yz}}$ are z-anti-symmetric while $G_{\mathrm{fs}_{zz}}$ is

symmetric in z. These properties would be reflected in the electron's density matrix.

We use Eq. (S8) for the Green's function and its explicit form and calculate the density

matrix from Eq. (S5). The result has a very similar form to Eq. (S8), and can be written as follows:

$$\rho_e(\boldsymbol{r}_{\mathrm{T}}, \boldsymbol{r}_{\mathrm{T}}', \omega) = \frac{\alpha}{\pi^2} \frac{1}{cS} \omega^2 \mu_0 \boldsymbol{\psi}(\mathbf{r}_T, \omega) \cdot \mathrm{Im}\{\bar{\bar{\boldsymbol{\alpha}}}(\omega)\} \cdot \boldsymbol{\psi}'^*(\mathbf{r}_{\mathrm{T}}', \omega) \tag{S9}$$

where α is the fine-structure constant. The functions $\boldsymbol{\psi}(\mathbf{r}_T, \omega) = \psi_T(r_T, \omega)\hat{\mathbf{r}}_T + \psi_z(r_T, \omega)\hat{\mathbf{z}}$ and

$\boldsymbol{\psi}'^*(\mathbf{r}_T', \omega) = \psi_T^*(r_T', \omega)\hat{\mathbf{r}}_T' + \psi_z^*(r_T', \omega)\hat{\mathbf{z}}'$ denote the spatial wavefunction of the electron after

interacting with an oscillating dipole with frequency ω in the transverse direction (ψ_T) or z

direction (ψ_z). The functions $\psi_{T,z}$ are the result of an overlap integral of the electron wavefunction

and the electromagnetic field (of a transverse- or z- oriented dipole), as written in Eq. (S5). Since

the Green's function is spherically symmetric, but the overlap integral is along the z-axis only, the

functions $\psi_{T,z}$ can be written in the following form:

$$\psi_T(\mathbf{r}_T) = \frac{1}{4\pi} \int_{-\infty}^{\infty} k \, dz \, e^{i\frac{c}{v_0}kz} \frac{k^2 |\mathbf{r}_T| z}{k^5 R^5} e^{ikR}(k^2 R^2 + 3ikR - 3) \tag{S10}$$

$$\psi_z(\mathbf{r}_T) = \frac{1}{4\pi} \int_{-\infty}^{\infty} k \, dz \, e^{i\frac{c}{v_0}kz} \frac{1}{k^3 R^3} e^{ikR}\left[k^2 R^2 + (ikR - 1) - \frac{z^2}{R^2}[(k^2 R^2 + 3ikR - 3)]\right] \tag{S11}$$

where here $R = R(\mathbf{r}_T, z) = \sqrt{|\mathbf{r}_T|^2 + z^2}$ is a function of z (the integration variable), and we

defined $k = \frac{\omega}{c}$. Notably, the functions $\psi_{T,z}$ are dimensionless and depend on $\mathbf{r}_T$ both explicitly

(through $|\mathbf{r}_T|$) and implicitly (through R). The similarity between the expressions of $G_{\mathrm{fs}_{xz}}, G_{\mathrm{fs}_{yz}}$

and ψ_T, as well as $G_{\text{fs}_{zz}}$ and ψ_z, is apparent from the direct connection between the electric field that the electron produces and the way the electron wavefunction changes.

We note several facts about $\psi_{T,z}$. First, both have azimuthal symmetry (depend only on $|\mathbf{r}_T|$). Second, we can see the conjugation of the spatial variables z, R to k which leads that k determines the length-scale of the functions $\psi_{T,z}$. Third, the only dependence of these functions on the properties of the electron is through its velocity, v_0, inside the exponential term. As a result, different electron velocities "sample" different spatial Fourier-components of the electromagnetic field. The choice of different Fourier components by different electron velocities can be noticed also by the expressions of $G_{\text{fs}_{xz}}, G_{\text{fs}_{yz}}, G_{\text{fs}_{zz}}$. The functions $\psi_T(\mathbf{r}_T), \psi_z(\mathbf{r}_T)$ are depicted in Fig. 3(a) in the main text.

S.3.2 Investigation of the entanglement

In this subsection, we analyze properties of the interaction with nanoparticles in terms of the entanglement formed during the interaction. We start from the electron density matrix in this case (Eq. (S9)) and quantify the entanglement in different cases through the purity measure [3]. For the mathematical analysis, we note that in this case, the electron state can be regarded as a 3-level system, instead of the representation offered in Eq. (S9) in 2 spatial dimensions. This "dimensionality reduction", is possible due to the discrete number of different outcomes: the electron can be scattered by an x-, y- or z- dipole excitation, and for each excitation the electron (spatial) wavefunction is determined by Eq. (S10, S11). Using this approach, we use the bra-ket notation to represent the electron density matrix and calculate the necessary components for the calculation of the purity.

We transform the density matrix in Eq. (S9) to the bra-ket notation of a 3-level system. For that, let us define a three-dimensional vector basis, denoted as $|\psi_j\rangle$ for $j = x, y, z$, such that $\langle \mathbf{r}_T | \psi_j \rangle = \psi_j(\mathbf{r}_T)$. Specifically, this means that $\langle \mathbf{r}_T | \psi_x \rangle = \psi_T(|\mathbf{r}_T|) \cdot (\mathbf{r}_T \cdot \hat{\mathbf{x}})$, and similarly for y, and $\langle \mathbf{r}_T | \psi_z \rangle = \psi_z(|\mathbf{r}_T|)$. Each $|\psi_j\rangle$ denotes the electron wavefunction after interacting with a dipole oriented in the j direction. Although the basis $|\psi_{x,y,z}\rangle$ is an orthogonal set ($\langle \psi_i | \psi_j \rangle = 0 \Leftrightarrow i \neq j$), this set, and thus also the density matrix ρ_e, is not normalized because it possess information about the probability of interaction for each dipole orientation. The fact that ρ_e is not normalized for all orientations, but to each orientation, is important for the entanglement calculation. Using this notation, we rewrite Eq. (S9) in the ket-bra notation,

$$\rho_e(\omega) = \left[\frac{\alpha}{\pi^2} \frac{1}{cS} \omega^2 \mu_0 \right] \sum_{i,j=x,y,z} \text{Im}\{\bar{\bar{\alpha}}(\omega)\}_{ij} |\psi_i\rangle\langle\psi_j| \tag{S12}$$

In Eq. (S12), the density matrix in the $|\psi_{x,y,z}\rangle$ basis is exactly the imaginary part of the polarizability tensor, $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$, up-to a global factor which accounts for global cross-section of the interaction.

The connection between the matrices $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$ and ρ_e is not entirely straightforward. The matrix $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$ indeed dictate some properties of ρ_e, such as number of eigenstates. However, the exact numerical spread of the eigenvalues, which determines the numerical value of the entanglement, differs between $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$ and ρ_e. This difference arises from the difference in the weights of each axes x, y, z according to the normalization of its basis vector, $\langle \psi_i | \psi_i \rangle = ||\psi_i||^2$. In our setup, there is an azimuthal (x-y) symmetry in terms of the interaction, making $||\psi_x||^2 = ||\psi_y||^2 = ||\psi_T||^2 \neq ||\psi_z||^2$. Thus, only $\bar{\bar{\alpha}}$ can break this azimuthal symmetry, for example in case

of a nano-rod oriented along the x-y plane. As a result, the transformation from $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$ to ρ_e does not affect the relative strength of the x, y components, only their relative strength compared to the z components. Therefore, we also understand that the eigenstates of $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$ are equal to the eigenstates of ρ_e, up to re-scaling of the x, y components relative to the z component.

This analysis has several consequences. First, the number of non-zero eigenvalues of $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$ equals the number of non-zero eigenvalues of ρ_e (and of ρ_e^2). Consequently, the minimal electron purity is determined by the number of non-zero eigenstates of $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$, which in our case relates to the geometrical dimension of the nanoparticle. Second, if $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$ has no z components, then the matrices $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$ and ρ_e are exactly the same (up-to a pre-factor), both in eigenstates and eigenvalues. Third, by setting a different $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$ (e.g. by changing the geometry of the nanoparticle, rotating it, or choosing a different excitation energy), one can change the relative strength between the z- and the x, y- eigenvalues, thus varying the electron purity. A special consequence, presented in Fig. 4 in the main text, is that the electron purity depends on the energy of the dipolar excitation when both transverse (x, y) and longitudinal (z) components exists in the nanoparticle.

S.3.3 Calculating the entanglement from experimental data

In this subsection, we present how our formalism enables calculating the entanglement created in the interaction from electron intensity images. In the end of this subsection, we comment on possible generalization of this method to other scenarios in electron microscopy.

We exploit our previous knowledge on the form of the electron density matrix ρ_e from Eq. (S12), as an incoherent sum of known wavefunctions (ψ_T, ψ_z) with unknown coefficients

($\text{Im}\{\overline{\overline{\boldsymbol{\alpha}}}(\omega)\}$). The electron purity, quantifying the entanglement created in the interaction, can be calculated from eigenvalues of ρ_{e} (see elaborated discussion in section S.4). In principle, these eigenvalues can be either measured directly, or calculated from a full reconstruction of ρ_{e}. From Eq. (S12), we see that it is convenient to work in the basis of $\{|\psi_x\rangle, |\psi_y\rangle, |\psi_z\rangle\}$, in which ρ_{e} is essentially a 3-by-3 matrix, whose elements have a known spatial form, and with unknown coefficients. Therefore, our approach is to calculate the eigenvalues of ρ_{e} based on our partial knowledge on its eigenstates, from standard electron intensity images.

In our context, using our knowledge on the electron density matrix, the process of extracting the electron purity from a single electron image is equivalent to the process of extracting the coefficients of the matrix $\text{Im}\{\overline{\overline{\boldsymbol{\alpha}}}(\omega)\}$ from that image. This matrix is composed of only 4 independent parameters. To see why, we regard the nanoparticles as a 3D ellipsoid with general aspect ratios, oriented along a general direction. The ellipsoid is described by 2 aspects ratios (for example, z-axis to x-axis and z-axis to y-axis), and its orientation is described by 2 angles. This is the geometrical argument for the number of parameters. Another argument for the number of independent parameters of $\text{Im}\{\overline{\overline{\boldsymbol{\alpha}}}(\omega)\}$, more algebraic in nature, is that $\text{Im}\{\overline{\overline{\boldsymbol{\alpha}}}(\omega)\}$ is a real-valued and symmetric matrix, which has 6 independent parameters; from that, we subtract 1 due to the symmetry of the interaction (and thus – the entanglement) to azimuthal rotations around the z axis, and subtract 1 due to the fact that the determinant of ρ_{e} (and thus $\text{Im}\{\overline{\overline{\boldsymbol{\alpha}}}(\omega)\}$) does not affect the purity calculation (see Section S.4 for more details). Hence, this argument yields 4 independent parameters, exactly as the geometrical argument.

Therefore, using these considerations, the purity of the electron can be calculated from a single electron image of the interaction, by fitting these 4 parameters to experimental data. However, additional knowledge on the shape of the nanoparticle helps further reducing this

number. For example, if the nanoparticle is known to be a nanorod in an unknown orientation, the number of free parameters to fit is only 2 (the angles of its orientation). More generally, standard experiments are done with some knowledge on the shape of the nanoparticle, such as aspect ratios, acquired using other imaging or fabrication methods. In this case, the only unknowns are again the 2 rotation angles. **Therefore, in the common cases the purity can be found by fitting a single electron image with only 2 parameters.**

The opposite direction should be discussed as well. In this approach, we assume full knowledge and control over $\text{Im}\{\overline{\overline{\boldsymbol{\alpha}}}(\omega)\}$, and it is the spatial form of $\{|\psi_x\rangle, |\psi_y\rangle, |\psi_z\rangle\}$ that we are after. Here, we can construct the spatial form of each function by an appropriate experiment – for each type of nanoparticle, aligned such that $\text{Im}\{\overline{\overline{\boldsymbol{\alpha}}}(\omega)\}$ is diagonal (thus so as ρ_e), measure the resultant electron image, obtaining $\left|\psi_j(\mathbf{r}_T)\right|^2$ for $j = x, y, z$. Additionally, if desired, the phase of this function can be measured using electron holograph or other interference experiments.

These considerations and experimental procedures are a direct consequence of our formalism, linking the electron images to its quantum properties such as its entanglement with the plasmonic nanostructure, quantified by its purity. Furthermore, it could potentially be applied to more complex optical environments, such as larger plasmonic structures (supporting modes in additional to the dipole modes), with the same theoretical analysis. The difference would be the types and shapes of excitable modes, for each the theoretical cross section and spatial pattern must be calculated in advanced.

There are additional physical observables that can be measured and are linked to the formation of electron-plasmon entanglement. Apart from direct measurements of both parties (mentioned in the main text), there are some further measurements that can be made on the electron

itself, characterizing its decoherence, from which the created entanglement can be calculated. For example, the process of nanoparticle-parameter fitting can be done on additional images other than the electron intensity image, for example its coherence images (presented in Fig. 3(b) in the main text), its diffraction images (similarly to the case of SPPs), and using any other optical manipulation done on the electron wave.

In fact, in terms of purity calculations, the coherence measurement has an intrinsic advantage over calculations from intensity images: in some cases, the coherence of the electron does not depend on the rotation of the nanoparticle, only on its aspect ratios (i.e. the relative size of the eigenvalues of $\text{Im}\{\bar{\bar{\alpha}}(\omega)\}$). Specifically, as explained in the caption of Fig. 3(b) in the main text, interaction with a nanorod does not create any entanglement, and a coherence measurement of the electron in this case would yield perfect coherence regardless of the nanoparticles' orientation. Therefore, it could be beneficial (yet not always mandatory) to have a coherence measurement of the electron, in addition to its intensity image, to measure the purity. This approach gets more similar to the approach of full quantum state reconstruction done in finite quantum systems, and its exact manifestation might depend on the available optical modes.

We note that in the aspects of experimental feasibility of our proposed methods, the required resolution for this kind of experiments depends on many parameters, such as the spatial resolution, the scattering probability, the electron energy spread, and the EELS resolution. Yet, the main requirement from these parameters is the ability to faithfully distinguish between electron images that result from transverse nanoparticles (xy disk) and longitudinal ones (z rod), and between the x and y directions. Generally, the need for a geometrical knowledge sets a requirement on the spatial resolution of the detector. As stated in Section S.3.1, the spatial images of the energy-

filtered electron scales as the excitation wavelength, which means that higher wavelengths can be chosen to match this requirement on the spatial resolution.

S.3.4 nanoparticle simulation parameters

In the results presented in the paper, we have used a nanoparticle of radius $10\ nm$, relative permittivity of $-30 + 5i$, and electron energy of 200 keV, post-selected for energy loss of 5 eV with zero filter bandwidth. For wider energy filters, the bandwidth will convolve with the numerical results, e.g., smear the intensity images of Fig. 3(a) and, and decrease the spatial coherence in Fig. 3(b).

S.4 The purity of the electron in a general scenario

In this section, we evaluate the purity of the electron after interacting with optical excitations in a general scenario. The main focus here is on the behavior of the purity under different "cardinalities" of the excitations' spectrum, that is, whether the electron interacts a *discrete* set of excitations or a *continuous* one. The number of available excitations to excite determines the number of non-zero eigenvalues of the electron density matrix, which affects its purity. Although the purity itself is affected by the relative magnitude of the non-zero eigenvalues, we find that **the purity can *vanish* altogether when there is a *continuum* of excitations**, regardless of the relative excitation strengths. In particular, this means that the purity of the electron interacting with SPPs is zero, and positive in the case of nanoparticles.

Being able to connect the purity with the excitation dimensionality has several experimental implications. The purity of the electron is a measure of the electron's overall coherence. Therefore, an electron exciting a continuum of resonances would have a greatly-impaired coherence, compared to an electron exciting a discrete amount of resonances. The gap in coherences could impair the ability to use the electron as a *quantum* particle, for example for measurements which are based on its spatial or temporal coherence.

This statement is intuitive in the case where energy-filtering is *not* used: having a continuous energy distribution of the electron (by having continuous distribution of resonance energies) should decrease its coherence. Equivalently, in classical optics a bandwidth of frequencies decreases wave coherence. However, in the quantum case of the electron, the statement holds even for single-frequency electron, i.e. even after energy-filtering. As a result, energy filtering will not always "save" the electron coherence after interaction. For example, in the SPPs case the purity is always zero, even after energy-filtering.

To show the purity analysis mathematically, we write the post-interaction electron density matrix in a diagonal form $\rho_{\mathrm{e}} = \sum_i c_i |i\rangle\langle i|$, where the c_i-s are the eigenvalues and the $\{|i\rangle\}$ are the corresponding eigenstates. The eigenvalues and states are determined by the specific optical environment, but for this derivation we shall keep them general. The purity can be calculated directly from the eigenvalues of ρ_{e}, in the following way (see S.3.2): $\frac{\mathrm{Tr}(\rho_{\mathrm{e}}^2)}{\mathrm{Tr}^2(\rho_{\mathrm{e}})}$. Using the general form of ρ_{e}, the purity can be written as $\frac{\sum_i c_i^2}{(\sum_i c_i)^2}$.

In the continuous case, the summation over the eigenvalues turns into an integral. In the case of an interaction with an infinite surface, there is a continuum of directions of emission of surface plasmons, and the purity then goes to 0.

Let us investigate the purity in the discrete and continuous cases. It is easy to see that for a finite number of non-zero eigenvalues (c_i-s), the purity in the discrete version is strictly larger than zero. Consequently, an electron interacting with a finite amount of modes always keeps some of its purity. As discussed in the main text, this larger-than-zero purity usually means that the electron maintains a larger area of spatial coherence (see Fig. 3 in the main text).

To summarize this discussion, we have shown that fundamentally **an electron interacting with a surface of SPPs has zero purity, even after energy filtering**. This claim is related to the fact that the plasmons have a continumu of propagation angles. Equivalently, this intrinsically relates to the dimensionality: two dimensions provide a continuum of modes. i.e., even after filtering the interaction for a single energy, there is still a continuum of modes corresponding to the momentum direction, which is manifested in ρ_{e} as a continuum of eigenvalues that yield zero purity. In contrast, a one dimensional structure, like a nanowire, can have two propagation directions and thus a finite purity value. It remains to be seen whether any infinite structure in 2D

and 3D will necessarily have a zero purity, or whether certain resonance structures could have a

finite value.

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