Modulation of Cathodoluminescence Emission by Interference with External Light

– SUPPLEMENTARY INFORMATION –

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S1. COHERENCE IN ELECTRON MICROSCOPY

The term *coherence* is employed to denote different things depending on the physical processes under consideration. We thus provide a brief discussion on several possible uses of this concept in the context of electron microscopy.

Coherence in the sampled excitations. Plasmons and other types of polaritons excited by electron beams (e-beams) can be out-coupled to radiation at different regions of the specimen, and eventually produce far-field CL interference. In this sense, the coherence of these excitations is a property of the specimen, independent of whether we excite them with fast electrons or with localized point emitters (*e.g.*, quantum dots). Even Smith-Purcell radiation fits into this general description: there is a continuum of degenerate light modes for each emission frequency (*i.e.*, different directions of emission and two polarizations) and the electron just provides a practical way of accessing a particular superposition of them (*i.e.*, the electron velocity and beam orientation relative to the grating select which modes are excited, corresponding to the emission of radiation along specific frequency-dependent directions).

Coherence in this context then refers to the interference between different excited modes (polaritons and photons) when the quantum mechanical state of the specimen remains unchanged after interaction with the electron [1]. An example of incoherent excitations according to this definition is provided by those associated with the luminescence resulting from the decay of interband electronic transitions in a semiconductor that are initially created by the e-beam and subsequently undergo de-excitation to an intermediate state that introduces a random phase (*e.g.*, *via* an Auger process): the sample is not left in the same quantum-mechanical state after interaction with the electron, so the emission intensity builds up from the (incoherent) sum of intensities associated with different excitations triggered by the electron at different locations.

Coherence of the electron as a source of optical excitations. Coherence in this sense depends on the electron wave function (or in general the electron density matrix if it is prepared in a mixed state). It manifests during the interaction of the sample with several synchronized electrons (see point *iii* below) and also by means of interference of CL with external light (points *iv-v*). To complement this discussion, several additional elements related to coherence can be demonstrated from first principles [2] (*i.e.*, with independence of the type of specimen and the mechanism of interaction with the electron) under the assumption of nonrecoil:

i. For interaction with an individual electron, the excitation probability for both EELS and CL reduces to the average of the probability $P(x,y)$ obtained for a classical point particle passing by (x,y) over the e-beam transverse density profile [3] (*i.e.*, the resulting probability is $\iint dxdy\ |\psi_\perp(x,y)|^2 P(x,y)$, where $\psi_\perp(x,y)$ is the lateral component of the wave function and the electron velocity is taken along z). This result was first obtained by Ritchie and Howie [3].

ii. The individual-electron probability $P(x,y)$ is actually independent of the longitudinal wave function $\psi_\parallel(z)$.

iii. For interaction with more than one electron during the lifetime of the sampled excitation, the probability can depend on the electron wave functions if they are mutually synchronized. This dependence comes through factors given by $M_{\omega/v}$ (eq 9 in the main text).

Additionally, we might wonder whether the excitations produced by the electron maintain some degree of coherence with respect to any external illumination. In the main text, we show that, in the limit of a point-particle electron, the CL emission is completely coherent with respect to external light if this is synchronized to a high precision relative to the optical cycle of the sampled excitation: the electron acts as a classical source that is phase-locked to the external light, so the generated far-field amplitude is the sum of contributions coming from each of them (i.e., the solution of Maxwell's equations for the combined electron and light sources). Now, the question arises, is this also true when the electron is not a point particle? We find the following answers from first-principles theory:

iv. The CL emission can partially interfere with external light if the electron and the light are mutually phase-locked. Interference comes through a term proportional to the so-called *degree of coherence* $|M_{\omega/v}|^2$ [4], where $M_{\omega/v}$ is the same quantity that rules the interference between the excitations produced by multiple synchronized electrons [2]). Maximum coherence corresponds to $|M_{\omega/v}|^2 = 1$, which can be achieved if the electron probability density consists of a series of δ-function peaks separated by a distance $2\pi v/\omega$ [2].

v. As we show in the main text, the CL emission can even be partially suppressed if it is mixed with mutually coherent light. The maximum fraction of emission that can be suppressed is given by $|M_{\omega/v}|^2$.

For electrons prepared in Gaussian wavepackets, the factor $|M_{\omega/v}|^2 = \mathrm{e}^{-\omega^2\sigma_t^2}$ depends on their duration σ_t relative to the optical cycle of the sampled excitation $2\pi/\omega$ (*e.g.*, $2\pi/\omega \approx 4.1\,$fs for $\hbar\omega = 1\,$eV). A practical way to achieve a significant value of $|M_{\omega/v}|^2$ consists in using PINEM-modulated electrons, and then the PINEM laser is automatically synchronized with the electron modulation. However, under cw illumination, this leads to $|M_{\omega/v}|^2 < 0.34$, unless the electron is already prepared as a short pulse (Figure S1). The quest for achieving the maximum possible value of $|M_{\omega/v}|^2 = 1$ defines an exciting avenue of research.

S2. ALTERNATIVE DESCRIPTION FOR A DIPOLAR SCATTERER: ANALYSIS OF ENERGY PATHWAYS

We present an alternative treatment of a dipolar scatterer that hosts a single optical mode. This approach does not require photon quantization and it can be applied to any two-level system that can be characterized by a transition dipole. As a starting point, we write the Hamiltonian

$$\begin{aligned}\hat{\mathcal{H}} =&\hbar\omega_0\, \hat{a}^\dagger\hat{a} + \hbar\sum_q \varepsilon_q \hat{c}_q^\dagger\hat{c}_q \\ &+ g(t)\left(\hat{a}^\dagger + \hat{a}\right) + \sum_{qq'} g_{qq'}\hat{c}_q^\dagger\hat{c}_{q'}\left(\hat{a}^\dagger + \hat{a}\right),\end{aligned} \quad \text{(S1)}$$

where ω_0 is the mode frequency, $\hat{a}^\dagger$ and $\hat{a}$ represent the corresponding creation and annihilation operators, $\hat{c}_q^\dagger$ and $\hat{c}_q$ create and annihilate an electron of wave vector q and kinetic energy $\hbar\varepsilon_q$ along the e-beam direction, the real coefficient $g(t)$ describes the mode coupling to classical external light, and $g_{qq'}$ are electron-scatterer coupling coefficients.

In what follows, we ignore transverse coordinates under the nonrecoil approximation, together with the assumption that the e-beam is focused around a lateral position $\mathbf{R}_0 = (x_0, y_0)$ relative to the scatterer, with a small focal spot compared to both c/ω_0 and R_0. A basis set of longitudinal wave vector states $\langle z|q\rangle = \mathrm{e}^{\mathrm{i}qz}/\sqrt{L}$ is then used to describe the electron, where L is the quantization length along the e-beam direction. In addition, the scatterer is considered to be prepared in its ground state before interaction with the external light and the electron. We further assume typical conditions in electron microscopy, characterized by a weak electron-scatterer interaction, so that we can work to the lowest possible order of perturbation theory. The external light is taken to be dimmed, such that its interaction strength becomes commensurate with that of the electron. Under these conditions, the density matrix of the combined electron-scatterer system can be written as

$$\hat{\rho} = \sum_{nn',qq'} \alpha_{nn',qq'}(t)\, \mathrm{e}^{\mathrm{i}(n'-n)\omega_0 t + \mathrm{i}\varepsilon_{q'q}t}\, |nq\rangle\langle n'q'|, \quad \text{(S2)}$$

where $|nq\rangle \equiv (\hat{a}^\dagger)^n\hat{c}_q^\dagger|0\rangle/\sqrt{n!}$ and we adopt the notation $\varepsilon_{q'q} = \varepsilon_{q'} - \varepsilon_q$. A finite lifetime τ_0 of the optical mode is now introduced through the equation of motion

$$\frac{d\hat{\rho}}{dt} = \frac{\mathrm{i}}{\hbar}\left[\hat{\rho}, \hat{\mathcal{H}}\right] + \frac{1}{2\tau_0}\left(2\hat{a}\hat{\rho}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}\hat{\rho} - \hat{\rho}\hat{a}^\dagger\hat{a}\right). \quad \text{(S3)}$$

Before interaction, the coefficients of the density matrix are $\alpha_{nn',qq'}(-\infty) = \delta_{n0}\delta_{n'0}\alpha_q^0\alpha_{q'}^{0*}$, where α_q^0 defines the incident longitudinal electron wave function

$$\psi_\parallel(z) = \sum_q \alpha_q^0\langle z|q\rangle = \sqrt{L}\int_{-\infty}^{\infty}\frac{dq}{2\pi}\,\alpha_q^0\,\mathrm{e}^{\mathrm{i}qz}. \quad \text{(S4)}$$

Here, we have used the prescription $\sum_q \to (L/2\pi)\int_{-\infty}^{\infty} dq$ to transform the sum over the electron wave vector q into an integral.

We consider external light characterized by an electric field $\mathbf{E}^{\rm ext}(\mathbf{r}, t)$ at the position of the scatterer, so we have

$$g(t) = -\mathbf{p}_0 \cdot \mathbf{E}^{\rm ext}(0, t), \quad \text{(S5)}$$

where $\mathbf{p}_0$ is the transition dipole, which is taken to be real. Additionally, the electron-scatterer coupling coefficients are given by [5]

$$g_{qq'} = g_{q'q}^* = -\frac{v}{L}\,\mathbf{p}_0 \cdot \mathbf{g}_{q'-q}, \quad \text{(S6)}$$

where

$$\mathbf{g}_q = \frac{2e}{v\gamma}\left[|q|\,K_1\left(|q|R_0/\gamma\right)\,\hat{\mathbf{R}}_0 + \frac{\mathrm{i}q}{\gamma}\,K_0\left(|q|R_0/\gamma\right)\,\hat{\mathbf{z}}\right],$$

v is the average electron velocity, and $\gamma = 1/\sqrt{1 - v^2/c^2}$.

The excitation probabilities here investigated are determined by the diagonal elements $\alpha_{nn,qq}(t)$, which we calculate to the lowest order of perturbation theory by plugging eqs S1 and S2 into eq S3. Identifying the coefficient of each $|nq\rangle\langle n'q'|$ term in both sides of the resulting equation, iteratively evaluating the correction to $\alpha_{nn',qq'}$ at perturbation order $l+1$ by inserting the order-l correction into the $[\hat\rho,\hat{\mathcal{H}}]$ term of eq S3, and starting with $\alpha_{nn',qq'}(-\infty)$ for $l=0$ (see above), we find

$$\frac{d\alpha_{01,qq'}(t)}{dt} = \frac{\mathrm{i}}{\hbar}g(t)\,\alpha_q^0\,\alpha_{q'}^{0*}\;\mathrm{e}^{-\mathrm{i}\omega_0 t} + \frac{\mathrm{i}}{\hbar}\sum_{q''} g_{q''q'}\,\alpha_q^0\,\alpha_{q''}^{0*}\;\mathrm{e}^{-\mathrm{i}(\omega_0+\varepsilon_{q'q''})t} - \frac{1}{2\tau_0}\alpha_{01,qq'}(t), \tag{S7a}$$

$$\frac{d\alpha_{11,qq}(t)}{dt} = \frac{2}{\hbar}g(t)\,\mathrm{Im}\left\{\alpha_{01,qq}(t)\;\mathrm{e}^{\mathrm{i}\omega_0 t}\right\} + \frac{2}{\hbar}\sum_{q'}\mathrm{Im}\left\{g_{qq'}\,\alpha_{01,q'q}(t)\;\mathrm{e}^{\mathrm{i}(\omega_0+\varepsilon_{qq'})t}\right\} - \frac{1}{\tau_0}\,\alpha_{11,qq}(t), \tag{S7b}$$

$$\frac{d\alpha_{00,qq}(t)}{dt} = -\frac{2}{\hbar}g(t)\,\mathrm{Im}\left\{\alpha_{01,qq}(t)\;\mathrm{e}^{\mathrm{i}\omega_0 t}\right\} - \frac{2}{\hbar}\sum_{q'}\mathrm{Im}\left\{g_{q'q}\,\alpha_{01,qq'}(t)\;\mathrm{e}^{\mathrm{i}(\omega_0+\varepsilon_{q'q})t}\right\} + \frac{1}{\tau_0}\,\alpha_{11,qq}(t), \tag{S7c}$$

where we have used the Hermiticity of $\hat\rho$ and $\hat{\mathcal{H}}$. The integral of eq S7a can be readily written as

$$\alpha_{01,qq'}(t) = \frac{\mathrm{i}}{\hbar}\,\alpha_q^0\,\alpha_{q'}^{0*}\int_{-\infty}^{t} dt'\,g(t')\,\mathrm{e}^{-\mathrm{i}\omega_0 t'-(t-t')/2\tau_0} - \frac{1}{\hbar}\sum_{q''} g_{q''q'}\,\alpha_q^0\,\alpha_{q''}^{0*}\;\frac{\mathrm{e}^{-\mathrm{i}(\omega_0+\varepsilon_{q'q''})t}}{\omega_0+\varepsilon_{q'q''}+\mathrm{i}/2\tau_0}.$$

At this point, we express the coupling coefficients in terms of the scatterer mode dipole $\mathbf{p}_0$ through eqs S5 and S6, use the nonrecoil approximation to write $\varepsilon_{q'q''}\approx(q'-q'')v$, and convert the q'' sum into an integral by means of the prescription noted above. Following this procedure, we find

$$\alpha_{01,qq'}(t) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\mathrm{e}^{-\mathrm{i}\omega t}\,\tilde\alpha_{01,qq'}(\omega),$$

where

$$\tilde\alpha_{01,qq'}(\omega) = \frac{1}{\hbar}\,\frac{1}{\omega+\mathrm{i}/2\tau_0}\;\mathbf{p}_0\cdot\left[\mathbf{E}^{\mathrm{ext}}(0,\omega-\omega_0)\,\alpha_q^0\,\alpha_{q'}^{0*} + \mathbf{g}_{(\omega-\omega_0)/v}\,\alpha_q^0\,\alpha_{q'-(\omega-\omega_0)/v}^{0*}\right] \tag{S8}$$

and $\mathbf{E}^{\mathrm{ext}}(\mathbf{r},\omega)=\int_{-\infty}^{\infty}dt\,\mathrm{e}^{\mathrm{i}\omega t}\,\mathbf{E}^{\mathrm{ext}}(\mathbf{r},t)$.

We are interested in the time-integrated quantity

$$T_q = \int_{-\infty}^{\infty} dt\,\alpha_{11,qq}(t)$$

(see below). From eq S7b, we find $T_q=\int_{-\infty}^{\infty}dt\,\mathrm{e}^{-t/\tau_0}\int_{-\infty}^{t}dt'\,\mathrm{e}^{t'/\tau_0}\,F(t')=\tau_0\int_{-\infty}^{\infty}dt\,F(t)$, where $F(t)$ is given by the first two terms in the right-hand side of that equation. This leads to

$$T_q = \frac{2\tau_0}{\hbar}\int_{-\infty}^{\infty}dt\;\mathrm{Im}\left\{g(t)\,\alpha_{01,qq}(t)\;\mathrm{e}^{\mathrm{i}\omega_0 t} + \sum_{q'} g_{qq'}\,\alpha_{01,q'q}(t)\;\mathrm{e}^{\mathrm{i}(\omega_0+\varepsilon_{qq'})t}\right\}. \tag{S9}$$

As a first result, eq S9 can help us evaluate the change in electron kinetic energy ΔE_{el}, starting from the variation in the population of the sample ground state due to the interaction, $\alpha_{00,qq}(\infty)-|\alpha_q^0|^2$. Multiplying this quantity by the plane wave energy $\hbar\varepsilon_q$, summing over q, calculating $\alpha_{00,qq}(\infty)$ from the integral of eq S7c, and using eq S9, we obtain

$$\begin{aligned}\Delta E_{\mathrm{el}} &= \sum_q \hbar\varepsilon_q\;\left[\alpha_{00,qq}(\infty)-|\alpha_q^0|^2\right]\\ &= 2\sum_{qq'}\varepsilon_{qq'}\int_{-\infty}^{\infty}dt\;\mathrm{Im}\left\{g_{qq'}\,\alpha_{01,q'q}(t)\;\mathrm{e}^{\mathrm{i}(\omega_0+\varepsilon_{qq'})t}\right\}.\end{aligned}$$

We now convert the sum over q' into an integral, change the variable of integration to $\omega=\varepsilon_{qq'}$, adopt the nonrecoil approximation $\varepsilon_{qq'}\approx(q-q')v$, identify the time integral as the Fourier transform $\tilde\alpha_{01,q'q}(\omega_0+\omega)$ (see eq S8), and substitute the coupling coefficients from eqs S5 and S6 to find

$$\Delta E_{\mathrm{el}} = -\frac{1}{\pi\hbar}\int_{-\infty}^{\infty}\omega d\omega\;\mathrm{Im}\left\{\frac{1}{\omega_0+\omega+\mathrm{i}/2\tau_0}\;\left[\left(\mathbf{p}_0\cdot\mathbf{E}^{\mathrm{ext}}(0,\omega)\right)\,\left(\mathbf{p}_0\cdot\mathbf{g}^*_{\omega/v}\right)\,M_{\omega/v} + \left|\mathbf{p}_0\cdot\mathbf{g}_{\omega/v}\right|^2\right]\right\}, \tag{S10}$$

where we have used the normalization condition $\sum_q \left|\alpha_q^0\right|^2 = 1$ and defined

$$M_{\omega/v} = \sum_q \alpha^0_{q-\omega/v}\,\alpha_q^{0*} = \int_{-\infty}^{\infty} dz\; \mathrm{e}^{\mathrm{i}\omega z/v}\;|\psi_\parallel(z)|^2 \tag{S11}$$

(eq 9 in the main text). In the derivation of the integral in eq S11, we have exploited the relation between α_q^0 and $\psi_\parallel(z)$ given in eq S4. We now consider an isotropic particle characterized by three degenerate modes of real transition dipoles $p_0\hat{\mathbf{x}}$, $p_0\hat{\mathbf{y}}$, and $p_0\hat{\mathbf{z}}$, each of them contributing to $\Delta E_{\rm el}$ with a term given by eq S10, in which $\mathbf{p}_0$ is substituted by the corresponding mode dipole. The sum of these contributions yields

$$\Delta E_{\rm el} = -\frac{1}{\pi\hbar}\int_{-\infty}^{\infty}\omega d\omega\; \mathrm{Im}\left\{\frac{|p_0|^2}{\omega_0+\omega+\mathrm{i}/2\tau_0}\;\left[\mathbf{E}^{\rm ext}(0,\omega)\cdot\mathbf{g}^*_{\omega/v}\,M_{\omega/v} + \left|\mathbf{g}_{\omega/v}\right|^2\right]\right\}.$$

Finally, separating the integral in positive and negative frequency parts, and changing $\omega\rightarrow-\omega$ in the latter, we can write $\Delta E_{\rm el} = \int_0^\infty \hbar\omega\, d\omega\; d\Gamma_{\rm el}/d\omega$, where

$$\boxed{\frac{d\Gamma_{\rm el}}{d\omega} = -\frac{1}{\pi\hbar}\,\mathrm{Im}\left\{\alpha(\omega)\,\mathbf{E}^{\rm ext}(0,\omega)\cdot\mathbf{E}^{\rm el*}(\mathbf{R}_0,\omega)\,M_{\omega/v}\right\} - \frac{1}{\pi\hbar}\,\left|\mathbf{E}^{\rm el}(\mathbf{R}_0,\omega)\right|^2\,\mathrm{Im}\left\{\alpha(\omega)\right\}} \tag{S12}$$

acts as an electron energy-change probability, in which we identify

$$\alpha(\omega) = \frac{|p_0|^2}{\hbar}\left(\frac{1}{\omega_0-\omega-\mathrm{i}/2\tau_0} + \frac{1}{\omega_0+\omega+\mathrm{i}/2\tau_0}\right) \tag{S13}$$

as the particle polarizability [6] and we have renamed $\mathbf{g}_{\omega/v} = \mathbf{E}^{\rm el}(\mathbf{R}_0,\omega)$ (see eq 8 in the main text). The opposite of the rightmost term in eq S12 coincides with the well-known expression of the EELS probability for a dipolar particle [1], $(4e^2\omega^2/\pi\hbar v^4\gamma^2)\left[K_1^2(\omega R_0/v\gamma) + K_0^2(\omega R_0/v\gamma)/\gamma^2\right]\mathrm{Im}\{\alpha(\omega)\}$, whereas the first term arises as a result of the particle-assisted interaction between the electron and the external light field. Although we assign the latter to an $\omega > 0$ component in the integral of $\Delta E_{\rm el}$, it should actually be interpreted as the net balance between energy losses and gains of energies $\pm\hbar\omega$.

Assuming a radiative decay rate $\gamma_{\rm rad}$ of the excited particle state, the number of photons emitted into the far field accumulates over time to yield

$$\Gamma_{\rm rad} = \gamma_{\rm rad}\sum_q T_q.$$

We can work out this expression from eq S9 by expressing $\alpha_{01,qq'}(t)$ in terms of its Fourier transform (eq S8), following similar steps as in the derivation of eq S10, and eventually summing over three orthogonal transition dipoles to describe an isotropic particle. This results in

$$\Gamma_{\rm rad} = \frac{\gamma_{\rm rad}}{2\pi\hbar^2}\int_{-\infty}^{\infty} d\omega\;\frac{|p_0|^2}{(\omega_0-\omega)^2+1/4\tau_0^2}\;\left[|\mathbf{E}^{\rm ext}(0,\omega)|^2 + |\mathbf{E}^{\rm el}(\mathbf{R}_0,\omega)|^2 + 2\,\mathrm{Re}\left\{\mathbf{E}^{\rm ext}(0,\omega)\cdot\mathbf{E}^{\rm el*}(\mathbf{R}_0,\omega)M_{\omega/v}\right\}\right],$$

where we have performed the q sum by using $\sum_q \left|\alpha_q^0\right|^2 = 1$ and eq S11. Neglecting for now the interference between scattered and externally incident photons (*i.e.*, we ignore the change in the probability of some of the decay channels stimulated by the photon population of such channels), we have [7] $\gamma_{\rm rad} = 4|p_0|^2\omega_0^3/3\hbar c^3$, so we can write $\Gamma_{\rm rad} = \int_0^\infty d\omega\;(d\Gamma_{\rm rad}/d\omega)$, where

$$\boxed{\frac{d\Gamma_{\rm rad}}{d\omega} \approx \frac{1}{\pi\hbar}\,\frac{2\omega^3\,|\alpha(\omega)|^2}{3c^3}\;\left[|\mathbf{E}^{\rm ext}(0,\omega)|^2 + |\mathbf{E}^{\rm el}(\mathbf{R}_0,\omega)|^2 + 2\,\mathrm{Re}\left\{\mathbf{E}^{\rm ext}(0,\omega)\cdot\mathbf{E}^{\rm el*}(\mathbf{R}_0,\omega)M_{\omega/v}\right\}\right]} \tag{S14}$$

represents the spectrally resolved photon emission probability, in which we have assumed $\omega_0\tau_0 \gg 1$ and taken $\omega\approx\omega_0$ in the multiplicative factors. After minor rearrangements, eq S14 becomes eq 7 in the main text.

We also note that the accumulated probability of decay from the excited state of the particle is given by $\Gamma_{\rm decay} = (1/\tau_0)\sum_q T_q$, which, following the same procedure as above and neglecting the nonresonant term in eq S13, is found to lead to

$$\boxed{\frac{d\Gamma_{\rm decay}}{d\omega} \approx \frac{1}{\pi\hbar}\,\mathrm{Im}\{\alpha(\omega)\}\;\left[|\mathbf{E}^{\rm ext}(0,\omega)|^2 + |\mathbf{E}^{\rm el}(\mathbf{R}_0,\omega)|^2 + 2\,\mathrm{Re}\left\{\mathbf{E}^{\rm ext}(0,\omega)\cdot\mathbf{E}^{\rm el*}(\mathbf{R}_0,\omega)M_{\omega/v}\right\}\right].} \tag{S15}$$

Importantly, in the final energy balance of the entire electron-particle-radiation system, a term

$$\boxed{\begin{aligned}\frac{d\Gamma_{\rm forward}}{d\omega} &= -\frac{1}{\pi\hbar}\,{\rm Im}\big\{\alpha(\omega)\big\}\,|\mathbf{E}^{\rm ext}(0,\omega)|^2 + \frac{1}{\pi\hbar}\,{\rm Im}\big\{\alpha^*(\omega)\,\mathbf{E}^{\rm ext}(0,\omega)\cdot\mathbf{E}^{\rm el*}(\mathbf{R}_0,\omega)M_{\omega/v}\big\} \\ &= -\frac{1}{\pi\hbar}\,{\rm Im}\big\{\alpha(\omega)\,\mathbf{E}^{\rm ext*}(0,\omega)\cdot[\mathbf{E}^{\rm ext}(0,\omega)+\mathbf{E}^{\rm el}(\mathbf{R}_0,\omega)M^*_{\omega/v}]\big\}\end{aligned}} \tag{S16}$$

is missing in order to conserve energy for each ω component according to the condition

$$\boxed{\frac{d\Gamma_{\rm el}}{d\omega}+\frac{d\Gamma_{\rm decay}}{d\omega}+\frac{d\Gamma_{\rm forward}}{d\omega}=0.} \tag{S17}$$

We interpret $\Gamma_{\rm forward}$ as the change in photon forward emission (*i.e.*, toward the direction of propagation of the incident light beam) associated with interference between emitted and externally incident photons (*i.e.*, the type of stimulated process that we neglected in $\gamma_{\rm rad}$ above). The first term in the right-hand side of eq S16 corresponds to the depletion of the incident light, as described by the optical theorem [8] (*i.e.*, $(1/\pi\hbar){\rm Im}\{\alpha(\omega)\}\,|\mathbf{E}^{\rm ext}(0,\omega)|^2=\sigma_{\rm ext}(\omega)I(\omega)/\hbar\omega$, where $\sigma_{\rm ext}(\omega)=(4\pi\omega/c){\rm Im}\{\alpha(\omega)\}$ is the extinction cross section and $I(\omega)=(c/4\pi^2)|\mathbf{E}^{\rm ext}(0,\omega)|^2$ is the light intensity per unit frequency), whereas the remaining term originates in electron-light interference.

Finally, part of the energy is absorbed by the particle due to internal inelastic transitions, so the total decay of the particle excited state can be separated as

$$\boxed{\frac{d\Gamma_{\rm decay}}{d\omega}=\frac{d\Gamma_{\rm rad}}{d\omega}+\frac{d\Gamma_{\rm abs}}{d\omega},}$$

where

$$\boxed{\frac{d\Gamma_{\rm abs}}{d\omega}\approx\frac{1}{\pi\hbar}\left[{\rm Im}\{\alpha(\omega)\}-\frac{2\omega^3\,|\alpha(\omega)|^2}{3c^3}\right]\left[|\mathbf{E}^{\rm ext}(0,\omega)|^2+|\mathbf{E}^{\rm el}(\mathbf{R}_0,\omega)|^2+2\,{\rm Re}\big\{\mathbf{E}^{\rm ext}(0,\omega)\cdot\mathbf{E}^{\rm el*}(\mathbf{R}_0,\omega)M_{\omega/v}\big\}\right].} \tag{S18}$$

is the spectrally resolved absorption probability. This completes our analysis of energy pathways during the interaction of the particle with external light and an incident electron. The contributions to the energy balance in eq S17 are thus given by eqs S12, S15, and S16, while the decay in S15 can in turn be expressed as the sum of two terms corresponding to radiative and absorptive channels, as given by eqs S14 and S18, respectively.

We remark that the boxed equations derived above apply to isotropic dipolar particles. Repeating the same analysis without summing over three orthogonal transition dipole orientations, we obtain similar expressions for a particle characterized by a polarizability tensor $\alpha(\omega)\,\hat{\mathbf{u}}\otimes\hat{\mathbf{u}}$ (*i.e.*, with a single transition dipole $\mathbf{p}_0$ along a direction $\hat{\mathbf{u}}$), for which the partial probabilities are given by eqs S12, S14, S15, S16, and S18 after substituting $\mathbf{E}^{\rm ext}$ and $\mathbf{E}^{\rm el}$ by $\hat{\mathbf{u}}\cdot\mathbf{E}^{\rm ext}$ and $\hat{\mathbf{u}}\cdot\mathbf{E}^{\rm el}$, respectively.

A. Energy pathways from the quantum-electrodynamics formalism

The above results can be corroborated using the quantum-electrodynamics formalism developed in the Methods section of the main text. In particular, an extension of eq S16 is readily obtained by evaluating the Poynting vector along the forward direction with respect to the incident laser, assuming illumination with a well-defined incident wave vector $\mathbf{k}_{\rm inc}$. Using the notation $2{\rm Re}\left\{\mathbf{E}^{\rm ext}(0,\omega){\rm e}^{{\rm i}\mathbf{k}_{\rm inc}\cdot\mathbf{r}-{\rm i}\omega t}\right\}$ for the time-dependent external light electric field, the frequency-space light electric far-field ($kr\gg1$) takes the form $\mathbf{E}^{\rm light}(\mathbf{r},\omega)\approx\mathbf{E}^{\rm ext}(0,\omega)\,{\rm e}^{{\rm i}\mathbf{k}_{\rm inc}\cdot\mathbf{r}}+\mathbf{f}^{\rm scat}_{\hat{\mathbf{r}}}(\omega)\,{\rm e}^{{\rm i}kr}/r$, where $k=|\mathbf{k}_{\rm inc}|=\omega/c$. When inserting this expression in eq 33 of the main text, we can separate $d\Gamma_{\rm ff}/\Omega_{\hat{\mathbf{r}}}d\omega=(d\Gamma_{\rm rad}/\Omega_{\hat{\mathbf{r}}}d\omega)+(d\Gamma_{\rm forward}/\Omega_{\hat{\mathbf{r}}}d\omega)$ into the contributions coming from the $1/r$ part (*i.e.*, $d\Gamma_{\rm rad}/\Omega_{\hat{\mathbf{r}}}d\omega$, which is extensively discussed in the main text) and the remaining interference between $\mathbf{E}^{\rm ext}(0,\omega){\rm e}^{{\rm i}\mathbf{k}_{\rm inc}\cdot\mathbf{r}}$ and $\mathbf{f}^{\rm CL/scat}_{\hat{\mathbf{r}}}$ terms (see also eqs 4 in the main text). The latter generates $d\Gamma_{\rm forward}/\Omega_{\hat{\mathbf{r}}}d\omega$, which can be integrated over angles $\Omega_{\hat{\mathbf{r}}}$ following a similar asymptotic analysis as used in the derivation of the optical theorem [8], based on the integral $\int d^2\Omega_{\hat{\mathbf{r}}}\,{\rm e}^{{\rm i}(k+{\rm i}0^+)r-{\rm i}\mathbf{k}_{\rm inc}\cdot\mathbf{r}}=2\pi{\rm i}/kr$ (valid in the $kr\to\infty$ limit), where k is supplemented by an infinitesimal imaginary part ${\rm i}0^+$, in accordance with the retarded formalism here adopted. This leads to

$$\frac{d\Gamma_{\rm forward}}{d\omega}=-\frac{1}{\pi\hbar k^2}{\rm Im}\left\{\mathbf{E}^{\rm ext*}(0,\omega)\cdot\left[\mathbf{f}^{\rm scat}_{\hat{\mathbf{k}}_{\rm inc}}(\omega)+M^*_{\omega/v}\mathbf{f}^{\rm CL}_{\hat{\mathbf{k}}_{\rm inc}}(\omega)\right]\right\},$$

which, using eqs 37 and 38 in the main text, reduces to eq S16 for a dipolar particle.

Likewise, we can obtain eq S12 starting from the electron mean energy after interaction at $t \to \infty$:

$$\Delta E_{\rm el} = \langle \hat{\mathcal{S}}^\dagger(\infty,-\infty)\hat{\mathcal{H}}_{\rm el}\hat{\mathcal{S}}(\infty,-\infty)\rangle - \langle \hat{\mathcal{H}}_{\rm el}\rangle,$$

where the average $\langle\cdot\rangle$ is defined as in the main text. Noticing that the interaction Hamiltonian (eq 25) is linear in the total current $\hat{\mathbf{j}}$, we use the evolution operator (eq 26) and retain terms just up to quadratic order in $\hat{\mathbf{j}}$ to find

$$\Delta E_{\rm el} \approx \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \left\langle \left[\hat{\mathcal{H}}_{\rm int}(t)\hat{\mathcal{H}}_{\rm el}\hat{\mathcal{H}}_{\rm int}(t') - \frac{1}{2}\left\{\hat{\mathcal{H}}_{\rm int}(t)\hat{\mathcal{H}}_{\rm int}(t'),\hat{\mathcal{H}}_{\rm el}\right\}\right]\right\rangle - {\rm i}\left\langle\left[\hat{\chi}(\infty,-\infty),\hat{\mathcal{H}}_{\rm el}\right]\right\rangle. \tag{S19}$$

Following the same approach as in the main text, we consider the total current to be the sum of the classical laser source $\mathbf{j}^{\rm ext}$ and the electron current operator $\hat{\mathbf{j}}^{\rm el}$ (eq 29). An important technical point refers to the operator $\hat{\chi}(\infty,-\infty) = ({\rm i}/2\hbar^2)\int_{-\infty}^{\infty} dt' \int_{-\infty}^{t'} dt'' \left[\hat{\mathcal{H}}_{\rm int}(t),\hat{\mathcal{H}}_{\rm int}(t')\right]$, in which only the terms that are linear in $\hat{\mathbf{j}}^{\rm el}$ are not commuting with $\hat{\mathcal{H}}_{\rm el}$. In the absence of external illumination, such linear terms disappear and the remaining part of $\hat{\chi}$ gives rise to an image-potential interaction with the sample, which produces elastic diffraction of the electron, but does not change its energy [9]. However, in the present scenario of combined electron and light interactions with the sample, $\hat{\chi}$ gives rise to changes in the electron energy, so it needs to be retained in the calculation. We now use eqs 18 and 20-22, together with the Onsager reciprocity relation $G_{i,i'}(\mathbf{r},\mathbf{r}',\omega) = G_{i',i}(\mathbf{r}',\mathbf{r},\omega)$, to rewrite eq S19 as

$$\begin{aligned}\Delta E_{\rm el} \approx \frac{4{\rm i}}{\hbar}\sum_{i,i'}\int_0^\infty d\omega \int d^3\mathbf{r}\int d^3\mathbf{r}' \Big\{ {\rm i}\,{\rm Im}\{G_{i,i'}(\mathbf{r},\mathbf{r}',\omega)\} \left\langle \hat{j}_i^\dagger(\mathbf{r},\omega)\hat{\mathcal{H}}_{\rm el}\hat{j}_{i'}(\mathbf{r}',\omega) - \frac{1}{2}\left\{\hat{j}_i(\mathbf{r},\omega)\hat{j}_{i'}(\mathbf{r}',\omega),\hat{\mathcal{H}}_{\rm el}\right\}\right\rangle \\ + \frac{1}{2}{\rm Re}\{G_{i,i'}(\mathbf{r},\mathbf{r}',\omega)\}\left\langle \left[\hat{j}_i^{\rm el\dagger}(\mathbf{r},\omega),\hat{\mathcal{H}}_{\rm el}\right] j_{i'}^{\rm ext}(\mathbf{r}',\omega) + j_i^{\rm ext*}(\mathbf{r},\omega)\left[\hat{j}_{i'}^{\rm el}(\mathbf{r}',\omega),\hat{\mathcal{H}}_{\rm el}\right]\right\rangle\Big\}.\end{aligned}$$

Finally, we evaluate the averages $\langle\cdot\rangle$ using eq 33 and the definition of $\hat{\mathcal{H}}_{\rm el}$. After some algebra, this leads to $\Delta E_{\rm el} = \int_0^\infty d\omega\,\hbar\omega\,d\Gamma_{\rm el}/d\omega$ with

$$\frac{d\Gamma_{\rm el}}{d\omega} \approx -\frac{4e}{\hbar}\int d^3\mathbf{r}\int d^3\mathbf{r}'{\rm Im}\left\{{\rm e}^{-{\rm i}\omega z/v}M_{\omega/v}(\mathbf{R})\,\hat{\mathbf{z}}\cdot G(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{j}^{\rm ext}(\mathbf{r}',\omega)\right\} - \int d^2\mathbf{R}\,M_0(\mathbf{R})\,\Gamma_{\rm EELS}(\mathbf{R},\omega), \tag{S20}$$

where $M_{\omega/v}(\mathbf{R})$ is the same as in eq 3 and $\Gamma_{\rm EELS}(\mathbf{R},\omega)$ is the classical EELS probability for an electron beam focused at $\mathbf{R}$ [1]. Equation S20 represents a generalization of eq S12 to arbitrary samples and incident electron wave functions. Indeed, this result reduces to eq S12 if the electron wave function can be factorized as $\psi^0(\mathbf{r}) = \psi_\perp(\mathbf{R})\psi_\parallel(z)$ with $|\psi_\perp(\mathbf{R})|^2 \approx \delta(\mathbf{R}-\mathbf{R}_0)$ (*i.e.*, the tightly focused beam limit) and the sample can be described by a dipolar polarizability $\alpha(\omega)$. Under such conditions, taking the particle at the origin, we can write the scattered part of the Green tensor as $G^{\rm scat}(\mathbf{r},\mathbf{r}',\omega) = -4\pi\omega^2\alpha(\omega)G^{\rm free}(\mathbf{r},\omega)\cdot G^{\rm free}(\mathbf{r}',\omega)$, in terms of the free-space component $G^{\rm free}(\mathbf{r},\omega) = (-1/4\pi\omega^2)(k^2+\nabla\otimes\nabla)\left({\rm e}^{{\rm i}kr}/r\right)$, and then, combining all of these elements, using the integral $\int_{-\infty}^{\infty} dz\,{\rm e}^{{\rm i}\omega(z/v+r/c)}/r = 2K_0(\omega R/v\gamma)$ (see eq 3.914-4 in ref 10), and identifying $\mathbf{E}^{\rm ext}(0,\omega) = -4\pi{\rm i}\omega\int d^3\mathbf{r}\,G^{\rm free}(\mathbf{r},\omega)\cdot\mathbf{j}^{\rm ext}(\mathbf{r},\omega)$, we obtain eq S12.

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SUPPLEMENTARY FIGURES

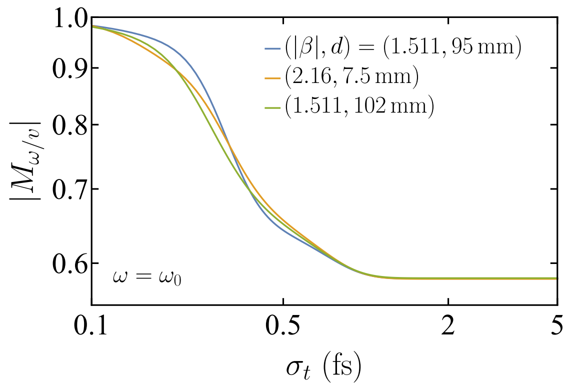

FIG. S1: **Dependence of the coherence factor on Gaussian wavepacket duration.** We show $|M_{\omega/v}|$ for a PINEM-modulated electron with three different combinations of parameters $|\beta|$ and d (see legend) along the blue line of maxima in Figure 3a in the main text as a function of the duration σ_t of a superimposed Gaussian wavepacket envelope. The excitation energy is $\hbar\omega_0 = 1.3\,\mathrm{eV}$.

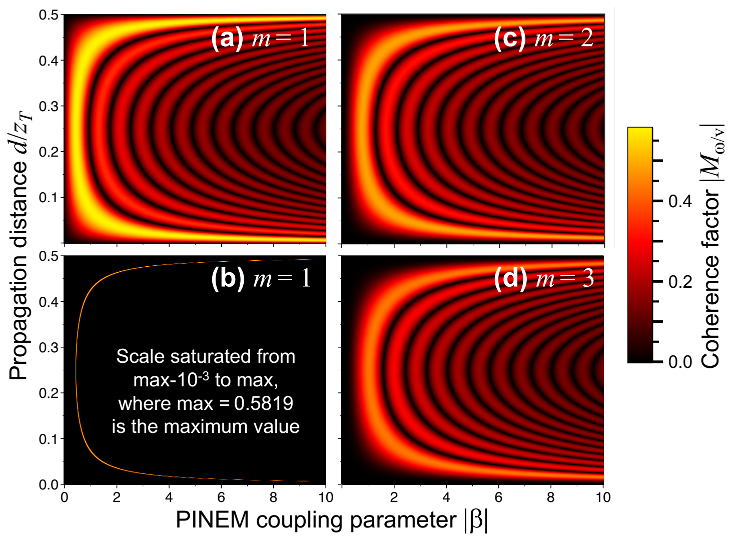

FIG. S2: **Coherence factor at harmonic frequencies of the PINEM laser frequency ω_P.** We show plots similar to that of Figure 4a in the main text, but for excitation frequencies $\omega = m\omega_P$ at different harmonics m of the PINEM laser frequency. Panel (a) is reproduced from Figure 4a in the main text for comparison. Panel (b) is extracted from panel (a) by plotting only the region corresponding to $|M_{\omega/v}| > 0.580865$. The maximum values of $|M_{\omega/v}|$ are 0.581865, 0.486499, and 0.434394 for $m = 1$, 2, and 3, respectively.