Supporting Information for: Capturing Plasmon-Molecule Dynamics in Dye Monolayers on Metal Nanoparticles using Classical Electrodynamics with Quantum Embedding

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Supporting Information Available

Optical Cross Sections

Consider a surface A which encloses a volume V. A normal vector, $\hat{n}$, is chosen along every point of A such that it has a positive magnitude facing outwards. The rate of electromagnetic energy that is transferred across A is given by

$$\mathbf{W} = -\oint \mathbf{S} \cdot \hat{n} dA \tag{1}$$

where $\mathbf{S}$ is the time-average poynting vector. $\mathbf{S}$ indicates the average rate of energy transferred per unit area and is given by

$$\mathbf{S} = \frac{1}{2} Re\left\{\mathbf{E} \times \mathbf{H}^*\right\} \tag{2}$$

with dimensions of power density (e.g. W/m^2).[1] Negative values for W corresponds to energy being transferred out of the surface and a positive values for W corresponds to energy being transferred into the surface. Now consider an arbitrary scatterer (e.g., nanoparticle) enclosed by A that is excited via light with a particular frequency and polarization. At every point along A, the time-average Poynting vector is given by Eq. 2. Because the energy of the system is conserved, $\mathbf{S}$ can also be written as a sum of three components,

$$\mathbf{S} = \mathbf{S}_{inc} + \mathbf{S}_{scat} + \mathbf{S}_{ext} \tag{3}$$

where $\mathbf{S}_{inc}$ is the time-averaged Poynting vector due to the incident light, $\mathbf{S}_{scat}$ is the time-averaged Poynting vector due to the scattered light, and $\mathbf{S}_{ext}$ is the time-averaged Poynting vector due to the interaction between the incident and scattered light. Each of these can be expressed in terms of incident and scattered electric and magnetic fields:

$$\mathbf{S}_{inc} = \frac{1}{2} Re\left\{\mathbf{E}_{inc} \times \mathbf{H}^{*}_{inc}\right\} \tag{4a}$$

$$\mathbf{S}_{scat} = \frac{1}{2} Re\left\{\mathbf{E}_{scat} \times \mathbf{H}^{*}_{scat}\right\} \tag{4b}$$

$$\mathbf{S}_{ext} = \frac{1}{2} Re\left\{\mathbf{E}_{inc} \times \mathbf{H}^{*}_{scat} + \mathbf{E}_{scat} \times \mathbf{H}^{*}_{inc}\right\} \tag{4c}$$

Therefore, the rate of energy flow into the surface A is given by

$$\mathbf{W}_{inc} = -\oint \mathbf{S}_{inc} \cdot \hat{n} dA \tag{5}$$

and the rate of energy that gets scattered and transferred out of A is given by

$$\mathbf{W}_{scat} = -\oint \mathbf{S}_{scat} \cdot \hat{n} dA \tag{6}$$

The resulting time dependent electric and magnetic fields can readily Fourier transformed to obtain the corresponding frequency dependent quantities (i.e., $\mathbf{E}(\omega)$ and $\mathbf{H}(\omega)$).

If we assume the surface A completely encloses the scattering particle, the rate at which scattered energy ($\mathbf{W}_{scat}$) is transferred out of this surface is given by the integral of the Poynting vector (units of W/m^2) over the whole surface. This scattering power is defined as

$$P_{scat}(\omega) = Re\left\{\hat{n} \cdot \oint_{monitors} \mathbf{E}_{scat}(\omega) \times \mathbf{H}^{*}_{scat}(\omega)\right\} \tag{7}$$

where

$$\mathbf{E}_{scat}(\omega) = \mathbf{E}_{total}(\omega) - \mathbf{E}_{inc}(\omega) \tag{8}$$

Likewise, we can define an absorption power that indicates the rate of energy transferred into the entire surface:

$$P_{abs}(\omega) = Re\left\{\hat{n} \cdot \oint_{monitors} \mathbf{E}_{total}(\omega) \times \mathbf{H}^{*}_{total}(\omega)\right\} \tag{9}$$

Typically, the absorption and scattering quantities are expressed as cross sections. By normalizing the absorption and scattering powers by the incident field intensity (I_{inc}), we obtain the corresponding cross sections:

$$\sigma_{abs}(\omega) = \frac{P_{abs}(\omega)}{I_{inc}(\omega)} \tag{10a}$$

$$\sigma_{scat}(\omega) = \frac{P_{scat}(\omega)}{I_{inc}(\omega)} \tag{10b}$$

A cross section has units of area and is typically expressed in m^2.

Calculating Cross Section in FDTD

To calculate these cross sections in FDTD, we must construct 6 flux monitors within the main TF/SF boundary for the absorption cross section σ_{abs} and 6 flux monitors outside the main TF/SF boundary for the scattering cross section σ_{scat} (2D slice of setup is illustrated in Fig. 1). Total fields (scattering + incident) inside the total field region are collected on the absorption flux monitor (See Fig. 1 B). Outgoing (scattered) electric and magnetic fields are collected on the scattering flux monitor (See Fig. 1 C).

Basic FDTD requires the electric and magnetic fields to be offset by half-steps both spatially (i.e., $\Delta x/2$) and temporally (i.e., $\Delta t/2$). The staggered nature of the grid, however, poses difficulty in collating the electric and magnetic fields for coarse grid spacings. This problem can be mitigated by correcting for the spatial and temporal offsets of both the $\mathbf{E}$ and $\mathbf{H}$ fields.[2] Additionally, the errors from calculating the near field scattering cross section can be minimized by using a near to far field (NTFF) transformation which extrapolates the scattered electric fields out to infinity by exploiting Green's theorem.[3]

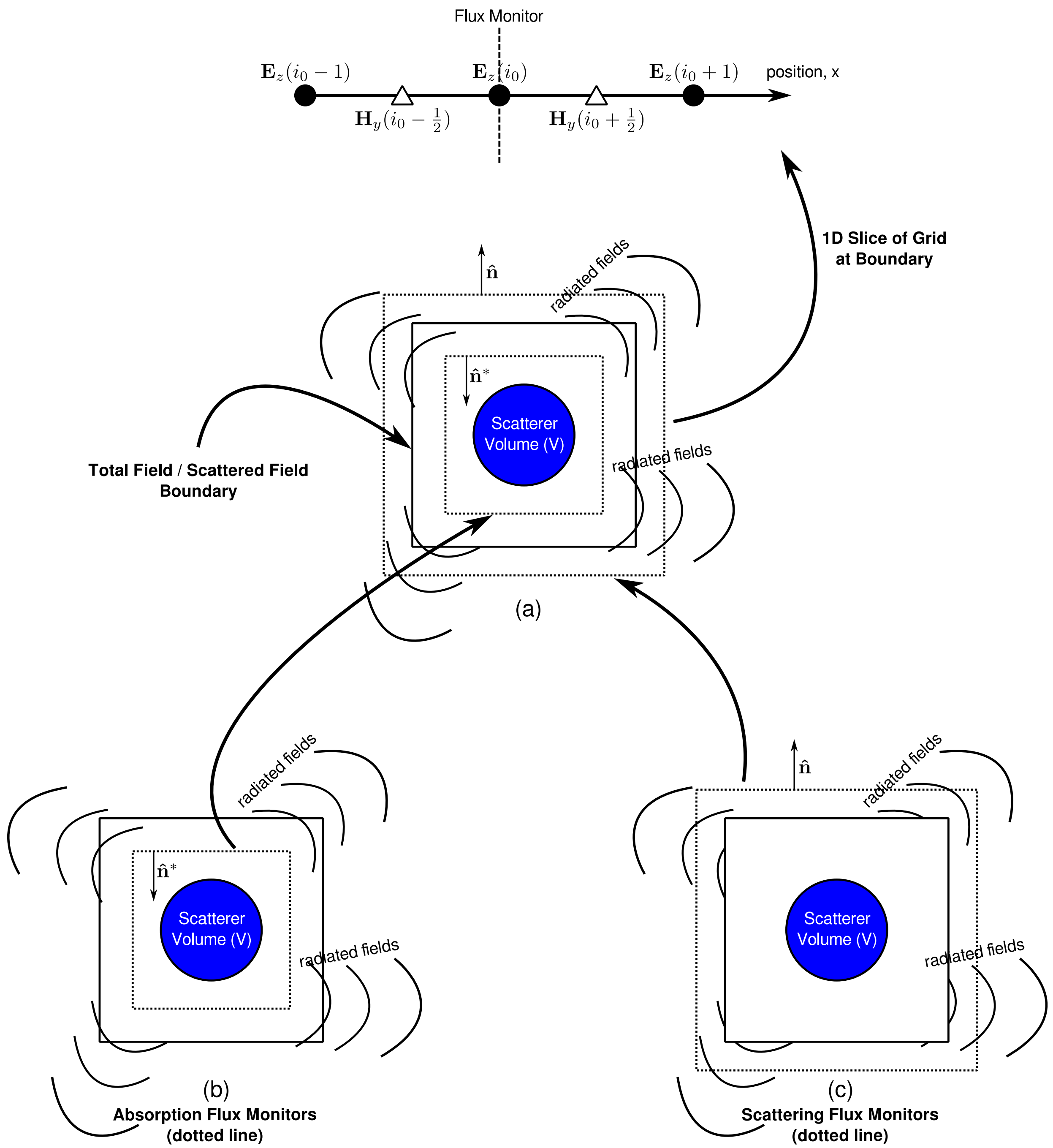

Figure 1: Schematic of a typical FDTD setup (in 2 dimensions) with TF/SF boundary and flux monitors. Panel A shows both the absorption and scattering monitors, while panels B and C show only absorption flux monitors inside the TF/SF boundary with inward pointing normals and scattering flux monitors outside the TF/SF boundary with outward pointing normals, respectively. Absorption flux monitors are located inside the TF/SF and scattered flux monitors are located outside the TF/SF.

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References

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