Optimized 3D Finite-Difference-Time-Domain Algorithm to Model the Plasmonic Properties of Metal Nanoparticles with Near-Unity Accuracy

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Supplementary Material: 3D FDTD Numerical Equations for Ag NP Modelling by Using Lorentz-Drude Fitting Terms

In a practical FDTD simulation, the Maxwell's equations are addressed by [1]:

$$\nabla \times \overrightarrow{H} = \overrightarrow{J} + \frac{\partial \overrightarrow{D}}{\partial t} \tag{1}$$

$$\nabla \times \overrightarrow{E} = -\frac{\partial \overrightarrow{B}}{\partial t}$$

$$\overrightarrow{D}(t) = \varepsilon(t) * \overrightarrow{E}(t)$$

$$\overrightarrow{B}(t) = \mu(t) * \overrightarrow{H}(t) \tag{S1}$$

Where $\varepsilon(t)$ is permittivity in F/m and $\mu(t)$ is permeability in H/m, D is electric flux density (also called dielectric displacement) in C/m², B is magnetic flux density (also known as magnetic induction) in Wb/m², H is the magnetic field intensity in A/m and E is electric field intensity in V/m. J is the material electric current density (A/m²) and can be obtained from material conductivity (σ (1/Ω)) by $\overrightarrow{J} = \sigma \overrightarrow{E}$.

By expanding these vector equations into scalar Equations [2], the complete 3D Maxwell's equations and constitutive relations are obtained in each axis. The final form of the update equations and constitutive relations for obtaining H field in only x-axis are:

$$H_x\big|_{t+\frac{\Delta t}{2}}^{i,j,k} = (m_{Hx1}\big|^{i,j,k})H_x\big|_{t-\frac{\Delta t}{2}}^{i,j,k} + (m_{Hx2}\big|^{i,j,k})C_x^E\big|_t^{i,j,k} + (m_{Hx3}\big|^{i,j,k})I_{CEx}\big|_t^{i,j,k} + (m_{Hx4}\big|^{i,j,k})I_{Hx}\big|_t^{i,j,k}$$

$$C_x^E\big|_t^{i,j,k} = \frac{E_z\big|_t^{i,j+1,k} - E_z\big|_t^{i,j,k}}{\Delta y} - \frac{E_y\big|_t^{i,j,k+1} - E_y\big|_t^{i,j,k}}{\Delta z}$$

$$I_{Hx}\big|_{t=\frac{\Delta t}{2}}^{i,j,k} = \sum_{T=\frac{\Delta t}{2}}^{t-\frac{\Delta t}{2}} H_x\big|_T^{i,j,k}$$

$$\tag{S2}$$

$$I_{CEx}\big|_t^{i,j,k} = \sum_{T=0}^{t} C_x^E\big|_T^{i,j,k}$$

$$m_{Hx0}\big|^{i,j,k} = \frac{1}{\Delta t} + \left(\frac{\sigma_y^H\big|^{i,j,k} + \sigma_z^H\big|^{i,j,k}}{2\varepsilon_0}\right) + \frac{(\sigma_y^H\big|^{i,j,k})(\sigma_z^H\big|^{i,j,k})\Delta t}{4\varepsilon_0^2}$$

$$m_{Hx1}\big|^{i,j,k} = \frac{1}{m_{Hx0}\big|^{i,j,k}} \left[\frac{1}{\Delta t} - \left(\frac{\sigma_y^H\big|^{i,j,k} + \sigma_z^H\big|^{i,j,k}}{2\varepsilon_0}\right) - \frac{(\sigma_y^H\big|^{i,j,k})(\sigma_z^H\big|^{i,j,k})\Delta t}{4\varepsilon_0^2}\right]$$

$$m_{Hx2}|^{i,j,k} = -\frac{1}{m_{Hx0}|^{i,j,k}}\frac{c_0}{\mu_{xx}|^{i,j,k}}$$

$$m_{Hx3}|^{i,j,k} = -\frac{1}{m_{Hx0}|^{i,j,k}}\frac{c_0\Delta t}{\varepsilon_0}\frac{\sigma_x^H|^{i,j,k}}{\mu_{xx}|^{i,j,k}}$$

$$m_{Hx4}|^{i,j,k} = -\frac{1}{m_{Hx0}|^{i,j,k}}\frac{\Delta t}{\varepsilon_0^2}(\sigma_y^H|^{i,j,k})(\sigma_z^H|^{i,j,k})$$

The final form of the update equations and constitutive relations for D in x-axis are:

$$D_x|_{t+\Delta t}^{i,j,k} = (m_{Dx1}|^{i,j,k})D_x|_t^{i,j,k} + (m_{Dx2}|^{i,j,k})C_x^H|_{t+\frac{\Delta t}{2}}^{i,j,k} + (m_{Dx3}|^{i,j,k})I_{CHx}|_{t-\frac{\Delta t}{2}}^{i,j,k} + (m_{Dx4}|^{i,j,k})I_{Dx}|_{t-\Delta t}^{i,j,k}$$

$$C_x^H|_{t+\frac{\Delta t}{2}}^{i,j,k} = \frac{H_z|_{t+\frac{\Delta t}{2}}^{i,j,k} - H_z|_{t+\frac{\Delta t}{2}}^{i,j-1,k}}{\Delta y} - \frac{H_y|_{t+\frac{\Delta t}{2}}^{i,j,k} - H_y|_{t+\frac{\Delta t}{2}}^{i,j,k-1}}{\Delta z}$$

$$I_{Dx}|_t^{i,j,k} = \sum_{T=0}^{t} D_x|_T^{i,j,k}$$

$$I_{CHx}|_{t-\frac{\Delta t}{2}}^{i,j,k} = \sum_{T=\frac{\Delta t}{2}}^{t-\frac{\Delta t}{2}} C_x^H|_T^{i,j,k} \tag{A3}$$

$$m_{Dx0}|^{i,j,k} = \frac{1}{\Delta t} + \left(\frac{\sigma_y^D|^{i,j,k}+\sigma_z^D|^{i,j,k}}{2\varepsilon_0}\right) + \frac{(\sigma_y^D|^{i,j,k})(\sigma_z^D|^{i,j,k})\Delta t}{4\varepsilon_0^2}$$

$$m_{Dx1}|^{i,j,k} = \frac{1}{m_{Dx0}|^{i,j,k}}\left[\frac{1}{\Delta t} - \left(\frac{\sigma_y^D|^{i,j,k}+\sigma_z^D|^{i,j,k}}{2\varepsilon_0}\right) - \frac{(\sigma_y^D|^{i,j,k})(\sigma_z^D|^{i,j,k})\Delta t}{4\varepsilon_0^2}\right]$$

$$m_{Dx2}|^{i,j,k} = \frac{c_0}{m_{Dx0}|^{i,j,k}}$$

$$m_{Dx3}|^{i,j,k} = \frac{1}{m_{Dx0}|^{i,j,k}}\frac{c_0\,\Delta t\,\sigma_x^D|^{i,j,k}}{\varepsilon_0}$$

$$m_{Dx4}|^{i,j,k} = -\frac{1}{m_{Dx0}|^{i,j,k}}\frac{\Delta t}{\varepsilon_0^2}(\sigma_y^D|^{i,j,k})(\sigma_z^D|^{i,j,k})$$

Afterwards, the final form of the update equations and constitutive relations for E field in x-axis are:

$$E_x|_{t+\Delta t}^{i,j,k} = (m_{Ex1}|^{i,j,k})D_x|_{t+\Delta t}^{i,j,k}$$
$$m_{Ex1}|^{i,j,k} = \frac{1}{\varepsilon_{xx}|^{i,j,k}} \tag{A4}$$

By using the same interoperation, the final form of the update equations and constitutive relations for other axis (y and z) can also be achieved. Note that, in the above equations, the terms are defined in 3D matrices in which i, j and k indicates the grid cell location (in x, y and z vectors respectively) in a 3D Yee grid. "m" terms are constitutive relations. "σ" terms are including all conductivity and loss values in the grid. "I" terms are integration terms which are the summation of curl (C) terms. Δt is the time step in second which is depended to the grid resolutions and calculated based on the Courant stability condition [3]:

$$\Delta t \leq \frac{1}{c_0\sqrt{\frac{1}{(\Delta x)^2} + \frac{1}{(\Delta y)^2} + \frac{1}{(\Delta z)^2}}} \tag{A5}$$

Where c_0 is the speed of the light in the medium in m/s. Δx, Δy and Δz are grid discretization (Δd) in x, y and z vectors in meter which are calculated by:

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$$\Delta d = \frac{\lambda_{min}}{N_\lambda} \tag{A6}$$

Where N_λ is grid resolution and λ_{min} is the shortest wavelength of the irradiated input spectrum obtaining by using the maximum refraction index inside the medium (η_{max}) and highest frequency of the irradiated input spectrum (f_c) as follows:

$$\lambda_{min} = \frac{c}{f_c \eta_{max}} \tag{A7}$$

While updating Maxwell's equations, the input source radiation spectrum is added to the system. The incident electric field of the source radiation spectrum is only polarised in x-y plane [1]; therefore, it is imported to grid as:

$$E_x^{src}|_t^{i,j,k_{src}} = P_x \cos(\omega t - k_0 \eta_{inc} z)$$

$$E_y^{src}|_t^{i,j,k_{src}} = P_y \cos(\omega t - k_0 \eta_{inc} z) \tag{A8}$$

Where P terms are calculating from the polarization vector ($\vec{P} = \vec{P_x} + \vec{P_y}$), $k_0 = \frac{2\pi}{\lambda_0}$, is the radiation's free space wavelength which is constant and η_{inc} is the refraction index of the incident source perimeter. The incident source magnetic field is achieved by using the Maxwell's curl equation ($\nabla \times \vec{E} = -\mu \frac{\partial \vec{H}}{\partial t}$) and is defined as:

$$H_x^{src}|_t^{i,j,k_{src}} = -P_y \sqrt{\frac{\varepsilon_{inc}}{\mu_{inc}}} \cos(\omega t - k_0 \eta_{inc} z)$$

$$H_y^{src}|_t^{i,j,k_{src}} = P_x \sqrt{\frac{\varepsilon_{inc}}{\mu_{inc}}} \cos(\omega t - k_0 \eta_{inc} z) \tag{A9}$$

In the updating process of Maxwell's equations, the permittivity can be interpreted differently for various materials. Linear isotropic materials don't show spatial and temporal dispersion; therefore, their permittivity is defined as a constant number called dielectric constant. However, the optical response of real anisotropic materials; such as MNPs, clearly depends on frequency and wave vector; thus, their dispersive properties are described by complex dielectric function ($\tilde{\varepsilon}_r(\omega)$). The measured dielectric function of Ag NPs was reported by Johnson and Christy [4] which can be mathematically fitted by Lorentz-Drude Model [5]:

$$\tilde{\varepsilon}_r(\omega) = \varepsilon_r(\infty) + \sum_{m=1}^N \frac{f_m \omega_P^2}{\omega_{0,m}^2 + j\Gamma_m \omega - \omega^2} \tag{A10}$$

Where ω is frequency, N is the number of resonators, f_m is the strength of the resonator "m", $\omega_{0,m}$ is the natural frequency of the resonator "m" and Γ_m is the damping rate of the of the resonator "m". $\varepsilon_r(\infty)$ is the offset value of permittivity of the host material in which the metal is solved. Table A.1 presents Lorentz-Drude parameters for Ag NPs.

Table S1. Lorentz-Drude parameters for Ag NPs [5].

$\omega_P = 9.01\ ev$		$\varepsilon_r(\infty) = 1\ F/m$
$\omega_0 = 0\ ev$	$f_0 = 0.84$	$\Gamma_0 = 9.01\ ev$
$\omega_1 = 0.816\ ev$	$f_1 = 0.065$	$\Gamma_1 = 0.053\ ev$
$\omega_2 = 4.481\ ev$	$f_2 = 0.124$	$\Gamma_2 = 3.886\ ev$
$\omega_3 = 8.185\ ev$	$f_3 = 0.011$	$\Gamma_3 = 0.065\ ev$
$\omega_4 = 9.083\ ev$	$f_4 = 0.84$	$\Gamma_4 = 0.916\ ev$
$\omega_5 = 20.29\ ev$	$f_5 = 5.646$	$\Gamma_5 = 2.419\ ev$

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