Genetically Engineered Plasmonic Nano-Arrays

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Supporting Information Available

Generalized Multiparticle Mie Theory. This section introduces the basic concepts of the Generalized Multiparticle Mie (GMM) theory and it is mainly based on the works of Xu.^{1,2} We refer to these works and to the references therein for further details.

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Let us consider a set of L non-overlapping spherical particles, shown in Figure 1, whose j^{th} element has radius a^j and is centered at (x^j, y^j, z^j) in the *primary* reference system $(0, X, Y, Z)$. We introduce a number L of *local* reference systems $(0, X^j, Y^j, Z^j)$ with $j = 1 \dots L$, centered on the j^{th} particle and with parallel axes to those of the primary system. The field scattered by the j^{th} particle

Figure 1: Geometry of the scattering problem.

can be expressed in terms of the radiating Vector Spherical Wave Functions (VSWFs) set centered on the j^{th} particle itself, that is

$$\begin{cases} \mathbf{E}_s^{jj} = \sum_{n=1}^{\infty} \sum_{m=-n}^n j E_{mn} [a_{mn}^{jj} \mathbf{N}_{mn}^3(k_0 r^j, \theta^j, \phi^j) + b_{mn}^{jj} \mathbf{M}_{mn}^3(k_0 r^j, \theta^j, \phi^j)] \\ \mathbf{H}_s^{jj} = \frac{k_0}{\omega \mu_0} \sum_{n=1}^{\infty} \sum_{m=-n}^n E_{mn} [b_{mn}^{jj} \mathbf{N}_{mn}^3(k_0 r^j, \theta^j, \phi^j) + a_{mn}^{jj} \mathbf{M}_{mn}^3(k_0 r^j, \theta^j, \phi^j)] \end{cases} \quad (1)$$

The same field scattered by the j^{th} particle, can be also expanded into the VSWF set centered on

the i^{th} particle, as follows:

$$\begin{cases} \mathbf{E}_s^{ji} = \sum_{n=1}^{\infty} \sum_{m=-n}^n jE_{mn} [a_{mn}^{ji} \mathbf{N}_{mn}^3(k_0 r^i, \theta^i, \phi^i) + b_{mn}^{ji} \mathbf{M}_{mn}^3(k_0 r^i, \theta^i, \phi^i)] \\ \mathbf{H}_s^{ji} = \frac{k_0}{\omega \mu_0} \sum_{n=1}^{\infty} \sum_{m=-n}^n E_{mn} [b_{mn}^{ji} \mathbf{N}_{mn}^3(k_0 r^i, \theta^i, \phi^i) + a_{mn}^{ji} \mathbf{M}_{mn}^3(k_0 r^i, \theta^i, \phi^i)] \end{cases} \quad (2)$$

The *vector addition theorem* for VSWF enables the transformation of the series expansion coefficients a_{mn}^{jj} and b_{mn}^{jj} for the scattered fields of the j^{th} particle into an expansion in the local coordinate system associated with the i^{th} particle a_{mn}^{ji} and b_{mn}^{ji} , as follows:

$$\begin{cases} a_{mn}^{ji} = \sum_{v=1}^{\infty} \sum_{\mu=-v}^v A_{mn,\mu v}^{ji} a_{\mu v}^{jj} + B_{mn,\mu v}^{ji} b_{\mu v}^{jj} \\ b_{mn}^{ji} = \sum_{v=1}^{\infty} \sum_{\mu=-v}^v B_{mn,\mu v}^{ji} a_{\mu v}^{jj} + A_{mn,\mu v}^{ji} b_{\mu v}^{jj} \end{cases} \quad (3)$$

The translation matrices $A_{mn,\mu v}^{ji}$ and $B_{mn,\mu v}^{ji}$ only depend on the distance and direction of the translation vector from the center of the i^{th} NP to the center of the j^{th} NP. The derivation of the translational matrices can be greatly simplified by decomposing the overall translation into a combination of two rotations and a translation along the z-axis, according to the Mackowski three-step procedure.^{2,3}

The external field incident on the i^{th} sphere can be expanded into regular VSWFs associated to the reference system $(0^i, X^i, Y^i, Z^i)$

$$\begin{cases} \mathbf{E}_e^{ii} = - \sum_{n=1}^{\infty} \sum_{m=-n}^n jE_{mn} [p_{mn}^{ii} \mathbf{N}_{mn}^1(k_0 r^i, \theta^i, \phi^i) + q_{mn}^{ii} \mathbf{M}_{mn}^1(k_0 r^i, \theta^i, \phi^i)] \\ \mathbf{H}_e^{ii} = - \frac{k_0}{\omega \mu_0} \sum_{n=1}^{\infty} \sum_{m=-n}^n E_{mn} [q_{mn}^{ii} \mathbf{N}_{mn}^1(k_0 r^i, \theta^i, \phi^i) + p_{mn}^{ii} \mathbf{M}_{mn}^1(k_0 r^i, \theta^i, \phi^i)] \end{cases} \quad (4)$$

In the reference system $(0^i, X^i, Y^i, Z^i)$ the electric field on the i^{th} sphere due to all other particles and the external field, is:

$$\mathbf{E}_i^{ii} = \sum_{\substack{j=1 \\ j \neq i}}^L \mathbf{E}_s^{ji} + \mathbf{E}_e^{ii} \quad (5)$$

Therefore, since the problem has been reduced to single scattering we can now utilize the single particle Mie theory¹ to calculate the overall scattering coefficients of the i^{th} sphere:

$$\begin{cases} a_{mn}^{ii} = a_n^i \left(p_{mn}^i - \sum_{\substack{j=1 \\ j \neq i}}^L a_{mn}^{ji} \right) \\ b_{mn}^{ii} = b_n^i \left(q_{mn}^i - \sum_{\substack{j=1 \\ j \neq i}}^L b_{mn}^{ji} \right) \end{cases} \quad (6)$$

where $i \in \{1, 2, \dots, L\}$, $n \in \{1, 2, \dots, \infty\}$, $|m| \leq n$, while a_n^i and b_n^i are the single sphere Mie theory coefficients.⁴ By using the addition theorem, i.e. eqs. 3, into eqs. 6 we have:

$$\begin{cases} a_{mn}^{ii} + a_n^i \sum_{\substack{j=1 \\ j \neq i}}^L \sum_{v=1}^{\infty} \sum_{\mu=-v}^v \left[A_{mn,\mu v}^{ji} a_{\mu v}^{jj} + B_{mn,\mu v}^{ji} b_{\mu v}^{jj} \right] = a_n^i p_{mn}^i \\ b_{mn}^{ii} + b_n^i \sum_{\substack{j=1 \\ j \neq i}}^L \sum_{v=1}^{\infty} \sum_{\mu=-v}^v \left[B_{mn,\mu v}^{ji} a_{\mu v}^{jj} + A_{mn,\mu v}^{ji} b_{\mu v}^{jj} \right] = b_n^i q_{mn}^i \end{cases} \quad (7)$$

where $i \in \{1, 2, \dots, L\}$, $n \in \{1, 2, \dots, \infty\}$, and $|m| \leq n$. In order to numerically solve the system of eqs. 7 we truncate the scattered field and the incident field expansion of the particles to a finite order N_{max} , namely:

$$\begin{cases} a_{mn}^{ii} + a_n^i \sum_{\substack{j=1 \\ j \neq i}}^L \sum_{v=1}^{N_{max}} \sum_{\mu=-v}^v \left[A_{mn,\mu v}^{ji} a_{\mu v}^{jj} + B_{mn,\mu v}^{ji} b_{\mu v}^{jj} \right] = a_n^i p_{mn}^i \\ b_{mn}^{ii} + b_n^i \sum_{\substack{j=1 \\ j \neq i}}^L \sum_{v=1}^{N_{max}} \sum_{\mu=-v}^v \left[B_{mn,\mu v}^{ji} a_{\mu v}^{jj} + A_{mn,\mu v}^{ji} b_{\mu v}^{jj} \right] = b_n^i q_{mn}^i \end{cases} \quad (8)$$

where $i \in \{1, 2, \dots, L\}$, $n \in \{1, 2, \dots, N_{max}\}$, and $|m| \leq n$. The system of eqs. 8 was solved iteratively using the approach proposed by Xu.¹

Genetic Algorithm. In the framework of GAs,⁵ a feasible solution of the given optimization problem, usually referred to as an individual, is represented by a binary string, namely a chro-

mosome. Each chromosome is in turn subdivided into N genes; the j^{th} gene represents, through Gray coding, the j^{th} degree of freedom of the problem. The choice of Gray coding guarantees that two consecutive values of a given degree of freedom are represented by binary sequences that differ only in one digit. Each chromosome is given a fitness value. The implemented GA works as follows: **i)** the population, which consists of W individuals, is randomly initialized. **ii)** The fitness of each individual is evaluated and the selection of the mating pool among the population is performed. The implemented selection criterion is the roulette wheel selection: each wheel's slot is proportional to the individual fitness. Indeed, a fit individual has a better probability of being selected for mating. **iii)** Once the mating has been performed the crossover process between two chromosomes can take place. The two mating chromosomes are cut at the same randomly selected point and the resulting strings are swapped between them. **iv)** In order to prevent the GA from becoming trapped in local minima, and to preserve the genetic diversity of the population, the chromosomes are subjected to mutation. The implemented mutation consists of inverting the value of one bit along the chromosome with a given probability P_m . **v)** Eventually the old generation is killed, replaced by new individuals, providing that the best individual in the old population is maintained (elitism). **vi)** Once the iteration number reaches the maximum value N_{iter} the GA stops, otherwise the iterative process restarts from step ii. In all the GA optimizations performed in this paper we have assumed a population W of 48 individuals, a number of iterations $N_{iter} = 10000$, and a probability of mutation of $P_m = 0.1$.

Two Dimensional Optimization with Varying NPs Size. This analysis consists in the synthesis of both the NPs centers and radii, assuming $\delta = 3nm$, $R_{min} = 5nm$, $R_{max} = 150nm$, and an incident wavelength $\lambda^{(Ag)} = 370nm$ for Ag and $\lambda^{(Au)} = 535nm$ for Au. The optimized patterns follow the same physical rules found on the basis of the analysis discussed in the text, even if the additional degree of freedom leads to better performances.

We found that regardless of the metal choice the $N = 2$ configuration of NPs results in an asymmetric dimer, i.e. composed of particles with different radii, aligned along the polarization direction, with the minimum allowed edge-to-edge spacing. We show this configuration in Figure 2

(a) for Au and (e) for Ag, while the exact particle coordinates are listed in Table 1. When more particles are added to the system, for instance when $N = 6$ as shown in Figure 2 (b), we find that Au NPs assemble to form asymmetric dimers, placed symmetrically with respect to the probing point along the vertical direction in order to provide an in-phase radiative contribution. In the Ag NP array with $N = 6$, shown in Figure 2 (f), the near field resonance supported by the central dimer is boosted by the far field radiative coupling of the remaining particles. The radius of the particles in the far zone turns out to be the maximum allowed ($R_{max} = 150nm$), in this way the radiative contribution is maximized and the achieved field enhancement is twice what is found in the corresponding fixed radius scenario.

Figure 2: Electric field magnitude on the equatorial plane of the optimized NP arrays composed of (a,e) $N=2$, (b,f) 6, (c,g) 10 and (d,h) 12 Au and Ag spheres, respectively. The achieved values of field enhancement in $\mathbf{r}_0$ ($\mathbf{r}_0$ is the center of each simulation box) are (a) 64 (b) 121 (c) 154 (d) 165 for Au and (e) 218, (f) 557, (g) 676 (h) 760 for Ag. The color maps are in logscale.

When increasing the NP number to $N = 10$ we find that, in the Au case, a second order grating

contribution is required to further enhance the field as shown in Figure 2 (c). In Ag case, shown in Figure 2 (g), the central dimer is surrounded by a NP necklace⁶ responsible for the radiative boosting, which leads to a FE increase of more than 20% with respect of the N=6 case. Finally, by adding further NPs, we found that also for Ag arrays the last two particles are placed further away to maximize the near-field at the probing point *via* in phase second order radiative contribution. However, we can notice that, as in the two dimensional optimization with fixed radius, the fundamental NP units turn out to be the isolated particle in the case of Ag aggregates and NP dimers for Au patterns, with the difference that they are asymmetric.

Table 1: Optimized 2D arrays of Au and Ag NPs.

	Au				Ag			
N	x[nm]	y[nm]	R[nm]	FE ₀	x[nm]	y[nm]	R[nm]	FE ₀
1	64	0	61		36	0	33	
2	-29	0	29	63	-6.5	0	6.5	218
3	215	-340	108		480	0	150	
4	-119	-364	108		-433	0	150	
5	-128	390	127		17.6	-328	150	
6	187	362	108	121	37.2	337	150	557
7	138	871	150		354	309	150	
8	501	0	99		-284	327	150	
9	256	-860	135		-392	-362	150	
10	-129	-865	140	154	378	-355	143	676
11	-463	0	96		156	776	106	
12	-200	833	108	165	156	-776	106	760

FDTD Analysis Details All particles are modeled using material dispersion data from Johnson and Christy,⁷ using particle shapes and sizes based on SEM of the fabricated particles. Meshing in the x and y (in-plane) dimensions is $2.5nm$ around all nanoparticles, and 2 nm in the z dimension (out-of-plane) in order to ensure numerical convergence. All arrays are simulated on a glass substrate in order to exactly describe our experimental conditions. In all simulations, plane wave excitation was used at normal incidence to the substrate. All periodic structures were simulated with periodic boundary conditions, otherwise perfectly matched layer (PML) boundary conditions were used to absorb all electromagnetic radiation at the simulation boundaries.⁸ In the case of geometries requiring PML, twelve layers were used to minimize reflections from the boundary; the

normalized maximum absorption coefficient, σ , was 0.25 and increased cubically as fields propagated through the PML layers. The simulations were performed using the commercial software Lumerical FDTD Solutions.⁹

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