Selected Topics in

Advanced Experimental Physics

Markus Lippitz

December 1, 2023

Contents

Part I

Concept: Fourier Transformation

Part II

Concept: Hybridization

Part III

Example: All Together

Chapter 8
Lattice of plasmonic particles

Markus Lippitz
December 1, 2023

Overview

Now we combine everything. We have three ingredients: the plasmonic resonance of a small silver particle, a periodic arrangement of these particles in a two-dimensional lattice, and the narrow optical resonance of the TDBC dye. The particles hybridized with each other, combining the plasmon hybridization of Chapter XXX with lattice modes, as in a chain of masses and in solid-state physics in general. As we will see below, this results in an X-shaped dispersion relation, which we measure using Fourier optics.

In a second step, this lattice plasmon mode hybridizes with the optical transition of the dye, leading to characteristic anti-crossing features in the dispersion relation, where the X crosses the horizontal dye dispersion. Microscopically, we can model the influence of the dye by taking into account the refractive index of the medium.

This chapter is based on the master thesis of Simon Durst[1]. All figures are taken from his thesis, sometimes slightly modified.

[1] Durst, 2021.

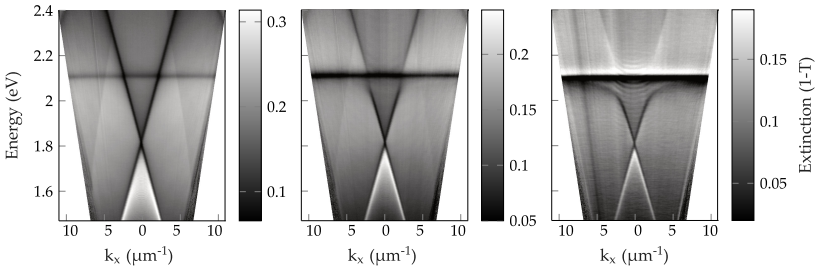

Figure 8.1: Dispersion relation of a lattice plasmon hybridized (X-shaped) with a dye (horizontal), for different concentrations of the dye (left to right: 1, 10, 60 weight %). The grey scale gives the extinction.

How this is measured

The samples consist of a rectangular lattice of silver particles on a glass substrate. It is fabricated by electron beam lithography. An electron sensitive resist is exposed in a (slightly modified) electron microscope and then

developed. At the exposed areas, the glass surface is accessible. The unexposed areas are still covered by the resist. A gold or silver film is deposited by thermal evaporation. When the resist is chemically removed, it takes with it the metal film on the unexposed areas. The metal remains only where it adheres directly to the glass surface. In this way, arbitrary two-dimensional structures can be fabricated with a resolution limited by the electron beam to about 50–80 nm in our case.

We have chosen a particle size of 80×80 nm. The lattice constant p_y is always 200 nm, p_x varies (see below). The lattice is coated with a polymer film containing the TDBC dye in variable concentration. Everything is covered with immersion oil ($n = 1.5$) and a second glass substrate, so that the particles are embedded in a homogeneous dielectric environment.

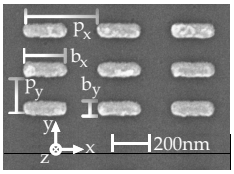

Figure 8.2: SEM micrograph of gold nanorods in a lattice. Indicated are the dimensions of the rods and the lattice constants.

For a dispersion relation we need an energy E and a wave vector k. Since the sample is only two-dimensional, this is an in-plane wave vector, which we have chosen to be along the x-direction, i.e. k_x. The signal measured as the function of E and k_x is the transmission T or the extinction[2] $1 - T$. We measure transmission spectra for white light as a function of angle of incidence. Electron beam lithography results in a finite size lattice of 30×30 µm. It is difficult to keep the sample in the beam when rotating either the sample or the beam. So we keep everything fixed and measure all the angles at the same time. To do this, we illuminate the sample with a light cone with a large aperture angle (NA = 0.9, max. angle = $64°$). The transmitted light is collected by a second microscope objective. Fourier optics tells us that the front focal plane is Fourier transformed into the back focal plane. We can no longer use a small angle of incidence, but an ideal imaging system must satisfy the Abbé-Sine condition that rays of equal angle of incidence θ intersect at the same point at a height h with

$$h = f \sin\theta \quad . \tag{8.1}$$

[2] In this sample, not only absorption but also scattering leads to a reduced transmission. Therefore, we call it extinction and not absorption.

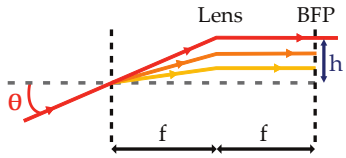

Figure 8.3: The back focal plane sorts rays by their angle in the front focal plane.

We image this back-focal plane (BFP) on the entrance slit of a spectrometer and thus get an image on the CCD camera which in one direction is angle of incidence, in the other wavelength of the light beam. This is converted into a E-k_x scale. As the maximum angle is fixed, but $k \propto E$, we observable region of the dispersion relation has a trapezoidal shape, i.e, the maximum value of k_x is lower at lower energy. The light beam is polarized before the sample such that we image the s polarization on the entrance slit of the spectrometer, i.e. along the x-direction of the sample coordinate system.

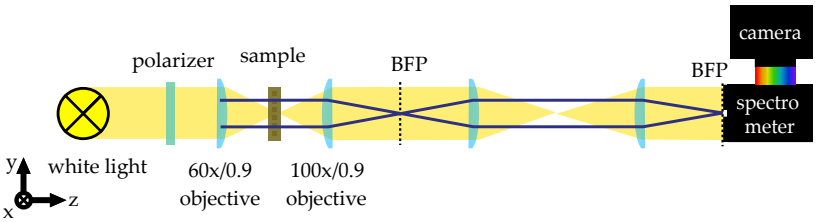

Figure 8.4: Setup to measure angle-dependent transmission spectra without moving parts.

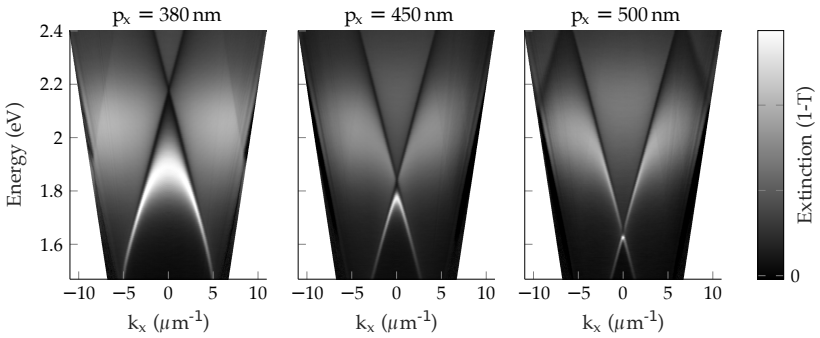

Figure 8.5: Angle-dependent extinction spectrum of an array of plasmonic particles.

How to understand the dispersion relation (without dye)

Each panel in Fig. 8.5 shows a dispersion relation, i.e., the relation between (in-plane) momentum and energy. Two features combine: the particle plasmon resonance and a lattice resonance. The particle resonance is at a given eigen-frequency (or energy), spectrally rather broad, and independent of the angle of incidence or k_x, as the particles are rather spherical. This gives the broad, medium gray band around an energy of 2 eV. The second feature is the lattice resonance. An optical wave travels parallel to the interface. Its dispersion relation is

$$E = \hbar \, (k_x + m \cdot G) \tag{8.2}$$

where $G = 2\pi/p_x$ is the fundamental reciprocal lattice vector and m an integer. This results in the X-shaped feature for $m = \pm 1$. With varying p_x the crossing point, i.e., the energy E at $k_x = 0$ varies, as

$$E(k_x = 0) = m\frac{2\pi}{p_x} \quad . \tag{8.3}$$

In the right-most panel of Fig. 8.5 we see the second order $m = \pm 2$.

The eigenmode of the lattice resonance is spatially extended over the whole lattice and spectrally narrow. The interaction of a broad (particle) and a narrow (lattice) resonance leads to characteristic spectral features that are visible in Fig. 8.5 and could be described as Fano resonance[3]. But that is beyond the scope of this chapter. Here we follow a more microscopic approach. We calculate the extinction spectrum of an arrangement of many small particles at positions $\mathbf{r}_i$. Each particle is modelled as sphere with a polarizability α_i given by the material properties and the volume of the small particle.

[3] Ugo Fano, 1912–2001

Radiating electric dipole

Let us first look at a single electric dipole $\boldsymbol{\mu}$ at the position $\mathbf{r}_0$. Its field at the position $\mathbf{r}$ is given by[4]

$$\mathbf{E}(\mathbf{r}) = \frac{k^2}{\epsilon_0 \, \epsilon_{out}} \, \mathbf{G}(\mathbf{r}, \mathbf{r}_0) \, \boldsymbol{\mu} \tag{8.4}$$

with the length k of the wave vector in the medium of dielectric function ϵ_{out}. The Greens function $\mathbf{G}$ is given by[5]

[4] Novotny and Hecht, 2012, eq. 8.52.

[5] This follows Novotny and Hecht, 2012 eq. 8.55 and differs by $4\pi k^2$ from eq. 2 in Yurkin and Hoekstra, 2007

$$\mathbf{G}(\mathbf{r},\mathbf{r}_0) = \frac{e^{ikR}}{4\pi\, k^2\, R^3}\left[\left(k^2R^2 + ikR - 1\right)\mathbf{1} + \left(3 - 3ikR - k^2R^2\right)\frac{\mathbf{RR}}{R^2}\right] \tag{8.5}$$

with $\mathbf{R} = \mathbf{r} - \mathbf{r}_0$, $R = |\mathbf{R}|$, $\mathbf{1}$ the unity 3×3-tensor, and $\mathbf{RR}$ the outer product of $\mathbf{R}$ with itself, i.e.

$$\mathbf{RR} = \begin{pmatrix} R_xR_x & R_xR_y & R_xR_z \\ R_yR_x & R_yR_y & R_yR_z \\ R_zR_x & R_zR_y & R_zR_z \end{pmatrix} \quad . \tag{8.6}$$

This is a convenient method to describe the full vectorial field emitted by a dipole at position $\mathbf{r}_0$ everywhere in space, including both near- and far-field components.

Test yourself

1. Convince yourself that eq. 8.5 agrees with the other commonly used form

$$\mathbf{E} = \frac{e^{i\,kr}}{4\pi\epsilon_0\,\epsilon_{out}}\frac{1}{r^3}\left\{(kr)^2\,(\hat{\mathbf{r}}\times\boldsymbol{\mu})\times\hat{\mathbf{r}} + (1-ikr)\,(3\hat{\mathbf{r}}\,[\hat{\mathbf{r}}\cdot\boldsymbol{\mu}] - \boldsymbol{\mu})\right\} \quad . \tag{8.7}$$

Scattering sphere

We need to know the oscillation amplitude of the emitting dipole $\mathbf{p}$ to use eq. 8.5. As in chapter 6, it is related by the polarizability α to the incoming optical field $\mathbf{E}_{inc}$

$$\mathbf{p} = \epsilon_0\,\epsilon_{out}\,\alpha\,\mathbf{E}_{inc} \tag{8.8}$$

with the dielectric function ϵ_{out} of the embedding medium. When we assume that the scattering nanoobject is a sphere, we can calculate

$$\alpha = 3V\,\frac{\epsilon_{in} - \epsilon_{out}}{\epsilon_{in} + 2\epsilon_{out}} \quad , \tag{8.9}$$

where V is the volume of the sphere and ϵ_{in} the dielectric function of it. The sphere radiates a scattered field $\mathbf{E}_S$

$$\mathbf{E}_S(\mathbf{r}) = \frac{k^2}{\epsilon_0\,\epsilon_{out}}\,\mathbf{G}(\mathbf{r},\mathbf{r}_0)\,\mathbf{p} \tag{8.10}$$

$$= \frac{1}{4\pi\,\epsilon_0\,\epsilon_{out}}\frac{e^{ikR}}{R^3}\,[\ldots]\,\mathbf{p} \tag{8.11}$$

where the contents of the square brackets is the same as in eq.8.5 above. k is again the length of the wave vector in a medium with dielectric function ϵ_{out}.

Multiple particles

When we have more than one particle, each particle i sees the incident field $\mathbf{E}_{i,inc}$ at the position $\mathbf{r}_i$ plus the sum over all scattered fields $\mathbf{E}_{j,S}$ from all the other induced dipoles j

$$\mathbf{E}_{i,loc} = \mathbf{E}_{i,inc} + \sum_{j\neq i}\mathbf{E}_{j,S} = \mathbf{E}_0\,e^{i\mathbf{k}\cdot\mathbf{r}_i} + \sum_{j\neq i}\frac{k^2}{\epsilon_0\,\epsilon_{out}}\mathbf{G}(\mathbf{r}_i,\mathbf{r}_j)\,\mathbf{p}_j \tag{8.12}$$

with the dipole moment $\mathbf{p}_j$ of the particle at position $\mathbf{r}_j$. The position of the 'receiving' particle $\mathbf{r}_i$ takes the role of $\mathbf{r}$ in the Greens function; the position of the scattering particle $\mathbf{r}_j$ takes the role of the dipole at position $\mathbf{r}_0$ above.

The local field $\mathbf{E}_{i,loc}$ then induces a dipole moment again

$$\mathbf{p}_i = \epsilon_0 \, \epsilon_{out} \, \alpha_i \, \mathbf{E}_{i,loc} \quad . \tag{8.13}$$

Both equations together form a coupled equation system for the dipole moments $\mathbf{p}_i$

$$\mathbf{E}_0 \, e^{i\mathbf{k}\cdot\mathbf{r}_i} = \frac{1}{\epsilon_0 \epsilon_{out} \alpha_i} \, \mathbf{p}_i \; - \sum_{j \neq i} \frac{k^2}{\epsilon_0 \, \epsilon_{out}} \mathbf{G}(\mathbf{r}_i, \mathbf{r}_j) \, \mathbf{p}_j \tag{8.14}$$

which can be written as

$$\mathbf{E}_{inc} = \mathbf{A} \, \mathbf{p} \quad , \tag{8.15}$$

where $\mathbf{p}$ and $\mathbf{E}_{inc}$ are column vectors containing the induced dipole moment and the incident field of all dipoles and $\mathbf{A}$ is an interaction matrix. Its elements are 3×3-sub-matrices given by[6]

$$\mathbf{A}_{ii} = \frac{1}{\epsilon_0 \epsilon_{out} \alpha_i} \, \mathbf{1} \tag{8.16}$$

$$\mathbf{A}_{ij} = - \frac{k^2}{\epsilon_0 \, \epsilon_{out}} \mathbf{G}(\mathbf{r}_i, \mathbf{r}_j) \quad . \tag{8.17}$$

[6] This assume an isotropic polarizability. Otherwise, the diagonal elements should be $1/\alpha_{x,y,z}$ instead of $\mathbf{1}/\alpha$.

Some publications put the minus sign of the last equation into the Greens function.

The extinction cross-section can be calculated by the optical theorem from the interference of the forward-scattered wave with the incident wave. We get[7]

$$\sigma_{ext} = \frac{k}{\epsilon_0 \epsilon_{out} \, |\mathbf{E}_{inc}|^2} \sum_i \Im(\mathbf{p}_i \cdot \mathbf{E}^{\star}_{i,inc}) \quad . \tag{8.18}$$

[7] Draine, 1988; Yurkin and Hoekstra, 2007.

The term $\Im(\mathbf{p} \cdot \mathbf{E}^{\star}_{inc})$ is very similar to the term for absorption, in which not the incident field $\mathbf{E}_{inc}$ but the local field $\mathbf{E}_{loc}$ would be used.

With this we have now everything at hand to calculate the extinction spectra of arrangements of small scattering spheres or dipoles. We solve eq. 8.15 for $\mathbf{p}$ and then calculate the cross-section. Depending on the community (and the distance between the dipoles) this is called discrete dipole approximation (DDA) or coupled dipole approximate (CDA).

Test yourself

2. Which size / dimension have $\mathbf{A}$ and $\mathbf{p}$ in eq. 8.15 ?
3. Sketch the interaction matrix $\mathbf{A}$ and its components.

Lattice sum

Things become easier when we are interested in infinite lattices of identical scatterers. As we are on a lattice, all lattice points are equal, especially in the amplitude and vectorial direction $\hat{\mathbf{n}}$ of the local field. It is then convenient to re-arrange eq. 8.12

$$\mathbf{E}_{i,loc} = \mathbf{E}_0 \, e^{i\mathbf{k}\cdot\mathbf{r}_i} \; + \sum_{j \neq i} k^2 \, \mathbf{G}(\mathbf{r}_i, \mathbf{r}_j) \, \alpha \, \mathbf{E}_{j,loc} \tag{8.19}$$

to

$$E_{i,loc}\, e^{-i\mathbf{k}\cdot\mathbf{r}_i} = \hat{\mathbf{n}}\cdot\mathbf{E}_0 + \sum_{j\neq i} k^2\, \hat{\mathbf{n}}\mathbf{G}(\mathbf{r}_i,\mathbf{r}_j)\hat{\mathbf{n}}\,\alpha\, E_{j,loc}\, e^{-i\mathbf{k}\cdot\mathbf{r}_i} \tag{8.20}$$

so that we get

$$\hat{\mathbf{n}}\cdot\mathbf{E}_0 = E_{loc}\left(1-\alpha\sum_{j\neq i} k^2\,\hat{\mathbf{n}}\mathbf{G}(\mathbf{r}_i,\mathbf{r}_j)\hat{\mathbf{n}}\; e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)}\right) = E_{loc}\,(1-\alpha\, S) \tag{8.21}$$

with the retarded lattice sum S. The induced dipole moment becomes

$$\mathbf{p} = \epsilon_0\,\epsilon_{out}\,\alpha\,\mathbf{E}_{loc} = \epsilon_0\,\epsilon_{out}\,\frac{\alpha}{1-\alpha\, S}\,\mathbf{E}_0 \tag{8.22}$$

or we define an effective (lattice) polarizability

$$\alpha_{\text{lattice}} = \frac{\alpha}{1-\alpha\, S} \quad . \tag{8.23}$$

The extinction cross-section then becomes[8]

$$\sigma_{ext} = k\,\Im(\alpha_{\text{lattice}}) \quad . \tag{8.24}$$

[8] somehow a 4π is missing here....

The simulated dispersion relations agree well with the measured ones, as Fig.8.6 shows.

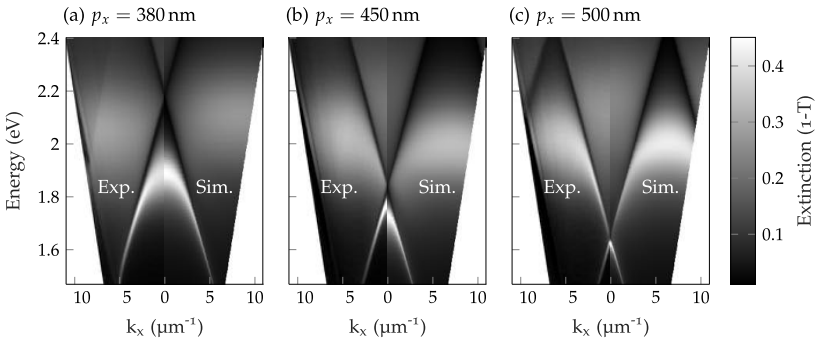

Figure 8.6: Simulations compared to experiment.

Coupling to a dye

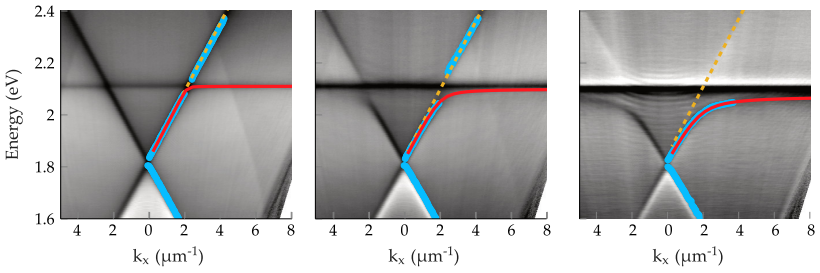

Figure 8.7: Anticrossing.

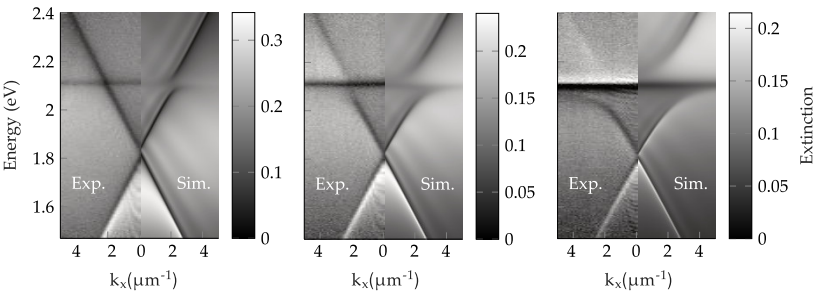

Figure 8.8: Full sim.

References

Draine, B T (1988). “The discrete-dipole approximation and its application to interstellar graphite grains”. In: *The Astrophysical Journal* 333, p. 848.

Durst, Simon (2021). “Excitonic Coupling to Surface Lattice Resonances : Experiment and Simulation”. Bayreuth.

Novotny, Lukas and Bert Hecht (2012). *Principles of nano-optics*. 2. ed. Cambridge Univ. Press.

Yurkin, Maxim A and Alfons G Hoekstra (2007). “The discrete dipole approximation: an overview and recent developments”. In: *Journal Of Quantitative Spectroscopy & Radiative Transfer* 106.1-3, pp. 558–589.

Bibliography

Draine, B T (1988). “The discrete-dipole approximation and its application to interstellar graphite grains”. In: *The Astrophysical Journal* 333, p. 848. .

Durst, Simon (2021). “Excitonic Coupling to Surface Lattice Resonances : Experiment and Simulation”. Bayreuth.

Novotny, Lukas and Bert Hecht (2012). *Principles of nano-optics*. 2. ed. Cambridge Univ. Press. .

Yurkin, Maxim A and Alfons G Hoekstra (2007). “The discrete dipole approximation: an overview and recent developments”. In: *Journal Of Quantitative Spectroscopy & Radiative Transfer* 106.1-3, pp. 558–589. .