Spontaneous emission control with plasmonic structures

1. Motivation
2. Classical RF sources
3. Fermi’s Golden Rule
4. Metals & plasmons
5. Redirecting light

Tutorial - May 2015
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Spontaneous emission control

Space
- Where to does the photon go?
- With what polarization?

Time
- How long does it take for the photon to appear?

Matter
- Selection rules
Motivation

Optical microscopy
Below $\lambda/2$ limit

Single photon sources
Quantum information
Quantum communication

Single molecules
Information from fluctuations

Quantum information in 1 photon can not be eavesdropped

Spectroscopy of molecules
Distance ruler, vibrations
THz, IR and VIS

Bates & Zhuang [PALM, STORM]
Liu & Alivisatos
Motivation

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Quantum information in 1 photon can not be eavesdropped

Blue LED

Nobel Physics 2014
Quantum source.. but..

still, it is useful to understand classical RF antenna sources

Example 1: radiation resistance
Example 2: phased array
\[ \nabla \times \mathbf{H} = \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t} \]

Radiation resistance – environment sets power to current ratio

The *work* you need to do keep current \( j \) going depends on environment
Radiation resistance

1) Dipole antenna
2) Ground plane

(Balanis Antenna Handbook)
Classical current dipole + mirror

1) Dipole antenna
2) Ground plane

(1918/ mast 212 m. f=24 kHz at 400 kW)
RF understanding of Drexhage?

Interference of the dipole field with that of its mirror image

*The same current* radiates a *different* far field power
Backaction viewpoint

In order to *maintain* constant current one does work against one’s own field

\[
W = \langle \mathbf{F} \cdot \frac{d\mathbf{v}}{dt} \rangle = \langle \mathbf{E} \cdot \frac{d\mathbf{p}}{dt} \rangle = \langle \text{Re}\mathbf{E}e^{i\omega t} \cdot \text{Re}(i\omega \mathbf{p}e^{i\omega t}) \rangle
\]

Suppose we call the dipole field

\[
\mathbf{E}(\mathbf{r}) = \mathbf{G}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{p}
\]

Resistance due to field \(\text{Im} \mathbf{G}\) that comes back to the source
Phased array physics

A set of coherent currents creates an arbitrary beam profile

RF: individual amplitude and phase control
1. Radiation *resistance*
   total power at fixed $J$

2. Directional gain
Single quantum emitter

- After one excitation, emits just one quantum of light
- Probabilistic timing of *when* emission occurs
- Spatial (and temporal) coherence of single photon wavepackets
- No such thing as setting up multiple *coherent* SpE sources

Radiation resistance

Analogy?

Isn’t a molecule a constant-output source (just 1 photon)

“Drexhage experiment” (1968)
25µm PS bead covered with 400nm Ag as mirror

PS bead glued to cleaved fiber

Lateral scanning in shear force varies emitter-mirror distance

Set up and measurement procedure

- Brightness (fluctuations)  
  how many counts per ~10 ms
- Lifetime  
  delay times APD ↔ laser
- Antibunching  
  delay times APD 1 ↔ APD 2

Time-tagging of photon & laser arrival times in 0.17 ns bins
Calibration example – single NV center

- Single NV center in a 100 nm nanodiamond (MicroDiamant AG)
- Decay rate varies with distance to the mirror
  - Radiative decay rate $\leftrightarrow$ Radiative impedance
  - (Nonradiative decay rate $\leftrightarrow$ Ohmic resistance)

Transition dipole moment

Dipole approximation – a small object $k.r \ll 1$ feels

$$E(r, t) = E e^{i k \cdot r - i \omega t} \approx E e^{i \omega t}[1 + i k \cdot r + \ldots]$$

As

$$V(t) = E \cdot (er) \cos \omega t$$

The probability of transitions is governed by

$$\mu = \langle \psi_{nlm} | er | \psi_{n' l' m'} \rangle \quad \text{‘Transition dipole moment’}$$

Note how this matrix element selects transitions

Loudon, The Quantum Theory of Light
Fermi’s Golden Rule

\[
V = -\mu \cdot E
\]

**Dipole operator**

**Light**

Perturbation that couples states can take the atom in initial state \( \psi_i \) to another state \( \psi_f \)

Fermi’s Golden Rule: rate of decay of the initial state \( \psi_i \)

\[
\Gamma = \frac{2\pi}{\hbar^2} \sum_{\text{all final states } f} \left| \langle \psi_f | V | \psi_i \rangle \right|^2 \delta(E_f - E_i)
\]

Loudon, The Quantum Theory of Light
Understanding Fermi’s Golden Rule

\[ \Gamma = \frac{2\pi}{\hbar^2} \sum_{\text{all final states } f} \left| \left\langle \psi_f \mid V \mid \psi_i \right\rangle \right|^2 \delta(E_f - E_i) \]

Matrix elements: Transition strength
Energy conservation
Selection rules

Spontaneous emission of a two-level atom:

**Initial state:** excited atom + 0 photons.

**Final state:** ground state atom + 1 photon in some photon state

**Question:** how many states are there for the photon ???

How many photon in a box of vacuum?

States in an \(L \times L \times L\) box:

\[
E(x,t) = Ae^{i\omega t} \sin(k \cdot r) \quad \text{with} \quad k = \frac{\pi}{L}(l,m,n)
\]

Number of states with \(|k|\) between \(k\) and \(k+dk\):

\[
N(k)dk = \frac{4}{8} \pi k^2 dk \left(\frac{L}{\pi}\right)^3 \cdot 2
\]

As a function of frequency \(\omega (=ck)\):

\[
N(\omega)d\omega = L^3 \frac{\omega^2}{\pi^2 c^2} \frac{dk}{d\omega}d\omega = L^3 \frac{\omega^2}{\pi^2 c^3}d\omega
\]

Loudon, The Quantum Theory of Light
Fluorescence decay rates

Fermi’s Rule: Fluorescence rate $\propto$ number of photon states

Visible light: $\sim 10^5$ photon states per Hz, per m$^3$ of vacuum

Loudon, The Quantum Theory of Light
Fluorescence in a cavity

Fermi’s Rule: Fluorescence rate $\propto$ number of photon states

Purcell factor

$$F = \frac{3}{4\pi^2} \lambda^3 \frac{Q}{V}$$

Purcell: One extra state per $\Delta \omega = \omega/Q$ in a volume $V$

Observations - 2D quantum well

Fujita et al., Science (2005)

Two-dimensional: Kyoto [Noda], Stanford [Vuckovic], DTU [Lodahl], WSI [Finley] ...

Three dimension: Lodahl et al. (Nature 2004), Leistikow et al. (PRL ’11)
Dispersion relation

Redistribution of states:
- photonic band gap
- flat bands imply high DOS

Local density of states

Consider a molecule / quantum dot / ...
- as located at a fixed position
- as oriented along a fixed direction

The available modes have to be weighted by how well the dipole orientation and position match to them

DOS: just count
\[ N(\omega) = \sum_{\text{all modes } k,n} \delta(\omega - \omega_{n,k}) \]

LDOS: local strength
\[ N(\omega, r, e_d) = \sum_{\text{all modes } k,n} |e_d \cdot E_{n,k}(r)|^2 \delta(\omega - \omega_{n,k}) \]

Reversible change of spontaneous emission rate

Metal wire provides a strongly *localized* resonance

Why relevant?

1. Calibrate photophysics of emitters

2. Make poor sources efficient
   *outcompete non-radiative processes by accelerating radiative decay*

   *accelerated decay means reduced timing uncertainty*
Why relevant?

\[ \Gamma_{\text{tot}} = \Gamma_{\text{non-rad}} + \Gamma_{\text{rad}} \]

\[ \Gamma_{\text{rad-vacuum}} \times \text{LDOS} \]

\[ \eta = \frac{\Gamma_{\text{rad}}}{\Gamma_{\text{tot}}} \]

Quantum efficiency:
probability that excitation actually results in light

heat/...
How can we understand Drexhage?

**Silver mirror**

*Perfect mirror: $E=0$ all modes $E_{||}=0$ at the mirror*

*Fermi says: inhibition*

**Image charge analysis**

*Net dipole doubled or zeroed*

*Classical flux reduced*

**Calculate back-acting Field for work done**

*Dissipated power*
Beyond ensemble-average rates

Per mirror-emitter distance: histogram of circa $3 \times 10^3$ “single”-dot traces

Single dot? $\langle N \rangle = 1.2$ from Poisson noise on brightness

Relevant 1

Slope: radiative rate
Axis intercept: non-radiative rate

This example (Invitrogen firefly beads - 77% quantum efficiency)
Essentially the *only* calibrated method to measure oscillator strength & quantum efficiencies

**Ensembles of emitters**
Snoeks, Lagendijk, Polman, PRL (’95)
Amos & Barnes, PRB (’95)
Leistikow, Blum, Vos, PRB & PCCP (’09)
Kwadrin & Koenderink, JPC (’12)

**Single nanosources**
Buchler, Sandoghdar, PRL (’05)
Frimmer, Mohtashami, Koenderink, APL (’13), PRL (’13)
Why relevant?

1. Calibrate photophysics of emitters

2. Make poor sources efficient
   *outcompete non-radiative processes*
   *by accelerating radiative decay*

   *accelerated decay means reduced timing uncertainty*
State of the art number summary

Microcavities

Narrowband $\Delta \omega / \omega = 10^{-5}$
Local (mode profile)
Theory: $F=10^3$
Data: $F=20$
Single $|E|^2$ LDOS

Photonic crystals

Broadband $\Delta \omega / \omega = 0.2$
Global
Theory: $F=0$ to 20
Data: $F=0.1$ to 10
Sum of $|E|^2$

Antennas

Broadband $\Delta \omega / \omega = 0.3$
Local
Theory: $F=10^4$
Data: $F=5$ to 1000
Phased array antenna

Picture: Verhagen

Picture: Moerner
Plasmonic antenna

Plasmon resonance

Circa $10^3$-$10^4$ free electrons

Incident field separates $e^-$ from ionic backbone

Linear restoring force implies a resonance

Resonant dipole scatterers

$\lambda \sim 300$-$1000$ nm, $Q \sim 5$-$30$
Plasma frequency – free charge oscillation

Suppose we displace the whole electron gas by a distance $d$

$n$ electrons at density $N$

$+Nde$

Surface charge

$n/Z$ ions

$-Nde$

Surface charge

$$nm\ddot{d} = -neE = -ne(\sigma/\epsilon_0) = -nNe^2d/\epsilon_0$$

Collective plasma oscillation: frequency

$$\omega_p = \sqrt{Ne^2/m\epsilon_0}$$
Quick estimate

Silver: 1 electron per atom
Mass density: 10.5 g/cm$^3$
Atomic weight: 108 g/mole

$N = 5.8 \times 10^{28}$ e- per m$^3$
e$= 1.6 \times 10^{-19}$ C
m$= 9 \times 10^{-31}$ kg
$\varepsilon_0 = 8.8 \times 10^{-12}$ F/m

$\omega_p = \sqrt{\frac{Ne^2}{m\varepsilon_0}}$

$\omega_p = 1.37 \times 10^{16}$ s$^{-1}$
$\lambda_p = 140$ nm

Actual value – renormalized by $m^*$, effective mass of conduction electrons
Measured data and model for Ag

**Drude model:**

\[ \varepsilon = 1 - \frac{\omega_p^2}{(\omega^2 + i\omega\gamma)} \]

**Modified Drude model:**

\[ \varepsilon = \varepsilon_\infty - \frac{\omega_p^2}{(\omega^2 + i\omega\gamma)} \]

Contribution of bound electrons

Ag: \( \varepsilon_\infty = 3.4 \)
Metal sphere – quasistatic plasmonics

\[ \vec{p} = \varepsilon_0 \varepsilon_m \alpha \vec{E}_0 \quad \text{with} \quad \alpha = 4\pi a^3 \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right) \]

Drude model for a metal: Lorentzian `plasmon resonance'

\[ \varepsilon = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad \text{means} \quad \alpha = V \left( \frac{\omega_0^2}{\omega_0^2 - \omega^2 + i\omega\gamma} \right) \]

- Resonance where \( \varepsilon(\omega_0) = -2 \varepsilon_m \)
- Response scales with the volume \( V \)
- \( \alpha \) exceeds \( V \) by factor 5 to 10
- Shape shift condition \( \varepsilon = -2 \varepsilon_m \)
Observables

Extinction cross section \([m^2]\)

Power removed from beam
Incident intensity

Extinction = scattering + absorption

removed from the beam
Re-radiated into all angles
Lost as heat in the scatterer
General properties

- Cross section $\sim 10 \times \pi r^2$
- Strong dipolar near field
- $Q \sim 5$ means 95% of loss is radiation into free space
- $\sigma$ and $\alpha$ as large as
  $$\sigma \approx \frac{3}{2\pi} \lambda^2$$

Plasmon particle is a solid state `strongest point-scatterer'
Plasmon antenna enhancement

- Simple metal particle: easily factors 3-10 enhancement
- LDOS enhancement due to enhanced effective dipole

\[ P = p_0 \left[ 1 + \frac{\alpha(\omega)}{r^3} \right] \]
Uses of particle plasmons

Very strong local fields $|E|^2$: $10^4$ x stronger than incident

Au spheres 5, 8, 20 nm, gaps of 1-3 nm

10,000 times enhanced optical field intensity
Record high Purcell factor

Single-crystal Ag-cube on Au
8 nm gap (PVP spacer)

Claim: up to 1000-fold Enhancement

50% lost in metal
50% appears as light

Akselrod et al.
Nat. Photonics
Vol 8, 835 (2014)
Flavours

M-I-M (Miyazaki)

Taper and wire (Polman)

Hybrid (X. Zhang)

V-groove (Bolzhevolnyi)

Wedge (Norris)
Scanning emitter microscope

Physics of this system: fivefold change in Fermi’s Golden Rule enhanced emission into guided plasmons

1. Only intrinsically poor sources improve in efficiency by Purcell

2. Yet you can gain brightness by redirecting photons

\[ I(\theta, \phi) = \text{extraction}(\theta, \phi) \times \text{efficiency} \times \text{pump} \]
Fluorescence correlation spectroscopy (FCS) uses photon correlations to reveal density and diffusion constant of an analyte. Problems: requires < 1 molecule per focal volume.

Pioneered by Levene et al. [2003] and Wenger et al. [2005].

A single nano-aperture confines geometrically for FCS. Plasmonic enhancements increase count rates and brightness.
Funneling light into a single beam

Sample: perforated Au film - hexagons of 440 nm pitch
Sources: dilute fluorophores Atto 640 dye diffusing in H₂O

We pump the central hole only in a confocal microscope

Collaboration with Institut Fresnel, Jérôme Wenger - Alexa 647 dye , 1 uM in water

140 nm holes/150 nm Au film/440 nm pitch

We only pump molecules in the central hole

FCS correlation
3.5 molecules/focus

Fluorescence lifetime

$\langle I(t) I(t + \tau) \rangle / \langle I(t) \rangle^2$

$\nu \sim \lambda^3 / 20$

LDOS Circa 4.4-fold enhanced

Funneling light into a single beam
Emission strongly redirected in a narrow beam

Single aperture: 10x brightness enhancement (full NA), pump $|E|^2$
Array: 40x enhancement in forward direction

Emission can be redirected

Emission strongly redirected in a narrow beam

Single aperture: 10x brightness enhancement (full NA), \( pumpe^2 \)

Array: 40x enhancement in forward direction

Quantitative per molecule improvement (FCS - \(<N>=3.5\))

Emission can be redirected

Single molecule
“phased array antenna”

Optimal for normal outcoupling

- Use a waveguide mode – in this case the gold/glass SPP
- Operate at 2nd order Bragg diffraction
- Plasmon also enhances *pump* light

Wave vector space

1. Sources emit mainly into the waveguide – in-plane isotropic

\[ k = n_{SPP} \frac{\omega}{c} \]

Radius increases with frequency
Wave vector space

1. Sources emit mainly into the waveguide – in-plane isotropic

$$k = n_{\text{SPP}} \frac{\omega}{c}$$

$$G = 2\pi/d$$
Wave vector space

1. Sources emit mainly into the waveguide – in-plane isotropic
2. Diffraction means $k_{||} \rightarrow k_{||} + G$
3. Repeated zone scheme dispersion couples out
Harrison construction

Bragg condition is met whenever circles cross
Wave vector space

1. Sources emit mainly into the waveguide – in-plane isotropic
2. Diffraction means $k_{||} \rightarrow k_{||} + G$
3. Repeated zone scheme dispersion couples out

Wave vectors that can be collected

$k_{||} \leq \omega/c \ n_{\text{substrate}}$
Particle lattice

Plasmon particle lattice in thin emissive waveguide

(450 nm thick SU8 with Rh6G, on glass)

Enhanced fluorescence extraction into folded band structure

Folded bands physics

Radiation pattern is essentially set by:
SPP isofrequency contour * finite size [blur]

Applications

"Fluorescence correlation spectroscopy"

- (40-fold)$^2$ faster acquisition
- $V=\lambda^3/20$ extends concentration range

Transit time through focus

Solid state lighting
‘Remote phosphor’ pumped by blue LED

- Better light extraction
- Thinner phosphor

Wenger, Inst. Fresnel

Verschuuren & Rivas, Philips
Barnes, Exeter
Enhanced LED lighting

Intrinsically efficient emitter, but in a thin layer
Directional emission

Circa 6-fold brightness enhancement from pump
Circa 10-fold brightness enhancement from directivity

Concept summary

Emission rates
Viewpoint 1) Fermi’s Golden Rule & counting of states
Viewpoint 2) Radiative impedance

Directivity
Phased array of secondary sources, driven by a single source

Plasmonics as a tool
Free electron sea provides high $|E|^2$ and strong scattering

Pump field enhancement $\times$ LDOS $\times$ redirection

Price to pay: possible absorption in the metal
Fluorescence decay rates

Fermi’s Rule: Fluorescence rate $\propto$ number of photon states

$\omega (10^{15} \text{s}^{-1})$

Visible light: ~10^5 photon states per Hz, per m^3 of vacuum