Quantum Plasmonics: Plasmon Enhanced Electron Transfer and Light Harvesting

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Plasmonics

Plasmons provide the mechanism for manipulating light at the nanoscale

Outline

- Introduction
- Quantum plasmonics
- Quantum Plexcitonics
- Plasmon-enhanced Light Harvesting
Localized Surface Plasmons (LSPR)

Plasmons are incompressible oscillations of the conduction electron liquid

Metal = ions + electron gas

E(t)

\[ \mathbf{E}_n = \hbar \omega_{pl} (n + \frac{1}{2}) \]

Plasmons typically excited to high \( n \) => Classical description

For resonant excitation, amplitude of motion becomes large. Large surface charges and field enhancements
Many different nanoshell plasmons are excited

Plasmons in real time, FDTD Simulations

Electromagnetic pulse hitting an Au(40,50)nm nanoshell

Many different nanoshell plasmons are excited
The plasmon energies of a nanoparticle depend on its shape!

**Bulk:**

\[ \omega_B = \sqrt{\frac{4\pi e^2 n}{m_e}} \]

**Surface:**

\[ \omega_{surf} = \frac{\omega_B}{\sqrt{2}} \]

**Sphere:**

\[ \omega_{S,l} = \omega_B \sqrt{\frac{l}{2l + 1}} \]

**Cavity:**

\[ \omega_{C,l} = \omega_B \sqrt{\frac{l + 1}{2l + 1}} \]

**Nanoshell (N.J. Halas 1998):**

**Nanorods**

Plasmon energies depend on aspect ratio \( x \) and can be tuned from UV to the IR.
Physical origin of the tunability of nanoshell plasmons


Plasmons on different surfaces interact and hybridize like atomic orbitals in molecules.

\[ \sigma^* \]

\[ \sigma \]

\[ |S> \]

\[ |S> \]

\[ |B> \]

\[ |C> \]

\[ |AB> \]

\[ \omega_s = \frac{\omega_B}{\sqrt{3}} \]

\[ \omega_c = \frac{2}{3}\omega_B \]

Anti-Bonding plasmon

Bonding plasmon
Tunability of Nanoshells

Analogy with molecular orbital theory provides simple and intuitive understanding of plasmons in composite nanoparticles.

Thick shell => weak interaction:

\[
\omega_{l=1\pm} \xrightarrow{x \to 0} \frac{\omega_B}{\sqrt{2}} \left(1 \pm \frac{1}{3}\right) = \begin{pmatrix} \omega_C \\ \omega_S \end{pmatrix}
\]

Thin shell => strong interaction:

where

\[
x = \frac{a}{b} = 1 - \Delta
\]

The \( \omega_- \) plasmon can be tuned from far IR to UV

The coupling to light is proportional to the admixture of the \(|S>\) plasmon
“Hot Spots”: electromagnetic field enhancement in nanoparticle dimer junctions

*Au sphere, D=60 nm; incident wavelength $\lambda = 475$ nm ($l=1$ plasmon resonance)*

E field is enormously enhanced in the junction!
Enhancement is larger than sum of individual nanoparticles
=> Collective effect, Plasmon interactions!

atom molecule atom

原子 分子 原子

\[ |\sigma^*\rangle \]

\[ |\sigma\rangle \]

\[ |S\rangle \]

\[ |S\rangle \]

Nanoparticle “dimers”

“antibonding” plasmon

“bonding” plasmon

NP plasmon

NP plasmon

Large Field
Nanoparticle dimers: Plasmon Hybridization  
(Nordlander et al., NL 4(2004)899)

In the dimer geometry, NP plasmons of different $l$ mix:

For large $D$, hybridization of modes of the same multipolar order $l$:

For small $D$, hybridization of NP plasmons with different $l$: 
Multipolar modes appear and large fields are induced

The large field enhancements are caused by admixture of high $l$ individual NP modes.
Nanoparticle dimers

Bonding dipole mode redshift and multipolar modes appear for small D

The dimer geometry is the canonical structure for SERS
Surface Enhanced Infrared Absorption (SEIRA)

Field enhancement in the IR due to (nonplasmonic) lightning rod effect

\[ E_{\text{Max}} = \frac{E_{\text{Ext}} (2D + d)}{d} \]

L.V. Brown et al., JACS 135(2013)3688
Plasmon-Enhanced 4-wave mixing
(Y. Zhang et al., PNAS 110(2013)9215)

\[ I(2\omega_2 - \omega_1) \propto |E(\omega_1)|^2 |E(\omega_2)|^4 \]

Plasmonic oligomer with dual Fano resonances tuned to \( \omega_1 \) and \( \omega_2 \)

Control 1: only \( \omega_1 \) tuned to FR
Control 2: only \( \omega_2 \) tuned to FR

Main: Both \( \omega_1 \) and \( \omega_2 \) tuned to FRs

Strong enhancement!

\[ \omega_{FWM} = 2\omega_2 - \omega_1 \]
Quantum Plasmonics

- Plasmon Tunability of metallic nanorods
- Electron tunneling in NP dimer: Charge transfer plasmons
- Nonlinear effects
  - Plasmon enhanced transport through conductive junctions
  - Coupled Plasmonic and Excitonic systems: Quantum plexcitonics
- Graphene plasmons

Time-dependent Local Density Approximation, RPA, jellium model, Nonequilibrium Green functions, Anderson Model, ……
1) Calculation of the electronic structure using the Local Density Approximation (LDA)

Density of states Au(40,80)a.u.

DOS is bulk like

Prodan & PN, CPL 352(2002)140

2) Calculation of the frequency dependent dielectric function using the Random Phase Approximation (RPA)

Efficient implementation on Beowulf cluster for nanoshells with more than a million inequivalent electrons
Quantum Plasmonics: Nanoshells

(TDLDA, and Mie theory for $\omega_+$ and $\omega_-$ modes)

More than a million electrons

The spectral features around $\omega_B$ are due to Friedel oscillations.

Excellent agreement between TDLDA, and Mie theory for $\omega_+$ and $\omega_-$ modes

Absorption

Photon energy (eV)

Aspect ratio

Aspect ratio

Single particle excitations

Tunability

Plasmon hybridization, Mie Theory

Plasmon Energy (eV)

$\omega_B$

$\omega_+$

$\omega_-$

$\omega$

$R_i / R_o$

$0.6$ $0.7$ $0.8$ $0.9$ $1.0$

$0$ $2$ $4$ $6$ $8$ $10$
Quantum description of silver nanorod plasmons
(J. Zuloaga et al., ACS Nano 4(2010)5269)

QM results for plasmon energies agree with classical theory!!

Longitudinal

Transverse

Field enhancements

Classical

QM

Quantum effects reduce the field enhancements near the NP surface

Enhancements agree beyond 0.5 nm

QM results for plasmon energies agree with classical theory!!
Physical origin of reduced field enhancements
(J. Zuloaga et al., ACS Nano 4(2010)5269)

Equilibrium electron density $n(\vec{r})$

Electron density at NP surface varies continuously, not abruptly “spill-out”

Plasmon-induced electron density $\delta n(\vec{r})$

Classical E&M predict $\delta n=\delta(d)$
QM calculation give smeared volume charge distribution

The effect can be modeled using nonlocal (k-dependent) permittivity

1 nm
Quantum Plasmonics: Charge Transfer Plasmons (CTP)

When nanoparticles near each other, a CTP appears
J.B. Lassiter et al., Nano Lett. 8 (2008)1212

Quantum calculations show a CTP for d<1nm. Strong reduction of the field Enhancement. CANNOT be modeled using nonlocal description
J. Zuloaga et al., Nano Lett. 9(2009)887;
Nonlinear optical response of a NP dimer

(C. Marinaca et al., Nano Lett. 12(2012)1333)

Field enhancement saturates due to electron tunneling!
Electron tunneling is nonlinear

Low intensity: Ohmic (low G)
Intermediate: Ohmic (large G, HE)
High: Non Ohmic (HE, AC Stark)

High harmonics are generated!
Quantum Corrected Model (QCM)
(R. Esteban et al., Nat Comm. 3(2012)825)

QM effects can be included in a classical E&M simulation by replacing the junction with a fictitious conductive material.

For typical timers, the field enhancement from QCM is an order of magnitude smaller than CEM!
Implementation of QCM
(R. Esteban et al., Nat Comm. 3(2012)825)

Local tunneling conductivity \( \text{Im}[\varepsilon] \) depends on \( l(x,y) \)

Tunneling rates calculated for planar junction

Practical implementation
Field enhancement from QCM is an order of magnitude smaller than CEM due to electron tunneling and nonlocal screening!
A conducting molecule blueshifts and broadens the dimer plasmon. For large conductance, a CTP appear in the mid IR.

Extinction spectrum depend sensitively on junction conductance.
Electric currents are enormously enhanced because of E field

Multi Na atom junctions

(P. Song, S.W. Gao et al., JCP 134(2011)074701, PRB 86(2012)121410)

CTP and BDP as in classical EM. New molecular resonance (MR) appears depending on molecular structure.

Electric currents are enormously enhanced because of E field

CTP and BDP as in classical EM. New molecular resonance (MR) appears depending on molecular structure.
Quantum Plexcitonics

The electromagnetic coupling between excitonic and plasmonic systems results in hybrid “plexciton” states

- Nonlinear Fano effect (Manjavacas et al., Nano Lett. 11(2011)2318)
- Plasmon blockade and antibunching (Manjavacas et al., ACS Nano 6(2012)1724)

Bosonic operators: Plasmons, Photons, Phonons, ...

Fermionic operators: Exciton, eh-pair excitations, ....

(N. Fofang et al., NL 8(2008)3481)
Plexciton formation in individual NP dimer
(A.E. Schlather et al., NL 13(2013)ASAP)

J-aggregates in NP junction

Giant Rabi splitting (250-400 meV)
meV for longitudinal polarization
Fano interference caused by a single quantum dot

Quantum plexcitonics, (A. Manjavacas et al., NL11(2011)2318)

Fano interference caused by a single quantum dot

Nonlinear absorption

Due to the fermionic nature of quantum dot excitations (Pauli Principle)

Nonlinear Fano effect (Govorov 2008)
Graphene plasmonics
(Z.Y. Fang et al., ACS Nano 7(2013)2388)

Nanodisks

Doping tunability

Nanorings

Diameter tunability

Doping tunability

Excellent agreement between experiments and theory

Q-factor for AB ring mode > 60!
Plasmon Blockade and antibunching

(A. Manjavacas et al., ACS Nano 6(2012)1724)

Graphene disks:
Ultranarrow and tunable plasmon modes

g/Γ_p >1

The coupling to a quantum emitter (exciton) results in plexcitonic states, a Jaynes-Cummings ladder

Energies no longer linear in n
⇔
Anharmonicity: E_{n+1} - E_n ≠ E_n - E_{n-1}

The presence of one plasmon quantum changes the energy of the next plasmon: **Plasmon Blockade**
Plasmon interaction changes many properties

Population of the different plexciton states
Black: w/o interaction
Red: interacting system
Plasmon Blockade restrict population of high $n$ states

Normalized absorption cross section
Dashed: w/o interaction
Colored: increasing interaction
Plasmon blockade result in saturable absorbtion and plasmon antibunching ($\langle b^+b^+bb \rangle < 1$)

$g$ (interaction), $\Omega$ intensity (Rabi frequency), $\Gamma_p$ plasmon width, $\omega_p$ plasmon energy
All realistic parameters from BEM and TDDFT calculations
Molecular Plasmons
(A. Manjavacas et al., ACS Nano 7(2013)3635)

TDDFT studies of Polycyclic Aromatic Hydrocarbons: reveals “Molecular Plasmons”

Highly tunable plasmon resonances in the visible
Stronger sensitivity to doping than graphene!
Plasmon-enhanced Light Harvesting

- Steam generation
- Hot electron generation and applications
Plasmon induced steam generation and distillation (O. Neumann et al., ACS Nano 7(2013)42)

Solar light generate steam (T>150°C) without heating the remaining liquid

Highly efficient process:
82% of light energy goes to direct vaporization of water;
18% goes to heating of the remaining liquid
Nanoparticle tuned to solar spectrum

Nanoparticles surrounded by bubbles move to the surface

Buoyancy after 4µs

Bubble coalescence after 20 ms
Nanoparticle on a substrate studied with conventional light sources (Z.Y. Fang et al., NL(2013)1736)

Bubble temperature from SERS Stokes anti-Stokes ratio

Once a complete nanobubble surrounds the NP, temperature increases drastically
Applications

- Water purification, desalination, and remediation
- Sterilization and sanitation: Autoclave; waste management
- Distillation: Biofuels and chemical industry

Solar Distillation in “the field”

Laser Distillation in “dry” environment

Distillate much richer than conventional distillation
Minimal heating of the remaining liquid
Plasmon decay

\[ E_n = \hbar \omega_{pl} (n + \frac{1}{2}) \]

The decay of plasmons occur one quantum at a time

\[ |n> \rightarrow |n-1> + \text{Photon or eh-pair} \]

The branching ratio between photons and eh-pairs is determined by the radiance of the mode

i) Subradiant modes favors eh-pairs
ii) Superradiant favors photons

Since plasmon typically is excited to high \( n \), many photons and eh-pairs are generated
Plasmon-induced Hot Electrons (HE)

Each plasmon quantum decays into a single hot eh-pair. Most HEs end up at $\varepsilon_F + \hbar \omega$

Plasmon enhanced yield of HE is $10^6$ times larger than for direct excitation ($Y_{\text{Plasmon}} = N_{el} \times Y_{DE}$)

HE ends up outside NP and can do things!
Hot electron applications

- Chemical reactions
- Photodetectors
- Photovoltaics
- Photoinduced graphene doping

\[ \text{H}_2 + e^- \rightarrow 2\text{H} \]
\[ \text{D}_2 + e^- \rightarrow 2\text{D} \]
\[ \text{H} + \text{D} \rightarrow \text{HD} \]
HE induced chemical reactions

Hot electrons are negative energy electrons and can transfer into specific molecular states.

Chemical reactions can be steered optically!

C. Frischkorn et al.,
Chem. Rev. 106(2006) 4207
The dissociation of closed shell molecules is the entrance channel barrier in many important chemical reactions $3\text{H}_2 + \text{N}_2 = 2\text{NH}_3$.

Dissociation of closed shell $\text{H}_2$ costs $4.6\text{eV}$. But $\text{H}_2^-$ auto dissociates!

Hot electrons do the impossible, dissociation of $\text{H}_2$ on Au!

HE transfer into $\text{H}_2$ and induce dissociation!

$\text{H}_2 + e \rightarrow 2\text{H}$
$\text{D}_2 + e \rightarrow 2\text{D}$
$\text{H} + \text{D} \rightarrow \text{HD}$
Dissociation of H₂ on Au by plasmon-induced hot electrons (S. Mukherjee et al., NL 13(2013)240)
HE triggered ssDNA release from Au nanoparticles
(R. Huschka et al., JACS 133(2011)12247)

dsDNA with one strand anchored to a NP and the other strand tagged with a fluorophore

Hot electron transfer to DNA induce DNA melting at physiological temperatures
NP on semiconducting substrate

(M. W. Knight et al., Science 332(2011)702)

Plasmon decay into hot electrons
Transport across the Schottky barrier

A nanoantenna-photodiode!
Simultaneous light collection and photocurrent generation
Hot-electron based photodetection  
(M. W. Knight et al., Science 332(2011)702)

Variations of this device geometry exhibit IQEs in the 20+ % range.

Device can be tuned into the visible.  
Novel approach for photovoltaics!
The use of a slit array enables the design of ultra narrow spectral photoresponse.

No ITO needed: More efficient device.

Embedding gold antenna in Si increases the quantum yield 25 times.

HEs are emitted in the polarization direction!
A Graphene-Antenna Sandwich Photodetector
(Z.Y. Fang et al., NL 12(2012)3808)

- Efficient HE production at the heptamer Fano resonance
- Efficient HE collection because “wrapping”
- High tunability
Primarily a hot e⁻ device:

IQE is 22% at 600nm. Photovoltaic applications
Hot electron doping of graphene
(Z.Y. Fang et al., ACS Nano 6(2012)10222)

Dirac point changes with illumination
Doping proportional to absorption.
Large effect!
Plasmon induced doping equivalent to 10V gate voltage.
Optically Induced Electronics
(Z.Y. Fang et al., ACS Nano 6(2012)10222)

Plasmons: n-doping
QDs: p-doping
(G. Konstantatos et al., Nat. Nano. 7(2012)363)

Electronic function only when “right “ light is incident!

Tunable effect:
Wavelength, polarization incidence angle, ……
Conclusions

QM effects reduce field enhancements in narrow NP junctions and for NR

Plasmon-induced hot electron processes
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Further reading


**Homodimer**

- "antibonding" Dark
- "bonding" Bright

**Dark and bright modes:**

AB mode cannot be excited with light but can be observed in EELS.


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**Heterodimer**

- Both B and AB can be excited by light.