LOCALIZED EIGENSTATES of the ELECTROMAGNETIC FIELD: the QUASI-STATIC REGIME and BEYOND

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Abstract

It was recently discovered that strongly localized eigenstates of a static electric field exist not only in disordered metal/dielectric composites [1], but also in small clusters of regular metallic inclusions embedded in an otherwise uniform dielectric host [2]. Applying these states to a non-static electromagnetic (EM) field in the quasi-static limit, it was found that the field can be restricted to have a large amplitude in spatial regions whose linear size is much smaller than the wavelength. This ultra-localization of an EM field (actually, the field is mostly electric—the magnetic field cannot build up a large amplitude over such a small region of space) is achieved with the help of surface plasmons in the metallic inclusions: These plasmons screen the electric field, essentially cancelling it outside the volume of the quasi-static eigenstate. This phenomenon has been proposed as the basis for a SPASER device, namely, "surface plasmon amplification by stimulated emission of radiation", which would be a source of strong, coherent EM radiation with a size that can be much smaller than the wavelength [3].

In this report we will present results for such states which go beyond the quasi-static approximation. That is necessary in order to analyze the radiative properties of those states, e.g., the radiative losses. It is also needed in order to study such states in the case where the metallic inclusions are not much smaller than the EM skin depth.

[1] M. I. Stockman, S. V. Faleev, and D. J. Bergman, *Localization versus Delocalization of Surface Plasmons in Nanosystems: Can One State Have Both Characteristics?*, Phys. Rev. Letters 87, 167401 (2001).

[2] K. Li, M. I. Stockman, and D. J. Bergman, *Self-similar chain of metal nanospheres as an efficient nanolens*, Phys. Rev. Lett. 91, 227402-1–227402-2 (2003).

[3] D. J. Bergman and M. I. Stockman, *Surface plasmon amplification by stimulated emission of radiation: Quantum generation of coherent surface plasmons in Nanosystems*, Phys. Rev. Letters 90, 027402 (2003).

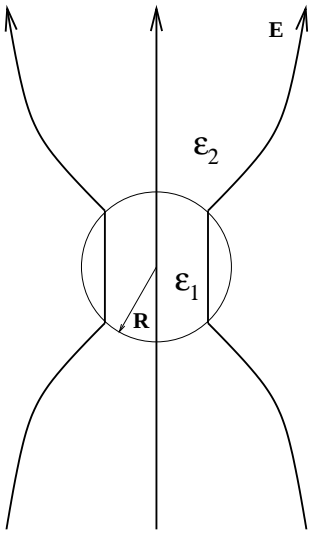
CONTENTS

INTRODUCTION

- **"Quasistatic resonances", also known as "surface plasmon resonances", can sometimes be localized in an extremely small volume of space.**
- **Such resonances, if they can be accessed and/or excited, have the capability of removing the lower bound restriction on spatial size of ac electric field. This can lead to the development of electromagnetic nano-probes and SPASERS (surface plasmon amplification by stimulated emission of radiation).**
- **The lifetime of these resonances arises from two different physical phenomena: (a) Intrinsic dissipation due to imaginary part of the electric permittivity of the metal spheres. (b) Radiation losses due to electromagnetic radiation—this is neglected in the leading order quasi-static treatment, but becomes important in higher order corrections, even when $ka << 1$ (a is the linear size of the resonance).**

Quasi-static Resonances in Two-Constituent Composite Media

- **States where a non-zero electric potential field $\varphi_n(\mathbf{r})$ can be found in the composite even though no external field or potential difference is applied to the system. Such states can only occur for special negative values of the electric permittivity ratio $\varepsilon_1/\varepsilon_2$.**
- **Example - dipole resonance in a spherical inclusion:**

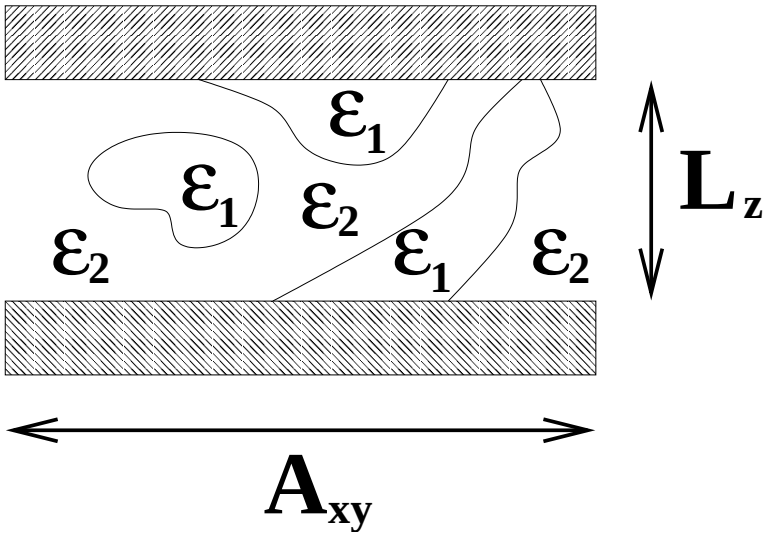


The induced dipole moment is

$$R^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}$$

The resonance occurs when $\varepsilon_1/\varepsilon_2 = -2$.

- **Similar resonances occur for induced higher multipole moments in a spherical inclusion.**



First introduced (Bergman 1977) as a basis for expanding the electric potential $\phi(\mathbf{r})$ in a real composite subject to an external or volume averaged electric field of amplitude 1 along z, namely $\mathbf{e}_z$

$$\phi(\mathbf{r}) = z + \sum_n \frac{s_n \langle \varphi_n | z \rangle}{s - s_n} \varphi_n(\mathbf{r}),$$

where

$$s \equiv \frac{\varepsilon_2}{\varepsilon_2 - \varepsilon_1},$$

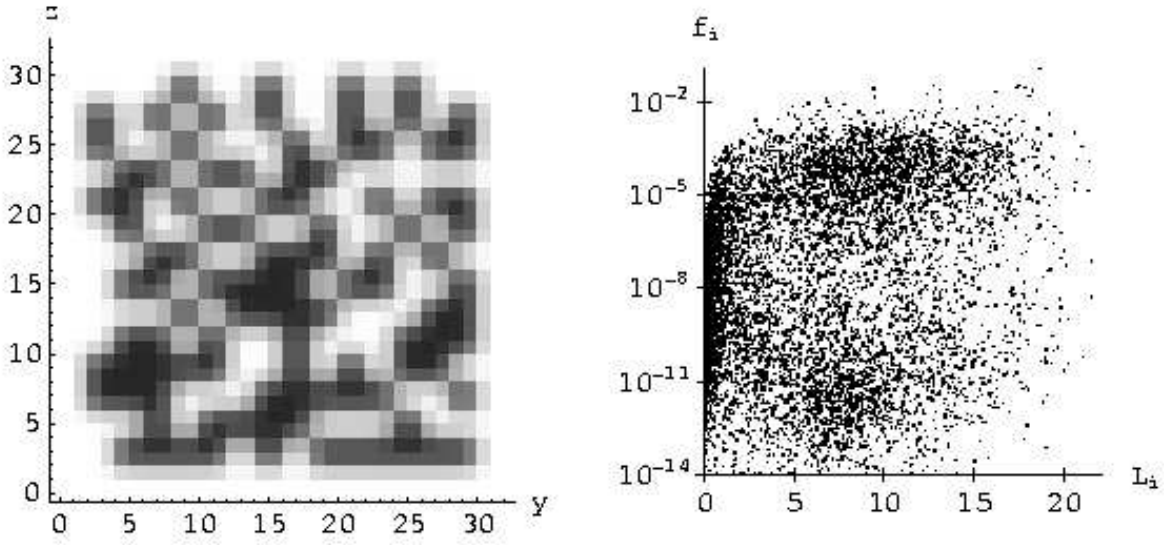
$s_n \in [0, 1)$ correspond to the "special (negative, real) values" (eigenvalues) of $\varepsilon_1/\varepsilon_2$, and

$$-\frac{\varepsilon_2}{s_n}\langle \varphi_n | z \rangle^* = -\frac{\varepsilon_2}{s_n}\langle z | \varphi_n \rangle = -\frac{\varepsilon_2}{s_n V}\int dV \theta_1 \frac{\partial \varphi_n}{\partial z}$$

$$= \frac{\varepsilon_2}{V}\int dV \left(1 - \frac{\theta_1}{s_n}\right)\frac{\partial \varphi_n}{\partial z} = \frac{1}{A_{xy}}\int_{z=\text{const}} dxdy D_z = \frac{Q_n}{A_{xy}}.$$

The last integral will vanish unless $\varphi_n(\mathbf{r})$ extends across the entire system all the way from $z = 0$ to $z = L_z$.

- **In a periodic microstructure, all the resonances are Bloch functions, i.e., delocalized. However, all the q $\neq 0$ functions are "dark states" with $\langle\varphi_n|z\rangle = 0$. Only the q $= 0$ functions are "luminous states" with $\langle\varphi_n|z\rangle \neq 0$.**
- **In a disordered microstructure the situation is more complicated:**



$L_n =$ **"localization length"**

$f_n \equiv \dfrac{V_1}{V}\,|\langle\varphi_n|z\rangle|^2 =$ **"oscillator strength"**
of the normalized eigenstate φ_n

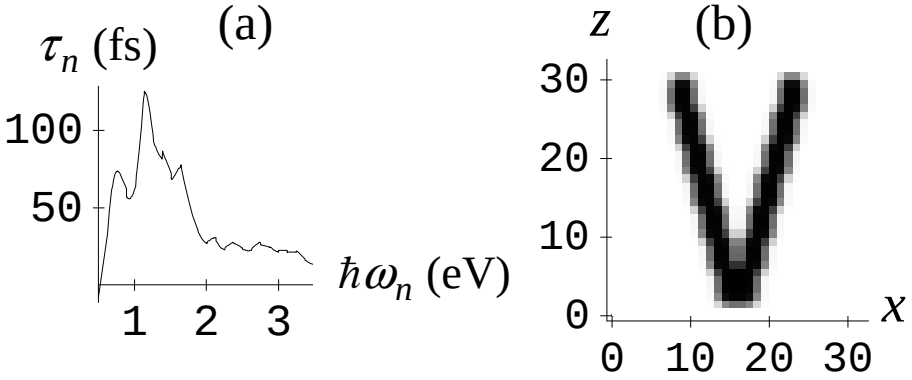
$$1 - \frac{\varepsilon_e}{\varepsilon_2} = \sum_n \frac{f_n}{s - s_n}$$

$$0 \leq s_n = \text{ real } < 1; \quad \sum_n f_n = 1$$

- **The actual SP frequencies Ω_n satisfy $s(\Omega_n) = s_n$ and are *complex*: $\Omega_n = \omega_n - i\gamma_n$.**
- **For weak relaxation, $\gamma_n \ll \omega_n$, one finds that ω_n satisfies an equation $\mathrm{Re}[s(\omega_n)] = s_n$ and that**

$$\frac{1}{\tau_n} = \gamma_n = \frac{\mathrm{Im}[s(\omega_n)]}{s'_n}, \qquad s'_n \equiv \left.\frac{d\mathrm{Re}[s(\omega)]}{d\omega}\right|_{\omega=\omega_n}$$

- **Assume a flat, V-shaped inclusion of metallic Ag embedded in a conventional dielectric host with $\varepsilon_h = 6.6$:**



- **Physical size of the inclusion is ~ 100 nm.**
- **Quasi-static regime is in effect when retardation is unimportant. This happens when all microstructural sizes are much smaller than the wavelength and/or skin depth.**

Interaction of Surface Plasmon (SP) Field with Matter

See Landau & Lifshitz, *Electrodynamics of Continuous Media*:

$$H = \frac{1}{4\pi T}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\int d^3r \frac{d[\omega\varepsilon(\mathbf{r},\omega)]}{d\omega}\,\mathbf{E}(\mathbf{r},\omega)\,\mathbf{E}(\mathbf{r},-\omega)$$

Quantization of SP electric field:

$$\phi(\mathbf{r},t) = \sum_n \sqrt{\frac{2\pi\hbar\ s_n}{\varepsilon_h s_n'}}\,\varphi_n(\mathbf{r})e^{-\gamma_n t}\left[a_n e^{-i\omega_n t} + a_n^\dagger e^{i\omega_n t}\right]$$

The Einstein coefficient for stimulated emission to the state φ_n is given by

$$A_n = \frac{4\pi}{3\hbar}\frac{s_n}{s_n'}\frac{|d_{10}|^2\, p_n q_n}{\varepsilon_h \gamma_n}$$

Here d_{10} is the matrix element for a dipole transition between two states of an excited element, e.g., a Quantum Dot. p_n is a spatial overlap factor of the population inversion and eigenmode intensity,

$$p_n = \int[\nabla\varphi_n(\mathbf{r})]^2[\rho_1(\mathbf{r}) - \rho_0(\mathbf{r})]d^3r$$

q_n is a spectral overlap factor

$$q_n = \int F(\omega)\left[1 + (\omega-\omega_n)^2/\gamma_n^2\right]^{-1} d\omega$$

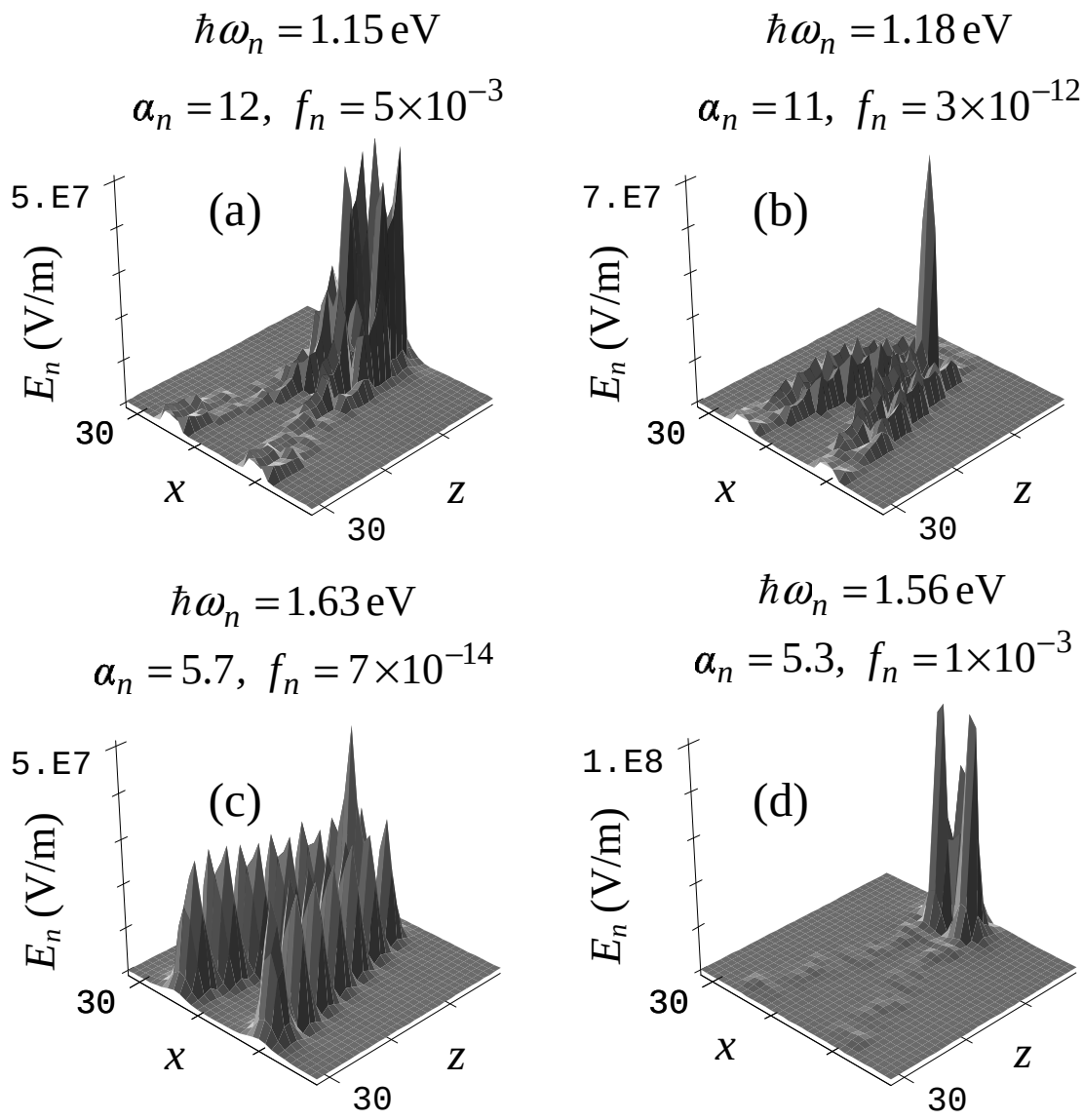
where $F(\omega)$ is the normalized-to-1 spectrum of dipole transitions in the active medium, close to its fluorescence peak. The Einstein spontaneous emission coefficient B_n is similar to A_n, but the excited state population ρ_1 replaces the population inversion $\rho_1 - \rho_0$ in the expression for p_n.

The rate equation for the number of surface plasmons (SP) in the state φ_n is

$$\frac{dN_n}{dt} = (A_n - \gamma_n) N_n + B_n$$

The net dimensionless gain is

$$\alpha_n = \frac{A_n - \gamma_n}{\gamma_n}$$

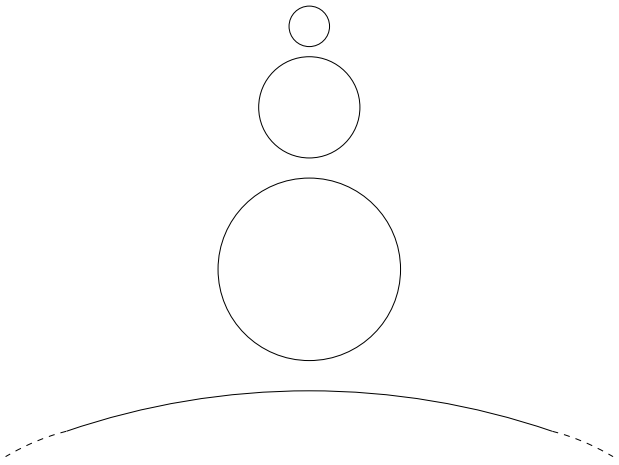


α_n is the enhancement factor due to stimulated emission of surface plasmons.

f_n is the "oscillator strength", proportional to the electric dipole moment of the resonance.

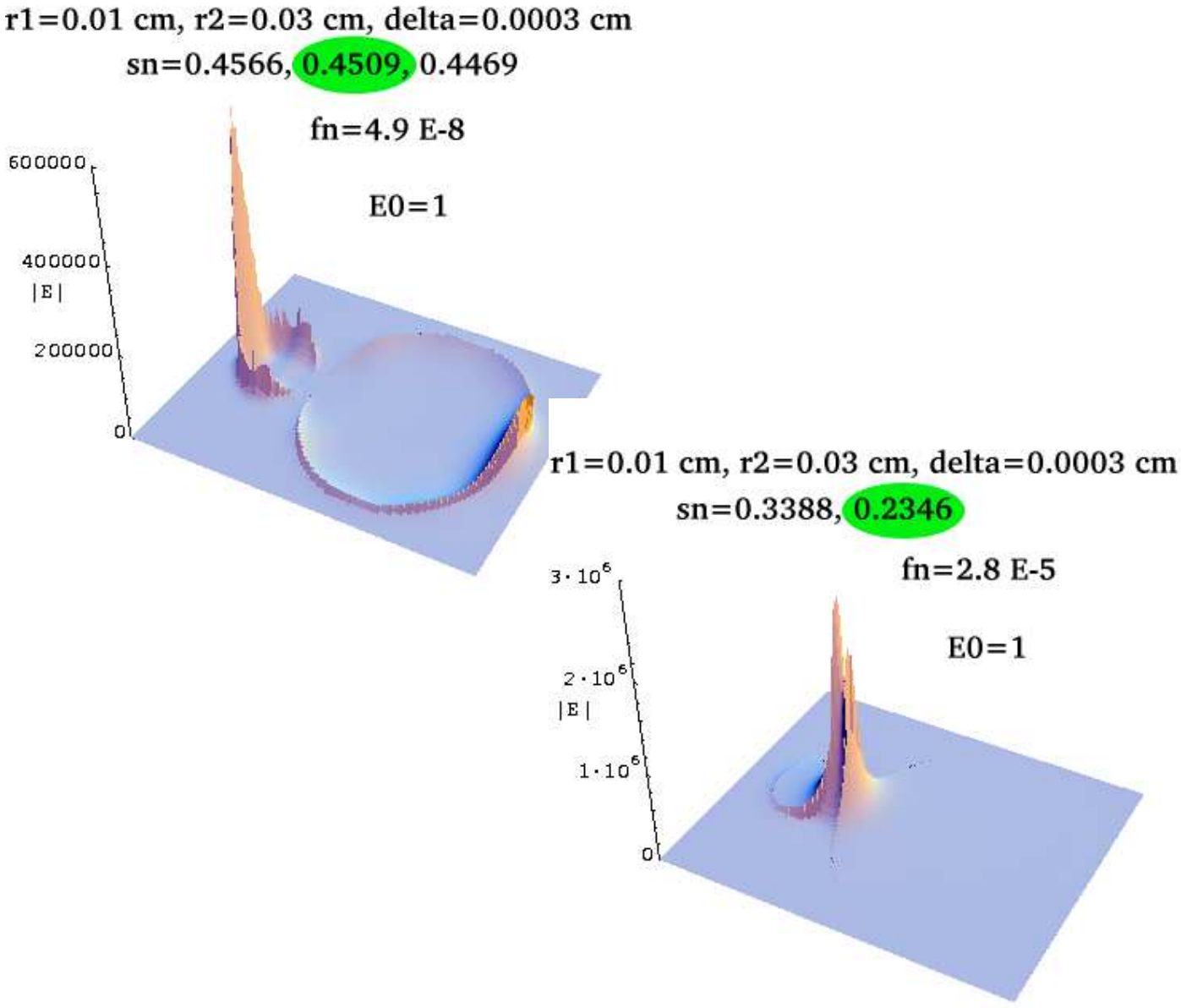
CLUSTERS OF NANOSPHERES

- **Such clusters, when properly constructed, have very small quasistatic resonances.**
- **Can be used to construct an electromagnetic nano-lens or nano-probe.**
- **Can perhaps be fabricated by exploiting forces between nanospheres induced by placing them in an external static electric field.**



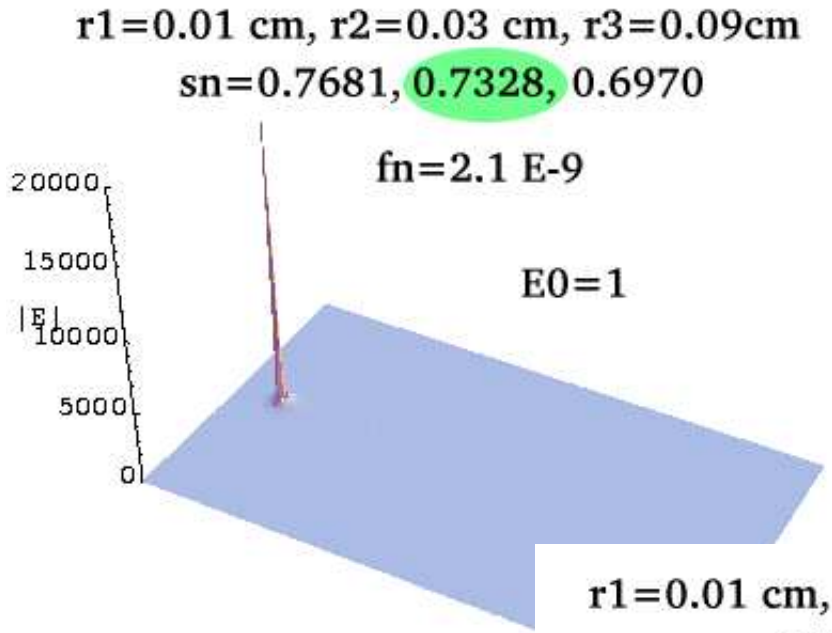
Two-sphere Eigenstates

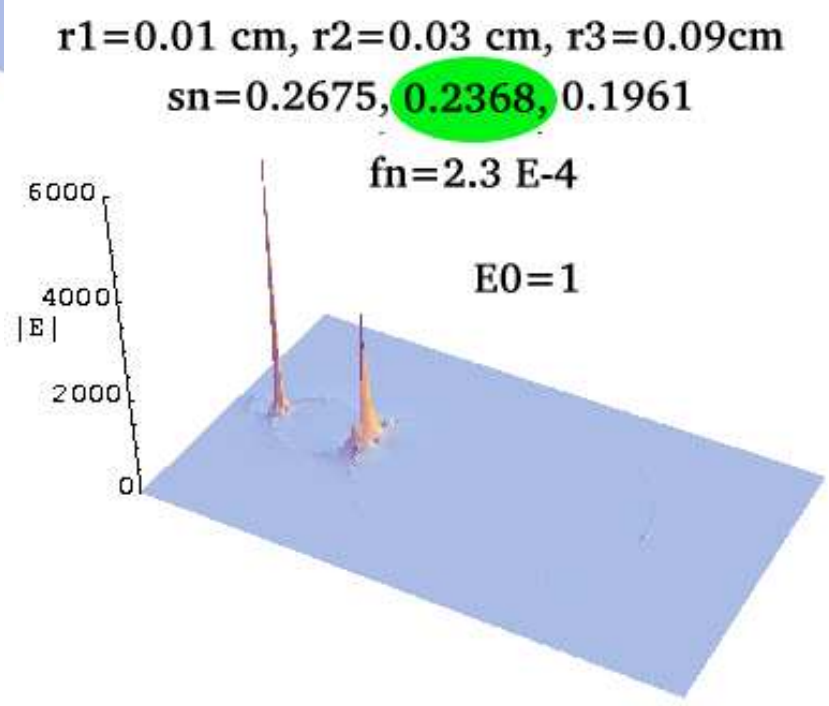
<u>Note</u>: Instead of cm we could have written μm !!



Note that the resonance at the bottom is well separated, in frequency, from its nearest neighbor.

Three-sphere Eigenstates





Scattering Resonances in Two-Constituent Composite Media

- **We assume $\mu = 1$ everywhere, but $\epsilon = \epsilon_1$ or $\epsilon = \epsilon_2$, depending on the constituent.**
- **We also assume that ϵ_2 is real and positive, and that the ϵ_1 material fills up a limited region in space—all the rest is ϵ_2 material. Nothing is assumed regarding ϵ_1, which can be either positive or negative or complex.**
- **Scattering resonances are monochromatic eigenstates of the wave equation for $\mathbf{E}(\mathbf{r}, t) \equiv \mathbf{E}(\mathbf{r})e^{-i\omega t}$ which are outgoing waves only:**

$$-\nabla \times (\nabla \times \mathbf{E}) + k^2\mathbf{E} = uk^2\theta_1\mathbf{E}$$

$$k^2 \equiv \epsilon_2\frac{\omega^2}{c^2} > 0$$

The eigenvalue $u \equiv 1 - \dfrac{\epsilon_1}{\epsilon_2}$ **is usually complex**

$$\theta_1(\mathbf{r}) = \begin{cases} 1 & \textbf{for r inside } \epsilon_1 \textbf{ material} \\ 0 & \textbf{for r inside } \epsilon_2 \textbf{ material} \end{cases}$$

Eigenstates of isolated sphere

TE states: $\mathbf{E}^{(M)}_{lmn}(\mathbf{r}) = f^{(M)}_{ln}(r)\mathbf{X}_{lm}(\Omega)$,
TM states: $\mathbf{E}^{(E)}_{lmn}(\mathbf{r}) = \frac{i}{k[1-u^{(E)}_{ln}\theta(a-r)]}[\nabla \times f^{(E)}_{ln}(r)\mathbf{X}_{lm}(\Omega)]$,

where

$$\mathbf{X}_{lm}(\Omega) \equiv \frac{\mathbf{L}Y_{lm}(\Omega)}{l(l+1)}; \quad \mathbf{L} \equiv \mathbf{r} \times \nabla$$

is a vector spherical harmonic, n is a "radial quantum number", and $f^{(M)}_{ln}(r)$, $f^{(E)}_{ln}(r)$ are the radial eigenfunctions. The radial functions have the following form for both cases $F = M$ and $F = E$:

$$f^{(F)}_{ln}(r) = \begin{cases} A^{(F)}_{ln} j_l[kr(1-u^{(F)}_{ln})^{1/2}] & \text{for } r < a, \\ B^{(F)}_{ln} h^{(1)}_l(kr) & \text{for } r > a, \end{cases}$$

where j_l and $h^{(1)}_l$ are spherical Bessel functions. The eigenvalues $u^{(F)}_{ln}$, as well as the coefficients $A^{(F)}_{ln}$, $B^{(F)}_{ln}$, are determined by continuity conditions at $r = a$. Note that $\theta(a-r)$ is the usual one-dimensional step function for the radial coordinate with origin at the sphere center.

Equations for the eigenvalues

$$x_{ln}^{(F)} \equiv ka\left(1-u_{ln}^{(F)}\right)^{1/2},$$

$$\left.\frac{xj_{l-1}(x)}{j_l(x)}\right|_{x=x_{ln}^{(M)}} = \left.\frac{xh_{l-1}^{(1)}(x)}{h_l^{(1)}(x)}\right|_{x=ka},$$

$$\left[\frac{j_{l-1}(x)}{xj_l(x)}-\frac{l}{x^2}\right]_{x=x_{ln}^{(E)}} = \left[\frac{h_{l-1}^{(1)}(x)}{xh_l^{(1)}(x)}-\frac{l}{x^2}\right]_{x=ka}.$$

When $ka \ll 1$, we get:

$$u_{ln}^{(M)} \approx \left(\frac{x_{l-1,n}}{ka}\right)^2 + i\frac{2(ka)^{2l-1}}{[(2l-1)!!]^2} \quad l \geq 1;\ n \geq 1,$$

$$u_{ln=0}^{(E)} \approx \frac{2l+1}{l} + i\frac{(l+1)(ka)^{2l+1}}{[l(2l-1)!!]^2} \quad l \geq 1,$$

$$u_{ln}^{(E)} \approx -\left(\frac{x_{l,n}}{ka}\right)^2 + i\frac{2(ka)^{2l+1}}{[l(2l-1)!!]^2} \quad l \geq 1;\ n \geq 1.$$

Here $x_{l,n}$, $n = 1, 2\ldots$ are the zeros of $j_l(x)$.

Note that when $ka \to 0$, the only eigenstates which survive are $\mathbf{E}_{lmn=0}^{(E)}$, which become the quasi-static or surface plasmon resonances. All the other eigenstates have eigenvalues $u_{ln}^{(F)}$ that tend to $\pm\infty$—they cannot be approached by the value of $u \equiv 1 - \epsilon_1/\epsilon_2$ in any real composite medium.

The physical meaning of $\mathrm{Im}(u_{ln}^{(F)})$

Since we assumed that ϵ_2 is real and positive, a nonzero value for $\mathrm{Im}(u_{ln}^{(F)})$ entails a nonzero value for $\mathrm{Im}(\epsilon_1) = -\epsilon_2 \mathrm{Im}(u_{ln}^{(F)})$ which has *the wrong sign* !!

This is due to the fact that the eigenstate radiates EM waves, therefore the sphere must generate (create) energy at a rate that compensates for the radiative losses, in order for the field to be an eigenfunction with a strictly periodic dependence on t. Thus, $\mathrm{Im}(\epsilon_1)$ is proportional to the rate of energy loss by radiation, while $\mathrm{Re}(\epsilon_1)$ is proportional to the energy stored by the electric field inside the sphere. Therefore, the *radiative lifetime* of the eigenstate $\tau_{ln}^{(F)}$) is given by

$$\frac{1}{\omega \tau_{ln}^{(F)}} = \left| \frac{\mathrm{Im}(u_{ln}^{(F)})}{\mathrm{Re}(u_{ln}^{(F)} - 1)} \right|.$$

Similar considerations show that the dissipative lifetime, due to generation of Joule heat by the field in the actual physical composite, is given by

$$\frac{1}{\omega\tau_{\rm diss}} = \left|\frac{{\rm Im}(\epsilon_1)}{{\rm Re}(\epsilon_1)}\right|$$

if the size of the metal particle is much less than the exponential decay length in it.

The total resultant lifetime τ of the excited resonance state is given by

$$\frac{1}{\tau} = \frac{1}{\tau_{ln}^{(F)}} + \frac{1}{\tau_{\rm diss}}.$$

It is useful to have quantitative estimates of both terms in this expression.

Lifetime of an electric field around an isolated sphere

Using the measured values of $\mathrm{Re}(\epsilon)$ **and** $\mathrm{Im}(\epsilon)$ **for metallic silver at** $\hbar\omega = 1.14\,\mathbf{eV}$ **or** $\lambda = 1.07\,\mu\mathbf{m}$**, we get**

$$\frac{1}{\omega\tau_{\mathrm{diss}}} \approx 0.01; \quad \tau_{\mathrm{diss}} \approx 60\,\mathrm{fs}.$$

A comparable value for $1/(\omega\tau^{(E)}_{l=1,n=0})$ **is obtained when** $ka = 0.22$**. This would require a sphere radius of** $a = 37\,\mathbf{nm}$**, which is somewhat larger than the exponential decay length (skin depth) in metallic silver** $\delta \approx 22\,\mathbf{nm}$**..**

A more comfortable sphere radius is obtained if we consider a quasi-static quadrupole eigenstate. In order to get a comparable value for $1/(\omega\tau^{(E)}_{l=2,n=0})$ we then need to have $ka = 0.71$. This would require a sphere radius of $a = 120\,$nm. Since this is considerably greater than the decay length, the dissipative lifetime will be smaller than the previous estimate by a factor of order δ/a (because the Joule heat is generated only in a surface layer of the sphere whose area is $\approx 4\pi a^2$ and thickness is $\approx \delta$, while the energy is stored also in a volume of the surrounding material of order a^3). Therefore we expect

$$\frac{1}{\omega\tau_{\rm diss}} \approx 0.002.$$

Thus, for a silver sphere of radius $a = 120\,$nm and an $l = 2$ quasi-static eigenstate, the radiative lifetime of 60 fs at $\lambda = 1.07\,\mu$m ($\nu \approx 3 \times 10^{14}\,$Hz), is about 5 times shorter than the dissipative lifetime, but 20 times longer than the period of the oscillating field.

Cluster of spheres

Of course, in order to have a strongly localized quasi-static eigenstate, we need to use not a single sphere, but a small cluster of spheres, with sizes and spacings chosen appropriately. The real part of the cluster eigenvalue will then be quite different from any of those of the isolated spheres, due to the non-weak electrical interactions between different spheres. However, as long as $ka \ll 1$, the imaginary part of the cluster eigenvalue will be approximately given by a weighted average of the isolated sphere values. The weights are determined by the expansion coefficients of the cluster eigenstate in terms of the isolated sphere eigenstates, and these can be either positive or negative.

The importance of symmetry

If the cluster has the symmetry of reflection through a point, which we can take to be the origin, then every eigenstate has a definite parity. Even eigenstates will have a vanishing dipole moment, i.e., the $l = 1$ (dipolar) eigenstates of the isolated spheres will make cancelling contributions to the overall dipole moment. In this case the relatively large dipolar contributions to the imaginary part of the cluster eigenvalue will also cancel. The contributions from higher multipole states are much smaller, as shown by our calculation of the quadrupole contribution.

SUMMARY and CONCLUSIONS

- **The radiative lifetime of scattering eigenstates of an isolated sphere was discussed, particularly for the most interesting case of the nearly quasi-static eigenstates in the case of a very small sphere with $a \ll \lambda$.**
- **For a cluster of spheres, it is important that the microgeometry have reflection symmetry through a point in order to allow even eigenstates with vanishing electric dipole moment and much longer radiative lifetime.**
- **A radiative lifetime that is comparable to the dissipative lifetime is achievable in the $l = 2$ resonance of an Ag metal sphere of radius 0.037 μm at a light wavelength of 1.07 μm in vacuum. The total lifetime is then about 10 times greater than the period $1/\nu$ of the oscillating EM field.**
- **For an Ag metal sphere of radius 0.12 μm, the lifetime of that state is mainly due to radiative losses and is about 20 times greater than the period of the oscillating field.**