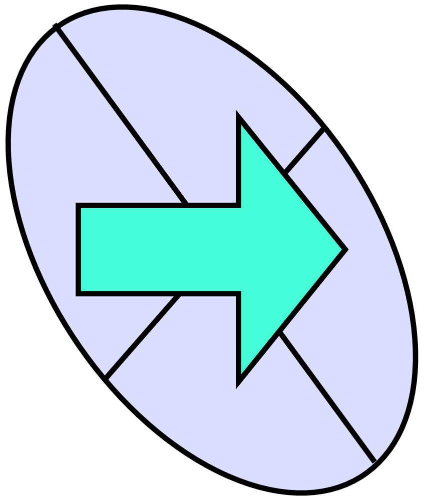
Quantum Faraday Rotation in Metallic Nanoparticles



Condensed Matter Seminar
Kansas State University
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collaboration with
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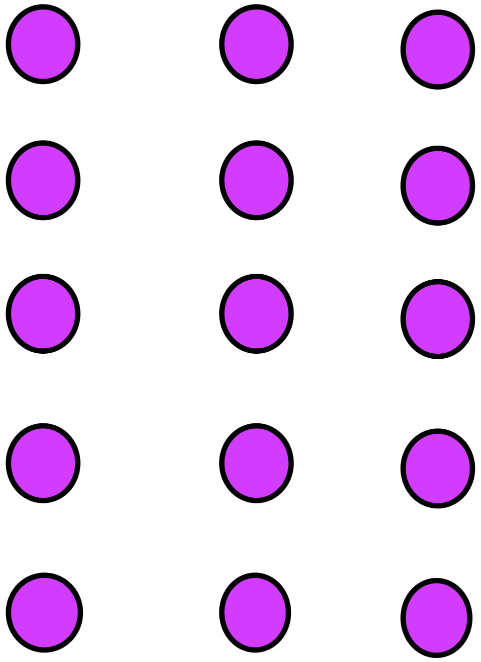


Why Study Nanoparticle Electromagnetics?

- NPs can be made much smaller than λ of the light → Rayleigh limit & collective electron motion.

- Experiment will measure the combined response of a collection of particles in a medium (composite system).

- The dielectric function $\epsilon(\omega)$ determines all EM responses, like absorption, scattering, and Faraday rotation and other polarization effects ⇒ better knowledge of the quantum electron physics.

- Faraday rotation can be affected by plasmon modes.

- It's fun. You get to use a lot of physics theory you learned in grad school.

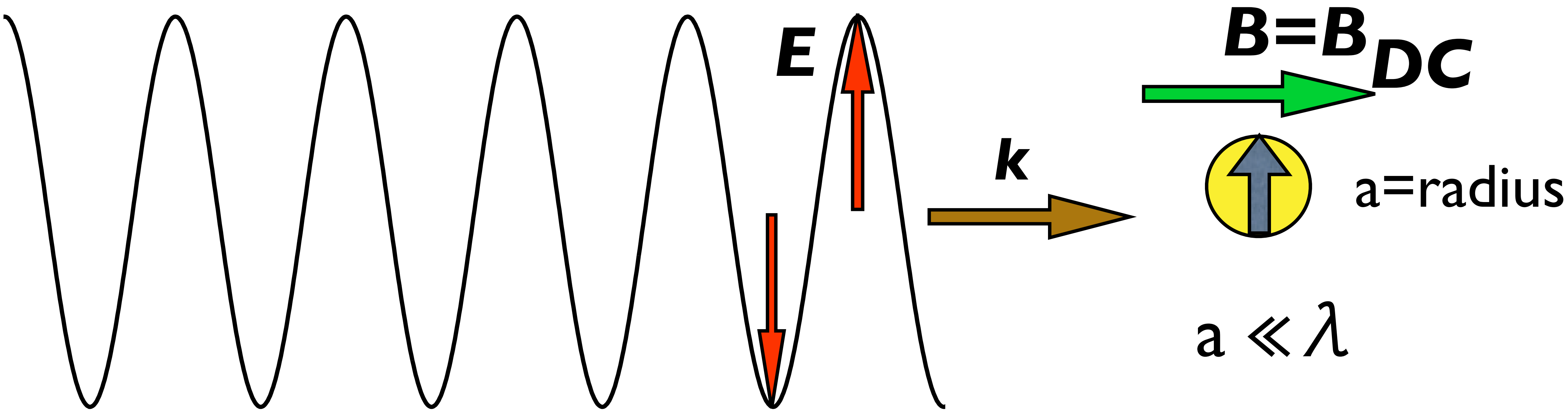
Today's topics

- plasmon oscillations in NPs
- light polarization, Faraday rotation, and $\epsilon(\omega)$
- Classical (Drude model) and quantum theory for the dielectric function $\epsilon(\omega)$
- the importance of bound electrons in $\epsilon(\omega)$
- how B_{DC} enters $\epsilon(\omega)$ in quantum vs. classical theory
- why electrons in NPs don't have Landau levels due to B_{DC}

EM
scattering

spherical dielectric
or conducting
particles

incident plane waves,
frequency ω, wave vector k



A nearly uniform polarization is induced in the NP.
Its amplitude depends on the dielectric function $\epsilon(\omega)$.
How to describe effects on the light?

Viktor Chikan’s core particles

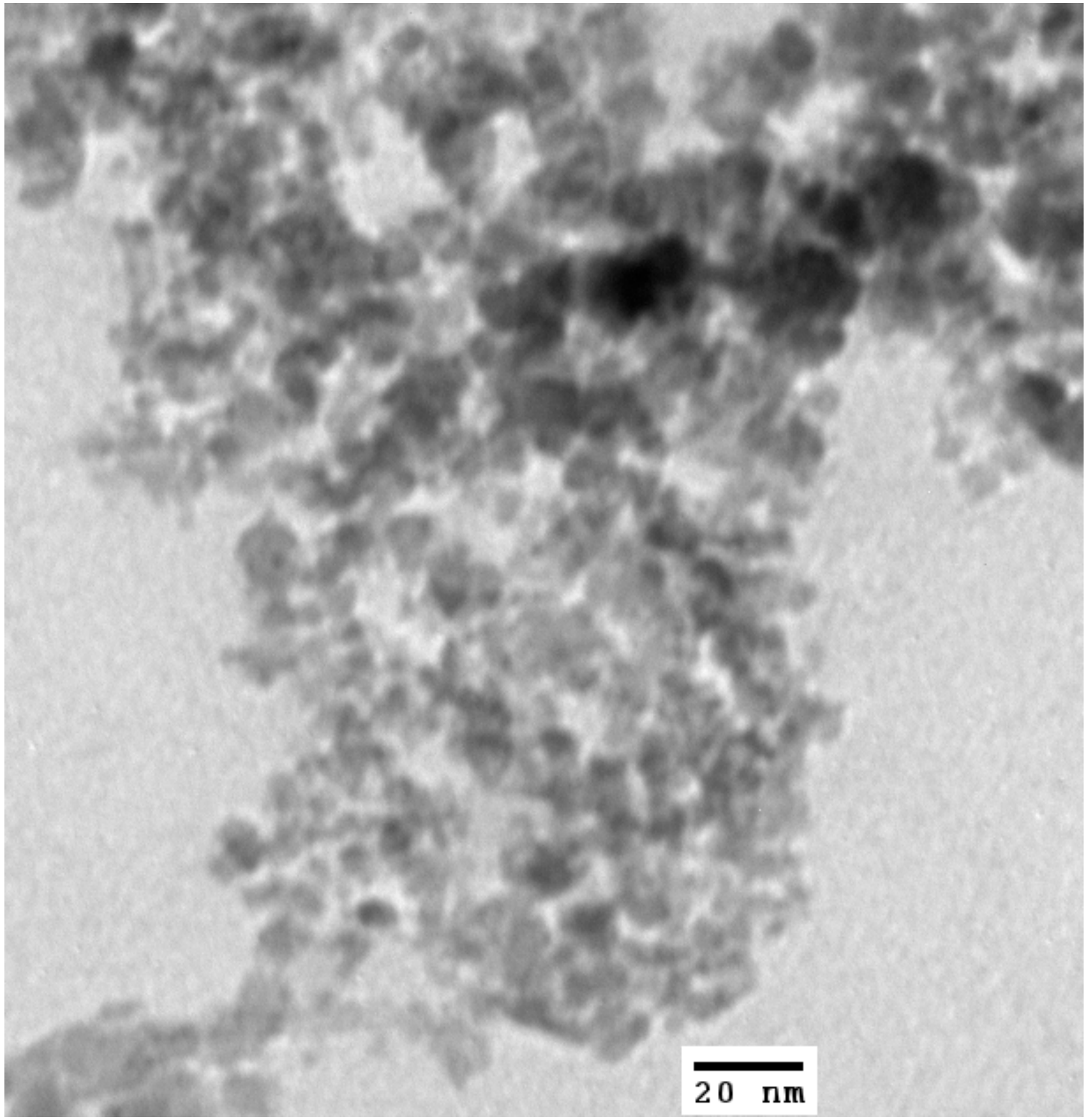


Figure 2 (a) TEM image of Fe_2O_3 nanoparticles used in the experiment.

gold-shell on maghemite (Fe_2O_3) cores (from Viktor Chikan's lab)

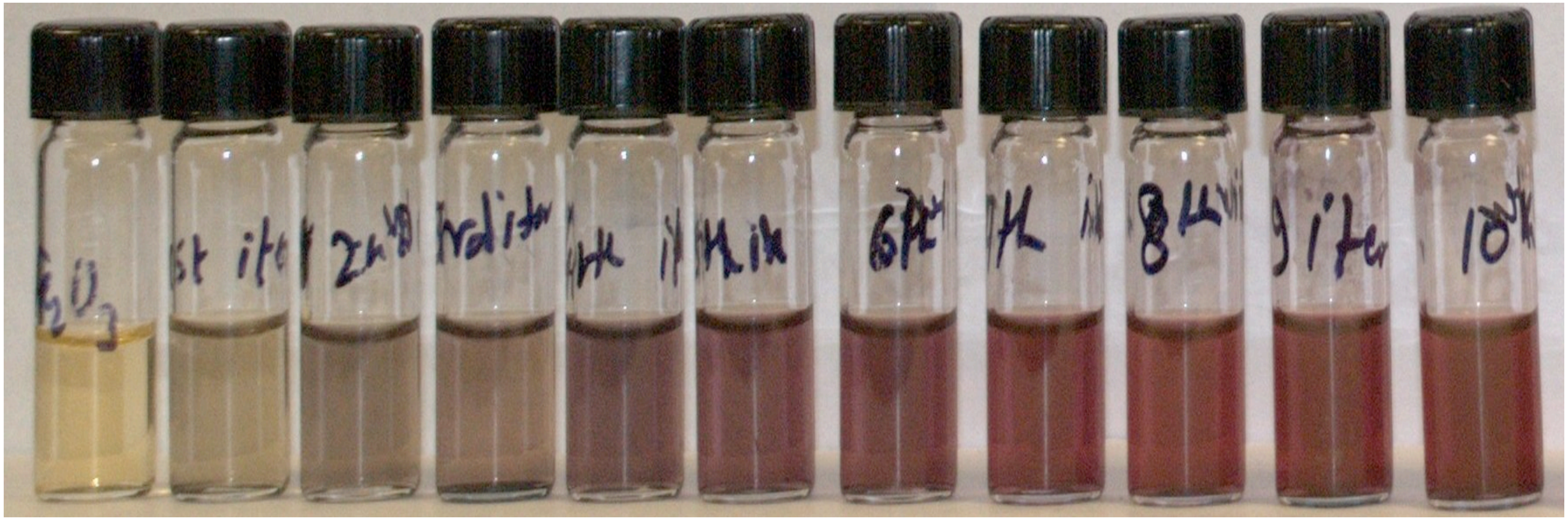


Figure 3 (b) Variation of color change when the thickness of gold onto the surface of the nanoparticles is increased.

Viktor Chikan’s core/shell particles

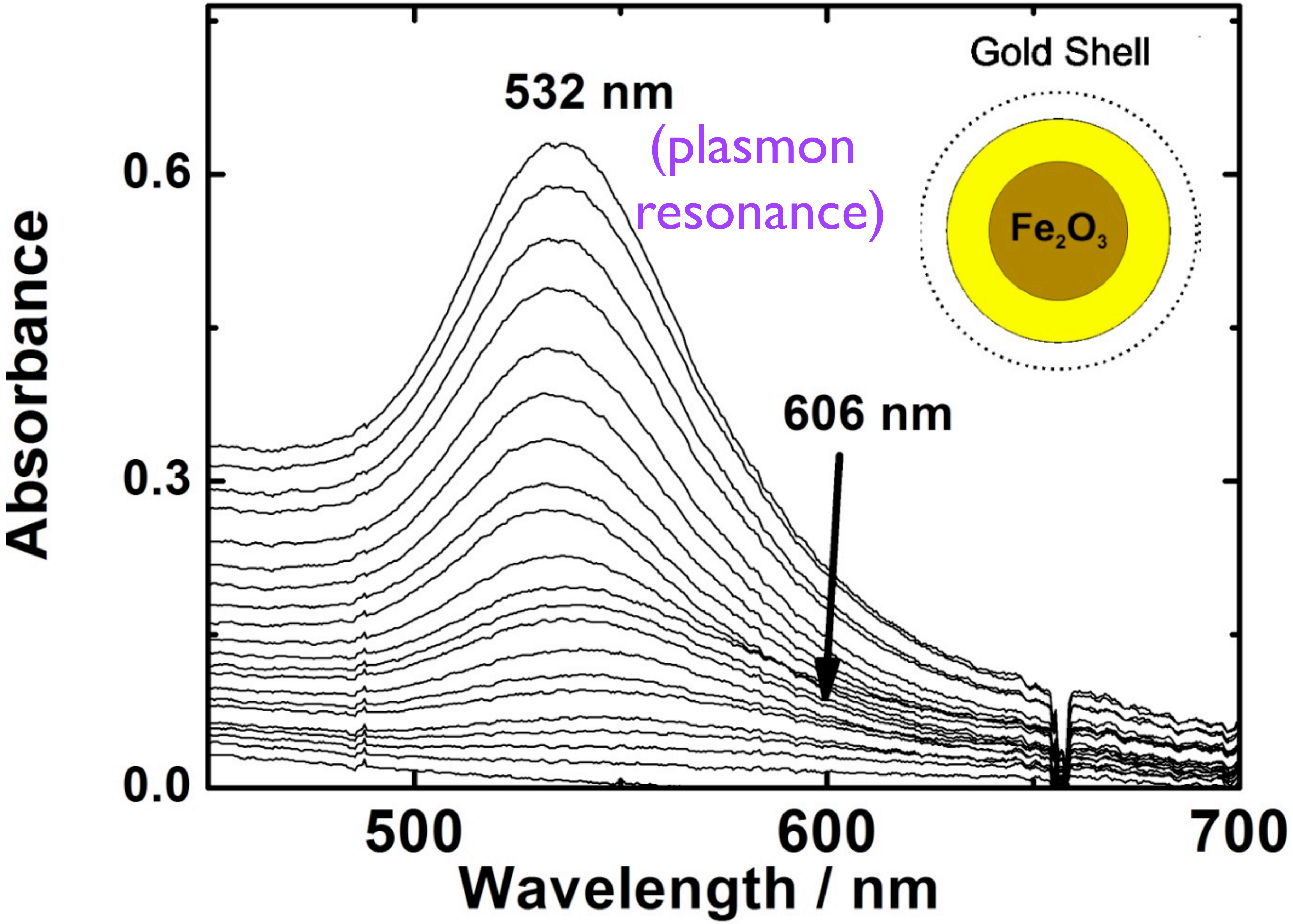


Figure 3 (a) UV-vis absorption spectrum of 3rd batch synthesis of gold coated Fe_2O_3 nanoparticles. The initial peak position is indicated by an arrow at 606 nm and shifts to 532 nm with increasing thickness of gold shell.

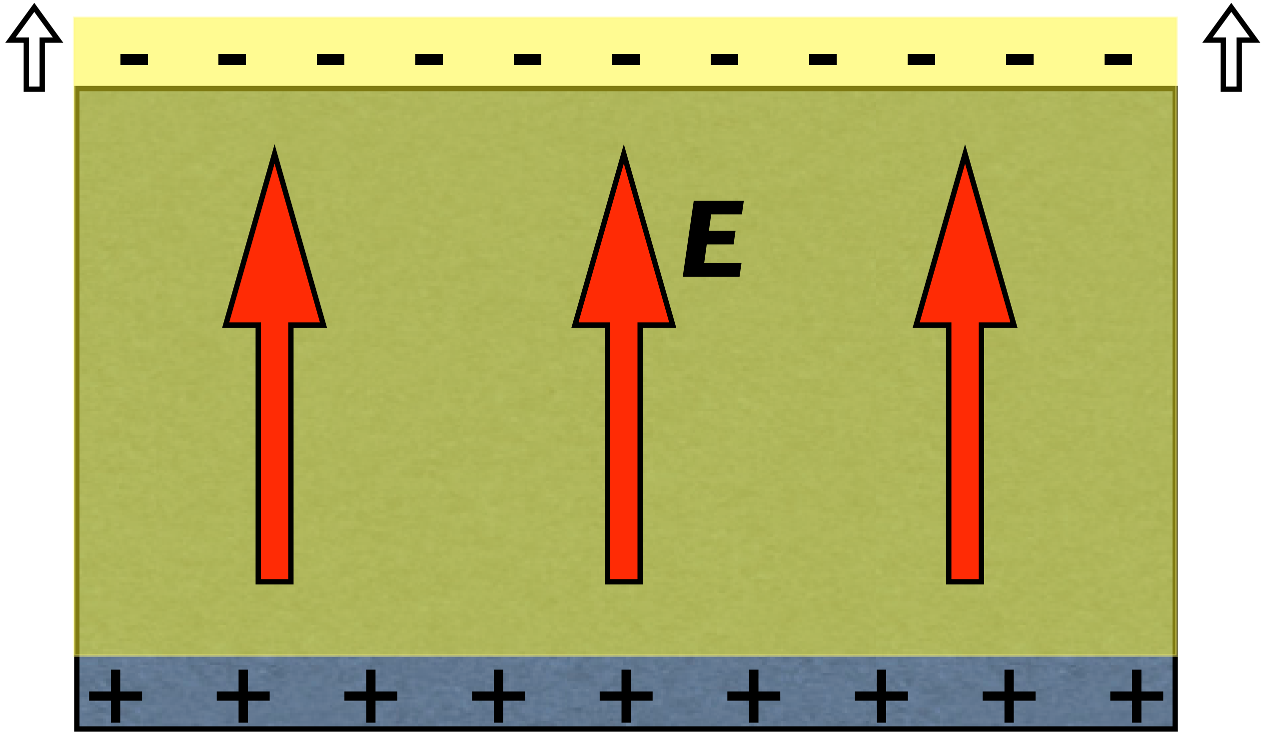
Bulk Plasma oscillations

$$\boxed{\omega_p = \sqrt{\frac{ne^2}{m\epsilon_0}}}$$

n = electron number density

z = electron gas displacement

$$\sigma = -enz$$



$$E = -\frac{\sigma}{\epsilon_0}$$

newtonian mechanics:

$$QE = M\ddot{z}$$

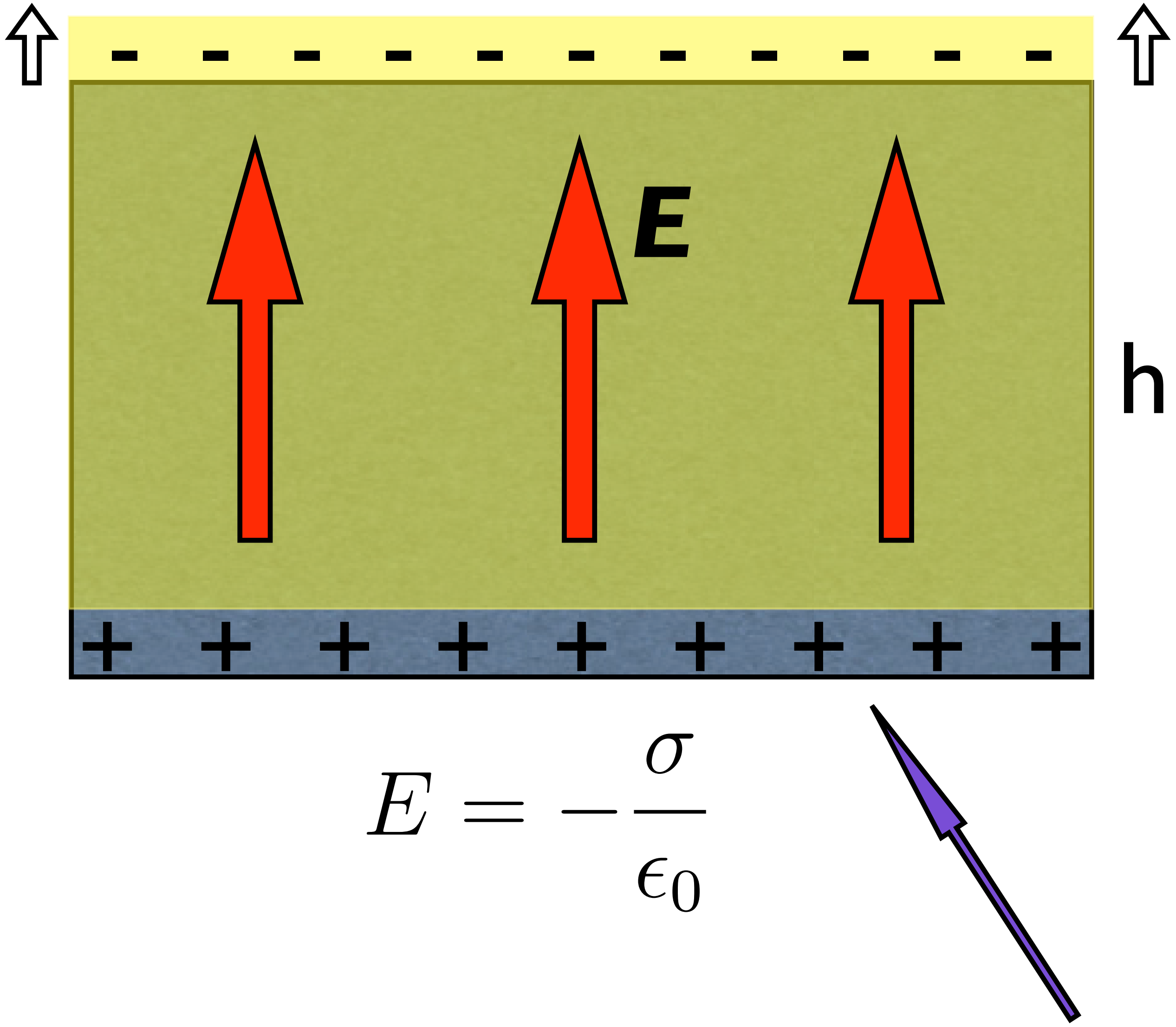
$$-\left(enV\right)\left(-\frac{\sigma}{\epsilon_0}\right) = \left(mnV\right)\ddot{z}$$

$$-\left(\frac{ne^2}{\epsilon_0}\right)z = m\ddot{z}$$

$$\boxed{\ddot{z} = -\frac{ne^2}{m\epsilon_0}\ z = -\omega_p^2\ z}$$

About electric polarization P

$$\sigma = -enz$$



$$E = -\frac{\sigma}{\epsilon_0}$$

A = top/bottom surface area

dipole moment:
$p = \sigma A h$

Polarization:
$P = p/V = \sigma = -enz$

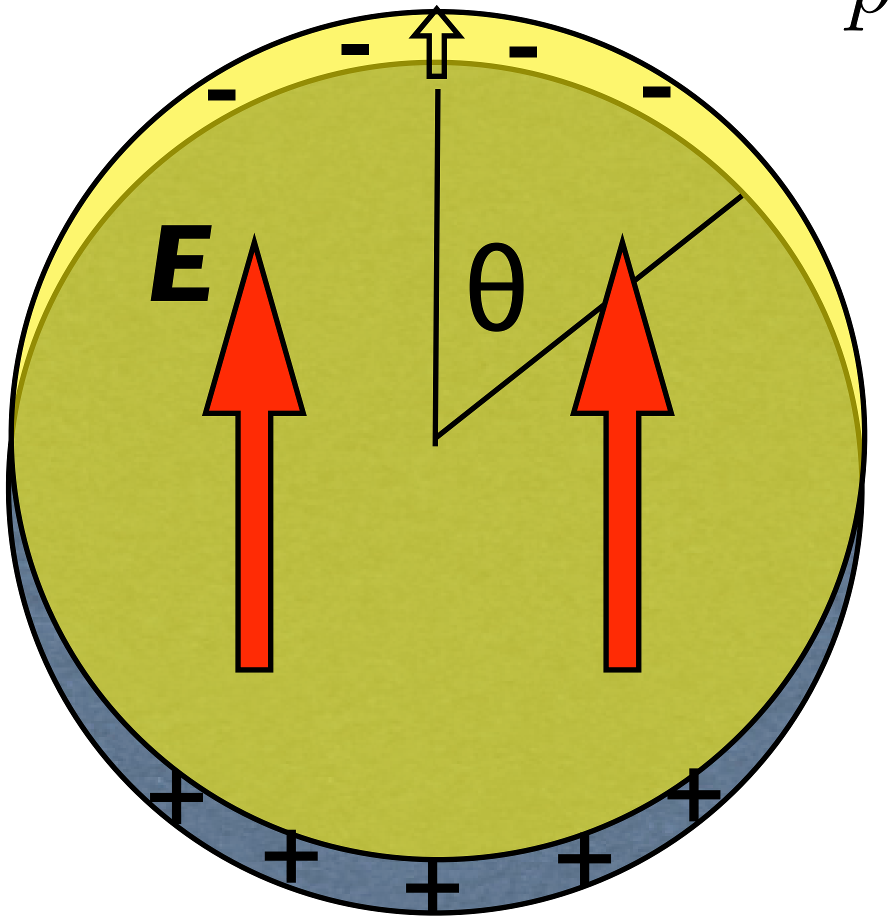
Spherical conductor, plasma oscillations

$$\boxed{\omega_s = \sqrt{\frac{ne^2}{3m\epsilon_0}} = \frac{\omega_p}{\sqrt{3}}}$$

z = electron gas displacement

$$\sigma = -nez\cos\theta$$

$$p_z = \int \sigma(a\cos\theta)dA = -\frac{4\pi a^3}{3}(nez)$$



Polarization: $\vec{P} = -(nez)\hat{z}$

newtonian mechanics: $QE = M\ddot{z}$

$$(-enV)\frac{nez}{3\epsilon_0} = (mnV)\ddot{z}$$

$$\vec{E} = -\frac{\vec{P}}{3\epsilon_0} = \frac{nez}{3\epsilon_0}\hat{z}$$

$$\ddot{z} = -\frac{ne^2}{3m\epsilon_0}z = -\omega_s^2 z$$

Therefore, Geometry affects the resonance frequency:

bulk gold:

$n = 5.90 \times 10^{28}/m^3$

$\omega_p = 1.36 \times 10^{16}$ rad/s

$\lambda_p = 138.5$ nm (very short)

spherical gold:

$n = 5.90 \times 10^{28}/m^3$

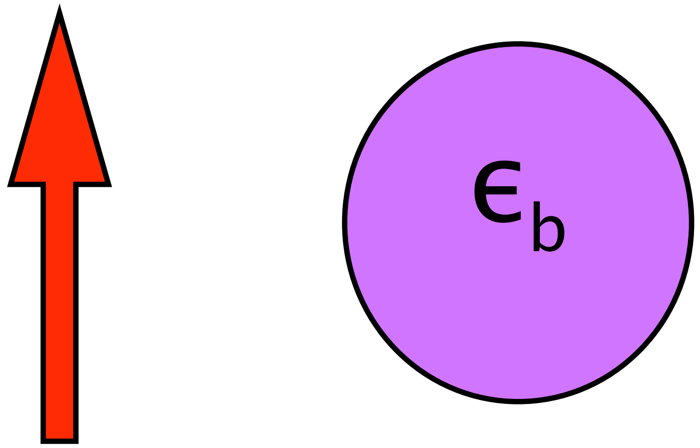
$\omega_s = 7.85 \times 10^{15}$ rad/s

$\lambda_s = 240$ nm (still too short)

Sphere in a host medium, dielectric response

Laplace eqn. solution.

E_0 = field in surroundings



ϵ_a=host

$$\Phi_{\text{inside}} = -\left(\frac{3\epsilon_a}{2\epsilon_a + \epsilon_b}\right) E_0 r \cos\theta$$

$$\vec{E}_{\text{inside}} = \frac{3\epsilon_a}{2\epsilon_a + \epsilon_b}\vec{E}_0$$ = uniform

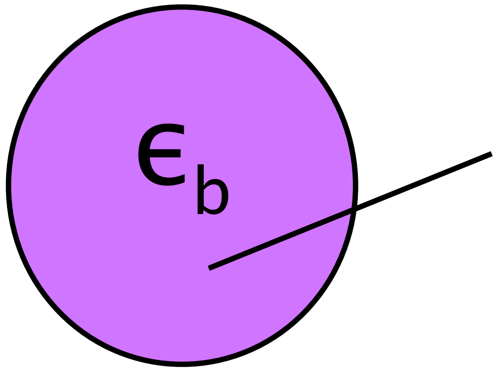
$$\Phi_{\text{outside}} = -\left[r - \left(\frac{\epsilon_b - \epsilon_a}{2\epsilon_a + \epsilon_b}\right)\frac{a^3}{r^2}\right] E_0 \cos\theta$$

$$\vec{E}_{\text{outside}} = \vec{E}_0 + \frac{\vec{p}\cdot\vec{r}}{4\pi\epsilon_a r^3}$$

induced electric dipole:

$$\vec{p} = \left(\frac{\epsilon_b - \epsilon_a}{2\epsilon_a + \epsilon_b}\right)\left(4\pi a^3 \epsilon_a \vec{E}_0\right)$$

Resonance of a conducting sphere



$$\vec{E}_{\text{inside}} = \frac{3\epsilon_a}{2\epsilon_a + \epsilon_b}\vec{E}_0$$

divergence when: $2\epsilon_a + \epsilon_b = 0$

Drude model, free electron gas: $\epsilon_b(\omega) = \epsilon_0\left[1 - \frac{\omega_p^2}{\omega^2}\right]$

resonance: $\Longrightarrow \quad 2\frac{\epsilon_a}{\epsilon_0} + 1 - \frac{\omega_p^2}{\omega^2} = 0 \quad \Longrightarrow$ $\boxed{\omega_{\text{SP}} = \frac{\omega_p}{\sqrt{2\frac{\epsilon_a}{\epsilon_0} + 1}}}$

for gold surrounded by H_20:

$n=(\epsilon_a/\epsilon_0)^{1/2}$
$=1.33$

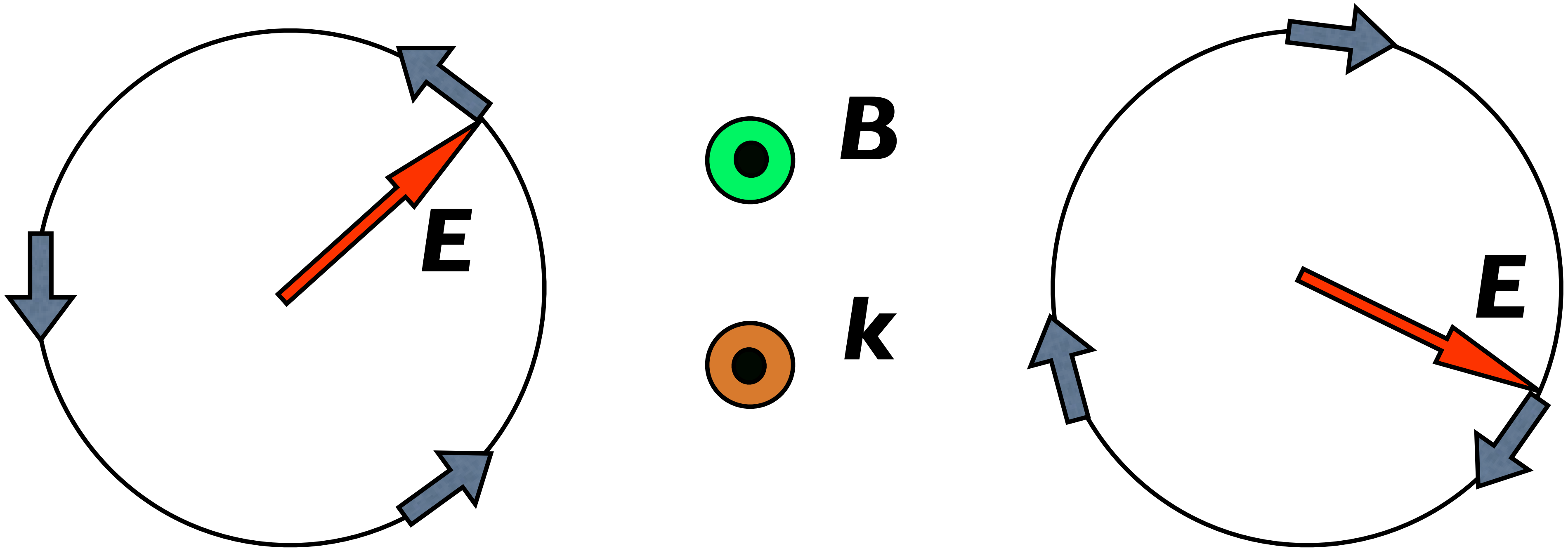
$$\omega_{\text{SP}} = \frac{\omega_p}{\sqrt{2(1.33)^2 + 1}} \approx 0.47\omega_p$$

$\Longrightarrow$ $\boxed{\lambda_{\text{SP}} = 295\text{ nm}}$

What about electron response and Faraday rotation?

Use circular polarization, and magnetic field ***B*** along ***k***=k***n***.

EM waves approaching you, the observer:



LEFT circular polarization
CCW rotation
positive helicity $\nu=\boldsymbol{\sigma}\cdot\boldsymbol{n}=+1$

$$\hat{u}_L = \frac{1}{\sqrt{2}}(\hat{x}+i\hat{y})\ e^{-i\omega t}$$

RIGHT circular polarization
CW rotation
negative helicity $\nu=\boldsymbol{\sigma}\cdot\boldsymbol{n}=-1$

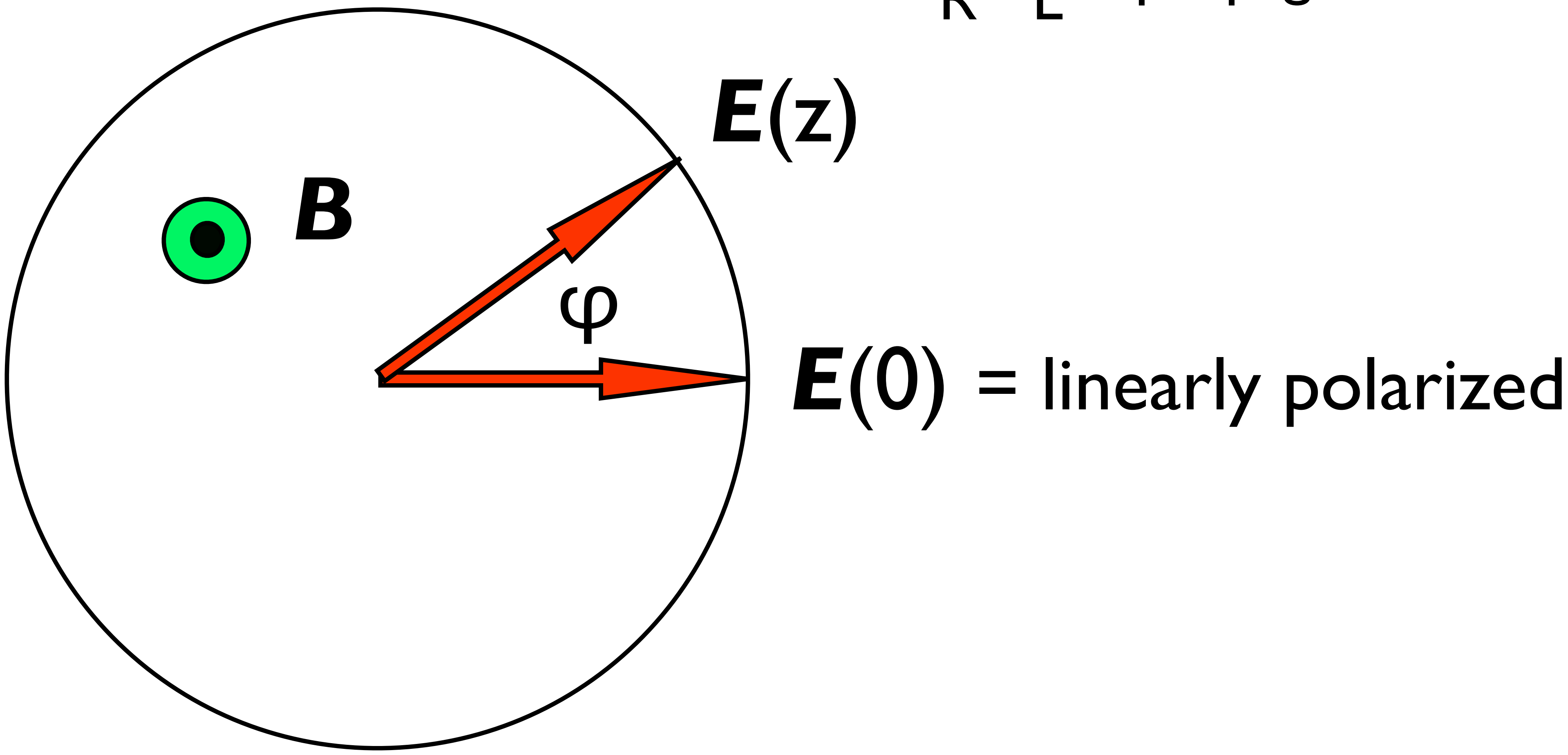
$$\hat{u}_R = \frac{1}{\sqrt{2}}(\hat{x}-i\hat{y})\ e^{-i\omega t}$$

Faraday Rotation angle:

$$\varphi=\tfrac{1}{2}\mathrm{Re}\{k_R-k_L\}z$$

z = propagation distance

k_R, k_L = propagation wave vectors

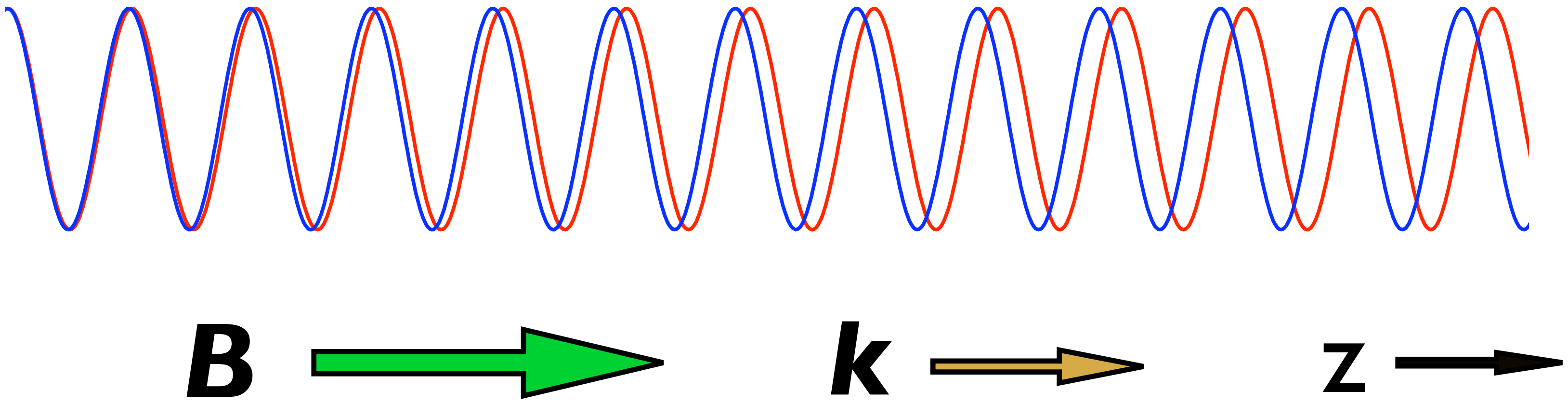


waves towards observer

Why is there Faraday rotation, and how large is it?

Incident linear polarization, at a single frequency ω:

$$\vec{E}_{\rm inc} = E_{\rm inc}\hat{x} = E_{\rm inc}\frac{1}{\sqrt{2}}(\hat{u}_R + \hat{u}_L)$$



red = λ_L $\quad \hat{u}_L = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{y})$

blue = λ_R $\quad \hat{u}_R = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{y})$

After propagation through z:

$$\vec{E}(z) = \frac{E_{\rm inc}}{\sqrt{2}}\left[\hat{u}_R e^{ik_R z} + \hat{u}_L e^{ik_L z}\right]$$

$$\vec{E}(z) = E_{\rm inc}\left[\hat{x}\cos\left(\frac{\Delta k}{2}z\right) + \hat{y}\sin\left(\frac{\Delta k}{2}z\right)\right]e^{i\bar{k}z}$$

Faraday rotation:

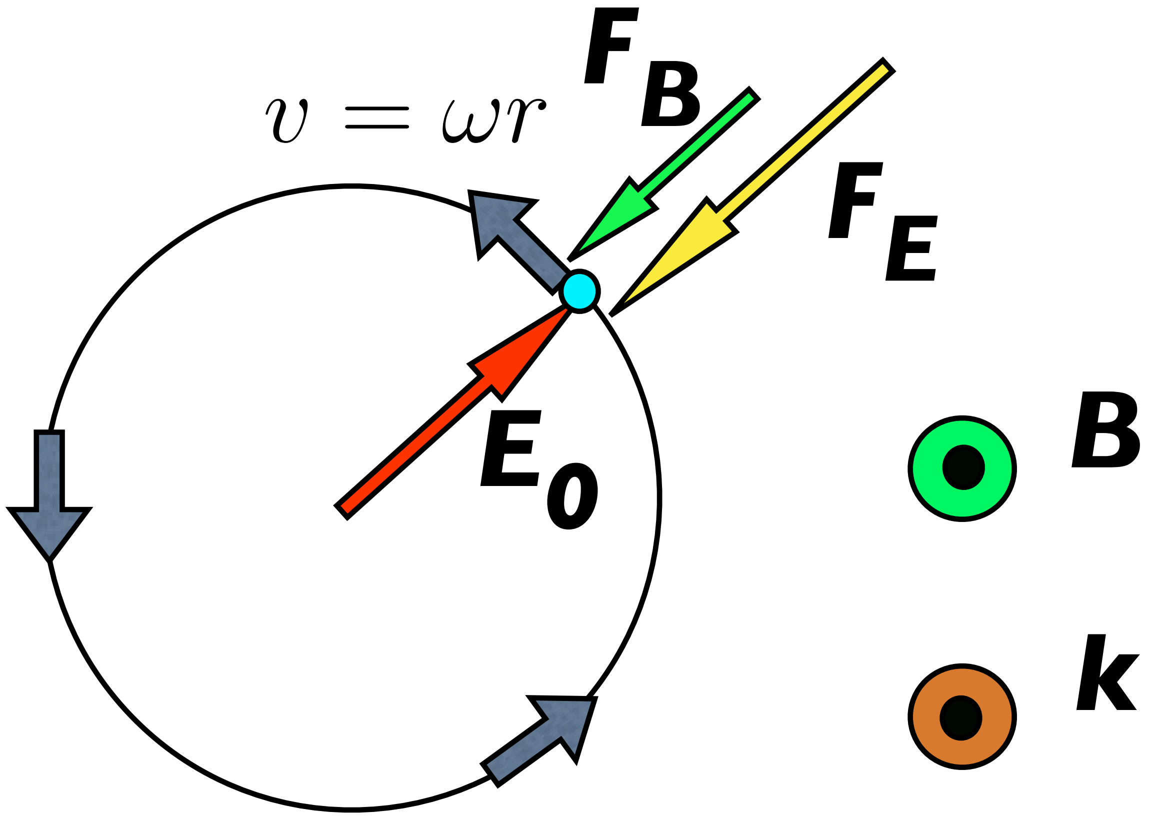
$$\psi = \frac{\Delta k}{2}z$$

$$\bar{k} \equiv \tfrac{1}{2}(k_R + k_L)$$

$$\Delta k \equiv k_R - k_L$$

Classical electron response, at frequency ω:

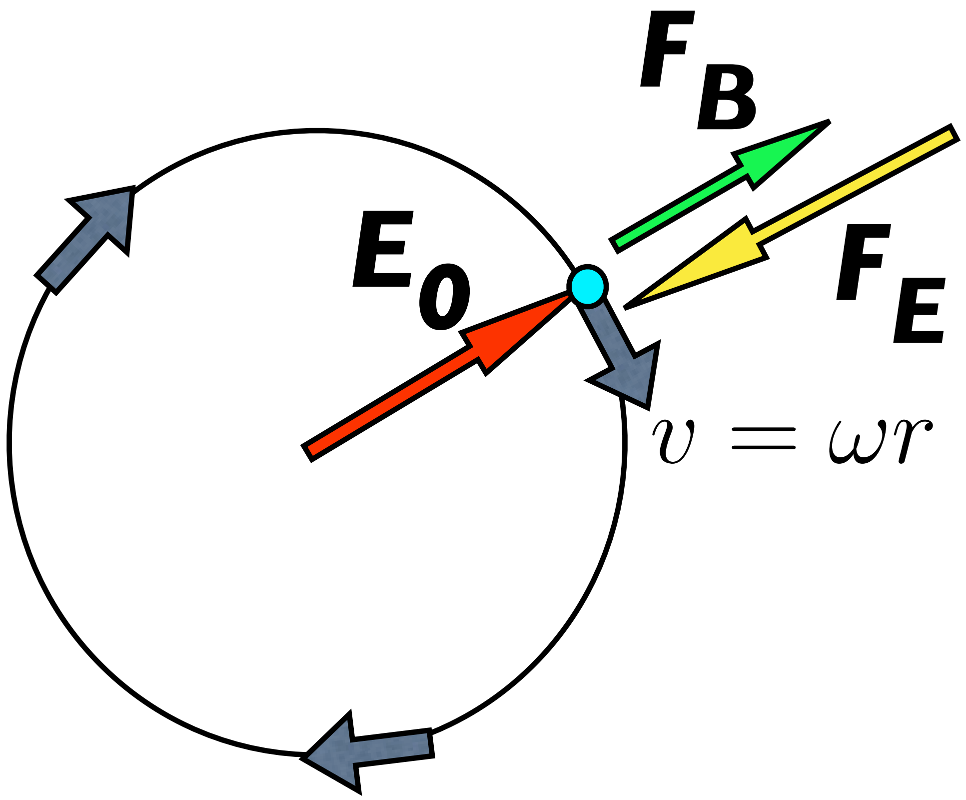
LEFT circular polarization



$$F_{\text{net}} = eE_0 + evB_z = m\omega^2 r$$

$$r = \frac{eE_0}{m\omega^2 - e\omega B_z} = \frac{eE_0}{m\omega(\omega - \omega_B)}$$

RIGHT circular polarization



$$F_{\text{net}} = eE_0 - evB_z = m\omega^2 r$$

$$r = \frac{eE_0}{m\omega^2 + e\omega B_z} = \frac{eE_0}{m\omega(\omega + \omega_B)}$$

cyclotron
frequency:

$$\boxed{\omega_B = \frac{eB_z}{m}}$$

LEFT polarization produces
larger orbit,
larger induced electric dipole

Effect on electric permittivity ϵ

permittivity ϵ:

$$\epsilon\vec{E} = \vec{D} = \epsilon_0\vec{E} + \vec{P}$$

polarization:

$$\vec{P} = n\vec{p}$$

electric dipole:

$$\vec{p} = -e\vec{r}$$

$$\epsilon = \frac{D_0}{E_0} = \frac{\epsilon_0 E_0 + P}{E_0} = \epsilon_0 + \frac{P}{E_0} \qquad \Longrightarrow \qquad \epsilon = \epsilon_0 - \frac{ne^2}{m\omega(\omega \pm \omega_B)}$$

$$\boxed{\epsilon = \epsilon_0\left[1 - \frac{\omega_p^2}{\omega(\omega \pm \omega_B)}\right]}$$

+ for RIGHT circular

- for LEFT circular

$$\lambda_R = \frac{2\pi}{k_R}$$

$$\lambda_L = \frac{2\pi}{k_L}$$

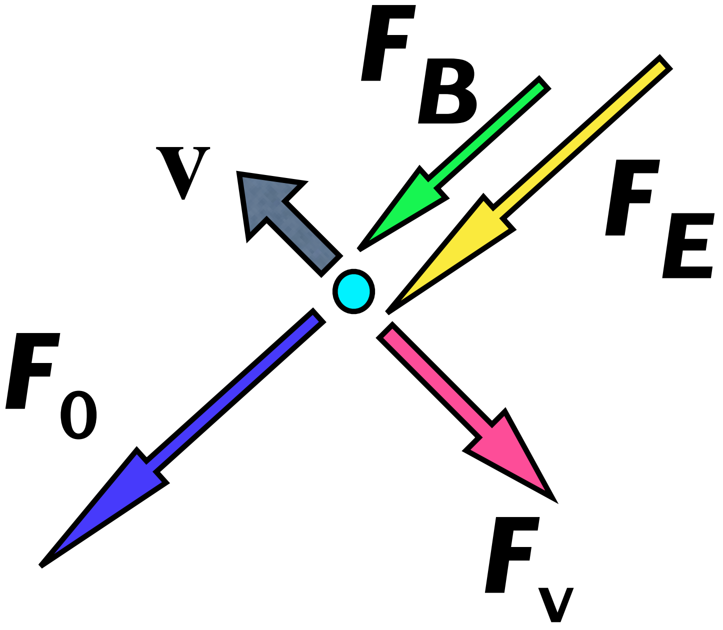
wave vectors:

$$k = \frac{2\pi}{\lambda} = \sqrt{\epsilon\mu}\,\omega$$

$$k = \frac{\omega}{c}\sqrt{1 - \frac{\omega_p^2}{\omega(\omega \pm \omega_B)}} \qquad \Longrightarrow \qquad \boxed{\lambda_R < \lambda_L}$$

Classical Faraday rotation: dielectric matrix ϵ

An electron is affected by several forces:



$$\vec{F} = -m\omega_0^2\vec{r} - e\vec{E} - e\dot{\vec{r}} \times \vec{B} - m\gamma\dot{\vec{r}} = m\ddot{\vec{r}}$$

binding electric Lorentz damping

harmonic motion: $\vec{r}(t) = \vec{r}_0 e^{-i\omega t}$

incident waves

$$m\left(\omega^2 - \omega_0^2 + i\omega\gamma\right)\vec{r} - i\omega e\vec{B} \times \vec{r} = e\vec{E}$$

electron response

$$\begin{pmatrix} m\left(\omega^2 - \omega_0^2 + i\omega\gamma\right) & i\omega eB_z \\ -i\omega eB_z & m\left(\omega^2 - \omega_0^2 + i\omega\gamma\right) \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} eE_{0x} \\ eE_{0y} \end{pmatrix}$$

form is: $\boxed{M \cdot \vec{r} = e\vec{E}}$

solution is: $\boxed{\vec{r} = \begin{pmatrix} x \\ y \end{pmatrix} = M^{-1} \begin{pmatrix} eE_{0x} \\ eE_{0y} \end{pmatrix}}$

Result for electric permittivity ϵ

$$\epsilon \vec{E} = \epsilon_0 \vec{E} + \vec{P} \qquad \vec{P} = -ne\vec{r} \qquad \vec{r} = M^{-1} \begin{pmatrix} eE_{0x} \\ eE_{0y} \end{pmatrix}$$

Then magic happens and

$$\boxed{\epsilon = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} \\ -\epsilon_{xy} & \epsilon_{xx} \end{pmatrix}}$$

$$\epsilon_{xx} = \epsilon_0 - \frac{(ne^2/m)\left(\omega^2 - \omega_0^2 + i\omega\gamma\right)}{\left(\omega^2 - \omega_0^2 + i\omega\gamma\right)^2 - (\omega e B_z/m)^2}$$

$$-i\epsilon_{xy} = \frac{(ne^2/m)(\omega e B_z/m)}{\left(\omega^2 - \omega_0^2 + i\omega\gamma\right)^2 - (\omega e B_z/m)^2}$$

What’s important: The eigenstates of ϵ are the RIGHT/LEFT circular polarization states!

$\lambda_1 = \epsilon_R = \epsilon_{xx} - i\epsilon_{xy}$ $\quad \hat{u}_1 = \hat{u}_R = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{y})$ RIGHT circular

$\lambda_2 = \epsilon_L = \epsilon_{xx} + i\epsilon_{xy}$ $\quad \hat{u}_2 = \hat{u}_L = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{y})$ LEFT circular

for the propagating eigenstates:

$$\boxed{\epsilon_{R/L} = \epsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2 - \omega_0^2 + i\omega\gamma \pm \omega\omega_B} \right)}$$

$$\Rightarrow$$

$$k_R = \sqrt{\epsilon_R \mu_0}\ \omega$$

$$k_L = \sqrt{\epsilon_L \mu_0}\ \omega$$

Complex Faraday rotation:

$$\psi = \tfrac{1}{2}(k_R - k_L)z$$

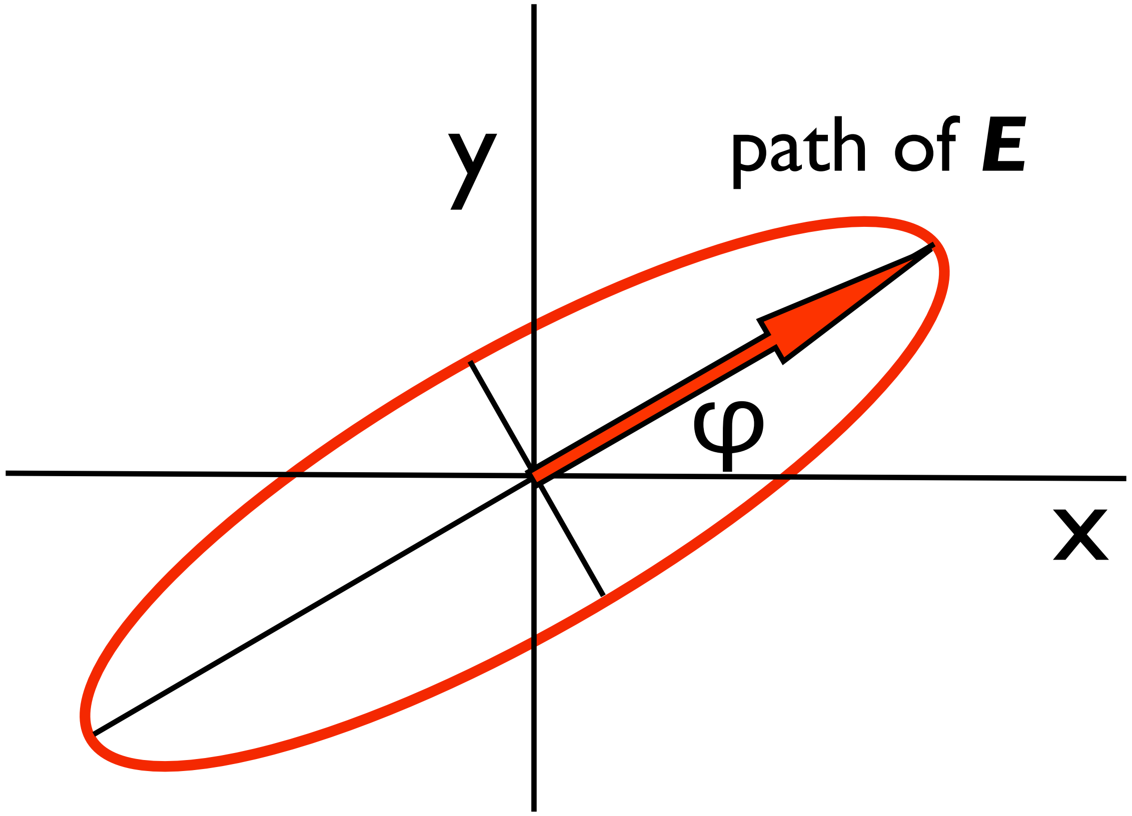
$$\Rightarrow$$

$$\boxed{\psi = -i\frac{\omega}{2c}\frac{\epsilon_{xy}}{\sqrt{\epsilon_{xx}}}z}$$

Real and Imag parts:

$$\varphi = \mathrm{Real}\left\{ -i\frac{\omega}{2c}\frac{\epsilon_{xy}}{\sqrt{\epsilon_{xx}}}z \right\}$$ = rotation

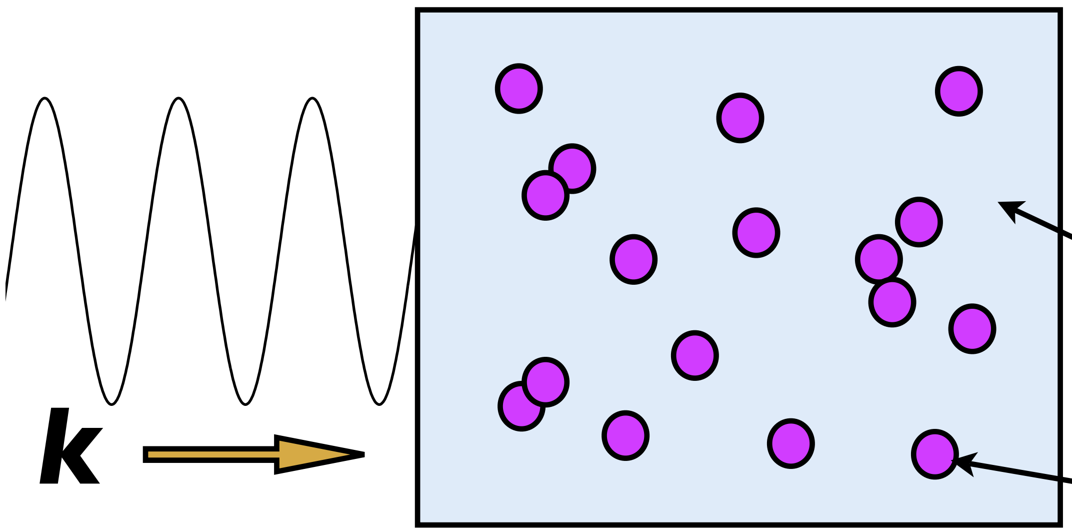
$$\chi = \mathrm{Imag}\left\{ -i\frac{\omega}{2c}\frac{\epsilon_{xy}}{\sqrt{\epsilon_{xx}}}z \right\}$$ = ellipticity



waves approaching observer

Scattering is from a collection of NPs. Use *effective medium theory*. (Maxwell-Garnet theory)

What are this sample's averaged ϵ_R, ϵ_L? N=# of NPs



$f_s = NV_s/V_{tot}$ = NP volume fraction

ϵ_h=host medium permittivity

$\boldsymbol{E}_h$=field in the host

ϵ_s=scatterers' permittivity

$\boldsymbol{E}_s$=field inside the scatterers

$$\begin{aligned}\mathbf{E}_{\rm av} &= f_s\mathbf{E}_s + (1-f_s)\mathbf{E}_h\\ \mathbf{P}_{\rm av} &= f_s\mathbf{P}_s + (1-f_s)\mathrm{P}_h\end{aligned}$$

$$\mathbf{P}_s = (\epsilon_s - 1)\,\epsilon_0\mathbf{E}_s$$

$$\mathbf{E}_s = \frac{3\epsilon_h}{\epsilon_s + 2\epsilon_h}\mathbf{E}_h$$

(Clausius-Mosotti eqn.)

$\Rightarrow$ $\Rightarrow$ $\Rightarrow$

$$\boxed{\beta_f = f_s\frac{\epsilon_s - \epsilon_h}{\epsilon_s + 2\epsilon_h}}$$

$\Downarrow$

$$\boxed{\epsilon_{\rm eff} = 1 + \frac{\mathbf{P}_{\rm av}}{\epsilon_0\mathbf{E}_{\rm av}} = \epsilon_h\frac{1+2\beta_f}{1-\beta_f}}$$

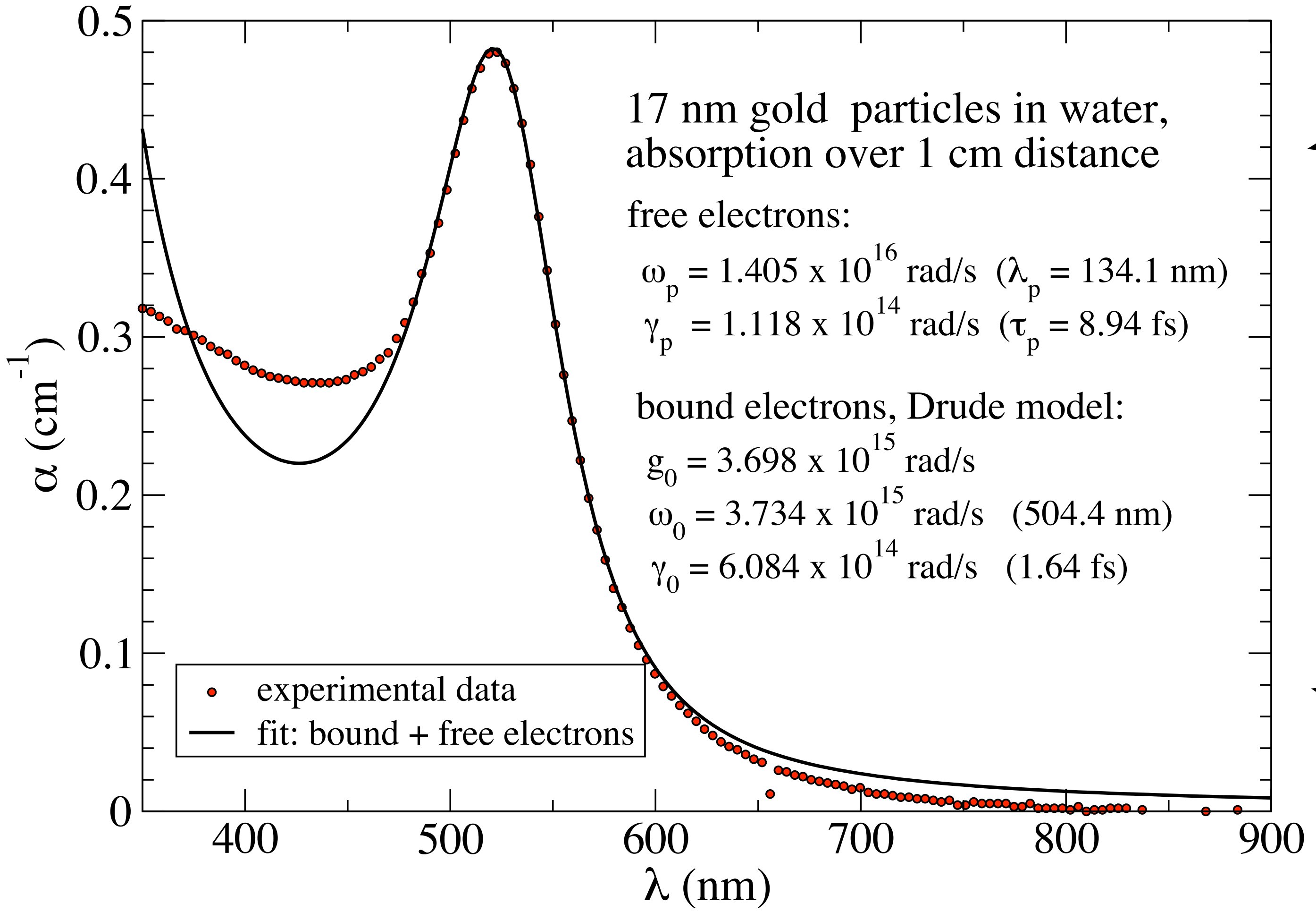
Find this for RIGHT/LEFT polarizations

Classical (Drude) model for pure gold NPs response:
(what we really do)

For ν=-1/+1, right/left circular polarizations

$$\epsilon_\nu(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_p + \nu\omega\omega_B} - \frac{g_0^2}{\omega^2 - \omega_0^2 + i\omega\gamma_0 + \nu\omega\omega_B}$$

(free electrons) (bound electrons)



17 nm gold particles in water, absorption over 1 cm distance

free electrons:

ω_p = 1.405 x 10^{16} rad/s (λ_p = 134.1 nm)

γ_p = 1.118 x 10^{14} rad/s (τ_p = 8.94 fs)

bound electrons, Drude model:

g_0 = 3.698 x 10^{15} rad/s

ω_0 = 3.734 x 10^{15} rad/s (504.4 nm)

γ_0 = 6.084 x 10^{14} rad/s (1.64 fs)

plasmon peak near 530 nm

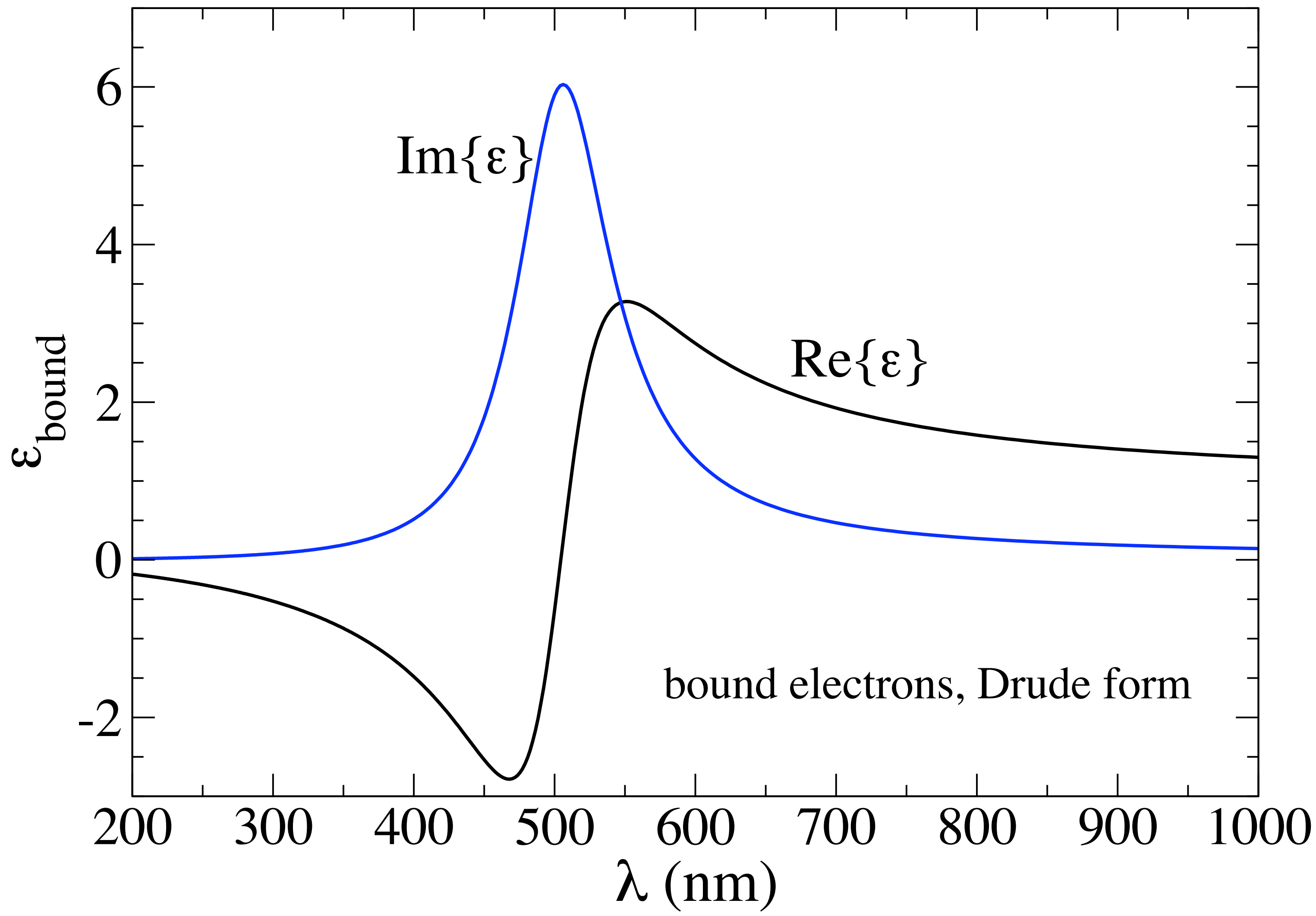
Fit parameters from absorption of a solution of gold particles:

$$\alpha = 2\,\mathrm{Im}\left\{k_{\mathrm{eff}}\right\} = 2\frac{\omega}{c}\mathrm{Im}\left\{\sqrt{\mu\epsilon_{\mathrm{eff}}}\right\}$$

for volume fraction of NPs

f_s=3.36x10^{-6}

Drude fitting, gold NPs, bound electron part:



negative real part below
505 nm probably is unphysical

Faraday rotation at $\omega_B \ll \omega$

cyclotron frequency at B=1.0 T

ω_B = eB/m = $1.8\text{x}10^{11}$ rad/s

$\ll$

optical frequency at λ=600 nm

$\omega = 2\pi c/\lambda = 3.1\text{x}10^{15}$ rad/s

Then the Faraday rotation is proportional to B:

$\upsilon = \varphi/(Bz) =$ Verdet constant

Also the Faraday rotation is proportional to volume fraction f_s:

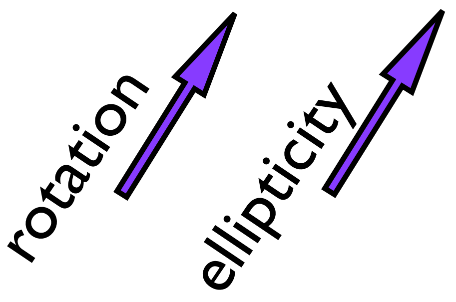
$\Upsilon = \varphi/(Bzf_s) =$ Verdet constant per volume fraction

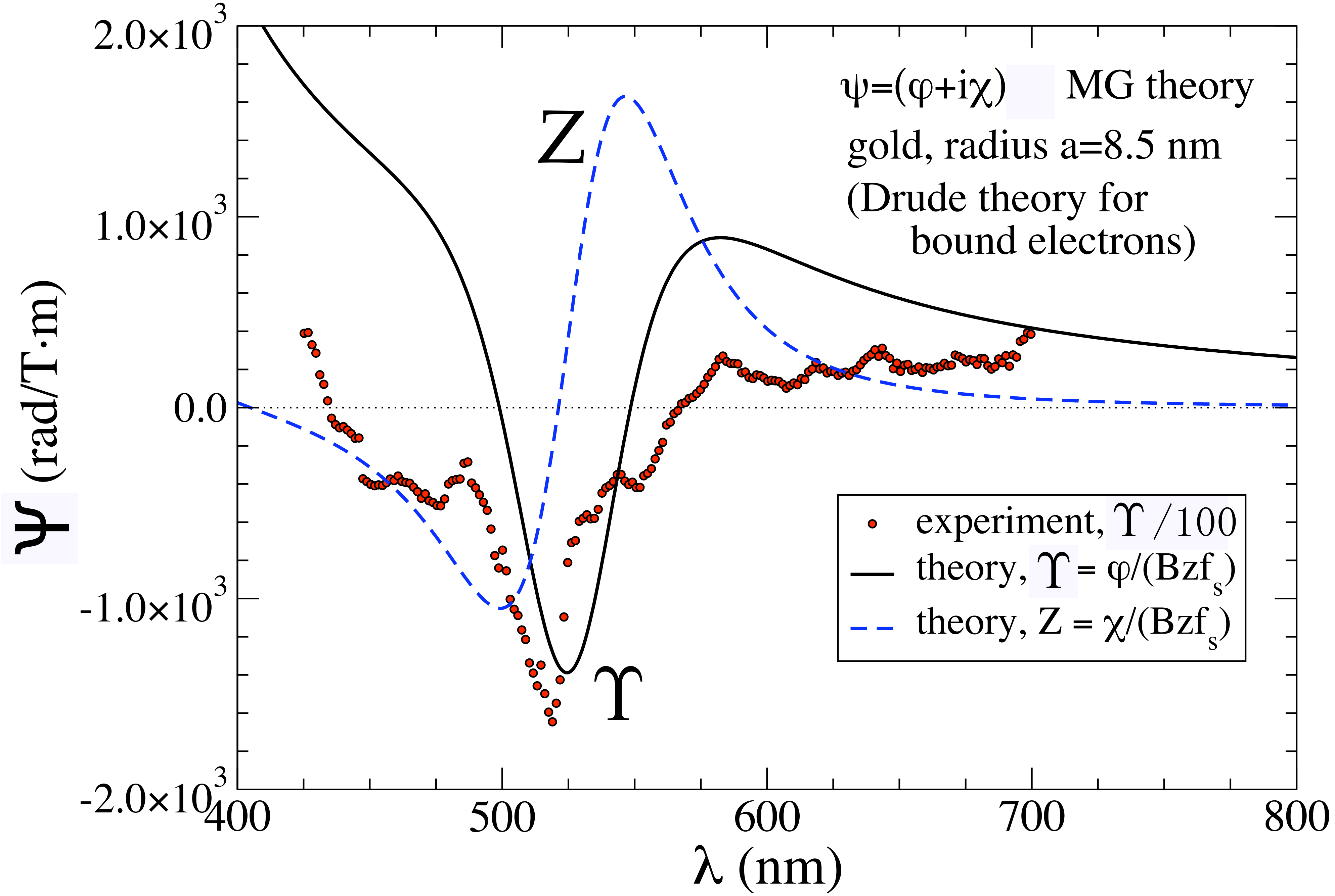
$Z = \chi/(Bzf_s) =$ ellipticity constant per volume fraction

Drude theory, 17 nm diameter gold NPs

scaled rotation & ellipticity

$$\Psi = \Upsilon + iZ$$





Drude theory result is much smaller than experiment.

Fig. 13-26 Giancoli 7th ed.
Nova Viçosa, Brazil

What about quantum electron dynamics with a DC magnetic field and the AC optical field?

$$A = A_0 + A_1$$

$$\boxed{\hat{H} = \frac{1}{2m_o}\left[\hat{\mathbf{p}} - e\hat{\mathbf{A}}(\hat{\mathbf{r}},t)\right]^2 + e\hat{\phi}(\hat{\mathbf{r}},t) + \hat{U}(\hat{\mathbf{r}})}$$

Apply perturbation theory to $H = H_0 + H_1$

The potential & A_0 determine the stationary states:

$$\hat{H}_0 = \frac{1}{2m_o}\left(\hat{\mathbf{p}} - e\hat{\mathbf{A}}_0\right)^2 + U(\mathbf{r})$$

At weak enough DC magnetic field:

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_o} + U(\mathbf{r}) - \vec{\mu}\cdot\mathbf{B}$$

This depends on the electron orbital magnetic dipole moment:

$$\vec{\mu} = \frac{e}{2m_o}\vec{L}$$

The optical field is a perturbation:

$$\boxed{\hat{H}_1 = -\frac{e}{m_o}\hat{\mathbf{A}}_1\cdot\left(\hat{\mathbf{p}} - e\hat{\mathbf{A}}_0\right)}$$

Perturbation theory* in thermal equilibrium … we want to find ϵ(ω).

Use density operator, in equilibrium:
(determined by states ψ_i of H_0)

$$\hat{\rho}_0 = \sum_i w_i |\psi_i\rangle\langle\psi_i|$$

$$w_i = \frac{1}{N} f_0(E_i), \quad f_0(E_i) = \frac{1}{e^{\beta(E_i - E_F)} + 1}$$

The perturbation.
Let light shine on the sample:

$$\hat{\rho} = \hat{\rho}_0 + \hat{\rho}_1$$

due to optical field ~ $e^{-i\omega t}$

quantum Liouville equation ⇒ dynamics:

$$\frac{\partial \hat{\rho}}{\partial t} = \frac{1}{i\hbar}[\hat{H}, \hat{\rho}]$$

leads to the time-dependence
of the density operator:

$$\boxed{\hat{\rho}_1 = \sum_{if} \frac{(w_i - w_f)|f\rangle\langle f|\hat{H}_1|i\rangle\langle i|}{\hbar(\omega + i\gamma) + (E_i - E_f)}}$$

*Approach used by Boswarva, Howard and Lidiard (1962); Adler (1962); Prange (2009).

Find permittivity $\epsilon(\omega)=1+\chi(\omega)$, from thermal averages, something like this:

electron's electric dipole operator:

$$\hat{\mathbf{d}}(\mathbf{r}) = e\hat{\mathbf{r}}|\mathbf{r}\rangle\langle\mathbf{r}|$$

averaged electric dipole at position r:

$$\mathbf{d}(\mathbf{r}) = \mathrm{Tr}\left\{\hat{\rho}\hat{\mathbf{d}}(\mathbf{r})\right\}$$

volume average ⇒
electric polarization:

$$\mathbf{P} = N\overline{\mathbf{d}} \ = \ \frac{N}{V}\int d^3r\,\mathbf{d}(\mathbf{r}) = \mathrm{Tr}\left\{\hat{\rho}ne\hat{\mathbf{r}}\right\}$$

E&M theory says:

$$\mathbf{P} = n\langle\mathbf{d}\rangle = \tilde{\chi}\cdot\epsilon_0\mathbf{E}$$

get susceptibility from:

$$\boxed{\chi_{ab} = \frac{ne^2}{\epsilon_0\hbar(\omega+i\gamma)}\sum_{if}\frac{(w_i - w_f)\langle i|\hat{v}_a|f\rangle\langle f|\hat{v}_b|i\rangle}{\omega_{if}\left(\omega+i\gamma+\omega_{if}\right)}}$$

velocity operator:

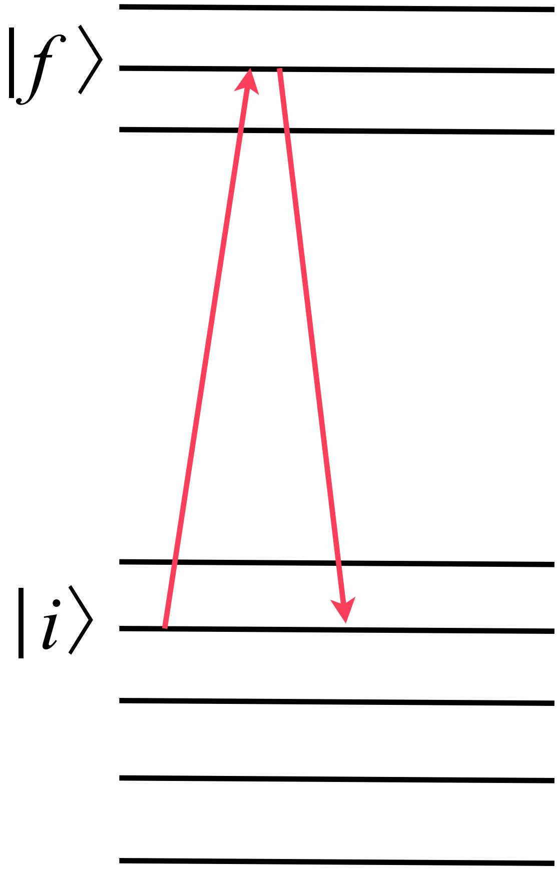
$$\hat{\mathbf{v}} = \frac{\vec{\pi}}{m_o} = \frac{1}{m_o}\left(\hat{\mathbf{p}} - e\hat{\mathbf{A}}\right)$$

transition frequencies:

$$\hbar\omega_{if} = E_i - E_f$$

What kinds of transitions are considered?

$$\boxed{\chi_{ab} = \frac{ne^2}{\epsilon_0 \hbar(\omega + i\gamma)} \sum_{if} \frac{(w_i - w_f)\langle i|\hat{v}_a|f\rangle\langle f|\hat{v}_b|i\rangle}{\omega_{if}\,(\omega + i\gamma + \omega_{if})}}$$



$$E_f \;=\; E_e = E_g + \frac{\hbar^2 \mathbf{k}_f^2}{2m_e^*} - \tfrac{1}{2} m_f \hbar\omega_B$$

Zeeman split states, $\Delta E = \frac{1}{2}\hbar\omega_B$

$$\boxed{\omega_B = \frac{eB_z}{m}}$$

$$E_i \;=\; E_h = -\frac{\hbar^2 \mathbf{k}_i^2}{2m_h^*} - \tfrac{1}{2} m_i \hbar\omega_B$$

under electric dipole transition rules like:

$$\Delta l \;=\; \pm 1,\; \Delta m \;=\; \pm 1. \qquad\qquad \Delta m \equiv m_f - m_i$$

Why don’t Landau levels appear as modifications of the band states?

For a free charge in a B-field:

$$H_0 = \frac{1}{2m_e}\vec{\pi}^2, \qquad \vec{\pi} = \mathbf{p} - \frac{e}{c}\mathbf{A}. \qquad \Rightarrow \qquad H_0 = \hbar\omega_B\left(a^\dagger a + \frac{1}{2}\right)$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_B, \quad n = 0, 1, 2, 3, \ldots$$

Landau ground state, n=0:

$$\boxed{\psi_0 = \frac{1}{\sqrt{\pi}\, r_0}\exp\left\{-\frac{r^2}{2r_0^2}\right\}, \qquad r_0 = \sqrt{\frac{2\hbar}{eB}}\, :}$$

The size of wavefunction depends on B.

At B=0.1 tesla, r_0 = 115 nm.

At B=1.0 tesla, r_0 = 36 nm.

At B=4.0 tesla, r_0 = 18 nm.

The Landau states do not fit into ~10 nm radius NPs!

A geometric confinement effect.

Why left/right circular polarizations couple differently to the medium.

$\boxed{\Delta m = \nu}$

matrix element / selection rules: $\langle l'm'|\hat{v}_y|lm\rangle = -i\Delta m\,\langle l'm'|\hat{v}_x|lm\rangle, \quad \Delta m = \pm 1$.

diagonal susc. elements:

$$\chi_{xx} \sim \sum_{fi} g_{fi}\,|\langle f|\hat{v}_x|i\rangle|^2 \;\; ,$$

off-diagonal susc. elements:

$$\chi_{xy} \sim \sum_{fi} (-i\Delta m)\,g_{fi}\,|\langle f|\hat{v}_x|i\rangle|^2 \;\; .$$

for right circular light (helicity ν=-1):

$$\chi_R \;=\; \chi_{xx} - i\chi_{xy} \sim \sum_{fi} (1-\Delta m)\,g_{fi}\,|\langle f|\hat{v}_x|i\rangle|^2$$

requires:

$$\Delta m \;=\; -1$$

for left circular light (helicity ν=+1):

$$\chi_L \;=\; \chi_{xx} + i\chi_{xy} \sim \sum_{fi} (1+\Delta m)\,g_{fi}\,|\langle f|\hat{v}_x|i\rangle|^2$$

requires:

$$\Delta m \;=\; +1$$

*As applied to 17nm diameter gold NPs.

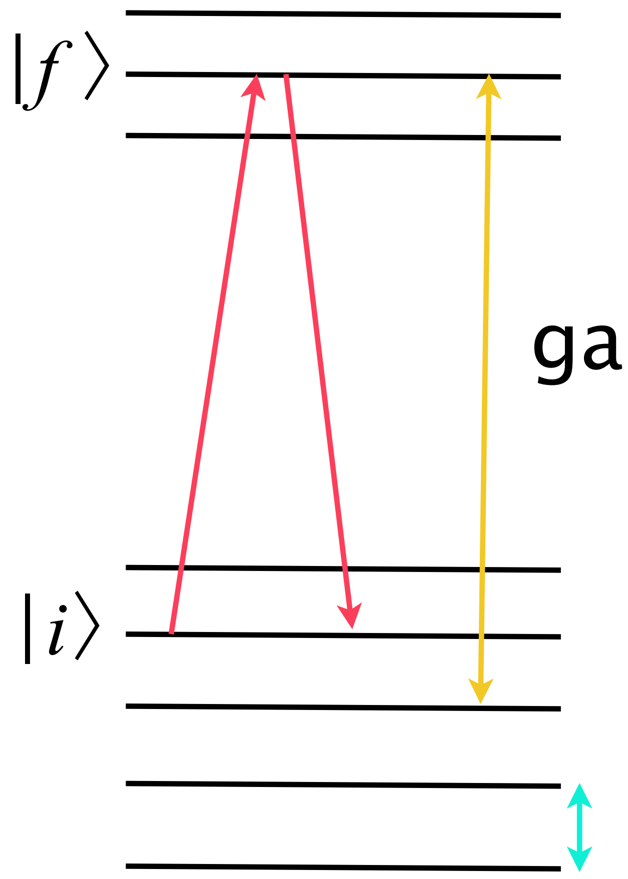
⇒ Integral* for interband transitions:

$\chi_\nu = Q\,T_\nu(\omega)$, ν=−1/+1 for R/L

$$\boxed{T_\nu = \frac{\omega_{2\nu}}{\omega + i\gamma} \sum_{m_f} \int_{\omega_g}^{x_F} dx \; \frac{g_{m_f}(x)\, x \sqrt{x - \omega_g}}{(x^2 - \frac{1}{4}\omega_B^2)(x^2 - \omega_\nu^2)}}$$

$\omega_\nu = \omega + i\gamma + \frac{1}{2}\nu\omega_B$

$$x = \omega_g + \frac{\hbar^2 k^2}{2m^*}$$



p-band, $E_f \;=\; E_e = E_g + \dfrac{\hbar^2 \mathbf{k}_f^2}{2m_e^*} - \frac{1}{2} m_f \hbar\omega_B$

gap=ħω_g≈2 eV

d-band, $E_i \;=\; E_h = -\dfrac{\hbar^2 \mathbf{k}_i^2}{2m_h^*} - \frac{1}{2} m_i \hbar\omega_B$

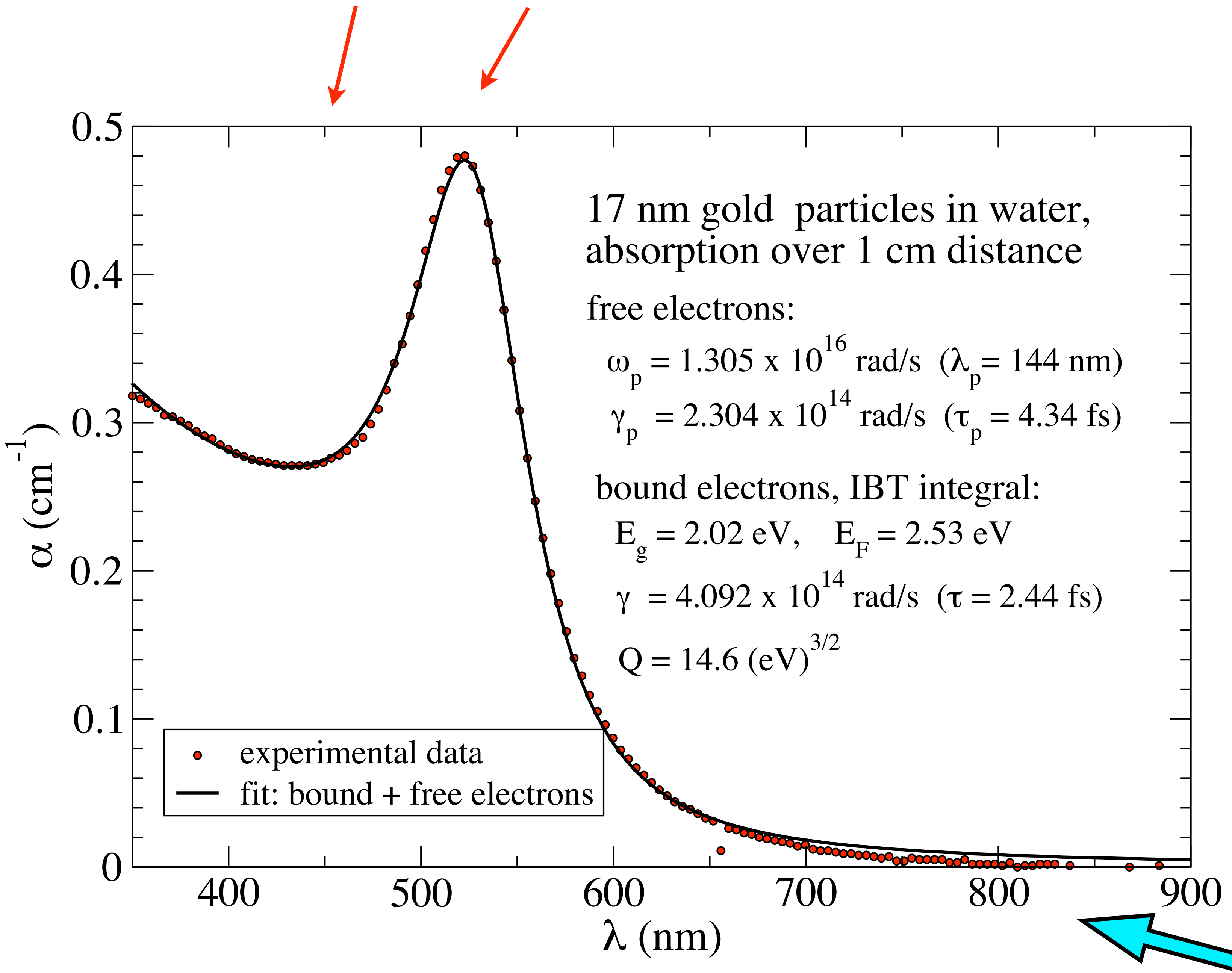
ΔE=½ħω_B

(along L-direction
in k-space)

*Generalized from approach of Inouye *et al.* and Scaffardi and Tocho, to add ω_B.

Using the quantum theory to fit parameters.

plasmon peak location & uv response is affected by the bound electrons.



$\epsilon = \epsilon_{free} + \epsilon_{bound}$

ϵ_{free}= Drude theory

ϵ_{bound}= interband transitions integral

Fit parameters from absorption of a solution of gold particles:

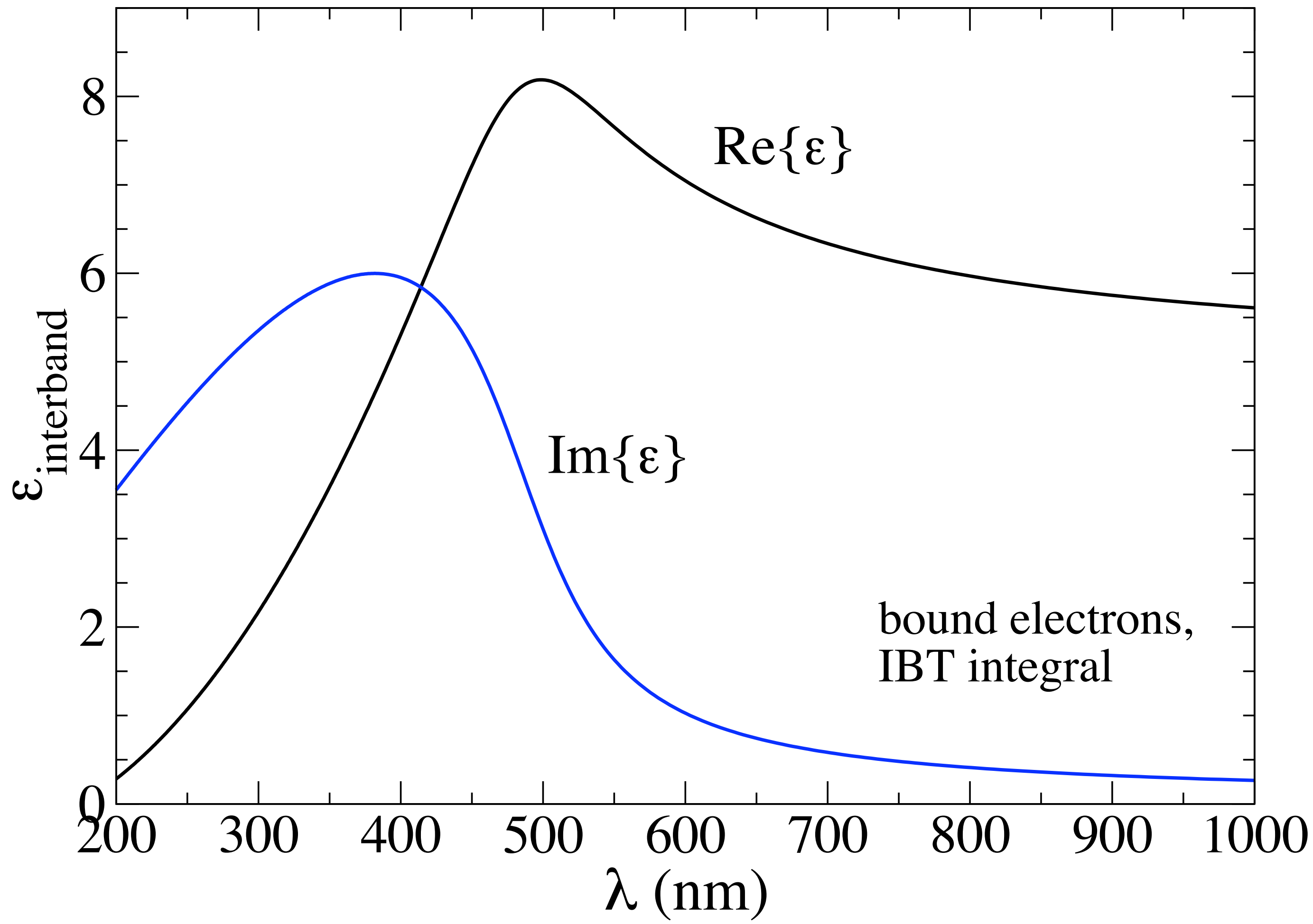
$$\alpha = 2\,\mathrm{Im}\left\{k_{\mathrm{eff}}\right\} = 2\frac{\omega}{c}\mathrm{Im}\left\{\sqrt{\mu\epsilon_{\mathrm{eff}}}\right\}$$

for volume fraction of NPs

$f_s = 5.95\mathrm{x}10^{-7}$

17nm diameter gold NPs.
From Integral for interband transitions:

Peak in Re{ϵ} due to Fermi energy (E_F=2.52 eV).



both parts stay positive.

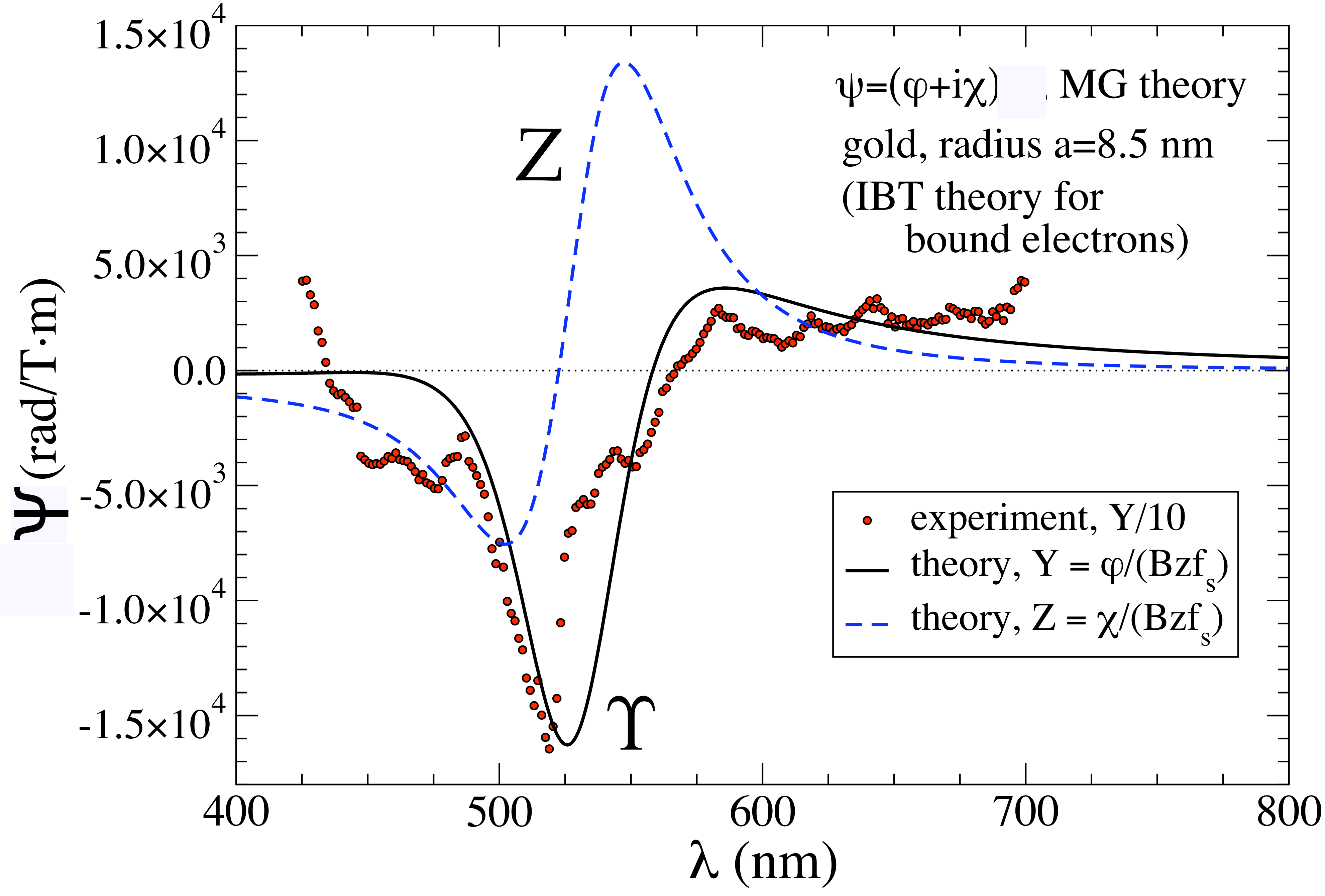
Using IBT integral for bound electrons, 17 nm diameter gold NPs

scaled rotation & ellipticity

$$\Psi = \Upsilon + iZ$$

rotation

ellipticity



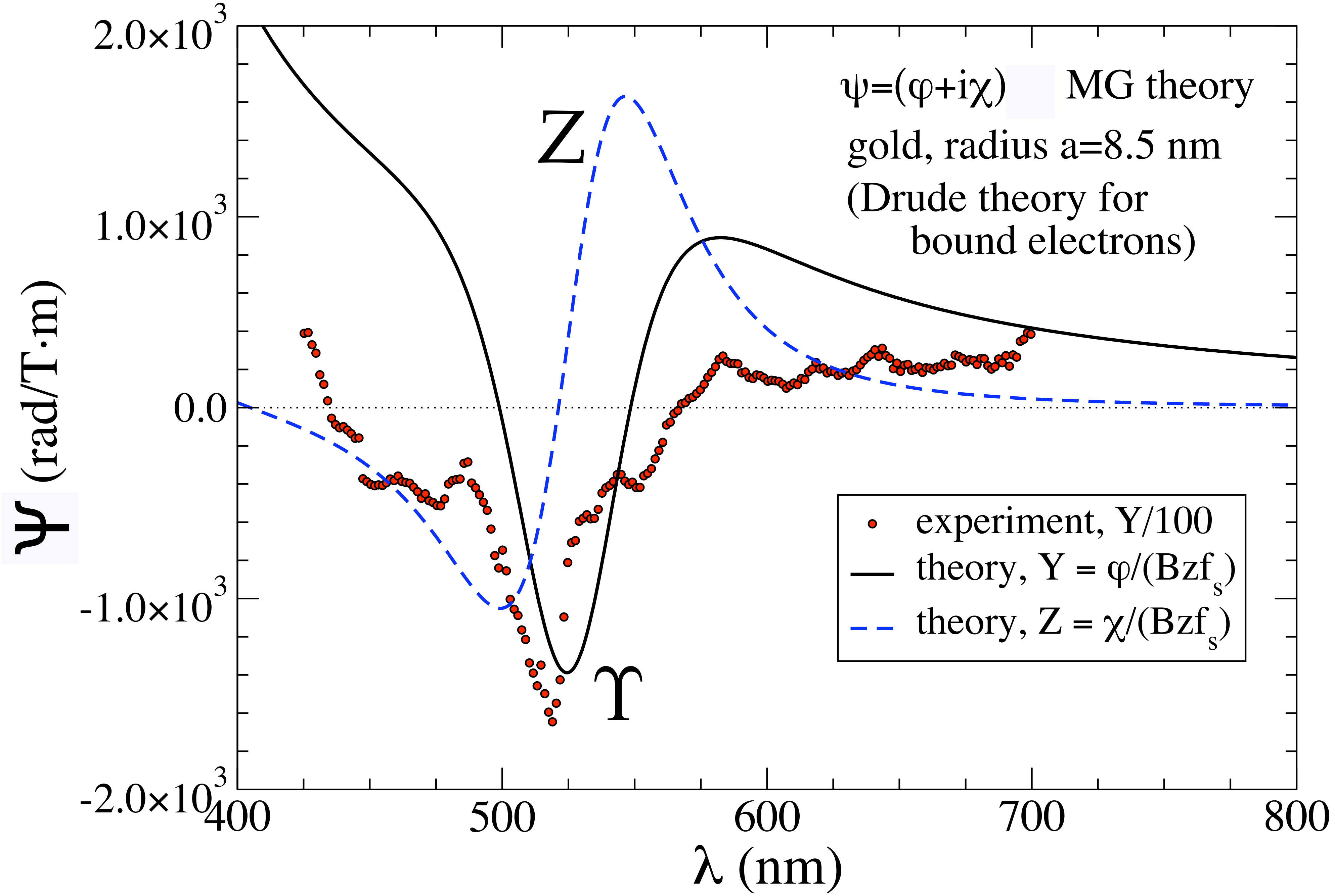
QM theory result is now closer to the experiment.

The tails of Υ go more quickly to zero.

scaled rotation & ellipticity

$$\Psi = \underset{\text{rotation}}{\Upsilon} + i\underset{\text{ellipticity}}{Z}$$

From the Drude theory for bound electrons, 17 nm diameter gold NPs



Drude theory result is much smaller than experiment.

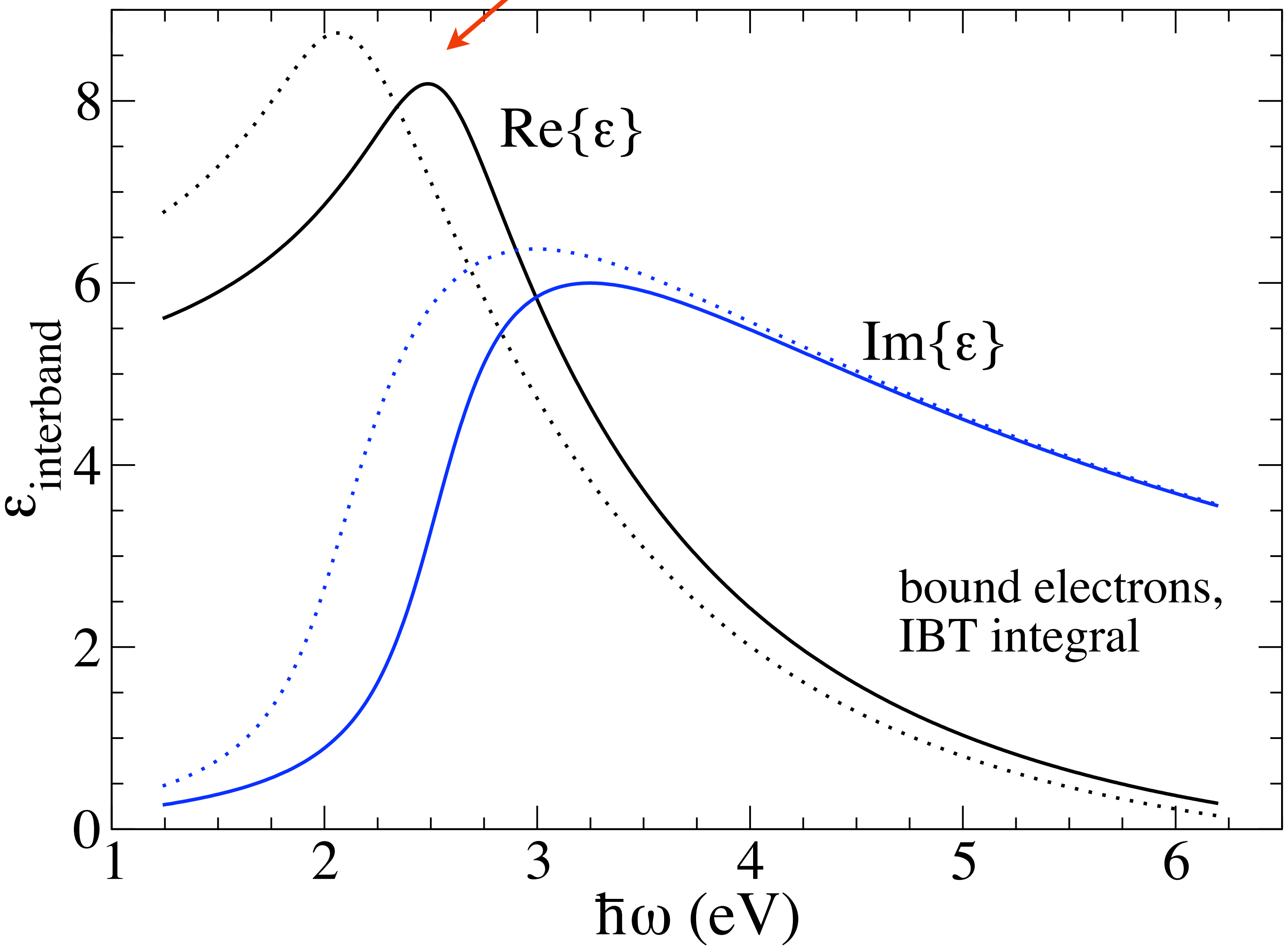
If you did an approximation of an unoccupied upper band:

dotted curves ⇒ unoccupied upper band.

peak at $\hbar\omega_g$=2.02.eV

peak at E_F=2.52.eV

⇐ solid curves: upper band has Fermi occupation probability for T=300 K.



Values of $\hbar\omega_g$ and E_F strongly control the bound electron responses.

Summary

- EM response [$\epsilon(\omega)$] in NPs is strongly affected by bound electrons.

- The plasmons are controlled by geometry and by $\epsilon(\omega)$, so avoid using a Drude approximation for the bound electrons if you want to get the correct plasmon frequencies.

- Applied DC magnetic field for typical NPs will not lead to Landau levels, but rather, Zeeman splittings that give a limited number of sub-states.

"Effects of interband transitions on Faraday rotation in metallic nanoparticles,"
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