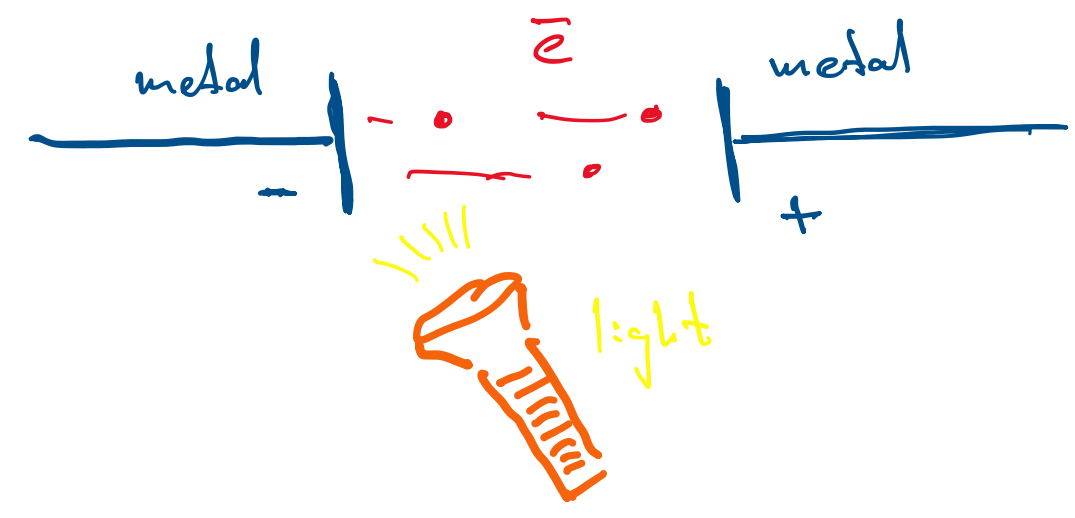
Inelastic scattering

Photoelectric effect

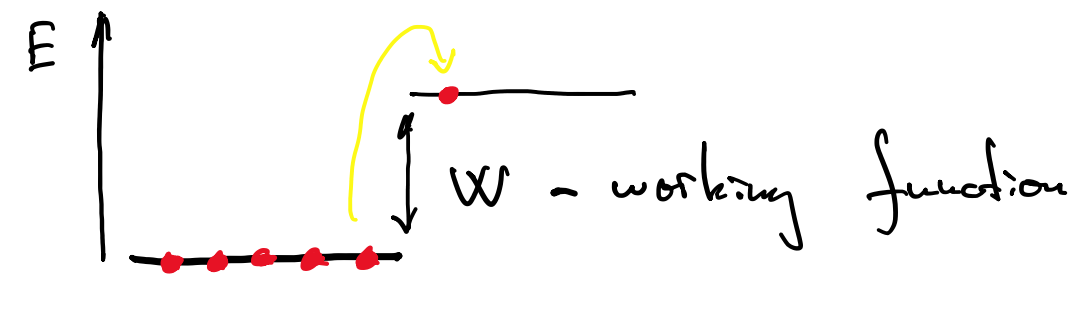
Hertz (1877)



Two important observations:

1) There is a threshold frequency ν_0
2) Above this ν_0, $E_{\bar{e}}$ (kinetic energy of an electron) increases linearly

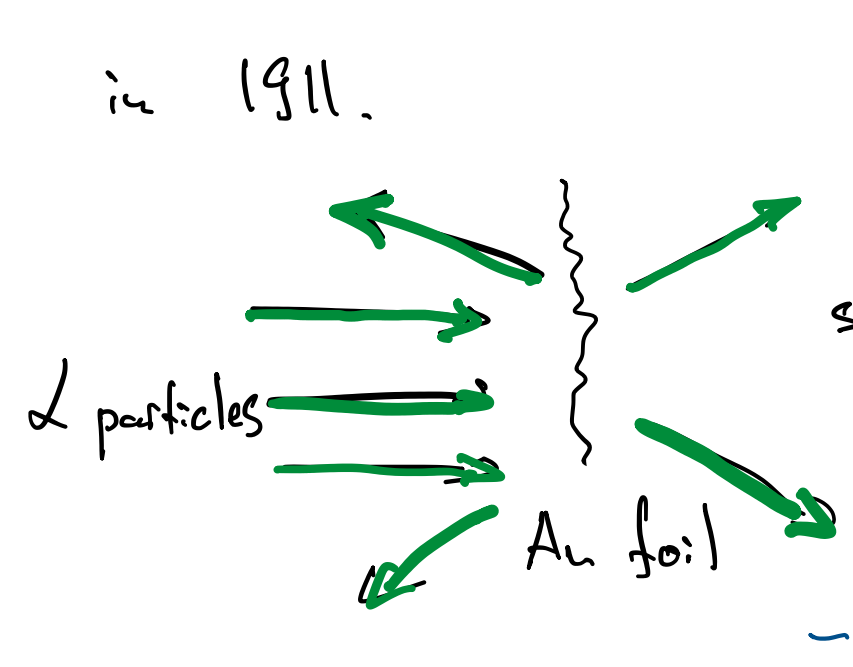
Einstein proposed working function (1905)



$$E_{\bar{e}} = \frac{1}{2}mv^2 = E_\gamma - W = h\nu - W$$

Millikan provided experimental proof only 10 years later in 1915.

For those times Rutherford already published his classic work on α-particle scattering experiment in 1911.

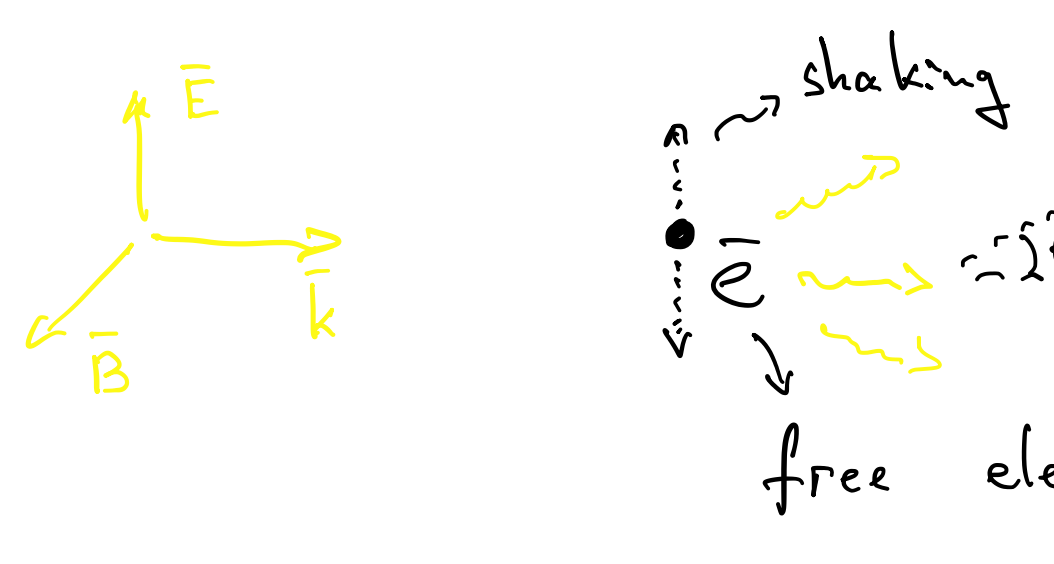


It allowed to suggest electrostatic nature of the scattering and assume nucleus as a circular objects, i.e. allowed Rutherford to propose planetary model.

This led later to Bohr's model.

While Einstein himself suggested light to have bundle „quanta" of energy, he was not happy, having „difficult struggle against idea of quantum, pulsed by small happy interludes of some discoveries".

Major problem was results of Thompson scattering:



$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{mc^2}\right)\frac{1}{2}(1+\cos^2\theta)$$

In fact, it is identical to Rayleigh, where

$$\nu_s = \nu_0$$

By 1916, Einstein has been already working on general relativety. Following his conclusions for photoelectric effect, he admitted the light must be „bundles" not only of energy, but of momentum.

$$\begin{cases} E = \dfrac{mc^2}{\sqrt{1-\frac{v^2}{c^2}}} \\ \bar{p} = \dfrac{m\bar{v}}{\sqrt{1-\frac{v^2}{c^2}}} \end{cases} \Rightarrow E^2 - p^2c^2 = m^2c^4$$

So, if you know the energy and the momentum you can know the particle mass.

This is relativistic version of what we know from Newton:

$$\begin{cases} E = \frac{1}{2}mv^2 \\ \bar{p} = m\bar{v} \end{cases} \Rightarrow E = \frac{p^2}{2m}$$

For the photon γ, since rest mass is zero:

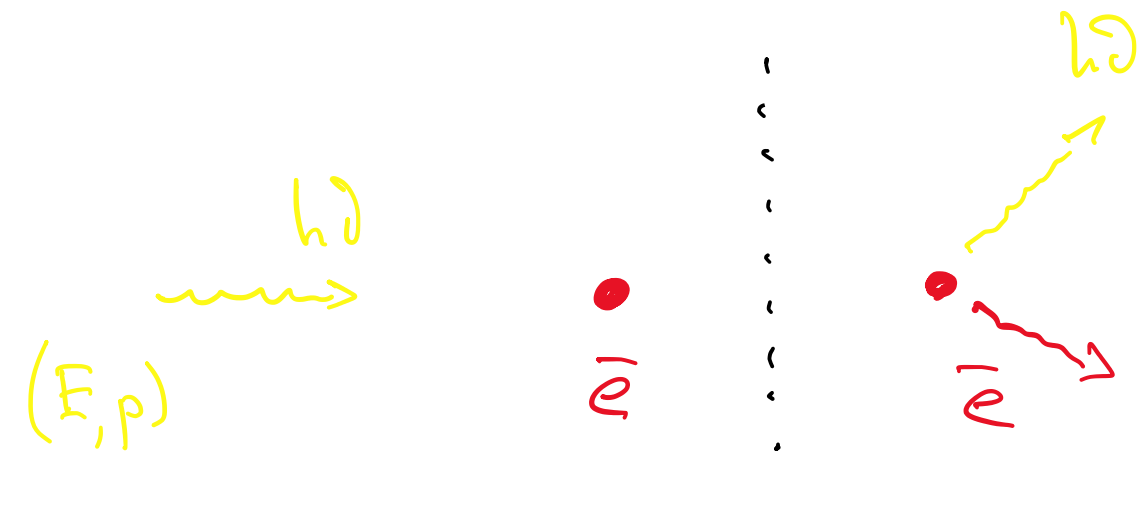
$$E_\gamma = p_\gamma c \quad (m_\gamma = 0)$$

$$\Downarrow$$

$$p_\gamma = \frac{E_\gamma}{c} = \frac{h\nu}{c} = \frac{h}{\lambda_\gamma}$$

Compton realized this idea only in 1923 !

He saw great deviation from Thompson scattering once momentum of photon starts to be comparable to „free" electron.

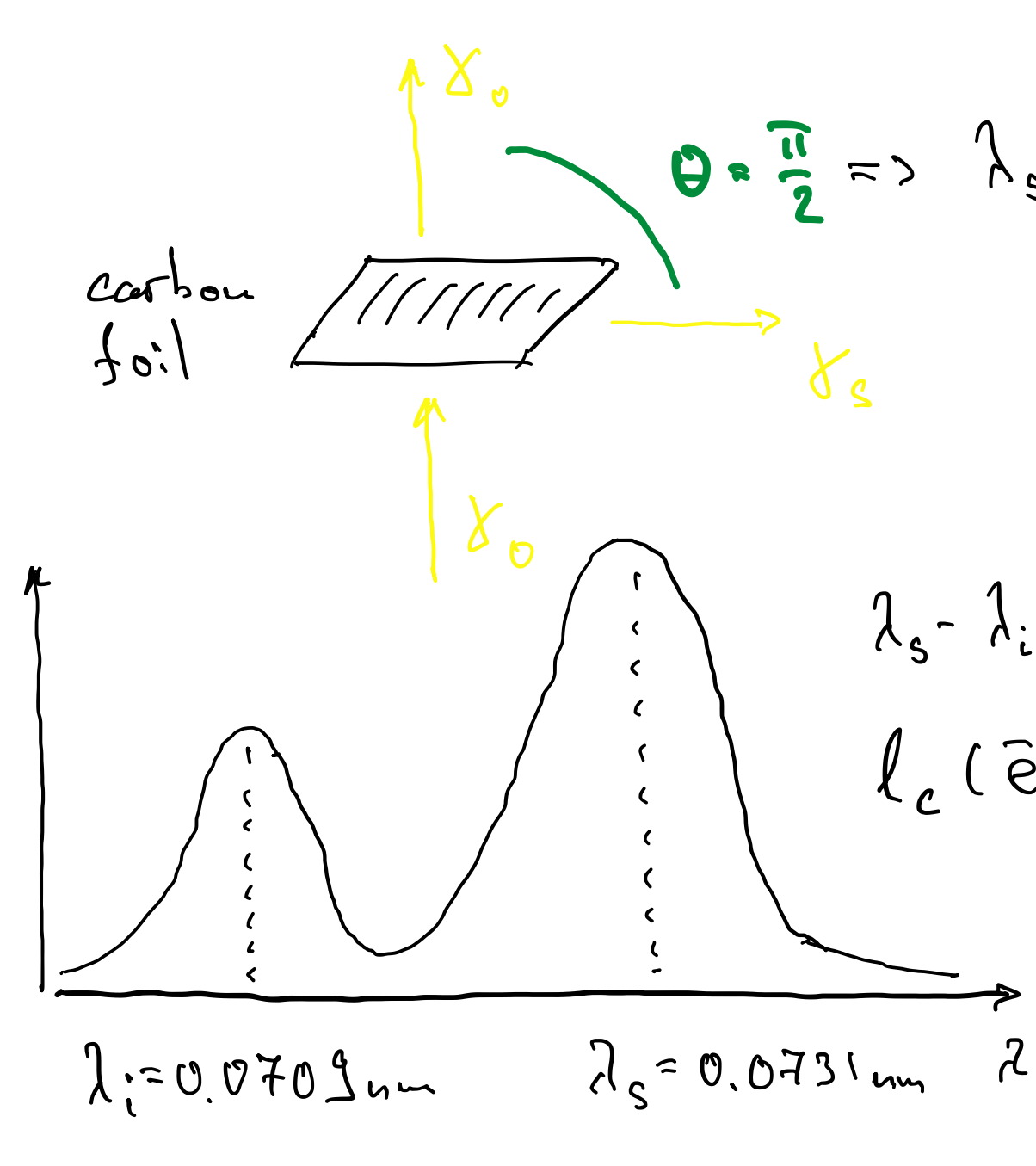


Free electron cannot absorb photon ! It will require change of rest mass, thus it can only scatter photon and change its own kinetic energy, i.e. momentum of electron will change.

Since E_k of electron has been changed, photon should lose some energy $\lambda_s > \lambda_i$

$$\lambda_s = \lambda_i + \frac{h}{m_e c}(1-\cos\theta)$$

$\frac{h}{m_e c} = l_c \rightarrow$ Compton wavelength of „free" electron.



$$\theta = \frac{\pi}{2} \Rightarrow \lambda_s = \lambda_i + \frac{h}{m_e c}$$

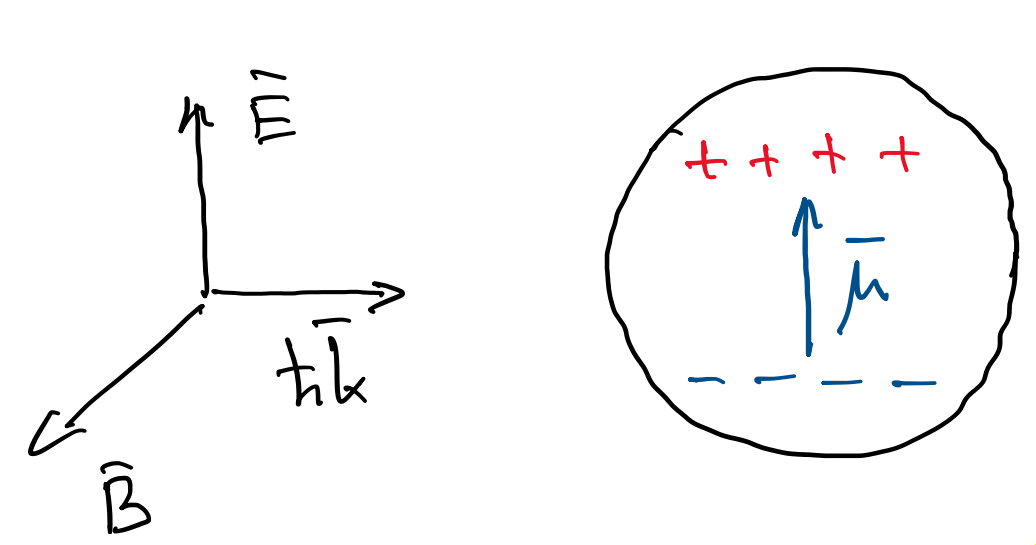
$$\lambda_s - \lambda_i = 0.0022\,nm$$

$$l_c(\bar{e}) = \frac{h}{m_e c} = 2.426\,pm$$

In 1928 Raman tried this experiment with visible light. Should that work? No.

However, he accidentally saw similar shifts, yet failed to explain origin of effect.

Same year, 3 month later, Mandelshtam-Landsberg reported their classic work!



$\bar{\mu} = \hat{\alpha}\bar{E}$ - dipole moment

↳ polarizability tensor

Remember, Fermi Golden Rule:

Time-dependent Schrödinger Equation

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\cdot\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi(x,t)$$

$$P_{fi} = \lim_{T\to\infty}\int_0^T\left[e^{-i(E_f-E_i-\hbar\omega)\frac{t}{\hbar}} + e^{-i(E_f-E_i+\hbar\omega)\frac{t}{\hbar}}\right]dt\cdot\frac{|V_{fi}|^2}{4\hbar^2}$$

$$V_{fi} = \int\Psi_f^*\hat{V}\Psi_i\,dx = \int\Psi_f^*(-\underbrace{q\bar{r}}_{\mu}\bar{E})\Psi_i\,dx$$

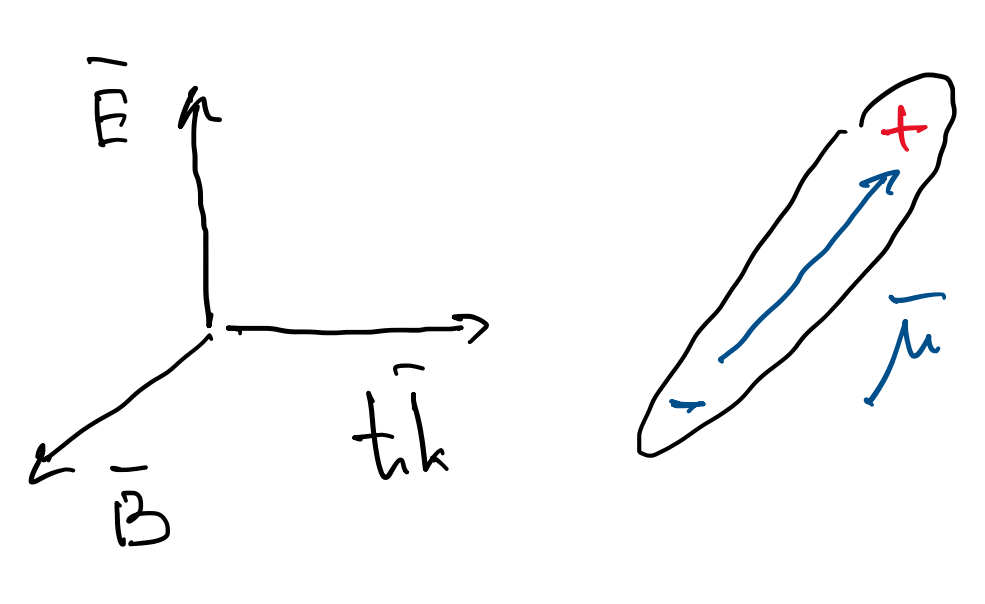
Why do we need tensor? Because matter can be anisotropic

Isotropic

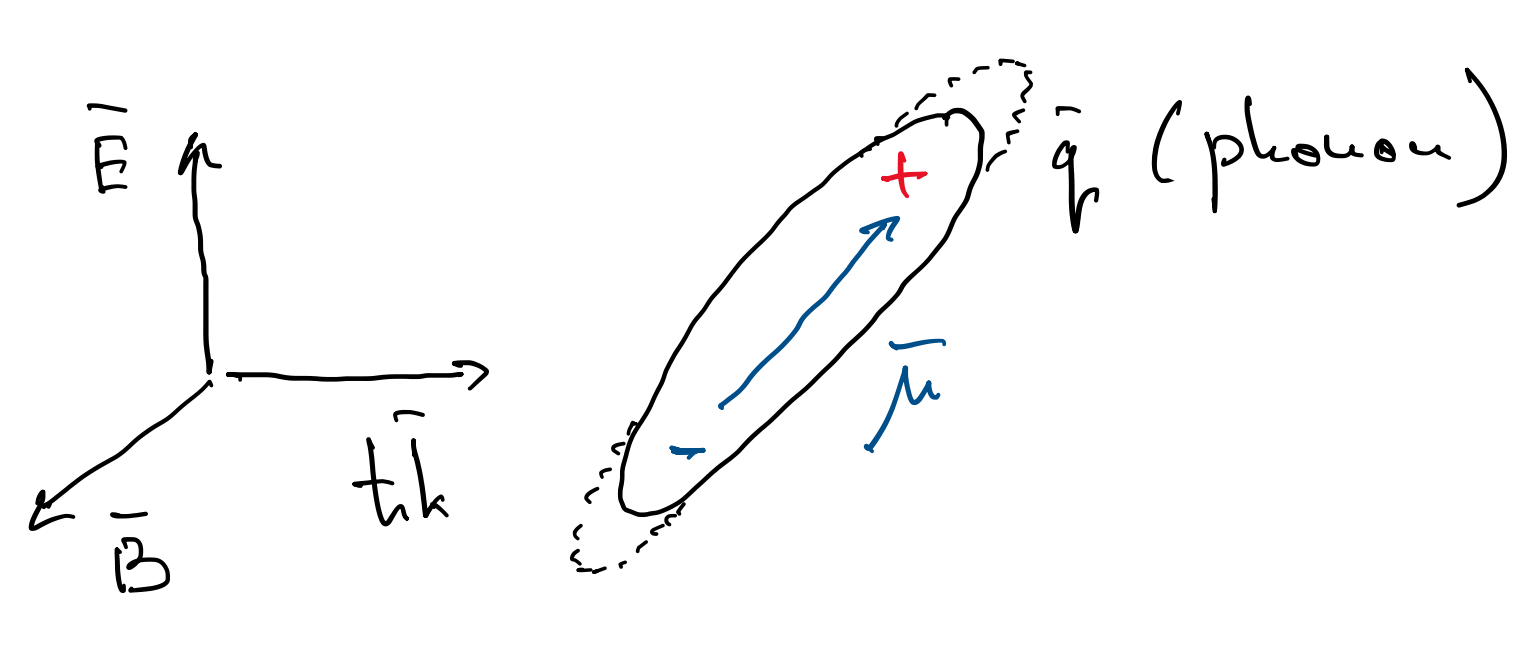
$$\hat{\alpha} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$$

Anisotropic

$$\hat{\alpha} = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & k \end{pmatrix}$$



While usually we have $\bar{\mu} = \hat{\alpha}\bar{E}$ as single dipole term, there will be always little displacement of lattice, that will affect polarizability!



Then $\hat{\alpha}$ can be open in Taylor expansion:

$$\hat{\alpha} = \hat{\alpha}_{q=0} + \bar{q}\left.\frac{\partial\hat{\alpha}}{\partial q}\right|_{q=0} + \dots$$

For dipole approximation: $E = E_0\cos\omega_0 t$

For harmonic displacement: $\bar{q} = \bar{q}_0\cos\omega_v t$

$$\bar{\mu} = \hat{\alpha}_{q=0} + \left.\frac{\partial\hat{\alpha}}{\partial q}\right|_{q=0} q_0\cos(\omega_v t)\,E_0\cos(\omega_0 t)$$

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$$2\cos a\cos b = \cos(a+b) + \cos(a-b)$$

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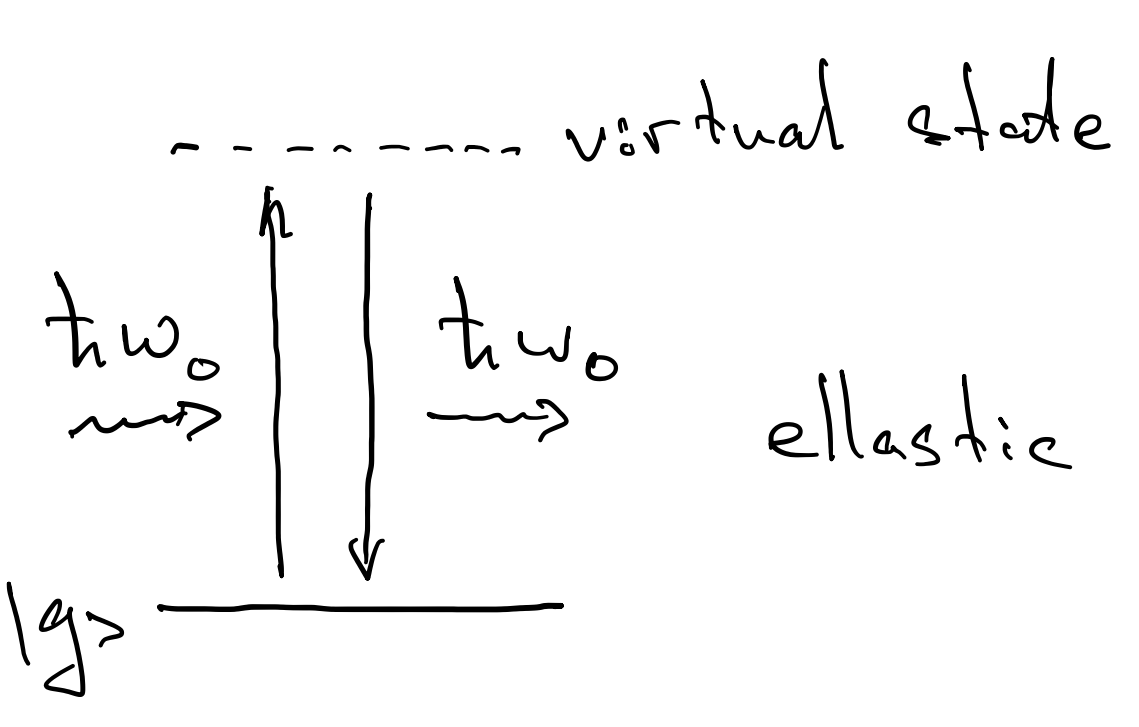
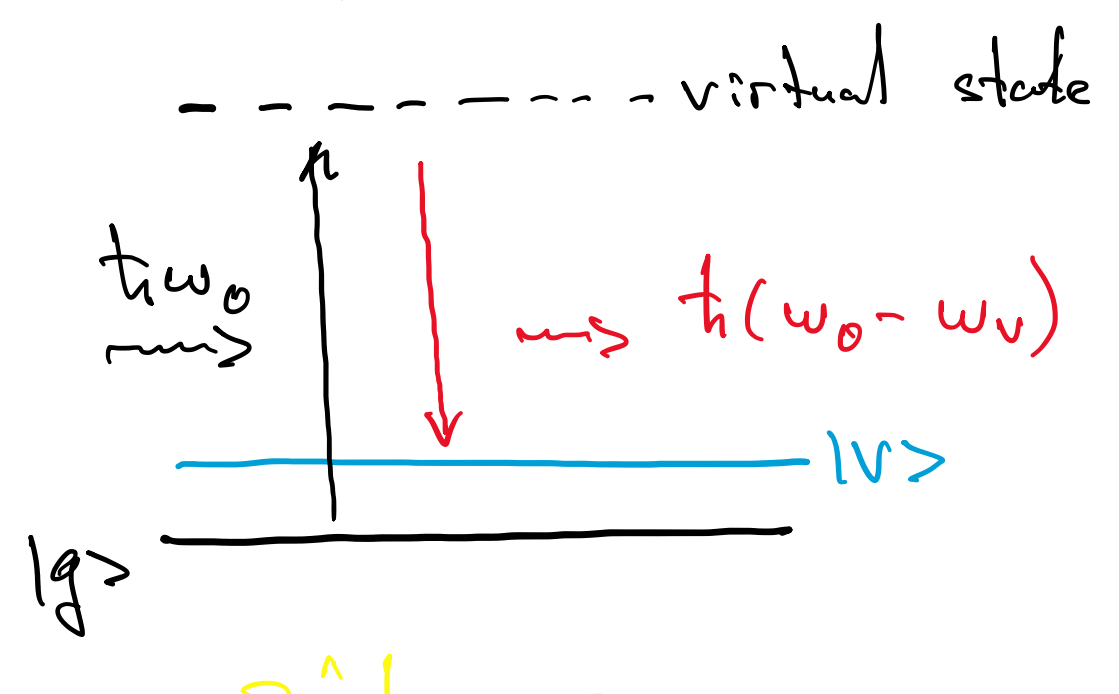
$$\bar{\mu} = \hat{\alpha}|_{q=0}E_0\cos\omega_0 t + \frac{1}{2}q_0\left.\frac{\partial\hat{\alpha}}{\partial q}\right|_{q=0}E_0\big(\cos(\omega_0-\omega_v)t + \cos(\omega_0+\omega_v)t\big)$$

1) $\hat{\alpha}_{q=0}\bar{E}_0\cos\omega_0 t$ - Rayleigh - Tyndall

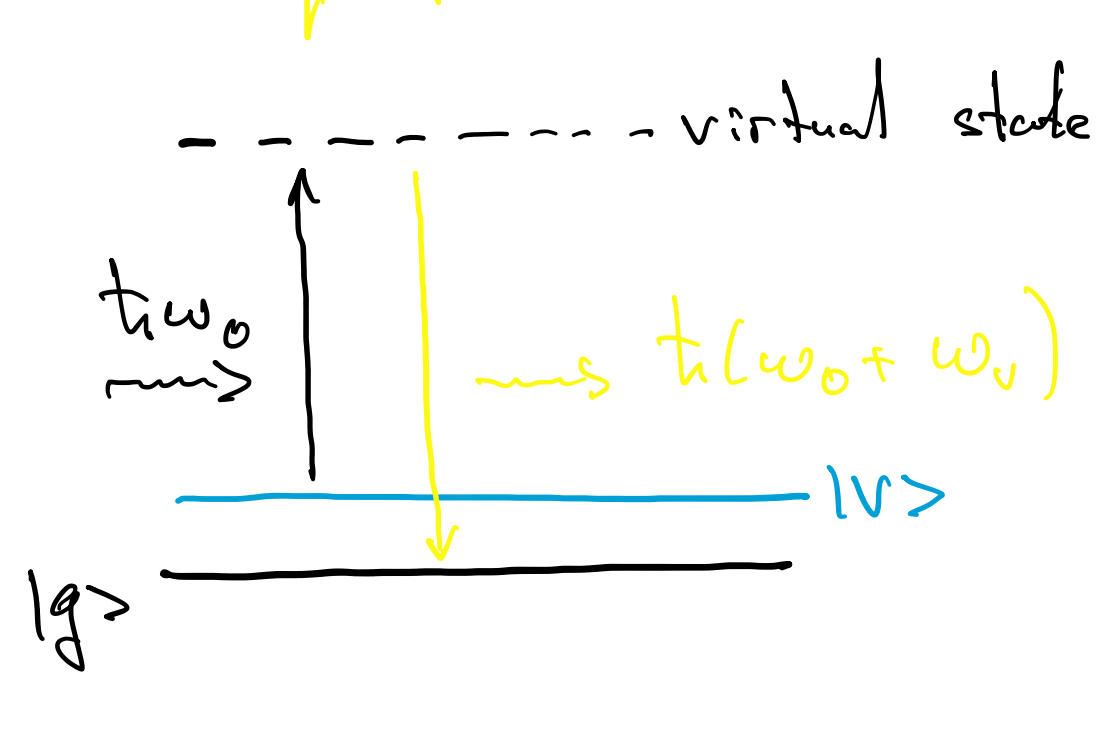


ellastic !

2) $\frac{1}{2}q_0\left.\frac{\partial\hat{\alpha}}{\partial q}\right|_{q=0}\bar{E}_0\cos(\omega_0-\omega_v)t$ — Stokes (Raman)

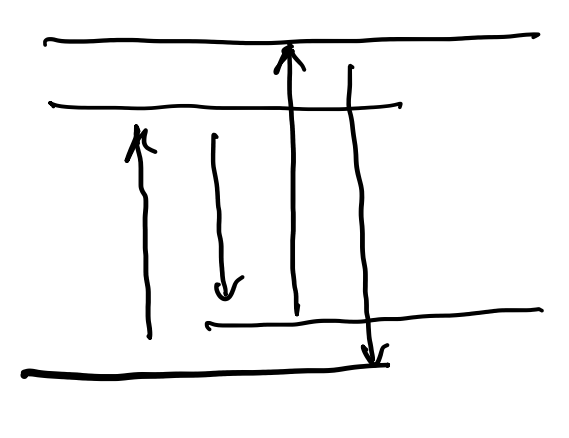


3) $\frac{1}{2}q_0\left.\frac{\partial\hat{\alpha}}{\partial q}\right|_{q=0}\bar{E}_0\cos(\omega_0+\omega_v)t$ — anti-Stokes Combinational scattering



Where energy can come from?

Alternative:



CARS (lost in translation)

Mandelshtam and Landsberg gave most full explanation of the effect on both Stokes and anti-Stokes sides, calling it combinational scattering.

But here we have problem as $\bar{q}$ is small, $\left.\frac{\partial\hat{\alpha}}{\partial q}\right|_{q=0}$ is small.

$$P_{fi} = \lim_{T\to\infty}\int_0^T\left[e^{-i(E_f-E_i-\hbar\omega)\frac{t}{\hbar}} + e^{-i(E_f-E_i+\hbar\omega)\frac{t}{\hbar}}\right]dt\cdot\frac{|V_{fi}|^2}{4\hbar^2}$$

$$V_{fi} = \int\Psi_f^*\hat{V}\Psi_i\,dx = \int\Psi_f^*(-q\bar{r}\bar{E}_0)\Psi_i\,dx$$

can we do something here?

Can we increas $\bar{E}_0$ locally near dipole?

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The idea of antenna

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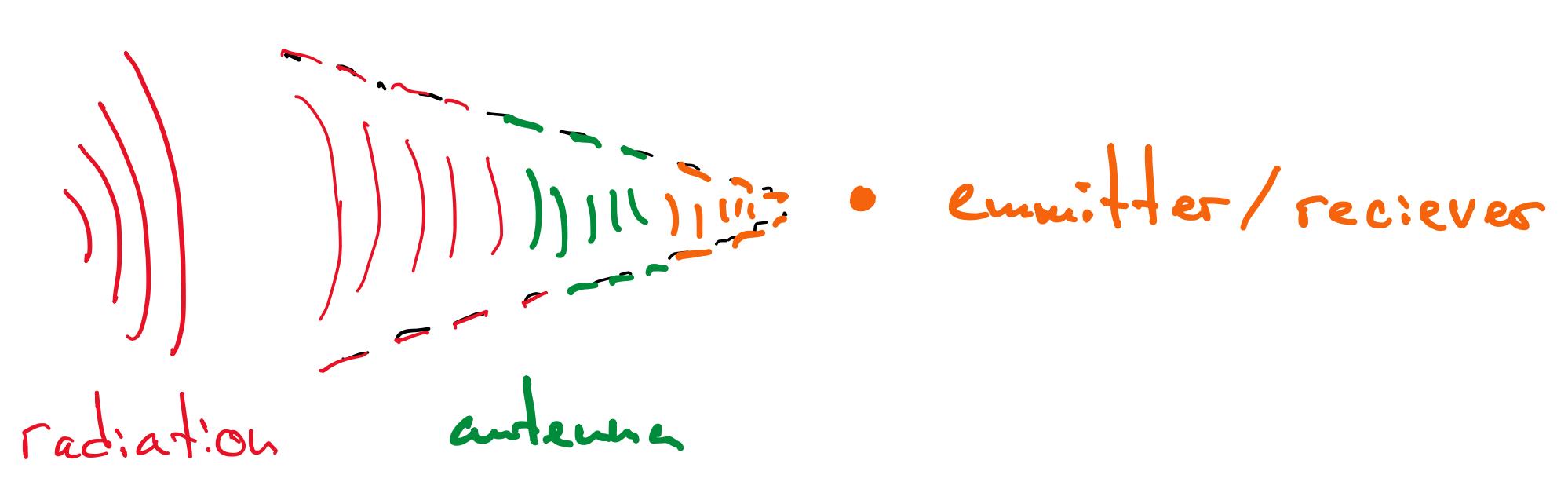
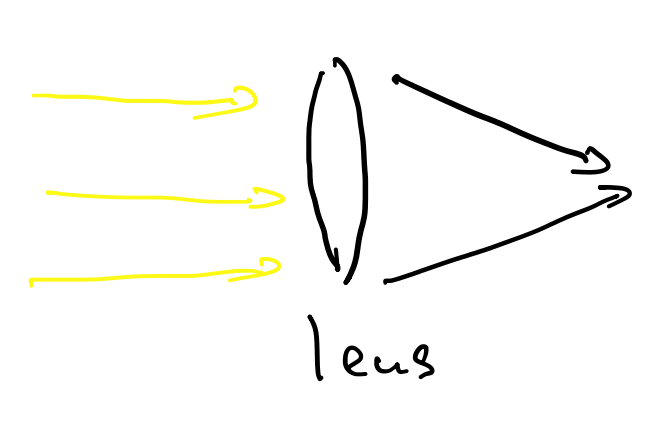
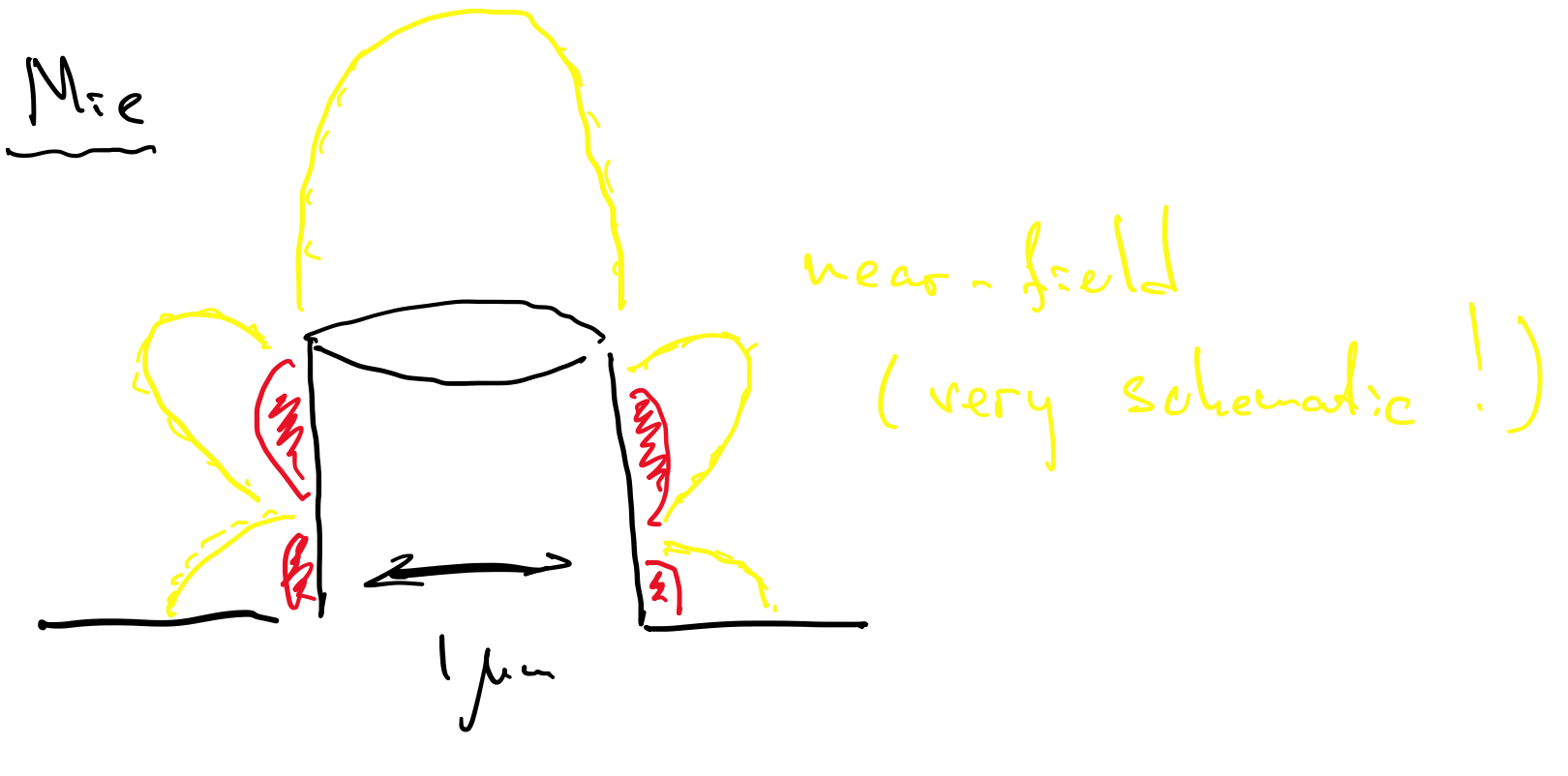


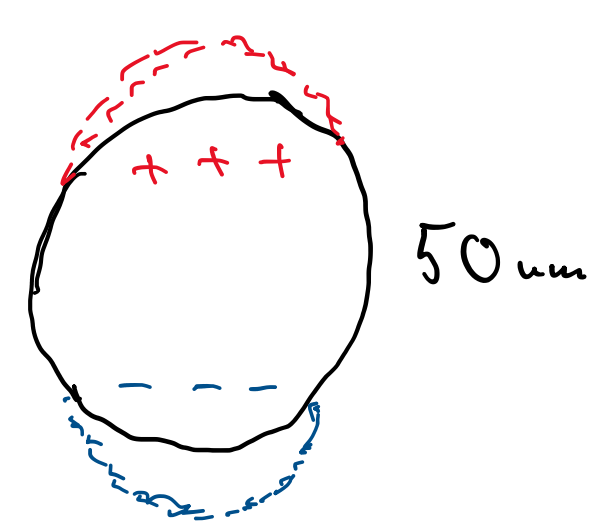
Lens



$\frac{\lambda}{2}$ confinement

Mie



Plasmonics