Theory of Surface Second Harmonic Generation

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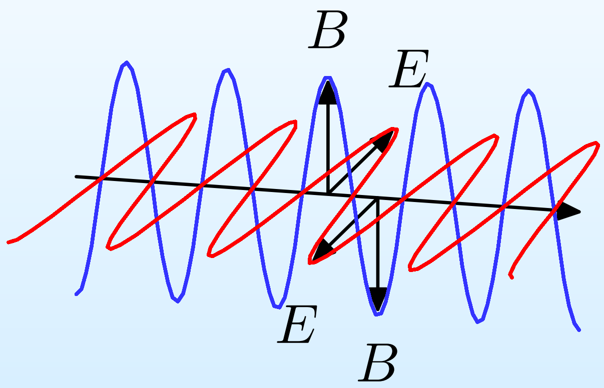
Electromagnetic Waves



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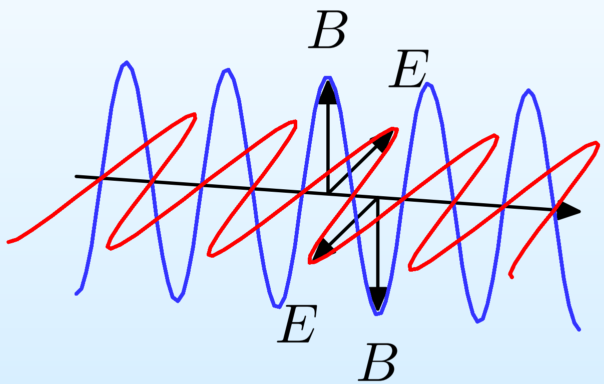
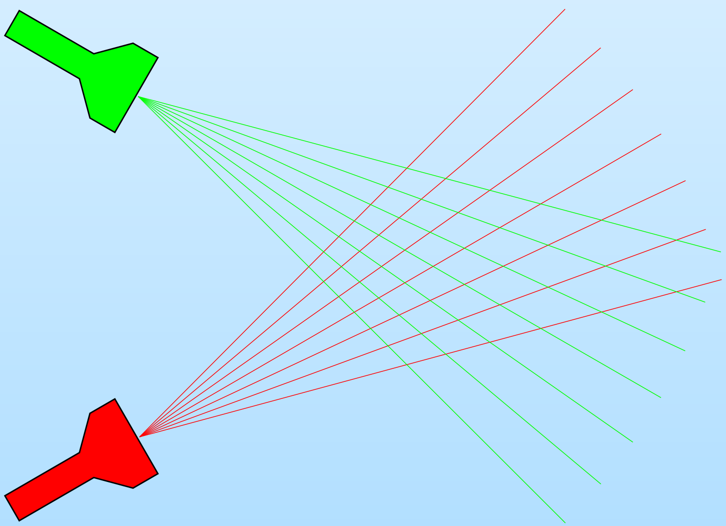


Light is transparent



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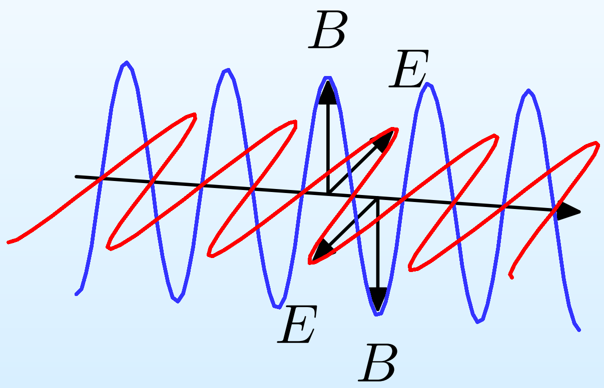

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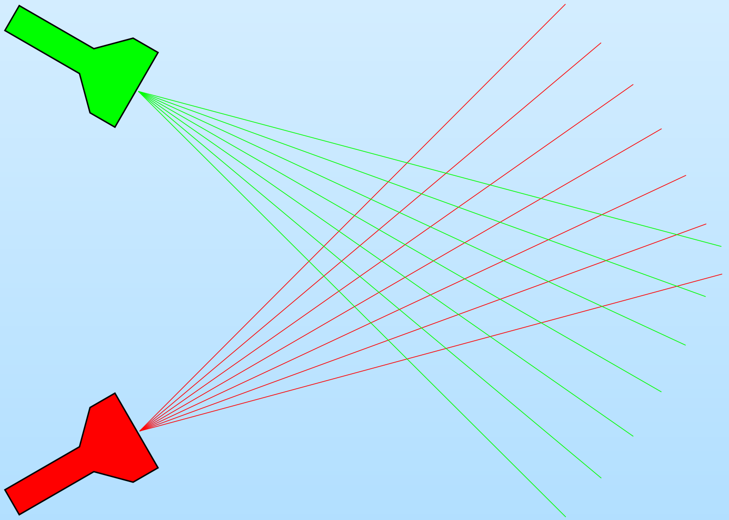
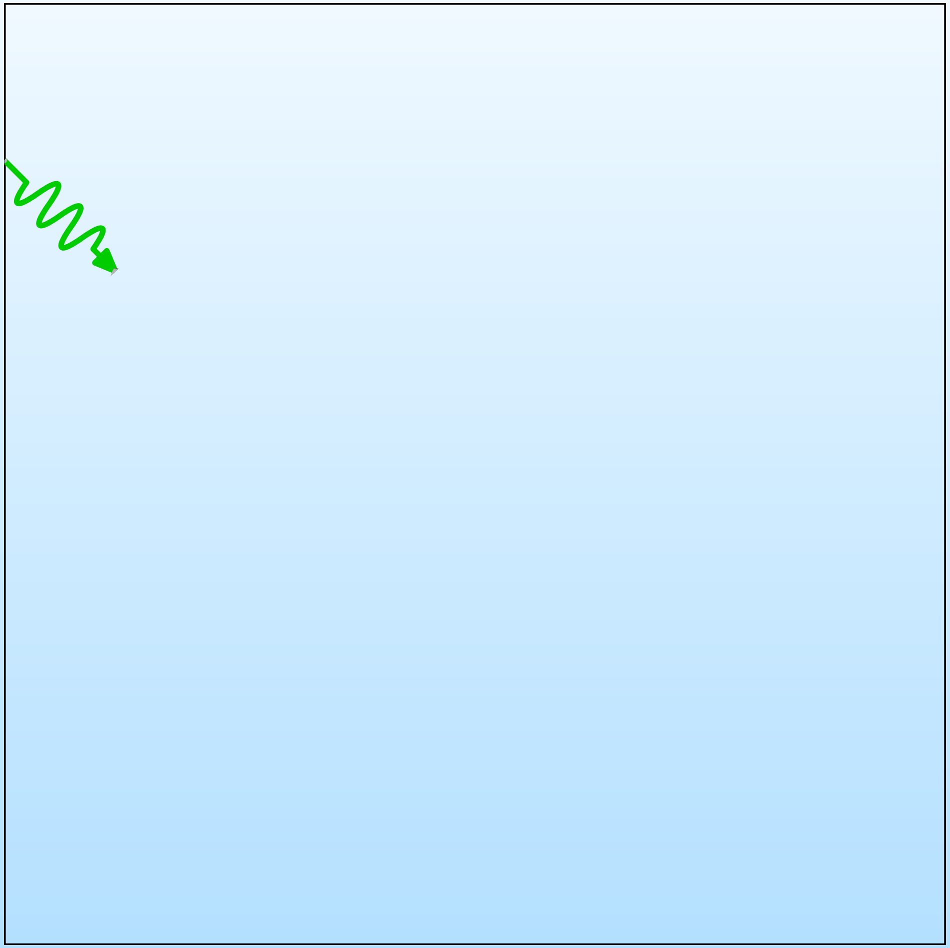


. . . almost.

Dressed Photons



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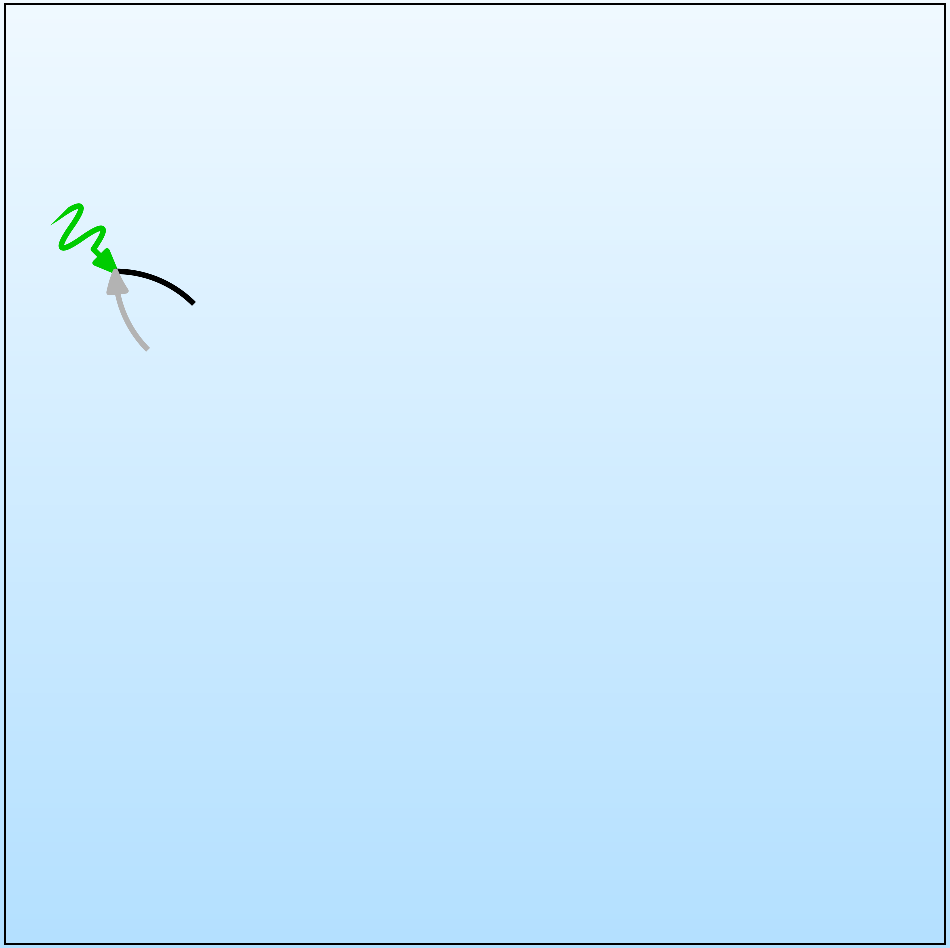

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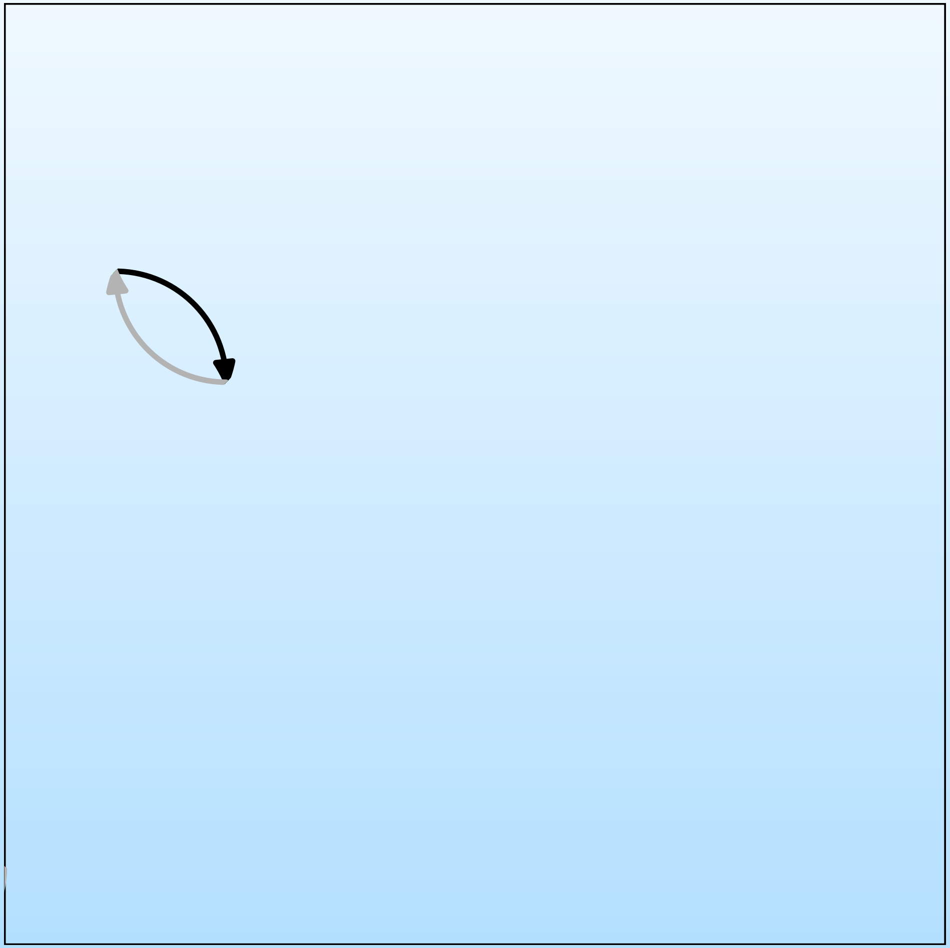

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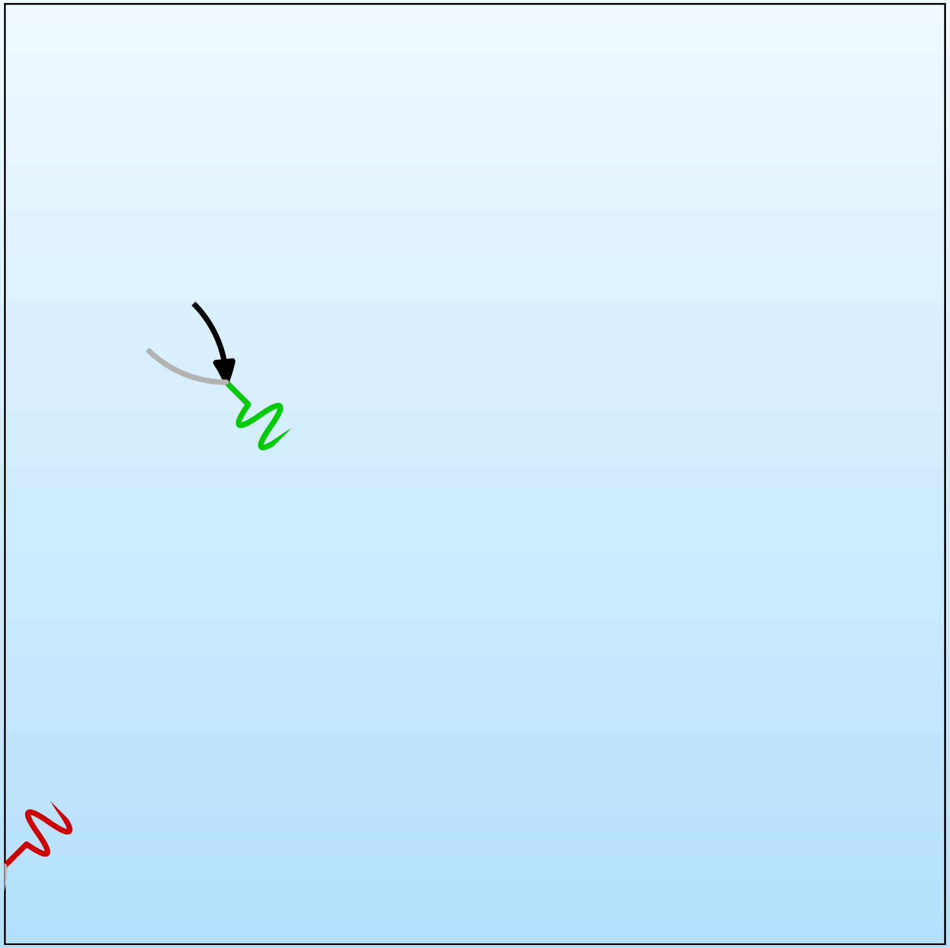

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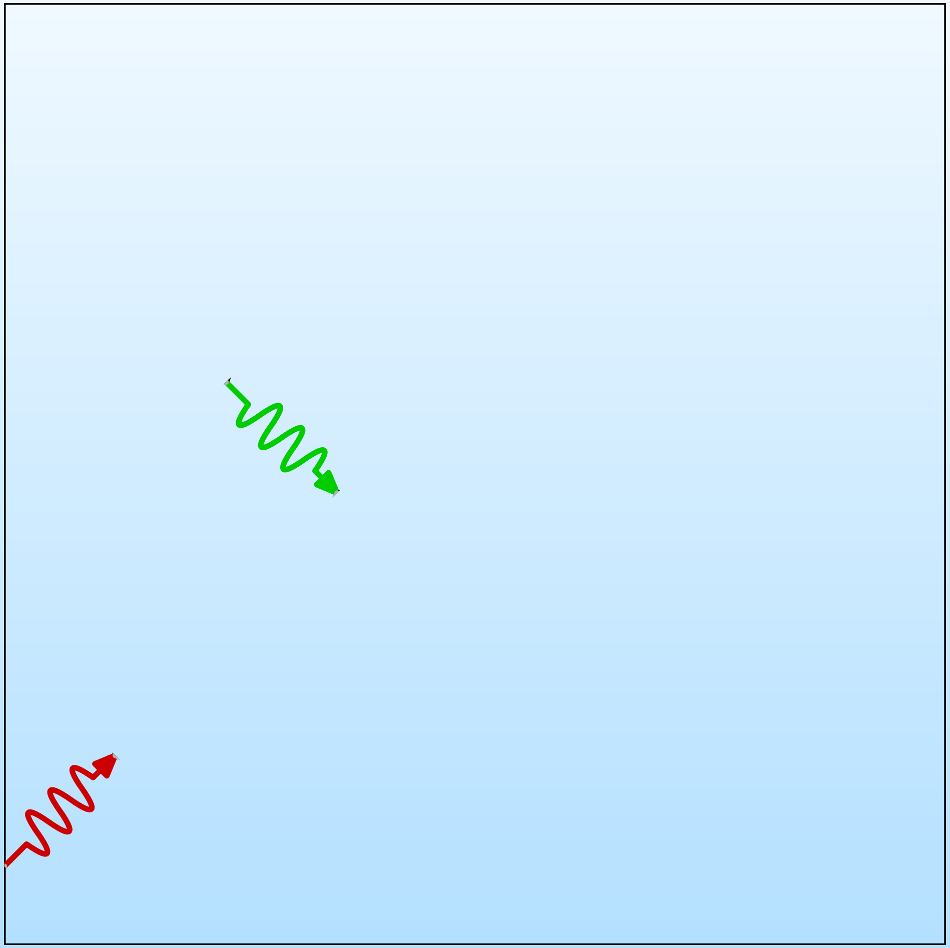

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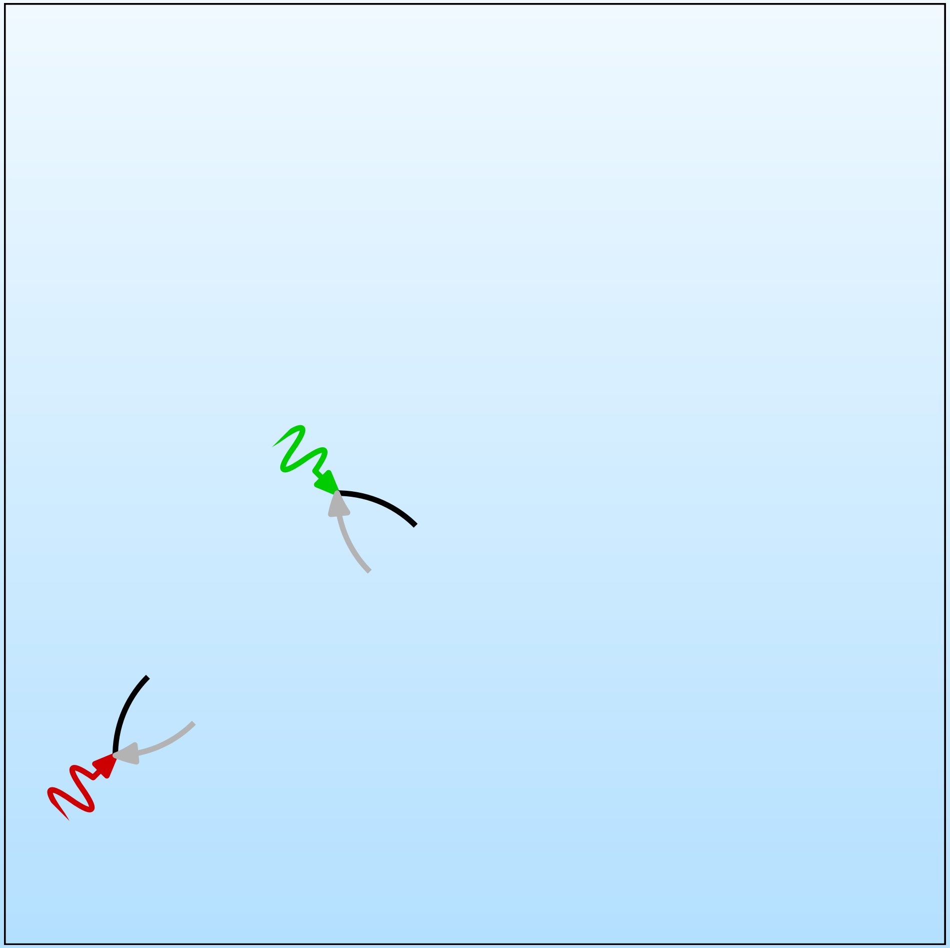

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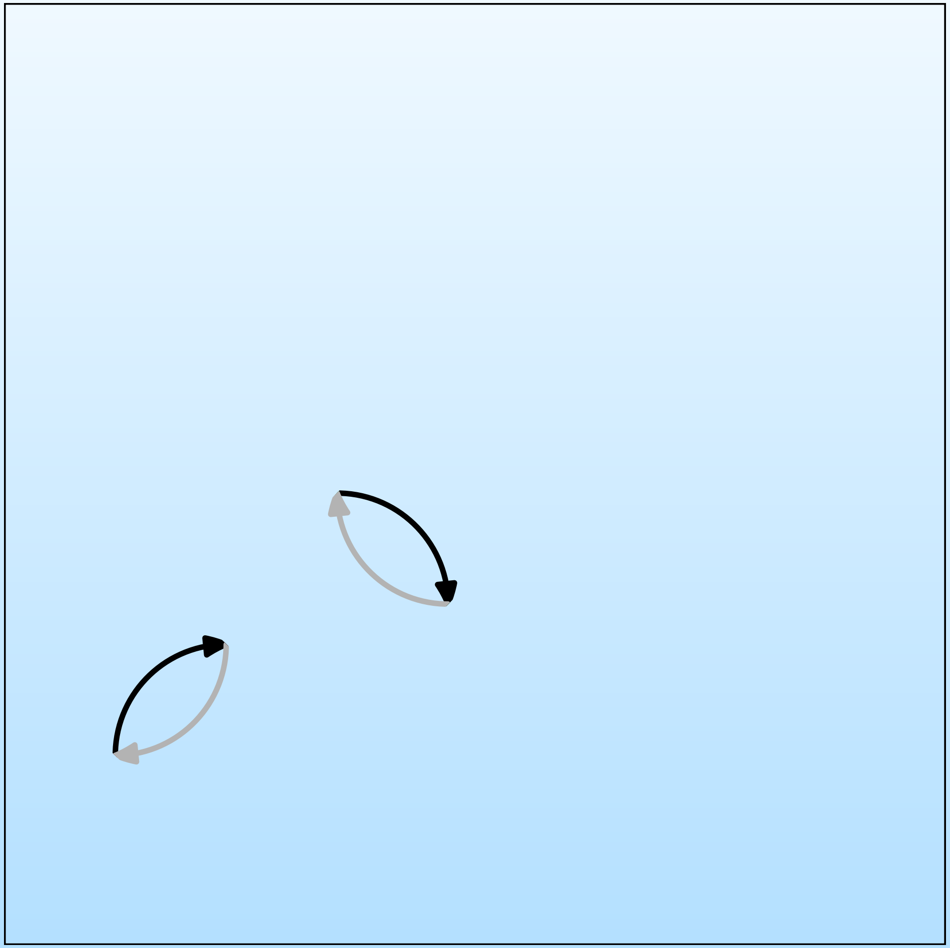

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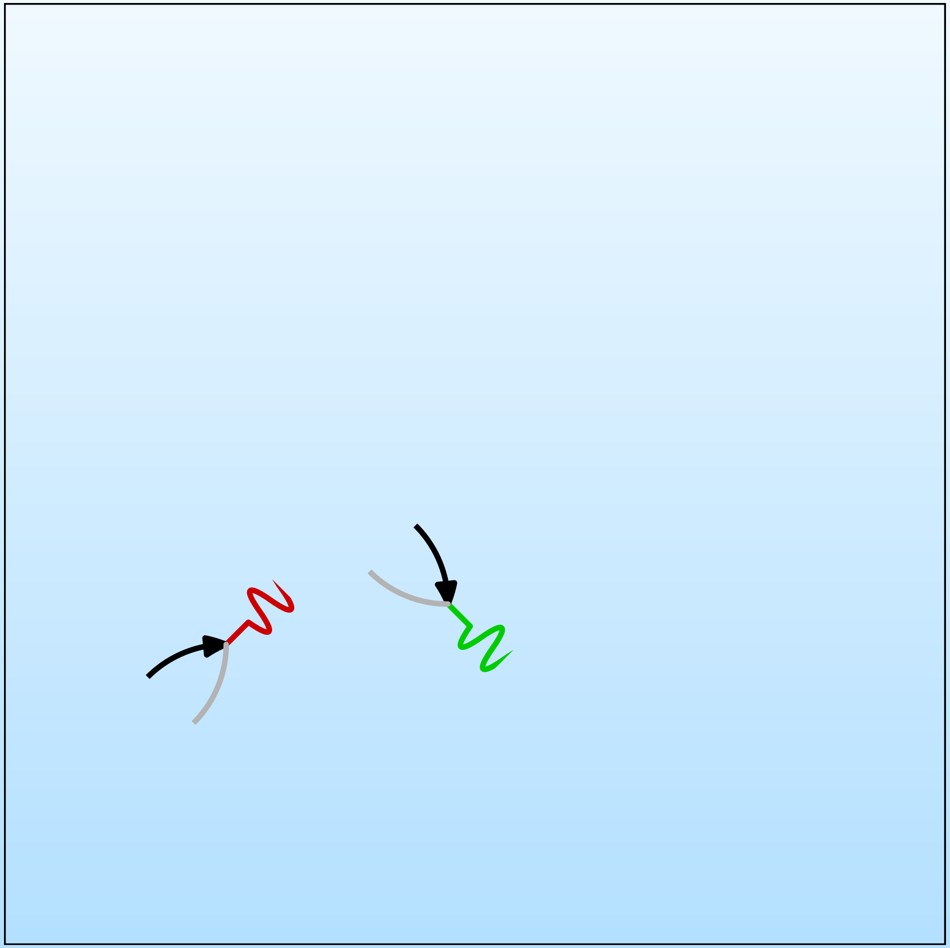

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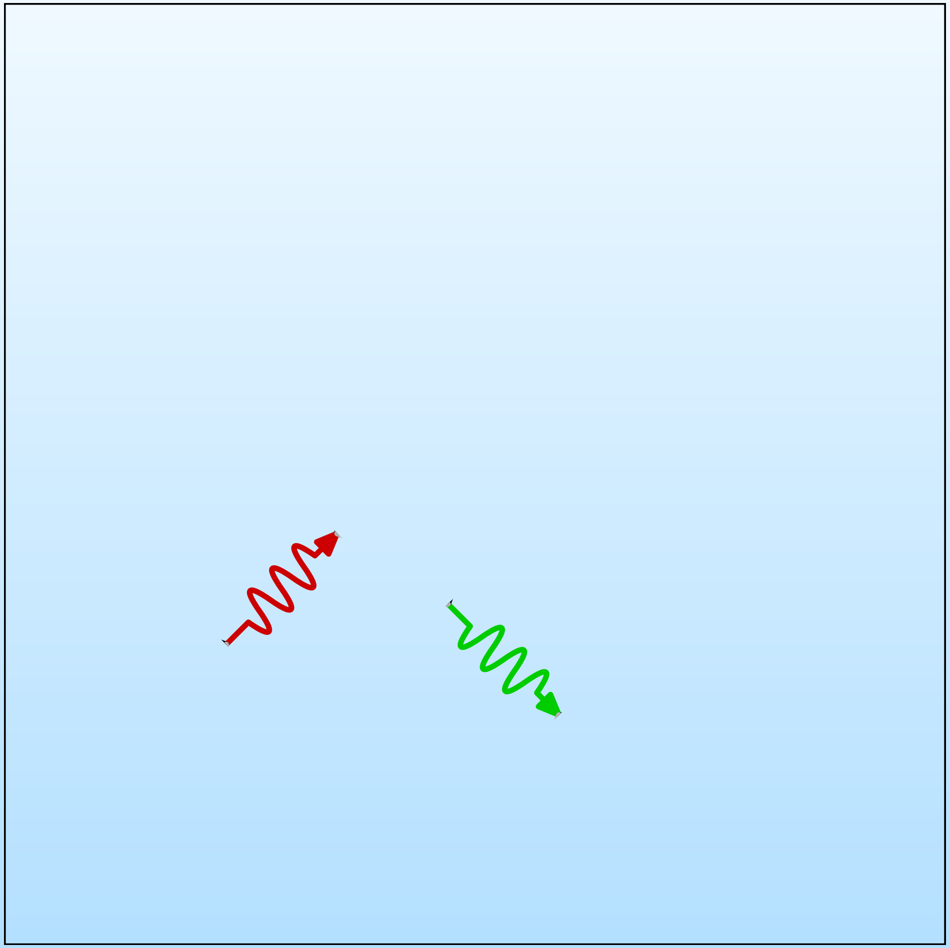

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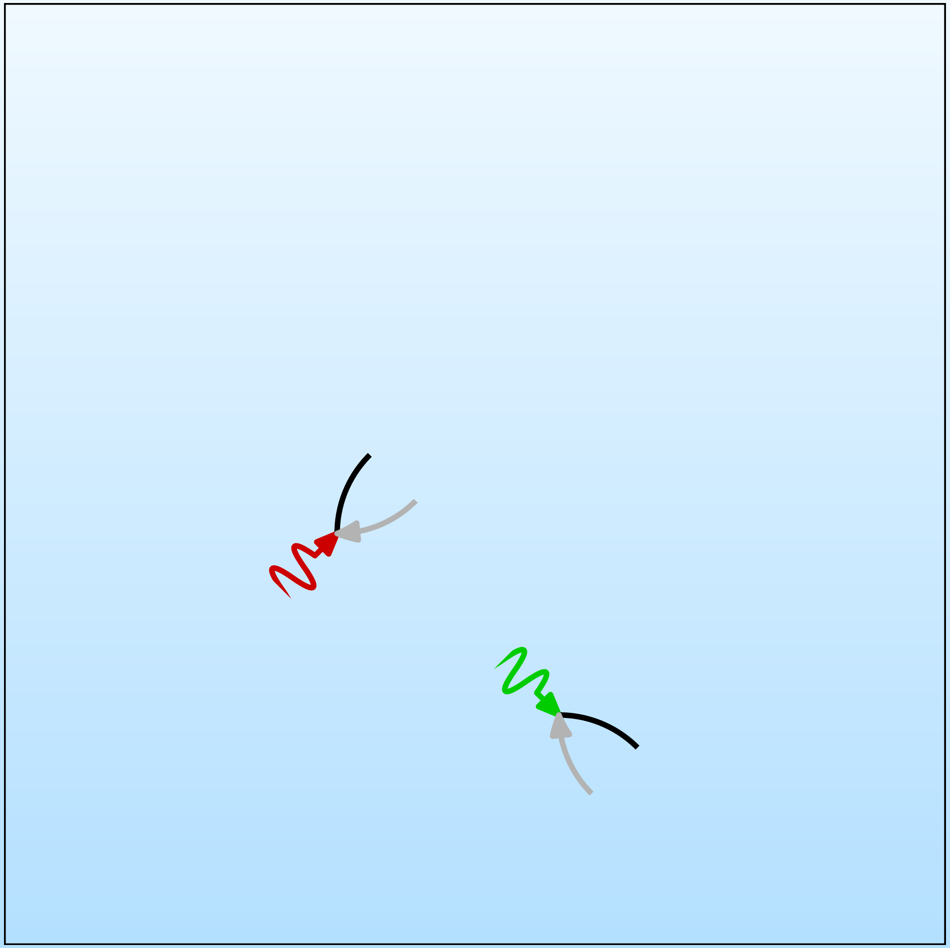

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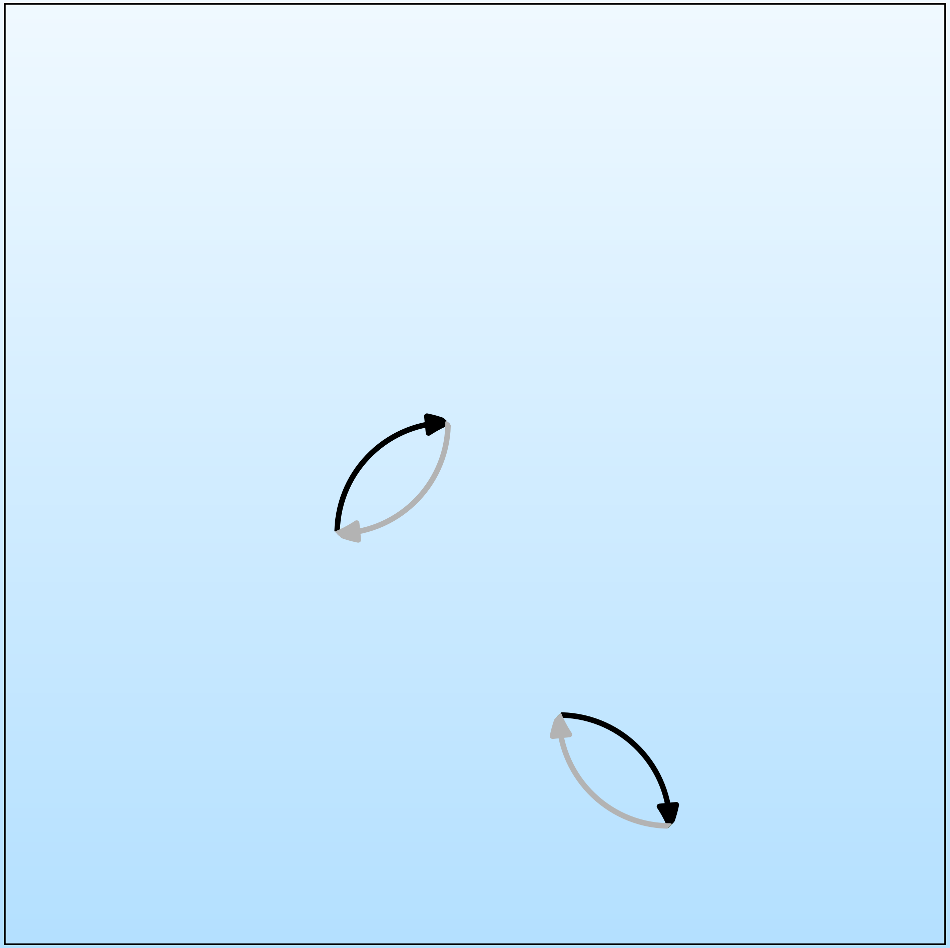

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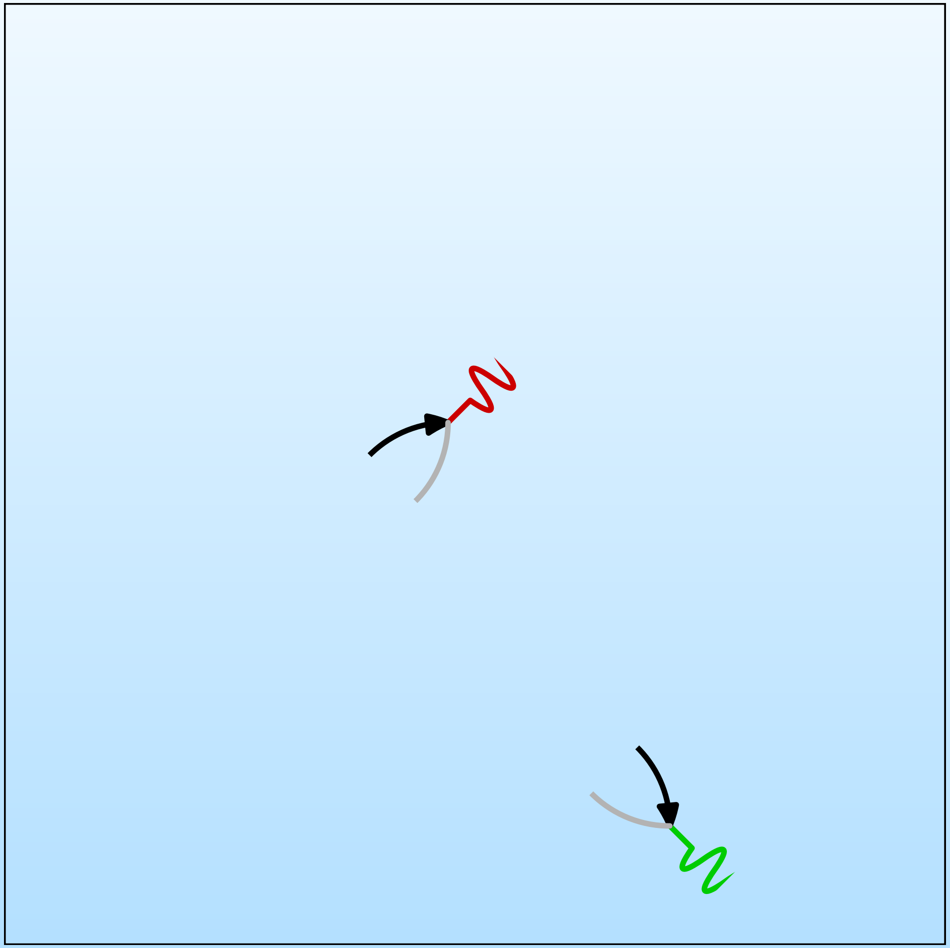

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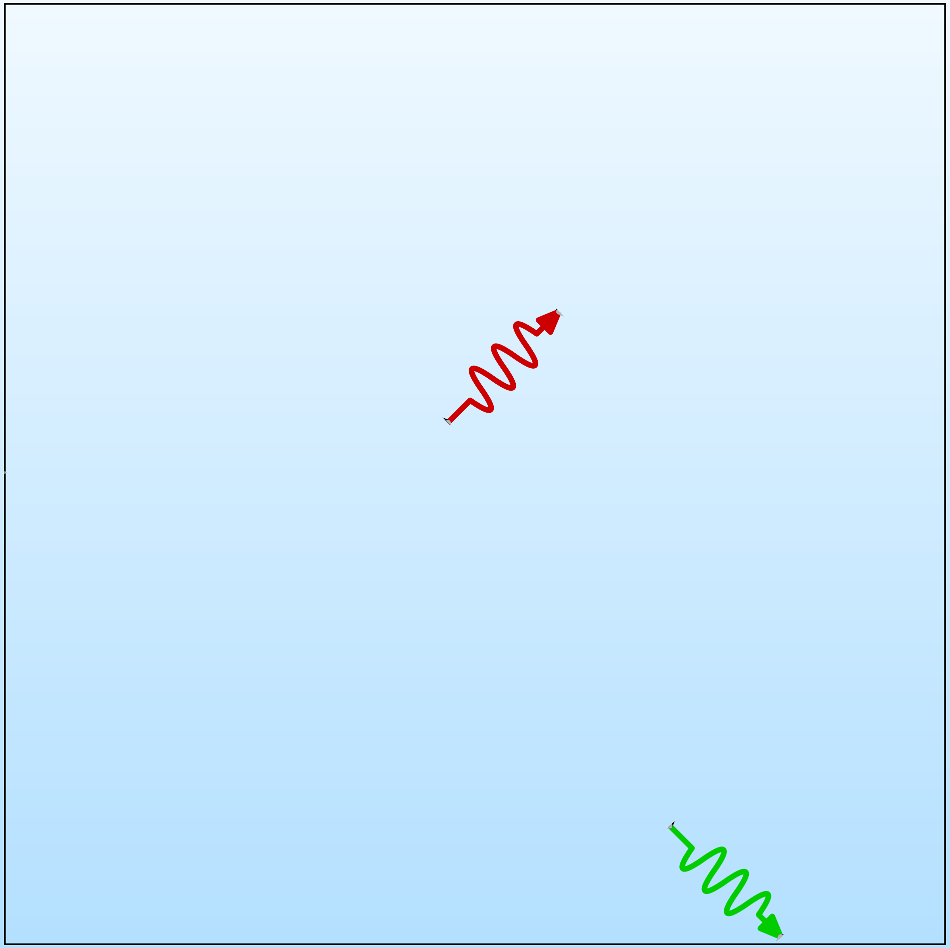

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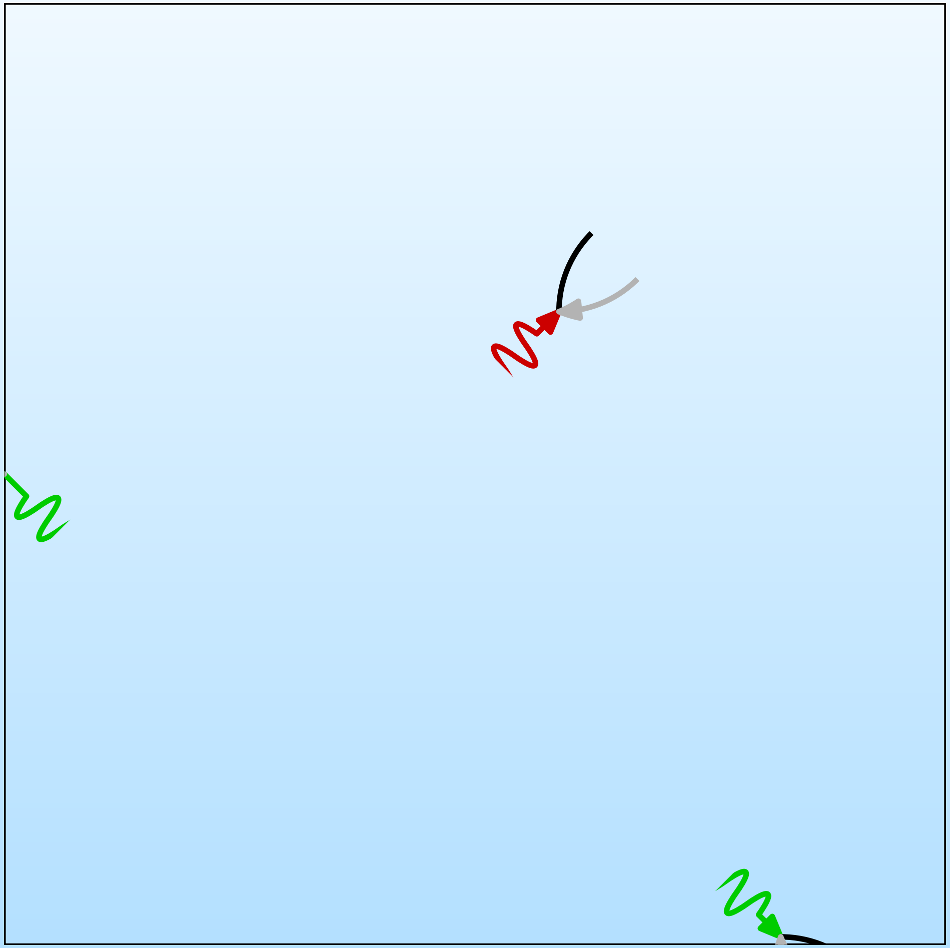

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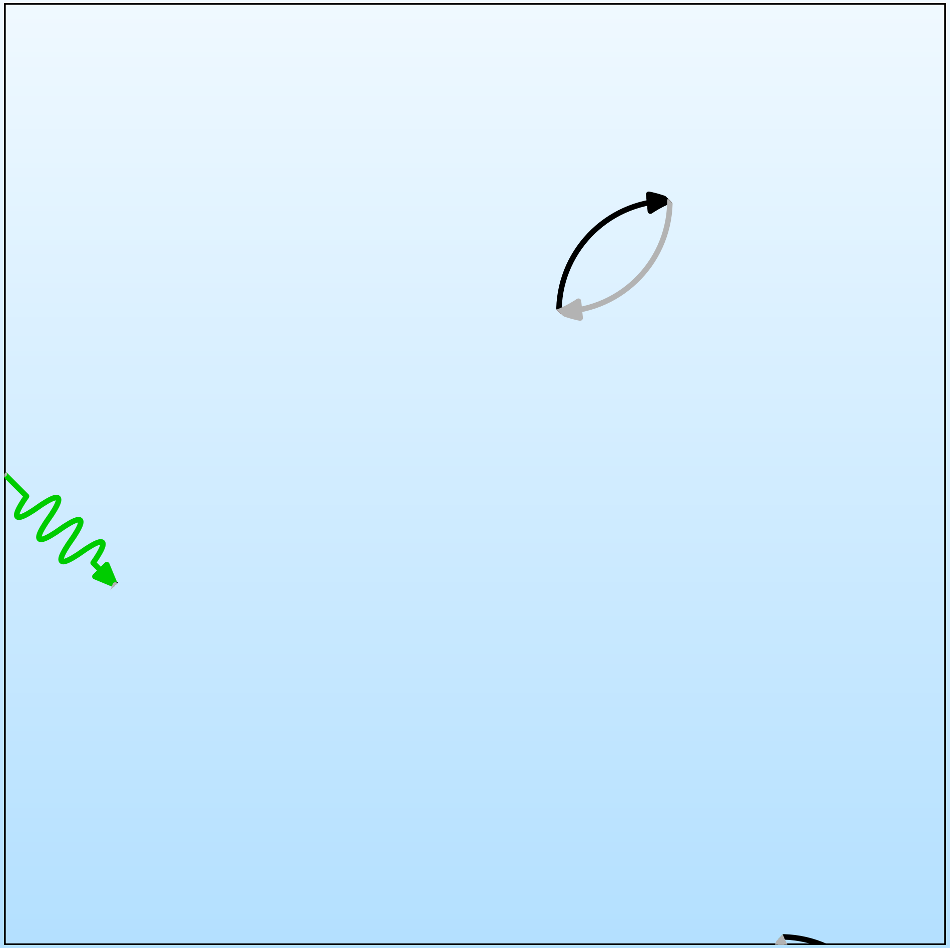

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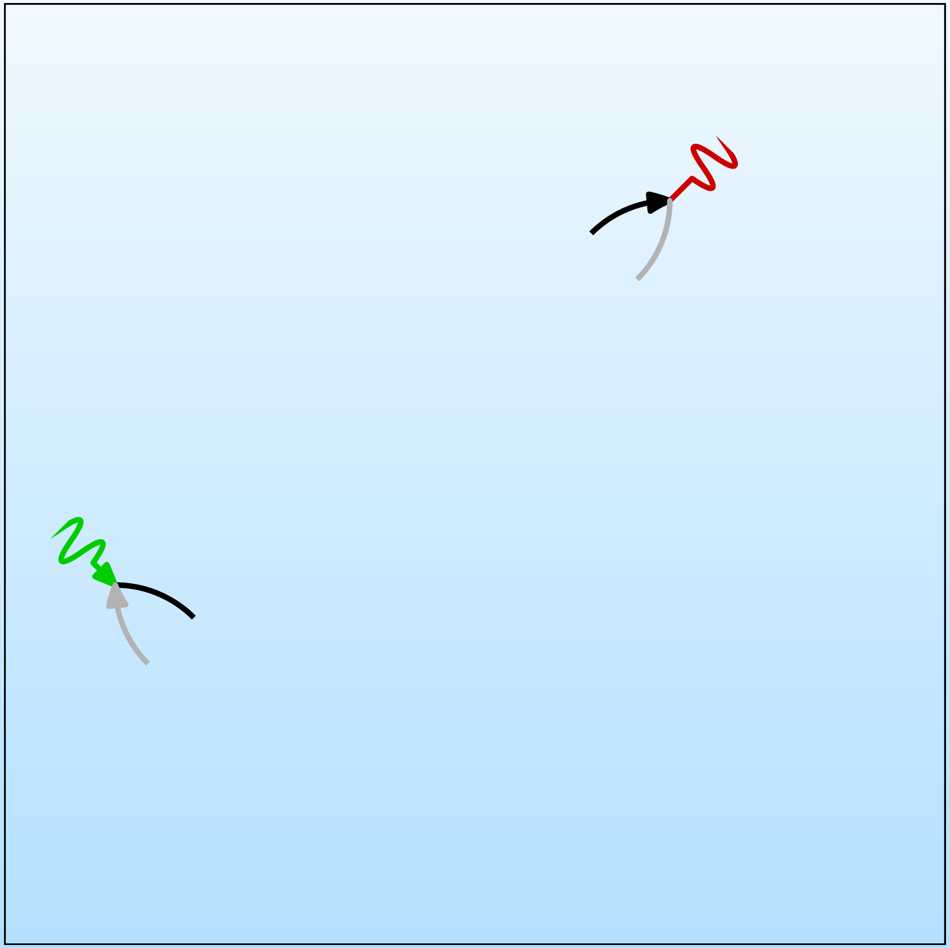

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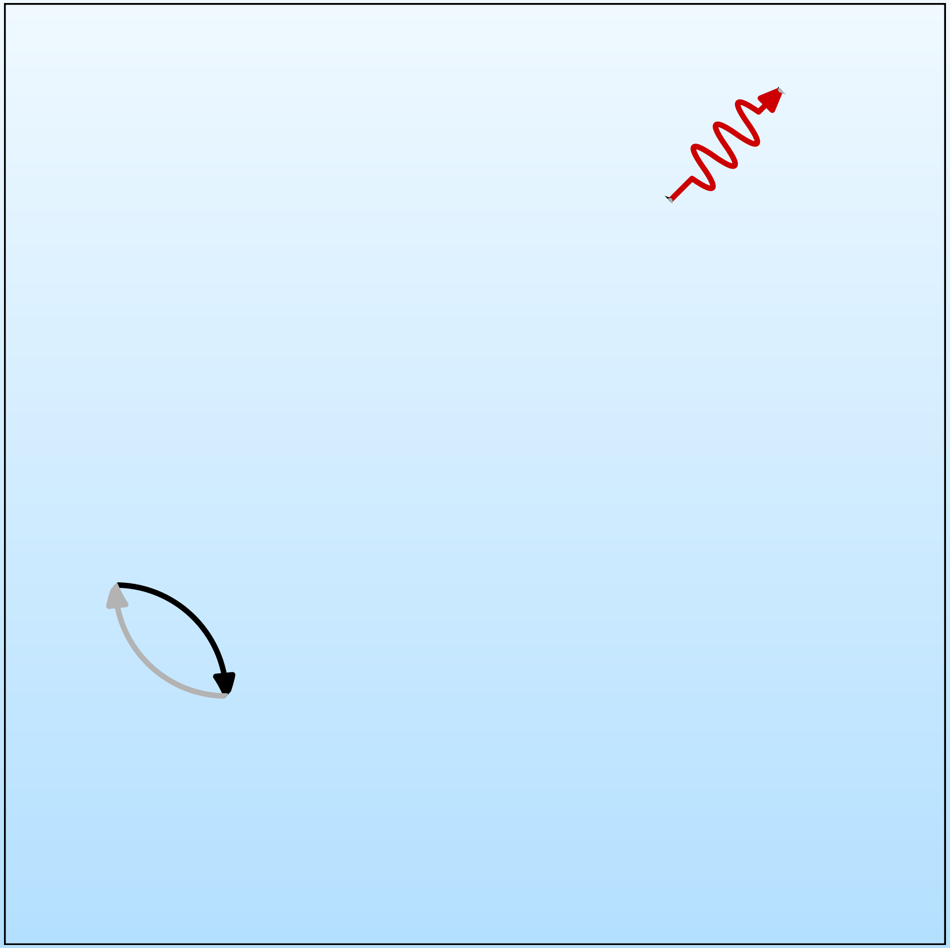
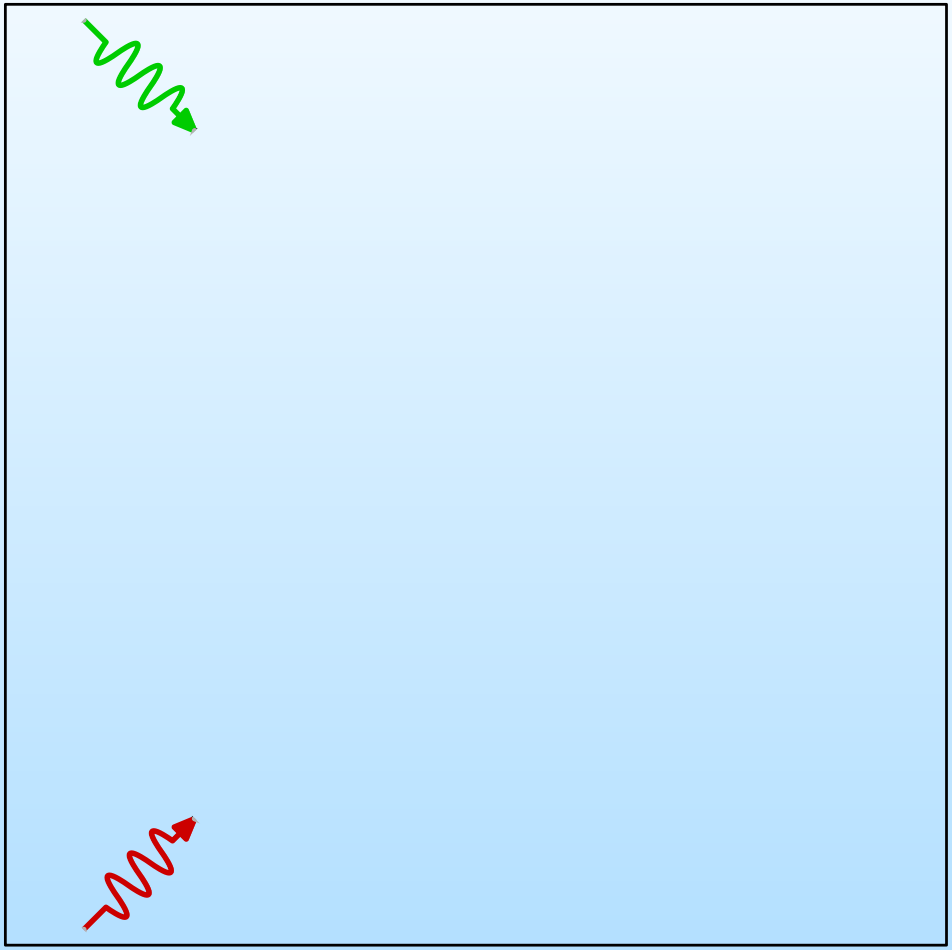


High Intensity



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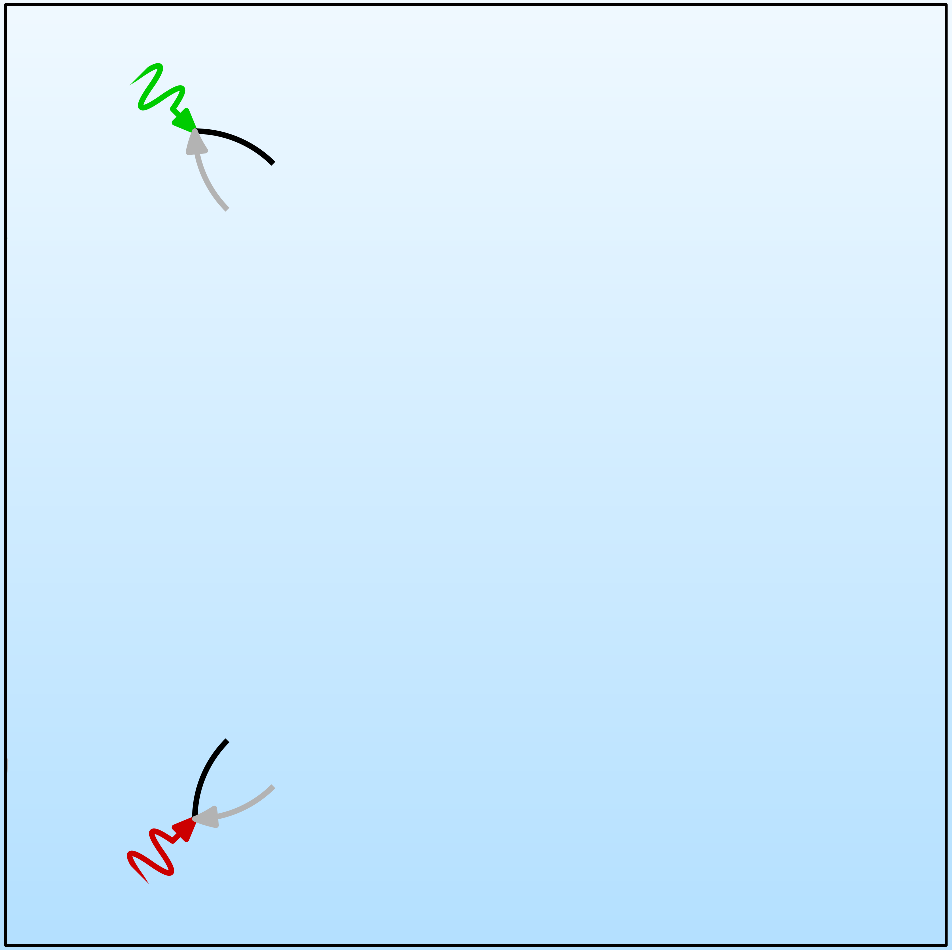

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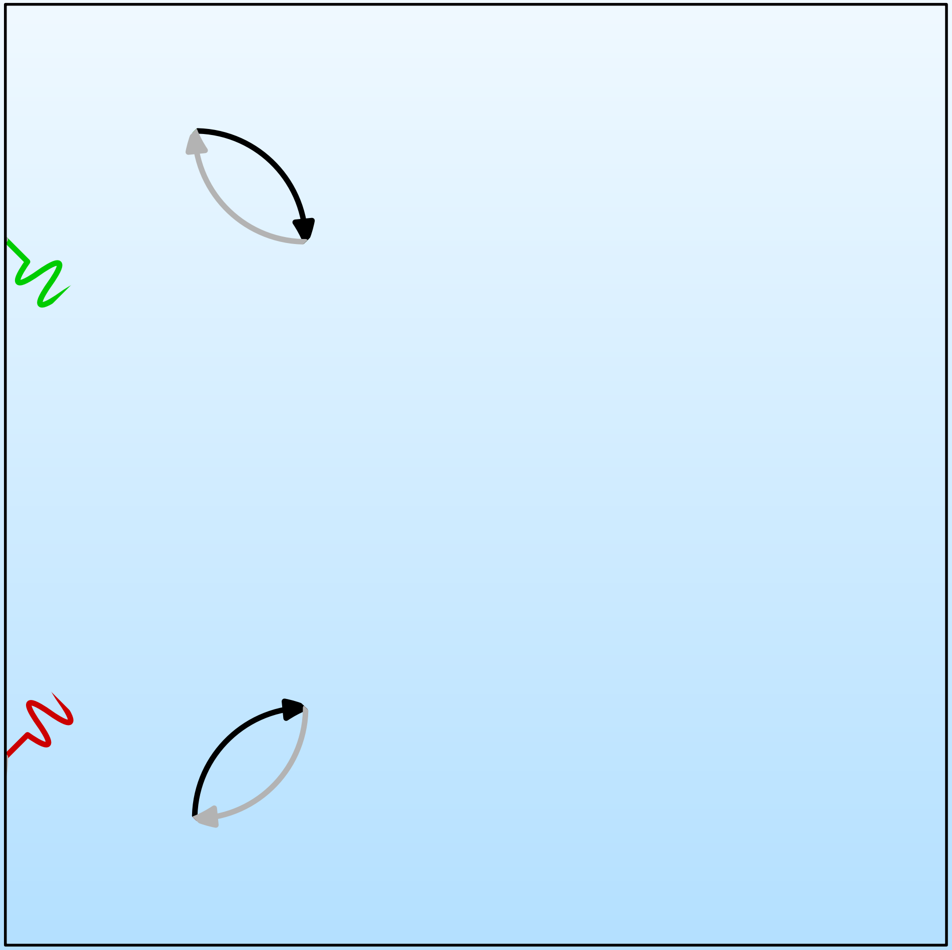

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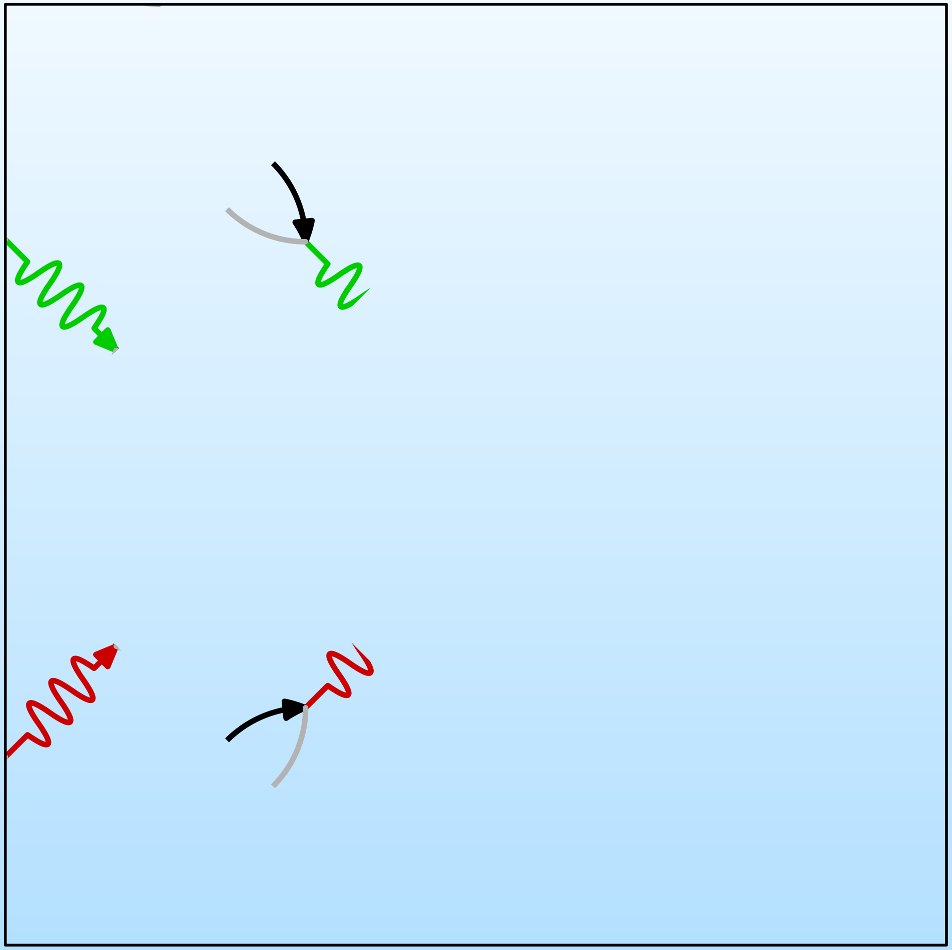

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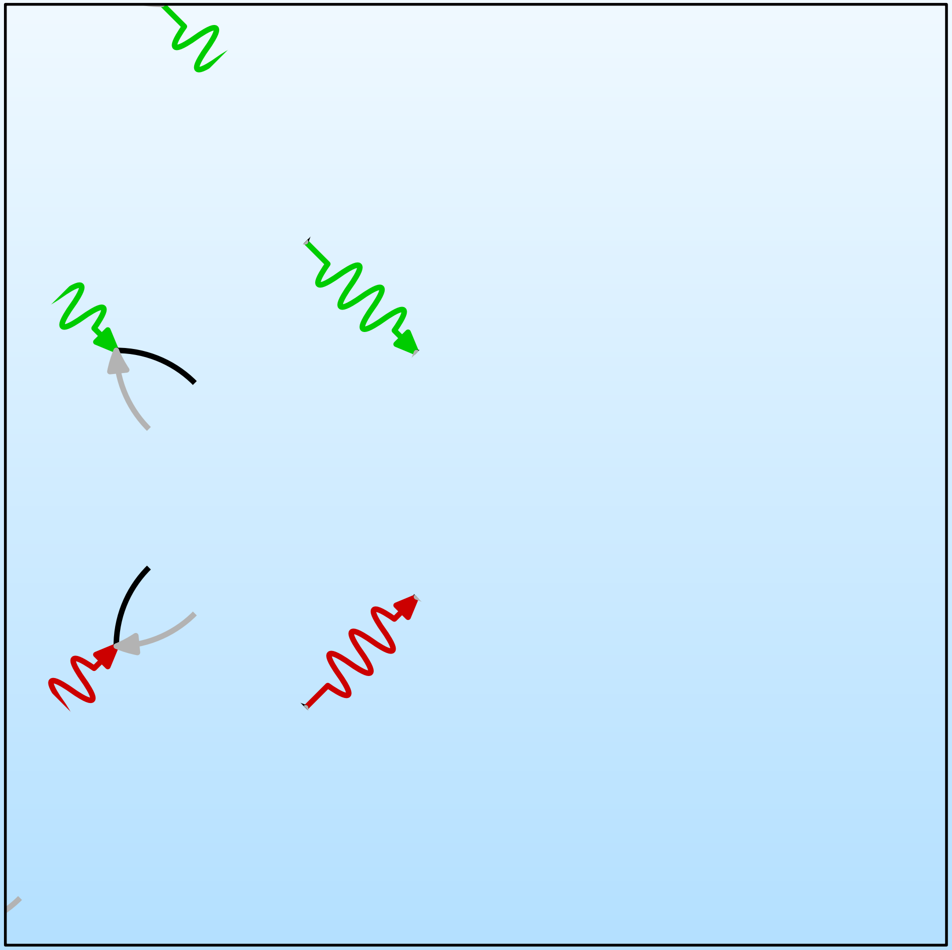

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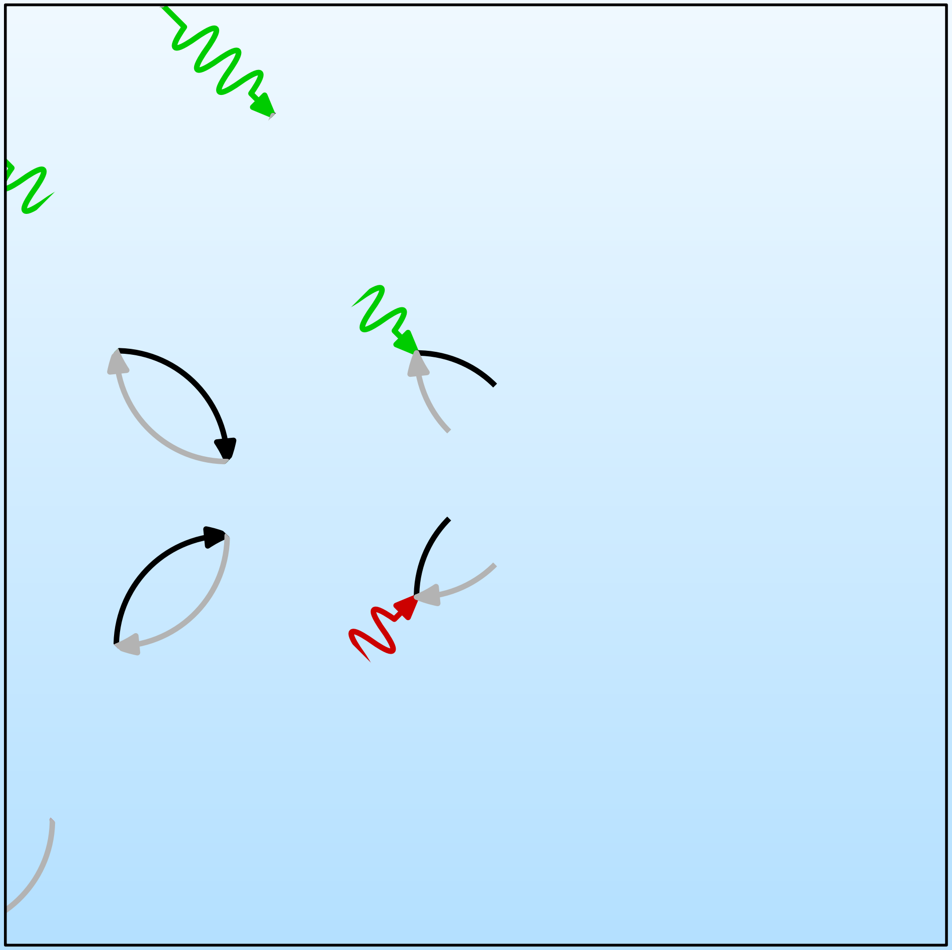

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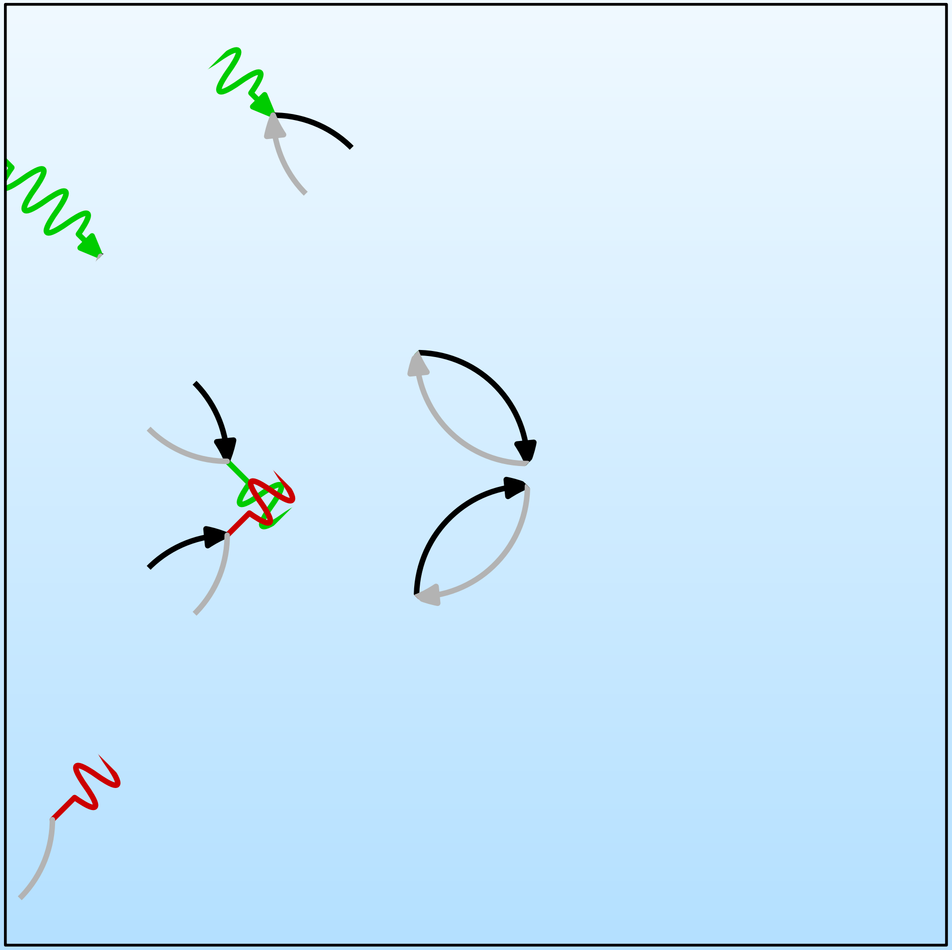

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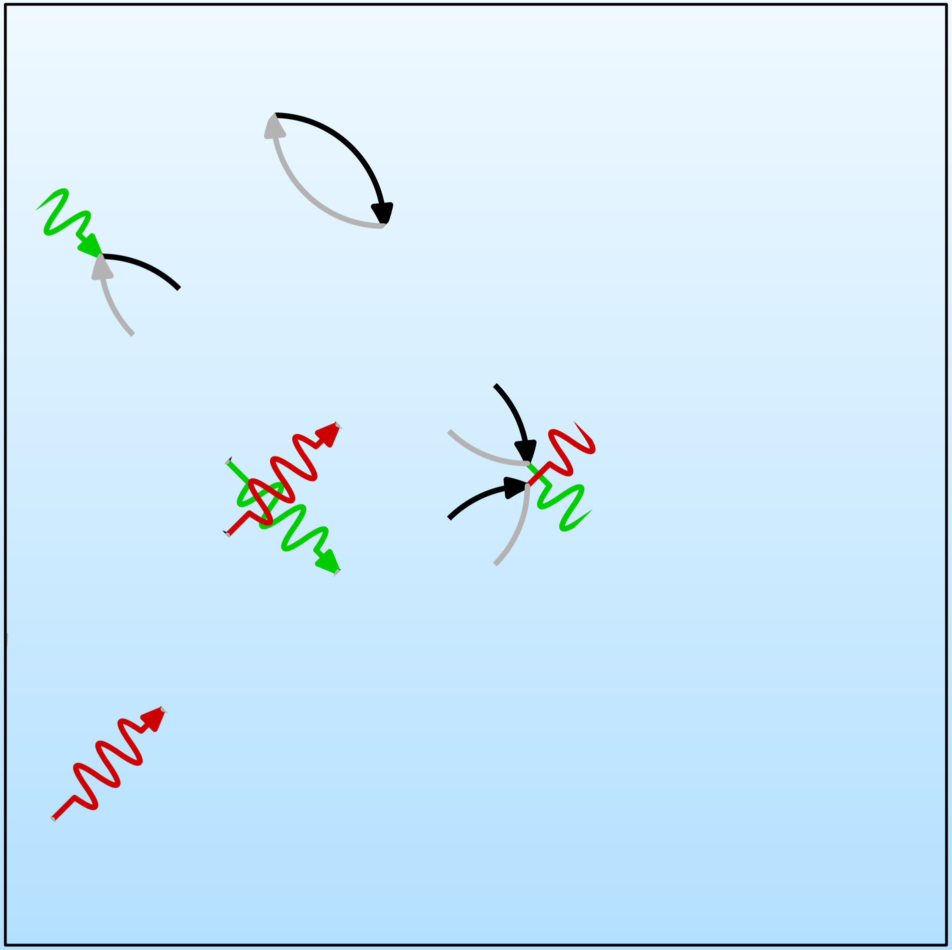

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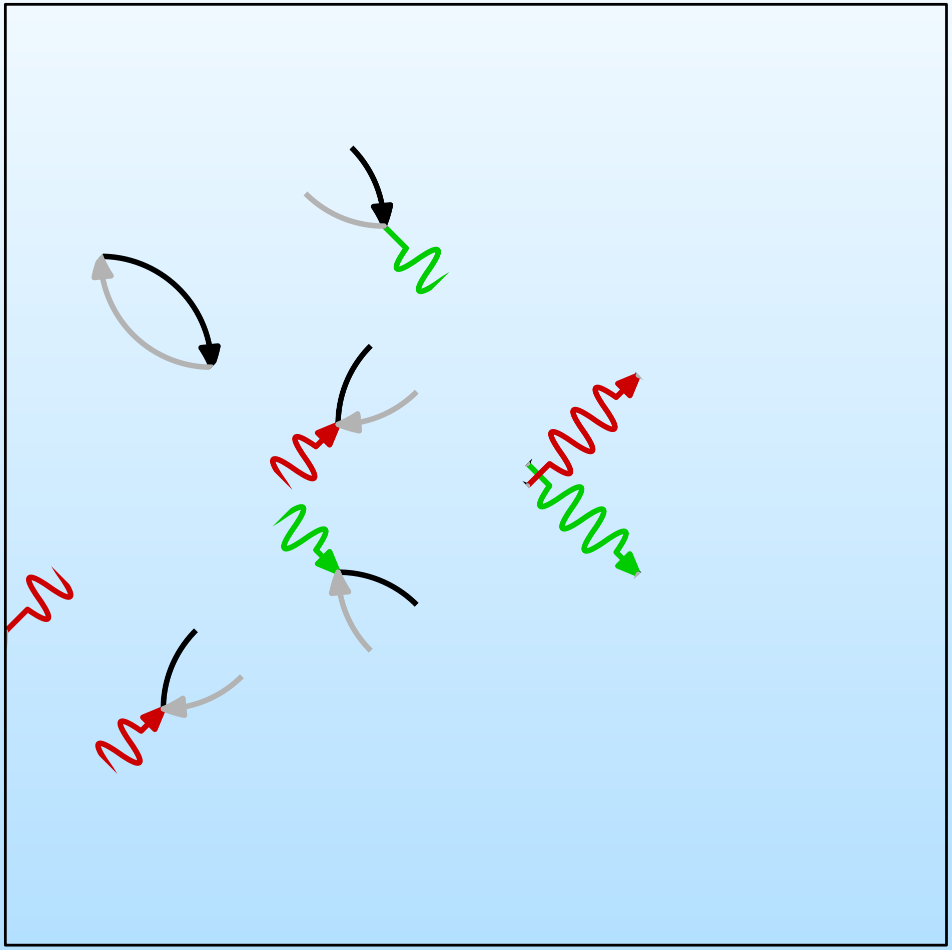

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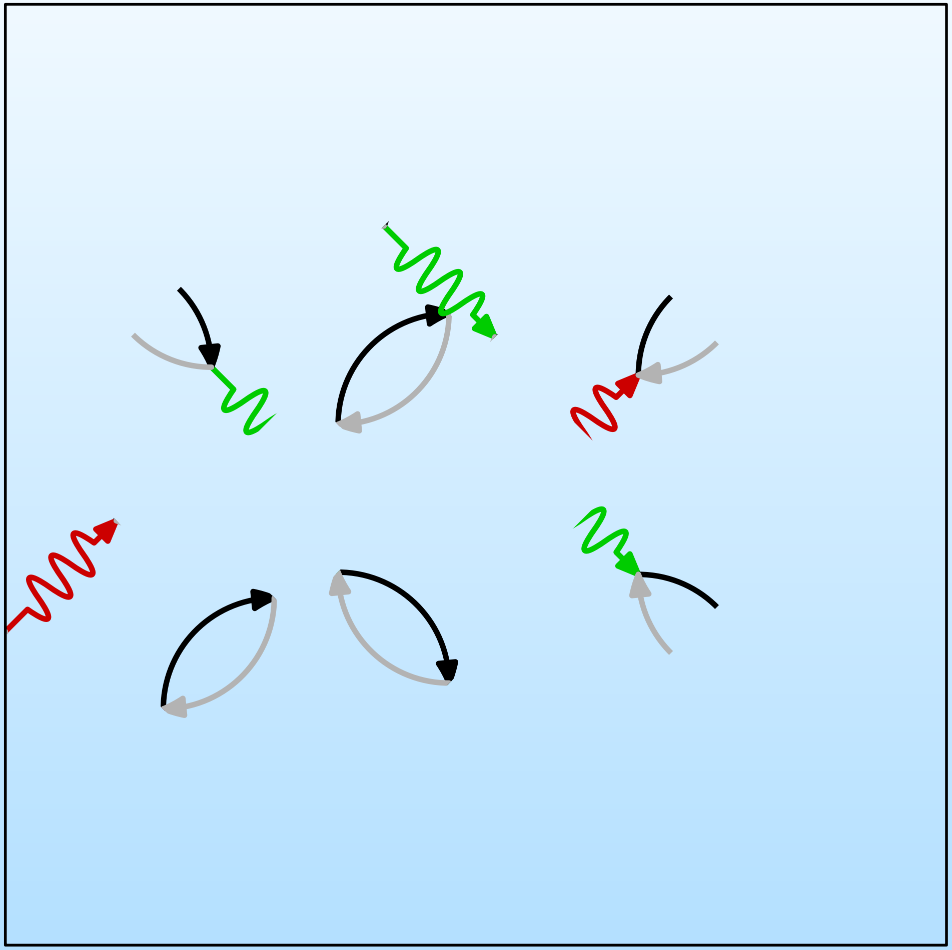

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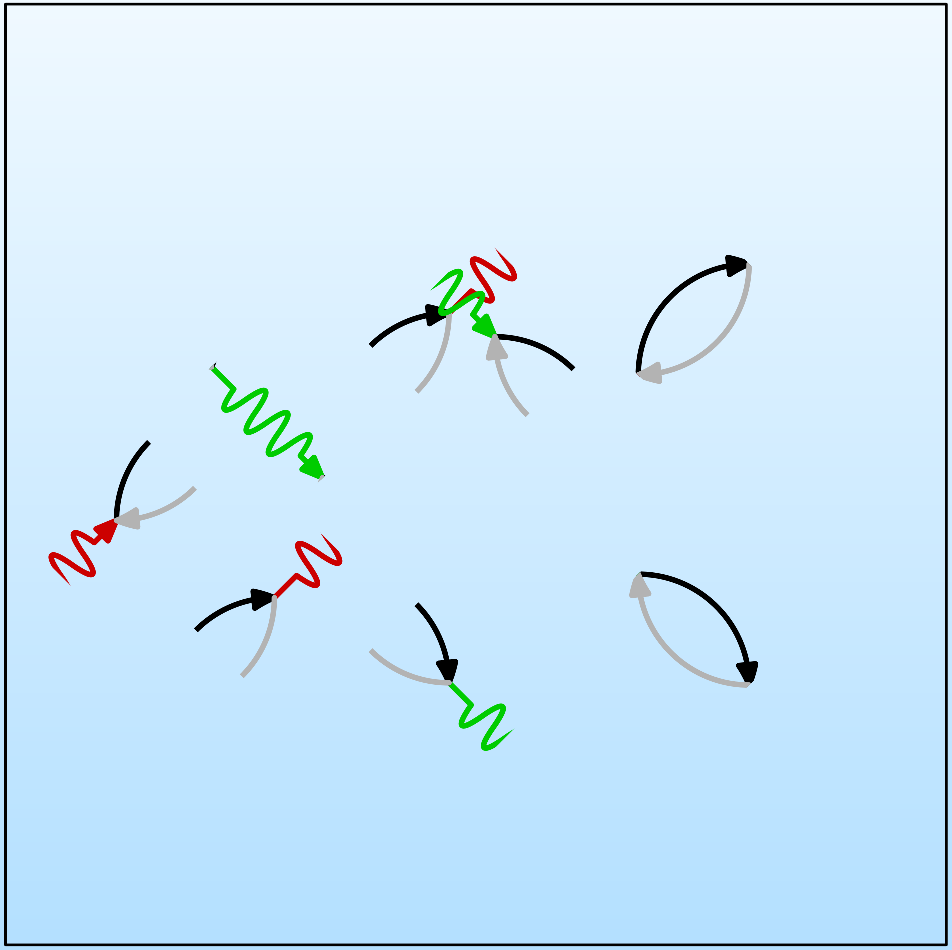

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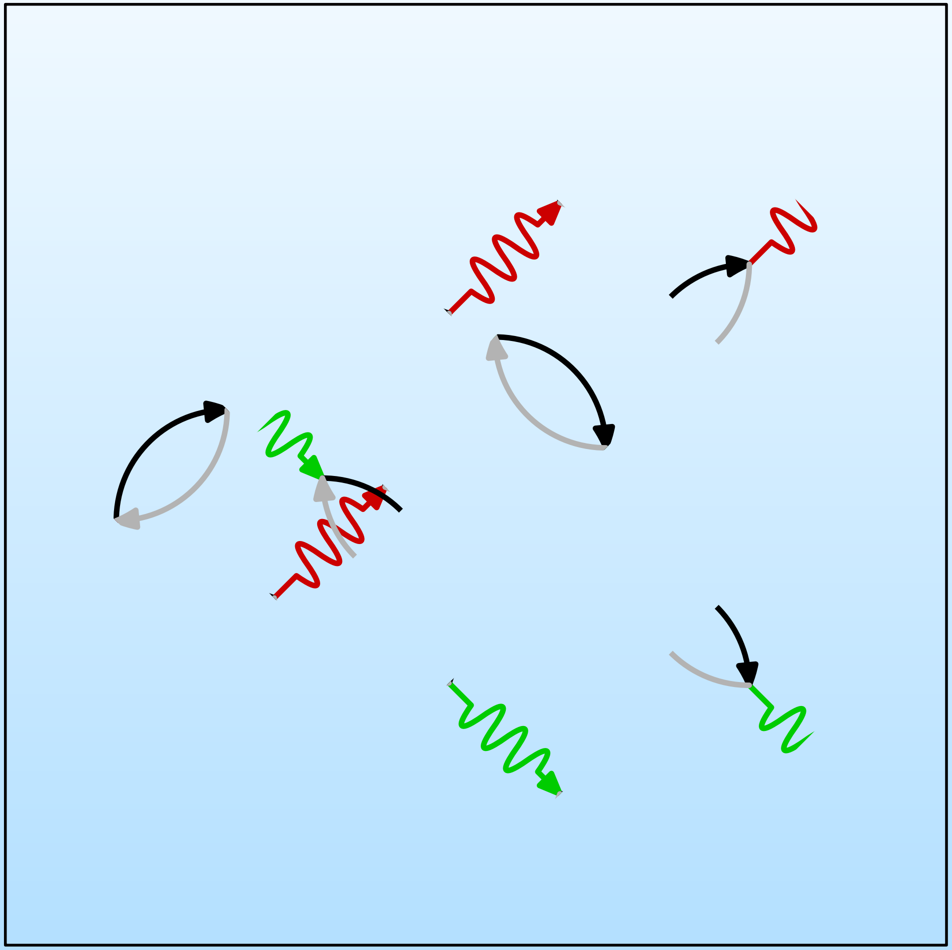
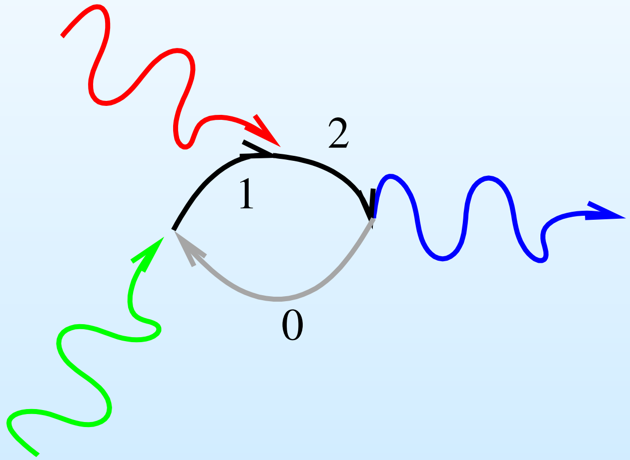
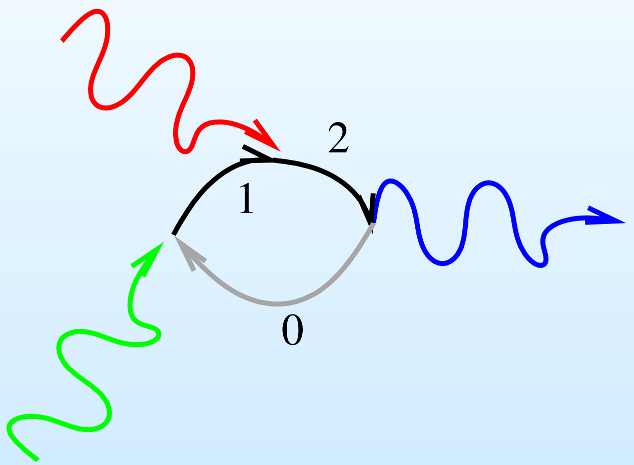


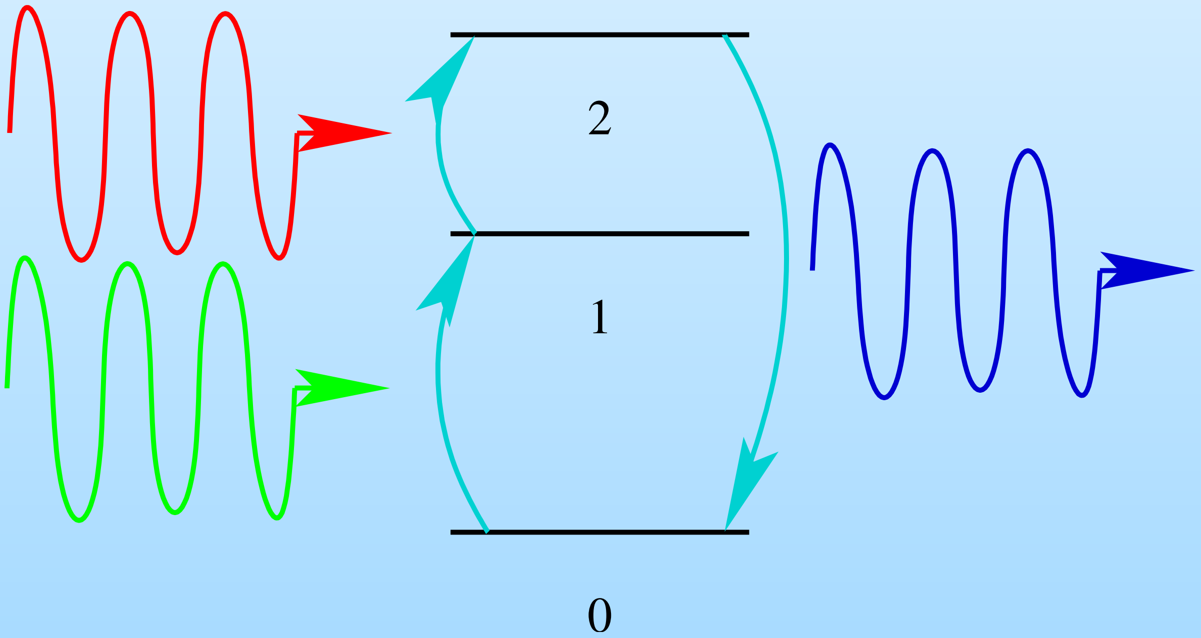
Photon-excited electron collision

Sum Frequency Generation



Sum Frequency Generation



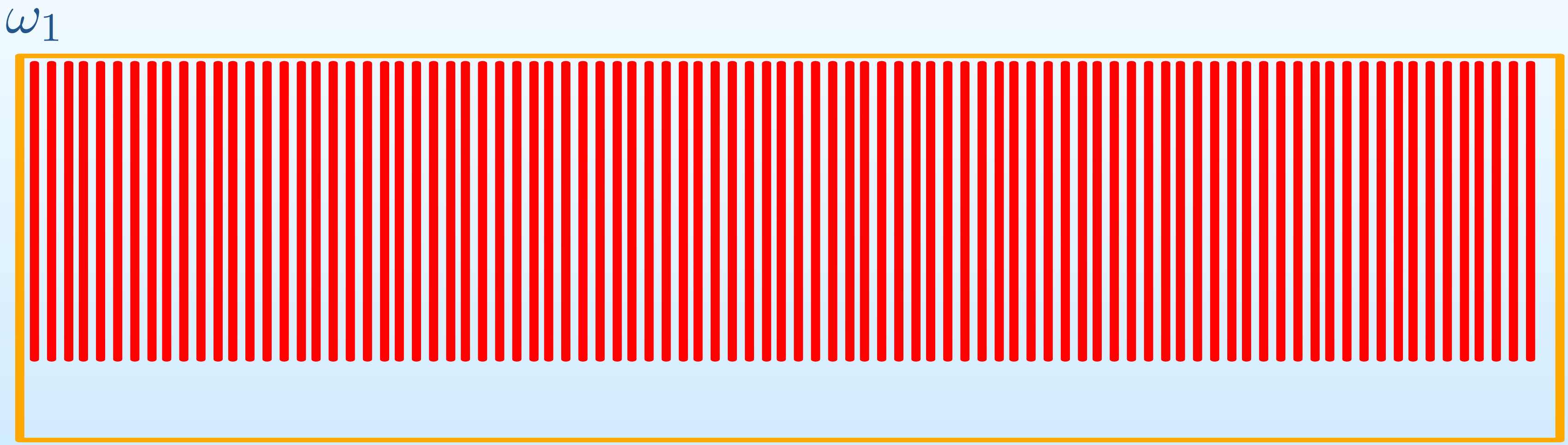


Multiplication Table

×	0	1
0	0	0
1	0	1

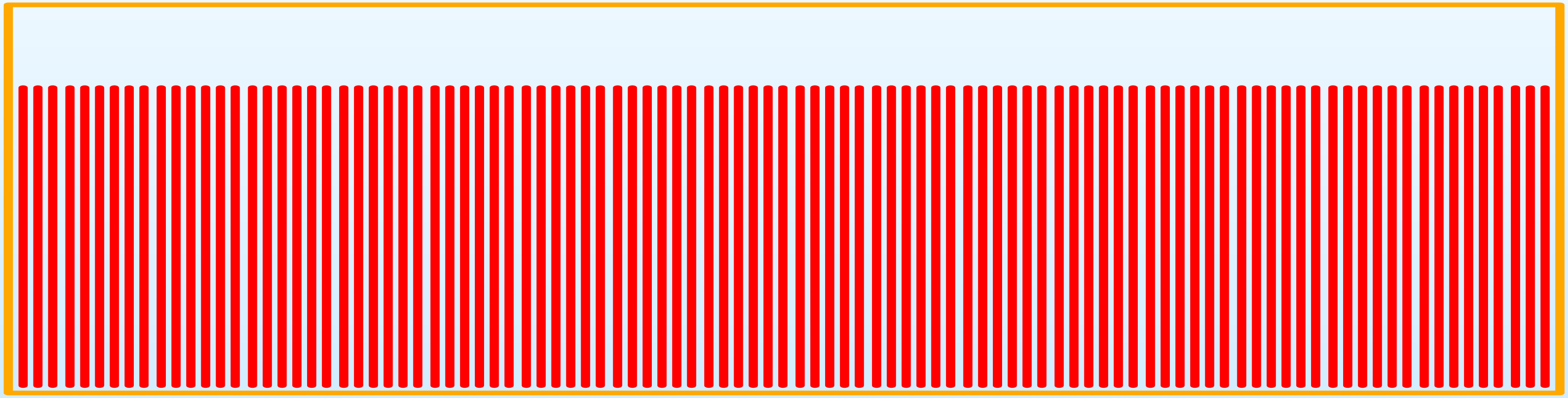
×	■	□
■	■	■
□	■	□

Wave Multiplication: DFG/SFG



Wave Multiplication: DFG/SFG

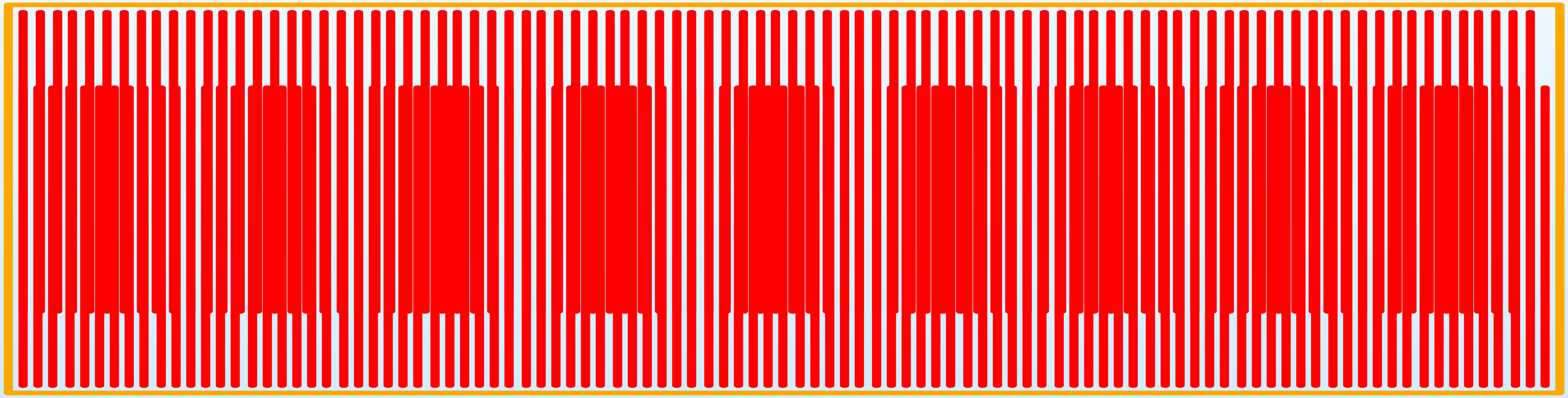
ω_1



$\omega_2 = 1.1\omega_1$

Wave Multiplication: DFG/SFG

ω_1

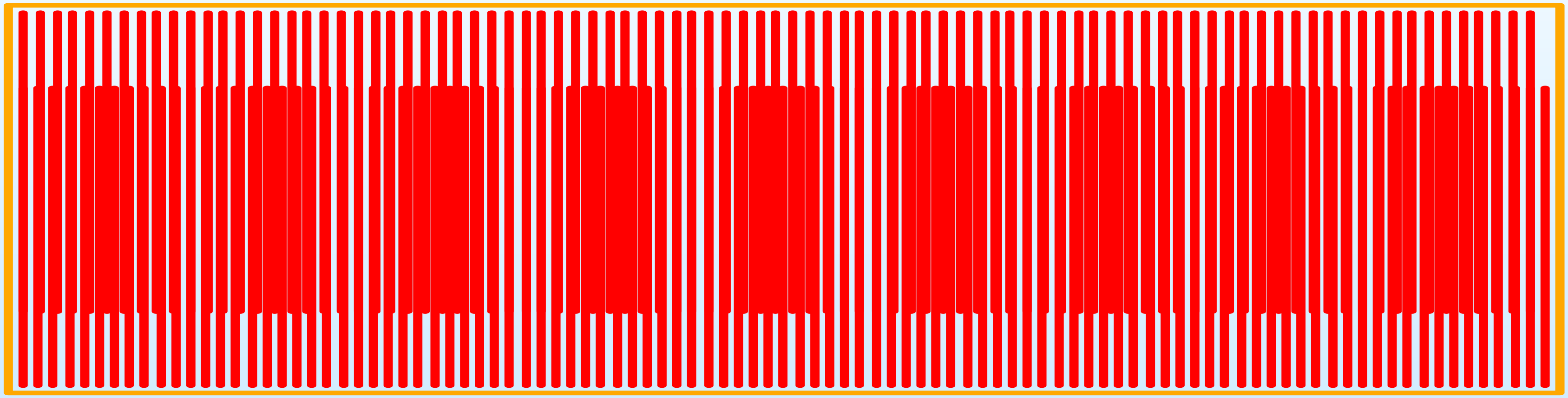


$\omega_2 = 1.1\omega_1$

$\Longrightarrow \omega_3 = 0.1\omega_1 = \omega_2 - \omega_1$

Wave Multiplication: DFG/SFG

ω_1



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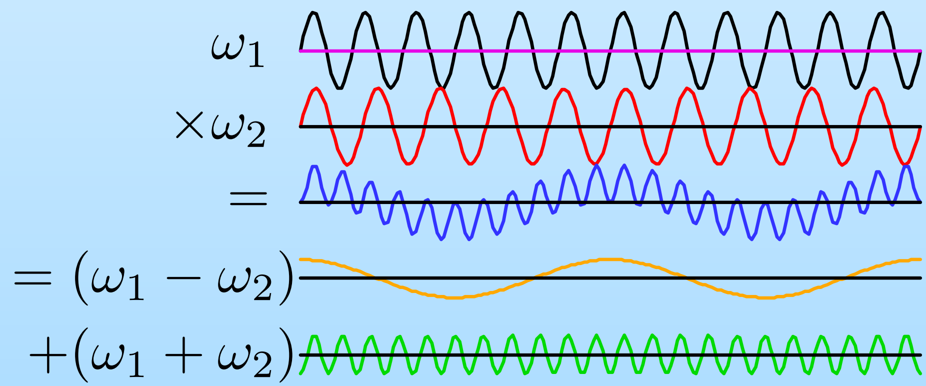
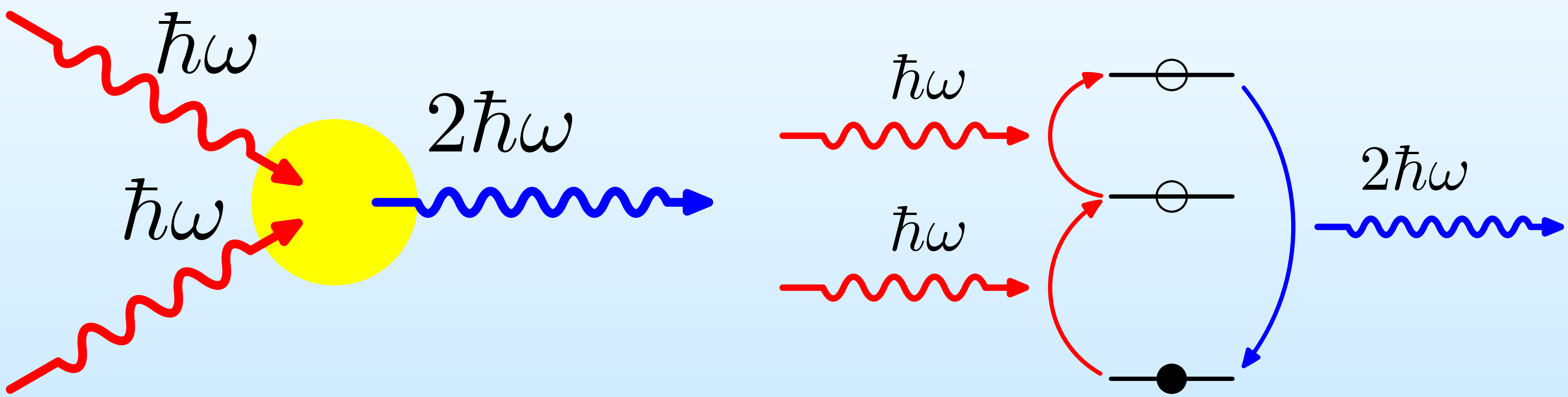


Second Harmonic Generation



$$\vec{P}(\vec{2}\omega) \propto \vec{E}(\omega)\vec{E}(\omega)$$

SHG and Symmetry

$$\vec{P}^{(2)} = \chi^{(2)} \vec{E}\vec{E}$$

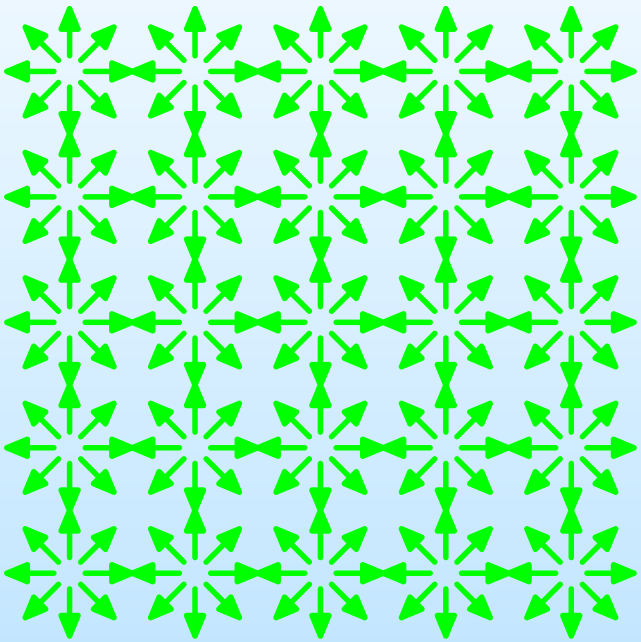
SHG and Symmetry

$$\vec{P}^{(2)} = \chi^{(2)} \vec{E}\vec{E}$$

After an inversion

$$-\vec{P}^{(2)} = \chi_I^{(2)} (-\vec{E})(-\vec{E})$$

SHG and Symmetry



$$\vec{P}^{(2)} = \chi^{(2)}\vec{E}\vec{E}$$

After an inversion

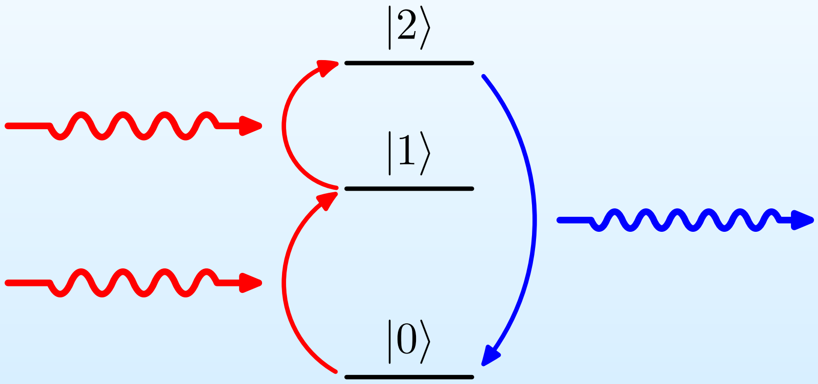
$$-\vec{P}^{(2)} = \chi_I^{(2)}(-\vec{E})(-\vec{E})$$

Centrosymmetry $\Rightarrow$

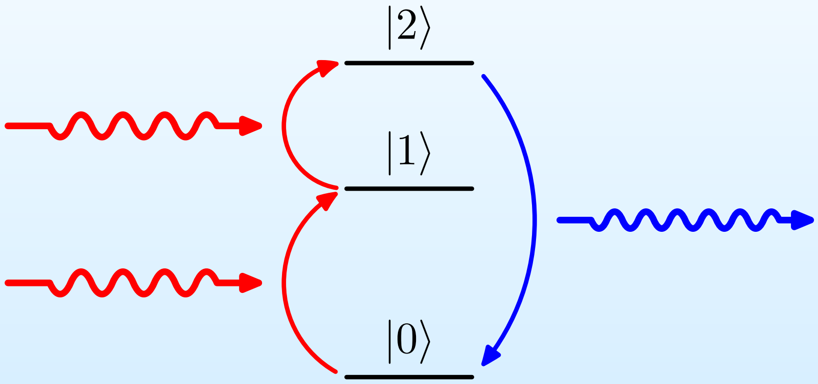
$$\chi_I^{(2)} = \chi^{(2)}$$

$$\Longrightarrow \vec{P}^{(2)} = 0, \quad \chi^{(2)} = 0$$

Centrosymmetry and Parity

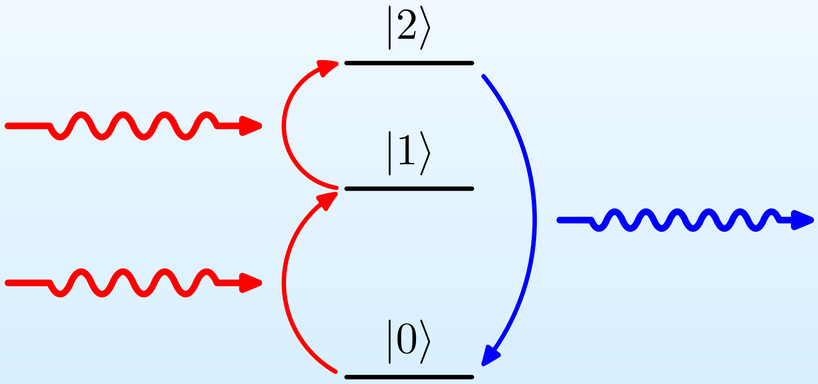


Centrosymmetry and Parity



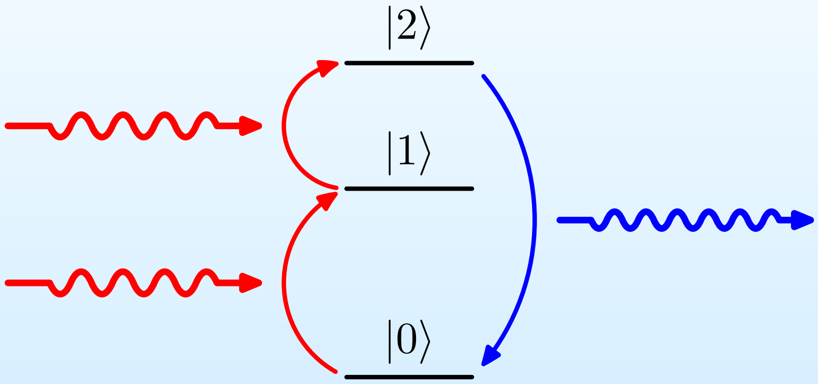
$|0\rangle$ even

Centrosymmetry and Parity



$|0\rangle$ even $\Rightarrow$ $|1\rangle$ odd

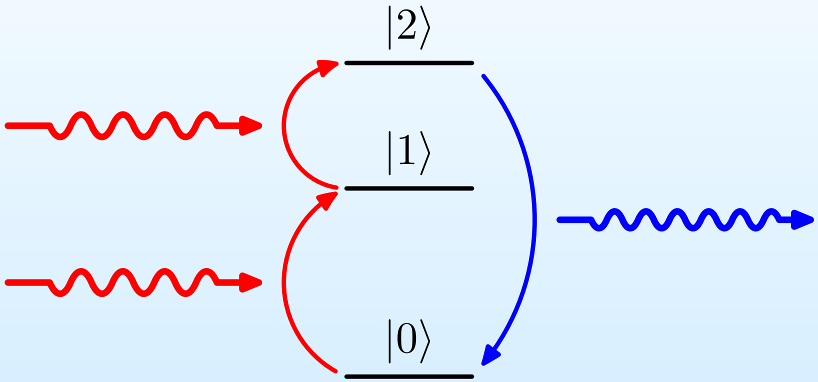
Centrosymmetry and Parity



$|0\rangle$ even $\Rightarrow$ $|1\rangle$ odd

$\Rightarrow$ $|2\rangle$ even

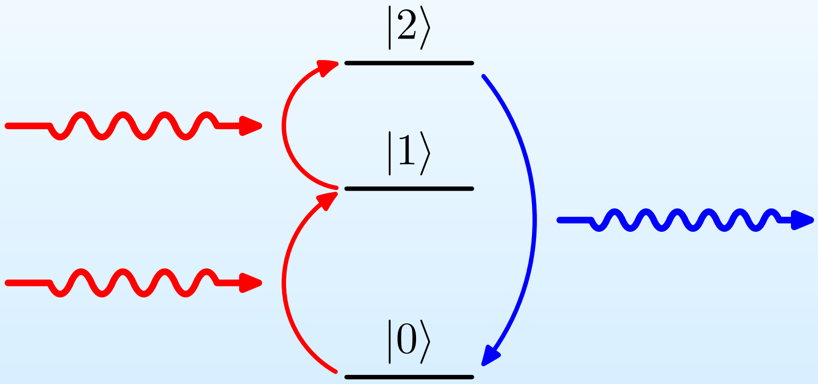
Centrosymmetry and Parity



$|0\rangle$ even $\Rightarrow$ $|1\rangle$ odd

$\Rightarrow$ $|2\rangle$ even $\Rightarrow$ $|0\rangle$ odd (!)

Centrosymmetry and Parity



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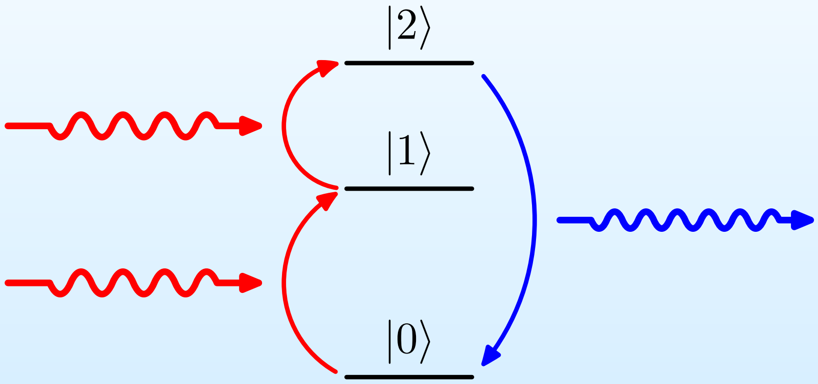
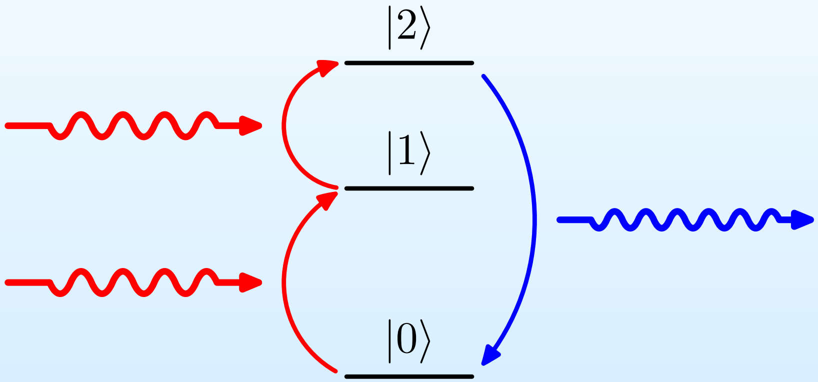
$\Rightarrow$ $|1\rangle$ even

Centrosymmetry and Parity



	$\|0\rangle$ even	$\Rightarrow$	$\|1\rangle$ odd
$\Rightarrow$	$\|2\rangle$ even	$\Rightarrow$	$\|0\rangle$ odd (!)
$\Rightarrow$	$\|1\rangle$ even	$\Rightarrow$	$\|2\rangle$ odd

Centrosymmetry and Parity



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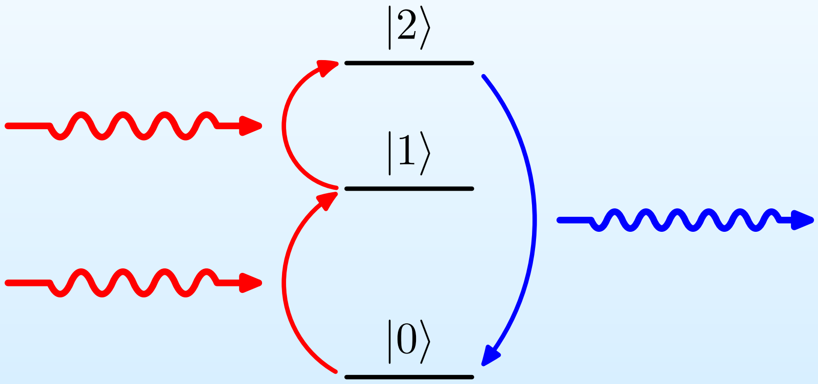
$\Rightarrow$	$\|0\rangle$ even (!!)		

Centrosymmetry and Parity



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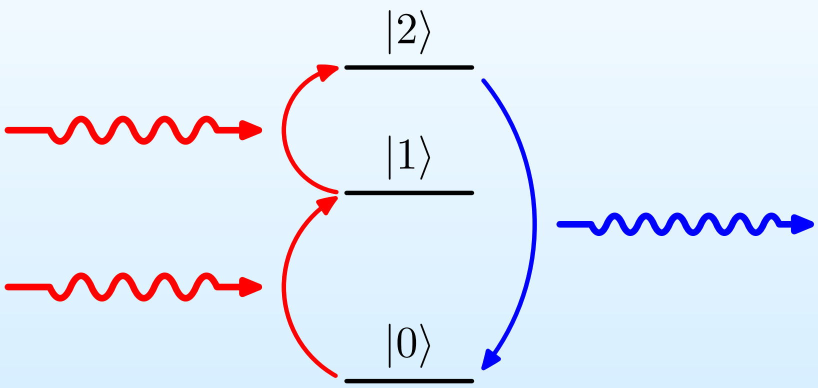
$\Rightarrow$	$	0\rangle$ even (!!)	$\Rightarrow$	$\ldots$

Centrosymmetry and Parity



	$|0\rangle$ even	$\Rightarrow$	$|1\rangle$ odd
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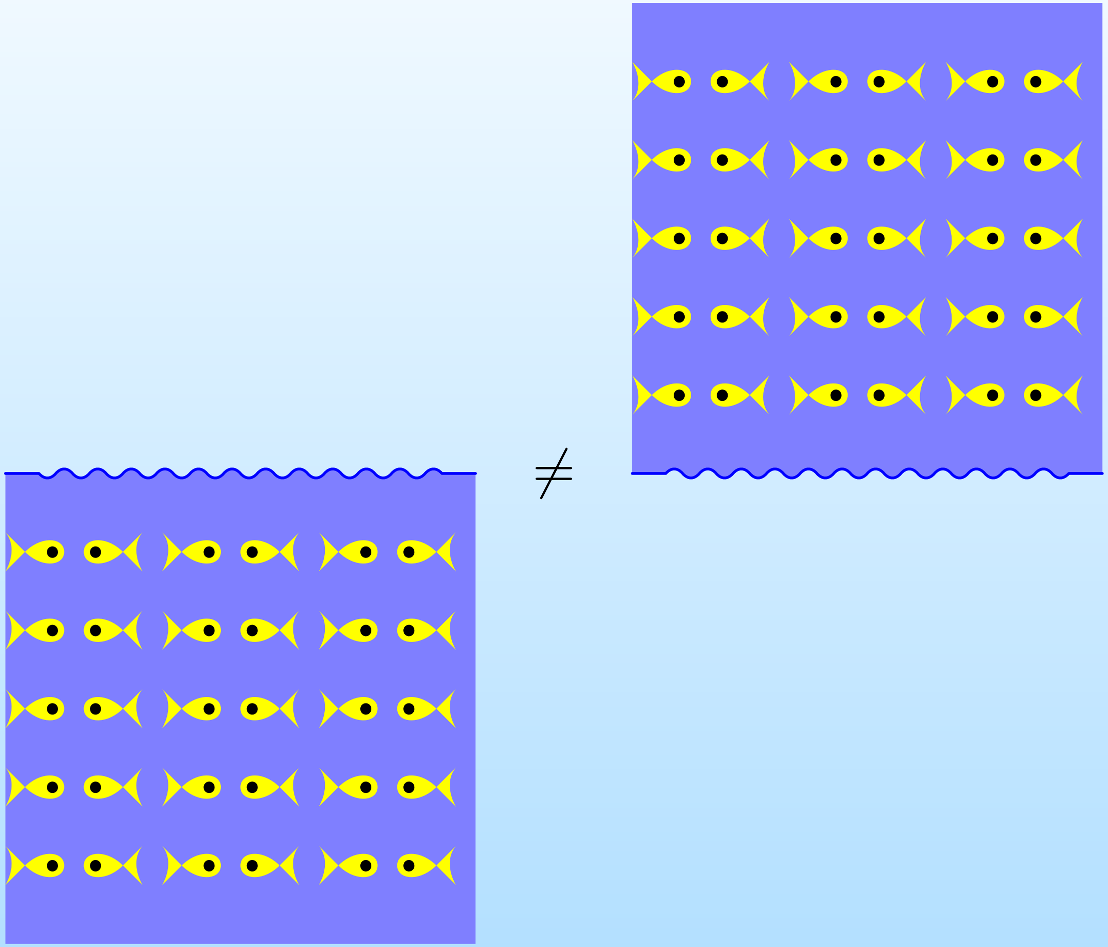
$\Rightarrow$	$|1\rangle$ even	$\Rightarrow$	$|2\rangle$ odd
$\Rightarrow$	$	0\rangle$ even (!!)	$\Rightarrow$	$\ldots$

$$\hat{H}_{int} = -\hat{p} \cdot \vec{E}.$$

$$\chi^{(2)} \propto \langle 0|\hat{p}|2\rangle\langle 2|\hat{p}|1\rangle\langle 1|\hat{p}|0\rangle = 0.$$

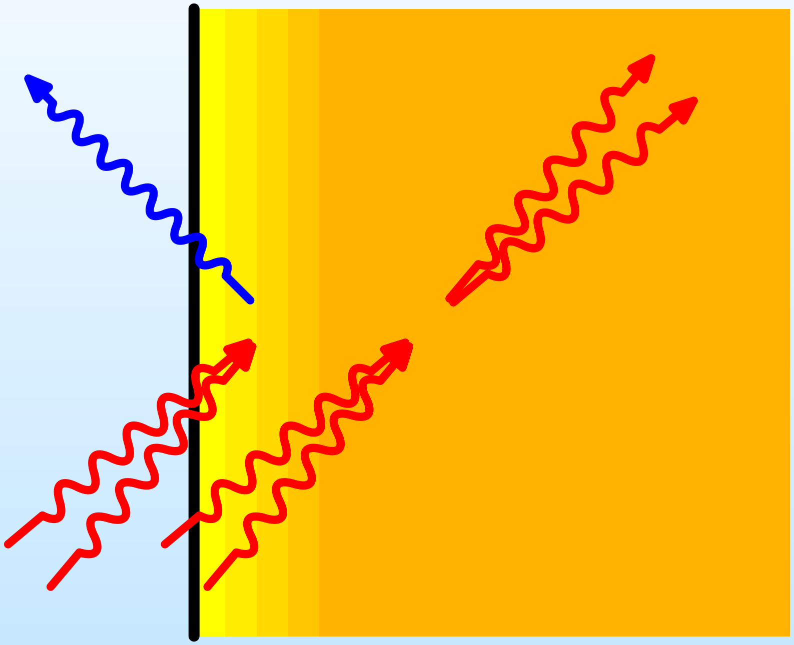
The second order *dipolar* susceptibility is null.

Centrosymmetry and Surfaces

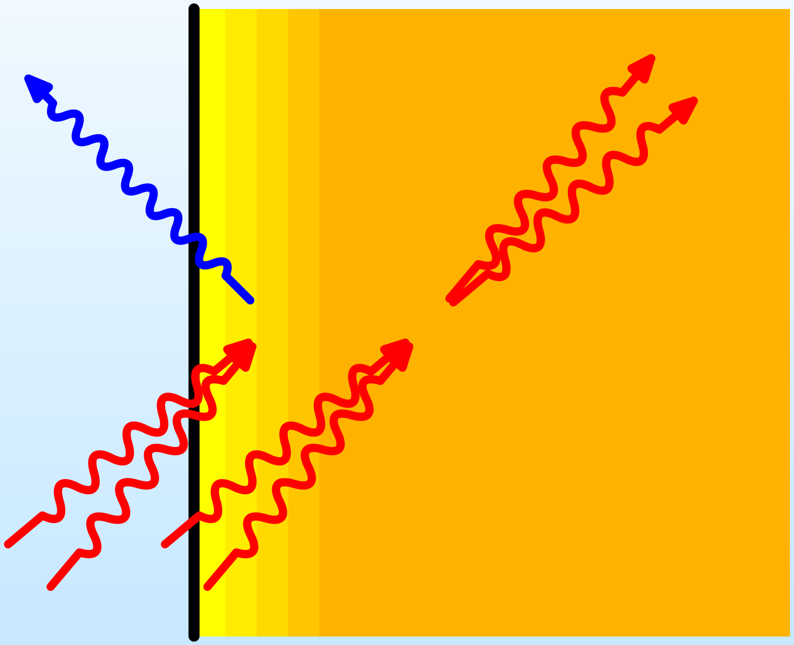


Surfaces are not centrosymmetric!

SHG and Surfaces

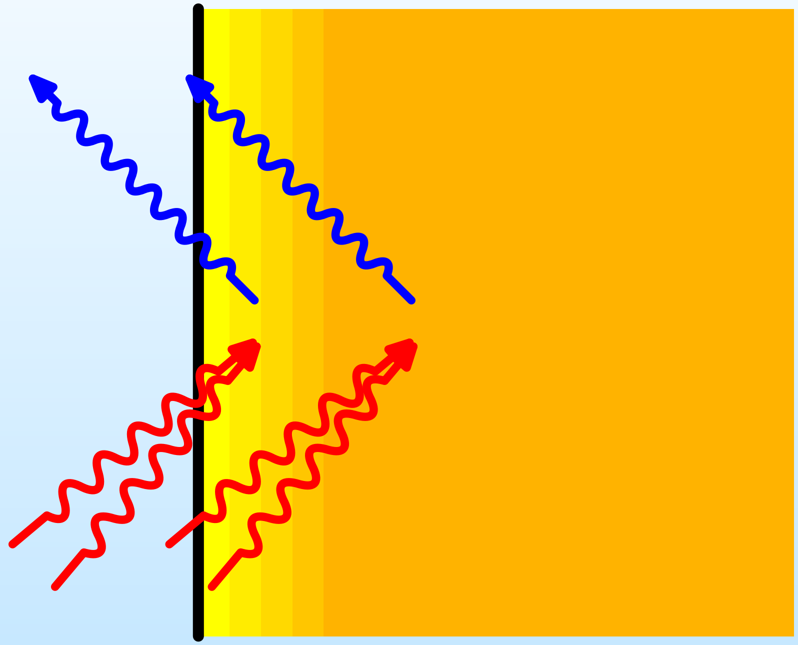


SHG and Surfaces



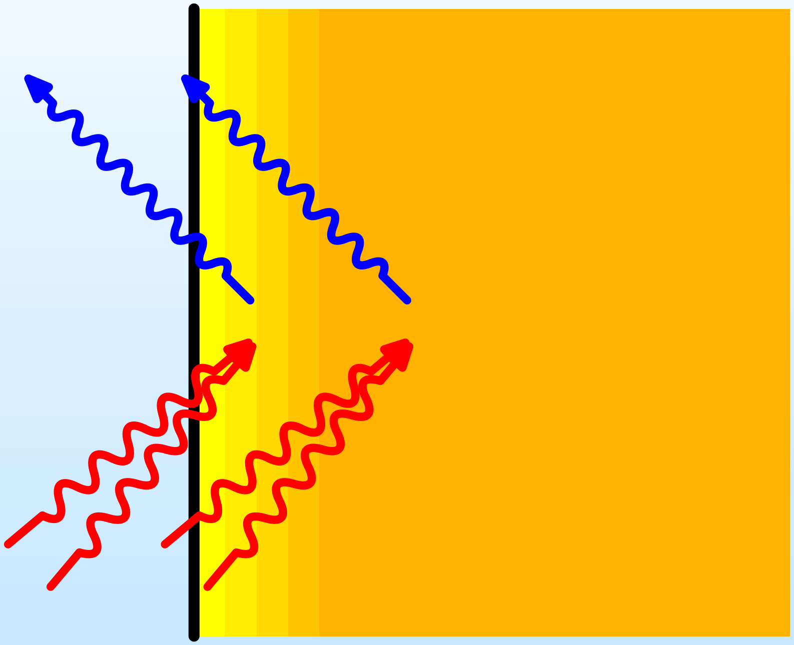
Dipolar SHG $P_i^{(2)} = \chi_{ijk} E_j E_k$ comes from the surface.

SHG and Surfaces



Dipolar SHG $P_i^{(2)} = \chi_{ijk} E_j E_k$ comes from the surface.
There might be SHG from bulk. . .

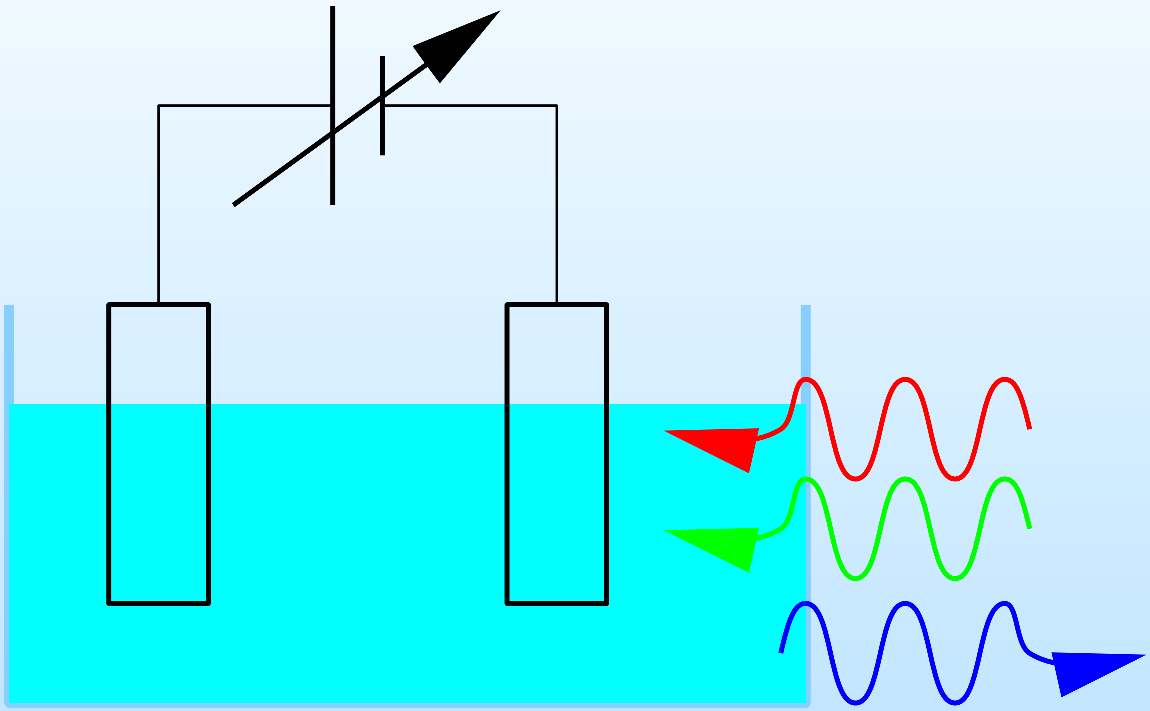
SHG and Surfaces



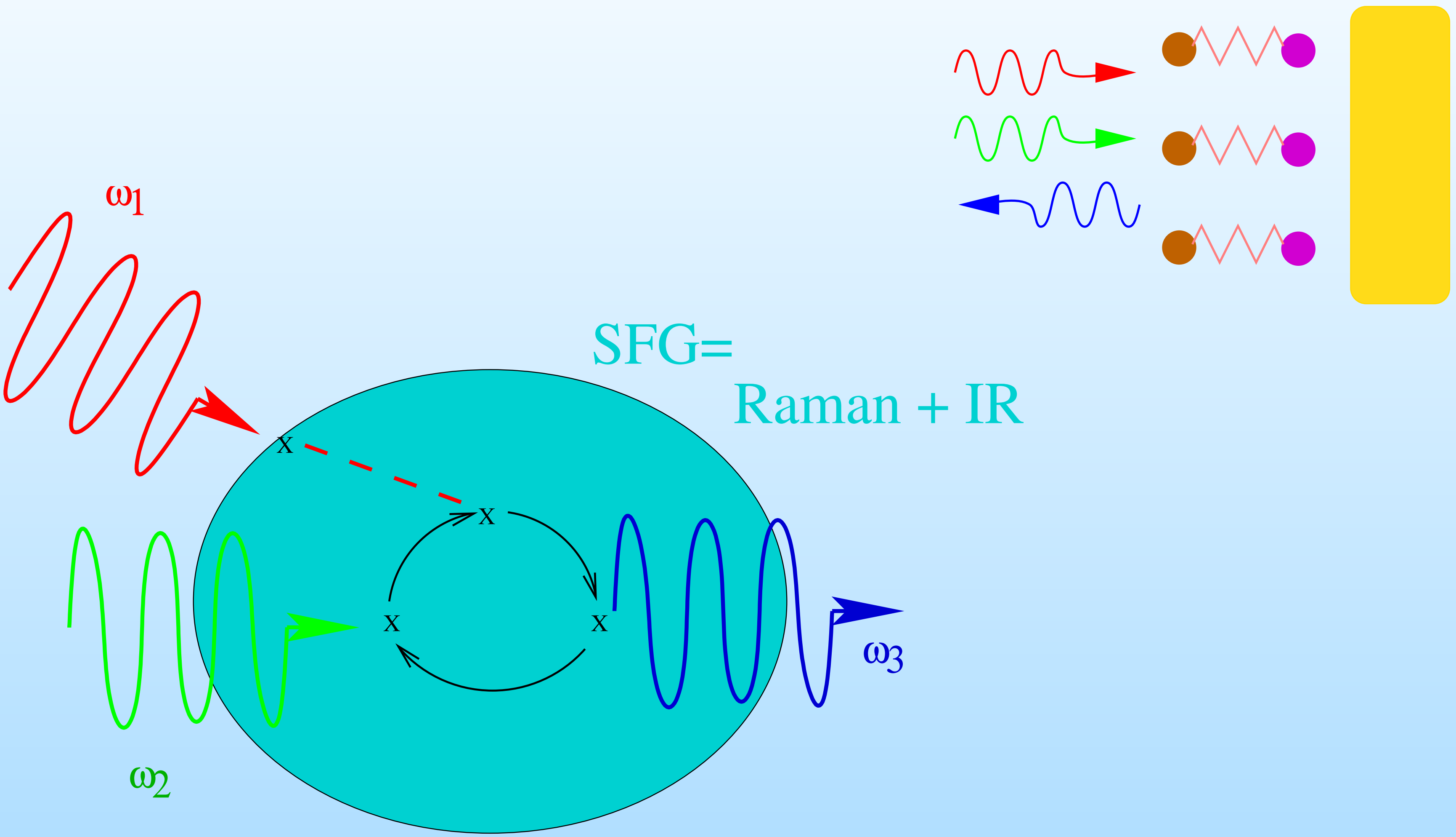
Dipolar SHG $P_i^{(2)} = \chi_{ijk} E_j E_k$ comes from the surface.
There might be SHG from bulk. . .
but it is *multipolar*

$$P_i^{(2)} = \chi_{ijkl} E_j \partial_k E_l.$$

Optical Observation of Surfaces



Adsorbates



Efficiency

- $E = \frac{p}{r^3} \rightarrow \frac{p}{\lambda^2 r}$

Efficiency

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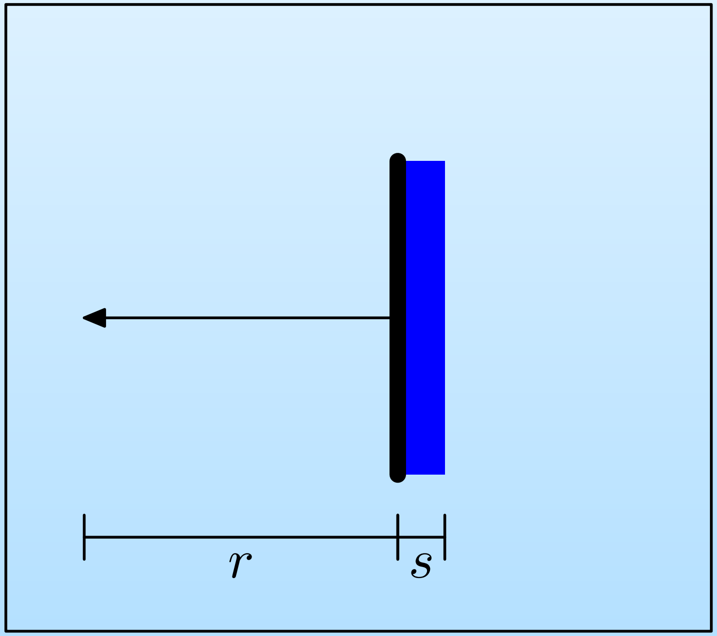
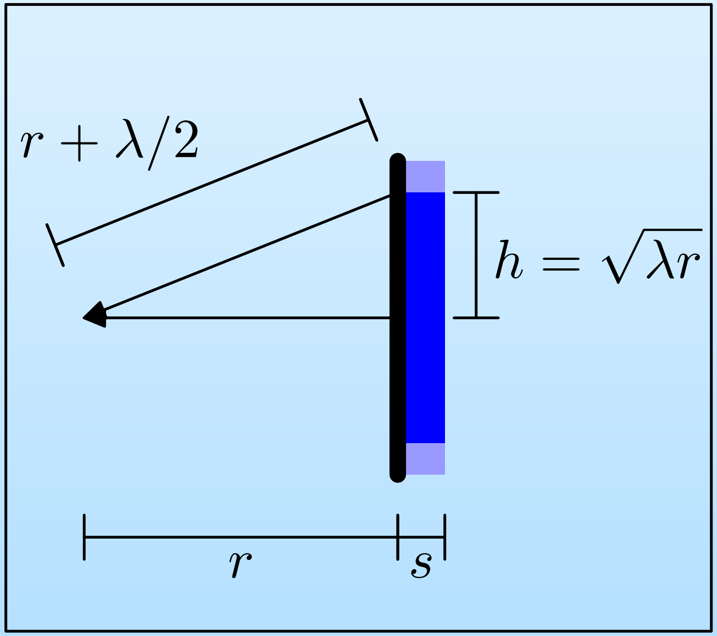
- $P \approx \frac{E^2}{e/a_B^2}$



Efficiency

- $E = \frac{p}{r^3} \to \frac{p}{\lambda^2 r}$
- $P \approx \frac{E^2}{e/a_B^2}$



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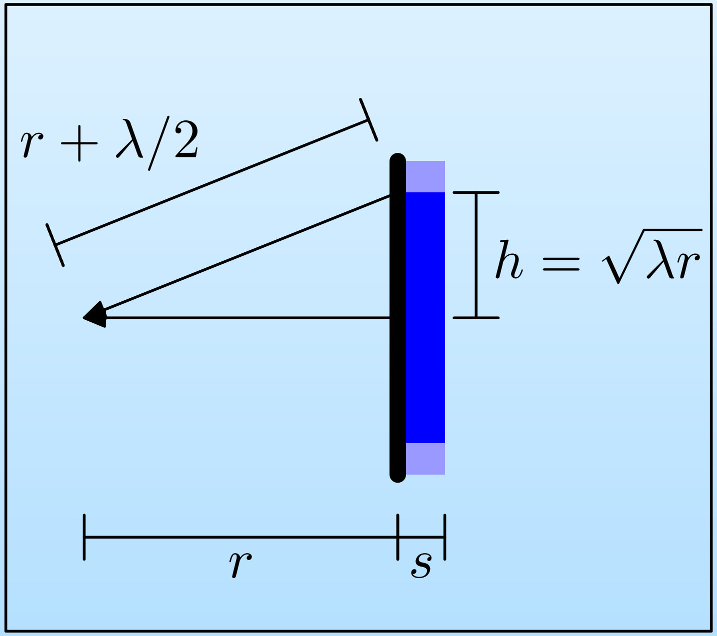

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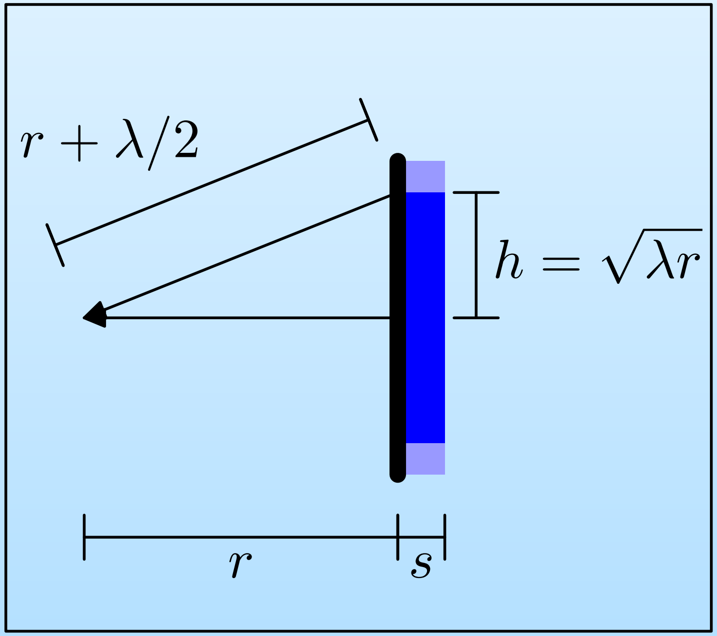

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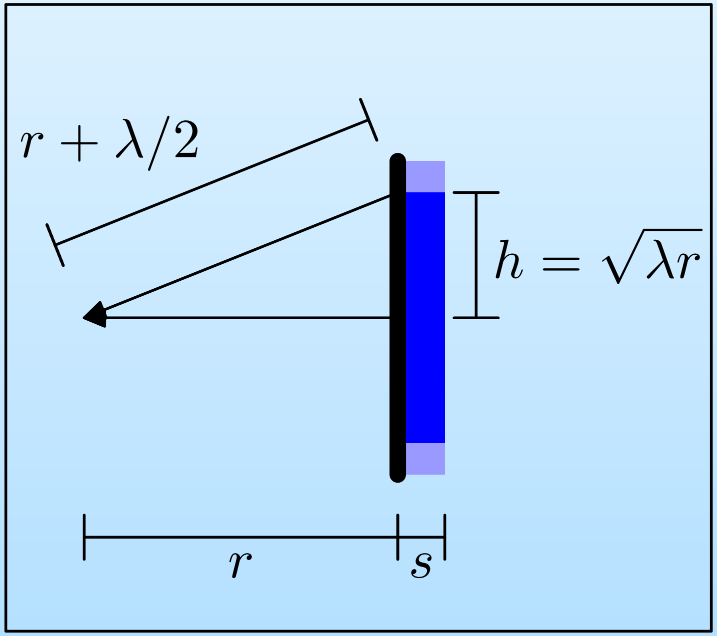
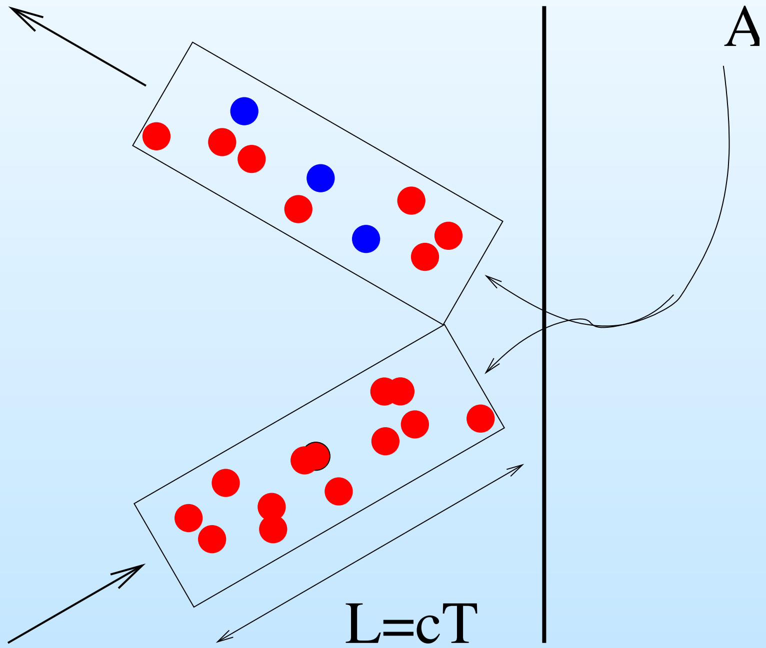


- $p \approx Ph^2 s \approx \frac{E^2}{e/a_B^2} \lambda r a_B$
- $E \approx \frac{a_B^3}{\lambda e} E^2$
- $I \approx cE^2 = RI^2 \approx Rc^2 E^4$
- $R \approx \left(\frac{a_B}{\lambda}\right)^2 \frac{a_B}{e^2} \frac{a_B}{c} a_B^2 \approx 10^{-24} \text{cm}^2/W$

Size of a photon

-



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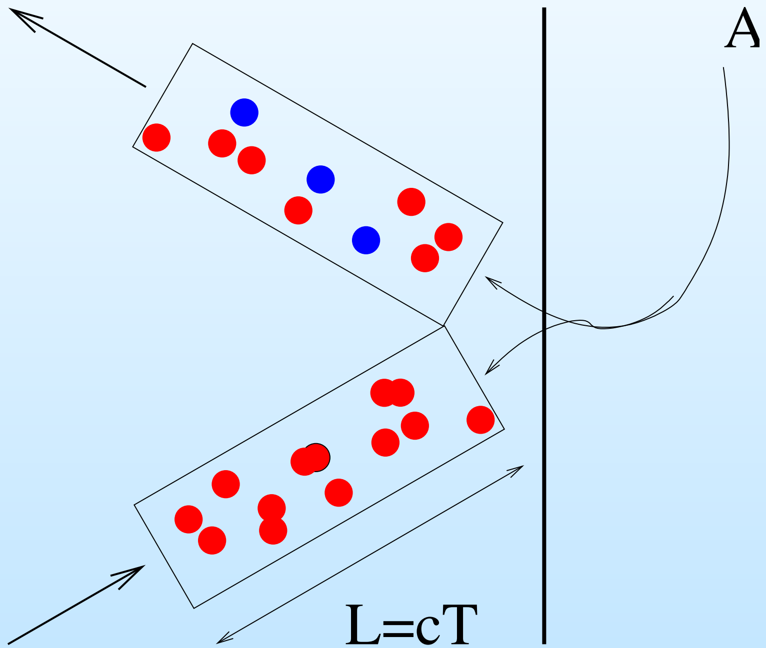
- 

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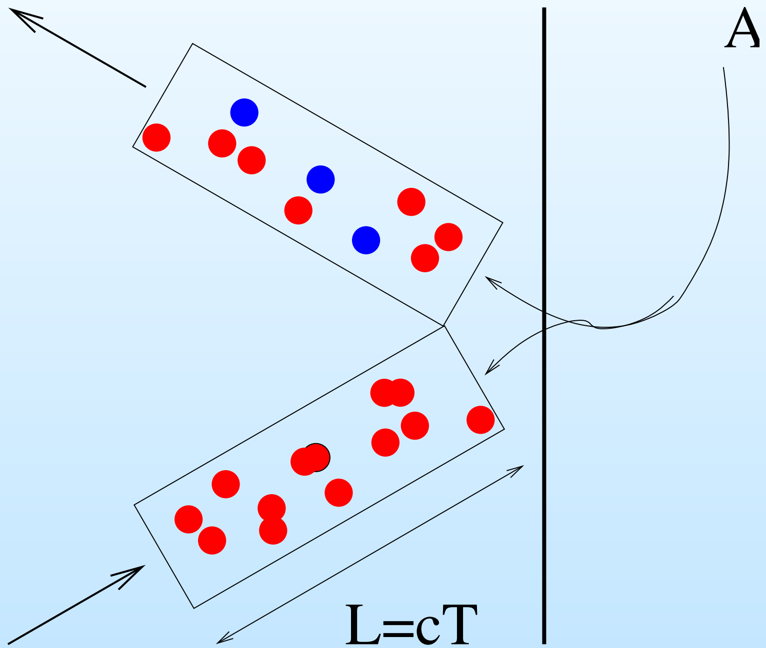
- 

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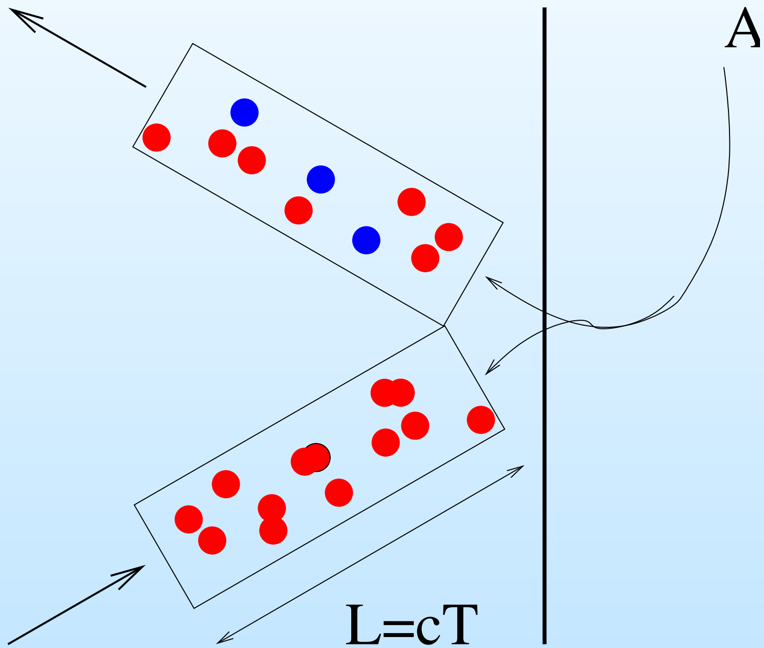
- 

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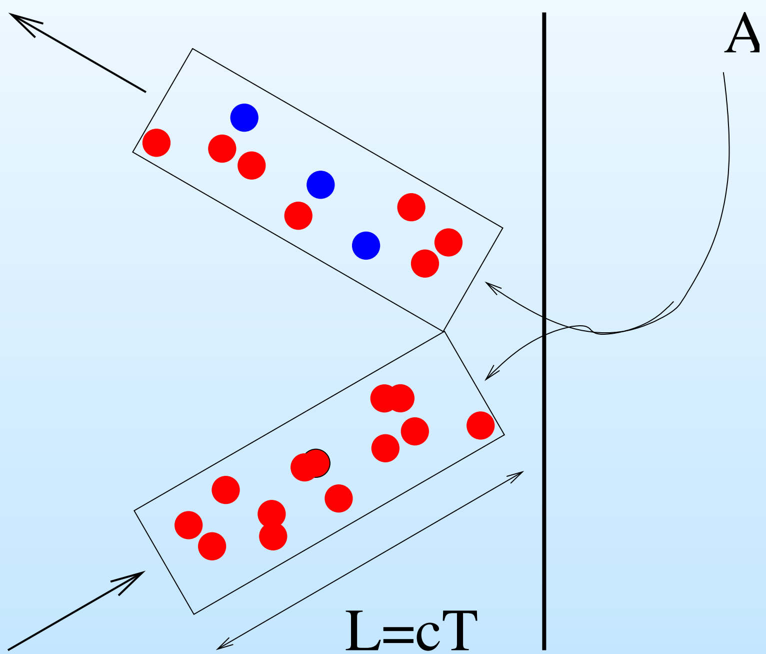
- 

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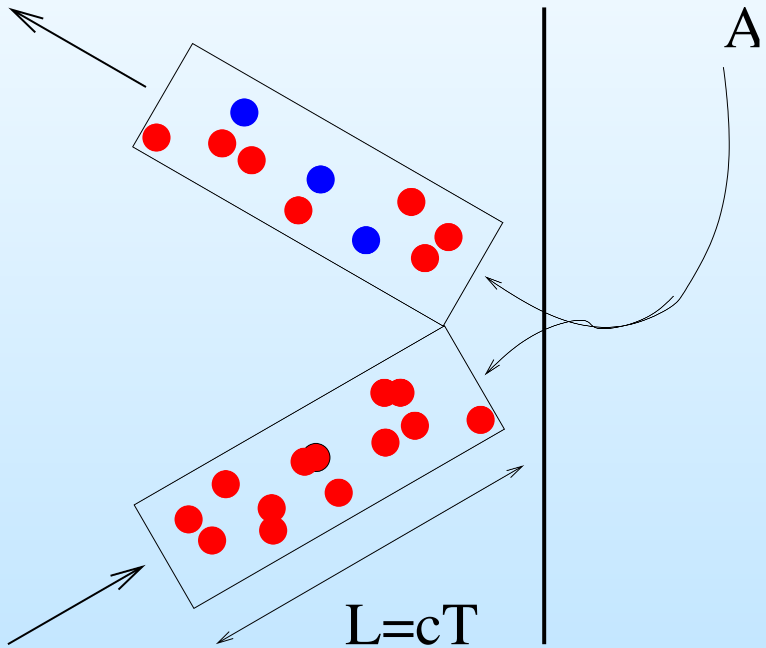
- 

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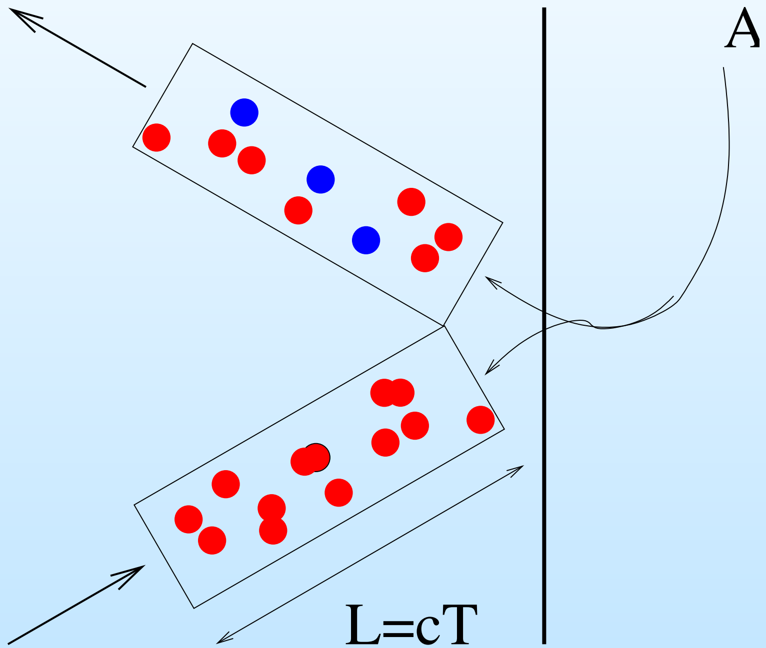
- 

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- Bulk SH is comparable to surface SH.

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Pulse duration: $\tau = 200$fs

Pulse energy: $\mathcal{E} = 0.3\mu$J

Focus size: $w = 10\mu$m

Repetition rate: $f = 250$kHz

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χ_{ijk} (cont.)

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- Susceptibility (time domain):

$$p_i^{(2)}(t) = \int dt' \int dt''\, \alpha_{ijk}(t, t', t'') E_j(t') E_k(t'')$$

χ_{ijk} (cont.)

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$$\alpha_{ijk}(t,t',t'') = -\frac{1}{\hbar^2}\Big\langle[[\hat{p}_i(t),\hat{p}_j(t')],\hat{p}_k(t'')]\Big\rangle_0$$

plus causality (zero unless $t > t' > t''$).

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\end{aligned}
$$

- Identify

$$
\alpha_{ijk} = -\frac{1}{\hbar^2} \frac{p_i^{0\mu} p_j^{\mu\nu} p_k^{\nu 0}}{(\omega_{\mu 0} - 2\omega)(\omega_{\nu 0} - \omega)} \pm \text{permutations}
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- 27 ω dependent quantities, resonant whenever $\hbar\omega =$ transition energy or a subharmonic

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- Similar, but using $H^I = -\hat{p}_l E_l - \hat{m}_l B_l - (1/6)\hat{Q}_{kl}\partial_k E_l$

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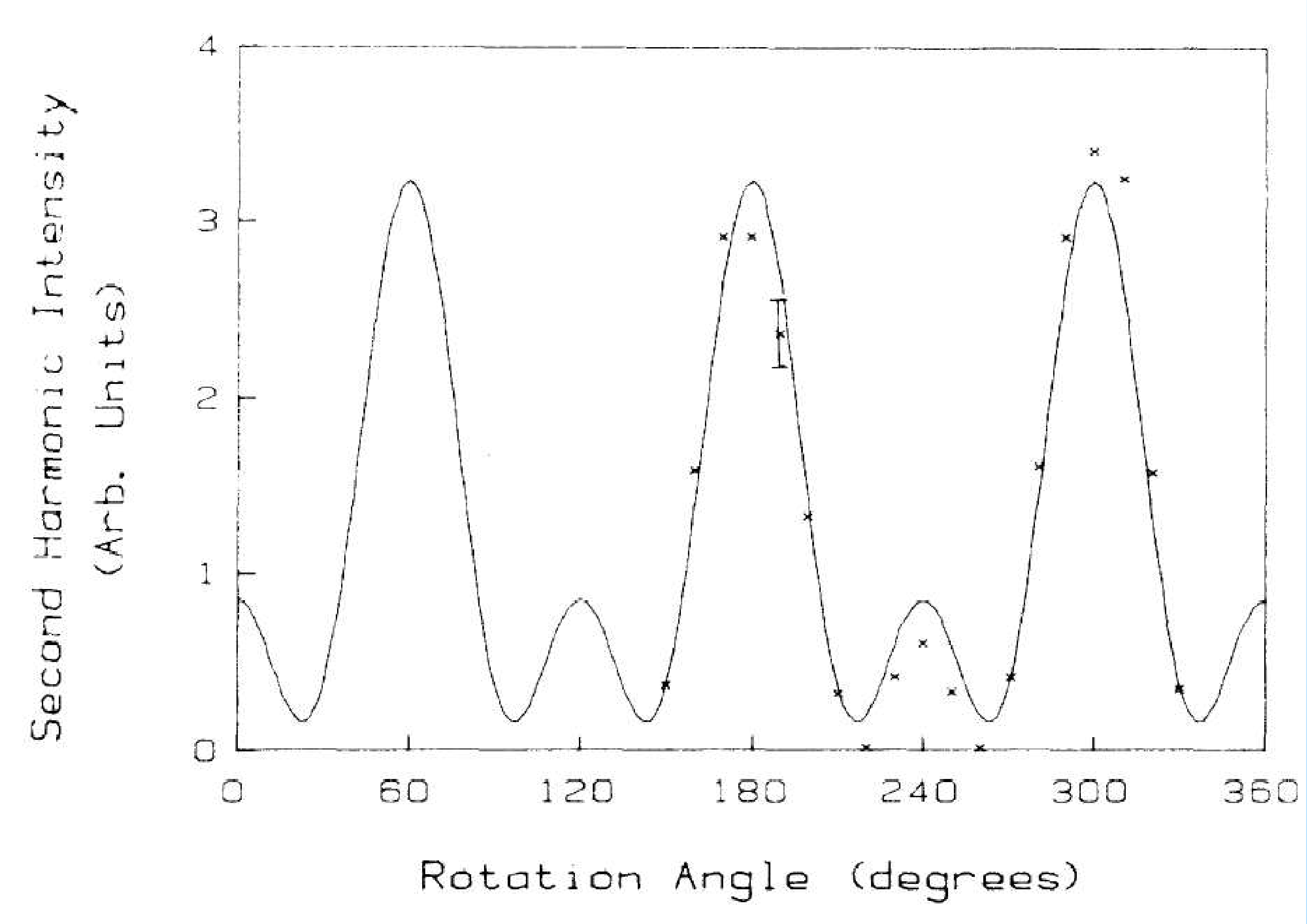
Surface Symmetry

$\chi_{ijk} = \chi_{ikj} = S_{ii'} S_{jj'} S_{kk'} \chi_{i'j'k'}$
$\Rightarrow$ only some independent non-null components of χ_{ijk}.
With $\hat{n}_\perp \| \hat{z}$:

Symmetry	χ_{ijk} non-null components
1	xxx, xxy, xyy, yxx, yxy, yyy, xxz, xyz, yxz, yyz, zxx, zxy, zyy, xzz, yzz, zxz, zyz, zzz
1m ($\perp y$)	xxx, xyy, xzz, xzx, yzy, yxy, zxx, zyy, zxz, zzz
2	xzx, xyz, yxz, yzy, zxx, zyy, zxy, zzz
2mm	xzx, yzy, zxx, zyy, zzz
3	$xxx = -xyy = -yyx$, $yyy = -yxx = -xyx$, $yzy = xzx$, $zxx = zyy$
3m ($\perp y$)	$xxx = -xyy = -yxy$, $xzx = yzy$, $zxx = zyy$, zzz
4, 6, ∞	$xxz = yyz$, $zxx = zyy$, $xyz = -yxz$, zzz
4mm, 6mm, ∞m	$xxz = yyz$, $zxx = zyy$, zzz

J. F. McGilp,J. Phys. D: Appl. Phys. **29**, 1812 (1999).

Example: Si(111) $p \leftarrow s$



Sipe et al., PRB **35**, 1129 (1987)

Surface Symmetry: Isotropic surface.

$$\overleftrightarrow{R}_{\theta} = \begin{pmatrix} 1-\delta\theta^2/2 & -\delta\theta & 0 \\ \delta\theta & 1-\delta\theta^2/2 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$I_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$I_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Isotropic surface (cont.)

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Isotropic surface (cont.)

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- I_x or I_y: $\chi_{zxy} \rightarrow -\chi_{zxy}$
  $\Rightarrow \chi_{xyz} = \chi_{yzx} = \chi_{zxy} = \chi_{xzy} = \chi_{zyx} = \chi_{yxz} = 0.$

Isotropic surface (cont.)

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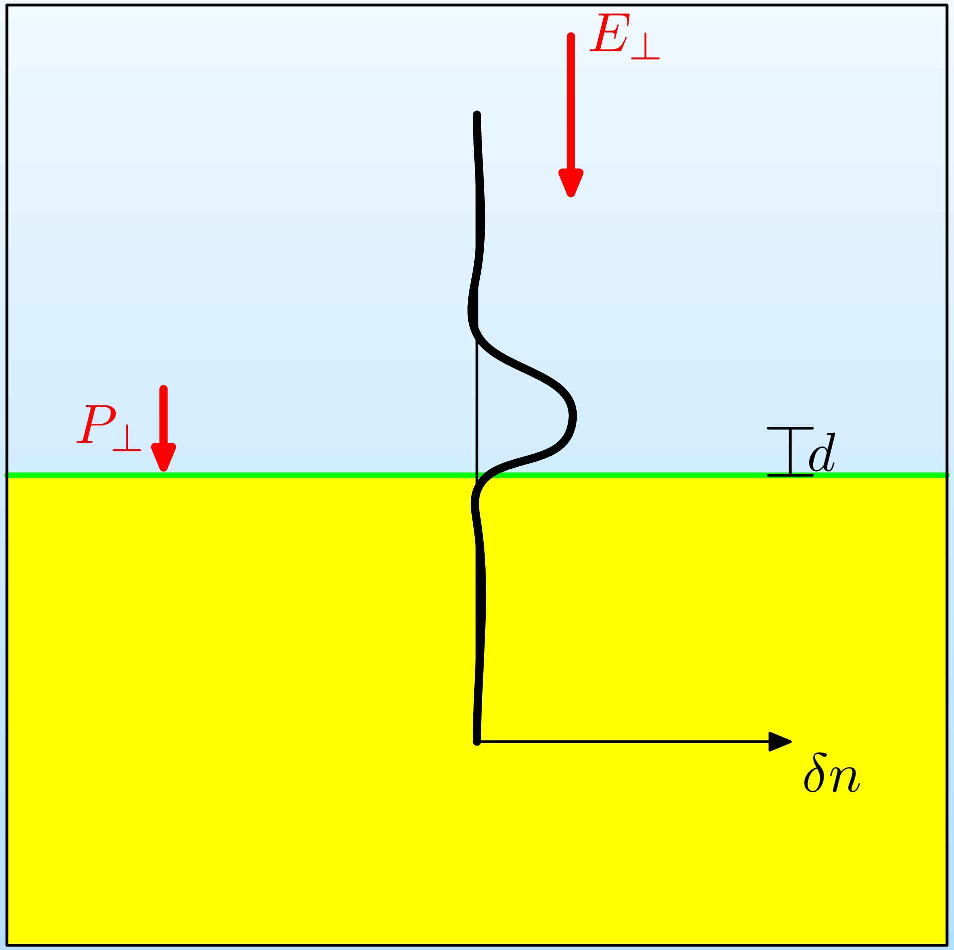
- I_x: $\chi_{zzx} \to -\chi_{zzx}$,
  $\Rightarrow \chi_{zzx} = \chi_{zzy} = \chi_{zxz} = \chi_{zyz} = \chi_{xzz} = \chi_{yzz} = 0.$
- I_x or I_y: $\chi_{zxy} \to -\chi_{zxy}$
  $\Rightarrow \chi_{xyz} = \chi_{yzx} = \chi_{zxy} = \chi_{xzy} = \chi_{zyx} = \chi_{yxz} = 0.$
- R_θ: $\chi_{zxx} \to (1 - \delta\theta^2)\chi_{zxx} + \delta\theta^2 \chi_{zyy}$
  $\chi_{zxx} = \chi_{zyy}$ =any

Isotropic surface (cont.)

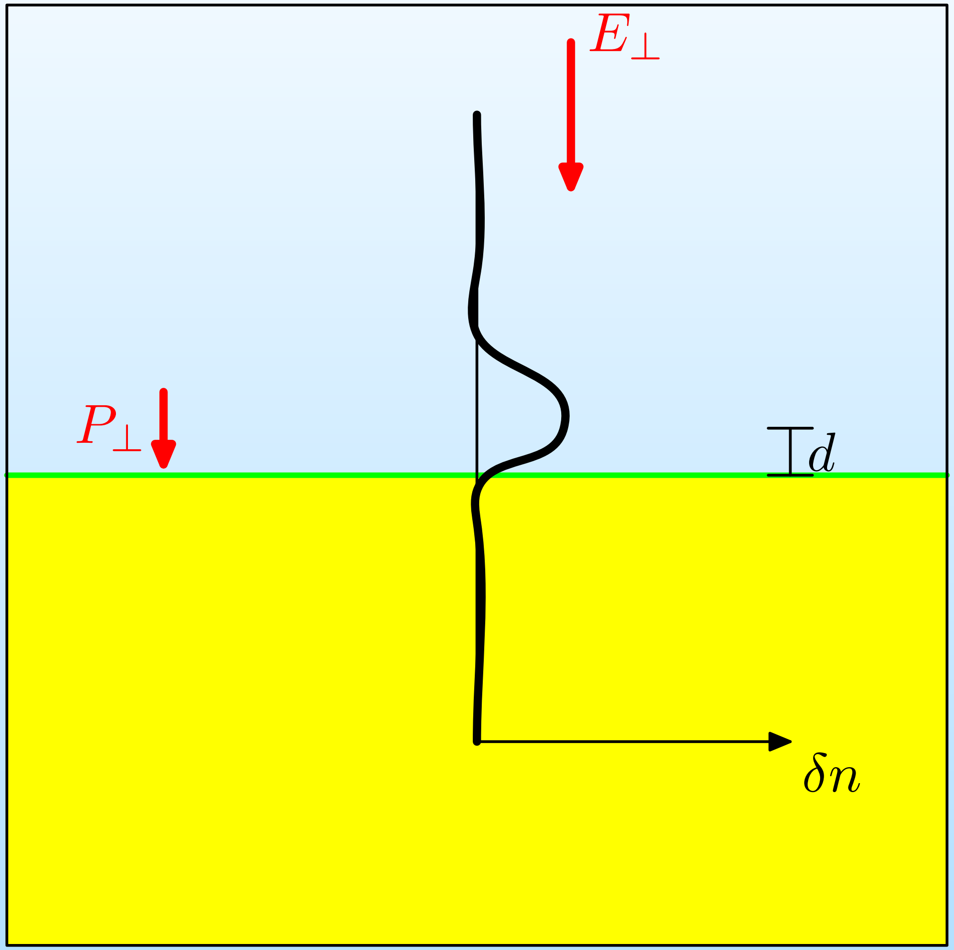
$$\chi_{ijk} = S_{ii'}S_{jj'}S_{kk'}\chi_{i'j'k'}$$

- Any: χ_{zzz} =any
- I_x: $\chi_{zzx} \to -\chi_{zzx}$,
  $\Rightarrow \chi_{zzx} = \chi_{zzy} = \chi_{zxz} = \chi_{zyz} = \chi_{xzz} = \chi_{yzz} = 0.$
- I_x or I_y: $\chi_{zxy} \to -\chi_{zxy}$
  $\Rightarrow \chi_{xyz} = \chi_{yzx} = \chi_{zxy} = \chi_{xzy} = \chi_{zyx} = \chi_{yxz} = 0.$
- R_θ: $\chi_{zxx} \to (1-\delta\theta^2)\chi_{zxx} + \delta\theta^2\chi_{zyy}$
  $\chi_{zxx} = \chi_{zyy}$ =any
- R_θ: $\chi_{xzx} = (1-\delta\theta^2)\chi_{xzx} + \delta\theta^2\chi_{yzy}$
  $\chi_{xzx} = \chi_{yzy}$ =any
- Three independent components: $\chi_{\perp\perp\perp}$, $\chi_{\parallel\perp\parallel}$, and $\chi_{\perp\parallel\parallel}$.

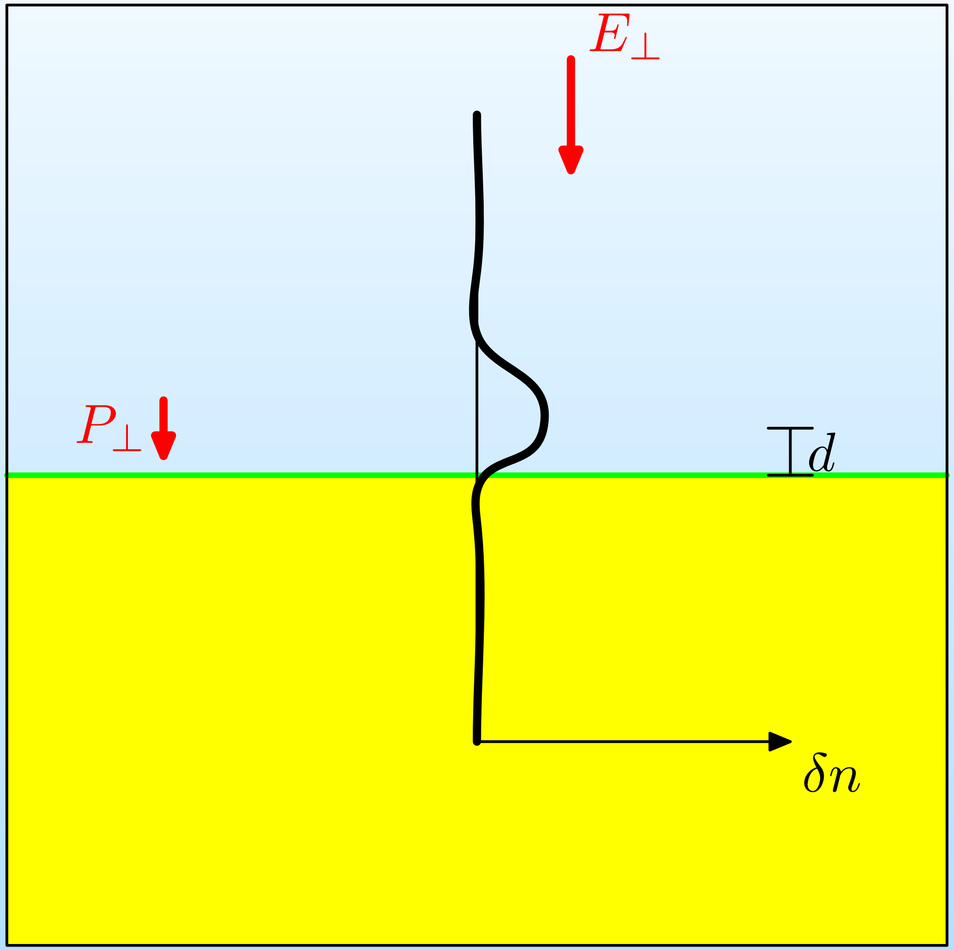
Nonlinear Surface Response: a



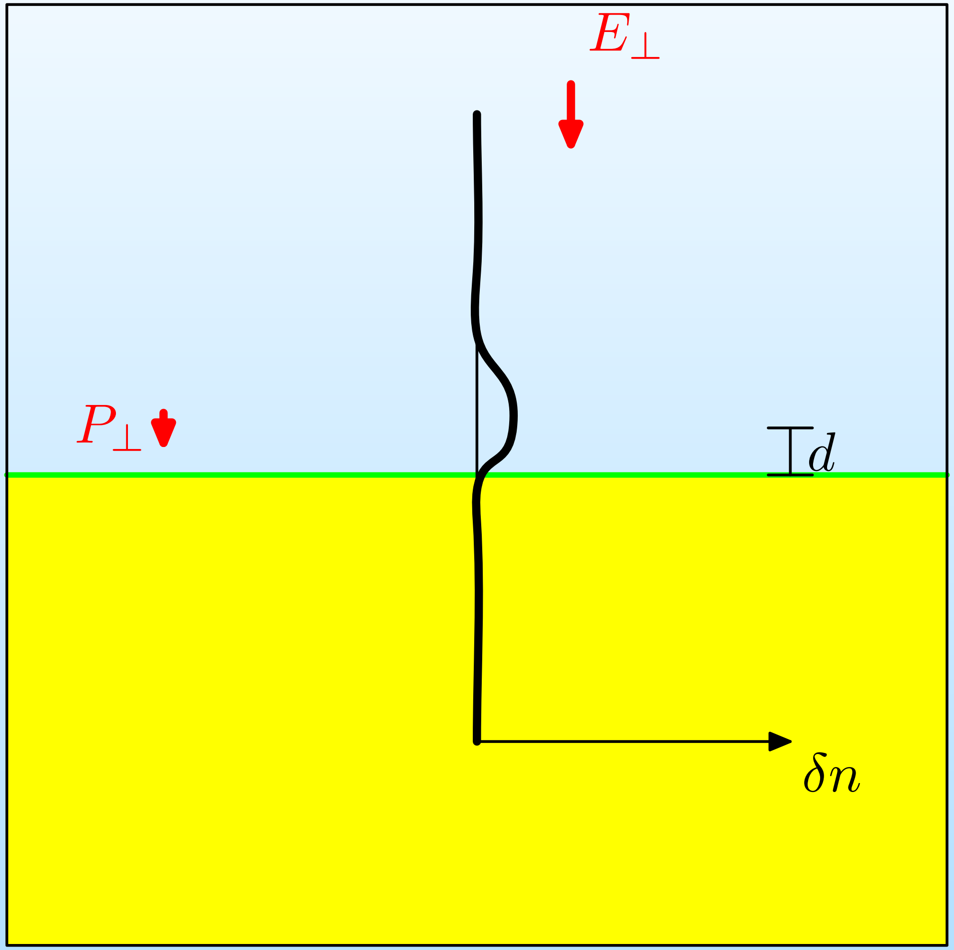
Nonlinear Surface Response: a



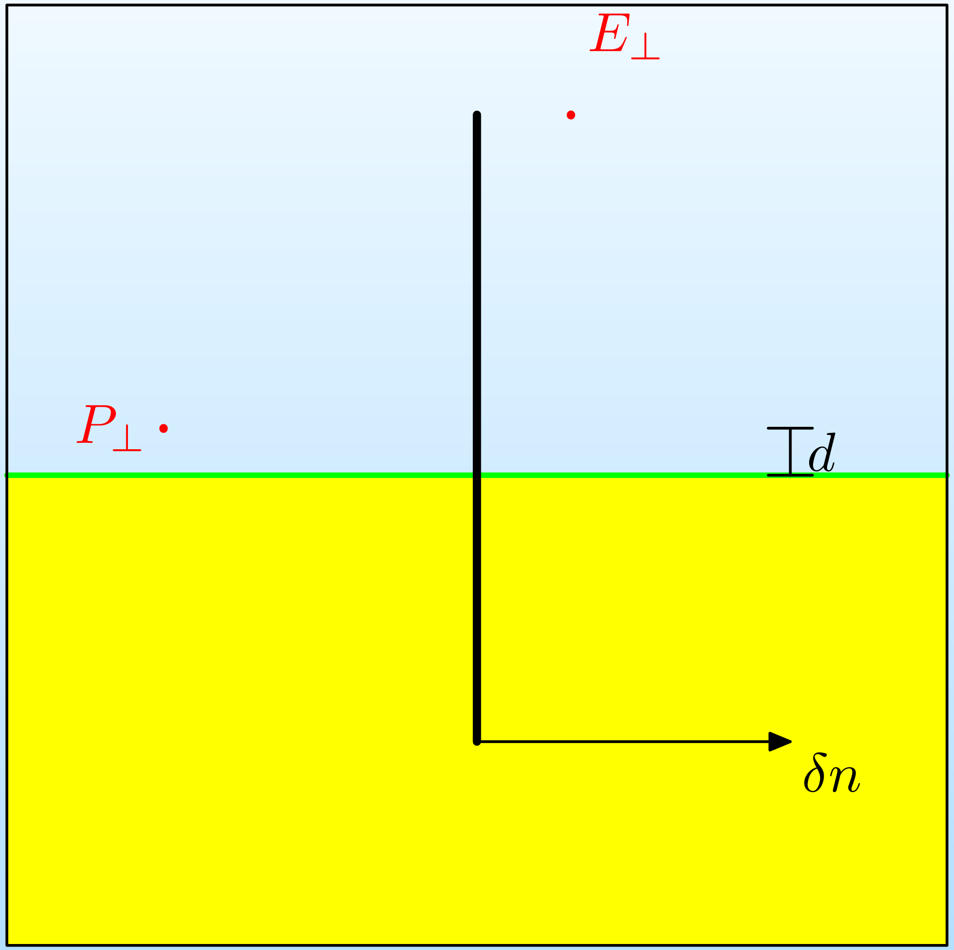
Nonlinear Surface Response: a



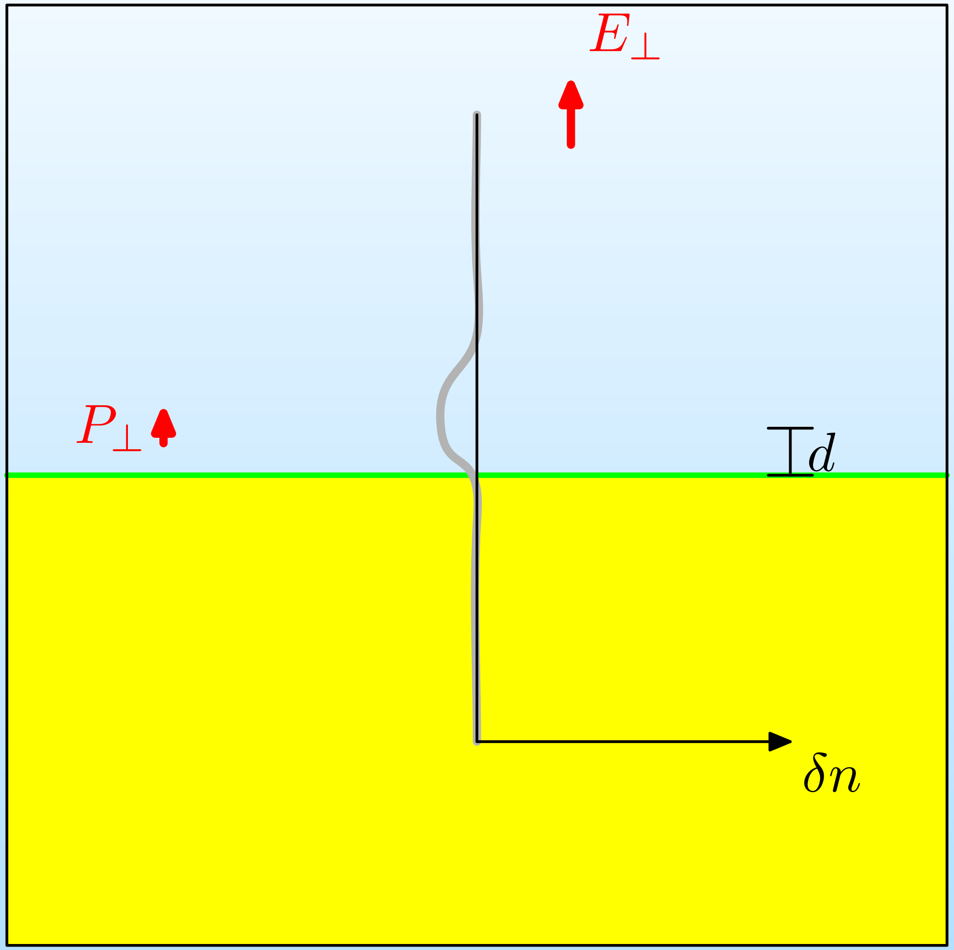
Nonlinear Surface Response: a



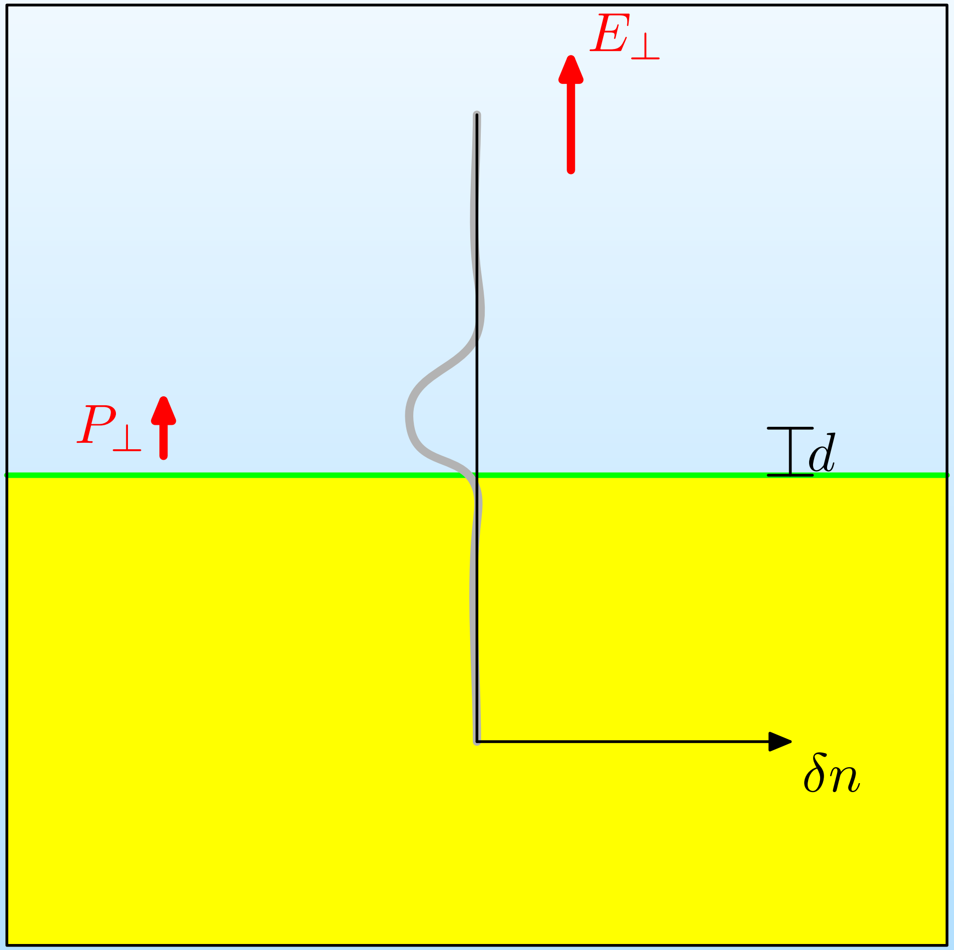
Nonlinear Surface Response: a



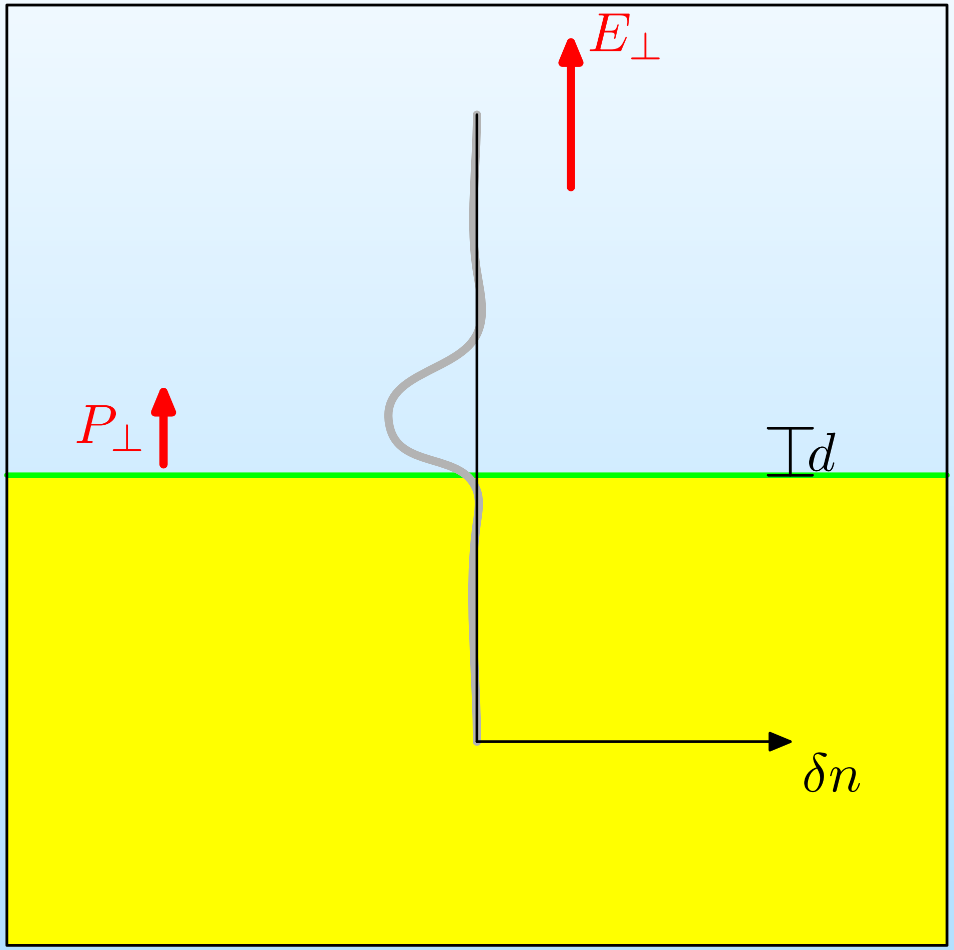
Nonlinear Surface Response: a



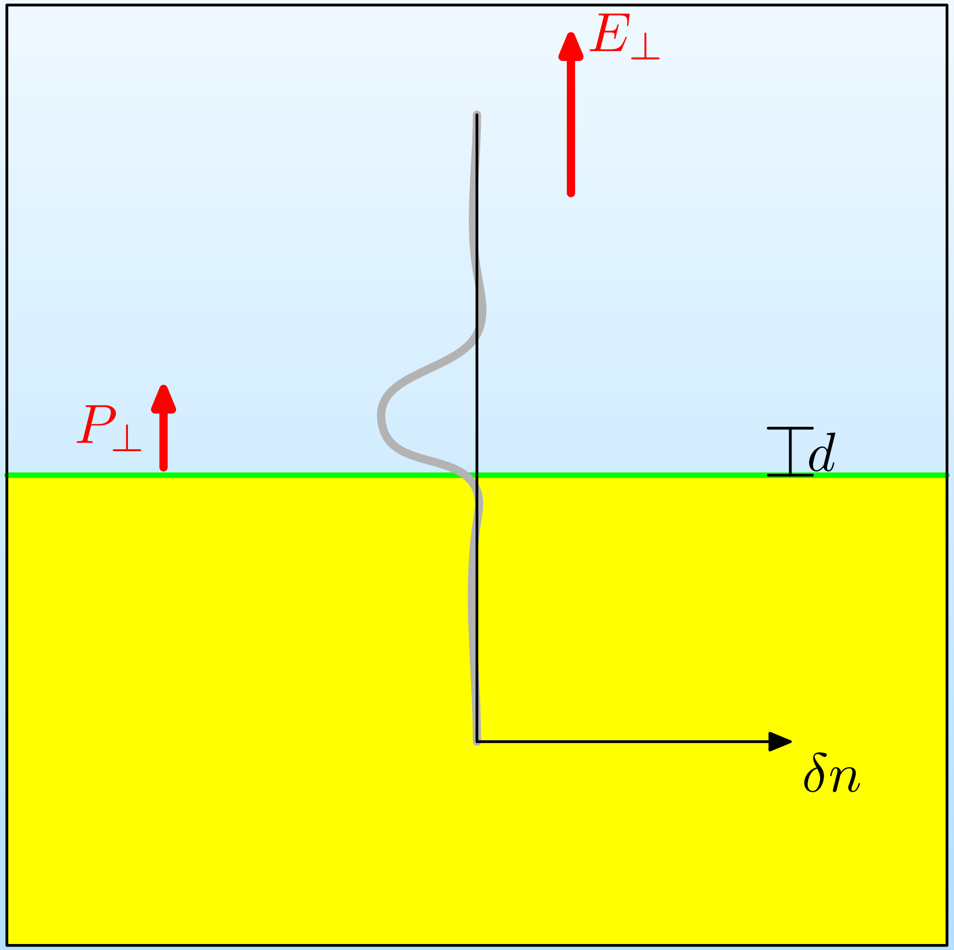
Nonlinear Surface Response: a



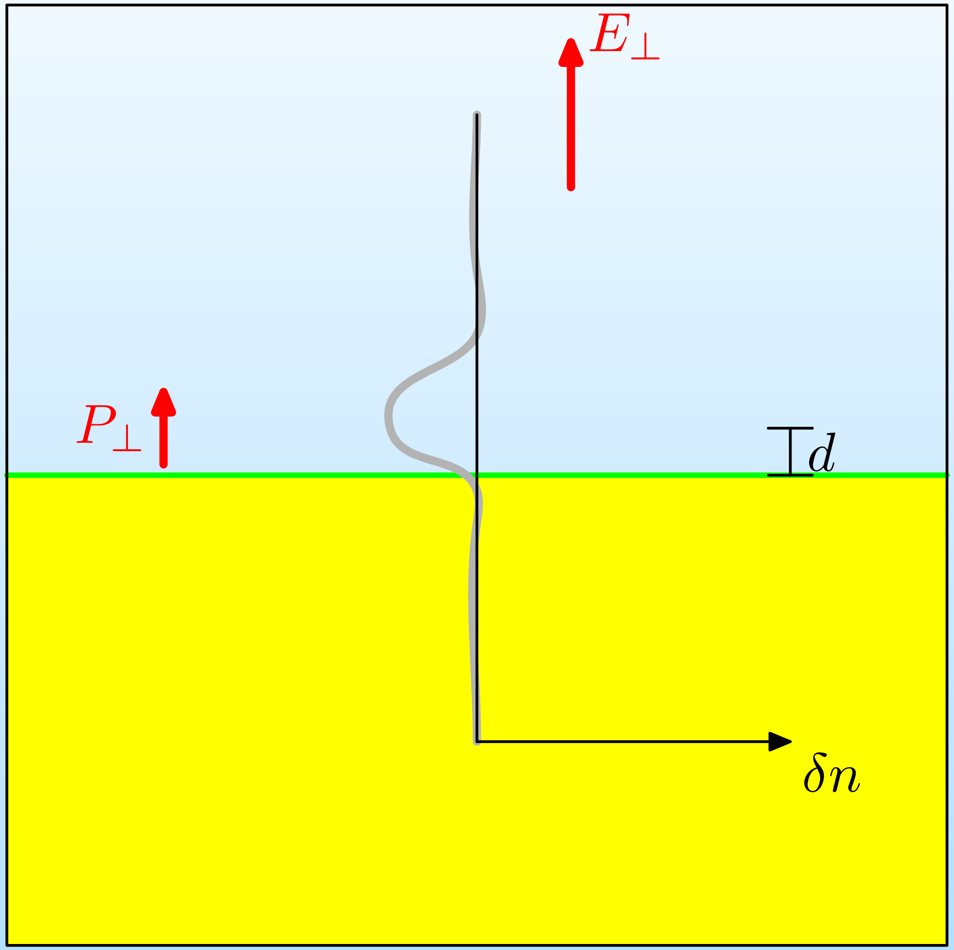
Nonlinear Surface Response: a



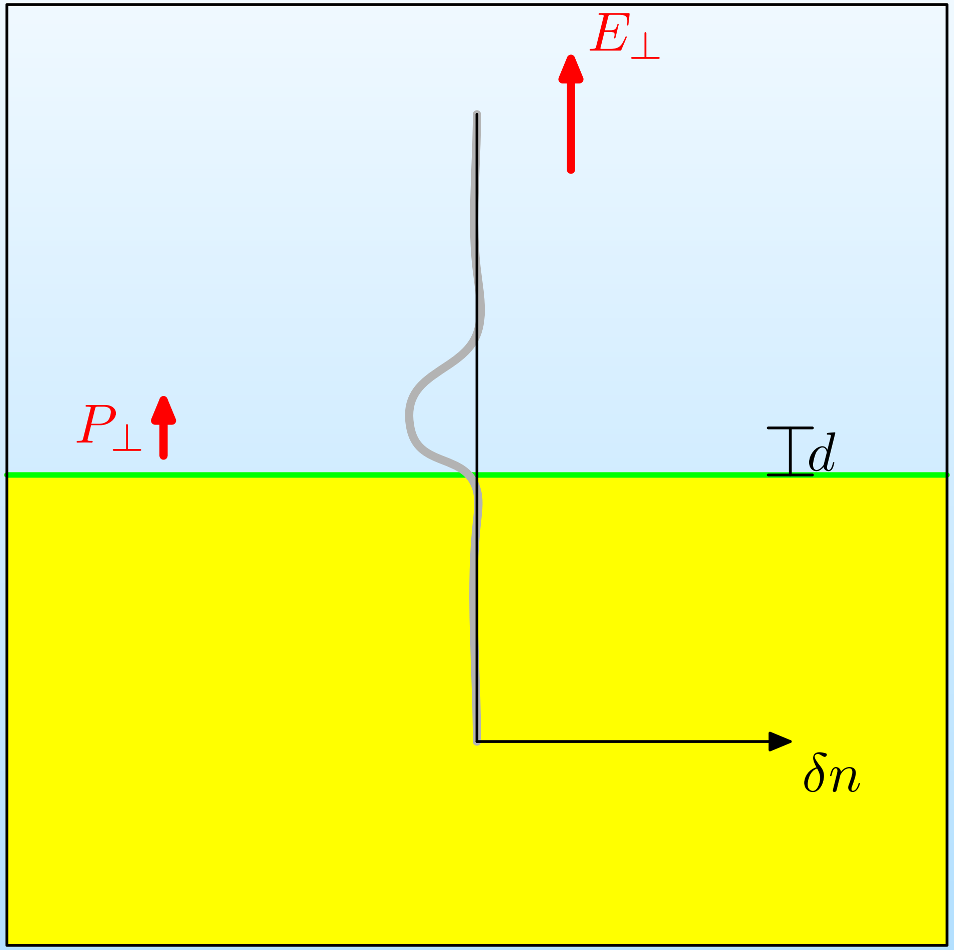
Nonlinear Surface Response: a



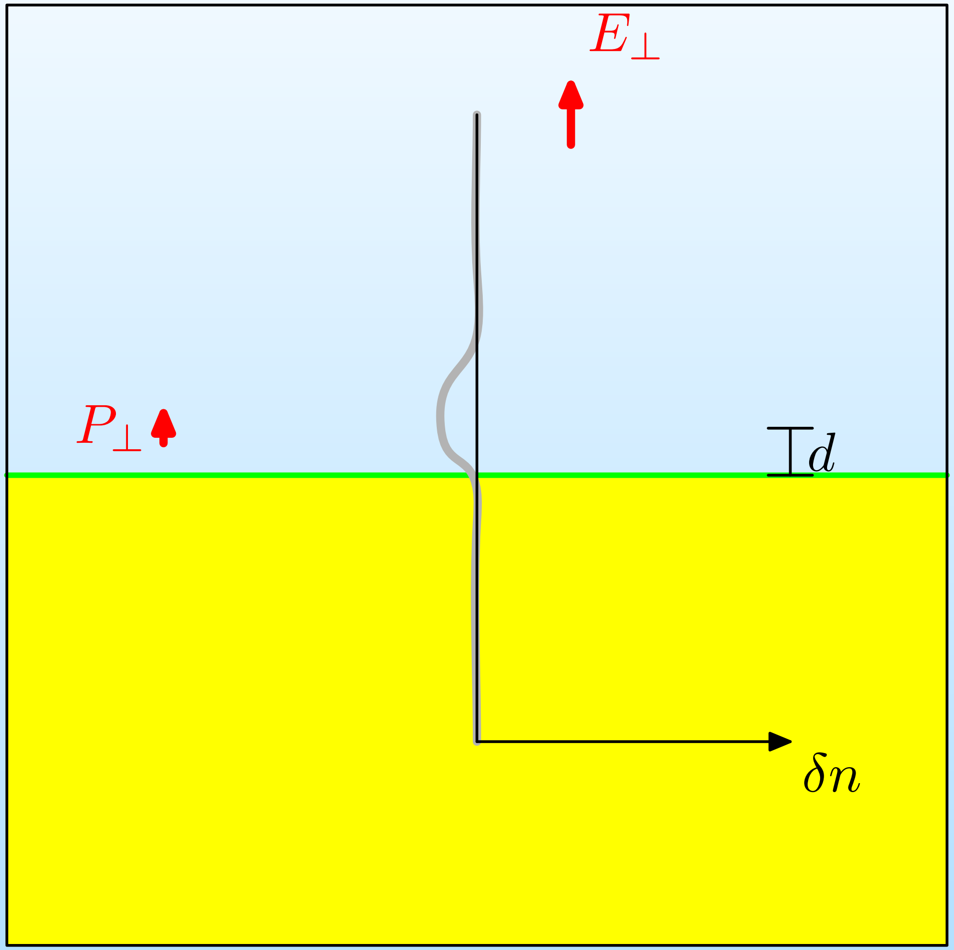
Nonlinear Surface Response: a



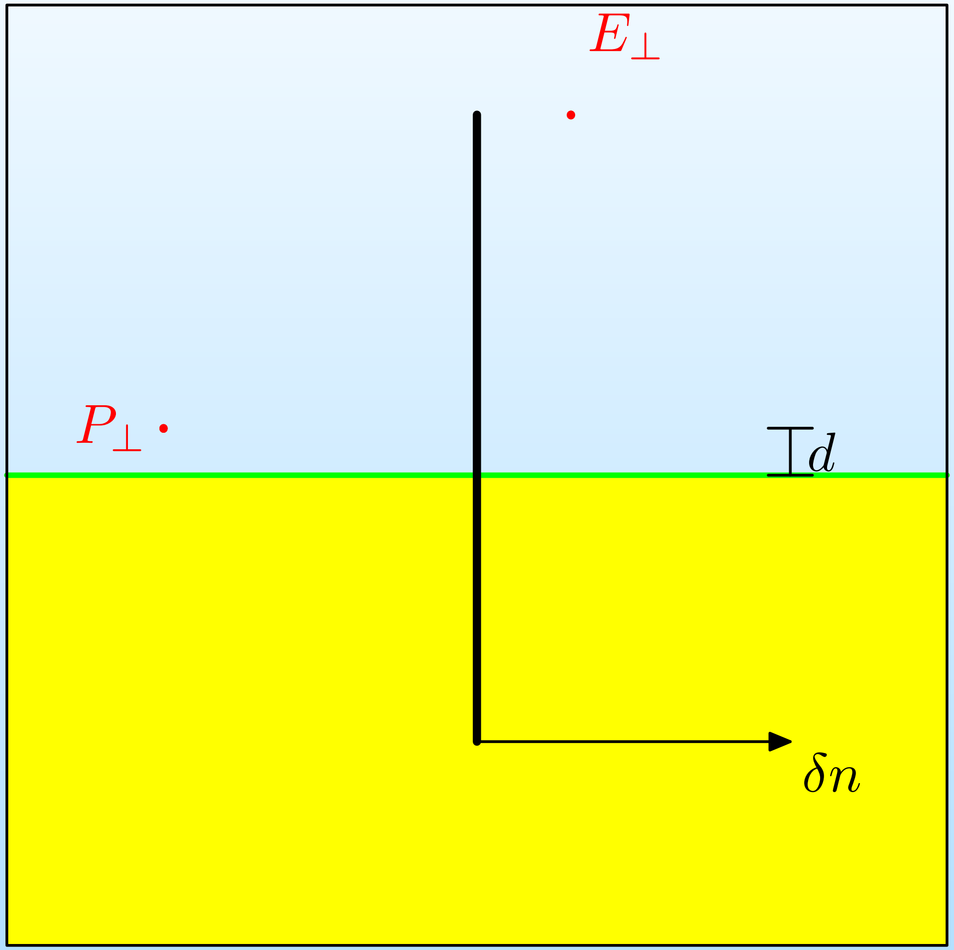
Nonlinear Surface Response: a



Nonlinear Surface Response: a



Nonlinear Surface Response: a



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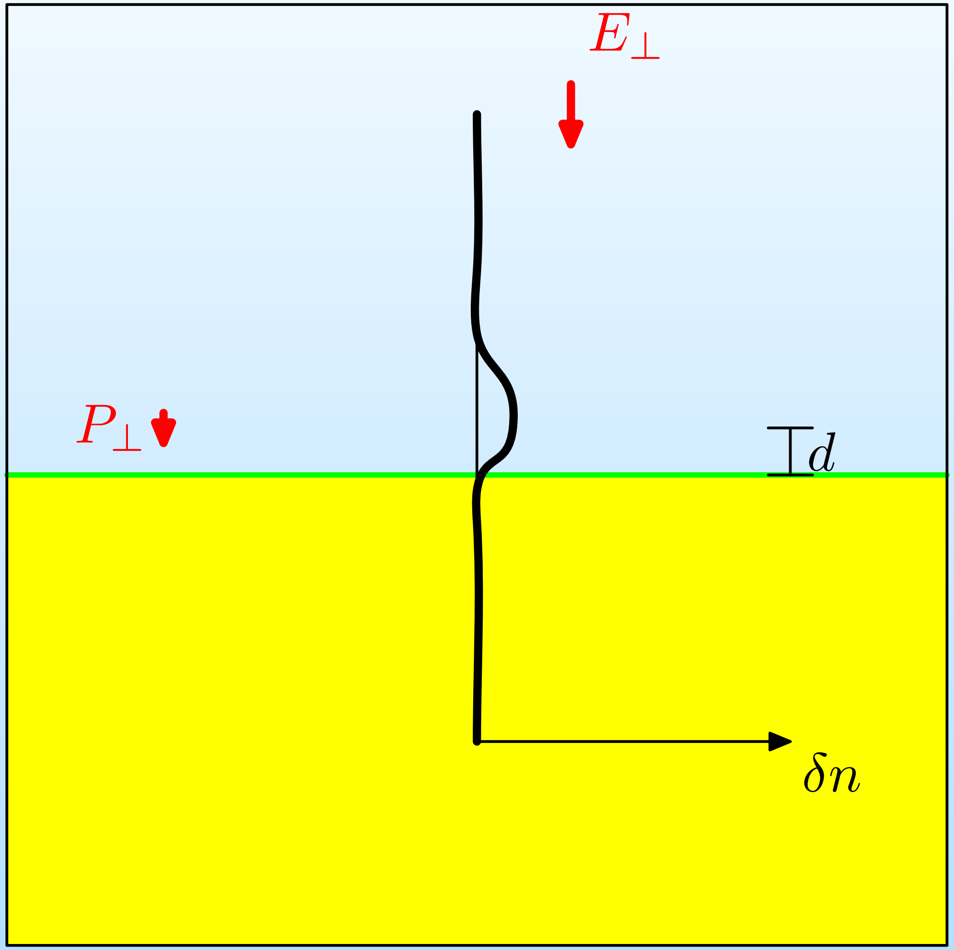
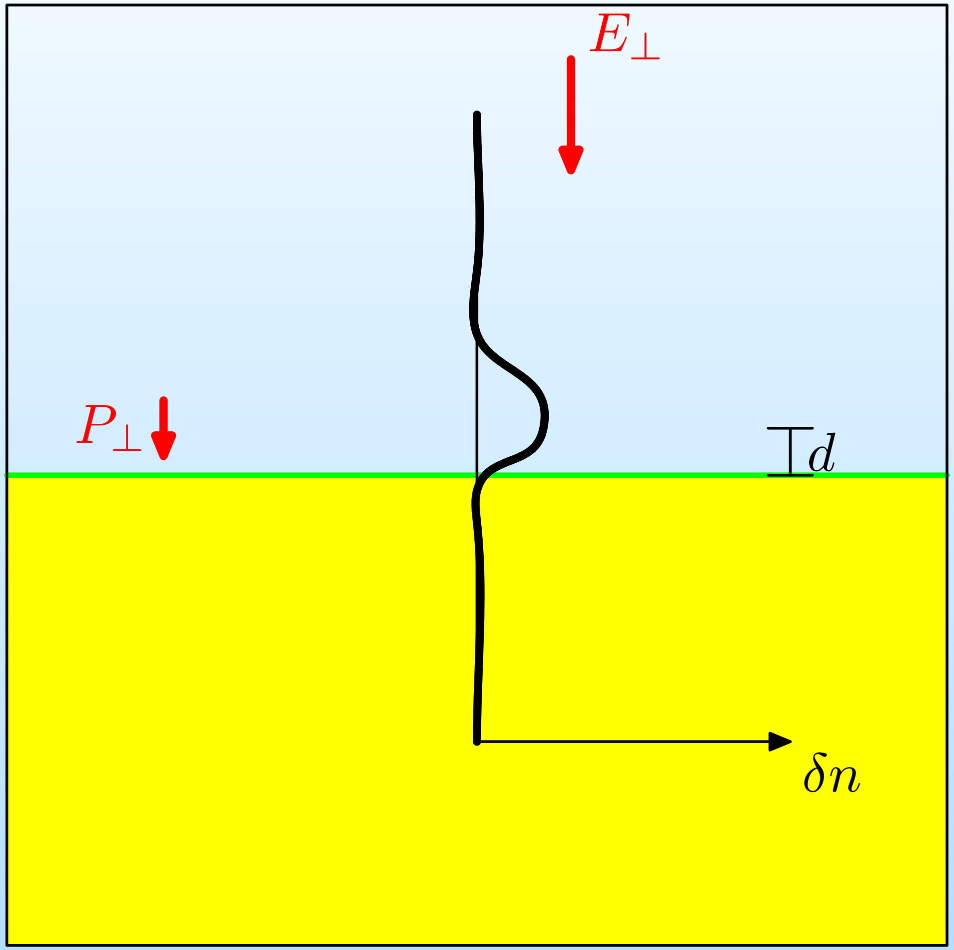
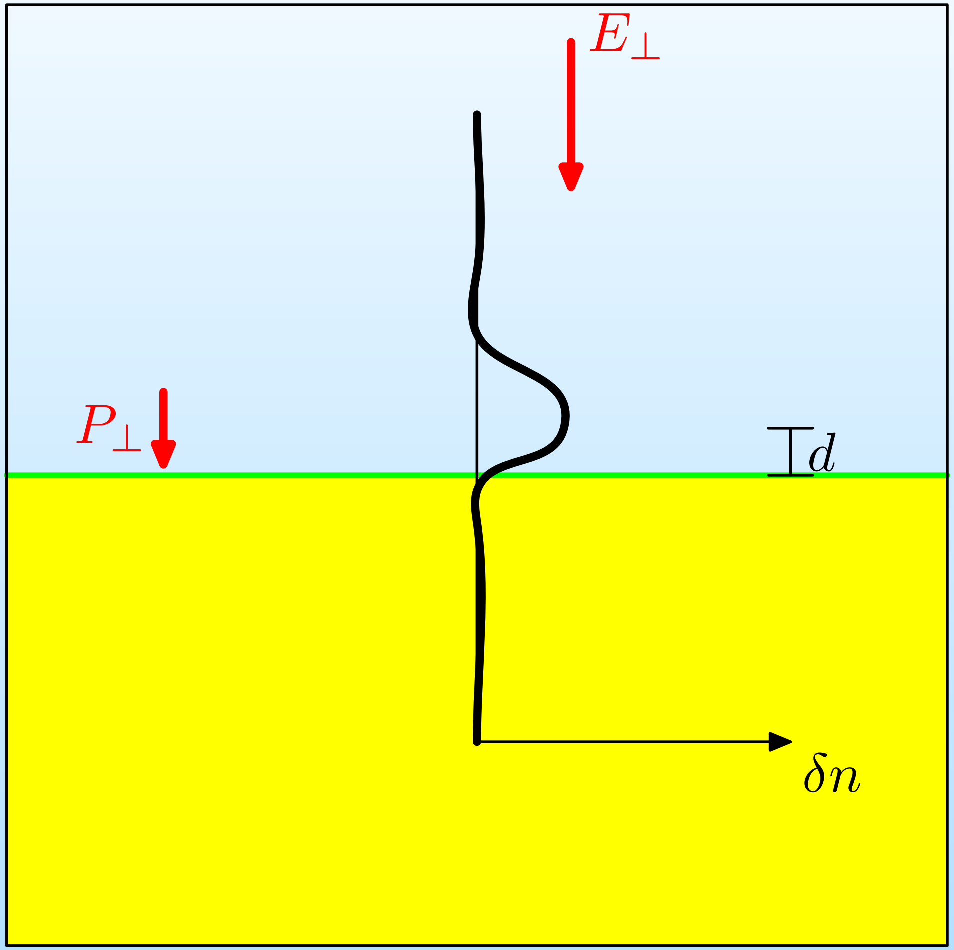


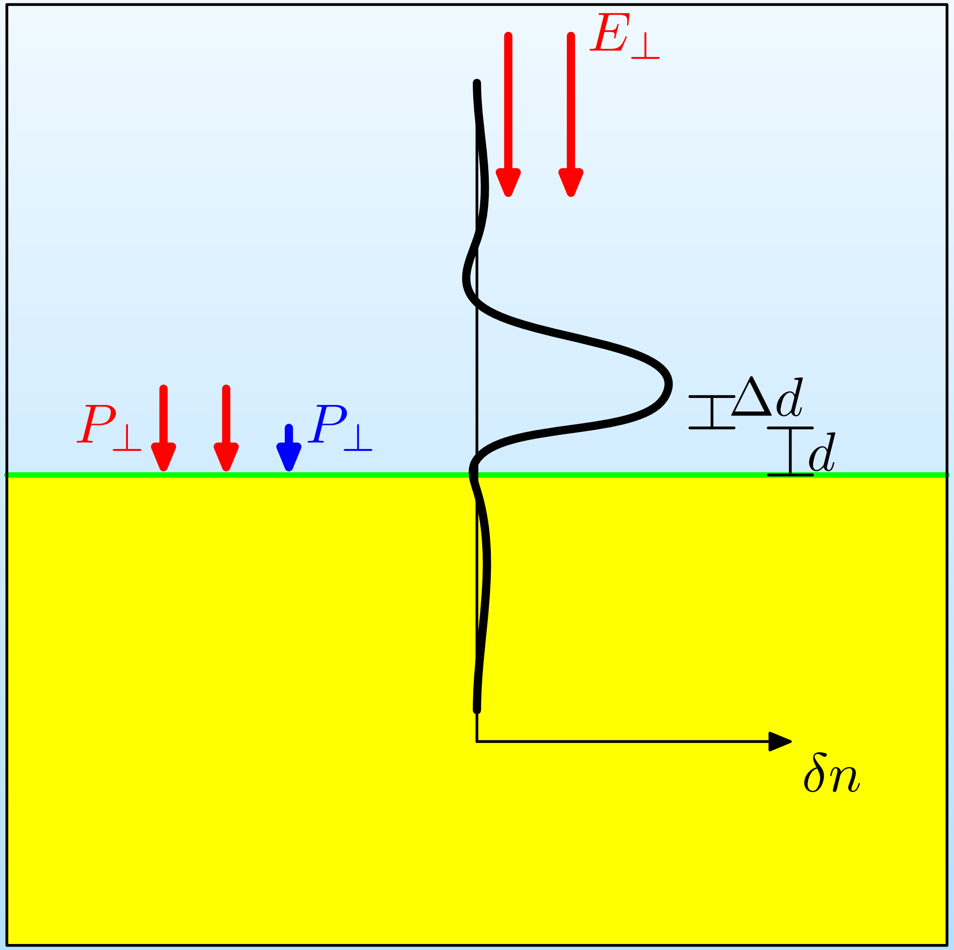
Nonlinear Surface Response: a



Nonlinear Surface Response: a

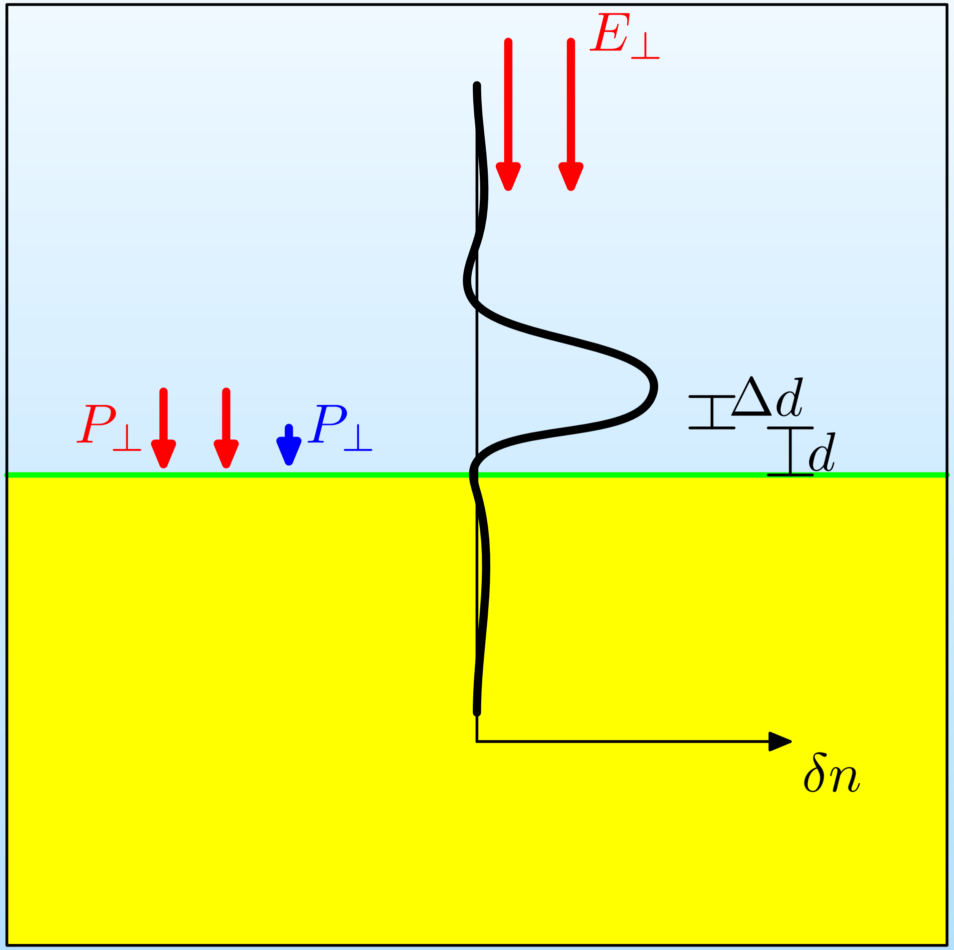


Nonlinear Surface Response: a



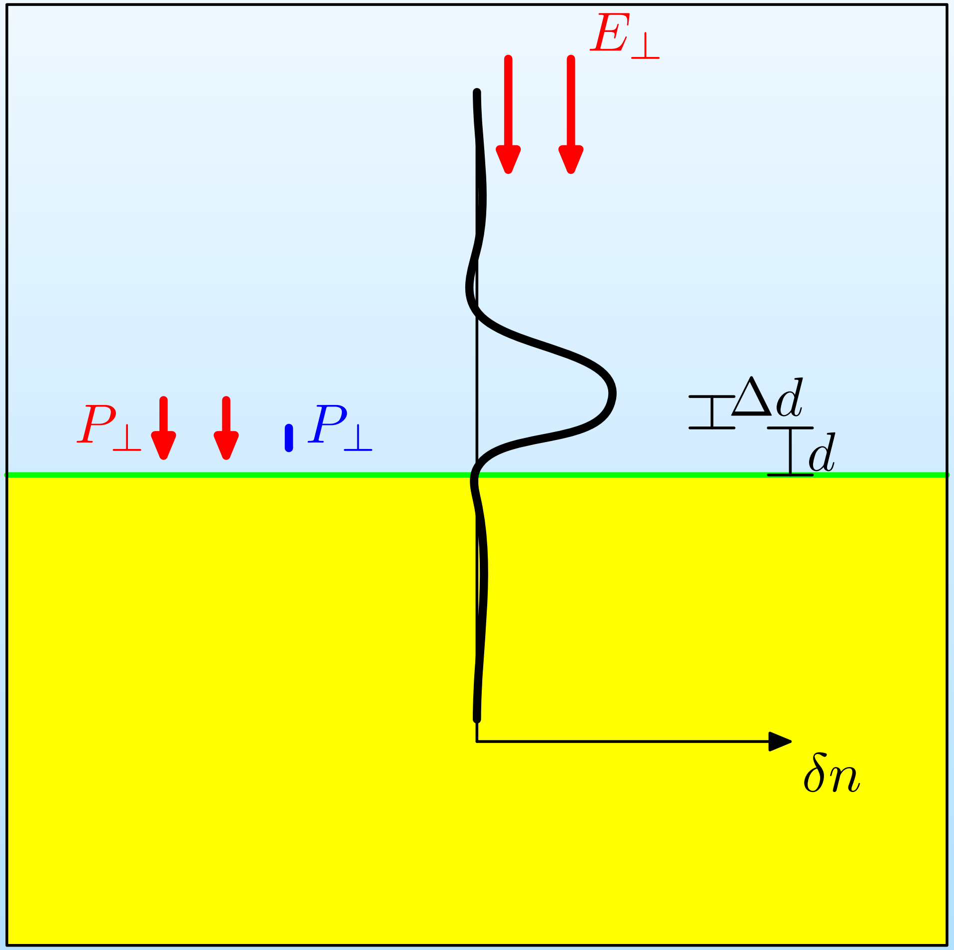
$$\chi_{\perp\perp\perp} \propto a \propto \Delta d$$

Nonlinear Surface Response: a



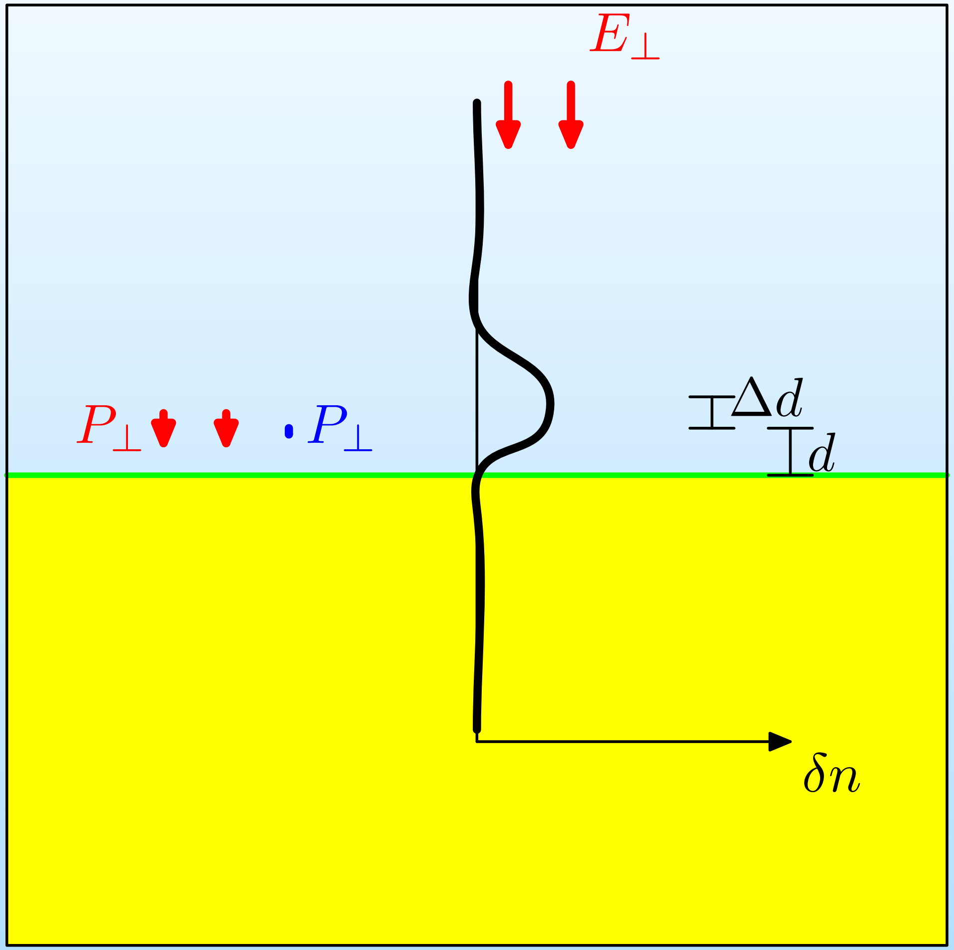
$$\chi_{\perp\perp\perp} \propto a \propto \Delta d$$

Nonlinear Surface Response: a



$$\chi_{\perp\perp\perp} \propto a \propto \Delta d$$

Nonlinear Surface Response: a



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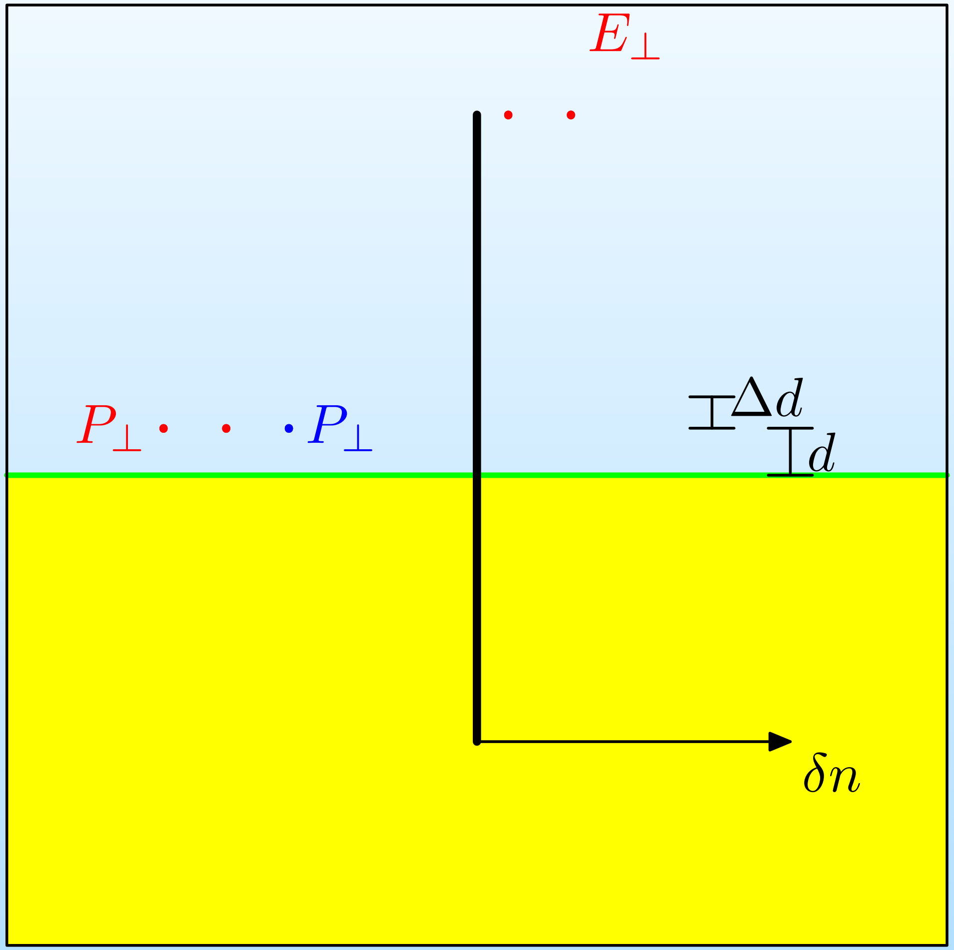
Nonlinear Surface Response: a



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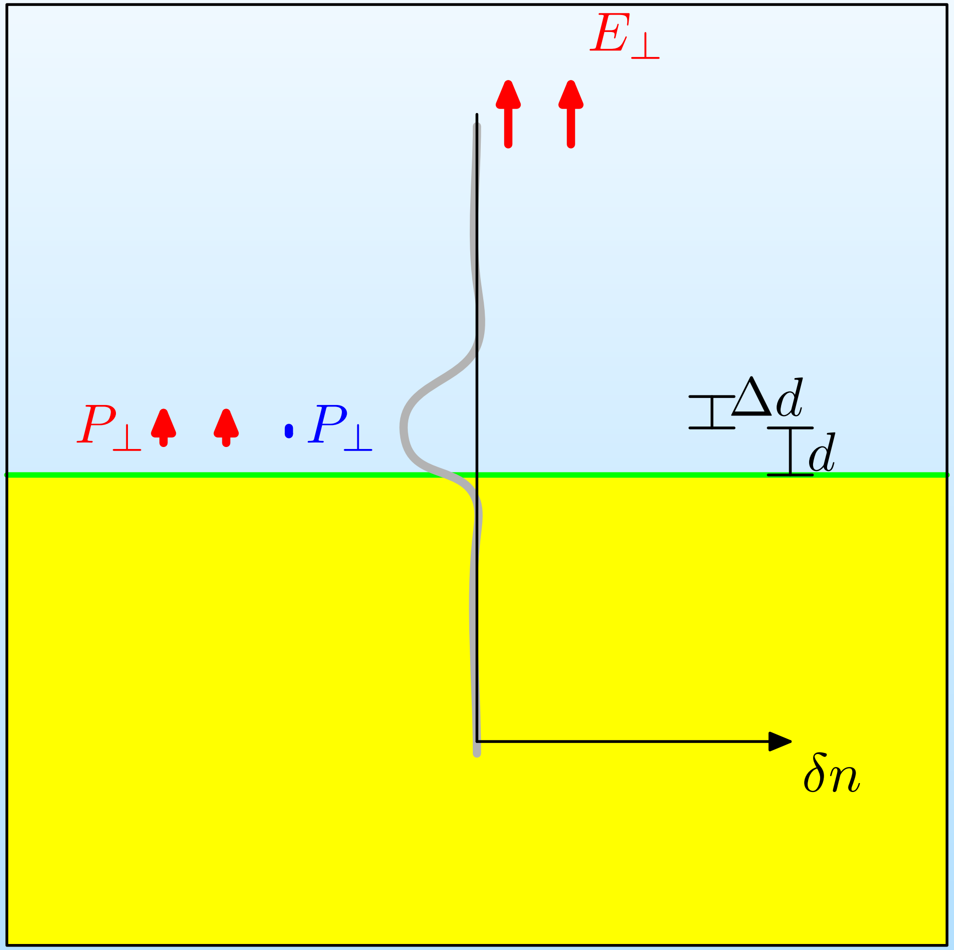

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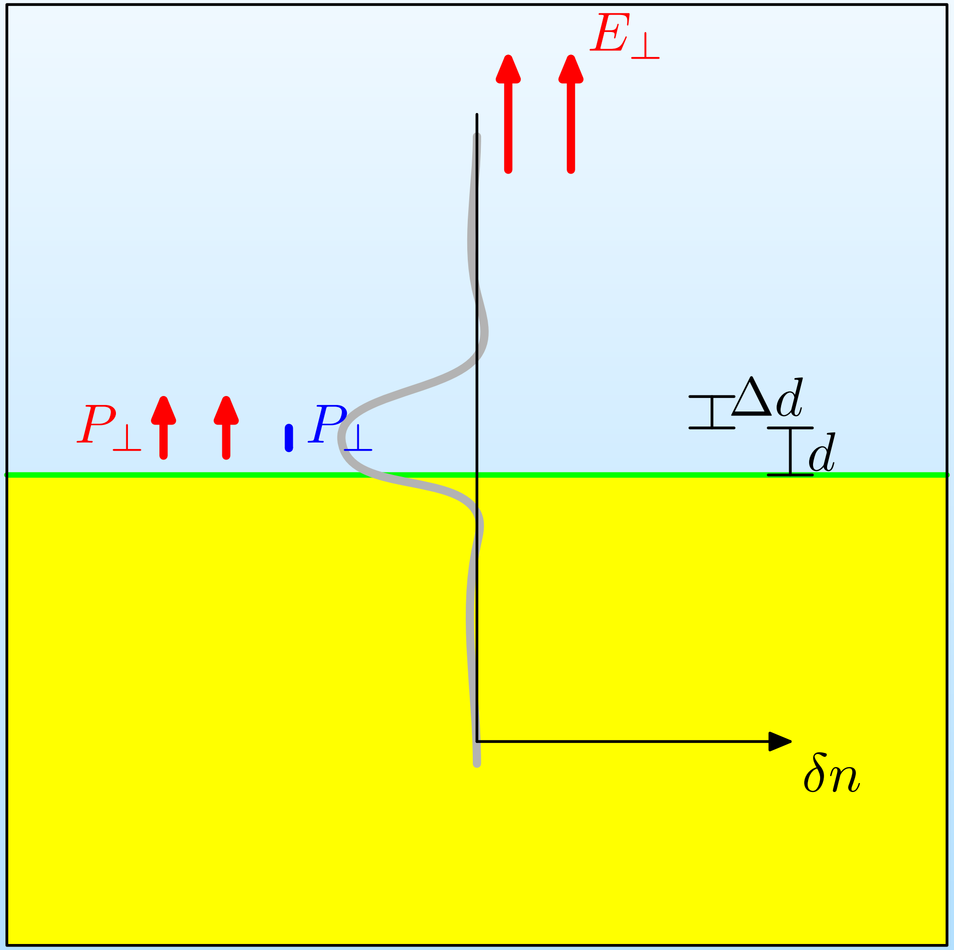

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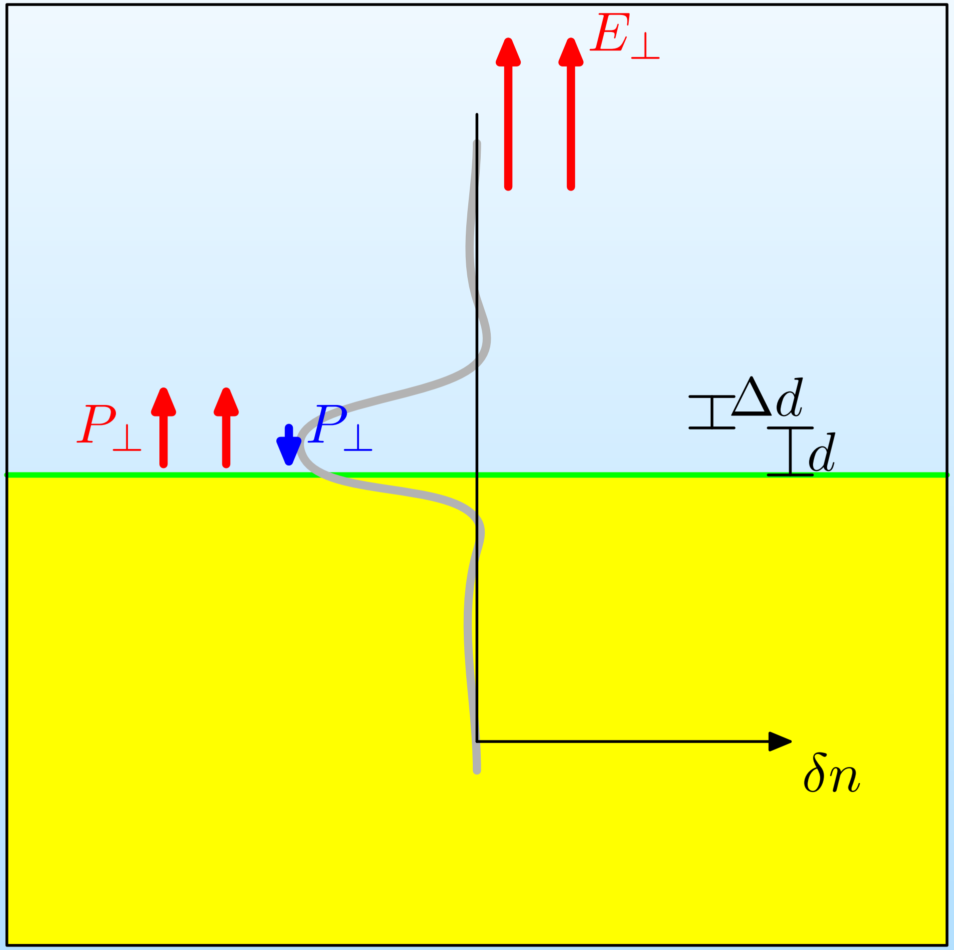

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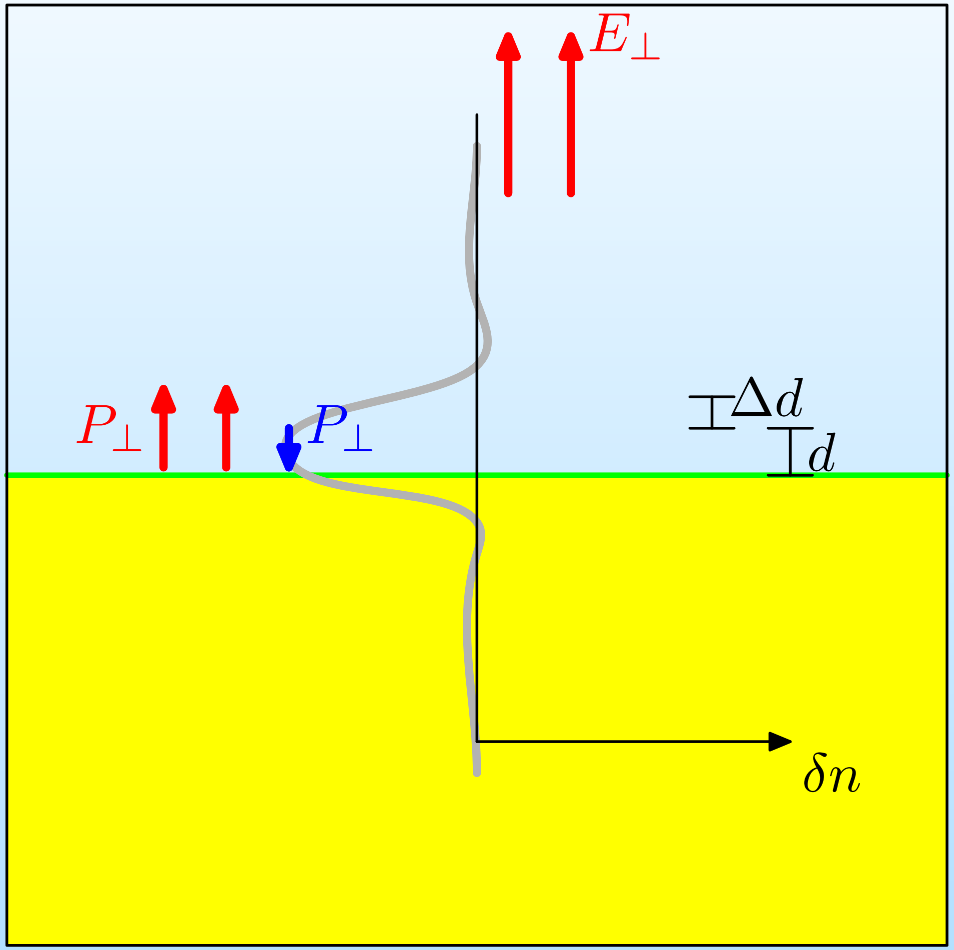

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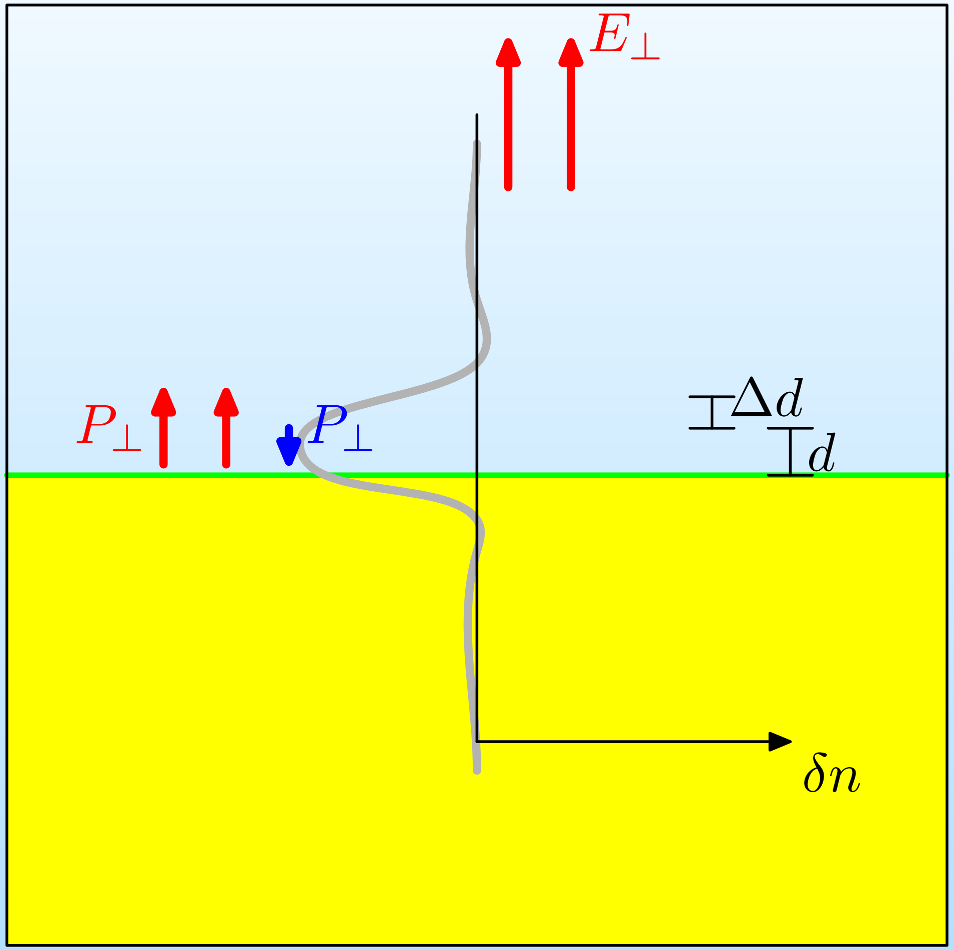
Nonlinear Surface Response: a



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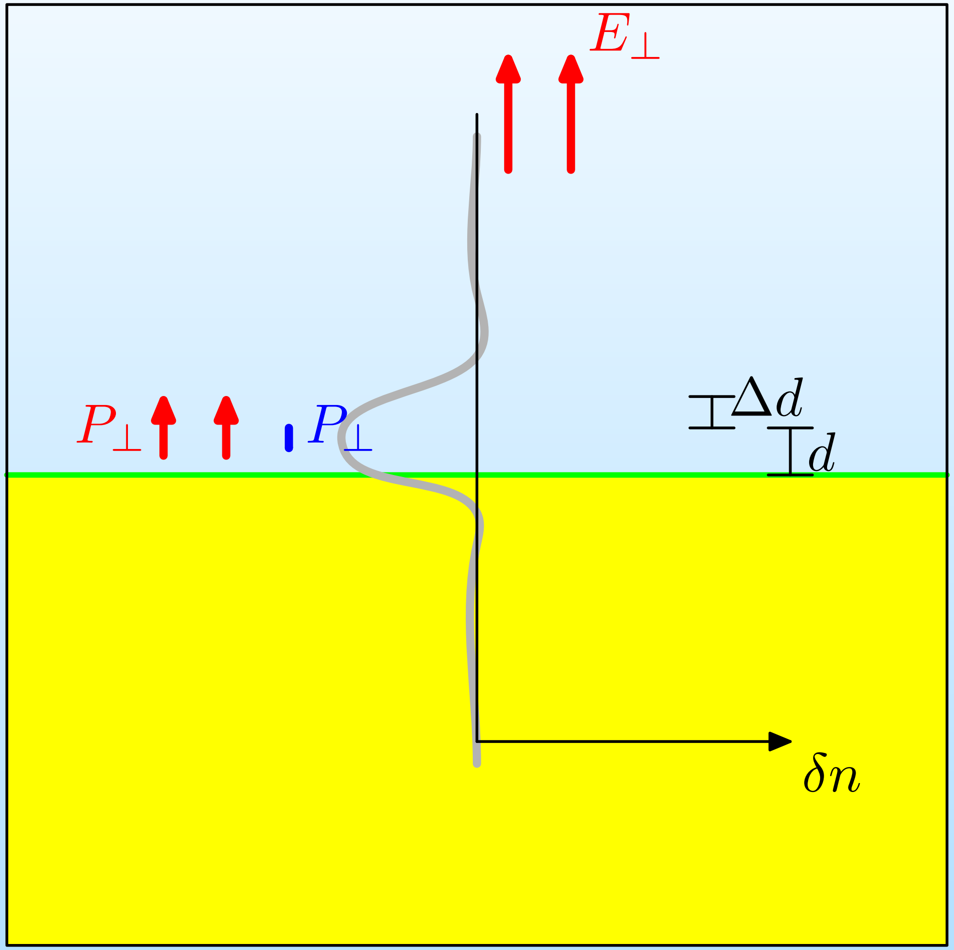

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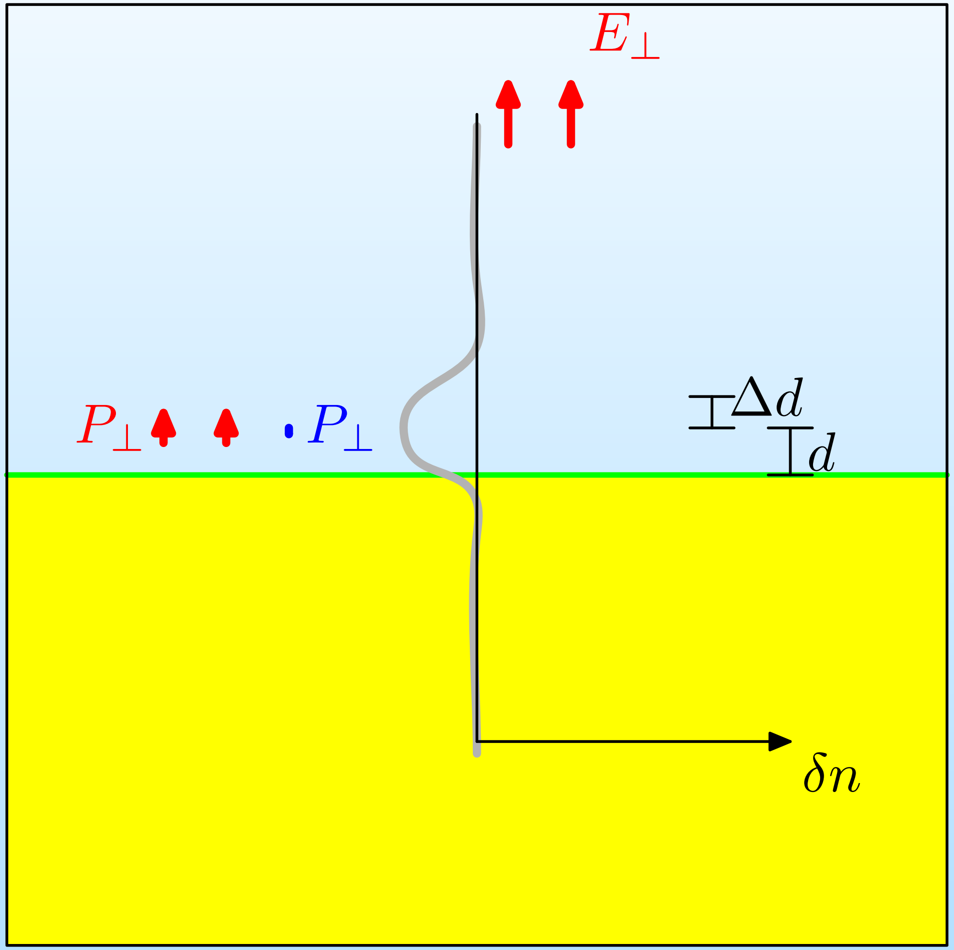
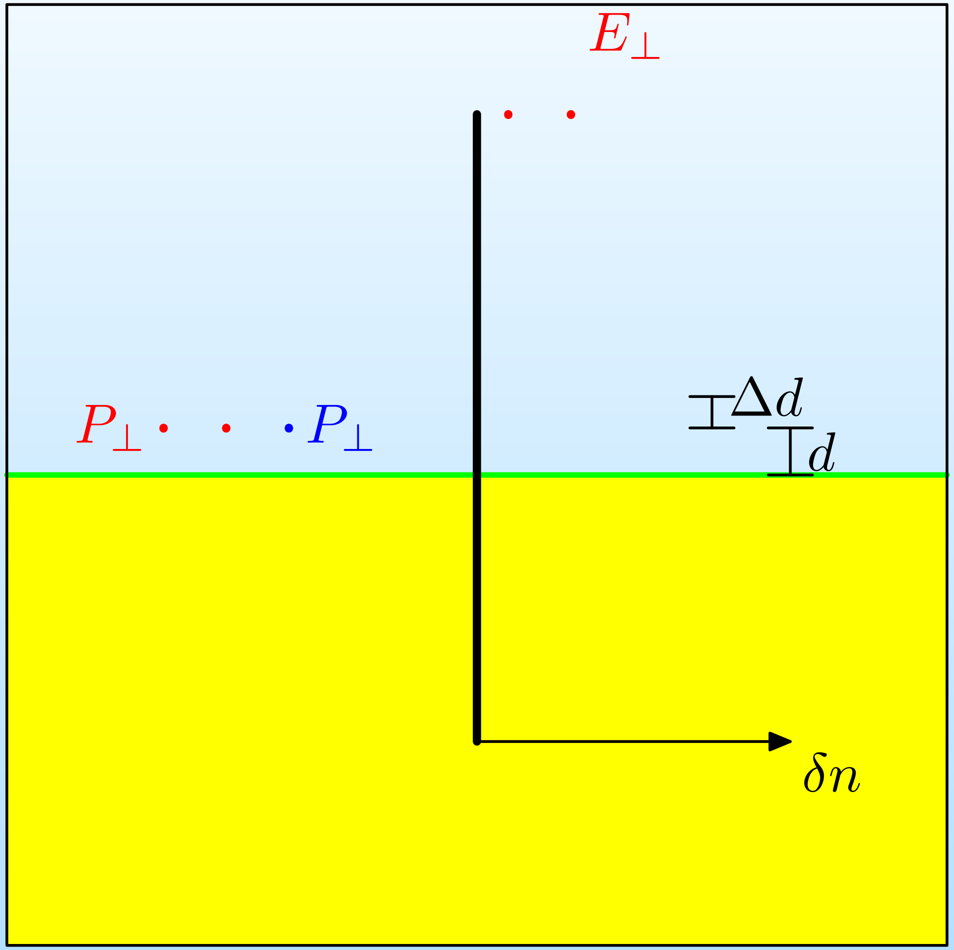


$$\chi_{\perp\perp\perp} \propto a \propto \Delta d$$

Nonlinear Surface Response: a



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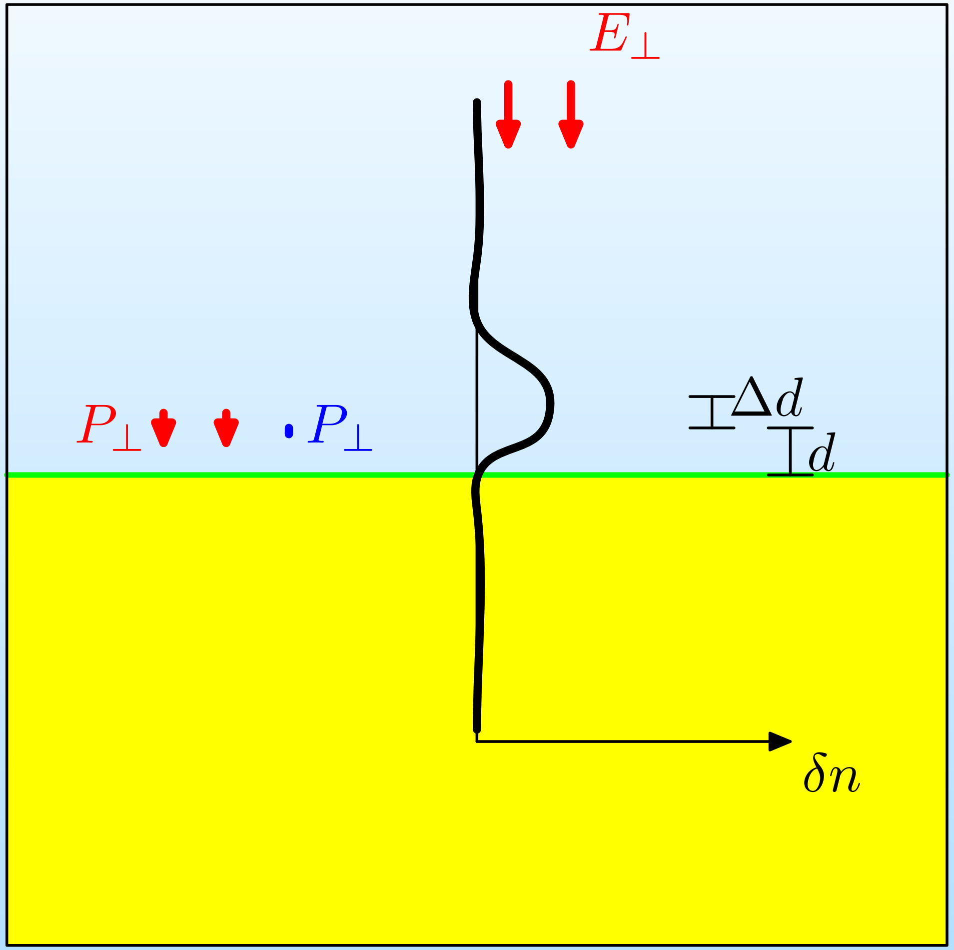
Nonlinear Surface Response: a



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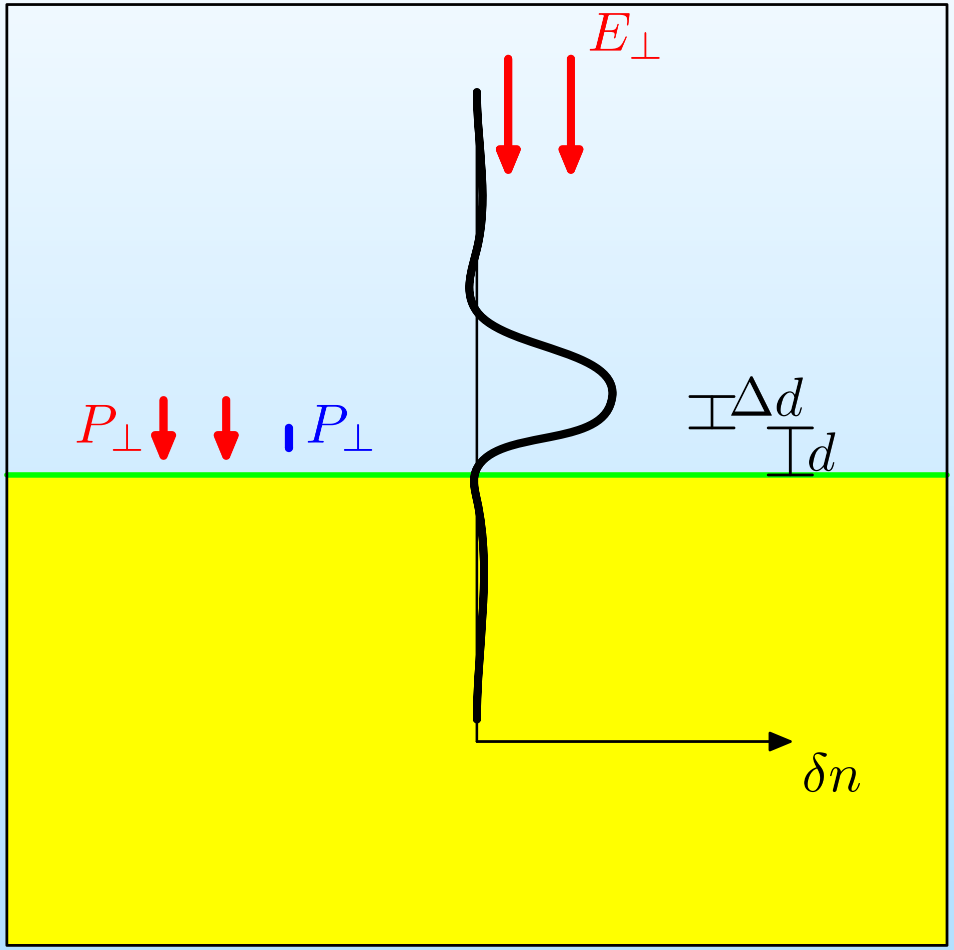
Nonlinear Surface Response: a



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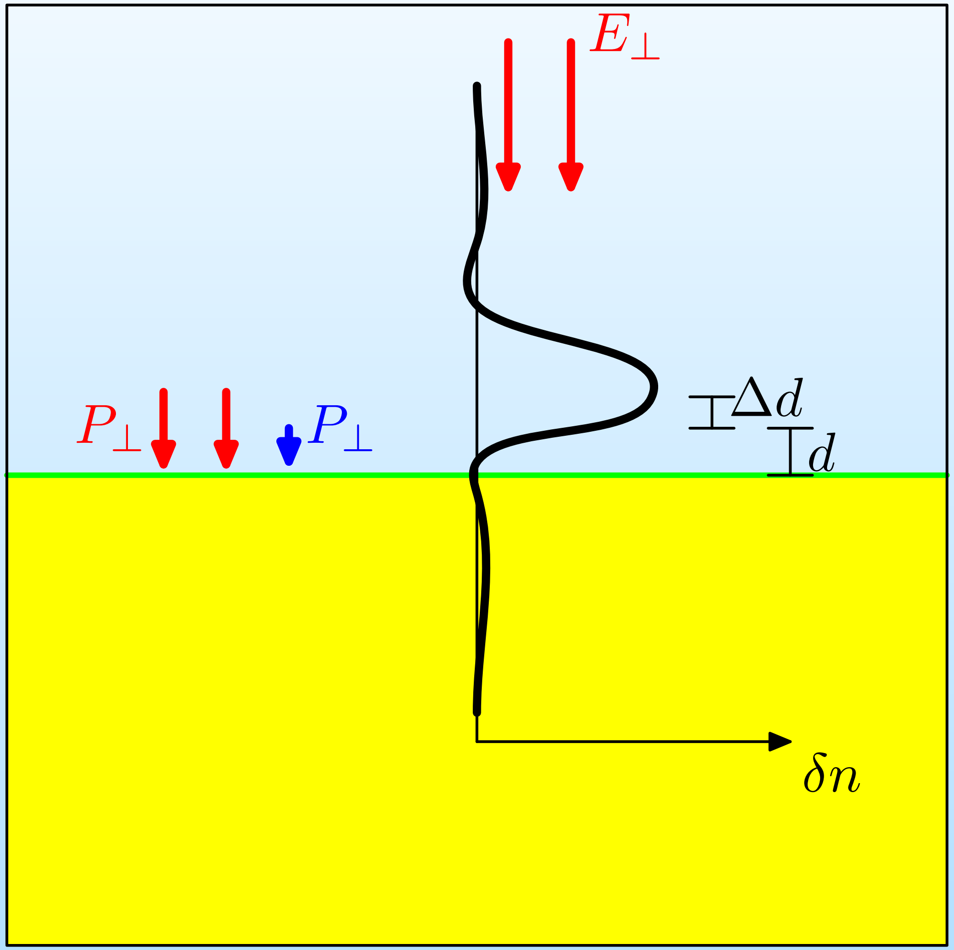
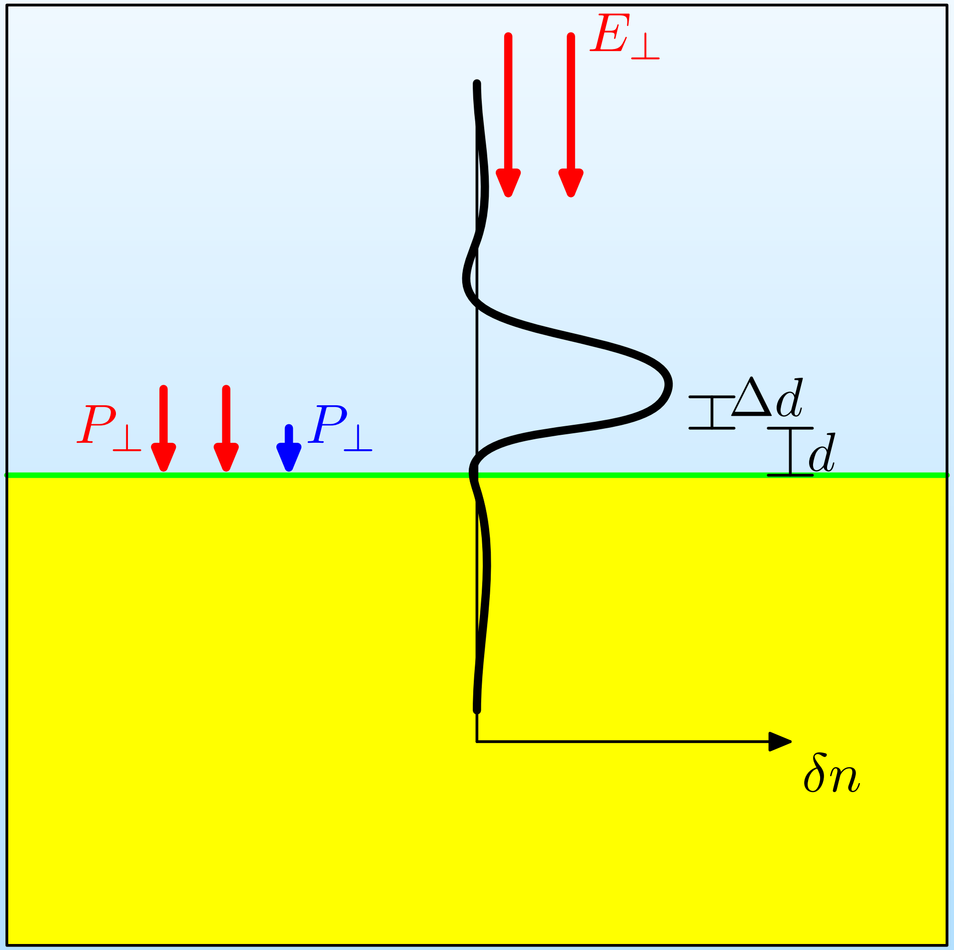


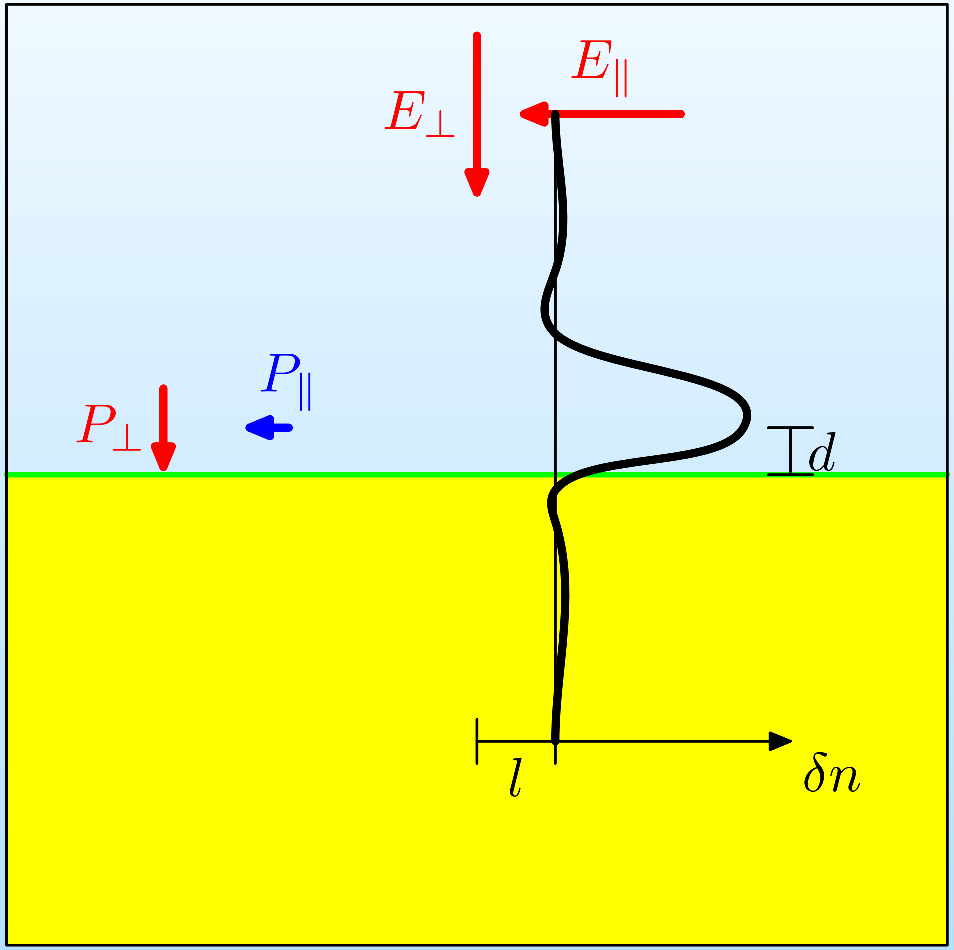
$$\chi_{\perp\perp\perp} \propto a \propto \Delta d$$

Nonlinear Surface Response: a



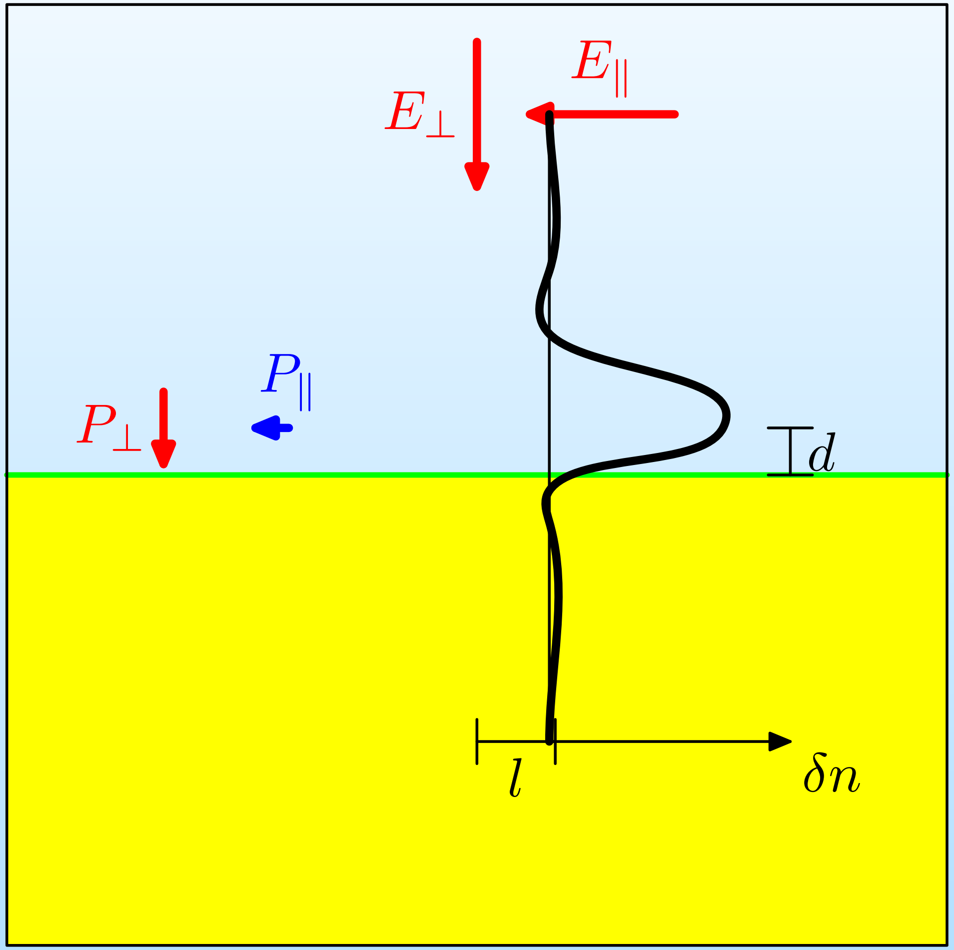
$$\chi_{\perp\perp\perp} \propto a \propto \Delta d$$

Nonlinear Surface Response: b



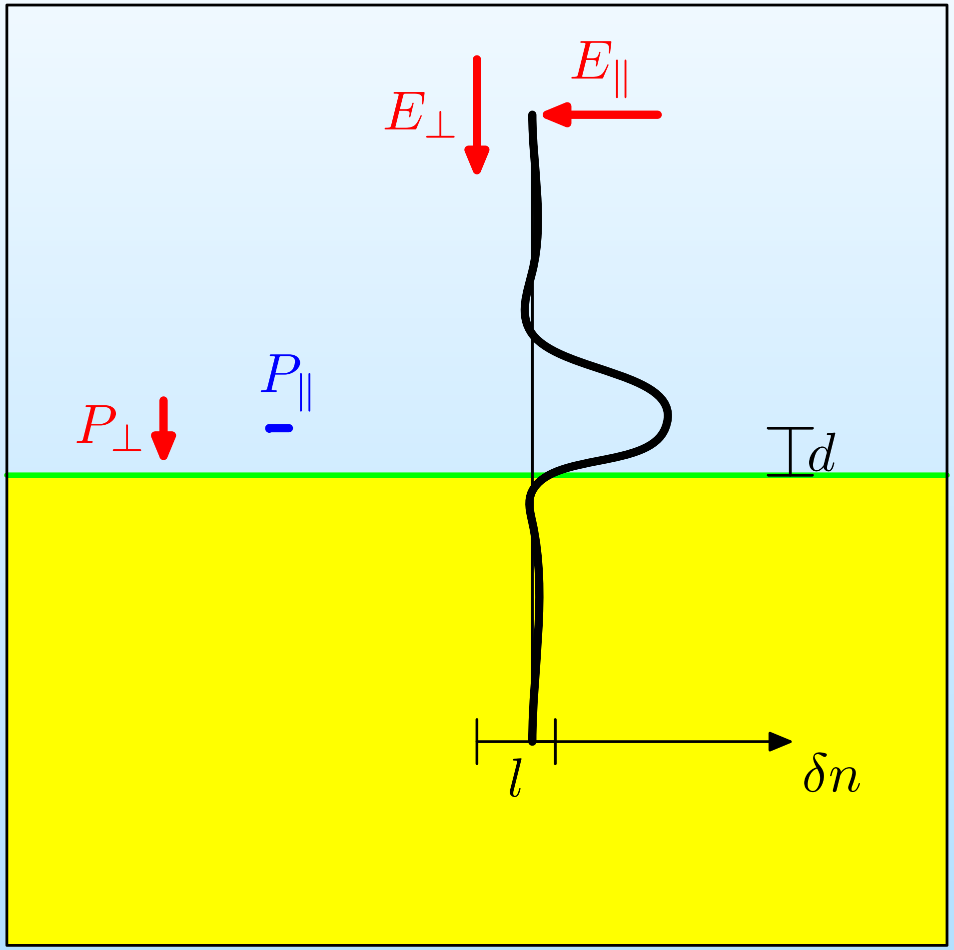
$$\chi_{\perp\parallel\parallel} \propto b \propto l$$

Nonlinear Surface Response: b



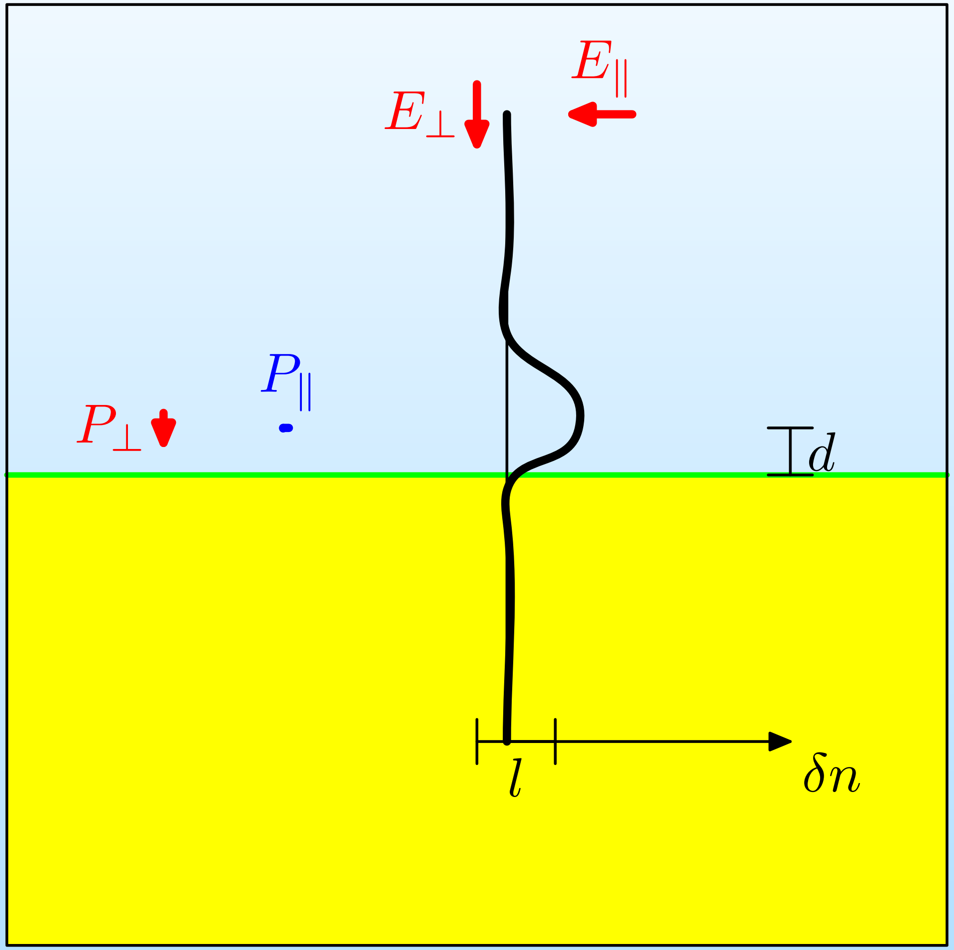
$$\chi_{\perp\parallel\parallel} \propto b \propto l$$

Nonlinear Surface Response: b



$$\chi_{\perp\parallel\parallel} \propto b \propto l$$

Nonlinear Surface Response: b



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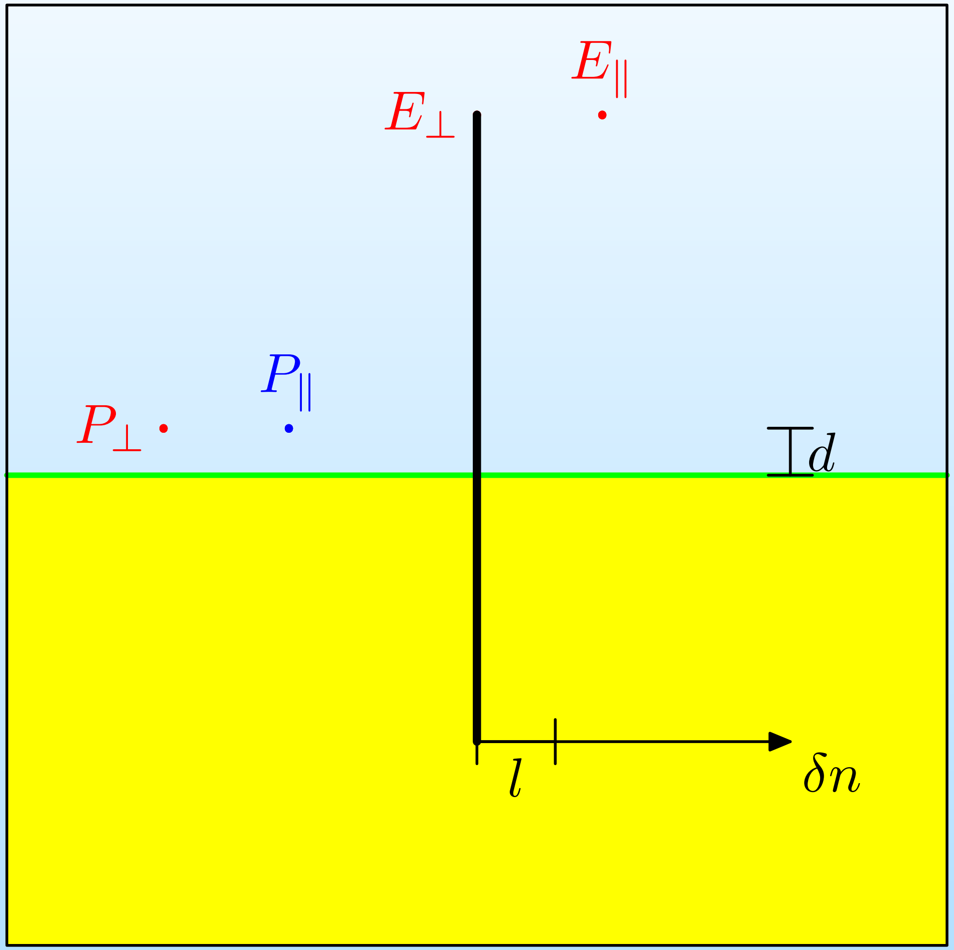
Nonlinear Surface Response: b



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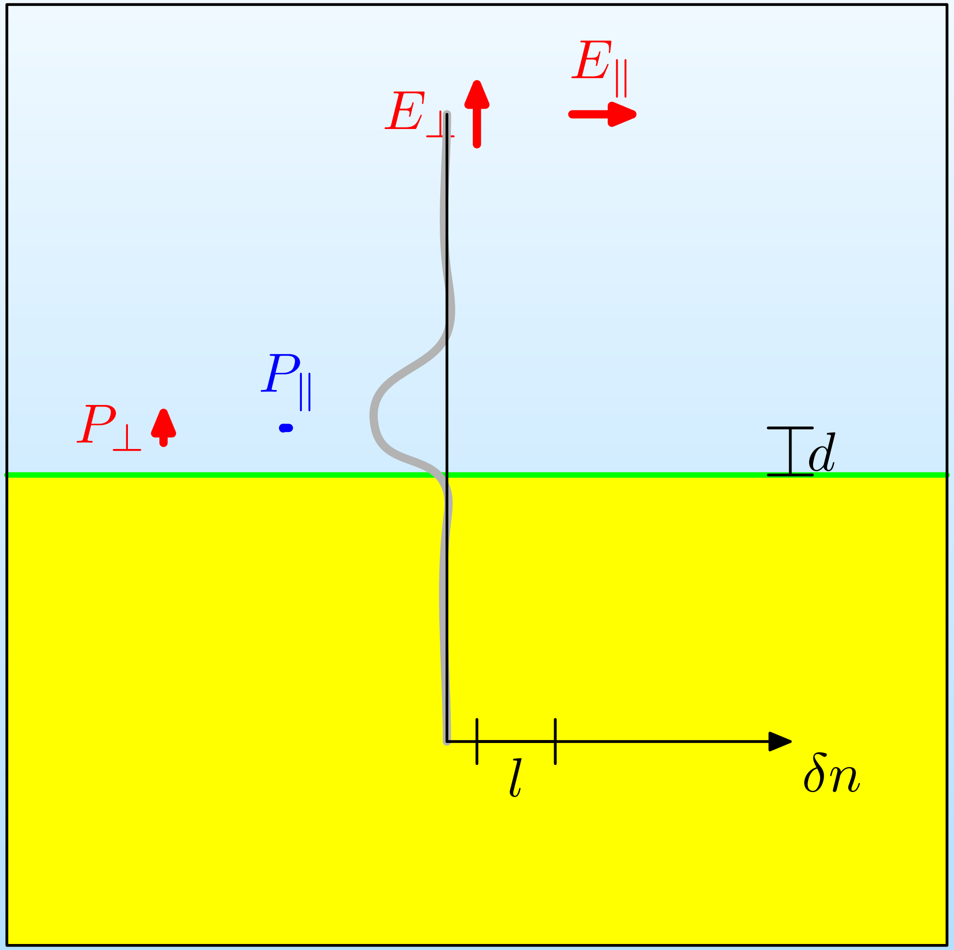
Nonlinear Surface Response: b



$$\chi_{\perp\parallel\parallel} \propto b \propto l$$

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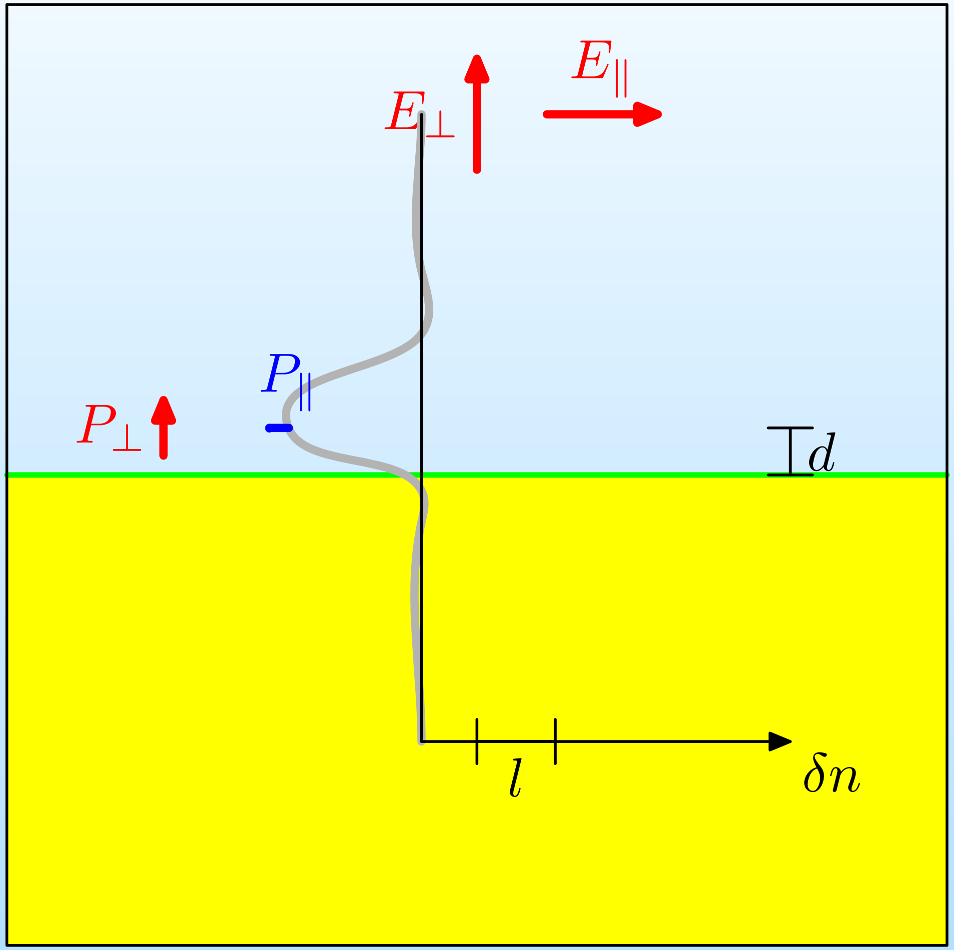

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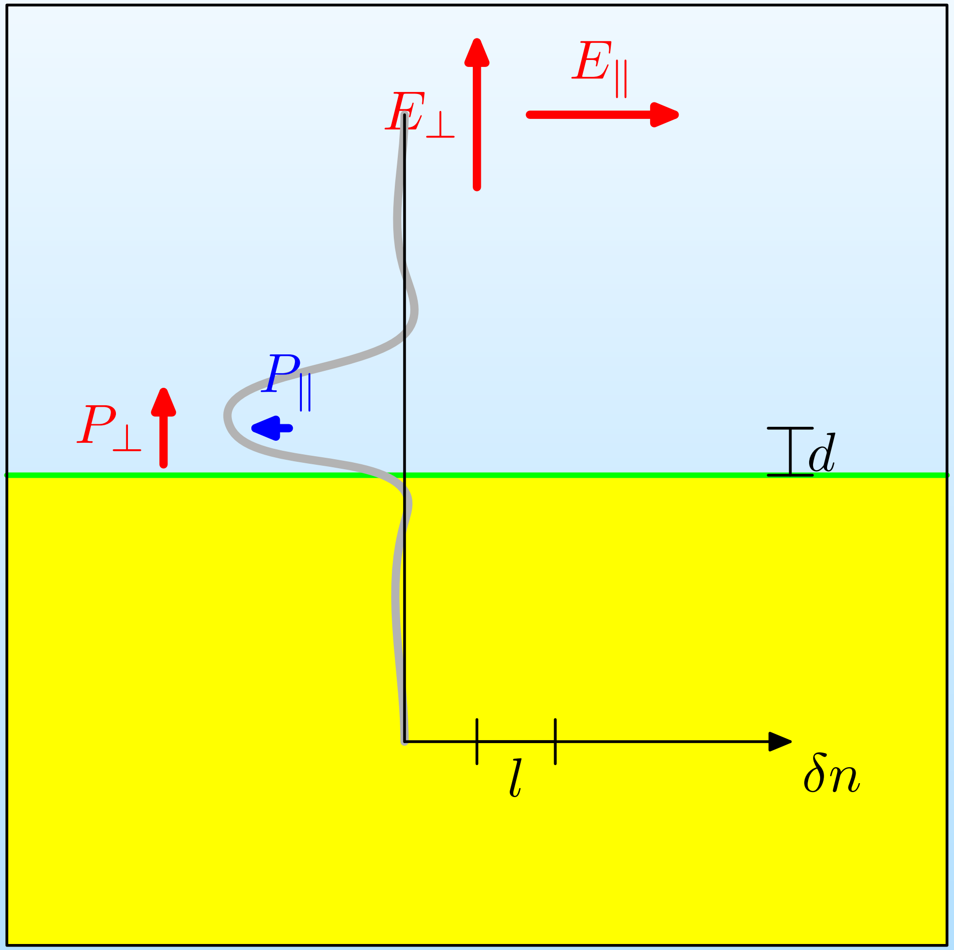

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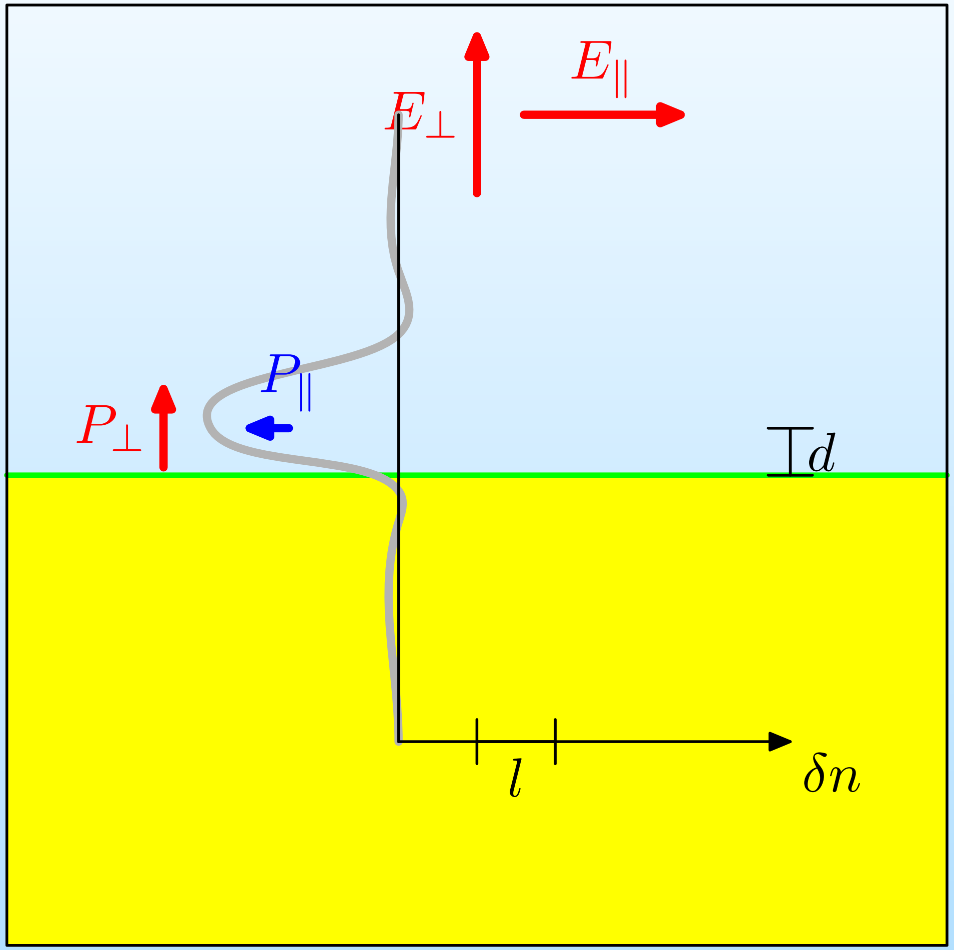
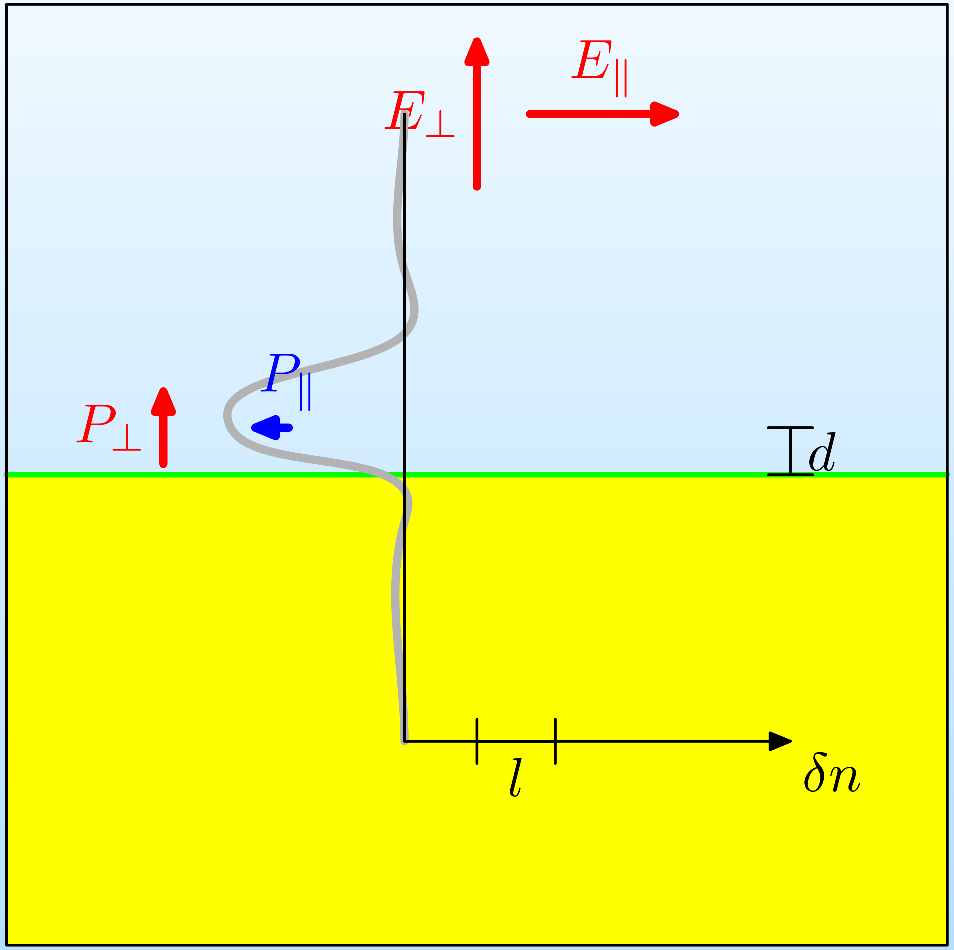


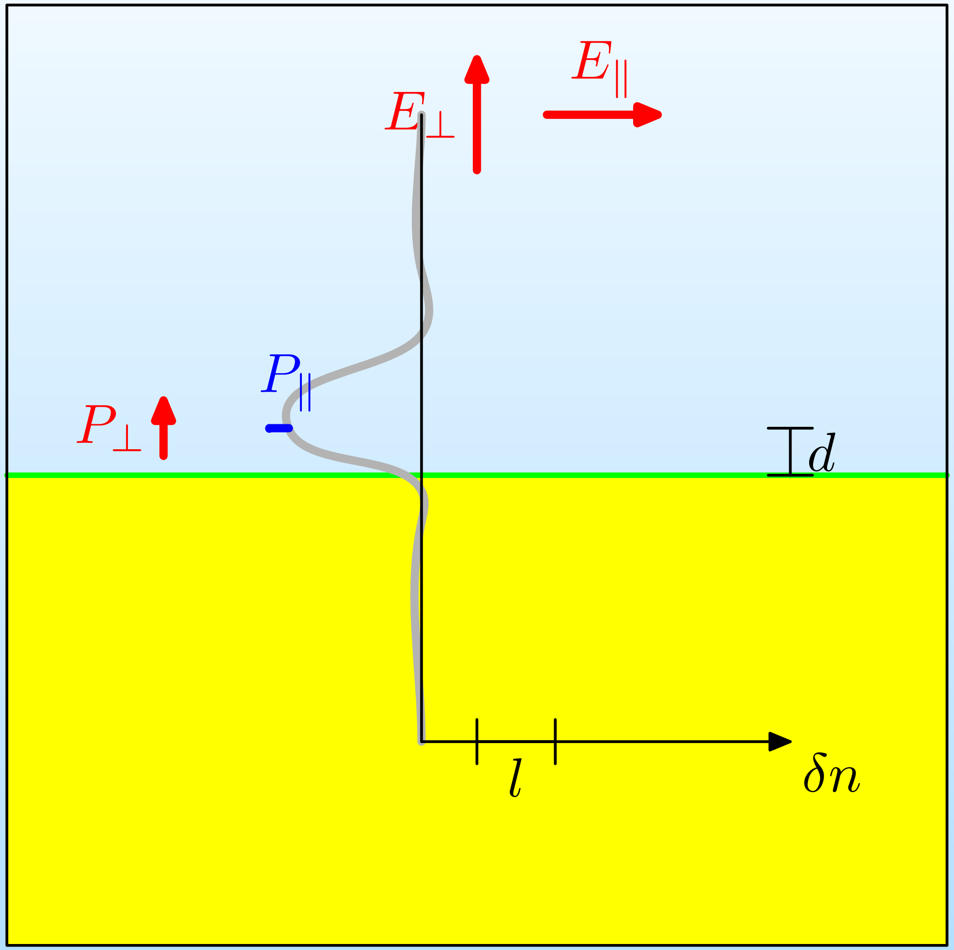
$$\chi_{\perp\parallel\parallel} \propto b \propto l$$

Nonlinear Surface Response: b



$$\chi_{\perp\|\|} \propto b \propto l$$

Nonlinear Surface Response: b



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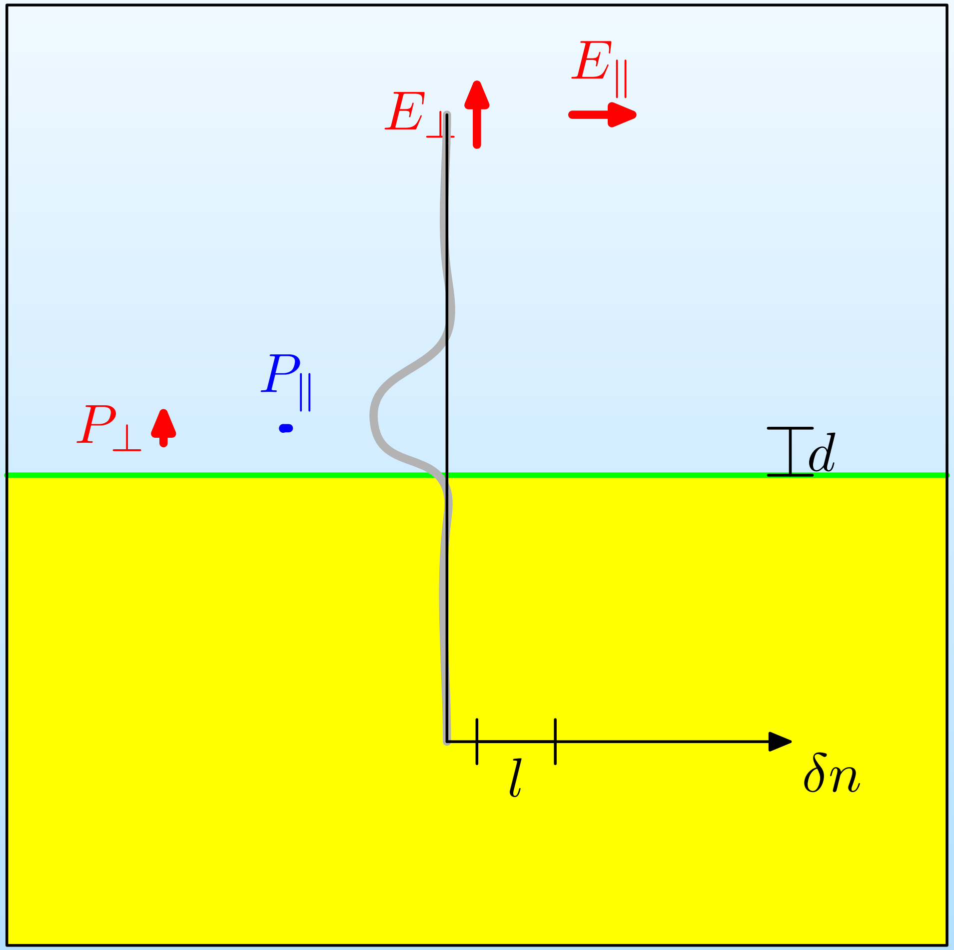
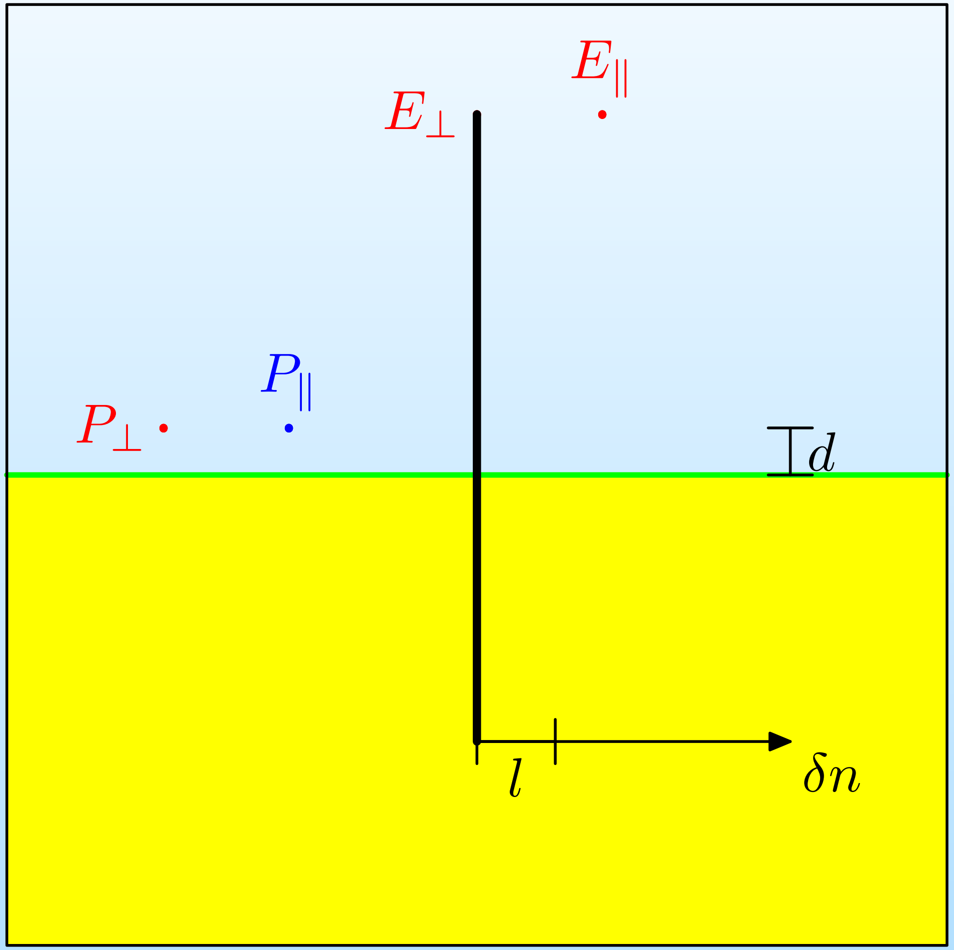
Nonlinear Surface Response: b



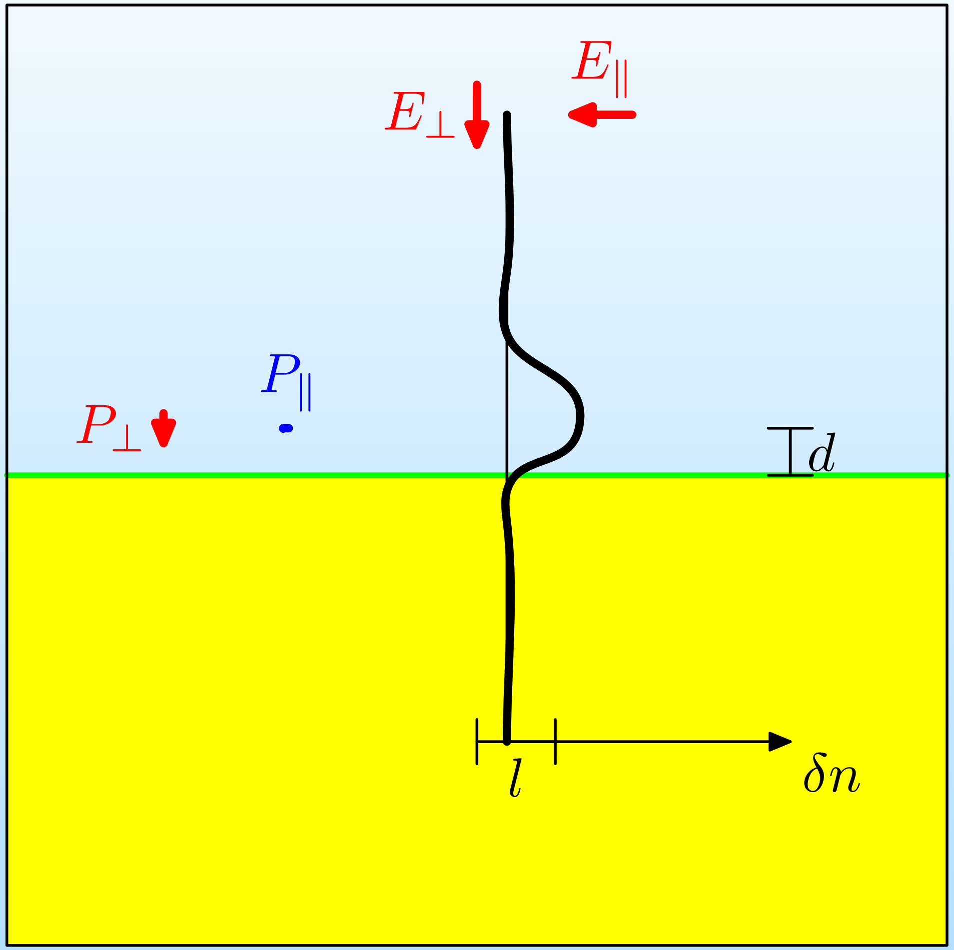
$$\chi_{\perp\parallel\parallel} \propto b \propto l$$

Nonlinear Surface Response: b



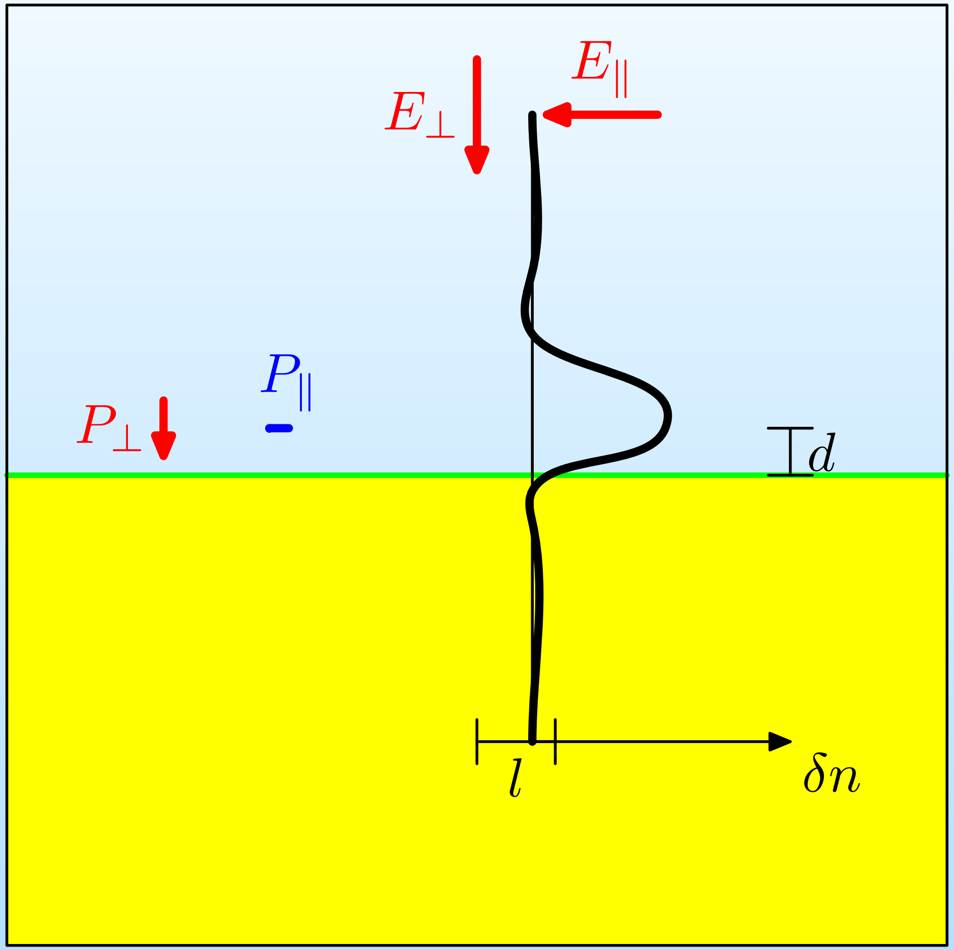
$$\chi_{\perp\parallel\parallel} \propto b \propto l$$

Nonlinear Surface Response: b



$$\chi_{\perp\|\|} \propto b \propto l$$

Nonlinear Surface Response: b



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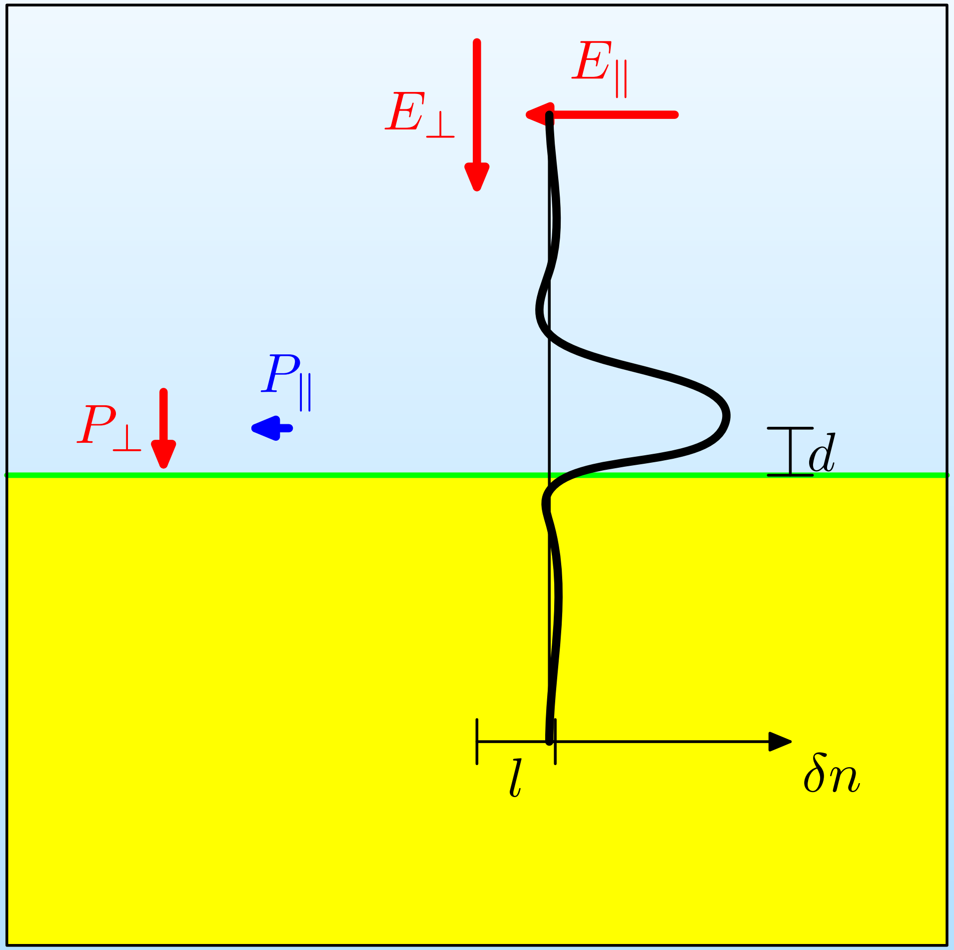
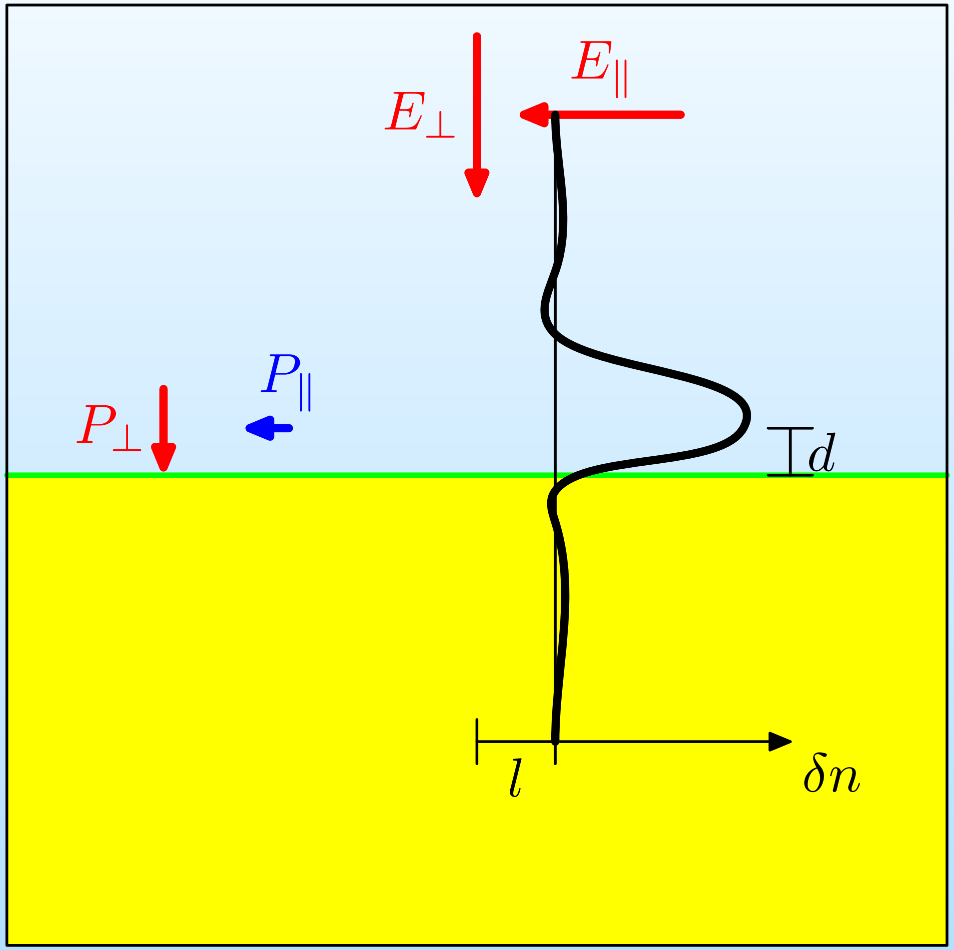


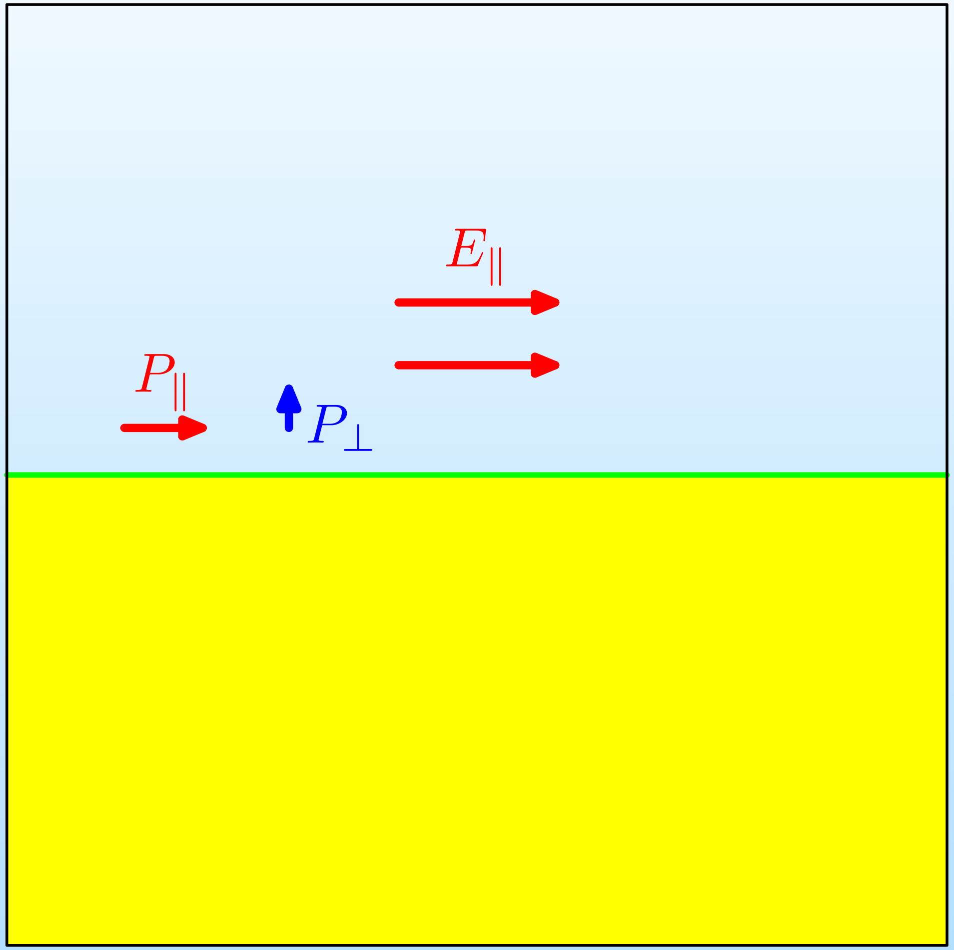
$$\chi_{\perp\parallel\parallel} \propto b \propto l$$

Nonlinear Surface Response: b



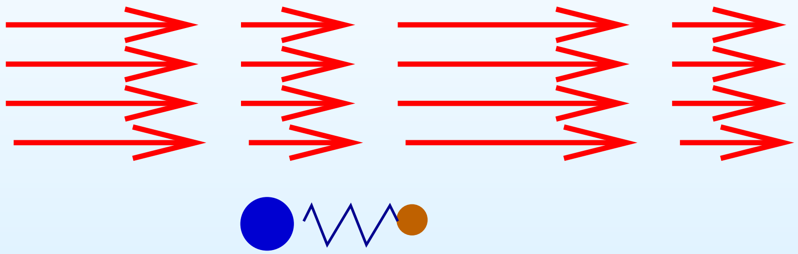
$$\chi_{\perp\|\|\|} \propto b \propto l$$

Nonlinear Surface Response: f



$$\chi_{\perp\|\|} \propto f$$

Continuum dipolium model



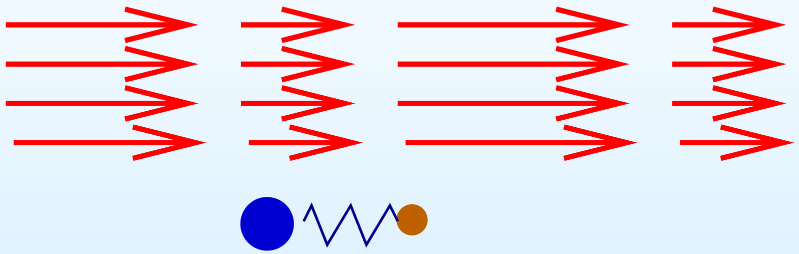
Harmonic oscillator

$$\vec{E}(\vec{r}) = \vec{E}(0)$$

$$m\ddot{\vec{r}} \;=\; -e\vec{E}(0,t) - m\omega_0^2\vec{r} - \frac{m}{\tau}\dot{\vec{r}}$$

Bernardo S. Mendoza y W. Luis Mochán, Phys. Rev. B **53**, 4999 (1996)

Continuum dipolium model



Harmonic oscillator

$$\vec{E}(\vec{r}) = \vec{E}(0) + \vec{r} \cdot \nabla \vec{E}(0) + \dots$$

$$\begin{aligned} m\ddot{\vec{r}} &= -e\vec{E}(0,t) - m\omega_0^2 \vec{r} - \frac{m}{\tau}\dot{\vec{r}} \\ &\quad -e\vec{r} \cdot \nabla \vec{E}(0,t) - \frac{e}{c}\dot{\vec{r}} \times \vec{B}(\vec{0},t) \end{aligned}$$

$\Rightarrow$ parametric oscillator if field $\vec{E} \neq$homogeneous.

Bernardo S. Mendoza y W. Luis Mochán, Phys. Rev. B **53**, 4999 (1996)

Response of a single molecule

$$\vec{p}^{(1)} = \alpha(\omega)\vec{E}(0,1)$$

$$\alpha(\omega) = \frac{e^2/m}{\omega_0^2 - \omega^2 - i\omega/\tau}$$

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$$\vec{p}^{(2)} = -\frac{1}{2e}\alpha(\omega)\alpha(2\omega)[\nabla E^2 - 4\vec{E} \times (\nabla \times \vec{E})]$$

Response of a single molecule

$$\vec{p}^{(1)} = \alpha(\omega)\vec{E}(0,1)$$

$$\alpha(\omega) = \frac{e^2/m}{\omega_0^2 - \omega^2 - i\omega/\tau}$$

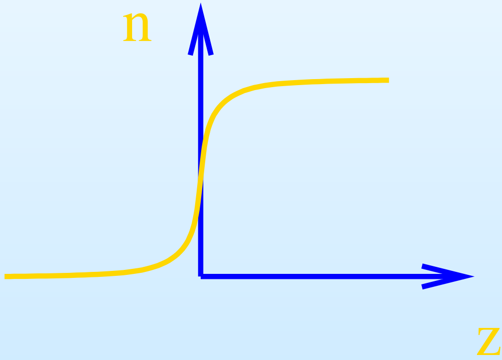
$$\vec{p}^{(2)} = -\frac{1}{2e}\alpha(\omega)\alpha(2\omega)[\nabla E^2 - 4\vec{E} \times (\nabla \times \vec{E})]$$

$$\overleftrightarrow{Q}^{(2)} = -\frac{3}{e}\alpha(\omega)^2\vec{E}_i\vec{E}_j$$

Macroscopic Response

$$\vec{P}^{(2)} = n\vec{p}^{(2)} - \frac{1}{6}\nabla \cdot n \overleftrightarrow{Q}^{(2)}$$

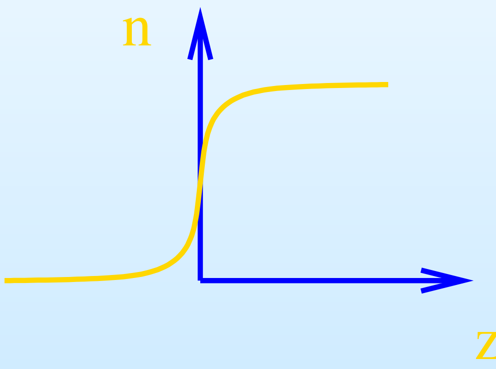
Macroscopic Response

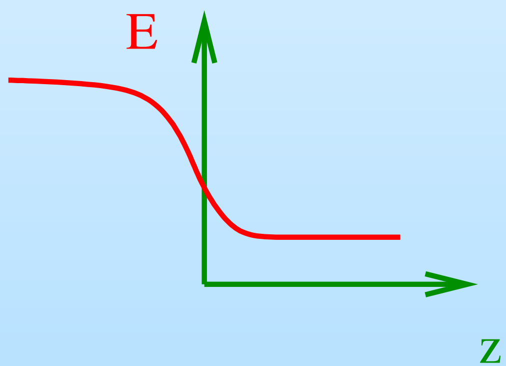


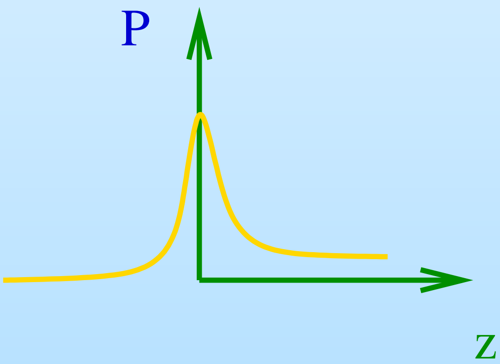
$$\vec{P}^{(2)} = n\vec{p}^{(2)} - \frac{1}{6}\nabla \cdot n \overleftrightarrow{Q}^{(2)}$$

Macroscopic Response

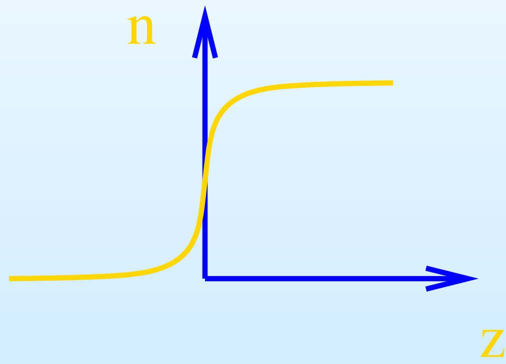
$$\vec{P}^{(2)} = n\vec{p}^{(2)} - \frac{1}{6}\nabla \cdot n \overleftrightarrow{Q}^{(2)}$$





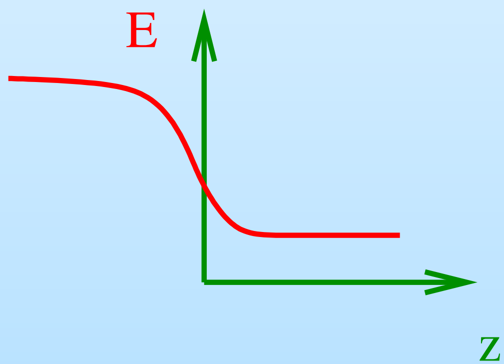


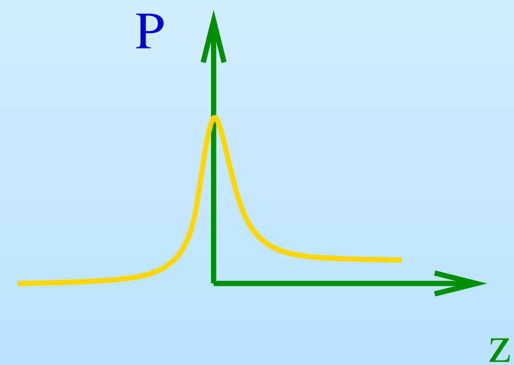
Macroscopic Response



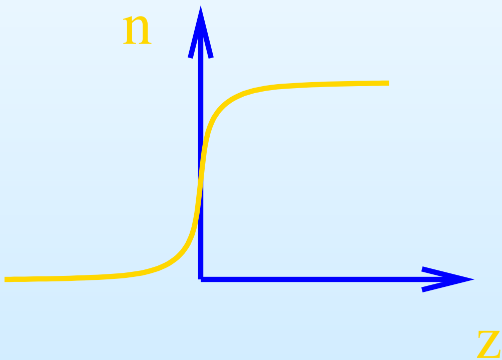
$$\vec{P}^{(2)} = n\vec{p}^{(2)} - \frac{1}{6}\nabla \cdot n \overleftrightarrow{Q}^{(2)}$$

$$\vec{P}_s^{(2)} = \int dz\, \vec{P}^{(2)}$$





Macroscopic Response



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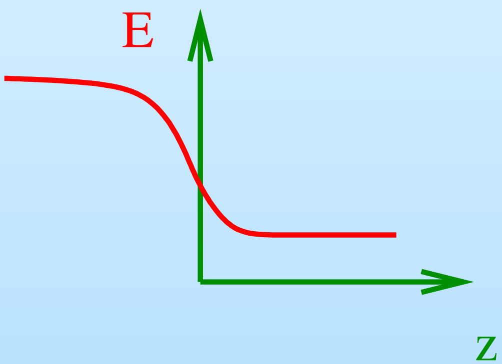

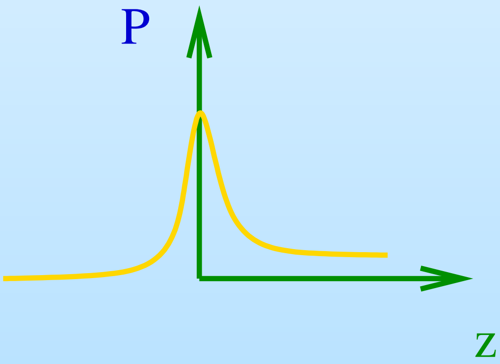

Strong polarization $\propto 1/a_B$ within thin $\sim a_B$ surface region, weak bulk polarization $\propto 1/\lambda$

Surface polarization

$$\vec{P}^{(2)} = n\alpha(2\omega)\vec{E}^{(2)} - \frac{n}{2e}\alpha(\omega)\alpha(2\omega)\nabla E^2 + \frac{1}{2e}\alpha^2(\omega)\nabla\cdot(n\vec{E}\vec{E}),$$

Surface polarization

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$$\begin{aligned} P_z^{(2)}(z) \quad &= \quad n(z)\alpha(2\omega)E_z^{(2)}(z) - \frac{n(z)}{2e}\alpha(\omega)\alpha(2\omega)\frac{\partial}{\partial z}E_z^2(z) \\ &\quad + \frac{1}{2e}\alpha^2(\omega)\frac{\partial}{\partial z}\left(n(z)E_{\omega,z}^2(z)\right), \end{aligned}$$

Surface polarization

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$$\begin{aligned} P_z^{(2)}(z) &= n(z)\alpha(2\omega)E_z^{(2)}(z) - \frac{n(z)}{2e}\alpha(\omega)\alpha(2\omega)\frac{\partial}{\partial z}E_z^2(z) \\ &+ \frac{1}{2e}\alpha^2(\omega)\frac{\partial}{\partial z}\left(n(z)E_{\omega,z}^2(z)\right), \end{aligned}$$

$$E_z^{(2)}(z) \approx -4\pi P_z^{(2)}(z),$$

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$$E_z^{(2)}(z) \approx -4\pi P_z^{(2)}(z),\ \ E_z(z) = D_z/\epsilon(\omega, z),$$

Surface polarization

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$$E_z^{(2)}(z) \approx -4\pi P_z^{(2)}(z),\;\; E_z(z) = D_z/\epsilon(\omega,z),\;\; \epsilon(z) \approx 1 + 4\pi n(z)\alpha$$

Surface polarization (cont.)

$$P_z^{(2)}(z) = \frac{1}{2e\epsilon(2\omega, z)} \Big[-\alpha(\omega)\alpha(2\omega)n(z)\frac{\partial}{\partial z}\frac{1}{\epsilon^2(\omega, z)} + \alpha^2(\omega)\frac{\partial}{\partial z}\frac{n(z)}{\epsilon^2(\omega, z)} \Big] D_z^2.$$

Surface polarization (cont.)

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$P_z^{(2)}(z)$ depends on z through $n(z)$ and $\partial n(z)/\partial z$ and is (almost) null within bulk

Surface polarization (cont.)

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$P_z^{(2)}(z)$ depends on z through $n(z)$ and $\partial n(z)/\partial z$ and is (almost) null within bulk
Surface polarization:

$$\vec{P}_s^{(2)} \equiv \int_{-\infty}^{\infty} dz \vec{P}^{(2)}(z).$$

Surface susceptibility (cont.)

Trick: $\int dz\, f(n(z)) \partial g(n(z))/\partial z = \int dn\, f(n) \partial g(n)/\partial n$

Surface susceptibility (cont.)

Trick: $\int dz\, f(n(z))\partial g(n(z))/\partial z = \int dn\, f(n)\partial g(n)/\partial n$

Integrate: $P_{s,z}^{(2)} = \chi_{zzz} D_z^2,$

Surface susceptibility (cont.)

Trick: $\int dz\, f(n(z))\partial g(n(z))/\partial z = \int dn\, f(n)\partial g(n)/\partial n$
Integrate: $P^{(2)}_{s,z} = \chi_{zzz} D_z^2$,
Identify:

$$\chi^s_{zzz}(\omega) = \frac{\alpha^2(\omega)}{8\pi e}\frac{\alpha(2\omega)\log(\epsilon_B(\omega)/\epsilon_B(2\omega))}{(\alpha(\omega)-\alpha(2\omega))^2} + \frac{\alpha(\omega)}{8\pi e}\frac{\epsilon_B(\omega)-1}{\epsilon_B(\omega)}\left(\frac{1}{\epsilon_B(\omega)} + \frac{\alpha(2\omega)}{\alpha(2\omega)-\alpha(\omega)}\right),$$

Surface susceptibility (cont.)

Trick: $\int dz\, f(n(z))\partial g(n(z))/\partial z = \int dn\, f(n)\partial g(n)/\partial n$
Integrate: $P_{s,z}^{(2)} = \chi_{zzz} D_z^2$,
Identify:

$$\begin{aligned}\chi_{zzz}^{s}(\omega) &= \frac{\alpha^2(\omega)}{8\pi e}\frac{\alpha(2\omega)\log(\epsilon_B(\omega)/\epsilon_B(2\omega))}{(\alpha(\omega)-\alpha(2\omega))^2} \\ &+\frac{\alpha(\omega)}{8\pi e}\frac{\epsilon_B(\omega)-1}{\epsilon_B(\omega)}\left(\frac{1}{\epsilon_B(\omega)}+\frac{\alpha(2\omega)}{\alpha(2\omega)-\alpha(\omega)}\right),\end{aligned}$$

independent of the density profile $n(z)$!

a

$$a(\omega) \equiv -64\pi^2 n_B e \left(\frac{\epsilon_B(\omega)}{\epsilon_B(\omega) - 1} \right)^2 \chi^s_{zzz}(\omega).$$

a

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$$\begin{aligned} a(\omega) = \quad & 2 \quad ([\epsilon_B(2\omega) - \epsilon_B(\omega)][2\epsilon_B(\omega) - \epsilon_B(2\omega) - \epsilon_B(\omega)\epsilon_B(2\omega)] \\ & \quad +[\epsilon_B(\omega)]^2[1 - \epsilon_B(2\omega)] \log[\epsilon_B(\omega)/\epsilon_B(2\omega)]) \\ & / \quad [\epsilon_B(2\omega) - \epsilon_B(\omega)]^2. \end{aligned}$$

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a depends only on the bulk dielectric functions $\epsilon_B(\omega)$ and $\epsilon_B(2\omega)$, analytically.

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a depends only on the bulk dielectric functions $\epsilon_B(\omega)$ and $\epsilon_B(2\omega)$, analytically.

Approximate expression for *arbitrary* ϵ_B (?). Accounts for strong field variation at surfaces. Ignores surface states, surface modified polarizability, surface local field corrections . . .

$b,\ f$

$$\vec{P}_{\parallel}^{(2)}(z) = \frac{1}{2e}\alpha^2(\omega)\frac{\partial}{\partial z}n(z)\vec{E}_{\parallel}E_z(z),$$

b, f

$$\vec{P}^{(2)}_{\|}(z) = \frac{1}{2e}\alpha^2(\omega)\frac{\partial}{\partial z}n(z)\vec{E}_{\|}E_z(z),$$

Integrate: $\vec{P}^{(2)}_{s,\|} = 2\chi_{\|\|z}\vec{E}_{\|}D_z,$

b, f

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Integrate: $\vec{P}^{(2)}_{s,\parallel} = 2\chi_{\parallel\parallel z}\vec{E}_{\parallel}D_z,$

Identify:

$$\chi_{\parallel\parallel z}(\omega) = \chi_{\parallel z\parallel}(\omega) = \frac{1}{4e}\frac{n_B\alpha^2(\omega)}{\epsilon_B(\omega)}.$$

b, f

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Identify:

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Parametrize:

$$b(\omega) \equiv -64\pi^2 n_B e\frac{\epsilon_B(\omega)}{(\epsilon_B(\omega)-1)^2}\chi^s_{\|\|z}(\omega) = -1$$

b, f

$$\vec{P}^{(2)}_{\parallel}(z) = \frac{1}{2e}\alpha^2(\omega)\frac{\partial}{\partial z}n(z)\vec{E}_{\parallel}E_z(z),$$

Integrate: $\vec{P}^{(2)}_{s,\parallel} = 2\chi_{\parallel\parallel z}\vec{E}_{\parallel}D_z,$

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Parametrize:

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Finally: $f \propto \chi_{z\parallel\parallel} = 0$.

Bulk response: d

$$\vec{P}^{(2)} = -\frac{n_B}{e}\alpha(\omega)\alpha(2\omega)\left(2\vec{E}\cdot\nabla\vec{E} - \frac{1}{2}\nabla E^2\right) - \frac{n_B}{2e}\alpha^2(\omega)\nabla\cdot(\vec{E}\vec{E}).$$

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Plane wave: ∇ *perpendicular* to $\vec{E}$.

Bulk response: d

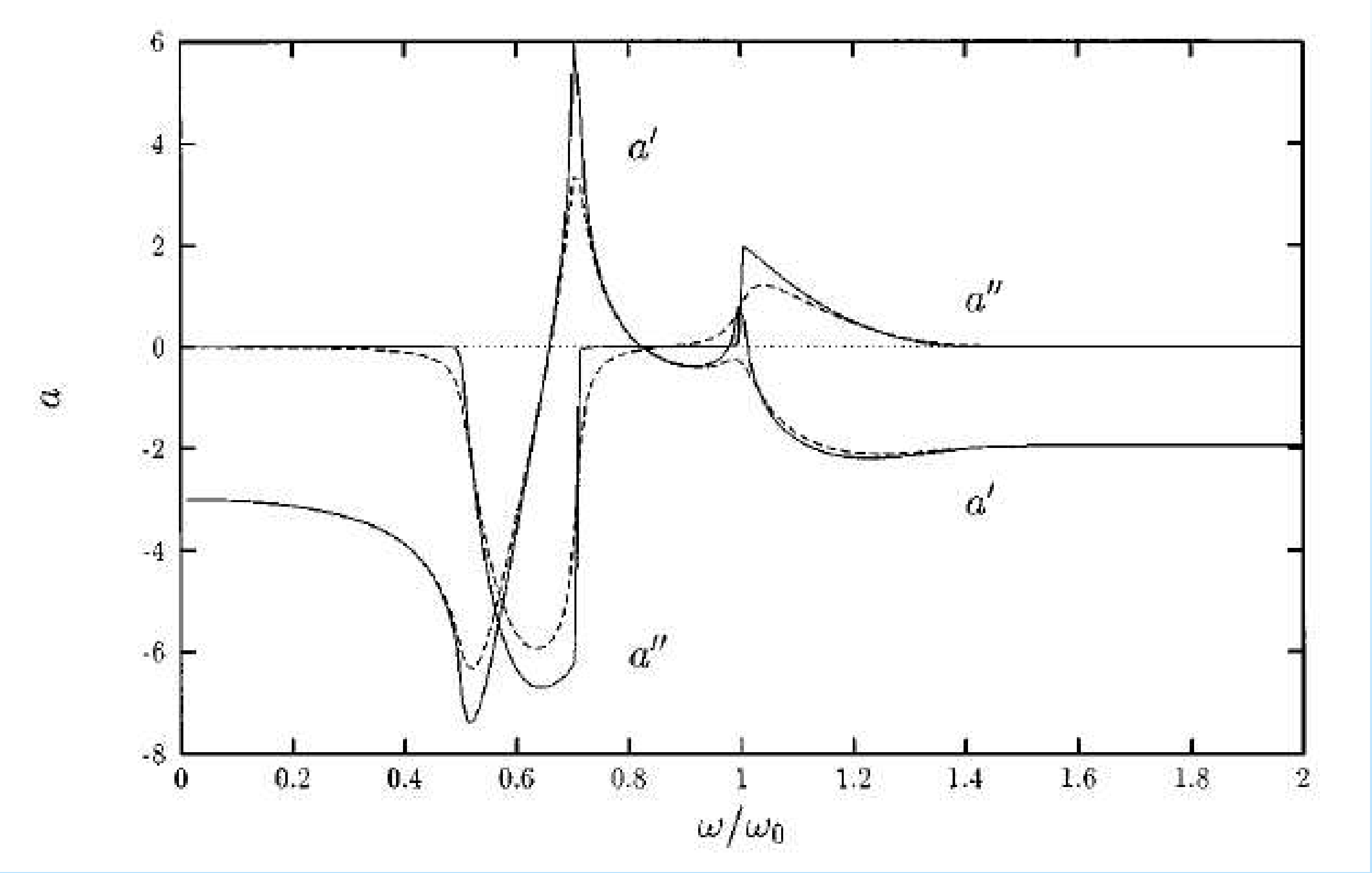
$$\vec{P}^{(2)} = -\frac{n_B}{e}\alpha(\omega)\alpha(2\omega)\left(2\vec{E}\cdot\nabla\vec{E} - \frac{1}{2}\nabla E^2\right) - \frac{n_B}{2e}\alpha^2(\omega)\nabla\cdot(\vec{E}\vec{E}).$$

Plane wave: ∇ *perpendicular* to $\vec{E}$. Then,

$$P^{(2)} \equiv \frac{1}{32\pi^2 ne}(\epsilon_B(\omega)-1)(\epsilon_B(2\omega)-1)d(\omega)\nabla E^2$$

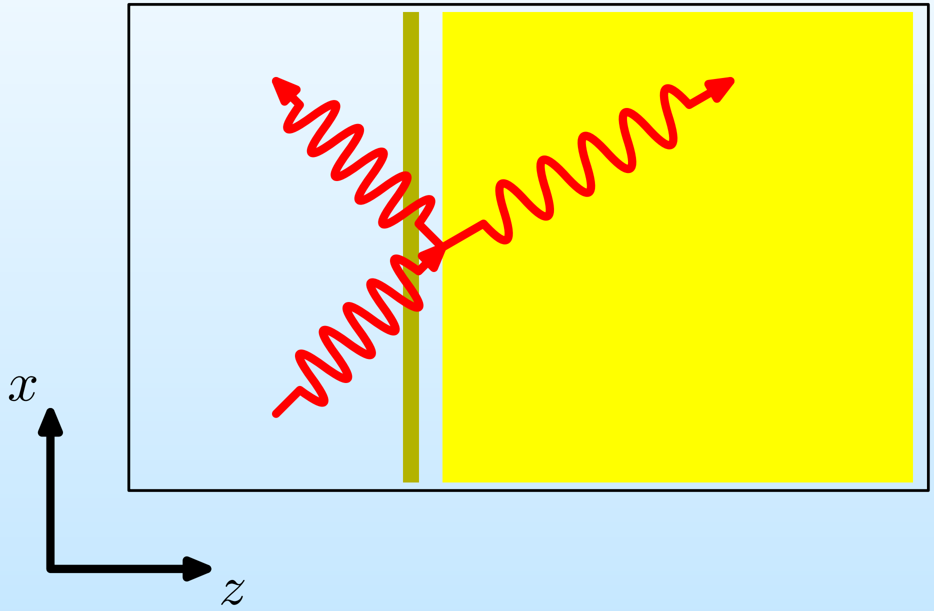
where: $d = 1$.

a for Harmonic Dipolium



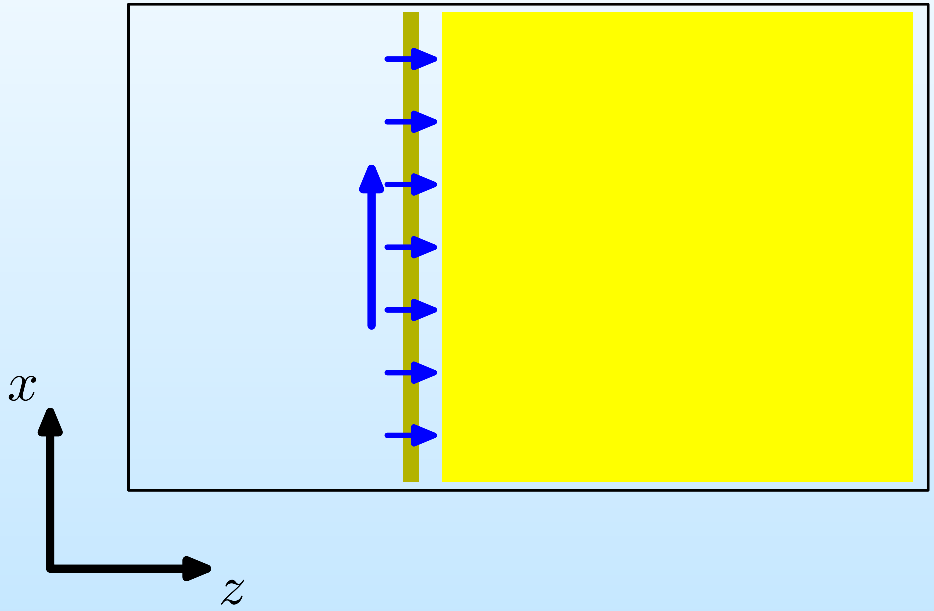
Efficiency

Solve linear problem ($t(\omega)$)



Efficiency

Solve linear problem ($t(\omega)$)
Obtain surface polarization

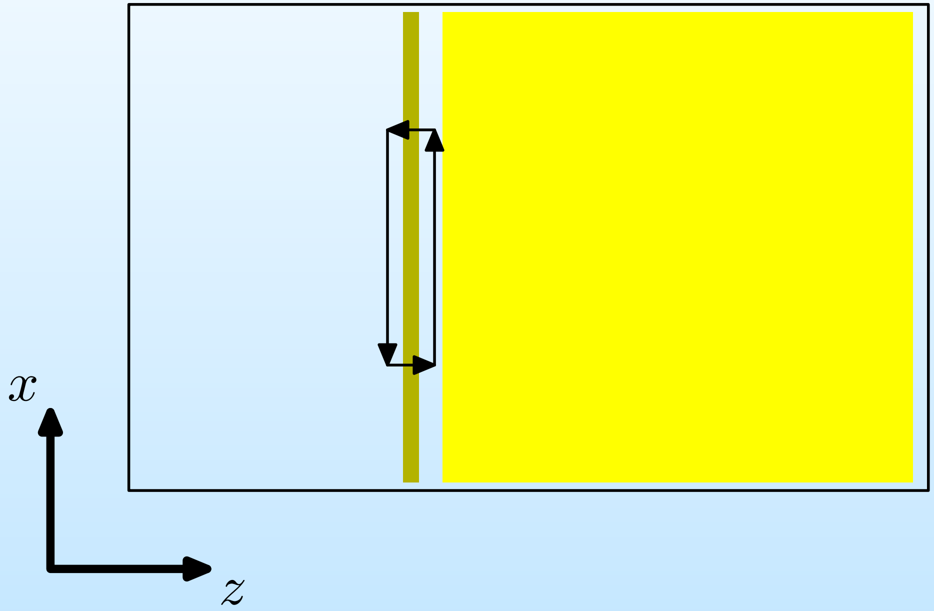


Efficiency

Solve linear problem ($t(\omega)$)
Obtain surface polarization
Get SH boundary conditions:

$$H_y(-) = H_y(+) - 8\pi i\omega/c\, P_{sx}$$

$$E_x(-) = E_x(+) + 8\pi i Q P_{sz}$$



Efficiency

Solve linear problem ($t(\omega)$)
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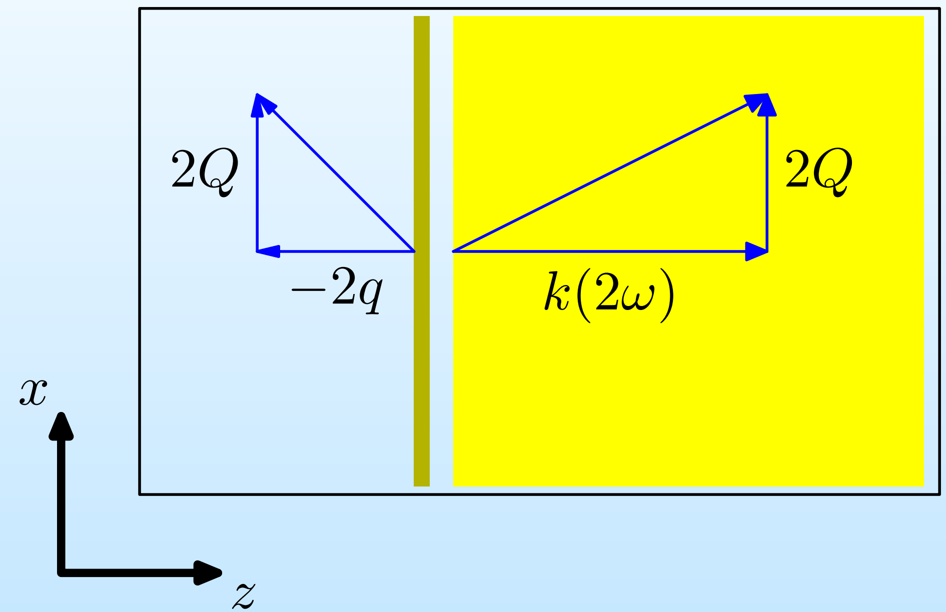
Get SH boundary conditions:
$H_y(-) = H_y(+) - 8\pi i\omega/c\,P_{sx}$
$E_x(-) = E_x(+) + 8\pi i Q P_{sz}$
Introduce surface impedance:
$Z_p(2\omega) = E_x(+)/H_y(+)$
$= k(2\omega)c/2\omega\epsilon_B(2\omega)$
$Z_p^v \;=\; -E_x(-)/H_y(-) \;=\; qc/\omega$



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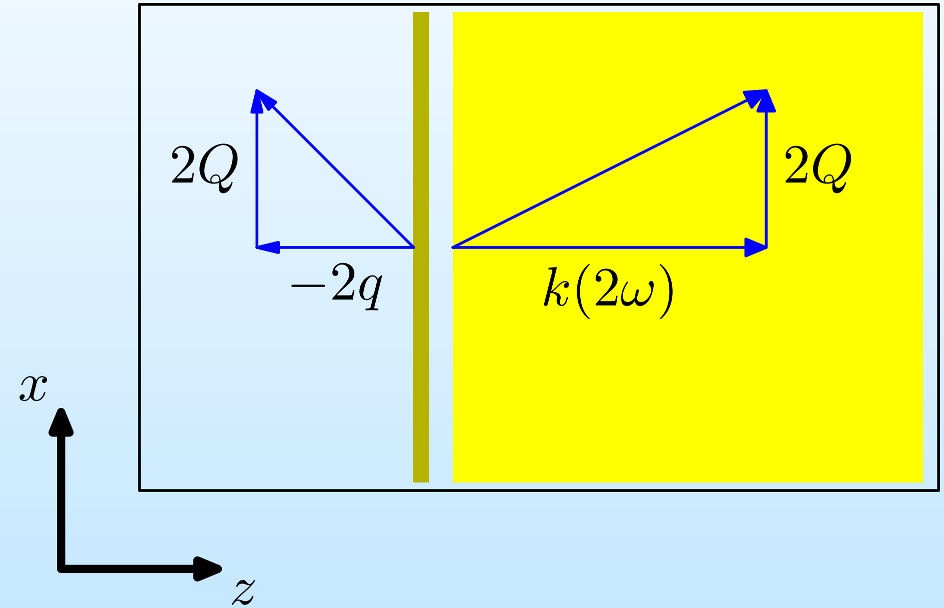
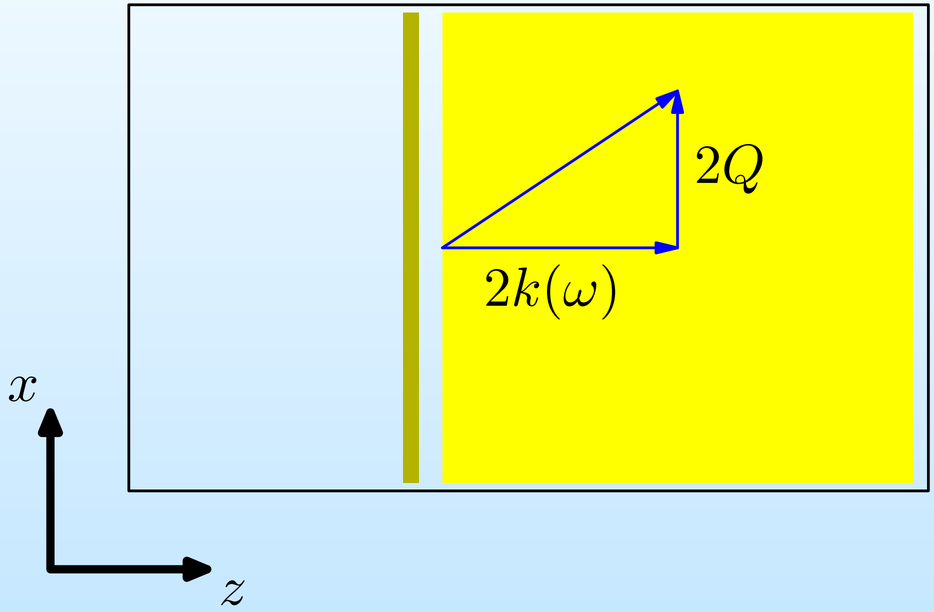
$= k(2\omega)c/2\omega\epsilon_B(2\omega)$
$Z_p^v = -E_x(-)/H_y(-) = qc/\omega$
Solve for $H_y(-)$ and surface radiated SH



Efficiency (cont)

Obtain bulk polarization



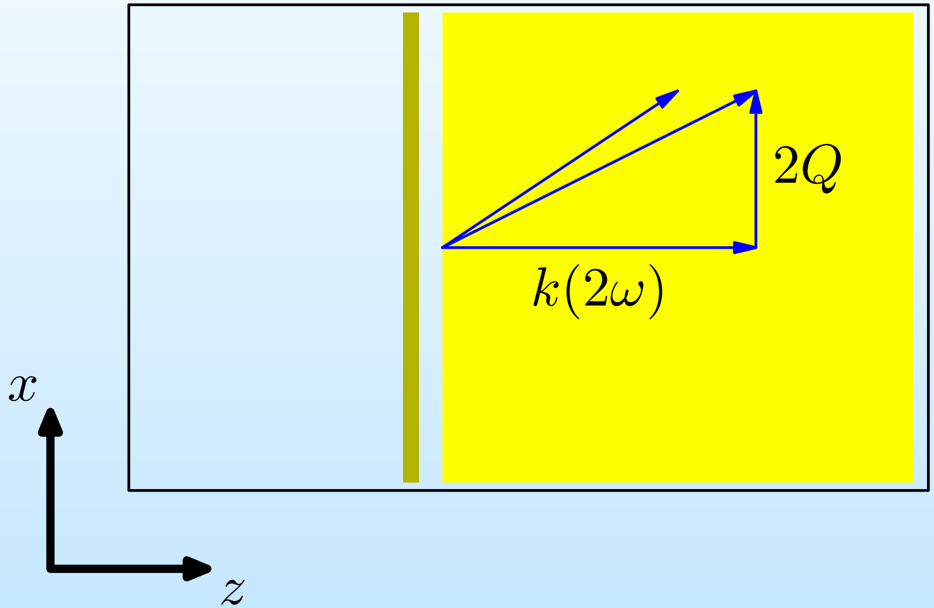
Efficiency (cont)

Obtain bulk polarization

Solve wave equation:

$$\nabla^2 \vec{E} - \left(\frac{2\omega}{c}\right)^2 \epsilon_B(2\omega)\vec{E}$$

$$= 4\pi \left(\frac{2\omega}{c}\right)^2 \vec{P}^{(2)} e^{2i(Qx+k(\omega)z)}$$



Efficiency (cont)

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Solve wave equation:

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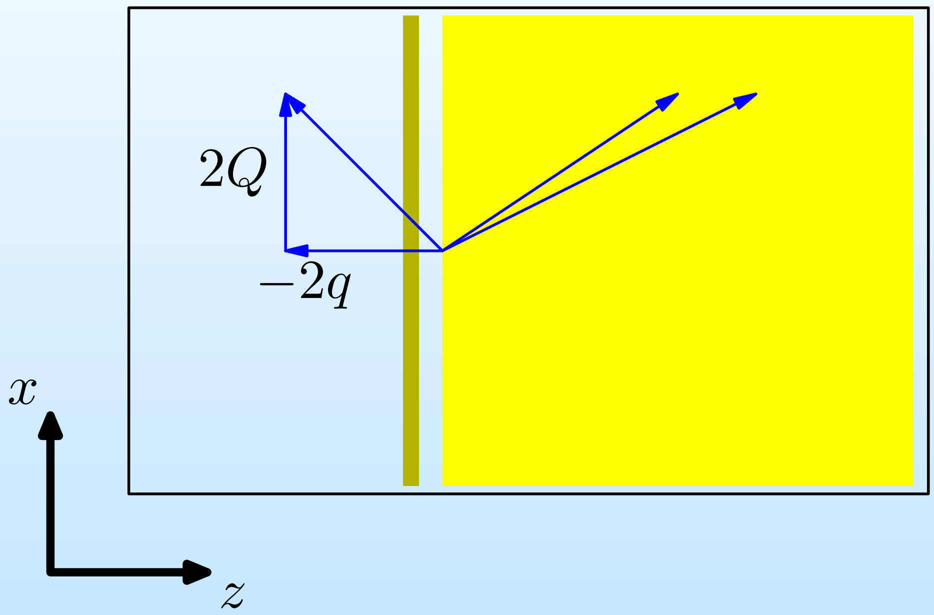
Match fields to bulk radiated SH



Efficiency (cont)

Obtain bulk polarization

Solve wave equation:

$$\nabla^2 \vec{E} - \left(\frac{2\omega}{c}\right)^2 \epsilon_B(2\omega)\vec{E}$$

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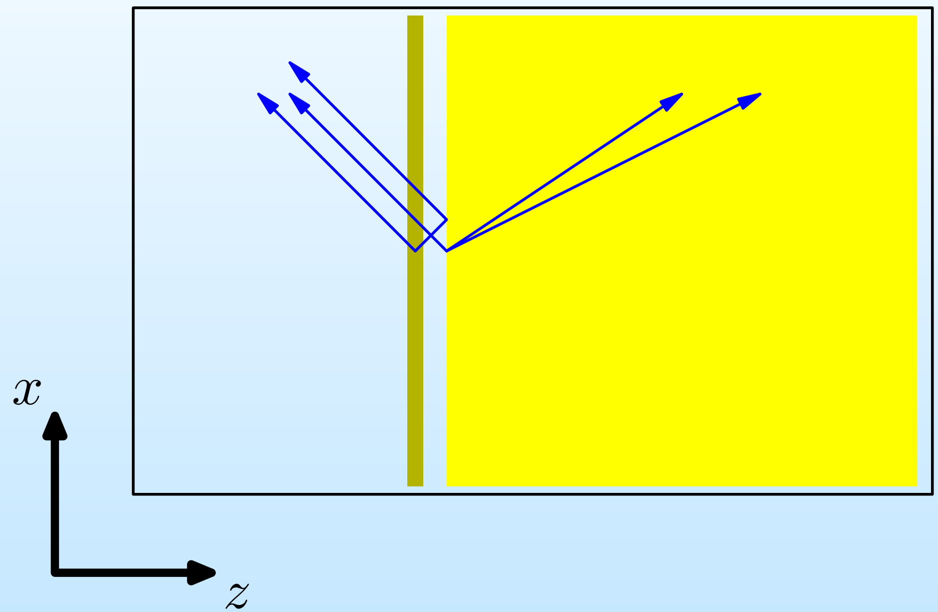
Match fields to bulk radiated SH

Add bulk and surface contributions

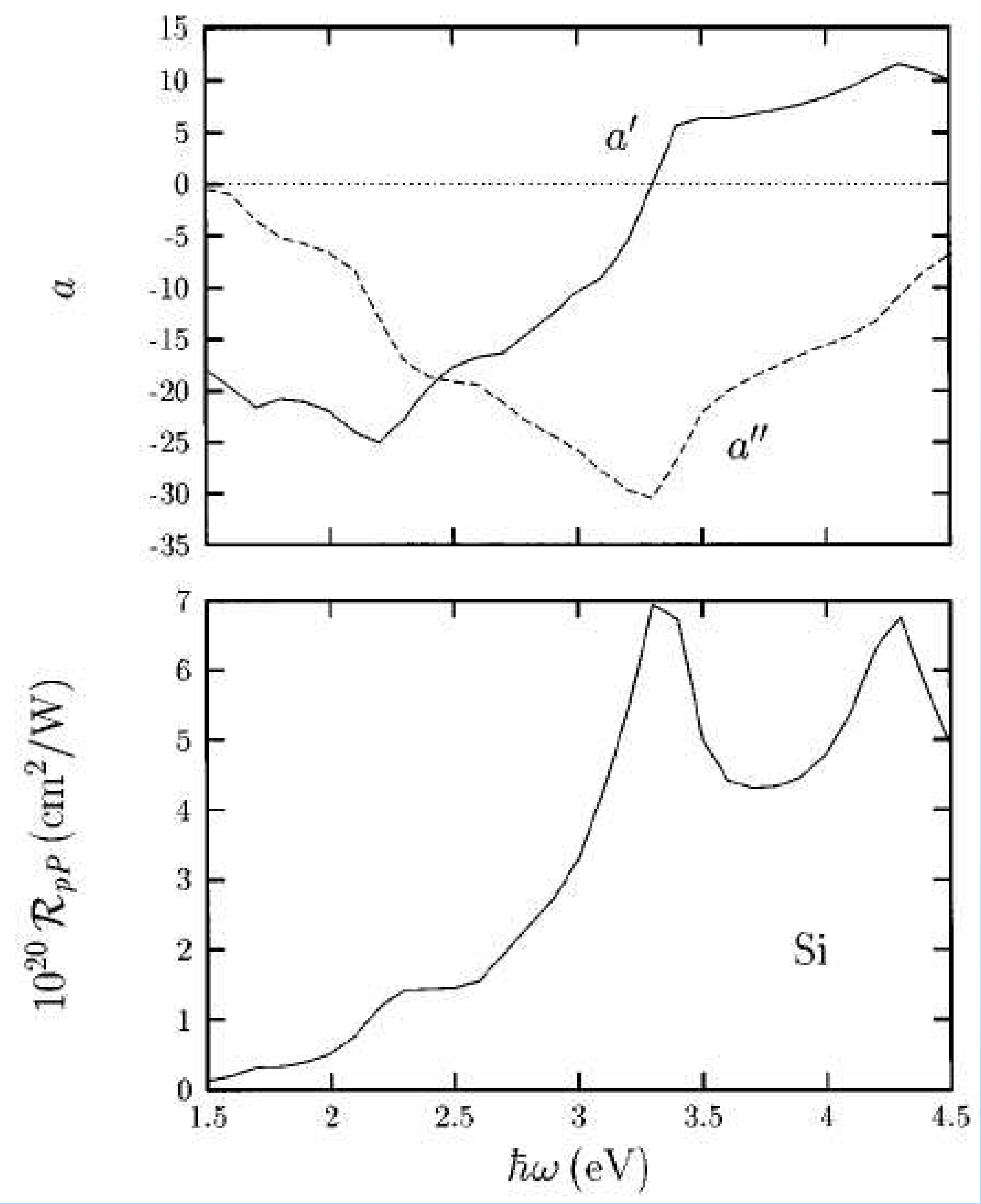


Efficiency (cont.)

$$\mathcal{R}_{pP} = \frac{2\pi^3\omega^2}{(n_B e)^2 c^3} |r_{pP}|^2,$$

$$\begin{aligned} r_{pP} \quad = \quad & \frac{Q}{q} \left(\frac{\epsilon_B(\omega) - 1}{4\pi} \right)^2 \frac{t(2\omega) t^2(\omega)}{\epsilon_B(2\omega)\epsilon_B(\omega)} \\ & \times \left(\frac{\epsilon_B(2\omega)}{\epsilon_B(\omega)} \left(\frac{Q(\omega) c}{\omega} \right)^2 a(\omega) - \frac{k(\omega) k(2\omega) c^2}{\omega^2 \epsilon_B(\omega)} b(\omega) \right. \\ & \left. + 2 \frac{\epsilon_B(2\omega) - 1}{\epsilon_B(\omega) - 1} d(\omega) \right) . \end{aligned}$$

Example: Si



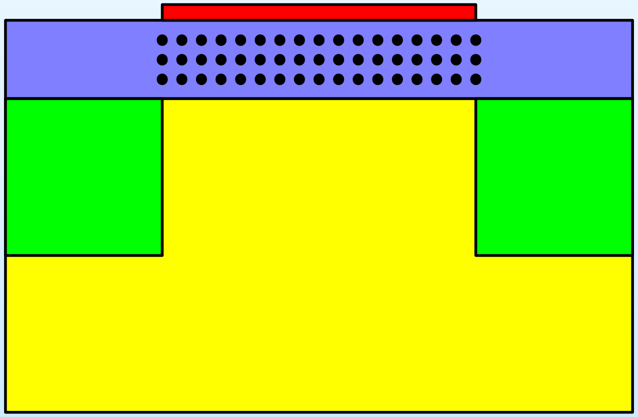
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
a
a′
a″
7
6
5
4
3
2
1
0
$10^{20}\,\mathcal{R}_{pP}\,(\mathrm{cm}^2/\mathrm{W})$
Si
1.5
2
2.5
3
3.5
4
4.5
$\hbar\omega$ (eV)

Further work

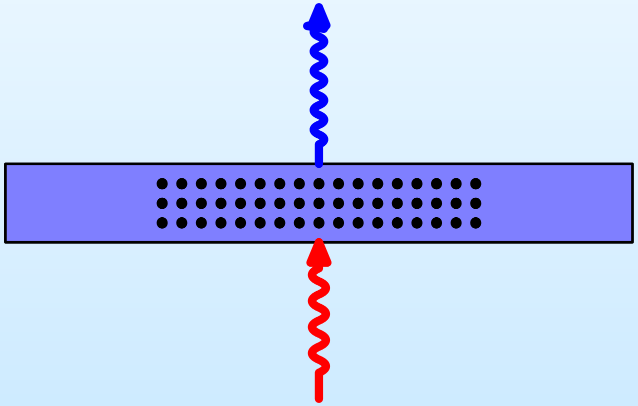
- Surface crystalline structure: Polarizable bonds
- Metals
- Adsorbates
- Chiral films
- Magnetic systems
- SFG/DFG
- . . .

Buried interfaces: nanoparticles

Flash memories



Observe interfaces with SHG



Experiment

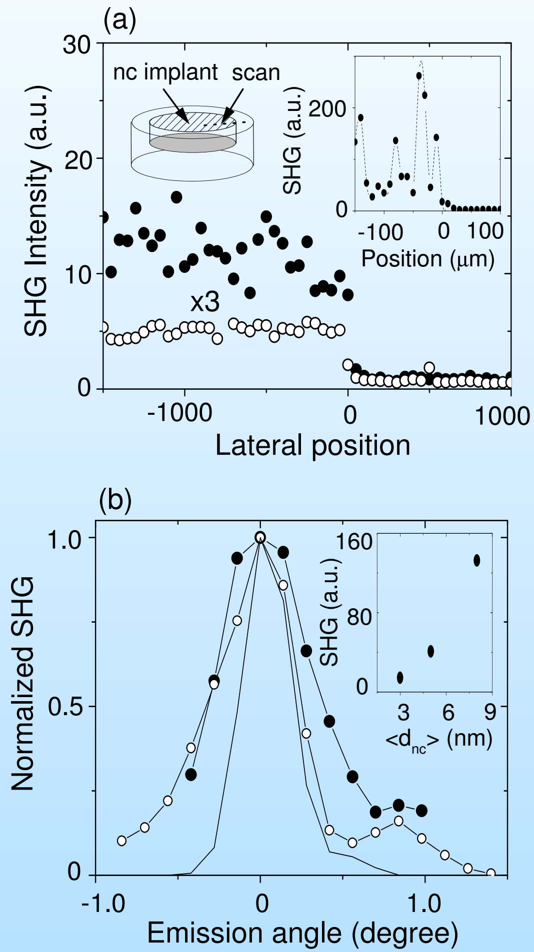


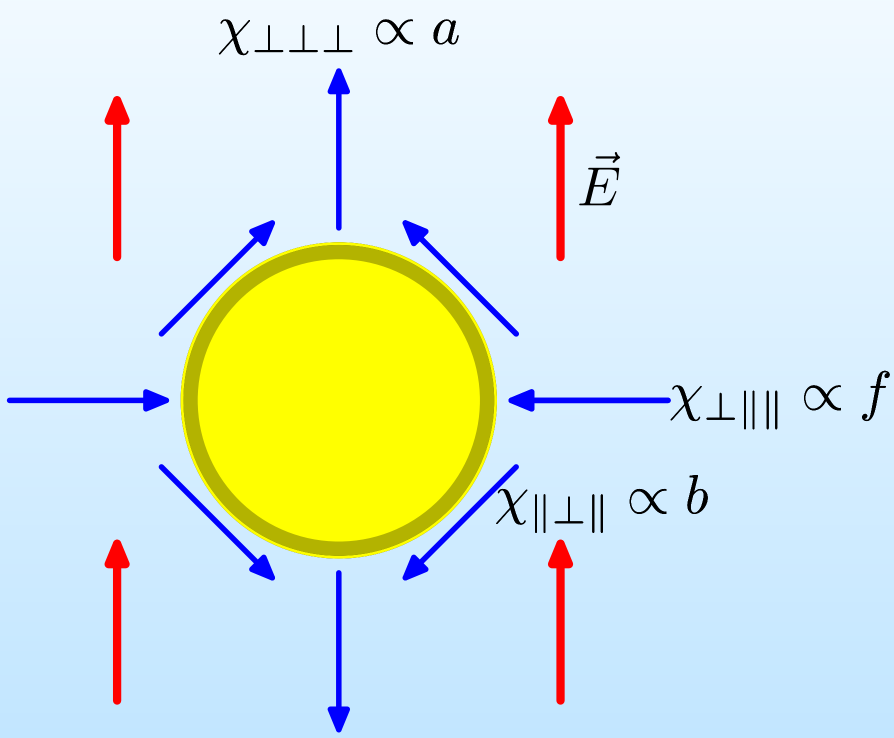
FIG. 3

13

Y. Jiang, P. T. Wilson, M. C. Downer, C. W. White, and S. P. Withrow, Appl. Phys. Lett. **78**, 766 (2001).

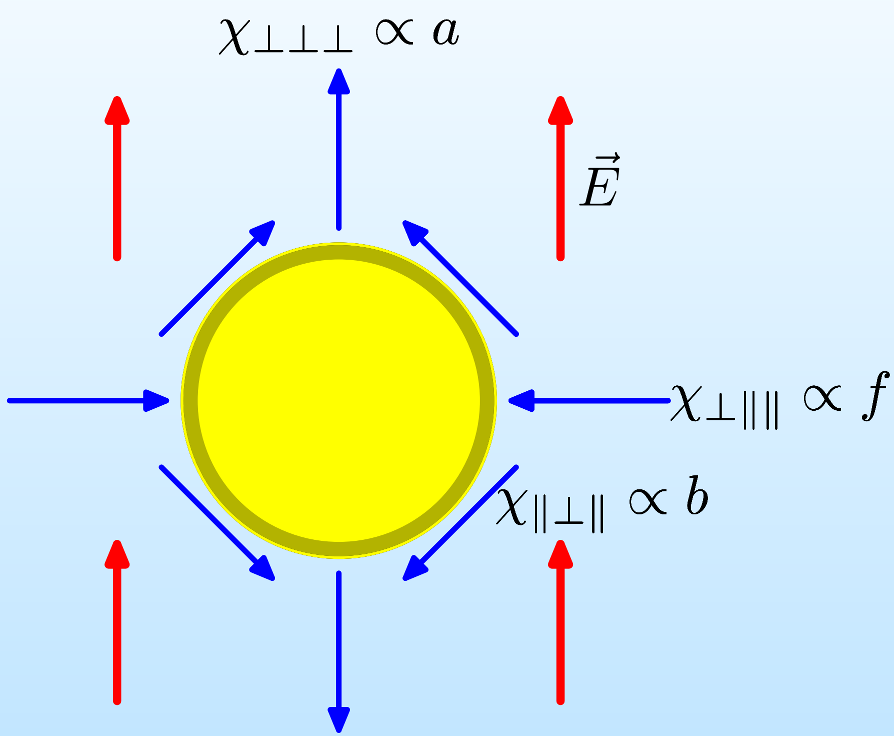
- Signal comes from nanospheres.
- Interface sensitive (annealed in Ar vs. Ar/H_2).
- Forward SHG.
- Edge vs. *bulk*.

Single sphere SHG



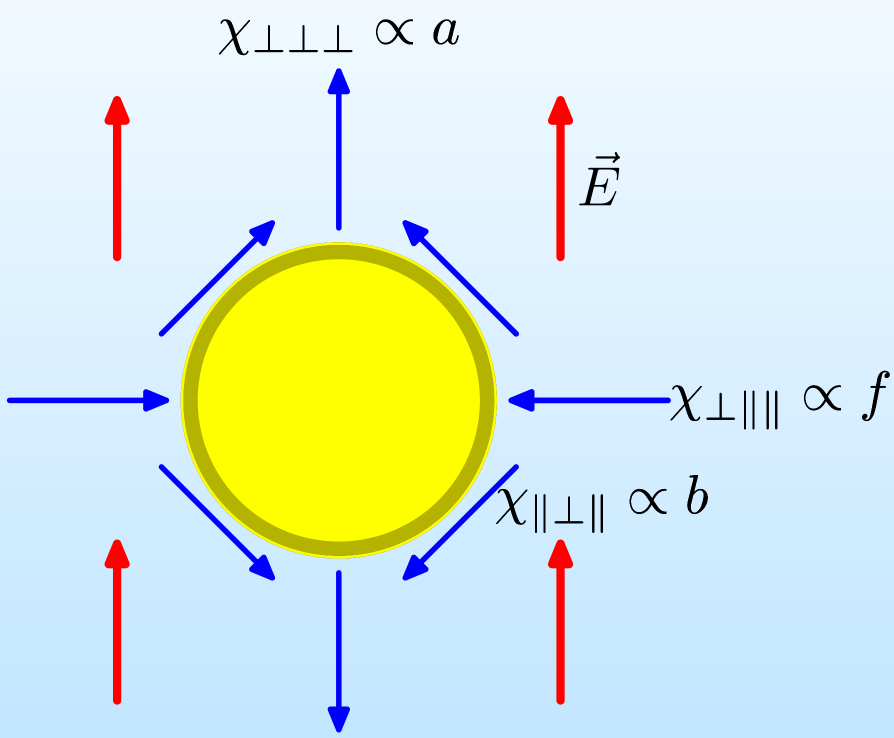
- Centrosymmetry is locally lost. . .

Single sphere SHG



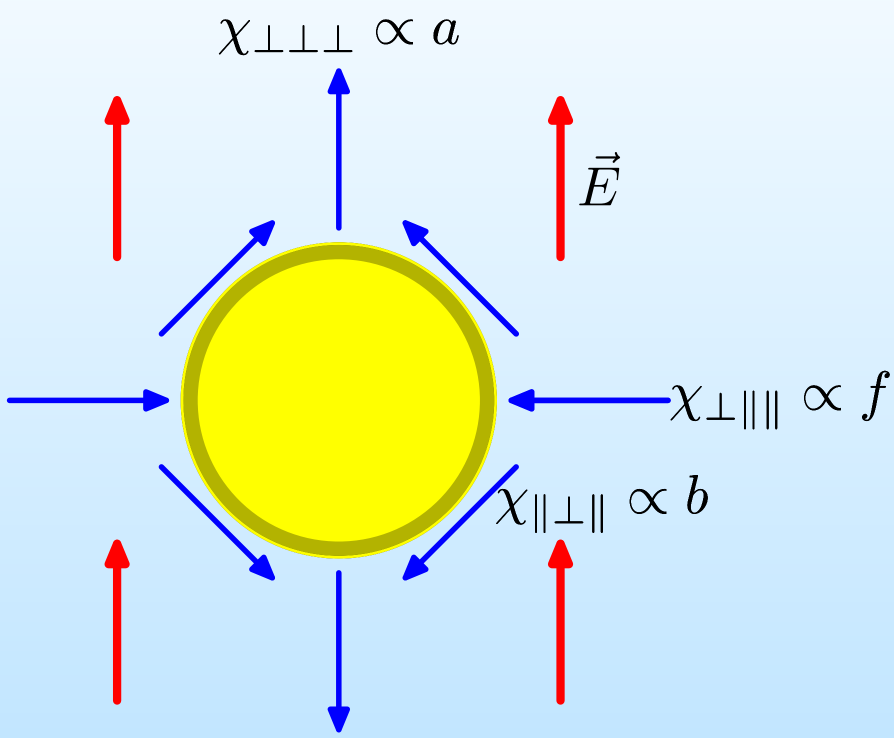
- Centrosymmetry is locally lost. . .
- but globally recovered.

Single sphere SHG



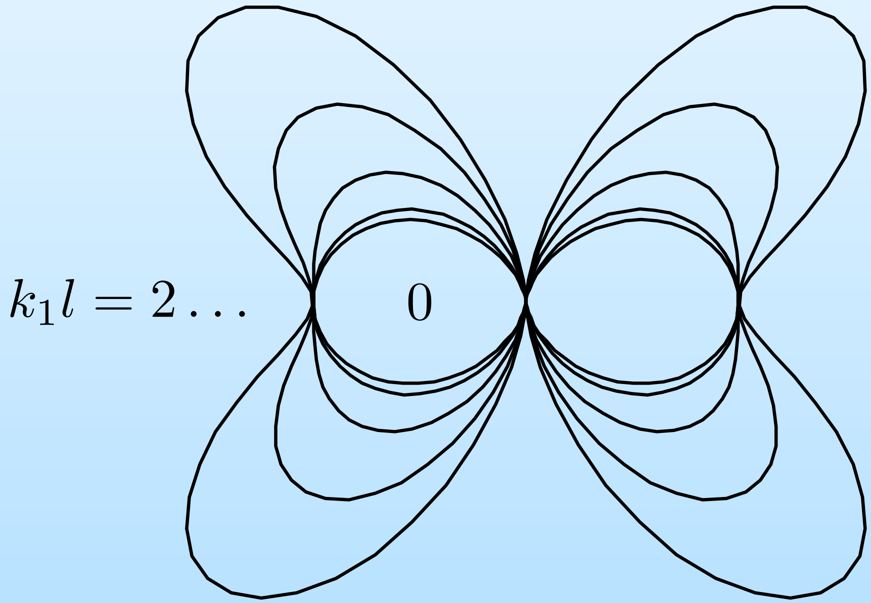
- Centrosymmetry is locally lost. . .
- but globally recovered.
- Total dipole is null. . .

Single sphere SHG

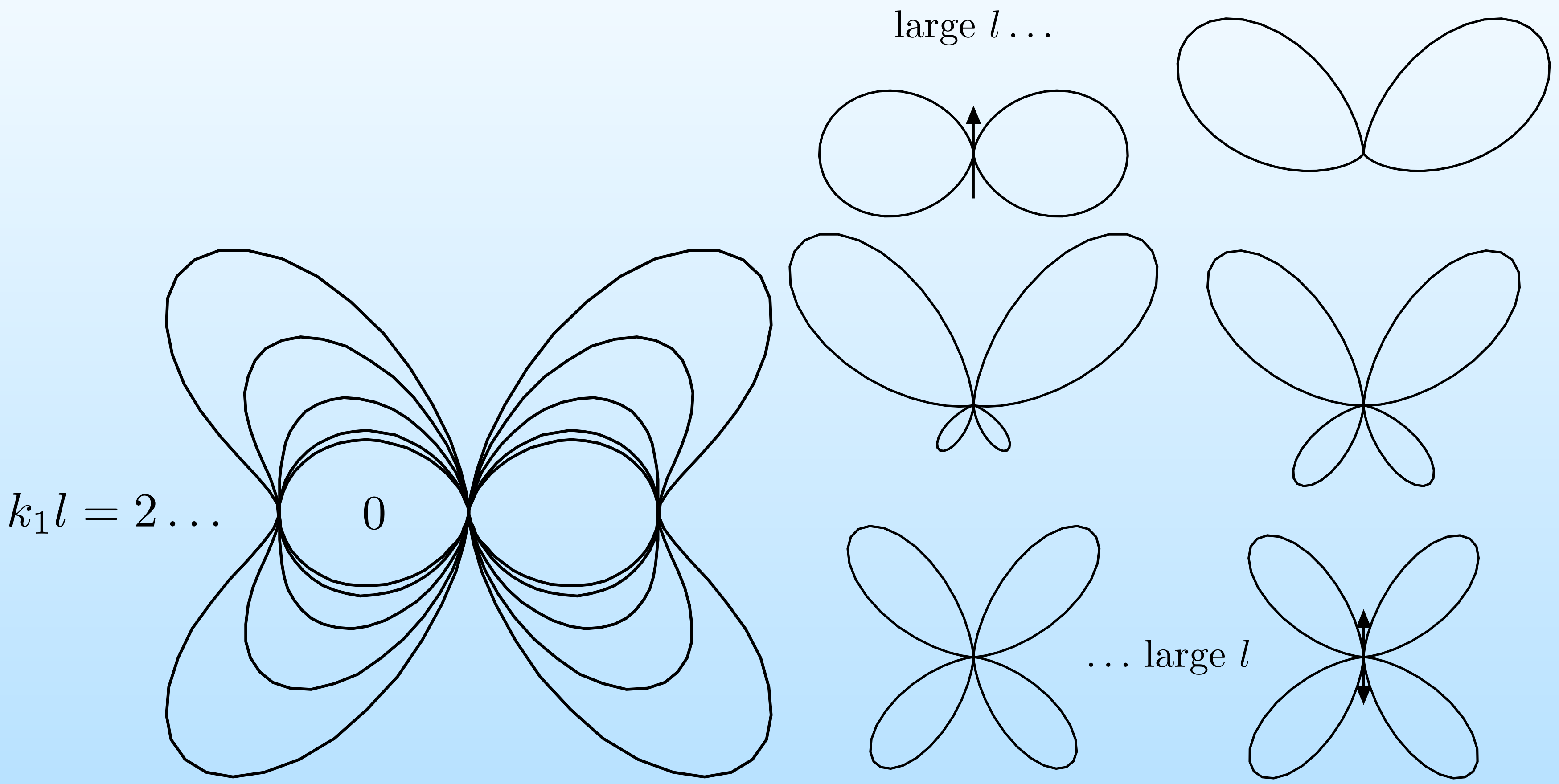


- Centrosymmetry is locally lost. . .
- but globally recovered.
- Total dipole is null. . .
- unless field is inhomogeneous.

Dipolar vs. quadrupolar radiation

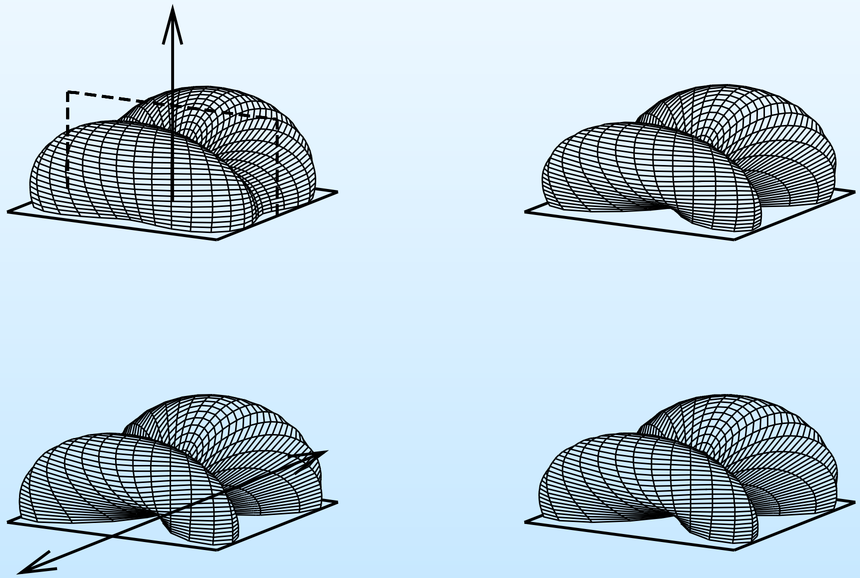


Dipolar vs. quadrupolar radiation

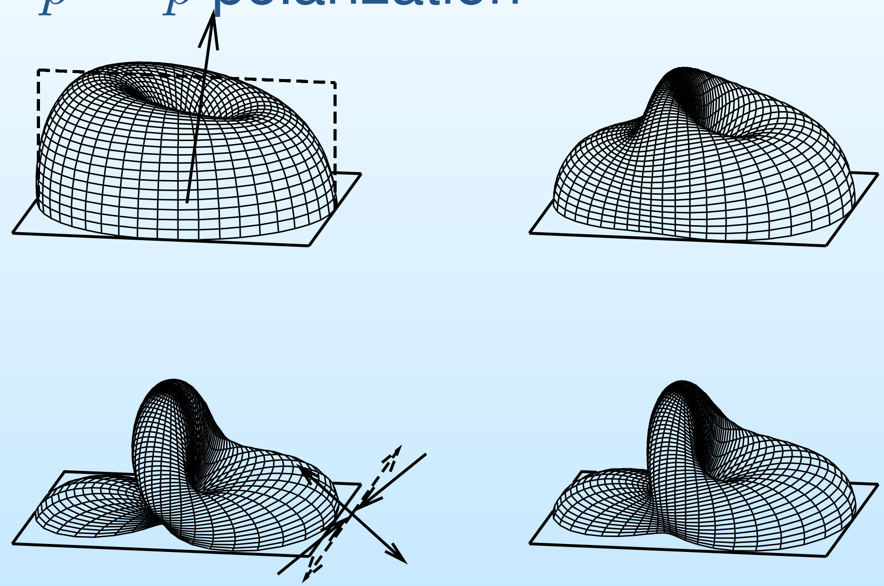


SHG efficiency for nanosphere over substrate

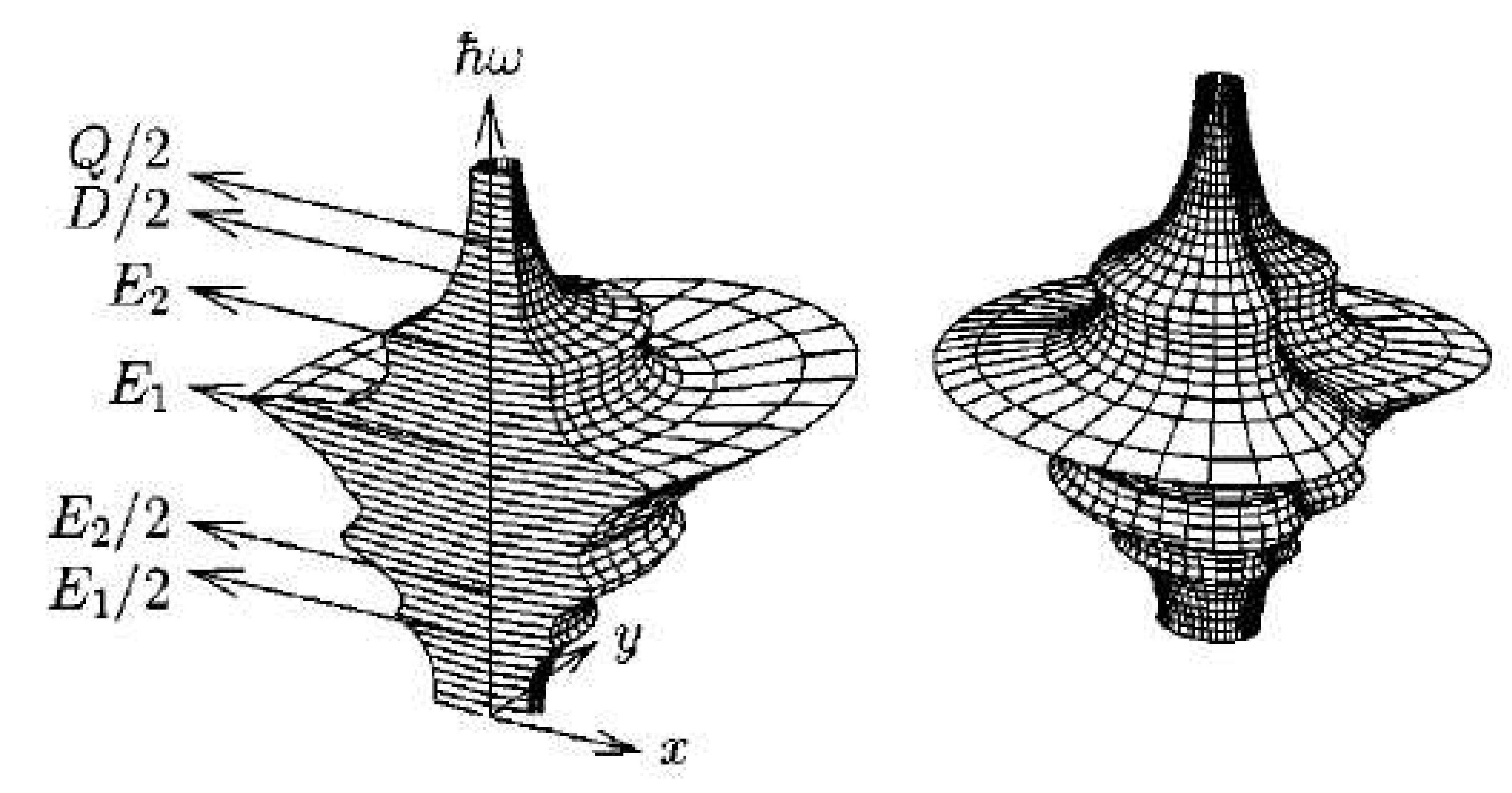
$s \to p$ polarization



$p \to p$ polarization



Spectral features: p in, $\theta = \pi/4$



Comparison

No forward radiation and wide distribution
vs.
Narrow distribution along forward direction!

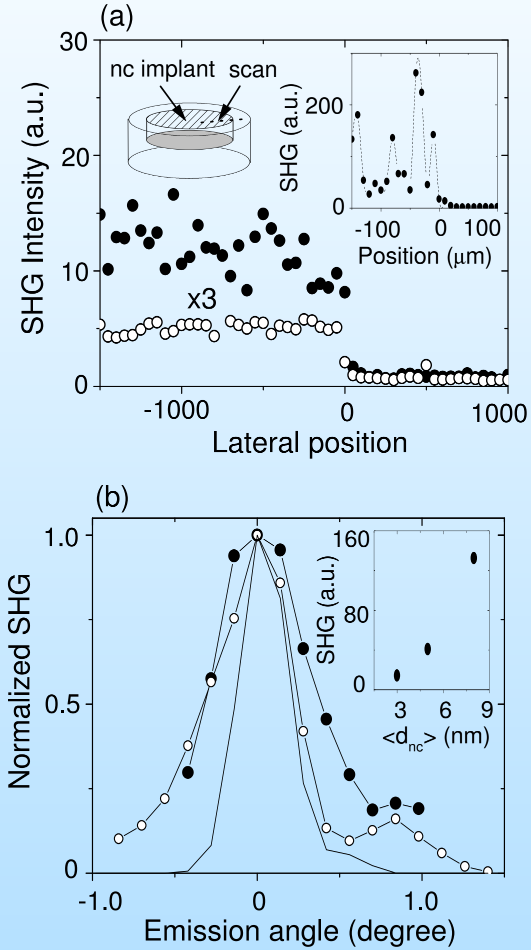


FIG. 3

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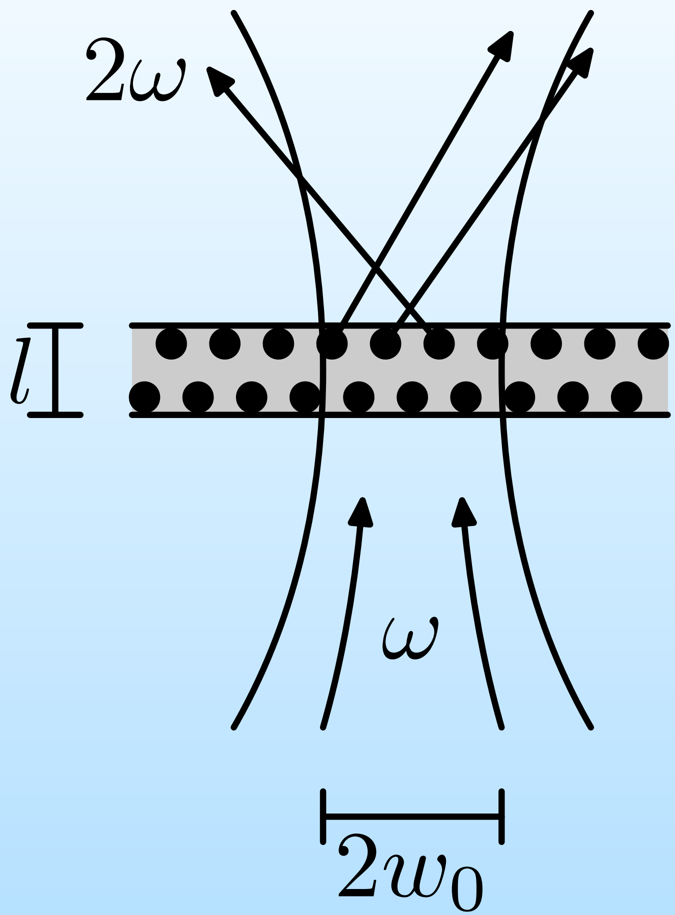
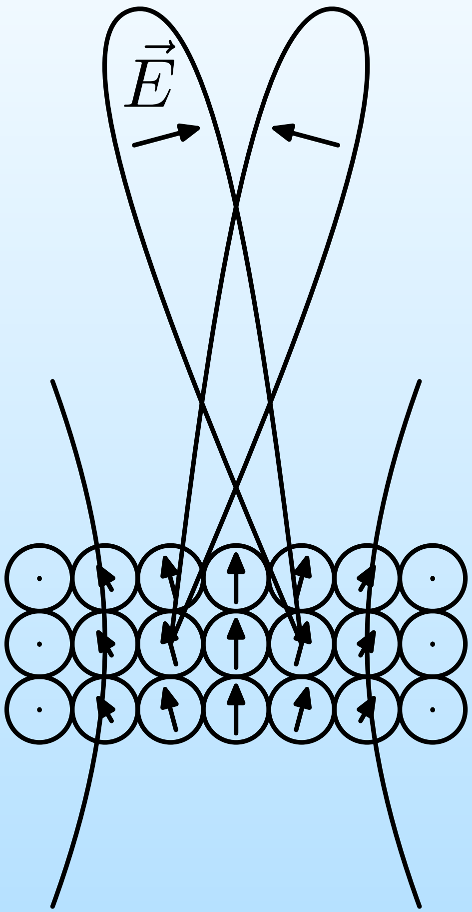
SHG from composite film





Theory

$$\vec{P}^{nl} = n_s \vec{p}^{(2)} - \frac{1}{6}\nabla \cdot \overset{\leftrightarrow}{Q}^{(2)} \Longrightarrow \vec{j}^{(2)}$$

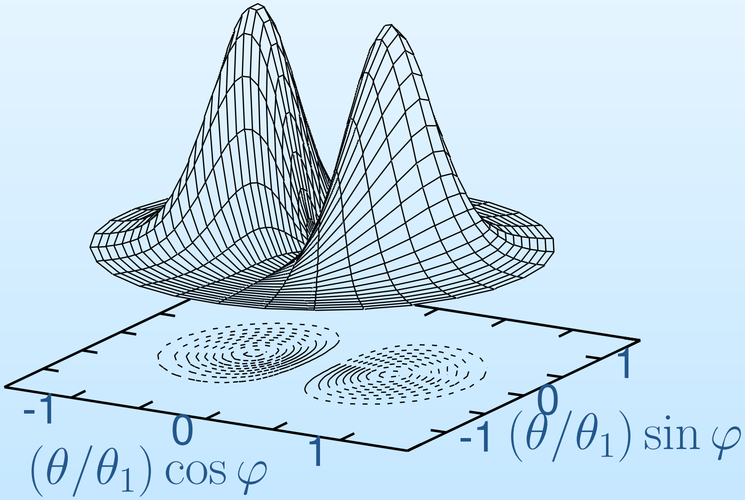
$$= \Gamma \nabla E^2 + \Delta' \vec{E} \cdot \nabla \vec{E} \Longrightarrow \vec{A}^{(2)}$$

$$\Longrightarrow \vec{E}^{(2)}, \vec{B}^{(2)}$$

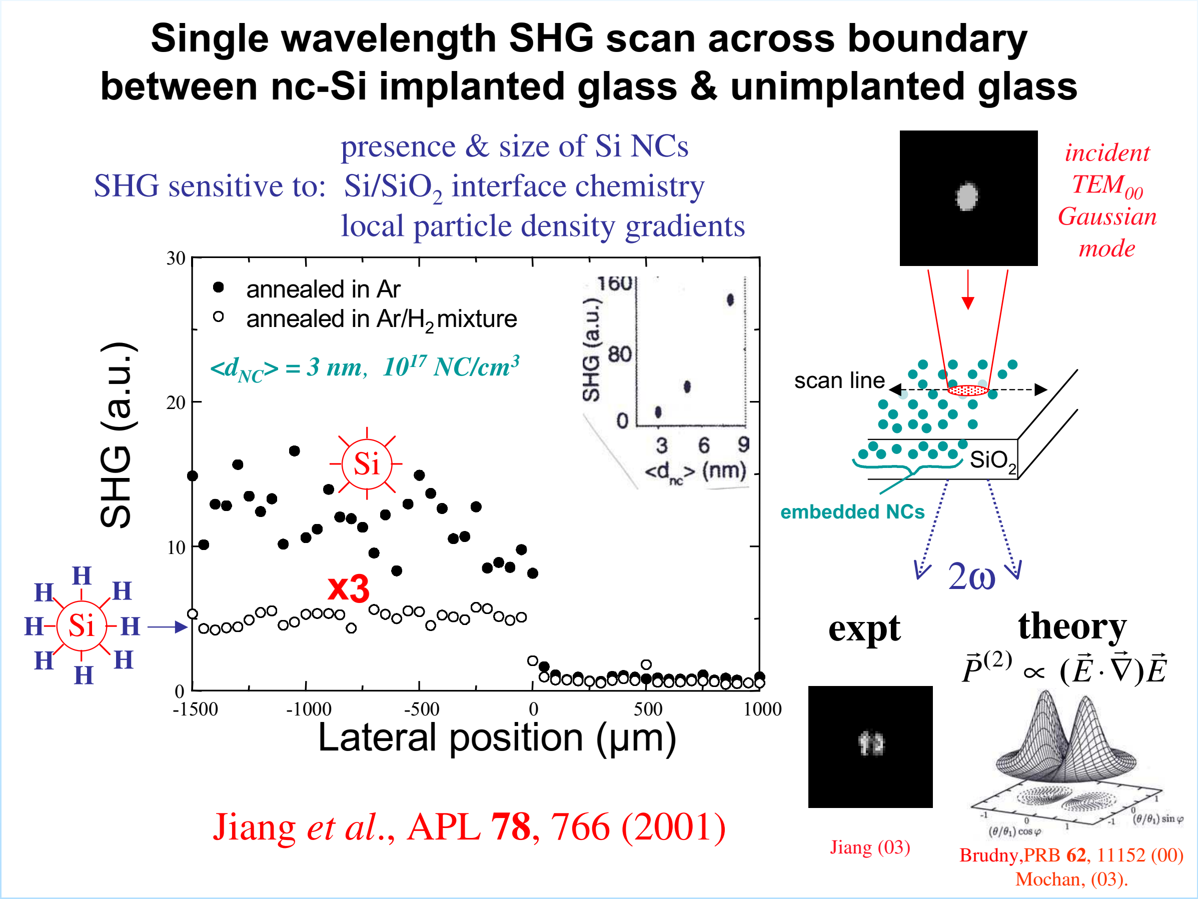
$$\Gamma = \frac{n_b}{18}(9\gamma^m + \gamma^q - 3\tilde{\gamma}^q) \Longrightarrow \vec{S}^{(2)}$$

$$\Delta' \equiv n_b(\gamma^e - \gamma^m - \gamma^q/6), \Longrightarrow \frac{d\mathcal{E}}{d\Omega} = \frac{1}{\mathcal{P}^2}\frac{dI^{(2)}}{d\Omega}$$

Angular distribution

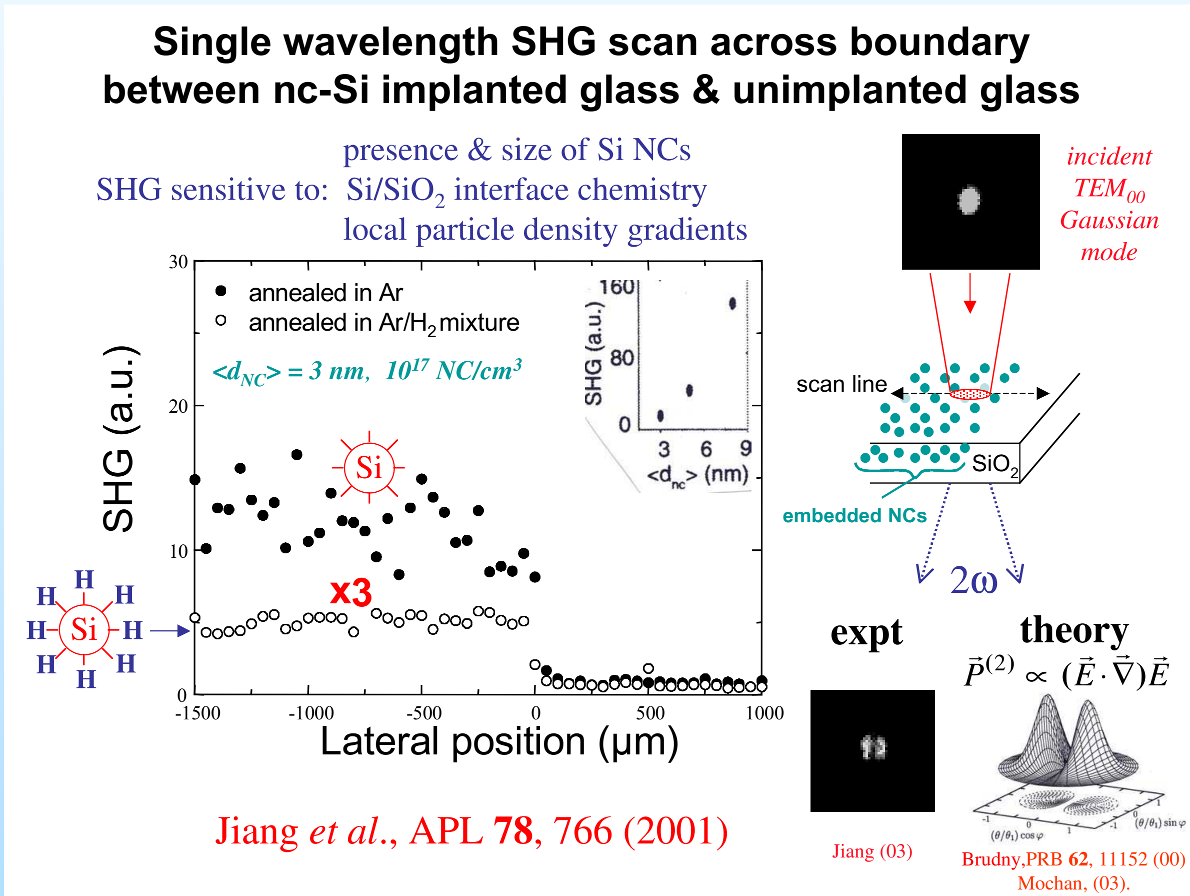


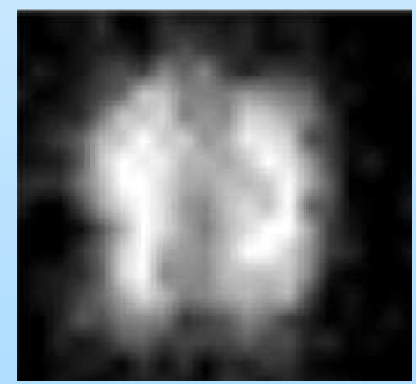
Experiment



Single wavelength SHG scan across boundary
between nc-Si implanted glass & unimplanted glass
SHG sensitive to: presence & size of Si NCs
Si/SiO2 interface chemistry
local particle density gradients
annealed in Ar
annealed in Ar/H2 mixture
<dNC> = 3 nm, 10^17 NC/cm^3
SHG (a.u.)
Lateral position (μm)
x3
Si
H
<dnc> (nm)
incident TEM00 Gaussian mode
scan line
SiO2
embedded NCs
2ω
expt
theory
P(2) ∝ (E·∇)E
Jiang et al., APL 78, 766 (2001)
Jiang (03)
Brudny,PRB 62, 11152 (00)
Mochan, (03).

Experiment





Figliozzi et al., submitted to PRL

Efficiency

$$\mathcal{E} = 10^{-2}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4 \frac{1}{e^2/a_B}\frac{1}{c/a_B}$$

$$\approx 10^{-4}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4\,\mathrm{W}^{-1}$$

$$\approx 10^{-24}\mathrm{W}^{-1}.$$

Efficiency

$$\mathcal{E} = 10^{-2}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4 \frac{1}{e^2/a_B}\frac{1}{c/a_B}$$
$$\approx 10^{-4}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4\,\mathrm{W}^{-1}$$
$$\approx 10^{-24}\mathrm{W}^{-1}.$$

- As $P \propto \vec{E}\nabla\vec{E} \sim E^2/w_0$, efficiency is proportional to incoming intensity, not power!

Efficiency

$$
\begin{aligned}
\mathcal{E} &= 10^{-2}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4 \frac{1}{e^2/a_B}\frac{1}{c/a_B} \\
&\approx 10^{-4}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4\,\mathrm{W}^{-1} \\
&\approx 10^{-24}\mathrm{W}^{-1}.
\end{aligned}
$$

- As $P \propto \vec{E}\nabla\vec{E} \sim E^2/w_0$, efficiency is proportional to incoming intensity, not power!
- Larger input power might actually yield less output power!

Efficiency

$$\begin{aligned}\mathcal{E} &= 10^{-2}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4 \frac{1}{e^2/a_B}\frac{1}{c/a_B} \\ &\approx 10^{-4}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4\,\mathrm{W}^{-1} \\ &\approx 10^{-24}\mathrm{W}^{-1}.\end{aligned}$$

- As $P \propto \vec{E}\nabla\vec{E} \sim E^2/w_0$, efficiency is proportional to incoming intensity, not power!
- Larger input power might actually yield less output power!
- Solution: Enhance transverse gradients with two beam SHG.

Conclusions

- Three wave mixing yields surface-sensitive optical spectroscopies.
- The bulk contribution is strongly suppressed (but not eliminated. . .) in centrosymmetric systems.
- Efficiency is *small*.
- Crystalline symmetry along surface is manifested by angular distribution of SHG radiation.
- Spectral dependence displays resonances at excitation energies and their subharmonics.
- The continuous *dipolium* model accounts (only. . .) for the strong surface field gradient.It produces simple analytical expressions for SHG in terms of the bulk linear response. It may be generalized. . .

Conclusions (cont.)

- The surface of isolated nanoparticles, deposited at surfaces and buried within composites may be observed with SHG.
- Quadrupolar and dipolar contributions may be comparable, giving rise to complex radiation patterns.
- There is no forward radiation, but there is nearly forward radiation from composites.
- Output power cannot be boosted simply by increasing input power.
- SHG may be enhanced orders of magnitude in two-beam geometry.