Microscopic model for electric-field-induced second-harmonic generation on various silicon and zincblende interfaces

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5. **Relation between THG and EFISH**

1. *Difference between SHG*

$$P_i = \varepsilon_0 \sum_{j,k} \chi_{ijk} E_j E_k$$

and electric field induced EFISH(G):

Optical second-harmonic generation induced by a dc electric field at the Si–SiO$_2$ interface

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3 fields present

$$E_x(\omega),$$

$$E_x(\omega' = \omega),$$

$$E_z(\omega = 0) \quad \parallel \mathbf{k},$$

$$P_i^{(3)}(2\omega_m) = (\varepsilon_0) \sum_{jkl} \chi_{ijkl}^{(3)}(2\omega_m, \omega_m, \omega_m, 0)$$

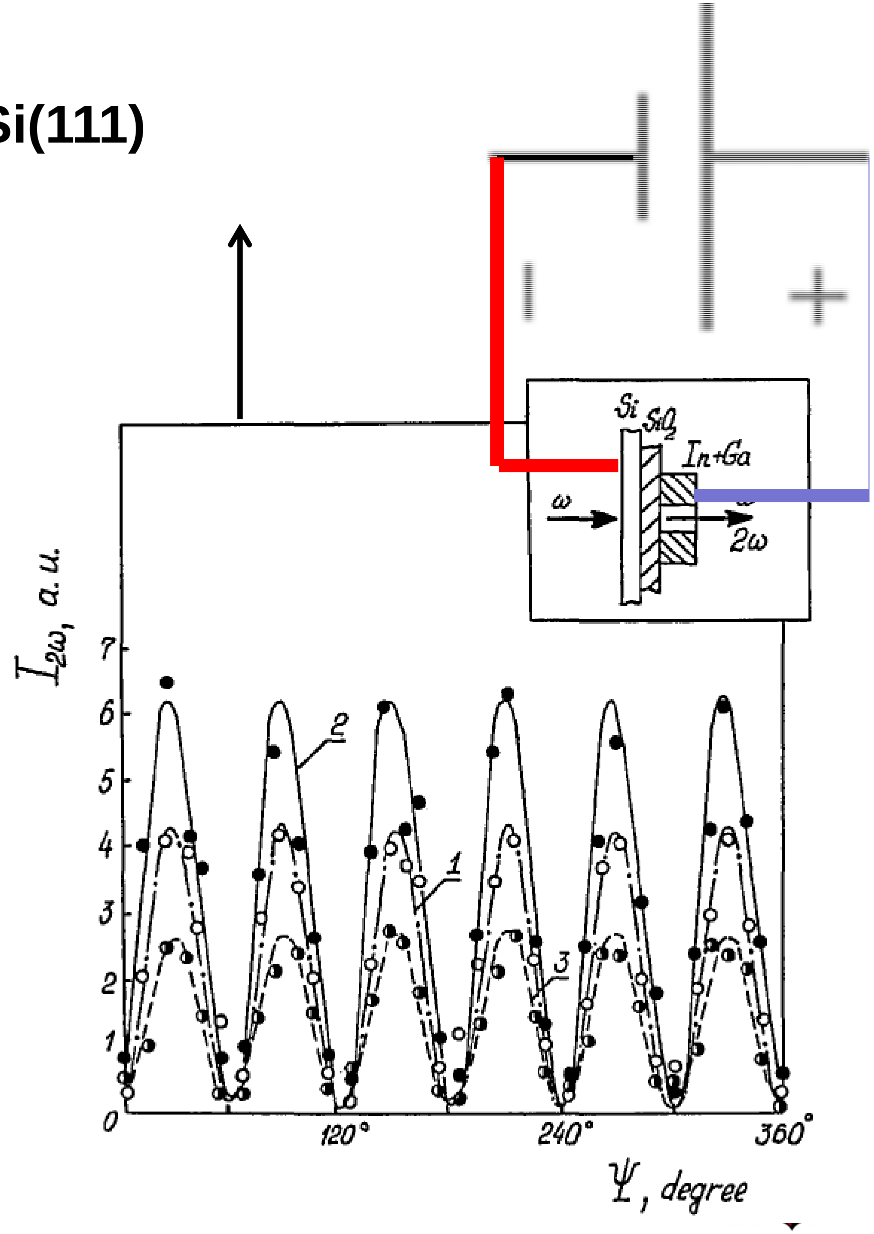
$$E_j(\omega_m) E_k(\omega_n = \omega_m) E_l(\omega_p = 0)$$

Bulk effect,

Phase matching not critical

(~ 100nm depl. region)

Si(111)



2. Group Theory for 4th rank tensors

The most general 4th rank tensor for T_d (O_h) has 4 independent elements (R. C. Powell *Symmetry, Group Theory and the Physical Properties of Crystals, Springer 2010*)
In Voigt (engineering) notation the 81 possible elements are displayed as a (6 x 6) matrix

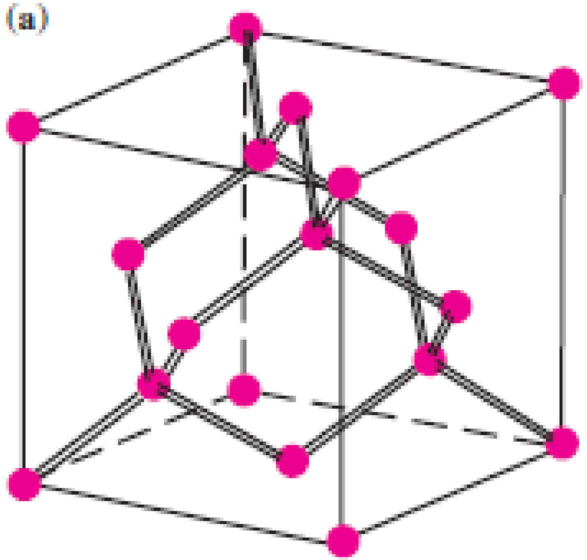
Table 3.6 Relationships between tensor subscripts

Reduced matrix ubscripts:	1	2	3	4	5	6
Tensor subscripts:	11	22	33	23,32	31,13	12,21
Numerical factors:	$s_{mn} = s_{ijkl}$ when m and n are 1, 2, 3					
	$s_{mn}=2s_{ijkl}$ when either m or n is 4, 5, 6					
	$s_{mn}=4s_{ijkl}$ when both m and n are 4, 5, 6					

T, T_h, T_d, O, O_h

$$\begin{pmatrix} s_{11} & s_{12} & s_{12} & 0 & 0 & 0 \\ s_{21} & s_{11} & s_{12} & 0 & 0 & 0 \\ s_{21} & s_{21} & s_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{44} \end{pmatrix}$$

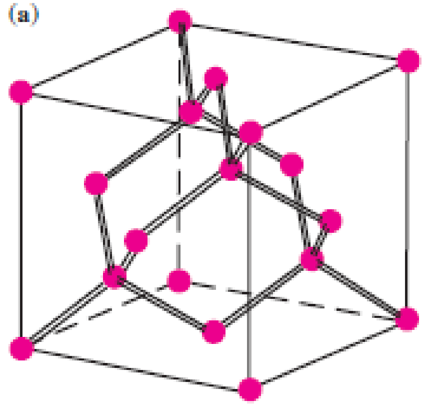
(a)



This matrix is given in the coordinate system of IUPAC!

2. Group Theory for 4th rank tensors

$$\chi^{(3)}(\omega_p,\omega_q,\omega_r,\omega_s)=\begin{pmatrix}
\begin{pmatrix} s_{11} & 0 & 0 \\ 0 & s_{12} & 0 \\ 0 & 0 & s_{12} \end{pmatrix} &
\begin{pmatrix} 0 & \frac{s_{44}}{4} & 0 \\ \frac{s_{44}}{4} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} &
\begin{pmatrix} 0 & 0 & \frac{s_{44}}{4} \\ 0 & 0 & 0 \\ \frac{s_{44}}{4} & 0 & 0 \end{pmatrix} \\
\begin{pmatrix} 0 & \frac{s_{44}}{4} & 0 \\ \frac{s_{44}}{4} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} &
\begin{pmatrix} s_{21} & 0 & 0 \\ 0 & s_{11} & 0 \\ 0 & 0 & s_{12} \end{pmatrix} &
\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{s_{44}}{4} \\ 0 & \frac{s_{44}}{4} & 0 \end{pmatrix} \\
\begin{pmatrix} 0 & 0 & \frac{s_{44}}{4} \\ 0 & 0 & 0 \\ \frac{s_{44}}{4} & 0 & 0 \end{pmatrix} &
\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{s_{44}}{4} \\ 0 & \frac{s_{44}}{4} & 0 \end{pmatrix} &
\begin{pmatrix} s_{21} & 0 & 0 \\ 0 & s_{21} & 0 \\ 0 & 0 & s_{11} \end{pmatrix}
\end{pmatrix}$$



This tensor is still given in the coordinate system of IUPAC!

T_d: 3 parameters

2. Group Theory for 4^th^ rank tensors - THG for T_d Symmetry

THG: (3ω, ω,ω,ω) : 2 independent elements, because the last 3 E's can be permuted, if there is only one – undistinguishable- incident fundamental!

The same can be done with EFISH: the two fields with ω can be permuted=> 2 independent elements remain.

$$\chi^{(3)}_{ijkl-EFISH}(2\omega,\omega,\omega,0) = \tfrac{1}{2}\left(\chi^{(3)}_{ijkl-EFISH} + \chi^{(3)}_{ikjl-EFISH}\right) \qquad s_{44}/4 = s_{12} = s_{21}$$

$$\chi^{(3)}_{ijkl-EFISH}(2\omega,\omega,\omega,0) = \begin{pmatrix} \begin{pmatrix} s_{11} & 0 & 0 \\ 0 & s_{12} & 0 \\ 0 & 0 & s_{12} \end{pmatrix} & \begin{pmatrix} 0 & s_{12} & 0 \\ s_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & s_{12} \\ 0 & 0 & 0 \\ s_{12} & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & s_{12} & 0 \\ s_{12} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} s_{12} & 0 & 0 \\ 0 & s_{11} & 0 \\ 0 & 0 & s_{12} \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & s_{12} \\ 0 & s_{12} & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 & s_{12} \\ 0 & 0 & 0 \\ s_{12} & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & s_{12} \\ 0 & s_{12} & 0 \end{pmatrix} & \begin{pmatrix} s_{12} & 0 & 0 \\ 0 & s_{12} & 0 \\ 0 & 0 & s_{11} \end{pmatrix} \end{pmatrix}$$

2. Group Theory for 4th rank tensors- EFISH for (001) surfaces

For calculating EFISH for (001) facets: Contract the tensor

normal inc.: χ. $\{0,0,Ez_{DC}\}$. $\{Ex,Ey,0\}$. $\{Ex,Ey,0\}]=$

$$\mathbf{P}_{001}(2\omega)=\begin{pmatrix}0\\0\\s_{12}Ez_{DC}\left(Ex^2+Ey^2\right)\end{pmatrix}$$

Cannot radiate into z- direction in a homogeneous material;

Radiation with ***k*** || to x,y will be discussed later (hardly observeable)

Oblique incidence with p-polarized light, but θ is (usually- high index) small=>

$$\mathbf{P}_{001}(2\omega)=\begin{pmatrix}E_p^2Ez_{DC}\ s_{12}\sin(2\theta),\\0,\\E_p^2Ez_{DC}\left(s_{11}\sin^2(\theta)+s_{12}\cos^2(\theta)\right)\end{pmatrix}$$

2. Group Theory for 4th rank tensors- EFISH (111) surfaces

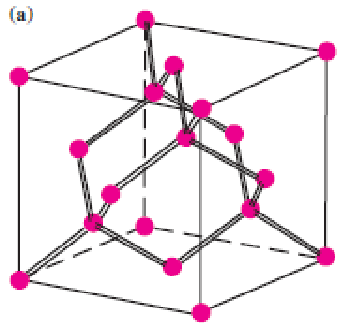
For all other coordinate systems (i.e. facets… relative orientations of ***E(ω)*** to the bonds), it has to be rotated- where $R_{ab}(\phi)$ is the rotation matrix.

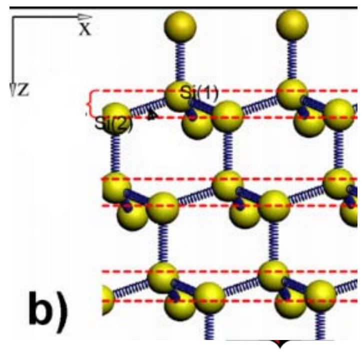
$$\chi'_{ijkl}(\phi) = R_{im}(\phi)\, R_{jn}(\phi)\, R_{ko}(\phi)\, R_{lp}(\phi)\, \chi_{mnop} \qquad R_y = \begin{pmatrix} \cos(\phi) & 0 & \sin(\phi) \\ 0 & 1 & 0 \\ -\sin(\phi) & 0 & \cos(\phi) \end{pmatrix}$$

Rotating χ, such that <111> direction || to z and one bond in the x-z plane yields: *($R_y(109.47°/2)\ R_z(45°)$)*

$$\chi_{111-EFISH}(2\omega,\omega,\omega,0) = \begin{pmatrix}
\begin{pmatrix} \frac{1}{2}(s_{11}+3s_{12}) & 0 & \frac{s_{11}-3s_{12}}{3\sqrt{2}} \\ 0 & \frac{1}{6}(s_{11}+3s_{12}) & 0 \\ \frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 & \frac{s_{11}}{3} \end{pmatrix} &
\begin{pmatrix} 0 & \frac{1}{6}(s_{11}+3s_{12}) & 0 \\ \frac{1}{6}(s_{11}+3s_{12}) & 0 & -\frac{s_{11}-3s_{12}}{3\sqrt{2}} \\ 0 & -\frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 \end{pmatrix} &
\begin{pmatrix} \frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 & \frac{s_{11}}{3} \\ 0 & -\frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 \\ \frac{s_{11}}{3} & 0 & 0 \end{pmatrix} \\
\begin{pmatrix} 0 & \frac{1}{6}(s_{11}+3s_{12}) & 0 \\ \frac{1}{6}(s_{11}+3s_{12}) & 0 & -\frac{s_{11}-3s_{12}}{3\sqrt{2}} \\ 0 & -\frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 \end{pmatrix} &
\begin{pmatrix} \frac{1}{6}(s_{11}+3s_{12}) & 0 & -\frac{s_{11}-3s_{12}}{3\sqrt{2}} \\ 0 & \frac{1}{2}(s_{11}+3s_{12}) & 0 \\ -\frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 & \frac{s_{11}}{3} \end{pmatrix} &
\begin{pmatrix} 0 & -\frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 \\ -\frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 & \frac{s_{11}}{3} \\ 0 & \frac{s_{11}}{3} & 0 \end{pmatrix} \\
\begin{pmatrix} \frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 & \frac{s_{11}}{3} \\ 0 & -\frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 \\ \frac{s_{11}}{3} & 0 & 0 \end{pmatrix} &
\begin{pmatrix} 0 & -\frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 \\ -\frac{s_{11}-3s_{12}}{3\sqrt{2}} & 0 & \frac{s_{11}}{3} \\ 0 & \frac{s_{11}}{3} & 0 \end{pmatrix} &
\begin{pmatrix} \frac{s_{11}}{3} & 0 & 0 \\ 0 & \frac{s_{11}}{3} & 0 \\ 0 & 0 & \frac{1}{3}(s_{11}+6s_{12}) \end{pmatrix}
\end{pmatrix}$$

(a)





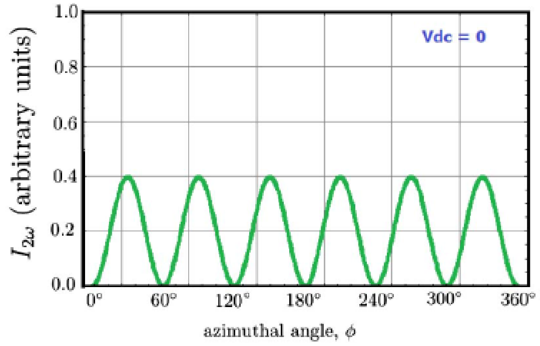
b)

2. Group Theory for 4th rank tensors- EFISH (111) facets

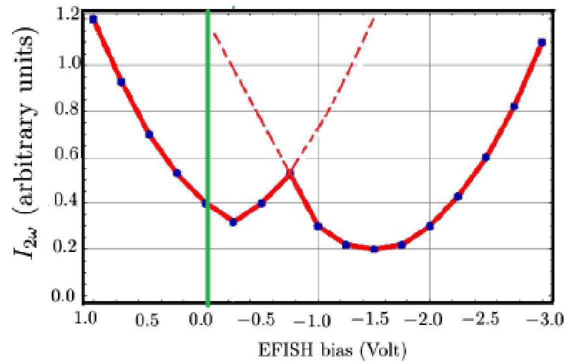
Normal incidence on (111) facets :

$$\mathbf{P}_{111}(2\omega)=\begin{pmatrix}\frac{1}{3\sqrt{2}}\left(s_{11}-3s_{12}\right)Ez_{DC}(Ex^2-Ey^2)\\ -\frac{\sqrt{2}}{3}\left(s_{11}-3s_{12}\right)Ez_{DC}\;Ex\;Ey\\ \frac{1}{3}s_{11}Ez_{DC}\left(Ex^2+Ey^2\right)\end{pmatrix}$$

Simulation for (111) on AOI and E_{DC}



(a)

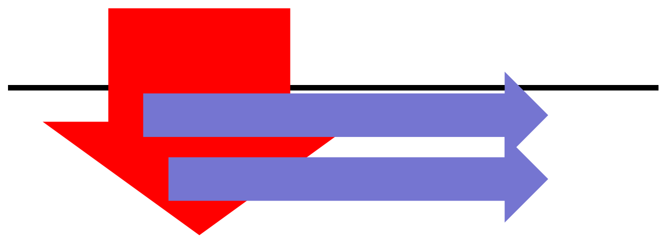


(b)

EFISH (110) facets:

$$\mathbf{P}_{110}(2\omega)=\begin{pmatrix}0\\ 0\\ \frac{1}{2}Ez_{DC}\left(Ex^2s_{11}-\left(Ex^2-2Ey^2\right)s_{12}\right)\end{pmatrix}$$

ω ***For (100) & (110) facets:***



Destructive superposition

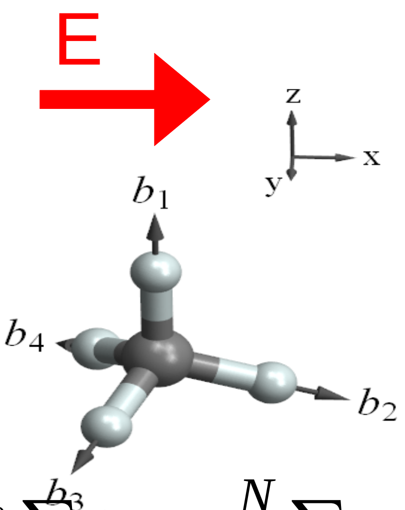
Would the in-plane radiation with z-component be measureable (e.g. waveguide)?

Hardly, because destructive interference of the dipoles due to non phasematching,

3. Comparison to SBHM: Simplified bond hyperpolarizibility

Classical model: Introduced by D.E. Aspnes PRB 2002 for SHG, THG, SFG of surfaces

- each accelerated charge radiates (anharmonically), driven by the external field
- each e- sitting on a bond between the ion and the electron is described by an equation of motion
- the movement is given by Newton’s, second law, just only along the bond
- the radiation field can be determined by Hertz´s vectors and has to be summed up



$$m\frac{d^2x}{dt^2} = q_j\vec{E}\cdot\hat{b}_j e^{-i\omega t} - \kappa_1(x-x_0) - \kappa_2(x-x_0)^2 - \gamma\frac{dx}{dt}$$

$$\vec{p}_{1j} = q_j\Delta x_1\hat{b}_j = \frac{q_j^2\vec{E}\cdot\hat{b}_j}{\kappa_1 - m\omega^2 - i\gamma\omega}\hat{b}_j = \beta_{1j}\hat{b}_j(\hat{b}_j\cdot\vec{E})$$

$$\vec{p}_{2j} = q_j\Delta x_2\hat{b}_j = \frac{q_j^2\kappa_2\Delta x_1^2}{\kappa_1 - 4m\omega^2 - 2i\gamma\omega}\hat{b}_j = \beta_{2j}\hat{b}_j(\hat{b}_j\cdot\vec{E})^2$$

$$\vec{P} = \frac{\epsilon_0}{V}\sum_j \vec{p}_j = \epsilon_0\frac{N}{V}\sum_j(\alpha_{1j}\hat{b}_j\otimes\hat{b}_j)\cdot\vec{E} + \epsilon_0\frac{N}{V}\sum_j(\alpha_{2j}\hat{b}_j\otimes\hat{b}_j\otimes\hat{b}_j)\cdot\cdot(\vec{E}\otimes\vec{E}) = \chi_1\vec{E} + \chi_2\vec{E}\vec{E}$$

All χs by SBHM are symmetric tensors fulfill Kleinman symmetry automatically

3. Comparison to SBHM: Simplified bond hyperpolarizibility

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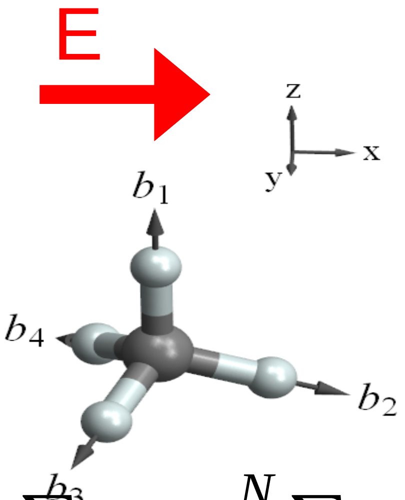

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$$\vec{p}_{2j} = q_j\Delta x_2\hat{b}_j = \frac{q_j^2\kappa_2\Delta x_1^2}{\kappa_1 - 4m\omega^2 - 2i\gamma\omega}\hat{b}_j = \beta_{2j}\hat{b}_j(\hat{b}_j\cdot\vec{E})^2$$

$$\vec{P} = \frac{\epsilon_0}{V}\sum_j\vec{p}_j = \epsilon_0\frac{N}{V}\sum_j(\alpha_{1j}\hat{b}_j\otimes\hat{b}_j)\cdot\vec{E} + \epsilon_0\frac{N}{V}\sum_j(\alpha_{2j}\hat{b}_j\otimes\hat{b}_j\otimes\hat{b}_j)\cdot\cdot(\vec{E}\otimes\vec{E}) = \chi_1\vec{E} + \chi_2\vec{E}\vec{E}$$

$$\propto \chi^{(2)}$$

$$\chi^{(3)}{}_{ijkl} \propto \alpha_{3b}(3\omega)\sum_{bonds=b}(\hat{b}_b\otimes\hat{b}_b\otimes\hat{b}_b\otimes\hat{b}_b)$$

All χs by SBHM are symmetric tensors fulfill Kleinman symmetry automatically

3. Comparison to SBHM: Simplified bond hyperpolarizibility

$\alpha_3(2\omega,\omega,\omega,0)$ could be frequency dependent..

and could be different from

$\alpha_3(3\omega,\omega,\omega,\omega)$

$$\vec{\chi}_{SBHM}^{(3)} = (\varepsilon_0)\frac{8N}{9V}\alpha_3(2\omega,\omega,\omega,0)\begin{pmatrix} \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} & \begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix} & \begin{pmatrix}0&0&1\\0&0&0\\1&0&0\end{pmatrix} \\ \begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix} & \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} & \begin{pmatrix}0&0&0\\0&0&1\\0&1&0\end{pmatrix} \\ \begin{pmatrix}0&0&1\\0&0&0\\1&0&0\end{pmatrix} & \begin{pmatrix}0&0&0\\0&0&1\\0&1&0\end{pmatrix} & \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} \end{pmatrix}$$

$$\chi^{(3)}(\omega_p,\omega_q,\omega_r,\omega_s) \propto \begin{pmatrix} \begin{pmatrix}s_{11}&0&0\\0&s_{12}&0\\0&0&s_{12}\end{pmatrix} & \begin{pmatrix}0&\frac{s_{44}}{4}&0\\\frac{s_{44}}{4}&0&0\\0&0&0\end{pmatrix} & \begin{pmatrix}0&0&\frac{s_{44}}{4}\\0&0&0\\\frac{s_{44}}{4}&0&0\end{pmatrix} \\ \begin{pmatrix}0&\frac{s_{44}}{4}&0\\\frac{s_{44}}{4}&0&0\\0&0&0\end{pmatrix} & \begin{pmatrix}s_{21}&0&0\\0&s_{11}&0\\0&0&s_{12}\end{pmatrix} & \begin{pmatrix}0&0&0\\0&0&\frac{s_{44}}{4}\\0&\frac{s_{44}}{4}&0\end{pmatrix} \\ \begin{pmatrix}0&0&\frac{s_{44}}{4}\\0&0&0\\\frac{s_{44}}{4}&0&0\end{pmatrix} & \begin{pmatrix}0&0&0\\0&0&\frac{s_{44}}{4}\\0&\frac{s_{44}}{4}&0\end{pmatrix} & \begin{pmatrix}s_{21}&0&0\\0&s_{21}&0\\0&0&s_{11}\end{pmatrix} \end{pmatrix}$$

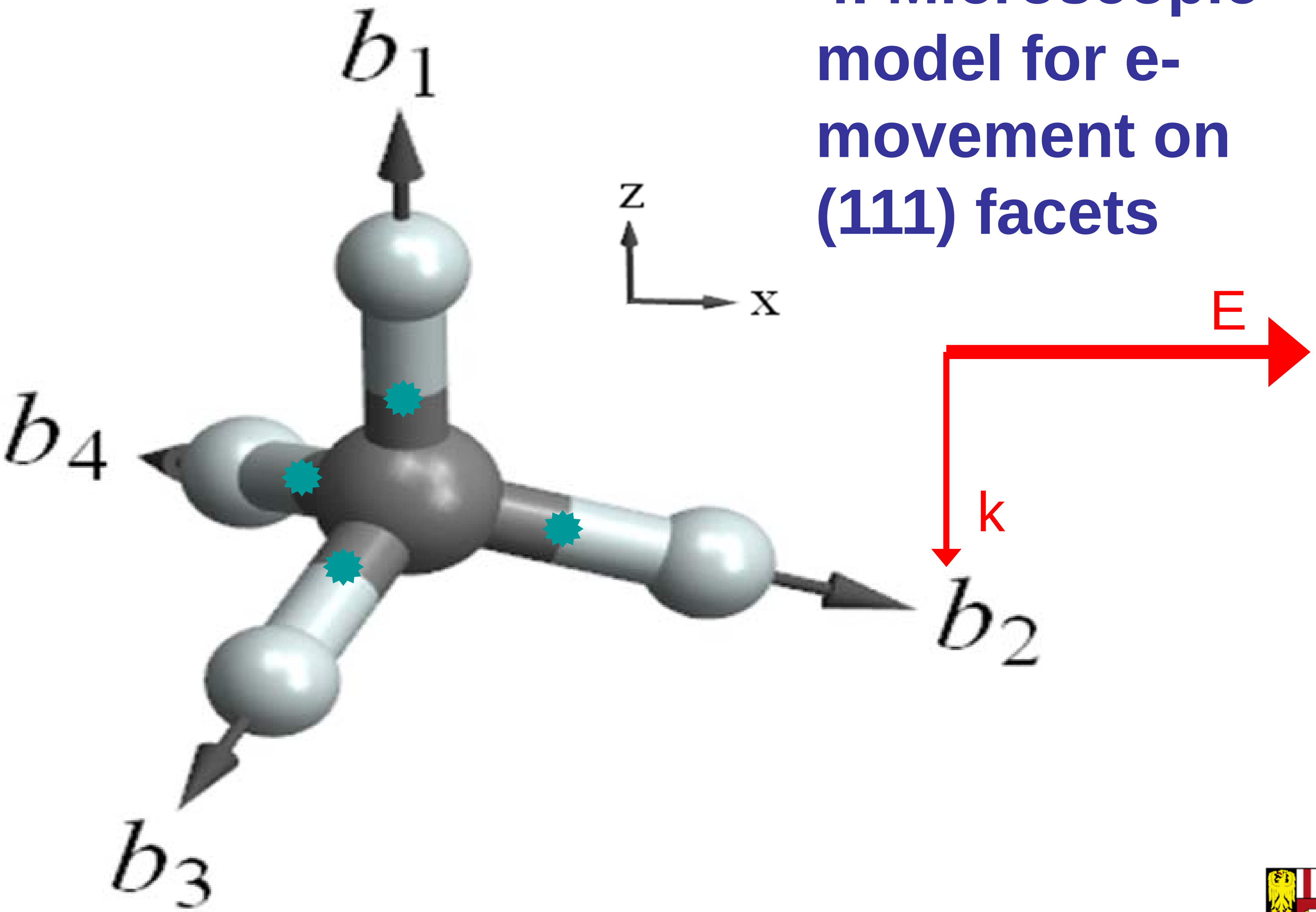
$$\boxed{\frac{8N}{9V}\alpha_3(2\omega,\omega,\omega,0) = s_{11} = s_{12} = s_{21} = \frac{s_{44}}{4}}$$

$\Rightarrow$ Has to be tested by ab initio theory

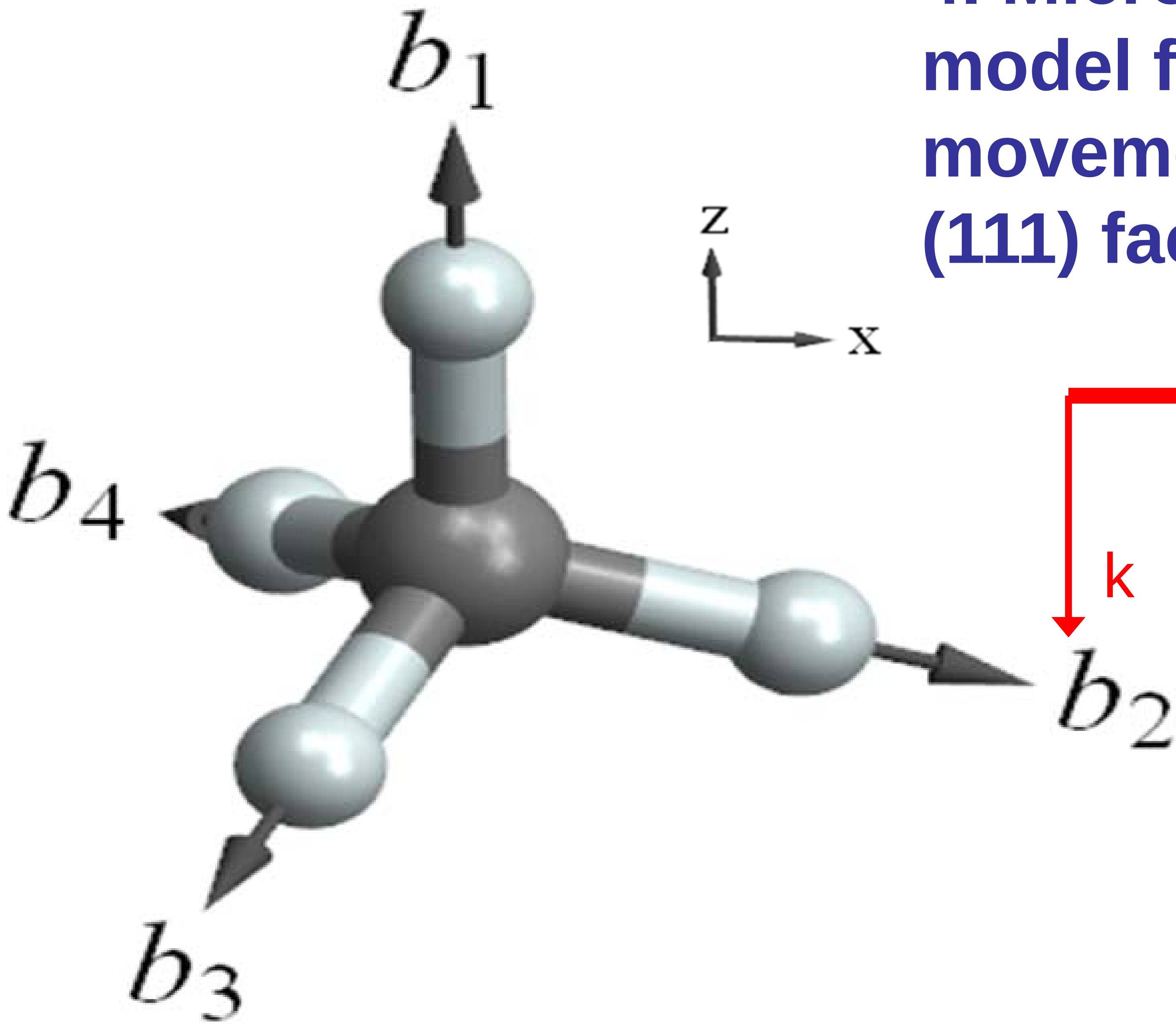
or experiment.

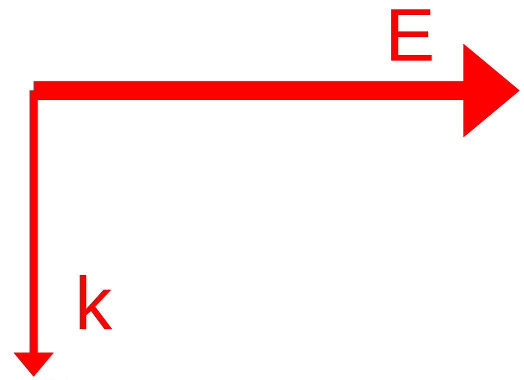
K. Kikuchi and K. Tada, “Theory of electric field-induced optical second harmonic generation in semiconductors,” Opt. Quantum Electron. 12, 199–205 (1980).

4. Microscopic model for e- movement on (111) facets

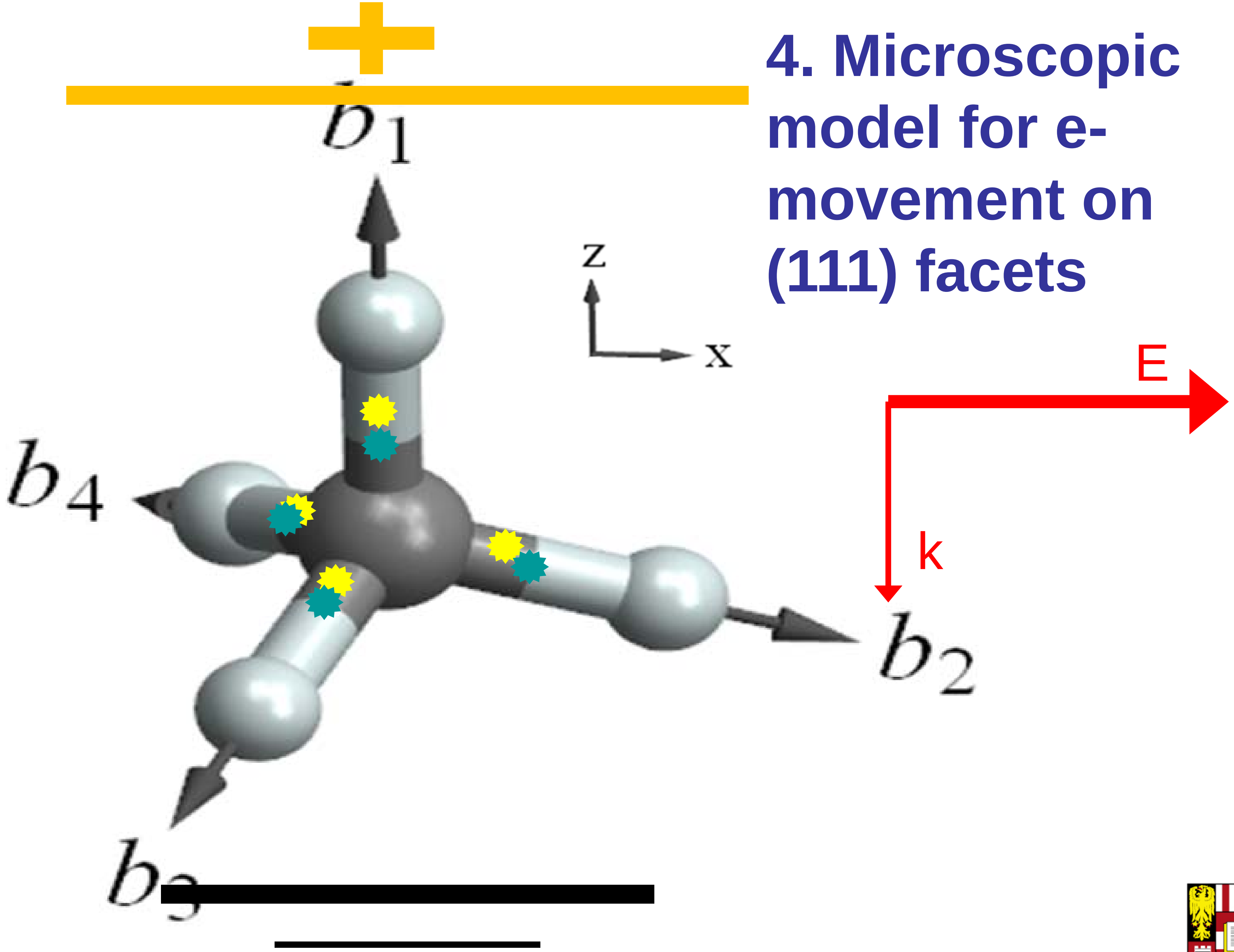


4. Microscopic model for e- movement on (111) facets

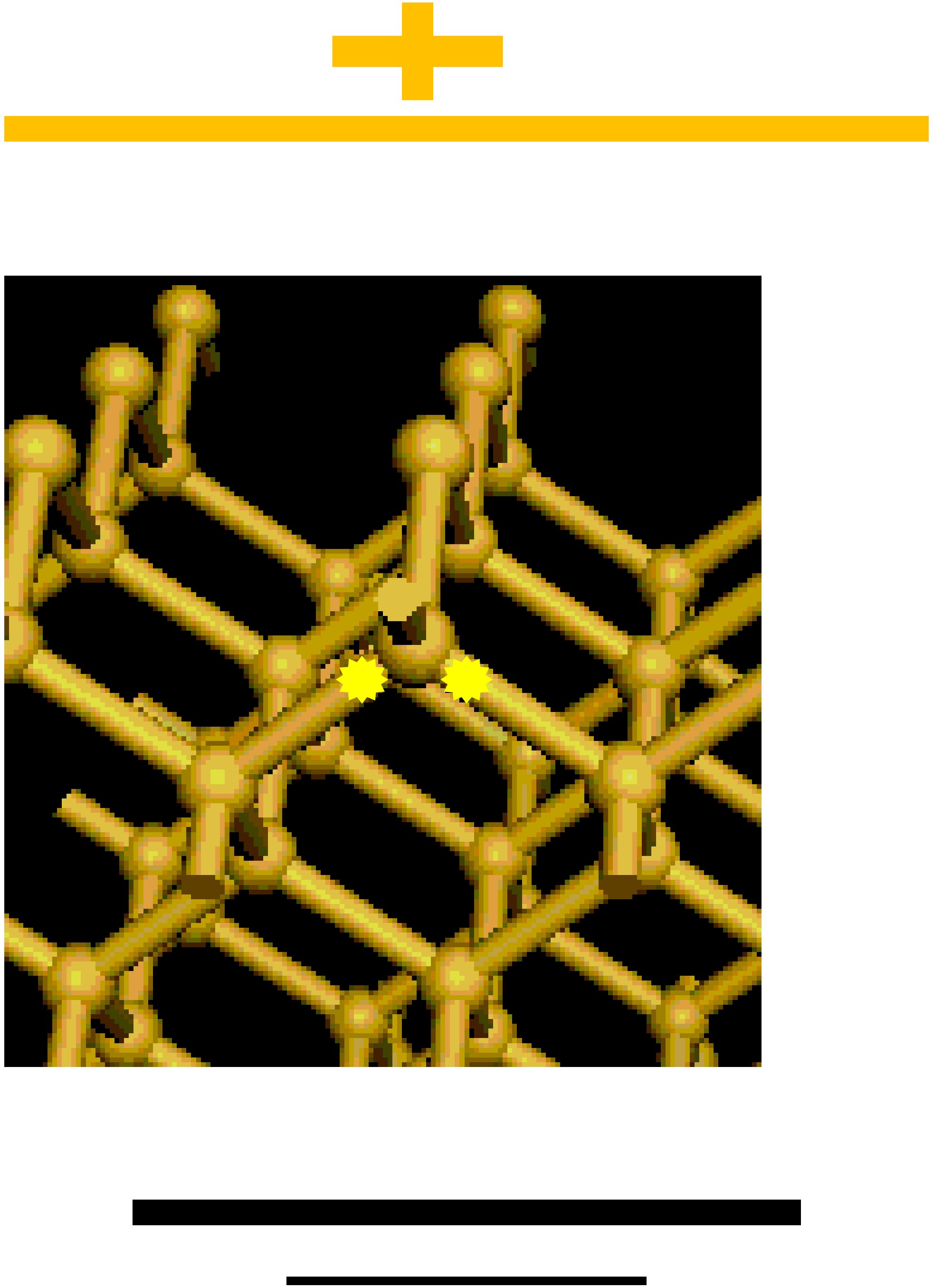




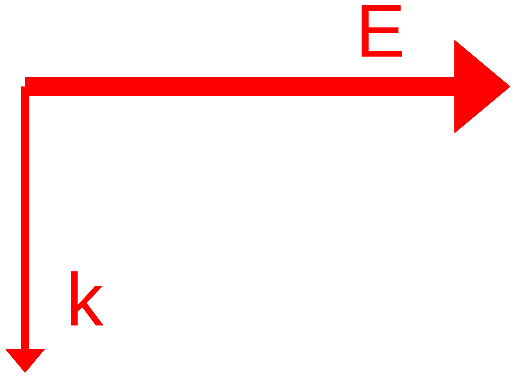
4. Microscopic model for e- movement on (111) facets



Microscopic model for e- movement on (001) facets:



For normal incidence the DC field does not break the symmetry w.r.t. the field direction of the light

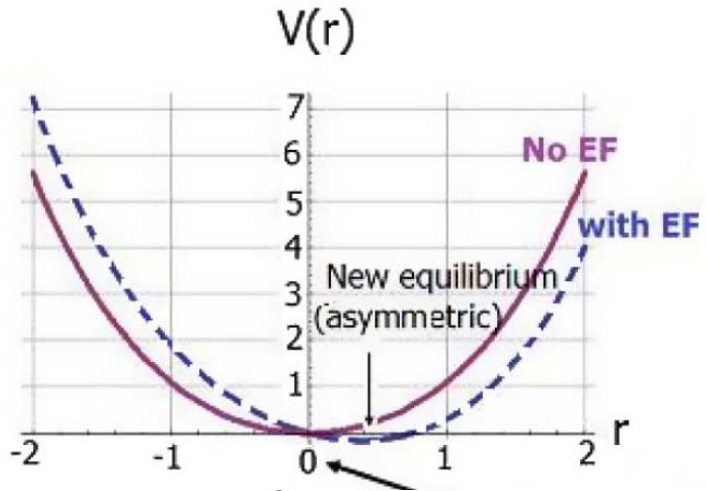


5. Relation between THG and EFISH

can be stablished formally via (at least in a good approximation– Kleinman symmetry)

$$\chi^{(3)}_{ijkl} . E^{DC}_{l} = \chi^{(2)eff}_{ijk}$$

... $\alpha_3\,(2\omega, \omega, \omega, 0)$ could be frequency dependent..and different from $\alpha_3(3\omega, \omega, \omega, \omega)$



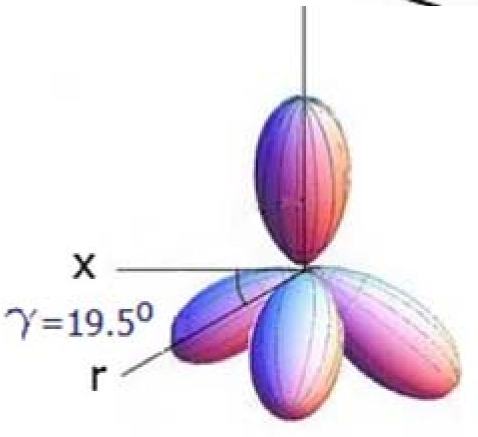
Or microscopically for the 3 backbonds:

$$V(r) = m\omega_0 r^2 - mbr^4 -->$$

$$V(r) = m\omega_0 r^2 - mbr^4 - r\ e\ E_{dc}\sin(\gamma)$$

New equilibrium position: $$r \simeq r_0 - \frac{eE_{dc}\sin(\gamma)}{2\omega_0}$$

Taylor expansion around n.e.p. yields a term in V prop. to r^3*: =>*



$$\alpha^{(2)}_{2eff}(2\omega) = \frac{6bE_{dc}\sin\gamma}{\omega_0}$$

connects THG and EFISH!

Summary:

a) **EFISHG is clearly a bulk effect**

b) **Group theory the right tool to describe EFISHG, two independent parameters. (as well as for THG)**

c) **SBHM for bulk seems to be a VERY reasonable one parameter model, but has to be checked.**

d) **(Zincblende bulk SHG: GT=> 1 parameter -**_here not derived_**)**

e) **Diamond and Zincblende (111) facets deliver EFISHG, (110) and (001) facets none (at normal incidence).**

f) **Microscopic model relates THG and EFISH efficiency.**

g) **EFISH in reflection will be measureable- despite bad phase matching- especially if space charge region is narrow.**

Details can be found in J. Opt. Soc. Am. **B32**, 562, (2015)

Thanks for your attention!