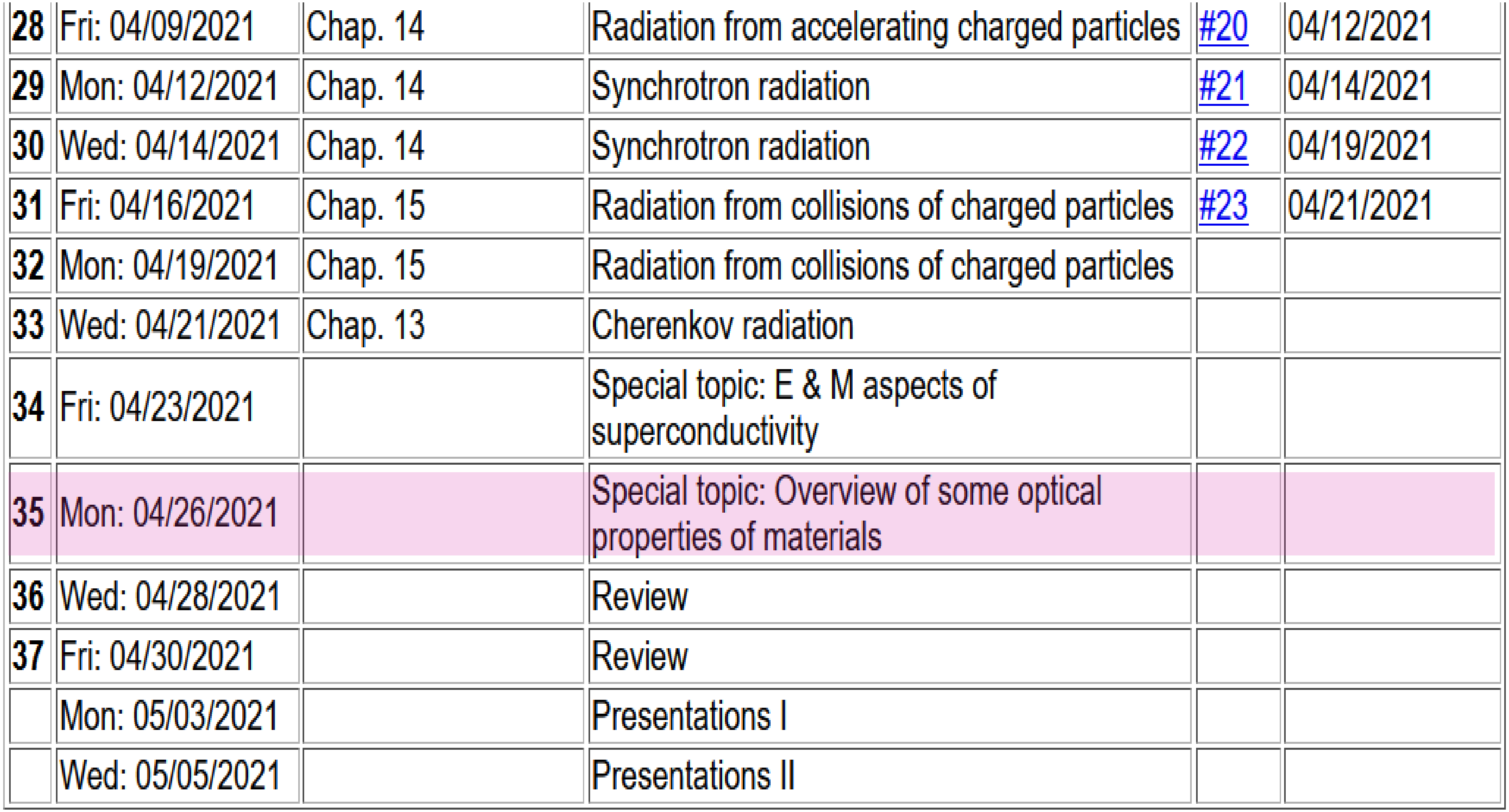
PHY 712 Electrodynamics
10-10:50 AM MWF Online

Discussion for Lecture 35:

Special Topics in Electrodynamics:

Some optical properties of materials**

**previously advertised as more details on superconductors



28	Fri: 04/09/2021	Chap. 14	Radiation from accelerating charged particles	#20	04/12/2021
29	Mon: 04/12/2021	Chap. 14	Synchrotron radiation	#21	04/14/2021
30	Wed: 04/14/2021	Chap. 14	Synchrotron radiation	#22	04/19/2021
31	Fri: 04/16/2021	Chap. 15	Radiation from collisions of charged particles	#23	04/21/2021
32	Mon: 04/19/2021	Chap. 15	Radiation from collisions of charged particles		
33	Wed: 04/21/2021	Chap. 13	Cherenkov radiation		
34	Fri: 04/23/2021		Special topic: E & M aspects of superconductivity		
35	Mon: 04/26/2021		Special topic: Overview of some optical properties of materials		
36	Wed: 04/28/2021		Review		
37	Fri: 04/30/2021		Review		
	Mon: 05/03/2021		Presentations I		
	Wed: 05/05/2021		Presentations II		

Timelines –

May 6 – take home exam available

May 14 – all course materials due; outstanding homework, projects, and completed exams

Aspects of optical properties of solids

1. **Quantum effects cause discrete energy levels for electrons; EM radiation can couple the ground state of a material to its excited states**
2. **In solid materials with ~10^{23} atoms, discrete states become bands of states**
   1. **Metals**
   2. **Insulators**
3. **Anisotropic effects**

Note: We can analyze effectively single particle systems with high accuracy. Analysis of several/many particle systems can be accomplished with a series of approximations. We will also use a linear combination of atomic orbital approach to get the qualitative picture.

Electronic structure of an atom

For simplicity we will first consider a single electron system; a H-like ion with atomic charge of +*Ze and one electron of charge –e:*

According to Quantum Mechanics:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$H\Psi_{nlm}(r,\theta,\phi) = E_{nlm}\Psi_{nlm}(r,\theta,\phi)$$

$$E_{nlm} = -\frac{Z^2e^2}{4\pi\epsilon_0 a_0}\frac{1}{2n^2} \equiv \frac{E_{100}}{n^2} \qquad a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

E_{100}=-13. 60569253 Z^2 eV

a_0 = 0. 52917721092 Å

The following few slides address the question of the expected distribution of energy levels of materials.

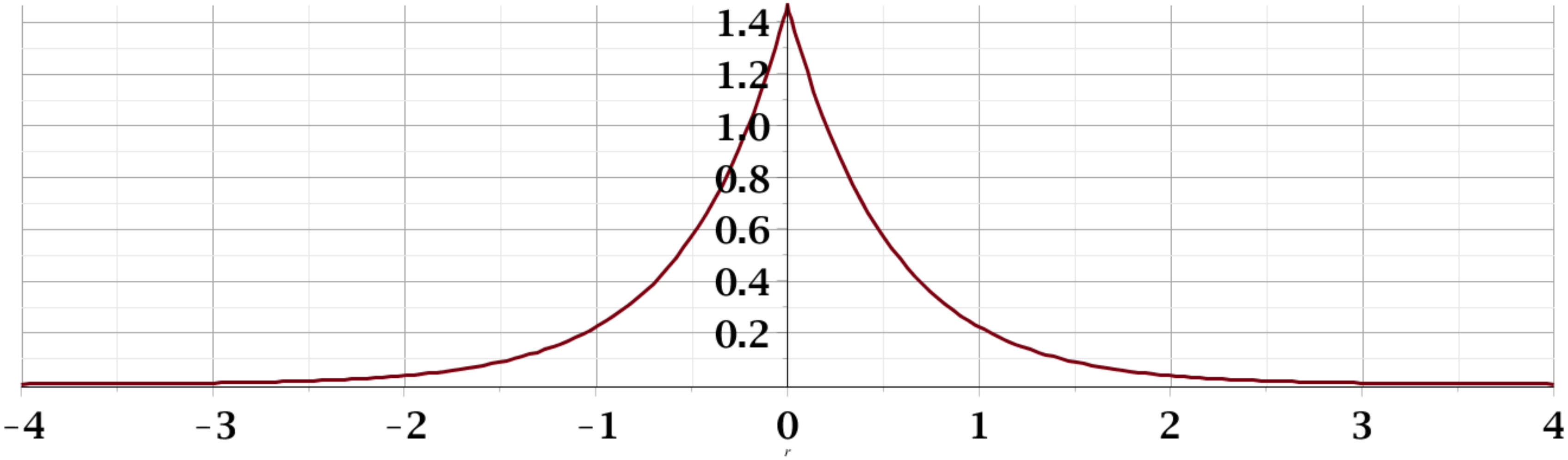
Note that isolated atoms and molecules have discrete and continuum states while solids have only continuum states.

How is the distribution of states of materials related to their spectra?

1. Optical properties of materials are determined by transitions between states.
2. Transitions between discrete states → discrete spectral features.
3. Transitions between continuum states → broad spectral features.

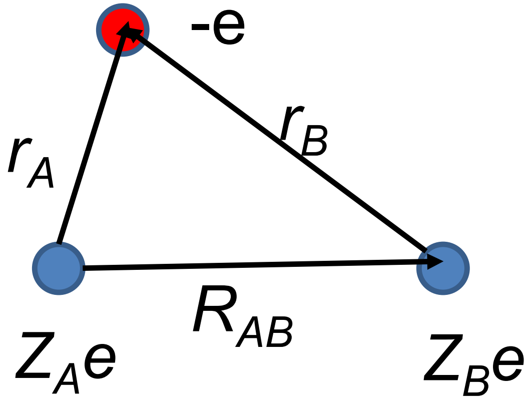
Probability amplitude for electron in the ground state of H atom:

$$\Psi_{100}(r,\theta,\phi)=\sqrt{\frac{Z^3}{\pi a_0^3}}e^{-Zr/a_0}$$



Now consider one electron in the presence of two H-like ions:

Electronic structure of H-like molecular ion (within Born-Oppenheimer approximation)



$r_A = |\mathbf{r} - \mathbf{R}_A|$ $\qquad$ $r_B = |\mathbf{r} - \mathbf{R}_B|$

$R_{AB} = |\mathbf{R}_B - \mathbf{R}_A|$

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Z_Ae^2}{4\pi\epsilon_0 r_A} - \frac{Z_Be^2}{4\pi\epsilon_0 r_B} + \frac{Z_AZ_Be^2}{4\pi\epsilon_0 R_{AB}}$$

Approximate wavefunction:

$$\Psi(\mathbf{r},\mathbf{R}_A,\mathbf{R}_B) = X_A\Psi_{100}(\mathbf{r}-\mathbf{R}_A) + X_B\Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

X_A and X_B can be determined variationally by optimizing

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

Electronic structure of H-like molecular ion – continued

Ref. Pauling and Wilson, *Introduction to Quantum Mechanics* (1935) (now published by Dover)

Necessary integrals:

$$\Delta \equiv \int d^3r \Psi^*_{100}(\mathbf{r}-\mathbf{R}_A)\Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

$$H_{AA} \equiv \int d^3r \Psi^*_{100}(\mathbf{r}-\mathbf{R}_A) H \Psi_{100}(\mathbf{r}-\mathbf{R}_A) = H_{BB}$$

$$H_{AB} \equiv \int d^3r \Psi^*_{100}(\mathbf{r}-\mathbf{R}_A) H \Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

Generalized eigenvalue problem for energy E in the variational approximation:

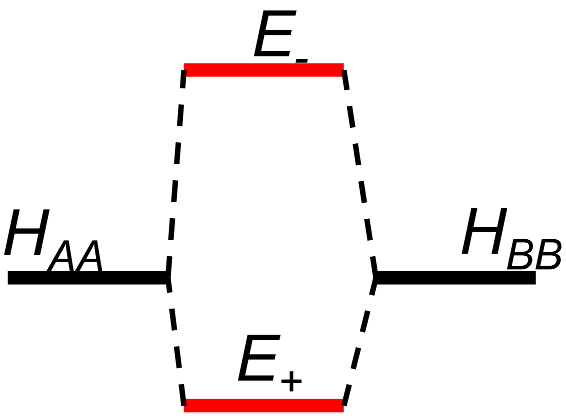
$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}\begin{pmatrix} X_A \\ X_B \end{pmatrix} = E\begin{pmatrix} 1 & \Delta \\ \Delta & 1 \end{pmatrix}\begin{pmatrix} X_A \\ X_B \end{pmatrix}$$

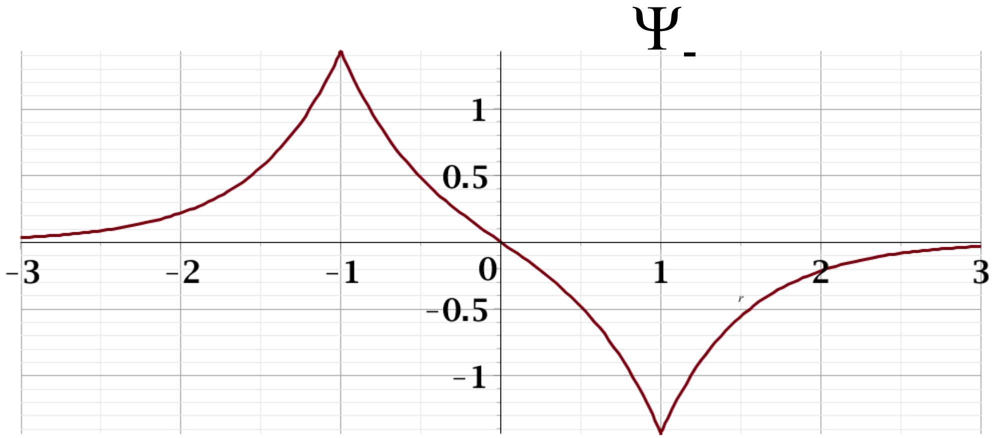
Eigenstates:

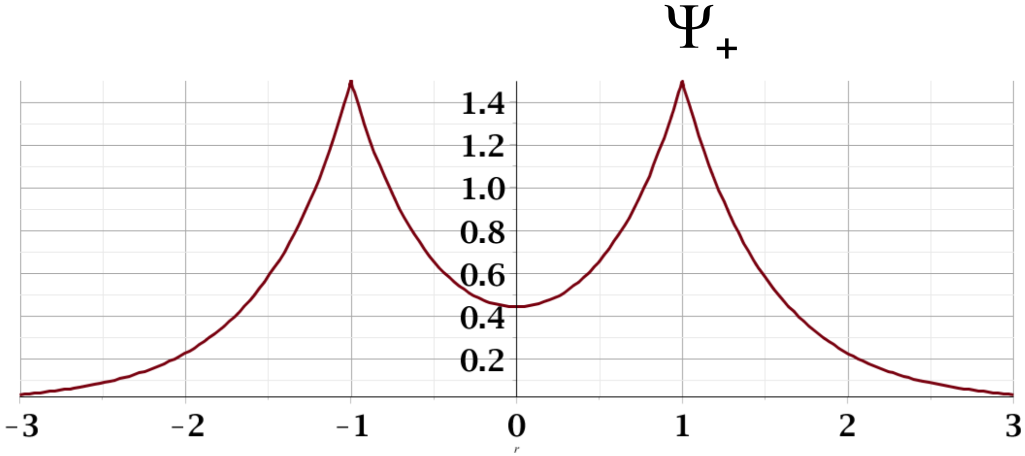
$$\begin{pmatrix} X_A \\ X_B \end{pmatrix}_+ = \frac{1}{\sqrt{2(1+\Delta)}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \mathrm{E}_+ = \frac{H_{AA}+H_{AB}}{1+\Delta}$$

$$\begin{pmatrix} X_A \\ X_B \end{pmatrix}_- = \frac{1}{\sqrt{2(1-\Delta)}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad \mathrm{E}_+ = \frac{H_{AA}-H_{AB}}{1-\Delta}$$

Electronic structure of H-like molecular ion – continued




Ψ_-


Ψ_+

In the previous slide, we showed two states for the H_2^+ molecular ion. Are these the only states?

1. Yes
2. No

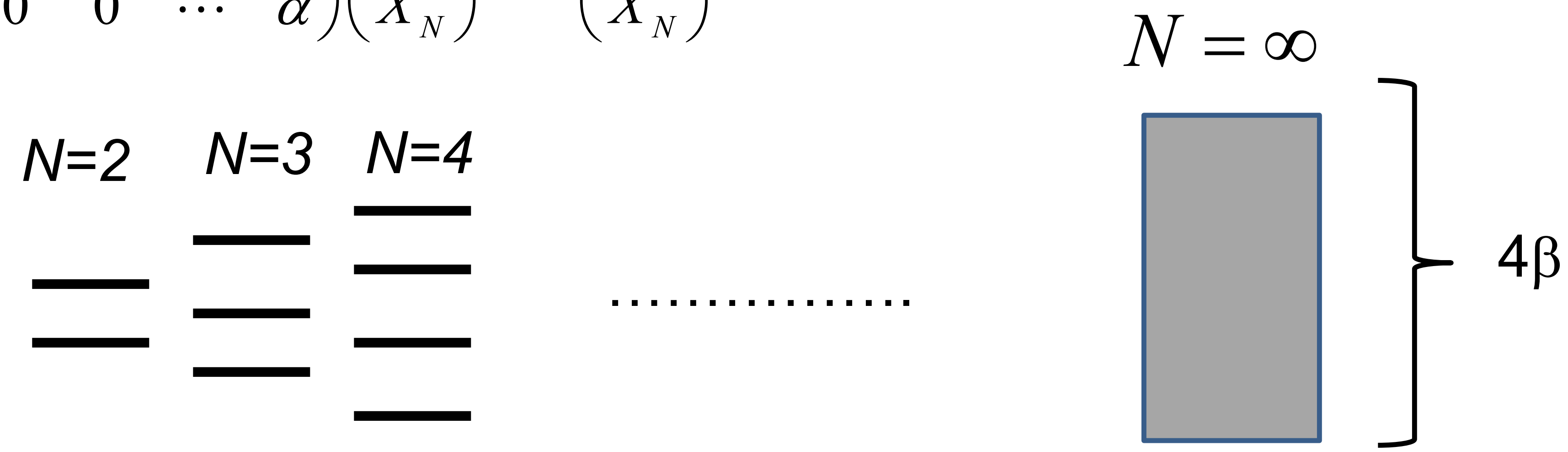
Formation of “energy bands” with a large number of atoms --

Extension of approximate “linear combination of atomic orbital” idea to larger systems

Idealized model Hamiltonian with only nearest neighbor interactions:

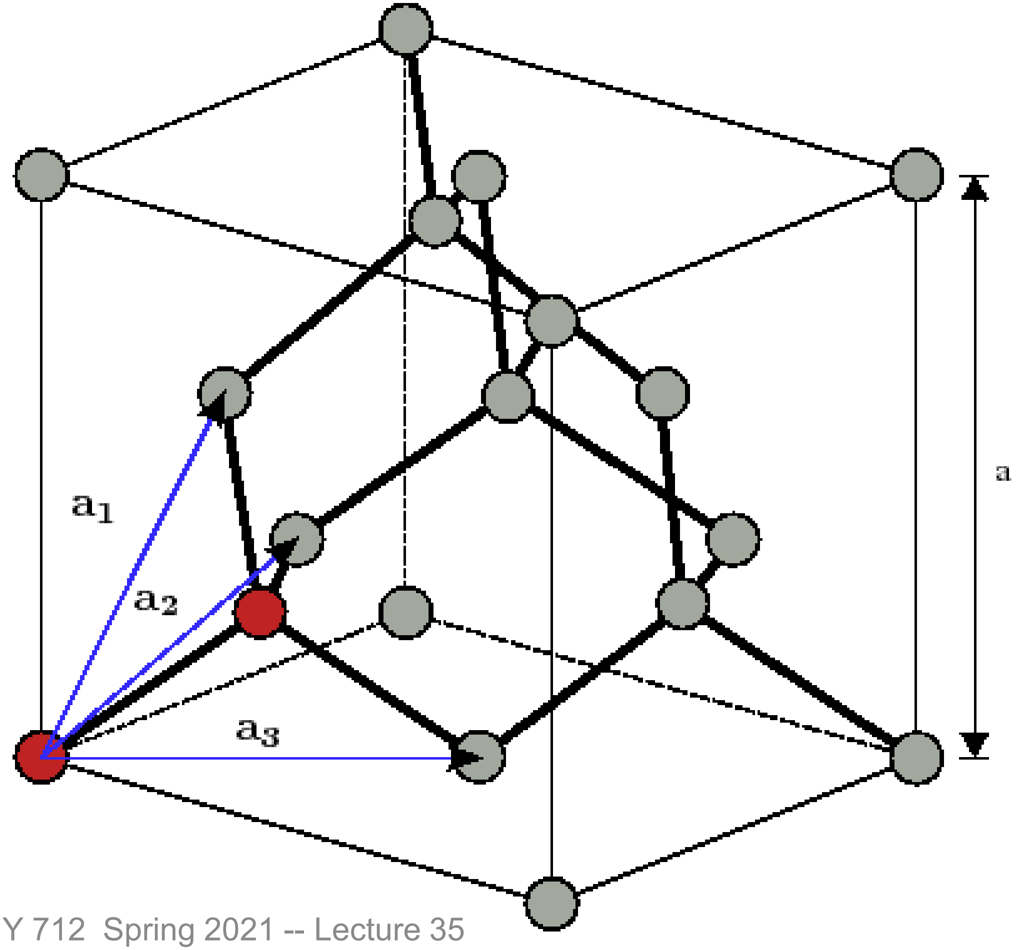
$$\begin{pmatrix} \alpha & \beta & \cdots & 0 \\ \beta & \alpha & \cdots & 0 \\ \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & \cdots & \alpha \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix} = E \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix}$$

Here we have idealized the analysis assuming an orthogonal basis with $\alpha \Leftrightarrow H_{AA}$ and $\beta \Leftrightarrow H_{AB}$.



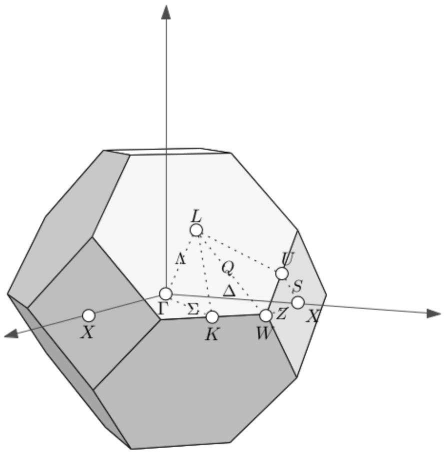
In practice, the "energy band" structure of materials is affected by competing effects of structure and composition

Example: Diamond lattice (2 C atoms per primitive unit cell)



Ref. PRB **2**, 2054 (1970) $E_n(k)$

Note: Valence bands must accommodate 8 valence electrons from two C $1s^2 2s^2 2p^2$ atoms per unit cell



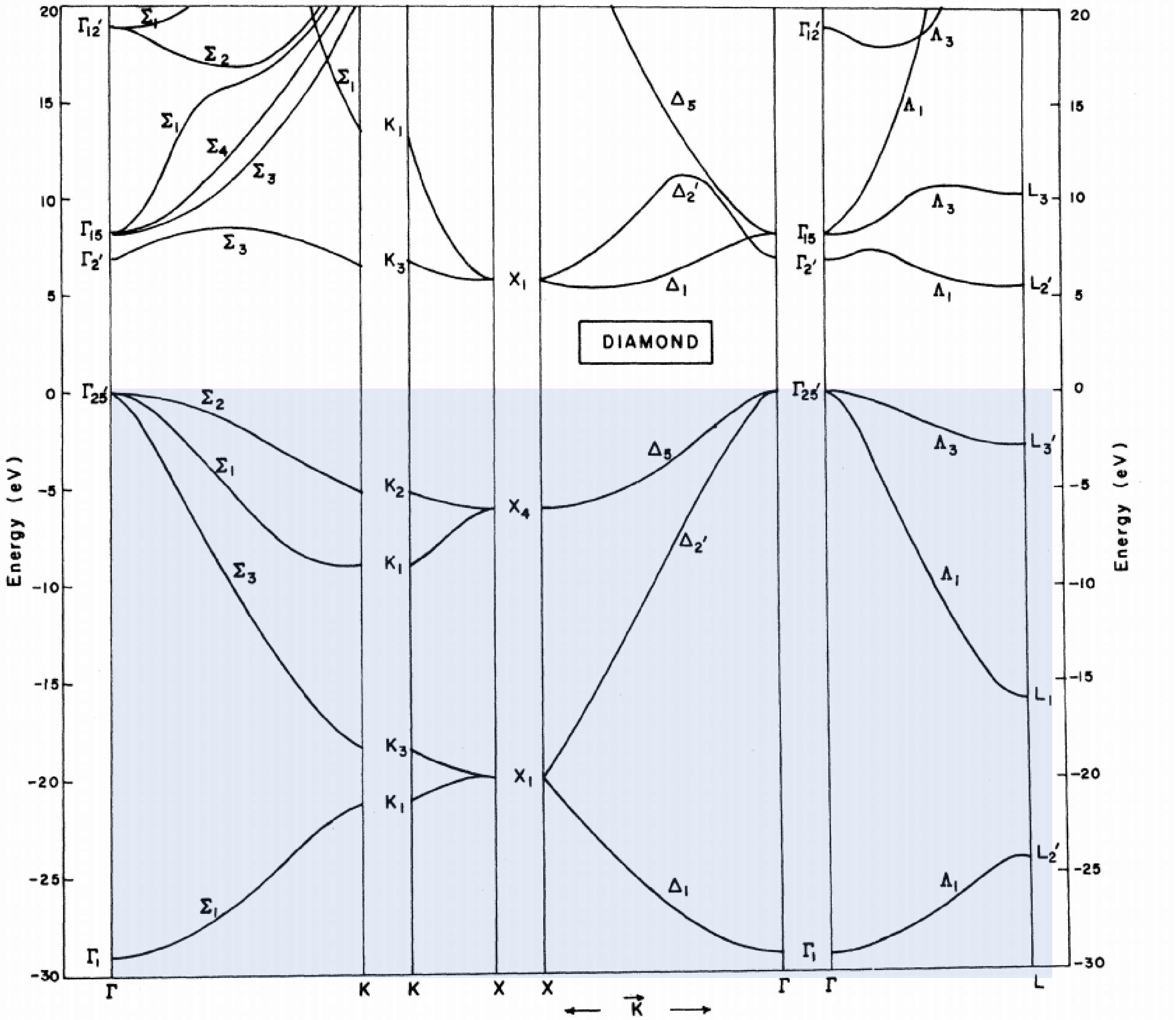
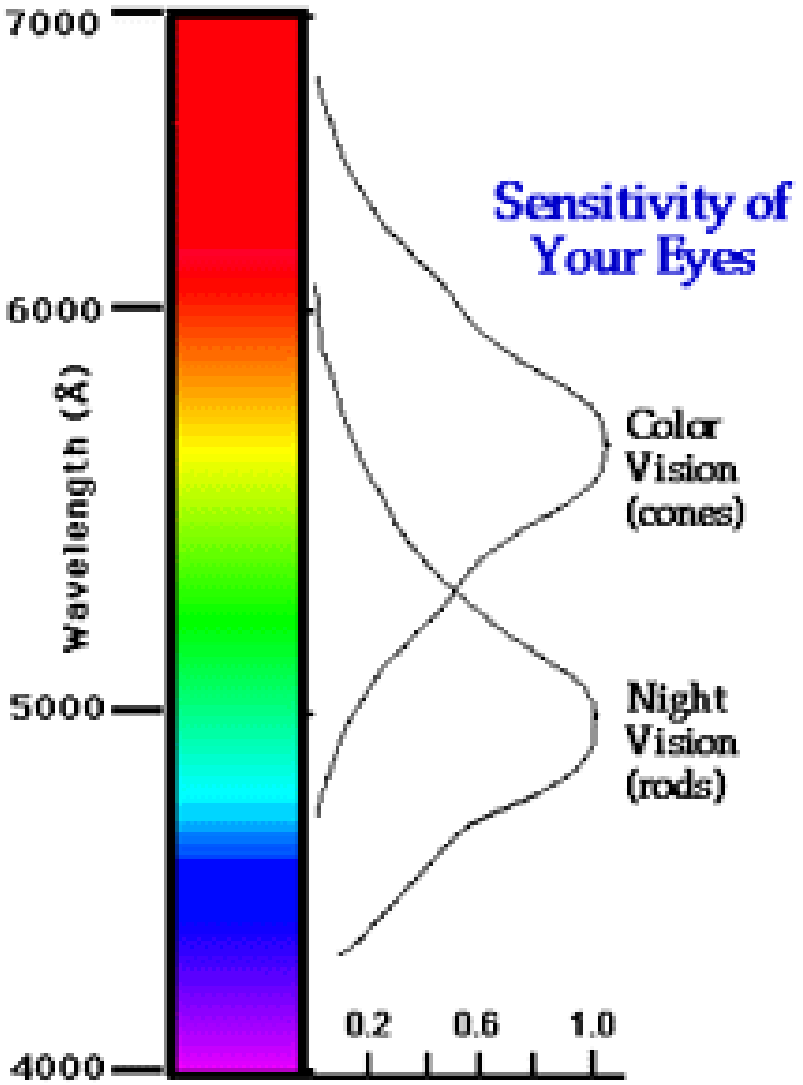


FIG. 1. Energy bands along principal symmetry lines.

Visible light for humans

2 eV

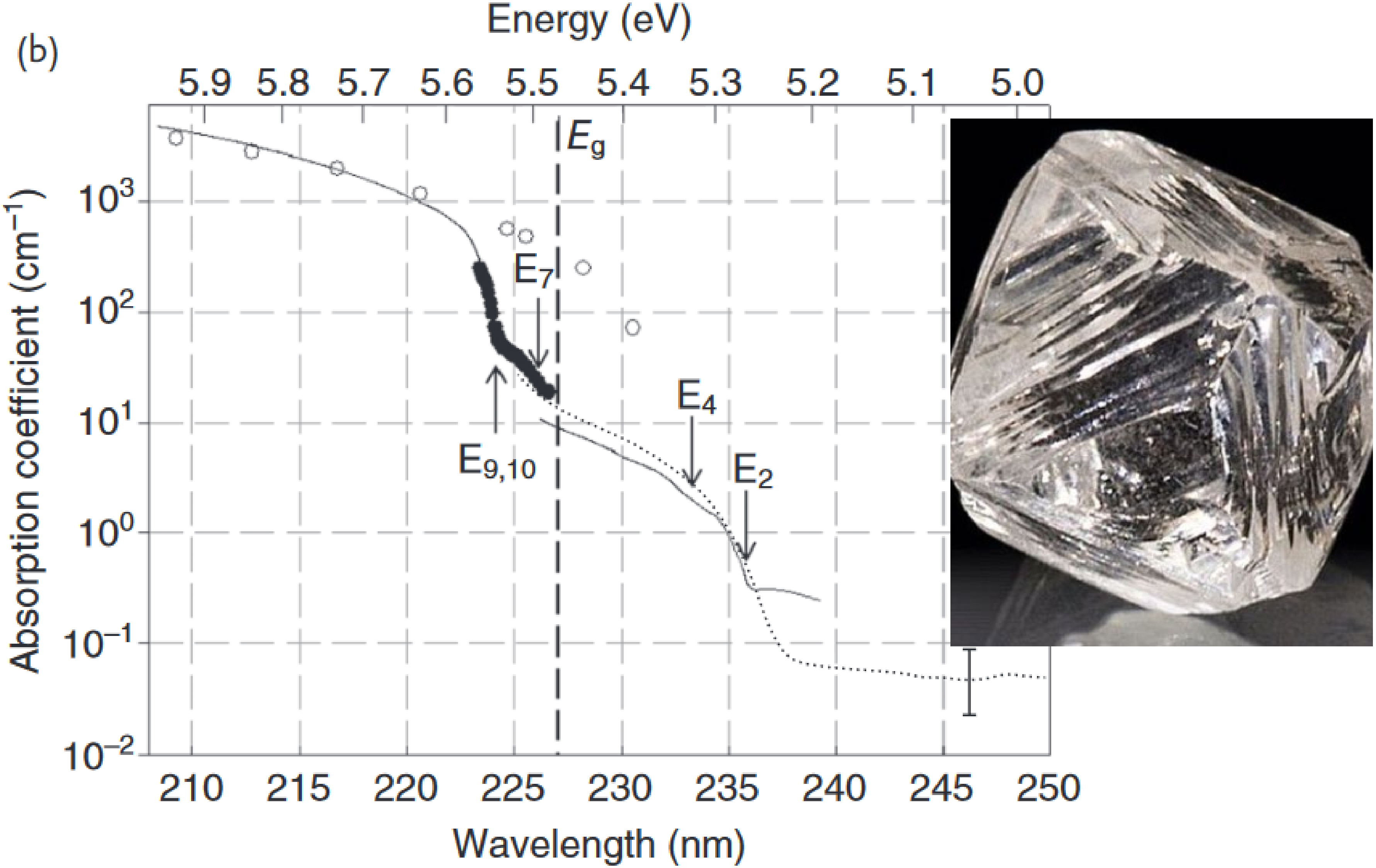
3 eV



How do you expect a diamond crystal to look when illuminated by visible light?

1. It will be opaque.
2. It will be completely transparent
3. It will be partially transparent.

Absorption spectrum of diamond



Optical Engineering of Diamond, First Edition. Edited by Richard P. Mildren and James R. Rabeau.
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Images of natural diamonds

How is it possible for these diamonds to have absorption in the visible spectrum?

$E_n(k)$

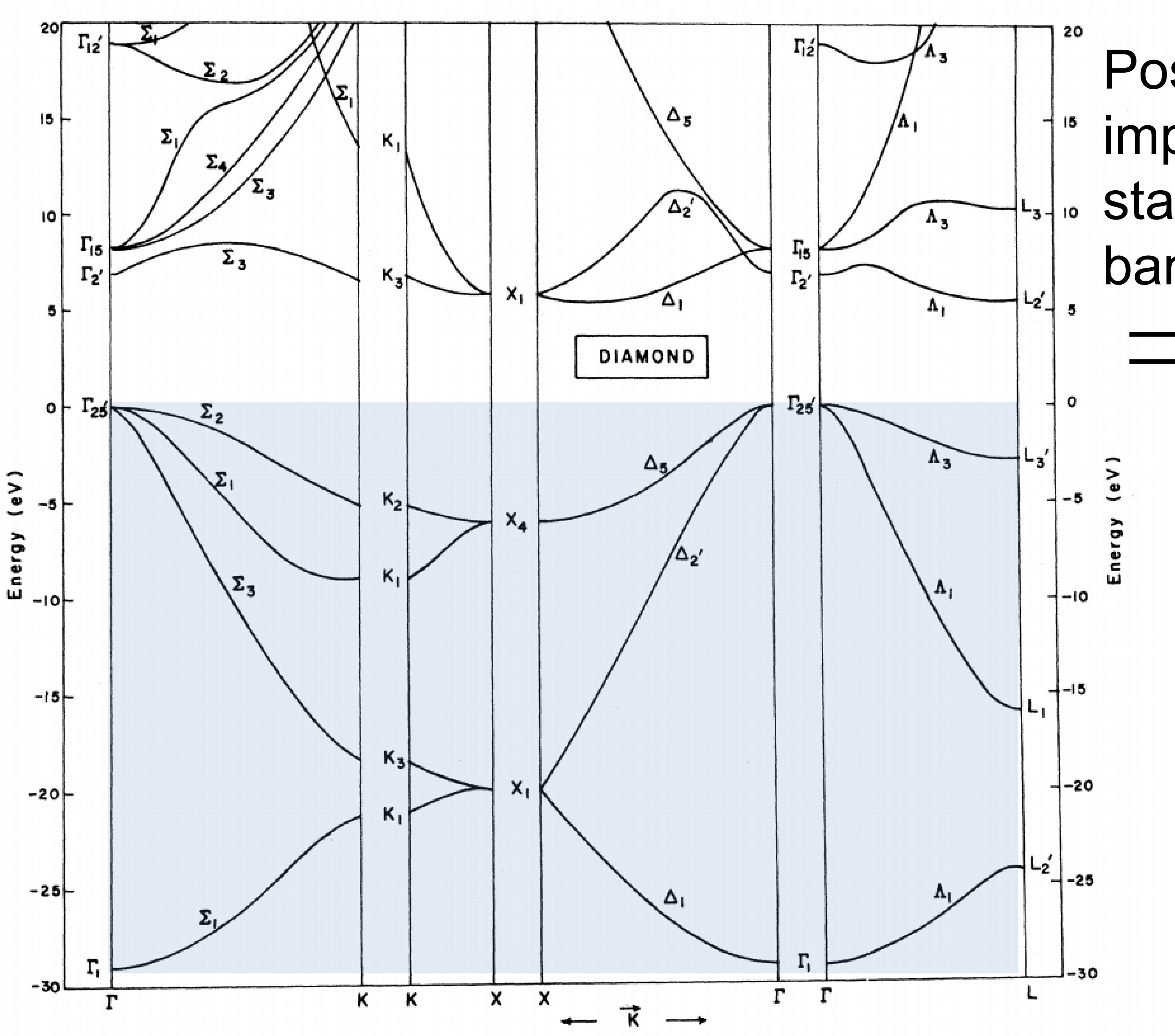
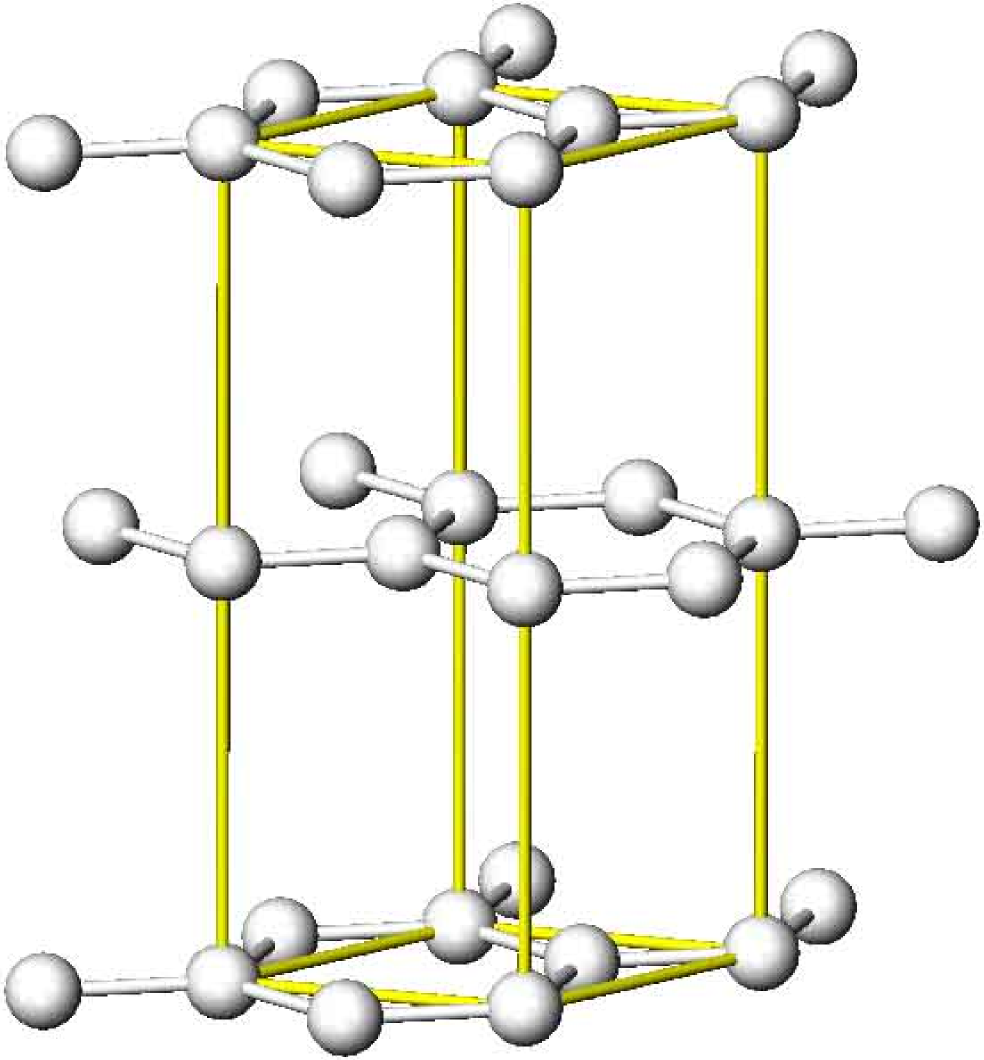


FIG. 1. Energy bands along principal symmetry lines.

Possible impurity states in band gap

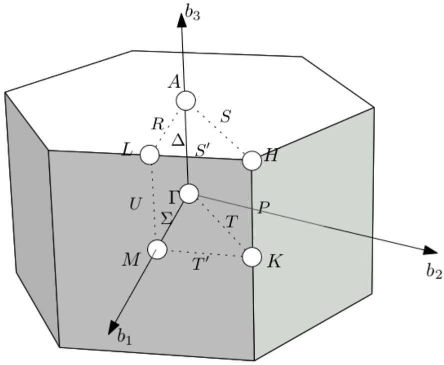
Another example --

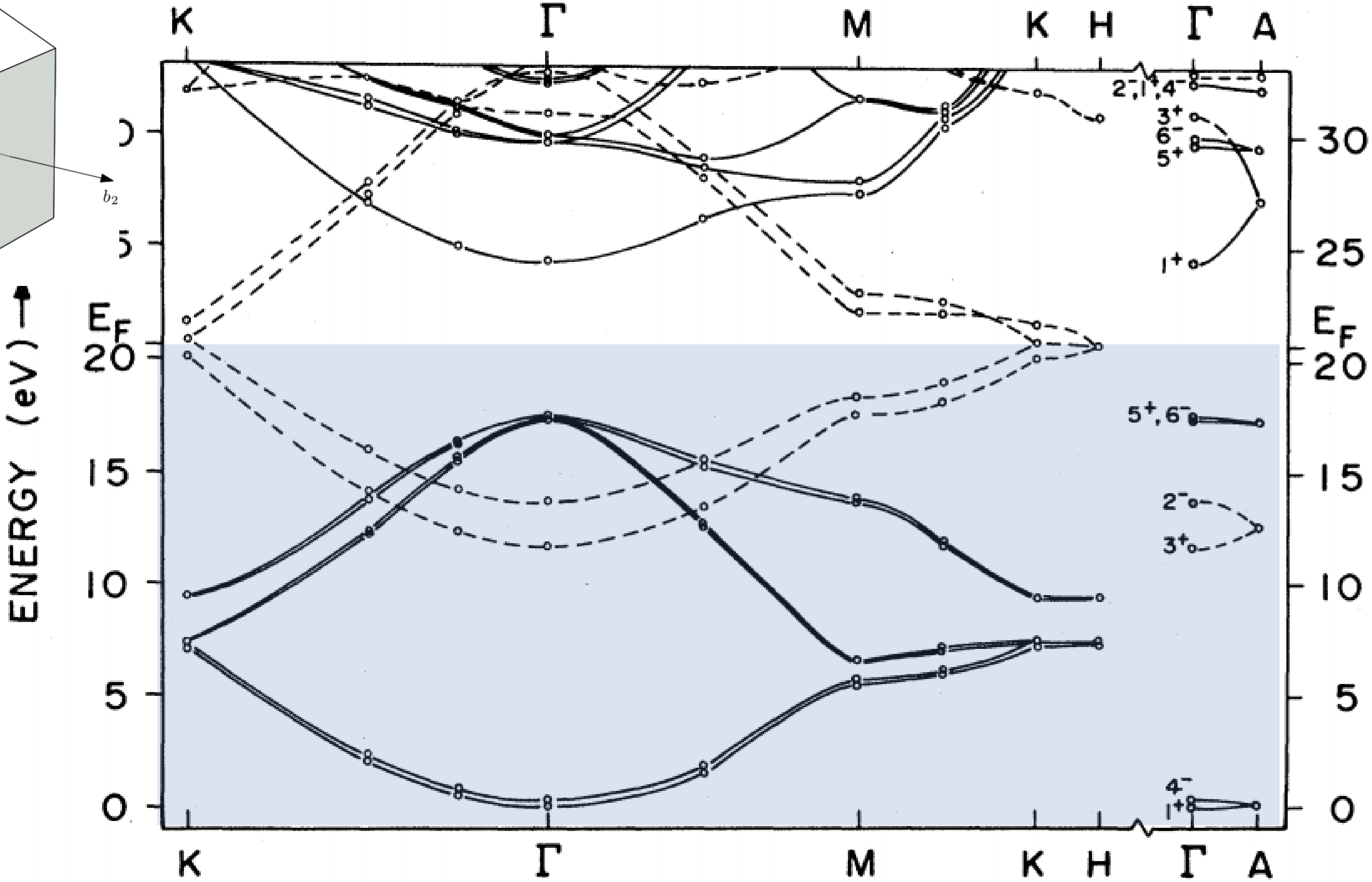
Example: Graphite (4 C atoms per unit cell)



Ref. *PRB* **26**, 5382 (1982)

Note: Valence bands must accommodate 16 valence electrons from four C $1s^2 2s^2 2p^2$ atoms per unit cell





Band diagram for graphite

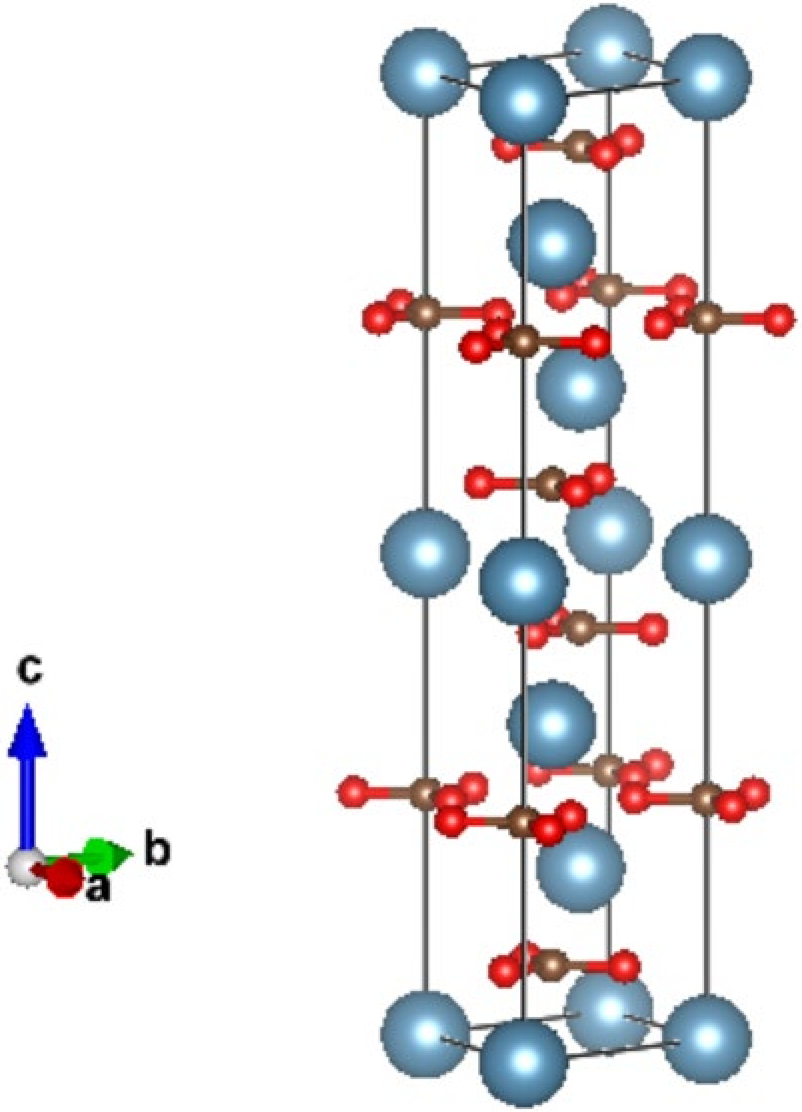
How different is the band structure of diamond and graphite?

1. They look slightly different, but it is hard to tell because they were analyzed using different approximations.
2. They look drastically different because ….

Image of natural graphite (semi metal)

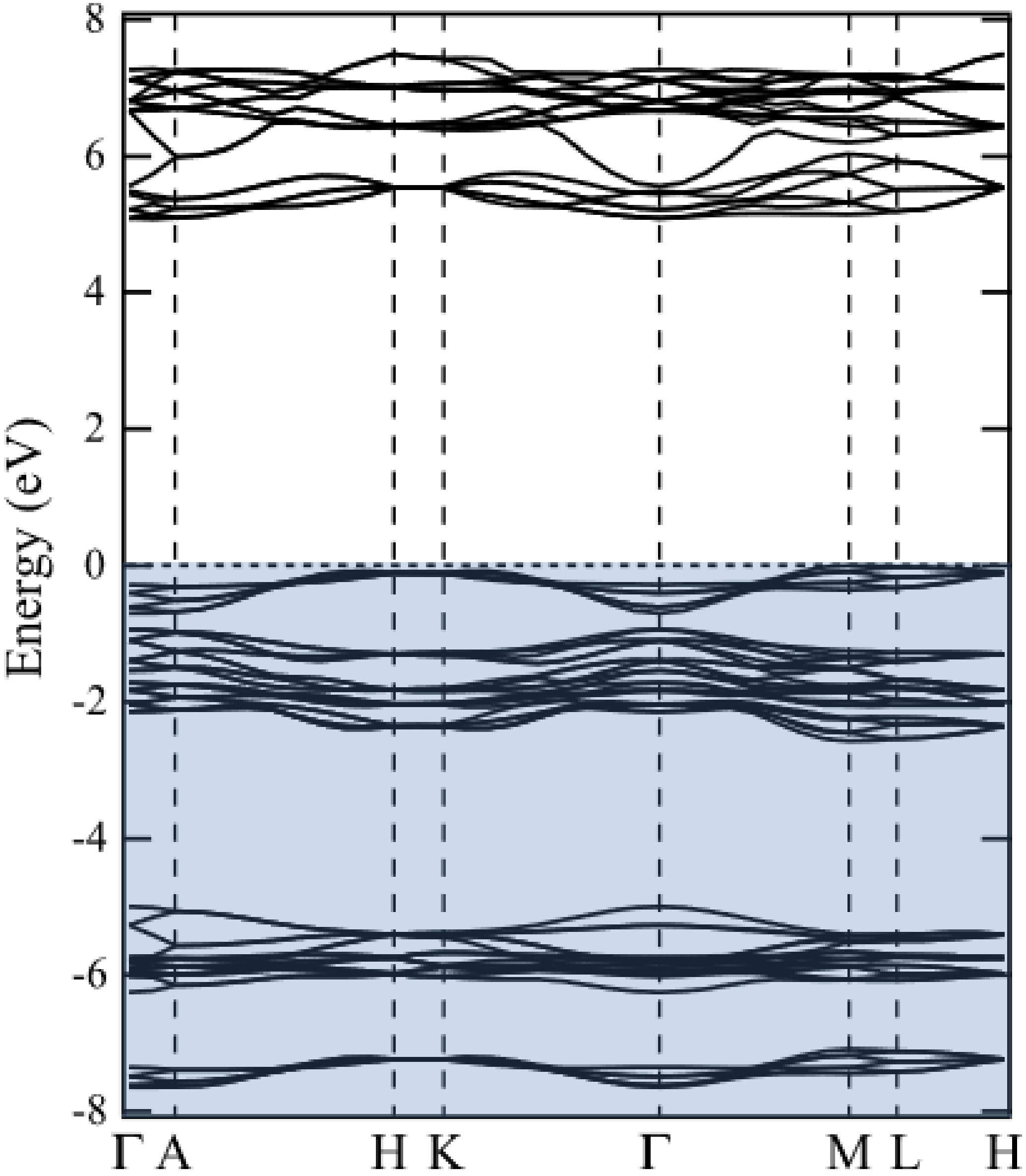
Another example --

Example: Calcite $CaCO_3$




Calcite
Calcite

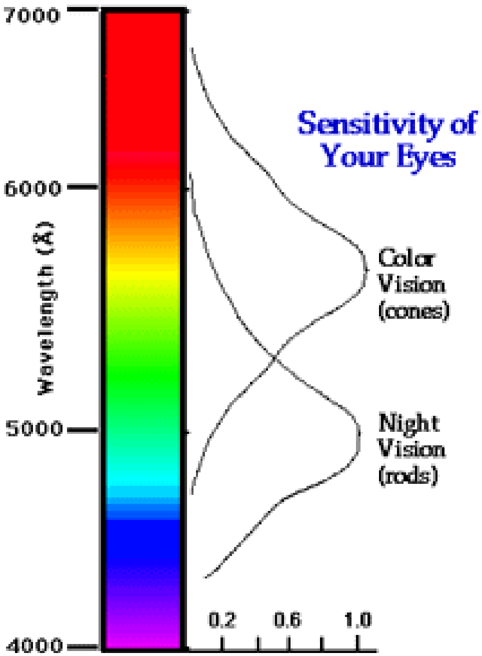
F.M. Hossain et al. / Solid State Communications 149 (2009) 1201–1203



$CaCO_3$ Calculated optical properties

2 eV

3 eV



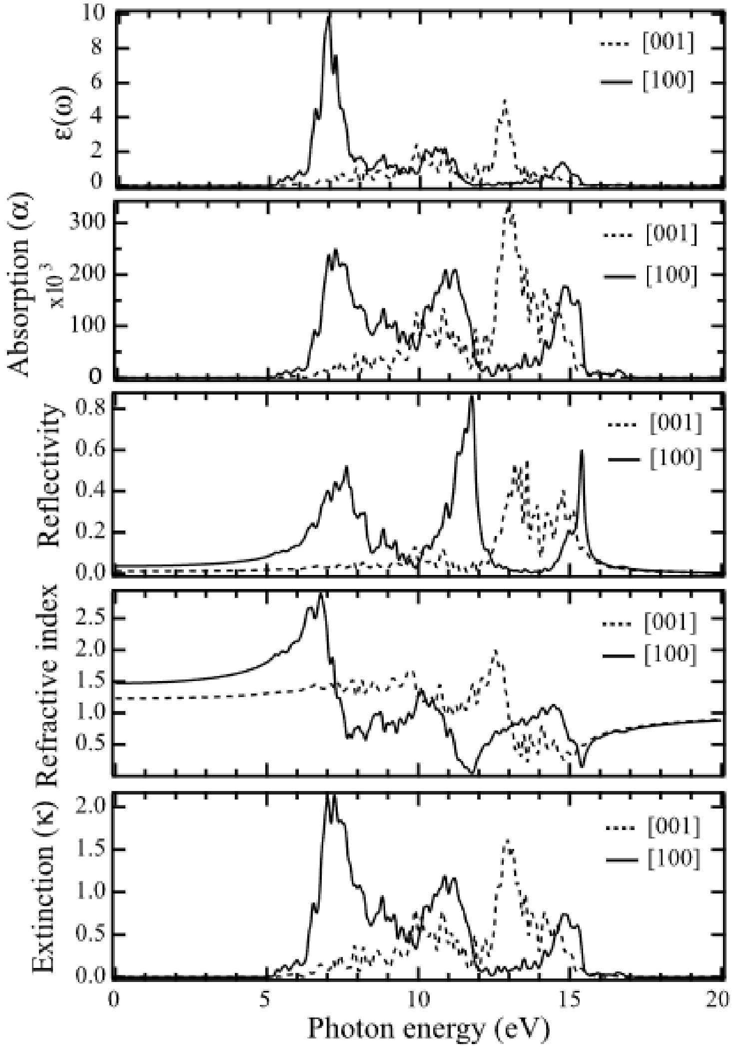


Fig. 3. The frequency dependent optical properties evaluated for the two directions (dashed and solid lines are along [001] and [100] directions respectively) of incoming light w.r.t. the crystal axis.

n_o=1.7

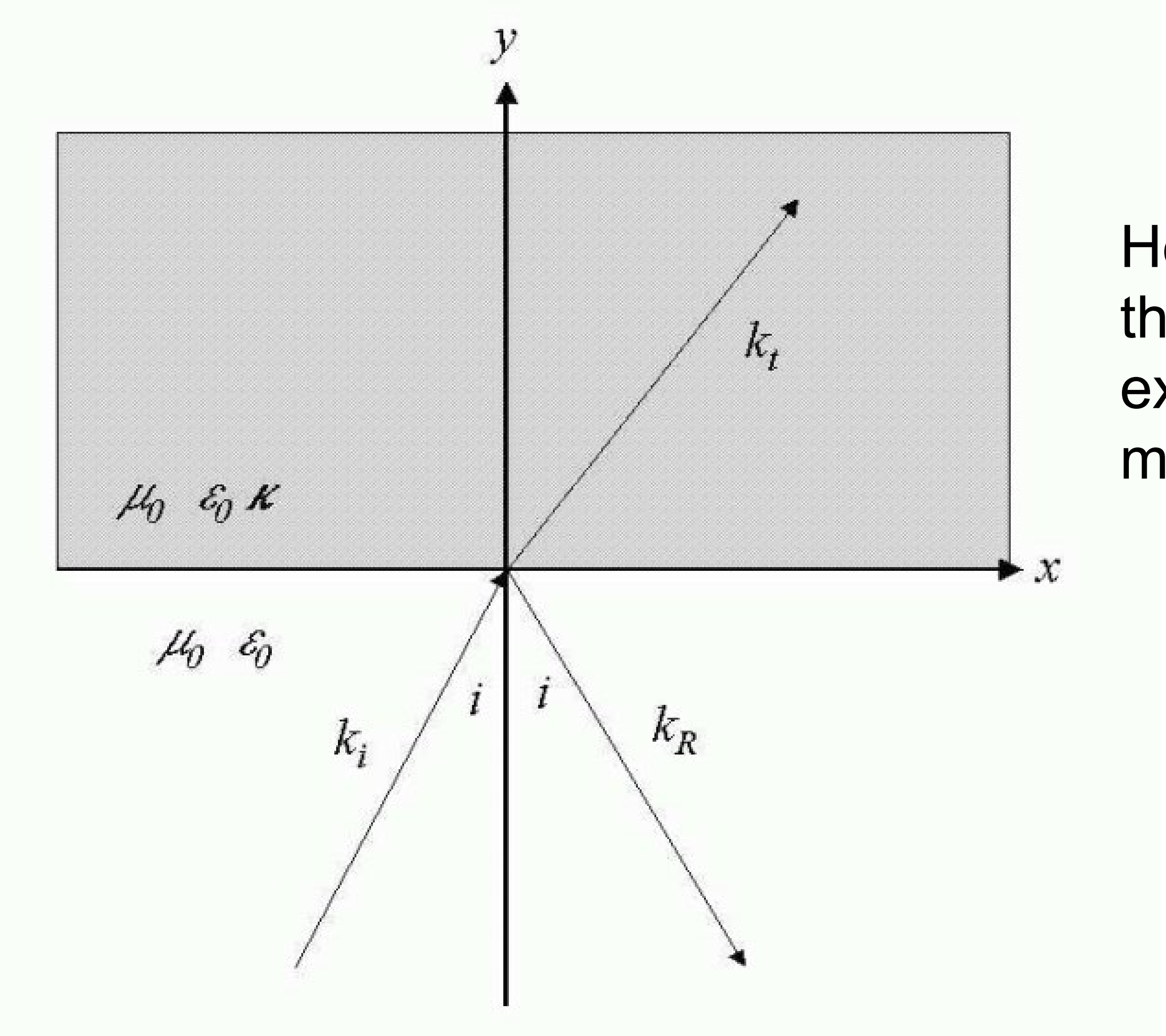
n_e=1.5

How are the results on the previous slide related to each other?

1. They are all independent of eachother
2. Some of them are related because …

What determines the birefringence that we observe?

Reflectance and transmittance in an anisotropic crystal --



Here we assume that the birefringence is expressed in the $\boldsymbol{\kappa}$ matrix.

Consider the problem of determining the reflectance from an anisotropic medium with isotropic permeability μ_0 and anisotropic permittivity $\varepsilon_0 \boldsymbol{\kappa}$ where:

$$\boldsymbol{\kappa} \equiv \begin{pmatrix} \kappa_{xx} & 0 & 0 \\ 0 & \kappa_{yy} & 0 \\ 0 & 0 & \kappa_{zz} \end{pmatrix}$$

By assumption, the wave vector in the medium is confined to the *x-y* plane and will be denoted by

$$\mathbf{k}_t \equiv \frac{\omega}{c}(n_x \hat{\mathbf{x}} + n_y \hat{\mathbf{y}}), \text{where } n_x \text{ and } n_y \text{ are to be determined.}$$

The electric field inside the medium is given by:

$$\mathbf{E} = (E_x \hat{\mathbf{x}} + E_y \hat{\mathbf{y}} + E_z \hat{\mathbf{z}}) \mathrm{e}^{i\frac{\omega}{c}(n_x x + n_y y) - i\omega t}.$$

Inside the anisotropic medium, Maxwell's equations are:

$$\nabla \cdot \mathbf{H} = 0 \qquad \nabla \cdot \boldsymbol{\kappa} \cdot \mathbf{E} = 0$$

$$\nabla \times \mathbf{E} - i\omega\mu_0 \mathbf{H} = 0 \qquad \nabla \times \mathbf{H} + i\omega\epsilon_0 \boldsymbol{\kappa} \cdot \mathbf{E} = 0$$

After some algebra, the equation for **E** is:

$$\begin{pmatrix} \kappa_{xx} - n_y^2 & n_x n_y & 0 \\ n_x n_y & \kappa_{yy} - n_x^2 & 0 \\ 0 & 0 & \kappa_{zz} - (n_x^2 + n_y^2) \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} = 0.$$

From **E, H** can be determined from

$$\mathbf{H} = \frac{1}{\mu_0 c} \left\{ E_z (n_y \hat{\mathbf{x}} - n_x \hat{\mathbf{y}}) + (E_y n_x - E_x n_y) \hat{\mathbf{z}} \right\} \mathrm{e}^{i\frac{\omega}{c}(n_x x + n_y y) - i\omega t}.$$

The fields for the incident and reflected waves are the same as for the isotropic case.

$$\mathbf{k}_i = \frac{\omega}{c}(\sin i\,\hat{\mathbf{x}} + \cos i\,\hat{\mathbf{y}}),$$

$$\mathbf{k}_R = \frac{\omega}{c}(\sin i\,\hat{\mathbf{x}} - \cos i\,\hat{\mathbf{y}}).$$

Note that, consistent with Snell's law: $n_x = \sin i$

Continuity conditions at the *y=0* plane must be applied for the following fields:

$$\mathbf{H}(x,0,z,t),\;\; E_x(x,0,z,t),\;\; E_z(x,0,z,t),\;\; \text{and}\;\; D_y(x,0,z,t).$$

There will be two different solutions, depending of the polarization of the incident field.

Solution for s-polarization

$$E_x = E_y = 0 \qquad \Rightarrow \; n_y^2 = \kappa_{zz} - n_x^2$$

$$\mathbf{E} = E_z \hat{\mathbf{z}} \mathrm{e}^{i\frac{\omega}{c}(n_x x + n_y y) - i\omega t} \qquad \mathbf{H} = \frac{1}{\mu_0 c}\left\{E_z (n_y \hat{\mathbf{x}} - n_x \hat{\mathbf{y}})\right\} \mathrm{e}^{i\frac{\omega}{c}(n_x x + n_y y) - i\omega t}$$

E_z must be determined from the continuity conditions:

$$E_0 + E_0'' = E_z \qquad (E_0 - E_0'')\cos i = E_z n_y \qquad (E_0 + E_0'')\sin i = E_z n_x$$

$$\frac{E_0''}{E_0} = \frac{\cos i - n_y}{\cos i + n_y}.$$

$$\frac{E_z}{E_0} = \frac{2\cos i}{\cos i + n_y}.$$

Some details for s-polarization

$$\mathbf{E}_0 = E_0\hat{\mathbf{z}}\ \mathrm{e}^{i\frac{\omega}{c}(\sin i\ x+\cos i\ y)-i\omega t} \qquad \mathbf{E}_0'' = E_0''\hat{\mathbf{z}}\ \mathrm{e}^{i\frac{\omega}{c}(\sin i\ x-\cos i\ y)-i\omega t}$$

$$\mathbf{H}_0 = \frac{E_0}{\mu_0 c}\left(\hat{\mathbf{x}}\cos i - \hat{\mathbf{y}}\sin i\right)\mathrm{e}^{i\frac{\omega}{c}(\sin i\ x+\cos i\ y)-i\omega t}$$

$$\mathbf{H}_0'' = \frac{E_0''}{\mu_0 c}\left(-\hat{\mathbf{x}}\cos i - \hat{\mathbf{y}}\sin i\right)\mathrm{e}^{i\frac{\omega}{c}(\sin i\ x-\cos i\ y)-i\omega t}$$

$$\mathbf{E} = E_z\hat{\mathbf{z}}\mathrm{e}^{i\frac{\omega}{c}(n_x x+n_y y)-i\omega t} \qquad \mathbf{H} = \frac{1}{\mu_0 c}\left\{E_z(n_y\hat{\mathbf{x}} - n_x\hat{\mathbf{y}})\right\}\mathrm{e}^{i\frac{\omega}{c}(n_x x+n_y y)-i\omega t}$$

Continuity conditions:

$$E_0 + E_0'' = E_z \qquad (E_0 - E_0'')\cos i = E_z n_y \qquad (E_0 + E_0'')\sin i = E_z n_x$$

Conventionally this s-polarization wave is called the "ordinary" wave since it satisfies Snell's law:

$$\sin\,\theta = \frac{n_x}{\sqrt{n_x^2 + n_y^2}} = \frac{\sin i}{\sqrt{\kappa_{zz}}}$$

Solution for p-polarization

$$E_z = 0 \qquad \Rightarrow \; n_y^2 = \frac{\kappa_{xx}}{\kappa_{yy}}(\kappa_{yy} - n_x^2).$$

Note that for $\kappa_{xx} = \kappa_{yy}$

$$n_y = \sqrt{\kappa_{xx} - sin^2 i}$$

$$\mathbf{E} = E_x \left(\hat{\mathbf{x}} - \frac{\kappa_{xx} n_x}{\kappa_{yy} n_y} \hat{\mathbf{y}} \right) \mathrm{e}^{i\frac{\omega}{c}(n_x x + n_y y) - i\omega t}.$$

$$\mathbf{H} = -\frac{E_x}{\mu_0 c} \frac{\kappa_{xx}}{n_y} \hat{\mathbf{z}} \mathrm{e}^{i\frac{\omega}{c}(n_x x + n_y y) - i\omega t}.$$

E_x must be determined from the continuity conditions:

$$(E_0 - E_0'') \cos i = E_x \qquad (E_0 + E_0'') = \frac{\kappa_{xx}}{n_y} E_x \qquad (E_0 + E_0'') \sin i = \frac{\kappa_{xx} n_x}{n_y} E_x.$$

$$\frac{E_0''}{E_0} = \frac{\kappa_{xx} \cos i - n_y}{\kappa_{xx} \cos i + n_y}.$$

$$\frac{E_x}{E_0} = \frac{2\kappa_{xx} \cos i}{\kappa_{xx} \cos i + n_y}.$$

Some details for p-polarization

$$\mathbf{E}_0 = E_0\left(\hat{\mathbf{x}}\cos i - \hat{\mathbf{y}}\sin i\right)\ \mathrm{e}^{i\frac{\omega}{c}(\sin i\ x+\cos i\ y)-i\omega t}$$

$$\mathbf{E}_0'' = E_0''\left(-\hat{\mathbf{x}}\cos i - \hat{\mathbf{y}}\sin i\right)\ \mathrm{e}^{i\frac{\omega}{c}(\sin i\ x-\cos i\ y)-i\omega t}$$

$$\mathbf{H}_0 = -\frac{E_0}{\mu_0 c}\hat{\mathbf{z}}\ \mathrm{e}^{i\frac{\omega}{c}(\sin i\ x+\cos i\ y)-i\omega t} \qquad \mathbf{H}_0'' = -\frac{E_0''}{\mu_0 c}\hat{\mathbf{z}}\ \mathrm{e}^{i\frac{\omega}{c}(\sin i\ x-\cos i\ y)-i\omega t}$$

$$\mathbf{E} = E_x\left(\hat{\mathbf{x}} - \frac{\kappa_{xx}n_x}{\kappa_{yy}n_y}\hat{\mathbf{y}}\right)\mathrm{e}^{i\frac{\omega}{c}(n_x x+n_y y)-i\omega t} \qquad \mathbf{H} = -\frac{E_x}{\mu_0 c}\frac{\kappa_{xx}}{n_y}\hat{\mathbf{z}}\mathrm{e}^{i\frac{\omega}{c}(n_x x+n_y y)-i\omega t}.$$

Continuity conditions:

$$(E_0 - E_0'')\cos i = E_x \qquad (E_0 + E_0'') = \frac{\kappa_{xx}}{n_y}E_x \qquad (E_0 + E_0'')\sin i = \frac{\kappa_{xx}n_x}{n_y}E_x.$$

Conventionally this is called the extraordinary wave since it does not necessarily satisfy Snell’s law.