

PHY 712 Electrodynamics

12-12:50 AM MWF via video link:

<https://wakeforest-university.zoom.us/my/natalie.holzwarth>

Extra notes for Lecture 34:

**Special Topics in Electrodynamics:
Some optical properties of materials**

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In this lecture we will examine some optical properties of crystalline materials.

21	Mon: 03/23/2020	Chap. 9	Radiation from localized oscillating sources	#17	03/25/2020
22	Wed: 03/25/2020	Chap. 9	Radiation from oscillating sources	#18	03/27/2020
23	Fri: 03/27/2020	Chap. 9 and 10	Radiation from oscillating sources	#19	03/30/2020
24	Mon: 03/30/2020	Chap. 11	Special Theory of Relativity	#20	04/03/2020
25	Wed: 04/01/2020	Chap. 11	Special Theory of Relativity		
26	Fri: 04/03/2020	Chap. 11	Special Theory of Relativity	#21	04/06/2020
27	Mon: 04/06/2020	Chap. 14	Radiation from accelerating charged particles	#22	04/08/2020
28	Wed: 04/08/2020	Chap. 14	Synchrotron radiation		
	Fri: 04/10/2020	No class	<i>Good Friday</i>		
29	Mon: 04/13/2020	Chap. 14	Synchrotron radiation	#23	04/15/2020
30	Wed: 04/15/2020	Chap. 15	Radiation from collisions of charged particles	#24	04/17/2020
31	Fri: 04/17/2020	Chap. 15	Radiation from collisions of charged particles		
32	Mon: 04/20/2020	Chap. 13	Cherenkov radiation		
33	Wed: 04/22/2020		Special topic: E & M aspects of superconductivity		
34	Fri: 04/24/2020		Special topic: Aspects of optical properties of materials		
35	Mon: 04/27/2020		Review		
36	Wed: 04/29/2020		Review		

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Reminder about the schedule. Please send me topics for the review next week.

Discussion --

- Vote on review next week
 - Review course materials? (need topic suggestions)
 - Review qualifier questions? (password protected)
 - http://users.wfu.edu/gutholdm/Graduate_Exams/Graduate%20Exams.htm

Classical Mechanics	E&M	Quantum Mechanics	Thermo/Stat. Mech.
2010	2010	2010	2010
2011	2011	2011	2011
2012	2012	2012	2012
2013	2013	2013	2013
2014	2014	2014	2014
2015	2015	2015	2015
2016	2016	2016	2016
2017	2017	2017	2017
2018	2018	2018	2018
2019	2019	2019	2019

Timelines –

May 1 – take home exam available

May 11 – 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 $\sim 10^{23}$ atoms, discrete states become bands of states**
 - a. Metals**
 - b. 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.

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Outline.

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:

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

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

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

$$E_{100} = -13.60569253 Z^2 \text{ eV}$$

$$a_0 = 0.52917721092 \text{ \AA}$$



Starting with the ground state of an hydrogen-like atom.

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

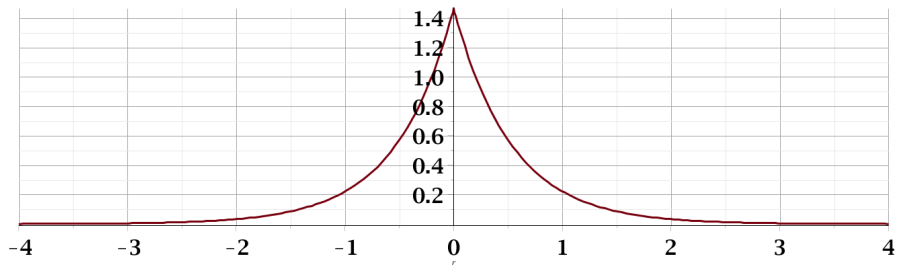
Why is it that isolated atoms and molecules have discrete states while solids have continua of states?

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

1. Optical properties of materials are determined by transitions between states.
2. #1 is true but optical properties may also be determined by response to EM fields without transitions between states.
3. Experiments will tell us all we need to know.

Probability amplitude for electron in the ground state:

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



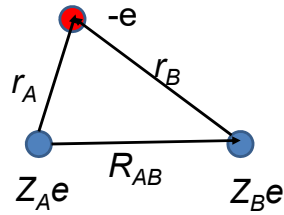
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Ground state wavefunction.

Now consider one electron in the presence of two H-like ions:
 Electronic structure of H-like molecular ion
 (within Born-Oppenheimer approximation)



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

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

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Z_A e^2}{4\pi\epsilon_0 r_A} - \frac{Z_B e^2}{4\pi\epsilon_0 r_B} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}$$

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

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

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Now consider what happens when you have two atoms. Find the approximate ground state using a linear combination of atomic orbitals.

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:

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

$$\begin{pmatrix} X_A \\ X_B \end{pmatrix}_- = \frac{1}{\sqrt{2(1-\Delta)}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad E_- = \frac{H_{AA} - H_{AB}}{1 - \Delta}$$

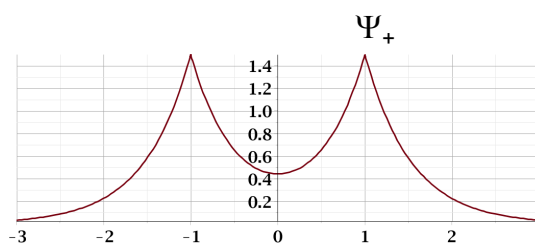
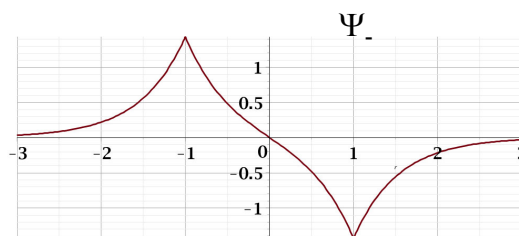
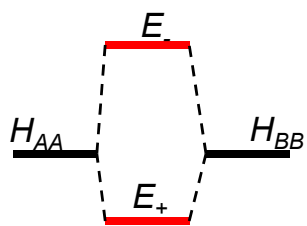
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Finding two solutions for the linear coefficients corresponding to two approximate states.

Electronic structure of H-like molecular ion – continued



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Energy levels and their corresponding eigenstates. Note that there are many more states for this system than these.

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 $\beta \Leftrightarrow H_{AB}$.



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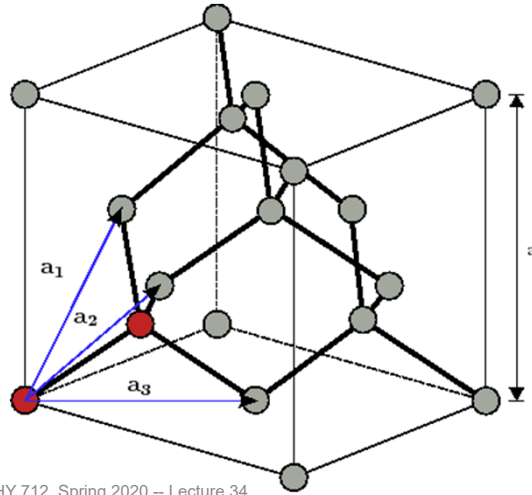
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Now imagine extending this type of analysis to a chain of N atoms. There are more and more states asymptotically leading to a continuum. In this way, we can understand why the states of solid materials correspond to continua of states.

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)



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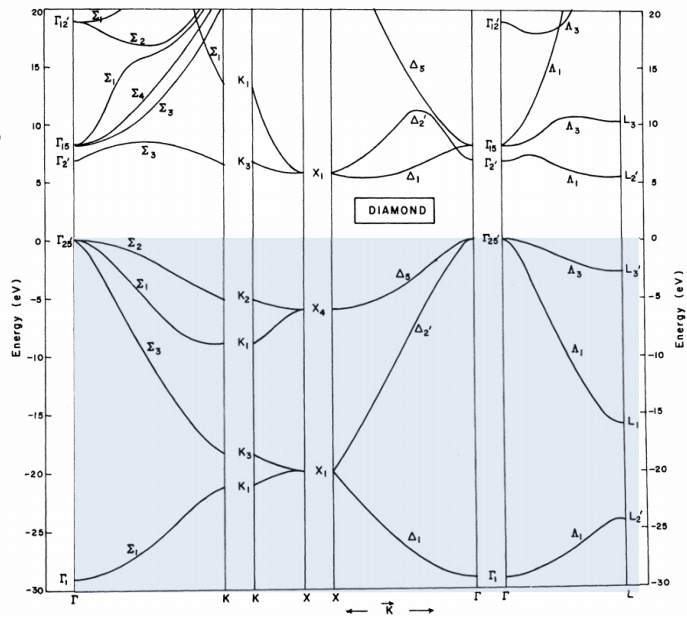
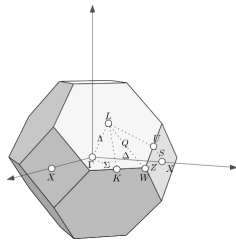
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Consider first an ideal crystal of carbon in the diamond structure. There are two atoms per primitive unit cell and ? atoms in the cubic cell.

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



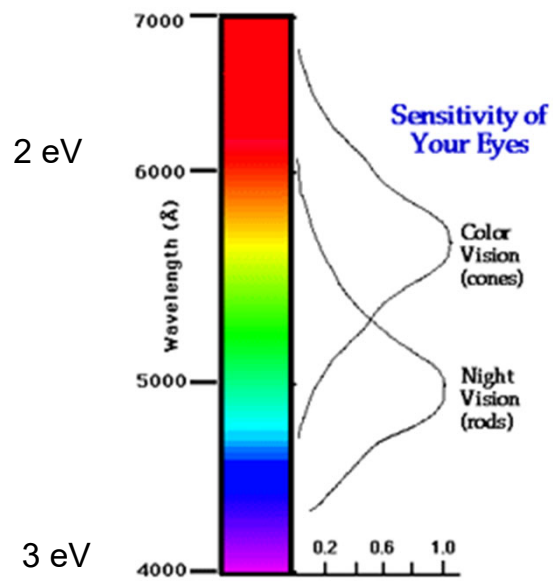
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PHY 712 Spring 2022 Energy states along principal symmetry lines.

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This is a plot of the band structure of diamond. The valence band spans ~ 30 eV. The conduction band is separated from the occupied states by ~ 5.1 eV.

Visible light for humans



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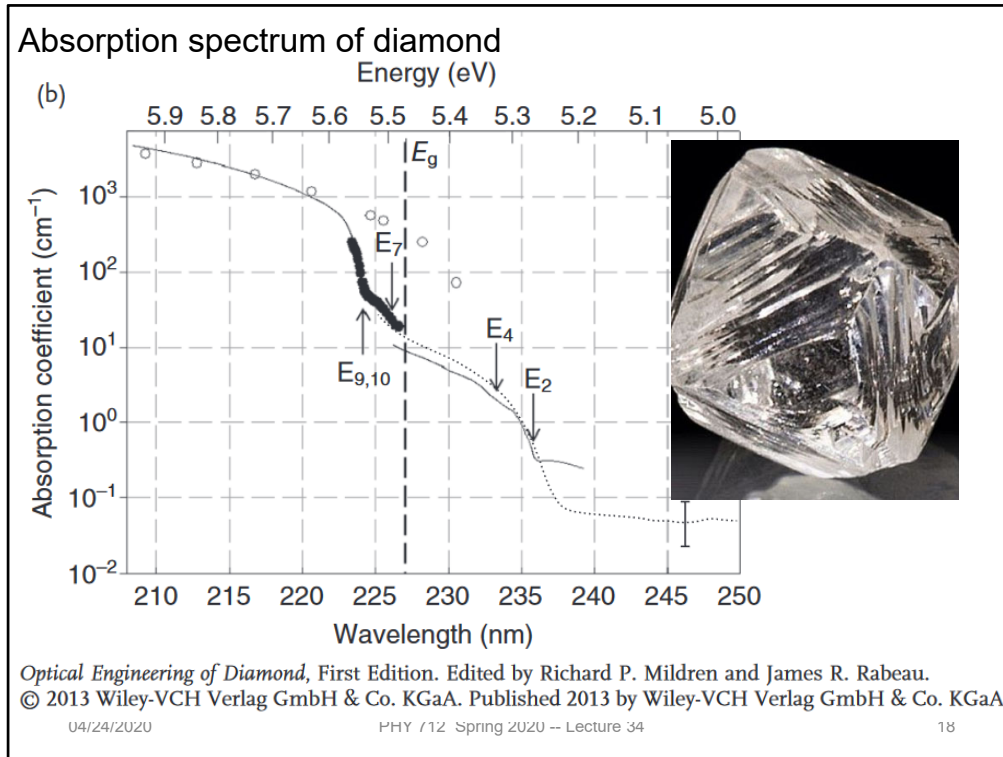
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Before asking what you might see when viewing a diamond crystal, here is reminder about the visible light and its energy equivalent.

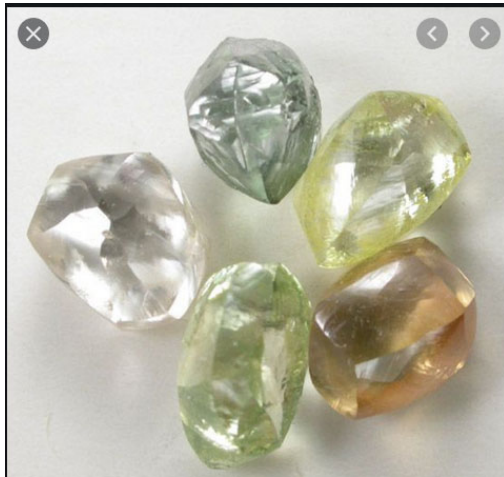
How do you expect a diamond crystal to look when illuminated by visible light?

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



Here is an absorption spectrum for diamond. The image on the right is that of a natural diamond crystal.

Images of natural diamonds



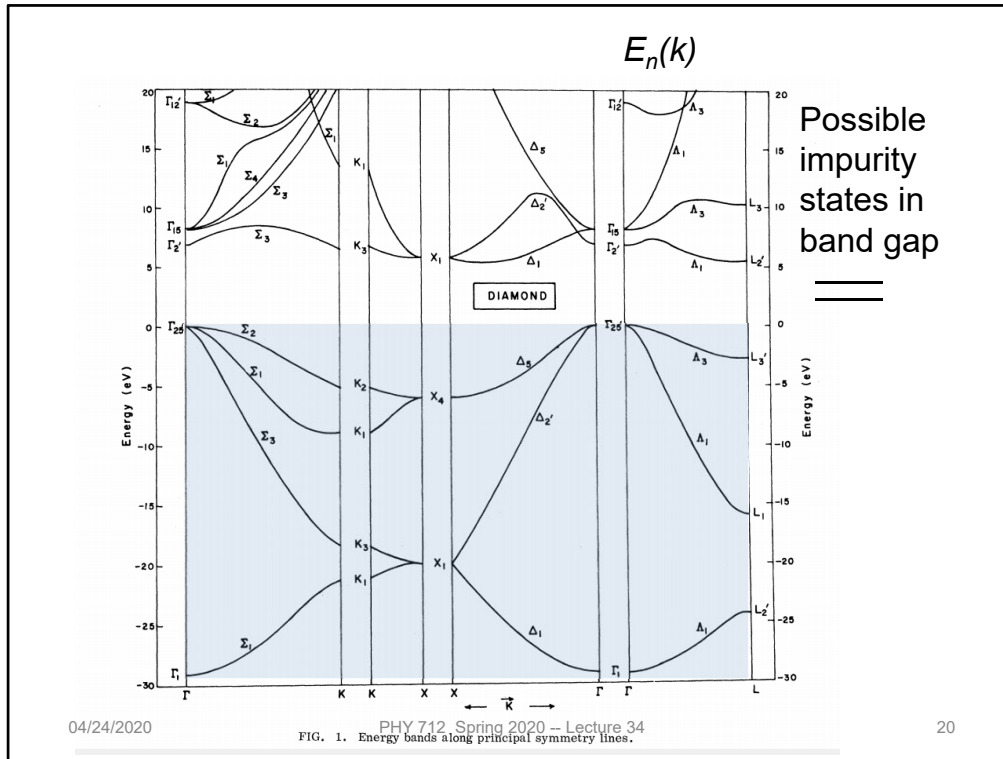
How is it possible for these diamonds to have absorption in the visible spectrum?

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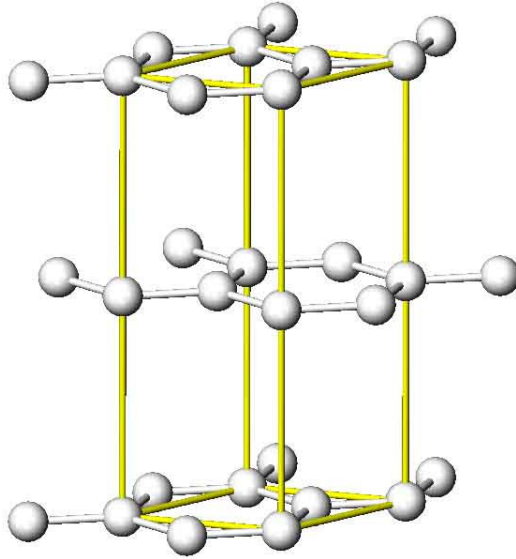
Here is an image of diamond crystal that are not completely transparent. How can this happen?



From the viewpoint of the band structure, it is not possible to absorb sub band gap light. Impurity states do not fit into the band picture since they are not part of the periodic structure.

Another example --

Example: Graphite (4 C atoms per unit cell)



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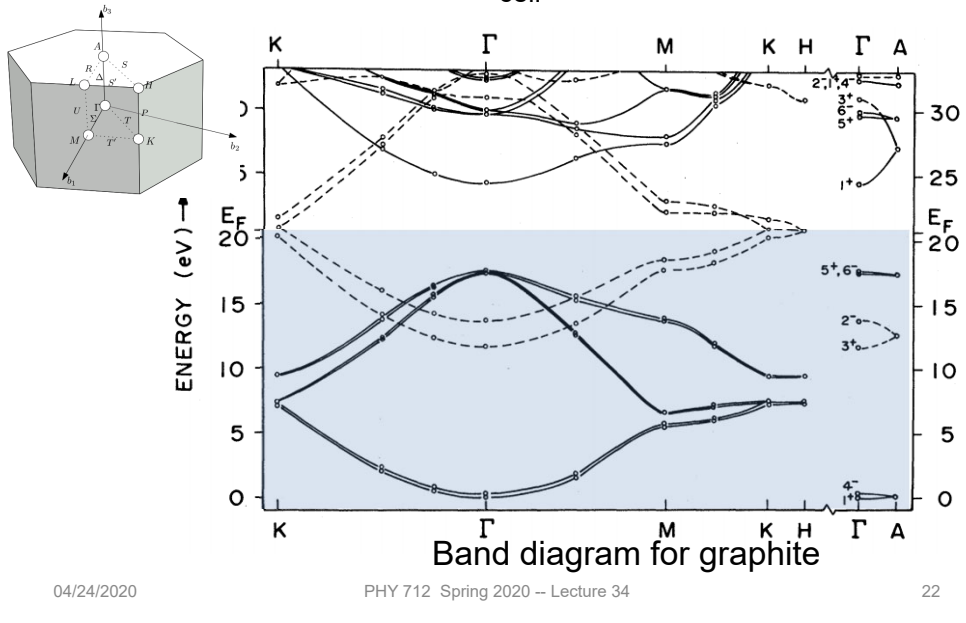
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Now consider another form of carbon in the graphite structure.

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



This is a band diagram of the electronic states of graphite. What do you think that graphite would look like?

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)

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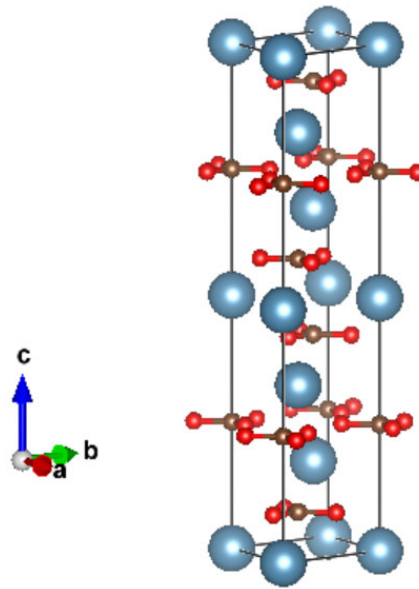
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This looks similar to the sample in my office. Graphite is called a semi metal.

Another example --

Example: Calcite CaCO_3



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Now consider another example of a transparent but anisotropic material, calcite.

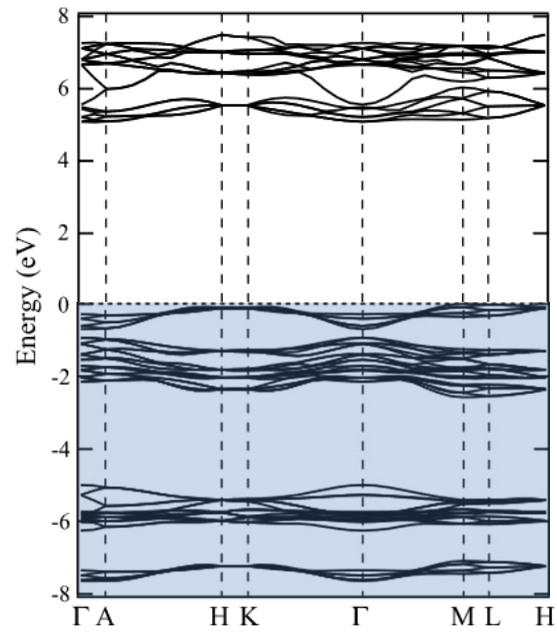


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Image of a calcite crystal

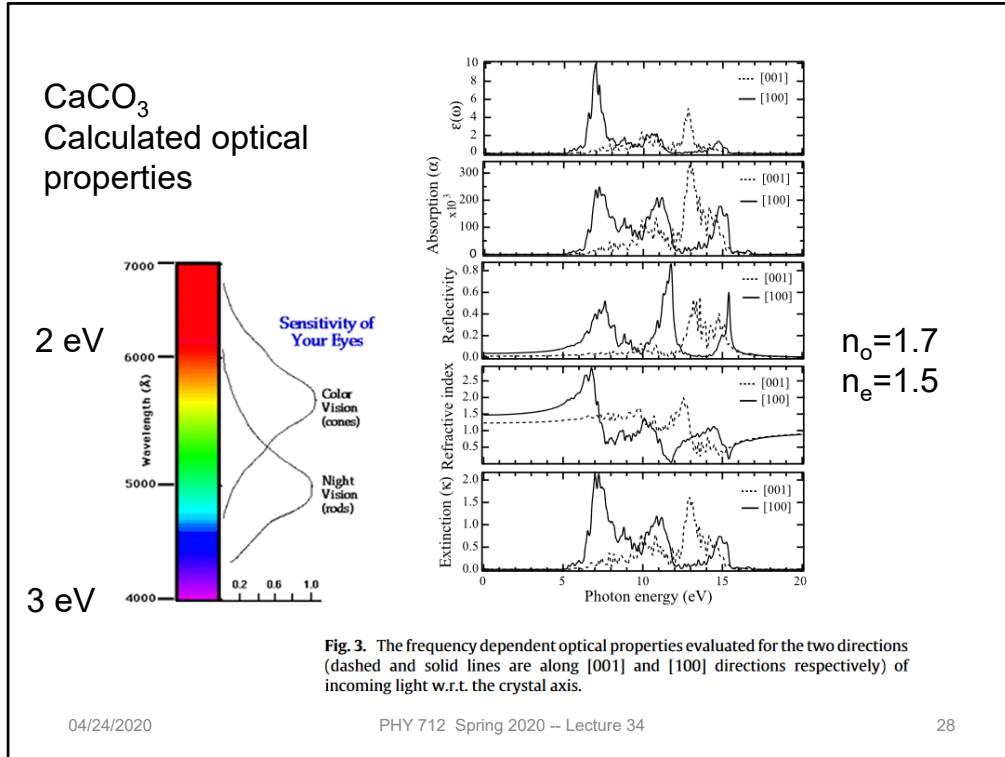


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Band structure of calcite



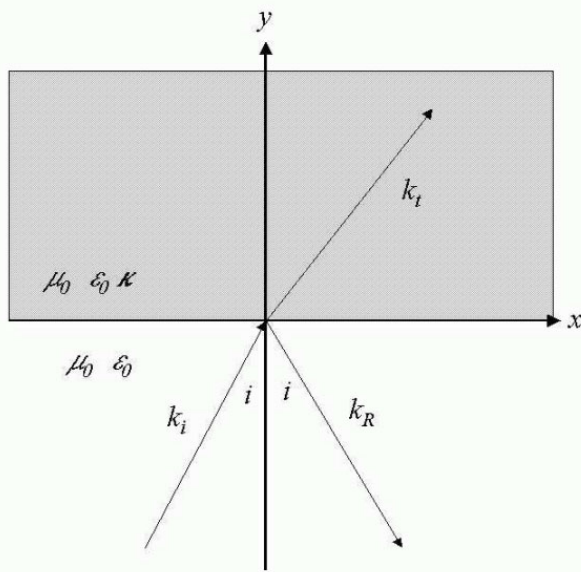
Calculated optical properties.

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

1. They are all independent of each other
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 κ matrix.

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Analysis of the reflectivity and transmittance of a birefringent crystal. This was covered briefly when we discussed the isotropic case in Chapter 7.

Consider the problem of determining the reflectance from an anisotropic medium with isotropic permeability μ_0 and anisotropic permittivity $\epsilon_0 \boldsymbol{\kappa}$ 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:

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

Inside the anisotropic medium, Maxwell's equations are:

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

After some algebra, the equation for \mathbf{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 \mathbf{E} , \mathbf{H} can be determined from

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

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:

$\mathbf{H}(x, 0, z, t)$, $E_x(x, 0, z, t)$, $E_z(x, 0, z, t)$, 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

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

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

E_z must be determined from the continuity conditions:

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

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

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

Some details for s-polarization

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

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

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

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

Continuity conditions:

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

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

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

Here we identify the s polarization with the "ordinary" wave.

Solution for p-polarization

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

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

$$\mathbf{E} = E_x \left(\hat{\mathbf{x}} - \frac{\kappa_{xx} n_x}{\kappa_{yy} n_y} \hat{\mathbf{y}} \right) e^{i\frac{\omega}{c}(n_x x + n_y y) - i\omega t} \quad n_y = \sqrt{\kappa_{xx} - \sin^2 i}$$

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

E_x must be determined from the continuity conditions:

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

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

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

Some details for p-polarization

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

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

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

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

Continuity conditions:

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

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

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Here we identify the "extraordinary" wave with p polarization.