Linear Spectroscopy

Source of Radiation or Excitation

Sample

Processes in the SAMPLES
- Transmission / Reflection / Absorption
- Linear Spectroscopy
- Dielectric function approach

Spectrometer + Detector

The interaction of radiation with matter

The interaction of radiation with matter:
- Ionization energy
- X-rays
- X-ray ionization
- Compton scattering
- Longer wavelength X-ray
- Diffraction
- Reflection
- Scattering
- Transmission
- Absorption

The interaction of radiation with matter:
- Ultraviolet
- Visible
- Infra-red
- Molecular vibration
- Molecular rotation and torsion

The interaction of radiation with matter:
- Increasing Frequency (v)
- Increasing Wavelength (λ)
- Visible spectrum

The interaction of radiation with matter:
- Transparency
- Absorption and Emission

Transparency:
- Taking the electron transitions associated with visible and ultraviolet interactions with matter as an example, absorption of a photon will occur only when the quantum energy of the photon exactly matches the energy gap between the initial and final states. In the interaction of radiation with matter, if there is no pair of energy states such that the photon energy can excite the system from the lower to the upper states, the matter will be transparent to that radiation.

Absorption and Emission:
- A downward transition involves emission of a photon of energy:
- Energy levels associated with molecules, atoms and nuclei in general are discrete, quasi-continuous energy levels. Transitions between these levels typically involve the absorption or emission of photons. Electron energy levels have been used in the development of radiometric energy levels for the nuclear, electronic, vibration and rotation absorption. Transitions between different energy states typically occur at the emission and transition between rotational quantum states are typically in the infrared region of the electromagnetic spectrum.
The interaction of radiation with matter

**X-ray Interactions**

X-ray photon energies are far above the ionization energies of atoms. X-rays can interact with an electron only by knocking it completely out of the atom. This is known as Compton scattering. At sufficiently high energies, the x-ray photon can create an electron-positron pair.

http://www4.nau.edu/microanalysis/Microprobe/Course%20Overview.html

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**Visible Light Interactions**

The primary mechanism for the absorption of visible light is the elevation of electrons to higher energy levels. There are many available states, so visible light is strongly absorbed. With a strong light source, red light can be transmitted through the hand or a fold of skin, showing that the red end of the spectrum is not absorbed as strongly as the violet end.

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**Infrared Interactions**

The quantum energy of infrared photons is in the range 0.001 to 1.7 eV which is in the range of energies separating the quantum states of molecular vibrations. Infrared is absorbed more strongly than microwaves, but less strongly than visible light. The result of infrared absorption is heating of the tissue since it increases molecular vibrational activity. Infrared radiation does penetrate the skin further than visible light and can thus be used for photographic imaging of subcutaneous blood vessels.
The interaction of radiation with matter

**Microwave Interactions**

The quantum energy of microwave photons is in the range 0.00001 to 0.001 eV, which is in the range of energies separating the quantum states of molecular rotation and torsion. The interaction of microwaves with matter other than metallic conductors will be to rotate molecules and produce heat as a result of that molecular motion. Conductors will strongly absorb microwaves and any lower frequencies because they will cause electric currents which will heat the material. Most matter, including the human body, is largely transparent to microwaves. High intensity microwaves, as in a microwave oven where they pass back and forth through the food millions of times, will heat the material by producing molecular rotations and torsions. Since the quantum energies are a million times lower than those of x-rays, they cannot produce ionization and the characteristic types of radiation damage associated with ionizing radiation.

**Materials equations**

Maxwell’s equations (c.g.s. units)

\[
\begin{align*}
\nabla \times \vec{H} - \frac{1}{c} \frac{\partial \vec{D}}{\partial t} &= \frac{4\pi}{c} \vec{J} \\
\nabla \times \vec{E} + \frac{1}{c} \frac{\partial \vec{B}}{\partial t} &= 0 \\
\n\nabla \cdot \vec{D} &= 0 \\
\n\nabla \cdot \vec{B} &= 0
\end{align*}
\]

\[
\vec{D} = \varepsilon \vec{E}
\]

\[
\vec{B} = \mu \vec{H}
\]

\[
\vec{J} = \sigma \vec{E}
\]

**Solution**

**EM wave**

\[
\vec{E} = \vec{E}_0 e^{i(\vec{K} \cdot \vec{r} - \omega t)}
\]

\[
-\vec{K}^2 = -\frac{\varepsilon \mu \omega^2}{c^2} - \frac{4\pi i \sigma \mu \omega}{c^2}
\]

Loss part of K-vector

\[
\nabla^2 \vec{E} = \frac{\varepsilon \mu \omega^2}{c^2} + \frac{4\pi \sigma \mu \omega}{c^2} \frac{\partial \vec{E}}{\partial t}
\]

The interaction of radiation with matter

**Complex Dielectric Function**

\[
\begin{align*}
\varepsilon_{\text{complex}} &= \varepsilon + \frac{4\pi i \sigma}{\omega} = \varepsilon_1 + i \varepsilon_2 \\
\vec{N}(\omega) &= \sqrt{\varepsilon_{\text{complex}}} = \sqrt{\varepsilon_\mu \left(1 + \frac{4\pi i \sigma}{\varepsilon \omega}\right)} = \vec{n}(\omega) + ik(\omega)
\end{align*}
\]

\[
\varepsilon_1 = \vec{n}^2 + k^2 \\
\varepsilon_2 = 2\vec{n}k
\]

we will relate these quantities in two ways:

1. to observables such as the reflectivity which we measure in the laboratory,

2. to properties of the solid such as the carrier density, relaxation time, effective masses, energy band gaps, etc.

\[
\vec{E}(z, t) = \vec{E}_0 e^{-i\omega t} \exp \left(i \frac{\omega z}{c \sqrt{\varepsilon \mu}} \sqrt{1 + \frac{4\pi i \sigma}{\varepsilon \omega}}\right)
\]

\[
\lambda \gg \sigma_o \rightarrow q \ll 0
\]

\[
I(z) = I_0 e^{-\alpha_{\text{abs}}(\omega)z}
\]

**Typical absorption length**

\[
\frac{1}{\alpha_{\text{abs}}} = \frac{c}{2\omega k(\omega)}
\]
Dielectric function is a tensor

$\tilde{D} = \tilde{\varepsilon}(\omega) \tilde{E}$

$\tilde{j} = \tilde{\sigma}(\omega) \tilde{E}$

$j = \hat{\sigma} \cdot \tilde{E}$.

Optical birefringence spectroscopy

$\varepsilon_{zz}(\omega) \neq \varepsilon_{xx}(\omega) = \varepsilon_{yy}(\omega)$

$\Delta n = (n_\perp - n_\parallel)$.

$\Delta n(\lambda)d = M\lambda$,

$I(\omega) \sim \sin^2 \left[ \frac{d}{2c} \Delta n(\omega) \right]$.

Linear spectroscopy

Schematic diagram for normal incidence reflectivity

$\mathcal{R} = \left| \frac{E_2}{E_1} \right|^2$

$\mathcal{R} = \left| \frac{1 - \tilde{N}_{\text{complex}}}{1 + \tilde{N}_{\text{complex}}} \right|^2 \leq \left( \frac{1 - \tilde{n}^2}{1 + \tilde{n}^2} \right)^2 1 = \mathcal{R} + \mathcal{A} + \mathcal{T}$

Contributions to Dielectric Function

The Free Carrier Contribution

The Plasma Frequency

$\omega_p^2 = \frac{4\pi ne^2}{m\varepsilon_{\text{core}}}$
Linear spectroscopy of semiconductors and dielectrics

Frequency dependence of the absorption coefficient near a threshold for interband transitions.

Ionic polarizability / Phonon contribution

Evaluate the dielectric constant of an ionic crystal.

Ionic polarizability is related to the motion of ions.

Recall the linear chain model we used to describe lattice vibrations:

Equations of motion in the presence of external field:

\[ M_1 \frac{d^2 u_n}{dt^2} = -C(2u_n - u_{n+1} - u_{n-1}) - e^* E \]
\[ M_2 \frac{d^2 u_{n+1}}{dt^2} = -C(2u_{n+1} - u_{n+2} - u_n) + e^* E \]

Also assume long wavelength, \( \lambda > a_0 \Rightarrow q \approx 0 \Rightarrow 
\[ u_n = u_0 e^{-i\omega t} \quad u_{n+1} = u_0 e^{-i\omega t} \]

Substitute this solution into equations of motion, solve for \( u_0^+ \), \( u_0^- \).

Get
\[ u_0^- = -\frac{e^*}{M_1(\omega_i^2 - \omega^2)} E_0 \quad u_0^+ = \frac{e^*}{M_2(\omega_i^2 - \omega^2)} E_0 \]

where \( \omega_i = \sqrt{2C \left( \frac{1}{M_1} + \frac{1}{M_2} \right)} \) - transverse optical phonon frequency at \( q = 0 \)

The ionic polarization \( P_i \) is then
\[ P_i = n_m e^*(u_0^+ - u_0^-) \]

\( n_m \) - number of dipoles per unit volume; \( P = \varepsilon_0 \varepsilon E \)

Relative permittivity:
\[ \varepsilon_r = \varepsilon \varepsilon_0 = 1 + \chi \; \chi = \chi_{el} + \chi_i \]

Get
\[ \varepsilon_r(\omega) = 1 + \chi_{el} + \frac{n_m e^*}{M_R \varepsilon_0(\omega_i^2 - \omega^2)} \]

where \( M_R = \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{-1} = \frac{M_1 M_2}{M_1 + M_2} \) - reduced mass
At high frequencies, $\omega >> \omega_t$, the ionic term vanishes: $\varepsilon_{r,\infty} = 1 + \chi_{el}$

At $\omega = 0$,

$$\varepsilon_{r,0} = 1 + \chi_{el} + \frac{n_m e^*}{M_R \varepsilon_0 \omega_t^2}$$

can rewrite

$$\varepsilon_r(\omega) = 1 + \chi_{el} + \frac{n_m e^*}{M_R \varepsilon_0 \omega_t^2 (1 - \omega^2/\omega_t^2)} = \varepsilon_{r,\infty} + \frac{\varepsilon_{r,0} - \varepsilon_{r,\infty}}{1 - \omega^2/\omega_t^2}$$

Note that $\varepsilon_r(\omega) \rightarrow \infty$. Also, $\varepsilon_r(\omega) = 0$ at $\omega = \left(\frac{\varepsilon_{r,0}}{\varepsilon_{r,\infty}}\right)^{1/2} \omega_t$

Between $\omega_t$ and $\omega$, $\varepsilon_r(\omega) < 0 \Rightarrow$ index of refraction is imaginary:

$$N(\omega) = \sqrt{\varepsilon_r} = i \cdot k(\omega) \quad \text{wave is reflected}$$

**Physical meaning of $\omega_l$ - the frequency of longitudinal optical phonon**

$$\nabla \cdot \mathbf{D} = \varepsilon (\nabla \cdot \mathbf{E}) = 0$$

TO phonons: no field in $z$ direction;

LO phonons: macroscopic field along $z$

from the symmetry of the problem:

$$\frac{\partial E_x}{\partial z} = 0 \Rightarrow \nabla \cdot \mathbf{E} = 0$$

only if $\varepsilon(\omega) = 0$

**Lyddane-Sachs-Teller relation**

We had

$$\varepsilon_r(\omega) = \varepsilon_{r,\infty} + \frac{\varepsilon_{r,0} - \varepsilon_{r,\infty}}{1 - \omega^2/\omega_t^2} \quad \text{and} \quad \omega_l^2 = \frac{\varepsilon_{r,0}}{\varepsilon_{r,\infty}} \omega_t^2$$

combine, get

$$\varepsilon_r(\omega) = \varepsilon_{r,\infty} \frac{\omega_l^2 - \omega^2}{\omega_t^2 - \omega^2} \quad \text{or} \quad \frac{\varepsilon_{r,0}}{\varepsilon_{r,\infty}} = \frac{\omega_l^2}{\omega_t^2}$$

If many phonon branches:

$$\varepsilon(\omega) = \varepsilon_{\infty} \prod_j \frac{\omega_{LO,j}^2 - \omega^2}{\omega_{TO,j}^2 - \omega^2}$$

**Electronic polarizability**

For an accurate quantitative description, quantum mechanics is needed

But we can get some general ideas with classical approach

Recall our model of atom:

Displaced electronic cloud feels a restoring force, which is linear (for small displacements)

$$\text{Total force } \mathbf{F} = e \mathbf{E} - \kappa \Delta \mathbf{r} = m \frac{d^2 \Delta \mathbf{r}}{dt^2}$$

$$\kappa = \text{spring constant} \quad m = \text{mass}$$

For simplicity consider one-dimensional case ($\Delta \mathbf{r}$ parallel to $x$)
Without an external field:
\[-kx = m \frac{d^2x}{dt^2}\]

Equation for harmonic oscillator. Solution: harmonic vibration
\[x(t) = x_0 e^{-i\omega_0 t} \quad \text{with frequency} \quad \omega_0 = \sqrt{k/m}\]

Now, have electromagnetic wave with field \(E(t) = E_0 e^{i\omega t}\)

Force \(F(t) = eE_0 e^{i\omega t}\)

Equation of motion becomes (forced oscillator)
\[eE_0 e^{i\omega t} - m\omega_0^2 x = m \frac{d^2x}{dt^2}\]

Look for a solution \(x(t) = x_0 e^{i\omega t}\)

get
\[x(t) = \frac{e/m}{\omega_0^2 - \omega^2} E_0 e^{-i\omega t} = \frac{e/m}{\omega_0^2 - \omega^2} E(t)\]

Now, consider damping force proportional to speed:
\[F_{\text{damp}} = -m\gamma \frac{dx}{dt}\]

Equation of motion becomes (damped oscillator):
\[eE_0 e^{i\omega t} - m\omega_0^2 x - m\gamma \frac{dx}{dt} = m \frac{d^2x}{dt^2}\]

Again, look for a solution \(x(t) = x_0 e^{i\omega t}\)

get
\[x(t) = \frac{e/m}{\omega_0^2 - \omega^2 + i\omega\gamma} E(t)\]

Therefore
\[n^2(\omega) = \frac{\varepsilon}{\varepsilon_0} = 1 + \frac{NZe^2}{\varepsilon_0 m} \left( \frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} \right)\]

Expect strong response (large \(x\)), \(\Rightarrow\) large susceptibility \(\chi \Rightarrow\) large refractive index \(n\) at \(\omega \approx \omega_0\)

Dipole moment \(p = qx\), so polarization \(P = eNZx\)

\(N\) atoms per unit volume, \(Z\) electrons per atom \(\Rightarrow\)
\[P = \varepsilon_0 \chi E \quad \text{and} \quad \varepsilon = \varepsilon_0 \left( 1 + \chi \right)\]

get
\[\chi = \frac{NZe^2}{\varepsilon_0 m \left( \omega_0^2 - \omega^2 \right)} \quad \text{or} \quad \varepsilon = \varepsilon_0 \left( 1 + \frac{NZe^2}{\varepsilon_0 m \left( \omega_0^2 - \omega^2 \right)} \right)\]

and
\[n^2(\omega) = \frac{\varepsilon}{\varepsilon_0} = 1 + \frac{NZe^2}{\varepsilon_0 m \left( \omega_0^2 - \omega^2 \right)}\]

Amplitude decays as wave propagates – absorption; results from damping

Usually write \(\tilde{n} \rightarrow n + i\frac{\alpha}{2k_0}\) Then \(\tilde{E}_0 = E_0 e^{-\alpha x/2}\)

\[\alpha - \text{absorption coefficient} \quad (\text{m}^{-1})\]
Reflectivity at normal incidence (in air)

Field amplitude: $r = \frac{n-1}{n+1}$ power (intensity): $R = |r|^2 = \frac{(n-1)^2}{(n+1)^2}$

If $\tilde{n} = n_R + in_I$ then $R = |r|^2 = n_R^2 - n_I^2$;
$\varepsilon_r' = n_R^2 - n_I^2$; $\varepsilon_r'' = 2n_Rn_I$

$n_I$ is called extinction coefficient

As we've seen, the dielectric function and refractive index are generally complex: $\varepsilon_r = \varepsilon_r' + i\varepsilon_r''$  $\tilde{n} = n_R + in_I$

We obtained

$$n^2(\omega) = \frac{\varepsilon}{\varepsilon_0} = 1 + \frac{N\varepsilon^2}{\varepsilon_0 m} \left( \frac{1}{\omega_0^2 - \omega^2 + i\gamma} \right)$$

Quantum mechanics gives similar result:

$$\alpha_e(\omega) = \frac{\varepsilon^2}{m} \sum f_j \frac{\omega_j}{\omega_j^2 - \omega^2 + i\gamma_j}$$

Many resonant frequencies $\omega_j$ correspond to energy transitions

Weighting factors $f_j$ called oscillator strengths (related to transition matrix elements)

Optical properties of conductive solids (metals)

conductivity of a medium $\sigma$: $J = \sigma E$

Including conductivity in Maxwell's equations in the medium:

$\nabla \times B = \mu J + \mu e \frac{\partial E}{\partial t}$

leads to wave equation:

$\nabla^2 \mathbf{E} = \mu \sigma \frac{\partial E}{\partial t} + \mu e \frac{\partial^2 E}{\partial t^2}$

Differs from a "standard" wave equation by the first term in the right part

Still, look for plane wave solution: $E(r, t) = E_0 e^{i(k \cdot r - \omega t)}$

applying $\nabla^2$ to plane wave gives $\nabla^2 \mathbf{E} = -k^2 \mathbf{E}$

$\partial^2 / \partial t \rightarrow -i\omega$; $\partial^2 / \partial t \rightarrow -\omega^2$ get $-k^2 \mathbf{E} = -i\omega\mu\mathbf{E} - \mu e\omega^2 \mathbf{E}$

so

$k^2 = \mu e\omega^2 + i\omega\mu\sigma = \mu_0 e_0 \omega^2 \left( \frac{\mu e}{\mu_0 e_0} + i \frac{\mu\sigma}{\mu_0 e_0 \omega} \right)$

$k_0 = \mu_0 e_0 \omega^2 \frac{\omega^2}{c^2}$

assume nonmagnetic: $\mu = \mu_0$ get $k = k_0 \sqrt{\frac{\varepsilon_0 + i \frac{\sigma}{\varepsilon_0 \omega}}{\varepsilon_0 \omega}} = \tilde{n}k_0$

complex refractive index: $\tilde{n} = \left( \frac{\varepsilon}{\varepsilon_0} + i \frac{\sigma}{\varepsilon_0 \omega} \right) = n_R + in_I = n_R + i \frac{\alpha}{2k_0}$

$\alpha$ - absorption coefficient (m$^{-1}$); $\tilde{E}_0 = E_0 e^{-\alpha y/2}$ and $I = I_0 e^{-\alpha x}$

...
Reflection from metals

Have complex refractive index $n_i$: 

$$n = \left( \frac{\varepsilon + i \sigma}{\varepsilon_0 \omega} \right)^{1/2} = n_I + i \frac{\alpha}{2k_0}$$

$n_R, n_I = \alpha/2k_0$ are real

Reflectivity at normal incidence (in air) 

$$R = |r|^2 = \frac{(n_R - 1)^2 + n_I^2}{(n_R + 1)^2 + n_I^2}$$

Consider a very good metal: large $\sigma$ (e.g. silver: $\sigma \approx 6 \times 10^7 \Omega^{-1}m^{-1}$)

For $\lambda = 500$ nm and $\varepsilon \approx \varepsilon_0$

$$\frac{\sigma}{\varepsilon_0 \omega} \approx 2000$$

then 

$$\frac{\alpha}{2k_0} = n_I \gg n_R - 1$$

$\Rightarrow R \to 1$

Dispersion equation in metals

The dispersion we got in a model of oscillating electrons:

$$n^2(\omega) = 1 + \frac{Ne^2}{\varepsilon_0 m} \left( \frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} \right)$$

$\omega_0 = \sqrt{k/m_e}$

$k -$ "spring constant"

$m_e -$ electron mass

in metal, there are free electrons – no restoring force $\Rightarrow \omega_0 = 0$

Still, there may be bound electrons, too.

So

$$n^2(\omega) = 1 + \frac{Ne^2}{\varepsilon_0 m} \left( \frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} + \sum f_j \frac{\omega_0^2 - \omega^2 + i\omega\gamma}{\omega_0^2 - \omega_0^2 + i\omega\gamma} \right)$$

free electrons

bound electrons

(like in dielectric)

The Free Carrier Contribution

Where carrier concentration is higher? Choose between $a$ and $b$. Show work

Plasma edges observed in the room temperature reflectivity spectra of $n$-type InSb with carrier concentration $n$ varying between $3.5 \times 10^{17}$ cm$^{-3}$ and $4.0 \times 10^{18}$ cm$^{-3}$.

$$\omega_p^2 = \frac{4\pi ne^2}{m\varepsilon_{core}}$$
Ionic contribution to dielectric function is related to lattice vibrations and exhibits dispersion in infrared region, given by the Lyddane-Sachs-Teller relation:

$$\varepsilon(\omega) = \varepsilon_\infty \prod_j \frac{\omega_{LOj}^2 - \omega^2}{\omega_{TOj}^2 - \omega^2}$$

Electronic polarizability is given by

$$\alpha(\omega) = \frac{e^2}{m} \left( \frac{1}{-\omega^2 + i\omega \gamma_e} + \sum_j \frac{f_j}{\omega_{0j}^2 - \omega^2 + i\omega \gamma_j} \right)$$

Dielectric function and refractive index are generally complex:

$$\varepsilon_r = \varepsilon_r' + i\varepsilon_r'' \quad \tilde{n} = n_R + i n_I \quad \varepsilon_r' = n_R^2 - n_I^2 \quad \varepsilon_r'' = 2n_R n_I$$

absorption coefficient $\alpha = 2k_0 n_I$  $n_I$ - extinction coefficient