Theory and Application of Nanomaterials
Lecture 8: Optical Spectroscopy

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Introduction

Interaction of light with matter can reveal details about electronic transitions described by quantum mechanics. One need is to probe ever-smaller volumes of materials, e.g. nano-materials. Below, a Micro-spectroscopy method is employed to look at sub micron features at varying temperatures.

Figure: A micro-spectroscopy set-up capable of examining sub-micron regions of materials at temperatures down to 4K. The solid immersion lens sits on the sample surface, and enhances the resolution of the far-field objective by increasing the refractive index.
# Outline

## 1. Optical Transitions
- Light Scattering
- Selection Rules
- Energy Relaxation or ‘Carrier Cooling’

## 2. Optical Spectroscopy
- Measuring Emission (Fluorescence/Luminescence)
- Measuring Absorption (PLE)
- Time Resolved Luminescence
- Interpretation of Time Resolved Luminescence
- Ultrafast Transient Absorption

## 3. Excitons, Defects and Symmetry Effects
- Excitons
- Donor Acceptor Pairs
- Valence Band Splitting
Light Scattering

Due to electron-photon coupling, energy and momentum can be exchanged with matter via interaction with electromagnetic radiation. Energy and momentum conservation require:

\[ E_2 - E_1 = h\nu \quad \rightarrow \quad \text{Energy conserved} \]
\[ \hbar k_2 - \hbar k_1 = \hbar k_p \quad \rightarrow \quad \text{Momentum conserved} \]

**Figure:** A Feynman diagram describing the evolution of an optical transition wherein an electron of energy \( E_1 \) and momentum \( k_1 \) absorbs a photon of energy \( h\nu \) and momentum \( \hbar k_p \). Time axis is by convention implied from left to right, but shown here explicitly.
Emission Processes

Below are shown to emission processes involving emission of light by change of electron energy level (fluorescence or luminescence) and by inelastic scattering of light of lattice vibrations or phonons (Raman scattering).

**Figure:** Feynman diagrams describing the evolution of an electron transition wherein an electron of energy $E_1$ and momentum $k_1$ emits a photon of energy $E = h\nu = E_1 - E_2$ and momentum $\hbar k_p = \hbar (k_1 - k_2)$ (above) or phonon of energy $\hbar \Omega$ and momentum $\hbar k_{ph}$ (below).
Optical Transitions

Having computed the wave function, we wish to describe general properties of optically-induced transitions. We will assume the wave function has the general form:

\[ |\psi\rangle = |n, l, m_l; s \rangle \]

In general, a transition will involve a change of quantum state, for instance between two Eigenstates here represented as atomic levels:

\[ |n, l, m_l, s\rangle \]
\[ |n_o, l_o, m_{l_o}, s_o\rangle \]

**Figure:** Energy level diagram showing an absorption of a photon of energy \( h\nu \), resulting in an atomic transition between to quantum states.
Selection Rules

The transition rate is given by Fermi’s golden rule:

\[
W_{fi} = \frac{2\pi}{\hbar} |\langle n, l, ml, s | \hat{H}_{int}(0) | n_o, l_o, m_{lo}, s_o \rangle|^2 \delta(\Delta E_{nn_o} - \hbar \omega)
\]

as we saw in our previous discussion of quantum mechanics and transitions between quantum states. Evaluating the expression for the matrix element, we can quote some selection rules:

\[
\langle \psi_f | \hat{H}_{int} | \psi_i \rangle = \langle s_f | s_i \rangle \langle n, l, ml | \hat{H}_{int}(0) | n_o, l_o, m_{lo} \rangle
\]

\[
\langle s_f | s_i \rangle = \delta_{if} \quad \text{spin allowed for } i = f
\]

\[
\langle n, l, ml | \hat{H}_{int}(0) | n_o, l_o, m_{lo} \rangle \neq 0 \quad \text{dipole allowed}
\]

Where the spin dependent part of the wave function is independent of the spatial coordinates and we can therefore factor the expression out. We say the transition is spin allowed if the spin portion of the matrix element is non-zero, and, since we used \( \hat{H}_{int} = -p \cdot E \) to calculate the matrix element (see discussion of Fermi’s golden rule), if the spatial portion of the matrix element is non-zero we say the transition is dipole allowed.
Energy Relaxation in Solids

\[ \Delta E = 2U \{ \begin{array}{c} \omega (k+nG) \\ \vdots \\ \omega (k+2G) \\ \omega (k+G) \\ \omega (k) \end{array} \]

\[ k \]

\[ \omega \]

**Figure:** (left): Band filling in extended zone scheme. (right): Scattering diagram showing the processes which lead to light emission from a semiconductor: light absorbed at \( E = h\nu \geq E_g \). Excess energy is lost by rapid phonon emission and emission at energy \( E = h\nu \approx E_g \).
Energy Relaxation in Molecules

A similar mechanism in molecules is depicted in figure 6, the conduction and valence bands are now replaced with their molecular counterparts, the so-called LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) energy levels. The molecular counterpart to the phonons in crystals are the normal modes of vibration of the molecule, with discrete energies.

**Figure:** An energy level diagram describing the absorption and emission of a photon in a molecule. Note the energy of the emitted photon is less than the absorbed photon due to internal energy relaxation.
Measuring Fluorescence / Luminescence

Typical apparatus for measuring fluorescence or luminescence, e.g. what might exist in a fluorescence microscope. An example luminescence spectra is also shown, the details of the various signatures will be discussed in what follows.

**Figure:** (left): Experimental apparatus for measuring fluorescence or luminescence. An excitation source is reflected off a dichroic mirror, and focused onto the sample by an achromatic lens. Longer wavelengths are emitted from the sample and transmitted by the dichroic mirror to be analyzed (right): Example $\mu$-photoluminescence spectra from $\text{Ga}_x\text{In}_{1-x}\text{P}$. 

Deep level Bound exciton

Impurity luminescence

Band-edge bound exciton

Counts/sec

0

500

1000

1500

2000

1.910

1.922

1.933

1.945

Energy (eV)
Density of States

In the figure below, the parabolic band approximation for a type-I semiconductor (e.g. GaAs) is shown. Plotted alongside the dispersion relation is the density of states (DOS). The DOS, or $\rho_{c(\nu)}(E)$, is dependent on the volume of a shell in $k$-space, and will be zero at the gaps, thus the shape of $\rho_{c(\nu)}(E)$ should be similar to what is sketched.

Figure: The density of states (DOS), or $\rho_{c/\nu}(E)$, is shown alongside the energy dispersion relation in the parabolic band approximation for a direct-gap semiconductor.
Absorption Spectroscopy, Photoluminescence Excitation

The principle of Photoluminescence excitation spectroscopy, or PLE, is based on energy relaxation, which results in emission at a lower energy than absorption. In the left part of the figure, an emission spectra is shown, centered around an energy $E_g - E_b$, if a spectrometer can be set to an energy below this, a laser excitation source (whose energy range is represented by the green arrow in the figure) can be scanned continuously towards higher energy.

**Figure:** (Left): A photoluminescence (PL) spectra resulting from excitonic recombination, a narrow energy range near the low energy tail of the spectra is selected as the PLE detection energy. The green arrow shows the range of excitation energies which will be used to obtain the PLE spectra. (Right): Photoluminescence intensity at the PLE detection energy plotted as a function of excitation energy is proportional to the density of states $\rho(E)$. 

$$I(E)$$

$$E_{detect} \leq E_g - E_b$$

$$\Delta E = E_b$$

$$\rho(E)$$
Measuring Time Resolved Photo-Luminescence (TRPL)

The most basic time-dependent measurement is time-resolved PL or TRPL, a prototypical example is shown below. The measurement can be made using a number of methods, including time-correlated single photon counting (TCSPC) with a time-resolution on the order of 500ps, or using a streak-camera, with a resolution in the sub-picosecond range.

**Figure:** (Left): Photo-luminescence, or PL, is initiated by an excitation pulse (blue), and time-resolved to show the recombination as function of time (red). (Right): A typical decay trace will be dominated by the recombination lifetime, but in principle is influenced by carrier thermalization, which takes place on a timescale typically very short compared to recombination.
Interpreting Time Resolved Photo-Luminescence (TRPL)

The measured fluorescence or luminescence decay time can often be characterized by a single exponential decay, e.g.:

\[ I(t) = I_0 e^{-t/\tau} \]

but the decay rate \( \tau \) may have other contributions beyond the radiative decay rate based on the quantum transition rate, which are usually sub-divided into radiative and non-radiative components, related as so:

\[ \frac{1}{\tau} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}} \]

where the possibility that a transition which does not involve emitting a photon may contribute to the observed decay \( \tau \). For instance, phonon emission where the optical energy of the photon is converted to heat.
Transport contributions to recombination

Mobile carriers (electrons and holes) can freely diffuse, and therefore the recombination rate will depend on the probability that two carriers of opposite type (electron/hole) will occupy the same site in the crystal.

\[ R = n_e n_h P_{eh} = \frac{1}{\tau} \]

\[ R_c = \frac{n_e n_h}{n_i^2} R = \frac{1}{\tau} \]

**Figure:** In a system where the excited state is mobile, such as a semiconductor or molecular crystal, transport effects influence the measured recombination rate or fluorescence / luminescence decay.
Ultrafast Transient Absorption

For optically thin samples, differential transmission, also known as transient absorption, is a well-known method which measures directly the changes in absorption on a femtosecond time scale. An intense “pump” pulse fills some fraction of the available states, resulting in increased transmission (reduced absorption) which will be dependent on the choice of time delay $\tau$ between the “pump” and “probe” pulse.

Figure: (Left): Differential transmission utilizes an intense pump pulse and typically a less intense probe pulse, delayed by a time $\tau$. Transmission is then a function of time delay $\tau$ due to state-filling effects. (Right): Typically the differential transmission, $\Delta T/T(\tau)$ is plotted vs. delay $\tau$. Illustrating the ultrafast hot carrier cooling and slower recombination processes for $\tau \gg \tau_c$, the carrier cooling rate.
Excitons

An electron in a conducting state may be bound to the positively charged hole, and the centro-symmetric system forms a so-called “quasi-particle” known as an exciton. The coulomb attraction between the electron and hole results in a binding energy:

\[
E_b = \frac{m^* q^4}{2\hbar^2 c^2} \frac{1}{n^2} = \frac{13.6\text{eV}}{(\epsilon/\epsilon_o)^2} \frac{1}{m_0 n^2}
\]

- quantum number \(n\), which specifies the \(s\)-wave character exciton states.
- \(E_{\text{bind}} \sim 10\text{meV}\) in GaAs, \(< k_B T\) at room temperature (23meV).
- Integral spin, due to the combination of electron and hole spin, behaving as a Boson, thus Excitons are candidates for Bose-Einstein condensation.

**Figure:** Schematic of quasi-particle referred to as an Exciton – an electron-hole pair bound together in an orbital system by coulomb attraction.
Impurities in Semiconductors

An impurity in a perfect crystal breaks the translational symmetry and creates a localized defect state. The impurity can either give up a charge (donor) which is transferred into one of the Bloch states of the crystal, or take up a charge (acceptor). The carrier concentration due to the presence of these impurities can be calculated from statistical physics, for instance the carrier concentration due to the density $N_d$ donors is:

$$n \approx (n_o N_d)^{1/2} e^{-E_d/2k_B T}$$

where

$$n_o = 2\left(\frac{mek_B T}{2\pi \hbar^2}\right)^{3/2}$$

These levels can also trap excitons, and as a result, below-gap emission can occur, as seen in the figure below.

![Energy level diagram showing donor and acceptor levels and recombination for donor acceptor pairs.](image)

**Figure:** Energy level diagram showing donor and acceptor levels and recombination for donor acceptor pairs.
Donor Acceptor Pairs

The energy of this emission is observed in discrete lines, corresponding to integral numbers of lattice spacings, for which the coulomb attraction varies discretely, resulting in a series of lines corresponding to varying donor-acceptor separation are observed:

\[ \Delta E = E_g - E_D - E_A - \frac{q^2}{\varepsilon r} \]

**Figure:** Donor-acceptor emission is modulated by discrete fluctuations in the nearest neighbor distance, which modulate the coulomb interaction energy.
Valence Band Splitting

One notes the varying curvature of the bands in the figure, and this is described in terms of the “effective mass”, derived from the curvature of the energy dispersion relation:

\[ E = \frac{\hbar^2 k^2}{2m} \rightarrow \frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \]

Based on the curvature, the two degenerate bands at the valence band maxima are labelled “heavy” and “light” hole bands (designated hh and lh), an additional band due to the spin-orbit interaction is also shown:

**Figure:** Parabolic band approximation for typical direct gap semiconductor, showing degeneracy in valence band at \( k = 0 \), so-called heavy and light hole bands and split-off band.