PHY 752 Solid State Physics
11-11:50 AM MWF Olin 103

Plan for Lecture 26:

- **Optical properties of semiconductors and insulators (Chap. 12 in GGGPP)**
  - **Dielectric function**
  - **Band-to-band optical transitions**

13	Wed, 9/23/2015	Chap. 4	Density functional theory	#12
14	Fri, 9/25/2015	Chap. 5	Implementation of density functional theory	#13
15	Mon, 9/28/2015	Chap. 5	Implementation of density functional theory	#14
16	Wed, 9/30/2015	Chap. 5	First principles pseudopotential methods	#15
17	Fri, 10/02/2015	Chap. 6	Example electronic structures	#16
18	Mon, 10/05/2015	Chap. 6	Ionic and covalent crystals	#17
19	Wed, 10/07/2015	Chap. 6	More examples of electronic structures	#18
20	Fri, 10/09/2015	Chap. 1-6	Review	Start exam
	Mon, 10/12/2015		No class	Take-home exam
	Wed, 10/14/2015		No class	Exam due before 10/19/2015
	Fri, 10/16/2015		Fall break -- no class	
21	Mon, 10/19/2015	Chap. 10	X-ray and neutron diffraction	#19
22	Wed, 10/21/2015	Chap. 10	Scattering of particles by crystals	#20
23	Fri, 10/23/2015	Chap. 11	Optical and transport properties of metals	#21
24	Mon, 10/26/2015	Chap. 11	Optical and transport properties of metals	#22
25	Wed, 10/28/2015	Chap. 11	Transport in metals	#23
26	Fri, 10/30/2015	Chap. 12	Optical properties of semiconductors and insulators	
	Wed, 12/02/2015		Student presentations I	
	Fri, 12/04/2015		Student presentations II	
	Mon, 12/07/2015		Begin Take-home final	

Optical transitions between states of a quantum system

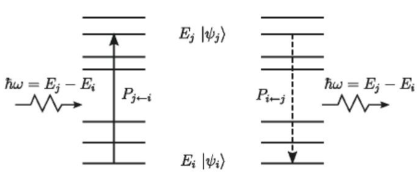

Figure 12.1 Schematic representation of the radiative transition probability between a pair of electronic states $|\psi_i\rangle$ and $|\psi_j\rangle$, of energy E_i and E_j; any transition between these two states involves the absorption, or the emission of a photon with energy $\hbar\omega = E_j - E_i$.

Example -- Ge

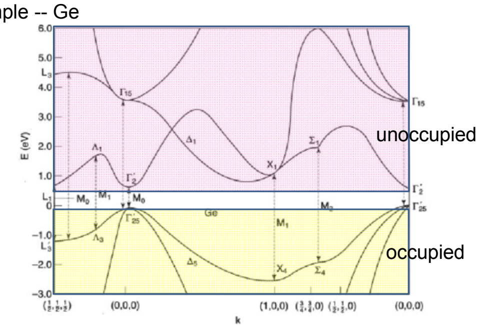

Figure 12.3 Energy bands of germanium along symmetry directions, with the empirical pseudopotential method. The **k** wavevector is in units of $2\pi/a$. Relevant direct interband edges are indicated by arrows [With permission from Figs. 1, 2, Phys. Rev. Lett. *9*, 94 (1962)].

Analysis

Ground state Hamiltonian

$$H_0 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}),$$

Hamiltonian with electromagnetic field

$$H = H_0 + \frac{eA_0}{mc} e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}\, \widehat{\mathbf{e}}\cdot\mathbf{p} + \frac{eA_0}{mc} e^{-i(\mathbf{q}\cdot\mathbf{r}-\omega t)}\, \widehat{\mathbf{e}}\cdot\mathbf{p}\,.$$

$$\mathbf{A}(\mathbf{r},t) = A_0\, \widehat{\mathbf{e}}\, e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)} + \text{c.c.} \qquad \widehat{\mathbf{e}} \perp \mathbf{q}\,,$$

Including linear terms in electromagnetic field

$$H = \frac{1}{2m}\left[\mathbf{p} + \frac{e}{c}\mathbf{A}(\mathbf{r},t)\right]^2 + V(\mathbf{r}) = H_0 + \frac{e}{mc}\mathbf{A}(\mathbf{r},t)\cdot\mathbf{p} + \frac{e^2}{2mc^2}\mathbf{A}^2(\mathbf{r},t),$$

Fermi Golden Rule for one-photon absorption

$$P_{j\leftarrow i} = \frac{2\pi}{\hbar}\left(\frac{eA_0}{mc}\right)^2 |\langle\psi_j| e^{i\mathbf{q}\cdot\mathbf{r}}\, \widehat{\mathbf{e}}\cdot\mathbf{p}|\psi_i\rangle|^2 \delta(E_j - E_i - \hbar\omega).$$

Fermi Golden Rule for one-photon emission

$$P_{i\leftarrow j} = \frac{2\pi}{\hbar}\left(\frac{eA_0}{mc}\right)^2 |\langle\psi_i| e^{-i\mathbf{q}\cdot\mathbf{r}}\, \widehat{\mathbf{e}}\cdot\mathbf{p}|\psi_j\rangle|^2 \delta(E_i - E_j + \hbar\omega).$$

Transition rate

$$W(\mathbf{q},\omega) = \frac{2\pi}{\hbar}\left(\frac{eA_0}{mc}\right)^2 2\sum_{ij} |\langle\psi_j| e^{i\mathbf{q}\cdot\mathbf{r}}\, \widehat{\mathbf{e}}\cdot\mathbf{p}|\psi_i\rangle|^2 \delta(E_j - E_i - \hbar\omega)[f(E_i) - f(E_j)],$$

Viewing transition rate in terms of the system's linear response to the electromagnetic field, it can be related to the dielectric function:

$$\boxed{\varepsilon_2(\mathbf{q},\omega) = \frac{2\pi\hbar c^2}{\omega^2}\frac{1}{V}\frac{W(\mathbf{q},\omega)}{A_0^2}}.$$

Explicitly:

$$\varepsilon_2(\mathbf{q},\omega) = \frac{8\pi^2 e^2}{m^2\omega^2}\frac{1}{V}\sum_{ij}|\langle\psi_j|e^{i\mathbf{q}\cdot\mathbf{r}}\,\widehat{\mathbf{e}}\cdot\mathbf{p}|\psi_i\rangle|^2\delta(E_j - E_i - \hbar\omega)[f(E_i) - f(E_j)].$$

Using the Kramers-Kronig transform:

$$\varepsilon_1(\mathbf{q},\omega) = 1 + \frac{1}{\pi}P\int_{-\infty}^{+\infty}\frac{\varepsilon_2(\mathbf{q},\omega')}{\omega'-\omega}\,d\omega';$$

Complex dielectric function

$$\boxed{\varepsilon(\mathbf{q},\omega) = 1 + \frac{8\pi e^2}{m^2}\frac{1}{V}\sum_{ij}\frac{|\langle\psi_j|e^{i\mathbf{q}\cdot\mathbf{r}}\,\widehat{\mathbf{e}}\cdot\mathbf{p}|\psi_i\rangle|^2}{(E_j - E_i)^2/\hbar^2}\,\frac{[f(E_i) - f(E_j)]}{E_j - E_i - \hbar\omega - i\eta}},$$

with $$\lim_{\eta\to 0^+}\frac{1}{x - i\eta} = P\frac{1}{x} + i\pi\delta(x),$$

Explicit form:

$$\varepsilon_2(\mathbf{q},\omega) = \frac{8\pi^2 e^2}{m^2\omega^2}\frac{1}{V}\sum_i^{\text{(occ)}}\sum_j^{\text{(unocc)}}|\langle\psi_j|e^{i\mathbf{q}\cdot\mathbf{r}}\,\widehat{\mathbf{e}}\cdot\mathbf{p}|\psi_i\rangle|^2\delta(E_j - E_i - \hbar\omega).$$

Details of optical transitions

Effects of wavevector

$$\langle\psi_{c\mathbf{k}_j}|e^{i\mathbf{q}\cdot\mathbf{r}}\,\widehat{\mathbf{e}}\cdot\mathbf{p}|\psi_{v\mathbf{k}_i}\rangle = \int\psi^*_{c\mathbf{k}_j}(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}\,\widehat{\mathbf{e}}\cdot\mathbf{p}\,\psi_{v\mathbf{k}_i}(\mathbf{r})\,d\mathbf{r}.$$

Non-trivial matrix element when $\mathbf{k}_j = \mathbf{q} + \mathbf{k}_i + \mathbf{g}$.

Note that $|\mathbf{q}| << |\mathbf{g}|$

$\Rightarrow$ $\mathbf{k}_i \approx \mathbf{k}_j$ (vertical transitions)

$$\begin{aligned}\varepsilon_2(\omega) &= \frac{8\pi^2 e^2}{m^2\omega^2}\frac{1}{V}\sum_{cv}\sum_{\mathbf{k}}|\langle\psi_{c\mathbf{k}}|\widehat{\mathbf{e}}\cdot\mathbf{p}|\psi_{v\mathbf{k}}\rangle|^2\delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega)\\ &= \frac{8\pi^2 e^2}{m^2\omega^2}\sum_{cv}\int_{\text{B.Z.}}\frac{d\mathbf{k}}{(2\pi)^3}|\widehat{\mathbf{e}}\cdot\mathbf{M}_{cv}(\mathbf{k})|^2\delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega);\end{aligned}$$

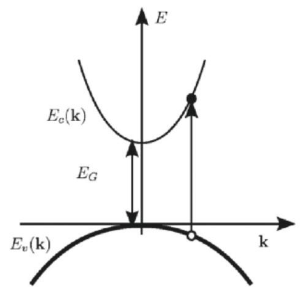

Figure 12.2 Schematic representation of the top valence band and bottom conduction band of a direct gap semiconductor or insulator. Optical transitions are vertical in the energy band diagram. [The valence band has been reported in bold to remind its full occupancy by electrons.]

In general the matrix element $M_{cv}(\mathbf{k})$ is a smooth function of **k** and the joint density of states often determines the frequency dependence of the optical properties:

$$J_{cv}(\omega) = \int_{\mathrm{B.Z.}} \frac{d\mathbf{k}}{(2\pi)^3} \delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega).$$

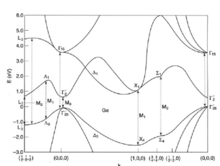

Figure 12.3 Energy bands of germanium along symmetry directions, with the empirical pseudopotential method. The **k** wavevector is in units of $2\pi/a$. Relevant direct interband edges are indicated by arrows [With permission from Figs. 1, 2, Phys. Rev. Lett. *9*, 94 (1962)].

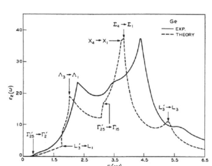

Figure 12.4 Spectral structure of $\varepsilon_2(\omega)$ (solid line) compared with the theoretical results of interband transitions for Ge (dashed line with edges emphasized to account for critical points) [reprinted with permission from D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Lett. *9*, 94 (1962) and D. Brust, Phys. Rev. *134*, A1337 (1964); copyright 1964 by the American Physical Society].

Another example – BN in the hexagonal structure

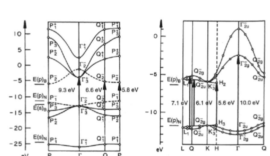

Figure 12.5 Two-dimensional (left) and three-dimensional (right) band structures of hexagonal boron nitride. Relevant optical transitions are also indicated [the calculations are due to E. Doni and G. Pastori Parravicini, Nuovo Cimento *64* B, 117 (1969); interpretation of experimental data is due to D. M. Hoffman, G. L. Doll, and P. C. Eklund, Phys. Rev. B *30*, 6051 (1984)].

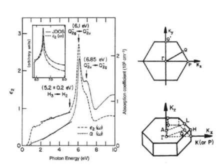

Figure 12.6 Imaginary dielectric constant $\varepsilon_2(\omega)$ and absorption coefficient $\alpha(\omega)$ due to interband electronic transitions in hexagonal boron nitride from experimental measurements [With permission from Fig. 6, Phys. Rev. B *30*, 6051 (1984)]. The inset is the joint density-of-states and $\varepsilon_2(\omega)$ calculated in the two-dimensional approximation near the saddle point singularity. The Brillouin zone of two-dimensional and three-dimensional hexagonal boron nitride are also reported for convenience.

Example – simple two-band semiconductor

$$E_c(\mathbf{k}) = E_G + \frac{\hbar^2 k^2}{2m_c^*}; \qquad E_v(\mathbf{k}) = -\frac{\hbar^2 k^2}{2m_v^*} \qquad m_c^* > 0,\ m_v^* > 0$$

$$E_c(\mathbf{k}) - E_v(\mathbf{k}) = E_G + \frac{\hbar^2 k^2}{2\mu}; \qquad \frac{1}{\mu} = \frac{1}{m_c^*} + \frac{1}{m_v^*}.$$

$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{m^2\omega^2}\int_{\mathrm{B.Z.}} \frac{d\mathbf{k}}{(2\pi)^3}|\widehat{\mathbf{e}}\cdot\mathbf{M}_{cv}(\mathbf{k})|^2\delta(E_G + \frac{\hbar^2 k^2}{2\mu} - \hbar\omega).$$

$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{m^2\omega^2}|C_1|^2\int_0^\infty \frac{1}{(2\pi)^3}4\pi k^2\,\delta(E_G + \frac{\hbar^2 k^2}{2\mu} - \hbar\omega)\,dk.$$

$$\boxed{\text{first-class transitions:} \quad \varepsilon_2(\omega) = \frac{A_1}{\omega^2}(\hbar\omega - E_G)^{1/2} \qquad \hbar\omega > E_G},$$

$$A_1 = (2e^2/m^2)|C_1|^2(2\mu/\hbar^2)^{3/2}$$

$$\boxed{\text{second-class transitions:} \quad \varepsilon_2(\omega) = \frac{A_2}{\omega^2}(\hbar\omega - E_G)^{3/2} \quad \hbar\omega > E_G},$$

$$\mathbf{M}_{cv}(\mathbf{k}) \approx C_2\mathbf{k}. \qquad A_2 = (2e^2/3m^2)|C_2|^2(2\mu/\hbar^2)^{5/2}.$$

Non-vertical transitions – effects of phonons

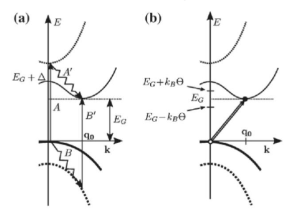

Figure 12.7 Model band structure for estimating the absorption coefficient due to indirect transitions. In (a) we indicate schematically possible second-order processes contributing to the scattering of an electron from the top of the valence band $\psi_{v\mathbf{k}_1}(\mathbf{k}_1 \approx 0)$ to the bottom of the conduction band $\psi_{c\mathbf{k}_2}(\mathbf{k}_2 \approx \mathbf{q}_0)$. The mechanism AA' consists of a direct transition from $\psi_{v\mathbf{k}_1}$ to a virtual state $\psi_{\alpha\mathbf{k}_1}$ (occupied or empty), followed by a phonon-assisted scattering to $\psi_{c\mathbf{k}_2}$. The mechanism BB' consists of a phonon-assisted scattering from $\psi_{v\mathbf{k}_1}$ to a virtual state $\psi_{\beta\mathbf{k}_2}$ (occupied or empty), followed by a direct transition to $\psi_{c\mathbf{k}_2}$ (energy conservation and Pauli exclusion principle can be ignored in the virtual states, as discussed in the text). In (b) the so evaluated second-order scattering amplitude is indicated with a double line. The energy thresholds for photon absorption, with absorption or emission of a phonon of energy $k_B\Theta$, are also indicated.

Electron-phonon coupling Hamiltonian

$$H_{\mathrm{ep}}(\mathbf{r},t) = \frac{1}{\sqrt{N}}\sum_{\mathbf{q}}^{\mathrm{B.Z.}} V_p(\mathbf{q},\mathbf{r})e^{-i\omega_{\mathbf{q}}t}a_{\mathbf{q}} + \mathrm{h.c.}$$

here $\mathbf{q}$ denotes wavevector of phonon of frequency $\omega_{\mathbf{q}}$

and $a_{\mathbf{q}}$ denotes a phonon anhilation operator

Probability of absorbing both photon and phonon:

$$P_{c\mathbf{k}_2\leftarrow v\mathbf{k}_1} = \frac{2\pi}{\hbar}|t_{c\mathbf{k}_2\leftarrow v\mathbf{k}_1}|^2\delta(E_{c\mathbf{k}_2} - E_{v\mathbf{k}_1} - \hbar\omega - \hbar\omega_{\mathbf{q}});$$

$$t_{c\mathbf{k}_2\leftarrow v\mathbf{k}_1} = \frac{eA_0}{mc}\sqrt{n_{\mathbf{q}}}\frac{1}{\sqrt{N}}\left[\sum_\alpha \frac{\langle\psi_{c\mathbf{k}_2}|V_p(\mathbf{q},\mathbf{r})|\psi_{\alpha\mathbf{k}_1}\rangle\langle\psi_{\alpha\mathbf{k}_1}|\widehat{\mathbf{e}}\cdot\mathbf{p}|\psi_{v\mathbf{k}_1}\rangle}{E_v(\mathbf{k}_1) - E_\alpha(\mathbf{k}_1) + \hbar\omega} + \sum_\beta \frac{\langle\psi_{c\mathbf{k}_2}|\widehat{\mathbf{e}}\cdot\mathbf{p}|\psi_{\beta\mathbf{k}_2}\rangle\langle\psi_{\beta\mathbf{k}_2}|V_p(\mathbf{q},\mathbf{r})|\psi_{v\mathbf{k}_1}\rangle}{E_v(\mathbf{k}_1) - E_\beta(\mathbf{k}_2) + \hbar\omega_{\mathbf{q}}}\right],$$

where

$$n_{\mathbf{q}} = \frac{1}{\exp(\hbar\omega_{\mathbf{q}}/k_BT) - 1}$$

Summing the probability over all initial and final states and assuming that the matrix elements are weakly dependent on wavevector, the rate of phonon-assisted transitions depends on the density of states for phonon absorption:

$$J_{(\text{phonon abs})}(\omega) = \int_{\text{B.Z.}} \int_{\text{B.Z.}} \frac{1}{(2\pi)^3 (2\pi)^3} d\mathbf{k}_1\, d\mathbf{k}_2\, \delta(E_{c\mathbf{k}_2} - E_{v\mathbf{k}_1} - \hbar\omega - k_B\Theta)\,;$$

where $\hbar\omega_{\mathbf{q}} \approx \hbar\omega_{\mathbf{q}_0} \equiv k_B\Theta$

For parabolic valence and conduction bands:

$$J_{(\text{phonon abs})}(\omega) = \frac{(4\pi)^2}{(2\pi)^6} \int_0^\infty \int_0^\infty k_1^2 k_2^2\, \delta\!\left(\frac{\hbar^2 k_2^2}{2m_c^*} + \frac{\hbar^2 k_1^2}{2m_v^*} + E_G - \hbar\omega - k_B\Theta\right) dk_1\, dk_2.$$

$$J_{(\text{phonon abs})}(\omega) = \frac{(4\pi)^2}{(2\pi)^6} \int_0^\infty \int_0^\infty k_1^2 k_2^2\, \delta\!\left(\frac{\hbar^2 k_2^2}{2m_c^*} + \frac{\hbar^2 k_1^2}{2m_v^*} + E_G - \hbar\omega - k_B\Theta\right) dk_1\, dk_2.$$

To perform the integral, we make the substitutions

$$\frac{\hbar^2 k_2^2}{2m_c^*} = x, \quad \frac{\hbar^2 k_1^2}{2m_v^*} = y, \quad k_2\, dk_2 = \frac{m_c^*}{\hbar^2}\, dx, \quad k_1\, dk_1 = \frac{m_v^*}{\hbar^2}\, dy$$

and obtain

$$J_{(\text{phonon abs})}(\omega) = \frac{(m_c^* m_v^*)^{3/2}}{2\pi^4 \hbar^6} \int_0^\infty \int_0^\infty \sqrt{x}\sqrt{y}\, \delta(x + y - b)\, dx\, dy\,,$$

where $b = \hbar\omega - E_G + k_B\Theta$. The δ-function under the sign of integral can be different from zero only for positive values of b. Performing the integral over dy one gets

$$J_{(\text{phonon abs})}(\omega) = \frac{(m_c^* m_v^*)^{3/2}}{2\pi^4 \hbar^6} \int_0^b \sqrt{x}\sqrt{b - x}\, dx = \frac{\pi b^2}{8} \qquad (12.21\text{a})$$

$$J_{(\text{phonon abs})}(\omega) = \frac{(m_v^* m_c^*)^{3/2}}{16\pi^3 \hbar^6} (\hbar\omega - E_G + k_B\Theta)^2 \quad \text{for} \quad \hbar\omega > E_G - k_B\Theta.$$

Similar expression holds for phonon emission

Form of optical absorption coefficient with both phonon absorption and emission:

$$\boxed{\alpha(\omega) = C\left[\frac{(\hbar\omega - E_G + k_B\Theta)^2}{e^{\Theta/T} - 1} + \frac{(\hbar\omega - E_G - k_B\Theta)^2}{1 - e^{-\Theta/T}}\right]}.$$

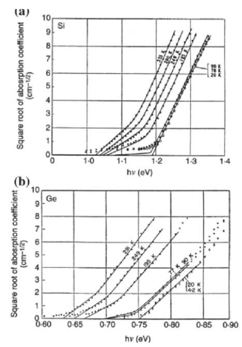

Figure 12.8 (a) Indirect transitions in silicon; dots indicate experimental measurements; the full lines are calculated using Eq. (12.22) of the text. (b) Indirect transitions in germanium [With permission from Fig. 1, Phys. Rev. *98*, 1865 (1955) and Fig. 1, Phys. Rev. *97*, 1714 (1955)].