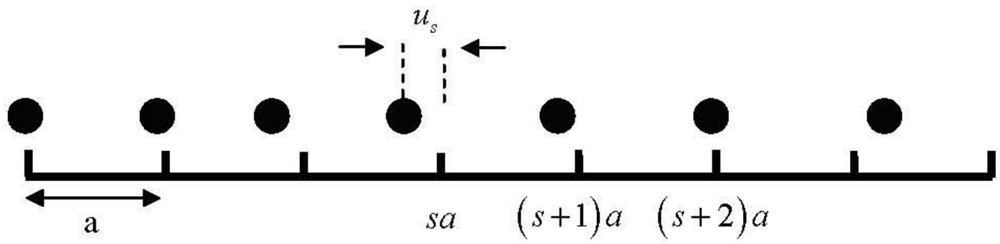
MSE 423 Fall 2025 – Week 14

Fermi's golden rule

Last week:

- Semiconductors – basic electrical and optical properties
- Density of carriers at thermal equilibrium
- Density of available states
- Law of mass action
- Intrinsic carriers and chemical potential
- Impurity levels
- Temperature dependence of majority carriers
- Carrier densities and chemical potentials in doped semiconductors
- p-n junction and built-in voltage
- p-n junction as a photovoltaic cell, as a diode
- (remember – do in-depth evaluations)

1-dimensional monoatomic chain



MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2022)

Properties

- Unique solutions for k in the first BZ

$$\frac{u_{s+1}}{u_s}$$

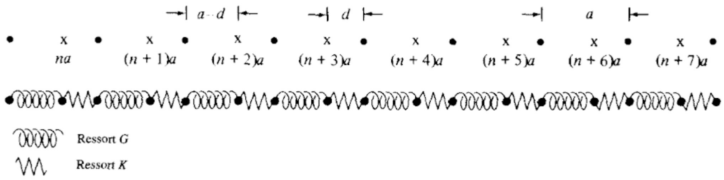
- Phase velocity and group velocity

Properties

- Standing waves

- Long wavelength limit

1-dimensional diatomic chain



III. Equations of motion

$$M\frac{d^2u_{1,s}}{dt^2} = K\left(u_{2,s} - u_{1,s}\right) + G\left(u_{2,s-1} - u_{1,s}\right)$$

$$M\frac{d^2u_{2,s}}{dt^2} = K\left(u_{1,s} - u_{2,s}\right) + G\left(u_{1,s+1} - u_{2,s}\right)$$

IV. Solutions

$$u_{1s} = u_1 e^{iksa} e^{-i\omega t}, \quad u_{2s} = u_2 e^{iksa} e^{-i\omega t}$$

V. Dispersion relations

$$\left(M\omega^2 - (K+G)\right)u_1 + \left(K + Ge^{-ika}\right)u_2 = 0$$

$$\left(K + Ge^{ika}\right)u_1 + \left(M\omega^2 - (K+G)\right)u_2 = 0$$

The homogenous linear equations have a solution only if the determinant of the coefficients is zero:

$$\begin{vmatrix} \left(M\omega^2 - (K+G)\right) & \left(K + Ge^{-ika}\right) \\ \left(K + Ge^{ika}\right) & \left(M\omega^2 - (K+G)\right) \end{vmatrix} = 0$$

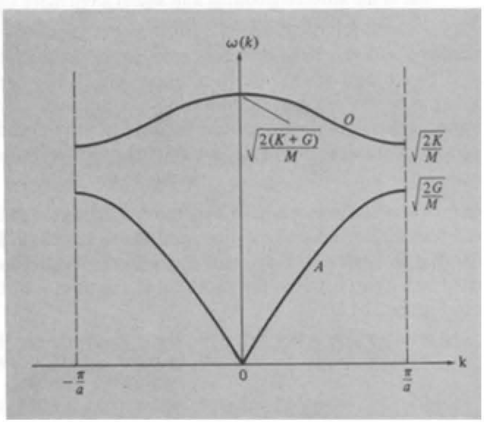
with solutions:

$$\omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\sqrt{K^2 + G^2 + 2KG\cos ka}$$

$$\frac{u_1}{u_2} = \mp \frac{K + Ge^{-ika}}{\left|K + Ge^{ika}\right|}$$

for each k there are two solutions which are called the two branches of the dispersion curves.

Figure 22.10
Dispersion relation for the diatomic linear chain. The lower branch is the acoustic branch and has the same structure as the single branch present in the monatomic case (Figure 22.8). In addition, there is now an optical branch (upper branch.)



The perfectly harmonic crystal

Phonon: lattice vibration of wave-vector $\mathbf{q}$ and frequency $\omega_j(\mathbf{q})$ (j: band index). Frequencies are calculated from the second derivatives of the energy (**interatomic force constants**) versus atomic displacements:

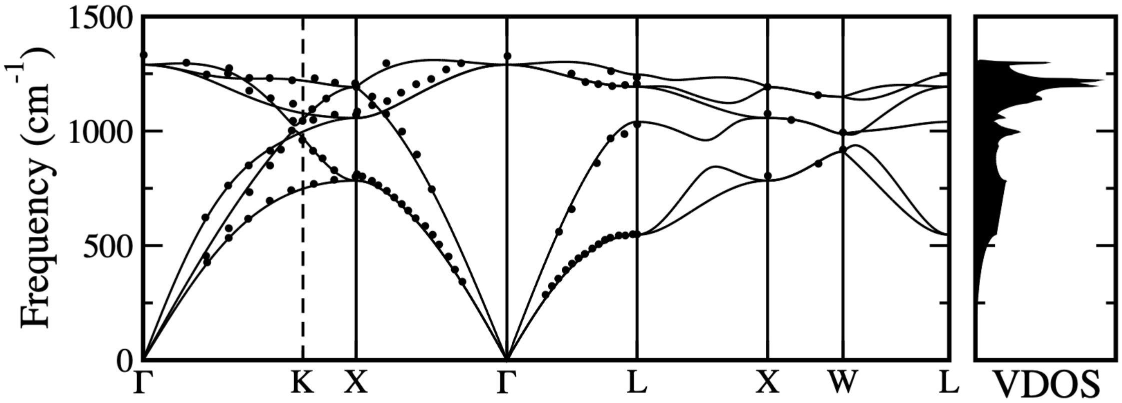
$$C_{\alpha i,\,\beta j}(\mathbf{R}_L, \mathbf{R}_{L'}) = \left.\frac{\partial^2 E}{\partial u_{\alpha i,\,L}\partial u_{\beta j,\,L'}}\right|_{equilibrium} = C_{\alpha i,\,\beta j}(\mathbf{R}_L - \mathbf{R}_{L'})$$

Precisely, phonon frequencies are the eigenvalues of the **dynamical matrix** $\tilde{D}_{\alpha i,\,\beta j}(\mathbf{q})$, Fourier transform of $C_{\alpha i,\,\beta j}(\mathbf{R}_L)$:

$$\tilde{D}_{\alpha i,\,\beta j}(\mathbf{q}) = \sum_L C_{\alpha i,\,\beta j}(\mathbf{R}_L)\, e^{-i\mathbf{q}\cdot\mathbf{R}_L}$$

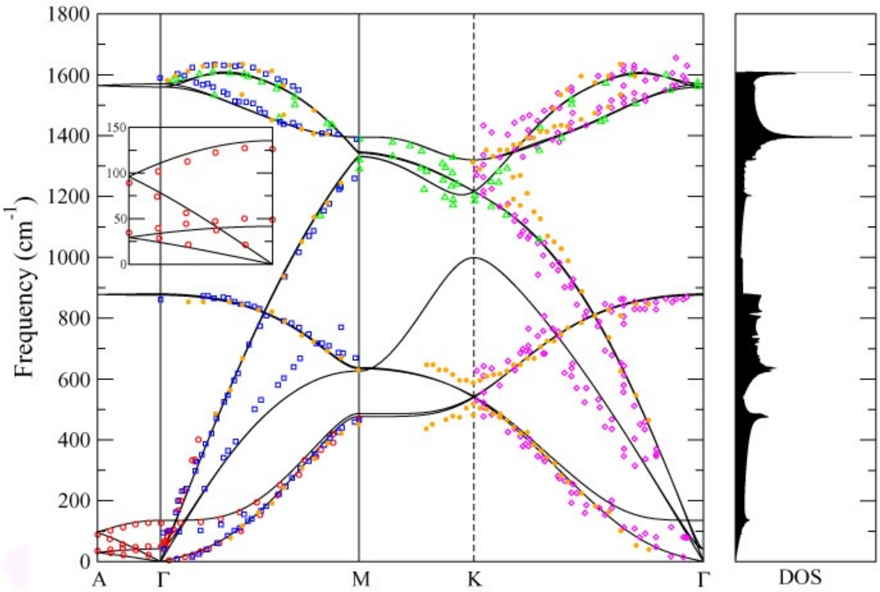
$$\omega^2 u_{\alpha i} = \sum_{\beta j} u_{\beta j} \tilde{D}_{\alpha i,\,\beta j}(\mathbf{q})$$

Phonon dispersions in diamond



Mounet PRB 2005

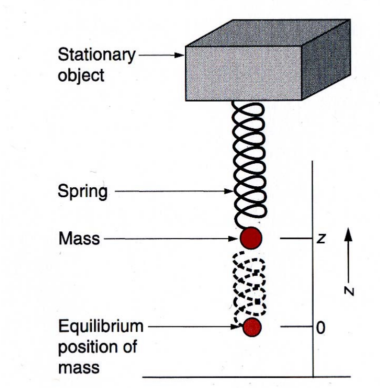
Phonon dispersions in graphite

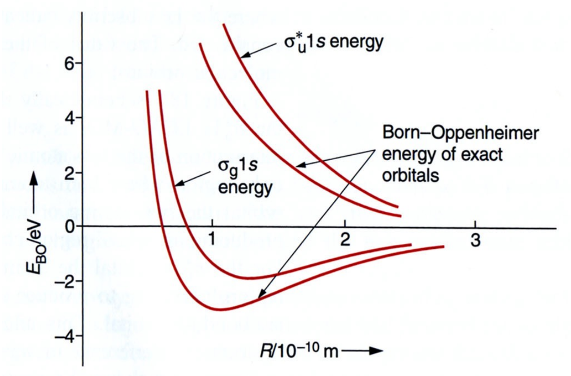


The quantization of vibrations

- Electrons are much lighter than nuclei ($m_{proton}/m_{electron}$~1800)
- Electronic wave-functions always rearrange themselves to be in the ground state (lowest energy possible for the electrons), even if the ions are moving around
- Born-Oppenheimer approximation: electrons in the instantaneous potential of the ions (so, electrons can not be excited – FALSE in general)

Nuclei have some quantum action…

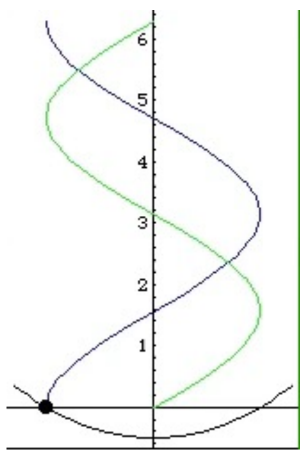




The quantum harmonic oscillator (I)

$$\left(-\frac{\hbar^2}{2M}\frac{d^2}{dz^2}+\frac{1}{2}kz^2\right)\varphi(z)=E\varphi(z)$$

$$\omega=\sqrt{\frac{k}{m}} \qquad a=\frac{\sqrt{km}}{\hbar}$$

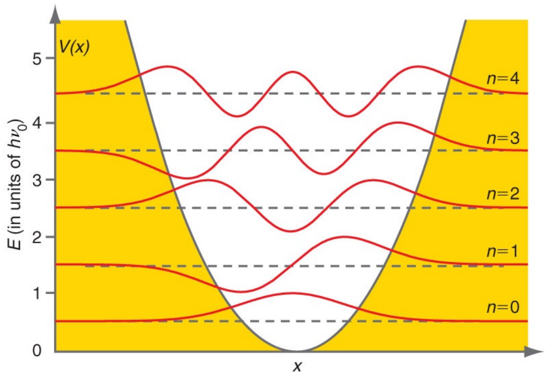


The quantum harmonic oscillator (II)

$$\psi_0 = \left(\frac{a}{\pi}\right)^{1/4} e^{-az^2/2}$$

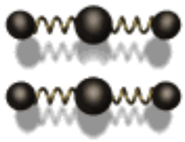
$$\psi_1 = \left(\frac{4a^3}{\pi}\right)^{1/4} z e^{-az^2/2}$$

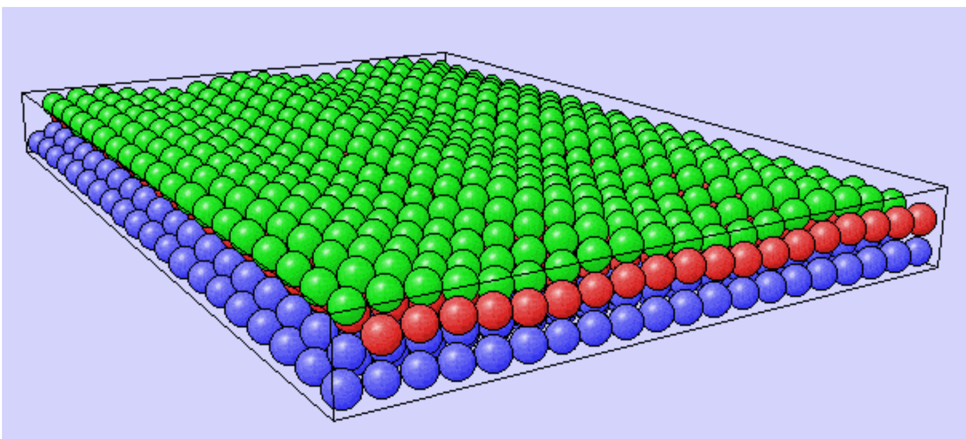
$$\psi_2 = \left(\frac{a}{4\pi}\right)^{1/4} (2az^2 - 1) e^{-az^2/2}$$



$$E = \hbar\omega\left(n + \frac{1}{2}\right)$$

Quantized atomic vibrations





Harmonic crystal's free energy

Quantization of phonons' energy:

$$E_j(\mathbf{q}) = \hbar\omega_j(\mathbf{q})(n + \frac{1}{2})$$

Partition function of one phonon (microcanonical ensemble - T & V constant):

$$Z_{\mathbf{q},j} = \sum_n \exp(-\frac{\hbar\omega_j(\mathbf{q})}{k_B T}(n + \frac{1}{2})) = \frac{1}{2\sinh\frac{\hbar\omega_j(\mathbf{q})}{k_B T}}$$

Total partition function:

$$Z_{total} = \prod_{\mathbf{q},j} Z_{\mathbf{q},j} = \frac{1}{\prod_{\mathbf{q},j} 2\sinh\frac{\hbar\omega_j(\mathbf{q})}{k_B T}}$$

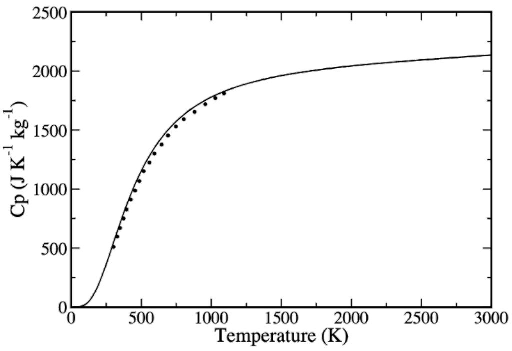
Free energy: ($\{a_i\}$ = lattice parameters)

$$\begin{aligned} F(\{a_i\},T) &= E(\{a_i\}) + F_{vib} \\ &= E(\{a_i\}) - k_B T \ln Z_{total} \\ &= E(\{a_i\}) + \sum_{\mathbf{q},j} \frac{\hbar\omega_{\mathbf{q},j}}{2} + k_B T \sum_{\mathbf{q},j} \ln(1 - \exp(-\frac{\hbar\omega_{\mathbf{q},j}}{k_B T})) \end{aligned}$$

Heat capacity

Constant volume heat capacity given by:

$$\begin{aligned} C_v &= -T\frac{\partial^2 F}{\partial T^2} \\ &= \sum_{\mathbf{q},j} c_v(\mathbf{q},j) = k_B \sum_{\mathbf{q},j} \left(\frac{\hbar\omega_{\mathbf{q},j}}{2k_B T}\right) \frac{1}{\sinh^2\left(\frac{\hbar\omega_{\mathbf{q},j}}{2k_B T}\right)} \end{aligned}$$



$$C_p - C_v = TV_0 B_0 \alpha_V^2$$

The quasi-harmonic approximation: principle

$$F(\{a_i\},T) = E(\{a_i\}) + \sum_{\mathbf{q},j} \frac{\hbar\omega_{\mathbf{q},j}}{2} + k_B T \sum_{\mathbf{q},j} \ln(1 - \exp(-\frac{\hbar\omega_{\mathbf{q},j}}{k_B T}))$$

If phonon frequencies assumed constant (harmonic crystal), no dependence of the vibrational free energy on structure

$\rightarrow$ no thermal expansion, no temperature dependence of elastic constants, heat capacity reaching a limit a high temperature, ie. **no anharmonic effects**.

Quasi-harmonic approximation: use harmonic expression of the free energy but add additional dependence of the phonon frequencies on the **lattice parameters** $\{a_i\}$.

Thermal expansion

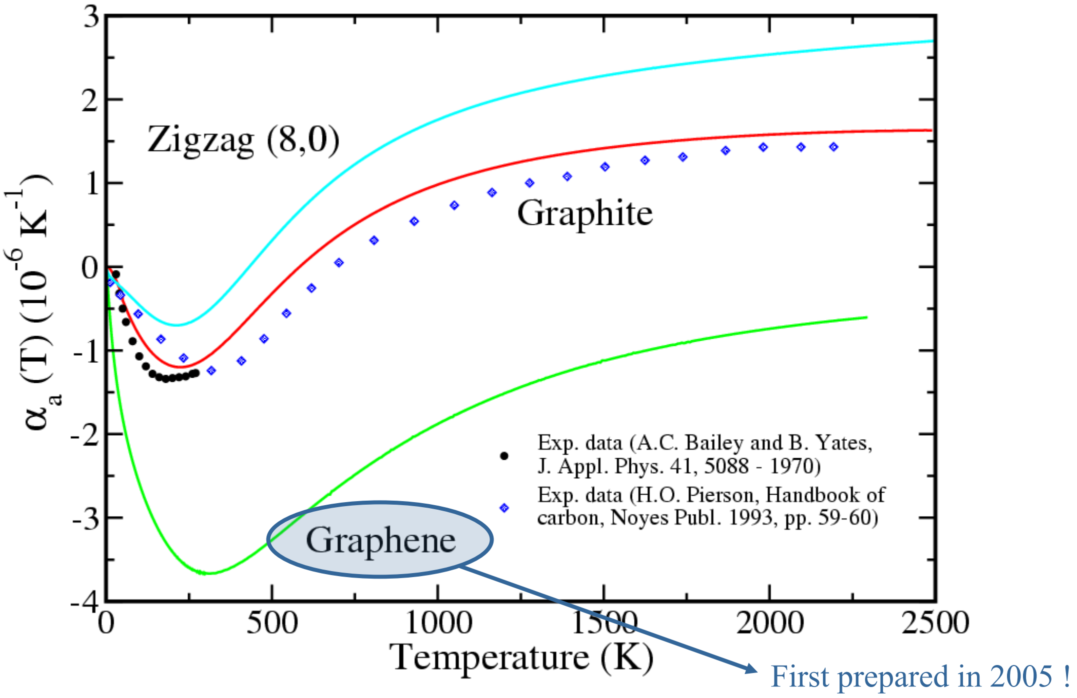
Minimization of quasi-harmonic free energy vs. lattice parameters $\{a_i\}$:

$$F(\{a_i\},T) = E(\{a_i\}) + \sum_{\mathbf{q},j} \frac{\hbar\omega_{\mathbf{q},j}(\{a_i\})}{2} + k_B T \sum_{\mathbf{q},j} \ln(1 - \exp(-\frac{\hbar\omega_{\mathbf{q},j}(\{a_i\})}{k_B T}))$$

Equilibrium lattice parameters given by that minimization change with temperature $\rightarrow$ **Thermal expansion** (or contraction):

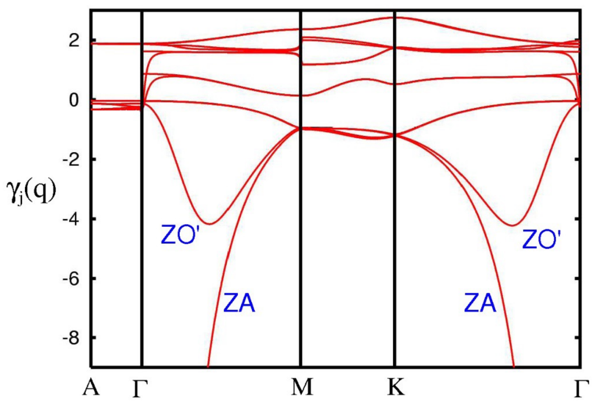
$$\alpha_i = \frac{1}{a_i}\frac{\partial a_i}{\partial T}$$

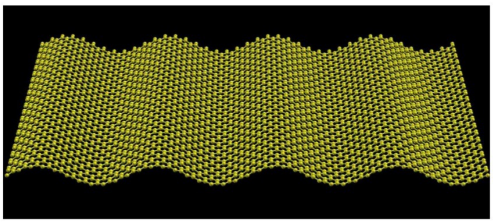
Thermal Contraction in 2-d and 1-d Carbon



Grüneisen parameters for graphene

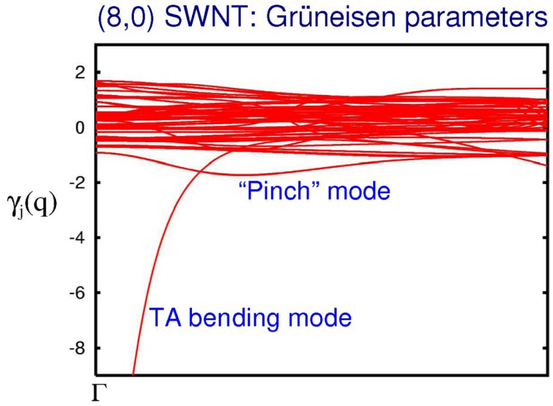
Grüneisen parameters $$\gamma_k(\mathbf{q},j) = \frac{-a_{0,k}}{\omega_{0,\mathbf{q},j}} \frac{\partial \omega_{\mathbf{q},j}}{\partial a_k}\bigg|_0$$

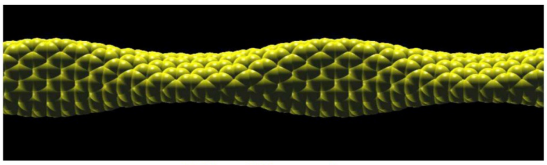




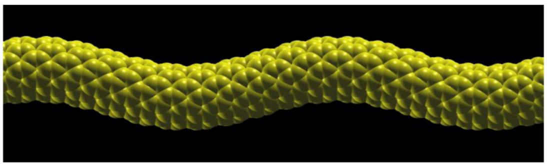
ZA bending mode

Grüneisen parameters for SWNT



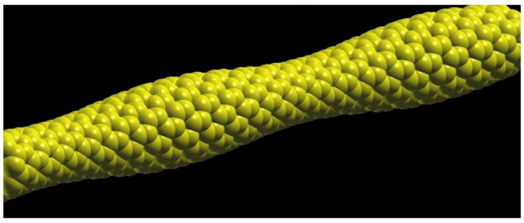


"Pinch" mode

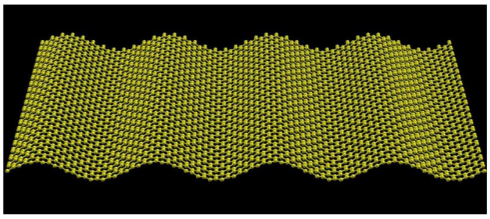


TA bending mode

Radial breathing mode



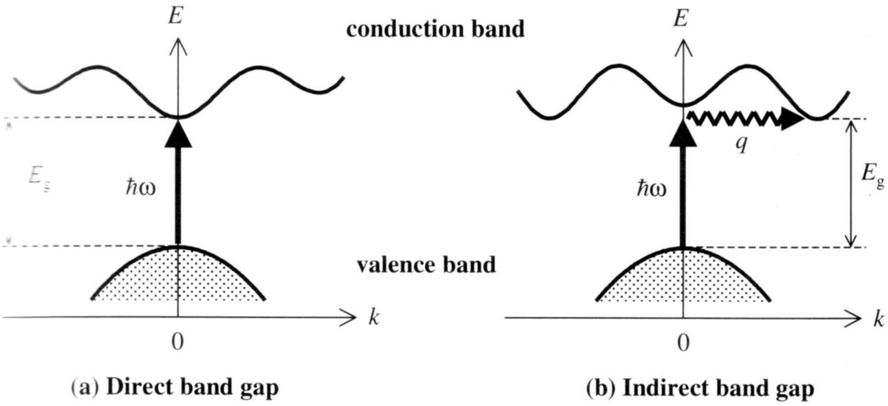
ZA bending mode of graphite



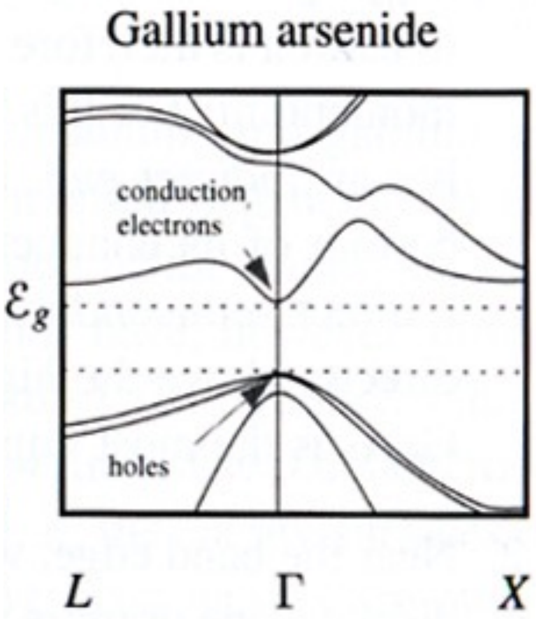
Optical processes

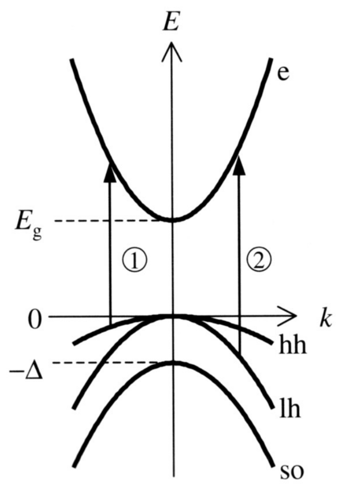
- Reflection and refraction
- Absorption
- Luminescence
- Scattering

Direct and indirect transitions



Transition rate for direct absorption





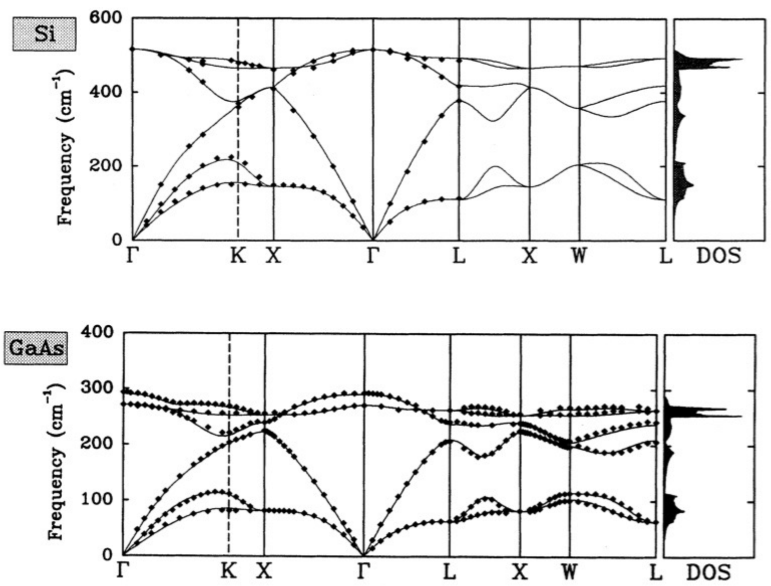
Dipole-allowed selection rules

These are for atoms…

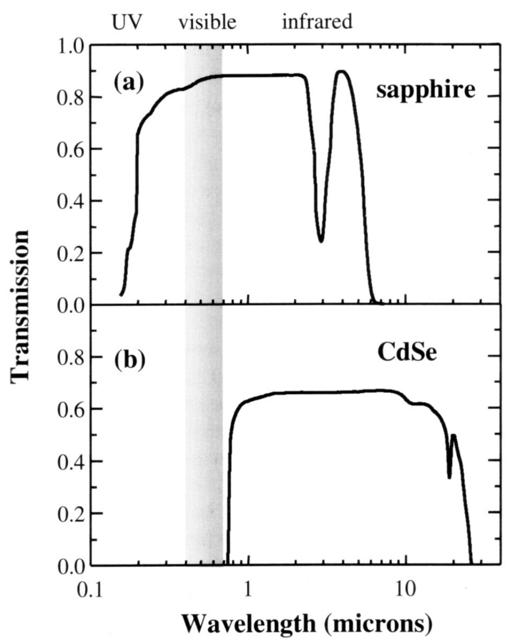
- Parity of initial and final state are opposite
- Δm=-1, 0 or 1
- Δl=-1 or 1

E.g. phosphorence involves dipole-forbidden transitions that are mediated by higher order terms (magnetic dipole, electronic quadrupole)

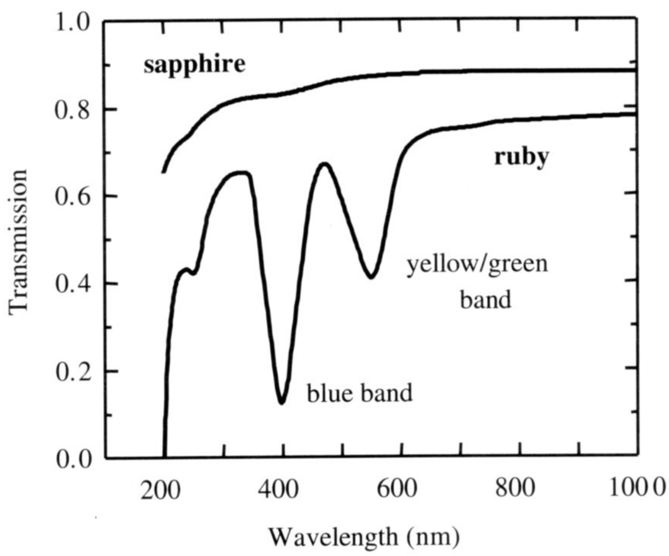
Infrared active modes



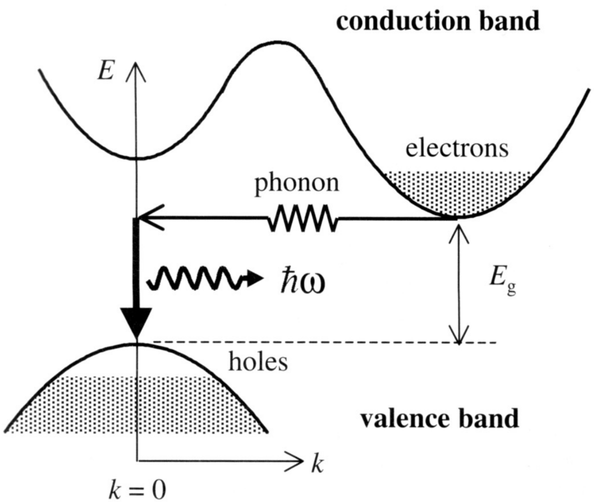
Transmission coefficient



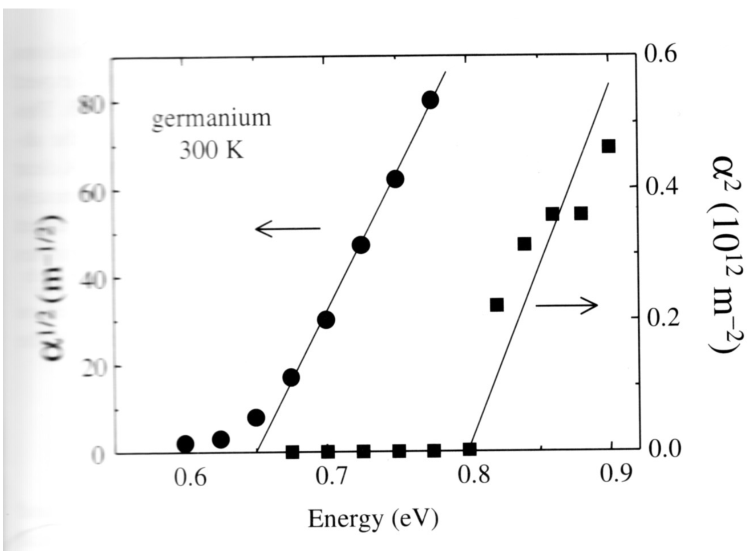
Transmission: amorphous vs optical



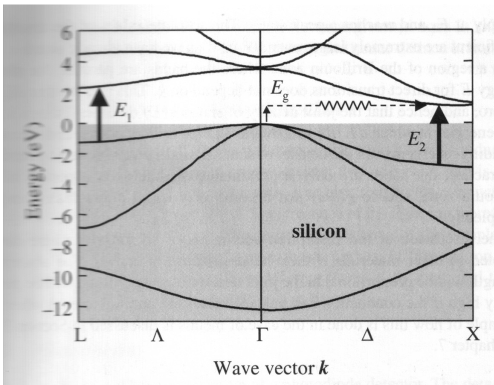
Indirect band gap materials

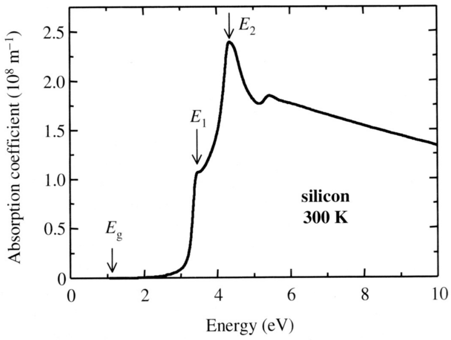


Indirect gap semiconductors

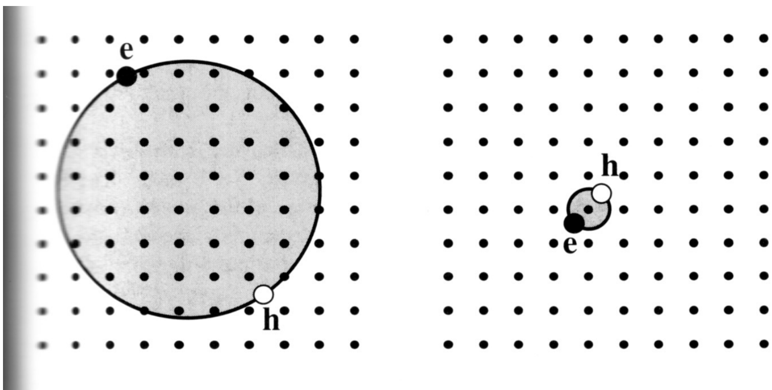


Absorption above the band edge



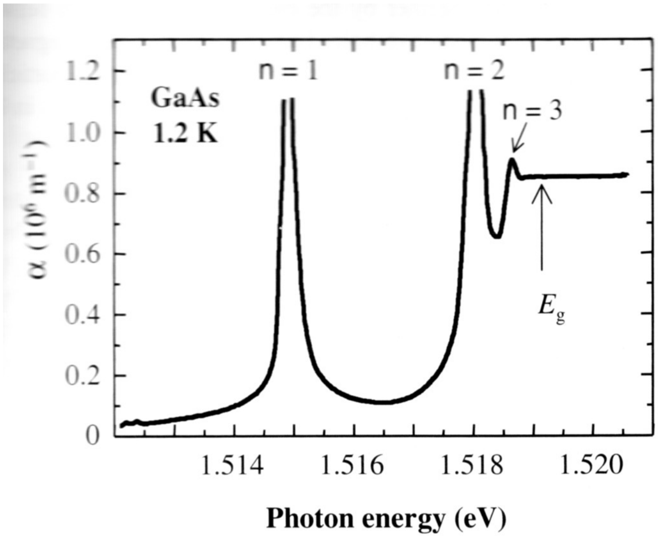


Excitons

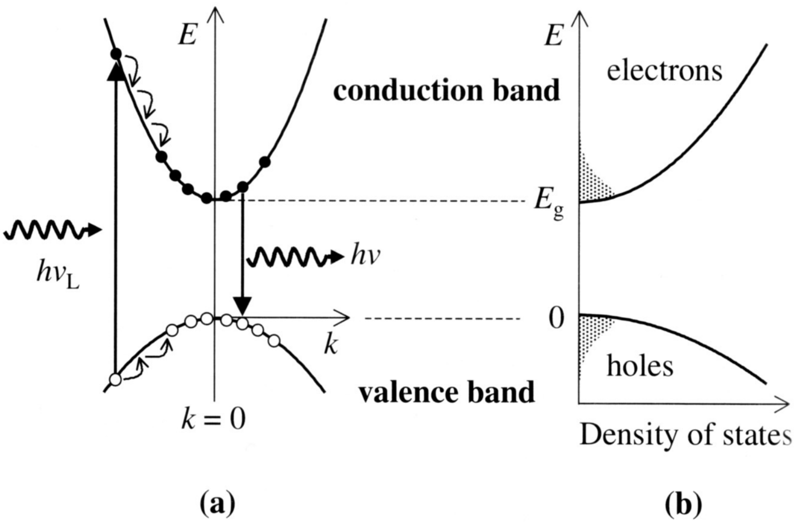


(a) Free exciton (b) Tightly bound exciton

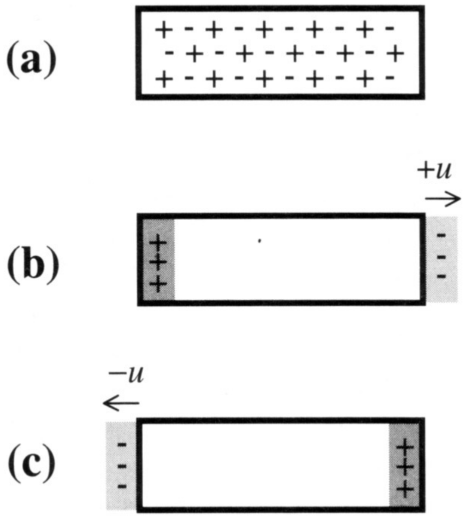
Excitons absorption



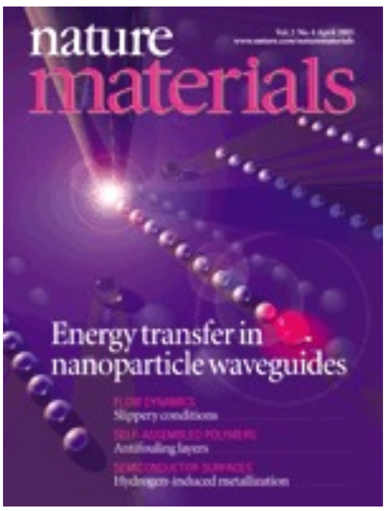
Photoluminescence: excitation, relaxation



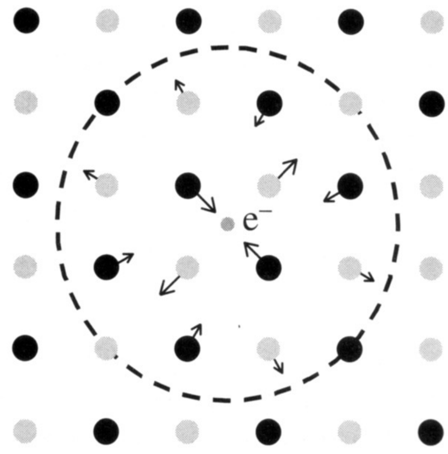
Plasmons



Plasmonics



Polarons



Exam: Tuesday 20 Jan 2025
15h15 to 18h15 (in room AAC 2 31)

We will have a written exam: 3 hours, 4 questions. Two theory questions, and two exercises. **Closed book, you cannot have any material with you – at most a basic calculator. Bring pen/pencil, we'll bring paper. No cell phones, not even as a watch (we'll announce time every 1h).** In the next slide you find a list of the theory questions that could be asked (in part or in full). The exercises will closely follow the ones you did during the semester.

MSE 423 F25: Questions for the oral exam

- **Schroedinger equation (time dependent, stationary); solutions for a free particle, for square wells in 1, 2 and 3 dimensions, for a potential barrier (graphical)**
- **Dirac notation, operators (Hermiticity, commutators), proof of the variational principle**
- **Five postulates of quantum mechanics**
- **Solving a differential equation as a diagonalization in a basis**
- **Angular momentum, spherical coordinates and Laplacian, spherical harmonics, Hamiltonian in a central potential**
- **Radial wavefunctions and nodal surfaces for the hydrogen atom, and the 3 quantum numbers n, l, m; spin; emission and absorption lines**
- **2- and many-electron wavefunctions; Hartree equations, connection to spin-statistics, Hartree-Fock concepts; atomic energy levels and the periodic table**
- **Schroedinger equation for molecules; molecular states and energy levels (diatomic homonuclear molecules); potential energy surfaces (energy vs distance).**
- **The method of Linear Combination of Atomic Orbitals (LCAO), sp^n hybridization, Huckel approach (by diagonalization)**
- **Symmetry operations – point group symmetries, and translational symmetries; Bravais lattices and reciprocal lattices; Wigner-Seitz cells and Brillouin zones**
- **Hamiltonian in a periodic potential; Bloch theorem and Bloch wavefunctions**
- **Band structure of the free electron gas, relation with the empirical pseudopotential method; band structures of semiconductors (Si, Ge, GaAs, and their conduction band pockets), of metals, of perovskites**
- **Bloch eigenstates of an atomic (exploded) crystal as Bloch sums of atomic orbitals; Bloch eigenstates of a real crystal as Bloch sums of linear-combinations of atomic orbitals; tight binding method – from levels to bands.**
- **Filling the bands: Fermi energy and Fermi surfaces; Fermi-Dirac statistics and Fermi-Dirac distribution; group velocity, effective mass; density of states in different cases.**
- **Homogeneous semiconductors: number of carriers at thermal equilibrium; density of available states; law of mass action; temp. dependence of the chemical potential on temperature.**
- **Impurity levels, temperature dependence of majority carriers; p-n junction; charge/field/voltage; built-in voltage**
- **1-dimensional monoatomic and diatomic chain; dispersion relations for monoatomic/diatomic chain; phonons; vibration free energy and thermomechanical properties.**
- **Optical properties; direct and indirect transitions, absorption; excitons, plasmons, polarons.**