Exercise-sheet 2 (October 27, 2017)

1 In-class exercises

1.1 Mathieu's equation

Consider Schrödinger's equation for an electron in a chain of atoms with lattice spacing a, where the potential felt by the electron and due to the atoms is modelled by the function $V(x) = V_0 \cos\left(\frac{2\pi}{a}x\right)$.

(a) Use Floquet's theorem to write the electronic wavefunction as $\psi(x) = e^{ikx}u_k(x)$ and substitute a Fourier series for the periodic function $u_k(x)$. Show that the coefficients of the series satisfy a three-term recurrence relation.

(b) Assuming that $V_0 << 1$, find an approximate expression for the electronic wavefunction and its energy.

1.2 Tight-binding approximation

Consider a linear lattice of atoms which are well separated such that their atomic orbitals have only small overlaps. In such a situation, the electronic states are fairly well represented by localized atomic orbitals ψ_n, for which

$$H_{\text{at}}(R)\psi_n(r-R) = \epsilon_n\psi_n(r-R), \tag{1}$$

where the atomic Hamiltonian (H_{at}) is given by

$$H_{\text{at}}(R) = \frac{p^2}{2m} + V_{\text{at}}(r-R), \tag{2}$$

with V_{at} the atomic potential.

Let us consider a single-particle Hamiltonian for an electron in the lattice which combines all the potential of the atoms as follows

$$H = \frac{p^2}{2m} + \sum_R V_{\text{at}}(r-R) = H_{\text{at}}(R) + \Delta V(r-R) \tag{3}$$

(a) Approximate the extended Bloch function with the function

$$\psi_k(r) = \sum_R e^{ikR}\phi(r-R), \tag{4}$$

with $\phi(r) = \sum_n b_n\psi_n(r)$, where the $\psi_n(r)$ are a set of localized atomic wave functions. Find an expression for determining the b_n constants.

(b) Find the dispersion relation for an s-band arising from a single atomic s-level.

2 Homework - due date: November 3, 2017 (30 points).

2.1 Atoms as Dirac delta potentials (25 points)

Consider a one-dimensional lattice of atoms with lattice spacing a, where each atom is represented by the potential $V(x) = V_0\delta(x)$.

(a) Assuming that between the atoms the electronic wavefunction is given by

$$\psi(x) = A\, e^{iKx} + Be^{-iKx}, \tag{5}$$

where A and B are two constants and $K = \sqrt{\frac{2mE}{\hbar^2}}$, with m the electron mass and E its energy, show that the derivative of $\psi(x)$ is discontinuous at the location of the atoms.

(b) One can extend the solution (5) to the full lattice by using Floquet's theorem, i.e. by writing $\psi(x) = e^{ikx}u_k(x)$ which implies

$$u_k(x) = Ae^{i(K-k)x} + Be^{-i(K+k)x}. \tag{6}$$

Use the fact that at the location of the atoms $\psi(x)$ is continuous and $\frac{d\psi}{dx}(x)$ is discontinuous to show that the electron energy E and the wavenumber k satisfy the relation

$$\cos ka = \frac{\alpha}{K}\sin Ka + \cos Ka, \tag{7}$$

where $K = \sqrt{\frac{2mE}{\hbar^2}}$ and α is to be determined.

(c) Plot the function $f(E) = \frac{\alpha}{K(E)}\sin K(E)a + \cos K(E)a$.

Given that $|f(E)| \leq 1$, do all values of E satisfy this condition?

(d) Consider the nearly free electron limit at $k = \frac{\pi}{a}$, i.e. assume $K = \frac{\pi}{a} + \nu$ with $\nu << 1$. Use the relation (7) to find some approximate value for ν. What is the electron energy to first order in ν?

2.2 Sodium in hcp and bcc (5 points)

Sodium transforms from body-centered cubic to hexagonal close-packed (hcp) at about $23K$. Assuming that the density remains fixed through this transition and that the $\frac{c}{a}$ ratio has the ideal value of $\sqrt{8/3}$, calculate the lattice constant a of the hcp phase, given that the cubic lattice spacing is $a = 4.23\mathring{A}$.