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# Solid State Theory

## Problem set 1

*Winter Term 2016*

**Website**: `http://www.thp.uni-koeln.de/trebst/Lectures/2016-SolidState.shtml`
**Due date:** Discussed in class on **Thursday, November 10th**.

If you turn in your solutions by Wednesday noon (November 9th), they will be graded.
Please submit your solutions to Henry Legg at hlegg@uni-koeln.de.

# 1. Fourier transformation

Consider a periodic function $f$ with period $L$, i. e. a function that satisfies the condition $f(x) = f(x+L)$. The Fourier transform $\tilde{f}(q)$ of $f(x)$ is defined via

$$f(x) = \frac{1}{L}\sum_q \tilde{f}(q)e^{iqx}\,. \tag{1}$$

Show that the allowed values for $q$ are $q = 2\pi n/L$, with $n$ integer. The inverse transformation is

$$\tilde{f}(q) = \int_0^L dx\, f(x)e^{-iqx}\,. \tag{2}$$

(Note that definitions are not unique, but there is a freedom to choose the prefactors.)

**a)** Calculate the Fourier transform of $f_1(x) = \cos(2\pi x/L)$ according to Eq. (2).
(Only 2 of the $\tilde{f}(q)$ are non-zero.) Check your result using Eq. (1).

**b)** Consider a function $g$, which is defined only at discrete points $x_n = na$ ($n = 0, \ldots, N$), and which is periodic: $g(x_0) = g(x_N)$. We define its Fourier transform via

$$g(x_n) = \frac{1}{Na}\sum_q \tilde{g}(q)e^{iqx_n}\,. \tag{3}$$

Then, the inverse transformation reads

$$\tilde{g}(q) = a\sum_{n=1}^{N} g(x_n)e^{-iqx_n}\,. \tag{4}$$

Show that $\tilde{g}(q) = \tilde{g}(q + 2\pi m/a)$ ($m$ integer). Therefore it is sufficient to restrict the $q$ values to the interval $-\pi/a < q \leq \pi/a$. What are the allowed values of $q$ in this interval? How many different $q$-values do we need?
Show that (**Hint:** Geometric series)

$$\sum_{n=1}^{N} e^{-i(q-q')x_n} = \begin{Bmatrix} N, & q = q' \\ 0, & q \neq q' \end{Bmatrix} = N\delta_{q,q'}\,, \tag{5}$$

and that

$$\sum_{q \in 1.BZ} e^{iq(x_n - x_m)} = \begin{Bmatrix} N, & n = m \\ 0, & n \neq m \end{Bmatrix} = N\delta_{n,m}\,, \tag{6}$$

where the *first Brillouin zone* (1. BZ) is the set of allowed $q$-values in the interval $(-\pi/a, \pi/a]$: $1.\text{BZ} = \{q| - \pi/a < q \leq \pi/a \text{ and } e^{iqN} = 1\}$.

**c)** Show that we recover Eqs. (1) and (2) from Eqs. (3) and (4) in the limit $N \to \infty, a \to 0$, with $Na = L = \text{const.}$

**d)** Now consider the limit $L \to \infty$ (*thermodynamic limit*).
Show that Eq. (1) becomes

$$f(x) = \int_{-\infty}^{\infty} \frac{dq}{2\pi}\, \tilde{f}(q)\, e^{iqx}\,, \tag{7}$$

and that Eq. (3) becomes ($L = Na, a = $const.)

$$g(x_n) = \int_{-\pi/a}^{\pi/a} \frac{dq}{2\pi}\, \tilde{g}(q)\, e^{iqx_n}\,. \tag{8}$$

# 2. Fourier representation of the $\delta$-function

Show that

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} = \delta(t). \tag{9}$$

Remember that *"the Fourier transform of a constant is a delta function (and vice versa)"*. What is $\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t_0)}$?
Check your result by calculating the inverse transformation $\int_{-\infty}^{\infty} dt\, e^{i\omega t}\, \delta(t - t_0)$.

**Hints:**
Calculate $\int_0^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t - \varepsilon\omega}$ and $\int_{-\infty}^{0} \frac{d\omega}{2\pi} e^{-i\omega t + \varepsilon\omega}$ for $\varepsilon > 0$.
Then, use that $\lim\limits_{\varepsilon \to 0+} \frac{\varepsilon}{\varepsilon^2 + (x - x_0)^2} = \pi\delta(x - x_0)$.

# 3. Covalent bonds

In the context of atomic physics, the wave function is referred to as an atomic orbital. When two atoms are brought together, their orbitals begin to overlap which may lead to the formation of a chemical bond. Let us consider the situation where each atom has an orbital that is occupied by a single electron and these orbitals are brought in contact such that they overlap. The picture of orbitals belonging separately to their respective atoms is now no longer valid. Instead, new orbitals are formed that can come in a variety of forms: If the orbital is concentrated around one of the atoms, then the bond it forms is referred to as an **ionic bond**. In the case when the electron pair is shared between the two atoms, the bond is said to form a **covalent bond**. A special case of this bond is the **metallic bond**, where many atoms are brought into contact and the orbitals themselves span and interact over multiple atoms. In this exercise, we will explore why the scenario of sharing electrons between atoms is energetically favorable.

Let us consider the simplified scenario of two nuclei separated by a distance $R$ and one electron, see Fig. 1. Applying the Born-Oppenheimer approximation, we will treat the nuclei as resting.

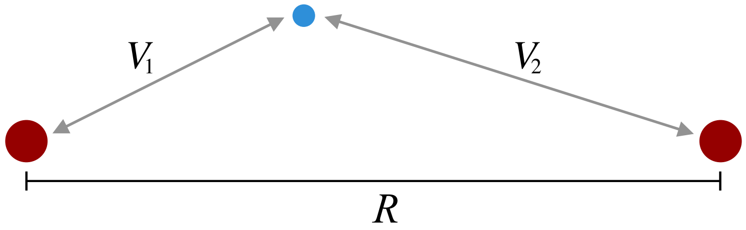

Figure 1: The setup considered in this exercise: Two nuclei depicted in red are separated by a distance $R$. They interact with a freely moving electron (blue) via an interaction $V_i$, indicated by the grey lines.

The Hamiltonian of the system is given by

$$H = P + V_1 + V_2, \tag{10}$$

where $P$ is the kinetic term of the electron and the $V_i$s represent the Coulomb interaction of the electron with the nucleus. The problem of the electron traveling around each of the nuclei without the presence of the other is easily solved. In fact, even the problem of the electron moving the presence of the two nuclei is possible to solve exactly, although more tedious. For a more general solution, we will use a **variational approach**.

In this approach, we construct a variational wave function $|\psi\rangle = \phi_1 |1\rangle + \phi_2 |2\rangle$ where the $\phi_i$ are complex coefficients, and the wavefunctions $|1\rangle$ and $|2\rangle$ are chosen to be the lowest energy solutions to the one electron, one nucleus problem described above, i.e.

$$(P + V_i) |i\rangle = \varepsilon_i |i\rangle . \tag{11}$$

This *ansatz* is also called the **Linear Combination of Atomic Orbitals** (LCAO), and in general, more than one orbital from each atom is chosen.

Our goal is to minimize the energy $E$, given as

$$E = \frac{\langle\psi| H |\psi\rangle}{\langle\psi|\,\psi\rangle} . \tag{12}$$

1. Evaluate the inner products $\langle\psi|H|\psi\rangle$ and $\langle\psi|\,\psi\rangle$. In doing so, you will come across the following terms:
   - $\langle i|\,(P+V_i)\,|i\rangle = \varepsilon_i$ is simply the eigenvalue problem of the simpler system with only nucleus $i$ present.
   - $\langle 1|\,V_2\,|1\rangle = V$ is the potential energy the electron in orbital 1 feels from the nucleus 2.
   - $\langle 1|\,V_2\,|2\rangle = -t$ is called the hopping amplitude that lets the electron move between the nuclei, mediated by their mutual interaction.
   - $\langle 1|\,2\rangle = S$ is the overlap of the two orbitals.
2. Now calculate the partial derivatives of the energy $E$ with respect to $\phi_i^*$, $\partial_{\phi_i^*}E$. For the energy to be minimal, these derivatives have to be zero. Enforce this constraint and rewrite the result set of equations as a system of equations that has the form of a generalized eigenvalue problem
$$H\phi = E\mathcal{S}\phi\,, \tag{13}$$
where $\mathcal{S}$ is a matrix of the form
$$\mathcal{S} = \begin{pmatrix} 1 & S \\ S^* & 1 \end{pmatrix}. \tag{14}$$
3. Continue by solving for the eigenvalues and eigenvectors. In this case, the finite overlap $S$ can be neglected to simplify the calculation to a regular eigenvalue problem. You are of course welcome to keep the overlap and study the limit of $S \to 0$ after solving for the eigenvalues and eigenvectors, but you will find that it does not add anything fundamental to the qualitative features of the problem at hand.

   Remember that the eigenvalues of a $2\times 2$ matrix
$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} \tag{15}$$
are given by
$$v_{1,2} = \frac{1}{2}(a+d) \pm \sqrt{\frac{1}{4}(a+d)^2 - (ad-bc)}\,, \tag{16}$$
and the eigenvectors are
$$\begin{pmatrix} E_\pm - d \\ c \end{pmatrix}. \tag{17}$$
4. Now imagine filling the resulting energy levels with a spin up and spin down electron and compare the overall energy of the system with that of the individual systems where each nuclei is surrounded by one electron. How does the probability density depend on the difference of $\varepsilon_1$ and $\varepsilon_2$ in comparison to the hopping strength $t$?