

Quantum transport with Green's functions:

A brief hands-on tutorial

3-weeks course (33442), DTU-Nanotech, Dept. for Micro- and Nanotechnology

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Abstract

This note contains a hands-on introduction to quantum transport in nano-systems meant for the 3-weeks DTU course 33442 *Quantum mechanics modeling of nanoelectronics*. The main point is to enable the reader to make simple computer programs for calculating electronic (or heat) transport through nano-systems using tight-binding and Green's function methods. The requirements are an introductory course on quantum mechanics, and preferably also a beginners solid-state physics background. In the back is a list of recommended further reading. Sections 1-5 are core-material while section 6 contains different more specialized topics.

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1 Introduction

If you ever wonder or is asked when nanotechnology will ever appear for real and change peoples life the answer is that this has already happened! The computer or mobile telephone contains a lot of nanotechnology and is without doubt the biggest success of nanotechnology so far. The great computer power available even in the smallest devices is due to a huge number of transistors present in their chips. This is only possible due to down-scaling of the individual transistors. This has followed Moore's "law" with a doubling of transistors every two years. Today transistors are a few 10s of nm, and is expected to even reach below 10 nm corresponding to a few hundred atoms in length in near future, see Fig. 1(a,b) ².

The down-scaling has provoked many fundamental technological and scientific questions. For instance, how to describe the electrical current when electrons are squeezed through nanoscale structures down to a few atoms? The flow of electronic current is in the end controlled by the underlying atomic and electronic structure. In the end one have to employ quantum mechanics when trying to establish the link between underlying materials, structure, and functionality, and this to a much greater extend than before when going to the nanoscale. One interesting direction of research is the search for new principles for electronic signal processing based on the quantum nature of the electrons in nanoscale devices. With the down-scaling in electronics the paradigm of electronic transport is shifting away from the traditional drift-diffusion description, where the distance between scattering of electrons (mean-free path, ℓ) is much smaller than the conductor length, so many scattering events take place throughout the length of the conductor. At the nanoscale around or below ℓ this is replaced by the *ballistic, quantum-coherent regime*, where only a single or few scattering events takes place through the most important part of the device.

A few decades back the ballistic regime was restricted to low temperature. Today two trends make ballistic, quantum-coherent transport increasingly important. Firstly, the down-scaling of traditional "top-down" silicon transistors reach the ballistic nanometer length scale where "every atom matters". Secondly, novel 2D materials, such as graphene, show near ballistic behavior up to micrometers even at room temperature. Thus there is a great interest in understanding, modeling, and design of nano-electronics starting from the atoms. For instance a long term vision is to build functionality into single molecules, so-called molecular electronics, possibly in combination with new materials, as f.ex. shown in Figure 1(d). The number of possibilities explode when moving away for a single materials such as silicon, and a single device type, such as the transistor. Computer "experiments"/simulations based on

² See also f.ex. www-03.ibm.com/press/uk/en/pressrelease/44363.wss
and wccfttech.com/tsmc-promises-10nm-production-2016-7nm-2017

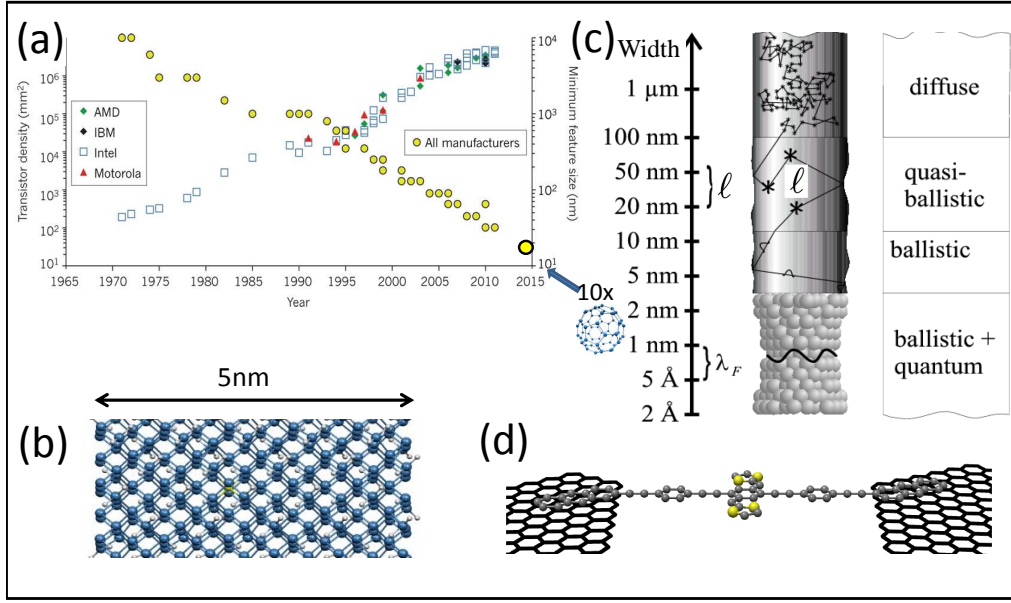


Figure 1: Moore's law. (a) The increase in transistor density and concomitant shrinking of transistor size to the 10nm range. The size of a C_{60} molecule (~ 1 nm) is shown for comparison. (b) 5nm long silicon nanowire. (c) The different transport regimes illustrated by a metallic nanowire shrinking its width. (d) Molecular junction device at 1nm length scale using graphene as electrodes.

atomistic calculations with predictive power play an important role in the investigations for this research. These are used to understand experiments providing a link between the atomic and electronic structure and measured transport properties, such as current as a function of voltage. But such calculations are also used to explore new directions and propose new experiments, which in the end may pave the way for technological breakthroughs.

The aim of this note is to provide the reader with basic theoretical tools, most notably the Green's function formalism, to treat quantum transport through nanoscale structures "starting from the atoms".

1.1 The Landauer Formula

For good metallic conductors, such as gold, the distance travelled by an electron before encountering a "scattering" event (mean-free path ℓ), is tenths of nanometers at room temperature. When electrons are accelerated and are considered on a length-scale smaller than ℓ they are said to be "ballistic" electrons. If the device we consider involve dimensions comparable to the relevant electronic wavelength, namely the Fermi wavelength, λ_F , the term quantum conduction is used. It is illustrated in Fig. 1(c) and is the regime we are interested in here. It was realized in the early 1990ies that this regime can be explored also in rather simple experiments: You break a contact between two gold wires like when you switch a contact and turn out the light and measure its resistance during break in the last few microseconds. The macroscopic contact surfaces are rough on the atomic scale, and the contact is made up of many contact points. In the end, just before the contact finally is broken, a single contact will remain, and since gold is rather soft it will elongate and typically end with a single-atom wide gold contact (like pulling the cheese on pizza). The contact often elongate atom-by-atom until it snaps at some length, see Fig. 2a. The conductance, G , of the atomic-scale junction connected to wide electrodes can be measured by a

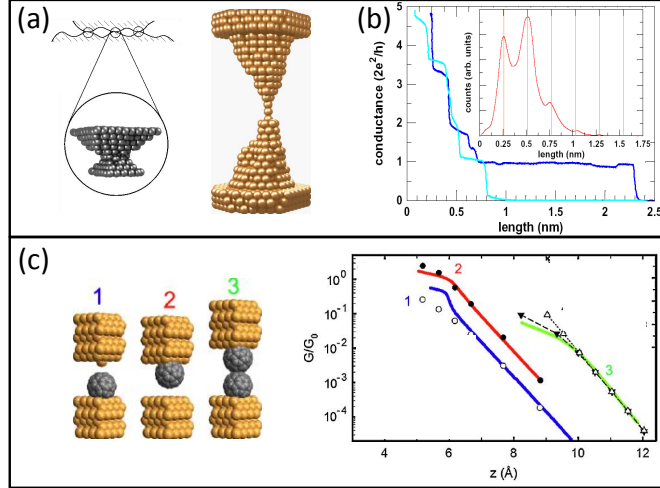


Figure 2: (a) A macroscopic contact between two metals is made up by many atomic scale contacts. When a gold contact is broken it will often contain just a single atom before breaking, or even a small one-atom wide chain. (b) Conductance when pulling a one-atom gold chain stays close to $G = 2e^2/h$, from [1]. (c) Single-molecule electrical contacts consisting of Cu electrodes connected by a single or two C_{60} molecules, from [2]. The conductance is in units of the *quantum unit of conductance*, $G_0 = 2e^2/h$, and is measured as a function of distance between electrodes in a Scanning Tunneling Microscope.

fast oscilloscope running a low voltage (millivolts) through the contact.

Interestingly, it turns out to be very close to a number given by natural constants $G = 2e^2/h$. This value is also denoted G_0 and called the *quantum of conductance*. In well controlled experiments at cryogenic temperatures the single atom gold contact can be pulled out to a chain more than 10 atoms long. Classically from Ohm's law one should expect the resistance to grow proportional to chain length, but it stays basically constant independent of number of atoms in the chain cf. Fig. 2b. The reason is that electrons move as ballistic waves with well defined phase ("quantum coherent") through the contact rather than by diffusion. Moreover, the value of $2e^2/h$ indicates that the atomic gold chain acts as a one-dimensional conductor. In this regime one should consider the wavefunction of the electrons spreading from electrode to electrode via the contact and, in particular, the transmission amplitudes for passing through the contact. Other experiments show that there is a small chance of inelastic scattering where the electrons loose energy to the atomic vibrations, but this only affects about 1% of the electrons and require a voltage above the energy above roughly 10meV in order to excite phonons in the chain.

Rolf Landauer (Fig. 3(a)) working for IBM introduced already in 1957(!) – way before nanotechnology – a theory for electrical resistance in the quantum coherent regime and for low-dimensional conductors. It took about 30 years before phase-coherent conductors were produced in experiments, and his ideas were brought to real tests. On the other hand a cornerstone of transport in nanoscale ballistic systems where charge carriers, the by now famous Landauer formula is getting increasingly more relevant as transistors are scaled to the quantum-coherent limit. The Landauer formula carriers move without experiencing inelastic scattering. In its simplest form the Landauer formula simply states that *conductance is transmission*. The electrical conduction at low voltage always takes place at the Fermi energy (E_F , highest occupied electron level).³ The formula for conductance, G , of a one-dimensional metallic conductor with a single "obstacle" or "defect" which allows electrons to pass with transmission probability, $T(E_F)$, is given by,

$$G = \frac{2e^2}{h} T(E_F) = G_0 T(E_F) . \quad (1)$$

³This is like water flow between reservoirs with a slight difference in water level takes place at the water surface.

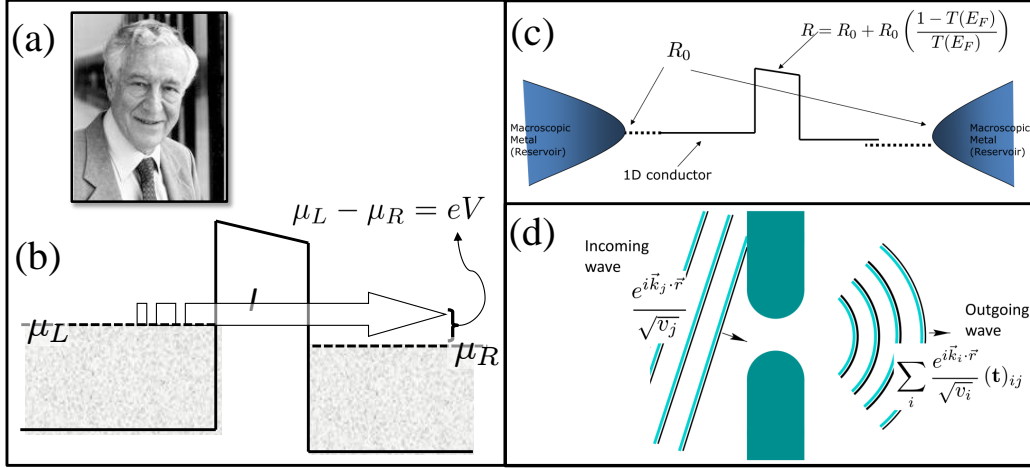


Figure 3: (a) Rolf W. Landauer (1927-1999) worked for IBM. (b) Landauer transport for a 1D system: A barrier between two 1D electrodes ("electron reservoirs"). (c) The total resistance given by the barrier resistance plus a "non-local" resistance due to the coupling to non-1D, wide reservoirs. (d) Multi-dimensional case: Transmission of a flux-normalized planewave with wavevector \vec{k}_j incoming from left and ending up as a superposition of planewaves to the right determined by a transmission amplitude matrix, \mathbf{t}_{ij} .

The "Landauer setup" is depicted in Figure 3(b): Two semi-infinite electrodes or electron reservoirs are coupled via a "defect" depicted as a simple square barrier. We need two ingredients to prove it in its most basic form. (i) Firstly, we need to remember (or learn) that for a one-dimensional infinite system with constant (or periodic) potential the quantum states make up a continuum, and we can count states per length in intervals of energy using that the number of states are proportional to the wavevector $dk/2\pi$ (the number of states within a range dk) or the density-of-states function (number of states per energy interval),⁴

$$g(E) = \frac{2}{2\pi} \frac{dk}{dE} = \frac{1}{\pi} \frac{1}{\hbar v_k}. \quad (2)$$

Here we have used the definition of group velocity of wavepackets with energy (or frequency ω), $v_k = d\omega/dk = (1/\hbar)dE/dk$. This can be computed from the bandstructure of the electrode, as we will see later. (ii) Secondly (and approximate), we assume that the electronic states to the left and right of the barrier are in thermodynamic equilibrium given each by the Fermi function, f_L and f_R ,⁵ The left and right Fermi energies are different due to the attachment of an external voltage source (f.ex. a battery), $\mu_L - \mu_R = eV$, with voltage V .

The electronic current from left to right electrode is then found by summing(integrating) all occupied electron states (per length) times their velocity, times the probability that they are transmitted to the right through the barrier, and finally times charge and spin-degeneracy (for non-magnetic systems),

$$I_{L \rightarrow R} = 2e \int_0^\infty \frac{dk}{2\pi} v_k T(E_k) f_L(E_k). \quad (3)$$

We only integrate over positive k since only half of the electronic states travel towards the right while

⁴Note also a factor of two since we have both positive and negative k corresponding to left and right-travelling waves. We did not include a factor of two for spin here yet.

⁵The Fermi function is here defined as $f(E) = (1 + e^{E/k_B T})^{-1}$ where e.g. $f_L(E) = f(E - \mu_L)$, μ_L being the left Fermi energy.

the other half goes the other way. The total left-to-right current is,

$$I = I_{L \rightarrow R} - I_{R \rightarrow L} = 2e \int_0^\infty \frac{dk}{2\pi} v_k T(E_k) [f_L(E_k) - f_R(E_k)] . \quad (4)$$

The important point realized by Landauer is that we can transform this integral over wavevector to an integral over energy using $dk = dE/(\hbar v_k)$ from Eq. 2,

$$I = \frac{2e}{h} \int dE T(E) [f_L(E) - f_R(E)] \approx \frac{2e}{h} T(E_F) (\mu_L - \mu_R) \approx G_0 T(E_F) V . \quad (5)$$

Here we have assumed small voltage, $eV = \mu_L - \mu_R$, in the last approximation. The conductance for a transparent barrier at the Fermi energy ($T(E_F) = 1$) then results in a conductance of $G = I/V = G_0$. This is close to the situation for the atomic gold chain above.

Exercise 1 (a) Go through the step from Eq. 4 to 5 (b) Convince yourself that the approximation is exact when the transmission, T , varies slowly on the energy scale corresponding to the applied voltage, eV . (c) Suppose we have zero voltage, i.e. $\mu_L = \mu_R = E_F$. Would it be possible to drive a current anyhow?

1.1.1 Relevant numbers and scales

The natural energy scale for electron transport and often nano-systems in general is electron-Volts (eV), that is, the kinetic energy of an electron (charge $e = -1.6 \cdot 10^{-19} \text{C}$) accelerated over a potential drop of 1V. This gives a nice link between a SI unit (namely Volts) and the microscopic energy scale of electrons in condensed matter (eV). For other quantities atomic units(a.u.) are natural. They have the nice feature that the constants of electron-mass (m), Planck's constant (\hbar), and the elementary charge (e) are all set to 1. The unit of energy in a.u. is "Hartree"(Ha) which is twice the binding energy of the electron in Hydrogen, $E_{\text{Ha}} = \hbar^2/(ma_0^2) = 27.2\text{eV}$. One therefore also often use "Rydberg"(Ry), $\text{Ry} = \text{Ha}/2$. The unit of length is "Bohr" ($a_0 = \hbar^2/(me^2)$), which corresponds to $a_0 = 0.53\text{\AA} = 0.05\text{nm}$. Planck's constant links frequency and energy, $h\nu = E$. An energy of 4meV corresponds to 1THz which is the time/energy scale of slow atomic vibrations. The electrostatics of atoms is also easy in these units since $e^2/(4\pi\epsilon_0 a_0) = E_{\text{Ha}}$.

Exercise 2 Use the information above and paper and pencil only to solve the following.

- (a) Estimate the time scale corresponding to an energy of 1eV, relevant for electrons in condensed matter.
- (b) Estimate the quantum of conductance in SI units, namely micro-Siemens (μS) and the corresponding quantum resistance $R_0 = 1/G_0$ in kilo-Ohm.
- (c) Calculate the current in μA for a fully transmitting channel when the applied voltage is 1V.
- (d) Calculate how many electrons pass per time for the current found in c. Compare this to the typical vibrational period of atoms.

The important input needed to obtain the conductance is thus the elastic quantum transmission. It turns out that the Landauer theory is relevant not only to describe electron transport in nanosystems, but it also useful for thermal (phonon) transport (specialized topic in section 6.6). In the note we will provide a hands-on way to calculate the transmission function for quite general systems defined in terms of atomic positions. It relies on the use of atomic orbital basis sets and Green's function techniques. As a refresher of introductory quantum mechanics where a square potential barrier is usually treated, we will now consider a simpler case of an energy barrier of height V and width w , but in the limit of $w \rightarrow 0$ while Vw is kept constant. In this limit the potential becomes a delta-function, $U(x) = Vw\delta(x)$.

Exercise 3 Consider a delta-function potential barrier.

- (a) Calculate⁶ the transmission amplitude, $t(E)$, through $U(x) = Vw\delta(x)$.
- (b) Plot $T(E) = |t(E)|^2$ for the delta-barrier as a function of energy for $Vw = 1$.
- (c) Now consider two similar delta-barriers separated by L , $U(x) + U(x - L)$. Use that the total amplitude is the sum of all possible paths, do the sum (its a geometric series), and calculate the transmission probability and plot it as a function of E and L .

1.1.2 No barrier = finite resistance?

You may wonder how the energy transferred by the battery to the electrons is dissipated as Joule heating in the Landauer setup. The answer is that this is assumed to take place in the macroscopic electrodes which feeds the one-dimensional system with particles. The Landauer formula includes how the electrons go through the "bottle-neck" or "rate-limiting step" of the system and includes only elastic (energy conserving) processes. The electrons are accelerated over the voltage drop (electric field) located at the barrier where they are scattered and potential energy is converted to kinetic energy. It is implicitly assumed that far away there are wide reservoirs at equilibrium which can feed electrons to the one-dimensional conductor, and in the end take up the energy that the electrons have gained from the voltage drop. We are used to calculate the power dissipated as Joule heating from the resistance, $P = IV = RI^2$. Thus even if there is no barrier, $T = 1$, we will have a resistance, $R = R_0$, due to the coupling of the conductor to the reservoirs.

It actually makes sense to define a resistance due to the barrier itself in series with a "non-local" resistance due to the coupling to electrodes,

$$R = G^{-1} = \frac{1}{G_0} \frac{1}{T} = R_0 \left(1 + \frac{1-T}{T} \right) = R_0 + R_b. \quad (6)$$

Here $R_0 = h/2e^2$ is the unavoidable resistance due to perfect coupling of a one-dimensional system to a multi-dimensional wide reservoir, and R_b the resistance of the "barrier itself". This is illustrated in Fig. 3(c). Note that $R_b = 0$ for $T = 1$. Although this looks like Ohm's law of resistors in series care must be taken for quantum transport. In general if two barriers are put in series Ohm's law will not hold as we will see below.

1.1.3 Beyond 1D

The Landauer-Büttiker formula generalize the one-dimensional formula to more dimensions. A typical situation is that the "device" contains a number of "channels" which transmit. For a two-dimensional system we may imagine planewaves (or Bloch waves) all at energy E_F but travelling in different directions impinging on the conductor. Consider one such wave with wavevector \vec{k}_j normalized to its flux in the transport direction, see Figure 3(d). This will end up in a superposition of waves with different wavevectors (\vec{k}_i) as "independent channels" on the right hand side as described by a quantum transmission *amplitude* matrix. The total transmission *probability* in Landauers 1D formula is now replaced by the sum of probabilities for entering all channels and exiting all channels,

$$T(E) = \sum_{ij} |t_{ij}|^2 = \text{Tr} [\mathbf{t}^\dagger \mathbf{t}]. \quad (7)$$

One may "diagonalize" the amplitude matrix and obtain a sum of individual "eigenchannels", $T = \sum_n T_n$, each with transmission as in 1D, $T_n \in [0; 1]$. This in turn means that we can have a *total* transmission bigger than 1 for multi-channel systems.

⁶Hint: Use that the wave-function must be continuous but with a kink at $x = 0$.

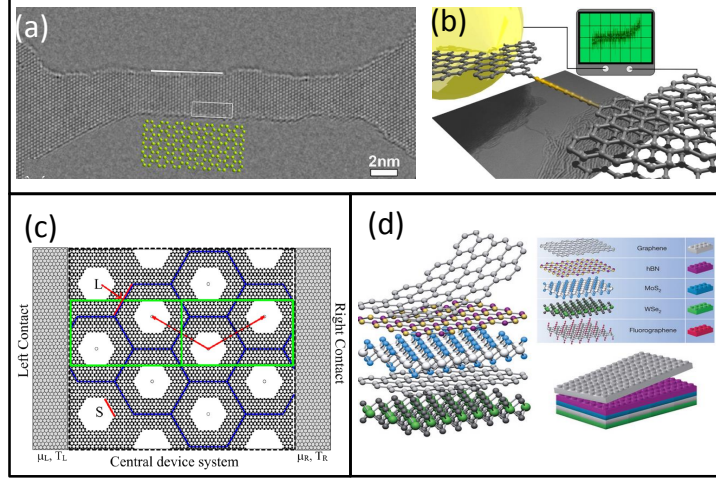


Figure 4: Examples of two-dimensional nanoconductors and materials. (a) A nanoscale graphene "constriction" sculpted by an electron beam [3]. (b) A single-atomic Carbon chain between graphene "electrodes", from [4]. The system can be observed in electron microscopy and its conductance can be measured. (c) A nanostructure consisting of a finite periodic rows of missing atoms ("finite anti-dot lattice") between graphene electrodes from [5]. (d) A range of different two-dimensional materials with varying electrical properties (conductors, semiconductors, insulators) exists and can even be combined, e.g. stacked and bonded by van der Waals interaction[6].

We will mainly base our examples in the note on planar carbon nanosystems derived from graphene. A major reason is one can get quite far and make relevant studies, even using simple tight-binding models for the electronic structure of graphene, as discussed in the next section. Examples of systems are shown in Fig. 4(a-d). For these systems the finite width transverse to the transport direction give rise to multiple channels as we will see later. An example which requires a multi-channel approach as sketched in Fig. 3(d), is a "constriction" formed in graphene shown in Fig. 4(a). The width of the narrowest point in the ribbon will determine the number of transport channels. The extreme case of a single chain of carbon, shown in Fig. 4(b), give rise to only a single conducting channel.

2 Schrödinger equation in matrix form: Tight-binding

Before we embark on the Green's functions we'll here briefly describe a simple but very useful description of the electronic structure relevant for graphene nanostructures and a big class of flat molecular carbon systems. This is used as an illustration of how one can think of a Hamiltonian operator as a matrix in the so-called tight-binding approximation⁷. In the tight-binding approximation one view the motion of the electrons as jumps between atomic orbitals (or atom-centered orbitals) on neighboring atoms. The reason for the term "tight-binding" is that the approximation works best, very roughly speaking, when electrons spend most of the time "tightly bound" in orbitals around atoms, and spend less time in between atoms. This is opposite to the "free electron approximation" where the electrons are assumed to spend equal time everywhere irrespective of the positions of atoms. In this approximation one expands the solutions to the Schrödinger equation in a basis-set involving the atomic orbitals, $\phi_\alpha(R)$, where R is the position of an atom and α denotes the specific valence orbitals of that atom such as $2s$, $2p_x$ and so on. The solutions for a molecule – the *molecular orbitals*, are thus described as a Linear Combination of

⁷This is also known as the Hückel model in chemistry.

the Atomic Orbitals and such methods are called LCAO,

$$\Psi_{\text{MO}} = \sum_{\alpha, R} c_{\alpha, R} \phi_{\alpha}(R). \quad (8)$$

When transport properties are in focus it is the electronic states on the molecule close to the Fermi level which are interesting. This is typically around the highest occupied molecular orbitals (the last one filled with electrons), known as the HOMO, or the lowest unoccupied molecular orbital (LUMO). In molecular electronics the organic molecules i.e. molecules based primarily on Carbon are used. As an important illustration of LCAO we will consider a simple but yet very important example, namely the situation where all carbon atoms are bonded to three other atoms and share 1 electron with each of these in the bonds. The molecules are typically planar, see Fig. 5, and can be thought of as being cut out of a hexagonal graphene lattice, see Fig. 7. The electronic structure of the transport can for all these carbon systems be described by a single orbital per carbon.

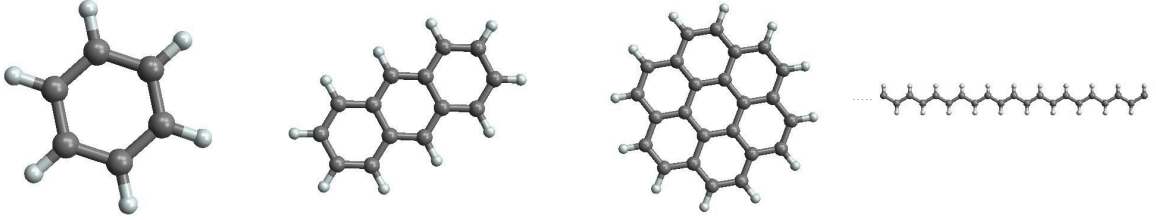


Figure 5: Benzene, Anthracene, Coronene, and Poly-Acetylene(PA). All are flat and their molecular orbitals can be described by a linear combination of a single so-called π -orbital (p_z orbital) on each atom. The carbon-carbon distance is about 1.4\AA and the angles involved are 120° .

We start by considering a graphene plane, say, lying in the xy plane. The carbon atoms has 4 valence orbitals (s, p_x, p_y, p_z) and 4 valence electrons. Three of the orbitals (s, p_x, p_y) make strong chemical bonds in the graphene plane - a so-called sp^2 hybrid. Three electrons from each carbon atom goes into this kind of bond. The last orbital is standing perpendicular to the plane (p_z) and contains 1 electron. These *perpendicular* p_z orbitals are also called π -orbitals. These orbitals have a node in the xy -plane and change sign across the graphene plane, see Fig. 6. They do not “mix” with the in-plane sp^2 -hybrid orbitals due to this symmetry. This means that the electrons in the π -orbitals - π -electrons - can only move around in these and not e.g. jump into one of the in-plane orbitals. The π -electrons make up a kind of 2-dimensional electron gas.

The electrons in the in-plane orbitals which make up the strong chemical bonds are bound more strongly and have lower energies compared to the π -electrons. Thus the π -electrons occupy the states at the Fermi level of graphene and therefore dominate the electron transport in graphene. Since this is our main interest here we will only describe graphene by the π -orbitals. The same argument goes for carbon nanotubes, but in this case the π -orbitals are perpendicular to the curved cylindrical surface of the tube. The model also works for the C-60 molecule where the π -orbitals are now in the radial direction, see Fig. 8.

The electron motion can be described by a kinetic energy parameter, often called the tight-binding overlap integral or *hopping matrix element* since it describes how the electron hops between neighboring orbitals,

$$V_{pp\pi} = \langle \phi_{\pi}(1) | \hat{H} | \phi_{\pi}(2) \rangle, \quad (9)$$

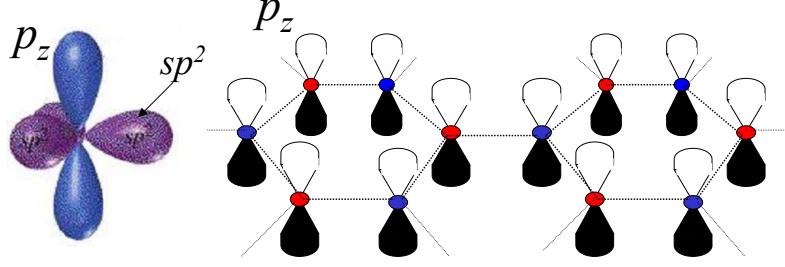


Figure 6: For graphene lying in the (x, y) -plane the in-plane orbitals make strong chemical bonds between the carbon atoms (so-called sp^2 hybrids). The last valence orbitals p_z perpendicular to the plane (shown) form separate electronic states (not shown) at higher energies around the Fermi level.

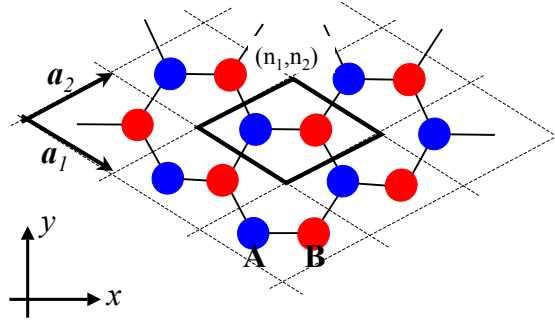


Figure 7: The unit cell of graphene contains two atoms A and B . We label a unit-cell by its coordinates (n_1, n_2) with respect to the lattice vectors \vec{a}_1, \vec{a}_2 .

where $\phi_\pi(1)$, $\phi_\pi(2)$ are π -orbitals located on neighboring atoms 1 and 2, and \hat{H} is the Hamiltonian operator. A typical value for graphene is $V_{pp\pi} = -2.7$ eV when the carbon atoms are $d_0 = 1.4$ Å apart. The hopping matrix element will increase its size when the atoms move closer since the orbitals will overlap more in the integral. This means that the electrons more easily can hop between the orbitals. One very roughly have the scaling[7],

$$V_{pp\pi}(d) = V_{pp\pi}(d_0) \left(\frac{d_0}{d} \right)^2. \quad (10)$$

We will neglect hopping beyond the nearest neighbor atoms. The matrix element,

$$\epsilon_0 = \langle \phi_\pi(1) | \hat{H} | \phi_\pi(1) \rangle, \quad (11)$$

is the average energy of the electron when present on atom 1. This is like a local potential of atom 1. Normally we define the energy relative to this, and set it equal to zero by choice ($\epsilon_0 = 0$). In the more general case of a non-flat molecule we have to take all s and p orbitals into account, and include not only the distance but also the angular dependence of hopping parameters. This is beyond the scope here but is touched upon later in section 6.4,

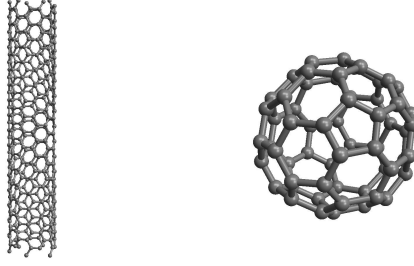


Figure 8: Carbon nanotube and the "football-molecule" or "Buckyball", C_{60} .

2.0.1 Example: The Benzene molecule

Benzene is the 6-membered carbon ring shown in Fig. 5. We will describe it by a single π -orbital on each carbon. The π -electrons makes up delocalized molecular orbitals which in the case of benzene makes the molecule strongly bonded together.

Exercise 4 Consider a benzene molecule described by the π -orbitals and a nearest-neighbor hopping. Argue that the Hamiltonian matrix can be written as,

$$\mathbf{H} = V_{pp\pi} \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}$$

Next we want to find the molecular orbitals and energies, that is, the eigenvalues and eigenvectors. We will use the the six-fold rotational symmetry around its center-axis. If we rotate the system $1/6$ around this axis we end up with an identical physical system and thus with an identical Hamiltonian. Now consider an energy eigenvector $\phi = (c_1, c_2, c_3, c_4, c_5, c_6)$, where c_i is the coefficient of the π -orbital on atom $i = 1, \dots, 6$, numbering the atoms around the ring. If we rotate indices/coordinates of this wavefunction we obtain,

$$C_6 \phi = (c_2, c_3, c_4, c_5, c_6, c_1), \quad (12)$$

where we have defined a rotation operator, C_6 . Since the rotated Hamiltonian is the same, or equivalently, \mathbf{H} commutes with C_6 , the rotated vector must equally well be an eigenvector with the same energy. We should be able to find simultaneous eigenvectors to \mathbf{H} and C_6 .

$$C_6 \phi = (c_2, c_3, c_4, c_5, c_6, c_1) = \lambda(c_1, c_2, c_3, c_4, c_5, c_6). \quad (13)$$

Note that acting 6 times, C_6^6 , amounts to doing nothing (identity). We can represent C_6 by the matrix,

$$\mathbf{C}_6 = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (14)$$

Exercise 5 (a) Show that Eq. 14 is correct and that $(\mathbf{C}_6)^{-1} = (\mathbf{C}_6)^T$. (b) Show that the vectors $\phi_n = \frac{1}{\sqrt{6}}(\lambda_n^0, \lambda_n^1, \lambda_n^2, \lambda_n^3, \lambda_n^4, \lambda_n^5)$ are normalized eigenvectors to C_6 with eigenvalues $\lambda_n = e^{-i2\pi n/6}$, $n = 0, 1, 2, 3, 4, 5$.

Now we have actually also found the eigenvectors of \mathbf{H} since in this case these vectors span the whole 6-dimensional space of the π orbitals.

(c) Show that these are eigenvectors of \mathbf{H} with eigenvalues $\varepsilon_n = \lambda_n + \lambda_{-n} = 2\cos(n\pi/3)$ in units of $V_{pp\pi}$.
(d) There are two π -electrons in each of these orbital⁸. Identify the HOMO and LUMO and calculate the energy difference between HOMO and LUMO, the so-called HOMO-LUMO gap. This is relevant for optical properties of the molecule.

We can have molecules with other ring-lengths. The eigenvalues can easily be found to be $2\cos(n2\pi/m)$ of a C_mH_m molecule. This is the same idea in Bloch's theorem for electrons in lattices using periodic boundary conditions except in the case of benzene we only have 6 "unit-cells".

Exercise 6 Consider polyacetylene which is a polymer – meaning many units of acetylene repeated, see Fig. 5. This is also a "flat", π -electron system. (a) We consider the "infinite" molecule. Argue that the eigenvalues in units of $V_{pp\pi}$ can be written as a bandstructure $E_k = 2\cos(k)$, where k can be considered to be a continuous variable in the range $[-\pi; \pi]$.

(b) Make a plot of the bandstructure and a plot of the corresponding velocity.

(c) The Density of States (DOS) measures how many states are available in a small energy-interval around a certain energy. Consider a finite but big number of units of polyacetylene: Around which energies do you expect a high DOS and where do you expect a low DOS?

2.0.2 Bandstructure of general "chain" systems

Next we will consider a more general example of a π -system, polyacene shown in Fig. 9, with more states in the unit-cell - labeled 1-4 as shown. We denote the right-going hopping-matrix by \mathbf{V} , and the on-site matrix by \mathbf{h} . These matrices are all 4×4 . The full (infinite) Hamiltonian for this system can be written as a Block matrix with (4×4) -Block-elements in the unit-cell index (n, m) as,⁹

$$\mathbf{H}_{nm} = \mathbf{h} \delta_{n,m} + \mathbf{V} \delta_{n+1,m} + \mathbf{V}^\dagger \delta_{n-1,m}. \quad (16)$$

In the same way as for the polyacetylene with a single state per unit cell, we transform to Bloch basis and write the wave-function as,

$$\Psi_k = \left(\sum_n e^{ikn} |n\rangle \right) \phi_k, \quad (17)$$

where now ϕ is a vector of length 4.

⁸The system has "spin-degeneracy" and each orbital comes in spin-up and spin-down versions.

⁹Alternatively one may write it is

$$\mathbf{H} = \sum_n \mathbf{h} |n\rangle \langle n| + \mathbf{V} |n+1\rangle \langle n| + \mathbf{V}^\dagger |n-1\rangle \langle n|, \quad (15)$$

where we write the wave-function as a direct product of a 4-vector $|\phi\rangle$ and a unit-cell state, $|\Psi\rangle = |\phi\rangle \otimes |n\rangle$.

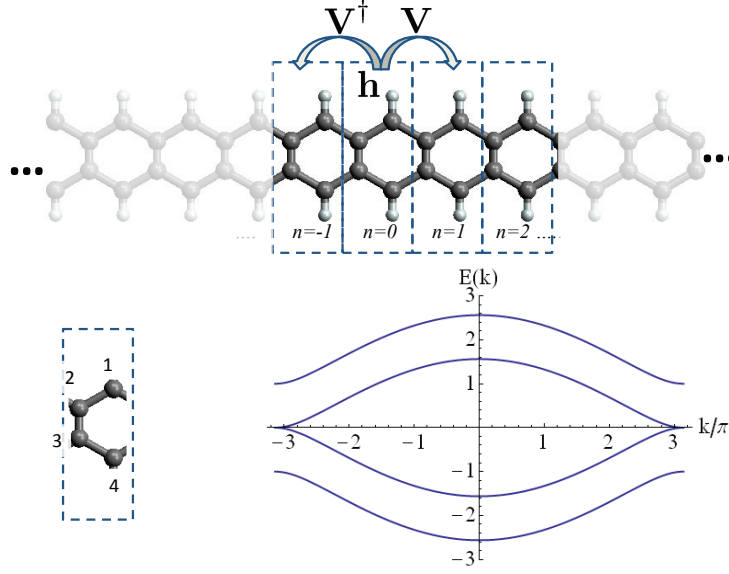


Figure 9: Bandstructure for a one-dimensional structure involving several atoms/basis states inside the repeated unit (dashed). Note the convention that \mathbf{V} is defined as a "hop" from left-to-right, while \mathbf{V}^\dagger is right-to-left.

Exercise 7 (a) Convince yourself that

$$\mathbf{h} = V_{pp\pi} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \text{ and, } \mathbf{V} = V_{pp\pi} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (18)$$

and that Schrödinger's equation for ϕ_k can be written as,

$$(\mathbf{h} + \mathbf{V}e^{-ik} + \mathbf{V}^\dagger e^{ik}) \phi_k = \varepsilon_b(k) \phi_k \quad (19)$$

where you now get 4 eigenstates/values (label b) for each k .

(b) Write a small Mathematica program to plot the bandstructure, $\varepsilon_b(k)$, $b = 1, 2, 3, 4$.

(c) The potential energy (on-site elements) of atom 2,3 will differ slightly from atoms 1,4. Investigate how this influence the bandstructure.

Extra: Use symmetry to reduce the problem to 2×2 and solve it by hand.

3 The retarded Green's function

Now we go through the basics of Green's functions and how they are related to the density of states and transport. To save ink we will leave out \hbar (that is use units where $\hbar = 1$), and reinstate it later on. We focus on tight-binding 1D-type systems and you may have polyacetylene in mind. We begin with Schrödinger's time-dependent equation (TDSE),

$$\mathbf{H}\phi(t) = i \frac{\partial}{\partial t} \phi(t). \quad (20)$$

We will in the entire note consider time-independent, steady-state transport, described by a *time-independent* Hamiltonian. We use bold-face \mathbf{H} to denote the (time-independent) Hamiltonian *matrix*

and the wavefunction, ϕ , is a vector. We want to solve it with the boundary condition,

$$\phi(t=0) = f = (f_1, f_2, \dots). \quad (21)$$

Now consider another equation,

$$\mathbf{H}\mathbf{G}(t) = i\frac{\partial}{\partial t}\mathbf{G}(t) \text{ with } \mathbf{G}(t=0) = \mathbf{1} \quad (22)$$

The Green's matrix \mathbf{G} contains a collection of solutions to the TDSE,

$$\mathbf{H}g_i(t) = i\frac{\partial}{\partial t}g_i(t) \quad (23)$$

where g_i is the i th column of \mathbf{G} and $g_i(t=0)$ is the vector with zeros except a 1 at the i th position. Once we have solved the equation for \mathbf{G} we can find the solution to TDSE for *any* initial f :

$$\phi(t) = \mathbf{G}(t)f. \quad (24)$$

The Green's matrix is also called the propagator because it propagates the initial value f at $t=0$ to an arbitrary time.

Exercise 8 (a) Prove that (24) is the solution to the TDSE. (b) What does it mean physically? Hint: Think about the superposition principle.

We can solve (22) formally,

$$\mathbf{G}(t) = e^{-i\mathbf{H}t} \equiv \sum_n \frac{(-i\mathbf{H}t)^n}{n!} \quad (25)$$

where the exponential to a matrix is defined from the series expansion.

Exercise 9 Prove that (25) is the solution to (22).

3.1 Retarded Green's function matrix in time

Instead of the Green's function defined in (25) the most common type of Green's function is the retarded Green's function defined by,

$$\mathbf{G}(t) = -i\theta(t)e^{-i\mathbf{H}t}. \quad (26)$$

The θ is the step function $\theta(t < 0) = 0$ and $\theta(t \geq 0) = 1$ (and a " $-i$ " in front is a matter of definition/taste). The propagator is "switched on" at $t=0$ and is zero before that: It only propagates the initial value into the future – the "response" come after the "excitation" at $t=0$. It is a solution to the equation:

$$i\frac{\partial}{\partial t}\mathbf{G}(t) - \mathbf{H}\mathbf{G}(t) = \delta(t)\mathbf{1} \quad (27)$$

where the delta "function" (see later) is the derivative of θ . The delta function source term corresponds to applying an external impulse force just at $t=0$.

3.2 Retarded Green's function in energy

When the Hamiltonian is time-independent we usually consider the time-independent solutions, ψ_E , where

$$\phi(t) = e^{-iEt}\psi_E, \quad (28)$$

and

$$\mathbf{H}\psi_E = E\psi_E. \quad (29)$$

In this case it is understood that all states at a certain energy, E , oscillates with the same complex phase e^{-iEt} . The retarded Green's function as a function of energy, $\mathbf{G}(E)$, corresponding to this situation is the solution to

$$[(E + i\eta)\mathbf{1} - \mathbf{H}]\mathbf{G}(E) = \mathbf{1}, \quad (30)$$

where η is an positive infinitesimal which we return to in a while. The retarded Green's function is also just called the Green's function. With this we can again solve,

$$[E - \mathbf{H}]\psi_E = f \quad (31)$$

by

$$\psi_E = \mathbf{G} f. \quad (32)$$

It corresponds to the TDSE with a driving force/source which is oscillating with the phase $e^{-iEt}f$ at all times,

$$(i\frac{\partial}{\partial t} - \mathbf{H})\psi_E e^{-iEt} = e^{-iEt}f. \quad (33)$$

The retarded Green's function in the time and energy domains, $\mathbf{G}(t)$ and $\mathbf{G}(E)$, are related by Fourier transformation,

$$\mathbf{G}(E) = \lim_{\eta \rightarrow 0_+} \int_{-\infty}^{\infty} dt e^{i(E+i\eta)t} \mathbf{G}(t). \quad (34)$$

The $\eta > 0$ factor takes care of the convergence for big times $t \rightarrow \infty$. The limit $\eta \rightarrow 0_+$ is taken in the end of all calculations. This is also discussed in Datta [8] p. 135.

Exercise 10 Show that Eq. (30) is fulfilled by the expression for $\mathbf{G}(E)$ in Eq. (34) using that $\mathbf{G}(t)$ is a solution to the Schrödinger equation with a source, Eq. 27, and the boundary condition $\mathbf{G}(t) = 0$ for $t < 0$. Hint: Use partial integration to get rid of the time-derivative.

If we insert equation (26) in (34),

$$\mathbf{G}(E) = -i \lim_{\eta \rightarrow 0_+} \int_{-\infty}^{\infty} dt e^{i(E+i\eta)t} \theta(t) e^{-i\mathbf{H}t}, \quad (35)$$

and treat \mathbf{H} as a number we can evaluate the integral and get

$$\mathbf{G}(E) = [(E + i\eta)\mathbf{1} - \mathbf{H}]^{-1}, \quad (36)$$

which also fits with (30).

Exercise 11 The energy eigenvectors diagonalize \mathbf{H} : $\mathbf{\Psi}^\dagger \mathbf{H} \mathbf{\Psi} = \text{diag}(\varepsilon_1, \varepsilon_2, \dots)$ where the columns of the matrix $\mathbf{\Psi}$ contains the eigenvectors ψ_q labeled by q corresponding to the eigenvalue ε_q , that is,

$$\mathbf{\Psi}_{lq} = \psi_q(l). \quad (37)$$

(a) Show that the matrix $\mathbf{G}(t)$ can be written in terms of the eigenvectors as,

$$\mathbf{G}_{lm}(t) = -i\theta(t) (e^{-i\mathbf{H}t})_{lm} = -i \sum_q \theta(t) \psi_q(l) e^{-i\varepsilon_q t} \psi_q(m)^* \quad (38)$$

Hint: Use that the eigenfunctions make up an orthonormal basis, $\Psi^\dagger \Psi = \mathbf{1}$, and show that you can write $\mathbf{H} = \Psi \text{diag}(\varepsilon_1, \varepsilon_2, \dots) \Psi^\dagger$.

(b) Show that $\mathbf{G}(E)$ can be written in terms of the eigenvectors as,

$$\mathbf{G}_{ij}(E) = \sum_q \frac{\psi_q(i) \psi_q(j)^*}{E + i\eta - \varepsilon_q} \quad (39)$$

Hint: Prove that

$$-i \int_{-\infty}^{\infty} dt \theta(t) e^{i(E+i\eta-\varepsilon_q)t} = \frac{1}{E + i\eta - \varepsilon_q} \quad (40)$$

and use (a).

3.3 Green's function and Density Of States (DOS)

If we take the imaginary part of the diagonal elements of the retarded Green's function we get,

$$\text{Im}[\mathbf{G}_{ll}] = \sum_q |\psi_q(l)|^2 \text{Im}\left[\frac{1}{E + i\eta - \varepsilon_q}\right] = - \sum_q |\psi_q(l)|^2 \frac{\eta}{(E - \varepsilon_q)^2 + \eta^2}. \quad (41)$$

Exercise 12 Use MATHEMATICA to plot the function $\eta/((E - \varepsilon_q)^2 + \eta^2)$ (it is called a *Lorentzian*) and show that the integral of it is exactly π .

In the limit of $\eta \rightarrow 0_+$ you get an infinitely narrow and high peak at the eigenenergy, ε_q , – the delta “function”:

$$\delta(x) = \frac{1}{\pi} \lim_{\eta \rightarrow 0_+} \frac{\eta}{x^2 + \eta^2}. \quad (42)$$

The *local density of states* (LDOS) at site l and can be found directly from the Green's function as,

$$\rho(l, E) \equiv \sum_q |\psi_q(l)|^2 \delta(E - \varepsilon_q) = -\frac{1}{\pi} \text{Im}[\mathbf{G}_{ll}(E)]. \quad (43)$$

The $P_l = |\psi_q(l)|^2$ gives the probability of finding the electron at site l while the $\delta(E - \varepsilon_q)$ make sure that we “count” states with a certain energy E only. Thus the LDOS measures the number of states around a certain energy E and in a certain state (or around a certain point in space).

3.3.1 Green's function in classical physics

For a classical analog we can think of the motion of a classical string in one dimension described by an amplitude along the string, $u(x)$. It follows an wave equation (c is the velocity),

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 u}{\partial t^2} \quad (44)$$

The corresponding retarded Green's function in frequency domain is the solution to

$$\left(\frac{\partial^2}{\partial x^2} - \frac{\omega^2}{c^2} \right) G(x, x') = \delta(x - x'). \quad (45)$$

The “row” $G(x, 0)$ (think of x as an index) corresponds to the response to a driving force with frequency $\omega/2\pi$ applied at zero. It is generating outgoing waves on the string. This is also described in Datta[8] page 133-134.

3.4 Retarded Green's function for an infinite chain

Consider the infinite tight-binding chain described by the (infinite) Hamiltonian matrix with constant on-site elements ε and hopping elements $-\beta$,

$$\mathbf{H}_{mn} = \varepsilon \delta_{m,n} - \beta(\delta_{m+1,n} + \delta_{m,n+1}). \quad (46)$$

The site indices, m and n goes from $-\infty$ to $+\infty$. We use an inter-site distance of unity $a = 1$.

From Bloch's theorem we know the eigenstates, $\psi_k(n) = e^{ikn}$, and eigenenergies, $E(k) = \varepsilon - 2\beta \cos(k)$. The expression for the retarded Green's function follows Datta [8] p. 134, except for the velocity $v = dE/dk$ which now is $v = 2\beta \sin(k)$:

$$\mathbf{G}_{mn}(E) = \frac{\exp(ik|n-m|)}{i2\beta \sin(k)}, \quad (47)$$

where we view $k = \arccos((\varepsilon - E)/2\beta)$ as a function of E .

Exercise 13 Prove that (47) actually fulfills (30). Hint: Insert it directly and calculate an arbitrary matrix element (l, m) and check it equals $\delta_{l,m}$.

4 The self-energy

4.1 The semi-infinite tight-binding chain

The Green's function is usually used for infinite systems - like the chain above - and thus corresponds to inverting an infinite matrix. But in actual calculations we are normally interested in the solution restricted to a finite piece of space. This is a situation which is ideally suited for using Green's functions.

As our prime example consider an semi-infinite chain described by the Hamiltonian,

$$\mathbf{H}_{mn}^c = \varepsilon \delta_{m,n} - \beta(\delta_{m+1,n} + \delta_{m,n+1}), \quad (48)$$

where the site indices now runs through $1, 2 \dots \infty$.

Now suppose we add a state at index 0 with on-site element ε' which couple to the infinite chain via a hopping matrix element β' ,

$$\mathbf{V}_{mn} = -\beta' \delta_{m,0} \delta_{n,1} \quad (49)$$

We can write our (infinite) Hamiltonian matrix as,

$$\mathbf{H} = \left(\begin{array}{ccc|c} \ddots & \ddots & \dot{0} & \vdots \\ \ddots & \ddots & -\beta & 0 \\ \dots 0 & -\beta & \varepsilon & -\beta' \\ \dots & 0 & -\beta' & \varepsilon' \end{array} \right) \quad (50)$$

and schematically as,

$$\mathbf{H} = \left(\begin{array}{cc} \mathbf{H}^c & \mathbf{V}^\dagger \\ \mathbf{V} & \varepsilon' \end{array} \right) \quad (51)$$

where our uncoupled Hamiltonian reads,

$$\mathbf{H}^0 = \left(\begin{array}{cc} \mathbf{H}^c & \mathbf{0} \\ \mathbf{0} & \varepsilon' \end{array} \right). \quad (52)$$

Suppose we know the Green's function for the semi-infinite chain with constant on-site and hopping elements (ideal) and with indices $n = 1, 2, \dots$:

$$\mathbf{G}^c = [z\mathbf{1} - \mathbf{H}^c]^{-1}. \quad (53)$$

We will use z as a short hand for $E + i\eta$. Then we can solve for the Green's function on site 0, \mathbf{G}_{00} ,

$$\begin{pmatrix} z\mathbf{1} - \mathbf{H}^c & -\mathbf{V}^\dagger \\ -\mathbf{V} & (z - \varepsilon')\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} & \mathbf{G}_{0c} \\ \mathbf{G}_{c0} & \mathbf{G}_{00} \end{pmatrix} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \quad (54)$$

$$\Rightarrow \begin{cases} (z\mathbf{1} - \mathbf{H}^c)\mathbf{G}_{0c} - \mathbf{V}^\dagger\mathbf{G}_{00} = \mathbf{0} \\ -\mathbf{V}\mathbf{G}_{0c} + (z - \varepsilon')\mathbf{G}_{00} = \mathbf{1} \end{cases} \quad (55)$$

and eliminating the unknown \mathbf{G}_{0c} yield¹⁰,

$$\mathbf{G}_{00}(z) = (z - \varepsilon' - \Sigma(z))^{-1}, \quad (56)$$

where we have introduced the so-called *self-energy*, $\Sigma(z)$, at site 0, which is found by solving the equations above,

$$\Sigma(z) = \mathbf{V}[z\mathbf{1} - \mathbf{H}_c]^{-1}\mathbf{V}^\dagger = \mathbf{V}\mathbf{G}^c(z)\mathbf{V}^\dagger = \beta' \mathbf{G}_{11}^c(z) \beta'. \quad (57)$$

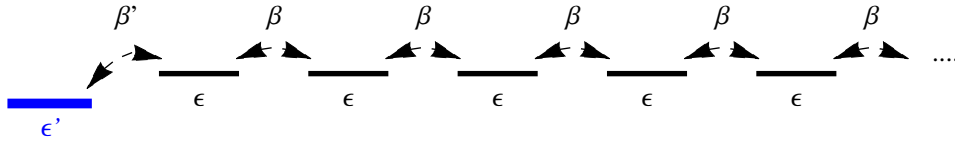


Figure 10: Pictorial representation of a semi-infinite tight-binding chain, ending in a "special" state with on-site energy(ε') and hopping (β') possibly different from the rest of the chain.

Exercise 14 Derive (57) from (55).

The self-energy $\Sigma(z)$ describes the effect of coupling site 0 to the chain. If there is no coupling we just have,

$$\mathbf{G}_{00} = \frac{1}{z - \varepsilon'}, \quad (58)$$

and $\Sigma = 0$. Of course the problem of finding \mathbf{G}_{11}^c remains. But this is actually quite easy. If $\beta' = \beta$ and $\varepsilon' = \varepsilon$ then we have a semi-infinite chain with an added site – which is again a semi-infinite chain (see Fig. 10)! Thus in this case $\mathbf{G}_{11}^c = \mathbf{G}_{00} \equiv g$. We then get an equation we can solve:

$$g = \frac{1}{z - \varepsilon - \beta^2 g}, \quad (59)$$

Exercise 15 (a) Find $\mathbf{G}_{11}^c(E)$ for the semi-infinite chain by solving the complex quadratic equation for g in (59), and sketch $\text{Im}(g)$ and $\text{Re}(g)$. Hint: You get of course two solutions, but have to use the physically meaningful one, i.e. the solution with positive LDOS, and where $g \rightarrow 0$ when $z \rightarrow \pm\infty$. Note that the choice of solution is different in the intervals $E - \varepsilon < -2|\beta|$ and $E - \varepsilon > -2|\beta|$. (b) Calculate $\mathbf{G}_{00}(E)$

¹⁰We do not want the Green's function inside the chain - we just call those elements \mathbf{X} .

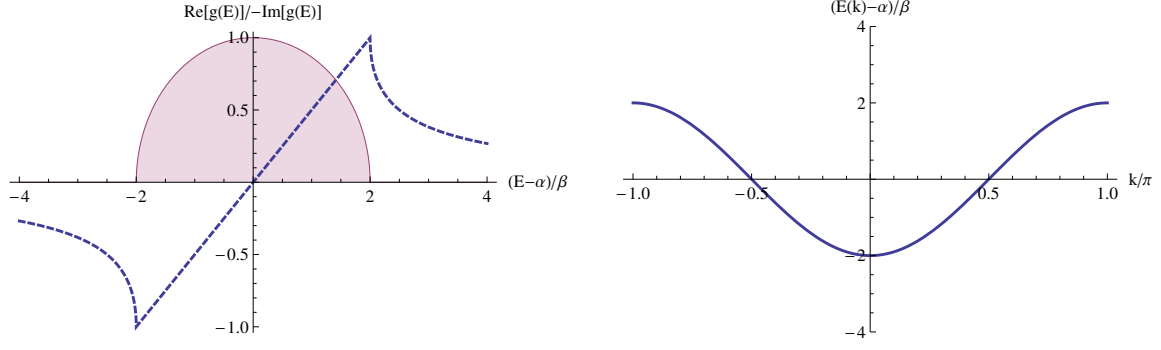


Figure 11: Left: The real(dashed line) and imaginary parts of the Green's function of a chain projected to the last site. Right: The bandstructure of the chain. Note that the imaginary part of the self-energy is zero outside the range of the band energies (the on-site is denoted α in the plot).

and plot the LDOS on site 0 for $\varepsilon = 0, \beta = 1$, varying ε' and β' . Compare to Fig. 11

Exercise 16 For the chain we know the eigenenergy is a function of the wavevector:

$$E(k) = \varepsilon - 2\beta \cos(k). \quad (60)$$

Use this to show that for $k > 0$,

$$\mathbf{G}_{11}^c(k) = -\frac{e^{-ik}}{\beta}. \quad (61)$$

Note: In order to obtain \mathbf{G}_{11}^c as a function of energy, E , we need to invert $E(k)$ which has multiple solutions. If you use `ArcCos` in MATHEMATICA you should define $k(E) = \pm \text{sign}(\beta) \arccos(-E/2\beta)$ with "-" for $E < |2\beta|$ and "+" otherwise.

4.1.1 So what does the self-energy mean?

Suppose we at $t = 0$ place an electron at site 0, that is

$$\phi(n, t = 0) = \phi_0 = \delta_{n,0}. \quad (62)$$

In the case of no coupling $\beta' = 0$ we just get an oscillating behavior for $t > 0$:

$$\phi(n, t) = (\mathbf{G}\phi_0)(n) = -i\delta_{n,0} e^{-i\varepsilon't}. \quad (63)$$

The probability of finding the electron at site 0 in this case is $P_0(t) = |\phi(t)|^2 = 1$ for all times and zero everywhere else.

Exercise 17 Use (24) and (26) to show that this is indeed the case.

Now assume that we couple site 0 to the rest of the chain ($\beta' \neq 0$). Physically the electron will now be able to propagate into the chain and therefore the probability of finding it on site 0 will go down with time. Since the chain is infinitely long it will eventually escape site 0 and never return again! We know

the retarded Green's function as a function of energy, and we can find the retarded Green's function in the time domain by inverse Fourier transformation,

$$\mathbf{G}_{00}(t) = \frac{i}{2\pi} \int_{-\infty}^{\infty} dE e^{-iEt} \mathbf{G}_{00}(E) \quad (64)$$

$$= \frac{i}{2\pi} \int_{-\infty}^{\infty} dE \frac{e^{-iEt}}{E + i\eta - \varepsilon' - \Sigma(E)} \quad (65)$$

If we for a second assume that $\Sigma(E)$ is a constant, just a complex number, $\Lambda - i\Gamma/2$, we will get an exponential decay¹¹,

$$P_0(t) = |\mathbf{G}_{00}(t)|^2 = e^{-\Gamma t}. \quad (66)$$

So this in turn means that now we get the decay corresponding to the electron escaping site 0 in time and it is the imaginary part Σ which determine the speed of decay.

Exercise 18 (a) Find the LDOS on site 0 when $\Sigma = \Lambda - i\Gamma/2$ is constant. The Γ is also called the level width or broadening.

(b) It is in general difficult to do the integral in (65) when Σ is not constant. Here we will get $P_0(t)$ for the first site of an semi-infinite chain ($\varepsilon = 0, \beta = 1$). Use that the eigenfunctions are the standing waves,

$$\psi_k(n) = \sqrt{2} \sin(k(n+1)), \text{ where } n = 0, 1, 2, 3... \quad (67)$$

$$\varepsilon_k = -2 \cos(k) \quad (68)$$

in (38) and do the sum (integral over $k \in]0; \pi[$ with using the measure dk/π) with MATHEMATICA to plot $P_0(t) = |\mathbf{G}_{00}(t)|^2$.

4.1.2 The mathematical trick

The mathematical trick we have used to get the self-energy can be refrased in more general terms. Suppose we have a general, possibly infinite, matrix,

$$\mathbf{M} = \left(\begin{array}{c|c} \mathbf{M}_{11} & \mathbf{M}_{12} \\ \hline \mathbf{M}_{21} & \mathbf{M}_{22} \end{array} \right).$$

and we want a part, say 22, of the inverse, $(\mathbf{M}^{-1})_{22}$. Note that we can not just pick out (\mathbf{M}_{22}) and invert it – this will not be right, except when the coupling elements (12, 21) are zero. Now, the following mathematical identity holds,

$$(\mathbf{M}^{-1})_{22} = [\mathbf{M}_{22} - \mathbf{M}_{21}(\mathbf{M}_{11})^{-1}\mathbf{M}_{12}]^{-1} \quad (69)$$

So this formula tells us to pick out (\mathbf{M}_{22}) and subtract a “correction”, Σ , before we invert to get the right answer,

$$\Sigma = \mathbf{M}_{21}(\mathbf{M}_{11})^{-1}\mathbf{M}_{12}, \quad (70)$$

Note that this of course has the same size as the 22-part.

Exercise 19 (a) Prove (69). Hint: Denote \mathbf{M}^{-1} by \mathbf{X} and use algebraic manipulations to get \mathbf{X}_{22} . (b) What is the corresponding formula for $(\mathbf{M}^{-1})_{11}$?

¹¹You have to do a contour integral to actually show this, but you can roughly understand how this result appears if you change integration variable to $E - \varepsilon' - \Lambda + i\Gamma/2$.

4.2 General case: Self-energy by recursion

In this section we consider how the self-energy in general can be obtained by an effective recursion method for 1D systems and systems which can be mapped to this "chain" geometry.¹²

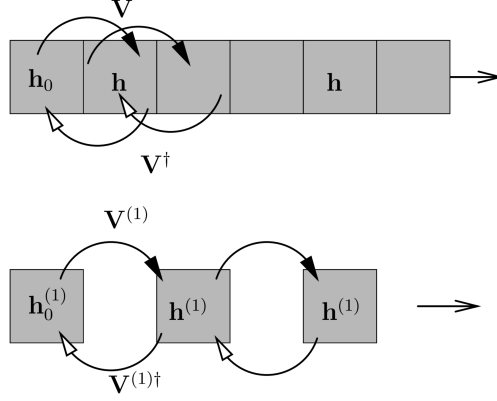


Figure 12: The idea in the recursion method we are describing here is to remove every 2nd cell and obtain an effective interaction between these cells instead. Repeating this procedure will in the end lead to a 1D chain of non-interacting cells.

Consider the semi-infinite system starting with unit-cells labelled $0, 1, 2, \dots$. All cells have the same dimension which is also the dimension of the on-site, h , and hopping Hamiltonians V and V^\dagger moving forwards and backwards, respectively. We consider the 0'th site to be a bit more special so we denote its on-site Hamiltonian h_s . We are interested in the self-energy corresponding to the first cell describing all effective interaction with the rest of the chain. We therefore consider the 0'th column in the equation,

$$[z\mathbf{1} - \mathbf{H}]\mathbf{G}(z) = \mathbf{1} \quad (71)$$

corresponding to the elements, $G_{00}, G_{10}, G_{20}, \dots$. The G_{00} is then the full retarded Green's function inside the first unit-cell while the others are between the 0th cell and the rest. The form of this reads,

$$(z\mathbf{1} - \mathbf{H})\mathbf{G} = \begin{pmatrix} z\mathbf{1} - h_s & -V^\dagger & 0 & 0 & 0 & \dots \\ -V & z\mathbf{1} - h & -V^\dagger & 0 & 0 & \dots \\ 0 & -V & z\mathbf{1} - h & -V^\dagger & 0 & \dots \\ 0 & 0 & \ddots & \ddots & \ddots & \\ \vdots & \vdots & & & & \end{pmatrix} \begin{pmatrix} \mathbf{G}_{00} & \mathbf{G}_{01} & \mathbf{G}_{02} & \dots \\ \mathbf{G}_{10} & \mathbf{G}_{11} & & \\ \mathbf{G}_{20} & & \ddots & \\ \vdots & & & \\ \vdots & & & \end{pmatrix} \quad (72)$$

Since we wish to obtain \mathbf{G}_{00} only, we need only to consider the 1st column of this equation where this lives. Now the idea is that we eliminate variables in this equation to solve it in the same spirit as done previously. We do it by removing every 2nd equation, *i.e.* involving all $\mathbf{G}_{(2n+1)0}$, $n = 0, 1, \dots$. So we after the first round have an effective set of equations describing $\mathbf{G}_{(2n)0}$, $n = 0, 1, \dots$. This "pruned" system is again an semi-infinite chain but now with "renormalized" on-site and hopping matrices. We are going

¹²**Important:** In the following it is important to make a consistent convention of "left" and "right": In general we will label a system with index from "left" to "right" and define all hopping matrices for left-to-right hops *without* a " \dagger " while right-to-left hops will have a " \dagger ". So we will call "forward" $L \rightarrow R$ and use hopping matrices without " \dagger " for that.

to use the notation for the effective matrix representing $(z - \mathbf{H})$ after j iterations (now dropping the explicit bold-face for matrices),

$$(z\mathbf{1} - \mathbf{H}) \mathbf{G}_{\text{1st column}} = \begin{pmatrix} z - \varepsilon_{sj} & -\alpha_j & 0 & 0 & 0 & \cdots \\ -\beta_j & z - \varepsilon_j & -\alpha_j & 0 & 0 & \cdots \\ 0 & -\beta_j & z - \varepsilon_j & -\alpha_j & 0 & \cdots \\ 0 & 0 & \ddots & \ddots & \ddots & \\ \vdots & \vdots & & & & \end{pmatrix} \mathbf{G}_{\text{1st column}} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix} \quad (73)$$

where the starting point $j = 0$ is given by $\alpha_0 = \mathbf{V}^\dagger$, $\beta_0 = \mathbf{V}$, $\varepsilon_{s0} = \mathbf{h}_s$, and $\varepsilon_0 = \mathbf{h}$.

Exercise 20

(a) Show that

$$\alpha_{j+1} = \alpha_j g_{bj} \alpha_j \quad (74)$$

$$\beta_{j+1} = \beta_j g_{bj} \beta_j \quad (75)$$

$$\varepsilon_{j+1} = \varepsilon_j + \alpha_j g_{bj} \beta_j + \beta_j g_{bj} \alpha_j \quad (76)$$

$$\varepsilon_{s(j+1)} = \varepsilon_{sj} + \alpha_j g_{bj} \beta_j \quad (77)$$

with the definition $g_{bj} = (z - \varepsilon_j)^{-1}$. Hint: Show it for $j = 1$ and convince yourself that we are back to a new semi-infinite chain.

- (b) Explain loosely why the effective interaction between the cells in the iterated chain goes to zero, $\alpha_j, \beta_j \rightarrow 0$?
- (c) Convince yourself that in the limit of $j \rightarrow \infty$ we can calculate $\mathbf{G}_{00} = (z - \varepsilon_{sj})^{-1}$.
- (d) Convince yourself, using the same argument, that the Green's function deep in the bulk of the chain, $\mathbf{G}_{\text{bulk}} = \mathbf{G}_{nn}$, $n \rightarrow \infty$, is obtained as the converged $\mathbf{G}_{\text{bulk}} = g_{bj}$, $j \rightarrow \infty$.
- (e) How can the self-energy in the 0th cell be obtained using \mathbf{G}_{00} ?
- (f) Convince yourself that after the recursion has converged you can get the left/right self-energies from the equations,

$$\varepsilon_s = \mathbf{h}_s + \Sigma_R \quad (78)$$

$$\varepsilon = \mathbf{h} + \Sigma_L + \Sigma_R. \quad (79)$$

This means that ε 's which in the limit are on-sites for an effective chain with zero coupling between cells are equal to the original on-site Hamiltonian plus a self-energy "correction".

Exercise 21 Consider an infinite chain with on-site \mathbf{h} and hopping in the right/left directions $\mathbf{V}/\mathbf{V}^\dagger$. If we cut it into two we get a left-going and a right-going semi-infinite chain.

- (a) Argue that in order to obtain the left self-energy matrix Σ_L from (74)-(77) you just have to exchange $\mathbf{V} \leftrightarrow \mathbf{V}^\dagger$.
- (b) Show that right self-energy be obtained from the left self-energy via the bulk Green's function.
- (c) Now your task is to make a MATHEMATICA routine which can calculate the first-cell self-energy. The input should be $\mathbf{h}_0 = \mathbf{h}$ and \mathbf{V} . As a check try out the simple 1D chain¹³ and compare to

¹³In MATHEMATICA you can do (1×1) -matrices as $\{\{\mathbf{x}\}\}$.

Fig. 11. Then check out the carbon system from Fig. 9. Note: Use a small finite imaginary $i\eta$ in $z \equiv E + i\eta$.

- (d) Make plots of the local DOS in a bulk cell and in the 0th cell. **Note that the sequence used for evaluating Eq. 74-77 matters!**

5 Green's functions, transport, and Landauer formula

The Green's function contains information on how an "excitation" at an arbitrary point in the system propagates to some other part of the system. So it is evident that it must contain the transmission probability an electron to move from one part of the system to another. Thus the Green's function is related to the transmission and this relation is called the Fisher-Lee relation¹⁴. To illustrate it assume that we have two semi-infinite chains, left ($n = \dots, -2, -1$) and right ($n = 1, 2, \dots$) acting as "electrodes", which are then coupled via a "molecule". For simplicity we could take the "molecule" to be a single site denoted by 0. If we make an excitation at $n = -1$ with energy, E , we will generate an outgoing transmitted wave in the right chain with amplitude proportional with the transmission amplitude $t(E)$ to go through the molecule at 0:

$$\mathbf{G}_{-1,1}(E) \propto t(E) \quad (80)$$

If the couplings are all equal, $\beta_L = \beta_R = \beta$, and the on-site element of the molecule is also unchanged compared to that of the chain, $\varepsilon' = \varepsilon$, we have the perfect infinite chain again and no scattering of our wave, that is perfect transmission, $|t(E)|^2 = 1$. We know the result for $\mathbf{G}_{-1,1}$ in this case, see (47), and if we assume that all dependence on ε' and β' is in t we can determine the constant of proportionality from the perfect case,

$$\mathbf{G}_{-1,1}(E) = t(E) \frac{\exp(i2k)}{i2\beta \sin(k)}, \quad (81)$$

and we get the transmission probability,

$$|t(E)|^2 = 4|\mathbf{G}_{-1,1}(E)|^2(\beta \sin(k))^2. \quad (82)$$

To calculate $\mathbf{G}_{-1,1}$ we have to invert the 3×3 matrix,

$$\mathbf{G}(E) = \begin{pmatrix} z - \varepsilon - \Sigma(E) & \beta_L & 0 \\ \beta_L & z - \varepsilon' & \beta_R \\ 0 & \beta_R & z - \varepsilon - \Sigma(E) \end{pmatrix}^{-1} \quad (83)$$

The two Σ 's take into account the coupling of site -1 and site 1 to the rest of the infinite left and right chains, respectively. In this case $\Sigma_L = \Sigma_R = \Sigma$ is just a number and will be the same for left and right chains. This is not always true, for example if the repeated unit in these involve several sites. Note that the left self-energy only involves the sites which couple to left chain sites, namely site -1. No other sites among $\{-1, 0, 1\}$ or in the right chain couple to the left chain and get a self-energy due to this. This is why the elimination of the left-chain variables only will involve site -1. Think about this and maybe consult Eq. 70 again. The same goes for the self-energy on site +1 where the right-chain variables have been eliminated.

Exercise 22 Now we consider two semi-infinite chains (with $\beta = 1, \varepsilon = 0$) coupled via a single site (or an infinite chain with a special site). Use MATHEMATICA and the expression you have obtained for the

¹⁴Fisher and Lee first derived it in the early 1980'ies [D. S. Fisher and P. A. Lee, Phys. Rev. B 23, R6851 (1981)].

self-energies of the perfect chain with $\beta = 1, \varepsilon = 0$ in (83) to calculate $|t(E)|^2$ from (82). Plot it for a number of ε' and couplings β_L, β_R . Check that the perfect homogenous chain has transmission 1.

The result in (82) can actually also be written in terms of \mathbf{G}_{00} for the 0th site,

$$|t(E)|^2 = |\mathbf{G}_{00}(E)|^2 \Gamma_L(E) \Gamma_R(E), \quad (84)$$

where

$$\Gamma_L(E) = -2\text{Im}[\Sigma_L(E)] \quad (85)$$

$$\Sigma_L(E) = -\beta_L^2 \frac{e^{ik}}{|\beta|} \quad (86)$$

is the self-energy on site 0 due to the coupling to the left chain (see (57) and (61)).

5.0.1 Heuristic derivation

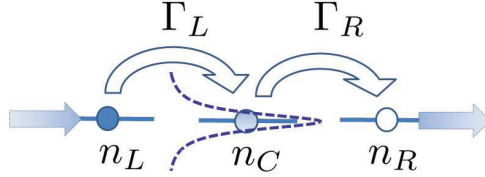


Figure 13: A simple heuristic picture to derive Eq. 84.

Let us try to make a simple derivation of Eq. 84 forgetting about quantum mechanics. We will consider 3 sites, left (L), right (R), and central (C) corresponding to "0" above in Exercise 23, and where L and R are representing the last/first sites in the left/right chains, see Fig. 13. We denote the electron occupation of the 3 sites by n_L, n_C, n_R . We can now write rate-equations for the occupations using the rates Γ_L and Γ_R (see 4.1.1 and the expression for $P(t)$),

$$\frac{dn_L}{dt} = -\Gamma_L(n_L - n_C) \quad (87)$$

$$\frac{dn_C}{dt} = -(\Gamma_L + \Gamma_R)n_C + \Gamma_L n_L + \Gamma_R n_R \quad (88)$$

$$\frac{dn_R}{dt} = -\Gamma_R(n_R - n_C) \quad (89)$$

Now suppose $n_L = 1$ meaning site L is always filled by incoming electrons, and $n_R = 0$ so site R is always emptying its electrons into the right chain. Steady-state in C , that is, $dn_C/dt = 0$, yield,

$$n_C = \frac{\Gamma_L}{\Gamma_R + \Gamma_L}. \quad (90)$$

We can also calculate the current flowing through C as,

$$I = \Gamma_R n_C = \Gamma_L (n_L - n_C) = \frac{\Gamma_L \Gamma_R}{\Gamma_R + \Gamma_L} \quad (91)$$

Exercise 23 (a) Show that the total particle number, $n = n_L + n_R + n_C$ is conserved, that is, $dn/dt = 0$.
(b) Derive Eq. 90 and Eq. 91.

Note that when the rates are equal $\Gamma_L = \Gamma_R = \Gamma$, the current is $I = (1/2)\Gamma$ corresponding to 50% chance of the particle to go left-right at rate Γ . In reality the wave-behavior of the electrons matter and the central state is not a single state at a certain energy (delta function), but the state is rather "smeared out" over a continuum of energies as described by the local density of states on site C ,

$$\text{LDOS}_C(E) = -\frac{1}{\pi} \text{Im}[\mathbf{G}_{00}(E)] = \frac{1}{2\pi} |\mathbf{G}_{00}(E)|^2 (\Gamma_L + \Gamma_R). \quad (92)$$

The current should therefore sum(integrate) over each small part of the C -site smeared over energy where the contribution from a dE -range around E , corresponding to a small voltage, is,

$$dI = \text{LDOS}_C(E) \frac{\Gamma_L \Gamma_R}{\Gamma_R + \Gamma_L} dE = |G_{00}(E)|^2 \Gamma_L \Gamma_R \frac{dE}{2\pi}, \quad (93)$$

and we can recognize the expression from Eq. 84.¹⁵

5.0.2 Simplest resonant model

In order to gain some more understanding of the tunneling rates and their use we will consider a simple, but very useful, model for transport through nano-scale systems. Here we will consider a "narrowest" point for the transmission consisting just of a single electronic state.

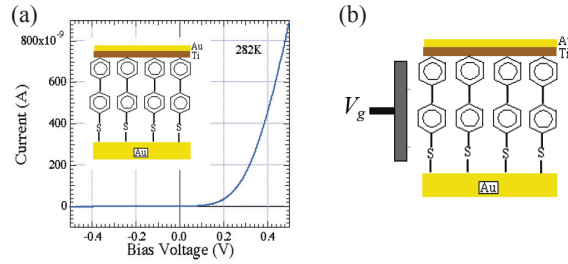


Figure 14: (a) Current-voltage characteristics of a molecular film between Au and Ti contacts. Note the rectifying (diode) behavior. [From C. Zhou *et al.*, Appl. Phys. Lett. **71**, 611 (1997)]. (b) Applying a gate potential V_g may shift the molecular levels.

Exercise 24 In this exercise we consider the simplest possible model for transport through molecules: Resonant tunneling through each molecular quantum level in parallel (see Fig. 14). We can model the transmission through a single molecular level with energy ε by,

$$T(E) = \frac{\Gamma_L \Gamma_R}{(E - \varepsilon)^2 + ((\Gamma_L + \Gamma_R)/2)^2} \quad (94)$$

where Γ_L , Γ_R are numbers (imaginary self-energies). We can interpret Γ_L/\hbar as the rate of electrons hopping from the left electrode onto the molecular level and like-wise Γ_R/\hbar . The total transmission through the molecule is then the sum of such transmissions for each molecular level in the system. Normally just a single or a few levels close to E_F matters, typically the HOMO or LUMO levels.

In this exercise we assume that the current is just going through a single level - this is typically the case when there is only one molecular level close to E_F . We use the Fermi energy $E_F = 0$ as our energy zero, and assume that the Fermi levels of the left and right electrodes are at $eV/2$ and $-eV/2$, respectively, where V is the applied voltage.

¹⁵Note that if we use atomic units and the Landauer formula $dI = |t(E)|^2 dE / (2\pi)$ since $\hbar = 2\pi$ when $\hbar = 1$.

We get the current from right to left electrode through the molecular level by the Landauer formula (neglecting temperature),

$$I = \frac{2e}{h} \int_{-eV/2}^{eV/2} T(E) dE, \quad (95)$$

where $T(E)$ is the transmission function of the level, and

$$G_0 = \frac{2e^2}{h} = 1/(12.9 \text{ k}\Omega). \quad (96)$$

Let us first assume that the level position, ε , is not depending on the applied voltage.

1. What is the current in μA if the applied voltage is $V = 1$ Volt and assuming we have $T(E) = 1$ instead of the expression (94) ?
2. Derive an analytic expression for the current through the level and sketch it.¹⁶
3. For very high voltages the current is going to be constant - find an expression for this constant current.
4. Calculate the maximum current in μA when $\Gamma_L = \Gamma_R = 0.1$ eV.
5. Calculate the maximum current in μA if $\Gamma_L = 0.1$ eV and $\Gamma_R = 0.001$ eV.
6. In the rest of the problems we assume that the level position depend on the voltage in the following way:

$$\varepsilon(V) = \varepsilon_0 + \frac{\Gamma_L - \Gamma_R}{\Gamma_L + \Gamma_R} \frac{eV}{2} \quad (97)$$

This model takes into account that the molecule can be bonded with different bondstrengths to the two electrodes.

Argue from (97) that $\varepsilon(V)$ follows the Fermi level of the left electrode if the tunneling to the right electrode is vanishing. This means that when the molecule is attached with a strong chemical bond to the left electrode (big Γ_L) the molecular level will tend to follow the potential of that electrode. With this we can model a *molecular diode*.

7. Consider the molecular diode in Fig. 14a. The HOMO level of the molecule is 0.5 eV below the Fermi level. We can neglect the other levels. The HOMO is coupled most strongly to one of the electrodes (say the left) by a strong Sulfur-Gold bond ($\Gamma_L = 0.05$ eV), whereas it is only weakly coupled to the other electrode (say the right) made up of a Titanium layer ($\Gamma_R = 10^{-6}$ eV), as shown in Fig. 14. Plot the IV characteristic of a device where 2000 of these molecules conduct in parallel.
8. Suppose we add an extra electrode (a "gate") to the molecules (see Fig. 14b) so we can shift the position of the molecular level, ε , with the gate voltage. Could this work as an transistor?

5.1 The current operator

Now we will describe a general expression for the transmission and as a start we consider Fig. 15 where the system consists of two parts, "left" L and "right" R , with a coupling described by an operator/matrix \mathbf{V} in the Hamiltonian,

$$\mathbf{H} = \mathbf{H}_L + \mathbf{H}_R + \mathbf{V} + \mathbf{V}^\dagger \quad (98)$$

¹⁶Use that $\int \frac{1}{1+x^2} dx = \arctan(x)$.

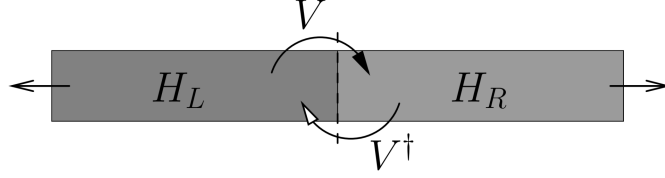


Figure 15: A generic system with a term in the Hamiltonian which couple left and right parts (which in general can be infinite).

Note that \mathbf{V} couples left to right (moves a particle from left into the right part) whereas \mathbf{V}^\dagger does the reverse. We have split the Hilbert space into these two parts and we can write Schrödinger's equation in a 2×2 form,

$$\mathbf{H}\psi = \begin{pmatrix} \mathbf{H}_L & \mathbf{V}^\dagger \\ \mathbf{V} & \mathbf{H}_R \end{pmatrix} \begin{pmatrix} \psi(L) \\ \psi(R) \end{pmatrix} = E \begin{pmatrix} \psi(L) \\ \psi(R) \end{pmatrix}, \quad (99)$$

Next we want to consider scattering states for this infinite system. That is, we want to consider solutions with scattering boundary conditions like we want to start the particle in a "in-coming" energy eigenstate (e.g. a standing wave in L) with energy E from left, ϕ_L . That is ϕ_L is a solution to $\mathbf{H}_L\phi_L = E\phi_L$. In the rest we evaluate all energy-dependent quantities at this particular energy, E , and do not specify it explicitly since the energy is conserved (elastic scattering). This amounts to a differential equation with a "source-term" given by this in-coming state and we wish to calculate the "response", ψ , of this in the whole system. So on the left-hand side we have the total wavefunction as a sum of the in-coming $-\phi_L$ (the sign is chosen for later convenience) and its response as a reflected wave $\psi(L)$, while on the right-hand side we have the response in terms of a transmitted wave $\psi(R)$. If we use that $\mathbf{H}_L\phi_L = E\phi_L$ we can incorporate this in (99),

$$\begin{pmatrix} \mathbf{H}_L & 0 \\ 0 & \mathbf{H}_R \end{pmatrix} \begin{pmatrix} \psi(L) - \phi_L \\ \psi(R) \end{pmatrix} + \begin{pmatrix} 0 & \mathbf{V}^\dagger \\ \mathbf{V} & 0 \end{pmatrix} \begin{pmatrix} \psi(L) \\ \psi(R) \end{pmatrix} = E \begin{pmatrix} \psi(L) - \phi_L \\ \psi(R) \end{pmatrix}. \quad (100)$$

An equation for this solution can be written using the retarded Green's function for the *isolated* left system, $\mathbf{g}_L = (z - \mathbf{H}_L)^{-1}$, and corresponding for *isolated* right system, \mathbf{g}_R ,

$$\Psi = \begin{pmatrix} \psi(L) \\ \psi(R) \end{pmatrix} = \begin{pmatrix} \phi_L \\ 0 \end{pmatrix} + \begin{pmatrix} \mathbf{g}_L & 0 \\ 0 & \mathbf{g}_R \end{pmatrix} \begin{pmatrix} 0 & \mathbf{V}^\dagger \\ \mathbf{V} & 0 \end{pmatrix} \begin{pmatrix} \psi(L) \\ \psi(R) \end{pmatrix}, \quad (101)$$

This is the so-called Lippmann-Schwinger equation.¹⁷ It can be solved iteratively using a start guess for the wave function ψ . Note that the incorporation of ϕ_L amounts to including the boundary condition by the "incoming" wave ϕ_L , which then yield ψ as the resulting total wave when we use the retarded version of \mathbf{g}_L and \mathbf{g}_R (the $i\eta$, $\eta > 0$).

Exercise 25 (a) Show that (100) can be rearranged into the Lippmann-Schwinger equation. (b) What is the solution when the coupling goes to zero, $\mathbf{V} \rightarrow 0$?

Next we wish to evaluate the particle current corresponding to the scattering state. Due to the coupling operator the original state on the left-hand side, ϕ_L , is transmitted to the right system. We can calculate the current generated by this by counting the number of particles per time which arrive in system R , i.e. the derivative of the number operator in R , \mathbf{N}_R . This number operator is simply the projection operator onto R ,

$$\mathbf{N}_R = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \quad (102)$$

¹⁷Note that $i\eta$ is implicitly included in E the limit $\eta \rightarrow 0$ is taken in the end.

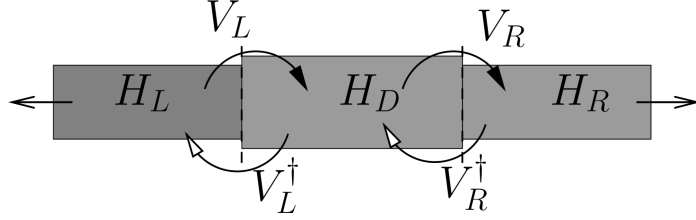


Figure 16: A generic system with a term in the Hamiltonian which couple left and right parts trough an intermediate "device" region. Note that V_L and V_R now in principle couple two regions of different dimensions and thus are not rectangular as for the V 's in the electrode "chains".

so we have

$$\langle \Psi | \mathbf{N}_R | \Psi \rangle = \langle \psi(R) | \psi(R) \rangle = \sum_n |\psi_n(R)|^2 \quad (103)$$

This is the probability of finding the particle in region R . The time-derivative of an operator can be found from the commutator (from now on we reinsert \hbar),

$$\dot{\mathbf{N}}_R = \frac{i}{\hbar} [\mathbf{H}, \mathbf{N}_R] = \frac{i}{\hbar} \begin{pmatrix} 0 & \mathbf{V}^\dagger \\ -\mathbf{V} & 0 \end{pmatrix} \quad (104)$$

Now we can get the particle current,

$$J = \langle \psi | \dot{\mathbf{N}}_R | \psi \rangle = \frac{i}{\hbar} (\langle \psi(L) | \mathbf{V}^\dagger | \psi(R) \rangle - \langle \psi(R) | \mathbf{V} | \psi(L) \rangle) . \quad (105)$$

Next we use the Lippmann-Schwinger equation (101) to get rid of $\psi(R)$,

$$J = \frac{i}{\hbar} (\langle \psi(L) | \mathbf{V}^\dagger \mathbf{g}_R \mathbf{V} | \psi(L) \rangle - \langle \psi(L) | \mathbf{V}^\dagger \mathbf{g}_R^\dagger \mathbf{V} | \psi(L) \rangle) . \quad (106)$$

Defining, Γ_R , (and using that \mathbf{V} is real and \mathbf{g} is symmetric),

$$\Gamma_R = i\mathbf{V}^\dagger (\mathbf{g}_R - \mathbf{g}_R^\dagger) \mathbf{V} = \mathbf{V}^\dagger (-2\text{Im}[\mathbf{g}_R]) \mathbf{V} = -2\text{Im}[\mathbf{V}^\dagger \mathbf{g}_R \mathbf{V}] \quad (107)$$

we can write,

$$J = \frac{1}{\hbar} \langle \psi(L) | \Gamma_R | \psi(L) \rangle . \quad (108)$$

Note that Γ_R is an operator describing the coupling to the right part of the Hilbert space, R , in the left part of the Hilbert space L . Note that Γ corresponds to the imaginary of the self-energy (times -2), see equations 57 and 70.

5.2 Left-Device-Right geometry

Finally we consider the situation where the left and right sides are coupled *via* a general "device" region, D . We want the "response" $\psi(D)$ in the device region and current through the right interface in the case when we send in an "incoming" wave, ϕ_L from the left where again $(E - \mathbf{H}_L)\phi_L = 0$. We write the total solution as incoming wave plus response (or scattered wave) as $(\psi(L) + \phi_L, \psi(D), \psi(R))$ and rearrange Schrödingers equation in a 3×3 form,

$$(E\mathbf{1} - \mathbf{H})\psi = \begin{pmatrix} E\mathbf{1} - \mathbf{H}_L & -\mathbf{V}_L^\dagger & 0 \\ -\mathbf{V}_L & E\mathbf{1} - \mathbf{H}_D & -\mathbf{V}_R^\dagger \\ 0 & -\mathbf{V}_R & E\mathbf{1} - \mathbf{H}_R \end{pmatrix} \begin{pmatrix} \psi(L) \\ \psi(D) \\ \psi(R) \end{pmatrix} = \begin{pmatrix} 0 \\ \mathbf{V}_L \phi_L \\ 0 \end{pmatrix} . \quad (109)$$

Now we employ the full retarded Green's function, $\mathbf{G}(E)[(E + i\eta)\mathbf{1} - \mathbf{H}] = \mathbf{1}$, to obtain the response in the device region,

$$\psi(D) = \mathbf{G}_D(E) \mathbf{V}_L \phi_L , \quad (110)$$

where \mathbf{G}_D is the full Green's function with index restricted to the "device" region, D . The current from the device region into the right electrode is then obtained as,

$$J = \frac{1}{\hbar} \langle \psi(D) | \mathbf{\Gamma}_R | \psi(D) \rangle = \frac{1}{\hbar} \langle \phi_L | \mathbf{V}_L^\dagger \mathbf{G}_D^\dagger \mathbf{\Gamma}_R \mathbf{G}_D \mathbf{V}_L | \phi_L \rangle. \quad (111)$$

This is the particle current when we are starting from "the single state" $\phi(L)$ on the left. In reality "a single state" does not make much sense. We have a number of in-coming (band) states each with a *continuum* of energies (bands) with a corresponding density of states, and the current is really a sum over all incoming L states within an "energy window", $[E_1, E_2]$. Using this (and now inserting the electron charge, e , explicitly to obtain the charge current),¹⁸ we consider the charge current I ,

$$I = e \frac{1}{\hbar} \int_{E_1}^{E_2} dE \sum_l \delta(\varepsilon_l - E) \langle \phi_l | \mathbf{V}_L^\dagger \mathbf{G}_D^\dagger \mathbf{\Gamma}_R \mathbf{G}_D \mathbf{V}_L | \phi_l \rangle \quad (112)$$

$$= \frac{e}{\hbar} \int_{E_1}^{E_2} dE \sum_l \langle \phi_l | \mathbf{V}_L^\dagger \mathbf{G}_D^\dagger \mathbf{\Gamma}_R \mathbf{G}_D \mathbf{V}_L \delta(\mathbf{H}_L - E) | \phi_l \rangle \quad (113)$$

$$= \frac{e}{\hbar} \int_{E_1}^{E_2} dE \sum_l \langle \phi_l | \mathbf{V}_L^\dagger \mathbf{G}_D^\dagger \mathbf{\Gamma}_R \mathbf{G}_D \mathbf{V}_L \left(-\frac{1}{\pi} \text{Im}[\mathbf{g}_L(E)] \right) | \phi_l \rangle. \quad (114)$$

We may extend the sum over all states included in the finite region (L, D, R) and not just the set of ϕ_l 's since the matrix inside the brackets is restricted to region L (and is zero otherwise), and introduce the matrix trace (Tr),

$$I = e \frac{1}{\hbar} \int_{E_1}^{E_2} dE \text{Tr} \left[\mathbf{V}_L^\dagger \mathbf{G}_D^\dagger \mathbf{\Gamma}_R \mathbf{G}_D \mathbf{V}_L \text{Im} \left[-\frac{1}{\pi} \mathbf{g}_L \right] \right] \quad (115)$$

$$= \frac{e}{\hbar} \int_{E_1}^{E_2} dE \text{Tr} \left[\mathbf{G}_D^\dagger \mathbf{\Gamma}_R \mathbf{G}_D \mathbf{V}_L \text{Im} \left[-\frac{1}{\pi} \mathbf{g}_L \right] \mathbf{V}_L^\dagger \right] \quad (116)$$

$$= \frac{e}{\hbar} \int_{E_1}^{E_2} dE \text{Tr} [\mathbf{G}_D^\dagger \mathbf{\Gamma}_R \mathbf{G}_D \mathbf{\Gamma}_L] = \frac{e}{\hbar} \int_{E_1}^{E_2} dE \text{Tr} [\mathbf{\Gamma}_R \mathbf{G}_D \mathbf{\Gamma}_L \mathbf{G}_D^\dagger] \quad (117)$$

$$(118)$$

Exercise 26

- Check for yourself the steps from (111) to (114) and (118) (Hint: use that Tr is cyclic meaning $\text{Tr}[AB] = \text{Tr}[BA]$ and the definition of $\mathbf{\Gamma}$).
- What is the dimension of the matrices inside the trace?

5.3 The Landauer formula yet again

The Landauer formula relates the conductance to the total transmission at the Fermi energy $T(E_F)$,

$$G = I/V = \frac{2e^2}{h} T(E_F). \quad (119)$$

If we take the Landauer formula for granted we can identify,

$$T(E) = \text{Tr} [\mathbf{\Gamma}_R \mathbf{G}_D \mathbf{\Gamma}_L \mathbf{G}_D^\dagger] \quad (120)$$

¹⁸Note that the quantities depend implicitly on the energy parameter in the integral, E .

The conductance is usually given in units of $G_0 = 2e^2/\hbar = 1/12.9 \text{ k}\Omega$ (the 2 is inserted for spin degeneracy) and we think of $[E_1; E_2]$ as an infinitesimal voltage window $E_2 - E_1 = eV$, between the left and right Fermi levels where the current is flowing. We can actually get to (120) by noting that the total transmission at a certain energy can be found from the sum of transmissions of all possible *flux-normalized* incoming states, that is, all possible states which carry unit current.¹⁹ The current (or velocity) of a Bloch state is the slope of the band $v = \frac{1}{\hbar} dE(k)/dk$. It can be noted that this is exactly equivalent to the inverse of the density of states of the corresponding Bloch wave, so,

$$\frac{1}{\sqrt{|v_l|}} |\phi_l\rangle = \sqrt{\hbar |\text{Im}[\mathbf{g}_L]|} |\phi_l\rangle. \quad (121)$$

Using this in (111) and using the definition of transmission, T , namely that this is the outgoing flux divided by the incoming flux, so T equals the current for *flux-normalized* incoming states (convince yourself about this!),

$$T = \frac{1}{\hbar} \sum_l \langle \phi_l | \sqrt{\hbar |\text{Im}[\mathbf{g}_L]|} \mathbf{V}_L^\dagger \mathbf{G}_D^\dagger \mathbf{\Gamma}_R \mathbf{G}_D \mathbf{V}_L \sqrt{\hbar |\text{Im}[\mathbf{g}_L]|} | \phi_l \rangle \quad (122)$$

$$= \text{Tr} \left[\mathbf{V}_L^\dagger \mathbf{G}_D^\dagger \mathbf{\Gamma}_R \mathbf{G}_D \mathbf{V}_L |\text{Im}[\mathbf{g}_L]| \right] \quad (123)$$

$$= \text{Tr}[\mathbf{G}_D^\dagger \mathbf{\Gamma}_R \mathbf{G}_D \mathbf{\Gamma}_L] = \text{Tr}[\mathbf{\Gamma}_R \mathbf{G}_D \mathbf{\Gamma}_L \mathbf{G}_D^\dagger]. \quad (124)$$

Here we have introduced the full trace in (123) over all possible states instead of just the L -sum in (122) since the DOS-operator $\text{Im}[\mathbf{g}_L]$ only counts L -states, $|\phi_L\rangle$, and yield zero on all other states, and the fact that the trace is cyclic (124). So to sum up the main results of our endeavors so far in a box:

$$\begin{aligned} T(E) &= \text{Tr}[\mathbf{\Gamma}_R \mathbf{G}_D \mathbf{\Gamma}_L \mathbf{G}_D^\dagger](E) \\ I(V) &= \int_{-\infty}^{\infty} dE (f_L(E) - f_R(E)) T(E) \end{aligned}$$

Here we have taken the filling of levels (finite temperature) in the left and right electrodes into account explicitly as discussed in the beginning of the note. It is important to note that not only does the filling of states in L and R depend on the voltage, V , via the difference in their chemical potentials ("Fermi energies"), $\mu_L - \mu_R = eV$. Also the Hamiltonian, and thus also \mathbf{G}_D inside the device, D , depends on the applied voltage since this will change the local potential landscape introducing an electrical field.

5.3.1 Spectral functions

The imaginary part of the Green's function contains the local (site) DOS in its diagonal as seen in Eq. 43. One also defines the spectral function/matrix, $\mathbf{A}(E) = -2\text{Im}[\mathbf{G}(E)]$. We can rewrite this as

$$\mathbf{A}(E) = -2\text{Im}[\mathbf{G}(E)] = \mathbf{G}(E) \mathbf{\Gamma}(E) \mathbf{G}^\dagger(E) \quad (125)$$

where $\mathbf{\Gamma}(E) = i(\mathbf{\Sigma}(E) - \mathbf{\Sigma}^\dagger(E)) = -2\text{Im}[\mathbf{\Sigma}(E)] = \mathbf{\Gamma}_L(E) + \mathbf{\Gamma}_R(E)$. The LDOS at site l is now given by (without spin), $\rho(l, E) = [\mathbf{A}(E)]_{ll}/2\pi$. Importantly, this allows us to define left and right spectral functions,

$$\mathbf{A}(E) = \mathbf{A}_L(E) + \mathbf{A}_R(E), \quad (126)$$

where,

$$\mathbf{A}_{L/R}(E) = \mathbf{G}(E) \mathbf{\Gamma}_{L/R}(E) \mathbf{G}^\dagger(E). \quad (127)$$

¹⁹This is the correct normalization which explicitly ensures that no particles disappear - current conservation.

The left electrode spectral function, \mathbf{A}_L , actually corresponds to the scattering states injected from the left electrode, and likewise for the right. We can rewrite the transmission as,

$$T(E) = \text{Tr}[\mathbf{\Gamma}_R \mathbf{G}_D \mathbf{\Gamma}_L \mathbf{G}_D^\dagger](E) = \text{Tr}[\mathbf{\Gamma}_R \mathbf{A}_L](E), \quad (128)$$

where one can view $\text{Tr}[\mathbf{\Gamma}_R \mathbf{A}_L]$ as the rate/current operator for escape into the right electrode, $\mathbf{\Gamma}_R$, acting on the states emerging from the left electrode, \mathbf{A}_L , cf. Eq. 108. For time-reversal symmetry one may easily show that $\text{Tr}[\mathbf{\Gamma}_L \mathbf{A}_R] = \text{Tr}[\mathbf{\Gamma}_R \mathbf{A}_L]$.

Exercise 27 Show Eq. 125. Hint: Show that $\mathbf{G}^{-1} - (\mathbf{G}^\dagger)^{-1} = -\mathbf{\Sigma} + \mathbf{\Sigma}^\dagger = i\mathbf{\Gamma}$.

5.4 Practical implementation

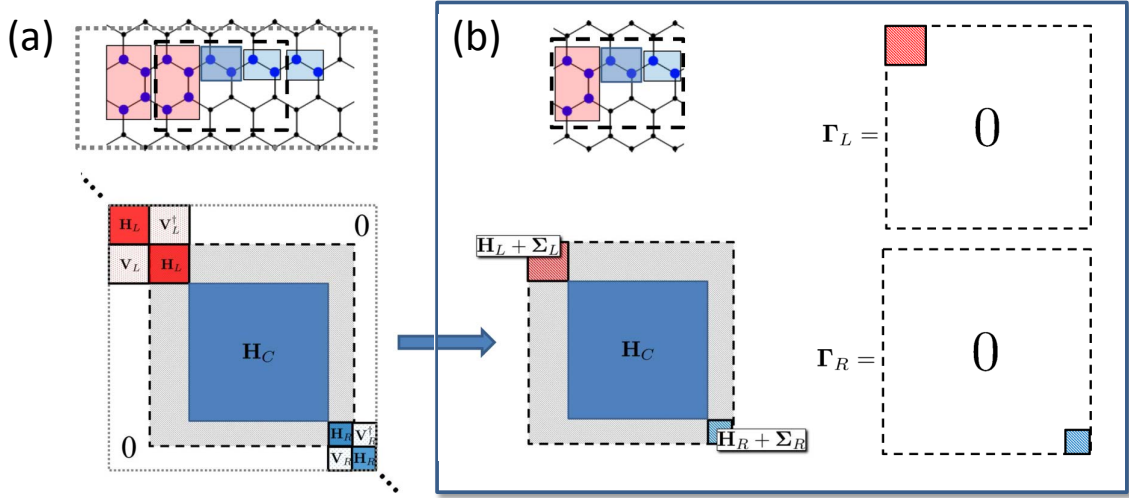


Figure 17: Going from coordinates to Hamiltonians. (a) All matrices needed to calculate the transmission from tight-binding can be generated from the coordinates of a system including two electrode unitcells in each end. Note coordinates and orbital sequence is sorted according to the transport direction from left to right. (b) The blocks $\mathbf{H}_{L/R}$, $\mathbf{V}_{L/R}$ describing the semi-infinite electrodes can be used to replace these by self-energies. These also yield the coupling matrices, $\mathbf{\Gamma}_{L/R}$. Note the dimensions of all matrices are the same.

There are several ways to use and implement the theory for numerical computation. These are basically related to how we divide the system into parts, but all will result in the same final transmission. We choose here the division outlined in Fig.16. The typical starting point is a set of atomic coordinates of the C atoms. From these we may set up a Hamiltonian. Maybe the simplest procedure is to set up the Hamiltonian for a system including two unit cells of both L and R electrodes following Fig.17a. From a "big" Hamiltonian matrix for this total system it is possible to pick out all sub-matrices we need to calculate the transmission, and left/right self-energies, in particular. Thus we can pick \mathbf{H}_L , \mathbf{V}_L to generate $\mathbf{\Sigma}_L$ and likewise for R . Once we have the self-energies we can directly put them into the Hamiltonian representing the smaller region with a single L/R unit cell in each end, see Fig. 17b. Inverting the infinite Green's matrix in Fig. 17a and picking out the smaller region part exactly corresponds to inverting the finite matrix in Fig. 17b. From the corresponding $\mathbf{\Gamma}$ -matrices, we can now do the product between matrices in Eq. 5.3 to get the transmission.

It is important to *sort* these in a way so there is a well-defined correspondence between sites and positions in matrices. In particular it is important that the ordering inside each "unit-cell" used in the

recursion is exactly the same. The typical way is to sort the coordinates along the transport direction, say x , first and secondly after the other direction, say y .

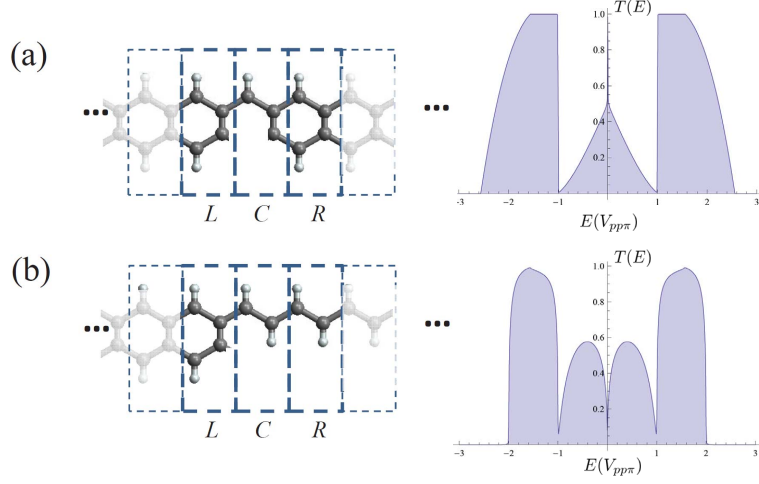


Figure 18: Systems considered in exercise 28 and their corresponding transmission functions.

In the example above the coupling matrices, $\mathbf{V}_{L/R}$, are the ones continued in the block-diagonal L/R parts. Alternatively (but slightly more complicated to implement) is to start with the "surface" or last-cell left and right Green's functions. Suppose these are the $l \times l$ matrix \mathbf{g}_L where l is the number of orbitals in the left repeated unit-cell, and likewise the $r \times r$ matrix, \mathbf{g}_R . We have the general $d \times d$ Hamiltonian matrix inside the device region, \mathbf{H}_D , and now the general matrices describing now how D couple to the left and right, \mathbf{V}_L^\dagger (with l rows and d columns) and \mathbf{V}_R (r rows and d columns) - see Fig.16. Then we can form the $d \times d$ matrices,

$$\Sigma_L = \mathbf{V}_L \mathbf{g}_L \mathbf{V}_L^\dagger \text{ and } \Sigma_R = \mathbf{V}_R^\dagger \mathbf{g}_R \mathbf{V}_R \quad (129)$$

$$\mathbf{G}_D = [\mathbf{1}(E + i\eta) - \mathbf{H}_D - \Sigma_L(E) - \Sigma_R(E)]^{-1} \quad (130)$$

$$\Gamma_L = i(\Sigma_L - \Sigma_L^\dagger) \text{ and } \Gamma_R = i(\Sigma_R - \Sigma_R^\dagger) . \quad (131)$$

and do the multiplications of the $d \times d$ matrices and their trace as in Eq. 124.

Exercise 28 Extend your previous routine for generating self-energies so it can calculate the transmission through a molecule described by a general tight-binding Hamiltonian \mathbf{H}_D . Note that the "molecule" region, D , as introduced in (109) includes the first unit-cell of the left/right electrodes. Use your code to calculate the transmission through the systems (a) and (b) in Fig. 18. Compare with the corresponding bandstructures of the L and R electrodes.

6 Special topics

Now we have the basics we will take a look at some more specialized topics.

6.1 Bond-currents

It is possible to obtain the *local* current flowing in the bonds between atoms. Given a solution to the time-dependent Schrödinger equation, ψ , we can consider the change in probability with time on a specific site, n , in the system,

$$\frac{dP_n}{dt} = \frac{d}{dt} |\psi_n(t)|^2. \quad (132)$$

Using Schrödinger's equation,

$$\frac{d\psi_n}{dt} = -\frac{i}{\hbar} \sum_m \mathbf{H}_{nm} \psi_m, \quad (133)$$

we can rewrite Eq. 132 as,

$$\frac{dP_n}{dt} = -\frac{2}{\hbar} \sum_m \text{Im}[\mathbf{H}_{nm} \psi_m^* \psi_n] = \sum_m J_{nm}. \quad (134)$$

Here we have defined the bond-current (probability) flow from site n to site m , J_{nm} , as,

$$J_{nm} = -\frac{2}{\hbar} \text{Im}[\mathbf{H}_{nm} \psi_m^* \psi_n]. \quad (135)$$

This is a so-called continuity equation stating that the change in probability equals with time equals the net flow of current at some point so no particles disappear at all times.

Exercise 29 (a) Derive Eq. 134 and show that $J_{nm} = -J_{mn}$. (b) Use Eq. 135 to show that the probability of finding the particle at any point, $\sum_n P_n(t)$, is independent of time.

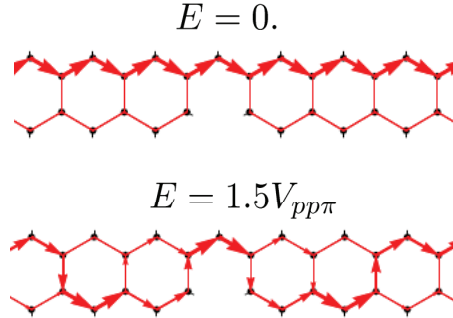


Figure 19: Bond-current starting from left for the two systems in Fig.18 at two different energies. The thickness of the arrow indicate the size of the bond-current. In each cross section of the structure it can be shown that the bond-currents sum up to the total current.

For a stationary state the probability is constant in time so the sum of bond-currents to each site is zero (flow-in equals flow-out), but J_{nm} will generally not be zero for a stationary scattering state. On the other hand a standing wave will have $J_{mn} = 0$ since ψ always can be chosen to be real in that case

(time-reversal symmetry). Now we will calculate the total bond-current flowing between n and m in the device region for a (flux normalized) scattering state incoming from the left, L ,

$$|\Psi_D\rangle = \mathbf{G}_D \mathbf{V}_L \left(\frac{1}{\sqrt{v_l}} |\phi_l\rangle \right). \quad (136)$$

In this case $\psi_n = \langle n | \Psi_D \rangle$ and we get the current flowing per energy interval, dE ,²⁰

$$J_{nm}(L) = -\frac{2}{\hbar} \text{Im} \left[\mathbf{H}_{nm} \langle n | \mathbf{G}_D \mathbf{V}_L \left(\frac{1}{\sqrt{v_l}} |\phi_l\rangle \langle \phi_l| \frac{1}{\sqrt{v_l}} \right) \mathbf{V}_L^\dagger \mathbf{G}_D^\dagger | m \rangle \right]. \quad (137)$$

Normally we just wish to find the total bond-current flowing in a given energy interval around an energy, E , starting from the left or right electrode. To get this we sum over all scattering states at that energy from, say, L ,

$$J_{nm} = -\frac{2}{\hbar} \sum_l \text{Im} \left[\mathbf{H}_{nm} \langle n | \mathbf{G}_D \mathbf{V}_L \left(\frac{1}{\sqrt{v_l}} |\phi_l\rangle \langle \phi_l| \frac{1}{\sqrt{v_l}} \right) \mathbf{V}_L^\dagger \mathbf{G}_D^\dagger | m \rangle \right] = \frac{1}{\hbar} \text{Im} \left[\mathbf{H}_{nm} \left(\mathbf{G}_D \mathbf{\Gamma}_L \mathbf{G}_D^\dagger \right) \right]_{nm}. \quad (138)$$

So we can finally write the (spectral) bond-current in terms of the spectral function,

$$J_{nm} = \frac{1}{\hbar} \text{Im} [\mathbf{H}_{nm} (\mathbf{A}_L)_{nm}]. \quad (139)$$

We have kept \mathbf{H}_{nm} inside the Im since it may be complex if we consider a certain transverse k-point (cf. Section 6.3) or a magnetic field. Here we have used the relation $1/v_l |\phi_l\rangle = \text{Im}[\mathbf{g}_L] |\phi_l\rangle$, and the definition of $\mathbf{\Gamma}_L$. The algebra is left as an extra exercise. Equivalent expressions can be derived for the bond-currents starting in electrode R . Notice the similarity with the expression for the Landauer formula in Eq. 5.3, where the main difference is that the internal- D quantity \mathbf{H}_{nm} is "replaced" by $\mathbf{\Gamma}_R$ describing the coupling out of D to the external R region. In Fig. 19 we show an example of calculated bond-currents.

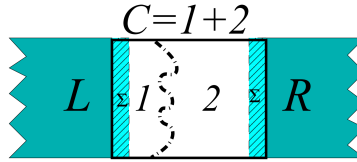


Figure 20: The device(central, C) region is divided into two sections, 1 and 2 where left and right self-energies are positioned in 1 and 2, respectively. The sum of bondcurrents over the arbitrary surface yield the total transmission. We can calculate the transmission by integrating the current-density of flux-normalized scattering states starting in right (or left) electrode, see section 6.5.

6.1.1 Bond-current conservation

We will now prove how the transmission is given by the sum over bond-currents crossing an *arbitrary* surface cutting the device region in two, 1 and 2, containing left and right self-energies, respectively – see Fig. 20. We introduce projectors onto these regions, P_1 and P_2 , and have,

$$\sum_{n \in 1, m \in 2} J_{nm} = \frac{1}{\hbar} \sum_{n \in 1, m \in 2} \mathbf{H}_{nm} \text{Im} \left[\mathbf{H}_{nm} \mathbf{G}_D \mathbf{\Gamma}_L \mathbf{G}_D^\dagger \right]_{nm} = \text{Im} \text{Tr} \left[(P_1 \mathbf{H} P_2) \mathbf{G}_D \mathbf{\Gamma}_L \mathbf{G}_D^\dagger \right] \quad (140)$$

$$= \text{Im} \text{Tr} \left[(P_1 \mathbf{H} P_2) (P_2 \mathbf{G}_D P_1) (P_1 \mathbf{\Gamma}_L P_1) (P_1 \mathbf{G}_D^\dagger P_1) \right] \quad (141)$$

²⁰Note that whenever we consider flux-normalization the absolute square of the scattering wavefunctions can be interpreted as the local density of states.

where we use that $P^2 = P$ and that $\mathbf{\Gamma}_L$ is inside region 1 only so, $\mathbf{\Gamma}_L = P_1 \mathbf{\Gamma}_L P_1$. We can rewrite,

$$P_2 \mathbf{G}_D P_1 = (P_2 \mathbf{g} P_2) (P_2 \mathbf{H} P_1) (P_1 \mathbf{G}_D P_1), \quad (142)$$

where $P_2 \mathbf{g} P_2$ is the Green's function for 2 *without* coupling to region 1 but including the coupling to the right electrode.

Using this we get,

$$\sum_{n \in 1, m \in 2} J_{nm} = \text{Tr} \left[\tilde{\mathbf{\Gamma}}_R \mathbf{G}_{11} \mathbf{\Gamma}_L \mathbf{G}_{11}^\dagger \right], \quad (143)$$

where we have introduced a new right self-energy and corresponding $\tilde{\mathbf{\Gamma}}_R$ which is the right self-energy propagated from region 2 into region 1,

$$\tilde{\mathbf{\Gamma}}_R \equiv (P_1 \mathbf{H} P_2) \text{Im} [P_2 \mathbf{g} P_2] (P_2 \mathbf{H}_D P_1). \quad (144)$$

So we have regained the usual expression for T , except now using the smaller region 1 as our new device region, D .

Exercise 30 (a) Prove "Dysons equation": $\mathbf{G} = \mathbf{g} + \mathbf{g} \mathbf{V} \mathbf{G}$, when $\mathbf{H} = \mathbf{h} + \mathbf{V}$ and $\mathbf{g} = (z - \mathbf{h})^{-1}$ is the "unperturbed" Green's function, while $\mathbf{G} = (z - \mathbf{H})^{-1}$ is the "full" Green's function.

(b) Now prove Eq. 142 using Dysons equation with $\mathbf{h} = P_1 \mathbf{H} P_1 + P_2 \mathbf{H} P_2$ and $\mathbf{V} = P_1 \mathbf{H} P_2 + P_2 \mathbf{H} P_1$.

6.2 Larger systems: More recursion

For very large systems we end up with quite large matrices. However, using a localized basis set (tight-binding) we typically get rather sparse matrices. In particular, for systems which are elongated along the transport direction it is faster to obtain the Green's function inside the central (device) region using a recursion where the initial left (or right) self-energy is propagated to the right end of the central region. This is illustrated in Fig. 21.

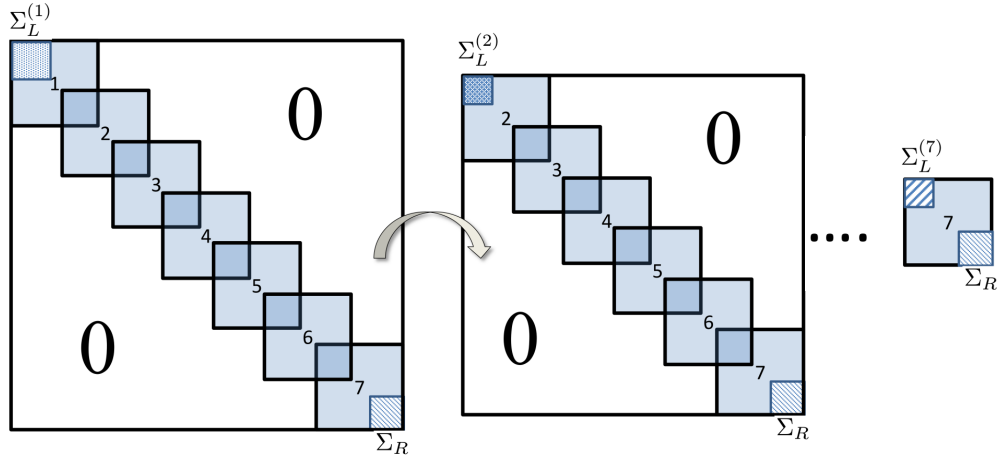


Figure 21: The left self-energy can be propagated to the end of a large device region to avoid inverting a large matrix for the Green's function of the total device region. Note that the matrices 1-7 can be different and of different size.

The self-energy in the left-most end of the device region can be propagated using the following

recursion (which you can show as an extra exercise),

$$\mathbf{g}_{11}(E) = \left(\mathbf{1}_{11}E - \mathbf{h}_{11} - \Sigma_L^{(1)}(E) \right) \quad (145)$$

$$\Sigma_L^{(l)}(E) = \mathbf{h}_{l,l-1} \mathbf{g}_{l-1,l-1}(E) \mathbf{h}_{l-1,l} \quad (146)$$

$$\mathbf{g}_{ll}(E) = \left(\mathbf{1}_{ll}E - \mathbf{h}_{ll} - \Sigma_L^{(l)}(E) \right). \quad (147)$$

Here we are left with a number (for example 7) inversions of smaller matrices which is nice since matrix inversion scales badly with matrix size. Another way which is numerical efficient is to solve the linear equations for vectors, \mathbf{x} and \mathbf{y} ,

$$(\mathbf{1}E - \mathbf{h} - \Sigma_L(E) - \Sigma_R(E)) \mathbf{x} = \mathbf{\Gamma}_L \quad (148)$$

$$(\mathbf{1}E - \mathbf{h} - \Sigma_L^\dagger(E) - \Sigma_R^\dagger(E)) \mathbf{y} = \mathbf{\Gamma}_R \mathbf{x} \quad (149)$$

where we get $\mathbf{y} = \mathbf{G}^\dagger \mathbf{\Gamma}_L \mathbf{G} \mathbf{\Gamma}_R$. The point is that here we define $\mathbf{\Gamma}_L$ as a matrix with n vectors of full device size length (N), where n is the size of $\Sigma_L^{(1)}$. The same goes for the equation of \mathbf{y} .

6.3 Periodic boundary conditions

Often the transverse direction to the transport can be better represented by periodic boundary conditions. Thus we will have a continuum of transport channels for each Bloch phase corresponding to different angles of waves impinging on the device region. This involves a simple extension of the theory so far. Namely all on-site and hopping matrices (\mathbf{h} and \mathbf{V}) will depend on the perpendicular wavenumber, $k_\perp \in [-\pi; \pi]$, see Fig. 22.

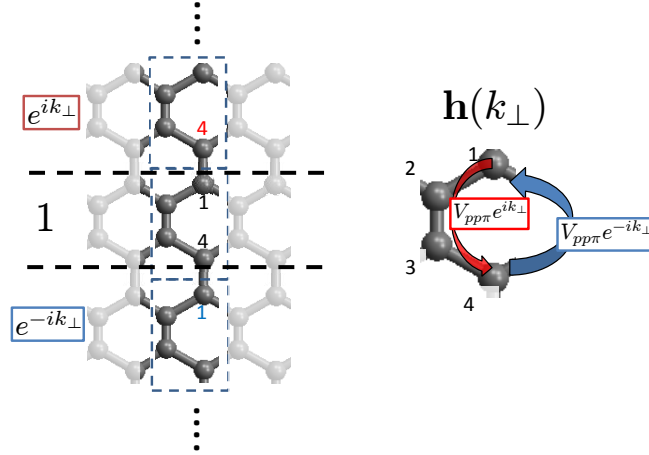


Figure 22: Periodic boundary conditions perpendicular to the transport direction makes all matrices dependent on transverse wavenumber, k_\perp . The Hamiltonian elements can be setup by considering to which transverse cell the sites belong.

6.4 Beyond single-orbital tight-binding: Slater-Koster approach

In order to describe the electronic structure of carbon systems with deviations from the flat situation or where atoms are bonded with sp^3 hybridization, e.g. with 4 neighbors we need to include at least all valence orbitals (s, p_x, p_y, p_z). This is done with the next step in approximation known as Slater-Koster theory. It is but is discussed in textbooks[7, 9]. Each carbon atom (that means on-site and hops) are

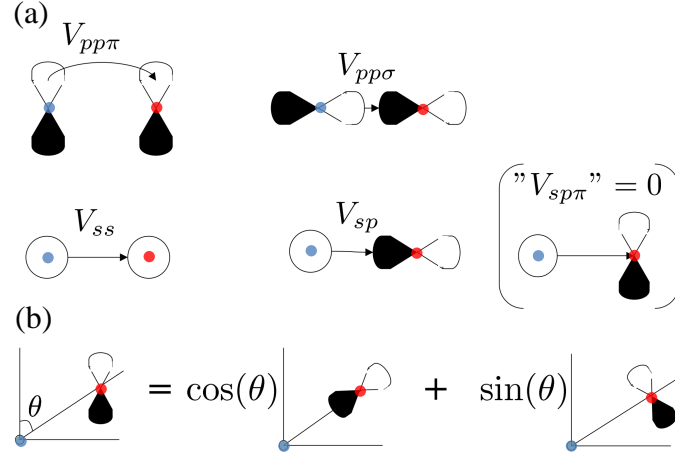


Figure 23: (a) Different possible matrix elements between s and p_x , p_y and p_z orbitals on two atoms. (b) For two atoms where the connecting unitvector is not along x, y, z we can split a p orbitals into two orbitals.

now represented by a 4×4 matrix. The on-site energy and hopping matrix elements in the Hamiltonian are replaced by 4×4 matrices representing the 4 orbitals (s, p_x, p_y, p_z) on each atom. The on-site is a diagonal matrix describing the energy difference between s and p orbitals,

$$\varepsilon = \Delta \left(\{ \varepsilon_s, \varepsilon_s, \varepsilon_s, \varepsilon_s \} \right), \quad (150)$$

and the hopping between nearest neighbours,

$$\mathbf{V}_{SK}(l, m, n) = \begin{pmatrix} V_{ss} & lV_{sp} & mV_{sp} & nV_{sp} \\ -lV_{sp} & l^2V_{pp\sigma} + (1-l^2)V_{pp\pi} & lm(V_{pp\sigma} - V_{pp\pi}) & ln(V_{pp\sigma} - V_{pp\pi}) \\ -mV_{sp} & lm(V_{pp\sigma} - V_{pp\pi}) & m^2V_{pp\sigma} + (1-m^2)V_{pp\pi} & mn(V_{pp\sigma} - V_{pp\pi}) \\ -nV_{sp} & ln(V_{pp\sigma} - V_{pp\pi}) & mn(V_{pp\sigma} - V_{pp\pi}) & n^2V_{pp\sigma} + (1-n^2)V_{pp\pi} \end{pmatrix} \quad (151)$$

The l, m, n are "direction-cosines" which can be found from the normalized vector connecting the two atoms, $\hat{e} = (l, m, n) = (\vec{r}_2 - \vec{r}_1)/|\vec{r}_2 - \vec{r}_1|$. For carbon we have parameters (in eV), $\varepsilon_s = -6$, $\varepsilon_p = 0$, $V_{ss} = -4.8$, $V_{sp} = 4.3$, $V_{pp\sigma} = 4.4$, and $V_{pp\pi} = 2.8$. The σ and π do not refer to orbitals but to the character (angular momentum) of the bonding around the axis connecting the two atoms. So p orbitals can make both a σ and a π type of bond depending on their orientation relative to the connecting axis.

For bilayer graphene (or, in general, coupling between two flat carbon systems each described only with pi -orbitals) we need a model including the interaction between π -orbitals inside a plane and *between* planes. For bilayer graphene the inter-planar distance is about $d_{gg} = 3.4\text{\AA}$ and while π -orbitals in different layers on top of each other are coupled by $V_{pp\sigma}$, and for general positions involve also a mix of $V_{pp\pi}$, but scaled according to the inter-atomic distance. One example of a model parameters²¹ for the hop between p_z -orbitals in graphenes lying in xy is,

$$V = V_{pp\pi} \sin(\theta)^2 + V_{pp\sigma} \cos(\theta)^2, \quad (152)$$

where

$$V_{pp\pi} = V_{pp\pi}^0 e^{-(R-d_0)/r_0} \text{ and } V_{pp\sigma} = V_{pp\sigma}^0 e^{-(R-d_{gg})/r_0} \quad (153)$$

with $r_0 \approx 0.45\text{\AA}$, $V_{pp\pi}^0 \approx -2.7 \text{ eV}$, and $V_{pp\sigma}^0 \approx -0.48 \text{ eV}$

²¹Interlayer interaction in general incommensurate atomic layers, M. Koshino, <http://arxiv.org/abs/1501.02116v1>.

6.5 Link to the real-space formulation

Here we will make connection to the formula for transmission (Eq. 120) to the usual expression for current-density in the real-space formulation of quantum mechanics. Consider the current originating from the single, right flux-normalized scattering states (labelled by r) at a particular energy, E . The flux of a flux-normalized scattering wavefunction integrated over a surface yields the transmission, T . Consider a surface, σ_{12} , located inside the scattering region (cf. Fig. 20),

$$T = \frac{\hbar}{m} \text{Im} \sum_r \int_{\sigma_{12}} d\vec{\sigma} \cdot (\Psi_r^*(\vec{r}) \vec{\nabla} \Psi_r(\vec{r})) \quad (154)$$

$$= \frac{\hbar}{m} \text{Im} \sum_r \int_{V_1} d\vec{r} \Psi_r^*(\vec{r}) \vec{\nabla}^2 \Psi_r(\vec{r}). \quad (155)$$

Here we have used Green's theorem to rewrite the surface integral as a volume integral over region 1. We have that in region 1 Ψ_r fulfil Schrödinger's equation where the boundary to the left is included as a self-energy²²,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + \int d\vec{r}' \Sigma_L(\vec{r}, \vec{r}') \right] \Psi_r(\vec{r}) = E \Psi_r(\vec{r}), \quad (156)$$

where the integral is over the support of Σ_L . The dividing surface, σ_{12} , is *arbitrary* as long as it is located within the freely chosen scattering region, where the current is defined in the NEGF formalism, and does not overlap with the support of Σ . Using Eq. 155 in Eq. 156 we can obtain,

$$T = \frac{\hbar}{m} \text{Im} \sum_r \int_{V_1} d\vec{r} (\Psi_r^*(\vec{r}) \vec{\nabla}^2 \Psi_r(\vec{r})) \quad (157)$$

$$= \frac{1}{\hbar} \sum_r \int d\vec{r} \int d\vec{r}' \Psi_r^*(\vec{r}) \Gamma_L(\vec{r}, \vec{r}') \Psi_r(\vec{r}'). \quad (158)$$

We can think of the expression in terms of an infinitely dense real-space grid basis where Γ_R is only non-zero at the dividing surface. This formula is again identical with Eq. 5.3 if we consider a discretization of real space(x),

$$T = \sum_{x, x'} \Gamma_L(x, x') A_R(x', x) = \text{Tr}[\mathbf{\Gamma}_L \mathbf{A}_R]. \quad (159)$$

Here we have defined the and the *right spectral function*,

$$\mathbf{A}_R = 1/\hbar \sum_r (|\Psi_r\rangle \langle \Psi_r|). \quad (160)$$

This function (matrix) actually describes the density of scattering states originating from the right electrode. We can interpret Eq. 159 as a measurement of current into the left electrode ($\mathbf{\Gamma}_L$) of states starting in the right electrode (\mathbf{A}_R). It can be shown (as an extra exercise) that $\mathbf{A}_R = \mathbf{G} \mathbf{\Gamma}_R \mathbf{G}^\dagger$ and that Eq. 160 is equivalent to Eq. 120. The local density of states of right-moving states on site l is given by $(\mathbf{A}_R)_{ll}(E)$, and equally for L .

6.6 Quantum heat transport

Heat can be carried by atomic vibrations (and electrons) between two reservoirs with different temperature. The transport of heat through a scattering region between two lattices via a nano-scale region can be calculated in complete analogue to the electronic case discussed previously if all interactions are assumed to be harmonic. As with electrons the simplest case of an semi-infinite "electrode" is again a 1D chain, see Fig. 24.

²²Check e.g. out the book by Datta [8].

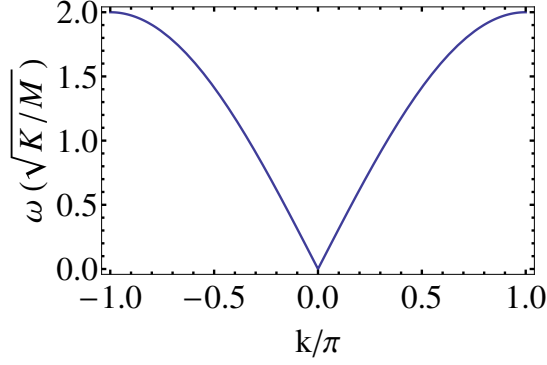
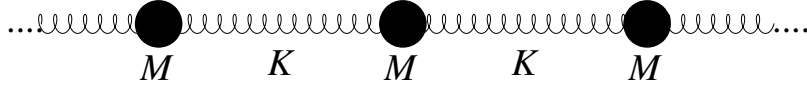


Figure 24: A simple model of a harmonic crystal consisting of a 1D chain of masses (M) which can move in 1D along the chain (longitudinal phonons). In the simplest case we may assume only nearest neighbor interactions via springs with spring-constant K .

For the electrons (particles) Schrödinger's equation yield a wavefunction which in the tight-binding case is a vector corresponding to the discrete atomic positions. For the chain we already in the classical case describe it by waves with an amplitude, a_j , at each position j . The amplitude simply describe the deviation from the equilibrium position of each mass, $a_j = \Delta x_j$. Interestingly, for harmonic systems the classical equation of motion for a_j is identical to the quantum equation²³ describing the quantum amplitude of the variable x_j . This is given by Newton's equation which can be written using the *dynamical matrix*, \mathbf{D} ,

$$\mathbf{D}a(t) = -\frac{\partial a(t)}{\partial t^2}, \quad (161)$$

where for the infinite chain we have,

$$\mathbf{D} = \frac{K}{M} \begin{pmatrix} \ddots & \ddots & \dot{0} & \vdots \\ \ddots & \ddots & -1 & \mathbf{0} \\ \mathbf{0} & -1 & 2 & -1 \\ \dots & 0 & \ddots & \ddots \end{pmatrix}. \quad (162)$$

This can be derived from the harmonic potential energy, $V(a)$,

$$V(a) = \frac{1}{2}K \sum_j (a_{j+1} - a_j)^2, \quad (163)$$

which yield give the force vector $F(a) = -\partial_a V(a)$ between atoms. In general $\mathbf{D}_{ij} = K_{ij}/\sqrt{M_i M_j}$, where K_{ij} is the spring-constant between atom i and j , which may have different masses M_i , M_j .

²³This can be seen if we use the harmonic oscillator, $\hat{H} = \frac{1}{2M}\hat{p}^2 + \frac{1}{2}K\hat{x}^2$. In this case Heisenberg's equation of motion $\frac{d\hat{p}}{dt} = i\hbar[\hat{p}, \hat{H}] = -K\hat{x}$, is exactly Newton's 2nd equation just replacing the classical variables with the corresponding quantum operators.

The dynamical matrix is symmetric and it looks exactly like the Hamiltonian matrix for electrons²⁴. As with electrons the time-independent states, or modes, are found using Fourier transform into frequency or energy,

$$\mathbf{D}a(\omega_k) = \omega_k^2 a(\omega_k). \quad (164)$$

This eigen-equation yields the vibrational mode vectors, a_k , and frequencies, ω_k , of these. In the infinite chain case we get the Bloch-modes $(v_k) = e^{ikj}$ and phonon-bandstructure $\omega(k) = \sqrt{K/M}(2 - 2\cos(k))$ (compare to electrons). Thus with respect to dynamics, as f.ex. presented by the retarded Green's function, we can instead of a tight-binding Hamiltonian representing the Schrödinger equation, consider the equation of motion (164), and formally replace,

$$\mathbf{H} \rightarrow \mathbf{D} \quad (165)$$

$$E + i\eta \rightarrow (\omega + i\eta)^2 \quad (166)$$

$$\mathbf{G}(E) = [\mathbf{1}(E + i\eta) - \mathbf{H}]^{-1} \rightarrow [\mathbf{1}(\omega + i\eta)^2 - \mathbf{D}]^{-1} \quad (167)$$

$$(168)$$

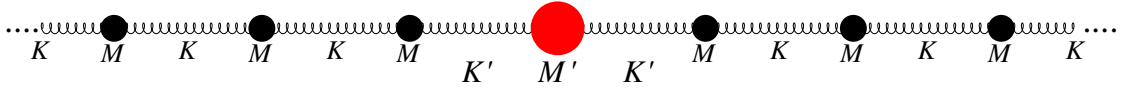


Figure 25: Simple setup for heat transport through a mass, M' , coupled via spring constants, K' , to homogeneous 1D atomic chains.

When it comes to transport of heat we can just follow the procedures for tight-binding. Again, we formally divide our system into a left, central, and right regions. The left and right contacts are modeled as two semi-infinite periodic harmonic structures just like the electronic case. The simplest case would be two harmonic chains with nearest neighbor springs, see Fig. 25. Unlike electrons which are fermions, the quantum harmonic vibrations or phonons are bosons. Thus these are occupied according to the Bose-Einstein distribution function, $n_B(\hbar\omega, T) = 1/(\exp(\hbar\omega/k_B T) - 1)$. Analogous to the Landauer formula for electron(charge) transport the heat or energy flow between the two reservoirs with temperatures,

$$I_{th} = \int_0^\infty d\omega \mathcal{T}_{ph}(\omega) \hbar\omega (n_B(\omega, T + \Delta T) - n_B(\omega, T)), \quad (169)$$

where $\mathcal{T}_{ph}(\omega)$ now is the transmission function for phonons. Here instead of charge (e) we are transporting energy ($\hbar\omega$). In the limit of small temperature difference we get the thermal conductance, $\kappa(T) = dI_{th}/dT$,

$$\kappa(T) = \frac{\hbar^2}{2\pi k_B T^2} \int_0^\infty d\omega \omega^2 \mathcal{T}_{ph}(\omega) \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}. \quad (170)$$

Exercise 31 Derive Eq. 170 from Eq. 169.

The calculation of the transmission, $\mathcal{T}_{ph}(\omega)$, for classical vibration-waves or quantum phonons in harmonic media does not differ. The equations of motion are similar for phonons/harmonic oscillators (but quantum mechanics kicks in when we consider the occupations).

²⁴However, there is additional symmetries of the dynamical matrix stemming from the fact that $\sum_i K_{ij} = \sum_j K_{ij} = 0$. This can be seen by the fact that the force on a single particle or degree of freedom (i) equals minus the force on all remaining particles (j).

Exercise 32 In the limit of low temperature only vibrations with a frequency approaching (long wavelength acoustic modes) will contribute to the conductivity. Since their wavelength is approaching infinity they will not be scattered and their corresponding $\mathcal{T}_{ph}(\omega) \rightarrow 1$ (1D). Derive that a single acoustic phonon-mode will yield the universal quantum of heat-conductance, $G_Q(T) = \pi^2 k_B^2 T / 3h$.

Further reading

- *Electronic Transport in Mesoscopic Systems* by Supriyo Datta, Cambridge University Press, Cambridge (1995). This is an oldie-but-goldie. There are other updated books by the same author.
- *Molecular Electronics: An Introduction to Theory and Experiment* by Juan-Carlos Cuevas and Elke Scheer, World Scientific Publishers (2010). Combination of both theory and experiments.

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