Chapter 6

Summary and Conclusions

In this thesis we investigated the transport properties of two-terminal devices in which carbon chains act as model interconnects between metal or graphene electrodes.

In the first part of the thesis, we investigated the electronic and charge transport properties of carbon chains contacted with two ideal metallic (silver) electrodes.

As a first step, we studied the binding properties of -C_n, -C_nH and -C_nH_2 radical species on the three highest symmetry sites (top, hollow and bridge) of the silver Ag(100) surface, finding that the binding energies strongly correlate with the coordination number between the terminal carbon atom of the chain and the surface: the higher the coordination number the more stable the adsorbed system.

Next we computed the zero-bias transmission spectra for chains from C_2 to C_{12}, observing a significative dependence on the adsorption site. Specifically both the chain-electrode coupling and the broadening of the resonances result strictly correlated to the coordination number: the higher the coordination number, the stronger the coupling and the wider the resonances. On the other hand, only a weak dependence on the chain length was found.

This, in turn, is reflected on the current-bias characteristics, with the hollow-bound chains providing the highest current as a consequence of higher transmission values across the Fermi level region.

To take a deeper look on the effect of electrode geometry on the transport properties, we further investigated systems where the carbon chain is bound to different silver (more realistic) tips. With respect to the binding on the ideal Ag(100) surface, we found minor differences in the transmission spectra, provided the appropriate binding model is chosen, due to some “incomplete” binding of the tip atoms. Hence, although the geometry of the electrode influences the transmission probabilities, the overall transport properties are mainly determined by the characteristics of the Ag-C bonds (*i.e.* the bond strength).

In order to better understand the role of the electrode-molecule junction, we also investigated the electronic and transport properties of sulfur- and silicon-capped C_4 chain, bound in the above mentioned sites. The linking atoms turn out to have significative effects on the transport properties, considerably reducing the chain-electrode coupling and causing an overall reduction of the transmission function.

Next, by performing phonon analysis, we observed that the vibrational motion of the atoms has negligible effects on the transmission and then on the transport properties, resulting in stable current values for a very large range of temperature as a consequence of the stiffness of polyynes.

Finally, we also critically discussed the reliability of our results, finding that the adopted setup leads to an underestimation of the bandgap, resulting in an overestimation of the current. However, this is a well-known problem related to the inaccuracy of the single-particle spectra calculated at Density Functional Theory level.

In the second part of the thesis, we examined the transport properties of carbon chains contacted with graphene electrodes.In particular we focused our attention on single chains bound on zigzag and armchair electrodes considering different junction geometries. We found close similarities between the two edge configurations. In fact, the formation of a ring at the junction causes (i) the BLA to be inverted, (ii) the chain to acquire a more marked radicalic character and (iii) the coupling with the electrodes to be weakened, if compared to single-bound chains. This, in turn, lead to a general reduction of the transmission probabilities and causes the resonances to approach the Fermi level, confirming the key role of the junction geometry in determining the transport properties. Moreover, for both edge-shaped electrodes, the chain-electrode coupling is strong enough to cause the identity of the ($\pi_\perp$) chain states to be lost, each one giving rise to a number of electronic states delocalized on the whole system as a consequence of the strong hybridization with the π electron clouds of graphene. This turns out to be one of the main differences between metallic and graphene electrodes. In fact, the chain-silver coupling is not strong enough to affect the geometric and electronic structure of the chain in a significative way, hence the chain states, although hybridized with the electrode ones, maintain their characteristics. As opposite, the chain-graphene junction can strongly modify the structural properties of the chain (BLA, linearity, etc), affecting, in turn, the electronic and the transport properties of the system. Another relevant difference between silver and graphene electrodes is the maximum theoretical value of the transmission, being 4 and 2, respectively, since in the latter case only the π chain states orthogonal to the electrode plane hold the conduction process.

We further investigated different electrode geometries, in particular we considered chains connected to pentagonal and triangolar tips, finding that, as opposite of the Ag-chain-Ag systems, the tip has significative effects on the transport properties. In particular, the triangular tips nullify the transmission in a large region across the Fermi level as a consequence of the complete decoupling of the $HOMO$ of the chain from the electrodes.

Next, we investigated double chains at different interchain distances, since these structures are expected to show quantum interference effects. We found different interference patterns depending on the chain length, on the interchain distance and on the contact geometry. We further considered the possibility to achieve chemical gating in such structures, finding that a Li atom can be used to this aim.

We also investigated molecules able to switch between high- and low-conductive states, making them good candidates for molecular switches applications. Specifically we considered systems in which an aromatic hydrocarbon is inserted in the middle of a chain, allowing the current to be switched on and off by mechanical rotation of the molecule. We found that some electronic states turn out to be conductive in the “off” configuration, while hydrogenation of the dangling bonds of the aromatic hydrocarbon lead to higher on/off ratio.

In conclusion, polyynes can find applications in molecular electronics as molecular wires, but with some important limitations, from an experimentally point of view, due to the high sensibility of the transport properties on the geometry of the system and on the characteristics of the junctions.

Appendix A

Green's Functions

A.1 Green's matrix

Suppose we wish to solve the following linear matrix equation for the column vector **f**:

$$(E\mathbf{I}-\hat{\mathbf{H}}_{\mathbf{0}})\mathbf{f}=\mathbf{g} \tag{A.1}$$

where E is a parameter, $\hat{\mathbf{H}}_{\mathbf{0}}$ is a N x N hermitian matrix and **f** and **g** are column matrixes. The most straightforward way to proceed is to calculate the inverse matrix $(E\mathbf{I}-\hat{\mathbf{H}}_{\mathbf{0}})^{-1}$, denoted as $\mathbf{G_0}$:

$$\mathbf{f}=(E\mathbf{I}-\hat{\mathbf{H}}_{\mathbf{0}})^{-1}\mathbf{g}=\mathbf{G_0}(E)\mathbf{g} \tag{A.2}$$

or, writing explicitly the matrix elements of $\mathbf{G_0}$:

$$f_i=\sum_j (G_0(E))_{ij}g_j \tag{A.3}$$

$\mathbf{G_0}$ is called the *Green's matrix* associated to the operator $\hat{\mathbf{H}}_{\mathbf{0}}$, and can be expressed in terms of its eigenvalues and eigenvectors:

$$\hat{\mathbf{H}}_{\mathbf{0}}\mathbf{c}^{\alpha}=\mathbf{E}_{\mathbf{0}}^{\alpha}\mathbf{c}^{\alpha} \tag{A.4}$$

as

$$(G_0(E))_{ij}=\sum_{\alpha}\frac{c_i^{\alpha}c_j^{\alpha *}}{E-E_0^{\alpha}} \tag{A.5}$$

Notice that each Green's matrix element has poles for values of E equal to the eigenvalues of $\hat{\mathbf{H}}_{\mathbf{0}}$, *i.e.* the eigenvalues represent values for which $\mathbf{G_0}$ does not exist. In a more general case, the Hamiltonian contains also a potential term $\mathbf{V}$:

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_{\mathbf{0}} + \mathbf{V} \tag{A.6}$$

The associated Green's matrix becomes:

$$\mathbf{G}(\mathbf{E}) = (E\mathbf{I} - \hat{\mathbf{H}}_{\mathbf{0}} - \mathbf{V})^{-1} \tag{A.7}$$

Using eq. A.7 and the expression for $\mathbf{G_0}$, one can easily derive the following equation:

$$\mathbf{G}(\mathbf{E}) = \mathbf{G_0}(\mathbf{E}) + \mathbf{G_0}(\mathbf{E})\mathbf{V}\mathbf{G}(\mathbf{E}) \tag{A.8}$$

This is the matrix form of the so-called *Dyson equation*.
As we will see in the following, the Green's function for a differential equation is simply a continuous generalization of the Green's matrix.

A.2 One-particle Green's function

Let's suppose we wish to solve the inhomogeneous differential equation for $f(x)$:

$$(E - \hat{H}_0)f(x) = g(x) \tag{A.9}$$

It is possible to expand $f(x)$ and $g(x)$ in terms of the eigenfunctions of $\hat{H}_0$:

$$\hat{H}_0 \psi^\alpha(x) = E_0^\alpha \psi^\alpha \tag{A.10}$$

as:

$$f(x) = \sum_\alpha f_\alpha \psi^\alpha(x) \tag{A.11}$$

$$g(x) = \sum_\alpha g_\alpha \psi^\alpha(x) \tag{A.12}$$

Since the eigenvectors form an orthogonal set and $g(x)$ is known, the coefficients g_α of the expansion can be calculated as:

$$g_\alpha = \int dx' \psi^{\alpha*}(x')b(x') \tag{A.13}$$

Substituting eq. A.11 and A.12 in the A.9 and using A.10 we obtain:

$$\sum_{\alpha}(E-\hat{H}_0)\psi^{\alpha}(x)=\sum_{\alpha}(E-E_0^{\alpha})\psi^{\alpha}(x)=\sum_{\alpha}g_{\alpha}\psi^{\alpha}(x) \tag{A.14}$$

Multiplying both sides by $\psi^{\alpha *}(x)$ and integrating over x we derive an expression for g_{α}:

$$g_{\alpha}=f_{\alpha}(E-E_0^{\alpha}) \tag{A.15}$$

Substituting eq. A.15 and A.12 into eq. A.11, we obtain an expression for $f(x)$:

$$f(x)=\sum_{\alpha}\frac{g_{\alpha}}{E-E_0^{\alpha}}\psi^{\alpha}(x)=\int dx'\left[\sum_{\alpha}\frac{\psi^{\alpha *}(x')\psi^{\alpha}(x)}{E-E_0^{\alpha}}\right]g(x') \tag{A.16}$$

Defining the *Green's function* as:

$$G_0(x,x',E)=\sum_{\alpha}\frac{\psi^{\alpha *}(x')\psi^{\alpha}(x)}{E-E_0^{\alpha}} \tag{A.17}$$

eq. A.16 can be rewritten as:

$$f(x)=\int dx' G_0(x,x',E)g(x') \tag{A.18}$$

Thus we have reduced the problem of solving the inhomogeneous differential equation A.9 to an integration (eq. A.18). Notice that $G_0(x,x',E)$ is independent on $g(x)$, thus once $G_0(x,x',E)$ is known, we can easily calculate $f(x)$ for any given $g(x)$.

Let's consider the case in which $g(x)$ is the δ Dirac function to find the differential equation obeyed by $G_0(x,x',E)$, *i.e.* in order to evaluate it:

$$g(x)=\delta(x-x') \tag{A.19}$$

for which eq. A.18 reads:

$$f(x)=\int dx'' G_0(x,x'',E)\delta(x-x')=G_0(x,x',E) \tag{A.20}$$

Thus the corresponding differential equation is:

$$(E-\hat{H}_0)G_0(x,x',E)=\delta(x-x') \tag{A.21}$$

then:

$$G_0(x,x',E)=\frac{\delta(x-x')}{E-\hat{H}_0} \tag{A.22}$$

In matrix form, this is analogues to:

$$(\mathbf{EI}-\hat{\mathbf{H}}_\mathbf{0})\mathbf{G_0}(\mathbf{E}) = (\mathbf{EI}-\hat{\mathbf{H}}_\mathbf{0})(\mathbf{EI}-\hat{\mathbf{H}}_\mathbf{0})^{-1} = \mathbf{I} \tag{A.23}$$

Thus the Green's function is defined by a problem where the inhomogeneous term in the differential equation is a delta function. If one knows the Green's function of a problem one can write down its solution in a closed form as the convolution of the Green's function and the functions appearing in the *r.h.s.* of the inhomogeneous equation. From a physical point of view, the Green's function represents the impulse response describing how the system reacts to a single point perturbation at x', represented by the delta function. Then, the integration over a distribution of source points x', given by $g(x')$, will lead to the total response of the system at point x, represented by $f(x)$.
Now let's consider the Hamiltonian

$$\hat{H} = \hat{H}_0 + V(x) \tag{A.24}$$

and we know the Green's function associated to $\hat{H}_0$. The differential equation associated to $\hat{H}$ is:

$$(E-\hat{H}_0 - V(x))G_0(x,x',E) = \delta(x-x') \tag{A.25}$$

After rearrangement and calculating the integral involving the δ function we obtain:

$$(E-\hat{H}_0)G(x,x',E) = \delta(x-x') + V(x)G(x,x',E) \tag{A.26}$$

$$G(x,x',E) = \int dx'' G_0(x,x'',E)\Big[\delta(x''-x') + V(x'')G(x'',x',E)\Big] \tag{A.27}$$

$$G(x,x',E) = G_0(x,x',E) + \int dx'' G_0(x,x'',E)V(x'')G(x'',x',E) \tag{A.28}$$

Eq. A.28 is called *Dyson equation* and is the continuous analogue of eq. A.8.

A.3 One-particle many-body Green's function

To generalize Green's function theory to many-body systems the first step is to consider an independent particle approximation, such as Hartree-Fock or density functional theory, for which:

$$\hat{H}_0 = \sum_i f(i) \tag{A.29}$$

Within this approximation we obtain a set of spin orbitals $\chi(x)$ and orbital energies ε by solving the equation:

$$f(i)\chi_i(x) = \varepsilon_i \chi_i(x) \tag{A.30}$$

Analogously to eq. A.17 we can define the Green's function as:

$$G_0(x,x',E) = \sum_i \frac{\chi_i^*(x)\chi_i(x')}{E-\varepsilon_i} \tag{A.31}$$

The matrix elements of the Green's function in the basis of spin orbitals are:

$$(G_0(E))_{ij} = \int\int dx dx' \chi_i^*(x) G_0(x,x',E)\chi_i(x') = \frac{\delta_{ij}}{E-\varepsilon_j} \tag{A.32}$$

Thus, in this basis, the Green's matrix reads as:

$$\mathbf{G_0(E)} = (E\mathbf{I} - \varepsilon)^{-1} \tag{A.33}$$

where ε is the diagonal matrix containing the orbital energies.

It is evident that $\mathbf{G_0(E)}$ has poles corresponding to the orbital energies, but recalling that Koopman's theorem states that these orbital energies are related to the ionization potentials and electron affinities of a N-particle system, these energies are also related to the (approximated) energy difference between the N- and the $N \pm 1$-particle system. Of course to get the exact ionization potentials or electron affinities, the Koopman's theorem must be corrected by the relaxation energies of the $N \pm 1$-particle system and the difference in correlation energy between the N- and $N \pm 1$-particle system.

Apparently it seems difficult to have an approximation of $G(E)$ better than G_0 retaining the one-particle picture, due to the two-particle term in the Hamiltonian. But this problem can be overcome introducing an effective energy dependent potential, called *self-energy*, in the Dyson equation:

$$\mathbf{G(E)} = \mathbf{G_0(E)} + \mathbf{G_0(E)}\Sigma\mathbf{(E)}\mathbf{G(E)} \tag{A.34}$$

where $\Sigma\mathbf{(E)}$ is the matrix representation of the exact self-energy in the base of the one-particle spin-orbitals. Rearranging eq. A.34 and using eq. A.33 we obtain:

$$(\mathbf{G_0(E)})^{-1} = (\mathbf{G(E)})^{-1} + \Sigma\mathbf{(E)} \tag{A.35}$$

$$\mathbf{G(E)} = (\mathbf{G_0(E)})^{-1} - \Sigma\mathbf{(E)})^{-1} = (E\mathbf{I} - \varepsilon - \Sigma\mathbf{(E)})^{-1} \tag{A.36}$$

It is worth highlight that the above formalism is exact, thus $\mathbf{G}(\mathbf{E})$ has poles corresponding to the exact ionization potentials and electron affinities of the N-particle system. Of course if one has to make approximations in Green's function theory, one approximates the self-energy. Expanding $\Sigma(\mathbf{E})$ in a perturbation series:

$$\Sigma(\mathbf{E}) = \Sigma^{(1)}(\mathbf{E}) + \Sigma^{(2)}(\mathbf{E}) + \Sigma^{(3)}(\mathbf{E}) + \dots \tag{A.37}$$

one can cut off this expansion at a given order. Notice that if $\Sigma(\mathbf{E}) = 0$, then $\mathbf{G}(\mathbf{E}) = \mathbf{G_0}(\mathbf{E})$.

A.4 Propagators

The dynamics of a system evolving in time is described by the time-dependent Schroedinger equation:

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \hat{H}\psi(x,t) \tag{A.38}$$

In order to describe a physical problem we need to specify the initial conditions. Such general initial condition problem can be solved through the introduction of the Green's functions. The Green's function $G(x,t,x',t')$ represents the solution to the Schroedinger equation for the particular condition where the particle is at position x' at time t':

$$\lim_{t \to t'} \psi(x,t) = \delta(x - x') \tag{A.39}$$

Thus the Green's function describes the time evolution of the particle from (x',t') to (x,t) and is usually called *propagator*. It is useful to introduce the *retarded propagator* as follows:

$$G^R(x,t,x',t') = \begin{cases} -iG(x,t,x',t') & \text{if } t \geq t' \\ 0 & \text{if } t < t' \end{cases} \tag{A.40}$$

or, introducing the heaviside function θ:

$$\theta(t - t') = \begin{cases} 1 & \text{if } t \geq t' \\ 0 & \text{if } t < t' \end{cases} \tag{A.41}$$

eq. A.40 can be rewritten as:

$$G^R(x,t,x',t') = -i\theta(t - t')G(x,t,x',t') \tag{A.42}$$

$G^R(x,t,x',t')$ satisfies the equation:

$$\left(i\hbar\frac{\partial}{\partial t} - \hat{H}\right)G^R(x,t,x',t') = \hbar\delta(x-x')\delta(t-t') \tag{A.43}$$

with the initial condition:

$$\lim_{t\to t'} G^R(x,t,x',t') = -i\delta(x-x') \tag{A.44}$$

The retarded propagator propagates the wavefunction forward in time and can have the following interpretation: prior to time t' the particle is absent, at time t' the particle is created at point x' and subsequently propagates accordingly to the Schroedinger equation. The wavefunction at time t is then given by:

$$\psi(x,t) = i\int dx' G^R(x,t,x',t')\psi(x',t') \tag{A.45}$$

Analogously we can define an *advanced propagator*:

$$G^A(x,t,x',t') = \begin{cases} 0 & \text{if } t \geq t' \\ iG(x,t,x',t') & \text{if } t < t' \end{cases} = -i\theta(t'-t)G(x,t,x',t') \tag{A.46}$$

which propagates the wavefunction backwards in time, but is still a solution of an equation analogue to eq. A.43.
It is also useful to introduce the advanced and retarded *Green's operators*, which are related to the time evolution operator $U(t,t')$ by:

$$G^R(t,t') = -i\theta(t-t')\hat{U}(t,t') \tag{A.47}$$

$$G^A(t,t') = i\theta(t'-t)\hat{U}(t,t') \tag{A.48}$$

Of course these operators satisfy the differential equation:

$$\left(i\hbar\frac{\partial}{\partial t} - \hat{H}\right)G^{R(A)}(t,t') = \delta(t-t') \tag{A.49}$$

Using the above relations, it turns out that the Green's function is related to the time evolution operator $\hat{U}(t,t')$ and to the Green's operators trough:

$$\begin{aligned} G(x,t,x',t') = \langle x|\,\hat{U}(t,t')\,|x'\rangle &= i[G^R(x,t,x',t') - G^A(x,t,x',t')] \\ &= i\,\langle x|\,G^R(t,t') - G^A(t,t')\,|x'\rangle \end{aligned} \tag{A.50}$$

thus:

$$\hat{U}(t,t') = i[G^R(t,t') - G^A(t,t')] = G(t,t') \tag{A.51}$$

The unitarity of the time-evolution operator is reflected into the hermitian relationship of the Green's operators:

$$G^R(t,t') = [G^A(t,t')]^\dagger \tag{A.52}$$

A.5 Propagation in a potential

Let's consider first the case of a free particle with momentum p and mass m propagating in time, whose Hamiltonian is:

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} \tag{A.53}$$

The propagator can be easily obtained in the momentum representation and depends only on the time difference:

$$G_0^R(p,t,p',t') = i\theta(t-t')\,\langle p|\, e^{-\frac{i}{\hbar}\hat{H}_0(t-t')}\,|p'\rangle \tag{A.54}$$

$$= i\theta(t-t')e^{-\frac{i}{\hbar}\hat{H}_0(t-t')}\,\langle p|p'\rangle \tag{A.55}$$

$$= i\theta(t-t')e^{-\frac{i}{\hbar}\frac{p^2}{2m}(t-t')} = G_0^R(p,t,t') \tag{A.56}$$

Fourier transforming we obtain the the propagator in the spatial representation:

$$G_0^R(x,t,x',t') = i\theta(t-t')\,\langle x|\, e^{-\frac{i}{\hbar}\hat{H}_0(t-t')}\,|x'\rangle \tag{A.57}$$

$$= i\theta(t-t')\left(\frac{m}{2\pi\hbar i(t-t')}\right)^{\frac{1}{2}} e^{-\frac{im}{2\hbar}\frac{(x-x')^2}{(t-t')}} \tag{A.58}$$

If a time-independent potential V is introduced in the Hamiltonian, such as in the case of an isolated system,

$$\hat{H} = \hat{H}_0 + V(x) \tag{A.59}$$

the propagator reads as:

$$G^R(x,t,x',t') = G^R(x,x',t-t') = \langle x|\, e^{-\frac{i}{\hbar}\hat{H}(t-t')}\,|x\rangle \tag{A.60}$$

Otherwise, if the environment influences the particle with a scalar time-dependent potential:

$$\hat{H} = \hat{H}_0 + \hat{V}_t \tag{A.61}$$

where the potential operator $\hat{V}_t$ is the potential function of the position operator $\hat{x}$, *i.e.* $\hat{V}_t = V(\hat{x},t)$. The retarded Green's function can be determined by evaluating the matrix elements of the time-evolution operator:

$$\begin{aligned} G^R(x,t,x',t') &= -i\theta(t-t')\,\langle x|\,U(t,t')\,|x\rangle \\ &= -i\theta(t-t')\,\langle x|\,Te^{-\frac{i}{\hbar}\int_{t'}^{t}dt''\hat{H}(t'')}\,|x\rangle \end{aligned} \tag{A.62}$$

where T is the time-ordered operator.

Those matrix elements can be calculated rewriting the time evolution operator in the interaction picture:

$$\begin{aligned} U(t,t') &= U_0(t,t_r)U_I(t,t')U_0^\dagger(t',t_r) \\ &= U_0(t,t_r)Te^{-\frac{i}{\hbar}\int_{t'}^{t}dt''\hat{V}_I(t'')}U_0^\dagger(t',t_r) \end{aligned} \tag{A.63}$$

where the potential operator in the interaction picture is given by:

$$\hat{V}_I(t) = U_0^\dagger(t,t_r)V(\hat{x},t)U_0(t',t_r) \tag{A.64}$$

and $\hat{U}_0(t,t_r) = e^{-\frac{i}{\hbar}H_0(t-t_r)}$. Notice that the potential operator $\hat{V}_I(t)$ is the potential function of the position operator in the interaction picture, *i.e.*:

$$\hat{V}_I(t) = V(\hat{x}_I(t),t) \tag{A.65}$$

where

$$\hat{x}_I(t) = U_0^\dagger(t,t_r)\,\hat{x}\,U_0(t',t_r) \tag{A.66}$$

Indicating with $|x,t\rangle$ the eigenstate of $\hat{x}_I(t)$:

$$\hat{x}_I(t)\,|x,t\rangle = x\,|x,t\rangle \tag{A.67}$$

the action of $\hat{V}_I(t)$ on such states is turned into the multiplication by the value of the potential at (x,t):

$$\hat{V}_I(t)\,|x,t\rangle = V(\hat{x}_I(t),t)\,|x,t\rangle = V(x,t)\,|x,t\rangle \tag{A.68}$$

In the following we will omit the index I, *i.e.* $\hat{x}_I(t) \equiv \hat{x}(t)$. Now we can calculate the perturbation expansion of the propagator by expanding the time-ordered exponential:

$$G^R(x,t;x',t') = -i\theta(t-t')\,\langle x,t|\,Te^{-\frac{i}{\hbar}\int_{t'}^{t}dt''V_I(t'')}\,|x',t'\rangle = \sum_{n=0}^{\infty} G_n^R(x,t;x',t') \tag{A.69}$$

where the n-th order term of the propagator reads as:

$$G_n^R(x,t;x',t') = -i\theta(t-t')\left(\frac{-i}{\hbar}\right)^n \frac{1}{n!}\int_{t'}^{t}\prod_{m=1}^{n}\langle x,t|\, T(V(\hat{x}(t_n),t_n)\times$$

$$\times V(\hat{x}(t_{n-1}),t_{n-1})\dots V(\hat{x}(t_1),t_1))\,|x',t'\rangle \tag{A.70}$$

By inserting a complete set of the above defined eigenstates:

$$\hat{I} = \int dx\, |x,t\rangle\,\langle x,t| \tag{A.71}$$

in between of operators $V(\hat{x}(t_i),t_i)$ in the perturbative expansion, we can easily evaluate the terms of the expansion. The zeroth-order term, *i.e.* the propagator in absence of the potential is given by:

$$G_0^R(x,t;x',t') = -i\theta(t-t')\,\langle x|\, e^{-\frac{i}{\hbar}H_0(t-t')}\,|x'\rangle \tag{A.72}$$

The first-order term of the propagator is given by:

$$G_1^R(x,t;x',t') = \frac{1}{\hbar}\int_{t'}^{t} dt_1\,\langle x,t|\, V(\hat{x}(t_1),t_1)\,|x',t'\rangle \tag{A.73}$$

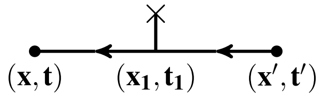
Since $t < t_1 < t'$, we can write the step function as:

$$\theta(t-t') = \theta(t-t_1)\theta(t_1-t') \tag{A.74}$$

and using eq. A.72 we obtain:

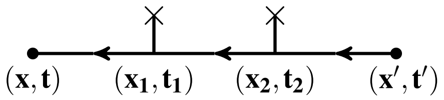
$$G_1^R(x,t;x',t') = -\frac{i}{\hbar}\int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dt_1 G_0^R(x,t;x_1,t_1)V(x_1,t_1)G_0^R(x_1,t_1;x',t') \tag{A.75}$$

where the time integral runs from $-\infty$ to $+\infty$ since the retarded propagators restrict the time integration to the original time interval. The first-order time propagator can be seen as the product of three terms: the amplitude for the free particle propagation from (x',t') to (x_1,t_1), where the particle experiences the effect of the potential described by the factor $V(x_1,t_1)$, and finally the amplitude for the free particle propagation from (x_1,t_1) to (x,t). Since the event of interaction with the potential can occur anywhere and at any times, we integrate over all such alternatives. It is helpful to rapidly evaluate the higher order term introduce the Feynman diagrammatic representation of G^R, in which a cross symbolize the interaction of the particle with the potential, let's say for instance a scattering event, and a line is used to represent the zeroth-order propagator:



$$\equiv \quad G_1^R(x,t;x',t')$$

Similarly we can built the second-order term of the propagator as:



$$\equiv \quad G_2^R(x,t;x',t')$$

Since integration is implied over the internal space-time points where interaction with the potential takes place, it becomes easy to write down the analytical equation corresponding to the above representation:

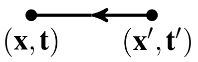
$$G_2^R(x,t;x',t') = -i\theta(t-t')\left(\frac{-i}{\hbar}\right)^2 \int_{t'}^{t} dt_2 \int_{t'}^{t_2} dt_1 \, \langle x,t|x_2,t_2\rangle \, V(x_2,t_2) \times$$
$$\langle x_2,t_2|x_1,t_1\rangle \, V(x_1,t_1) \, \langle x_1,t_1|x',t'\rangle = \tag{A.76}$$
$$= \frac{1}{\hbar^2}\int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{+\infty} dx_2 \int_{-\infty}^{+\infty} dt_2 G_0^R(x,t;x_2,t_2)V(x_2,t_2)\times$$
$$G_0^R(x_2,t_2;x_1,t_1)V(x_1,t_1)G_0^R(x_1,t_1;x',t') \tag{A.77}$$

where we have used the fact that for the time relationship $t' \leq t_1 \leq t_2 \leq t$ we can write the step function as:

$$\theta(t-t') = \theta(t-t_2)\theta(t_2-t_1)\theta(t_1-t') \tag{A.78}$$

With the same token, it is possible to sum the diagrams up to an infinite order, leading to the Dyson equation:

$$G^R(x,t;x',t') \quad \equiv$$



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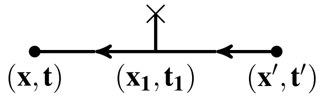

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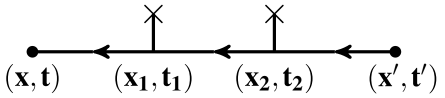

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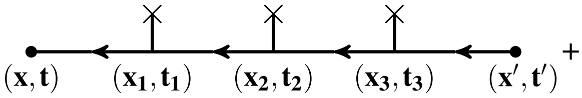
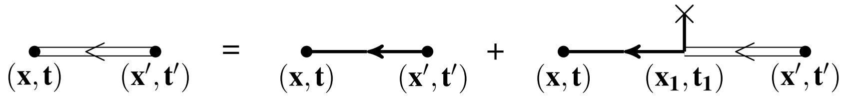


$+ \ldots$

This series of scattering processes is iterative, since each subsequent diagram has an extra interaction and propagator line. We indicate with a double line the propagator including further (infinite) scattering events, in order to distinguish it from the zeroth-order propagator. Thus the full propagator representation becomes:

$G^R(x,t;x',t') \equiv$



Analytically this corresponds to the equation:

$$G^R(x,t;x',t') = G_0^R(x,t;x',t') + \\ + \frac{i}{\hbar}\int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dt_1\, G_0^R(x,t;x_1,t_1)\, V(x_1,t_1)\, G^R(x_1,t_1;x',t') \tag{A.79}$$

Notice that all diagrams have the same type of structure, in the following sense: they are formed by an initial and a final Green's function (the same in all diagrams) and by a central part in which we can find the scattering processes. Obviously, this latter is the most interesting one. Such structure allows us to define the (improper) *self-energy* Σ_I as the sum of the central part of the diagrams of all orders.

$\Sigma_I \equiv$

Thus the expansion of the retarded Green's operators can be summarized in the following equation:

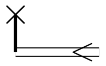
$$G^R(x,t;x',t') = G_0^R(x,t;x',t') + \\ \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{+\infty} dx_2 \int_{-\infty}^{+\infty} dt_2\; G_0^R(x,t;x_2,t_2)\, \Sigma_I(x_1,t_1,x_2,t_2)\, G_0^R(x_2,t_2;x',t') \tag{A.80}$$

or, in matrix notation

$$\mathbf{G^R} = \mathbf{G_0^R} + \mathbf{G_0^R}\, \Sigma_I\, \mathbf{G_0^R} \tag{A.81}$$

It is useful also introduce the proper self-energy Σ (called just self-energy in the following) as the part of the diagram that includes only a single scattering process and whose diagrammatic representation is simply:

$$\Sigma \equiv$$



If compared with the diagrammatic representation of Σ_I, it appears evident that the following relation holds (in matrix form):

$$\mathbf{\Sigma_I G_0^R} = \mathbf{\Sigma G^R} \tag{A.82}$$

allowing to write the Dyson's equation in its common form:

$$\mathbf{G^R} = \mathbf{G_0^R} + \mathbf{G_0^R}\Sigma\mathbf{G^R} \tag{A.83}$$

Notice that, due to the symmetry of the diagrammatic series, we could have chosen to write the above equation in an alternative way:

$$\mathbf{G^R} = \mathbf{G_0^R} + \mathbf{G^R}\Sigma\mathbf{G_0^R} \tag{A.84}$$

With the same token, we obtain for the advanced Green's function:

$$\mathbf{G^A} = \mathbf{G_0^A} + \mathbf{G^A}\Sigma\mathbf{G_0^A} \tag{A.85}$$

On the other hand notice that the Dyson's equation obtained for the one-particle problem is just a particular case of eq. A.83, which is valid for any electron systems.
The derivation of the analogue equations for the electron-electron interaction is more complicated and will not be reported here.

A.6 Analytic properties of Green's functions

For an isolated system, for which the Hamiltonian is time-independent, we can for any complex number E (which in the following will assume the meaning of an energy variable) with a positive imaginary part, transform the retarded Green's operator* defined in eq. A.47 according to:

$$G^+(E) = \frac{1}{\hbar}\int_{-\infty}^{+\infty} d(t-t')e^{\frac{i}{\hbar}E(t-t')}G^R(t-t') \tag{A.86}$$

---

*We use the notation ± for the retarded/advanced Green's operators in energy domain in order to distinguish them from time-domain operators where the Fourier transform is obtained as the analytic continuation from the upper half plane ($ImE > 0$). Of course the Green's operator must fulfill the equation:

$$(E-\hat{H})G^{+}(E)=\hat{I} \tag{A.87}$$

Analogously we obtain that the advanced operator satisfies an equation of the same form:

$$(E-\hat{H})G^{-}(E)=\hat{I} \tag{A.88}$$

for values of the energy E in the lower half-plane ($ImE < 0$), and by analytic continuation on the real axis we can evaluate the Fourier transform:

$$G^{-}(E)=\frac{1}{\hbar}\int_{-\infty}^{+\infty} d(t-t')e^{\frac{i}{\hbar}E(t-t')}G^{A}(t-t') \tag{A.89}$$

By inversion of the above equations we obtain the advanced and retarded Green's operators in time domain:

$$G^{R}(t)=\frac{1}{2\pi}\int_{-\infty+i\eta}^{+\infty+i\eta} dEe^{-\frac{i}{\hbar}Et}G^{+}(E) \tag{A.90}$$

$$G^{A}(t)=\frac{1}{2\pi}\int_{-\infty-i\eta}^{+\infty-i\eta} dEe^{-\frac{i}{\hbar}Et}G^{-}(E) \tag{A.91}$$

from which follows, in analogy with eq. A.52, the hermitian relationship:

$$G^{-}(E)=[G^{+}(E^{*})]^{\dagger} \tag{A.92}$$

Furthermore, always in analogy with the time-domain operators, we introduce the energy-domain Green's operator $G(E)$:

$$G(E)=\begin{cases} G^{+}(E) & \text{if } ImE>0 \\ G^{-}(E) & \text{if } ImE<0 \end{cases} \tag{A.93}$$

which admits spectral representation:

$$G(E)=\frac{1}{E-\hat{H}}=\sum_{\lambda}\frac{|\varepsilon_{\lambda}\rangle\langle\varepsilon_{\lambda}|}{E-\varepsilon_{\lambda}} \tag{A.94}$$

where $|\varepsilon_\lambda\rangle$ are the eigenstates of $\hat{H}$:

$$\hat{H}\,|\varepsilon_\lambda\rangle = \varepsilon_\lambda\,|\varepsilon_\lambda\rangle \tag{A.95}$$

and the identity representation has been used:

$$\sum_\lambda |\varepsilon_\lambda\rangle\,\langle\varepsilon_\lambda| = \hat{I} \tag{A.96}$$

The analytic properties of the retarded and advanced Green's operators leads, by an application of the Cauchy theorem, to the spectral representations:

$$G^+(E) = \int_{-\infty}^{+\infty} \frac{dE'}{2\pi} \frac{\hat{A}_{E'}}{E - E' + i\eta} \tag{A.97}$$

$$G^-(E) = \int_{-\infty}^{+\infty} \frac{dE'}{2\pi} \frac{\hat{A}_{E'}}{E - E' - i\eta} \tag{A.98}$$

where we have introduced the spectral operator $\hat{A}_E$, which accounts for the discontinuity of the Green's operator across the real axis:

$$\begin{aligned}\hat{A}_E = i(G^+(E) - G^-(E)) = i(G_{E+i\eta} - G_{E-i\eta}) = 2\pi\delta(E - \hat{H}) = \\ = 2\pi\sum_\lambda |\varepsilon_\lambda\rangle\,\langle\varepsilon_\lambda|\,\delta(E - \varepsilon_\lambda)\end{aligned} \tag{A.99}$$

as can be seen on using:

$$\begin{aligned}\frac{1}{E - E' + i\eta} - \frac{1}{E - i\eta - E'} = \frac{(E - i\eta - E') - (E - E' + i\eta)}{(E - E')^2 + \eta^2} = \\ = -\frac{2i\eta}{(E - E')^2 + \eta^2} = -\frac{2\pi i}{\pi}\frac{\eta}{(E - E')^2 + \eta^2}\end{aligned} \tag{A.100}$$

and taking the limit $\eta \to 0^+$:

$$G^+(E) - G^-(E) = -2\pi i\delta(E - \hat{H}) \tag{A.101}$$

where the density of state operator $\delta(E - \hat{H})$ has been introduced:

$$\delta(E - \hat{H}) = \lim_{\eta\to 0^+} \frac{1}{\pi}\frac{\eta}{(E - E')^2 + \eta^2} \tag{A.102}$$

By using eq. A.92 we can easily demonstrate that:

$$G^+(E) - G^-(E) = G^+(E) - G^+(E)^\dagger = 2iImG^+(E) \tag{A.103}$$

i. e.

$$ImG^+(E) = -\pi\delta(E - \hat{H}) \tag{A.104}$$

On the other hand the real part of $G^+(E)$ is given by:

$$ReG^+(E) = \lim_{\eta\to 0^+} \int Re\left[\frac{1}{E - E' + i\eta}\right] \delta(E' - \hat{H})dE' = \tag{A.105}$$

$$= \lim_{\eta\to 0^+} \int \frac{E - E'}{(E - E')^2 + \eta^2} \delta(E - \hat{H})dE' = \tag{A.106}$$

$$= P\int \frac{1}{E - E'} \delta(E - \hat{H})dE' = G^p(E) \tag{A.107}$$

where P indicates the principal value of the integral:

$$P\int \frac{f(E')}{E - E'}dE' = \lim_{\delta\to 0}\left\{ \int_{-\infty}^{E'-\delta} \frac{f(E')}{E - E'}dE' + \int_{E'+\delta}^{+\infty} \frac{f(E')}{E - E'}dE' \right\} \tag{A.108}$$

Of course,

$$ReG^-(E) = ReG^+(E) \tag{A.109}$$

and thus, separating the real and the imaginary part of $G^\pm(E)$, we get:

$$G^\pm(E) = G^p(E) \mp i\pi\delta(E - \hat{H}) \tag{A.110}$$

The relationship between real and imaginary part of the position representation matrix elements $\langle x| G^\pm(E) |x'\rangle$ can be determined by Kramers-Kronig relations, for the retarded operator analytic in the upper half plane:

$$ReG^+(x,x',E) = P\int_{-\infty}^{+\infty} \frac{dE'}{\pi} \frac{ImG^+(x,x'E')}{E' - E} \tag{A.111}$$

while for the advanced operator in the lower half plane:

$$ImG^-(x,x',E) = -P\int_{-\infty}^{+\infty} \frac{dE'}{\pi} \frac{ReG^-(x,x'E')}{E' - E} \tag{A.112}$$

Analogously to the time-domain Green's functions the perturbative expansion $G(E)$ in a static potential V reads as:

$$
\begin{aligned}
G_E = \frac{1}{E-\hat{H}} = \frac{1}{E-\hat{H}_0+V} = \frac{1}{(E-\hat{H}_0)}(1-(E-\hat{H}_0)^{-1}V) = \\
= \frac{1}{1-(E-\hat{H}_0)^{-1}V}\frac{1}{E-\hat{H}_0} = \\
= (1+(E-\hat{H}_0)^{-}1V+(E-\hat{H}_0)^{-1}V(E-\hat{H}_0)^{-1}V+\ldots)\frac{1}{E-\hat{H}_0} = \\
= G_0(E)+G_0(E)VG_0(E)+G_0(E)VG_0(E)VG_0(E)+\ldots \\
= G_0(E)+G_0(E)\Sigma_I(E)G_0(E)
\end{aligned}
$$

where the *improper* self-energy $\Sigma_I(E)$ has been introduced and where $G_0(E)$ is the Green's operator associated to the unperturbed Hamiltonian:

$$
G_0(E) = \frac{1}{E-\hat{H}_0} \tag{A.113}
$$

The space representation of the Green's propagators (the Green's function matrix elements) as a function of E can be obtained by evaluating the matrix elements:

$$
G^{+(-)}(x,x',E) = \langle x|\,G_E^{+(-)}\,|x'\rangle \tag{A.114}
$$

and recalling eq. A.92 we can deduce the hermitian property :

$$
[G^{+}(x,x',E)]^{*} = G^{-}(x',x,E^{*}) \tag{A.115}
$$

By using eq. A.96, we get the spectral representation in the space-domain:

$$
G^{+}(x,x',E) = \sum_{\lambda}\frac{\varepsilon_{\lambda}(x)\varepsilon_{\lambda}^{*}(x')}{E-\varepsilon_{\lambda}+i\eta} \tag{A.116}
$$

$$
G^{-}(x,x',E) = \sum_{\lambda}\frac{\varepsilon_{\lambda}(x)\varepsilon_{\lambda}^{*}(x')}{E-\varepsilon_{\lambda}-i\eta} \tag{A.117}
$$

The Green's function thus have singularities at the energy eigenvalues (the energy spectrum), constituting a branch cut for the continuum part of the spectrum and simple poles for the discrete part. Along a branch cut the spectral function measures the discontinuity in the Green's operator:

$$A(x,x',E) = i\langle x|\, G_{E+i\eta} - G_{E-i\eta}\, |x'\rangle = i(G^{+}(x,x',E) - G^{-}(x,x',E)) = \\ = -2ImG^{+}(x,x',E) = 2\pi\sum_{\lambda}\varepsilon_{\lambda}(x)\varepsilon_{\lambda}^{*}(x')\delta(E-\varepsilon_{\lambda}) \qquad \text{(A.118)}$$

Notice that $A(x,x',E)$ satisfies the completeness relation:

$$\int_{\sigma}\frac{dE}{2\pi}A(x,x',E) = \delta(x-x') \qquad \text{(A.119)}$$

where the integration (or summation) is over the energy spectrum.

Moreover the trace of $A(x,x',E)$ correspond to the local density of states per unit volume:

$$A(x,x,E) = 2\pi\sum_{\lambda}|\psi_{\lambda}(x)|^{2}\delta(E-\varepsilon_{\lambda}) = 2\pi\sum_{\lambda}|\langle x|\varepsilon_{\lambda}\rangle|^{2}\delta(E-\varepsilon_{\lambda}) \qquad \text{(A.120)}$$

i.e. the unnormalized probability per unit energy to find the particle at position x with energy E (or vice versa the probability density for the particle with energy E to be found at the point x). Thus the integral over x of the trace of $A(x,x',E)$ assumes the meaning of the number of energy levels per unit energy, *i.e.* it is a density of states $D(E)$:

$$\int dxA(x,x,E) = 2\pi\sum_{\lambda}\delta(E-\varepsilon_{\lambda}) = 2\pi D(E) \qquad \text{(A.121)}$$

where resolution of the identity has been used. It follows that the relative probability to find the particle with energy E somewhere in space is proportional to the number of states available at that energy.

The spectral function also allows to evaluate the density matrix elements. Consider the density operator (diagonal in energy representation)

$$\hat{\gamma} = \sum_{\lambda}p(\varepsilon_{\lambda})\,|\varepsilon_{\lambda}\rangle\,\langle\varepsilon_{\lambda}| \qquad \text{(A.122)}$$

where the spectral weights $p(\varepsilon_{\lambda})$ obeys

$$\sum_{\lambda}p(\varepsilon_{\lambda}) = 1 \qquad \text{(A.123)}$$

The density matrix elements take the form:

$$\gamma(x,x') = \langle x|\,\hat{\gamma}|x'\rangle = \int_{-\infty}^{+\infty} \frac{dE}{2\pi}\, p(E)A(x,x',E) = \int_{-\infty}^{+\infty} dE\, p(E)\,\delta(E-\hat{H}) \tag{A.124}$$

The trace of $\gamma(x,x')$ can be interpreted as the probability of finding at the position x, determined by the probability to find the particle with energy E at such position (represented by $A(x,x',E)$) times the probability it has energy E (represented by $p(E)$) and summed over all possible energy values.

These properties establish a connection between the energy eigenstates and the dynamics, making Green's functions suitable for describing transport across a nanostructure.

Bibliography

[1] L. Sun, Y. A. Diaz-Fernandez, T. A. Gschneidtner, F. Westerlund, S. Lara-Avilab, and K. Moth-Poulsen. *Chem. Soc. Rev.*, 43:7378, 2014.

[2] M. L. Perrin, C. J. O. Verzijl, C. A. Martin, A. J. Shaikh, R. Eelkema, H. v. Eschjan, J. M. v. Ruitenbeek, J. M. Thijssen, H. S. J. v. der Zant, and D. Dulic. *Nat. Nanotechol.*, 8:282, 2013.

[3] E. Wierzbinski, X. Yin, K. Werling, and D. H. Waldeck. *J. Phys. Chem. B*, 117: 4431, 2012.

[4] M. Frei, S. V. Aradhya, M. Koentopp, M. S. Hybertsen, and L. Venkataraman. *Nano Lett.*, 11:1518, 2011.

[5] T. Dadosh, Y. Gordin, R. Khrane, I. Khivrich, D. Mahalu, V. Frydman, J. Sperling, A. Yacoby, and I. Bar-Joseph. *Nature*, 436:677, 2005.

[6] W. Wang, T. Lee, and M. A. Red. *Phys. Rev. B*, 68:035416, 2003.

[7] X. Li, J. He, J. Hihath, B. Xu, S. M. Lindsay, and N. Tao. *J. Am. Chem. Soc.*, 128:2135, 2006.

[8] E. A. Weiss, M. R. Wasielewski, and M. A. Ratner. *Top. Curr. Chem.*, 257:103, 2005.

[9] A. Aviram and M. Ratner. *Chem. Phys. Lett.*, 29:277, 1974.

[10] C. P. Collier, E. W. Wong, M. Belohradsky, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams, and J. R. Heath. *Science*, 285:391, 1999.

[11] J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour. *Science*, 286:1550, 1999.

[12] M. A. Ratner and A. Aviram. *Chem. Phys. Lett.*, 29:277, 1974.

[13] M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. Von Hänisch, F. Weigend, F. Evers, H. B. Weber, and M. Mayor. *Proc. Natl. Acad. Sci. USA*, 102:8815, 2005.

[14] R. Liu, S. H. Ke, W. T. Yang, and H. U. Baranger. *J. Chem. Phys.*, 124:124718, 2006.

[15] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, and H. v. Löhneysen. *Phys. Rev. Lett.*, 88:176804, 2002.

[16] J. G. Kushmerick, C. M. Whitaker, S. K. Pollack, T. L. Schull, and R. Shashidhar. *Nanotechnology*, 15:S489, 2004.

[17] M. L. Chabinyc, X. Chen, R. E. Holmlin, H. Jacobs, H. Skulason, C. D. Frisbie, V. Mujica, M. A. Ratner, M. A. Rampi, and G. M. Whitesides. *J. Am. Chem. Soc.*, 4:11730, 2002.

[18] X. Xiao, B. Xu, and N. Tao. *Angew. Chem. Int. Ed.*, 43:6148, 2004.

[19] R. McCreery, J. Dieringer, A. O. Solak, B. Snyder, A. M. Nowak, W. R. McGovern, and S. DuVall. *J. Am. Chem. Soc.*, 125:10748, 2003.

[20] N. N. P. Moonen, A. H. Flood, J. M. Fernandez, and J. F. Stoddart. *Top. Curr. Chem.*, 262:99, 2005.

[21] M. A. Reed, J. Chen, A. M. Rawlett, D. W. Price, and J. M. Tour. *Appl. Phys. Lett.*, 78:3735, 2001.

[22] Z. K. Keane, Z. W. Ciszek, J. M. Tour, and D. Natelson. *Nano Lett.*, 6:1518, 2006.

[23] P. D. Nguyen, T. C. Nguyen, F. M. Hossain, D. H. Huynh, R. Evans, and E. Skafidas. *Nanoscale*, 7:289, 2015.

[24] N. J. Tao. *Nat. Nanotechnol.*, 1:173, 2006.

[25] M. Di Ventra, S. T. Pantelidis, and N. D. Lang. *Appl. Phys. Lett.*, 76:3448, 2000.

[26] P. Damle, T. Rakshit, M. Paulsson, and S. Datta. *Nanotechnol.*, 1:145, 2002.

[27] S. J. Tans, A. R. M. Verschuerer, and C. Dekker. *Nature*, 393:49, 1998.

[28] N. Tao. *Phys. Rev. Lett.*, 76:4066, 1996.

[29] E. Tran, M. A. Rampi, and G. M. Whitesides. *Angew. Chem. Int. Ed.*, 43:3835, 2004.

[30] L.-C. Cheng, X. Jiang, J. Wang, C. Chen, and R.-S. Liu. *Nanoscale*, 5:3547, 2013.

[31] S. Iijima. *Nature*, 354:56, 1991.

[32] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. *Science*, 306:666, 2004.

[33] F. Schwierz. *Nat. Nanotechnol.*, 5:487, 2010.

[34] A. D. Franklin, M. Luisier, S.-J. Han, G. Tulevski, C. M. Breslin, L. Gignac, M. S. Lundstrom, , and W. Haensch. *Nano Lett.*, 12:758, 2012.

[35] M. Liu, V. I. Artyukhov, H. Lee, F. Xu, and B. I. Yacobson. *ACS Nano*, 7:10075, 2013.

[36] V. I. Artyukov, M. Liu, and B. I. Yacobson. *Nano Lett.*, 14:4224, 2014.

[37] C. Lee, X. Wei, J. W. Kysar, and J. Hone. *Science*, 321:385, 2008.

[38] F. Liu, P. Ming, and J. Li. *Phys. Rev. B*, 76:064120, 2007.

[39] D. Sanchez-Portal, E. Artacho, J. M. Soler, A. Rubio, and P. Ordejón. *Phys. Rev. B*, 59:12678, 1999.

[40] K. E. Spear and J. P. Dismukes. *Synthetic diamond: Emerging CVD science and technology*. Electrochemical Society; Wiley: New York, 1994.

[41] W. D. Langer, T. Velusamy, T. B. H. Kuiper, and R. Peng. *Astrophys. J.*, 480: L63, 1997.

[42] R. Hayatsu, R. G. Scott, M. H. Studier, R. S. Lewis, and E. Anders. *Science*, 209: 1515, 1980.

[43] X. Gu, R I. Kaiser, and A. M. Mebel. *ChemPhysChem*, 9:350, 2008.

[44] V. Boudon, J.-P. Champion, M. Loëte T. Gabard, A. Coustenis, C. De Bergh, B. Bézard, E. Lellouch, P. Drossart, M. Hirtzig, A. Negrao, and C. A. Griffith. *DOI:10.1051/epn/2009601.*

[45] R. Thissen, V. Vuitton, P. Lavvas, J. Lemaire, C. Dehon, O. Dutuit, M. A. Smith, S. Turchini, D. Catone, R. V. Yelle, P. Pernot, A. Somogyi, and M.Coreno. *J. Phys. Chem. A*, 113:11211, 2009.

[46] C. C. Wang, P. Zielke, O. F. Sigurbjornsonn, C. R. Viteri, and R. Signorell. *J. Phys. Chem. A*, 113:11129, 2009.

[47] W. A. Chalifoux and R. R. Tykwinski. *C. R. Chimie*, 12:341, 2009.

[48] R. Eastmond, T. R. Johnson, and D. R. M. Walton. *Tetrahedron*, 28:4601, 1972.

[49] M. Tsuji, T. Tsuji, S. Kuboyama, S.-H. Yoon, Y. Korai, T. Tsujimoto, K. Kubo, A. Mori, and I. Mochida. *Chem. Phys. Lett.*, 355:101, 2002.

[50] M. Tsuji, S. Kuboyama, T. Matsukazi, and T. Tsuji. *Carbon*, 41:2141, 2003.

[51] F. Cataldo. *Tetrahedron*, 60:4265, 2004.

[52] F. Cataldo. *Carbon*, 42:129, 2004.

[53] L. Ravagnan, F. Silviero, C. Lenardi, P. Piseri, E. Barborini, and P. Milani. *Phys. Rev. Lett.*, 89:285506, 2002.

[54] L. Ravagnan, P. Piseri, M. Bruzzi, S. Miglio, G. Bongiorno, A. Baserga, C. S. Casari, A. Li Bassi, C. Lenardi, Y. Yamaguchi, T. Wakabayashi, C. E. Bottani, and P. Milani. *Phys. Rev. Lett.*, 98:216103, 2007.

[55] R. J. Lagow, J. J. Kampa, H.-C. Wei, S. C. Battle, J. W. Jenge, D. A. Laude, C. J. Harper, R. Bau, R. C. Stevens, J. F. Haw, and E. Munson. *Science*, 267:362, 1995.

[56] W. A. Chalifoux and R. R. Tykwinski. *Nat. Chem.*, 2:967, 2010.

[57] E. Kano, M. Takeguchi, J.-I. Fujita, and A. Hashimoto. *Carbon*, 80:382, 2014.

[58] T. Pino, H. Ding, F. Güthe, and J. P. Meyer. *J. Chem. Phys.*, 114:2208, 2001.

[59] R. Nagarajan and J. P. Maier. *Int. Rev. Phys. Chem.*, 29:521, 2010.

[60] S. Hino, Y. Okada, K. Iwasaki, M. Kijima, and H. Shirakawa. *Chem. Phys. Lett.*, 372:59, 2002.

[61] G. von Helden, N. G. Gotts, and M. T. Bowers. *Nature*, 363:60, 1993.

[62] J. Hunter, J. Fye, and M. F. Jarrold. *Science*, 260:784, 1993.

[63] C.-H. Kiang and W. A. Goddart. *Phys. Rev. Lett.*, 76:2515, 1996.

[64] G. Von Helden, N. G. Gotts, and M. T. Bowers. *J. Am. Chem. Soc.*, 115:4363, 1993.

[65] A. G. Rinzler, J. H. Hafner, P. Nicolaev, P. Nordlander, D. T. Colbert, R. E. Smalley, L. Lou, S. G. Kim, and D. Tománek. *Science*, 269:1550, 1995.

[66] Z. Whang, X. Ke, Z. Zhu, F. Zhang, M. Ruan, and J. Yang. *Phys. Rev. B*, 61: R2472, 2000.

[67] X. Zhao, Y. Ando, Y. Liu, M. Jinno, and T. Suzuki. *Phys. Rev. Lett.*, 90:187401, 2003.

[68] F. Börrnert, C. Börrnert, S. Gorantla, A. Bachmatiuk X. Liu, J.-O. Jogswig, F. R. Wagner, F. Schäffel, J. H. Warner, B. Rellinghaus, T. Gemming, J. Thomas, M. Knupfer, B. Büchner, and M. H. Rümmeli. *Phys. Rev. B*, 81:085439, 2010.

[69] C. Jin, H. Lan, L. Peng, K. Suenaga, and S. Iijima. *Phys. Rev. Lett.*, 102:205501, 2009.

[70] A. Chuvilin, J. C. Meyer, G. Algara-Siller, and U. Kaiser. *New Journal of Physics*, 11:083019, 2009.

[71] G. Casillas, A. Mayoral, M. Liu, A. Ponce, V. I. Artyukhov, B. I. Yacobson, and M. Jose-Yacaman. *Carbon*, 66:436, 2014.

[72] R. F. Egerton, P. Li, and M. Malac. *Micron*, 35:399, 2004.

[73] B. Song, G. F. Schneider, Q. Xu, G. Pandraud, C. Dekker, and H. Zandbergen. *Nano Lett.*, 11:2247, 2011.

[74] H. Ohnishi, Y. Kondo, and K. Takayanagi. *Nature*, 395:780, 1998.

[75] O. Cretu, A. R. Botello-Mendez, I. Janowska, C. Pham-Huu, J.-C. Charlier, and F. Banhart. *Nano Lett.*, 13:3487, 2013.

[76] P. Moreno-Garcia, M. Gulcur, D. Z. Manrique, T. Pope, W. Hong, V. Kaliginedi, C. Huang., A. S. Batsanov, M. R. Bryce, C. Lambert, and T. Wandlowski. *J. Am. Chem. Soc.*, 135:12228, 2013.

[77] A. La Torre, F. B. Romdhane, W. Baaziz, I. Janowska, C. Pham-Huu, S. Begin-Colin, G. Pourroy, and F. Bahnhart. *Carbon*, 77:906, 2014.

[78] W. Koch and M. C. Holthausen. *A chemist's guide to Density Functional Theory*. Wiley-VCH, 2001.

[79] R. G. Parr and W. Yang. *Density Functional Theory of atoms and molecules*. Oxford University Press, 1989.

[80] S. Datta. *Quantum Transport: Atom to Transistor*. Cambridge University Press, 2005.

[81] J. C. Cuevas and E. Scheer. *Molecular Electronics. An introduction to theory and experiment*. World Scientific Publishing Co., 2010.

[82] R. Martinazzo. Electronic transport at the nanoscale: the non-equilibrium green's function method. URL `http://users.unimi.it/cdtg/download/notes/NEGF.pdf`.

[83] Electron propagator (green's function) methods. URL `http://www.chemistry.mcmaster.ca/~ayers/chem770/Notes4.pdf`.

[84] Green's functions. URL `http://cns.gatech.edu/~predrag/courses/PHYS-6124-12/StGoChap5.pdf`.

[85] Eigenfunctions, eigenvalues and green's functions. URL `http://physics.bu.edu/~pankajm/LN/LNGF1.pdf`.

[86] P. Hohemberg and W. Kohn. *Phys. Rev.*, 136:B864, 1964.

[87] W. Kohn and L. J. Sham. *Phys. Rev.*, 140:A1133, 1965.

[88] D. M. Ceperley and B. J. Alder. *Phys. Rev. Lett.*, 45:566, 1980.

[89] J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.*, 77:3865, 1996.

[90] J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.*, 78:1396, 1997.

[91] A. D. Becke. *J. Chem. Phys.*, 98:5648, 1993.

[92] C. Lee, W. Yang, and R. G. Parr. *Phys. Rev. B*, 37:785, 1988.

[93] B. Miehlich, A. Savin, H. Stoll, and H. Preuss. *Chem. Phys. Lett.*, 157:200, 1989.

[94] T. Tsuneda and K. Hirao. *WIREs Comput. Mol. Sci.*, 4:375, 2014.

[95] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal. *J. Phys.: Condens. Matter*, 14:2745, 2002.

[96] M. Brandbyge, J. L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro. *Phys. Rev. B*, 65:165401, 2002.

[97] P. A. Serena and N. Garcia. *Molecular Electronics. An introduction to theory and experiment*. NATO ASI series (Kluwer, Dordrecht), 1997.

[98] R. H. M. Smit, C. Untiedt, A. I. Yanson, and J. M. van Ruitenbeek. Common origin for surface reconstruction and the formation of chains of metal atoms. *Phys. Rev. Lett.*, 87:266102, Dec 2001.

[99] J. Chen and M. A. Reed. *Chem. Phys.*, 281:127, 2002.

[100] N. Troullier and José Luriaas Martins. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B*, 43:1993–2006, Jan 1991.

[101] M. Paulsson and T. Frederiksen. Inelastica, a python package for siesta/transiesta dft codes. URL `http://sourceforge.net/projects/inelastica`.

[102] M. Paulsson and M. Brandbyge. *Phys. Rev. B*, 76:115117, 2007.

[103] Thomas Frederiksen, Magnus Paulsson, Mads Brandbyge, and Antti-Pekka Jauho. Inelastic transport theory from first principles: Methodology and application to nanoscale devices. *Phys. Rev. B*, 75:205413, May 2007.

[104] URL `http://schmeling.ac.rwth-aachen.de/cohp/index.php?menuID=2`.

[105] B. Xu and N. Tao. *Science*, 301:1221, 2003.

[106] W. Haiss, R. Nichols, H. Van Zalinge, S. Higgins, D. Bethell, and D. Schiffrin. *Phys. Chem. Chem. Phys.*, 6:4330, 2004.

[107] X. Li, J. He, J. Hihath, B. Xu, S. Lindsay, and N. Tao. *J. Am. Chem. Soc.*, 128: 2135, 2006.

[108] E. Leary, H. van Zalinge, S. J. Higgins, R. J. Nichols, F. F. de Biani, P. Leoni, L. Marchetti, and P. Zanello. *Phys. Chem. Chem. Phys.*, 11:5198, 2009.

[109] Z.-L. Cheng, R. Skouta, H. Vasquez, J. R. Widawsky, S. Schneebeli, W. Chen, M. S. Hybertsen, R. Breslow, and L. Venkataraman. *Nat. Nanotechnol.*, 6:353, 2011.

[110] C. R. Arroyo, E. Leary, A. C.-Gomez, G. Rubio-Bollinger, M. T. Gonzales, and N. Agrait. *J. Am. Chem. Soc.*, 133:14313, 2011.

[111] N. D. Lang and P. Avouris. *Phys. Rev. Lett.*, 81:3515, 1998.

[112] N. D. Lang and P. Avouris. *Phys. Rev. Lett.*, 84:358, 2000.

[113] Z. Crljen and G. Baranović. *Phys. Rev. Lett.*, 98:116801, 2007.

[114] K. Honkala L. Nykänen, H. Häkkinen. Computational study of linear carbon chains on gold and silver surfaces. *Carbon*, 50:2752, 2012.

[115] P. Moreno-Garcia, M. Gulcur, D. Z. Manrique, T. Pope, W. Hong, V. Kaliginedi, C. Huang, A. S. Batsanov, M. R. Bryce, C. Lambert, and T. Wandlowski. *J. Am. Chem. Soc.*, 135:12228, 2013.

[116] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D.J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, , and J. A. Pople and. *Gaussian09, Revision A.02*. Gaussian Inc., Pittsburgh PA, 2009.

[117] Ramya Nagarajan and John P. Maier. Electronic spectra of carbon chains and derivatives. *Int. Rev. Phys. Chem.*, 29:521–554, 2010.

[118] S. Yang and M. J. Kertesz. *Journal of Physical Chemistry A*, 110:9771, 2006.

[119] Joachim Paier, Martijn Marsman, and Georg Kresse. Why does the b3lyp hybrid functional fail for metals. *J. Phys. Chem.*, 127(2):024103, 2007.

[120] M. E. Casida. *J. Mol.Struc.- THEOCHEM*, 914:3, 2009.

[121] M. Liu, V. I. Artyukhov, H. Lee, F. Xu, and B. I. Yakobson. Carbyne from first principles: Chain of c atoms, a nanorod or a nanorope. *ACS Nano*, 11:10075, 2013.

[122] S. Das Sarma, S.Adam, E. H. Hwang, and E. Rossi. *Rev. Mod. Phys.*, 83:407, 2011.

[123] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim. *Rev. Mod. Phys*, 81:109, 2009.

[124] J. B. Oostinga, H. B. Heersche, X. Liu, A. F. Morpurgoa, and L. M. K. Vandersypen. *Nature Materials*, 7:151, 2008.

[125] D. Li and R. B. Kaner. *Science*, 320:5880, 2008.

[126] R. Balog, B. Jørgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi, M. Fanetti, E. Lægsgaard, A. Baraldi, S. Lizzit, Z. Sljivancanin, F. Besenbacher, B. Hammer, T. G. Pedersen, P. Hofmann, and L. Hornekær. *Nature Materials*, 9: 315, 2010.

[127] S. Dutta and S. K. Pati. *J. Mater. Chem.*, 20:8207, 2010.

[128] R. Baer and D. Neuhauser. *J. Am. Chem. Soc.*, 124:4200, 2002.

[129] E. H. van Dijk, D. J. T. Myles, M. H. van der Veen, and J. C. Hummelen. *Org. Lett.*, 8:2333, 2006.

[130] T. Markussen, J. Schiötz, and K. S. Thygesen. *J. Chem. Phys.*, 132:224104, 2010.

[131] R. Stadler, S. Ami, F. Forshaw, and C. Joachim. *Nanotechnology*, 15:S115, 2004.

[132] R. Stadler, F. Forshaw, and C. Joachim. *Nanotechnology*, 14:138, 2003.

[133] R. A. Webb, S.Washburn, C. P. Unbach, and R. B. Laibowits. *Phys. Rev. Lett.*, 54:2696, 1985.

[134] T. Markussen, R. Stadler, and K. S. Thygesen. *Phys. Chem. Chem. Phys.*, 13: 14311, 2011.

[135] J. P. Bergfield, H. M. Heitzer, C. Van Dyck, T. J. Marks, and M. A. Ratner. *acsNANO*, 9:6412, 2015.

[136] Y. Geng, S. Sangtarash, C. Huang, H. Sadeghi, Y. Fu, W. Hong, T. Wandlowsky, S. Decurtins, C. J. Lambert, and S.-X. Liu. *J. Am. Chem. Soc.*, 137:4469, 2015.

[137] G. C. Salomon, D. Q. Andrews, T. Hansen, R. H. Goldsmith, M. R. Wasielewsky, R. p. Van Duyne, and M. A. Ratner. *J. Chem. Phys.*, 129:154701, 2008.

[138] M. G. Reuter and T. Hansen. *J. Chem. Phys.*, 141:181103, 2014.

[139] H.-W Lee. *Phys. Rev. Lett.*, 82:11, 1999.

[140] P. Von R. Scheyer and A.-M. Sapse. *Lithium chemistry, a theoretical and experimental overview*. John Wiley & Sons, 1995.

[141] H. Qian and J.-Q. Lu. *Phys. Lett A*, 371:465, 2007.

[142] D. I. Gittins, D. Bethell, D. J. Schiffrin, and R. J. Nichols. *Nature*, 408:67, 2000.

[143] C. Sporer, I. Ratera, D. Ruiz-Molina, Y. Zhao, J. Vidal-Gancedo, K. Wurst, P. Jaitner, K. Clays, K. Persoons, C. Rovira, and J. Veciana. *Angew. Chem. Int. Ed*, 43:5266, 2004.

[144] Y. Chen, G.-Y. Jung, D. A. A. Ohlberg, X. Li, D. R. Stewart, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, and R. S. Williams. *Nanotechnology*, 14:5266, 2003.

[145] C. M. Guédon, H. Valkenier, T. Markussen, K. S. Thygesen, J. C. Hummelen, and S. J. van der Molen. *Nat. Nanotech.*, 7:305, 2012.