One dimensional conductors

Let us work in the single electron approximation, neglecting the electron correlation effects not included in a mean filed approximation. Let us take a conductor, a wire, with a square section of side d comparable to the Fermi wavelength $2\pi/k_F$, where k_F is the Fermi momentum, and with a length l much longer than d, but shorter of the mean free path λ of an electron. This means that, if we take a normal metal, d is comparable to the atomic dimensions and l is up to hundreds of ångstrom. Let us take the x axis along the axis of the wire, and y and z in the square section. Let us approximate the potential felt by one electron in the yz plane as a square potential well with walls of infinite height. This system is periodic along x, but not along y and z. The energy contribution of the confined motion of the electron in y and z will be
$E_{n,m} = \hbar^2\pi^2(n^2+m^2)/d^2$
with n and m integer numbers. The free motion of the electron along the axis of the wire will give rise to an additional energy term $E'_{n,m}(k_x)$ with a dependence on the crystal momentum in the x direction k_x similar to that of an energy band in the three-dimensional metal. These unidimensional (1D) energy band will have energy widths $W_{n,m}$. There will be a unidimensional band for each couple of n and m values. Let us assume that d is so small that energy differences between the values of $E_{n,m}$ is larger than W values, and therefore the unidimensional bands do not overlap. The Fermi level will cross one of these bands. This will be the only band contributing to the electrical conduction.

Let us connect the wire to two macroscopic conductors A and B, and let us apply potential difference V between A and B. The Fermi level of the negative conductor – let us say A- will be eV higher than that of the positive conductor, B. Therefore, electrons will be injected in the wire by the negative conductor A and they will flow in the states of the wire with an energy between E_{FA} and E_{FB}, $E_{FA} = E_{FB}+eV$, until they reach B.

The current is
$$I = \frac{2e}{2\pi} \int_{E_{FB}}^{E_{FB}+eV} v_{k_x} \frac{dk_x}{dE'} dE'$$

where v_{kx} is the electron velocity, $v_{kx} = 1/\hbar \; dE'(k_x)/dk_x$, and the factor 2 is there because there is spin degeneracy (for each k_x two states with opposite spin have the same energy) if the wire is paramagnetic. Therefore
$I = 2e^2V/h$
and the resistance and the conductivity are
$R = 1/(2e^2/h)$ $\sigma = 2e^2/h$ $(1/(2e^2/h) \approx 13 \text{ k}\Omega)$
independently from the material and the length of the wire.

If some unidimensional bands overlap the current is the sum of the current carried by each band. Therefore if the Fermi level crosses n bands, the current is ne^2V/h and the conductivity is
$\sigma = n2e^2/h$

If the wire is ferromagnetic the spin degeneracy is removed and in this case
$\sigma = ne^2/h$

The conductivity of a nanowire, if l is shorter of the mean free path λ of the electrons, is a multiple of the universal quantum of conductance $G_0 = 2e^2/\hbar$. Since there is no scattering in the wire, and therefore no loss of energy, the potential drops are at the

contacts between the macroscopic conductors and the wire, and not in the wire. If the length l is more than λ some electron scatter in the nanowire, but the only possible scattering is to go back. Therefore the conductivity decreases.

An electron that moves from the metal A to the nanowire feels a change in section of the conductor and/or a change in the potential. These may cause a reflection of the wavefunction back into the metal A. If only a fraction of the wavefunctions of the electron is transmitted into the wire the conductivity is

$$\sigma = \sum_n T_n e^2 / \hbar$$

with $T_n \le 1$. If the change in cross section going from the macroscopic conductor to the wire is smooth, the values of T are very close to 1.

La figura mostra a destra in alto come varia la conducibilita' di 5 nanofili d'oro mentre vengono allungati, e in basso l'istogramma dei valori della conducibilita' di migliaia di nanofili. I valori piu' frequenti di conducibilita' sono circa 1 G_0, 2 G_0, 3 G_0… Si nota che i picchi sono a un po' meno di 2 G_0, 3G_0... Questo e' dovuto alla parziale riflessione della funzione d'onda degli elettroni provenienti dai metalli macroscopici nelle giunzioni con i nanofili. Le misure sono fatte a temperatura ambiente in aria o in soluzione. (da Venkataraman et al., Nano Letters 6, 458 (2006))
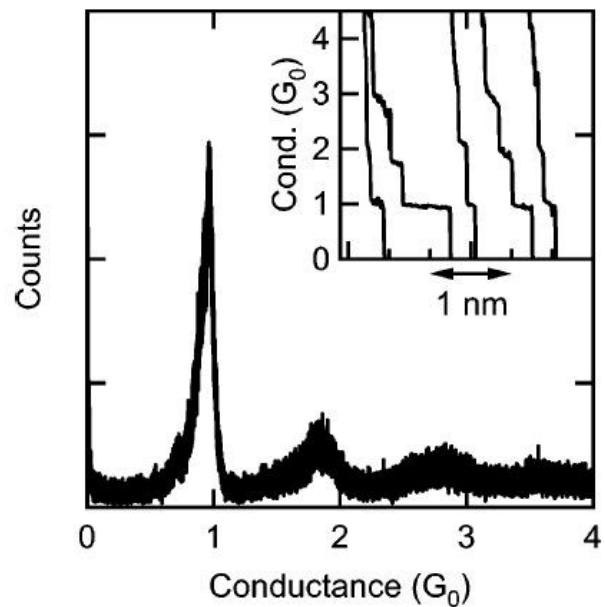
Effects of finite temperature

What is written above works if $k_B T$ is much less than the energy separation between the 1D bands in the nanowire. If this is not the case, electrons and holes are excited also in bands different from those cut by the Fermi level. The effect of this is a rounding of the steps in the conductance vs elongation plots and a broadening of the peaks in the histograms counts vs conductance.

What happens if a molecule is trapped between two pieces of nanowires when the nanowire breaks?

Let us assume a simple model for the molecule, that is a one-dimensional periodic arrangement of two types of atoms *A* and *B*, arranged in an alternating sequence *ABABABAB* . . . . (see J. K. Tomfohr et al. Phys. Rev. B65, 245105 (2002). The unit cell consists of an *A* and a *B* atom and the spacing between cells is *a* (the distance between *A* and *B* is *a*/2). The wave function in unit cell *m* is expressed as a linear combination of orthonormal orbitals ϕ_A and ϕ_B on each atom in that cell:

$$\Psi^{(m)} = C_A^{(m)} \phi_A + C_B^{(m)} \phi_B .$$

The motion of the electrons from one atom to the next is described in the Hamiltonian matrix by a coupling $-t$ between orbitals on nearest-neighbor atoms only and the onsite energies are E_A and E_B , with $E_A<E_B$.
Assuming the Bloch form for the eigenstates, $C^{(m)}=e^{ikma}C^{(0)}$, the energy eigenvalues are found to be

$$E_\pm(k)=\Sigma\pm\sqrt{\Delta^2 + 2t^2(1+\cos ka)}$$

where
$\Sigma=(E_A+E_B)/2$ and $\Delta=(E_A-E_B)/2$.

If the molecule has infinite length the physical solutions have a real k, like in a infinite solids (otherwise the wavefunctions diverge for m-> ∞ or - ∞). If the molecule is semi-infinite or finite (it has at least one end) complex k values are possible. Therefore let us plot the eigenvalues of the electron in this model of a molecule as a function of a complex k. The figure below, taken from the paper by Tomfohr cited above, shows the usual band structure (real k) at the right, while the left part shows the dependence of the energy on the imaginary k. In this calculation t is set equal to Δ.

Model Complex Bandstructure (t=Δ)
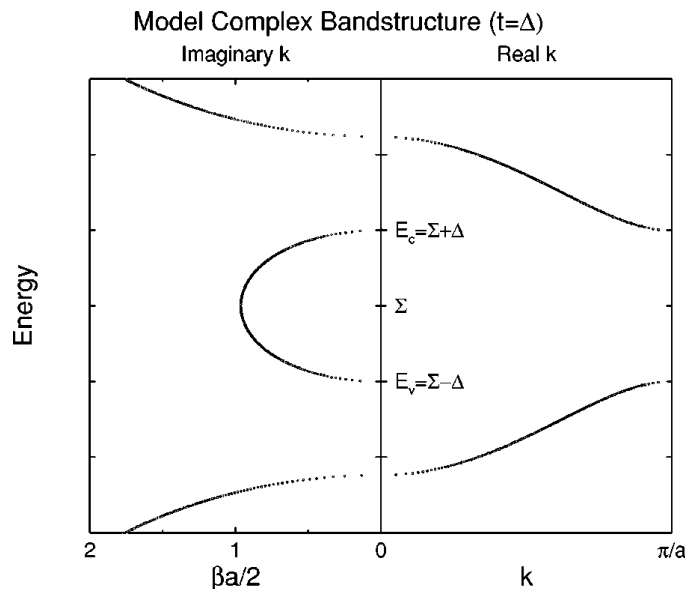
The band gap in the model is 2|Δ|. Besides the "normal" bands for real k that would exist in an infinite system also, there are physical solutions for complex k in gap and above and below the "normal bands". The two bands $E_+(k)$ and $E_-(k)$ are connected in the complex k plane at E=Σ.
If you have a molecule (or a nanowire) with at least one end, an electron can exist with an energy in the gap, but its wave function decays exponentially from the end into the molecule (or the nanowire).

You can apply a similar model to a solid with al least a surface, and you will find that because of this surface you can have states with energy in the gap of the infinite system, but the wavefunctions of these states decay exponentially if you move from the surface into the crystal (these state are called surface states).
The imaginary *k* region of the band structure determines how an electron with a given energy will tunnel through a finite region of the crystal. In the gap region, between Σ-Δ and Σ+Δ (~see Fig. above) |k| gives the rate of decay of the wave function from one cell to the next. As the energy approaches the band edge from the gap, |k| decreases so an electron with an energy in the gap will tunnel more effectively as its energy approaches the band edge. The band edges each act as the top of an effective potential barrier; like the top of the simple square barrier, they mark the crossover point from decaying states to propagating ones.
If a molecule has a finite length and an electron is injected in the middle of the gap from one end, its probability of reaching the other end is minimum. It will be much higher if the electron is injected with an energy close to that of the bands in the

molecule. The tunnelling probability of an electron through a molecule depends on its energy. The closer it is to that of a band, the higher the probability. If I have a molecule between two metals, and I apply a small potential difference between the two metals, electrons near the Fermi level will be injected from one metal to the other through the molecule. If the molecular levels are far from the Fermi level this molecule act like a potential barrier. There is tunnelling through it, and the decay of the electron wave functions, calculated in the way described above, depends on the energy distance between the Fermi level and the molecular state closer to it (the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital (LUMO)).