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RESISTANCE OF ATOMIC SODIUM WIRES*

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We systematically study the electrical transport through atomic sodium wires connected to two semi-infinite electrodes. The dependence of the resistance on the wire length and on the wire–electrode separation is investigated. For small wire–electrode distances the single sodium atom can show a larger resistance than the Na-dimer, confirming recent *ab initio* calculations [N.D. Lang, *Phys. Rev. Lett.* **79**, 1357 (1997)]. In our density functional theory based Landauer approach, this anomalous behaviour is shown to be dependent on the level of description of the wire (number of basis functions per atom) as well as on the strength of the electrode–wire coupling.

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1. Introduction

The low temperature resistance of atomic wires is the subject of intense theoretical and experimental investigations [1–5]. Well defined experimental conditions with 1 or two atoms in the wire have been established in STM experiments of Yazdani *et al.* [1] for the case of Xenon atoms. Moreover, a theoretical study of atomic sodium chains between uniform jellium modelled metal electrodes has revealed counter-intuitive behaviour as a function of the number of sodium atoms contained in the chain [3]. It has been argued that there is an anomalous resistance dependence with large resistances (of the order of 30 kΩ) for the 1 atom case decreasing to about half that value for two atoms.

In the following we will investigate this behaviour in detail. The theoretical methodology we use is based on the Landauer formalism as applied

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to molecular chain conductance calculations [6–8] combined with a Linear-Combination of Atomic-Orbitals (LCAO) approach based on Density Functional Theory (DFT) within the Local-Density-Approximation (LDA) [10]. Here we apply this methodology to the benchmark problem of atomic sodium chains, where analytical results for a single basis function per atom [8] as well as results from other numerical approaches are available. Anticipating the findings of this paper, the crucial parameter with respect to the anomalous behaviour mentioned above is the distance between the atomic wire and the metallic electrodes. We will show that if this distance is varied, both, the "anomalous" behaviour and the "normal" behaviour can be observed. Furthermore, also the basis set used to calculate the electronic structure of the wire has an influence on the predicted transport properties. The theoretical method is shortly outlined in Sec. 2. Numerical results and their discussion are given in Sec. 3.

2. Theoretical method

For calculating the linear conductance of atomic wires we will use the Landauer formalism [9]. The linear conductance $\mathcal{G}$ of an object coupled to two semi-infinite electrodes (L and R) is given at zero-temperature by

$$\mathcal{G} = \frac{2e^2}{h} T(E_f), \tag{2.1}$$

where $T(E_f)$ is the transmission function of the object evaluated at the equilibrium Fermi energy of the reservoirs. It is defined by

$$T(E) = \mathrm{Tr}(\boldsymbol{G}^\dagger(E)\boldsymbol{\Gamma}_\mathrm{R}(E)\boldsymbol{G}(E)\boldsymbol{\Gamma}_\mathrm{L}(E)). \tag{2.2}$$

The retarded Green's function $\boldsymbol{G}(E)$ is to be determined by solving the Dyson equation

$$(z\boldsymbol{S} - \boldsymbol{H} - \boldsymbol{\Sigma}_\mathrm{L}(z) - \boldsymbol{\Sigma}_\mathrm{R}(z))\boldsymbol{G}(z) = \mathbf{1}, \quad z = E + i\eta, \quad \eta \to 0^+, \tag{2.3}$$

where $\boldsymbol{H}$ and $\boldsymbol{S}$ are the Hamiltonian and overlap matrices for the object and $\boldsymbol{\Sigma}(z)$ is a self-energy resulting from the coupling to the electrodes. The self-energy has the form

$$\boldsymbol{\Sigma}_\mathrm{L,R}(z) = \boldsymbol{V}^\dagger_\mathrm{L,R}\boldsymbol{g}_\mathrm{L,R}(z)\boldsymbol{V}_\mathrm{L,R}. \tag{2.4}$$

Here, the matrices $\boldsymbol{V}^\dagger, \boldsymbol{V}$ describe the object–electrode interaction and $\boldsymbol{g}(z)$ is the electrode Green's function. Finally, the spectral functions are defined via the self-energies as

$$\boldsymbol{\Gamma}_\mathrm{L,R}(E) = i(\boldsymbol{\Sigma}_\mathrm{L,R}(E + i\eta) - \boldsymbol{\Sigma}_\mathrm{L,R}(E - i\eta)) \quad \eta \to 0^+. \tag{2.5}$$

In order to apply this approach to a specific system, one has to define a procedure to determine *(i)* the Hamiltonian and overlap matrices of the object, *(ii)* the interaction matrices appearing in the self-energy and *(iii)* a model for the electrodes. Concerning points *(i)* and *(ii)* we will use the LCAO-DFT-LDA approach [10], including sp^3 valence orbitals in the electronic structure calculations. The electrodes will be modelled by semi-infinite tight-binding metallic chains with one atomic orbital with energy ε per lattice site and lattice constant a, for which an analytic Green's function is available [11].

From the dispersion relation of this model, $E(k) = \varepsilon + 2t_0 \cos ka$ it follows that the Fermi energy lies at $E_f = \varepsilon$ at half-filling. The band parameters are fixed at $\varepsilon = -4$ eV and $t_0 = -2.7$ eV, values which are obtained from our LCAO-DFT-LDA approach.

Besides the usage of an sp^3 basis set, we will also study what happens if the electrons are described by a single basis function per atom only. In this case, analytical results are available for the transmission in Eq. (2.2) [8]. Denoting the relevant matrix elements of the spectral function Eq. (2.5) by $2\mathit{\Delta}$ and the hopping integral in the wire by β the results for the one and two atom chains are

$$T_1(E) = \frac{4\mathit{\Delta}^2}{(E-E_M)^2 + 4\mathit{\Delta}^2}, \tag{2.6}$$

$$T_2(E) = \frac{4\mathit{\Delta}^2\beta^2}{[(E-E_M)^2 - \mathit{\Delta}^2 - \beta^2]^2 + 4(E-E_M)^2\mathit{\Delta}^2}, \tag{2.7}$$

where E_{M} is the "molecular" energy, *i.e.* the diagonal matrix element of the unperturbed molecular Hamiltonian.

3. Results

We present in this section the numerical results for the resistance $\mathcal{R} = 1/\mathcal{G}$ of sodium atomic wires as a function of the electrode–wire separation d and of the wire length. The bond length in the wires was fixed at 6.00 a_{B}, which approximately corresponds to the equilibrium distance of a Na-dimer ($\mathrm{d_{eq}}$=5.67 a_{B}). For wires with more than four atoms dimerization of the wire is expected due to a Peierls transition. Such effects will not be considered here.

In Fig. 1, the dependence of the resistance $\mathcal{R} = 1/\mathcal{G}$ on the number of atoms in the chain is displayed for three different values of d. For comparison the wire resistance was also calculated using a single $3s$ valence orbital for each sodium atom in the wire. The result of Lang, who stated that $\mathcal{R}_{N=1} > \mathcal{R}_{N=2}$ [3], in our approach is only found in the case of the sp^3 basis and in addition only for strong coupling between the chain and the

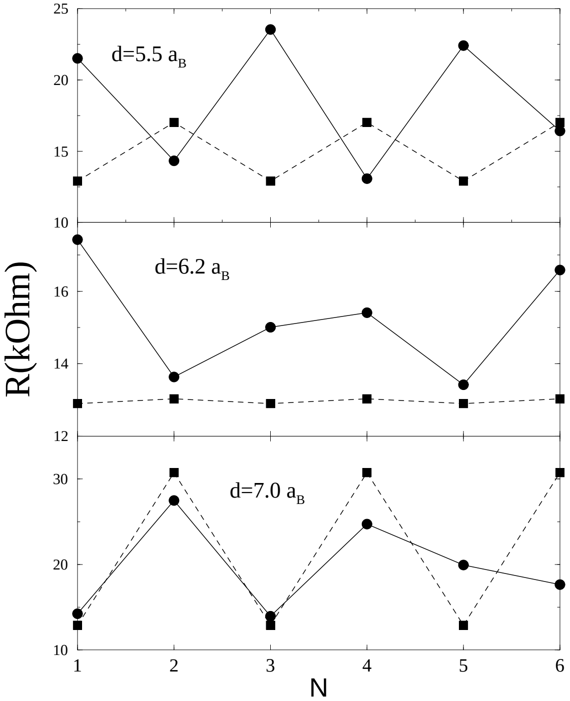

Fig. 1. Dependence of the resistance on the length of the atomic sodium wire for different electrode–wire separations. Dashed lines (connecting the squares) correspond to a resistance calculated with only the 3s-valence orbitals in the wire.

electrode. Concerning the coupling strength there exists a critical value d_{crit} where both, the single atom and the dimer, have approximately the same resistance. This can be seen in Fig. 2 where $\mathcal{R}_{N=1}$ and $\mathcal{R}_{N=2}$ are plotted *versus* d. The critical value lies at about 6.50 a_{B}, (for comparison, the distance considered by Lang [3] is about 5.7 a_{B}). For $d > d_{\text{crit}}$ the resistance of the dimer increases almost exponentially. The resistance of the single atom will also increase exponentially but at much larger electrode–atom separations (not shown). With respect to the basis set size, for an s-basis set only, the "normal" behaviour ($\mathcal{R}_{N=1} < \mathcal{R}_{N=2}$) is recovered with values of $\mathcal{R}$ very close to the resistance quantum of 12.9 kΩ for wires with an odd number of electrons. That this must be the case can be easily seen by considering the analytical results, Eqs. (2.6), (2.7), reviewed at the end of the last Section. For one atom connected to leads of the same material we have to consider the transmission at a Fermi energy which equals E_M. Thus $T(E_f)$ is always equal to unity resulting in the universal contact resistance of 12.9 kΩ. For two atoms, at $E = E_f$, the result for $T(E_f)$ depends on the relative magnitude of β and Δ, however, and can only be smaller than or equal to the one atom result. As expected from Eq. (6), the resistance of the single atom with an s-state is independent of the electrode–wire separation. This can be seen in Fig. 2(a). Thus the *s*-level basically acts like an ideal conduction channel.

For an sp^3 basis the behaviour displayed in Figs. 1 and 2 can be better understood by inspecting the transmission spectrum, as shown in Fig. 3. The value the linear resistance of the wire acquires, depends sensitively on the position of the Fermi level E_f with respect to the modified eigenenergies of the wire. In order to distinguish between the bare eigenenergies we have displayed the free wire density of states (DOS) together with the corresponding $T(E)$ for two different values of the electrode–wire separation. Intuitively one would expect that E_f lies in the HOMO–LUMO gap for a Na-dimer (the HOMO is twice occupied) and would almost touch the singly occupied HOMO in the one atom case. This picture is however only valid in the case of a weak coupling to the electrodes, where the position of the eigenvalues of the wire remains approximately the same as for an isolated wire and the broadening induced by the coupling is smaller than the energy spacing between the eigenvalues.

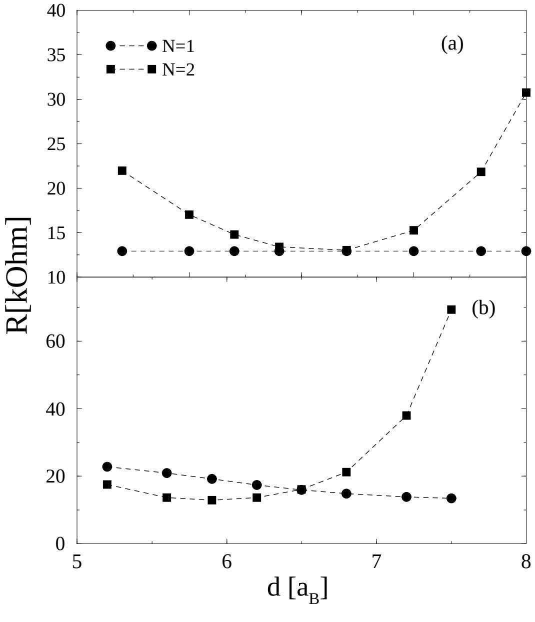

Fig. 2. Dependence of the resistances of the one and two-atom chains on the separation *d* to the reservoirs. The electronic structure of the wires was determined using (a) an *s* and (b) an sp^3 valence basis set.

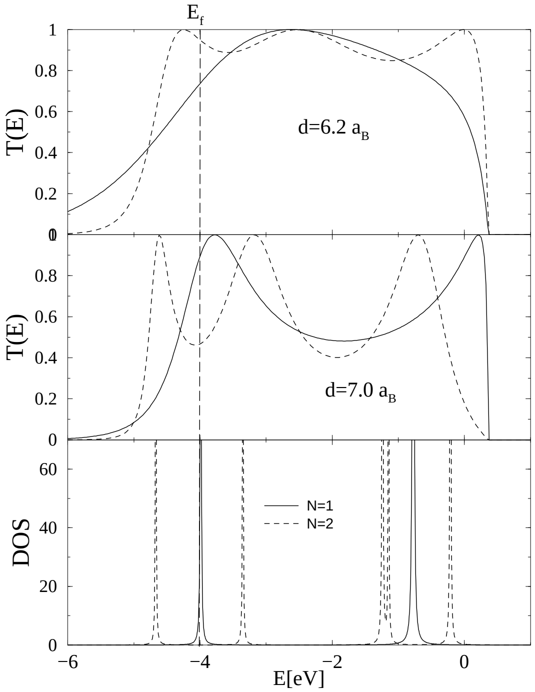

Fig. 3. The transmission coefficient as a function of energy for one and two atoms (using an sp^3 basis) between the electrodes for two different electrode–wire separations. The lowest panel shows the DOS of the isolated wires. Only the low-energy part of the spectra is shown.

For $d = 6.2\ a_\mathrm{B}$, the eigenstates of Na$_1$ and Na$_2$ are strongly broadened and shifted by the coupling to the leads, however. The HOMO and LUMO (3-fold degenerate) of the single atom cannot be clearly resolved any more but evolve into a rather broad single peak. Especially at E_f the transmission for a single atom becomes smaller than for the dimer. With increasing distance the coupling to the electrodes is reduced and thus the renormalization and broadening of the eigenstates become weaker. At $d = 7.0\ a_\mathrm{B}$, the "HOMO" and "LUMO" of the dimer are already "resolved" and the transmission $T(E_f)$ within the gap is reduced.

In conclusion, we have studied the electrical transport trough an atomic sodium wire as a function of the wire length and of the electrode–wire separation. The "anomalous" resistance dependence found by Lang has been reproduced. It turns out, however, that this effect sensitively depends on the electrode–wire separation and hence on the strength of the coupling to the electrodes as well as on the basis set used for describing the electronic structure of the wires. In our model the "anomalous" behaviour has been shown to be present in the strong coupling regime where renormalization of the wire eigenvalues becomes relevant.

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