

Anomalous Dependence of Resistance on Length in Atomic Wires

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The resistance of an atomic Na wire between two macroscopic metallic electrodes is found to decrease by a factor of 2 going from the 1- to the 2-atom wire, and then to stay roughly the same for the 2-, 3-, and 4-atom wires. The initial decrease in resistance is related to the phenomenon of incomplete valence resonances for an atom interacting with a continuum of states. Such resonances lead to what might be called incomplete conduction channels. [S0031-9007(97)03863-5]

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We discuss in this Letter the zero-temperature resistance of wires consisting of a chain of between one and four Na atoms connecting two macroscopic metal electrodes. Now in general, the resistance of a wire increases with its length, either linearly, or faster under certain circumstances (including strong localization [1], and far-off-resonance conduction in short atomic wires [2]). In the case of on-resonance conduction (such as occurs for most metal atoms) in short atomic wires connecting two macroscopic electrodes, the resistance is usually relatively constant with length [3], since these wires form an approximation to the situation of ballistic conduction through a narrow channel linking two reservoirs, as envisioned by Imry and Landauer [4]. In the circumstance in which this ideal channel is narrow enough to be considered one-dimensional, the resistance is in fact $\pi\hbar/e^2 = 12.9 \text{ k}\Omega$, independent of channel length [5]. What happens, by contrast, for the Na wires studied here and represented schematically in Fig. 1, is that the resistance *decreases* with length (by nearly a factor of 2) in going from the 1-atom wire to the 2-atom wire, and then stays relatively constant after that [6].

Now there have been a number of experiments [7] using either the scanning tunneling microscope (STM) or a mechanically controllable break-junction to draw a nanowire between two electrodes, in which the resistance of the wire is measured as a function of the separation between the electrodes. It has recently been seen by Barnett and Landman [8] in a molecular dynamics simulation, however, that such drawn wires can have a rather complex structure, and exhibit a complicated series of structural changes as a function of electrode separation (with substantial effects on the conductance), and so the results of these experiments cannot be immediately related to the calculations discussed here for a simple line of several atoms [9]. More relevant would be STM experiments such as those of Yazdani *et al.* [2], in which the resistance of a well-defined 1- or 2-atom wire was measured.

We will represent the metal electrodes using the uniform-background (jellium) model [10,11]; the Na atomic cores are represented using a pseudopotential [12]. The self-consistent, density-functional calculation

and the method of obtaining the current (and hence the conductance) due to the presence of the wire are the same as described in Ref. [3]. There the resistance R is defined as the reciprocal of the additional conductance due to the presence of the wire.

The results for R at low bias are given graphically in Fig. 2 [13]. In view of the properties of the ideal one-dimensional conductance channel [4], the fact that the R values for the 2-, 3-, and 4-atom wires are all similar, and not dramatically different from the ideal value of $12.9 \text{ k}\Omega$, is not surprising. The less expected result (pointed out earlier in Refs. [14] and [15]) is that the 1-atom R value is so much larger than the ideal value [16]. It should also be mentioned in this connection that R for a 1-atom Al wire is, by contrast, not so different from that for the 2- and 3-atom Al wire [3], so this is an additional point to be understood.

To further our discussion, we recall once again (as in Refs. [3] and [15]) the analysis of Kalmeyer and Laughlin [17], who consider a very wide square barrier between two semi-infinite regions of constant potential (corresponding to our electrodes). Within this barrier is a spherical well which by itself would support one discrete state. In the presence of the semi-infinite regions, this discrete state broadens into a resonance. For the energy at the center of the resonance, and for the well midway in the barrier, it is shown that the conductance of the barrier is, taking spin degeneracy into account, $e^2/\pi\hbar$ (whose reciprocal is $12.9 \text{ k}\Omega$). The well resonance thus gives rise, at the peak energy, to the same conductance as a

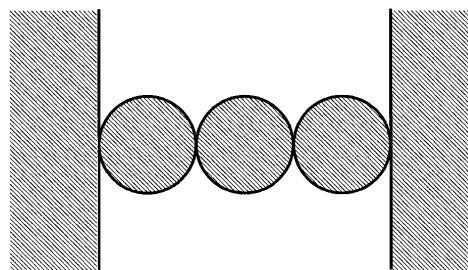


FIG. 1. Schematic diagram of (Na) atomic wire connecting two semi-infinite metallic electrodes.

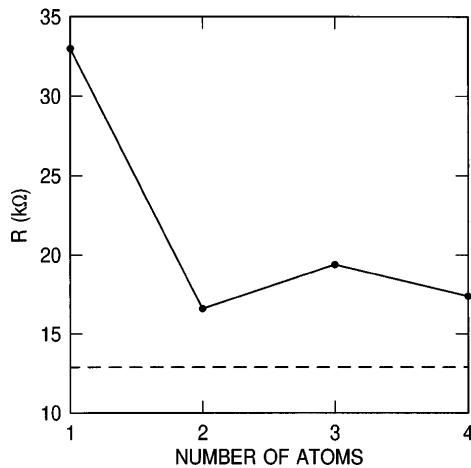


FIG. 2. Resistance R for the Na wire shown schematically in Fig. 1, as a function of the number of atoms in the wire. Dashed line is drawn at the ideal value of $R = \pi \hbar / e^2$ (12.9 k Ω).

one-dimensional ideal channel linking two reservoirs [4,18]. In our case, for the 1-atom wire, it is the Na valence resonance that corresponds to the well resonance in this model. This valence resonance is seen in Fig. 3 (solid curve), which gives the additional density of states [19] due to the presence of the Na atom. Since the Fermi level does not cut the resonance very far off peak, it is at first sight unexpected that R for the 1-atom wire is so much larger than the ideal value. However, the thick-barrier condition implicitly used by Kalmeyer and Laughlin does not hold for the Na atom in direct contact with the two electrodes. It was argued in general terms in Ref. [15] why this would lead to an increased resistance, but here we consider the question more specifically.

The reason why R for the 1-atom Na wire is particularly large appears to lie in the degree to which the atom's valence states maintain their integrity when the barrier is thin. As pointed out by Pendry [20], a valence

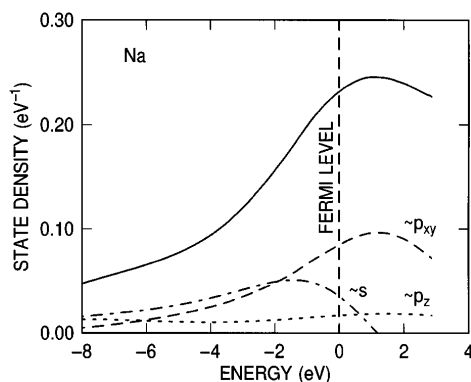


FIG. 3. Additional state density due to the presence of a single Na atom between two semi-infinite electrodes (solid curve) [11,19]. The broken curves give three of the components of this state density, as described in the text.

resonance for an atom interacting with a continuum of states can be “incomplete,” in that it need not contain a full complement of electrons—e.g., a filled resonant p state well below the Fermi level can have less than six electrons. The missing weight from an incomplete resonance, as he notes, is redistributed over a wide range of energies. The phase shift at the peak of the resonance will then in general be less than $\pi/2$, and the conductance for a configuration such as ours will be less than the quantum unit of conductance even when the resonance peak is right at the Fermi level.

The density of states shown as the solid curve in Fig. 3 can be decomposed into contributions that can be very roughly identified with the s , p_z (along the surface normal), and p_{xy} (transverse) states of the free Na atom as discussed in Ref. [21], by projecting the wave functions on the various spherical harmonics Y_{lm} . This decomposition is also shown in Fig. 3. We do not exhibit the $l = 2$ components, which are necessary to make the components given add up to the total for all lm (solid curve).

Now because of the fact that the valence resonances become less distinct at higher energies (and since the high-energy tail of the resonance is irrelevant to the phase shift at the Fermi level, which determines the low-bias conductance), we will discuss only the *lower segment* of each resonance. We define this as the part of the resonance lying at energies below that corresponding to the resonance peak. We also use the phrase *lower segment weight* to mean the area under this part of the curve in a density-of-states plot such as Fig. 3. If the resonance corresponded to an atomic state with negligible hybridization, it would, e.g., have a lower segment weight of 1 for an atomic s or p_z state ($m = 0$) and 2 for the degenerate p_{xy} state ($|m| = 1$); we will refer to these as the *ideal values*.

Most of the weight of the ($l = 0, m = 0$) and ($l = 1, m = 0$) components (labeled as $\sim s$ and $\sim p_z$) shown in Fig. 3, has clearly been redistributed to other energies: the lower segment weight of the $\sim s$ curve shown is only 0.2 states instead of the ideal value of 1, and the $\sim p_z$ curve hardly shows a trace of a resonant peak [22]. Even the ($l = 1, |m| = 1$) resonance (labeled $\sim p_{xy}$), which is somewhat more distinct, has a lower segment weight of only 0.4 states, instead of the ideal value of 2.

Even though several distinct channels make some contribution to the conductance of the 1-atom Na wire, the resonances associated with each of the channels are so incomplete that the sum of the contributions is still much less than $e^2/\pi \hbar$, as seen from the fact that the actual calculated R value is 33 k Ω (corresponding to a conductance of 40% of $e^2/\pi \hbar$). For Na wires with two or more atoms, we note that the end atoms are only in contact with a single semi-infinite electrode (and one atom on the other side), rather than two semi-infinite electrodes, and so the incompleteness of the resonances can be expected to be

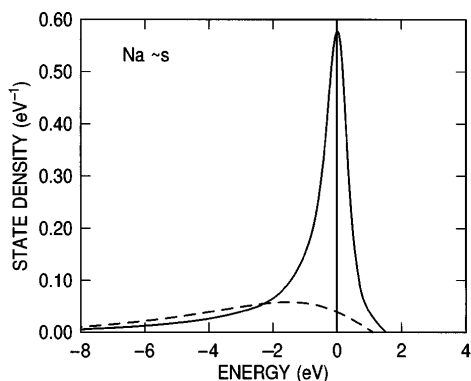


FIG. 4. The $\sim s$ component (taken about one atom) of the additional state density [19] due to the presence of a 1-atom (dashed curve) or a 2-atom (solid curve) Na wire between two semi-infinite electrodes.

less significant, since it is the interaction with the continuum of states that leads to incompleteness [20]. This is illustrated in Fig. 4, which shows the $\sim s$ contribution to the additional state density [19], computed in a sphere of radius 5 bohrs [23] centered on the atom in the 1-atom Na wire or on one of the two atoms in the 2-atom wire. The lower segment weight for the 1-atom wire is just 0.2, while it is 0.6 for the 2-atom wire, to be compared in both cases with the ideal value of 1. (In the 2-atom case, what is seen in Fig. 4 is the bonding resonance; the antibonding resonance is washed out [24].)

To understand why the 1-atom Al wire is so different (it in fact has $R = 6.6$ k Ω [3,25]), we show in Fig. 5 the corresponding additional state density and its lm decomposition. This is quite different from that seen in Fig. 3. The $\sim s$ component is well below the Fermi level, as expected from the fact that the Al 3s state is filled in the free atom. The $\sim p_z$ component remains somewhat indistinct. However, the $\sim p_{xy}$ resonance has a lower segment weight of 1.0 (as compared with the ideal value of 2), making it an appreciably more complete resonance than in the case of Na (where the $\sim p_{xy}$ lower segment weight was 0.4) [26]. A calculation of the type done for

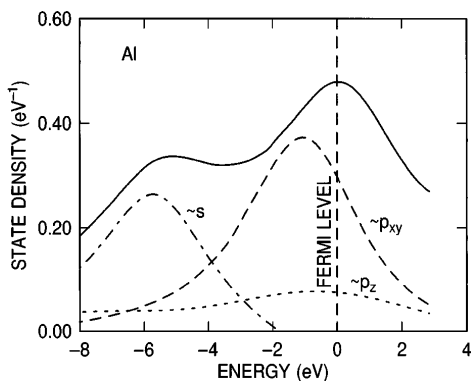


FIG. 5. Same as Fig. 3, except for Al atom.

Na in Fig. 4 shows only a small change in the degree of completeness of the $\sim p_{xy}$ resonance in going from the 1- to the 2-atom Al wire.

We have thus presented the particular case of an Na atomic wire, whose resistance decreases initially with wire length. This was seen to arise from the presence in the 1-atom wire of incomplete conduction channels that were a consequence of the substantial incompleteness of the valence resonances of the atom, which is strongly coupled to two macroscopic electrodes. This was contrasted with the more expected behavior of Al wires.

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- [2] A. Yazdani, D. M. Eigler, and N. D. Lang, *Science* **272**, 1921 (1996).
- [3] N. D. Lang, *Phys. Rev. B* **52**, 5335 (1995).
- [4] Y. Imry, in *Directions in Condensed Matter Physics: Memorial Volume in Honor of Shang-keng Ma*, edited by G. Grinstein and G. Mazenko (World Scientific, Singapore, 1986), p. 101; R. Landauer, *Z. Phys. B* **68**, 217 (1987); *J. Phys. Condens. Matter* **1**, 8099 (1989).
- [5] Note that we are defining the resistance here as the voltage difference between the reservoirs (the difference between the electrochemical potentials of the two reservoirs, measured deep in each reservoir, divided by the electron charge), divided by the current through the channel.
- [6] If we were discussing transmission through a series of one-dimensional barriers, then having two barriers in sequence with a small separation would lead to more transmission than a single barrier, because the double-barrier configuration has a resonant state. But in our case, each metal atom already corresponds to a double rather than a single barrier, for energies near the Fermi energy, so this is not relevant here.
- [7] C. J. Muller, J. M. Krans, T. N. Todorov, and M. A. Reed, *Phys. Rev. B* **53**, 1022 (1996); J. M. Krans, J. M. van Ruitenbeek, V. V. Fisun, I. K. Yanson, and L. J. de Jongh, *Nature (London)* **375**, 767 (1995); L. Olesen, E. Lægsgaard, I. Stensgaard, F. Besenbacher, J. Schiøtz, P. Stoltze, K. W. Jacobsen, and J. K. Nørskov, *Phys. Rev. Lett.* **72**, 2251 (1994); J. I. Pascual, J. Méndez, J. Gómez-Herrero, A. M. Baró, N. Garcia, and Vu Thien Binh, *Phys. Rev. Lett.* **71**, 1852 (1993); N. Agraït, J. G. Rodrigo, and S. Vieira, *Phys. Rev. B* **47**, 12345 (1993).
- [8] R. N. Barnett and U. Landman, *Nature (London)* **387**, 788 (1997).
- [9] We note here that for Al wires in the break-junction experiments described by J. M. Krans [Ph.D. Thesis, Rijksuniversiteit Leiden, 1996; see also J. M. Krans, C. J. Muller, I. K. Yanson, Th. C. M. Govaert, R. Hesper, and J. M. van Ruitenbeek, *Phys. Rev. B* **48**, 14721 (1993)], the last few conductance plateaus have a small positive slope

- with increasing distance. For example, the conductance increases (continuously) by $\sim 20\%$ with an increase of electrode separation of $\sim 1 \text{ \AA}$ (last plateau). (This is not seen for Na wires in these experiments.) The effective diameter of an Al atom is nearly 3 \AA , however, suggesting that such effects are due not to the elongation of a 1-atom-thick wire by the addition of an atom, as discussed in the present Letter, but rather to the structural distortions of a much more complex wire of the sort described by Barnett and Landman [8].
- [10] See, e.g., N. D. Lang, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, New York, 1973), Vol. **28**, p. 225. The use of the jellium model for the electrodes is not expected to have a significant effect on the results. Evidence for this is given by J. Bormet, J. Neugebauer, and M. Scheffler, *Phys. Rev. B* **49**, 17242 (1994), who study several different isolated atoms adsorbed on an Al(111) surface, and find that the density of states structure due to the presence of these atoms on the surface is rather similar to that found when the jellium model is employed for the surface.
- [11] In the calculations, we take the electrodes to have $r_s = 2$ bohrs, typical of a high-electron-density metal such as Al. Here $(4/3)\pi r_s^3 \equiv n^{-1}$, with n the mean interior electron number density in the electrodes.
- [12] D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979); G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
- [13] The bias used in the calculation is 0.01 V. The number of plane waves employed is specified by $N = 5$ for the transverse directions and by $N = 9$ for the surface-normal direction (see Ref. [3] for definition of N); the calculation is done in a box of width 12 bohrs in the transverse directions and 33 bohrs along the surface normal. The Na-surface bond length (measured from Na nucleus to positive-background edge of the electrode) is fixed at 3 bohrs, the calculated bond distance for one atom and a single surface. The Na-Na bond length is taken to be 7 bohrs, the bond distance in the bulk solid. We do not try to calculate bond lengths here because R is in general not very sensitive to their exact values (cf. Ref. [3]).
- [14] N. D. Lang, *Phys. Rev. B* **36**, 8173 (1987); **37**, 10395 (1988).
- [15] N. D. Lang, *Phys. Rev. B* **55**, 4113 (1997).
- [16] A recent STM measurement of the conductance of a single Gd atom on a Cu(100) surface (using an Au tip) has now found a similar result: the resistance was found to be 1.92 times the ideal value (A. Yazdani and L. Bürgi, private communication).
- [17] V. Kalmeyer and R. B. Laughlin, *Phys. Rev. B* **35**, 9805 (1987).
- [18] Cf. also A. G. Scherbakov, E. N. Bogachek, and U. Landman, *Phys. Rev. B* **53**, 4054 (1996); M. Büttiker, *Phys. Rev. B* **41**, 7906 (1990); A. Szafer and A. D. Stone, *Phys. Rev. Lett.* **62**, 300 (1989); J. A. Torres, J. I. Pascual, and J. J. Sáenz, *Phys. Rev. B* **49**, 16581 (1994).
- [19] We mean by this the difference in density of energy eigenstates between two systems: the pair of electrodes together with the atom between them, and the same pair of electrodes (with the same spacing) without the atom. The eigenstates referred to here are those of the single-particle equations of the density-functional formalism. The additional state density, since it is a difference of two positive quantities, can be negative (or have lm components that are negative) in some energy ranges; this is found for the high-energy tails of the $\sim s$ resonances here. Our figures do not show these negative regions, since they are irrelevant for our discussion. The state density plotted in Figs. 3 and 5 was computed as in Ref. [14]; contributions in a sphere of radius 7 bohrs were included.
- [20] J. B. Pendry, *J. Phys. C* **10**, 809 (1977). Cf. also J. P. Muscat and D. M. Newns, *Phys. Rev. B* **19**, 1270 (1979); R. M. Nieminen and M. Puska, *Solid State Commun.* **33**, 463 (1980).
- [21] N. D. Lang, in *Physics and Chemistry of Alkali Adsorption*, edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, Amsterdam, 1989); S. Holmström, *Physica Scripta* **36**, 529 (1987); H. Ishida, *Phys. Rev. B* **39**, 5492 (1989).
- [22] We use the symbol “ \sim ” to reflect the fact that l is not a good quantum number here (although m is).
- [23] For our decomposition to be most well-defined, we might consider taking it in a sphere of just half the Na-Na bond distance, i.e., a sphere radius of 3.5 bohrs. But this is somewhat too small to get a good estimate of the full contribution. The fact that in the 2-atom case, the sphere of radius 5 bohrs centered on one atom has a small overlap with the corresponding sphere centered on the other atom represents a negligible error, however.
- [24] The antibonding s resonance reappears distinctly if the electrodes are moved away from the Na dimer by ~ 3 bohrs, but even then it is much broader than the bonding resonance because it is closer in energy to the top of the potential barrier separating the dimer from the electrodes.
- [25] We note here the discussion of this same system by H. Mehrez, S. Ciraci, A. Buldum, and I. P. Batra, *Phys. Rev. B* **55**, R1981 (1997). They compute the local density of states at the “wire” atom but do not actually calculate the conductance, although they argue for its detailed connection with the local density of states.
- [26] We note here the experimental finding of incomplete conduction channels for Al contacts by E. Scheer, P. Joyez, D. Esteve, C. Urbina, and M. H. Devoret, *Phys. Rev. Lett.* **78**, 3535 (1997). Case (c) of their Fig. 1 is most comparable with the results given in Fig. 5 above. (The actual configuration of the contact in the experiment is not of course known.)