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Resistance of atomic wires

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The resistance of wires consisting of 1–3 atoms connecting two semi-infinite metallic electrodes is calculated for both small and large bias. The wires discussed consist of Al atoms, with one of the Al atoms substituted by S in certain cases. The resistances obtained are in the range 7–~30 kΩ. For the three-atom wire, the value of the resistance when the S atom is present depends on the order of the atoms in the wire. When the S is an end atom, the resistance at larger bias also shows a dependence on polarity (diode behavior). These studies involve a self-consistent calculation of the electron density distribution for the entire electrode/wire system.

I. INTRODUCTION

The development of the scanning tunneling microscope has brought with it the possibility of constructing (and measuring the resistance of) wires consisting of just several atoms that connect two macroscopic electrodes.[1] An early example of such a configuration (with the wire consisting of just one atom), was given by Gimzewski and Möller,[2] and was analyzed theoretically by Lang.[3,4] The theoretical calculation was done fully self-consistently, with electron-electron interactions included. The present paper extends this analysis to cases with more than one atom, which requires use of a different computational approach from that employed earlier.

The general aspects of the "constriction" resistance associated with the linking of two reservoirs by a very narrow channel have been discussed by Landauer,[5] Imry,[6] and Büttiker.[7–9] For an ideal one-dimensional channel (i.e., a channel with unit transmission probability that is narrow enough to have only one transverse state occupied) connecting two incoherent electron reservoirs, the resistance is $\pi\hbar/e^2 = 12\,900\ \Omega$. The resistance considered here is given by the voltage difference between the reservoirs (electrochemical potential difference divided by electron charge) divided by the current through the channel. We will see to what extent such a channel represents the properties of our atomic wires.

There are a number of recent studies of the resistance of constrictions that have a mesoscopic rather than atomic scale. The system usually considered is a two-dimensional electron gas in a semiconductor heterostructure with the constriction defined electrostatically by a split gate on top of the heterostructure.[10,11] This configuration permits studying, e.g., resistance as a function of constriction width (which is controlled by varying the voltage on the gate). Somewhat closer to the present problem are studies of the resistance of the neck that forms when a scanning tunneling microscope tip, after indenting a metal surface, is withdrawn, narrowing the neck until the contact is broken.[12] Simulations suggest that such necks show a gradual transition in width as their length is traversed,[12] rather than the abrupt transition envisioned in the present paper between the electrodes with flat, extended surfaces and the connecting wire consisting of a single line of atoms. (The former is closer to the adiabatic case as discussed by Glazman *et al.*[11]) More closely related to the present work are studies of microscopic wires connecting two reservoirs done using the tight-binding approximation.[13] These, however, are not self-consistent calculations: energy levels and coupling matrix elements are represented by simple parameters whose values are not calculated; and electron-electron interactions are either not taken into account, or are again included in a parametrized fashion. (The lack of electrostatic self-consistency in these treatments would also make it difficult to extend them to cases of large bias voltage, in which there can be substantial rearrangements of the electron distribution.)

II. GENERAL APPROACH

References 3, 14, and 15 calculated the current flow between two planar metallic electrodes, represented using the uniform-background (jellium) model,[16] with one atom in the region between them. The solution proceeded in the following way: First, within the framework of the density-functional formalism, the single-particle wave functions and self-consistent density distribution were found for the pair of bare metallic electrodes, assuming them for simplicity to be identical, in the presence of the bias voltage. Next, corresponding to each of these wave functions, a Lippmann-Schwinger equation involving a Green's function for the biased bimetallic junction was solved to obtain a single-particle wave function for the total system, consisting of the two electrodes plus the atom. From these wave functions, the density distribution for the total system was obtained, and the problem solved self-consistently using a modified iterative procedure. This same general approach is used here, except that the single atom is replaced by a group of atoms.

In the earlier treatments, each single-particle equation for the total system was solved within a large sphere centered on the atom by integrating an equivalent set of coupled radial equations outward from the origin. Each of these equations corresponded to a different $Y_{lm}(\Omega)$ to which the solution was taken to be proportional at the origin. This method is not practical when there is more than one atom, and we instead take the approach of representing the wave functions, within a box that includes the group of atoms, as a linear combination of plane waves that are periodic over the box, with the box made large enough to include the region where the potential is perturbed by the presence of the atoms. The behavior of the plane-wave representation outside of the box will be of no interest to us (we only want it to be good inside); and we will avoid the most important effects that would correspond to a periodic repetition of the group of atoms. In particular, we will use the Hockney method[17] for the Fourier-transform solution of Poisson's equation for isolated systems. The term "isolated" means that the only boundary condition is that the potential decays to zero correctly at infinity (as r^{-1} for a system with a net charge).[18] Thus, for example, if the group of atoms has a net dipole moment, we will not have as part of our computed electrostatic potential within the box the potential due to periodic repetitions of this dipole outside the box. We note also that the change in wave function induced by the presence of the group of atoms decays with distance, and so we will choose a box of sufficient size that the periodicity of the wave function at the box boundaries due to the representation does not have a significant effect on the quantities of interest.

III. THE EQUATIONS AND THEIR SOLUTION

A. Equations

As noted above, the analysis is based on the density-functional theory of many-electron systems, which requires the solution of effective one-electron Schrödinger-like equations.[19] These equations are here put into Lippmann-Schwinger form:[20,21]

$$\Psi^{MA}(\mathbf{r})=\Psi^{M}(\mathbf{r})+\int d^3\mathbf{r}'\,d^3\mathbf{r}''G^{M}(\mathbf{r},\mathbf{r}')\times\delta V(\mathbf{r}',\mathbf{r}'')\Psi^{MA}(\mathbf{r}'') \ . \tag{3.1}$$

The superscripts M and MA refer, respectively, to the pair of bare biased metal electrodes, and to the complete system consisting of the metal electrodes and the group of atoms between them. This equation embodies the motion that electrons in states of the electrodes impinge on and are scattered elastically by the potential $\delta V(\mathbf{r},\mathbf{r}')$, which describes the difference in potential between the complete system and the bare electrodes. It can be written

$$\delta V(\mathbf{r},\mathbf{r}')=v_{\mathrm{ps}}(\mathbf{r},\mathbf{r}')+\left[v_{\mathrm{xc}}(n^{MA}(\mathbf{r}))-v_{\mathrm{xc}}(n^{M}(\mathbf{r}))+\int d^3\mathbf{r}''\frac{\delta n(\mathbf{r}'')}{|\mathbf{r}-\mathbf{r}''|}\right]\delta(\mathbf{r}-\mathbf{r}') \ . \tag{3.2}$$

We use atomic units here (and below), with $|e|=m=\hbar=1$. The term $v_{\mathrm{ps}}(\mathbf{r},\mathbf{r}')$ is the sum of the (nonlocal) pseudopotentials representing the atomic cores, $v_{\mathrm{xc}}(n(\mathbf{r}))$ is the local-density approximation to the exchange-correlation potential,[22] $n^{M}(\mathbf{r})$ is the electron number density for the pair of biased metal electrodes, $n^{MA}(\mathbf{r})$ is the density for the complete system, and $\delta n(\mathbf{r})=n^{MA}(\mathbf{r})-n^{M}(\mathbf{r})$. We will use the atomic pseudopotentials introduced by Hamann, Schlüter, and Chiang.[23]

The nature of the wave functions Ψ^{M} has been discussed in Ref. 15. It will be recalled that $\Psi^{M}(\mathbf{r})$ has the form $e^{i\mathbf{K}_{\parallel}\cdot\mathbf{R}}u_{E\mathbf{K}_{\parallel}}(z)$, where $\mathbf{R}$ is the coordinate parallel to the surfaces and z the coordinate normal to them. Deep in the positively biased electrode (which we will take henceforth to be the left electrode), $u_{E\mathbf{K}_{\parallel}}(z)$ has the form of a linear combination of left-moving and right-moving plane waves with wave vector k_L. Here $\frac{1}{2}k_L^2=E-\frac{1}{2}|\mathbf{K}_{\parallel}|^2-v_{\mathrm{eff}}^{M}(-\infty)$, where E is the energy eigenvalue in the single-particle equations for the pair of biased electrodes and where $v_{\mathrm{eff}}^{M}(z)$ is the total effective potential (electrostatic plus exchange correlation) in these equations.

The character of $u_{E\mathbf{K}_{\parallel}}(z)$ (whether propagating or standing wave) depends, as discussed in Ref. 15, on the value of k_L: whether $\frac{1}{2}k_L^2$ is greater than or less than the potential step across the barrier, $v_{\mathrm{eff}}^{M}(\infty)-v_{\mathrm{eff}}^{M}(-\infty)$. We will specify this character by an additional subscript α: $u_{E\mathbf{K}_{\parallel}\alpha}$. For propagating states, we will replace α either by "+," which will correspond to a wave incident from the left (together with its reflected and transmitted parts) or by "−," which will correspond to a wave incident from the right. Thus, e.g.,

$$\Psi_{E\mathbf{K}_{\parallel}-}^{M}(\mathbf{r})=e^{i\mathbf{K}_{\parallel}\cdot\mathbf{R}}u_{E\mathbf{K}_{\parallel}-}(z) \ , \tag{3.3}$$

where

$$u_{E\mathbf{K}_{\parallel}-}(z)=(2\pi)^{-3/2}k_R^{-1/2}\times\begin{cases}e^{-ik_Rz}+Ae^{ik_Rz}, & z\rightarrow\infty \ ,\\ Be^{-ik_Lz}, & z\rightarrow-\infty \ .\end{cases} \tag{3.4}$$

Here k_L is as defined before and $\frac{1}{2}k_R^2=E-\frac{1}{2}|\mathbf{K}_{\parallel}|^2-v_{\mathrm{eff}}^{M}(\infty)$, and the coefficient has been chosen to accord with the continuum normalization which we will impose on the wave functions Ψ^{M}, specified by

$$\int d^3\mathbf{r}[\Psi_{E'\mathbf{K}_{\parallel}'\alpha}^{M}(\mathbf{r})]^*\Psi_{E\mathbf{K}_{\parallel}\alpha}^{M}(\mathbf{r})=\delta(E-E')\delta(\mathbf{K}_{\parallel}-\mathbf{K}_{\parallel}') \ . \tag{3.5}$$

The continuum wave functions Ψ^{MA} for the complete system, which are solutions to the Lippmann-Schwinger equation (3.1) will, via that equation, have the same labeling $(E,\mathbf{K}_{\parallel},\alpha)$ as the Ψ^{M}, even though of course $\mathbf{K}_{\parallel}$ no longer refers to a conserved quantity. These solutions will also have the same normalization as the Ψ^M (see Ref. 20), a fact that facilitates the calculation of the electron density distribution and the current. In the present paper, we will not be considering systems that have discrete states, and so, even though the treatment of such states is straightforward, we will not discuss them here. We note again that for $E_{FL} < E < E_{FR}$, where E_{FL} is the Fermi level in the left electrode and $E_{FR} = E_{FL} + \mathcal{V}$ is the Fermi level in the right electrode (bias $\mathcal{V}$ taken positive), we occupy only states corresponding to a wave incident from the right, i.e., only $\Psi^{MA}_{E\mathbf{K}_\parallel -}$ and not $\Psi^{MA}_{E\mathbf{K}_\parallel +}$ just as is done by McCann and Brown.[24]

The electron number density is given by the sum of squares of the occupied states $\Psi^{MA}_{E\mathbf{K}_\parallel \alpha}$, with a factor 2 included for spin degeneracy (we take the system to be unpolarized). The electric current density in the full system is given by

$$\mathbf{j}^{MA}(\mathbf{r}) = -2\int_{E_{FL}}^{E_{FR}} dE \int d^2\mathbf{K}_\parallel \, \mathrm{Im}\{[\Psi^{MA}_{E\mathbf{K}_\parallel -}(\mathbf{r})]^* \nabla \Psi^{MA}_{E\mathbf{K}_\parallel -}(\mathbf{r})\} \tag{3.6}$$

(recall that we are setting $|e|=1$), where the integral over $\mathbf{K}_\parallel$ is restricted by $|\mathbf{K}_\parallel| \leq \sqrt{2[E - v^M_{\mathrm{eff}}(\infty)]}$. Now let $\mathbf{j}^M$ be the current density for the pair of biased electrodes in the absence of the group of atoms. Then the quantity of interest to us is

$$\delta J = \int d^2\mathbf{R} \, \hat{z} \cdot [\mathbf{j}^{MA}(\mathbf{r}) - \mathbf{j}^M] \,, \tag{3.7}$$

which is independent of z since our system has no current sources or sinks. Here $\hat{z}$ is the unit vector pointing to the right and perpendicular to the surfaces of the electrodes. If we write $\Psi^{MA} = \Psi^M + \delta\Psi$, then

$$\begin{aligned} \delta J = -2\int_{E_{FL}}^{E_{FR}} dE \int d^2\mathbf{K}_\parallel \int d^2\mathbf{R} \, \mathrm{Im} \Bigg\{ & [\Psi^M_{E\mathbf{K}_\parallel -}(\mathbf{r})]^* \frac{d}{dz} \delta\Psi_{E\mathbf{K}_\parallel -}(\mathbf{r}) + \delta\Psi^*_{E\mathbf{K}_\parallel -}(\mathbf{r}) \frac{d}{dz} \Psi^M_{E\mathbf{K}_\parallel -}(\mathbf{r}) \\ & + \delta\Psi^*_{E\mathbf{K}_\parallel -}(\mathbf{r}) \frac{d}{dz} \delta\Psi_{E\mathbf{K}_\parallel -}(\mathbf{r}) \Bigg\} \,, \end{aligned} \tag{3.8}$$

where the integration range for $\mathbf{K}_\parallel$ is the same as in Eq. (3.6).

B. Calculation in plane-wave representation

We enclose the group of atoms introduced between the electrodes in a cubic box of side $2L$. The box is taken large enough that δV, the potential appearing in Eq. (3.1), is negligible outside the box.[25] We then represent, e.g., $\Psi(\mathbf{r})$ within the box as

$$\Psi(\mathbf{r}) = \sum_{\mathbf{n}} \Psi_{\mathbf{n}} e^{i\mathbf{k}_{\mathbf{n}} \cdot \mathbf{r}} \,, \tag{3.9}$$

where $\mathbf{n} = (n_x, n_y, n_z)$ and $\mathbf{k}_{\mathbf{n}} = \pi\mathbf{n}/L$. The n_i (with $i = x$, y, or z) are integers, and the sum extends over the ranges specified by $-N \leq n_i \leq N$. Similarly, e.g., we write

$$\delta V(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{n}, \mathbf{n}'} e^{i\mathbf{k}_{\mathbf{n}} \cdot \mathbf{r}} \delta V_{\mathbf{n}\mathbf{n}'} e^{-i\mathbf{k}_{\mathbf{n}'} \cdot \mathbf{r}'} \,. \tag{3.10}$$

With this representation, Eq. (3.1) becomes

$$\sum_{\mathbf{n}'} C_{E\mathbf{n}\mathbf{n}'} \Psi^{MA}_{E\mathbf{K}_\parallel \alpha \mathbf{n}'} = \Psi^M_{E\mathbf{K}_\parallel \alpha \mathbf{n}} \,, \tag{3.11}$$

where

$$C_{E\mathbf{n}\mathbf{n}'} = \delta_{\mathbf{n}\mathbf{n}'} - (2L)^6 \sum_{\mathbf{n}''} G^M_{E\mathbf{n}\mathbf{n}''} \delta V_{\mathbf{n}''\mathbf{n}'} \tag{3.12}$$

($\delta_{\mathbf{n}\mathbf{n}'}$ is a Kronecker delta). Now the Green's function satisfies the equation

$$[E + \tfrac{1}{2}\nabla^2 - v^M_{\mathrm{eff}}(z)] G^M_E(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{3.13}$$

and can be put in the form

$$G^M_E(\mathbf{r}, \mathbf{r}') = \frac{1}{2\pi^2} \int d^2\overline{\mathbf{K}}_\parallel \, e^{i\overline{\mathbf{K}}_\parallel \cdot (\mathbf{R} - \mathbf{R}')} \times \frac{u^L_{E\overline{\mathbf{K}}_\parallel}(z_<) u^R_{E\overline{\mathbf{K}}_\parallel}(z_>)}{W_{E\overline{\mathbf{K}}_\parallel}} \,, \tag{3.14}$$

where $z_<$ ($z_>$) is the lesser (greater) of z and z'. Here (as above)

$$\left[E + \frac{1}{2}\frac{d^2}{dz^2} - \frac{1}{2}|\overline{\mathbf{K}}_\parallel|^2 - v^M_{\mathrm{eff}}(z) \right] u^\beta_{E\overline{\mathbf{K}}_\parallel}(z) = 0 \,, \tag{3.15}$$

where $\beta = L$ or R, with

$$u^L_{E\overline{\mathbf{K}}_\parallel}(z) \propto \exp(-i\bar{k}_L z) \quad \text{as } z \to -\infty \,,$$

$$u^R_{E\overline{\mathbf{K}}_\parallel}(z) \propto \exp(i\bar{k}_R z) \quad \text{as } z \to \infty \,,$$

where

$$\tfrac{1}{2}\bar{k}_L^2 + v^M_{\mathrm{eff}}(-\infty) = \tfrac{1}{2}\bar{k}_R^2 + v^M_{\mathrm{eff}}(\infty) = E - \tfrac{1}{2}|\overline{\mathbf{K}}_\parallel|^2 \,;$$

i.e., G^M is an outgoing-wave Green's function (often denoted G^+). The quantity $W_{E\overline{K}_\parallel}$ in Eq. (3.14) is the Wronskian (which is z independent):

$$W_{E\overline{\mathbf{K}}_\parallel} = u^L_{E\overline{\mathbf{K}}_\parallel}(z) \frac{d}{dz} u^R_{E\overline{\mathbf{K}}_\parallel}(z) - u^R_{E\overline{\mathbf{K}}_\parallel}(z) \frac{d}{dz} u^L_{E\overline{\mathbf{K}}_\parallel}(z) \,. \tag{3.16}$$

(The wave functions denoted u^β here, unlike the similarly defined u_α discussed earlier, are not normalized.) The plane-wave representation for G^M is given in Appendix A.

We will in the present paper take the atom positions to be given by chemical bond lengths obtained from data on crystals, rather than by a minimization of the total system energy. Our results for resistance are found to be not very sensitive to the exact values of these bond lengths. We will typically start our calculation with a trial $\delta n(\mathbf{r})$ consisting of a superposition of atomic densities. From this we obtain $\delta V_{\mathbf{nn}'}$ (with use of Poisson's equation as discussed in Sec. II), and then $\Psi^{MA}_{E\mathbf{K}_\parallel \alpha \mathbf{n}}$ from Eq. (3.11). These wave functions give a new electron density, and the cycle is repeated using a modified iterative procedure until a self-consistent solution is obtained. The calculations were done using the IBM 9076 SP2 parallel computer.

C. Obtaining the current

We now discuss the calculation of the current. We might consider term-by-term differentiation of the plane-wave representation (3.9) for the wave function, in order to evaluate the current from Eq. (3.8), but this is not in fact a good procedure, because the differentiated series has very poor convergence properties. This poor convergence should not be surprising; the reader can easily understand the problem by evaluating in this way the current associated, e.g., with a simple plane wave of arbitrary wave vector. Convergence factors[26] can be used to produce some improvement in this procedure, but the results are still not adequate for values of N feasible to use in the present study. We employ instead a different approach, not involving term-by-term differentiation of the plane-wave expansion of the wave function.

The expression for $\delta\Psi(\mathbf{r})$ that will instead be differentiated is that given by the Lippmann-Schwinger equation (3.1). If we substitute the plane-wave expansions for $\delta V(\mathbf{r},\mathbf{r}')$ and $\Psi^{MA}(\mathbf{r})$ into the integrand in Eq. (3.1), we obtain

$$\delta\Psi_{E\mathbf{K}_\parallel -}(\mathbf{r}) = \int d^2\overline{\mathbf{K}}_\parallel \, e^{i\overline{\mathbf{K}}_\parallel \cdot \mathbf{R}} \sum_{\mathbf{n},\mathbf{n}'} F_{E\overline{\mathbf{K}}_\parallel \mathbf{n}}(z)\, \delta V_{\mathbf{nn}'} \Psi^{MA}_{E\mathbf{K}_\parallel -,\mathbf{n}'} , \tag{3.17}$$

where

$$F_{E\overline{\mathbf{K}}_\parallel \mathbf{n}}(z) = \frac{16L^5}{\pi^2} \frac{\sin(\overline{K}_x L - \pi n_x)\sin(\overline{K}_y L - \pi n_y)}{(\overline{K}_x L - \pi n_x)(\overline{K}_y L - \pi n_y)} \times \frac{1}{W_{E\overline{\mathbf{K}}_\parallel}} \int_{-L}^{L} dz'\, e^{ik_{n_z} z'} u^{L}_{E\overline{\mathbf{K}}_\parallel}(z_<) u^{R}_{E\overline{\mathbf{K}}_\parallel}(z_>) . \tag{3.18}$$

When this is substituted into Eq. (3.8) for the current, the derivative with respect to z can be done numerically on the $u^{\beta}_{E\overline{\mathbf{K}}_\parallel}(z)$, which are known to essentially arbitrary accuracy.[27]

IV. SELECTED RESULTS

A. One-, two-, and three-atom aluminum wires

We now consider the conductance of Al wires consisting of a small number of atoms connecting our pair of semi-infinite electrodes.[28] This conductance δG is given by $\delta G = \delta J / \mathcal{V}$, with the bias $\mathcal{V}$ as specified above and δJ as given in Eqs. (3.7) and (3.8). For purposes of discussion, we will express this conductance in terms of a resistance $R \equiv 1/\delta G$.

We first consider wires of one, two, and three Al atoms (with the two- and three-atom wires perpendicular to the surfaces).[29] For now we take a small bias $\mathcal{V} = 0.01$ V, which means that it is only the states close to the Fermi level that lead to a net current. The self-consistent electronic charge distribution for the three-atom case is shown in Fig. 1. The calculated resistances are given by the first three entries in Table I. It will be recalled in connection with this table that the ideal one-dimensional channel discussed in the Introduction has a resistance of 12.9 kΩ. If such a channel supports M independent transverse states instead of just one, with no interchannel scattering, the resistance is 12.9/M kΩ.

The various states of the Al atom that lie at the Fermi level in our problem correspond in some loose sense to these channels. It is the partially occupied $3p$ states of this atom that are cut by the Fermi level when the atom (as here) is bonded to a high-density metal; thus if there were really a true correspondence between this set of

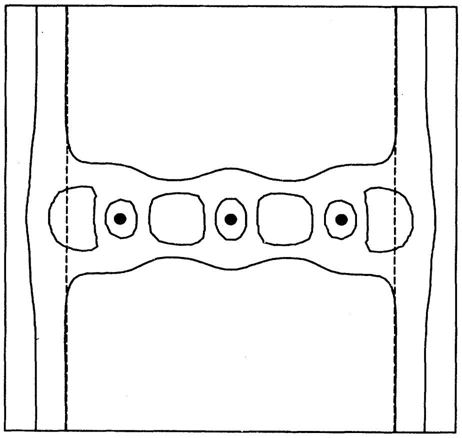

FIG. 1. Contours of constant electronic charge density for a three-atom straight Al wire perpendicular to a pair of biased semi-infinite electrodes that are represented using the uniform-background model ($r_s = 2$ bohrs). Contours are shown in a plane through the Al nuclei (black dots); the values are selected to be visually informative. The contours along the wire boundary and those surrounding the nuclei have a value of 0.014 electrons/bohr^3; the others have a value of 0.028 electrons/bohr^3. Bias $\mathcal{V} = 0.01$ V (left electrode positive). The nearest-neighbor Al separation is 5.4 bohrs, and the distance between the positive-background edge of each electrode (indicated by a dashed line) and the nucleus of the Al bonded to it is 2.6 bohrs. (1 bohr = 0.529 Å.)

TABLE I. Resistances R associated with one- to three-atom straight Al and Al/S wires, which are perpendicular to the electrode surfaces, at low bias ($\mathcal{V}=0.01$ V). The string of element symbols in the first column indicates the ordering of the atoms starting at the left electrode; e.g., S-Al-Al means a chain with a sulfur atom bonded to the left electrode, an aluminum at the center, and an aluminum bonded to the right electrode. Number of plane waves in computation is given by $N=6$. (In cases including S, the cubic box was replaced by a rectangular box as described in Ref. 25 and the N value for the z direction was increased to 7, while being reduced to 4 for the x and y directions.)

Composition	R (kΩ)
Al	6.6
Al-Al	9.0
Al-Al-Al	8.3
S-Al-Al	19
Al-S-Al	32

three orbital states (the two spin states are already taken into account in the ideal value of 12.9 kΩ), we would expect a wire resistance of 4.3 kΩ. Of course there is not such a close correspondence, which is why none of the values for Al wires in Table I is equal to this. (Also our geometry does not have the ideal "adiabatic" character mentioned in the Introduction.)

To understand one of the ways in which this correspondence is imperfect, we recall a calculation of Kalmeyer and Laughlin.[30] These authors 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 constant-potential regions, this discrete state broadens into a Lorentzian resonance (taking the discrete-state energy to be above the constant potential). 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 $e^2/\pi\hbar$ (taking spin degeneracy into account), but off resonance, this conductance is decreased by the ratio of the value of the Lorentzian state density at the energy of interest to the peak value.

The Fermi level will not, in general, cut the atomic resonances in a calculation such as ours at their peak. As an illustration of this point, we show in Fig. 2 the additional state density due to the presence of an Al atom adsorbed just on a single metal surface (identical to one of our electrodes); note that the Fermi level cuts the $3p_{xy}$ state density resonance substantially down from its peak value (p_z states have their lobes perpendicular to the surface and p_{xy} states have them parallel).

We expect that the $3p_{xy}$ states of an adsorbed Al atom have a greater total overlap with the states of the metal on which it is adsorbed than with those of an adjacent single Al atom (such as with those of the center atom in the three-atom wire). Thus, quite apart from questions of the resonance position, we expect the $3p_{xy}$ orbitals to form effective conduction channels between the electrodes when there is one Al atom, but to form less effective channels when there are three atoms (or two),[31,32] which is in accord with the results for Al wires given in Table I.

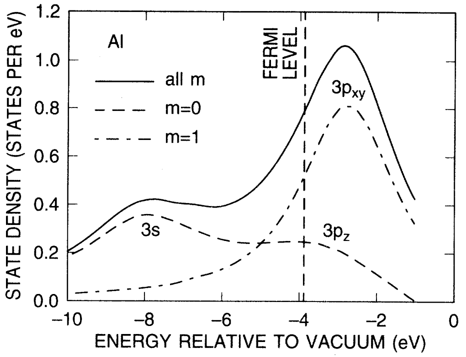

FIG. 2. Difference in eigenstate density between a single metal surface (uniform-background model, $r_s=2$ bohrs) with an Al atom bonded to it, and the same metal surface without the atom. Components with azimuthal quantum numbers $m=0$ and 1 are shown separately. The Al is at the calculated equilibrium distance for this configuration of 2.6 bohrs (measured between nucleus and positive-background edge). Peaks are labeled by the atomic state from which they arise. This calculation uses the procedure of Ref. 21.

B. Wires consisting of two aluminum atoms and one sulfur atom

If we replace one of the end Al atoms in the three-atom wire by a sulfur atom,[33] the low-bias resistance increases by a factor of ~2, as seen in Table I. This is understandable in view of the fact that since sulfur is electronegative, the $3p$ resonance is mostly filled and thus well below the Fermi level, with only a small tail at the Fermi level. This is illustrated by the curve of the density of states for S adsorbed just on a single surface, shown in Fig. 3. Sulfur thus forms a low-density-of-states bottleneck to the conduction.

If we change the position of the S atom from the end of the chain to the center, the resistance increases yet further, to a factor of ~4 relative to that of the Al chain.

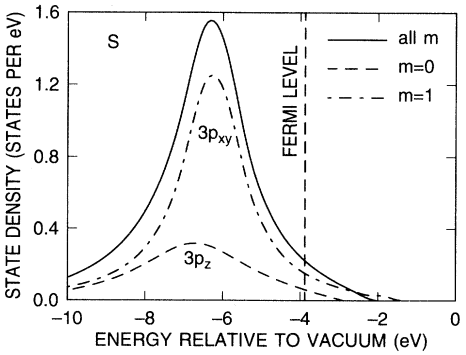

FIG. 3. Eigenstate density difference for S atom bonded to a metal surface. Details are the same as given in the caption of Fig. 2, except the metal-adatom distance is 1.9 bohrs.

TABLE II. Polarity dependence of the resistance R associated with the S-Al-Al chain. The sign of the bias $\mathcal{V}$ gives the polarity of the left electrode (i.e., the electrode bonded to the sulfer atom). Number of plane waves in computation is given in the caption of Table I.

$\mathcal{V}$ (V)	R (kΩ)
+2	21
−2	15

When the S atom is not in direct contact with the metal but only with an Al on each side, its $3p$ resonance becomes narrower, pulling the tail away from the Fermi level. It is for reasons such as this that we should expect the resistance of atomic wires composed of more than one kind of atom to depend on the order of these atoms in the chain.

Because of the asymmetry of the S density of states about the Fermi level,[34] we would expect the resistance at larger bias to be dependent on the polarity. This is seen in Table II for the S-Al-Al chain with a bias of ±2 V. For +2 V (see table caption for the sign convention), electrons are injected from the Al part of the chain into S states above the Fermi level, whose density is relatively small (cf. Fig. 3). A negative bias polarity involves instead the higher density of filled S states in the conduction process.

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APPENDIX A

The Green's function G^M in the plane-wave representation is given by

$$G^M_{E\mathbf{nn}'}=\frac{(-1)^{n_x+n_y+n'_x+n'_y}}{2\pi^2L^4}\int_0^\infty t\,dt\,g_{En_zn'_z}(t/L)\int_0^{\pi/2}d\phi\,\sin^2(t\cos\phi)\sin^2(t\sin\phi)$$
$$\times(t^2\cos^2\phi+\pi^2n_xn'_x)(t^2\sin^2\phi+\pi^2n_yn'_y)$$
$$\times[(t^2\cos^2\phi-\pi^2n_x^2)(t^2\cos^2\phi-\pi^2n_x'^2)$$
$$\times(t^2\sin^2\phi-\pi^2n_y^2)(t^2\sin^2\phi-\pi^2n_y'^2)]^{-1}\;,$$

where

$$g_{En_zn'_z}(|\overline{\mathbf{K}}_\parallel|)=\frac{1}{W_{E\overline{\mathbf{K}}_\parallel}}\int_{-L}^{L}dz\,e^{-ik_{n_z}z}$$
$$\times\left[u^R_{E\overline{\mathbf{K}}_\parallel}(z)\int_{-L}^{z}dz'u^L_{E\overline{\mathbf{K}}_\parallel}(z')e^{ik_{n'_z}z'}+u^L_{E\overline{\mathbf{K}}_\parallel}(z)\int_{z}^{L}dz'\,u^R_{E\overline{\mathbf{K}}_\parallel}(z')e^{ik_{n'_z}z'}\right].$$

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[29] We take the Al-surface bond length (measured from the Al nucleus to the positive-background edge of the electrode) to be fixed at 2.6 bohrs, which is the calculated bond distance for the case in which nothing else is bonded to the atom [see N. D. Lang, Phys. Rev. B **49**, 2067 (1994)]. We take the Al-Al bond length to be 5.4 bohrs, which is the bond distance calculated for bulk Al using the local-density approximation by V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978). We do not try to calculate the bond lengths here because our results are not very sensitive to the exact values of these lengths: for example, expanding all bond lengths in the three-atom Al wire by 0.2 bohr changes the calculated resistance by less than 1%.

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cal bond between atoms or between an atom and a surface is that the coupling is *not* small, i.e., that it is not capable of being treated perturbatively.

[32] The peak in the local density of states that can be associated with p_{xy} states is narrower on the center Al atom in the three-atom linear chain than on the end atoms. This supports the contention that the overlap between $3p_{xy}$ orbitals on the atom is larger with states of the metal than with these same orbitals on an adjacent Al atom.

[33] We take the bond length between the surface and the S atom (measured from the S nucleus to the positive-background edge of the electrode) to be fixed at 1.9 bohrs, which is the calculated bond distance for the case in which nothing else is bonded to the atom [see N. D. Lang, S. Holloway, and J. K. Nørskov, Surf. Sci. **150**, 24 (1985)]. We take the S-Al bond length to be 4.4 bohrs, which is the measured distance in β-Al_2S_3 crystals: R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1964), Vol. 2.

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