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Electrical conductance of parallel atomic wires

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The effects of lateral interactions on the conductance of two atomic wires connected in parallel are investigated using density-functional theory. Carbon-atom wires with a cumulene structure end bonded to two metal electrodes are used as the model system. Large variations of the low-bias conductance of the system as a function of the separation of the two wires on the atomic scale are predicted. This variation results from two types of interactions: (a) a direct bonding interaction between the atomic wires, and (b) an indirect interaction associated with the presence of the metal electrodes. The electrodes transfer an amount of charge to the carbon wires that varies with the separation *d* between the wires by as much as a factor of 2. The conductance changes, as a function of *d*, follow closely the variation of the density-of-states of the system at the Fermi level.

There is currently strong interest in measuring the electrical properties of atomic and molecular structures and understanding the factors that determine them. These studies are motivated by the possible use of such systems in future molecular electronic technologies.[1–7] Some of the simplest but very important atomic/molecular electronic components are wires composed of atomic or molecular chains.[8–31] In previous work,[12,18] we examined through first-principles calculations the electrical properties of wires composed of ''cumulene'' carbon atom chains, and compared them with the predictions of general theories of transport in low-dimensional systems.[32] In this paper, we report on the interaction between parallel conductors and its influence on the conductance and capacitance of the atomic system. Two straight carbon chains connected in parallel between two flat metal electrodes are used as the model system. Earlier discussions of parallel atomic-scale conductors have been given by Yaliraki and Ratner[33] and by Magoga and Joachim.[34]

It is of course well known that the equivalent conductance G_{total} of a number n of macroscopic conductors in parallel is simply the sum of the conductances of the individual wires, i.e., $G_{\text{total}}=\Sigma_{i=1}^{n}G_i$. To take advantage of the extreme miniaturization of future molecular electronic devices, the separation between the individual components should also be in the atomic/nanoscale regime. Currently, most studies of the conductance of molecular wires utilize dense layers of these molecules chemisorbed between flat metal electrodes.[35–39] The observed conductance is divided by the number of molecules between the electrodes to obtain the conductance of an individual molecule, i.e., the possible effects of interwire interactions on the electrical properties are typically ignored. From studies of chemisorption, on the other hand, it is well established that such interactions exist, and become very significant at short distances.[40] Here we explore how direct wire-wire interactions and the coupling of the wires through the metal electrodes affect their electrical properties, and to what extent the simple superposition law for parallel conductors is valid on the atomic scale. The metal electrodes are described using the semi-infinite uniform-background model,[41] while the carbon atomic cores are described using pseudopotentials.[42] The self-consistent density-functional calculation and the method used to calculate the current and hence the conductance of the wires have been described before.[43] The geometrical parameters of the carbon chains are the same as those in Ref. 12, i.e., the spacing between carbon atoms is 2.5 a.u. (Ref. 44) while the end carbon atoms of the chain are 1.4 a.u. inside the positive background edge of the uniform background model.[45]

In Fig. 1 we show the computed low-bias[46] conductance (in units of the quantum of conductance[47] $2e^2/h$) of pairs of five- and six-carbon-atom wires as a function of the separation d between the wires in the pair. The short-dashed bar at the right side of each panel indicates the sum of the conductances of the two wires at infinite separation, i.e., in the absence of any wire-wire interaction. It is clearly seen that at small separations, the conductance of the two-wire system is not the sum of the conductances of the separate wires. Instead, significant variations (increase or decrease) of the conductance of the two-wire system take place as the interwire separation d is varied. Furthermore, the details of the variation depend on the structure, i.e., number of carbon atoms in the wires.

To obtain insight into the causes of the conductance variation seen in Fig. 1, we investigated the electronic structure of the metal–two-wire–metal system as a function of the separation d. Figure 2 (top) shows for comparison the density-of-states (DOS)[48] of a single six-carbon chain between the two metal electrodes, while the center and bottom panels of this figure show the DOS of the metal–six-carbon-chains–metal system at $d=6.0$ and 3.5 a.u., respectively. It is clear that as d is varied, the electronic structure of the two-wire system undergoes significant changes in the region close to the Fermi energy. The character of the electronic structure changes can be elucidated by examining a plot of a difference in charge densities specified in the following way: We use the symbol $\rho(\mathbf{r};X)$ to denote the electron-density distribution of system X (but we will usually suppress the position variable $\mathbf{r}$ in our discussion). We are interested in the electron density $\delta\rho$ associated with the presence of the wires in the metal-wires-metal system, and so we define this as

$$\delta\rho(\text{wires})=\rho(\text{metal}-\text{wires}-\text{metal})-\rho(\text{metal}-\text{metal}),$$

i.e., the difference in electron densities of the metal-wires-metal system and the system consisting of just the two metal

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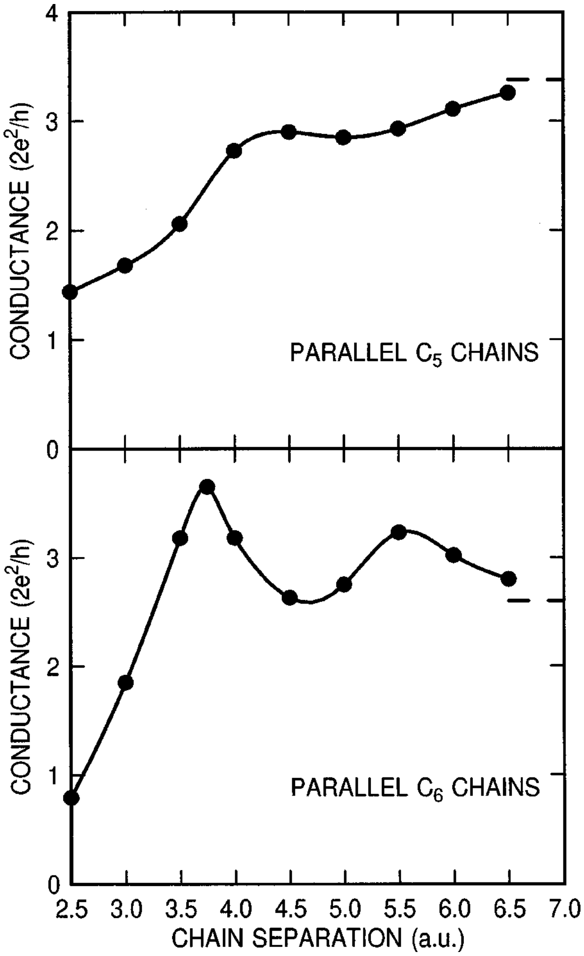

FIG. 1. Conductance (in units of the conductance quantum $2e^2/h$) of a pair of five- and six-carbon-atom wires as a function of the separation (in atomic units) between the wires. Short-dashed bar at right side of each panel indicates sum of the conductances of the two wires at infinite separation. Calculated values (dots) connected by a smooth curve. (1 a.u. = 0.529 Å.)

electrodes without the wires. Now using these definitions, the particular quantity we want to display is

$$\delta\rho(\text{pair of wires}) - 2\,\delta\rho(\text{single wire}),$$

where the notation used here is short for a subtraction in which each of the single wires is considered to be placed at the position of one of the two wires in the pair. This difference shows how the interaction between the wires alters the charge density. A plot of this quantity for $d = 3.5$ a.u. is given in Fig. 3. It shows a clear increase in charge density in the region between the two wires, indicating the development of interchain chemical bonds.

To further explore the nature of this bonding interaction, we performed local density functional (LDF) calculations on a pair of C_6 chains not attached to electrodes using the GAUSSIAN 98 program.[49] Changes in bond orders and Mulliken populations[50] were used to determine the nature of the changes in electronic structure brought about by the interchain interactions. The calculations show that when $d \leq 6$ a.u., the two chains interact via the p_y orbitals (the y axis is as shown in Fig. 3) that form the π bonds along each carbon atom chain. No corresponding interaction is found between the p_x orbitals (the x axis is normal to the plane of Fig. 3) of the carbon chains, indicating that the interchain bonds have σ character, i.e., that there is a conversion of π bonds along each chain to σ bonds linking the two chains. For example, at a chain separation of $d = 3.5$ a.u., the interchain bond orders between atom pairs 1-7, 2-8, and 3-9 are 0.69, 0.32, and 0.57, respectively. Formation of these bonds

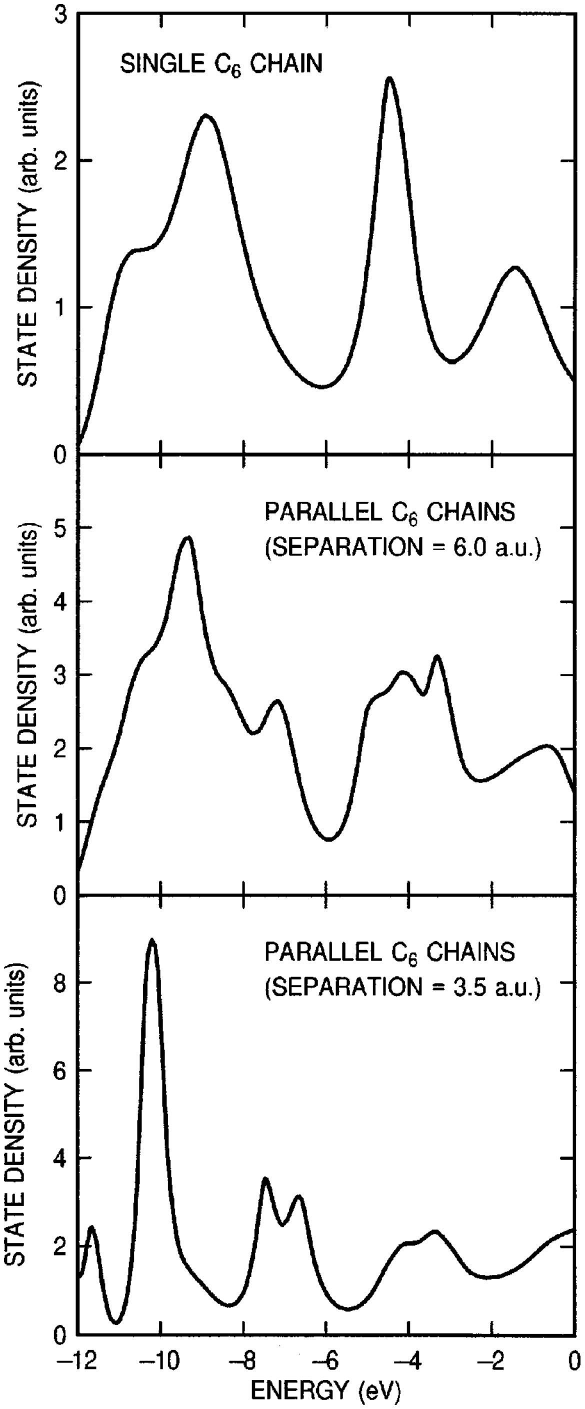

FIG. 2. Top: density-of-states (Ref. 48) for a single six-carbon chain between two metal electrodes. Center and bottom: density-of-states for the metal–six-carbon-chains–metal system at chain spacing of 6.0 and 3.5 a.u., respectively. The Fermi level is the zero of energy (we neglect the distinction between the right- and left-electrode Fermi levels here, since they are separated by just 0.01 eV).

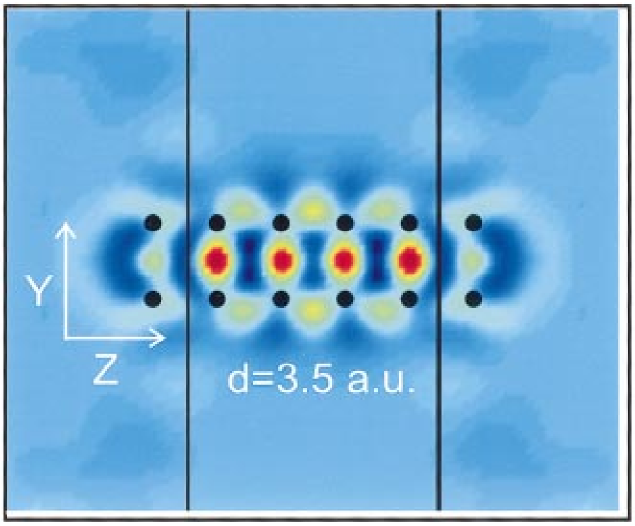

FIG. 3. (Color) Change in electron density due to the interaction between two six-carbon wires linking a pair of electrodes (defined explicitly in the text). Color scale extends from dark red (electron excess) to dark blue (electron deficit). Wire spacing is 3.5 a.u. Black dots indicate positions of the carbon atoms; black vertical lines indicate the edges of the electrode positive backgrounds.

decreases the bond order of π bonds along the individual chains. Specifically, the bond orders between atoms 2-3 and 3-4 are found to decrease by 0.52 and 0.16, respectively. The bond order between atoms 1-2 is not reduced because by bringing together the two carbon chains, the previously nonbonding electrons at the ends of the chains are rehybridized and participate in both intra- and interchain bonding.

The above results show that at short separations, lateral interactions between a pair of atomic wires attached to two electrodes are also present to some degree in the free pair (i.e., the pair not attached to electrodes). However, we also find that the metal electrodes play a major role in the interaction between the two wires. The influence of the electrodes can be clearly seen in Fig. 4, which gives the difference

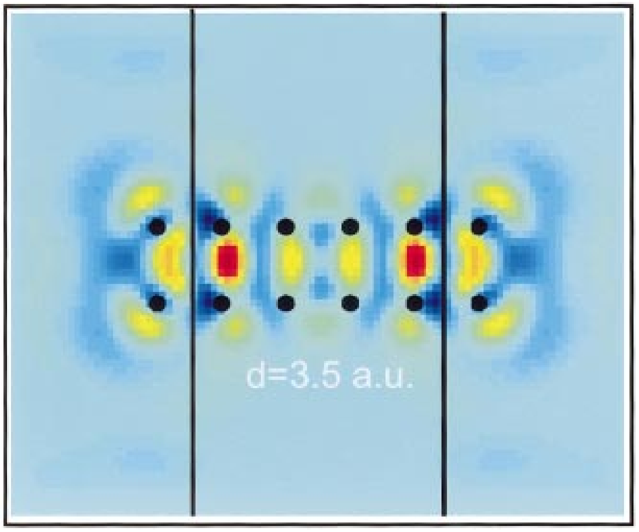

FIG. 4. (Color) Change in electron density associated with attaching a free pair of six-carbon chains to metal electrodes (defined explicitly in the text). See caption of Fig. 3 for other details.

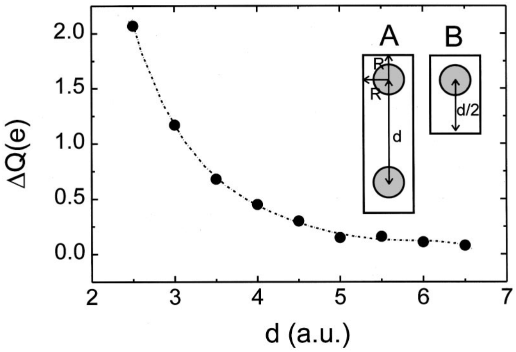

FIG. 5. Additional electronic charge transfer per wire ΔQ due to the presence of a second wire (C_5 wires) (defined explicitly in the text). ΔQ is shown as a function of wire spacing d, and is given in units of the electron charge (the positive values shown correspond to an electron excess). Inset figures show boxes over which electron density is integrated to get this result (see the text). $R = 1.75$ a.u.

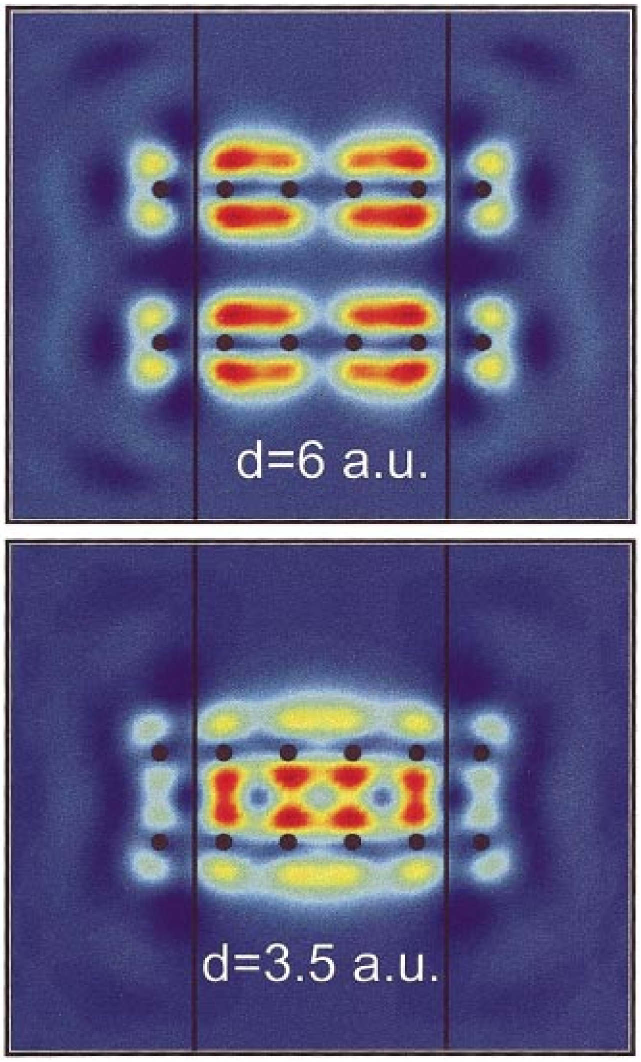

FIG. 6. (Color) Contribution to $\delta\rho$ for C_6 chains arising from the highest-energy peak in the occupied density-of-states, i.e., the HOMO, seen in Fig. 2 (for $d = 6$ a.u. and 3.5 a.u.). See Fig. 3 caption for other details. Note that since $\delta\rho$ is a difference of electron densities, it can exhibit negative values in some regions.

$$\delta\rho(\text{pair of wires}) - \rho(\text{free pair of wires})$$

for $d = 3.5$ a.u. An accumulation of charge in the interchain bonding region is observed, which helps to further bind the two atomic wires. In our previous study of single carbon wires we found that there is significant charge transfer from the electrodes to the wire. The amount of transferred charge increases with the length of the wire (i.e., the electrical capacitance of the wire). For a C_5 wire connected to a single electrode, the transferred charge was found to be 0.7 electrons.[18] The connection to a second electrode was found to increase the transferred charge by only $\sim 30\%$. It is important to find out if the charge transfer process in the two-wire system is affected by the interwire distance *d*. The fact that, as Fig. 4 shows, the charge is more delocalized than in the individual wires by occupying the interwire region, implies that the capacitance of the system should be increased at small *d*, allowing a larger charge transfer. To estimate the amount of charge transfer as a function of *d*, we perform the following calculation: We enclose the pair of wires in a rectangular box as shown in cross section in inset A of Fig. 5. The sides of the box are a distance *R* from the wires as shown, and the ends of the box are the same distance *R* from the ends of the wires. Let us denote the integral of $\delta\rho(\mathbf{r};\ \text{pair of wires})$ over this box by Q_2. Now enclose the wire in the system metal–single-wire–metal in the rectangular box shown in inset B of Fig. 5 (half of the box shown in inset A) and denote the integral of $\delta\rho(\mathbf{r};\ \text{single wire})$ over this box by Q_1. The additional electronic charge transfer per wire due to the presence of a second wire is then defined as $\Delta Q = \frac{1}{2}Q_2 - Q_1$. This quantity for C_5 wires is shown in Fig. 5 as a function of wire spacing *d*. A large variation in the additional charge transfer is observed, ranging from 0.1*e* per wire at $d = 6$ a.u. to 2.1*e* per wire at $d = 2.5$ a.u. This variation corresponds to as much as a doubling of the capacitance of the system of two noninteracting wires. As we saw above, the key change in electronic structure of the two-wire system as the interwire separation is reduced, involves a direct and through-the-electrode coupling (bonding) of the wires. While the strength of the interaction is monotonic, the conductance changes in a much more complex manner (see Fig. 1). As Fig. 6 shows, the spatial distribution of the partially occupied HOMO (highest occupied molecular orbital) of the two-wire system, which should be involved in the conduction process, changes significantly with the interchain distance. Nevertheless, a very good correlation is observed when comparing the calculated conductance of the two-wire system with the density-of-states at the Fermi energy $[\mathrm{DOS}(E_F)]$ of the combined system (see Fig. 7). This demonstrates that, as in the case of an isolated atomic wire,[12,18] the conductance of a two- (or more) wire system still depends primarily on the magnitude of the $\mathrm{DOS}(E_F)$. Conversely, any lateral interactions between molecular wires in parallel that affect $\mathrm{DOS}(E_F)$ would affect the overall conductance of the system.

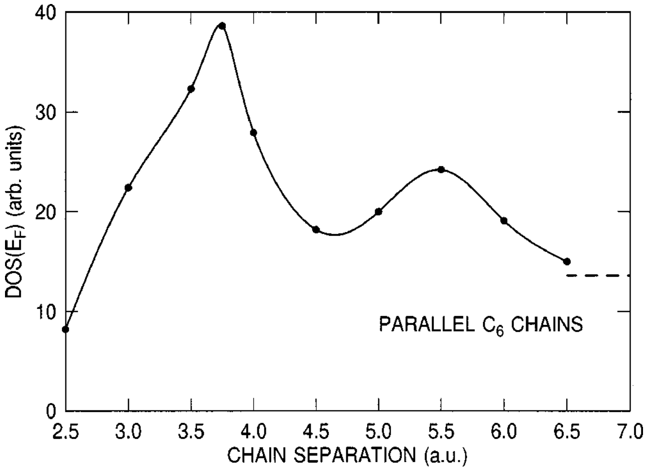

FIG. 7. Density-of-states (Ref. 48) at the Fermi level for a pair of C_6 wires as a function of wire separation. Dashed bar at right shows value for infinite separation. Calculated values (dots) connected by a smooth curve.

We have seen that the total low-bias conductance of a pair of carbon wires can be less than that for a single isolated wire, when the wire spacing becomes comparable to, e.g., the distance between threefold hollow sites on Ni(111) (2.7 a.u.). As the wire spacing is decreased toward this range, there is an oscillatory component (seen also in Ref. 34) of the total conductance. As the spacing is decreased from large values, there is a conversion of π bonds along the wires to σ bonds linking the wires. The variations of conductance follow roughly the variations in the density-of-states at the Fermi level for the system. It is also found as the spacing decreases that the electronic charge transferred to the wires from the electrodes increases monotonically.

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