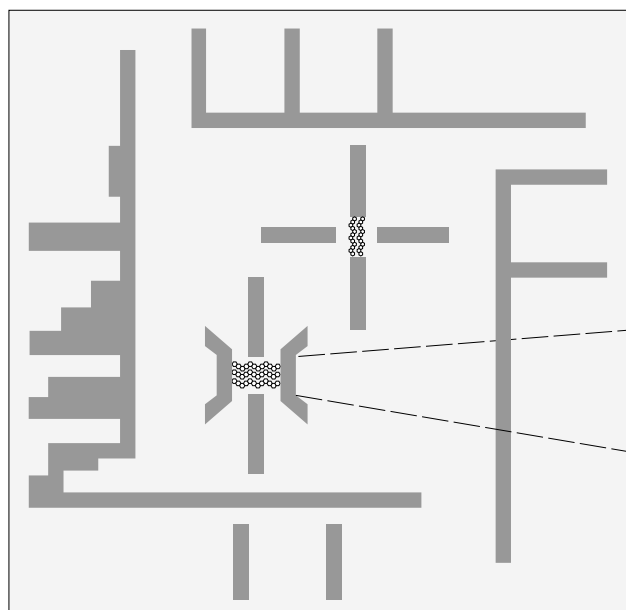
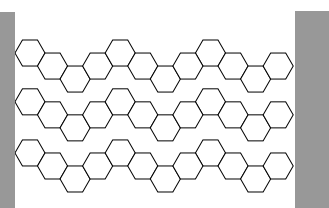


Molecular Wires for Ultrafast Circuits

Antonio Redondo



Integrated circuits containing conducting polymer molecules are now being tested



Electronic circuitry has undergone continuous miniaturization since transistors replaced vacuum tubes in the 1960s. A dominant force driving the miniaturization is the incessant demand for faster processing of ever-increasing amounts of information. Shown in Figure 1 are two measures of the rapid pace of miniaturization. The minimum dimension of devices that can be fabricated on a semiconducting chip (such as transistors, diodes, and switches) has decreased over the last twenty-five years from about 16 microns (1 micron = 10^{-6} meter) to about 0.5 micron, and the number of devices that can be included on a single chip has increased from 1 in 1958 to over 10 million. The remarkable increase in the scale of “integration” is due not only to development of techniques for producing smaller devices but also to improvements in circuit design.

The past rates of integration would seem to imply that gigascale integration (1 billion components per chip) may be reached by the year 2000. However,

such an extrapolation ignores limitations on the level of integration achievable with current semiconductor technology. Many of the limitations arise from inescapable physical laws and properties of matter. For example, as a device is made smaller, the electric field produced by a fixed voltage applied across its ends becomes larger. But the electric field cannot be allowed to exceed the value E_{\max} at which the material composing the device suffers electrical breakdown. The electric field can be kept below E_{\max} by reducing the voltage applied to the device. But that approach faces another fundamental limit. The voltage cannot be reduced below a certain minimum imposed by the thermal energy of the electrons in the device, which is given by kT , where k is Boltzmann’s constant and T is the temperature in kelvins. In particular, if an applied voltage is to produce a detectable response (an increase in current flow, say, or an electronic transition resulting in emission of light), the minimum applied voltage V_{\min} must be several times larger than the so-called

thermal voltage given by kT/e , where e is the electronic charge. At room temperature kT/e is about 0.025 volt.

The limits E_{\max} and V_{\min} are universal, applying to all materials. Another limit—one applicable to semiconductors and other solid materials—was expounded in the mid 1960s by Edward O. Johnson. He argued that there exists a maximum speed v_{\max} at which an electron can travel a distance L in a solid and that therefore the travel time t must be greater than L/v_{\max} . The existence of a maximum speed is due to the inevitable presence in any real solid of thermal excitations and lattice defects such as impurity atoms, vacancies, and randomness in the locations of the atoms that constitute the material. Defects in crystalline semiconductors are not only inevitable but also, in fact, deliberately introduced to achieve desirable properties. Collisions between such defects and an electron moving through a semiconductor cause the electron to lose kinetic energy and to undergo random changes in the direction of its motion. (Such collisions are

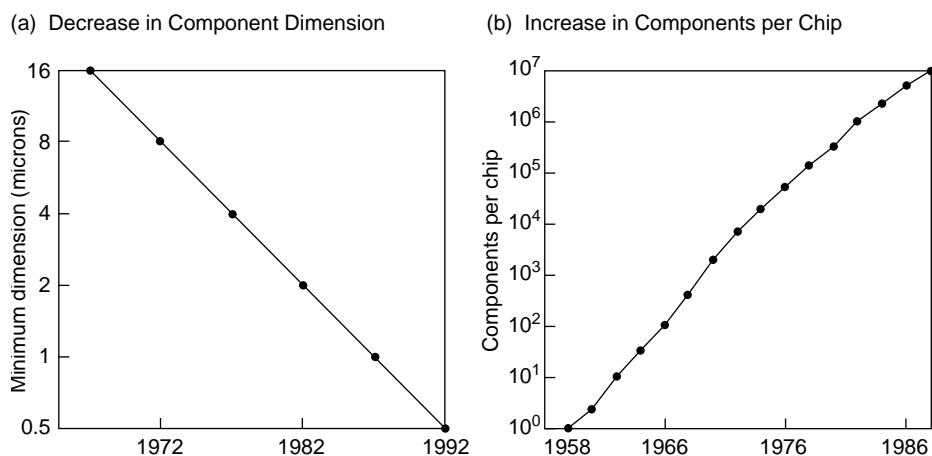


Figure 1. Measures of Electronic Miniaturization

(a) Continuing developments in photolithographic techniques have brought about an exponential decrease in the size of electronic components that can be fabricated on chips. (b) The decrease in component dimensions and improvements in circuit design have led to amazing increases in the number of components that can be included on a single chip. Although the rate of increase has decreased somewhat from an exponential rise during the 1960s, the number of components per chip has now reached 10 million.

the main cause of the electrical resistance of solid materials; the energy lost by the electrons appears in the form of heat.) If an electric field in a given direction is created in the semiconductor (by applying a voltage of fixed value across the semiconductor), then, between collisions, the electron is subject to a force in the direction of the electric field and thereby gains kinetic energy. Over time the electron moves as if it possessed a zero average velocity perpendicular to the field and a nonzero velocity component, a "drift velocity," in the direction of the field. Thus the electron executes a not-quite-random walk through the semiconductor. The drift velocity, or v_{\max} , of electrons in a semiconductor increases with the applied voltage and also varies with the composition of the semiconductor, its temperature, and the number and nature of the defects it contains. When 1 volt

is applied across 1 millimeter of a typical silicon crystal, electrons traverse the 1 millimeter with a drift velocity of about 100 meters per second and thus in a time of about 10 microseconds. (In contrast, if a crystal with no lattice defects were available and if 1 volt were applied across 1 millimeter of that "ideal" crystal, electrons would traverse the 1 millimeter at an average speed of about 6000 meters per second.)

Since the existence of a v_{\max} for a semiconducting material is an inescapable fact, the relation $t = L/v$ implies that the only way to reduce t below the value given by L/v_{\max} is to reduce L , the dimension of the device.

* It should be noted that another solution to the problem of increasing the speed of electron transfer along interconnects may lie in the existence of semiconducting devices in which, during sufficiently short times and over sufficiently short lengths, electron motion is not impeded by collisions and is instead "ballistic."

As mentioned above, however, the process of miniaturization can be carried only so far. In particular, since the electric field E created by applying a voltage V across a length L of semiconducting material is given by $E = V/L$ and since E cannot exceed the breakdown field E_{\max} nor can V be less than V_{\min} , there exists a minimum L given by V_{\min}/E_{\max} . Hence the travel time t must be greater than $V_{\min}/E_{\max} v_{\max}$.

How then can the speed of electronic circuits be increased beyond that dictated by the fundamental limit given above? One approach,* and the subject of this article, focuses (initially at least) on the connections along which electrons are transferred from one device to another. Today the "interconnects" on chips are made of semiconducting or metallic materials along which the speed of electron motion is limited by the drift velocity. Perhaps, though, the nearly random walk of electrons in such conventional interconnects can be replaced by a different, more rapid type of motion, one based on quantum-mechanical effects. The approach we are pursuing hinges on the fact that delocalized states are accessible to electrons in certain polymeric molecules.

The molecules in question belong to a class of organic compounds that are said to be conjugated. One of the simplest conjugated organic molecules, benzene, is of course not a polymer and therefore not a candidate for interconnects. However, consideration of that familiar compound can help define the terms "conjugated organic molecule" and "delocalized electron." As shown in Figure 2, the conventional representation of benzene—its Kekulé structure—includes a pathway of alternating single and double carbon-carbon bonds. Such a Kekulé structure suggests that one pair of electrons is confined, or localized, between carbon atoms 1 and 2;

two pairs are localized between carbon atoms 2 and 3; one pair is localized between carbon atoms 3 and 4; and so on. However, the Kekulé structure of benzene (or of any other molecule) is a simplification and hence leads to an idealized picture of where the nine electron pairs that bind its carbon atoms are likely to be found. An alternate picture is that each electron pair has the same probability of being found at any point around the benzene ring as does any other pair. Such electrons are said to be delocalized (in this case over the entire ring), and electron delocalization is a characteristic feature of all conjugated organic molecules.

Also shown in Figure 2 are the Kekulé structures of two conjugated organic polymers, polyacetylene and polythiophene. Like the Kekulé structure of benzene, the Kekulé structure of any conjugated organic polymer includes a sequence of alternating single and double carbon-carbon bonds, a "backbone." Furthermore, like the pairs of electrons that bind the carbon atoms of benzene, the electron pairs that bind the backbone of a conjugated organic polymer are delocalized, in some instances over extensive regions of the molecule.

Polyacetylene is an example of a conjugated organic polymer with a straight-chain backbone. Although the conductivity of very pure polyacetylene approaches that of copper, polyacetylene is not a candidate for interconnects because, like other straight-chain conjugated polymers, it oxidizes easily in air. Polythiophene is an example of a cyclic conjugated polymer. A number of such polymers, although they exhibit lower conductivities than that of polyacetylene, are extremely stable in air and are therefore possible candidates for interconnects.

Cyclic conjugated organic polymers

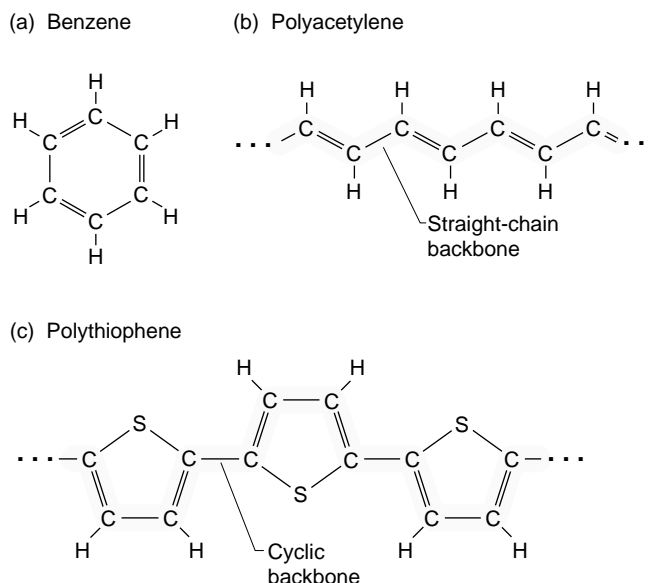


Figure 2. Kekulé Structures of Some Conjugated Organic Molecules

(a) The alternation of single and double carbon-carbon bonds in the Kekulé structure of benzene suggests that each of the nine electron pairs that bind its six carbon atoms into a cyclic configuration is localized between a pair of carbon atoms and that the number of localized electron pairs alternates around the ring between one and two. An alternate picture is that each of the nine electron pairs is delocalized around the entire ring. That is, each electron pair has the same probability of being found anywhere around the ring as does any other pair. (b) and (c) Single and double carbon-carbon bonds also alternate along the straight-chain and cyclic backbones of the polymers polyacetylene and polythiophene. The electron pairs that bind the polymer backbones, like the electron pairs that bind the benzene ring, are delocalized.

may offer several advantages over semiconducting materials as interconnects. First, the voltage that must be applied across such a "molecular wire" to bring about the transfer of electrons from one end to the other may be very low. (Like any material, the polymer cannot be subjected to an electric field greater than its breakdown field.) Second, the number of electrons that need to be transported along the polymer in order for it to function as an interconnect may be very low (possibly one or a few at a time). If so, the power consumption of circuits containing molecular wires can be reduced, together with the concomitant problems associ-

ated with heat dissipation. Finally, the transfer of electrons along a molecular wire may be very fast. An electron "moves" along a conjugated organic polymer primarily by undergoing transitions from one delocalized electronic state to another. Whereas times for the motion of electrons in the fastest semiconducting interconnects are on the order of picoseconds (1 picosecond = 10^{-12} second), times for electronic transitions are on the order of femtoseconds (1 femtosecond = 10^{-15} second). The optimism inspired by a simple comparison of those times must be tempered, however, by the fact that electronic transitions, though intrinsically fast,

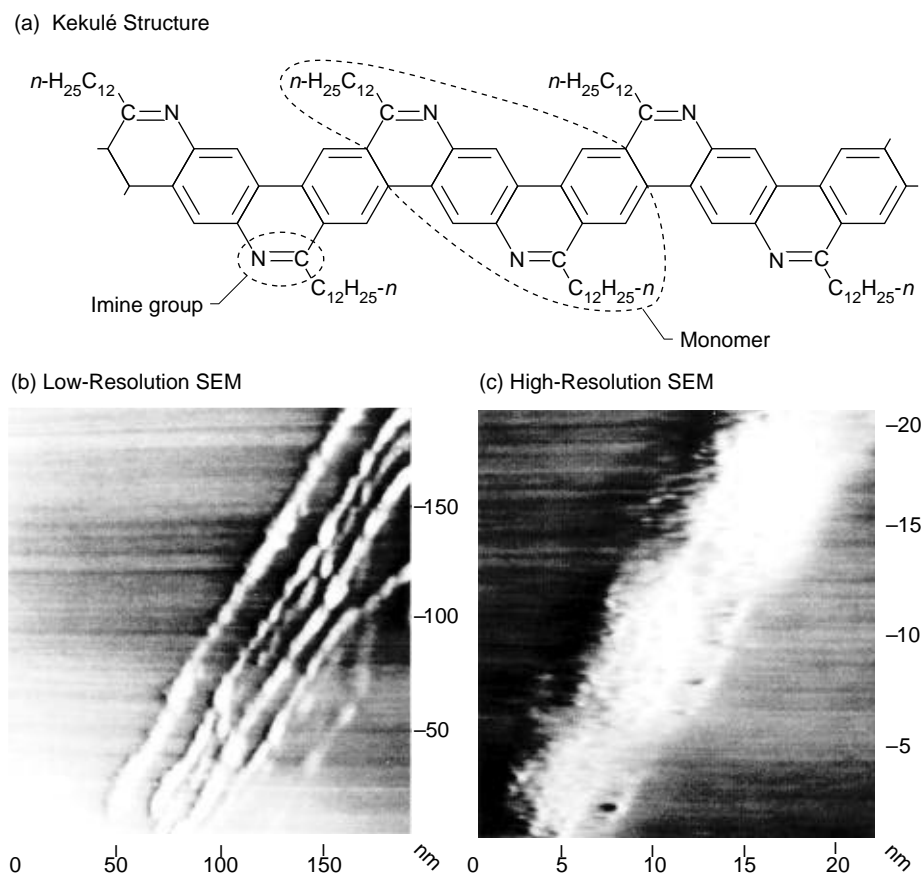


Figure 3. A Candidate Molecular Wire

(a) A conjugated organic polymer that may transfer electrons rapidly and efficiently from one electronic device to another has been synthesized by James M. Tour and Jay Lamba at the University of South Carolina. As shown by its Kekulé structure, the polymer consists of linked benzene residues (more precisely, linked para-phenylene residues) bridged by imine groups. (The carbon symbols have been omitted in the benzene residues.) Note the alternating single and double carbon-carbon bonds along the polyphenylene backbone. All the benzene rings along the backbone are coplanar. A monomer of the polymer is highlighted, and the symbol n indicates that the $-C_{12}H_{25}$ groups are unbranched. The advantages of using imine groups as bridges are discussed in the text. (b) This scanning tunneling electron micrograph of molecules of the polymer whose Kekulé structure is given in (a) was prepared by depositing a solution of the molecules on a substrate and allowing the solvent to evaporate. Note that the polymer molecules tend to form stacks whose orientation is driven by the rigid planarity of the polymer. That tendency will be ideal for establishing interconnects between electrodes. (c) This higher-resolution scanning electron micrograph shows that the polymer molecules are about 7.5 nanometers long (1 nanometer = 10^{-9} meter), a length that corresponds to the presence of eight monomers in each molecule. Both electron micrographs were taken at the University of South Carolina by Jay Lamba and John Cooper under the direction of M. Myrick.

may not occur very often, particularly at the interfaces of the polymer with the devices it connects.

During the past year researchers at Los Alamos National Laboratory, the University of South Carolina, and Yale University have started a collaborative experimental and theoretical study of the viability of conjugated organic polymers as components of ultrafast electronic circuits. The work is concentrating initially on the use of cyclic conjugated organic polymers as interconnects between the simplest of devices, namely metallic electrodes. The key to success will be the design of polymers possessing suitable electron-transfer properties and capable of being incorporated into real circuits. Figure 3 shows scanning tunneling electron micrographs of a candidate polymer designed and synthesized by James M. Tour and his graduate student Jay Lamba at the University of South Carolina. Each polymer molecule, which is only eight monomers long, consists of a polyphenylene backbone (a series of linked benzene rings) bridged with imine ($>C=N-$) groups. Although the polyphenylene backbone can, in principle, conduct electrons, it is not a particularly good intrinsic conductor because each benzene ring is free to rotate relative to its neighbors. Such rotation leads to a polymer with a nonplanar configuration that is less than optimally favorable for electron transfer along the backbone. But the imine bridges assure a configuration in which all the benzene rings are coplanar. The use of imine groups as bridges was motivated, in addition, by the fact that the imine groups, unlike other bridging groups that would also assure a strictly planar polymer, do not disturb the conjugation of the backbone.

Yale University's contribution to the collaborative effort will consist of ex-

perimental studies of the polymer shown in Figure 3 and of other candidate polymers synthesized by Tour's group. In particular, Mark A. Reed and his graduate student Rachel Lombardi will measure the conductivities of the polymers in specially designed chips.

Los Alamos National Laboratory's contribution to the project is theoretical analysis. Our aim is not only to understand the experimental results, but, just as important, to predict and provide feedback to the experimenters. For example, as mentioned above, the interfaces between a polymer and the electrodes (or other devices) it connects are crucial to efficient electron transfer. In fact, the polymer molecules must be designed so that they have terminal chemical fragments that efficiently transfer electrons from and to the electrodes. Unfortunately, experimental design and synthesis of a candidate polymer requires a minimum of six months. As a result, the number of candidate polymers that can be investigated experimentally is seriously curtailed by manpower and cost considerations. One role of theorists will be to make educated guesses about which polymers are the most promising candidates and should be synthesized for experimental study.

One of the properties of conjugated organic polymers we are trying to calculate is their capability to transfer electrons—their conductivities. The theoretical techniques available for studying the transfer of one or a few electrons at a time along a molecule are at the cutting edge of current research, and therefore their application to the question at hand is not cut and dried. Our calculation of the conductivities of conjugated organic polymers illustrates the problems that must be confronted.

Under many circumstances a macroscopic material obeys Ohm's law. That is, the current density J (the current per

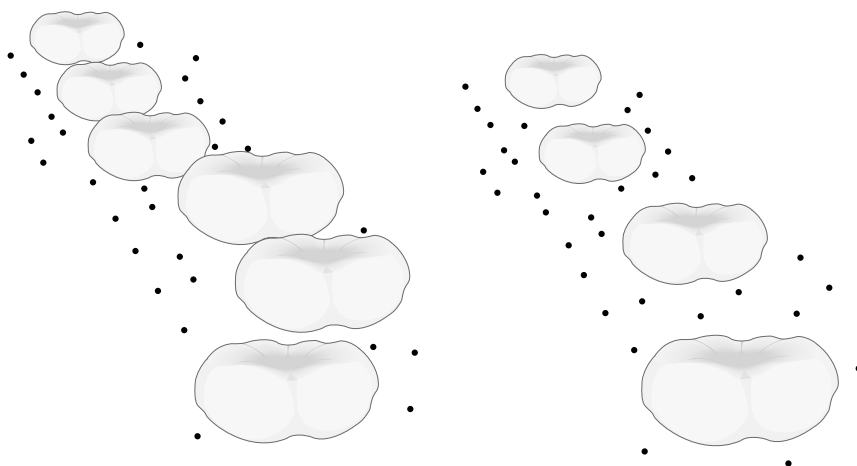


Figure 4. Orbitals for the Polymer of Figure 3

Shown here are an artist's renditions of two molecular orbitals. Each orbital is occupied by a certain pair of electrons along the polyphenylene backbone of the trimeric version of the polymer shown in Figure 3. The surfaces that make up each orbital define a volume within which the absolute value of the wave function is equal to or greater than a fixed low value (0.05 atomic units) and hence the volume within which the electron pair is most likely to be found. The shape of the orbital on the left indicates that the electron pair has equal probability of being found within a doughnut-like region around any of the six benzene residues in the trimer. The shape of the orbital on the right indicates that the other electron pair has an equal probability of being found within a doughnut-like region around only four of the six benzene residues in the trimer. The dots located near but outside each orbital denote atoms other than the carbon atoms of the backbone.

unit area) established in a material by an electric field E is directly proportional to the electric field. Symbolically, $J = \sigma E$; the constant of proportionality σ is the conductivity. When the flow of current induced in a material has the same direction as the applied electric field (as is true in many materials), the conductivity is a scalar, a single number. In some materials, however, the current does not flow in the same direction as the electric field. For example, some layered crystalline materials can exhibit a current parallel to the layers irrespective of the direction of the electric field. The conductivity

of such a material is not a scalar but a tensor, that is, a 3-by-3 matrix. The conductivities of conjugated organic polymers are expected to be tensors.

One of the approaches we are using to calculate the conductivity of a polymer molecule is based on macroscopic analogues. We start by assuming that the polymer satisfies Ohm's law. Although we expect that assumption to be valid at sufficiently small electric fields, we are not certain about its validity at the fields that will be imposed on the polymer molecules. Our criterion for acceptance of the applicability of Ohm's law and any other assumption

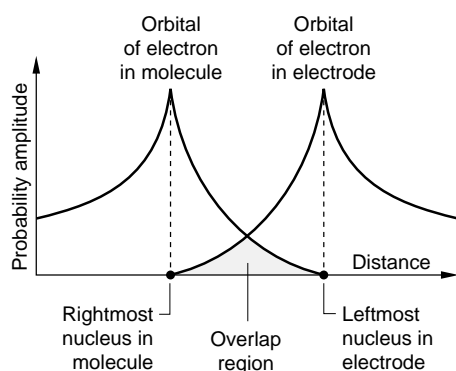


Figure 5. Overlapping Wave Functions and Transition Probabilities

The wave function on the left in this schematic illustration represents an orbital of an electron near the rightmost end of a molecule, which contacts the leftmost end of a metallic electrode. The local maximum in the wave function at the position of the nucleus of the rightmost atom in the molecule indicates that the electron has a high probability of being found close to the positively charged nucleus. The exponential decrease of the wave function toward the right indicates that the electron has an exponentially decreasing probability of being found to the right of the rightmost nucleus. The wave function on the right represents an orbital of an electron in the electrode near the interface between molecule and electrode. That wave function has a local maximum at the position of the nucleus of the leftmost atom in the electrode and decreases exponentially toward the left. The probability that an electron will undergo a transition from one orbital to the other increases with the extent of the overlap between the two orbitals.

will be a comparison of calculated and measured conductivities. If Ohm's law is applicable, we can calculate the conductivity tensor of a polymer molecule by using a theory developed by the

Japanese physicist Ryogo Kubo during the 1960s. Kubo's theory is called linear response theory because it relates the response of a system (here the current density) to the external agent causing the response (the electric field) by a general equation in which both the response and the agent are raised to the first power. Kubo developed a set of formulas for the conductivity tensor of a macroscopic body; we have had to extend the theory to produce a different set of formulas for the conductivity of a single polymer molecule.

Our method starts with the solution of Schrödinger's equation for a polymer molecule. We solve Schrödinger's equation by using standard techniques widely available and thoroughly tested during the last twenty years. The solution of Schrödinger's equation, the wave function, provides us with a set of orbitals, one for each pair of electrons along the backbone, and a set of corresponding electron energies. Each orbital is a function that describes the probability of finding the electron pair at any point in three-dimensional space; the corresponding energy indicates how tightly the electrons are bound to the molecule. Typical orbitals for the trimeric version of the polymer molecule shown in Figure 3 are depicted in Figure 4. The complete set of orbitals, one for each pair of electrons, can be combined to give the total wave function for the molecule.

Our approach to obtaining the conductivity tensor requires calculating the wave function of the polymer molecule for each of a sequence of values of the applied electric field. From the resulting sequence of wave functions, we then calculate the dipole-moment matrix for the molecule as a function of the applied electric field. (The dipole-moment matrix is a measure of how much the wave function distorts when a

voltage is applied across the ends of the molecule.) We then enter the dipole-moment matrix into the modified Kubo formulas we have developed to calculate the conductivity tensor of the molecule.

Although the procedure described above is conceptually straightforward, many as yet unanswered questions will have an impact on how our research will evolve. For example, our calculation of the dipole-moment matrix involves the assumption that the electric field is constant over the entire molecule. That assumption may or may not provide a calculated conductivity with the same level of accuracy as the measured conductivity but is most certainly invalid at high electric fields. Furthermore, the natural extensions of Ohm's law to high electric fields include nonlinear terms; that is, the current density is given by an equation such as $J = \sigma_1 E + \sigma_2 E^2 + \sigma_3 E^3 + \dots$. As a consequence, the formulas based on Kubo's formalism would have to be modified accordingly.

Other questions of a more practical nature also need to be addressed. Already mentioned is the question concerning transfer of electrons from electrode to polymer molecule and vice versa. Electrons may be transferred along the length of the polymer molecule very efficiently but face bottlenecks at the electrode-polymer interfaces. We know, however, that the probability of an electron "hopping" from an orbital in the molecule to an orbital in the electrode increases with the overlap between the orbitals (Figure 5). The hopping probability also depends in a dramatic manner on the difference between the energies of the electron in the two orbitals: the smaller the difference the larger the probability. Therefore, a crucial part of our research is the study of the conductivity between

a polymer molecule and a metallic electrode and the exact dependence of the conductivity on the overlap between the wave functions. Fortunately, the methods we have been developing are as applicable to polymer-electrode conductivity as they are to the conductivity of the polymer itself.

Another problem concerns depositing the polymer molecules at the desired locations on a chip, a task that cannot be accomplished by standard techniques. The most promising approach is "self-assembly," which involves designing the polymer to include terminal chemical groups that selectively bind to metallic electrodes. For example, the thiol group, $-SH$, is known to selectively bind to gold. The terminal groups must be chosen not only on the basis of their binding selectivity but also on their ability to provide maximum conductivity between the polymer and the metallic electrode. After the polymer molecules are equipped with appropriate terminal groups, a small quantity of a solution containing the molecules is deposited on the regions of a chip between electrodes. By natural chemical affinity the molecules then self-assemble at the correct positions.

After the feasibility of molecular wires has been demonstrated, a number of more advanced applications can be investigated. For example, introducing the appropriate chemical fragment (a porphyrin, say) in the middle of a conjugated organic polymer may create a device that acts as a switch. Or, if the fragment acts as a barrier to the passage of electrons, the result may be a tunnel device that allows passage of electrons only when the applied voltage is above a given threshold. A number of other relatively simple electronic devices that work at the molecular level can be envisioned. Indeed, at the present time, the possibilities seem limitless. ■

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