



Bypassing the Transistor Paradigm

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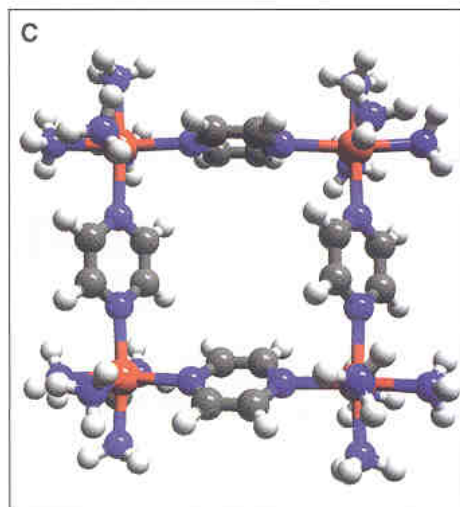
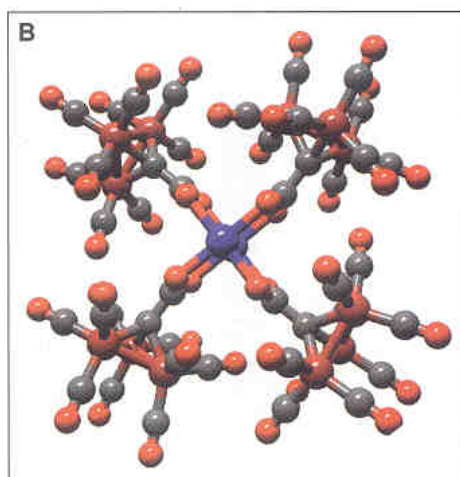
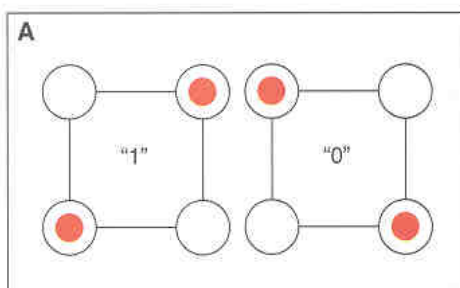
New technologies often initially attempt to reproduce the previous technology in form and function. For example, when word processors were first introduced, many were designed to emulate typewriters: Characters were entered along one line at the bottom of the screen, and white "electronic paper" had to be scrolled up and down to the "writing head." In the quest to develop truly molecular-scale electronics, the impulse to reproduce transistor action with molecules may one day be viewed similarly. But an alternative scheme of using molecules for electronics that bypasses the transistor paradigm may offer a more natural route to exploiting molecular functionality for computing.

Modern computers are the result of two very good ideas: to use binary numbers to represent information in a machine and to encode the binary "1" and "0" as the "on" and "off" states of a current switch. Initially, electromechanical relays were used as the current switches, which were later changed to vacuum tube triodes (then called "valves"). These were eventually replaced by the solid-state version, the modern transistor. Representing binary information by turning on or off a current stream has been one of the most fruitful ideas in the history of technology.

This paradigm does, however, have serious drawbacks as device sizes are reduced. The smaller the switch, the lower its ability to cleanly turn the current off and on. Also, the current through each single switch is reduced, making it more difficult to charge up the interconnect lines between devices. Finally, switching current requires electrons to move from the power supply through a resistance to ground, resulting in considerable energy dissipation. If present transistors could be magically shrunk to the size of single molecules, a chip with phenomenal device density could be fabricated, but such a chip would melt as soon as it was turned on from the heat it generated.

It is thus clear that if electronic devices are to be shrunk to the ultimate limit of molecular size, a new paradigm must be

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Toward molecular electronics. (A) In the QCA approach, binary information is stored in the charge configuration of a single molecule. Possible QCA molecules: synthesized dimolybdenum tetra-cluster carboxylate, $\text{Mo}_2[\text{O}_2\text{CCCO}_3(\text{CO})_9]_4$ (7) (B), and ruthenium-based molecule $\text{Ru}_4(\text{NH}_3)_{16}(\text{C}_4\text{H}_4\text{N}_2)_{410}^+$ proposed by Marya Lieberman and co-workers (C). Structures calculated by Olaf Wiest.

developed. The Quantum-dot Cellular Automata (QCA) paradigm (1, 2) retains the notion of a binary representation of information, but this binary information is stored in the charge configuration within a cell rather than in the on/off state of a current switch. Each cell consists of four dots and contains two mobile electrons, which occupy antipodal sites (see panel A in the figure). In a molecular implementation, each cell is a single molecule. No current flows between cells. Rather, the Coulomb interaction between cells is exploited, which tends to induce the same state in neighboring cells. Remarkably, this interaction is sufficient to support general purpose computing (2).

The QCA concept provides a natural route for exploiting molecular functionality. Molecules make good charge containers; they do not make good wires or current switches. QCA molecular devices would be true molecular circuits and may allow device densities in the 10^{11} to 10^{12} devices/cm² range. In these systems, power dissipation can approach the fundamental lower limits imposed by physics, and therefore a molecular QCA chip could be operated without melting.

QCA circuits have been constructed with small metallic islands forming the dots (3). Operation of a three-input majority logic gate has been demonstrated (4), and a line of cells has been shown to act as a binary wire (5). Because of the relatively large size and large interdot capacitances, these circuits only work at cryogenic temperatures (below 100 mK).

For the purposes of developing molecular electronics, the metallic systems can be viewed as low-temperature prototypes (6). Shrinking to molecular scales will increase the relevant energies and enable room temperature operation. QCA operation in a single molecule has not yet been demonstrated experimentally, but several candidate systems have been identified, and a considerable experimental effort is under way to synthesize and characterize these molecules. In QCA molecules, transition metal atoms play the role of the "dots." The metal d-orbitals act as localized states for electrons.

Fehlner and co-workers are exploring a class of molecules known as metal cluster carboxylates for use as QCA molecules. Each of the four dots is composed of a cluster of three metal atoms, with additional metal atoms forming a central bridge (see panel B in the figure) (7). Electrons hop from one outer dot to another through the central cluster, which also acts structurally

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to place the four dots on a plane. The molecules have been synthesized with several different clusters and centers in an effort to understand the role of the linkers in electron hopping and design molecules with appropriate switching behavior. Marya Lieberman and her team are investigating another kind of potential QCA molecules, in which each dot consists of a single ruthenium atom (see panel C in the figure).

The QCA approach to molecular electronics is very promising, but creating functional QCA molecules is just the first step. In a device, the molecules need to be

attached to a surface in a predetermined geometry, inputs and clocking signals need to be applied, and the state of the output cells must be read. Each of these steps presents substantial challenges. In addition, the whole approach to circuit architecture must be rethought if circuits are going to be based on QCA cells rather than transistors. Work along these lines is under way (8, 9).

References and Notes

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PERSPECTIVES: REACTION DYNAMICS

Detecting Resonances

George C. Schatz

An important advance in the field of chemical reaction dynamics was recently achieved with the observation of isolated resonances in gas phase bimolecular chemical reactions that have no intermediate bound states (1, 2). A “resonance” is a transient, metastable state produced during the reaction. Transient intermediates are well known in many kinds of chemical reactions (and also in nuclear and particle physics). What makes the newly observed resonances special is that they occur near the top of a reaction barrier (the “transition state”), where one would not normally expect to find metastable states.

Such nonintuitive resonances first showed up in theoretical simulations of simple gas phase reactions in the early 1970s (3, 4). Numerous attempts have been made to detect them experimentally, including ground-breaking molecular beam studies by Neumark and co-workers (5). But the several reported “sightings” of resonances were later shown to be either ambiguous or erroneous (6–8). The new observations show resonant behavior for several different properties of the reaction dynamics and are consistent with high-quality theoretical simulations: It appears that the long search is over.

The two reactions studied, $H + D_2 \rightarrow HD + D$ (1) and $F + HD \rightarrow HF + D$ (2), are deuterated variants of two fundamental chemical reactions, namely the $H + H_2$ and $F + H_2$ reactions. $F + H_2$ is an important reaction in chemical lasers. $H + H_2$ is often considered to be the simplest atom-transfer reaction, and interest in this reaction goes back to the discovery of quan-

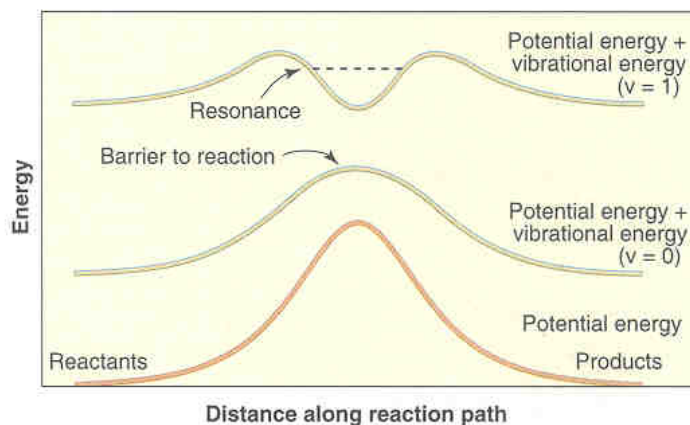
tum mechanics. London (9) and Eyring and Polanyi (10) used this reaction to determine the first potential energy surface for a chemical reaction. Such surfaces are now widely used in chemistry and biology to describe the forces on nuclei during chemical reactions.

On the $H + H_2$ surface, a 9.6 kcal/mol barrier separates reactants from products (see the figure below). The top of this potential energy barrier corresponds to the linear symmetrical species H-H-H. It is this intermediate that is used to determine reaction rate coefficients with transition state (“activated complex”) theory. The term “activated complex” might imply a metastable intermediate, but the latter term

is inappropriate for $H + H_2$, because the barrier is usually surmounted within a few femtoseconds—not enough time for a resonance to establish itself. Nevertheless, theoretical studies (3, 4) showed that there can be resonances in which the H-H-H intermediate oscillates across the barrier a few times before falling apart. The figure shows that these states can arise because vibrational frequencies associated with motion perpendicular to the reaction path are lower at the barrier top than in the reactants or products. A similar picture ap-

plies to the $F + H_2$ reaction, but in contrast to $H + H_2$, it is highly exothermic, with a barrier of only 1.5 kcal/mol.

In nuclear and particle physics, resonances are often seen in scattering experiments, where they show up as peaks in cross sections determined as a function of the collision energy. (A cross section is the effective area of a nucleus for a scattering or absorption process.) Analogous measurement of cross sections for chemical reactions can be done in either crossed molecular beam or laser photolysis experiments. But observing resonances in these experiments is extremely difficult, because the measurements are averaged over a range of orientations, translational energies, and directions of approach of the colliding species. Thus, although resonances are often seen in theoretical simulations (where no averaging is done), they often disappear when



Schematic reaction path from reactants to products for $H + H_2$. Lowest curve: potential energy function, showing the barrier that must be surmounted for reaction to occur. Middle curve: sum of the potential energy and the zero point energy ($v = 0$) associated with vibrational motion perpendicular to the reaction path. Top curve: potential plus vibrational energy associated with the first excited vibrational state ($v = 1$). Because the vibrational frequencies are lower near the barrier top than in the reactants or products, the vibrational energy is lowest at the barrier, and the potential plus vibrational energy shows a well for the first excited state. This well can support one or more metastable (resonance) states. It is these states that have now been observed in chemical reactions for the first time (1, 2).

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