Probing intramolecular circuit laws

Constructive quantum interference is verified experimentally in a parallel single-molecule circuit, potentially offering an intuitive approach to designing intramolecular circuits.

Christian Joachim

Kirchhoff’s superposition law states that the total conductance of an electronic circuit in a parallel configuration is the sum of the conductance of the individual branches (that is, for the two-branch case, \( G = G_1 + G_2 \) (ref. 1)). To construct complex electronic machines capable of calculating or recording data, engineers have based their designs on Kirchhoff’s node and mesh electronic circuit laws for almost 100 years. However, to boost running speed, minimize energy consumption and increase portability, circuit miniaturization is now approaching the molecular and even the atomic scale. In the future, it would be expected that computers be constructed from functional atoms or chemical-group building blocks, except that at this scale the Kirchhoff classical superposition laws may no longer be valid, because electrons tunnelling through molecular circuits obey quantum physics laws, rather than statistical physics laws, an occurrence that was not entirely foreseen by the pioneers of molecule circuit design\(^5\). Now, reporting in Nature Nanotechnology, researchers from Brookhaven National Laboratories and Columbia University in the US probe the superposition law for a parallel two-branched molecular circuit and find experimental evidences of constructive quantum interference between the two possible paths\(^6\).

When a molecule is connected between two metallic electrodes and enough voltage bias is supplied, a net tunnelling current flows through the molecular circuit as a result of billions of electron-transfer events per unit of time. The electron transfer rate of those events is dictated by the electronic coupling between the two metallic leads introduced by the molecular electronic states of the interconnecting molecule. On first approximation, the junction conductance is proportional to the square of the electron transfer rate\(^1\), but because of the wavelike character of the electrons tunnelling through the molecular wire the through-molecule electron transfer rate decays exponentially with the number of molecular units present along the circuit. As a result, in a molecule circuit in series, the total conductance is proportional to the product of the individual units\(^5\) (that is, for the simplest two-unit case, \( G \propto G_1 \times G_2 \); Fig. 1a).

Adding a second identical path in parallel increases the electron transfer rate by a factor of two and therefore the total conductance by a factor of four. But for this to occur, the branching must take place within the junction, and the two branches must be identical to each other so that there is no time shift in the electron transfer events through the two parallel paths. In this case, it was analytically proven that a constructive quantum interference term needs to be added to the classical Kirchhoff’s conductance law\(^5\) (that is, \( G = G_1 + G_2 + 2\sqrt{G_1 \times G_2} \); Fig. 1b). The Brookhaven–Columbia collaboration, led by Mark Hybertsen, Latha Venkataraman and Ronald Breslow, has experimentally demonstrated exactly this quantum scenario. However, two other different scenarios can arise. If there is a time shift in the electron transfer events between the two parallel branches, for example, due to a different chemical composition, destructive interference occurs and the overall conductance is drastically reduced (Fig. 1c). If now the two molecular branches are each directly and independently connected to the metallic leads, two electron-transfer paths in parallel are created bearing no phase relationship between each other and the standard \( G = G_1 + G_2 \) is recovered (Fig. 1d).

The researchers use the tunnel junction of a scanning tunnelling microscope (STM) to measure the conductance of their single-molecule circuit while increasing and decreasing the distance between the tips of the electrodes repeatedly, but it is the chemical design of the molecule circuit that plays a crucial role towards the success of the experiment\(^4\). They synthesize a series of molecular pairs consisting of one and two intramolecular electron transfer...
paths with a common linker at each end that does not electronically interact with the metallic electrode of the STM junction; rather, the linkers — or nodes, in standard circuit terminology — are part of the molecule itself, contributing to its molecular electronic states. Moreover, the linkers for the linear and branched molecules are chemically similar and electronically equivalent, allowing for a direct comparison between the two measured conductances.

But is it really necessary to synthesize a molecule in the shape of a circuit to miniaturize an electronic calculator to the limit? Quantum physics offers at least two more alternatives — each with its own superposition laws — to take advantage of intramolecular quantum resources that unlike the Brookhaven–Columbia system, which works in the real domain, can operate in a dual space (real and imaginary). One way is to structure the molecule as an array of qubits and have a well chosen initial quantum state carrying enough information to encode for a desired calculation to be computed by quantum evolution of the system7. This requires no intervention of intramolecular electron transfer. Alternatively, and without structuring the molecule in qubits, the computational information is encoded in the Hamiltonian as the system evolves quantum mechanically in time starting always from the same initial quantum state, which in this case would carry no quantum information6.

Thanks to the work by Hybertsen, Venkataraman, Breslow and co-workers, all three possible designs of intramolecular calculating systems can now be tested experimentally. The two dual-space quantum approaches described above have the advantage that an increase in circuit complexity does not lead to a large increase of the spatial extension of the corresponding molecule, whereas adding new chemical groups, however synthetically demanding it may be, is so intuitive an approach that it could have a more practical and broader appeal for circuit engineering, especially now that the parallel superposition law has been confirmed. It remains to certify, however, which of these approaches will lead to the maximum computing power per single molecule.

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References

QUANTUM DOTS

Strain is a problem no more

An elegant modification of nuclear magnetic resonance allows detailed structural analysis of self-assembled semiconductor quantum dots, so far hindered by the intrinsic strain in these nanostructures.

Daniel Gammon

Magnetic resonance of nuclear spin is a beautiful example of quantum control and measurement. It is conceptually a simple process: first, the application of a strong magnetic field causes the spin to precess around the magnetic field direction. Then a small periodically alternating magnetic field is applied in the direction perpendicular to that of the strong one. When the frequency of the oscillations is in resonance with the spin precession, the nuclear spin can be flipped. Because the spin precession depends on the type of nucleus, nuclear magnetic resonance (NMR) can be used to obtain structural information about materials and has been extremely useful in science and technology since it was first demonstrated in the 1930s.

One of the challenges of NMR is that it requires the presence of a great number of nuclear spins, mostly because a single spin normally has a very small net polarization, even at cryogenic temperatures. A powerful way to improve sensitivity is to use optical pumping (Fig. 1). This consists of using light to induce a polarization of the electron spins that is then transferred to the nuclei through the hyperfine interaction. Finally, any modulation of the nuclear spin is transferred back to the electron spin and can be detected with sensitive optical methods. This optically detected NMR (or simply ODNMR) can be used to measure the response of the nuclear spins even in a single semiconductor quantum dot (QD) that contains typically only $10^7$ nuclei.

The first ODNMR measurements of a single QD were made more than a decade ago on a GaAs QD (ref. 2), but there has been relatively little progress since then. This is because most QD research — in fact, most of nanostructures research in general — is on intrinsically strained materials, and strain reduces the sensitivity of ODNMR to an extent that obtaining structural information is practically impossible. Now, writing in Nature Nanotechnology, Chekhovich and co-workers report an elegant modification of ODNMR that not only allows the structure of strained QDs to be studied, but also gives information on strain itself3.

Strain leads to quadrupole splittings of the nuclear spin spectrum. For example, a nuclear spin with a total spin of $3/2$ is split in a magnetic field through the Zeeman interaction. Strain combined with quadrupole interactions adds additional energy shifts. As a result, the four spin states ($-3/2$, $-1/2$, 1/2 and 3/2) are split in energy, and the NMR transition spectrum is split into three resonance lines — not one as in the case of an unstrained QD. The strain is also inhomogeneous across the QD, and each line broadens. Knowledge of the spin splitting and of the inhomogeneity is important for understanding the physical properties of the QD. In the standard ODNMR experiment, when one of the resonances is matched by the frequency of the alternating magnetic field, the spins affected are only those of two adjacent levels, and their populations vary until they are equal. Unfortunately in this case, the populations of the other levels are not affected, and the signal is too low to be detected. The situation is particularly dramatic for atoms with higher nuclear spin,