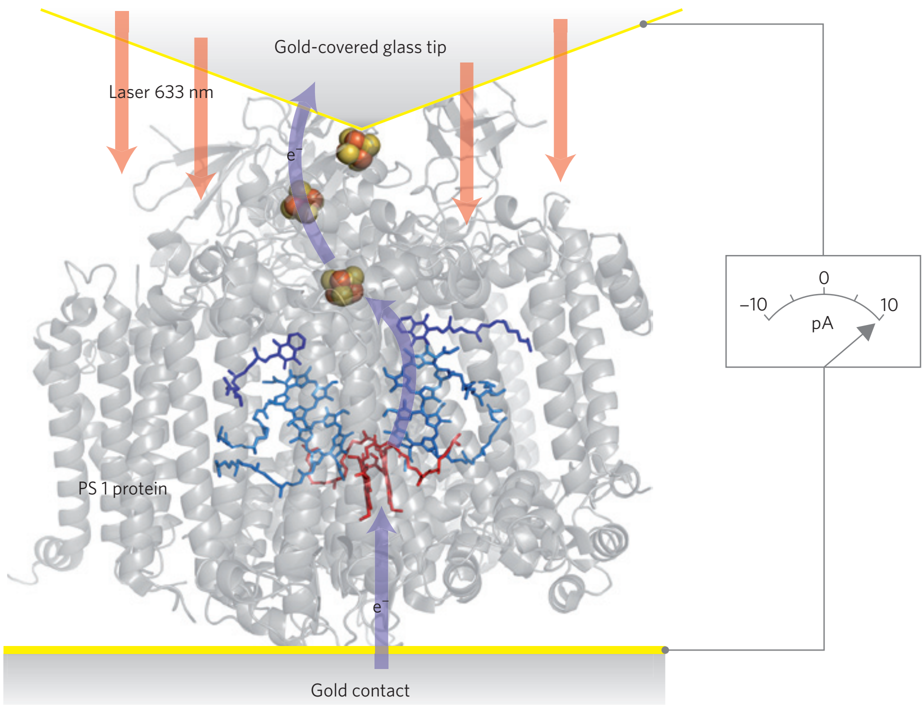

Figure 1 | Measuring the photocurrent of a single PS I protein. The PS I, which contains light-harvesting chlorophyll molecules, is covalently bound to two electrodes — a gold-covered glass tip and a gold surface — and is optically excited by laser light at 633 nm (red arrows) from the back of the tip. On illumination, the initial excitation of a special pair of chlorophyll molecules (P700; red) is followed by electron transfer to a monomeric chlorophyll (light blue). The excited electron then relaxes via intermediate phylloquinones (a polycyclic aromatic ketone; dark blue) to the iron–sulphur centres (yellow-red), before tunnelling to the gold-covered glass tip. The electron transfer path within the PS I is represented by the purple arrows.

self-assembled between two electrodes separated by a nanogap[7]. Second, the thermal expansion that can occur on illumination, and can dramatically alter the dimensions of the nanoscale gap between electrodes, must be addressed. Contacting via soft or flexible conducting interfaces might be necessary. Third, control over the direction in which the photocurrent will flow would be highly desirable. To achieve this, the thiol–gold interaction used to contact both electrodes to the protein should be complemented with a second attachment chemistry, which would allow each side of the protein to be contacted with a specific electrode.

If these issues could be solved, the extreme photocurrent value obtained by Reichert, Carmeli and colleagues for a single protein could be scaled up to an ensemble of proteins. This could ultimately lead to the development of significantly improved photobioelectrochemical devices for producing green fuels[8] and electricity[9].

Finally, from a fundamental perspective, the goal of single-enzyme electrochemistry remains elusive. Reichert, Carmeli and colleagues have made an important step in this direction, but their results were obtained under ultrahigh-vacuum conditions. Therefore, the next challenge will be to detect the photocurrent of a single protein in an electrochemical environment. Ultimately, the gap between electrochemistry and single-photosystem protein measurements could perhaps be bridged through a combination of protein self-assembly in nanogaps[7] and highly sensitive nanoelectrode-based instrumentation[4]. ❐

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QUANTUM INFORMATION

Blockade at a different level

Valley degeneracy in carbon nanostructures can be detrimental to electron spin control and readout based on spin blockade. As a way around this problem, it is now shown how to use a combined valley–spin blockade instead.

Guido Burkard

The spin of a single electron in a semiconductor quantum dot — a nanoscale structure in which the electron motion is confined in all directions — has several features that make it an ideal candidate for a quantum bit (qubit) for quantum information processing[1]. It is a quantum entity with two distinguishable states. Most importantly, quantum dots can be embedded in solid-state devices, and the electronic properties can be controlled by electric and magnetic fields.

A large part of the research on solid-state quantum information has focused on spins in GaAs quantum dots[2]. Indeed, a series of proof-of-principle experiments have demonstrated that these systems satisfy all the criteria that are commonly considered necessary to build a quantum processor[3]. Practically however, this is not enough, yet. The electron spin tends to lose

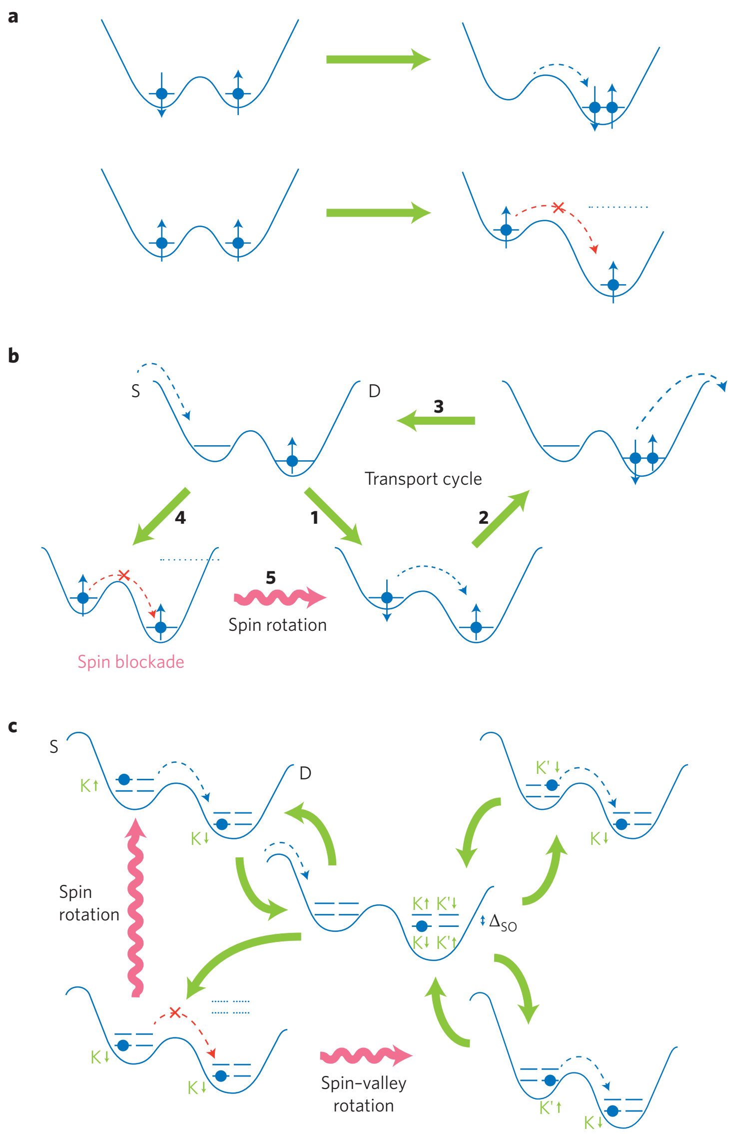

Figure 1 | Energy landscape in a double quantum dot filled with two electrons (blue dots), for example, in a carbon nanotube. **a**, If the electrons possess opposite spins (arrows), then a tilt in the potential will result in both electrons occupying the same dot, thus settling in the energetically favourable state. In the case with the two electron spins being the same, the transition of the left electron to the right is prevented by the Pauli principle, as long as no other state (dotted line) becomes available. **b**, Double quantum dots filled with one electron in the right dot and connected to source (S) and drain (D) leads in series (upper left). Tunnelling of an electron with opposite spin from the S lead to the left dot (1) initiates a transport cycle, in which an electron moves from the left dot to the right dot (2), and then out into the D lead (3). However, tunnelling of an electron from the S lead with the same spin (4) causes a spin-blocked state (lower left) from which the electrons only escape if one of the spins is rotated (5). **c**, Valley–spin blockade: same as in **b**, but every dot comprises four states K↑, K↓, K′↑, K′↓, representing all combinations of spin and valley. These are split into two pairs by the spin–orbit interaction Δ_{SO}. While three out of four valley–spin configurations of the electron entering from the S lead initiate a transport cycle (doubly occupied dot states omitted for simplicity), the other one blocks the transport (bottom left), and the electrons can only escape from it by a rotation of their spin and/or valley.

its quantum coherence in time, because of its interaction with the environment. In GaAs, the coupling of the electron spin with the spin of the surrounding nuclei is a substantial source of decoherence.

An interesting alternative to GaAs is represented by carbon materials, like nanotubes or graphene, because carbon has a much lower concentration of nuclear spins. Unfortunately, these materials also exhibit a couple of inconvenient features. The first is related to the so-called valley degeneracy. This is due to the fact that the electronic band structure of carbon nanotubes and graphene comprises two branches, or valleys. There are electrons with the same velocity, the same spin, the same energy, but different 'valley' index, usually denoted by K and K′. The existence of such a valley degeneracy interferes with the best proven and tested scheme for spin readout, based on the Pauli spin blockade effect. The second issue is that the spin–orbit interaction, which couples the spin to the motion of the electron, is generally quite weak in carbon. The spin–orbit interaction lies at the heart of all schemes to electrically control the electron spin. Now, writing in *Nature Nanotechnology*, Pei and co-workers describe an experiment on quantum dots obtained through gating of a bent carbon nanotube presenting solutions to both problems[4].

To understand why valley degeneracy is a problem, it is essential to consider how the spin of an electron is measured — or 'read out' to use the appropriate information storage terminology. Because it is much easier to detect the presence or absence of a single electron charge in a quantum dot than it is to measure its spin, a common procedure for single-spin readout is to first convert spin to charge. According to the Pauli exclusion principle, two electrons cannot exist in exactly the same state, that is, with the same spin value and wavefunction. Imagine now that the two electrons occupy one of two adjacent quantum dots, and the spin of the electron in the right dot is 'up' (Fig. 1a). When the potential of the left dot is increased, it becomes energetically favourable for both the electrons to occupy the right dot. However, this only happens if the spin on the left was 'down' because a state with both electrons on the right with both spins up would violate Pauli's principle. Measuring the amount of charge in the right dot is therefore an indirect way of measuring the spin of the electron that was in the left dot. In practical terms, if the two dots are wired up and connected in series to source and drain contacts (Fig. 1b), the Pauli spin blockade suppresses the electric current when there is a single unpaired electron in one dot and an electron with the same spin enters the other dot. The blocked state turns out to be very sensitive for spin readout: as soon as one of the two spins is flipped, the current can resume. If the spin is rotated continuously, the current will be roughly proportional to the spin-flip rate.

The problem with valley degeneracy is that there is, in principle, another way in

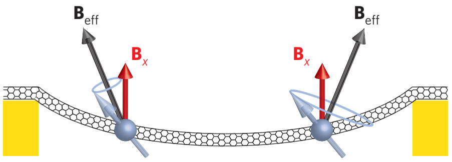

Figure 2 | The effective magnetic field $\mathbf{B}_{\mathrm{eff}}$ in a bent nanotube is the sum of the external field $\mathbf{B}_x$ and a field produced by the spin–orbit interaction $\mathbf{B}_{\mathrm{SO}}$ (ref. 4). While $\mathbf{B}_x$ is constant along the tube, $\mathbf{B}_{\mathrm{SO}}$ points along the local (axial) direction of the nanotube and thus varies along the tube. If an electron is moved back and forth along the tube using an alternating electric field, then the electron spin (blue arrow) is exposed to an alternating magnetic field $\mathbf{B}_{\mathrm{eff}}(t) = \mathbf{B}_x + \mathbf{B}_{\mathrm{SO}}(t)$, where t denotes time, which rotates the spin (electric dipole resonance).

which two electrons with the same spin (spin triplet) occupy the same dot, that is, if they have different valley indices. In a GaAs quantum dot, alternative states also exist, but usually only at a much higher energy. A way around the problem is to consider a combined valley–spin blockade, rather than a pure spin one[5]. In a nanotube, the two valleys and spin orientations lead to four states. Owing to the spin–orbit interaction, these states are split into two pairs (Fig. 1c). Previous experiments[6,7] have observed distinct signatures in the electric current for which the valley–spin blockade is responsible, but the small energy gaps in nanotube quantum dots provide easy access to additional states at relatively low energy, thus making the observation of spin blockade rather difficult. To render the valley–spin blockade more robust, Pei *et al.* tune their semiconducting nanotube double dot into an ambipolar regime, where the states in the right dot are just below the bandgap. This means that there are no other available states spoiling the blockade within a large energy range.

The researchers were then able to induce spin rotations through the so-called electric-dipole spin resonance. They exploited the fact that the spin–orbit interaction leads to an effective magnetic field along the axial direction of the tube[8] and its direction changes when an electron moves along a bent tube (Fig. 2). If an alternating electric field is used to shake the electron back and forth along the tube, an effective alternating magnetic field is produced, which then rotates the spin[9]. One reason why this works so well is that the spin–orbit interaction in the nanotubes studied by Pei and colleagues[4] is stronger than in tubes investigated earlier, for reasons that at this stage seem unclear.

The applied oscillatory electric field in fact couples to both the spin and the valley degrees of freedom in a bent tube[9], whereas in disordered straight tubes, pure valley rotations are possible[10]. It would be interesting if pure spin rotations could be achieved as well, and if spin and valley operations could be distinguished using the valley–spin blockade. After all, the valley index is a two-valued degree of freedom, and one may wonder if it is any good as a bit, or even a qubit. Finally, valley degeneracy occurs in other materials with low nuclear-spin content, such as silicon and germanium, which likewise are potential host materials for spin qubits. ❐

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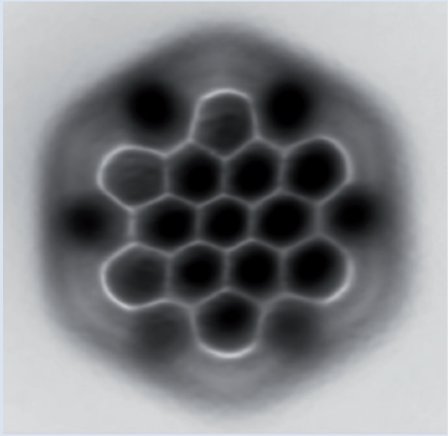
SCANNING PROBE MICROSCOPY

A discerning look at the bonds in a molecule

The resolution of a scanning probe microscope can be improved by attaching a small molecule to the tip of a probe and this has previously allowed individual atoms and bonds within adsorbed organic molecules to be resolved. Researchers at IBM's Zurich Research Laboratory, Universidade de Santiago de Compostela and CEMES-CNRS in Toulouse have now shown that an atomic force microscope (AFM) with a carbon monoxide molecule on its tip can also be used to discriminate between different types of chemical bonds (*Science* **337,** 1326–1329; 2012).

Leo Gross and colleagues imaged C_{60} molecules and polycyclic aromatic hydrocarbons adsorbed on a copper surface and found that carbon–carbon bonds within the molecules had different contrasts and apparent lengths, features that could be correlated with their bond orders. The images are formed by measuring the change in resonant frequency, or frequency shift, of the oscillating cantilever on which the tip is mounted: repulsive forces create a positive frequency shift, attractive forces a negative shift. Bonds with a higher bond order, which have a greater electron density, appeared brighter due to a stronger Pauli repulsion between the tip and the sample. The shorter length of such bonds could also be distinguished because the CO molecules at the apex of the tip tilt during imaging, which amplifies the apparent differences in length.



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The AFM image (pictured), which measures approximately 20 Å across, shows a polycyclic aromatic hydrocarbon composed of 13 fused benzene rings. The bonds of the ring at the centre of the planar molecule are of greater bond order than the bonds connecting the central ring to the outer rings, and accordingly appear brighter and have a shorter apparent length. The bonds can be distinguished despite the fact that they differ in length by only 0.03 Å. (The bonds at the periphery of the molecule are subject to a variety of effects, which obscure the bond-order differences.)

OWAIN VAUGHAN