Sense the Electrons that Come and Go

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In a recent paper in Nature, researchers from Rice University and Bell Laboratories have shown that charge fluctuations on a quantum dot can be measured with microsecond time resolution.[1] The quantum dot consisted of a well-defined region in a GaAs semiconductor crystal that was connected to a source and drain electrode and electrostatically coupled to a gate electrode. The charge on the quantum dot was probed, time-resolved, in a second electronic circuit that was capacitively coupled to the quantum dot. The results presented in the paper form an independent confirmation that electrons in a source – quantum dot – drain circuit tunnel one by one. In addition, the rates of single-electron tunneling into and out of the quantum dot can be directly measured. The work by W. Lu et al. complements previous work dealing with electron number fluctuations in quantum dot transistors[2] (and references cited in ref. [1]). Probing the tunneling dynamics in such an independent way, that is, via a second circuit, will add to the information obtained from conventional tunneling spectroscopy where the current in the source – quantum dot – drain system itself is measured. Here, we will highlight the role of electron tunneling dynamics in an electrically contacted quantum dot and speculate on the importance of the results obtained by W. Lu et al. for future research in this field.

A quantum dot is a semiconductor crystal with dimensions in the 1 – 100-nm range that is isolated from the outside world by energy barriers. In a quantum dot, the electron energy levels are well-separated due to confinement of the particle waves in the limited space of the nanocrystal. The energy separation between the levels depends on the dimensions of the dot. Crudely, two types of quantum dots can be distinguished. Quantum dots prepared by lithography in semiconductor crystals have dimensions in the 30 – 100-nm range. The confinement of the electron waves is rather weak, and the separation between the energy levels is in the order of 0.1 meV. Such a large quantum dot can contain up to 100 electrons. Lithographically defined quantum dots have been studied extensively in the last decade providing a wealth of information on quantum confinement and electron – electron charge and spin interactions.[3] The other type of quantum dots are chemically prepared from molecular precursors in a bottom-up approach. The dimensions in the 1 – 10-nm range ensure strong confinement of the electron waves; the discrete energy levels are separated by energies in the 100-meV range. This type of quantum dots may show quantum effects up to room temperature. The properties of quantum dots in the strong confinement regime have been studied extensively with optical spectroscopy. There are only a limited number of reports of electrical spectroscopy of such small quantum dots, due to problem of contacting such small crystals by two or three electrodes.[4] Electrical studies were mainly performed with an scanning tunneling microscope (STM), whose tip contacts a nanometer-sized quantum dot which is chemically attached to a substrate.

The electrons in a quantum dot occupy orbitals with symmetries similar to those found in an atom. Therefore, quantum dots are also indicated as artificial atoms. Figure 1 shows the first two conduction energy levels in a nanometer-sized quantum dot obtained from a tight-binding calculation,[5, 6] they show S and P orbital symmetry, respectively. The electron number N of an artificial atom plays the same role as the atom number and decides the optical and electrical properties. The ability to vary the electron number N in a controlled way is of primary importance. A semiconductor nanocrystal can be excited with photons, creating artificial atoms with one or more excitonic electron – hole pairs, which will decay to the ground state. This has allowed the study of the physics of artificial atoms by a number of optical pump-probe spectroscopies.[7, 8] On the other hand, electrical spectroscopy can be performed with a quantum dot contacted with a source and a drain electrode (two-terminal device). Electrons tunnel into the quantum dot from the source electrode, and leave the quantum dot by tunneling to a drain electrode. The source electrode can be the tip of an STM. The chemical potential of an electron that is injected into a quantum dot containing $N-1$ electrons can be denoted as[9] Equation (1):

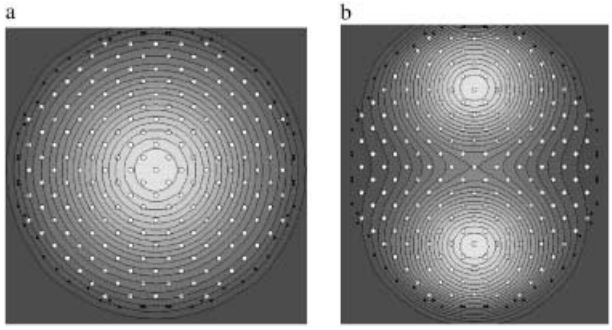

Figure 1. *A tight-binding calculation of the two first conduction orbitals in a nearly spherical but faceted nanocrystal (the atoms of the nanocrystal are shown as white points). The lowest energy level has S symmetry (a), and the second level has P-type symmetry (b).*

$$\mu_{N-1/N} = \varepsilon_N + P + (N-1)\,E_{ee} \qquad (1)$$

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where ε_N is the single-particle energy of the level occupied by the incoming electron; P is the dielectric polarization energy (self-energy) accounting for Coulomb repulsion between the incoming electron and valence electrons of the crystal, and $(N-1)E_{ee}$ accounts for the Coulomb repulsion between the entering electron and the $N-1$ delocalized electrons that already occupy the conduction levels of the quantum dot. For simplicity, we have neglected spin interactions between the electrons. In a two terminal device, the chemical potential is delivered by a bias V_{SD} between the source and drain electrode (Figure 2a). If the chemical potential of the source electrode equals the chemical potential $\mu_{N-1/N}$, a single electron from the source electrode can enter the quantum dot. The rate of this tunneling process (denoted as Γ_N^{in}) depends on the width and height of the barrier, and the density of states in the source electrode. Injection of a second electron into the dot is prevented until an electron escapes from the dot to the drain electrode (rate Γ_N^{out}). Thus the energetics in the quantum dot ensure single-electron tunneling via a well-defined energy level of the quantum dot. A step in the source–drain current I_{SD} is measured. If the chemical potential of the source electrode is further increased, a second resonance can be observed. Measurement of the I_{SD} (or the conductance G_{SD}) versus V_{SD} plot provides direct information on the energetics of the quantum dot (see further Figure 2).

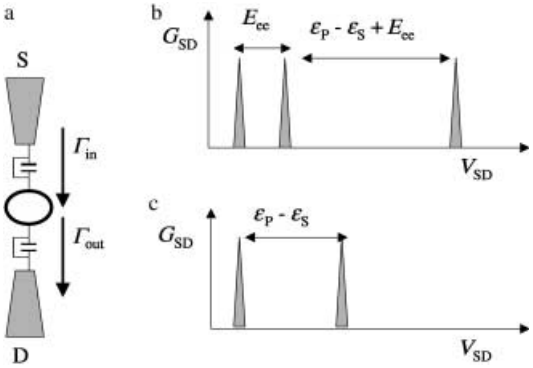

Figure 2. *a) A quantum dot in an electrical circuit; at sufficiently large bias between the source (S) and drain (D) electrode, electrons tunnel one by one from the source into the dot, and from the dot to the drain. b) Source–drain conductance under shell-filling conditions ($\Gamma^{in} \gg \Gamma^{out}$): the peaks indicate injection of the first and second electron into the S energy level, and third electron into the P level. c) Source–drain*

This form of resonant tunneling spectroscopy has been successfully employed to study the energy levels and Coulomb interactions in nanometer-sized chemically prepared quantum dots.[10–12] The tunneling dynamics have, however, a profound influence on tunneling spectra, as will be discussed below.

In a single-electron tunneling transistor (SET) a gate electrode is capacitively coupled to the quantum dot (Figure 3a). The chemical potential for electron injection can than be changed at will with an amount $U(V_{gate})$ via the potential of the gate electrode, thus resulting in Equation (2):

$$\mu_{N-1/N} = \varepsilon_N + P + (N-1)E_{ee} - U(V_{gate}) \qquad (2)$$

This means that by a proper polarization of the gate electrode a single-electron tunneling current can be achieved close to equilibrium, that is, at $V_{SD} \approx 0$. In such a way, the equilibrium and excited states of an N-electron artificial atom could be investigated with much success.[3]

When the bias V_{SD} is increased, the electron number $N(V_{SD})$ and thus the possible electronic configurations in the quantum dot are determined by the tunneling dynamics; that is, by the rate of tunneling from the source into the dot relative to the rate of tunneling out of the dot to the drain. We illustrate this for a semiconducting quantum dot with a spherical symmetry. The LUMO (lowest unoccupied molecular orbital) (denoted as S) has s-type symmetry and is two-fold degenerate; the second energy level is a six-fold degenerate P level (Figure 1). We first consider the situation where tunneling into the quantum dot is much faster than out of the quantum dot to the drain.[10] When the bias V_{SD} is increased from zero, a first tunneling resonance (current step) is observed at an electrochemical potential $\mu_{0/1} = \varepsilon_s + P$. A further increase of the bias leads to a second current step at $\mu_{1/2} = \varepsilon_s + P + E_{ee}$, followed by a third current step at $\mu_{2/3} = \varepsilon_P + P + 2E_{ee}$ (Figure 2b). Under these conditions, tunneling spectroscopy reflects the filling of the energy levels in order of increasing energy; that is, shell-filling spectroscopy. The electron–electron interactions are maximally present; therefore, this form of spectroscopy is also called resonant tunneling spectroscopy with charging. This is equivalent to building up atoms: H(S^1), He(S^2), Li (S^2P^1). In contrast, if the tunneling conditions are changed, such that tunneling into the dot is much slower than out of the dot, the average electron number is close to zero. Thus, the resonances $\mu_{1/2}$, $\mu_{2/3}$... do not occur. Instead, a second resonance reflects tunneling through the P level, while the S level is unoccupied (Figure 2c). This form of spectroscopy, called shell-tunneling spectroscopy or tunneling spectroscopy without charging, has been used to detect the single-particle energy levels (S, P, D...) of colloidal quantum dots.[12] In chemical language, the first resonance is equivalent to H(S^1), while the second, third etc. resonances are equivalent to excited hydrogen atoms H(P^1). Shell-tunneling spectra of a CdSe quantum dot (4.3 nm in diameter) showed resonances in the positive bias range that correspond to tunneling through the S, P, D, S′, and F conduction orbitals.[11] The limiting cases in the tunneling dynamics (shell-filling and shell-tunneling) give rise to electron configurations in the quantum dot that can be understood intuitively. In contrast, if the rates of tunneling into the dot are comparable to those out of the dot, a multitude of ground and excited-state elec-

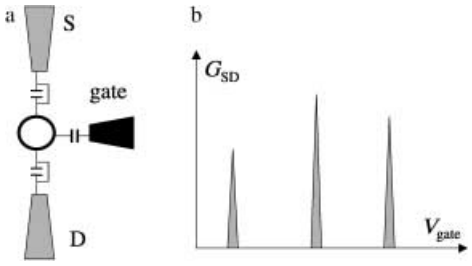

Figure 3. *A quantum dot contacted by a source (S) and drain (D) electrode, and capacitively coupled to a gate electrode (a). Changing the voltage of the gate electrode leads to resonant tunneling conditions close to $V_{SD} = 0$, indicated by peaks in the conductance (b). The number of electrons is increased by one at each conductance peak.*

tronic configurations are observed on increasing the bias V_{SD}. For example, we acquired tunneling spectra with a single CdSe quantum dot under conditions where tunneling into is as fast as tunneling out of the dot and observed resonances corresponding to the following electron configurations: (S^0P^0/S^1P^0), (S^1P^0/S^2P^0), (S^0P^0/S^0P^1), (S^2P^0/S^2P^1), (S^2D^0/S^2D^1), ($S^2S'^0/S^2S'^1$).[11] In addition, at large and constant bias, the electron number can fluctuate with more than one. Temporal fluctuations in the electronic configurations of the quantum dot are also important for the performance of nanodevices.

The report of W. Lu et al. shows that fluctuations in the electron number in a quantum dot can be probed, time-resolved, by capacitive coupling of the quantum dot to a second SET, the probe (Figure 4). The charge on the quantum dot influences the electrochemical potential of the probe quantum dot (a superconducting Al particle) and thus the steady-state current in the probe circuit. Measurement of DC (direct current) in the probe clearly detects the resonances (degeneracy points) $N-1/N$ of the quantum dot under investigation [given by Equation (2)] which occur periodically with increasing gate potential. In addition, the probe SET has been incorporated into a radiofrequency resonant circuit (RFSET) that allows charge fluctuations to be detected even at frequencies of 10 MHz, thus with a time-resolution in the 0.1-μs regime. At zero bias, the quantum dot resonances, occurring at certain gate potentials, were seen by the RFSET as a rapid switching between two states; these states correspond to the electron numbers $N-1$, and N in the quantum dot. Between two resonance potentials, the RFSET remained silent, indicating a constant number of electrons in the quantum dot. The on/off switching times seen with the RFSET provide the tunneling rates from the source to the quantum dot, and out of the quantum dot to the drain. The results show that the rates of single-electron tunneling are specific for a given resonant condition. This type of information is obtained independently from the conventional measurements in the source–quantum dot–drain circuit itself. The authors provide a simple illustration of this. They chose conditions at which a single electron can tunnel from the source to the dot, but not from the dot to the drain: I_{SD} is thus zero. Nevertheless $N-1/N$ fluctuations in the electron number of the quantum dot are detected by the RFSET due to back and forward single-electron tunneling between the source and quantum dot. We expect that independent detection of fluctuations in the electron number of a quantum dot and measurement of the rates of single-electron tunneling into and out of the quantum dot will become important for studies under strong non-equilibrium conditions, in which a number of tunneling paths are simultaneously operative and the electron number can vary with more than one, or under optical excitation of the quantum dot in the circuit. The results obtained by W. Lu et al. are also important for future applications, for instance, for quantum computing. Due to the complex technology, these studies will be limited to larger quantum dots that are defined in a semiconductor crystal by lithography.

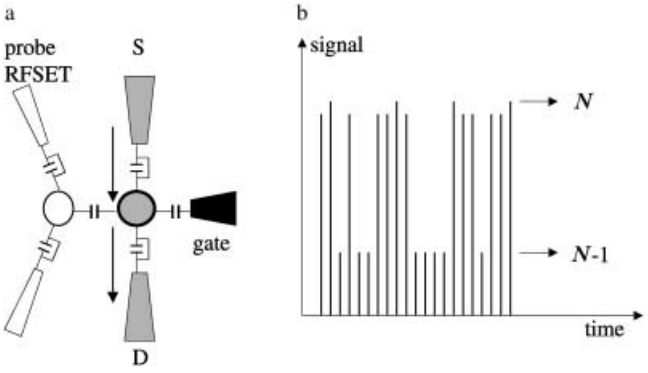

Figure 4. *A quantum dot with source (S), drain (D) and gate electrodes is capacitively coupled to a probe SET incorporated in a radiofrequency resonant circuit (RFSET) (a). The RFSET readout shows that, for certain well-defined gate potentials, the charge of the quantum dot fluctuates between* (N − 1)e *and* Ne *on a time scale of microseconds (b).*

Keywords: charge transport · confinement · dynamics · quantum dots · scanning probe microscopy

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