Probing the single-particle orbital energy spectrum of insulating nanocrystals with Scanning Tunneling Spectroscopy

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Current techniques in colloid chemistry permit the synthesis of a large variety of insulating nanocrystals with a tunable size in the 1-5 nm range, hence considerably smaller than what can be reached by lithography [1]. The energy level spectrum of these nanocrystalline quantum dots (Q-dots) in relation to their chemical identity, crystal structure, size and shape is a matter of experimental and theoretical interest. This is also true for the inter-particle Coulomb interactions in these confined insulating systems. There is a growing tendency to study these systems on the level of a single nanocrystal by optical and electrical techniques.

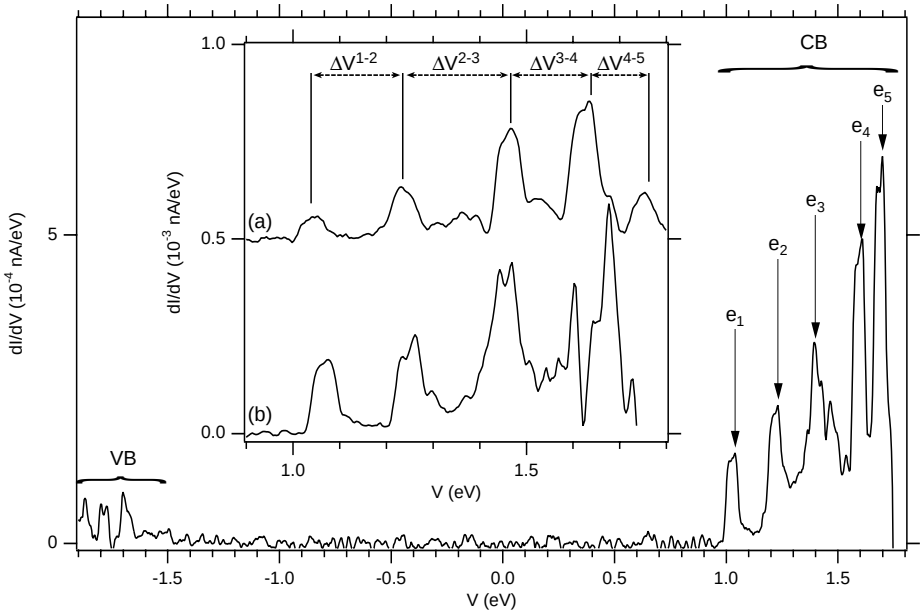
Resonant tunneling through a single Q-dot can be studied using a Scanning Tunneling Microscope. The colloidal crystals are anchored on a conducting substrate, the tip is positioned above a crystal and scanning and feedback controls are disabled. In such a way, a metal substrate / dot / tip Double-Barrier Tunnel Junction (DBTJ) is formed. In an *asymmetrical* configuration, the tunneling spectrum is related to the spectrum of discrete energy levels of the insulating nanocrystal, while the zero-conductivity gap is related to the (quasi-particle) band gap [2].

We report on a yet unexplored possibility of STS that may play a key role in the determination of the *single-particle orbital energy spectrum* of insulating nanocrystalline Q-dots [3]. The time-averaged electron occupation of a given (resonant) energy level of the nanocrystal is determined by the relative rates of electron transfer, *into* - and *out* of the energy level. A Scanning Tunneling Microscope offers the possibility to vary the tip-to-dot distance and, thus the time-averaged electron occupation of the resonant orbitals of the Q-dot. This means that Coulomb interactions between electrons in resonant orbitals can be turned on and off by variation of the tip-to-dot distance.

In *shell-tunneling spectroscopy*, electrons tunnel one at a time. The conductance spectrum corresponds to the single-particle orbital energy spectrum of the Q-dot. We obtained the orbital energy spectrum of a 4.3 nm CdSe Q-dot at 4.2 K and found a very good agreement with the results of pseudo-potential theory [see figure]. When the tip is brought closer to the dot, the orbitals are filled accumulatively with electrons (*shell-filling spectroscopy*). Electron-electron Coulomb interactions break down the spin and orbital degeneracy of the electron states of the Q-dot.

[1] **Distance-dependent electron transfer in Au/spacer/Q-CdSe assemblies.**
E.P.A.M. Bakkers, A.W. Marsman, L.W. Jenneskens and D. Vanmaekelbergh,
Angew. Chem. Int. Ed. English 39, 2297 (2000).
[2] **Resonant electron tunneling through semiconducting nanocrystals in a symmetrical and asymmetrical junction**. E.P.A.M. Bakkers and D. Vanmaekelbergh, Phys. Rev. B 62, R7743 (2000).
[3] **Single-particle orbital energy level spectrum of nanocrystalline CdSe quantum dots obtained by scanning tunneling spectroscopy.** D. Vanmaekelbergh et al. Submitted.

Below, a typical spectrum is shown for a 4.3 nm CdSe nanocrystal.



The spectrum shows tunneling through Valence Band orbitals (small peaks below –1.5 eV), a zero-conductivity gap (between –1.5 and 1 eV) and tunneling through discrete Conduction Band orbitals e_1,e_2,… (above 1 eV). The spectrum agrees well with the single-particle orbital spectrum obtained from pseudopotential theory: the zero-conductivity gap corresponds to the sum of the LUMO-HOMO gap and the electron and hole charging energies; the CB-peaks reveal the five first electron orbitals of a spherical 4.3 nm CdSe quantum dot: s-type (e_1), p-type (e_2), d-type (e_3), s-type (e_4), f-type (e_5).