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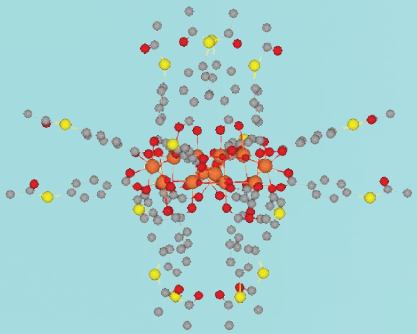


Mohammad Hadi Timachi
Supervisor: Prof. Dr. Piet Brouwer
06.06.2013

Electron Transport through Single Mn_{12} Molecular Magnet

H.B. Heersche, Z. de Groot, J.A. Folk & van der Zant
Physical Review Letters [PRL 96, 206801, May 2006]

Overview

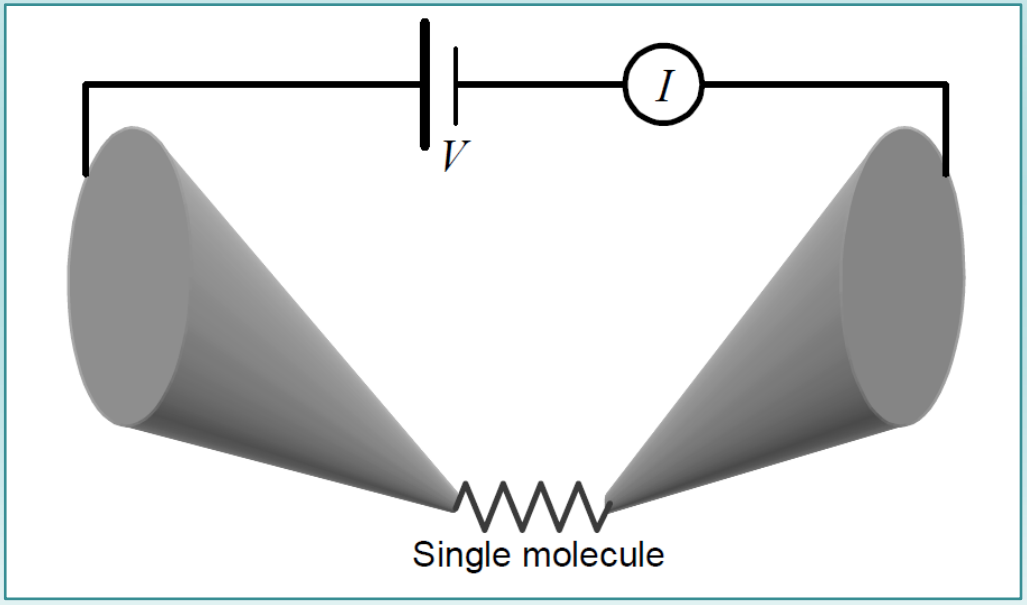
- **Electron Transport in single molecules**
  - Importance of Electron transport in single molecules
  - Ohm's law in microscopic scale
  - Experimental setup
  - Theoretical approach
  - Electric current of one level quantum dot molecule
  - Electric current of two level quantum dot molecule
  - Electric current of one level quantum dot molecule with excited state
- **Single molecular Magnets (SMMs)**
  - Single $\mathbf{Mn_{12}}$ Molecular Magnet
  - Transport through Single $\mathbf{Mn_{12}}$ Molecular Magnet
  - New model describing observed G spectra
- **Conclusion**
- **Resources**

Electron Transport In Single Molecule

Importance of electron transport study in single molecules :

Unique properties as an electronic unit:

- Very small size (several nm) → quantized energy levels ~ eV
- Self-assembly
- Diversity and functionality
- Exciting new behavior



Setup of Conductance measurement of a single molecule [2]

Ohm's Law in Microscopic Scale

Ohm's Law : Conductance G for a rectangular conductor

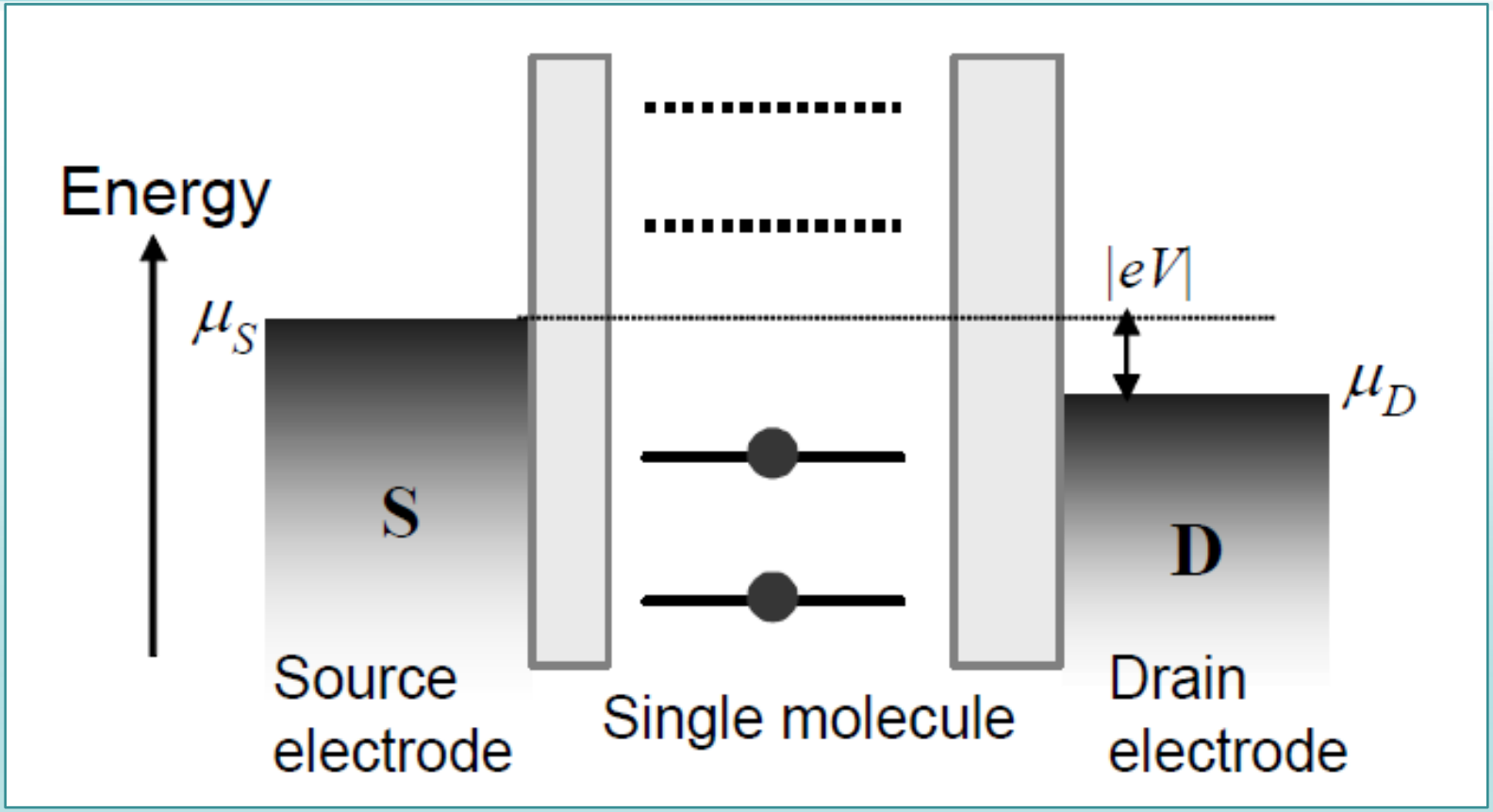
$$G = \frac{\sigma W}{L}$$

- W: Width of wire
- σ: Conductivity of conductor
- L: Length

Failure Reasons in Microscopic Scale (i.e. Single Molecule or nanostructures) **:**

- Size is smaller than electron mean free path
- Contact between electrodes and conductor
- Large charge addition energy and quantized excitation spectrum

Electron Transport In Single Molecule

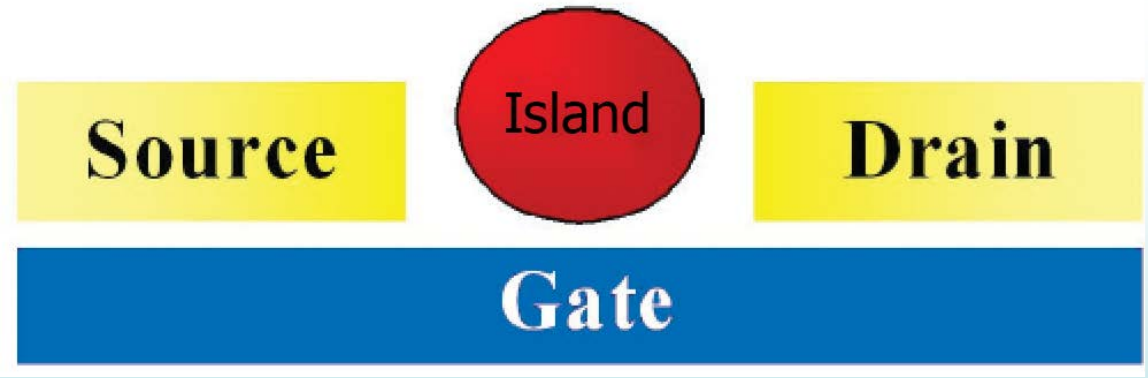


Schematic diagram of the energy landscape of a single molecule between two macroscopic electrodes (early experiments) [2]

- **On state**: available state between μ_S and μ_D (Fermi Level) → Large current
- **Off state**: no available states between μ_S and μ_D → blocked current

Electron Transport In Single Molecule

Scheme of electron transport using a capacitively connected gates



Types:

- **Coherent tunneling regime**
  - Strong coupling
  - Short stay
- **Incoherent (sequential, Coulomb Blockade) tunneling regime**
  - Weak coupling
  - Long stay and localization
  - There are tunnel barriers between electrodes and molecule

Electron Transport In Single Molecule

Total electrostatic energy for molecule with N electrons:

$$Q^2/_{2C} = (Ne)^2/_{2C}$$

C: Total capacitance (total interaction between e with other e on molecule or electrodes)

Total energy is:

$U(N) = \sum_{i=1}^{N} E_i + \frac{(Ne)^2}{2C}$ Adding 1 e to molecule $\rightarrow U(N+1) = \sum_{i=1}^{N} E_i + \frac{((N+1)e)^2}{2C}$

E_i: Chemical potential of molecule with i e

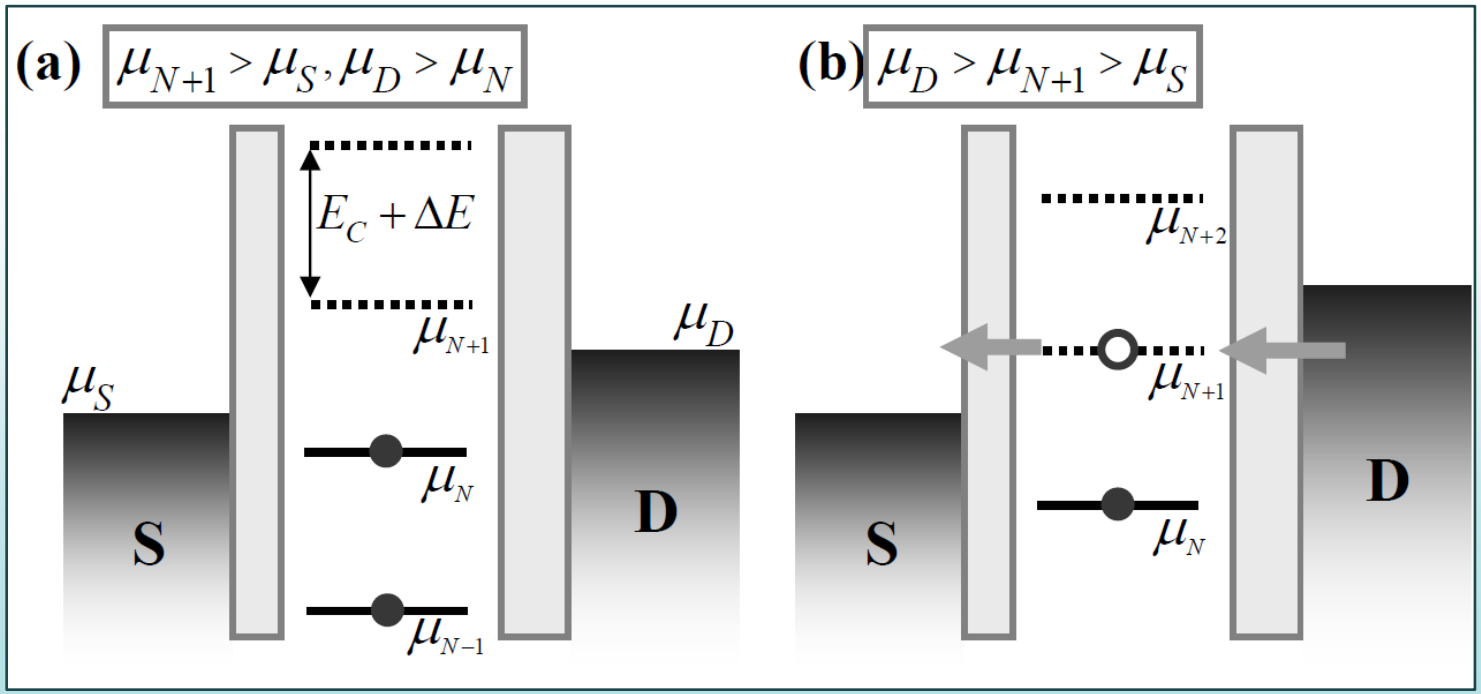
Electrochemical potential (min energy required for adding Nth e):

$$\mu_N \equiv U(N) - U(N-1) = E_N + (n - \frac{1}{2})\frac{e^2}{C}$$

To add one more e: $\mu_{N+1} = \mu_N + \frac{e^2}{C} + \Delta E = \mu_N + E_C + \Delta E$

- $\Delta E = E_{N+1} - E_N$
- E_C:Charging energy(energy required to overcome the Coulomb repulsion among different e)
- μ_{N+1}should be lower than μ_S & μ_D for N+1 e to be added to molecule

Electron Transport In Single Molecule

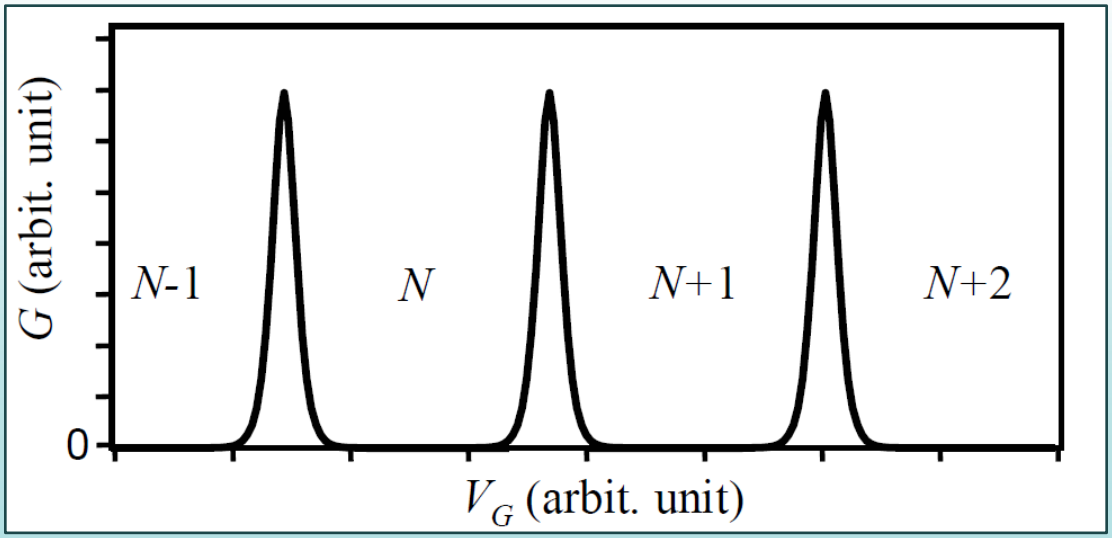


assumptions:

- There are tunnel barriers between molecule
- All interactions between e on molecule and all other electrons (on molecule or electrodes) is parameterized by total capacitance (C)
- ΔE does not change for different charge states of the molecule

Electron Transport In Single Molecule

Gate Voltage Role on the Conductance



Linear conductance [2]

To see Coulomb oscillation:

$E_C + \Delta E \gg k_B T$ (Molecule is a quantum dot ($\Delta E > k_B T$))

$R_{contact} \gg \frac{h}{e^2}$ (contact between the molecule and the leads to be resistive)

Electron Transport In Single Molecule

Electric current of One Level Quantum dot Molecule (N and N+1 states available):

$$\frac{I}{|e|} = -P_0\Gamma_S f_S + P_1\Gamma_S(1-f_S) = \frac{\Gamma_S\Gamma_D}{\Gamma_S+\Gamma_D}(f_D - f_S) \equiv \Gamma(f_D - f_S)$$

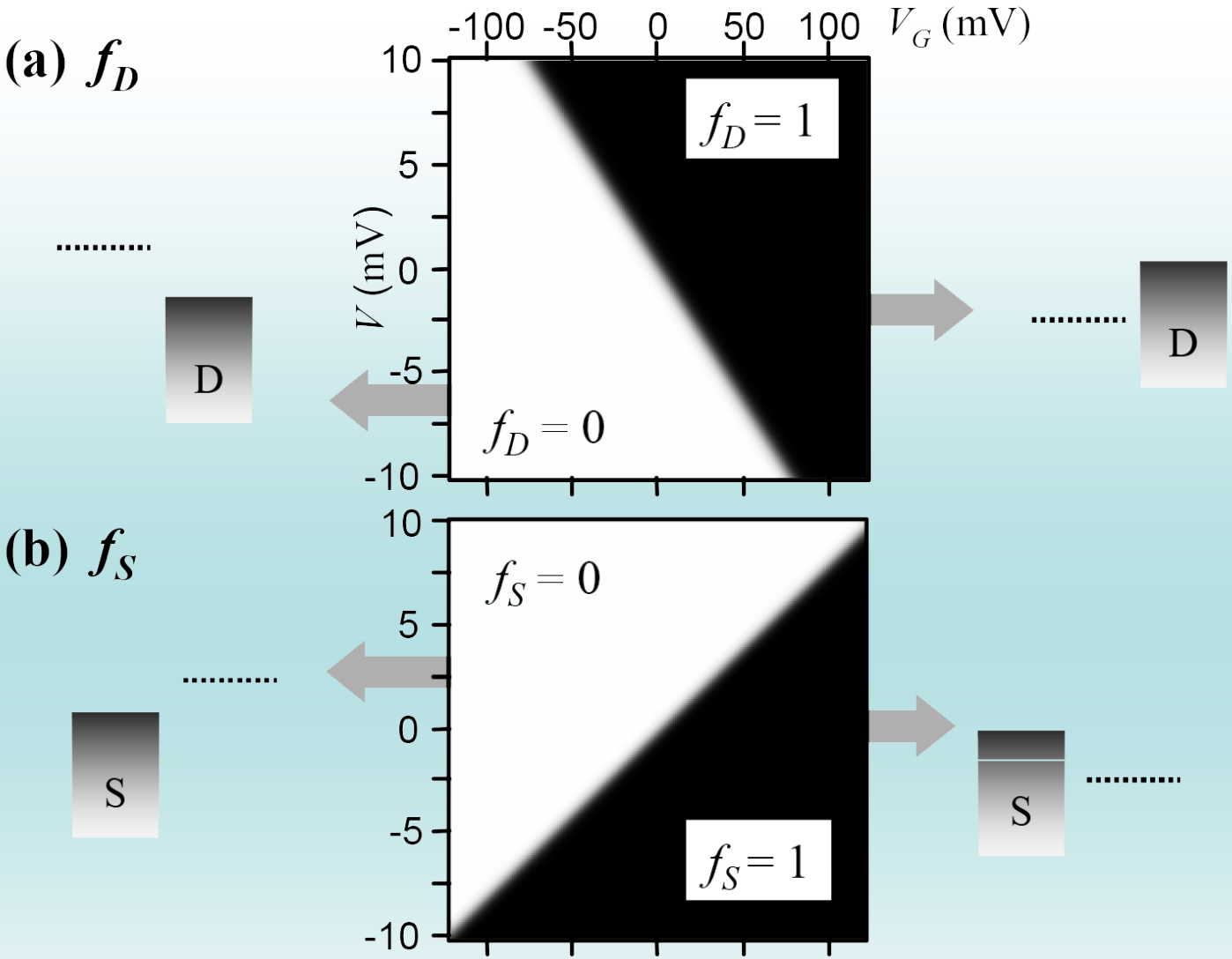
- f_S&f_D: Fermi functions calculated at μ_{N+1} for S&D
- Γ_S&Γ_D: e decay time to S&D
- P_0&P_1: Probability of N and N+1 state of quantum dot ($P_1 = 1 - P_0$)

Γ defines the amplitude of current

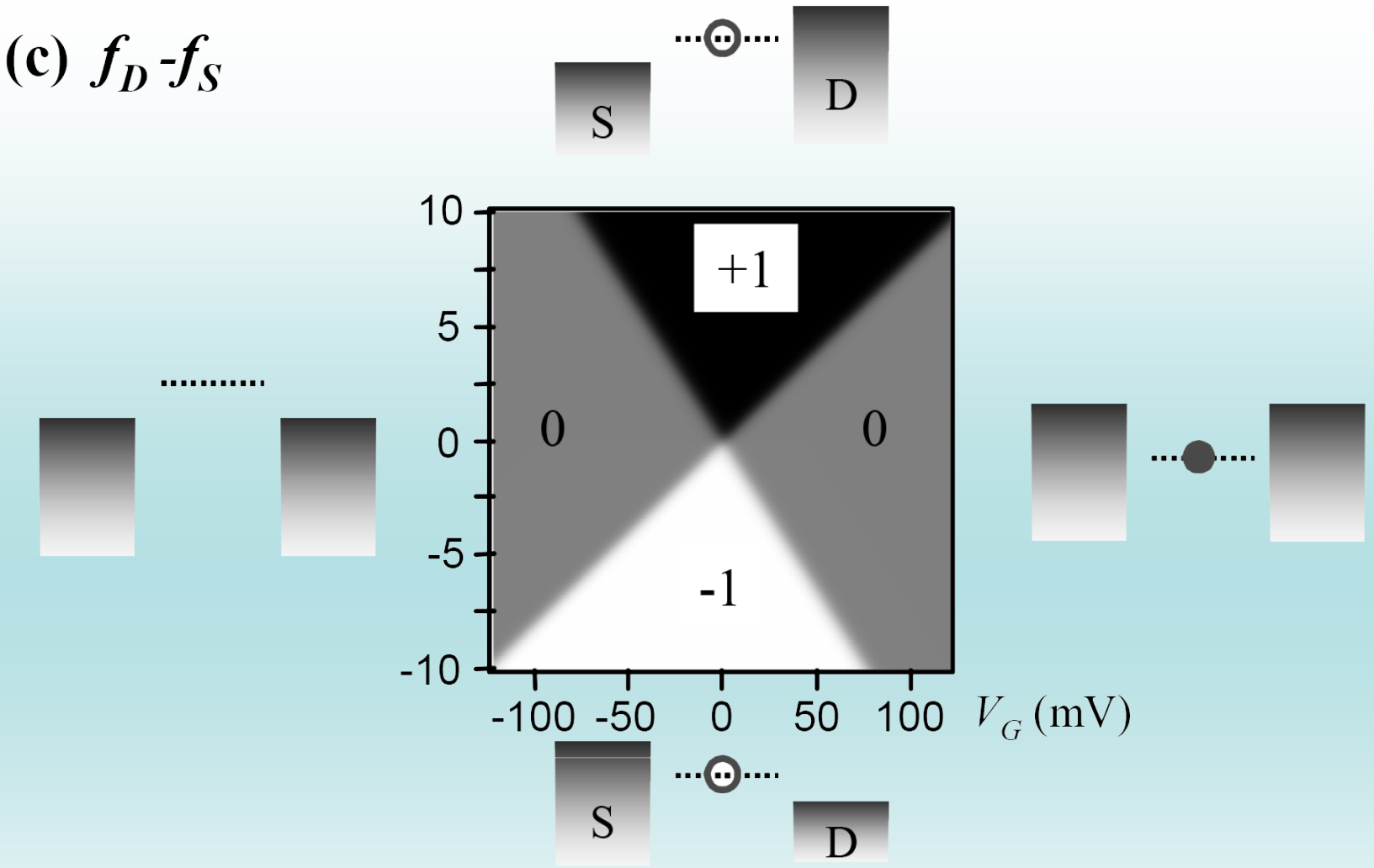
$(f_D - f_S)$ decides whether current flows or not
(f_D&f_S are either 0 or 1 in most cases at low temps.)

$\rightarrow$ Current becomes non-zero when f_D&f_S have different values $\rightarrow$ Conducting case is when μ_{N+1} is between μ_D& μ_S

Electron Transport In Single Molecule

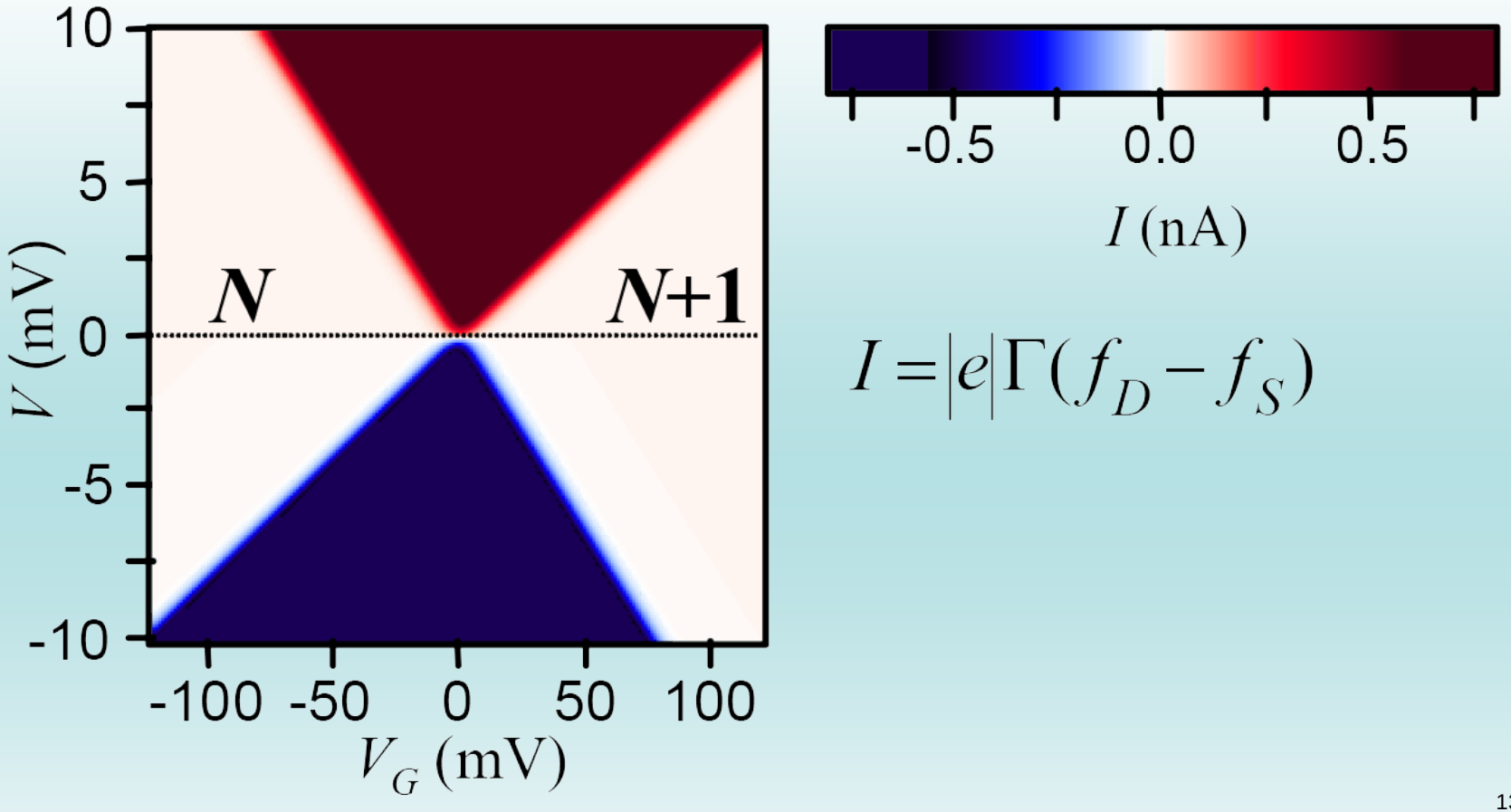


Electron Transport In Single Molecule



Electron Transport In Single Molecule

Calculated current (I) as a function of V and V_G (with $\Gamma_S = \Gamma_D = 10\ GHz$) [2]

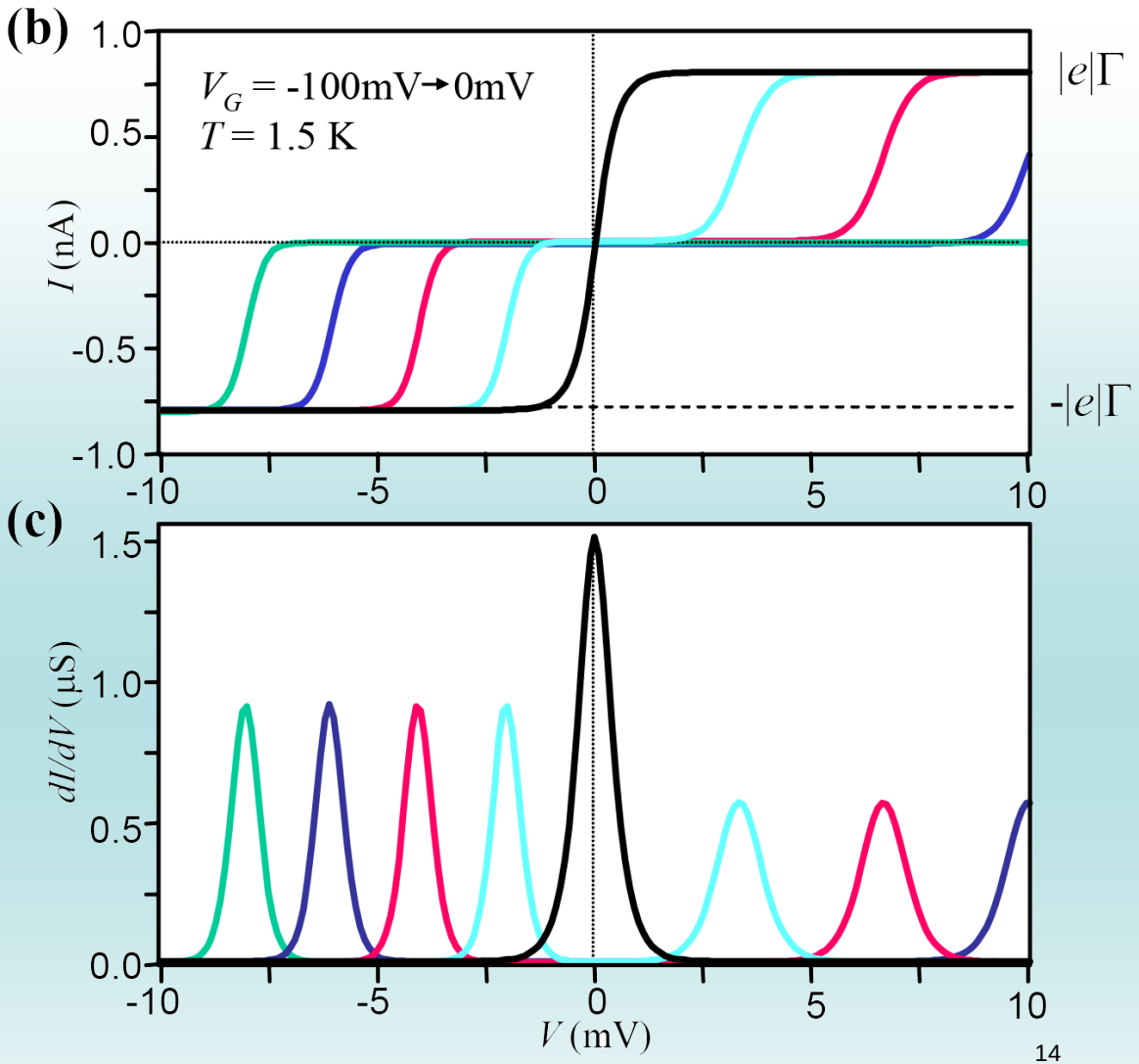


$$I = |e|\Gamma(f_D - f_S)$$

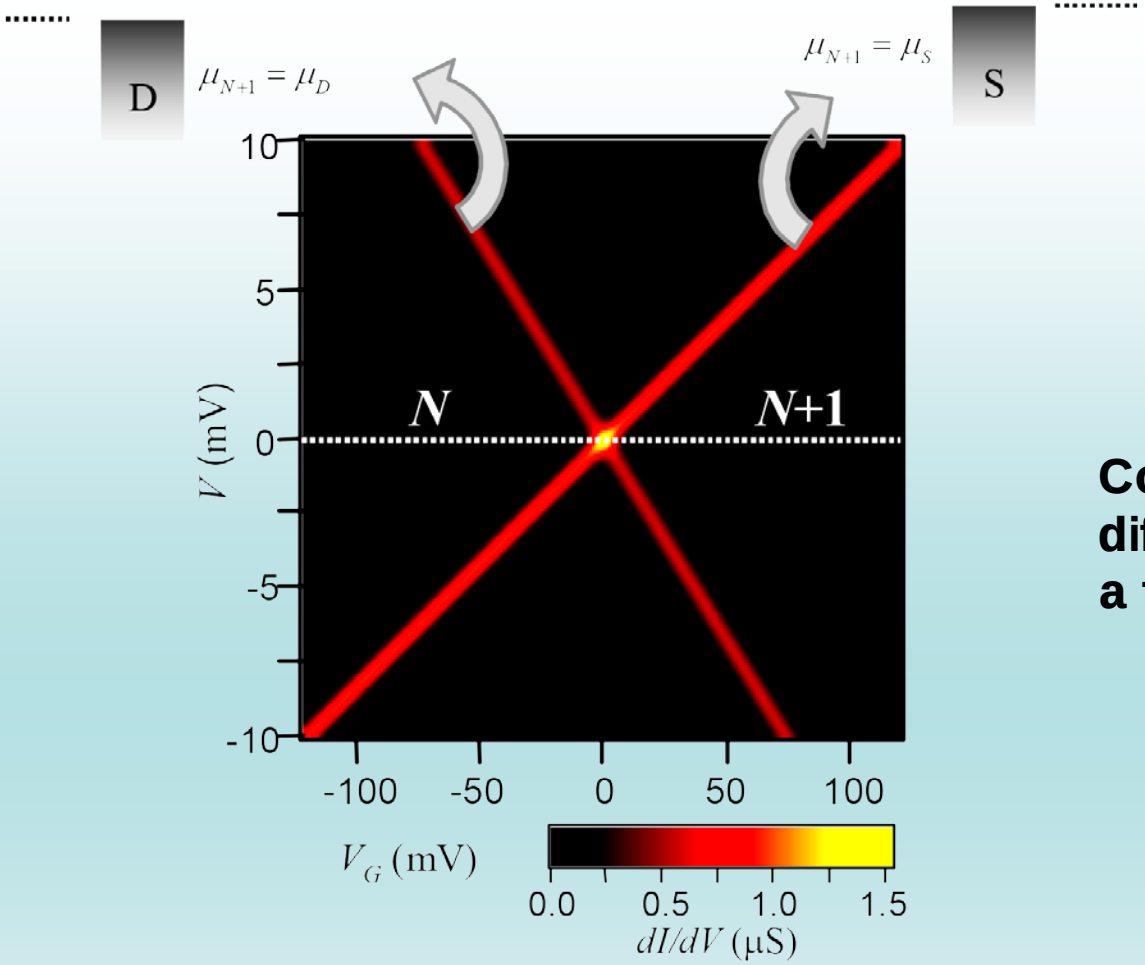
Electron Transport In Single Molecule

Calculated I-V curves at different gate voltages. [2]

Calculated dI/dV curves at different gate voltages. [2]



Electron Transport In Single Molecule

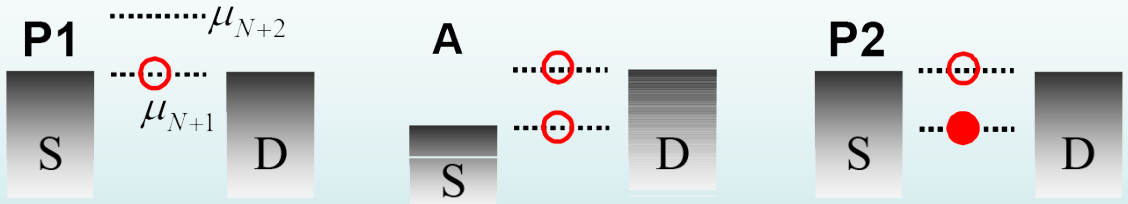


$$\frac{dI}{dV} = \frac{e^2\Gamma}{k_B T}\left((1-f_D) f_D \frac{C_S}{C_{total}} + (1-f_S) f_S \frac{C_D + C_G}{C_{total}} \right)$$

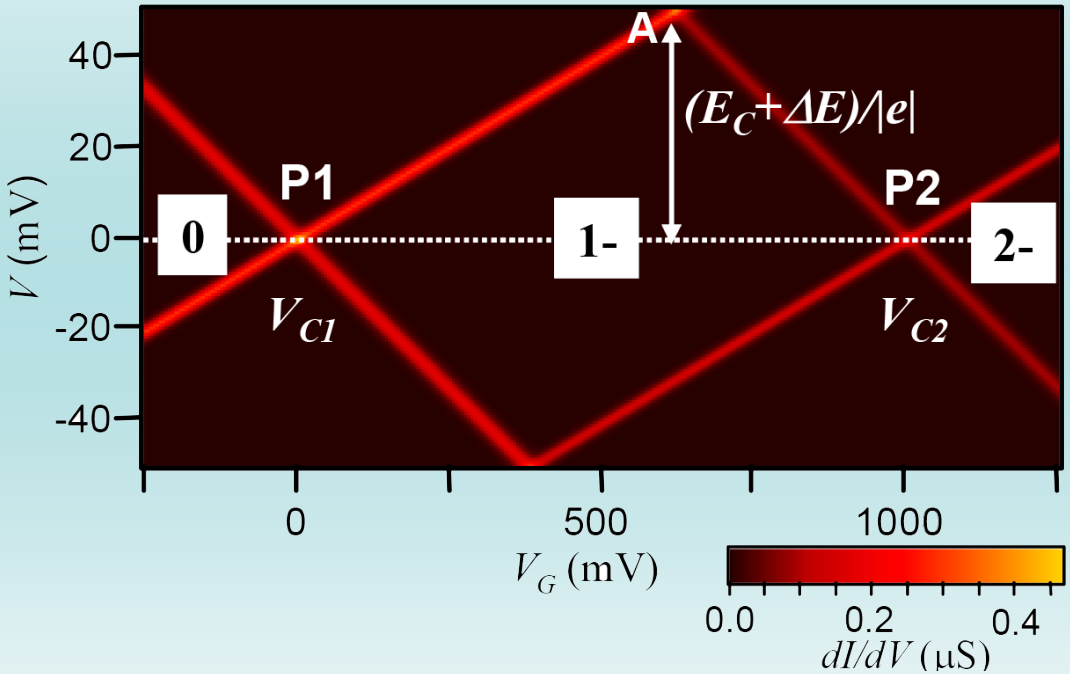
Color scale plot of the differential conductance as a function of V and V_G [2]

Electron Transport In Single Molecule

Electric current of Two Level Quantum dot Molecule (N, N+1 and N+2 states available & probabilities P_0, P_1, P_2):



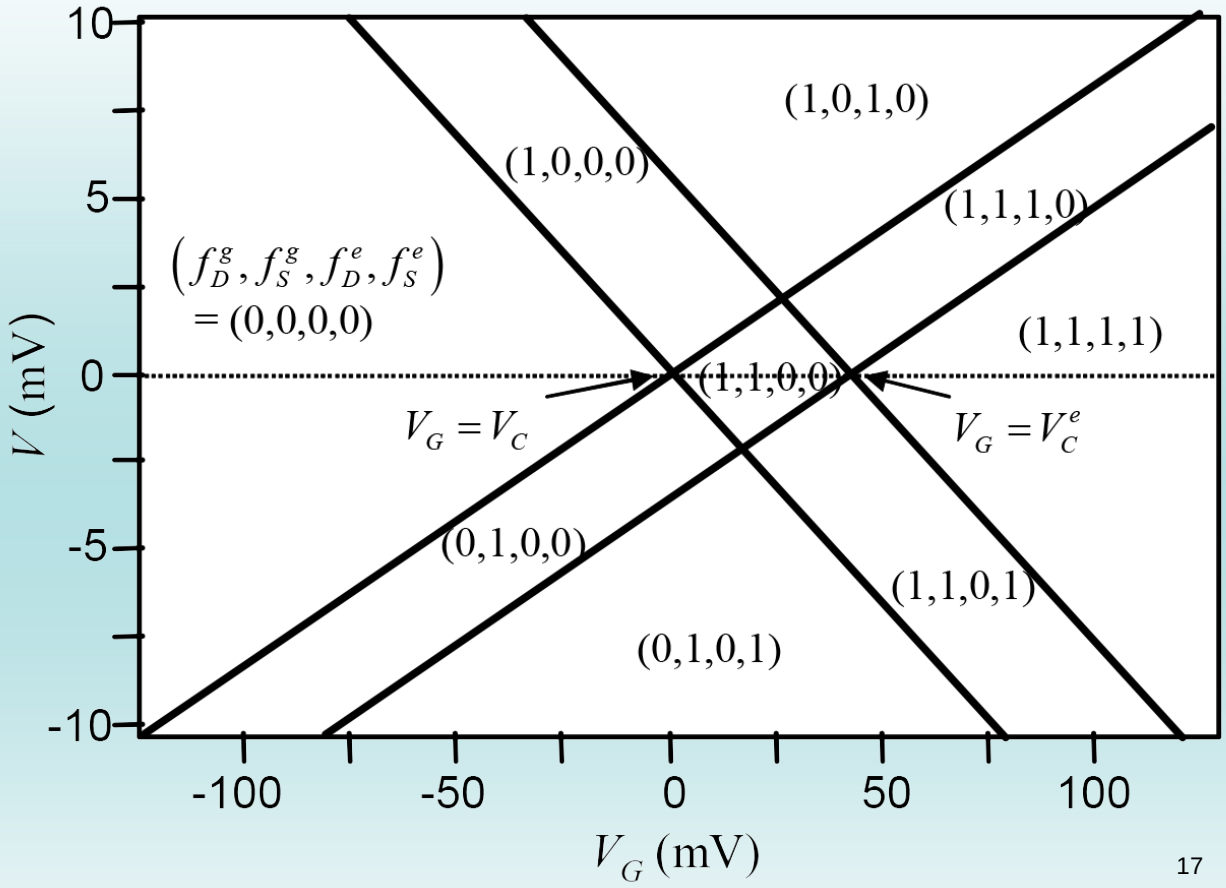
Color scale plot of the differential conductance as a function of V and V_G [2]



Electron Transport In Single Molecule

Electric current of One Level Quantum dot Molecule with excited state (N and N+1 states available & probabilities $P_0, P_1{}^g, P_1{}^e$):

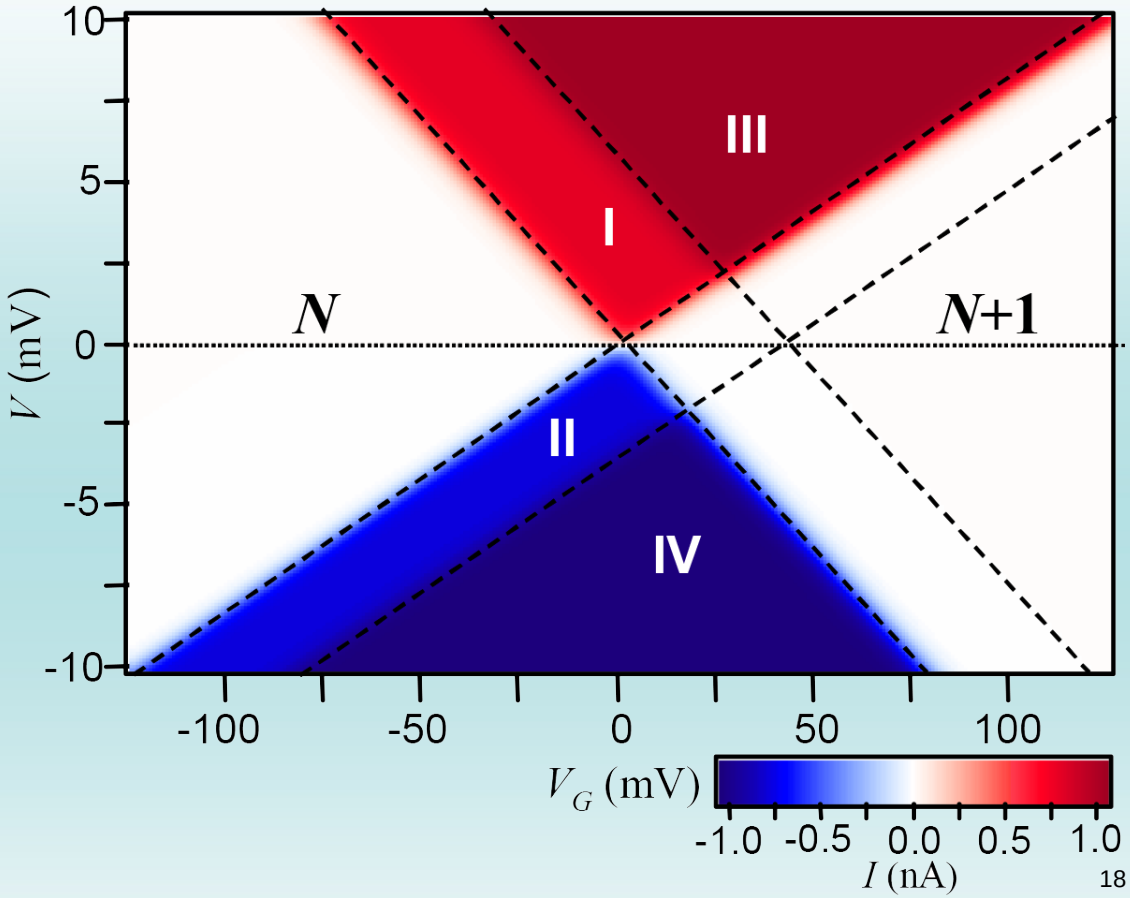
Fermi functions map in different regions of V and V_G [2]



Electron Transport In Single Molecule

Electric current of One Level Quantum dot Molecule with excited state (N and N+1 states available & probabilities $P_0, P_1{}^g, P_1{}^e$):

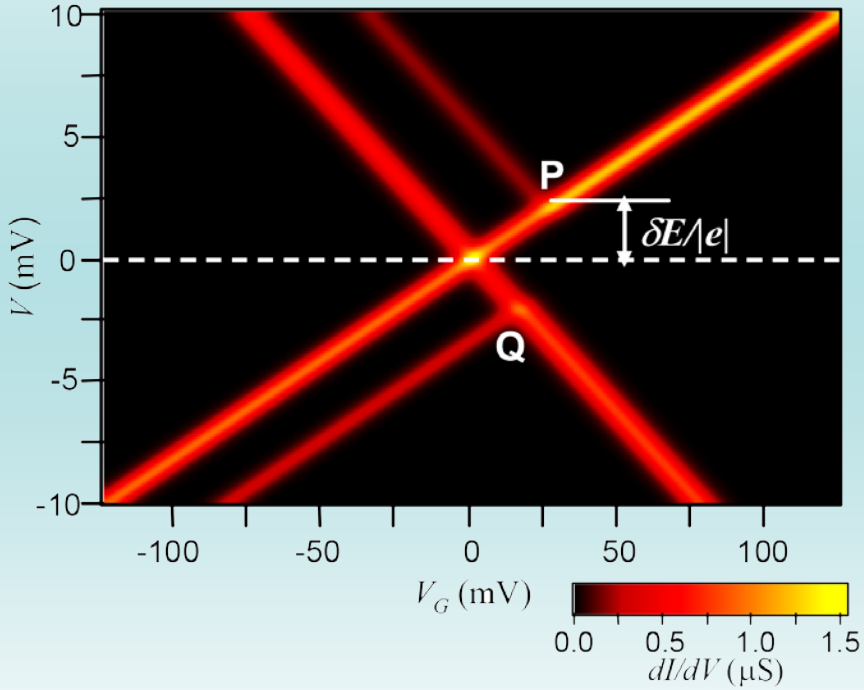
Current calculated for the one-level quantum dot. The number of electrons on the dot is shown in each blockade region of V and V_G [2]



Electron Transport In Single Molecule

Electric current of One Level Quantum dot Molecule with excited state (N and N+1 states available & probabilities $P_0, P_1{}^g, P_1{}^e$):

The differential conductance plot as a function of V and V_G for a one level quantum dot.



$$\delta E = U^e(N+1) - U^g(N+1)$$

Single Molecular Magnets (SMMs)

SMMs are nanoscale magnetic molecules that exhibit slow relaxation of the magnetization at low temperatures [4]

- Inner magnetic core with a surrounding shell of organic ligands
- Ligands can be tailored to bind molecule on surfaces or into junctions
- Variety of shapes and sizes, allow selective substitutions of the ligands to alter the coupling to the environment
- Crystallize into high-quality crystals and are soluble, thus allowing for a structural determination and rationalization of their properties

Importance of study on SMMs:

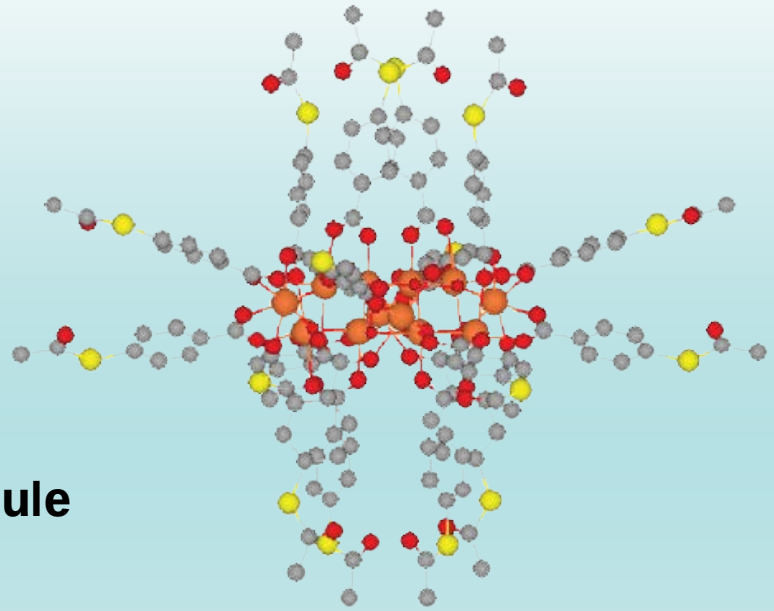
Properties:	**Influence:**	**Result:**
• large spin • high anisotropy barrier	hampers magnetization reversal process through quantum tunneling of magnetization (QTM)	magnetic hysteresis

Single $\mathbf{Mn_{12}}$ Molecular Magnet

Single $\mathbf{Mn_{12}}$ Molecular Magnet with tailor made ligands

$\boldsymbol{Mn_{12}O_{12}(O_2C-C_6H_4-SAc)_{16}(H_2O)_4}$ **(size: 3 nm)**

Thiol group :
Strong affinity for gold surfaces & serve as tunnel barriers



$\boldsymbol{Mn_{12}O_{12}(O_2C-C_6H_4-SAc)_{16}(H_2O)_4}$ **Molecule**

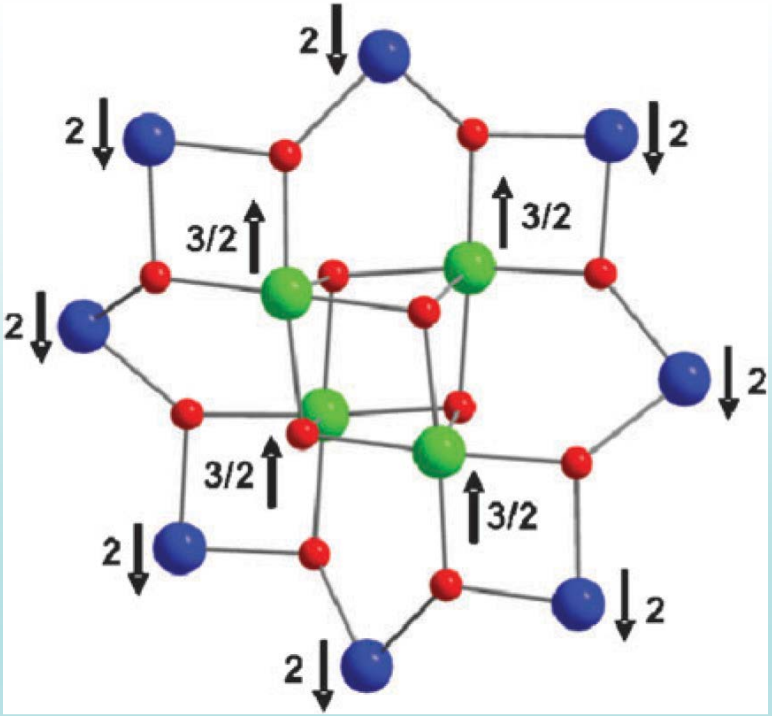
[3] Color labels:

- Manganese → orange
- Oxygen → dark red
- Carbon → gray
- Sulfur → yellow

Single $\mathbf{Mn_{12}}$ Molecular Magnet

Spin alignments in the ground state of $\mathbf{Mn_{12}}$ complexes that gives their S = 10 ground states.

Color scheme: MnIV green, MnIII blue, O red.[4]



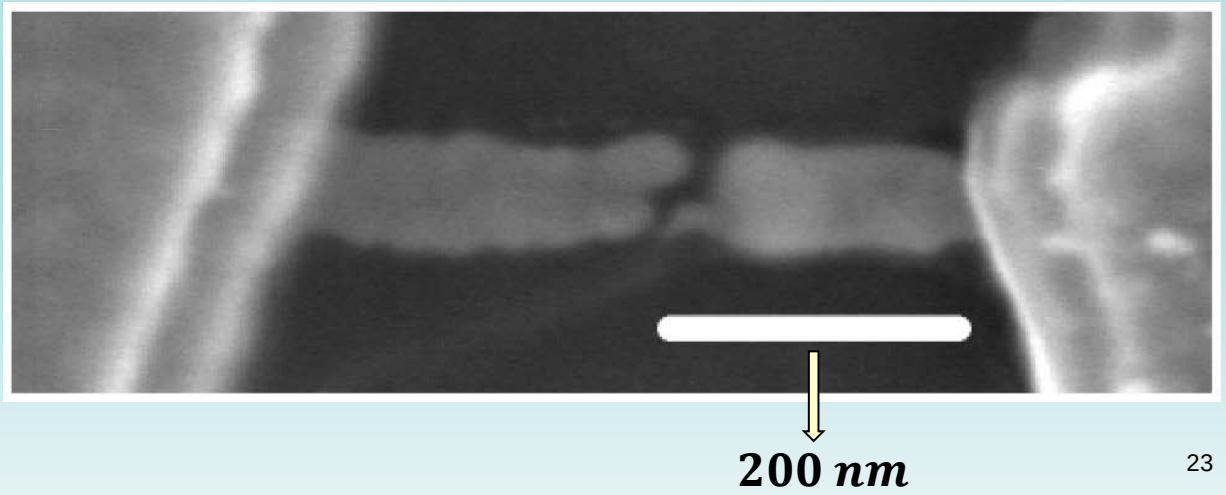
Verified by polarized neutron scattering experiments

Transport through Single $\mathbf{Mn_{12}}$ Molecular Magnet

Aim: To explore high spin ground state (& high anisotropy barrier) on electron transport

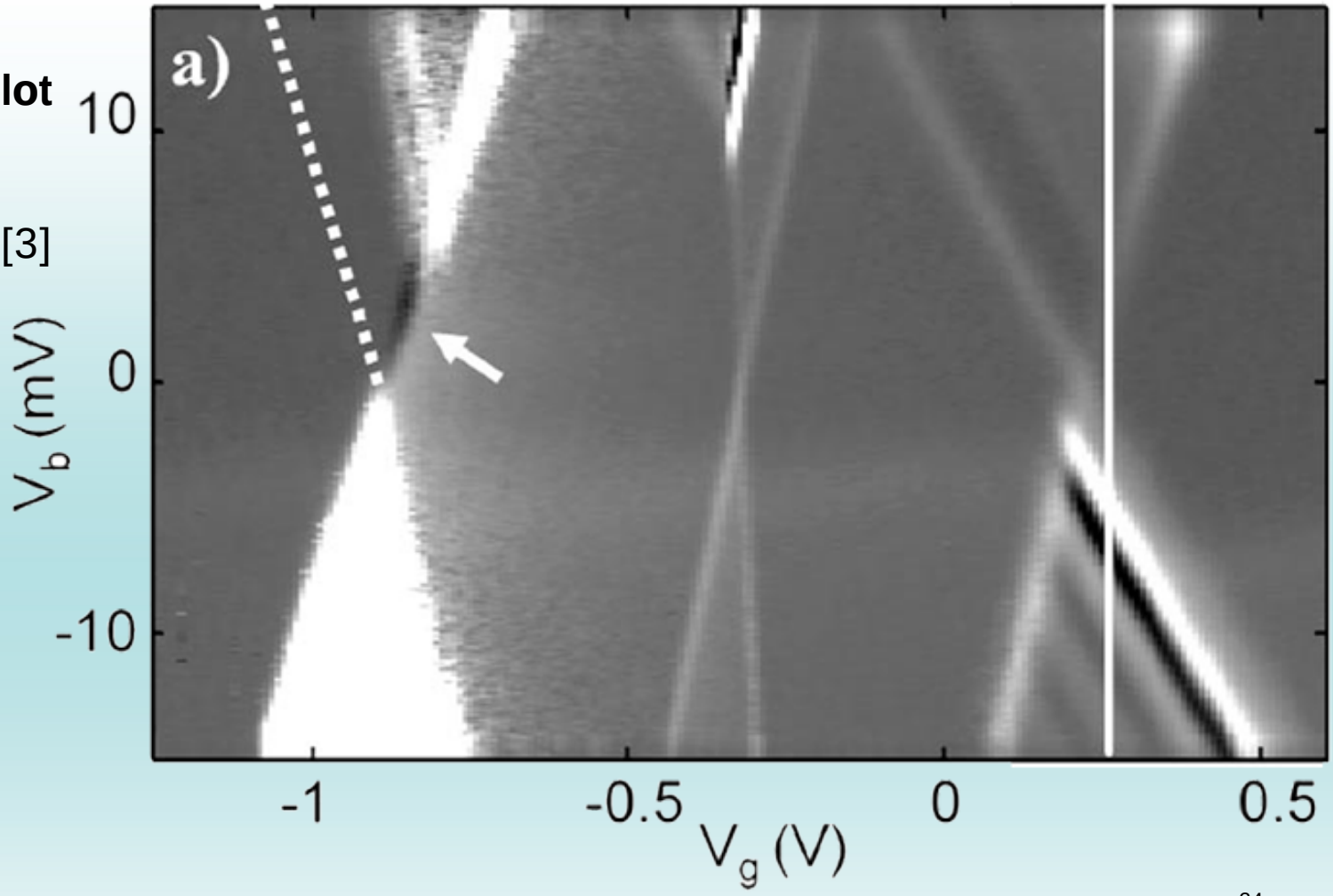
Schematic drawing of Mn_{12} trapped between electrodes [3]

Scanning electron microscope image (SEM) of electrodes[3]



Transport through Single $\mathbf{Mn_{12}}$ Molecular Magnet

Differential conductance plot as a function of V_b and V_G
(T =3K, R C_6H_4) [3]



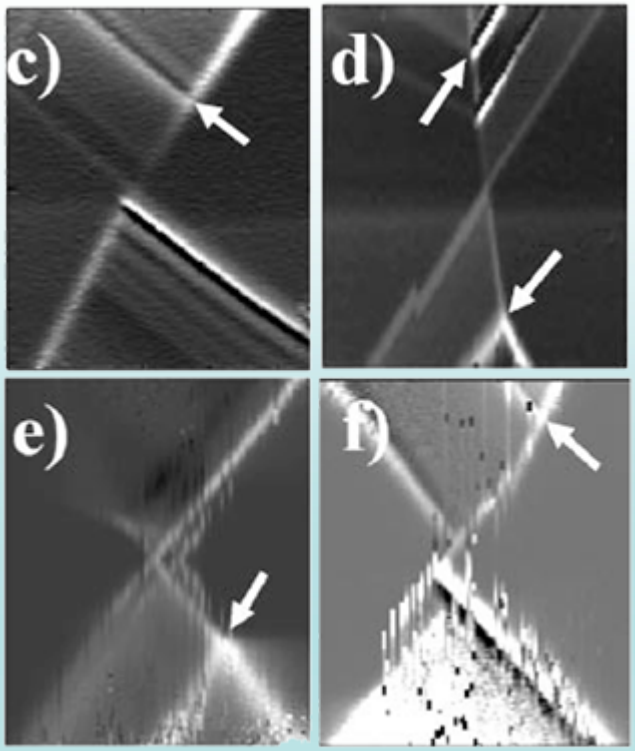
Transport through Single $\mathbf{Mn_{12}}$ Molecular Magnet

Excitation ot 14±1 meV in all 6 transport regions indicated with arrows [3]

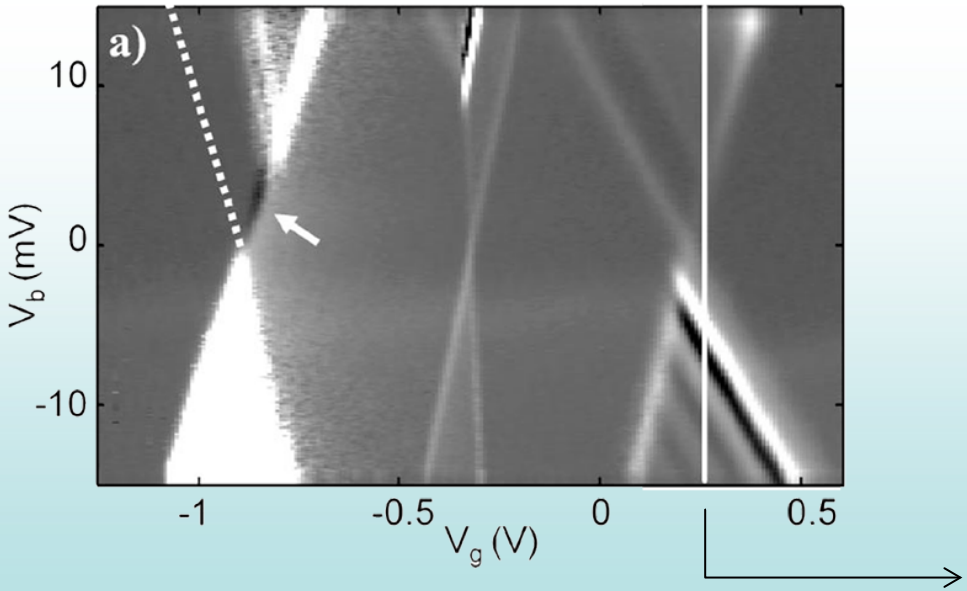
This is a fingerprint of molecule

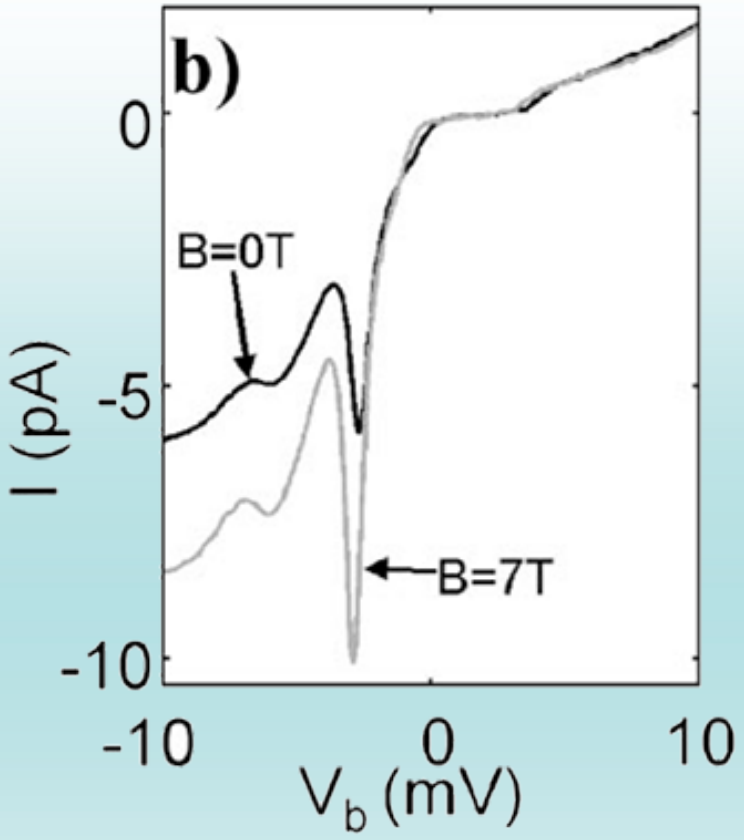
Raman spectrum exhibits strong peaks beyond this energy

This excitation origin is believed to be from vibrations of magnetic core of molecule



Transport through Single $\mathbf{Mn_{12}}$ Molecular Magnet





***I* - V_b at the gate voltage indicated in (a) with a line.** [3]

Transport through Single $\mathbf{Mn_{12}}$ Molecular Magnet

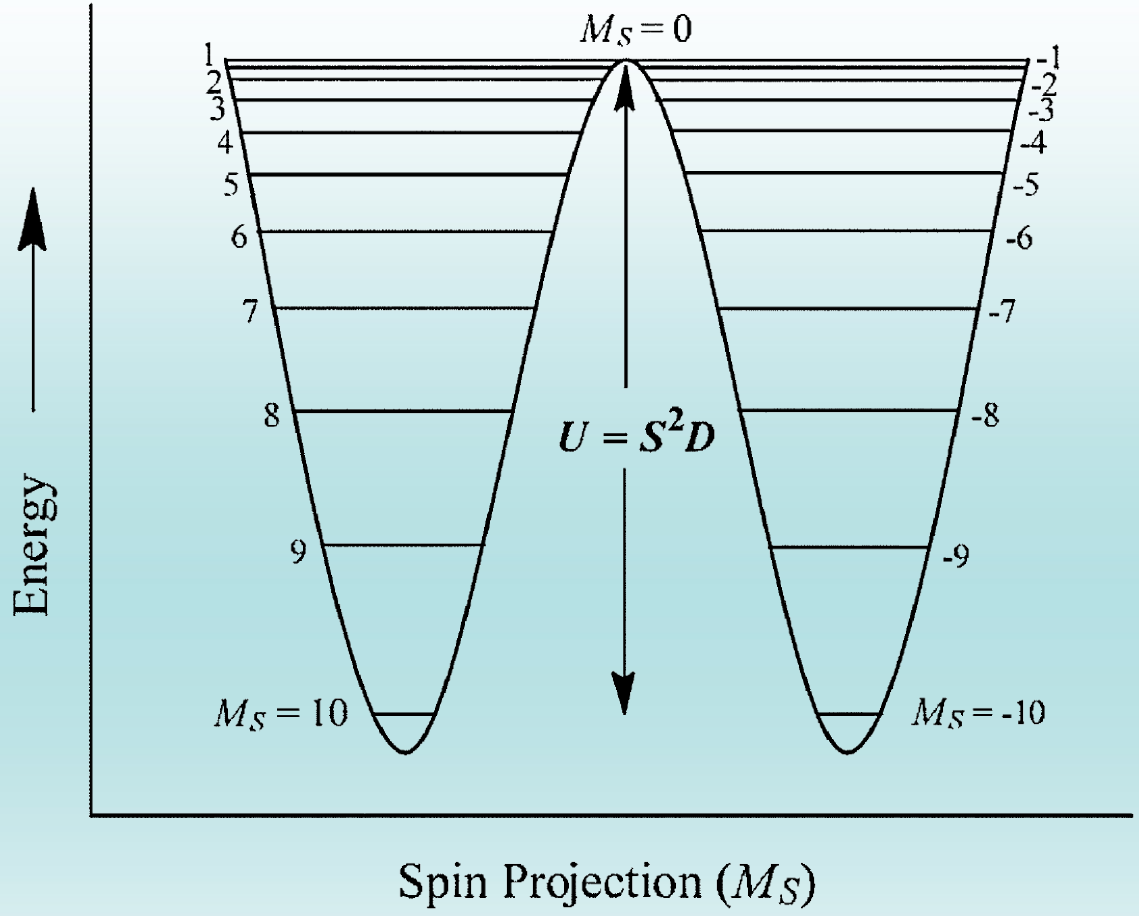
New sequential model that incorporates spin-Hamiltonian description of high-spin ground state of $\mathbf{Mn_{12}}$ and ladder spin excitation system for SMM in charge state N:

$$\boldsymbol{H_{N\alpha} = -D_{N\alpha} S_z^{\,2} + B_2 \left(S_x^{\,2} - S_y^{\,2}\right)}$$

$D_{N\alpha} > 0$: Anisotropy const.
B_2: the lowest order QTM perturbation due to deviations from perfect axial symmetry

For adding or subtracting e: $|\Delta S|, |\Delta M| = \frac{1}{2}$

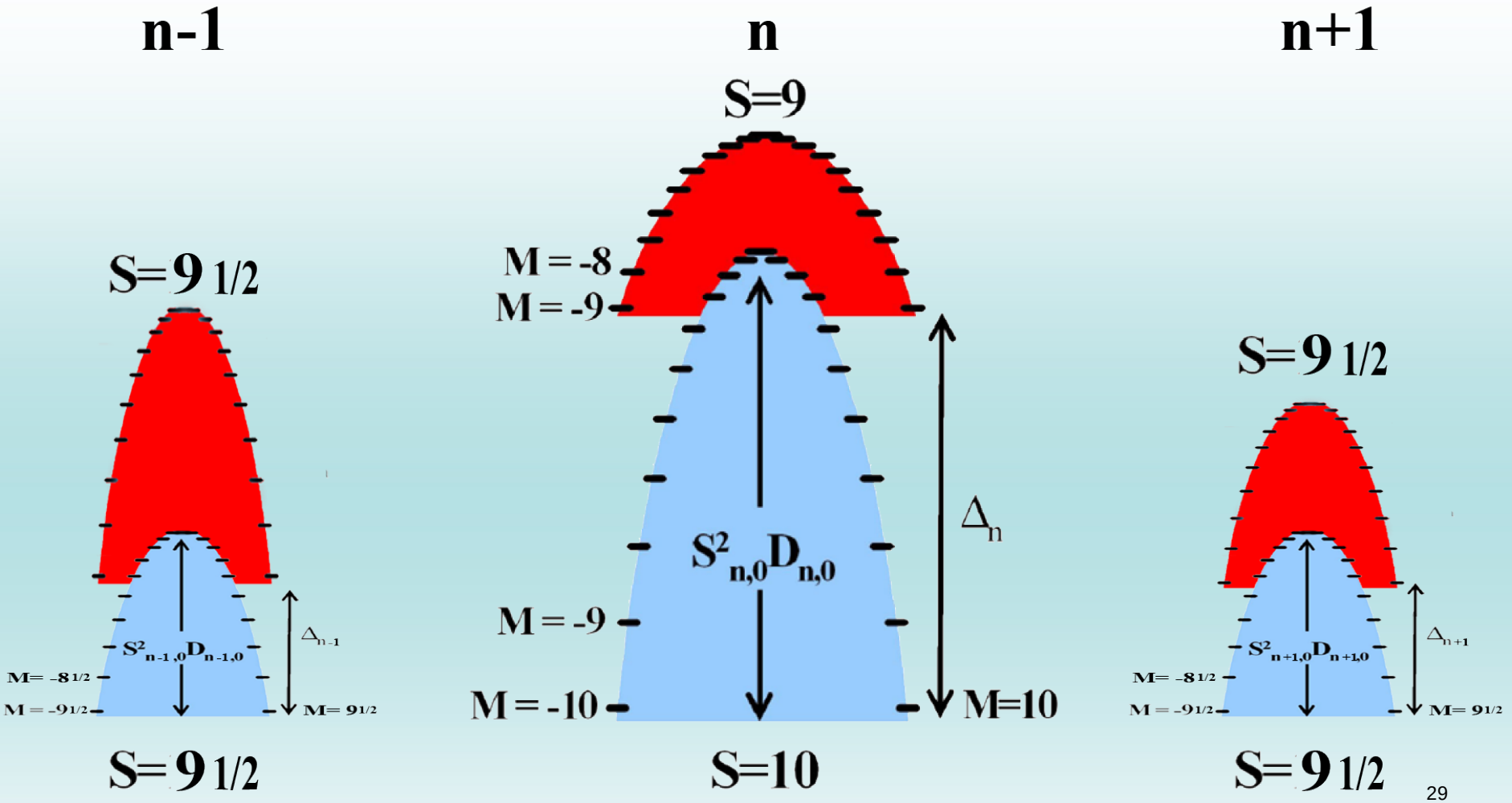
Transport through Single $\mathbf{Mn_{12}}$ Molecular Magnet



Plot showing the allowed, quantized orientations (M_S states) of the spin vector of a molecule such as $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ with S = 10 and negative D. energy increases with decreasing $|M_S|$ [4]

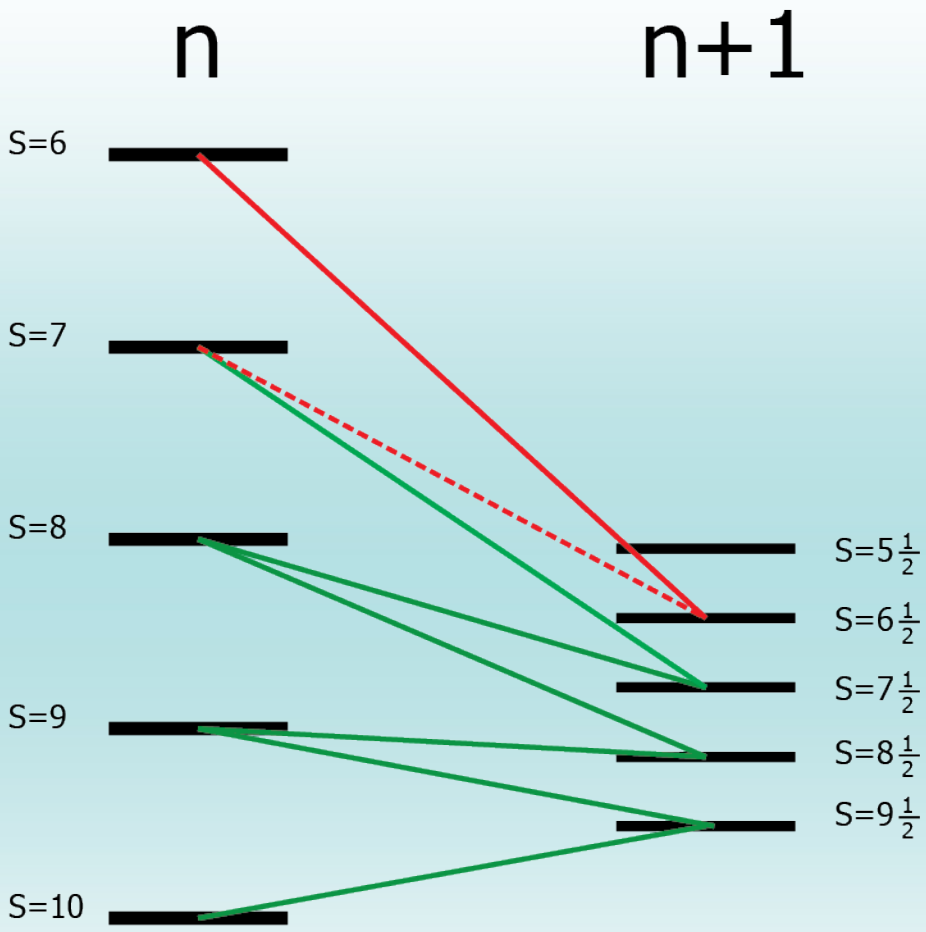
Transport through Single Mn_{12} Molecular Magnet

Spin Energy states for n, n+1 and n-1 in $V_G = 0$



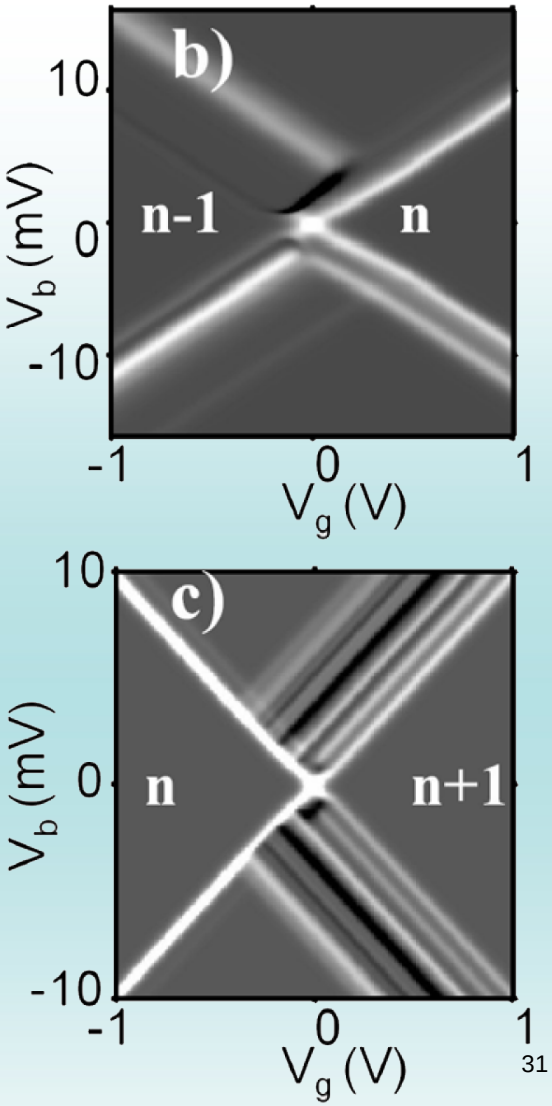
Transport through Single $\mathbf{Mn_{12}}$ Molecular Magnet

Spin Energy states and possible spin selection for n, n+1 and n-1 in $V_G \neq 0$



Transport through Single $\mathbf{Mn_{12}}$ Molecular Magnet

Calculated differential conductance for mentioned Hamiltonian (with 3 charge states) [2]

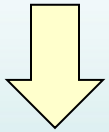


NDC and CCS are generic features when:

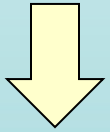
1) The MAB is charge state dependent
2) The spin multiplet within a charge state overlap in energy ($D_{N0}{S_{N0}}^2 > \Delta_N$)

Conclusion

Measured transport through single Mn_{12} Molecule → CCS and NDC on the energy scale of the anisotropy barrier observed



By using the mentioned model, it will be possible to combine spin properties of the SMM with standard sequential tunneling theory.



May lead to electronic control of nanomagnets to harvest magnetic hysteresis in molecular scales.

Resources

1. Angew. Chem. Int. Ed. 2003, 42, No. 3
2. Electron Transport in Single Molecule Transistors by Jiwoong Park
3. H.B. Heersche et al. Physical Review Letters [PRL 96, 206801, 2006]
4. Chem. Soc. Rev. –Vol38- 2009 - Rashmi Bagai and George Christou
5. Nature materials – vol7- March 2008 - Lapo Bogani and Wolfgang Wernsdorfer
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7. Nature nanotechnology –Vol1-December 2006 - N. J. Tao