Electron Transport Through Single-Molecule Magnets

European Union

Research Training Networks

Spintronics

HPRN-CN-2002-00302

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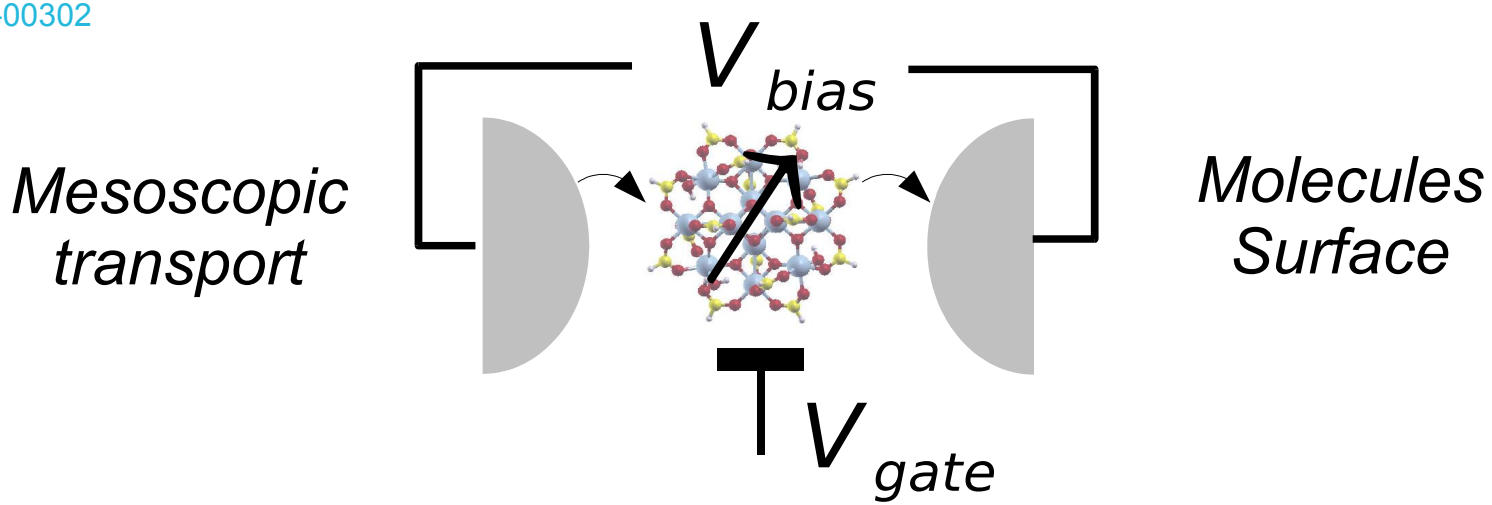

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Outline

(1) Transport through single molecules

- Experimental setups
- Theoretical framework

(2) Spin effects in transport through single molecule magnets (SMM):

- *Magnetic* excitations
- Magnetic & low-lying *electronic* excitations

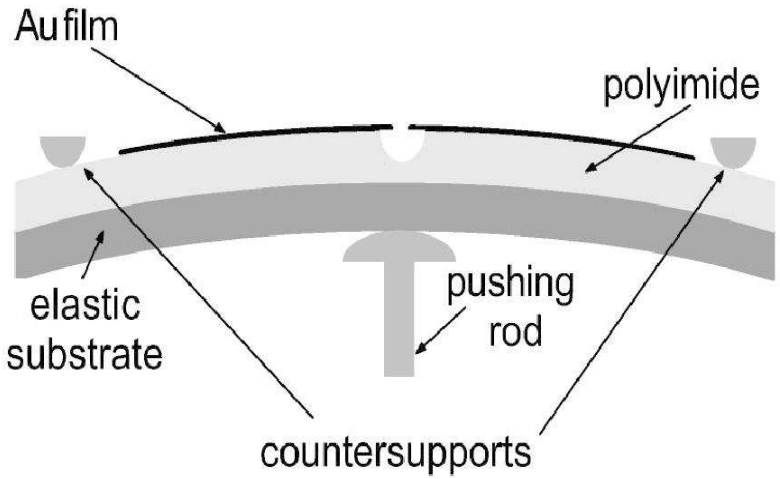
Experiment

Experimental approaches

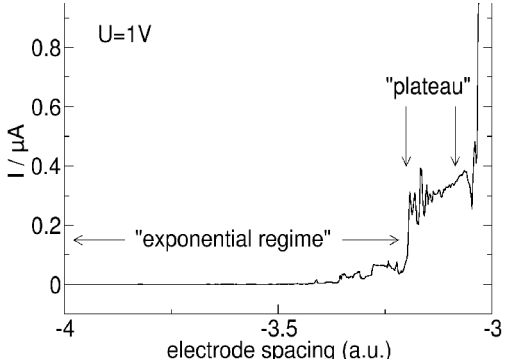
*STM: *no* gate *and* asymmetric

Mechanically-Controlled Break Junction (MCBJ)

- **Strong tunnel coupling**
- **Stable contact: high voltage and current levels**
- **Controlled** contact: stretch, rebond "symmetrize" tunnel coupling
- Good statistics possible



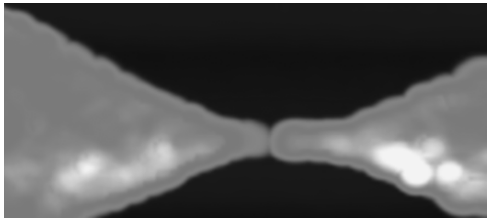
- Single I(V) traces
- "High" temperature T ~ 4 K

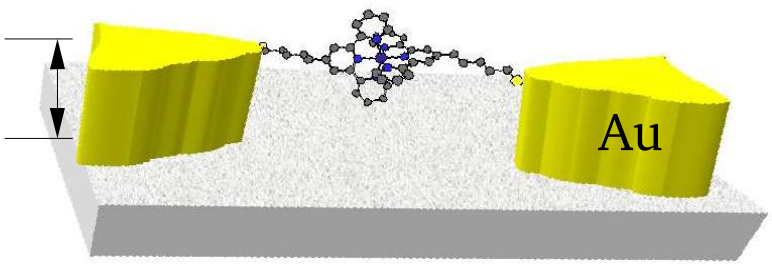


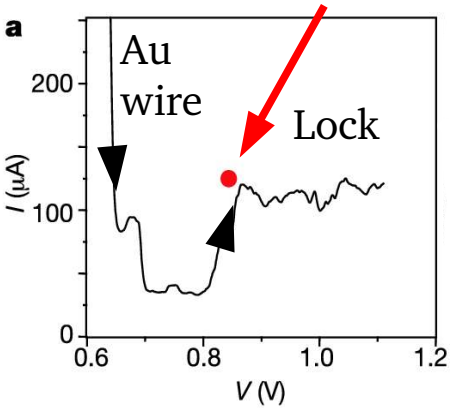
Electro-Migrated Junction (EMJ)

- **Gate voltage**: identification of resonances
- Weak / moderate tunnel coupling
- Very low temperature T (~ 50 mK)

- Asymmetric tunnel coupling
- Few devices "work" ~ 10 %
- Gold particles can *ly around*
- Low voltage & current levels
- *Fry* the molecules

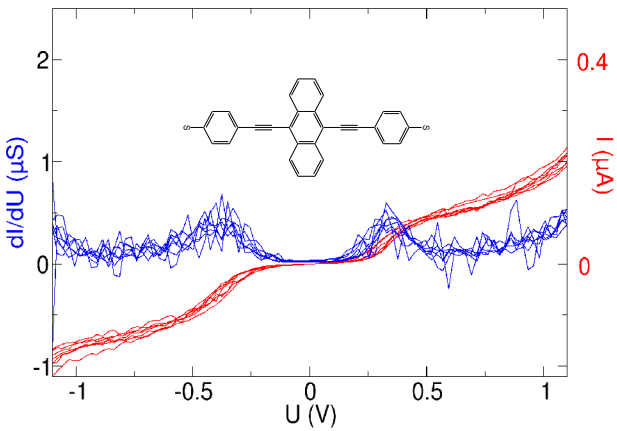




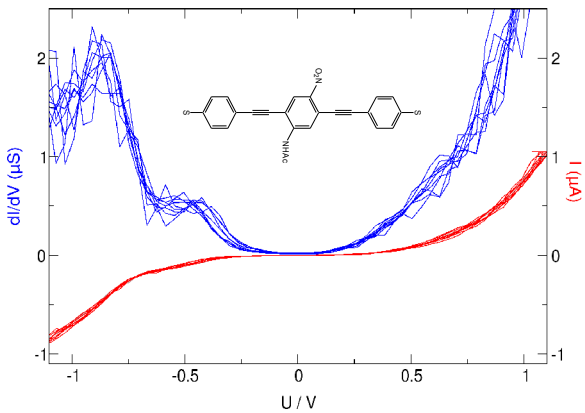


Mechanically Controlled Break Junction

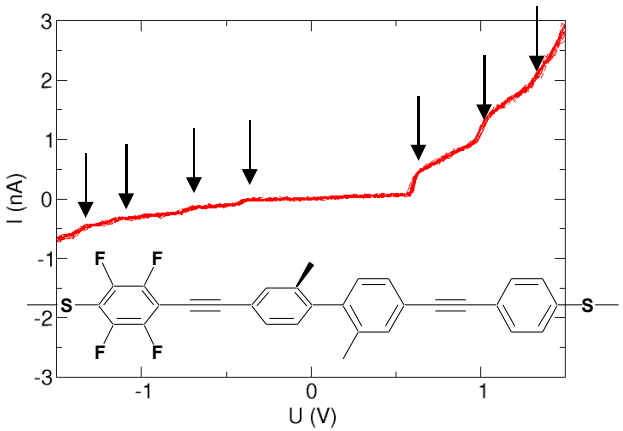
J. van Ruitenbeek
M. Reed
J. P. Bourgoin
H. Weber



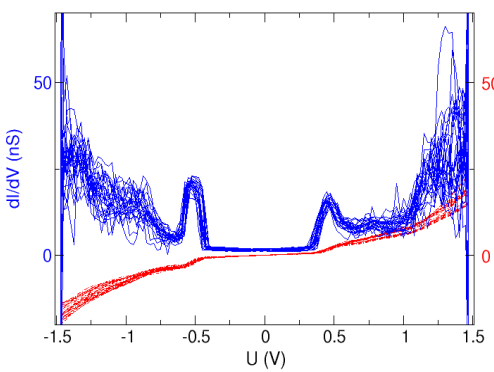
Symmetry of molecule

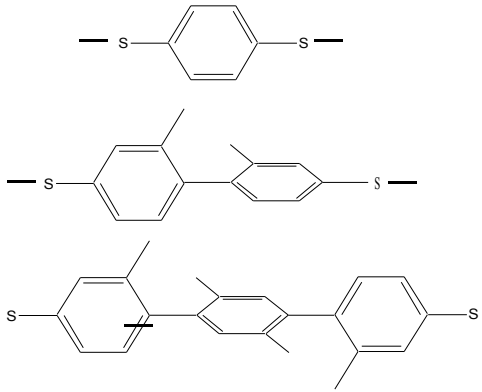


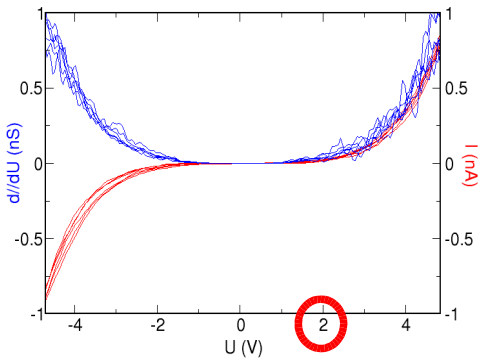
Gate-effect by sidegroups

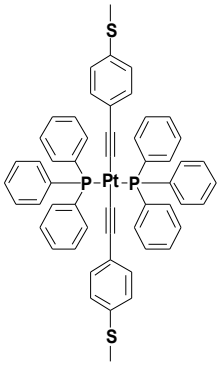


Intramolecular conjugation



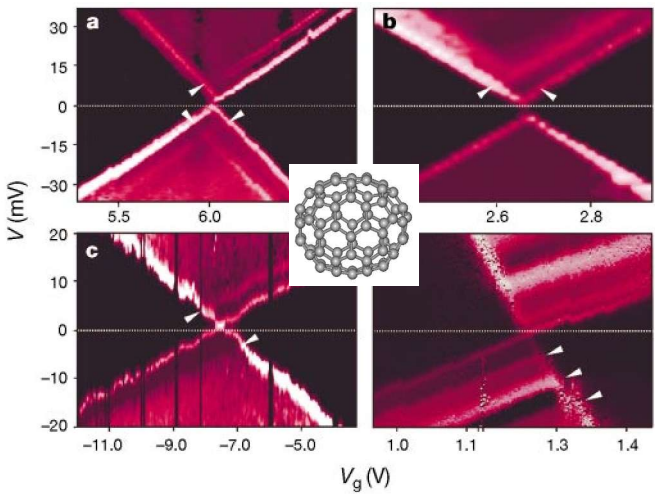


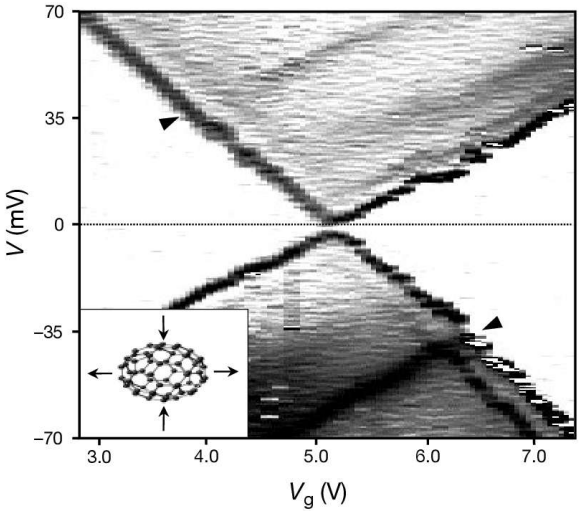


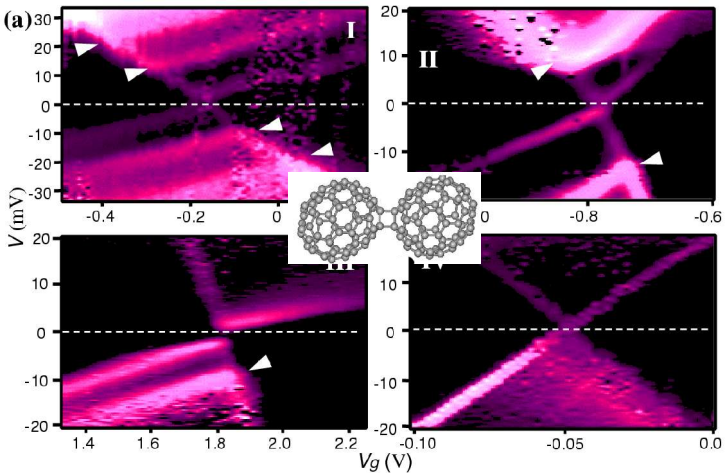


Courtesy H. Weber

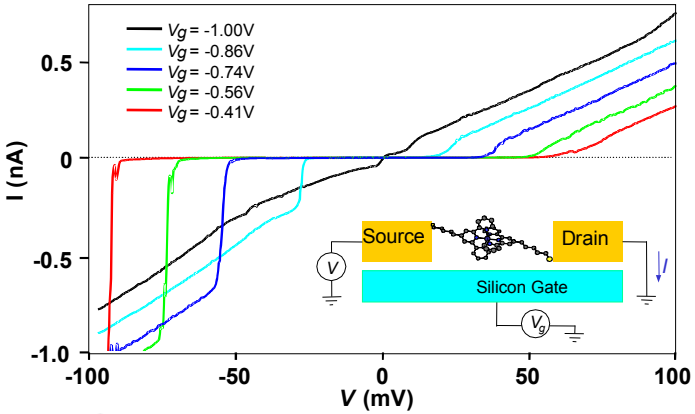
Electro-Migrated Junction

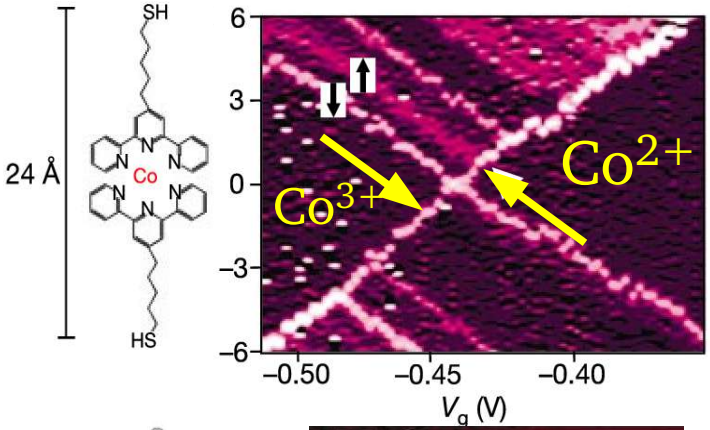




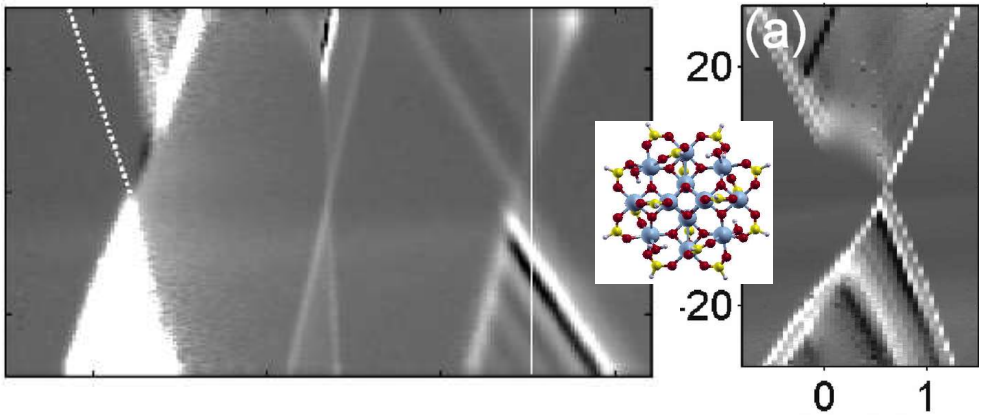


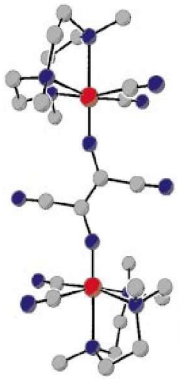
J. W. Park
P. McEuen
D. Ralph
H. K. Park

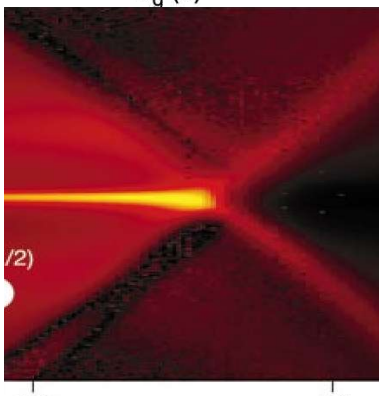




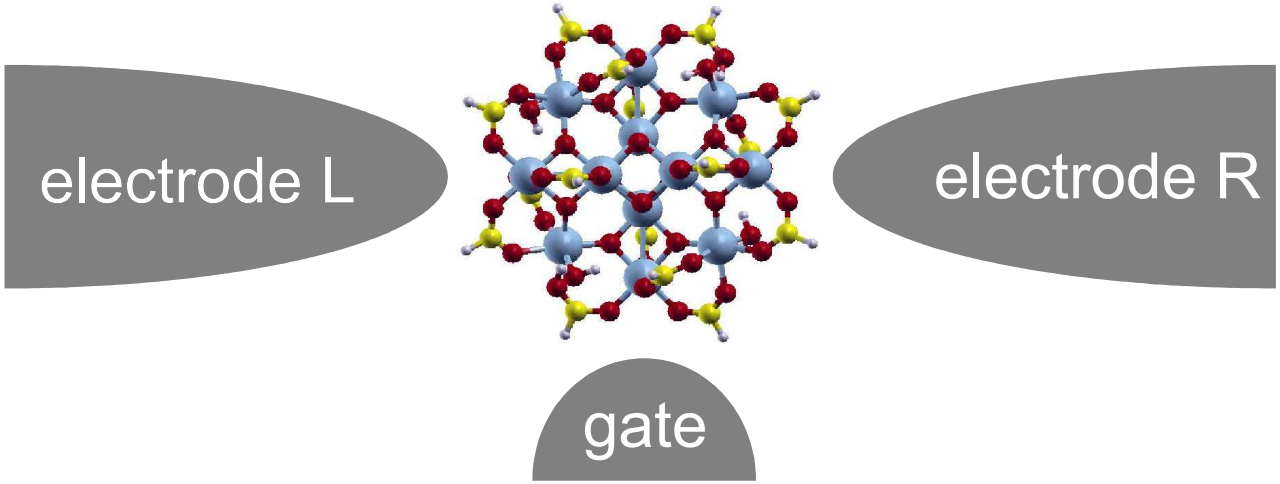
H. van der Zant



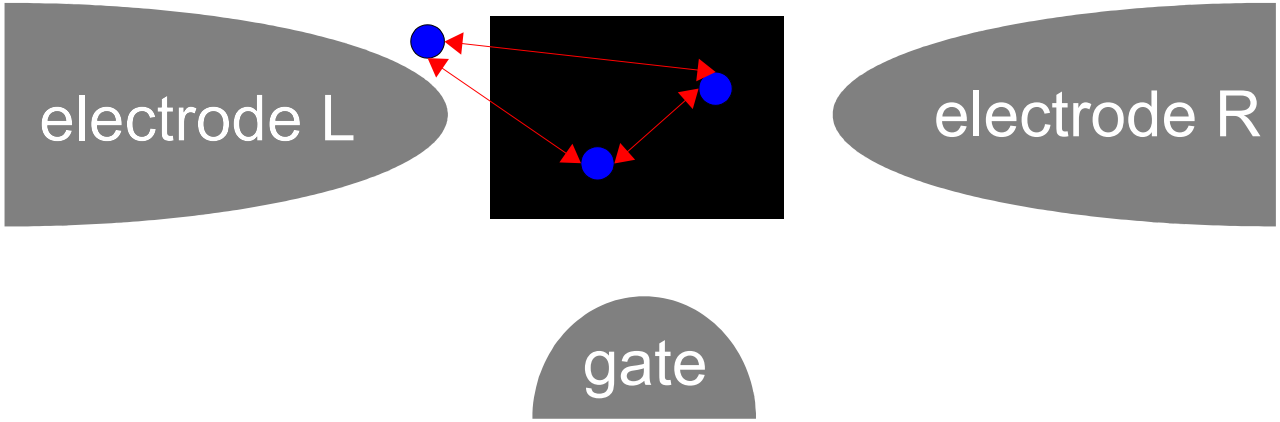


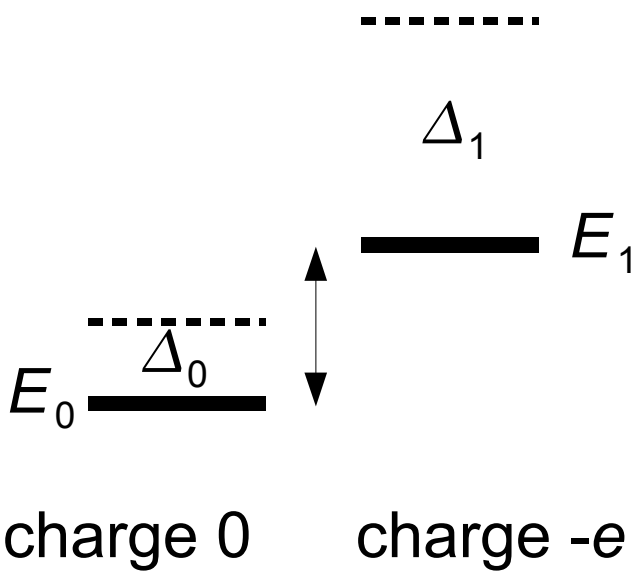


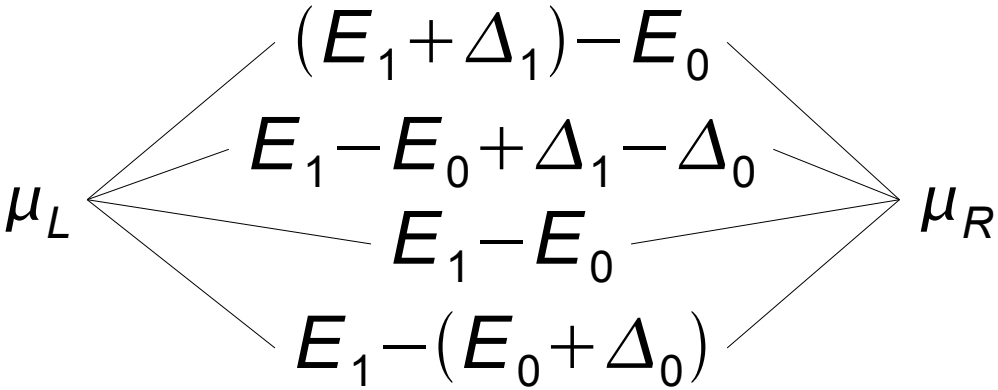
Theory - setup



Current spectroscopy

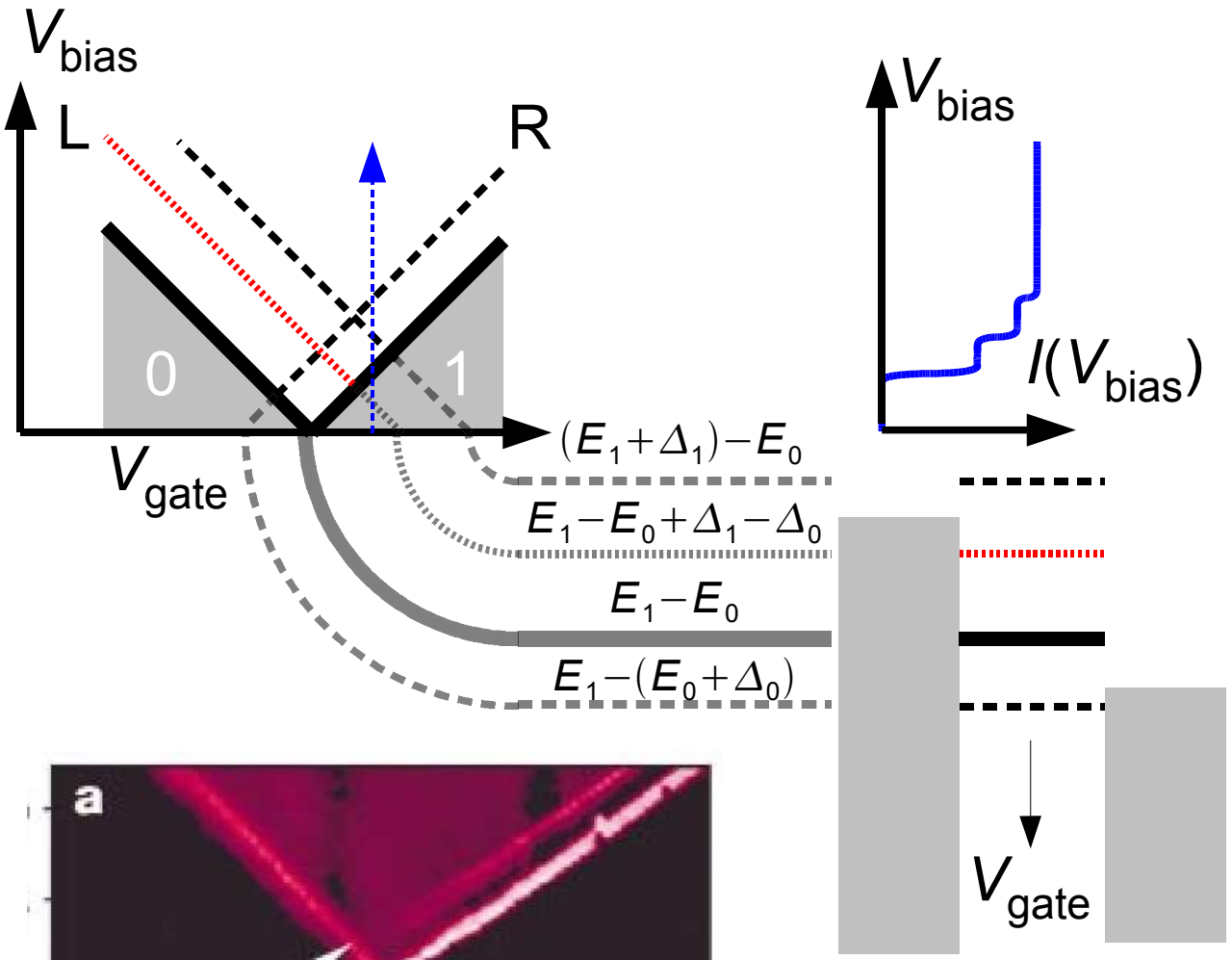




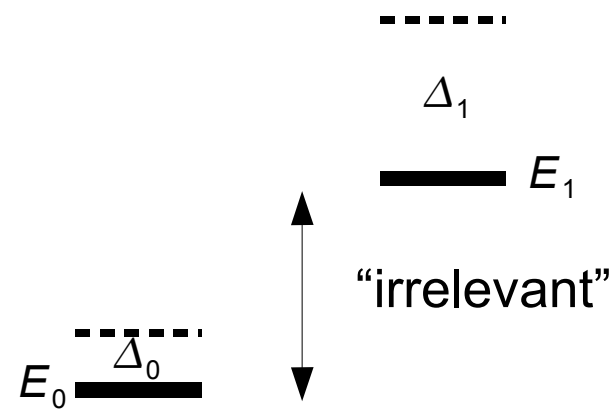


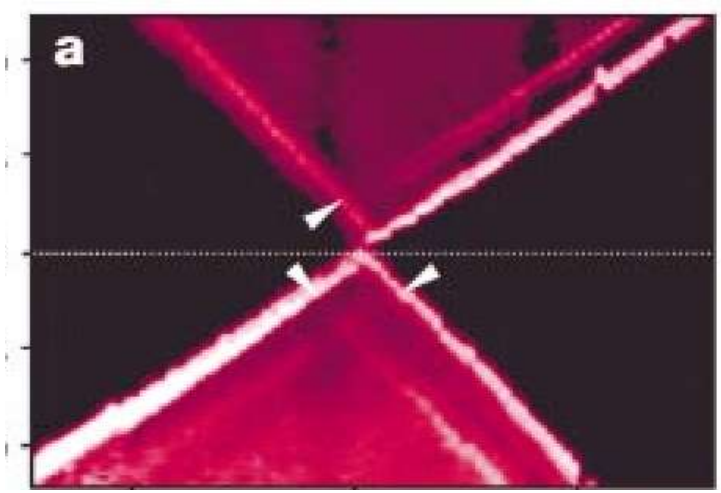
Current spectroscopy

2 Excitation spectra



2 Charge states





Energy conservation

Amplitudes ~ wavefunction

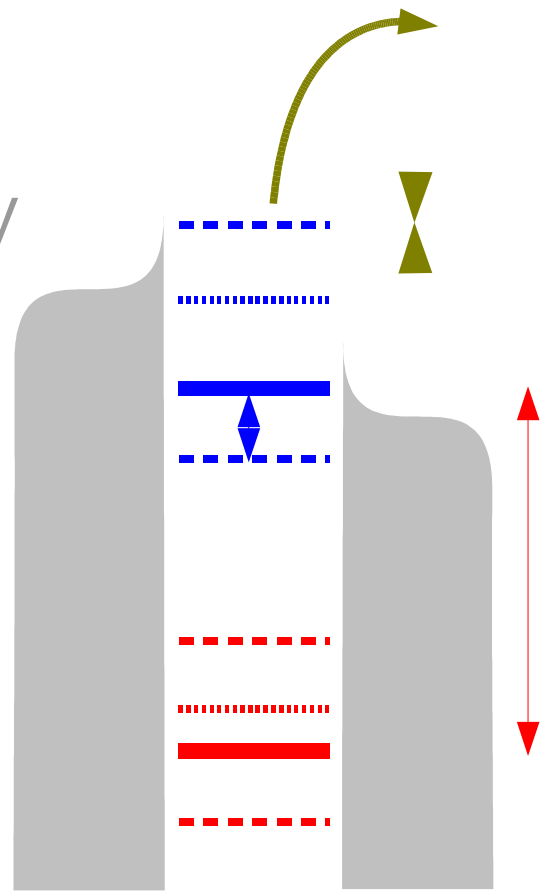
Non-equilibrium occupations

Energy scales

Higher order processes:
$\Gamma \sim T$

Tunnel coupling
$I \sim 0.5$ n A
$\Gamma \sim 0.1$ meV

Temperature
T ~ 50 mK - 5 K
~ 0.005 – 0.5 meV



Excitations
Vibrational ~ 1-100 meV
Magnetic ~ < 5 meV

Fingerprint
of single-molecule
transport

Addition energy
U ~ δ > 100 meV

Coulomb effect +
Energy quantization

Systematic approach

Model-based
Perturbative in tunnel coupling Γ
Theoretical starting point:
1st order: sequential tunneling
2nd order: co-tunneling
....
Non-perturbative: Kondo-tunneling

J. Lehmann

Basic physics
Large energy scales
Full non-equilibrium
Controlled

"***Ab-initio*** molecular non-equilibrium *transport theory*"
No DFT yet *in principle* for non-equilibrium
Mean-field .... strong interactions effects

Electronic
Magnetic
Vibrational

Sequential tunneling transport

Master equation approach

(*a,b* = molecular eigenstates)

Probabilities

$$\frac{dp_a}{dt} = 0 = \sum_b \{W_{a\leftarrow b} p_b - W_{b\leftarrow a} p_a\}$$

Current

$$I^L = \sum_{ab}^{N_a<N_b} W^L_{a\leftarrow b} p_b - \sum_{ab}^{N_a>N_b} W^L_{b\leftarrow a} p_a$$

Golden rule rates

$$W_{a\leftarrow b} = W^L_{a\leftarrow b} + W^R_{a\leftarrow b}$$

$$W^\alpha_{a\leftarrow b} = \Gamma^\alpha_{ab} f_\alpha(E_a - E_b) \qquad \alpha = L, R \quad \text{for} \quad N_a > N_b$$

$$W^\alpha_{a\leftarrow b} = \Gamma^\alpha_{ba}(1 - f_\alpha(E_b - E_a)) \qquad \text{for} \quad N_a < N_b$$

$$\Gamma^\alpha_{ab} = 2\pi \sum_{k\sigma} |t_{k\alpha}|^2 \delta(E - \epsilon_{k\alpha}) \times \sum_{i\sigma} \left|\left\langle a \middle| d^{dag}_{i\sigma} \middle| b \right\rangle\right|^2$$

Electron tunneling rate

Spin-blockade of electron tunneling:
rate = 0 unless
|S-S'|=1/2 and |M-M'| =1/2

- Spin selection rules
- Orbital symmetry
- Nuclear wavefunction overlap (Franck-Condon factors)

Sequential tunneling transport

A. Thielmann, M. H. Hettler, J. König, G. Schön
PRB **68**, 115105 (2003)

Schottky term ~ V
Thermal noise (fluctuation-dissipation)

Conditional-probabilities

$$0 = \mathrm{W}\,\mathrm{P}$$

Zero-frequency current noise

$$\mathrm{S}(\omega=0) = \mathrm{e}^{\mathrm{T}}(\mathrm{W}^{\mathrm{II}}\mathrm{p} + \mathrm{W}\,\mathrm{P}\,\mathrm{W}\,\mathrm{p})$$

Golden rule rates

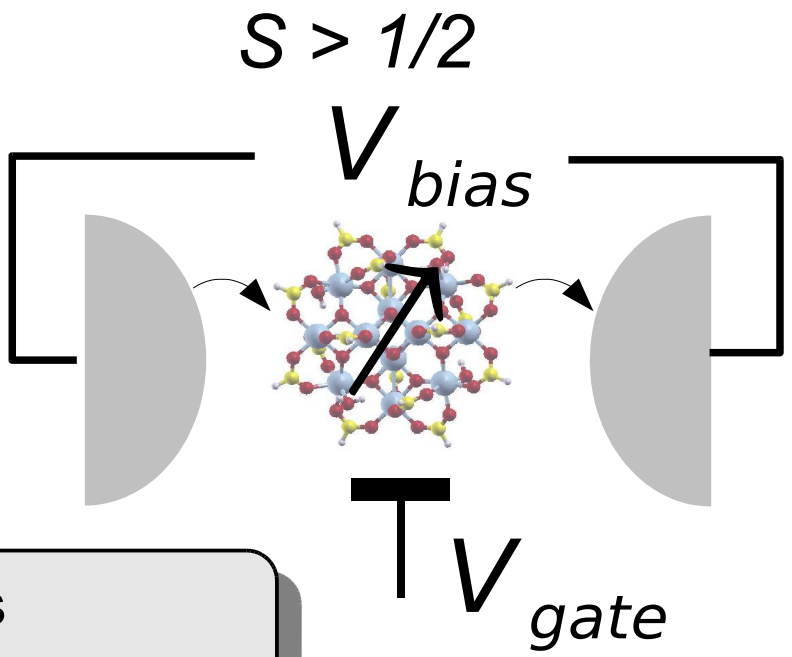
Slow processes:

- Suppressed current
- Enhanced noise

Tunneling transport through single molecule magnets (SMM)

Molecular Magnetism:
Access magnetic excitations in *multiple charge states*
Create *non-equilibrium* magnetic states

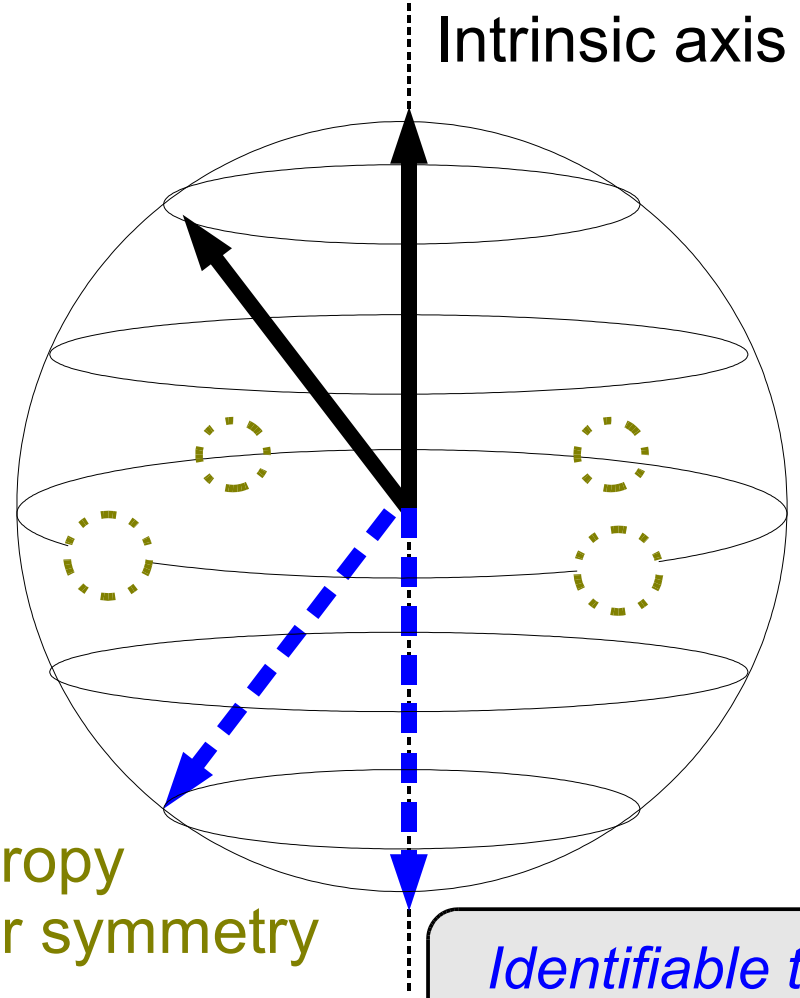
e.g.
Mn12,
S=10



- Hidden resonances
- “Fake” resonances
+ Negative dI/dV
+ Current & noise oscillations
+ Current suppression

Single Molecular Magnet (SMM)

Large S



Easy-axis anisotropy
Continuous axial symmetry

S_z

Molecular:

No preferred *direction*

Easy-plane anisotropy
Discrete molecular symmetry

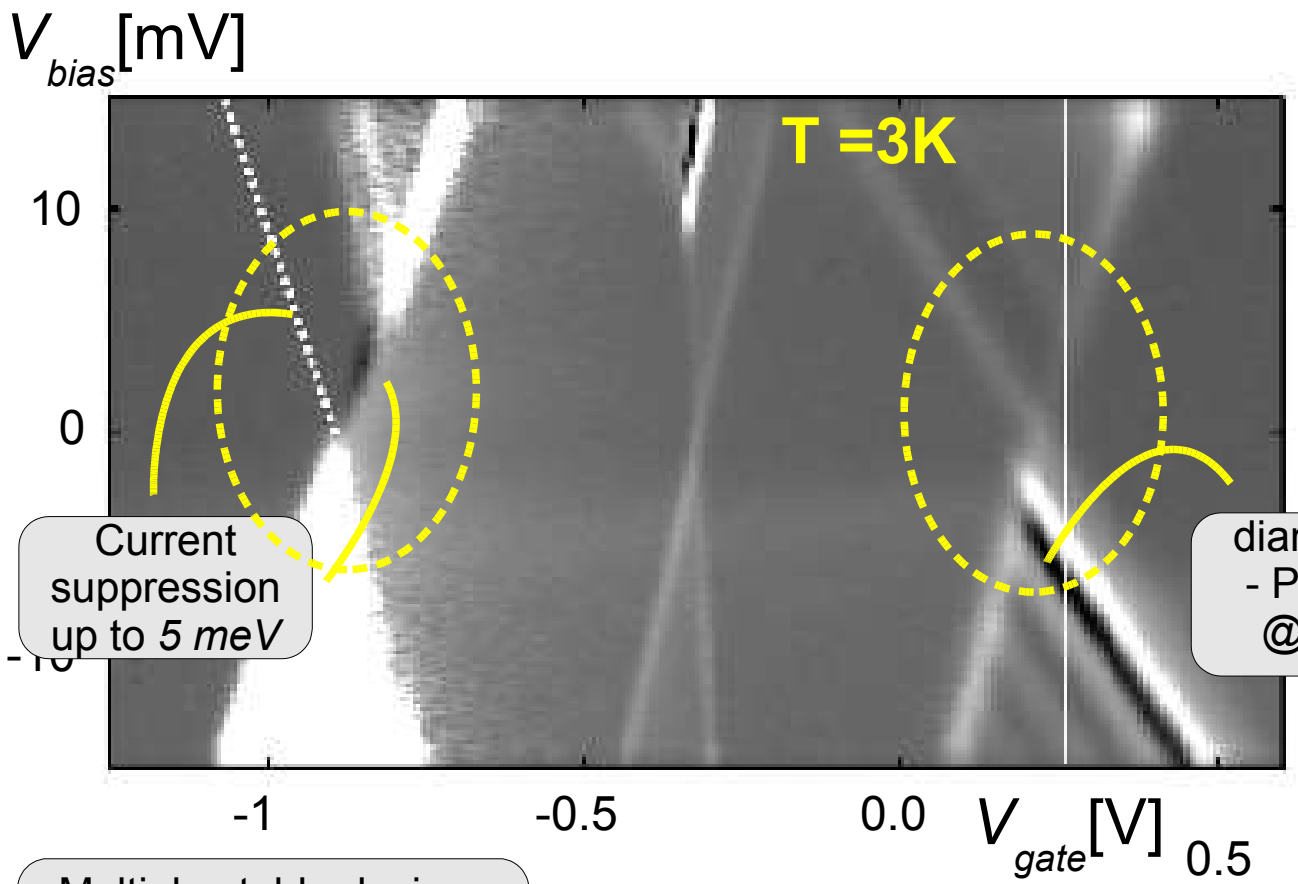
Quantum Tunneling of Magnetic moment (QTM)

Identifiable transport effects of QTM?
- *weak perturbation*
- *forbidden for S=n+ ½*

Electronic control of magnetic states?

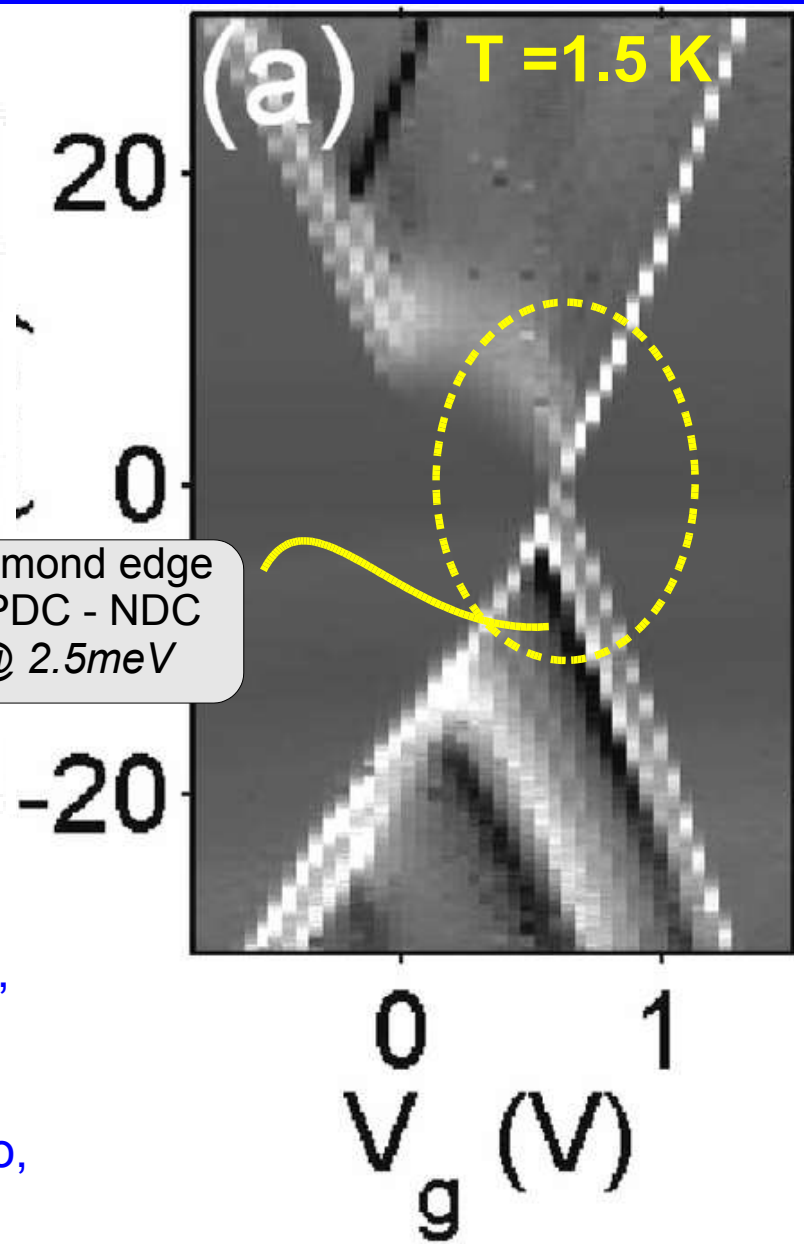
Experimental motivation

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



Current suppression up to *5 meV*

diamond edge - PDC - NDC @ *2.5meV*



Multiple stable devices

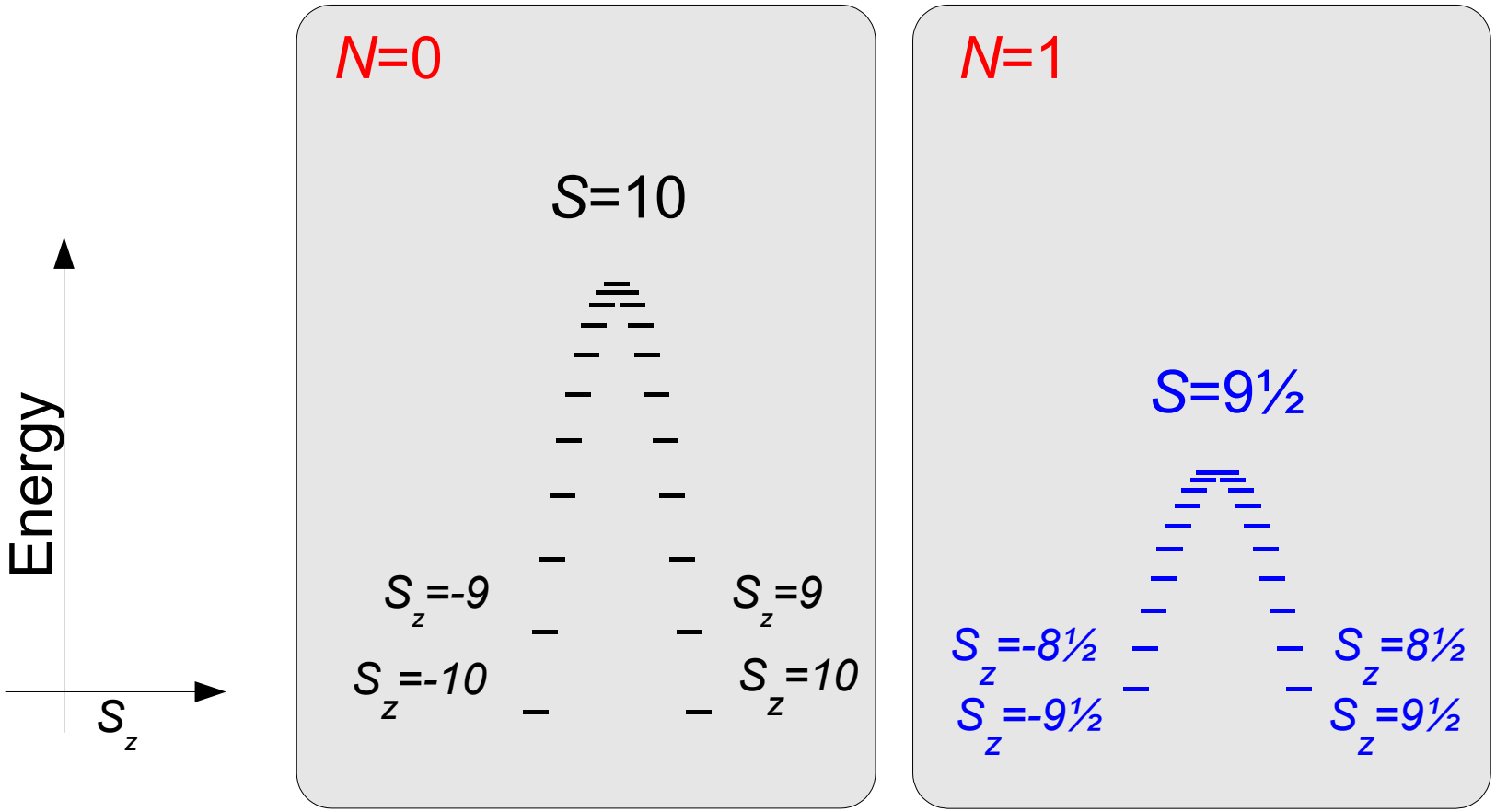
Reproducible features
16 meV
~ 5 meV

Two measurment *setups*

H. Heersche, Z. de Groot, J. Folk, H. van der Zant
Kavli Institute of Nano Science, Delft

L. Zobbi, D. Barrecca, E. Tondello, A. Cornia
University of Modena, Italy

Magnetic excitations: Magnetic Anisotropy Barrier (MAB)



Tunneling ⇒ spin selection rule for S and S_z

c.f. Park, Pederson, PRB (2004)

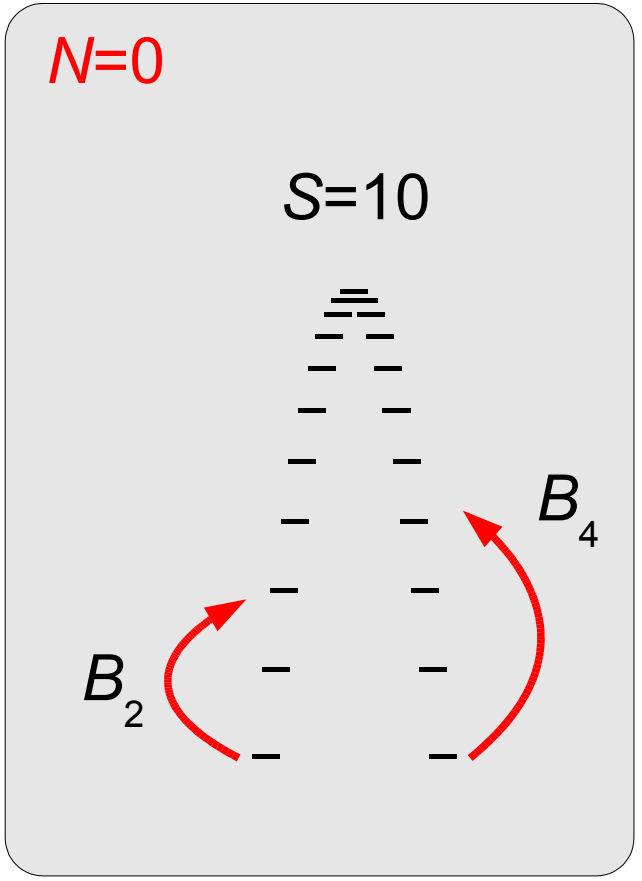
$$H_{MAB} = -D_N S_z^2$$

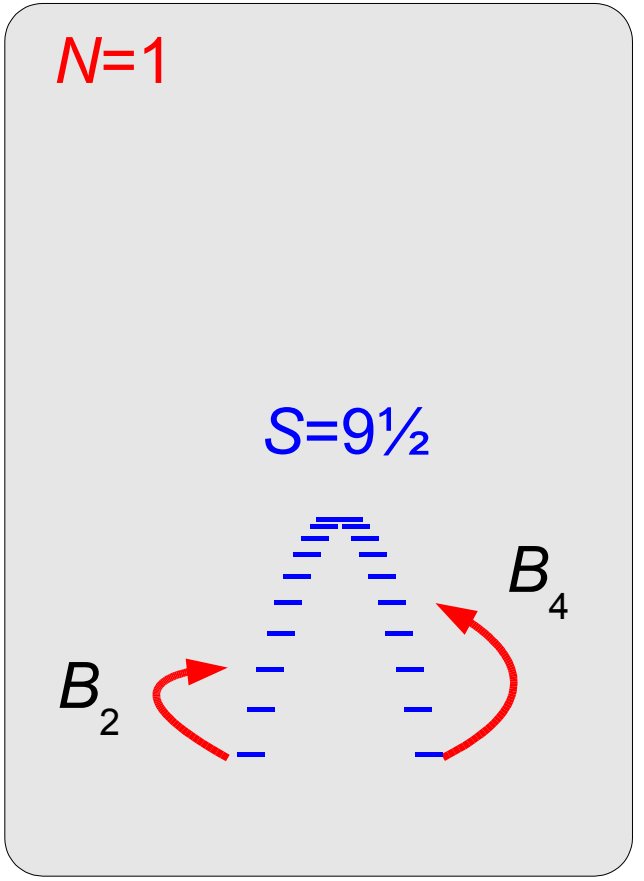
$$\cancel{S_z^4}$$

Charge-induced "magnetic distortion"

Sessoli 93,Takeda 97,Aubin 99,Soler 00 & 01
Kuroda-Sowa 01, Coronado 04

Magnetic excitations: (QTM)
Quantum Tunneling of Magnetic moment





$$H_{MAB} = -D_N S_z^2$$

$$H_{QTM} = \frac{1}{2} B_2 (S_-^2 + S_+^2) + \frac{1}{2} B_4 (S_-^4 + S_+^4)$$

QTM effect on non-linear transport?

Numbers: (~ Mn12)

S ~10

D ~ 5.10^{-2} meV

B_2 ~ 1.10^{-4} meV

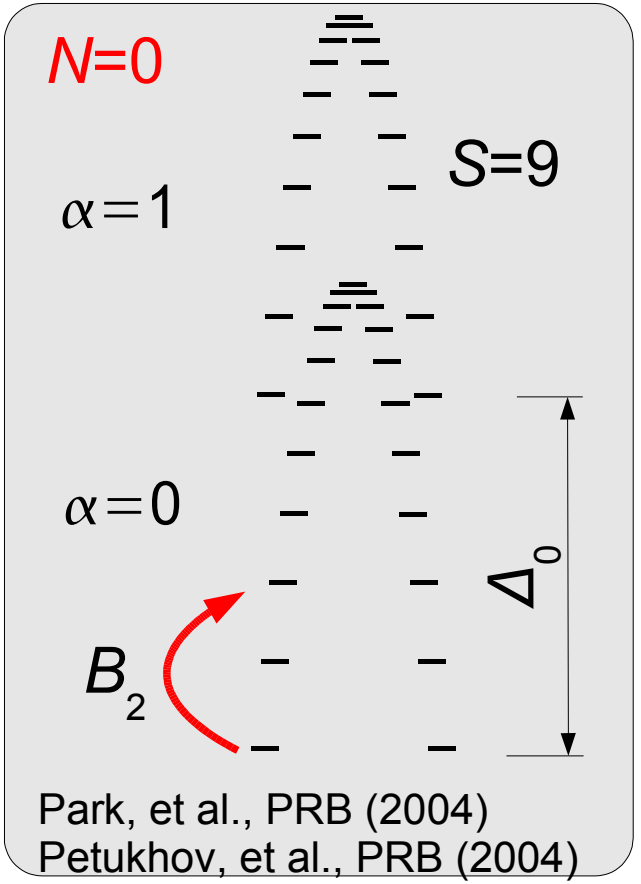
Small energy scale
but
violates selection rule!

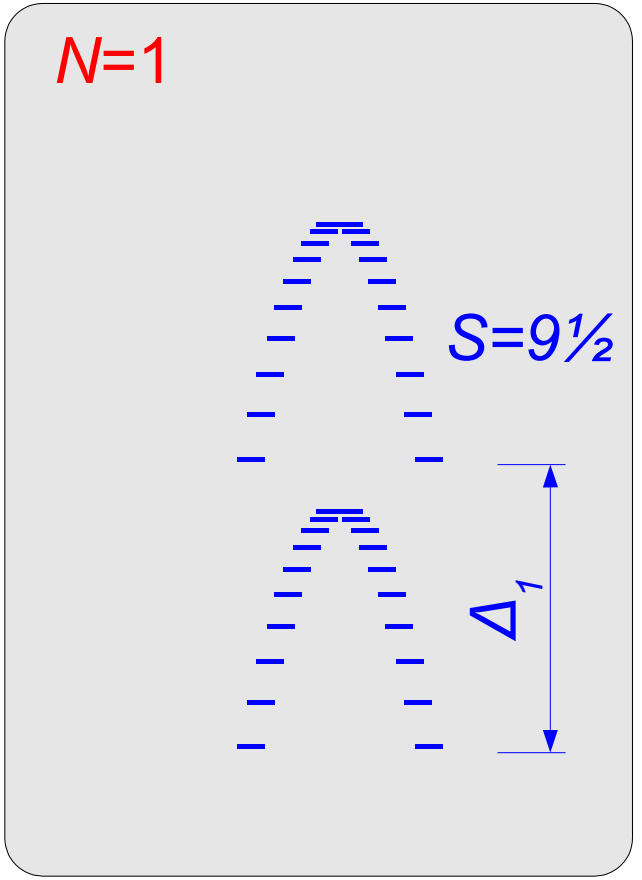
Lifts a strong restriction on non-equilibrium occupations magnetic states

Magnetic anisotropy barrier ~ $D\ S^2$ ~ 5 meV

Electronic Excitations ~ 5 meV

Magnetic & *electronic* excitations

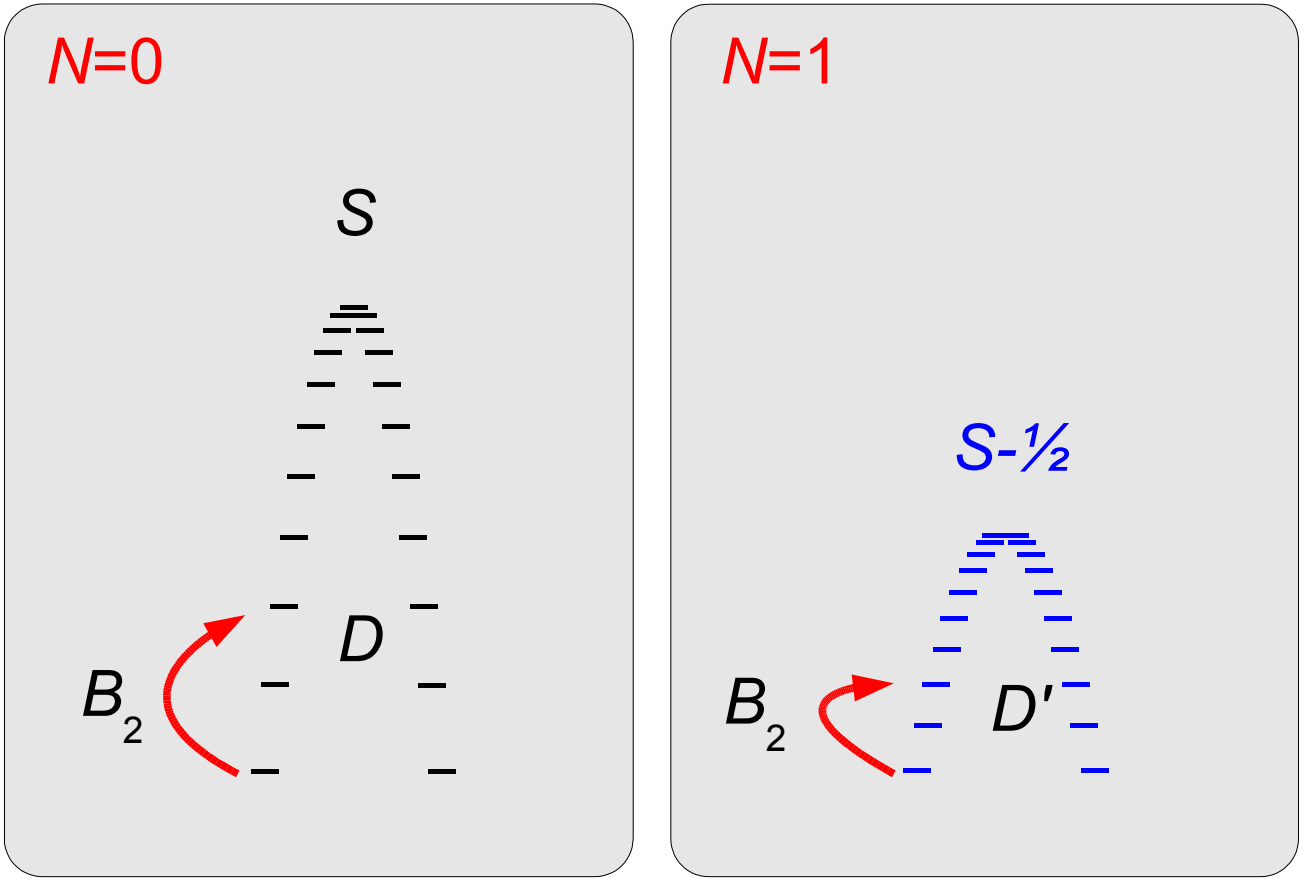




$$H_{MAB} = -D_{N\alpha} S_z^2 + \Delta_{N\alpha} \delta_{\alpha 1}$$

$$H_{QTM} = \frac{1}{2} B_2 (S_-^2 + S_+^2)$$

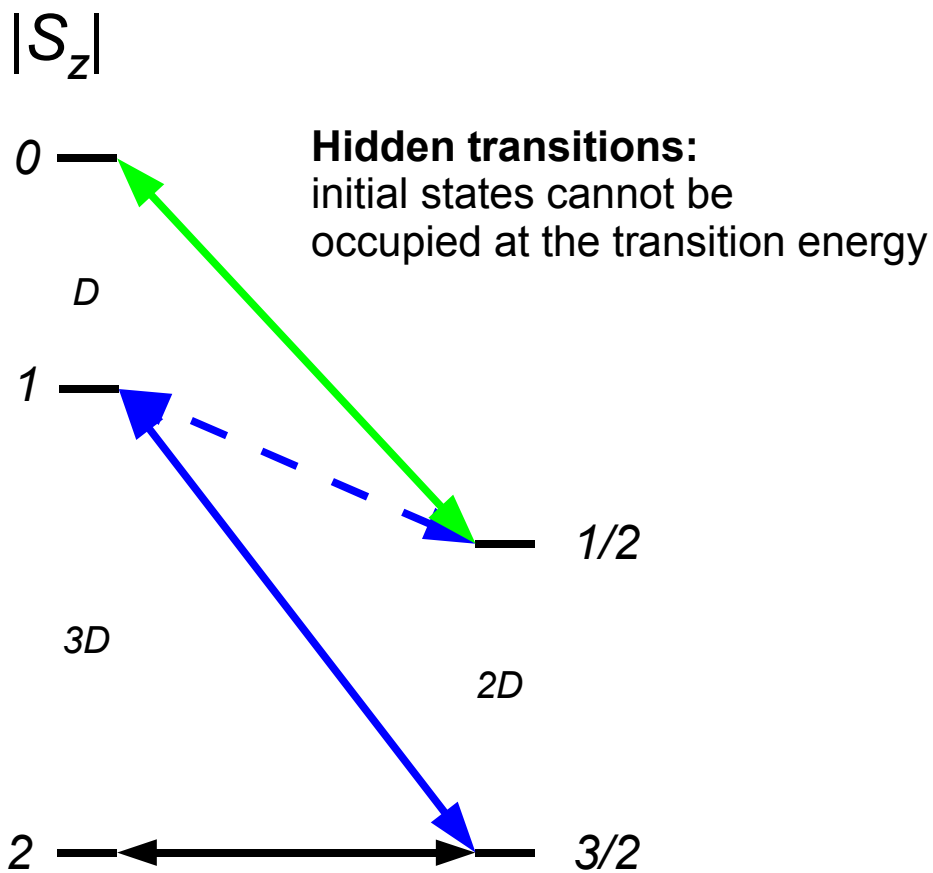
Low-symmetry QTM $B_2 >> B_4$



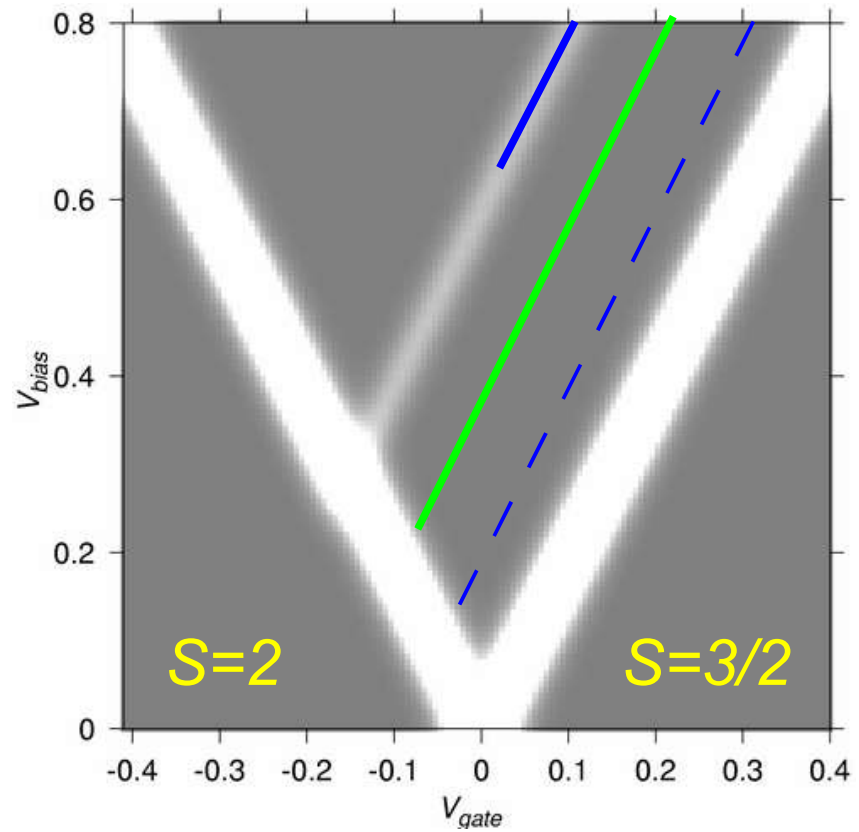
or $S+½$

Hidden lines: D=D', B_2=0

Eigenstates: S, S_z *approximately* good quantum numbers



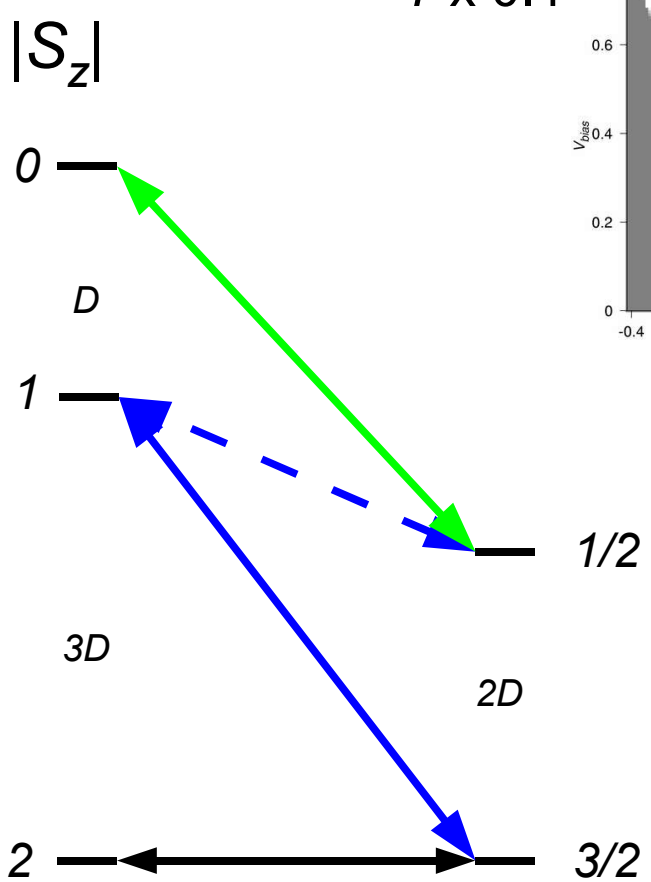
Hidden transitions:
initial states cannot be occupied at the transition energy

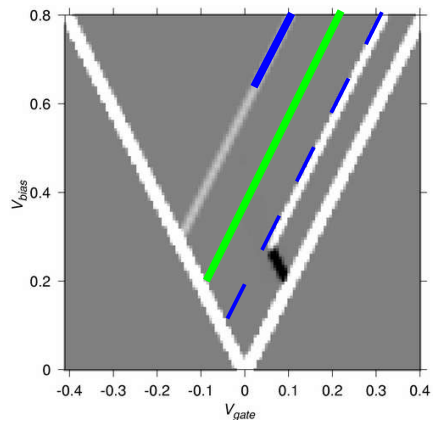


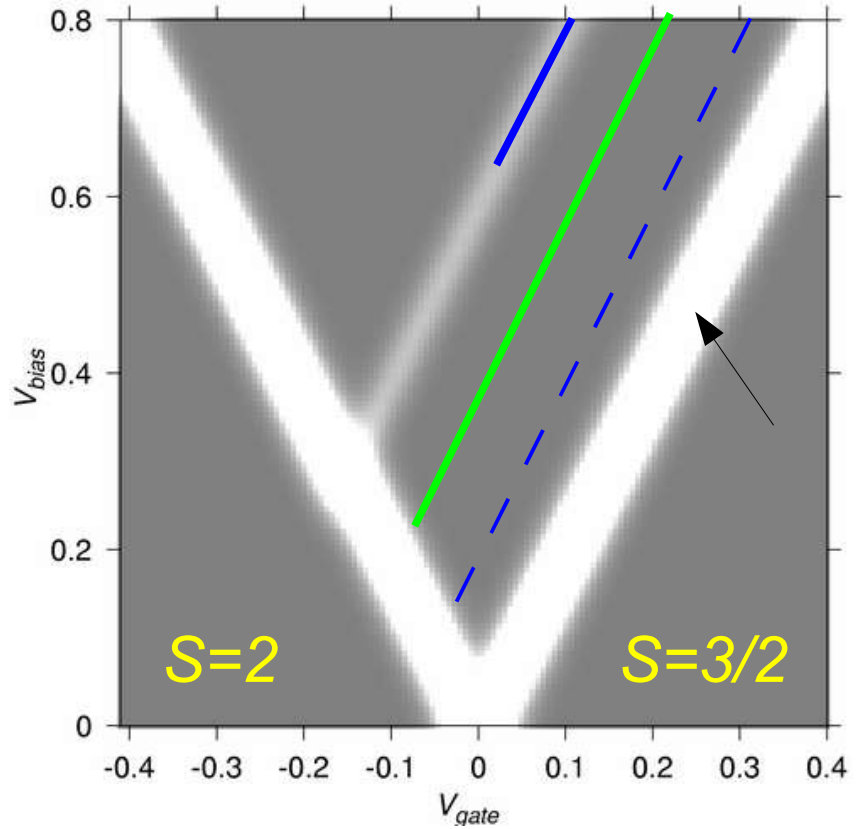
Inverted parabola
+ spin selection rules
Only 2 current steps
Others hidden

General result for
D=D' and *any* spin S

NDC and "fake" lines: $D = D'$, $B_2 > 0$



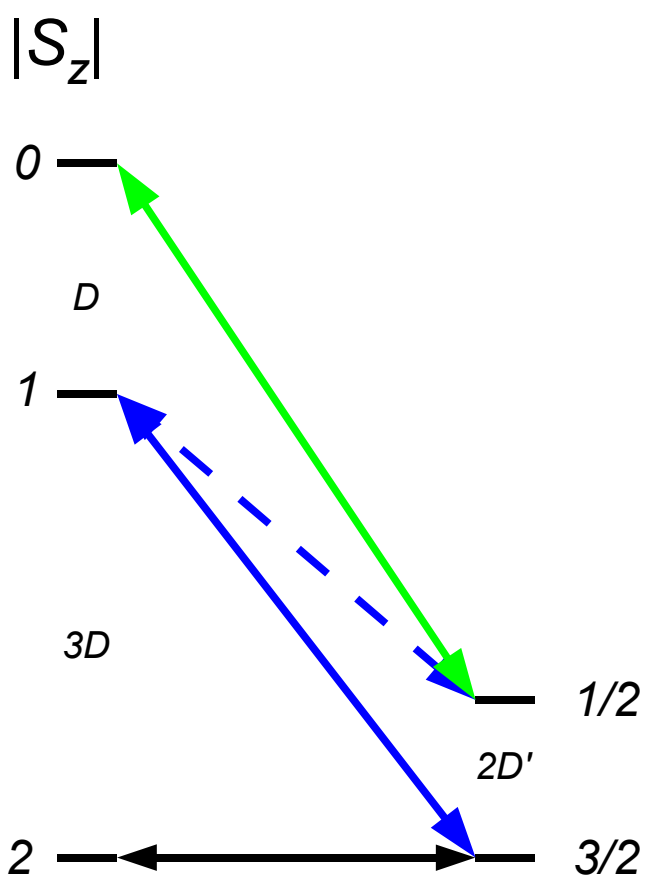


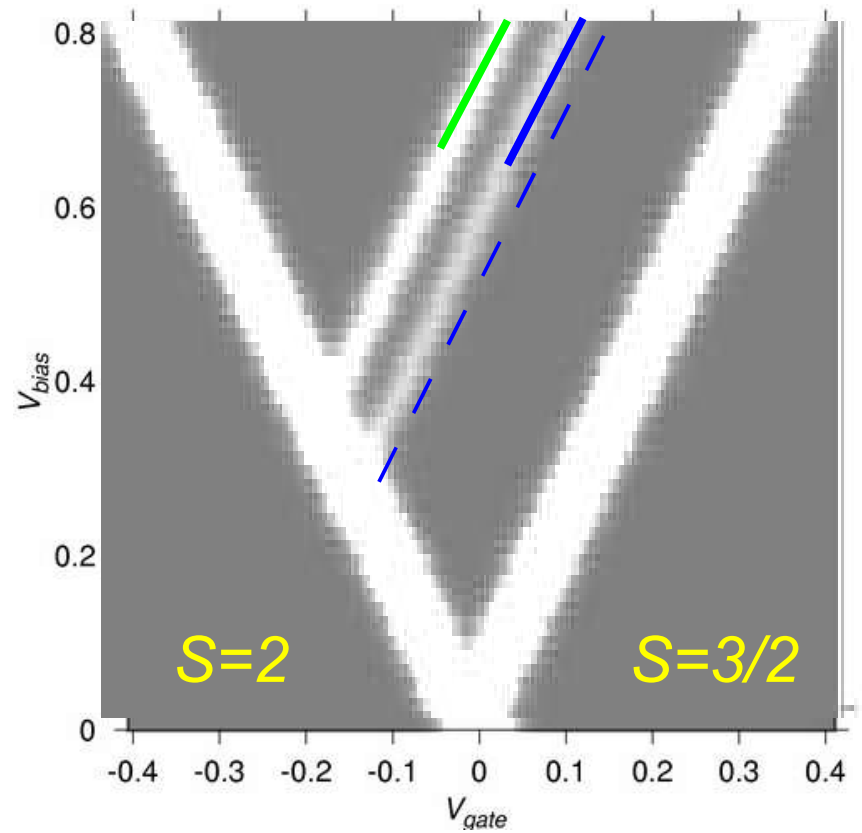


QTM:
"fake" resonance lines
+ negative resonance

Hidden lines: $D > D'$, $B_2=0$

Charge-induced "magnetic distortion"

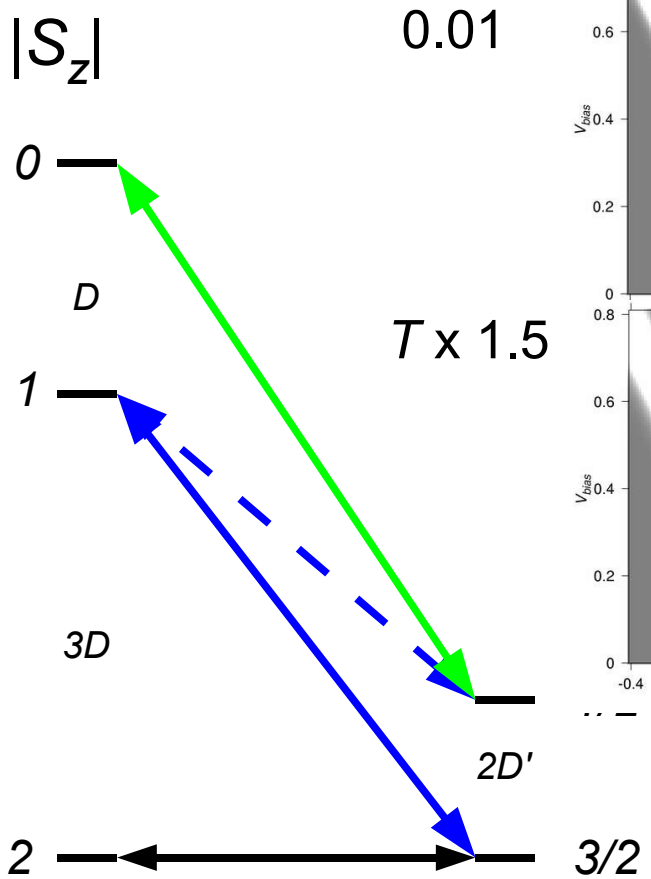


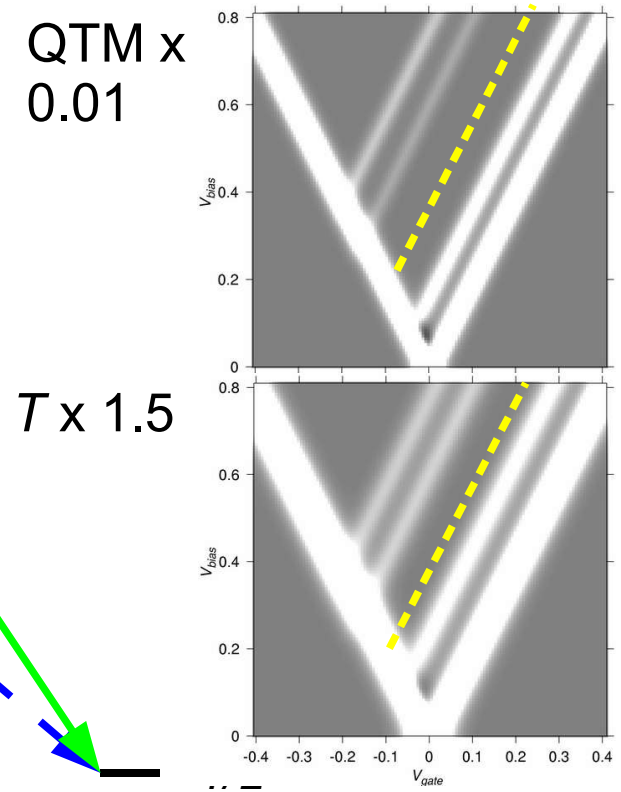


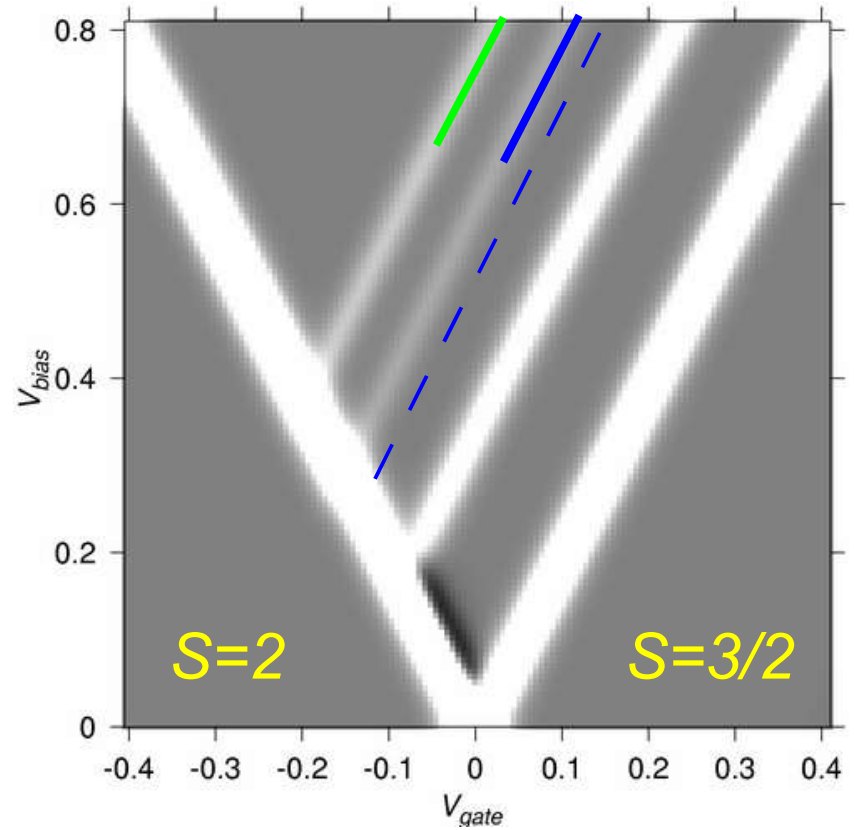
Anisotropy barrier
different in 2 charge states
⇒ more transition lines appear

NDC and "fake" lines: $D > D'$, $B_2 > 0$

Charge-induced "magnetic distortion"



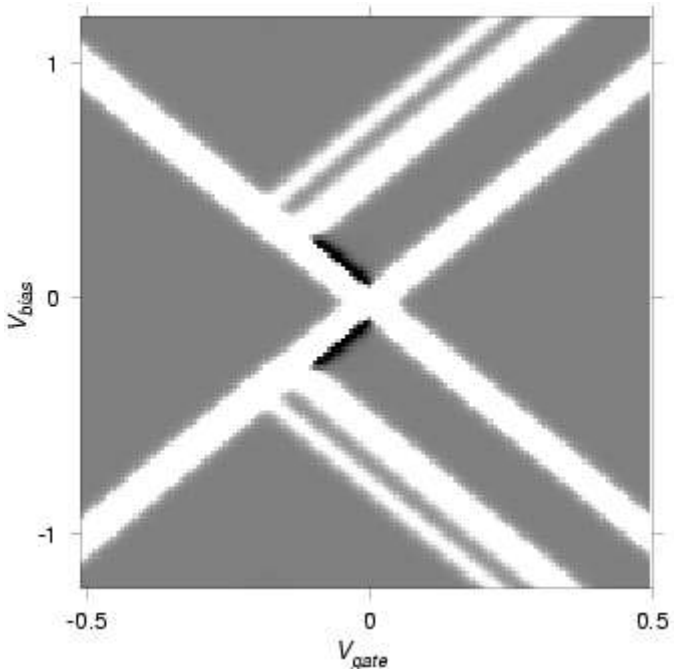




QTM:
"fake" resonance lines
+ negative resonance

NDC and "fake" lines: $D > D'$, $B_2 \neq 0$

D fixed
B_2 varied

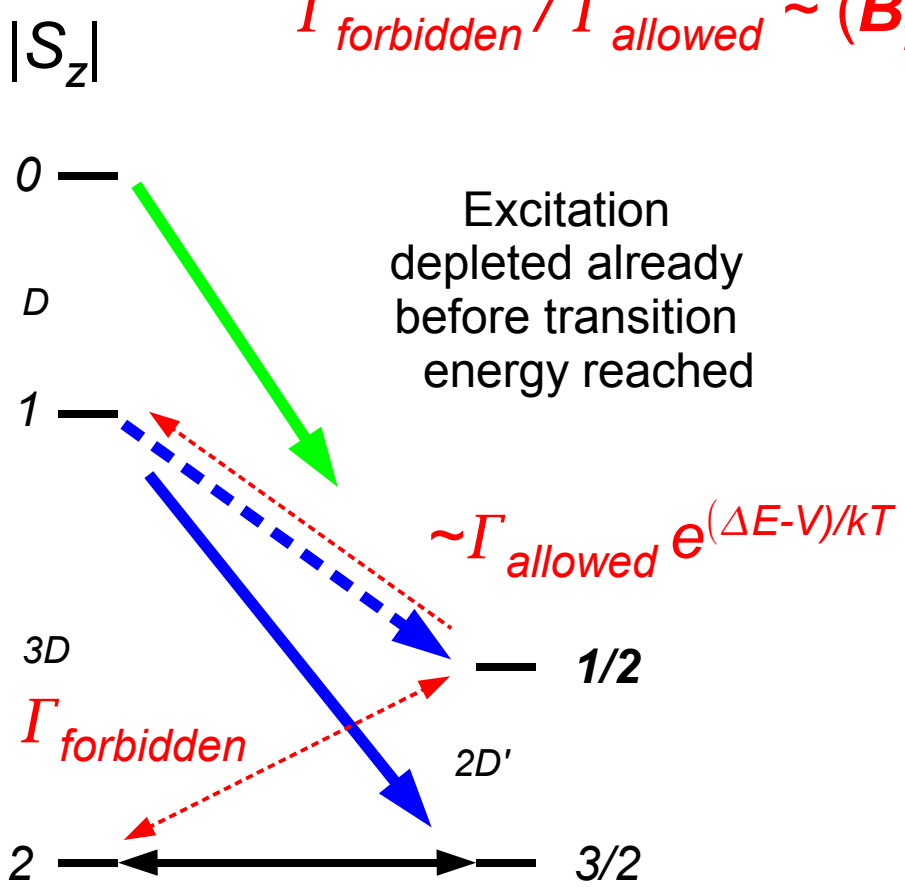


"Fake" resonances shift with QTM
....even though
addition spectrum is *not altered*!

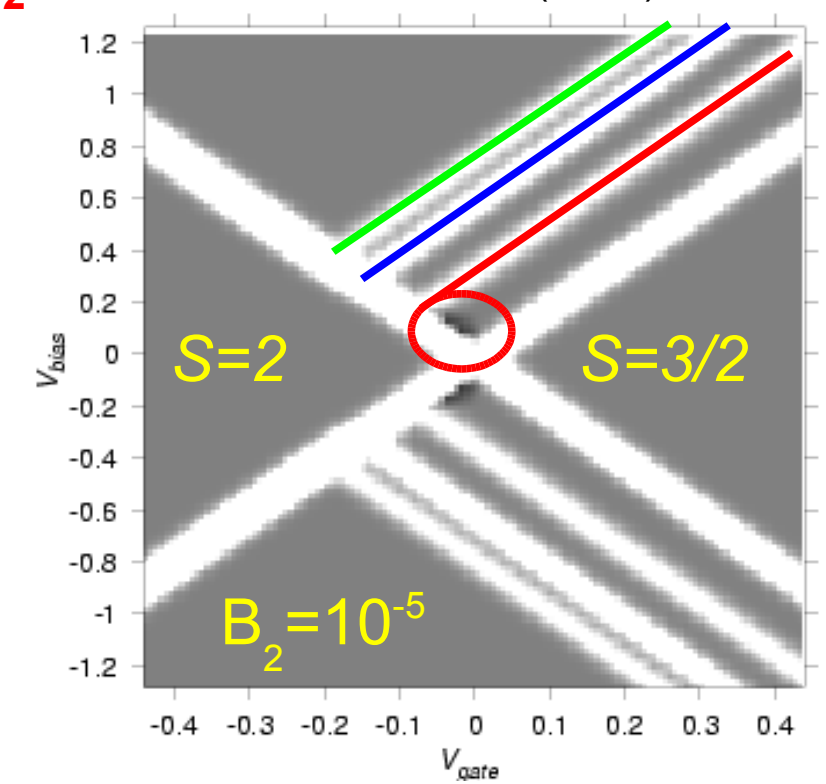
Negative Differential Conductance (NDC):
associated with "fake" lines
(black resonance)

QTM affects populations

$\Gamma_{forbidden} / \Gamma_{allowed} \sim (B_2 / D)^2$



Bonet, et al., PRB (2002)



Weak violation of spin selection rule

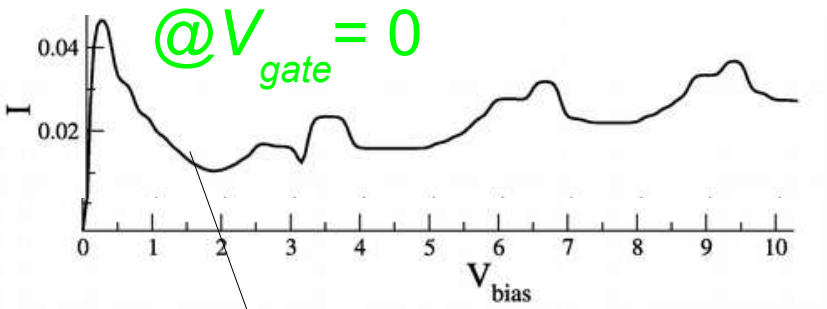
$\Rightarrow$

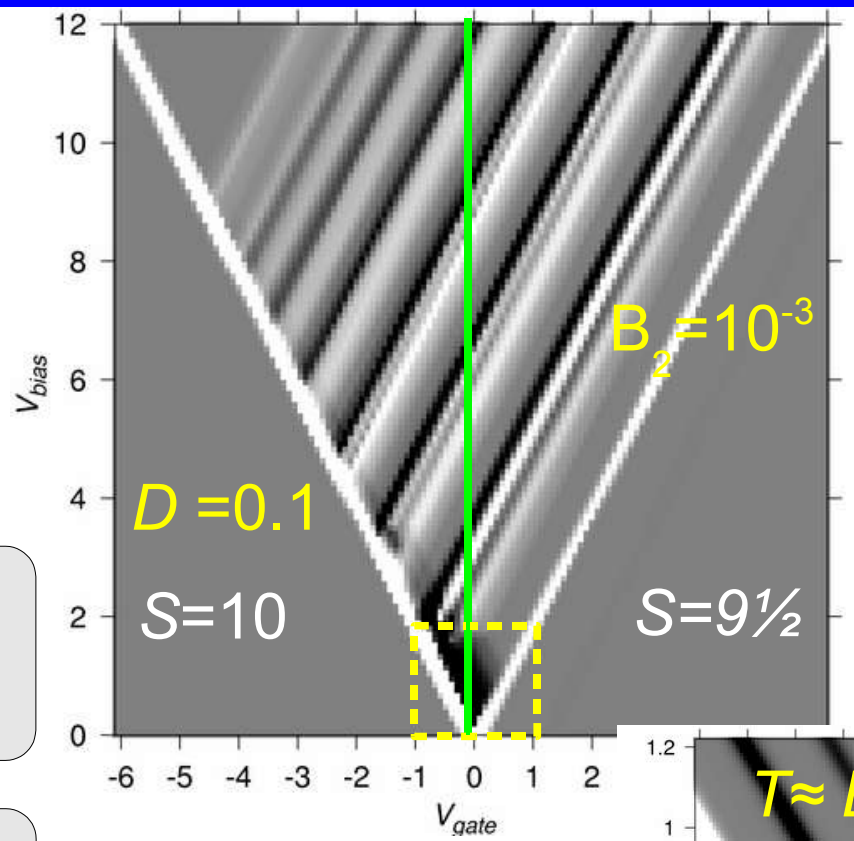
Shift ~ $T \ln B_2/D$

Line *moves* downwards:

- decreasing QTM
- increasing temperature

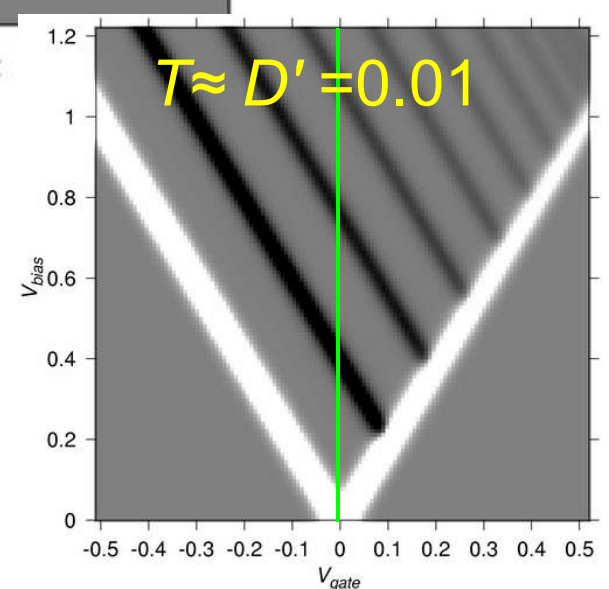
QTM-induced current oscillations





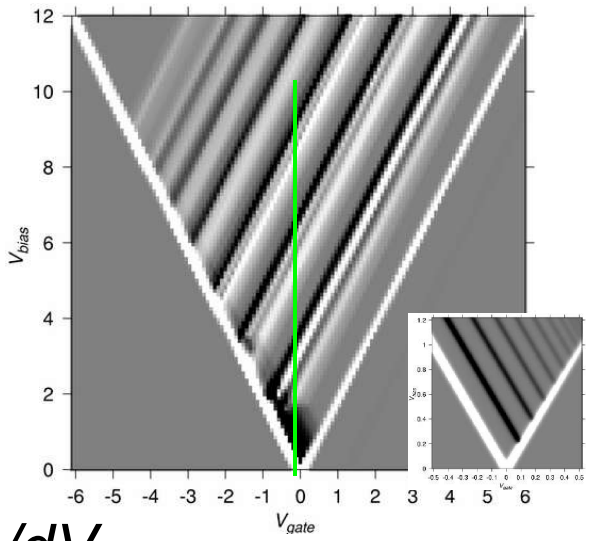
(1) N*egative* conductance resonances: map out **anisotropy barriers**

(2) Positive resonances shift with *T*: e***xtract*** B_2

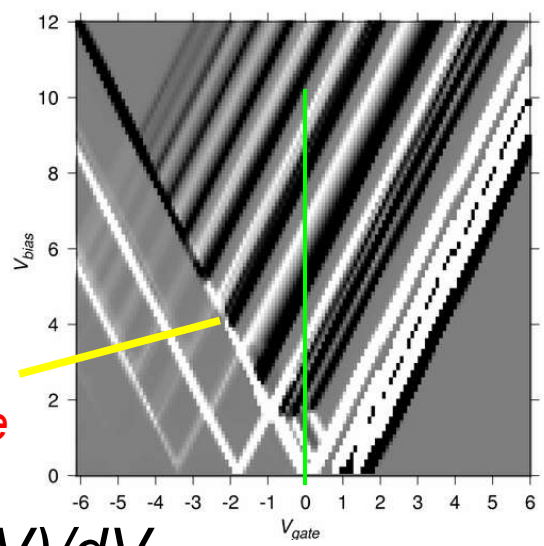


...even though QTM-splittings cannot be resolved!

Noise identifies "fake" resonances

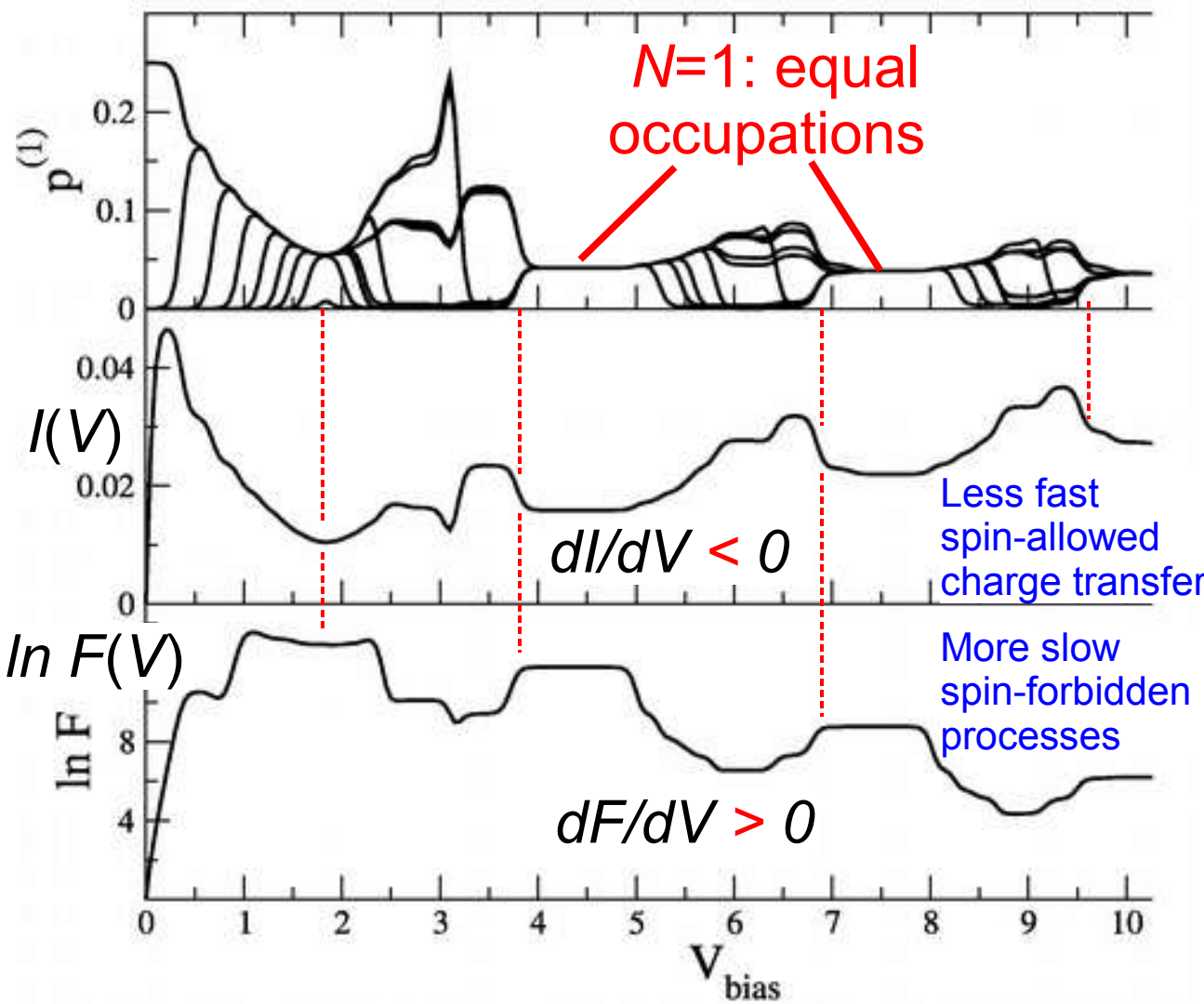


d*I(V)/dV*



"Fake" lines terminate

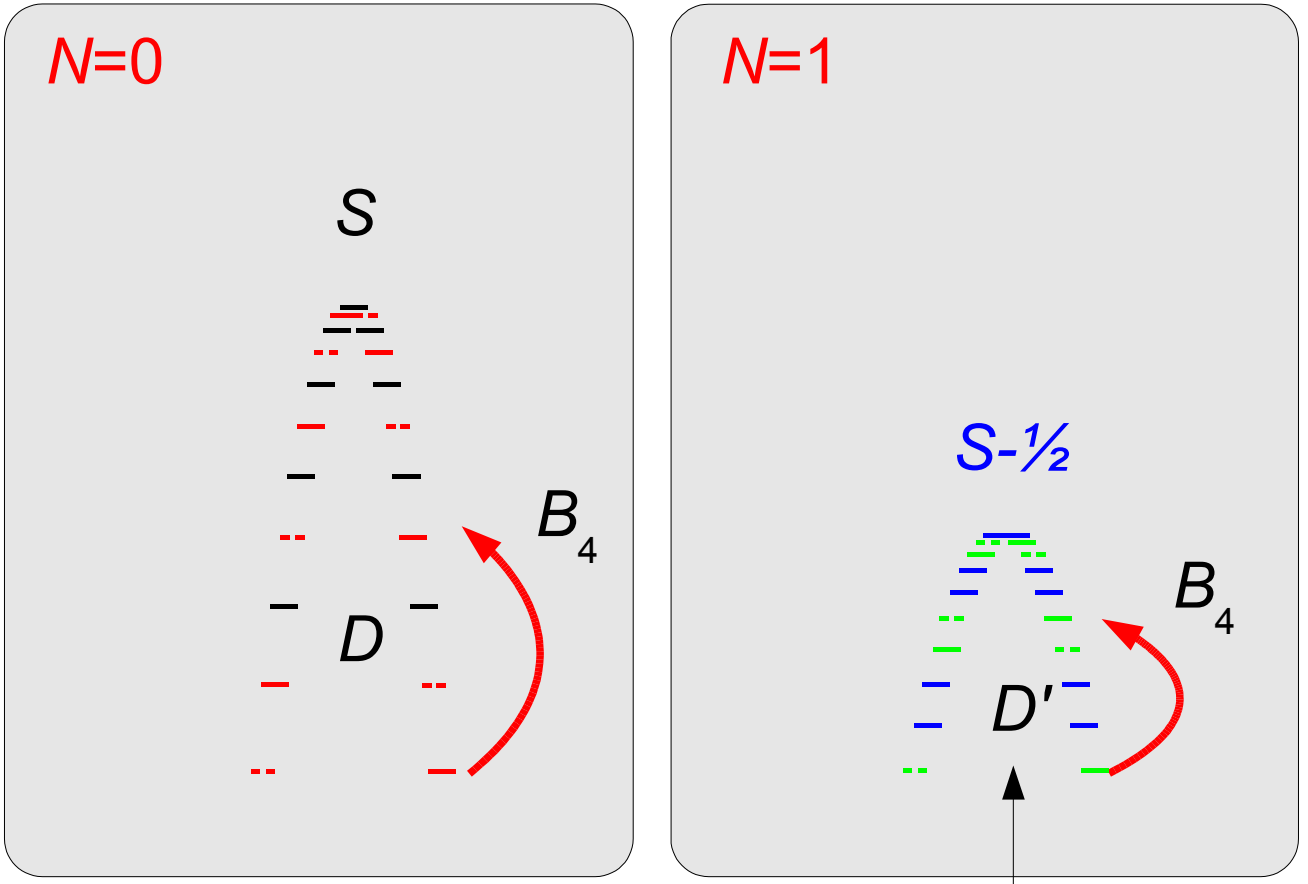
d ln*F(V)/dV*



Noise enhancement ~
Negative differential conductance

High-symmetry QTM $B_4 >> B_2$

2 groups of states with different magnetic symmetry

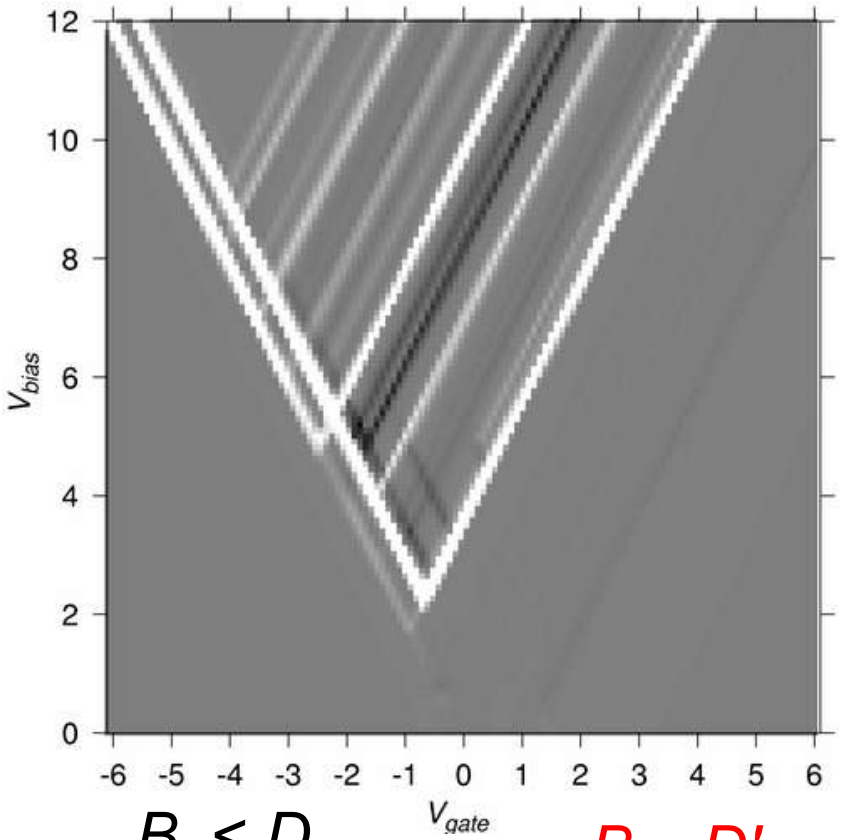


$B_4 < D$

$B_4 \sim D'$

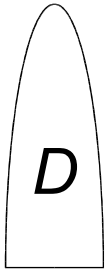
Level crossing: ground-state changes character

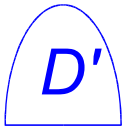
Current blockade: suppressed overlap

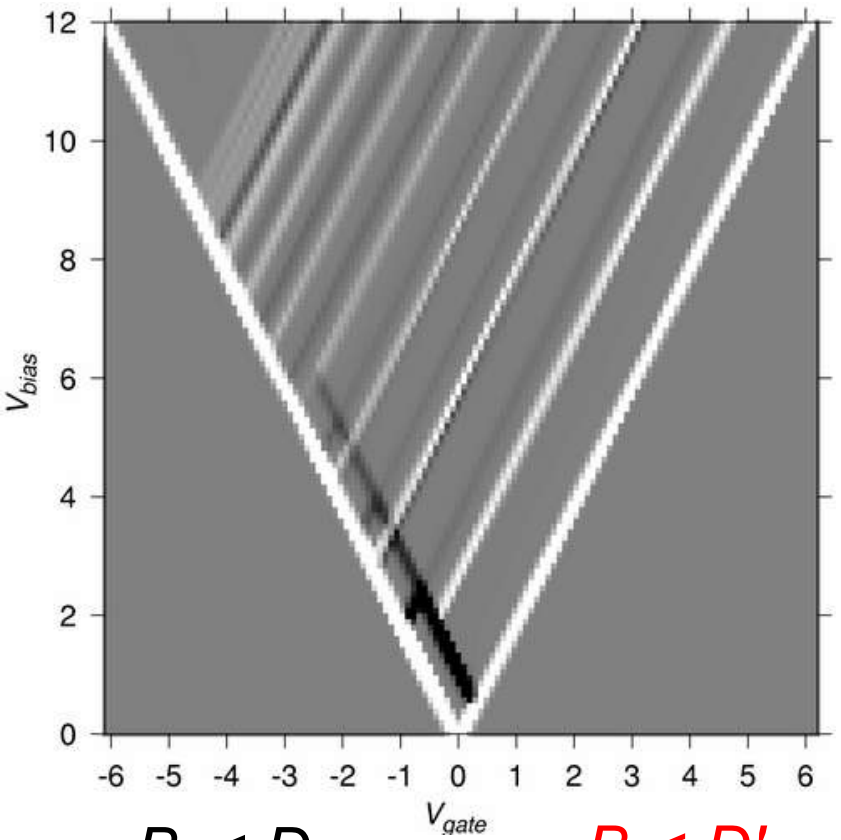


$B_4 < D$

$B_4 \sim D'$

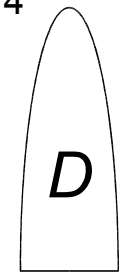


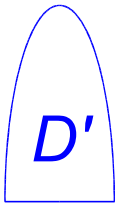




$B_4 < D$

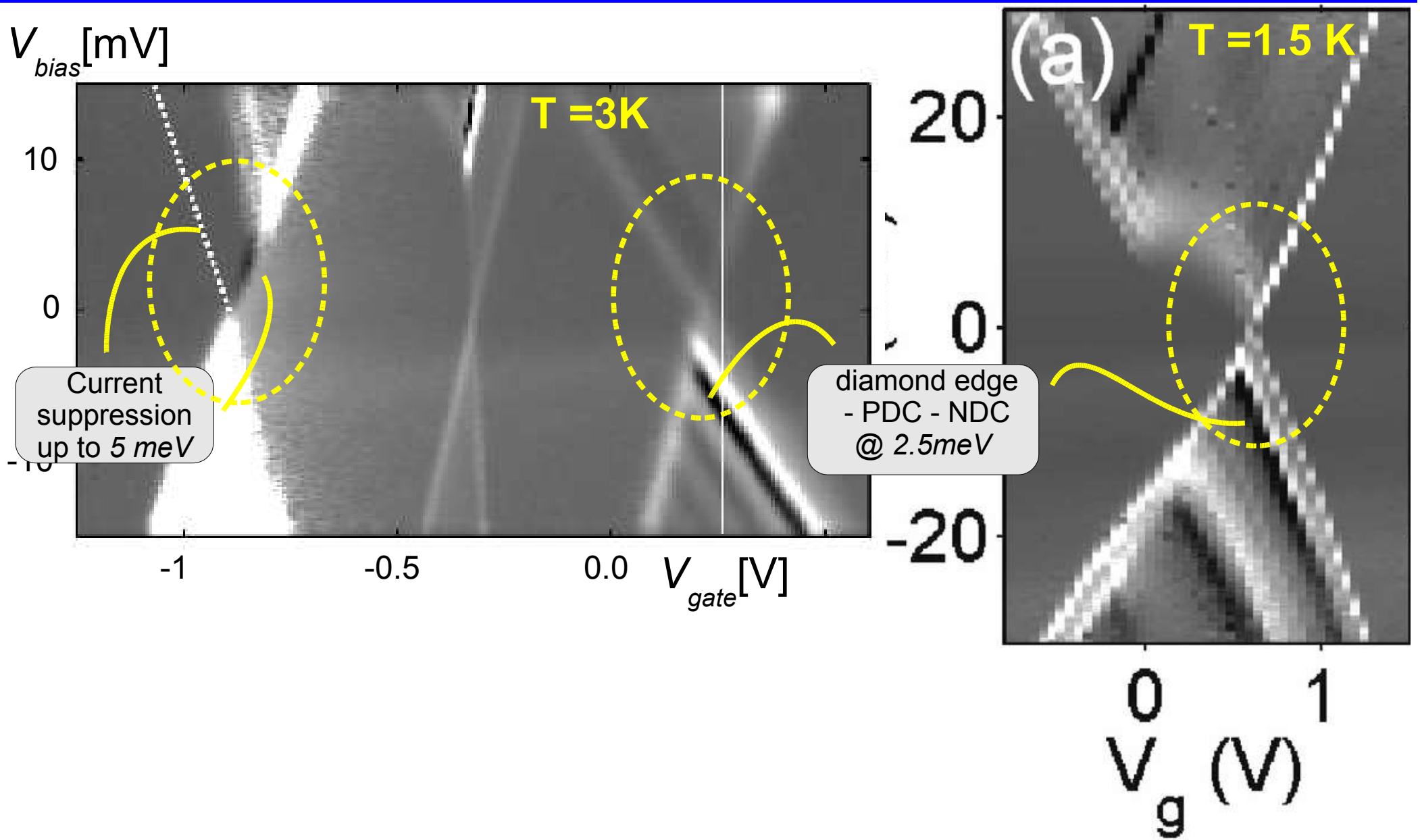
$B_4 < D'$





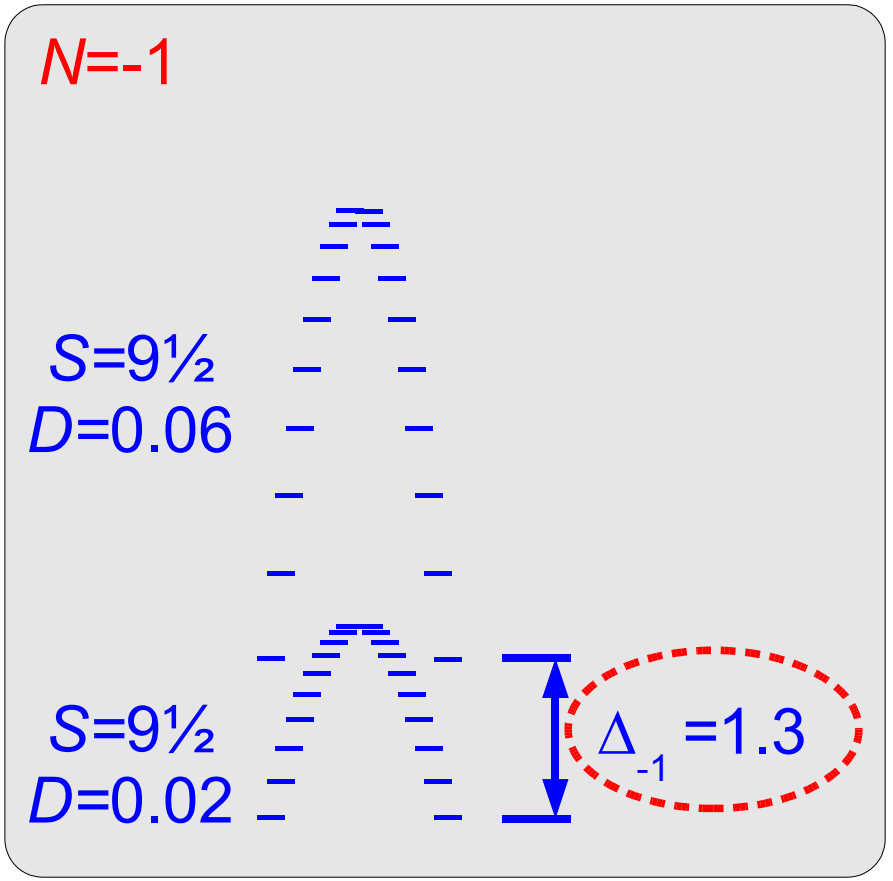
Magnetic & *electronic* excitations

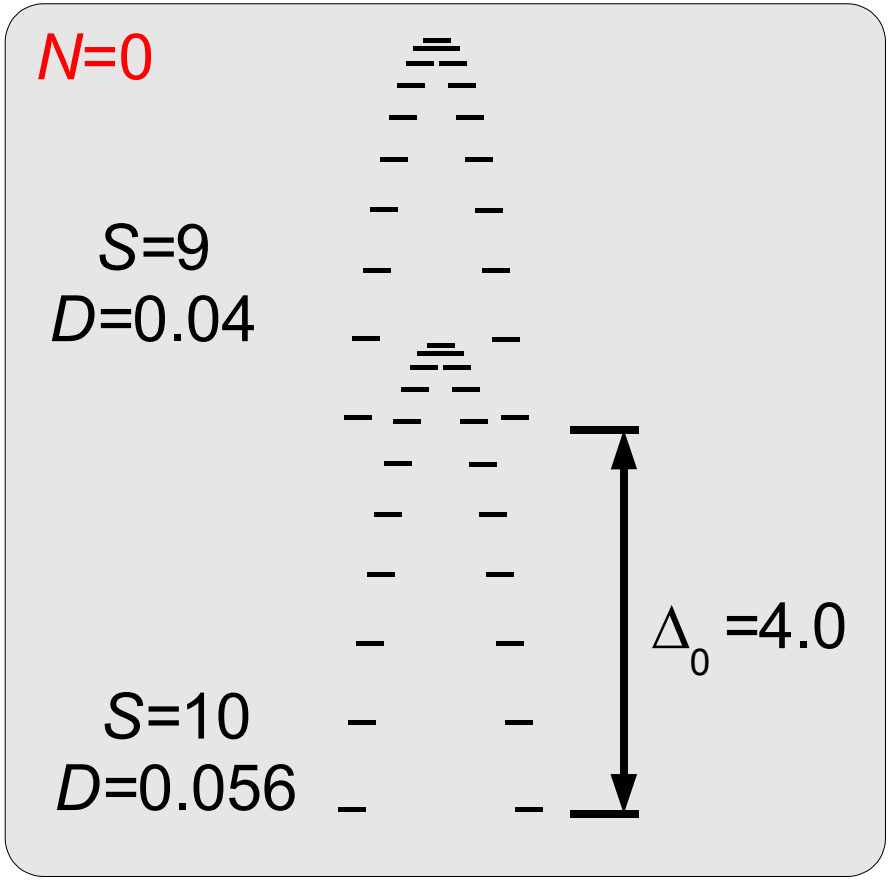
$Mn_{12}O_{12}(O_2C\text{-}C_6H_4\text{-}SAc)_{16}(H_2O)_4$



2 spin-multiplets / charge state

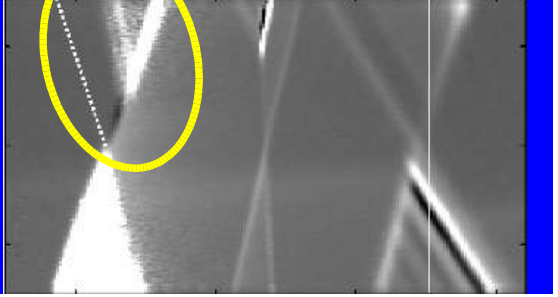
[Unit: meV]



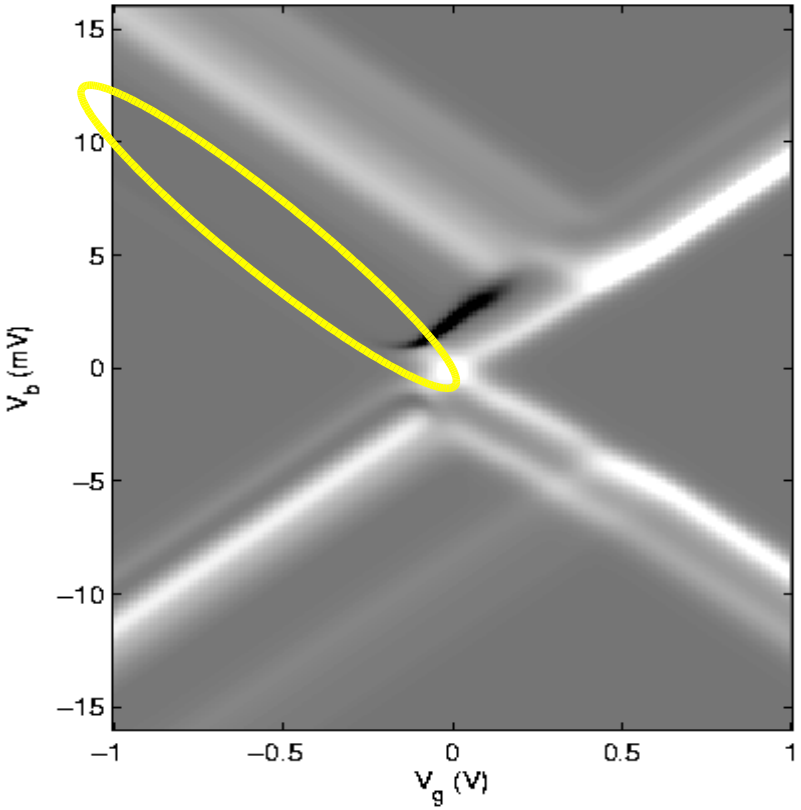


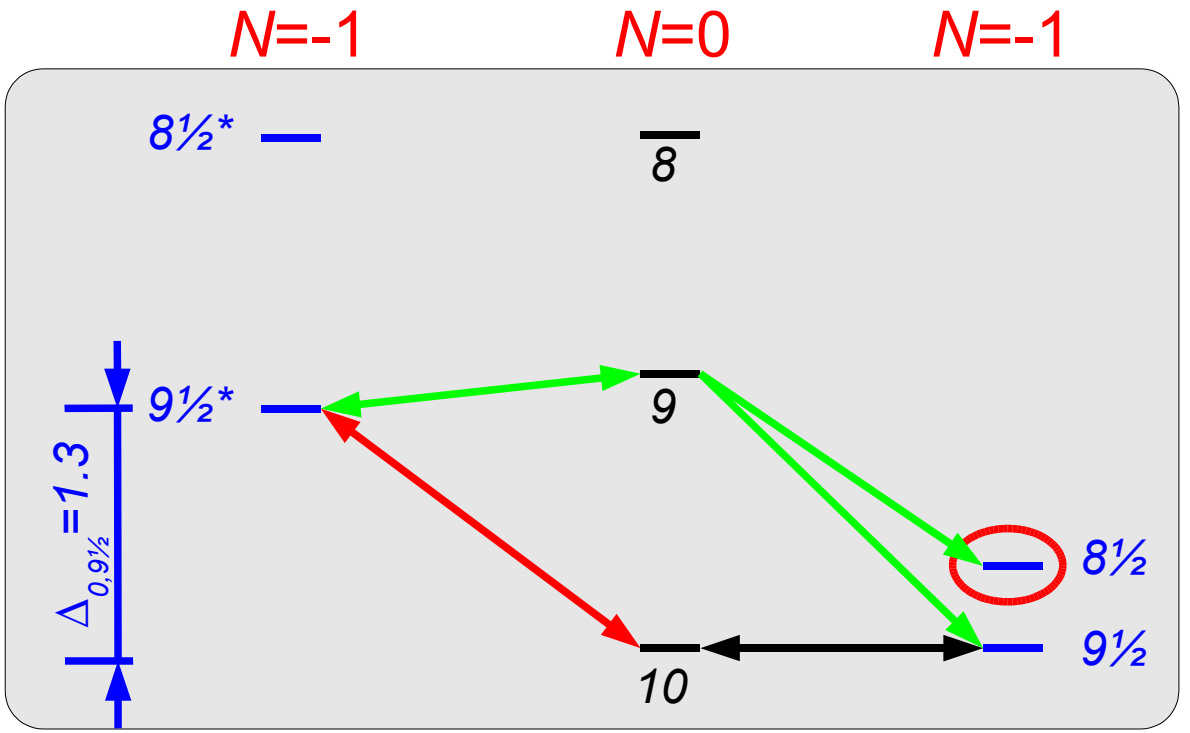
New type of spin-blockade:
electronic excitation ~ anisotropy barrier DS^2

Spin blockade due to S_z



CCS due to bias driven population inversion between $N=-1$, $S_z=9½$ and $S_z=8½$

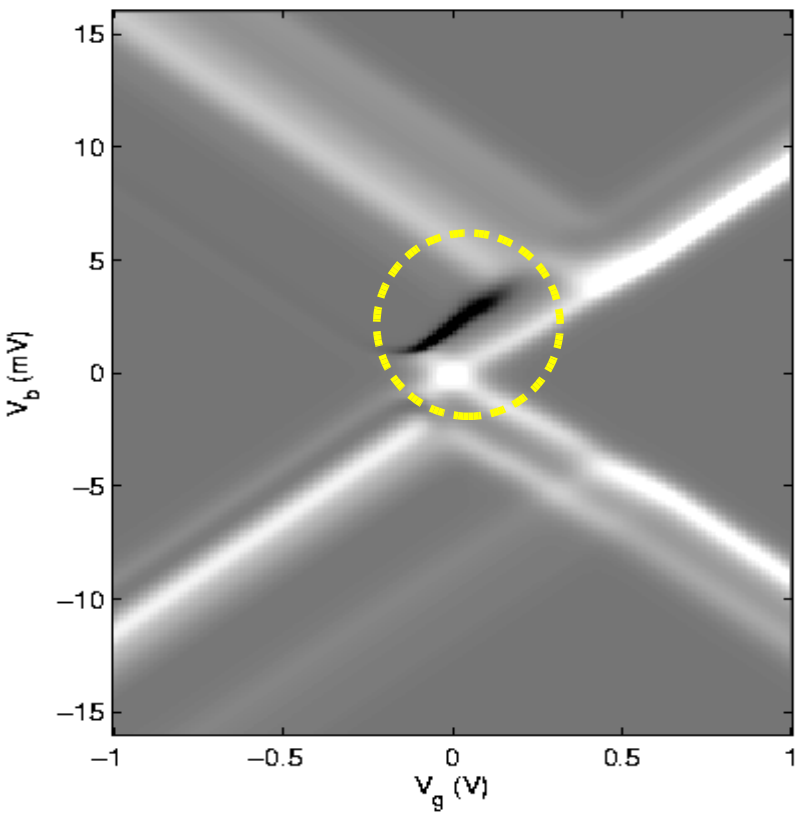


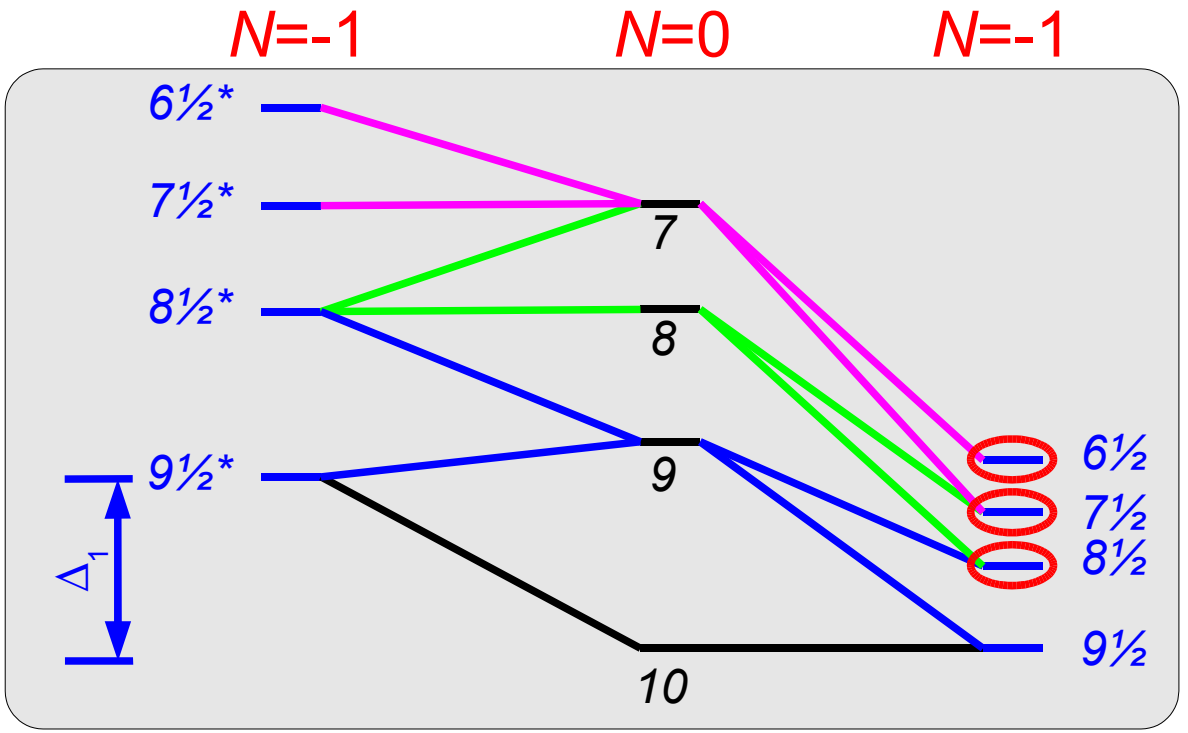


Cascade via excited state spin multiplet into blocking state of ground state spin multiplet

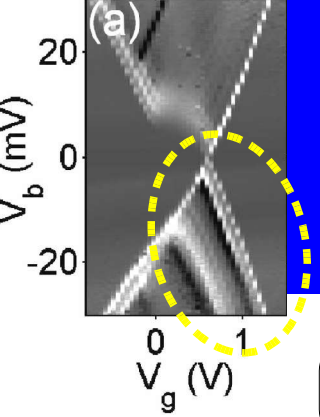
“Relay/Estafette” - mechanism

Sequence of blocking states
N=-1, S_z=8½...½

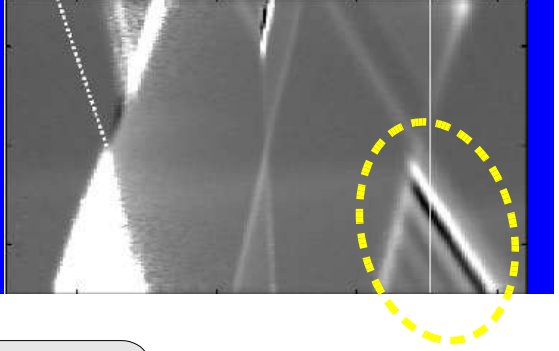




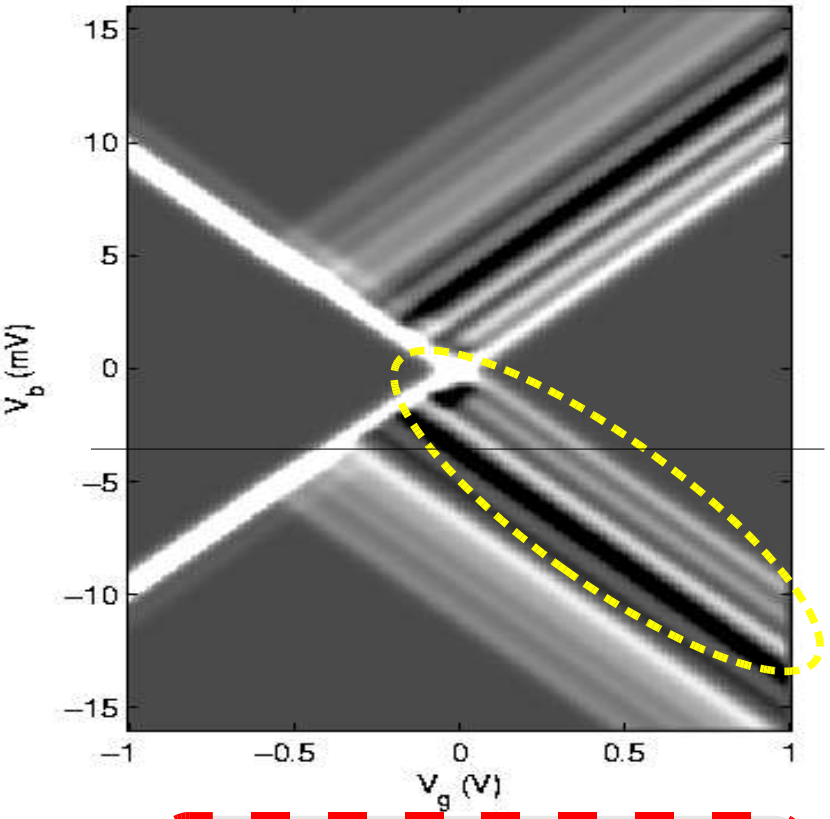
Connection to experiment:
Size of blocked region ~ MAB

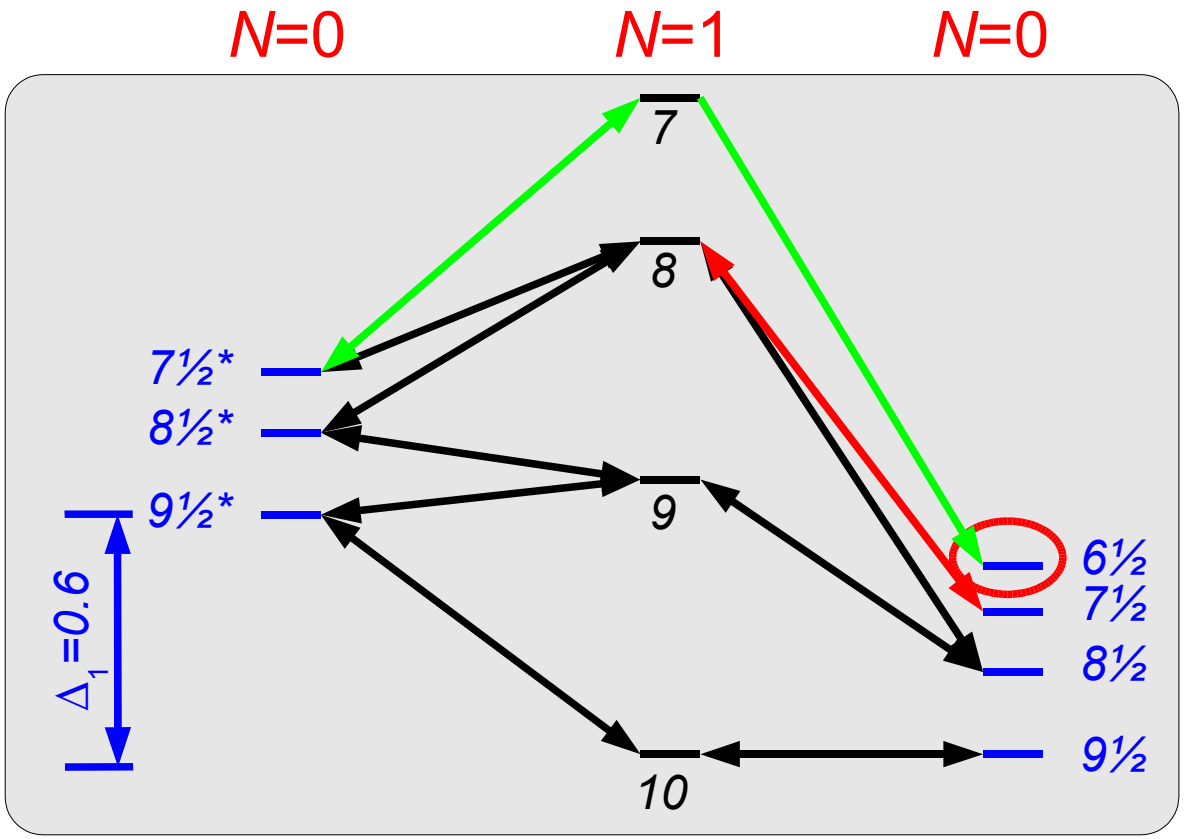


NDC



Cascade into higher excited states $N=1$, $S_z=6½$





Partially consistent with experiment...

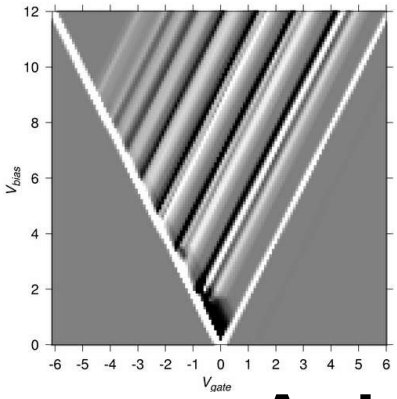
Blocking states "active" beyond some threshold

Advances *and prospects* ***in molecular magnetism***

Transport spectroscopy

Magnetic excitations in multiple charge states
Non-equilibrium magnetic states:
Detection
Control

QTM visible in transport

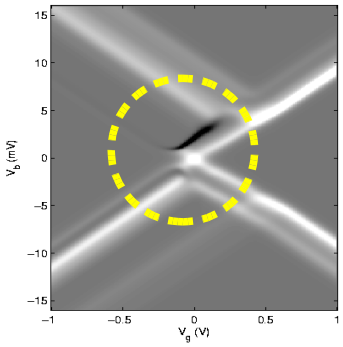


Non-equilibrium shift of *"fake" resonances*
Shot-noise identifies "fake" resonances
High-symmetry B_4 >> B_2
Blocking in ground-state

Anisotropy barriers + electronic excitations

Include
spin-relaxation

Magnetic state *population inversion*
- blocking in excited states
Persistent spin(M) - blockade



Advances and ***prospects in molecular magnetism***

Tunneling transport through SMMs

Charge-induced deformation

M. R. Wegewijs, K. Nowack,
Focus on NEMS, New. J. Phys. (2005)

Model-based transport theory

Charge-induced magnetic distortion

Multiple charge-state spin-Hamiltonian

Parameters,
Magnetic symmetry

Ab-inition methods

Microscopic picture of charging

Molecular structure