Coulomb blockade and magnetic effects in molecular tunnel junctions

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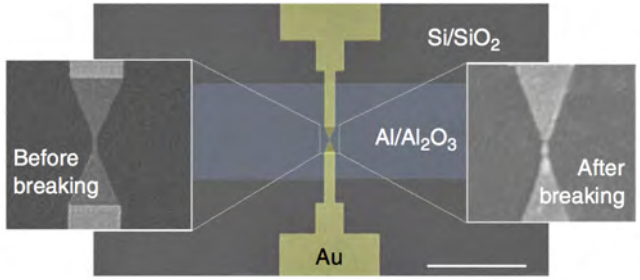
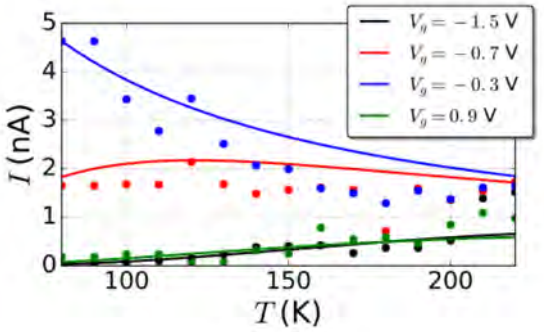
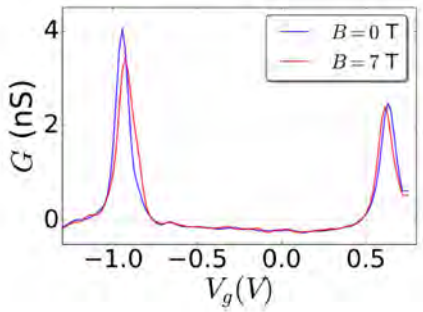
IFISC

SPICE Molecular Electro-Opto-Spintronics Workshop
Mainz (October, 2019)

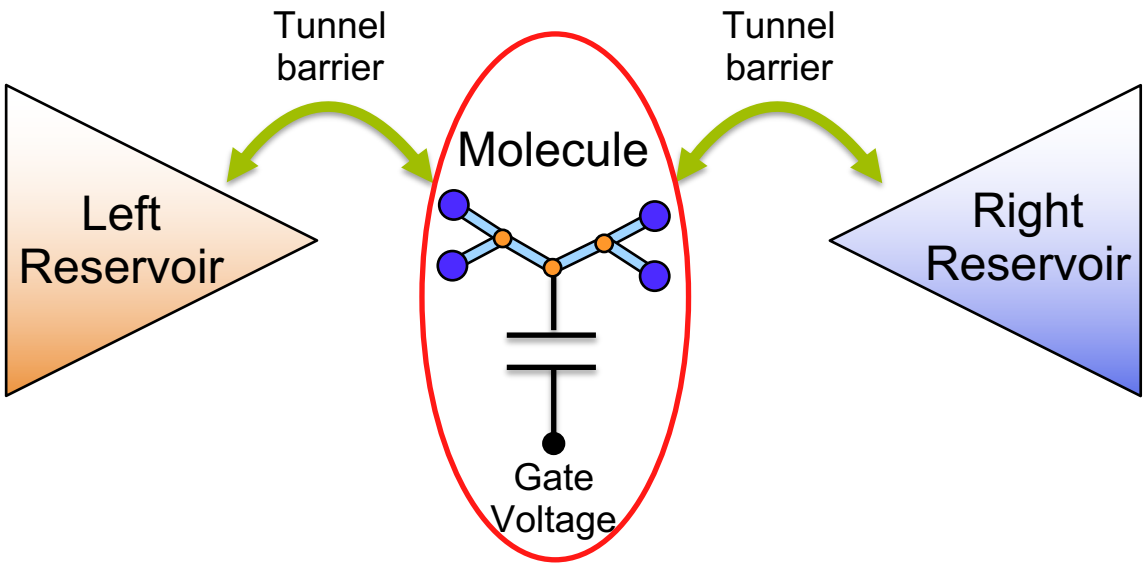
- **Introduction**
  - Molecular junctions
  - Previous work
  - Coulomb blockade
- **Model**
  - Hamiltonian
  - Electric Current
  - Green's function
  - Results
- **How to distinguish interacting and noninteracting models**
  - Magnetic effects
  - Experiment
- **Conclusions**





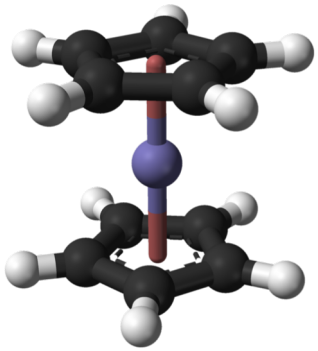


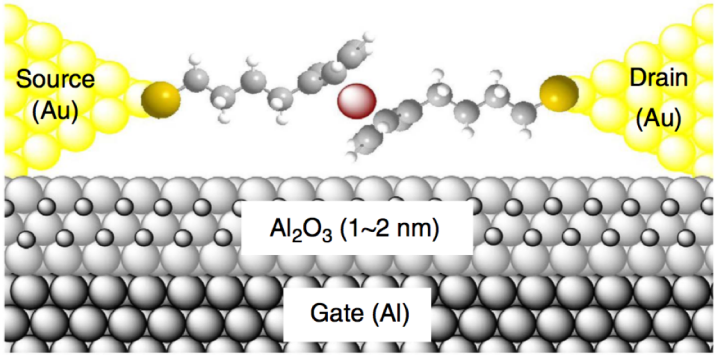
Organic molecule (~1 nm} bridges two bulk metallic electrodes

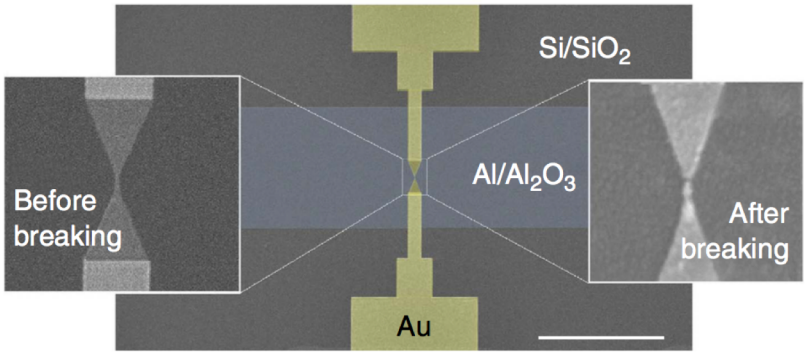


- Possibility to beat Moore's law with single-molecule electronic circuits
- **Transistors**, rectifiers, new functionalities?
- Fundamental questions: **transport mechanism**, vibrations, role of electrode-molecule binding, room-temperature quantum transport, interdisciplinarity!

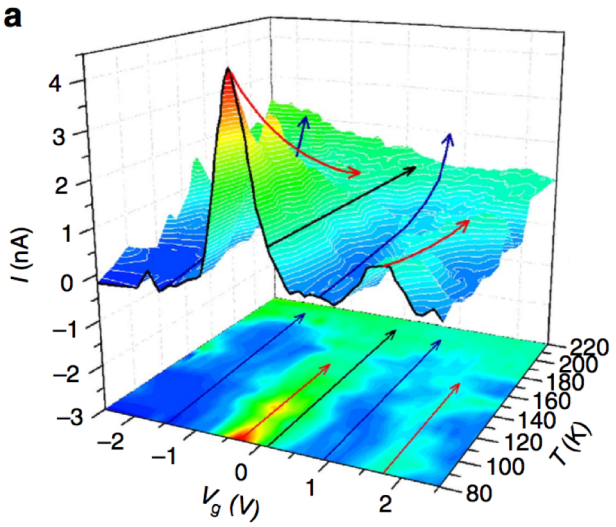
Molecular transistor with a Ferrocene-based molecule: S-$(CH_2)_4$-Fc-$(CH_2)_4$-S

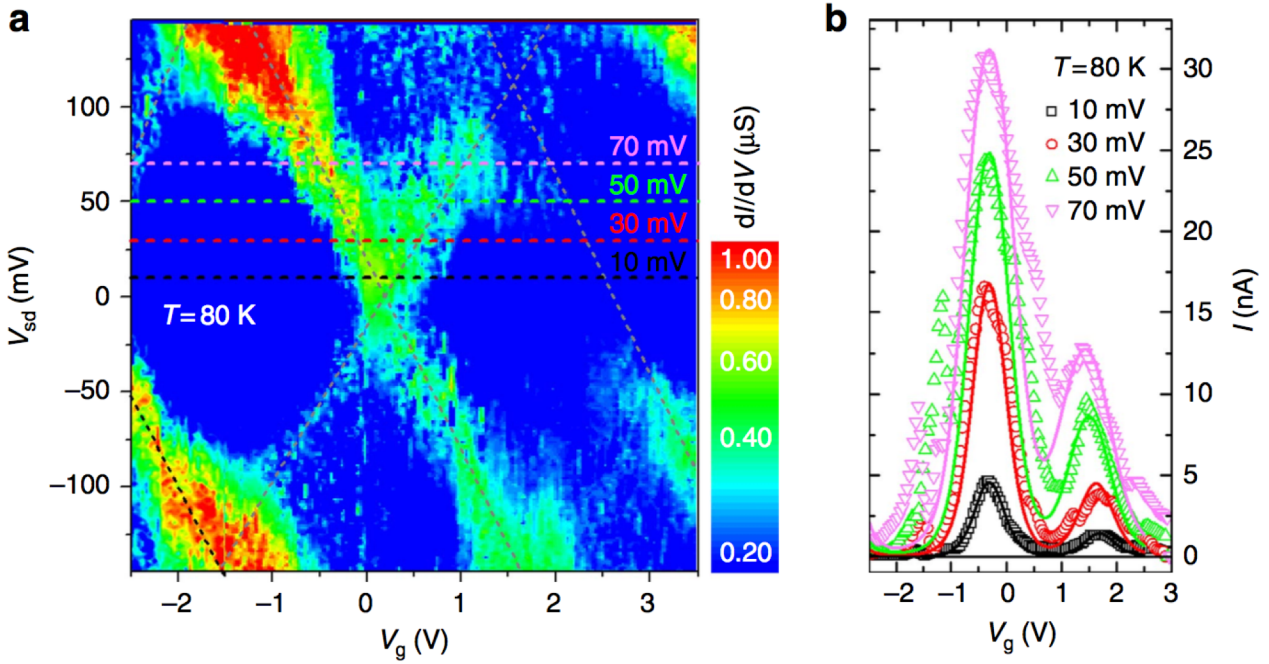






They study temperature dependence of the electric transport



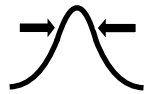


A. R. Garrigues *et al*. Nature Communications **7**, 11595 (2016)

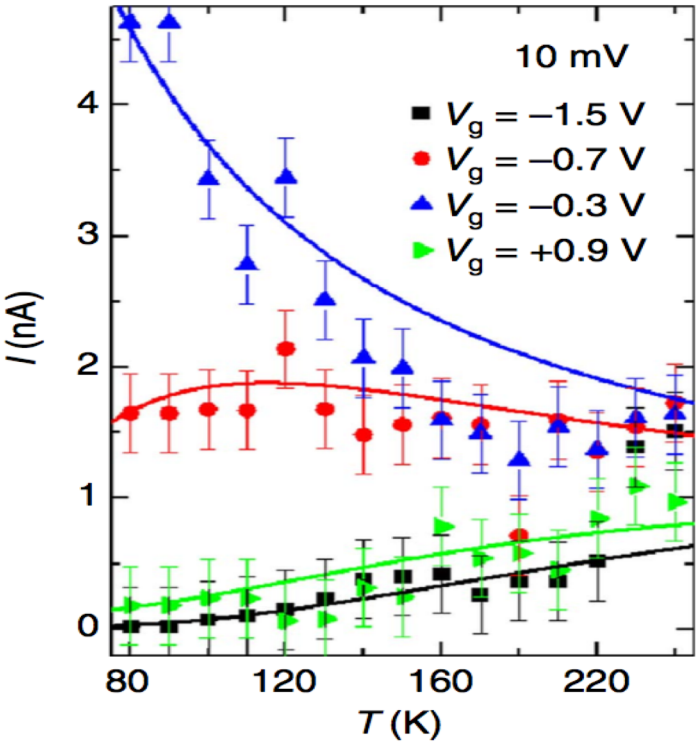
They consider a theoretical noninteracting model

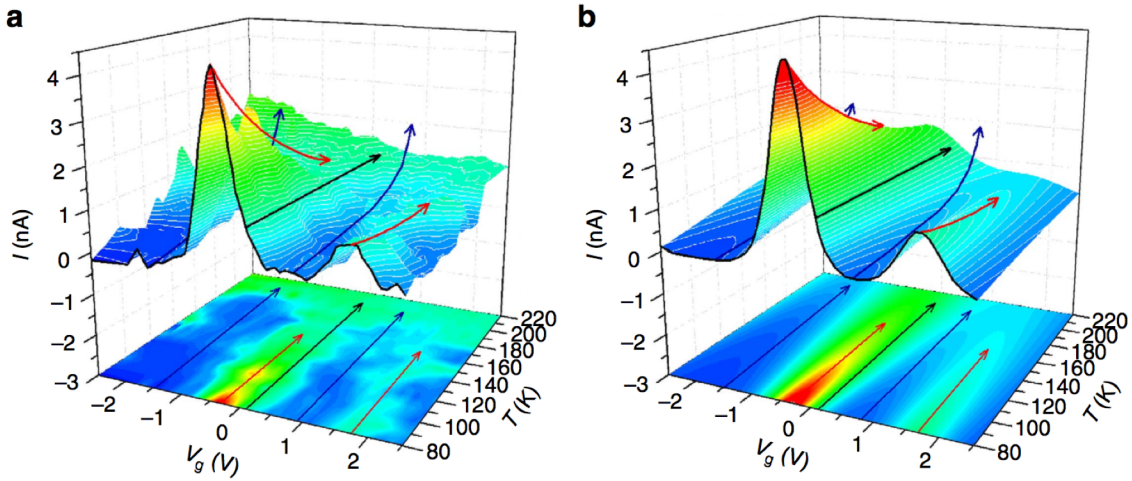
$$I = \frac{q}{h}\int_{\infty}^{\infty} d\omega D_{\varepsilon}(\omega)\frac{\Gamma_L\Gamma_R}{\Gamma_L+\Gamma_R}[f_L(\omega)-f_R(\omega)]$$

$$f_{\alpha}(\omega) = \frac{1}{1+\exp\frac{\omega-\mu_{\alpha}}{k_B T_{\alpha}}}$$ Lead Fermi function

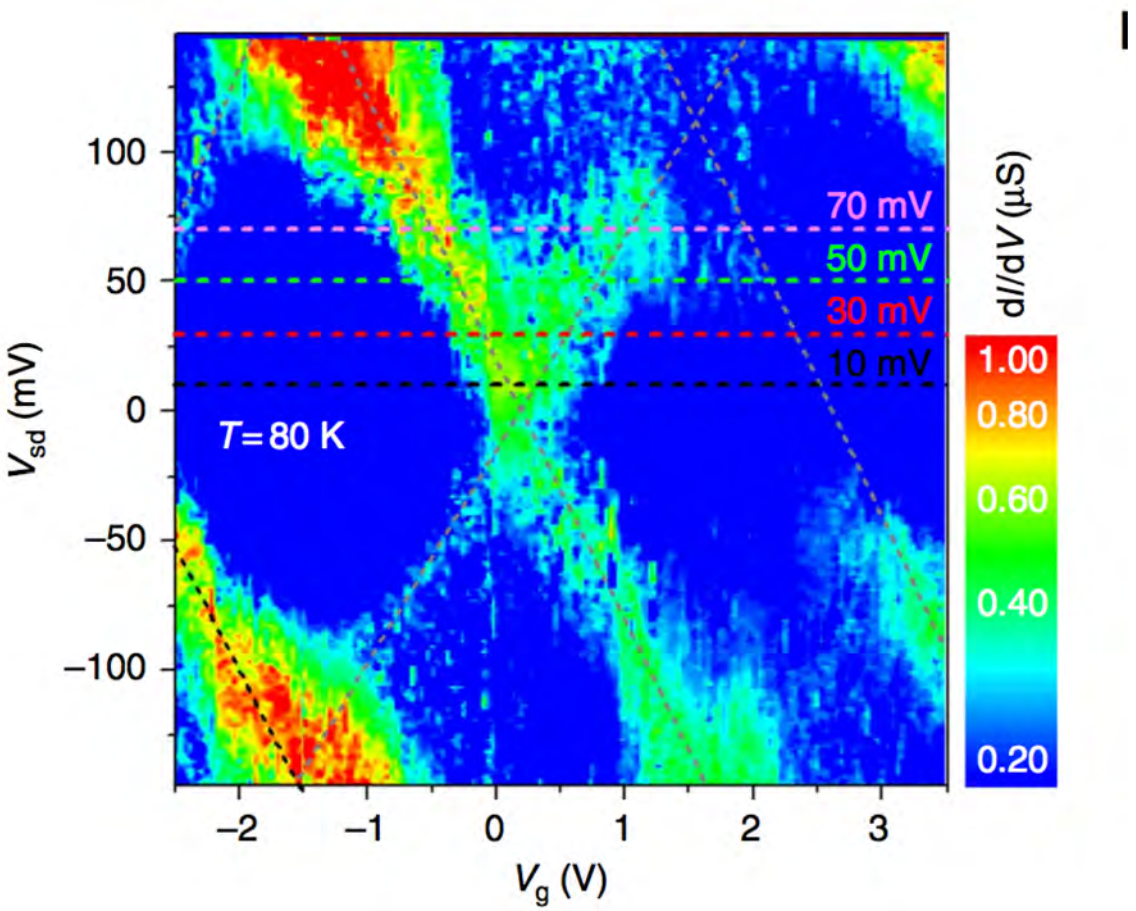
Γ_{α} Level Broadening 

$$D_{\varepsilon}(\omega) = \frac{\Gamma/2}{(\omega-\varepsilon)^2+(\Gamma/2)^2}$$

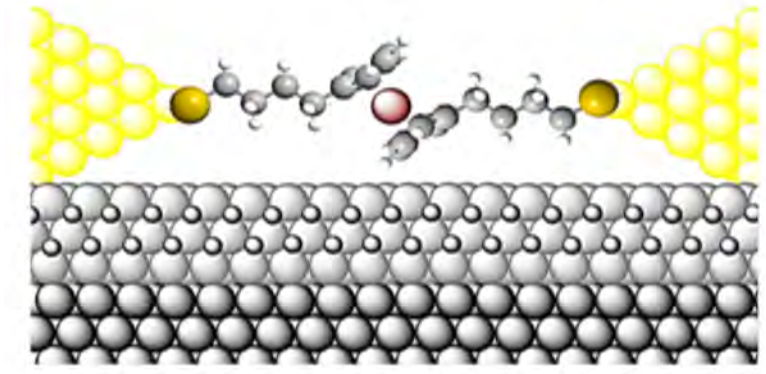




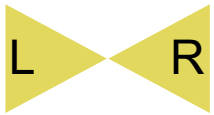
Alvar R. Garrigues *et al*. *Nature Communications* **7**, 11595 (2016)



Can we explain the same experiment using an interacting model?



$$\mathcal{H} = \mathcal{H}_{\text{mol}} + \mathcal{H}_{\text{leads}} + \mathcal{H}_{\text{tunnel}}$$



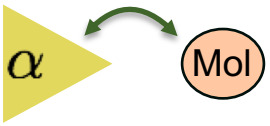
$\alpha = \{L, R\}$ Leads

k Wavenumber

σ Spin

ε_m Molecular level

U Charging energy



$t_{\alpha k}$ Tunnel amplitude

$$\mathcal{H}_{\text{leads}} = \sum_{\alpha k \sigma} \varepsilon_{\alpha k} c^{\dagger}_{\alpha k \sigma} c_{\alpha k \sigma}$$

$$\mathcal{H}_{\text{mol}} = \sum_{\sigma} \varepsilon_m d^{\dagger}_{\sigma} d_{\sigma} + U d^{\dagger}_{\uparrow} d_{\uparrow} d^{\dagger}_{\downarrow} d_{\downarrow}$$

$$\mathcal{H}_{\text{tunnel}} = \sum_{\alpha k \sigma} t_{\alpha k} C^{\dagger}_{\alpha k \sigma} d_{\sigma} + \text{h.c.}$$

- Time evolution of the lead occupation

$$I_\alpha \equiv -e\frac{d\langle n_\alpha\rangle}{dt} \qquad n_\alpha = \sum_{k\sigma} c^\dagger_{\alpha k\sigma} c_{\alpha k\sigma}$$

$$I_L + I_R = 0$$

- We apply the nonequilibrium Green's function formalism

$$I_{\alpha\sigma} = -\frac{2e}{h}\sum_\beta \int d\omega [f_\alpha(\omega) - f_\beta(\omega)] \frac{\Gamma_{\alpha\sigma}\Gamma_{\beta\sigma}}{\Gamma_\sigma} \mathrm{Im}[G^r_{\sigma,\sigma}]$$

$$G^r_{i\sigma,j\sigma}(t) = -\frac{i}{\hbar}\theta(t)\langle [d_{i\sigma}, d^\dagger_{j\sigma}]_+\rangle$$

Retarded Green's function

Broadening $\Gamma_\alpha = 2\pi\rho_\alpha |t_{\alpha k}|^2$

$$f_\alpha(\omega) = \frac{1}{1+\exp\frac{\omega-\mu_\alpha}{k_B T_\alpha}}$$

Lead Fermi function

We calculate the retarded Green's function using the equation-of-motion technique

$$\langle\langle A(t), B\rangle\rangle = -\frac{i}{\hbar}\theta(t)\langle[A(t), B]_+\rangle$$

$$i\hbar\partial_t \rightarrow \langle\langle A(t), B\rangle\rangle$$

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We consider the Hubbard-I scheme (atomic solution + broadening):

$$G^r_{\sigma,\sigma}(\omega) = \frac{\langle n_{\bar{\sigma}}\rangle}{\omega - \varepsilon_m - \Sigma} + \frac{1 - \langle n_{\bar{\sigma}}\rangle}{\omega - \varepsilon_m - U - \Sigma}$$

$$\Sigma \approx -\frac{i\Gamma}{2}$$ *Self-energy*

$$\Gamma = \Gamma_L + \Gamma_R$$

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$$\Sigma \approx -\frac{i\Gamma}{2}$$ *Self-energy*

$$\Gamma = \Gamma_L + \Gamma_R$$

We remark that we have a self-consistent problem:

$$\langle n_\sigma\rangle = -\int \frac{d\omega}{\pi}\frac{\Gamma_L f_L(\omega) + \Gamma_R f_R(\omega)}{\Gamma}\mathrm{Im}\left[G^r_{\sigma,\sigma}(\omega)\right]$$

We consider energy dependent hybridization witdths:

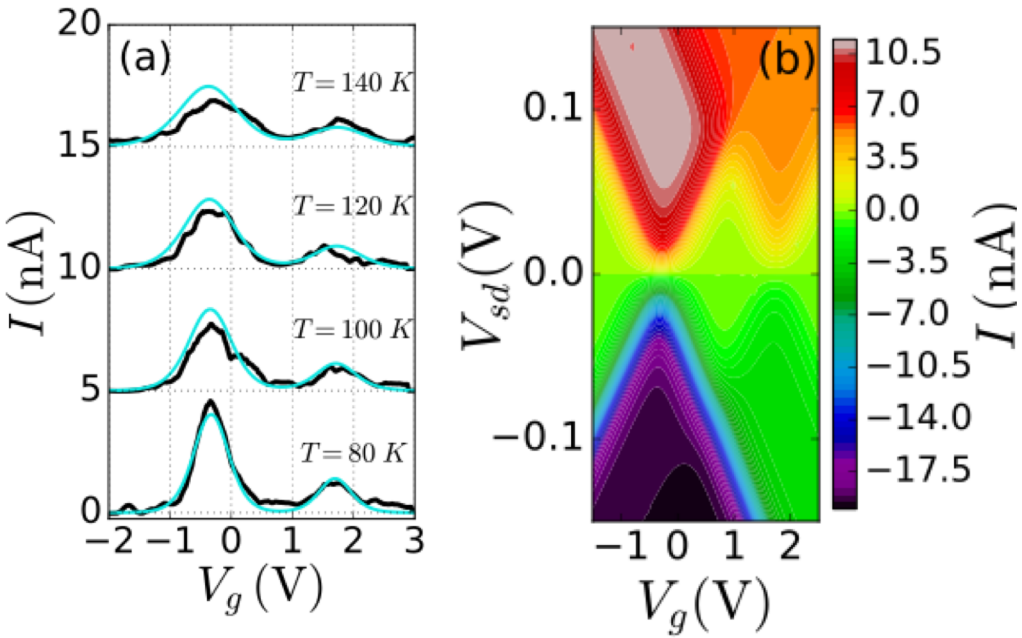
$$\Gamma_\alpha(\omega) = \begin{cases} \gamma_{\alpha 1} & \text{if } \omega < \varepsilon_d + U/2 \\ \gamma_{\alpha 2} & \text{if } \omega > \varepsilon_d + U/2 \end{cases}$$

Parameters are fitted with the experimental curves:

U	ε_N	γ_{L1}
76 meV	27 meV	0.4 meV
γ_{L2}	γ_{R1}	γ_{R2}
0.4 meV	0.05 meV	0.01 meV
C_g	C_L	C_R
0.525 e V^{-1}	5.78 e V^{-1}	6.83 e V^{-1}

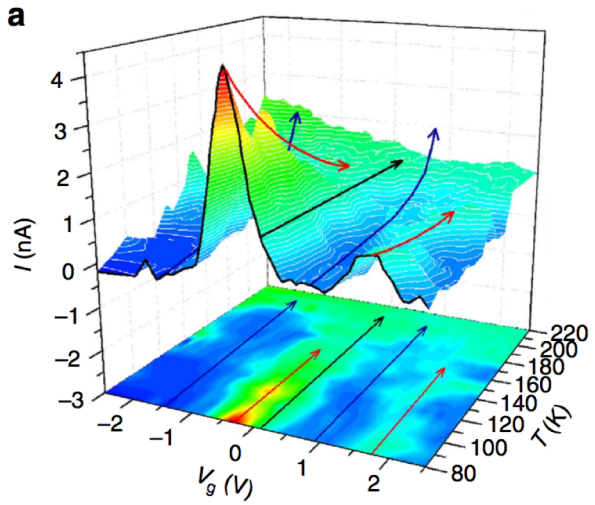
Current vs Gate voltage:

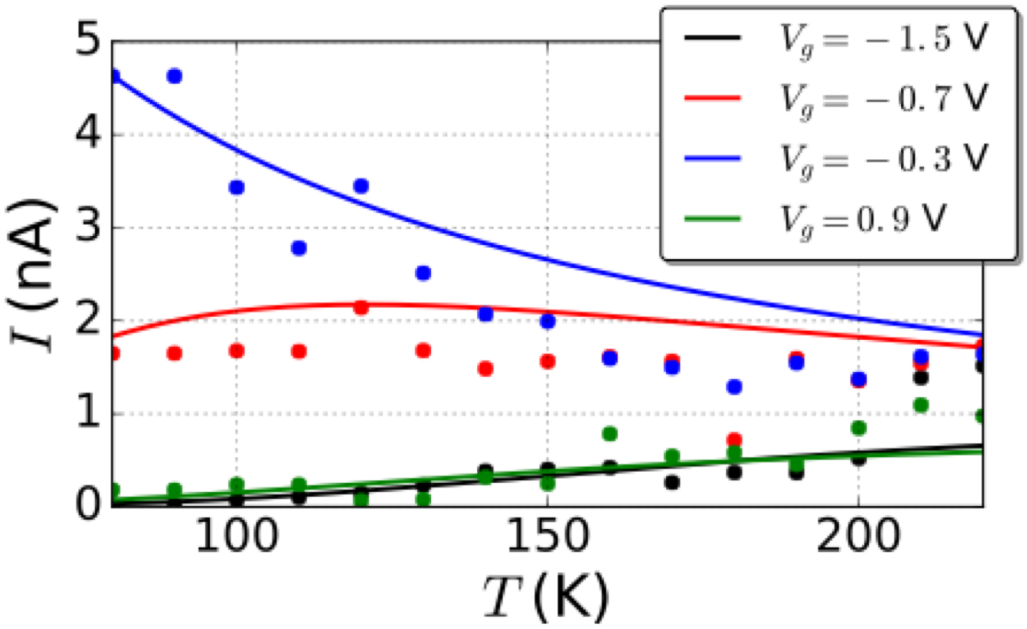
- **Two peaks**: Energy level and electron-electron interactions.
- **Good agreement** with experiments.
- **Coulomb diamonds** when we include voltage bias.



Current vs Temperature:

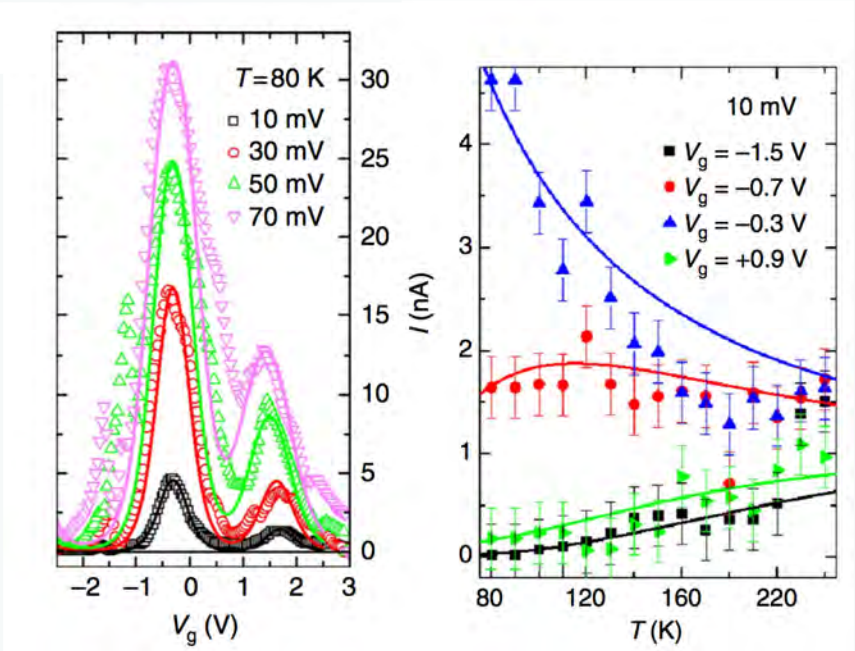
- **Resonances** decrease with increasing temperature.
- **Symmetry point** insensitive.
- **Coulomb blockade valley** slightly increases





Noninteracting model

Nature Communications **7**, 11595 (2016)



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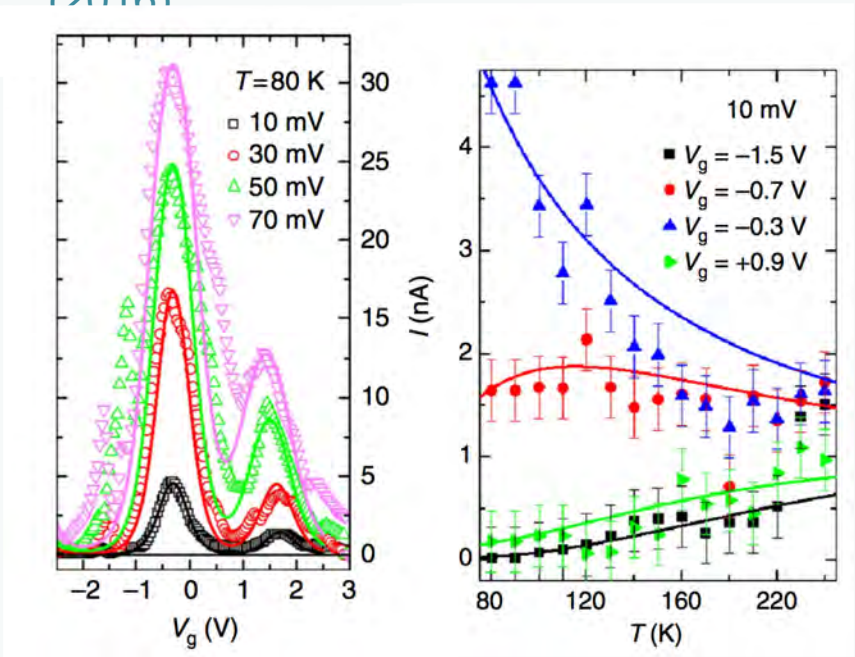
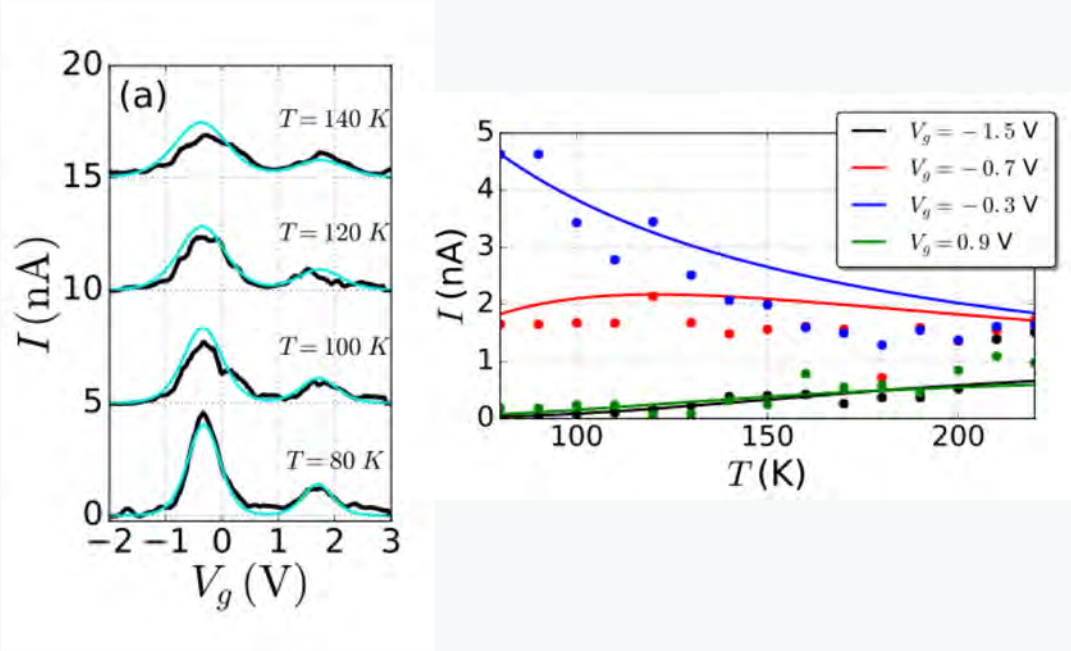


Interacting model

Our work



Noninteracting model

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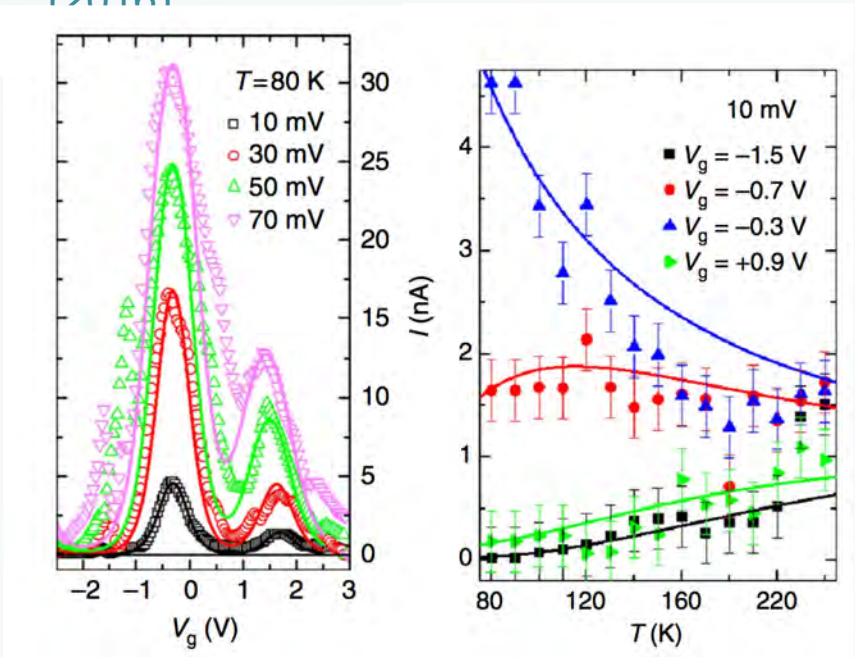

Interacting model

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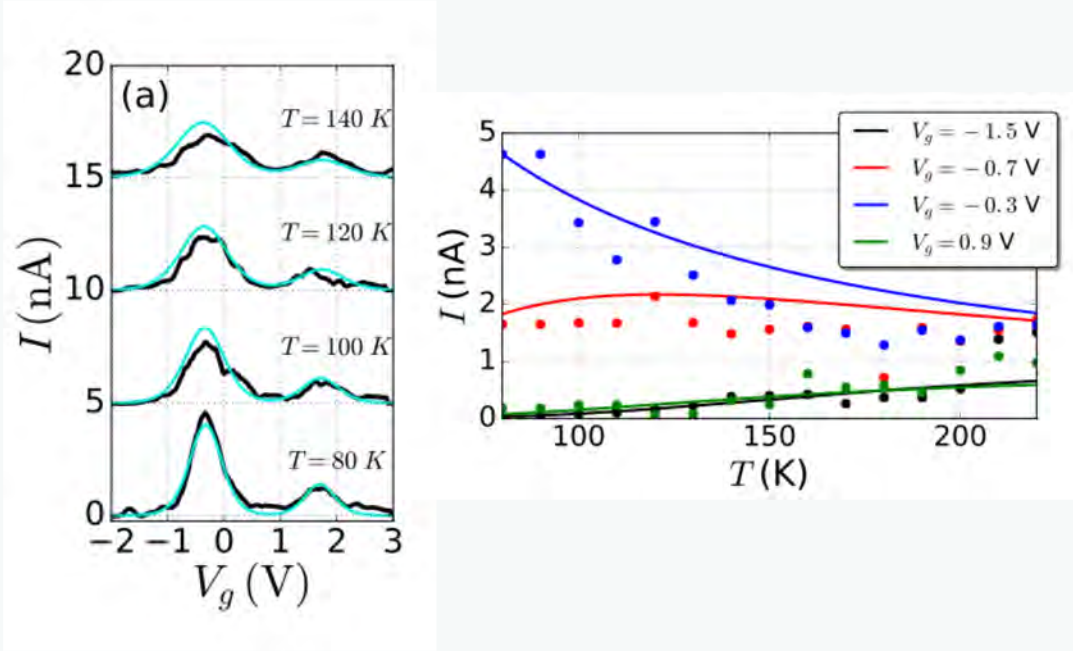
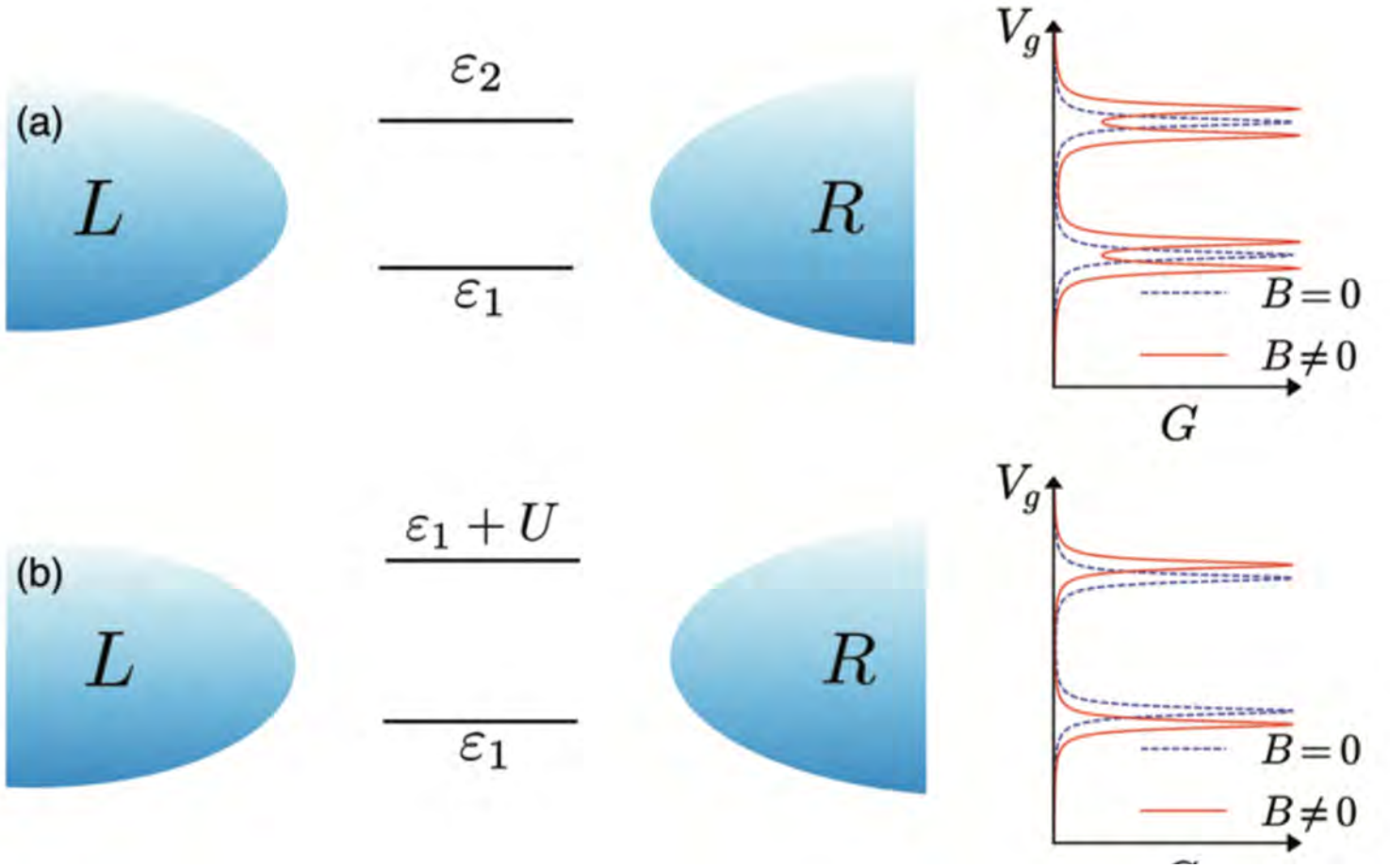


How to distinguish between the interacting and noninteracting case?



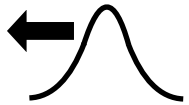
Noninteracting molecule (a):
Conductance splitting

Interacting molecule (b):
Conductance shift

We apply a **magnetic field**.

$$\mu_m = \frac{(2N-1)e^2}{2C} - e\frac{C_L V_L + C_R V_R + C_g V_g}{C} + \varepsilon_N + \Delta S g \mu_B B$$

If…

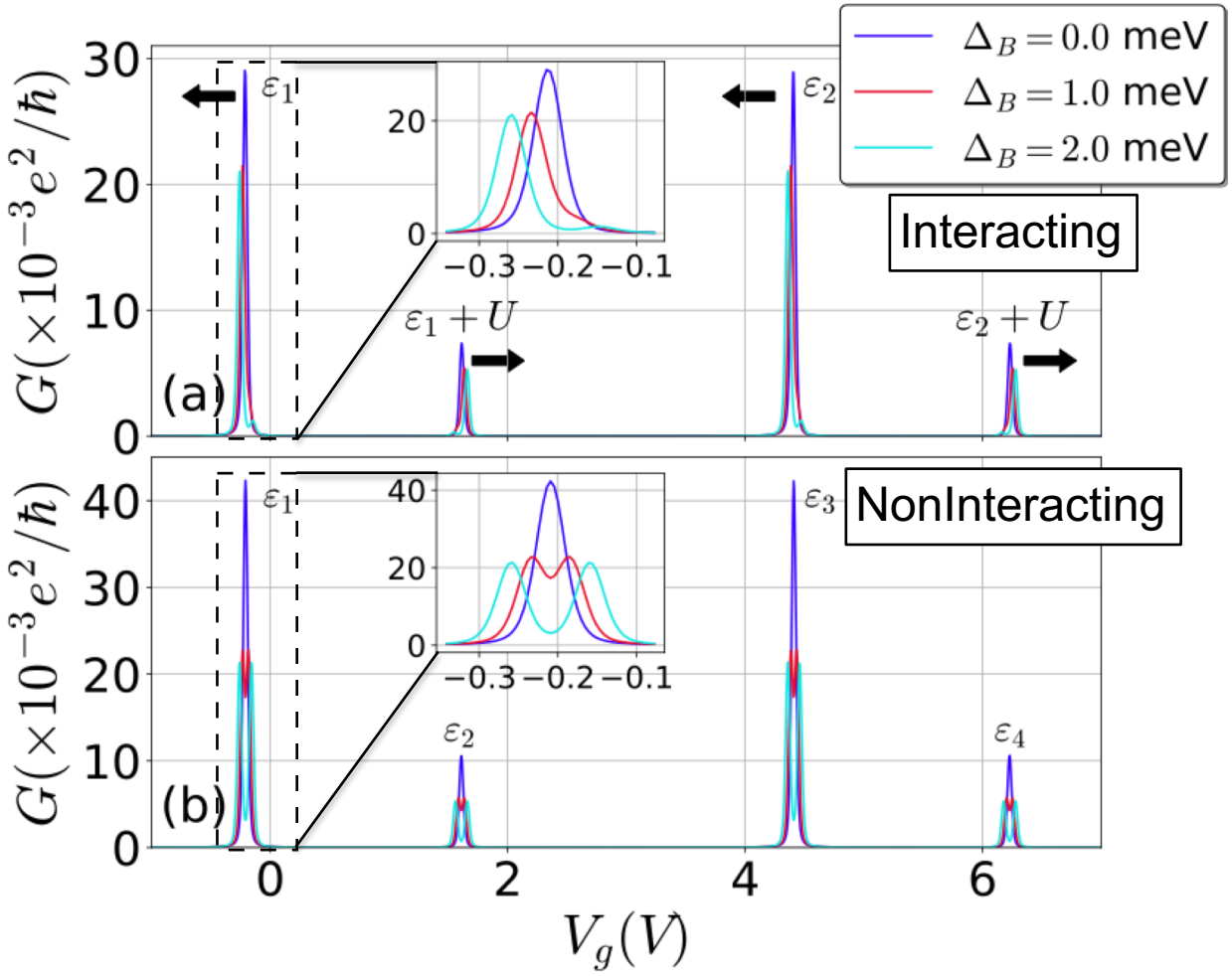
$\Delta S > 0$ 

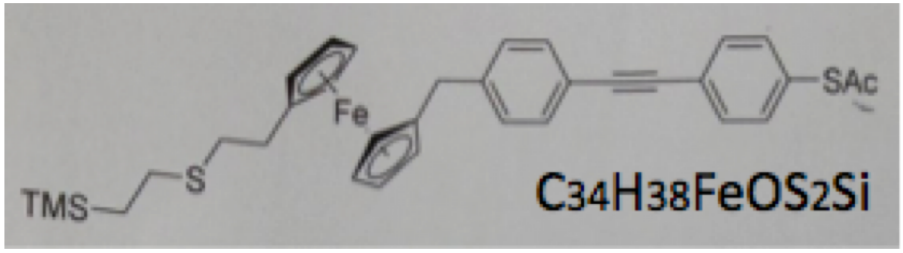
$\Delta S < 0$ 

Linear conductance *G*

Interacting model:
Increasing or decreasing separation.

Noninteracting model:
Resonance splitting.

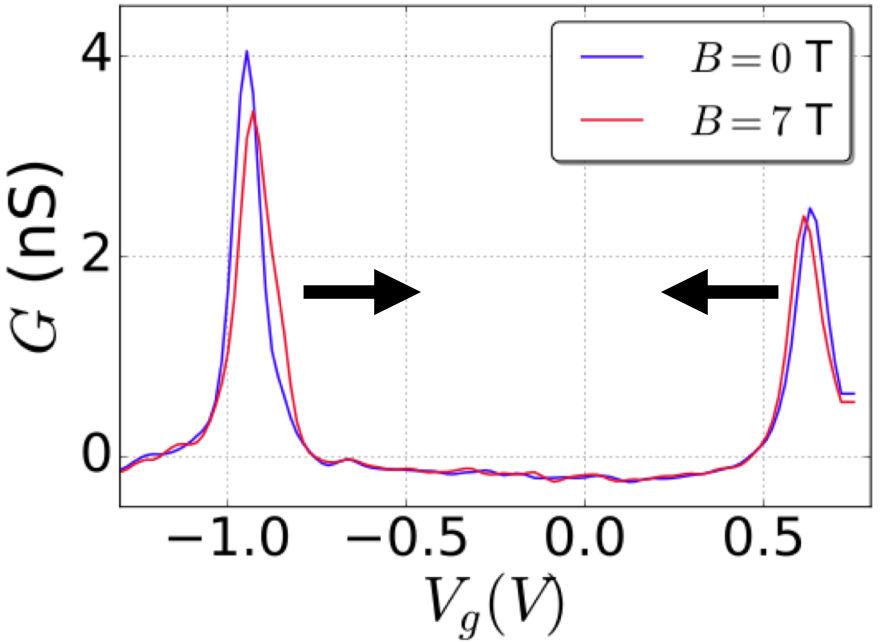


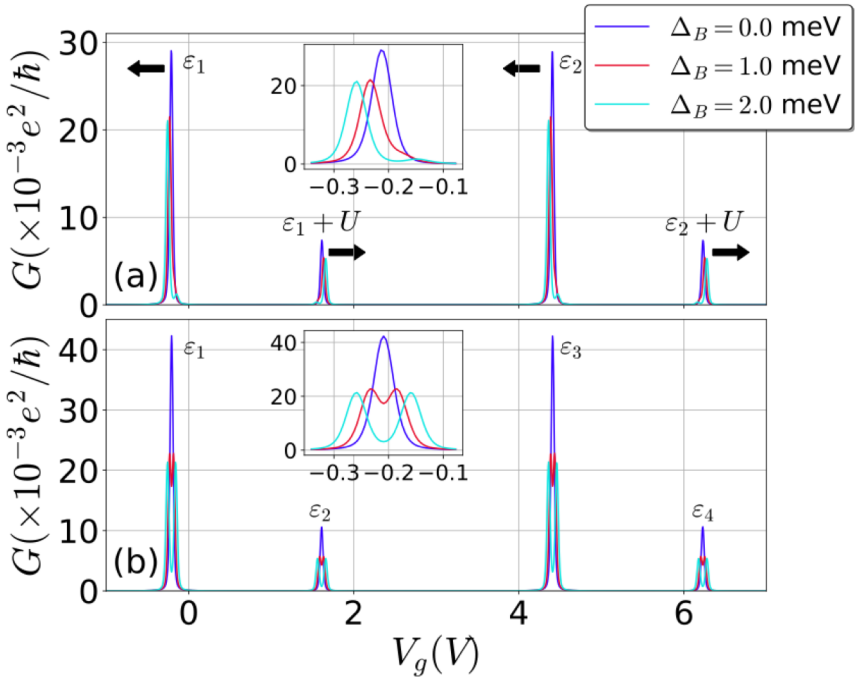


- Ferrocenyl molecule.
- Very low temperatures. $T = 4\ \mathrm{K}$
- Position shift as increasing magnetic field.
- **Interacting** molecule.
- Two different Coulomb blockade levels.

Comments:

At high T the shift is not observed.
From left to right we have Fe^{3+}, Fe^{2+}, Fe^{1+}
Instability.





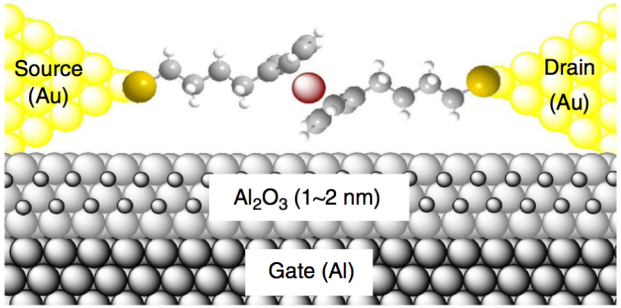
Our work

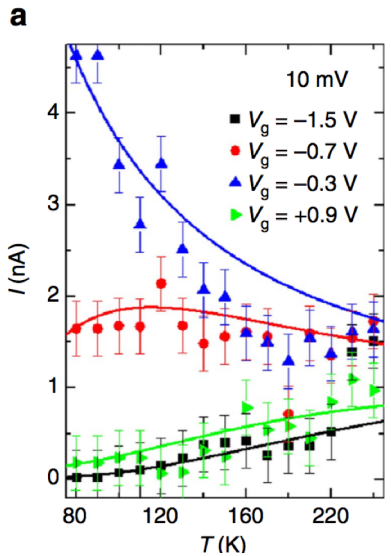
An **interacting model** reproduces the temperature dependence of the electronic transport across a Ferrocene tunnel junction

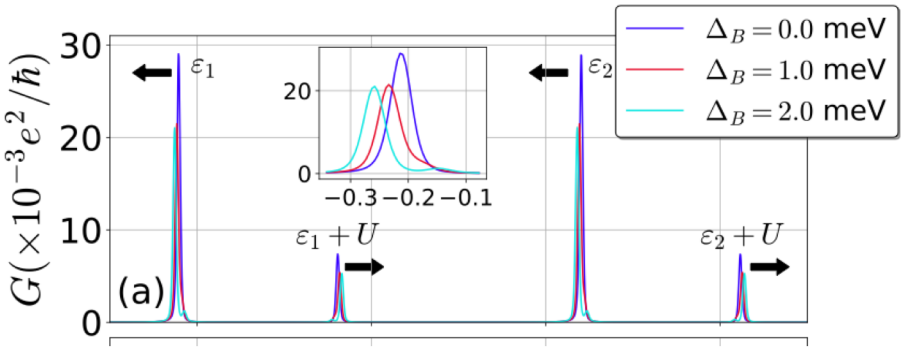
We can distinguish between interacting and noninteracting situations with a **magnetic field.**

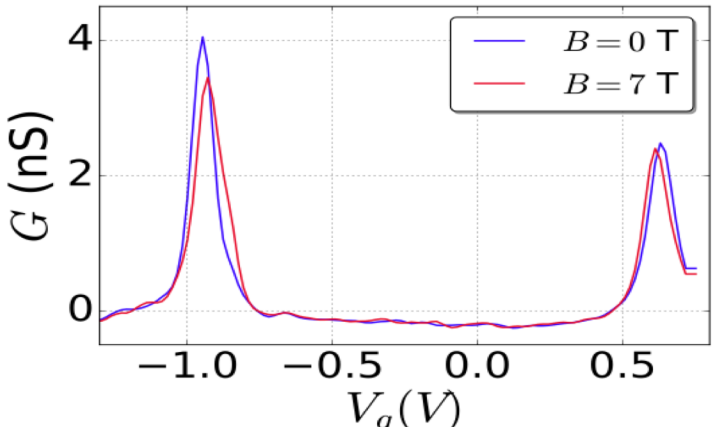
- Noninteracting particles: Resonance splitting.
- Interacting particles: Resonance shift.

Experimental data are consistent with the interacting scenario.









Miguel A. Sierra, D. Sánchez, A. R. Garrigues, E. del Barco, L. Wang and C. A. Nijhuis, Nanoscale **10**, 3904 (2018)

THANK YOU

for your attention