Kondo effect in mesoscopic and nanoscopic systems

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Recap Lectures 1 & 2

- Standard spin ½ Kondo model
  - Complicated quantum impurity problem
  - Needed the developments of new numeric tools to solve it
  - The low temperature strong coupling fixed point is a Fermi liquid
  - There a single energy scale in the Kondo regime: universal functions of $k_B T_K$

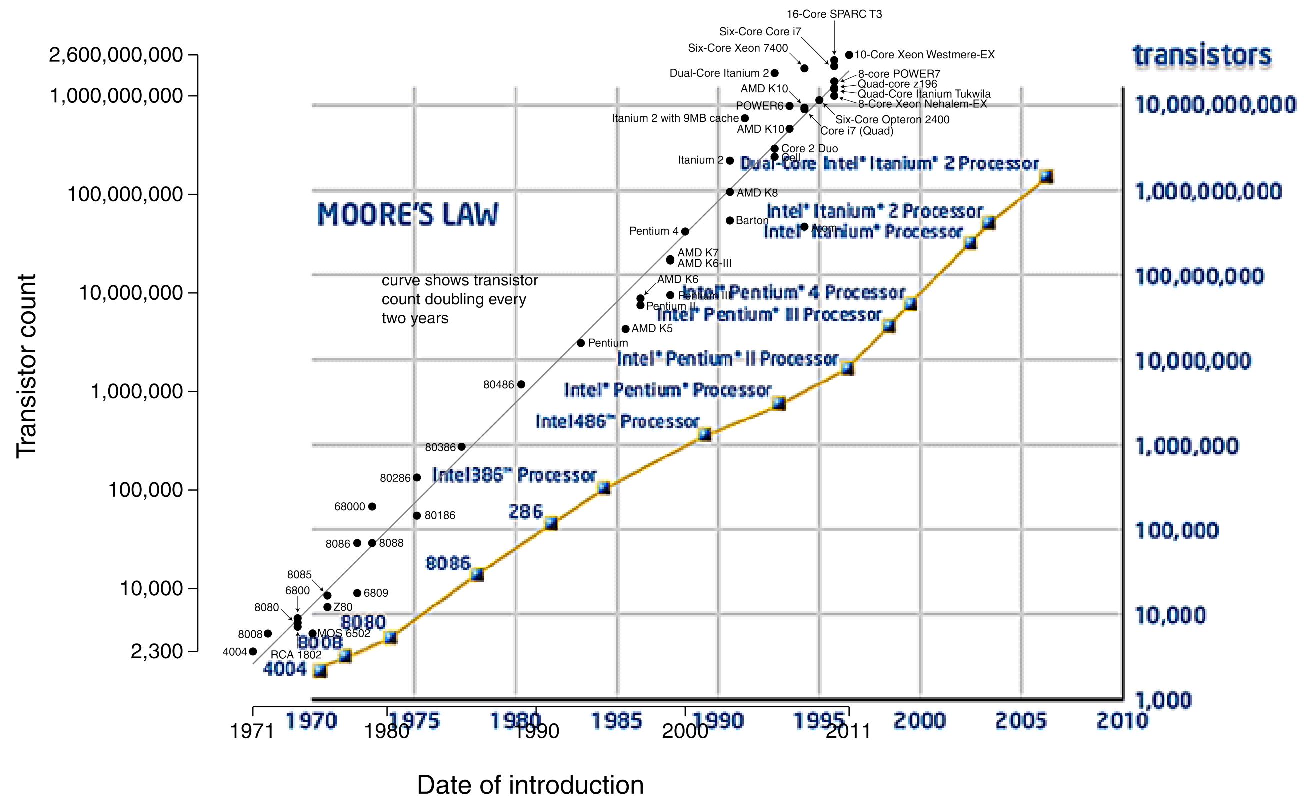
Outline of lecture 3

- Mesoscopic and nanoscopic devices
- Transport through quantum dots and molecular transistors
    - Meir and Wingreen conductance formula
- Molecular transistors.
    - Kondo effect in molecular transistors
    - The role of molecular vibrations

Moore’s law (1965)

The number of transistors in an processor doubles every two years while the price remains constant.

Microprocessor Transistor Counts 1971-2011 & Moore’s Law



Moore's law in aeronautics?

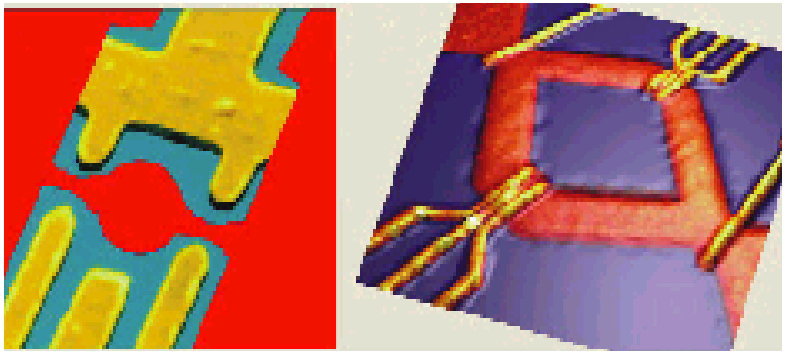
- A flight between New York and Paris was worth in 1975 $900 and lasted 9 hours.
- It should cost now 1 penny and last less than a second.

Why molecular transistors?

- Moore's law is expected to breakdown by 2020. (gate size ~6nm, tunneling, heating)
- An alternative to semiconductor based transistors may be needed.
- **Molecular based devices** offer the possibility of creating transistors with an area ~10^5 times smaller than current technology

Quantum dots

- The starting point is a two dimensional electron gas generated in a GaAs/$Al_xGa_{1-x}As$ heterostructure.
- The gas is protected by an insulated layer and metallic gates can be deposited on the surface and negatively charged to repel the electrons below.
- The electrons are confined in small regions forming a *quantum dot*
- Charging energies $U \sim 1K - 10K$
- Kondo temperatures $T_K < 1K$

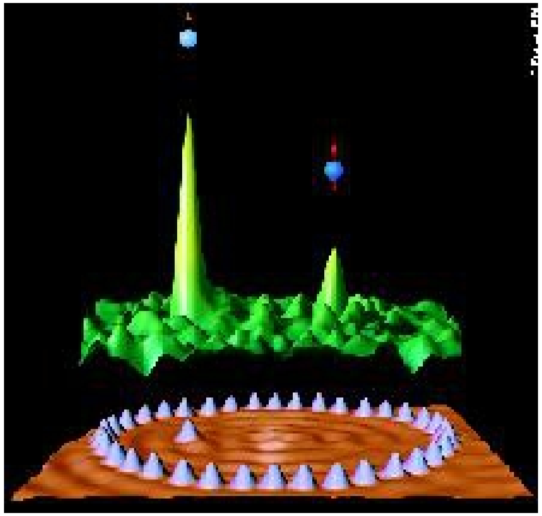


Molecular transistors

- Metal-metal junction:
  - Electromigration
  - Break junctions
- Add molecules at the junction to get one bridging the gap
  - Lack of reproducibility
- Charging energy $U \sim 1000K - 10000K$
- Kondo temperatures $T_K < 200K$

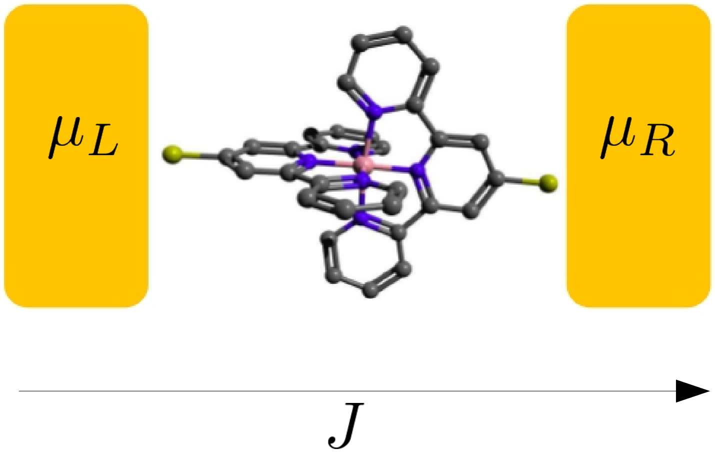
Atoms or molecules on surfaces

- Studied using Scanning tunneling microscopy (STM)
- Spectroscopy: access to spectral properties of the atom
- STM tip couples to bulk electrons: Fano lineshapes
- Lack of tunability
- Surface states that can be modified using quantum corrals
- Kondo effect given mostly by bulk states.



Transport through an interacting region

$$H = \sum_{\ell=L,R} \sum_{k\alpha} \epsilon_{\ell k} c^\dagger_{\ell k\alpha} c_{\ell k\alpha} + H_{\rm int}(\{d_n\};\{d^\dagger_n\})$$
$$+ \sum_{\ell=L,R} \sum_{k\alpha} \sum_{n} (V_{n\ell k\alpha} c^\dagger_{\ell k\alpha} d_n + V^*_{n\ell k\alpha} d^\dagger_n c_{\ell k\alpha})$$



Y. Meir, N. S. Wingreen, Phys. Rev. Lett. **68** 2512 (1992)

Transport through an interacting region

Meir and Wingreen showed that

$$J = \frac{ie}{2h} \int dE \left(\mathrm{Tr}[(f_L(E)\mathbf{\Gamma}^L - f_R(E)\mathbf{\Gamma}^R)(\mathbf{G}^r - \mathbf{G}^a) + (\mathbf{\Gamma}^L - \mathbf{\Gamma}^R)\mathbf{G}^<] \right)$$

where:

$$\mathbf{\Gamma}^L_{n,m} = 2\pi \sum_\alpha \rho_L(E) V_{nL\alpha}(E) V^*_{mL\alpha}(E)$$

$$G^<_{n,\ell k\alpha}(t) = i\langle\langle c_{\ell k\alpha}, d_n(t)\rangle\rangle$$

The calculation of out-of-equilibrium Green's functions for an interacting system in the strongly correlated regime is still an open problem. [some recent developments by F. Anders (2008) using NRG and J. Han and R. Heary (2009) using Quantum Monte Carlo]

$$eV = \mu_R - \mu_L$$

Transport through an interacting region

- Simplifications:
  - In the high temperature regime $k_B T \gg \Gamma_L, \Gamma_R$
    - No Kondo physics
  - Proportionate couplings: $\Gamma_L = \lambda \Gamma_R$
    - No need to calculate: $G^{<}_{n,\ell k\alpha}$
    - But $G^r(E, V)$
  - Zero bias: $V \to 0$
    - $G^r(E, 0)$ but $G^{<}_{n,\ell k\alpha}(E, V \to 0)$
  - Asymmetric couplings: $\Gamma_L \ll \Gamma_R$
    - Tunneling situation: $G^r(E, 0)$

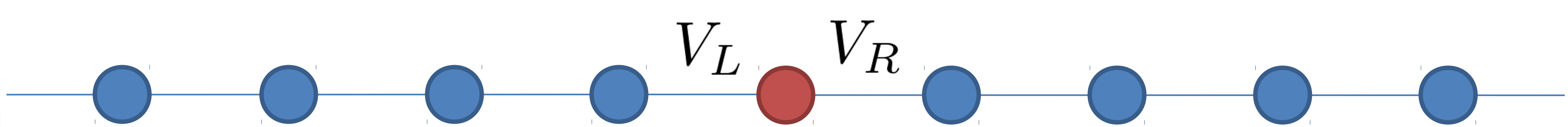
Single level quantum dot

$$H = \sum_{\sigma} \epsilon_d n_\sigma + U n_{d\downarrow} n_{d\uparrow} + \sum_{\ell k} \epsilon_{\ell k} c^\dagger_{\ell k \sigma} c_{\ell k \sigma} + \sum_{\ell k} (V_{\ell k} c^\dagger_{\ell k \sigma} d_\sigma + V^* d^\dagger_\sigma c_{\ell k \sigma})$$

$$\Gamma_L = \lambda \Gamma_R, \quad V \to 0$$

$$g_\sigma = \frac{4\pi e^2}{h} \int dE \, \frac{\Gamma^L \Gamma^R}{\Gamma^L + \Gamma^R} A_{d\sigma}(E, T, V = 0) \left(-\frac{\partial f}{\partial E} \right)$$

The Anderson impurity is coupled to a single effective electron bath with an hybridization $\Gamma = \Gamma^L + \Gamma^R$



The d-level couples to the symmetric combination $V_L f_{L0\sigma} + V_R f_{R0\sigma}$

Zero temperature conductance

$$g_\sigma(T=0) = \frac{4\pi e^2}{h}\frac{\Gamma^L\Gamma^R}{\Gamma^L+\Gamma^R} A_{d\sigma}(E=0,T=0,V=0)$$

Non-interacting system:

$$A_{d\sigma}(E=0,T=0,V=0) = \frac{\Gamma/\pi}{\epsilon_d^2+\Gamma^2} \qquad \Gamma = \Gamma^L+\Gamma^R$$

$$g_\sigma(T=0) = \frac{4e^2}{h}\frac{\Gamma^L\Gamma^R}{\epsilon_d^2+(\Gamma^L+\Gamma^R)^2}$$

$$g_\sigma(T=0) = \frac{4e^2}{h}\frac{\Gamma^L\Gamma^R}{(\Gamma^L+\Gamma^R)^2}\frac{1}{1+\epsilon_d^2/(\Gamma^L+\Gamma^R)^2}$$

$$g_\sigma(T=0) = \frac{4e^2}{h}\frac{\Gamma^L\Gamma^R}{(\Gamma^L+\Gamma^R)^2}\sin^2(\pi n_{d\sigma})$$

Zero temperature conductance

For $\Gamma^L = \Gamma^R$ and $\epsilon_d = 0$

$$g_\sigma(T=0) = \frac{e^2}{h}$$ (unitary limit)

The total conductance as a function of the gate voltage has a Lorentzian shape

For an interacting level, the occupation of the level has a two step behavior as predicted by the Hartree-Fock solution and we expect the conductance to have a plateau of height 2 e^2/h in the magnetic moment regime

$$g_\sigma(T=0) = \frac{4e^2}{h} \frac{\Gamma^L \Gamma^R}{(\Gamma^L + \Gamma^R)^2} \sin^2(\pi n_{d\sigma})$$

High temperature regime

$k_B T \gg \Gamma$

We can treat the hybridization as a perturbation. To lowest order
We use the spectral density of the isolated quantum dot (atomic limit)

$$A_{d\sigma}(E) = \frac{1}{Z}\sum_{i,j}(e^{-\beta E_i} + e^{-\beta E_j})\langle\Psi_j|d_\sigma^\dagger|\Psi_i\rangle\langle\Psi_i|d_\sigma|\Psi_j\rangle\delta[\epsilon - (E_j - E_i)]$$

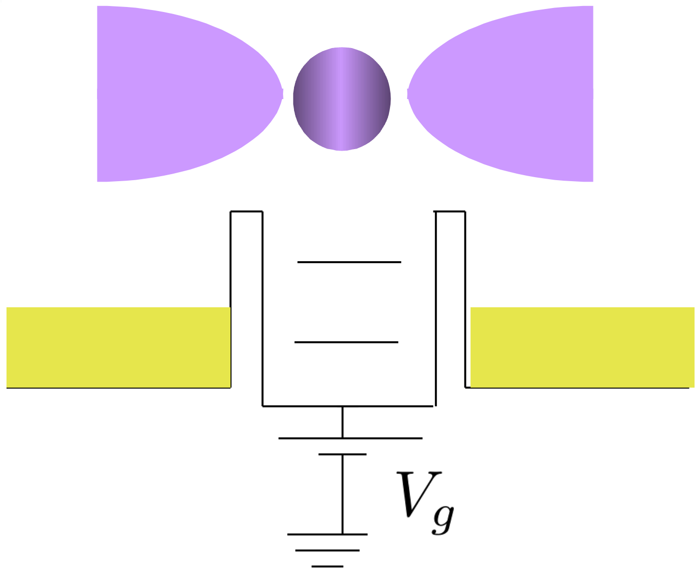
$$g = \frac{e^2}{\hbar}\frac{\Gamma}{k_B T}\sum_{i,j,\sigma}(P_i + P_j)f(E_i - E_j)f(E_j - E_i)|\langle\Psi_j|d_\sigma^\dagger|\Psi_i\rangle|^2$$

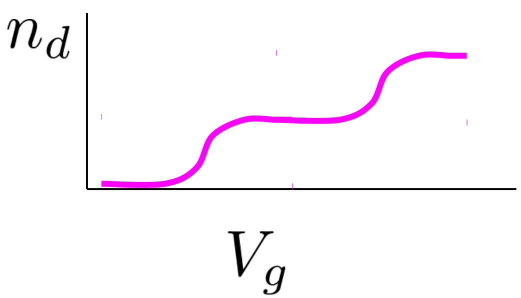
$$P_i = e^{-\beta E_i}/Z$$

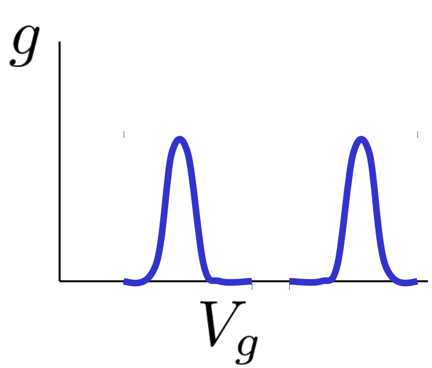
We expect two peaks of width $k_B T$ as a function of the gate voltage at $\epsilon_d = 0, -U$

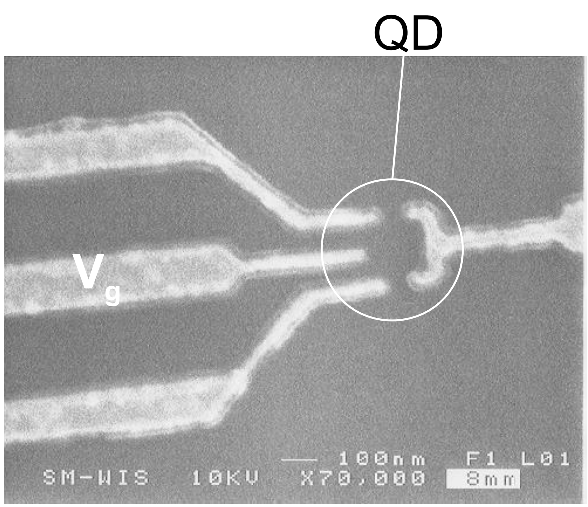
$$\epsilon_d \propto -V_g$$

At the charge degeneracy points.

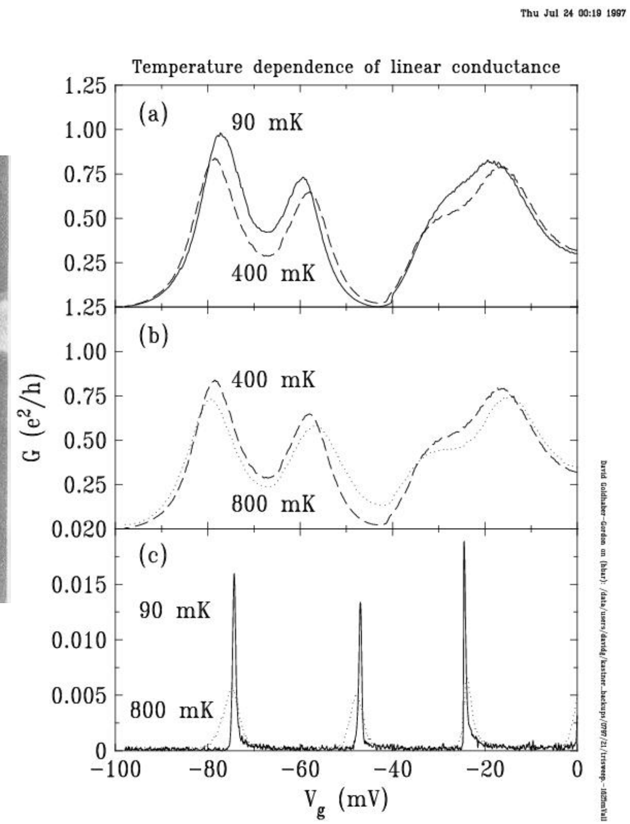




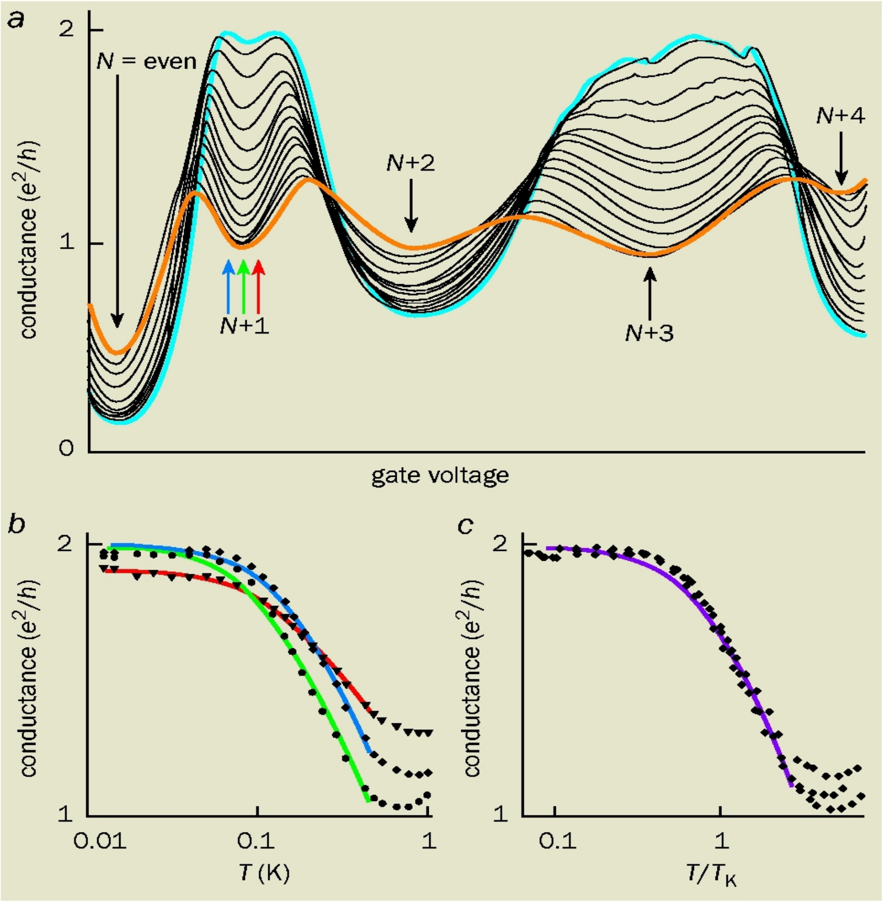


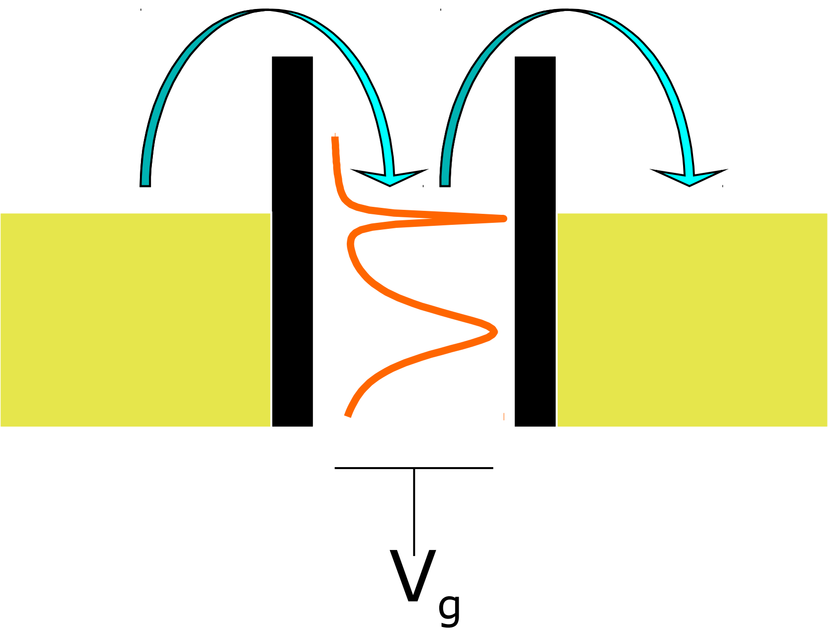


Goldhaber-Gordon et al
Nature 2000

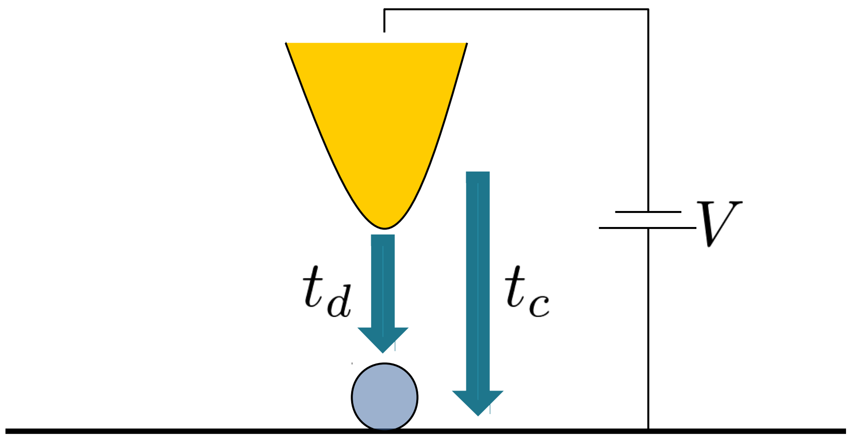


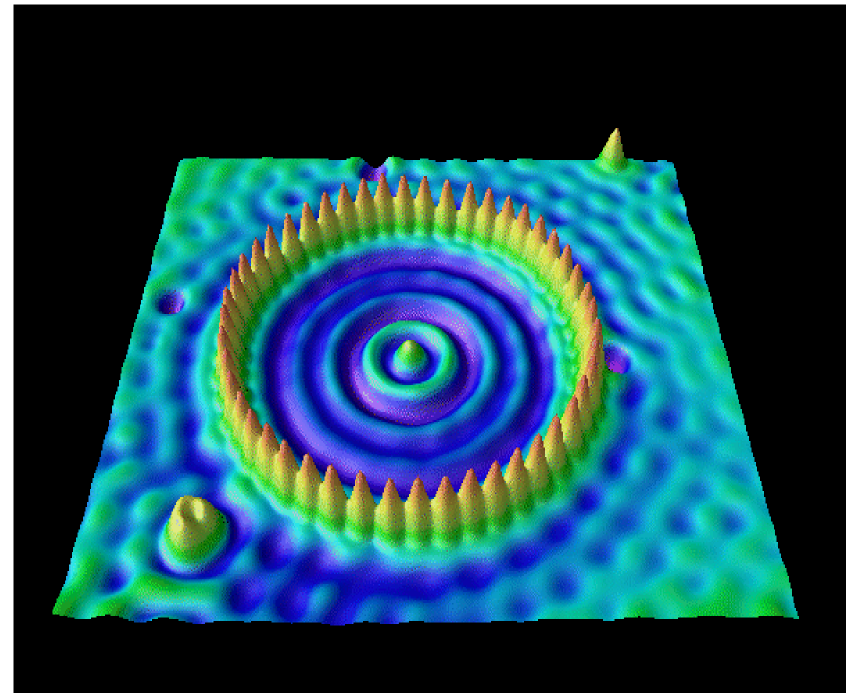
Kondo effect in quantum dots





Scanning tunneling miscroscopy



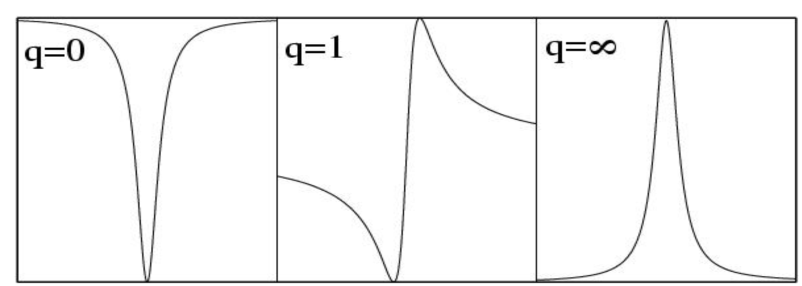


$$dI/dV \propto A_{STM}(V)$$

$$t_c \Psi_\sigma^\dagger + t_d d_\sigma^\dagger$$

Access to the spectral density

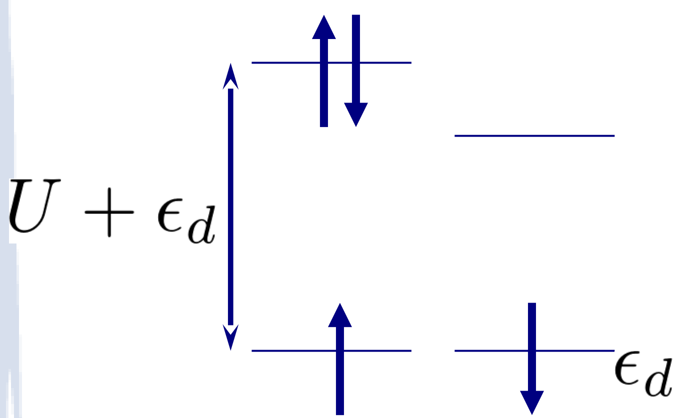
Fano lineshapes



$$q = t_d/t_c$$

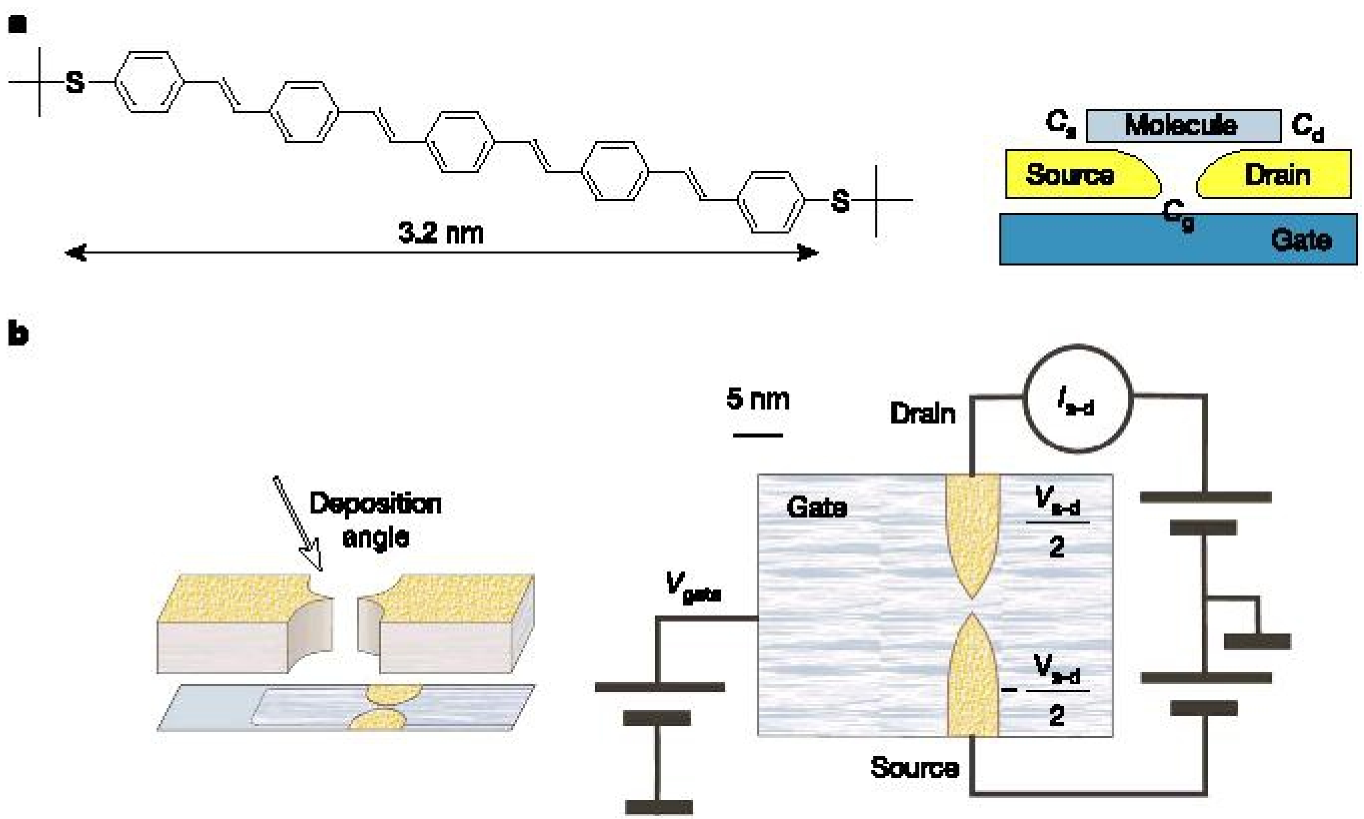
A molecule as a building block

- Large level quantization.
- Large charging energies.

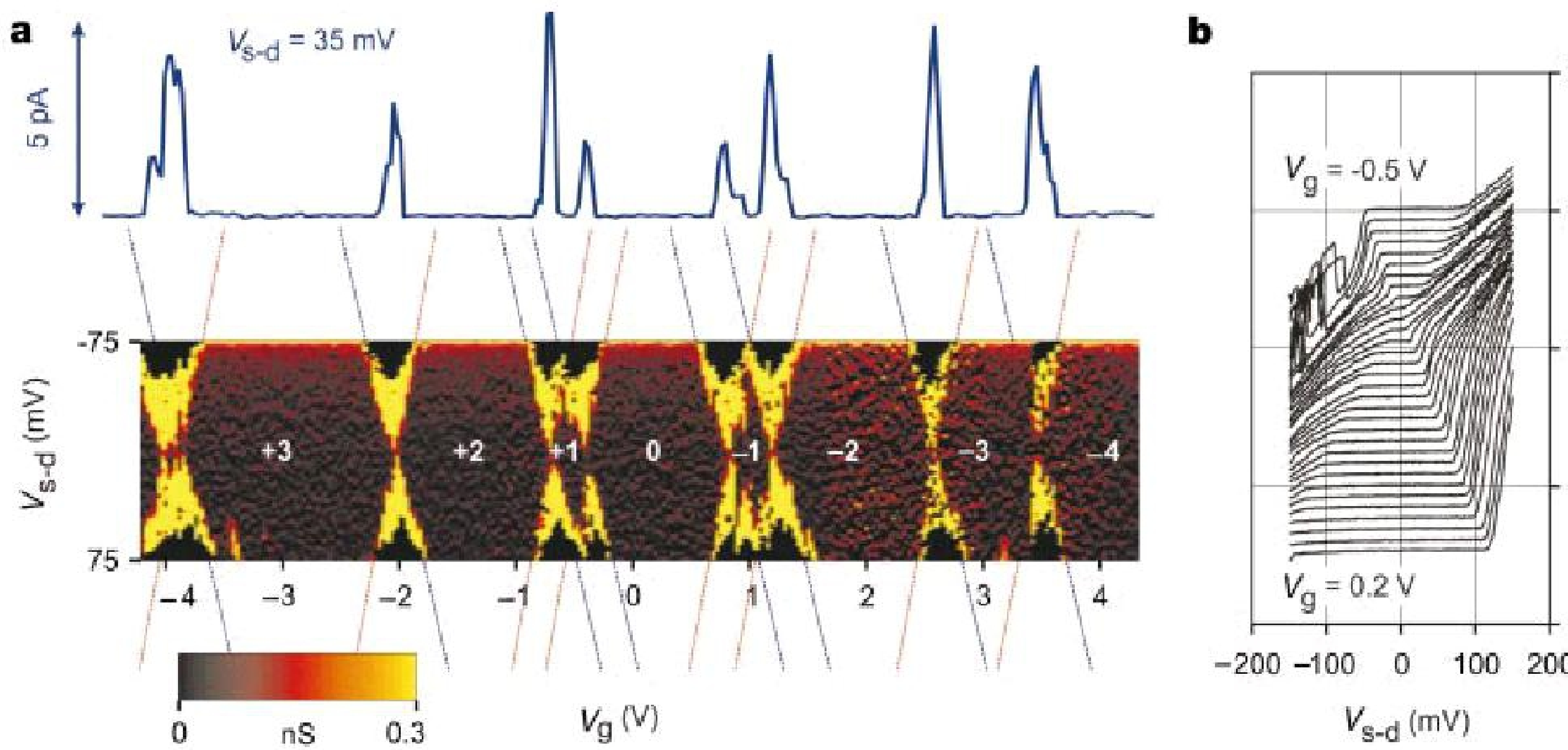


$$H_d = \epsilon_d(n_\uparrow + n_\downarrow) + U n_\uparrow n_\downarrow$$

Anderson model!

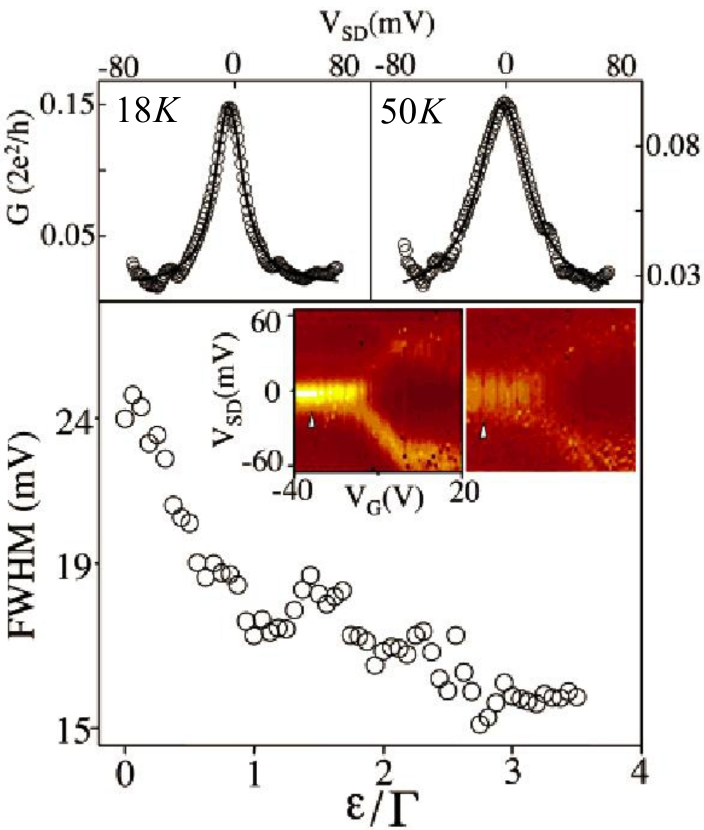


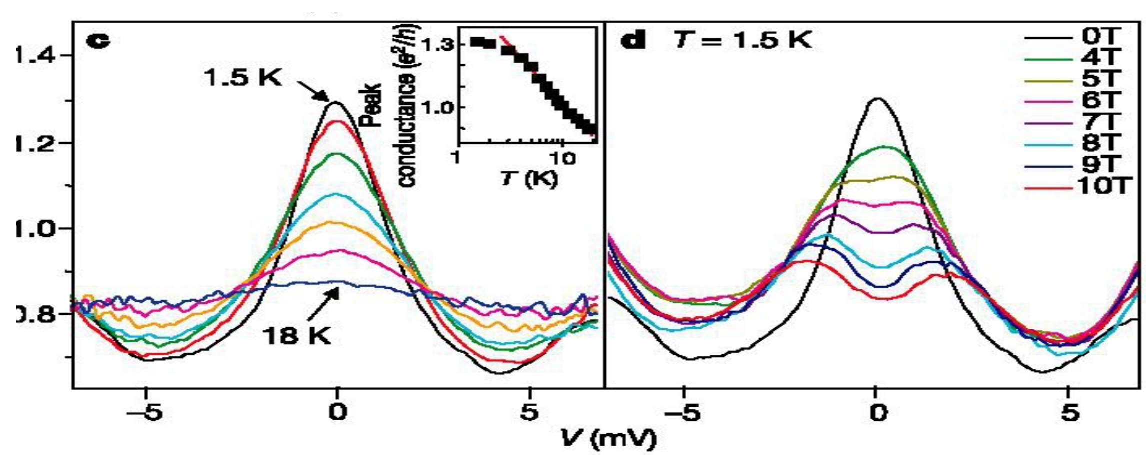
- S. Kubatkin et al., Nature 425, 698 (2003)



a
$V_{s\text{-}d}$ = 35 mV
5 pA
-75
$V_{s\text{-}d}$ (mV)
75
+3
+2
+1
0
−1
−2
−3
−4
−4
−3
−2
−1
0
1
2
3
4
0
nS
0.3
V_g (V)
b
V_g = -0.5 V
V_g = 0.2 V
25
0
−25
−50
−75
$I_{s\text{-}d}$ (pA)
−200
−100
0
100
200
$V_{s\text{-}d}$ (mV)

Kondo effect in molecules

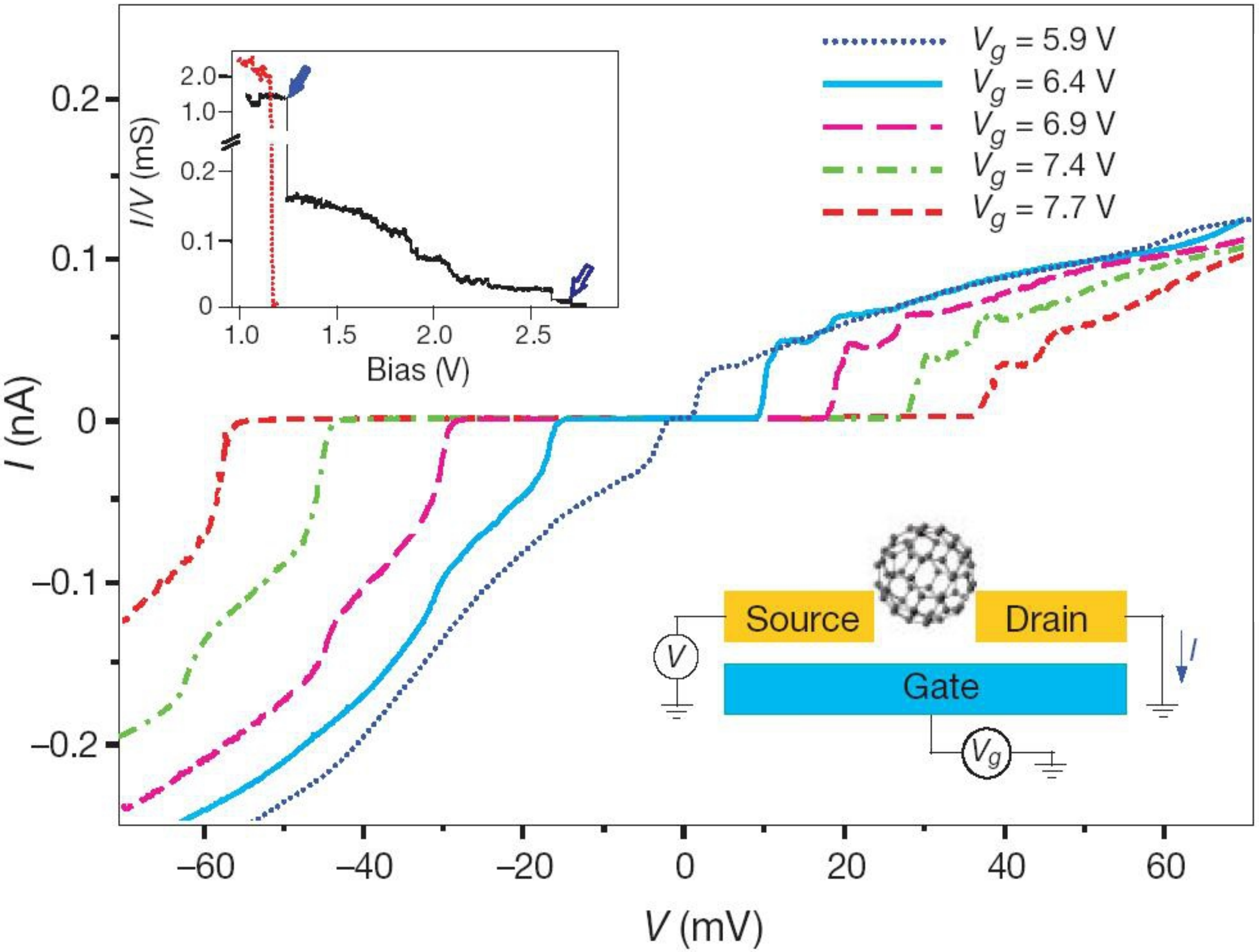


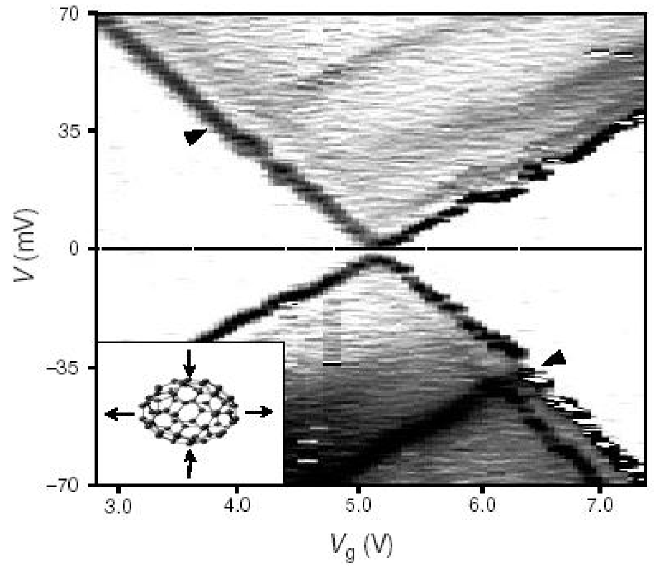


L.H. Yu and D. Natelson, Nano Lett. **4**, 79 (2004)

J. Park *et al.*, Nature **417**, 722 (2002)

Molecular vibrations





H. Park et al., Nature 407, 57 (2000)

Outline

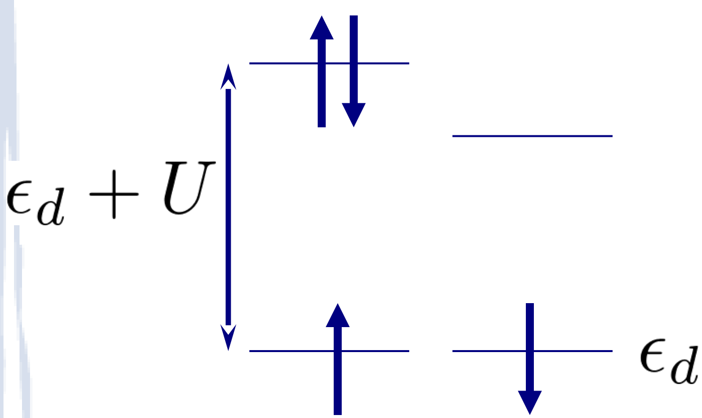
- Molecular vibrations
- Anderson-Holstein
- Negative U Kondo effect
- Franck Condon effect
- Franck Condon blockade and Kondo effect

Kondo effect in C60 molecular transistors:
L.H. Yu and D. Natelson, Nano Lett. 4, 79 (2004)
A.N. Pasupathy et al., Science 306, 86 (2004)

Phononic effects in Suspended Quantum dots:
E.M. Weig, et al., Phys. Rev. Lett. 92, 046804 (2004)

A molecule as a building block

- Large level quantization.
- Large charging energies.
- Electron vibron interaction: coupling to a mode with coordinate x and frequency ω_0



$$H_d = \epsilon_d(x)(n_\uparrow + n_\downarrow) + U n_\uparrow n_\downarrow + H_{phon}$$

$$\epsilon_d(x) \sim \epsilon_d + c_1(x - x_0) + \cdots$$

Quantum Harmonic Oscillator

$$H_{vib} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega_0^2 \hat{x}^2$$

$$a = \sqrt{\frac{m\omega_0}{2}} \left(\hat{x} + \frac{i}{m\omega_0}\hat{p}\right), \quad a^\dagger = \sqrt{\frac{m\omega_0}{2}} \left(\hat{x} - \frac{i}{m\omega_0}\hat{p}\right)$$

$$\hat{x} = \sqrt{\frac{1}{2m\omega_0}}(a + a^\dagger), \quad \hat{p} = i\sqrt{\frac{m\omega_0}{2}}(a^\dagger - a)$$

$$\mathrm{H}_{vib} = \omega_0 \left(a^\dagger a + \tfrac{1}{2}\right)$$

Isolated molecule

$$H_d = \epsilon_d n_d + U n_\uparrow n_\downarrow - \lambda(a^\dagger + a)(n_d - 1) + \omega_0 \left(\tfrac{1}{2} + a^\dagger a\right)$$

$$n_d = n_\uparrow + n_\downarrow$$

The Hamiltonian can be diagonalized on each charge sector using a phonon displacement operator

$$\tilde{U} = e^{\frac{\lambda}{\omega_0}(n_d - 1)(a^\dagger - a)} \qquad \tilde{U}^\dagger a \tilde{U} = a + \frac{\lambda}{\omega_0}(n_d - 1)$$

$$\tilde{H}_d = \tilde{U}^\dagger H_d \tilde{U}$$

$$\tilde{H}_d = \left(\epsilon_d + \frac{\lambda^2}{\omega_0}\right) n_d + \left(U - \frac{2\lambda^2}{\omega_0}\right) n_\uparrow n_\downarrow + \omega_0 \left(\tfrac{1}{2} + a^\dagger a\right) - \frac{\lambda^2}{\omega_0}$$

Isolated molecule

$$|0,m\rangle = |0\rangle e^{\frac{\lambda}{\omega_0}(a^\dagger - a)}|m\rangle$$
$$|\sigma,m\rangle = |\sigma\rangle|m\rangle$$
$$|2,m\rangle = |\uparrow\downarrow\rangle e^{-\frac{\lambda}{\omega_0}(a^\dagger - a)}|m\rangle$$

$$E_{0,m} = -\frac{\lambda^2}{\omega_0} + m\omega_0$$

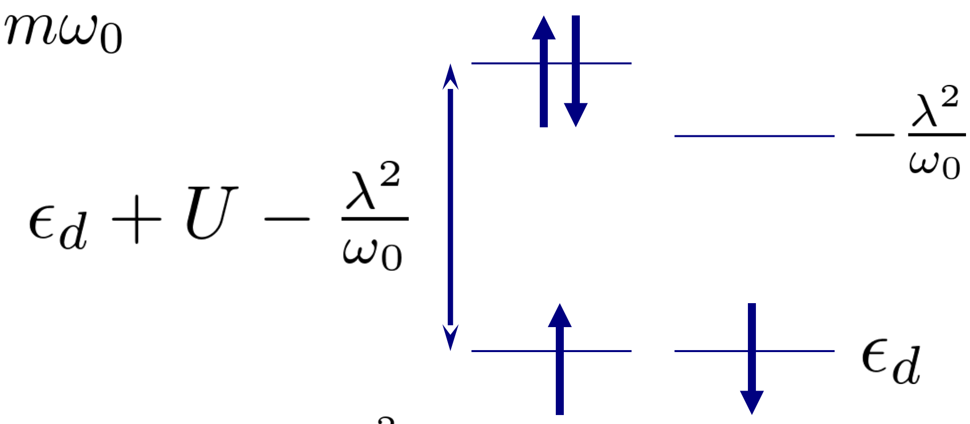
$$E_{\sigma,m} = \epsilon_d + m\omega_0$$

$$E_{2,m} = 2\epsilon_d + U - \frac{\lambda^2}{\omega_0} + m\omega_0$$

$$\tilde{U} = e^{\frac{\lambda}{\omega_0}(n_d - 1)(a^\dagger - a)}$$

$$\tilde{M}^+ = e^{\frac{\lambda}{\omega_0}(a^\dagger - a)}$$

$$\tilde{M}^- = e^{-\frac{\lambda}{\omega_0}(a^\dagger - a)}$$



$$U_{\text{eff}} = U - \frac{\lambda^2}{\omega_0}$$

Weak coupling to the leads $k_B T > \Gamma$

$$g = \frac{e^2}{\hbar}\frac{\Gamma}{k_B T}\sum_{\mu,\nu,m,n,\sigma} W(E_{\nu n}, E_{\mu m}, T)|\langle\Psi_{\nu n}|d_\sigma^\dagger|\Psi_{\mu m}\rangle|^2$$

$$W(E_{\nu n}, E_{\mu m}, T) = (P_{\mu m} + P_{\nu n})f(E_{\mu m} - E_{\nu n})f(E_{\nu n} - E_{\mu m})$$

$$P_{\mu m} = e^{-\beta E_{\mu,m}}/Z$$

$$|\langle\Psi_{\nu 0}|d_\sigma^\dagger|\Psi_{\mu 0}\rangle|^2 = |\langle\nu|d_\sigma^\dagger|\mu\rangle|^2|\langle 0|e^{\frac{\lambda}{\omega_0}(a^\dagger - a)}|0\rangle| = |\langle\nu|d_\sigma^\dagger|\mu\rangle|^2|e^{-\lambda^2/\omega_0^2}$$

Exponential supression of the tunneling due to the Franck-Condon effect: “Franck-Condon blockade”

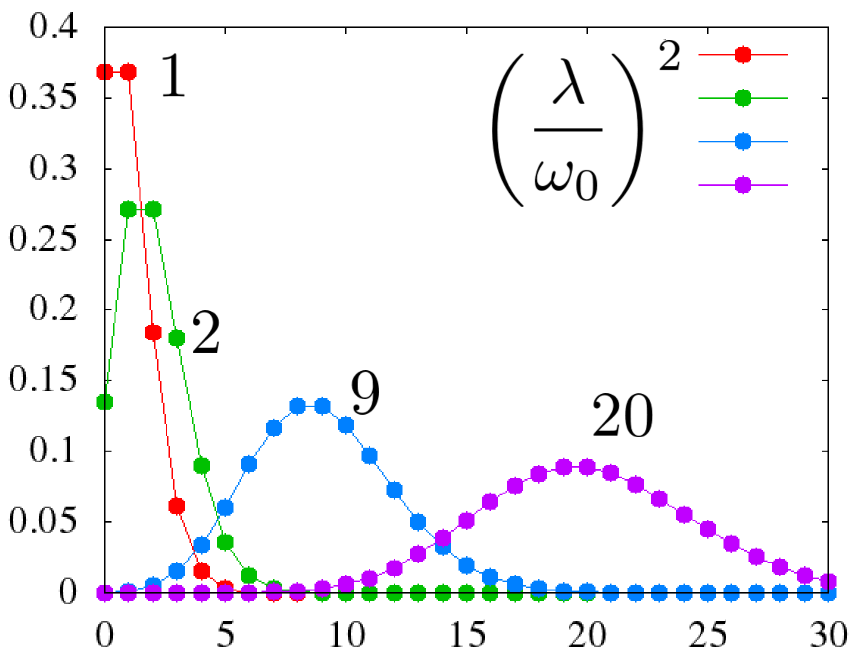
J. Koch and F. von Oppen Phys. Rev. Lett. **94**, 206804 (2005)
R. Leturcq *et al.* Nature Physics **5**, 327 (2009)

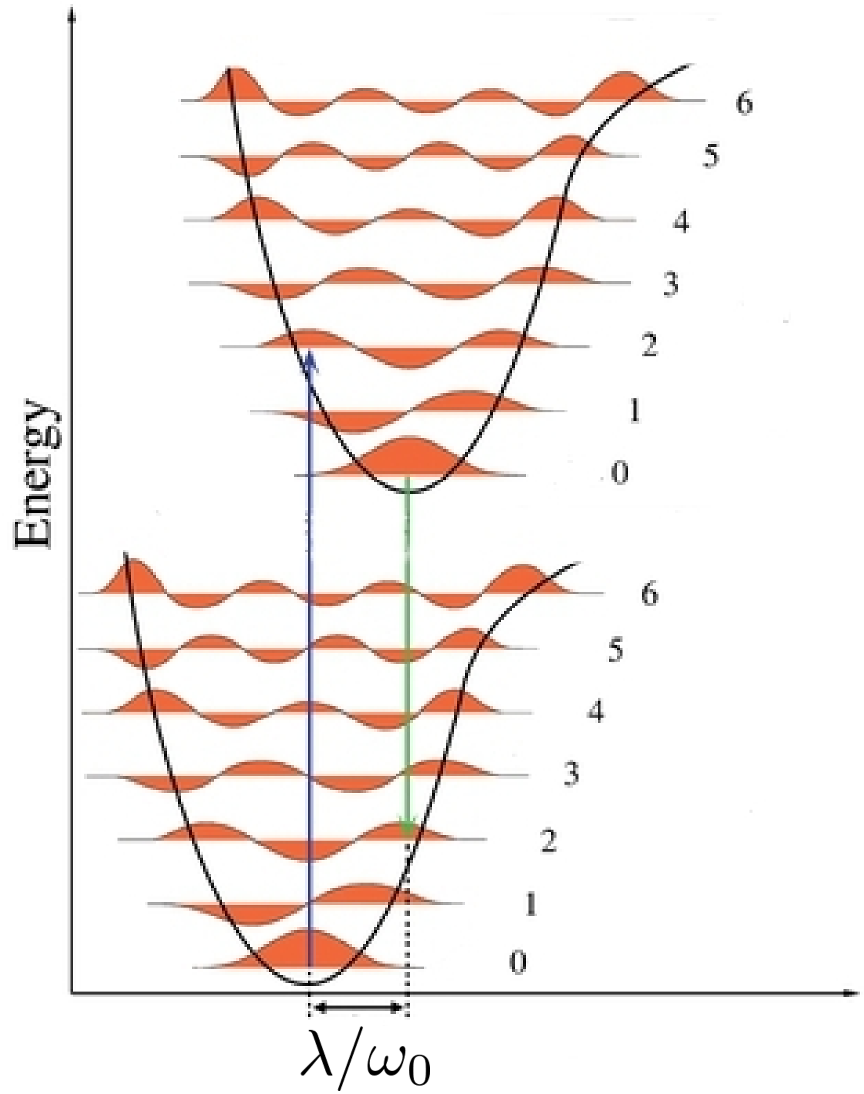
Franck Condon effect

$$|0,0\rangle \to |1,n\rangle$$

$$\gamma_{n,0}^2 = |\langle 0|e^{\frac{\lambda}{\omega_0}(a^\dagger - a)}|n\rangle|^2$$

$$= e^{-\lambda^2/\omega_0^2}\frac{\left(\frac{\lambda}{\omega_0}\right)^{2n}}{n!}$$

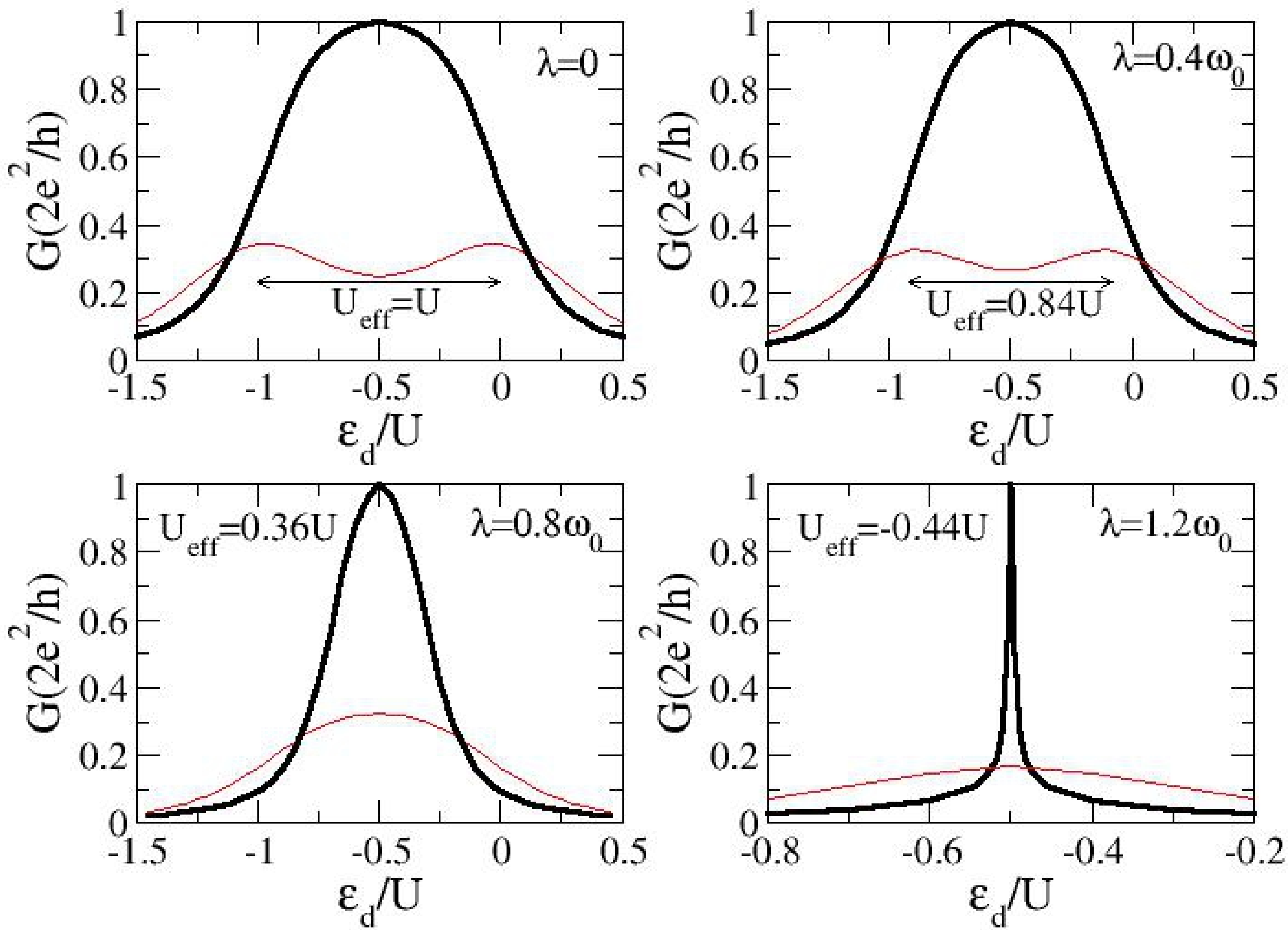




J. Franck Trans. Farad. Soc. ***21*** *536 (1926);*
E. Condon Phys. Rev. ***28*** *1182(1926)*

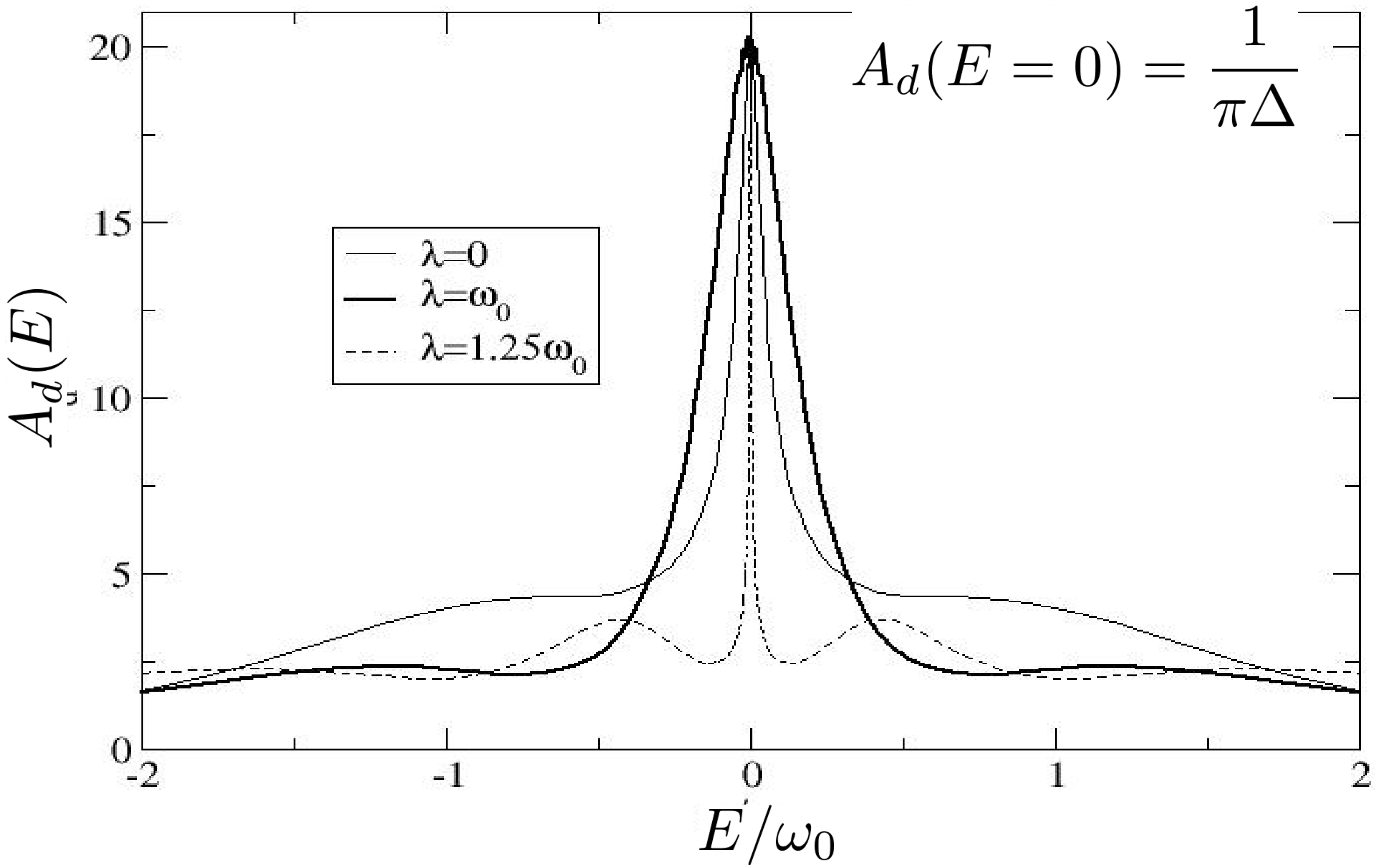
NRG results

Zero-bias conductance vs. gate voltage at low (black) and high temperatures.



[PRL 2004]

Spectral density $(\epsilon_d = -U/2)$



Schrieffer Wolff transformation

$U_{\text{eff}} > 0$

$|\uparrow\downarrow\rangle e^{-\frac{\lambda}{\omega_0}(a^\dagger - a)}|m\rangle$

H_V

$|0\rangle e^{\frac{\lambda}{\omega_0}(a^\dagger - a)}|m\rangle$

H_V

$$E_{2,m} = 2\epsilon_d + U - \frac{\lambda^2}{\omega_0} + m\omega_0$$

$|\downarrow\rangle|0\rangle$

$$E_{0,m} = -\frac{\lambda^2}{\omega_0} + m\omega_0$$

$|\uparrow\rangle|0\rangle$

$E_\downarrow = \epsilon_d$

intermediate states

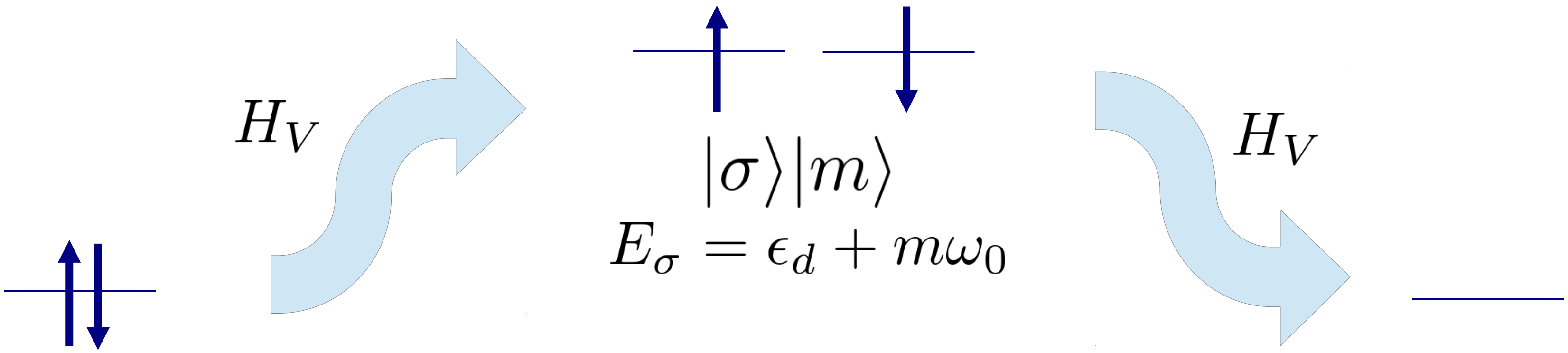
$E_\uparrow = \epsilon_d$

$$J_K = V^2 \sum_m \gamma_{0,m}^2 \left(\frac{1}{-\epsilon_d + m\omega_0 - \frac{\lambda^2}{\omega_0}} + \frac{1}{U + \epsilon_d + m\omega_0 - \frac{\lambda^2}{\omega_0}} \right)$$

Kondo Hamiltonian with modified couplings

Schrieffer Wolff transformation

$U_{\text{eff}} < 0$



$|\sigma\rangle |m\rangle$

$E_\sigma = \epsilon_d + m\omega_0$

$| \uparrow\downarrow\rangle e^{-\frac{\lambda}{\omega_0}(a^\dagger - a)}|0\rangle$

intermediate states

$|0\rangle e^{\frac{\lambda}{\omega_0}(a^\dagger - a)}|0\rangle$

$$J_K^\perp = V^2 \sum_m \gamma_{0,m}^2 \left(\frac{(-1)^m}{-\epsilon_d + m\omega_0 - \frac{\lambda^2}{\omega_0}} + \frac{(-1)^m}{U + \epsilon_d + m\omega_0 - \frac{\lambda^2}{\omega_0}} \right)$$

$$J_K^{||} = V^2 \sum_m \gamma_{0,m}^2 \left(\frac{1}{-\epsilon_d + m\omega_0 - \frac{\lambda^2}{\omega_0}} + \frac{1}{U + \epsilon_d + m\omega_0 - \frac{\lambda^2}{\omega_0}} \right)$$

Anisotropic Kondo Hamiltonian for the pseudospin:

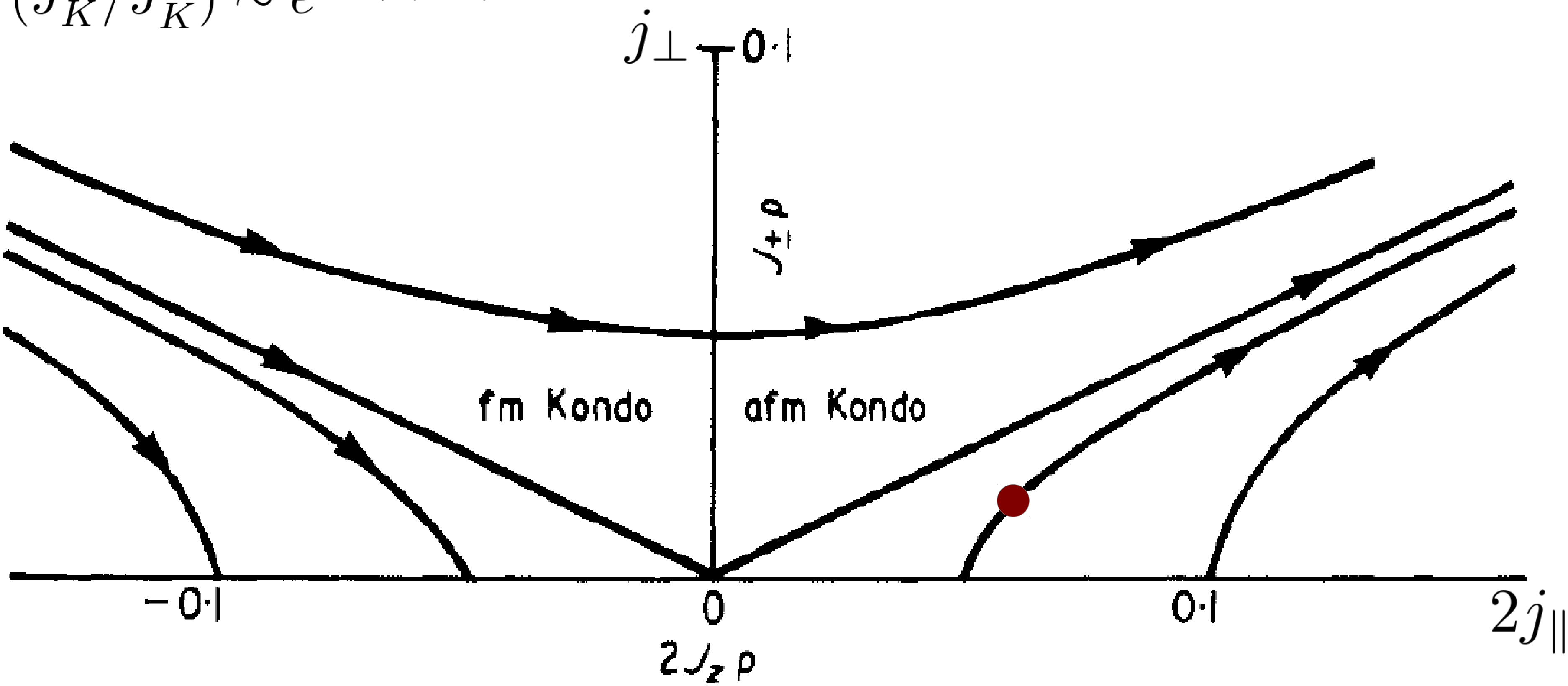
$| \Uparrow\rangle = |0\rangle, | \Downarrow\rangle = | \uparrow\downarrow\rangle$

Charge Kondo effect (anisotropic Kondo)

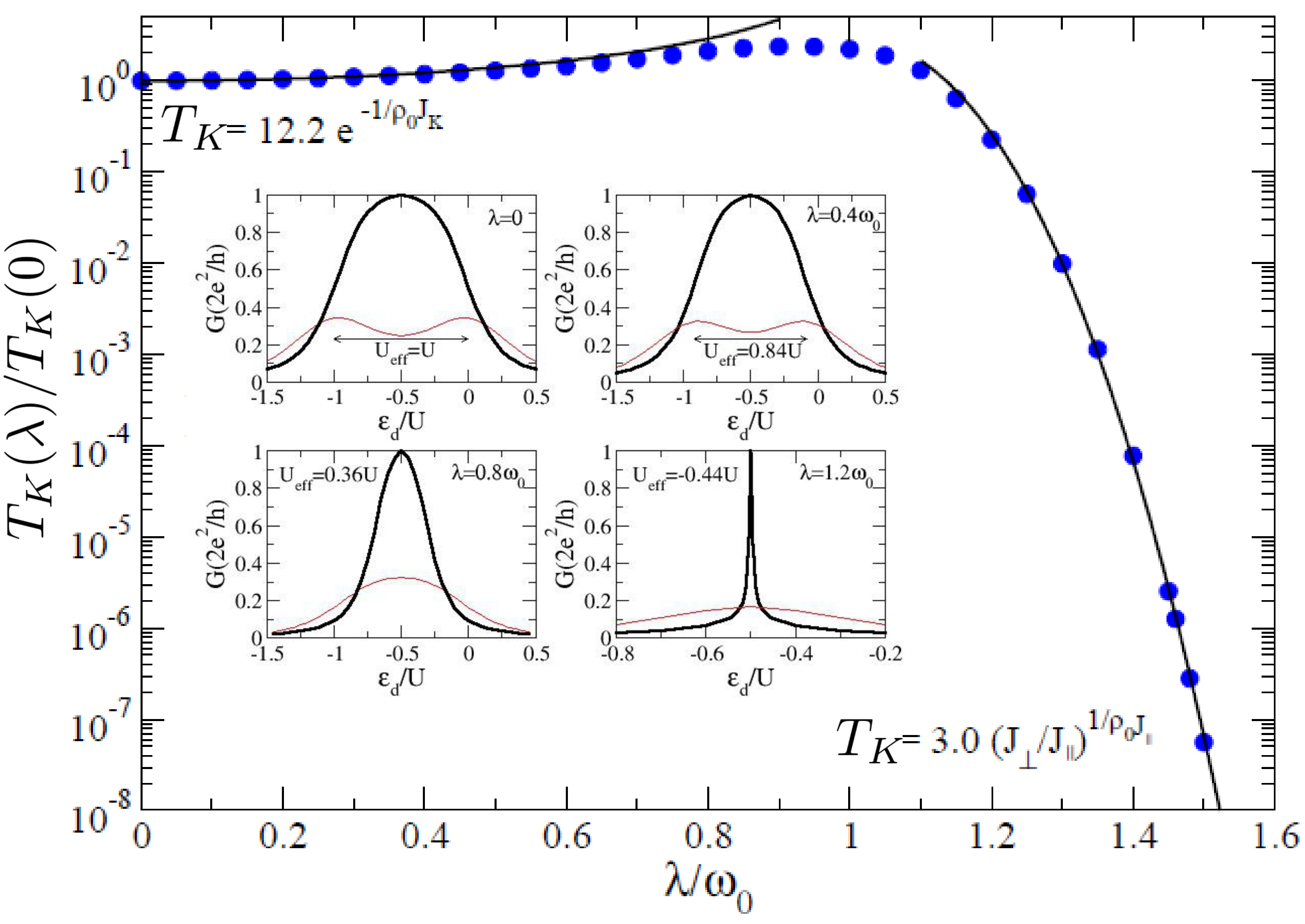
$$\frac{dj_\perp}{d\ln D} = -2j_\parallel j_\perp \qquad \frac{dj_\parallel}{d\ln D} = -2j_\perp^2$$

$$T_K \sim D(J_K^\perp/J_K^\parallel)e^{1/\rho_0 J_K^\parallel}$$

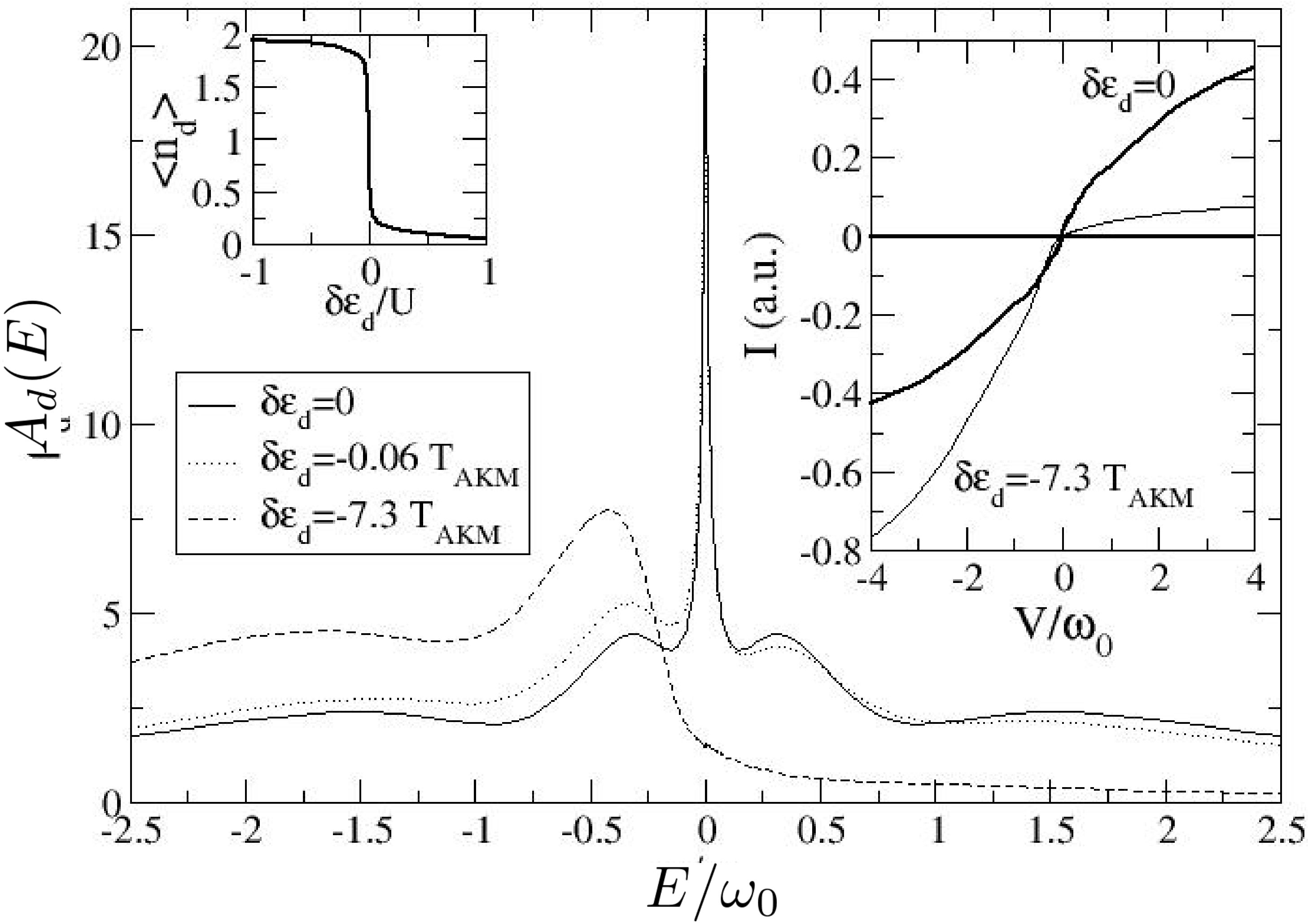
$$(J_K^\perp/J_K^\parallel) \sim e^{-2(\lambda/\omega_0)^2}$$



Kondo temperature



Charge Kondo effect

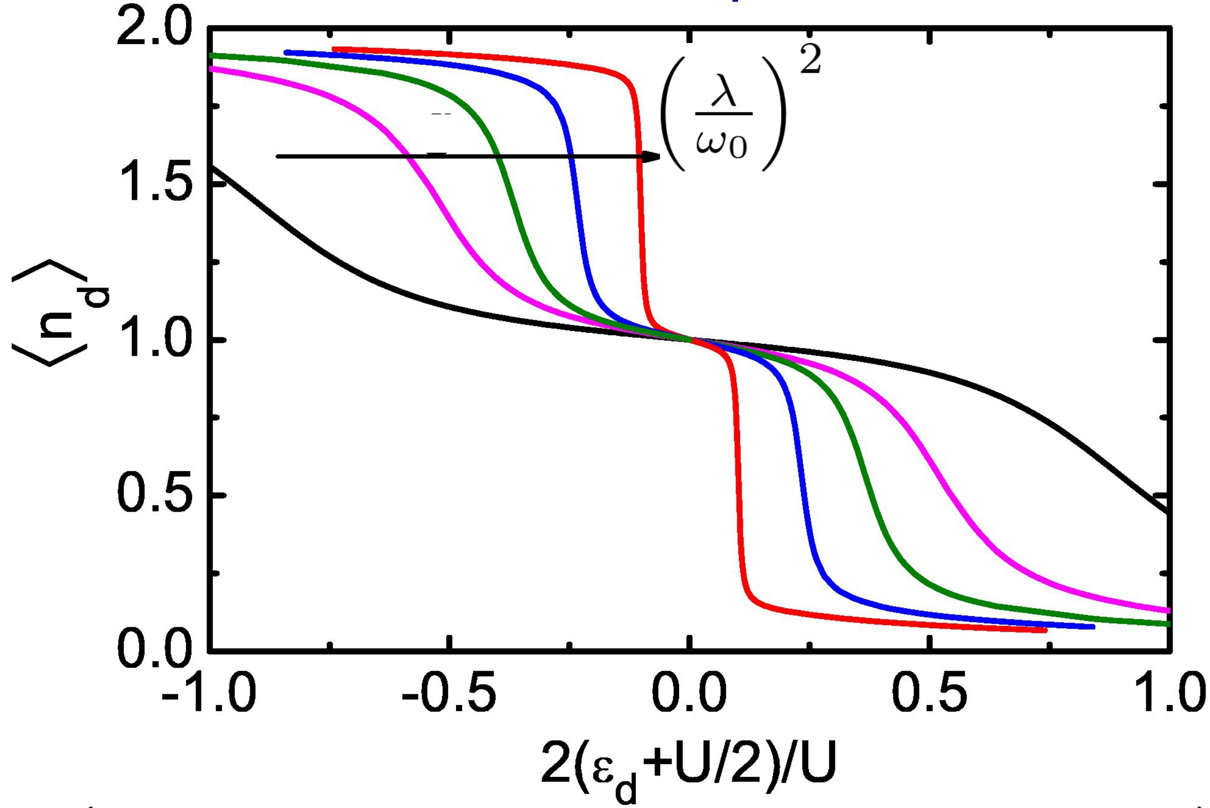


A small gate voltage destroys the charge Kondo effect but there no peak splitting as in the spin-Kondo with a magnetic field.

Spin-Kondo effect and vibrations

$$\Gamma \propto \Gamma_0 e^{-\lambda^2/\omega_0^2}$$

Level occupation



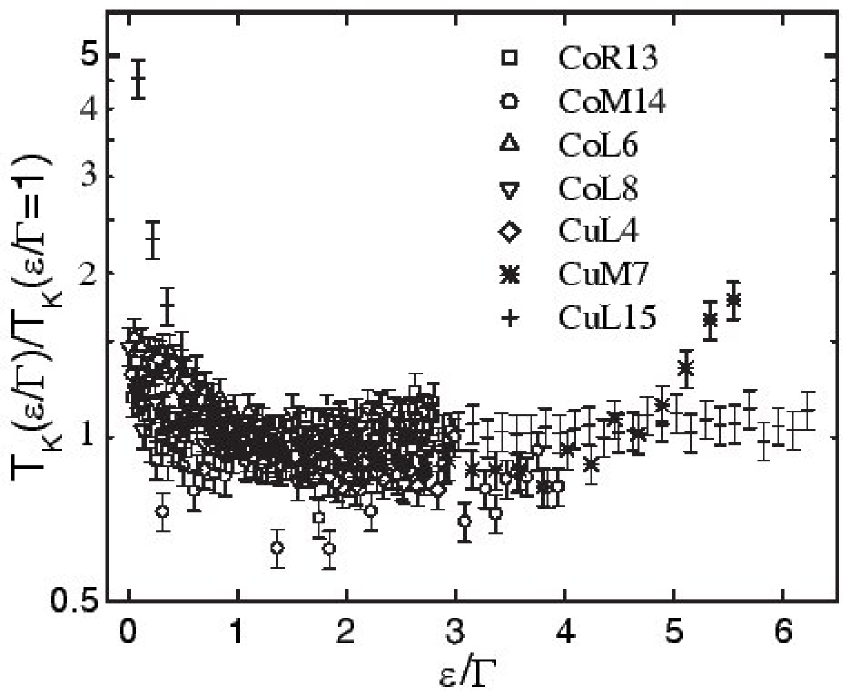
peaked at
$m^\star = (\lambda/\omega_0)^2$

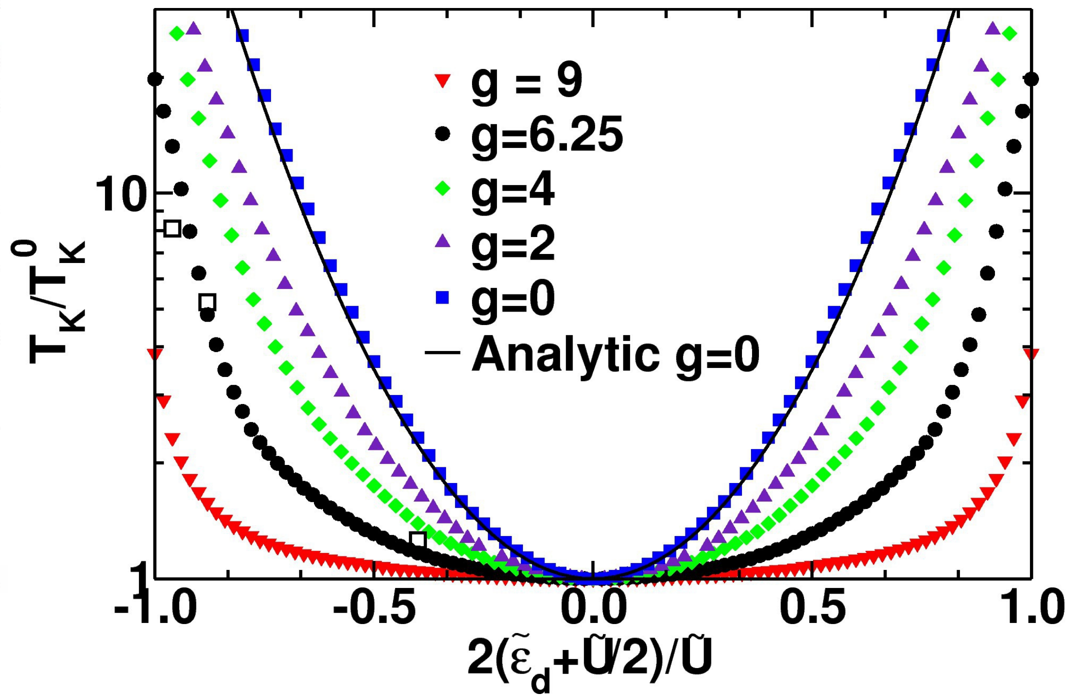
$$J_K = V^2 \sum_m \gamma_{0,m}^2 \left(\frac{1}{-\epsilon_d + m\omega_0 - \frac{\lambda^2}{\omega_0}} + \frac{1}{U + \epsilon_d + m\omega_0 - \frac{\lambda^2}{\omega_0}} \right)$$

$$\sim V^2 \left(\frac{1}{-\epsilon_d} + \frac{1}{U+\epsilon_d} \right) \equiv J_K(\lambda = 0)$$

Spin-Kondo effect and vibrations

$$g = \left(\frac{\lambda}{\omega_0}\right)^2$$



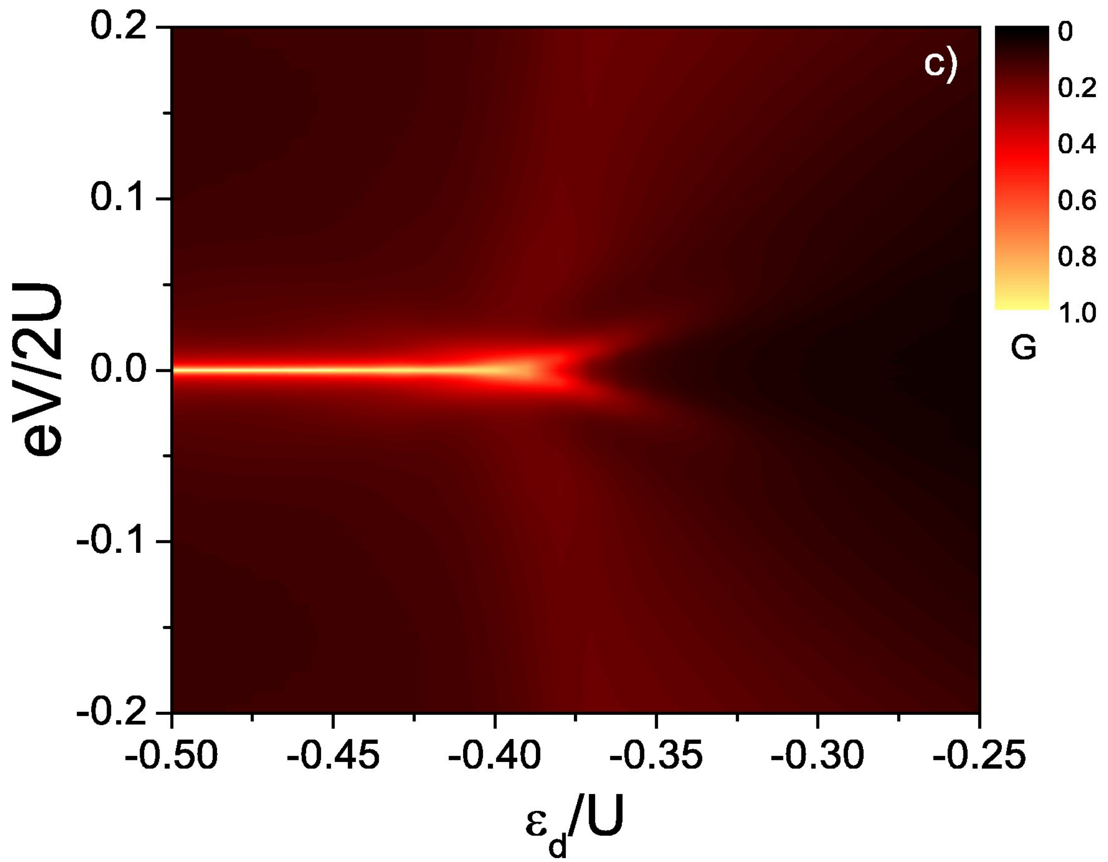


L.H. Yu et al. Phys. Rev. Lett. **95**, 256803 (2005)
PSC, G. Usaj, and C.A. Balseiro, PRB R (2007)

Other electron phonon couplings

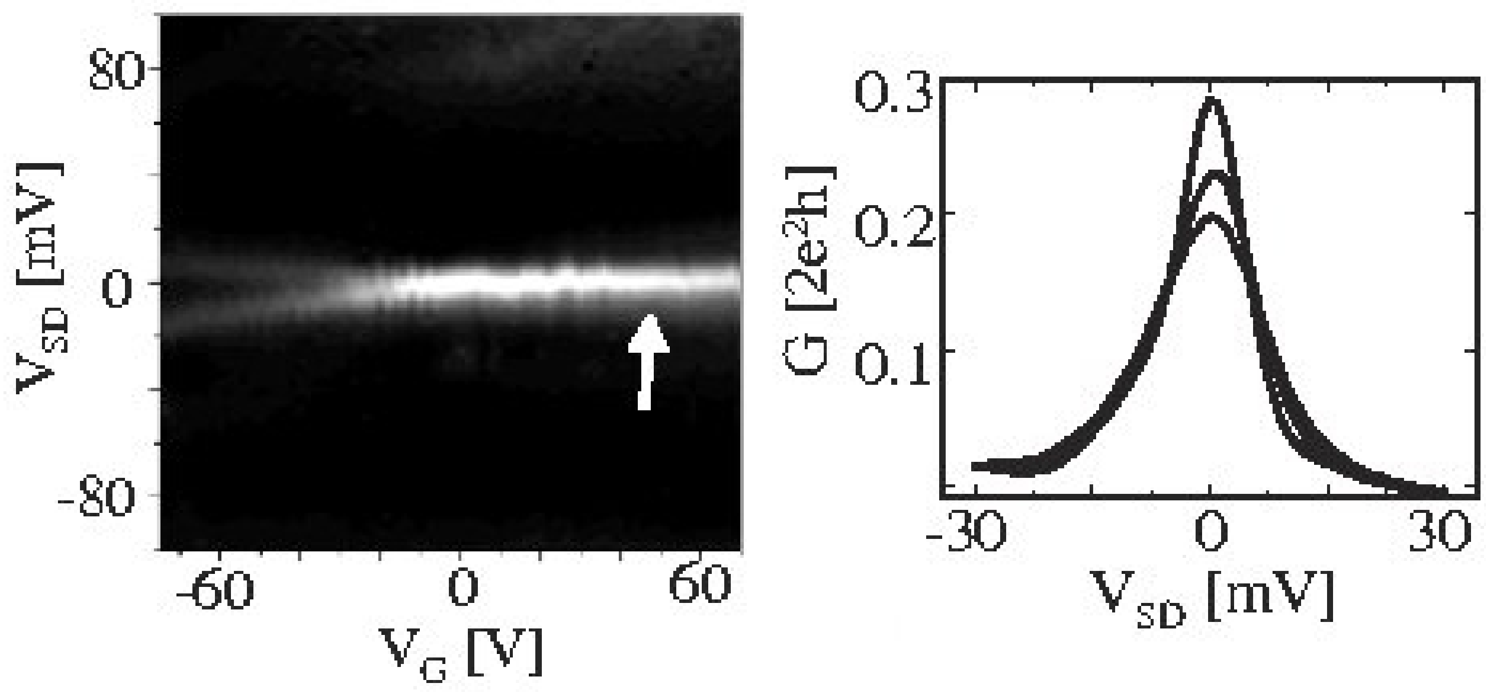
- Breathing modes
  - Effective hybridization
- Shuttle modes
  - New channel opening: no longer possible to map the left and right leads to a single electron bath.
- Stretching modes
  - Coupling to magnetic anisotropy can change the nature of ground state in magnetic molecules [PRB (2012)]

Coulomb blockade diamond edges



$$g(V) \sim \frac{2e^2}{h}\pi\Gamma\left[A_d(V/2) + A_d(-V/2)\right]$$

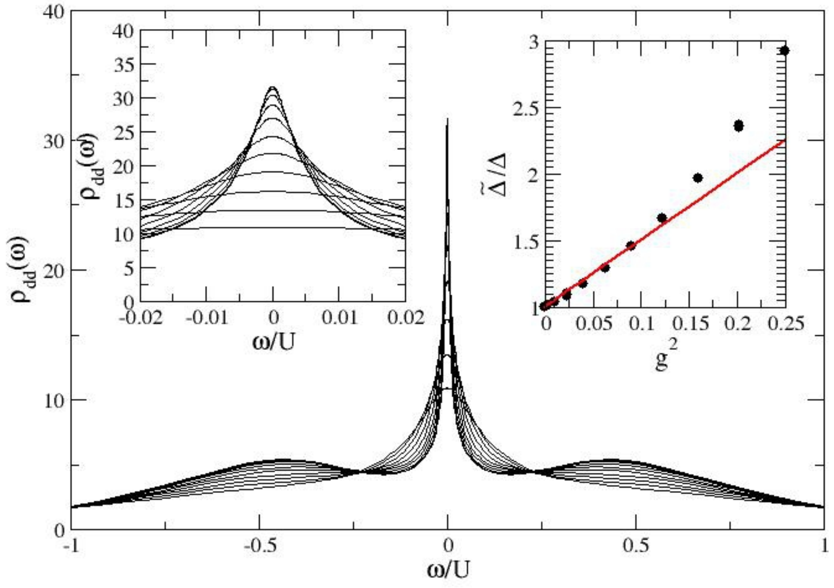
Coulomb blockade diamond edges

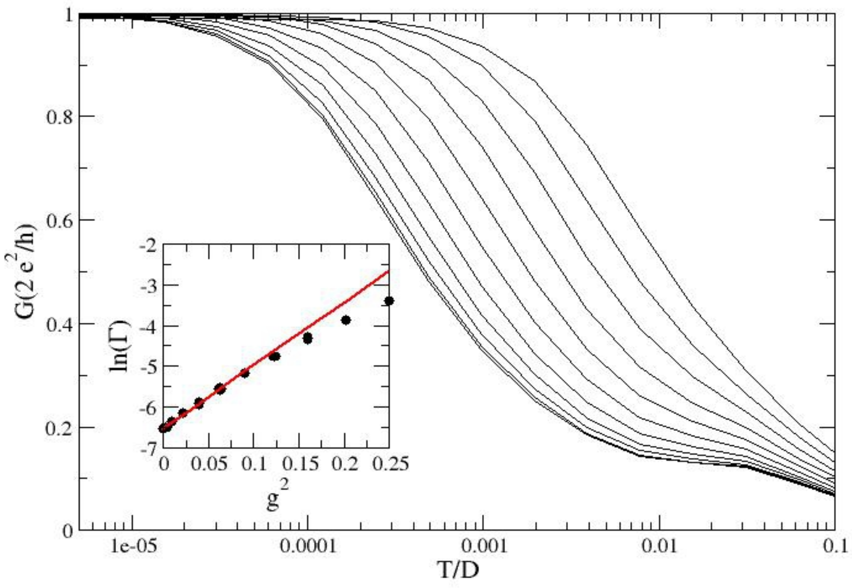


Conclusions

- The electron vibron interaction in molecular transistors leads to a rich variety of behavior:
  - New anisotropic charge Kondo effect
  - Anomalous gate-voltage dependence of the Kondo temperature.
  - Blurring of Coulomb-blockade diamond edges due to Franck-Condon effects.
  - Conduction channel opening (asymmetric coupling)
- Next lecture:
  - Exotic Kondo effects in double quantum dots and magnetic molecules.

Breathing mode





Breathing mode