STM – single molecule transport:

LUMO – HOMO current steps, charging effects, vibrational effects

D.A. Ryndyk

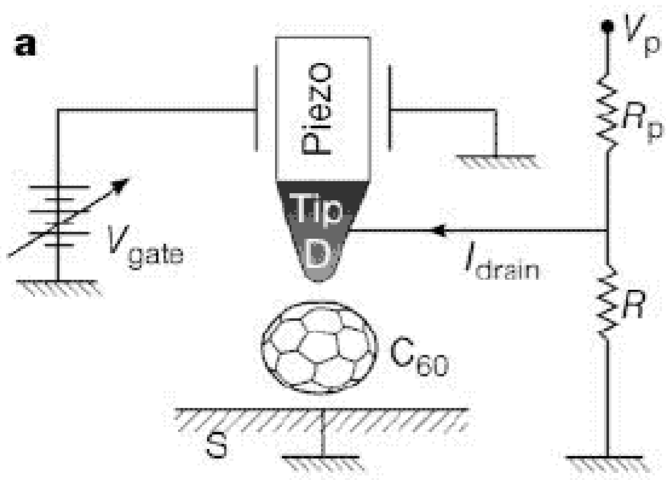
Universität Regensburg

Outline

- Recent experiments.
- Noninteracting transport.
- Charging effects.
- Vibrational effects.

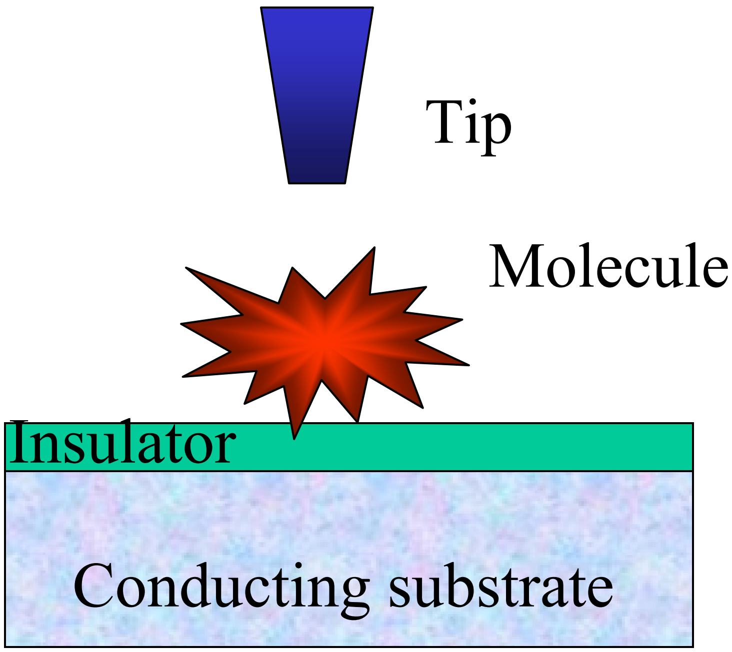
Recent experiments

- **STM-molecular junction**



(from Joachim, Gimzewski, Aviram, Nature 2000)

- **With insulating barrier**

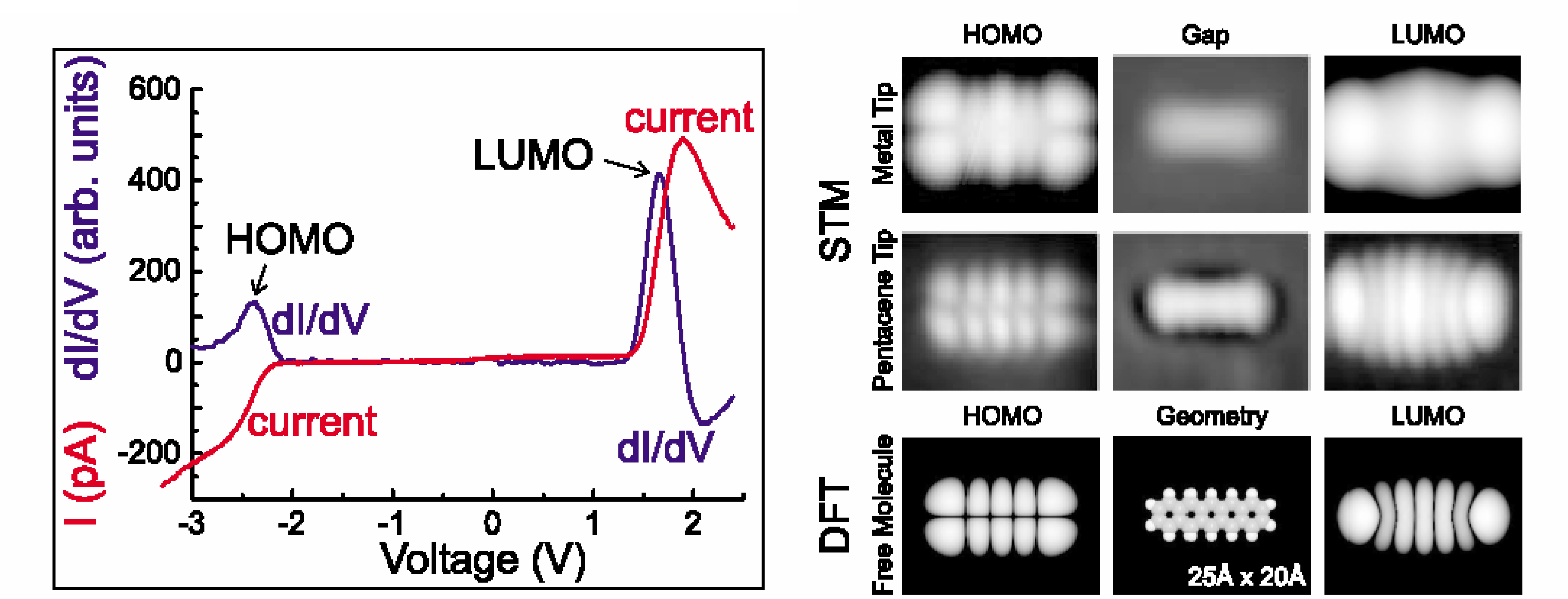


PRL 94, 026803 (2005) PHYSICAL REVIEW LETTERS week ending 21 JANUARY 2005

Molecules on Insulating Films: Scanning-Tunneling Microscopy Imaging of Individual Molecular Orbitals

Jascha Repp and Gerhard Meyer
IBM Research, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

Sladjana M. Stojković, André Gourdon, and Christian Joachim
CEMES-CNRS, 29 rue J. Marvig, P.O. Box 4347, F-31055 Toulouse Cedex, France
(Received 23 September 2004; published 19 January 2005)



Pentacene molecules on one and two layers of NaCl on Cu(111).

Atomic Scale Conductance Induced by Single Impurity Charging

N. A. Pradhan, N. Liu, C. Silien,* and W. Ho†

Department of Physics and Astronomy and Department of Chemistry, University of California, Irvine, California 92697-4575, USA

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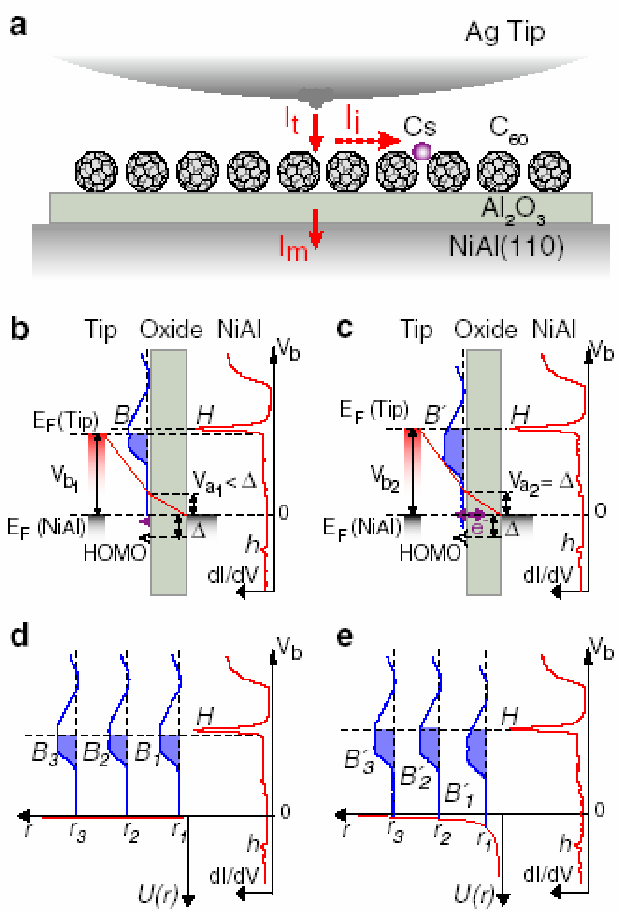
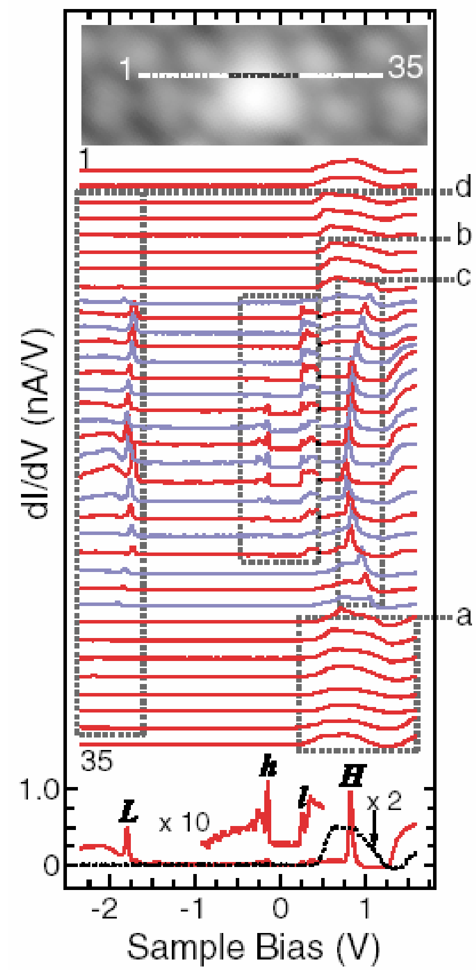
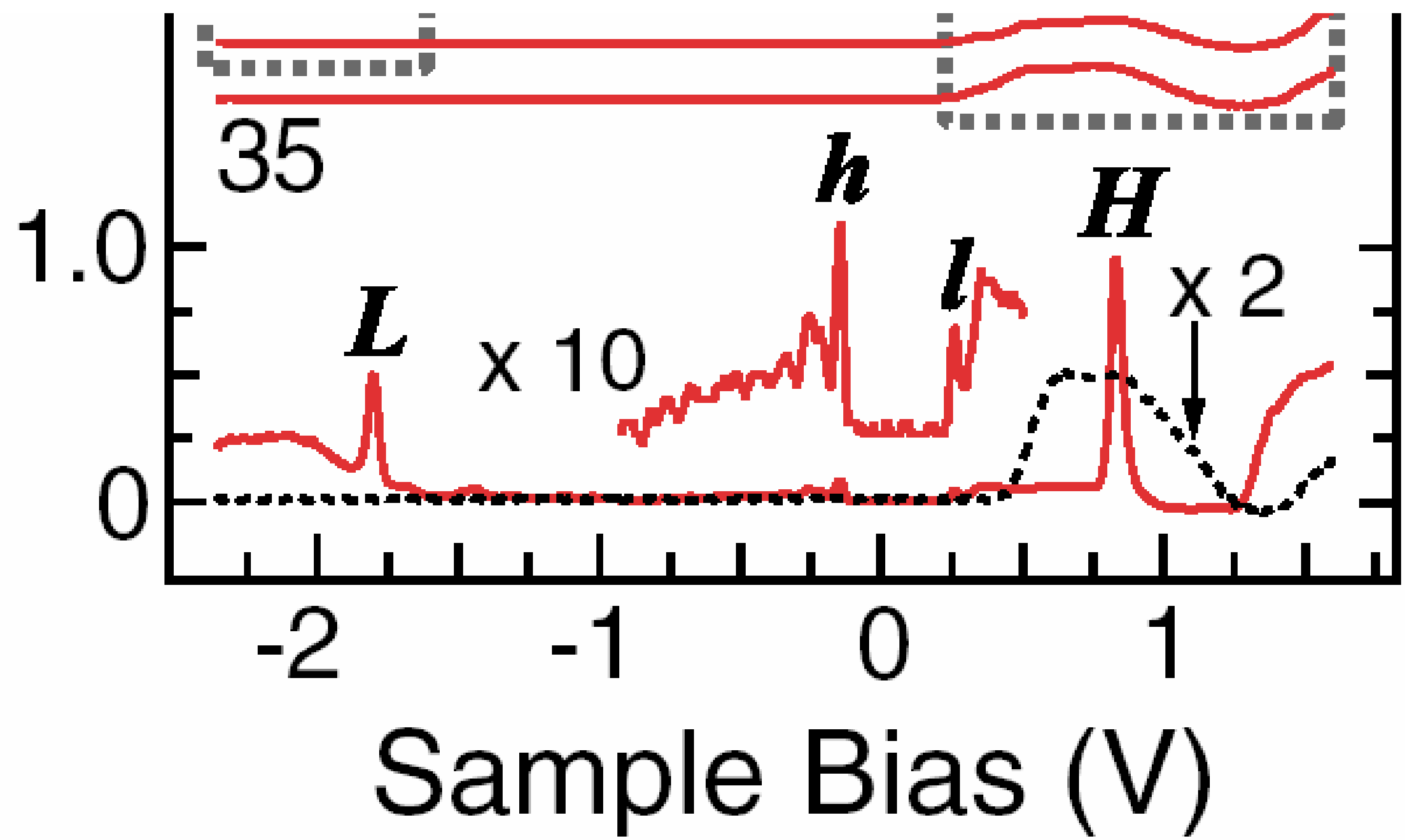
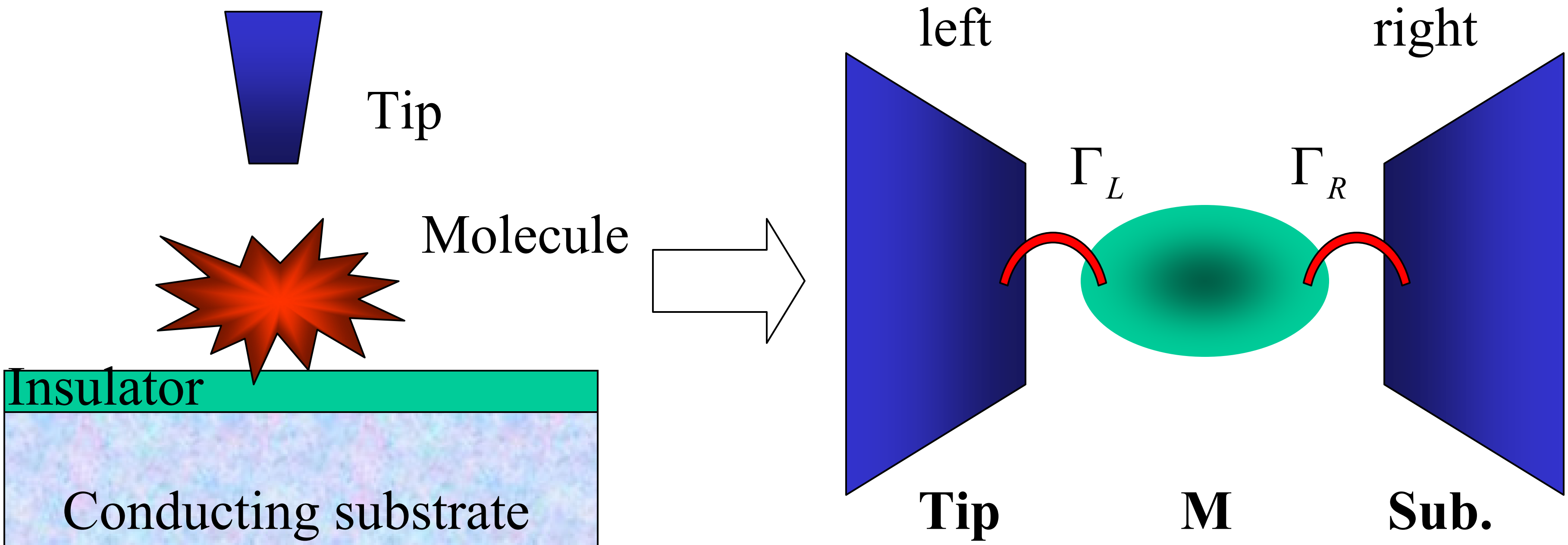






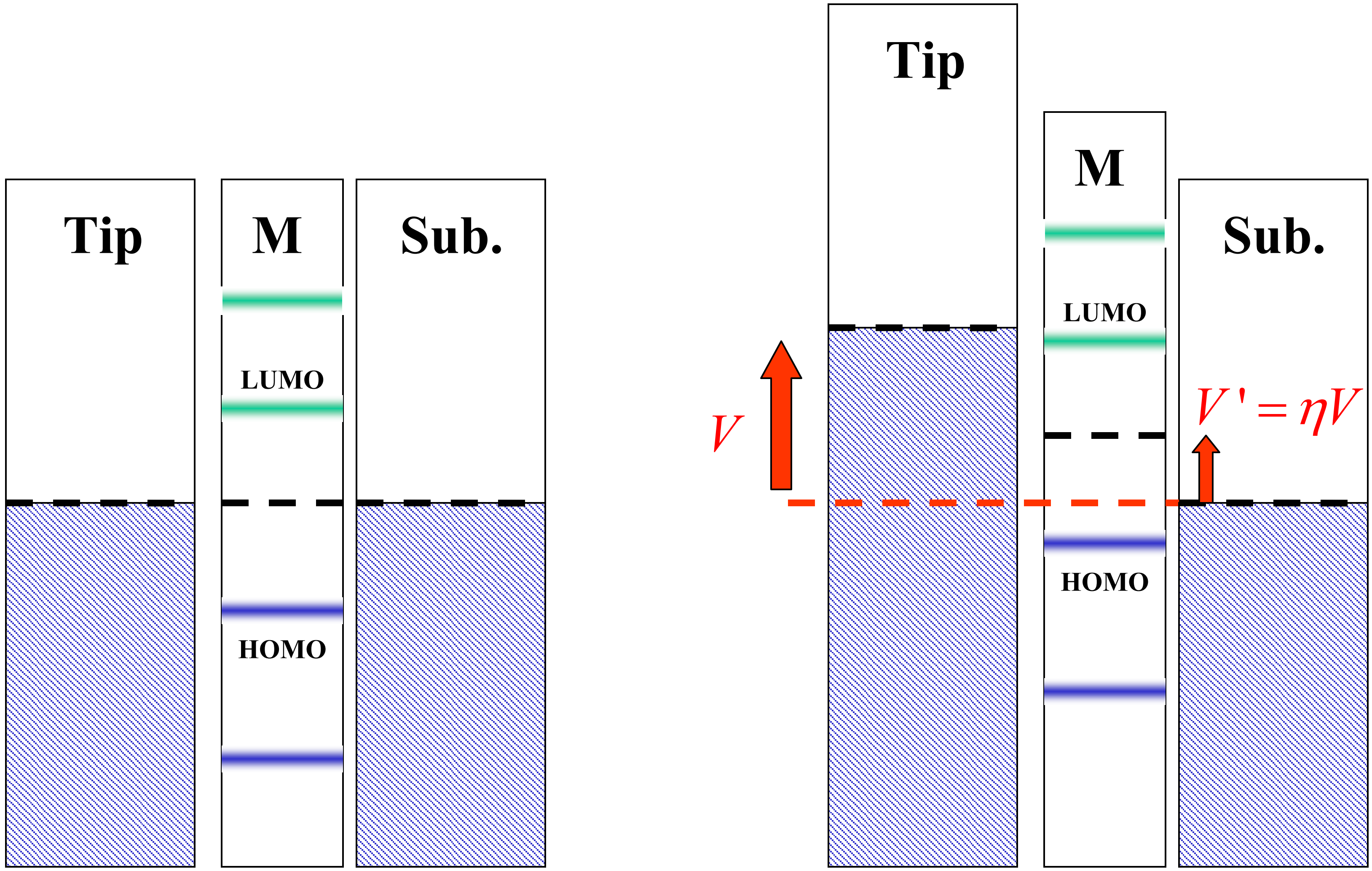
35
1.0
0
L
x 10
h
l
H
x 2
-2
-1
0
1
Sample Bias (V)

Noninteracting transport



$$\Gamma_L \ll \Gamma_R$$

Energy diagrams



Equilibrium

Finite voltage

Equations

$$J_{i=L,R} = \frac{ie}{\hbar}\int\frac{d\varepsilon}{2\pi}\mathrm{Tr}\left\{\boldsymbol{\Gamma}_i\left(\varepsilon - e\varphi_i\right)\left[\mathbf{G}^<\left(\varepsilon\right) + f_i^0\left(\varepsilon - e\varphi_i\right)\left[\mathbf{G}^R\left(\varepsilon\right) - \mathbf{G}^A\left(\varepsilon\right)\right]\right]\right\}$$

$$\boldsymbol{\Gamma}_{i=L(R)}\left(\varepsilon\right) = \Gamma_{i\alpha\beta} = 2\pi\sum_{k\sigma}V_{ik\sigma,\beta}V^*_{ik\sigma,\alpha}\delta\left(\varepsilon - \varepsilon_{ik\sigma}\right)$$

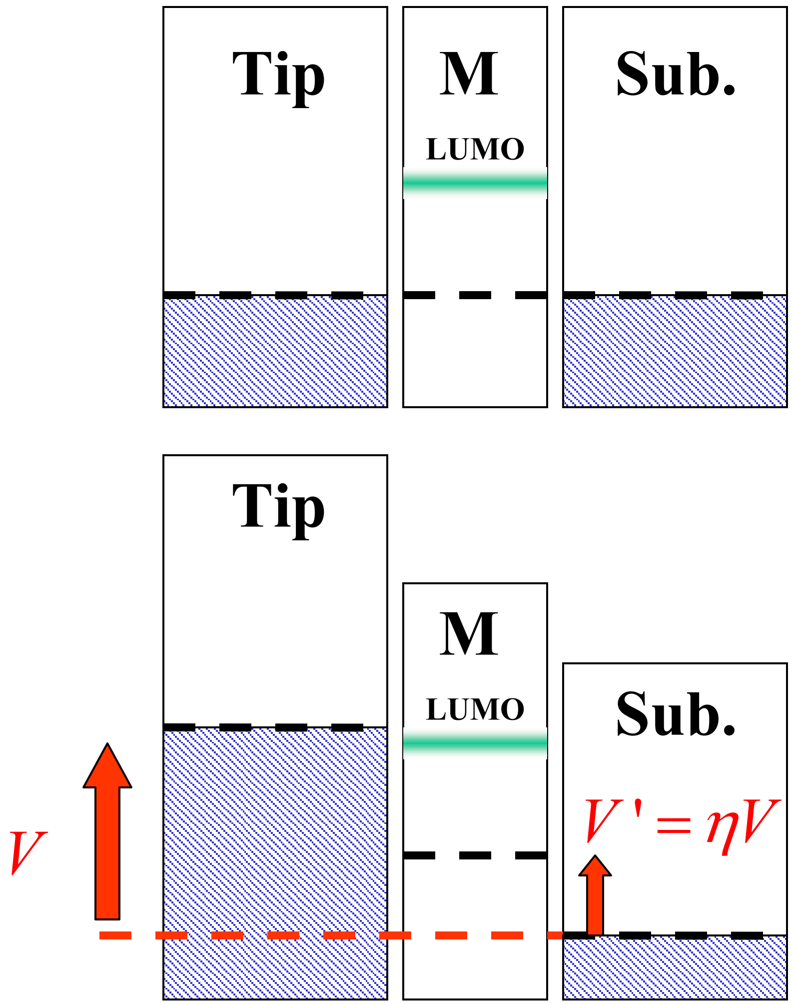
Assume that the spectral function $\mathbf{A}\left(\varepsilon\right) = i\left[\mathbf{G}^R\left(\varepsilon\right) - \mathbf{G}^A\left(\varepsilon\right)\right]$

is *equilibrium* and *diagonal*.

$$J_{i=L,R} = \frac{e}{\hbar}\int\frac{d\varepsilon}{2\pi}\sum_{\alpha}\left\{\Gamma_{i\alpha}\left(\varepsilon - e\varphi_i\right)A_\alpha\left(\varepsilon\right)\left[f_i^0\left(\varepsilon - e\varphi_i\right) - f_\alpha\left(\varepsilon\right)\right]\right\}$$

$$f_\alpha\left(\varepsilon\right) = \frac{\Gamma_{L\alpha}f_L^0\left(\varepsilon - e\varphi_L\right) + \Gamma_{R\alpha}f_R^0\left(\varepsilon - e\varphi_R\right)}{\Gamma_{L\alpha} + \Gamma_{R\alpha}}$$

One level (LUMO)



Quasiparticle approximation

$$A(\varepsilon) \approx 2\pi\delta(\varepsilon - \varepsilon_1)$$

$$J_{i=L,R} \approx \frac{e}{\hbar}\Gamma_{i1}\left[f_i^0(\varepsilon_1 - e\varphi_i) - n_1\right]$$

$$n_1 = \frac{\Gamma_{L1} f_L^0(\varepsilon_1 - e\varphi_L) + \Gamma_{R1} f_R^0(\varepsilon_1 - e\varphi_R)}{\Gamma_{L1} + \Gamma_{R1}}$$

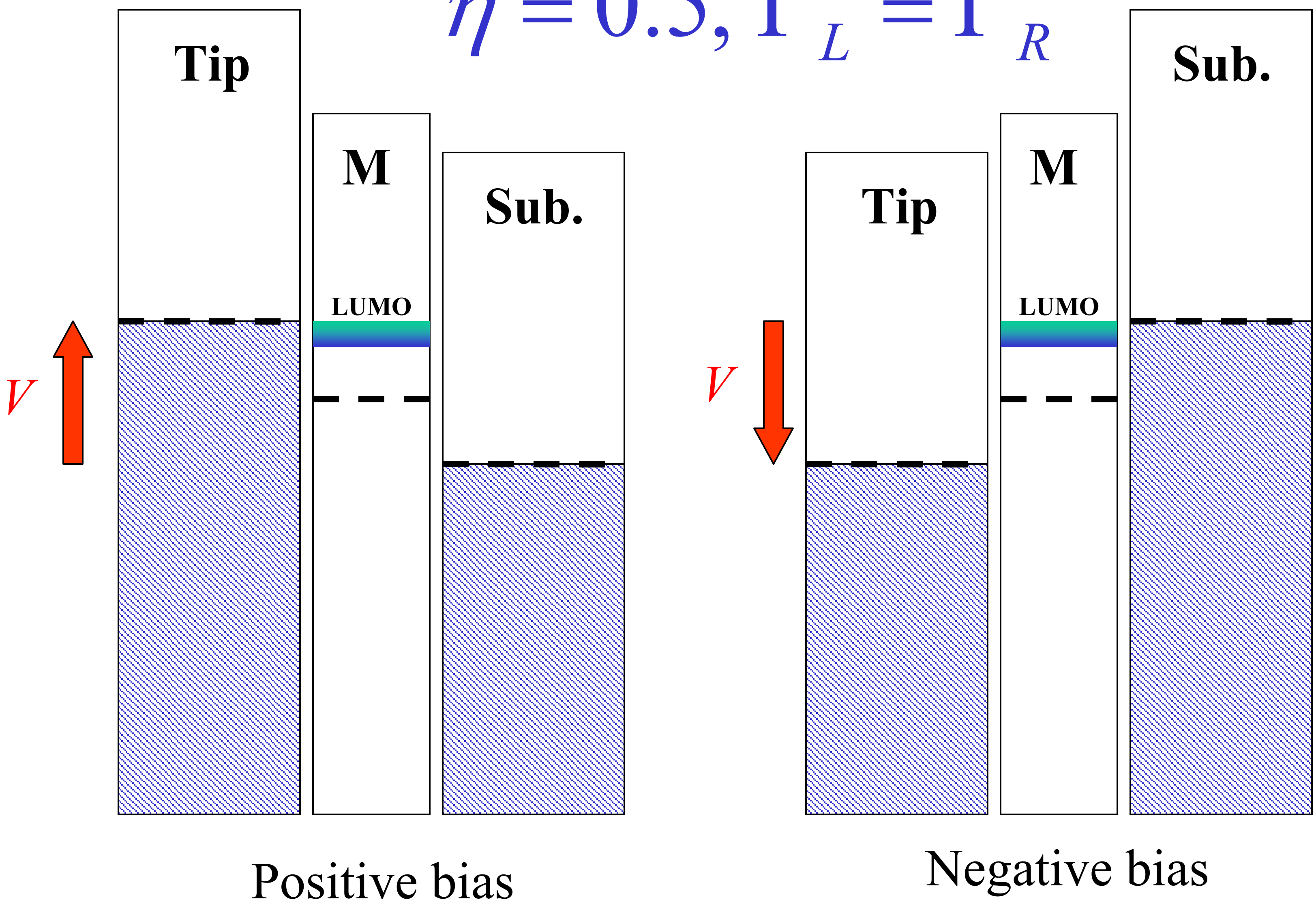
Extended q.p. approximation

$$G_\alpha^<(\varepsilon) \approx iA_\alpha(\varepsilon) n_\alpha$$

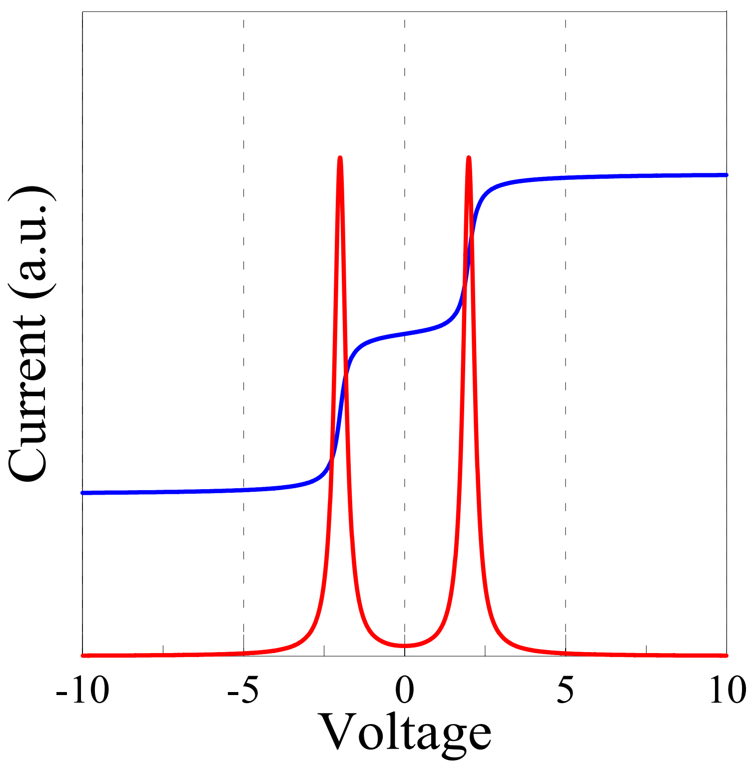
n_α is the number of electrons.

Symmetrical case

$$\eta = 0.5, \Gamma_L = \Gamma_R$$

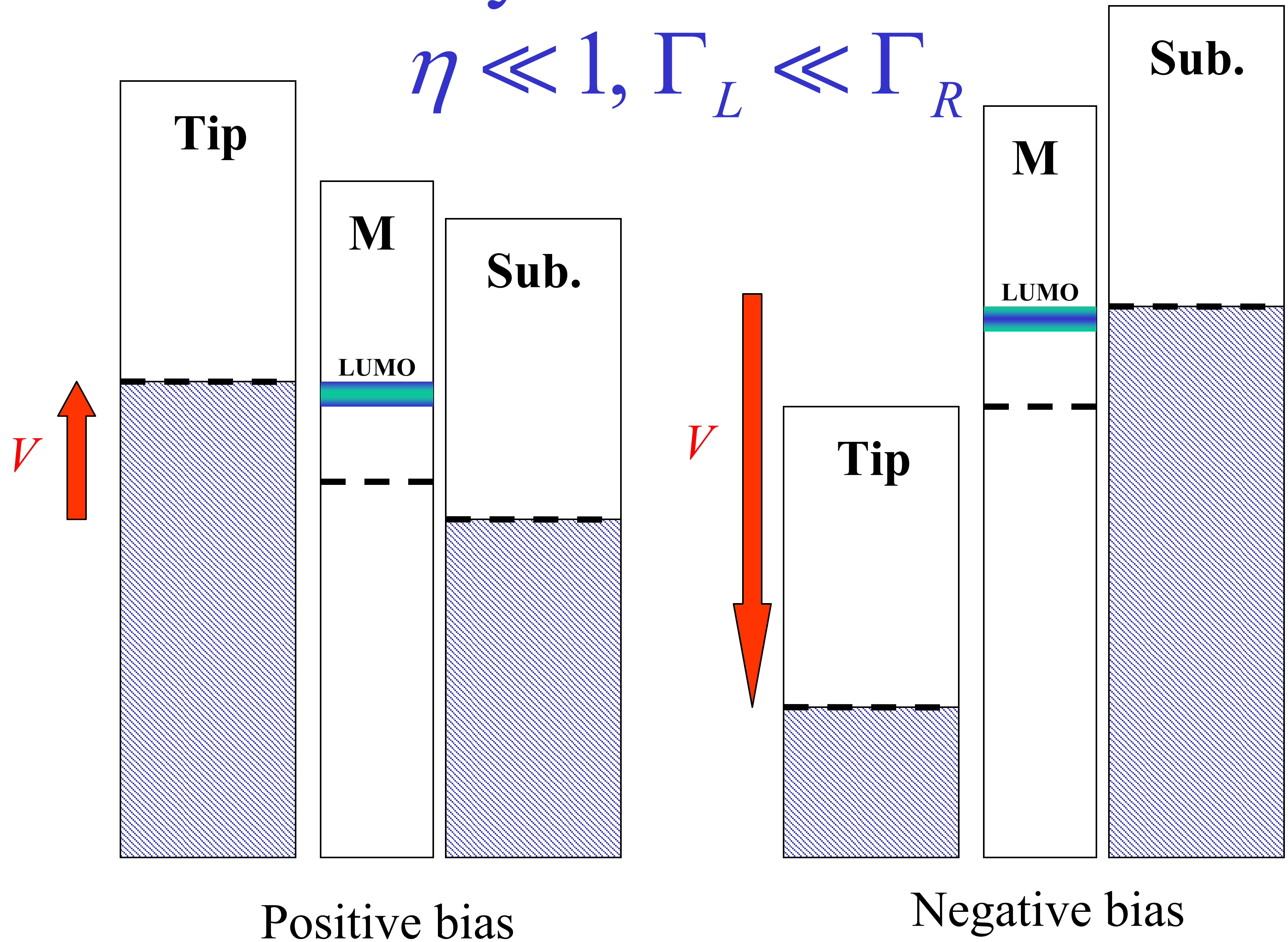


$$\varepsilon_1 = 1, \eta = 0.5,$$
$$\Gamma_L = 0.1, \Gamma_R = 0.1$$



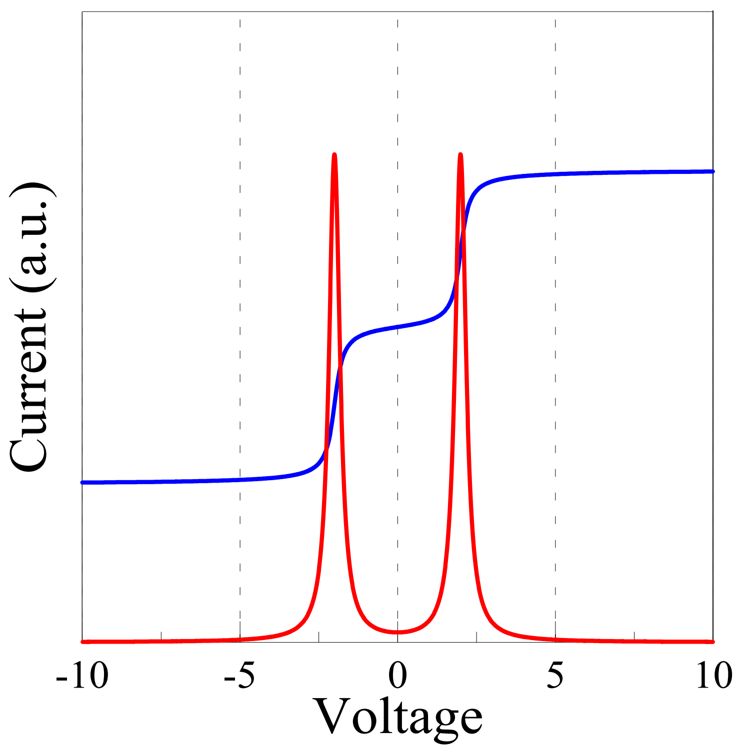
Asymmetrical case

$$\eta \ll 1, \Gamma_L \ll \Gamma_R$$



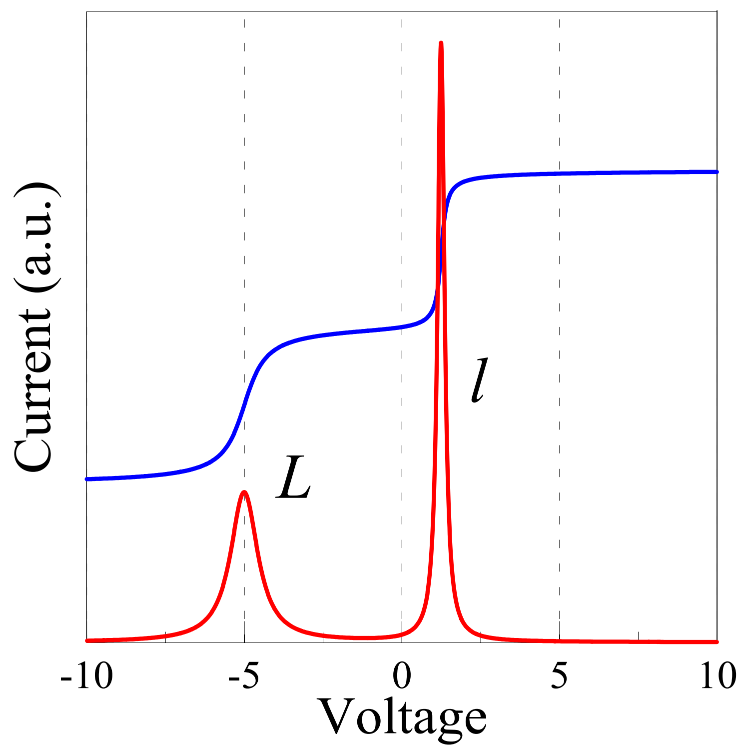
$\varepsilon_1 = 1,\ \eta = 0.5,$

$\Gamma_L = 0.1,\ \Gamma_R = 0.1$



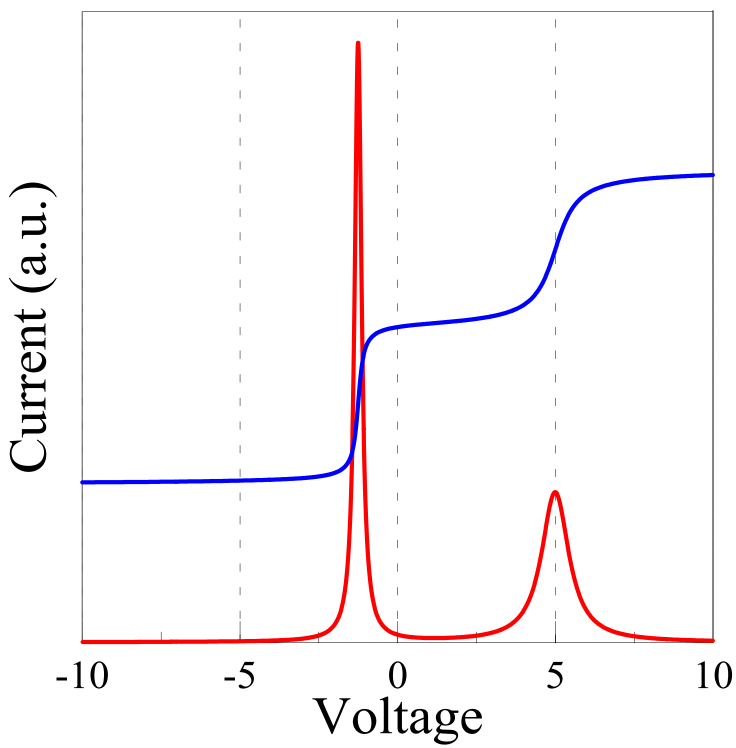
$\varepsilon_1 = 1,\ \eta = 0.2,$

$\Gamma_L = 0.1,\ \Gamma_R = 0.1$

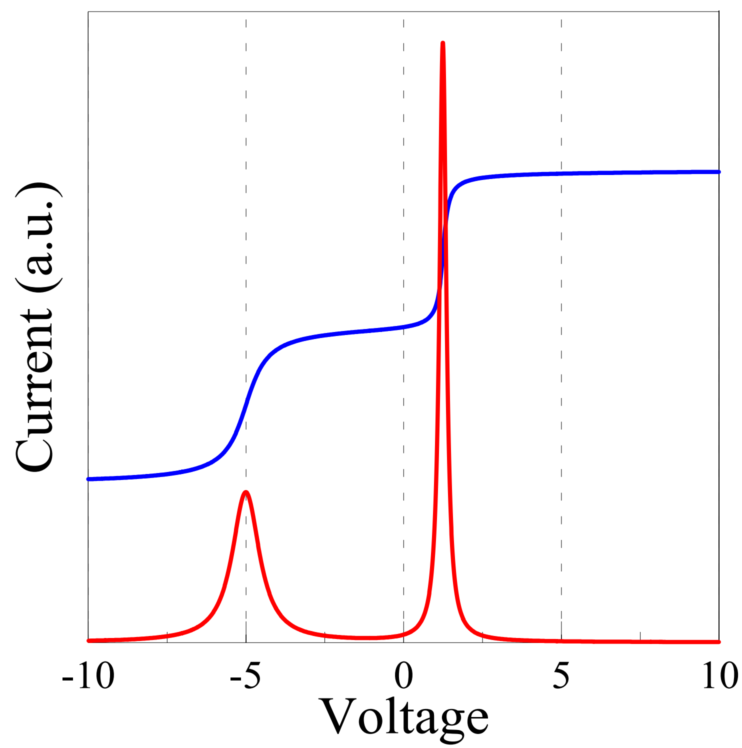


$$V_L = -\frac{\varepsilon_1}{\eta} \qquad V_l = \frac{\varepsilon_1}{1-\eta}$$

$$\varepsilon_1 = 1,\ \eta = 0.8,$$
$$\Gamma_L = 0.1,\ \Gamma_R = 0.1$$

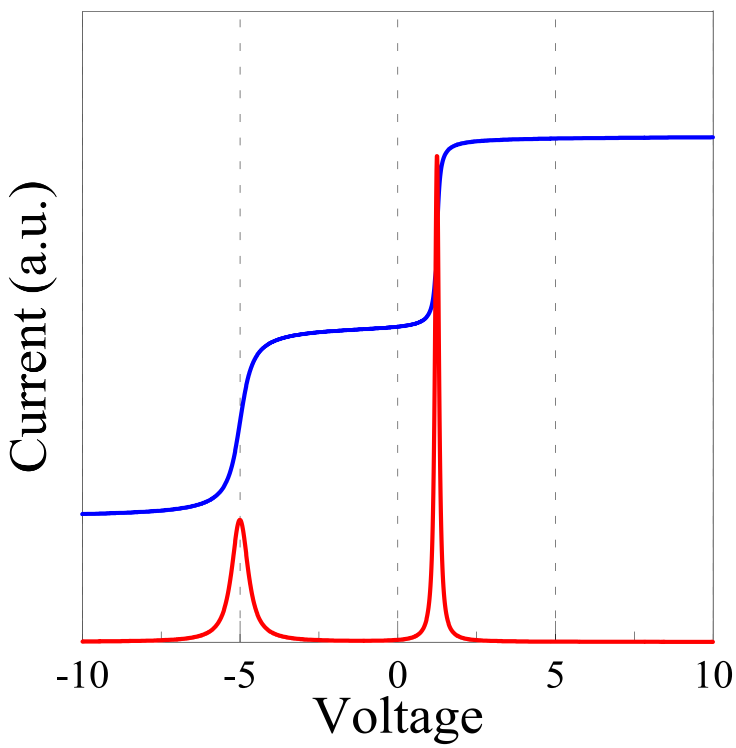


$$\varepsilon_1 = 1,\ \eta = 0.2,$$
$$\Gamma_L = 0.1,\ \Gamma_R = 0.1$$



$\varepsilon_1 = 1, \eta = 0.2,$

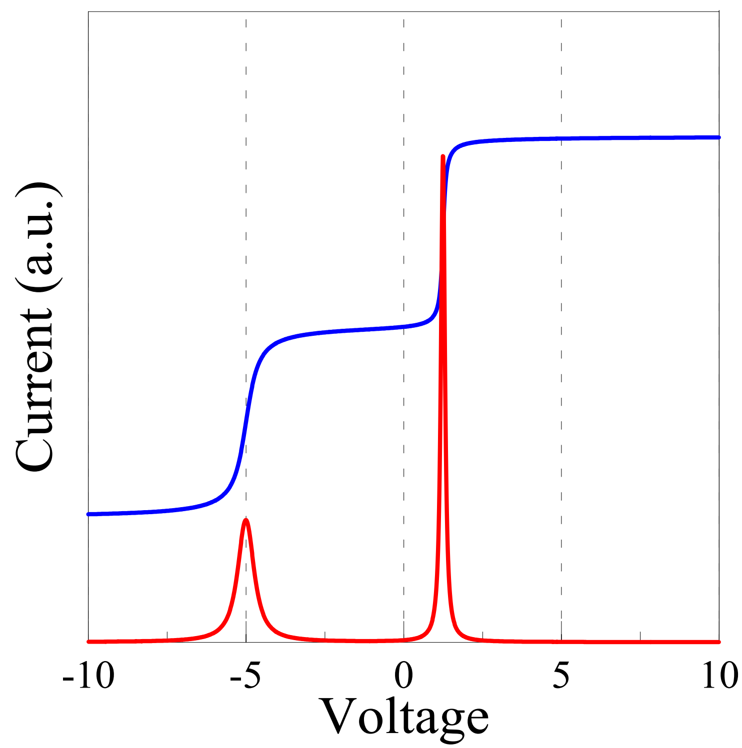
$\Gamma_L = 0.01, \Gamma_R = 0.1$



Typical case

$\varepsilon_1 = 1, \eta = 0.2,$

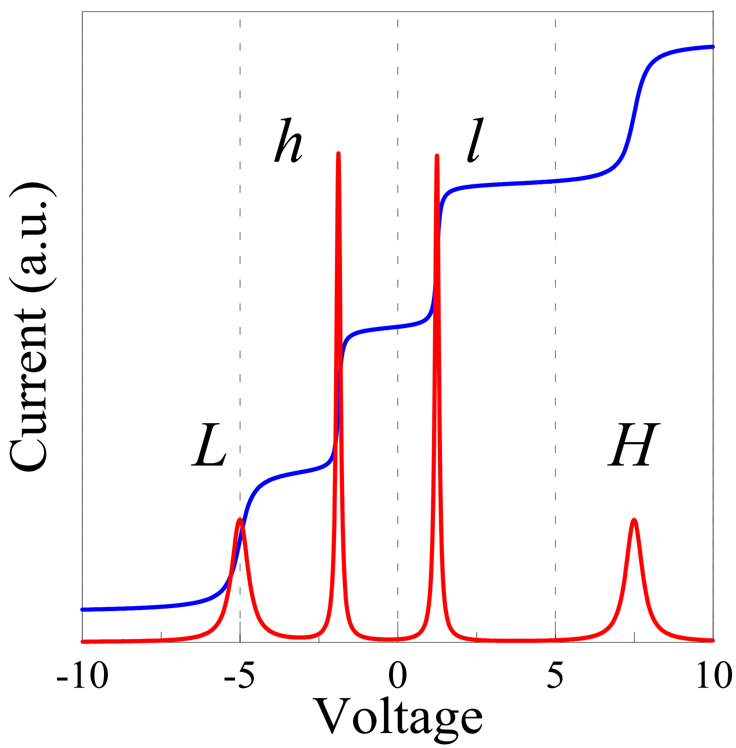
$\Gamma_L = 0.1, \Gamma_R = 0.01$

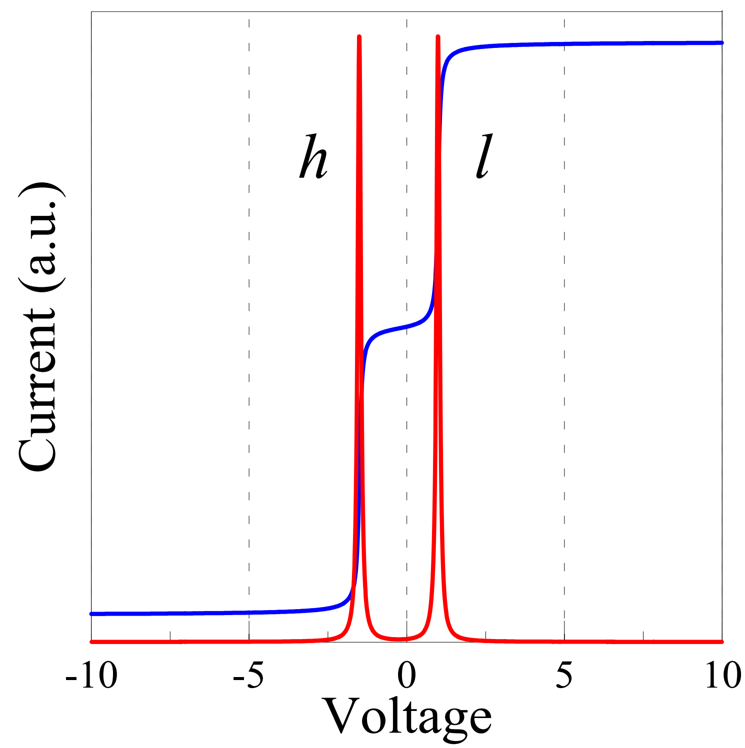


LUMO + HOMO

$\varepsilon_1 = 1,\ \varepsilon_{-1} = -1.5,\ \eta = 0.2,$
$\Gamma_L = 0.01,\ \Gamma_R = 0.1$

$\varepsilon_1 = 1,\ \varepsilon_{-1} = -1.5,\ \eta \to 0,$
$\Gamma_L = 0.01,\ \Gamma_R = 0.1$



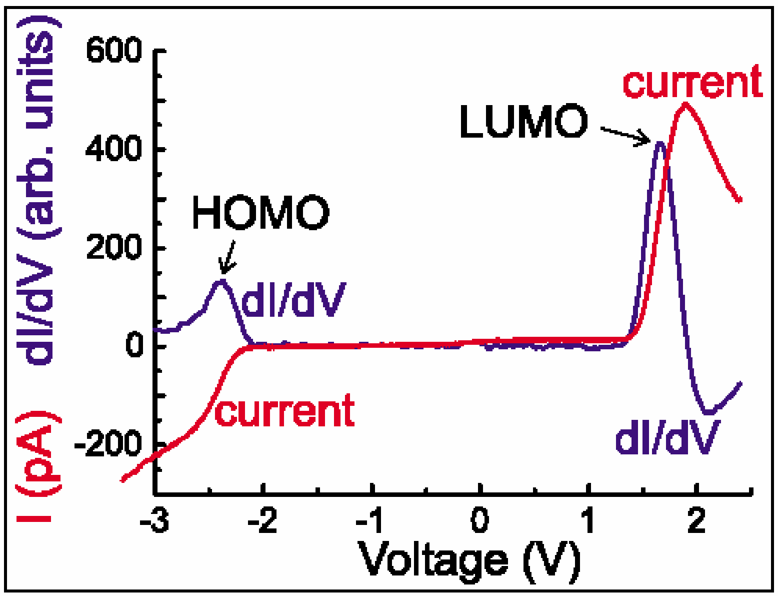


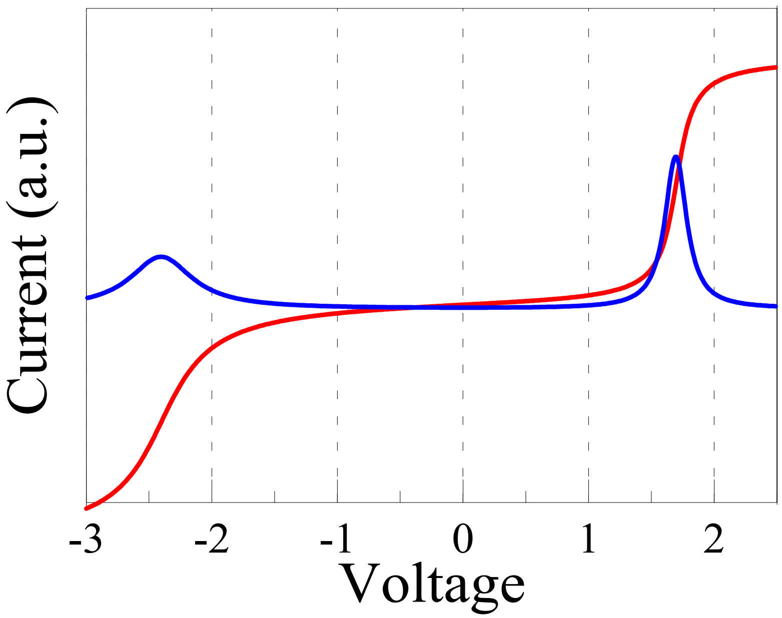
Repp et al., PRL **94**, 026803 (2005)

$\varepsilon_1 = 1.7,\ \varepsilon_{-1} = -2.4,\ \eta \to 0,$

$\Gamma_L = 0.01,\ \Gamma_R = 0.1,\ \gamma_{-1} = 0.2$

Experiment



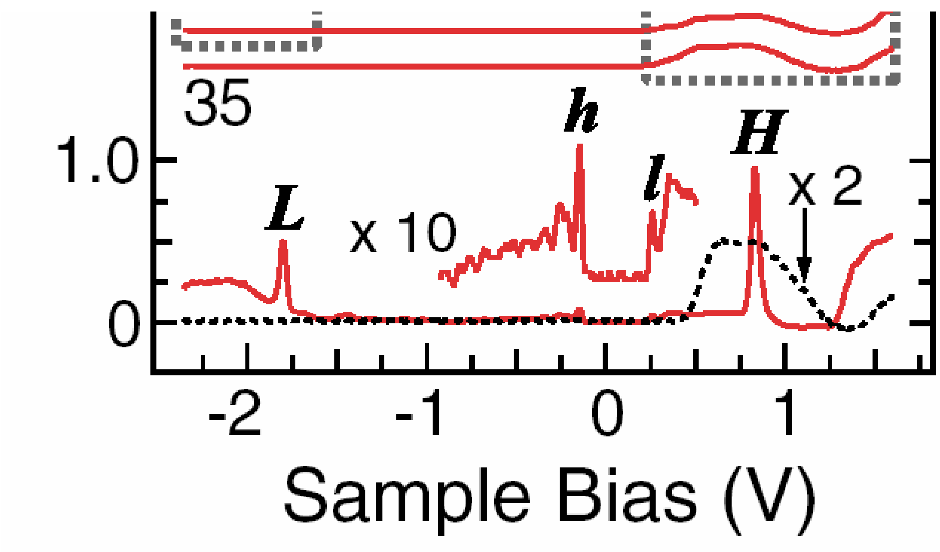


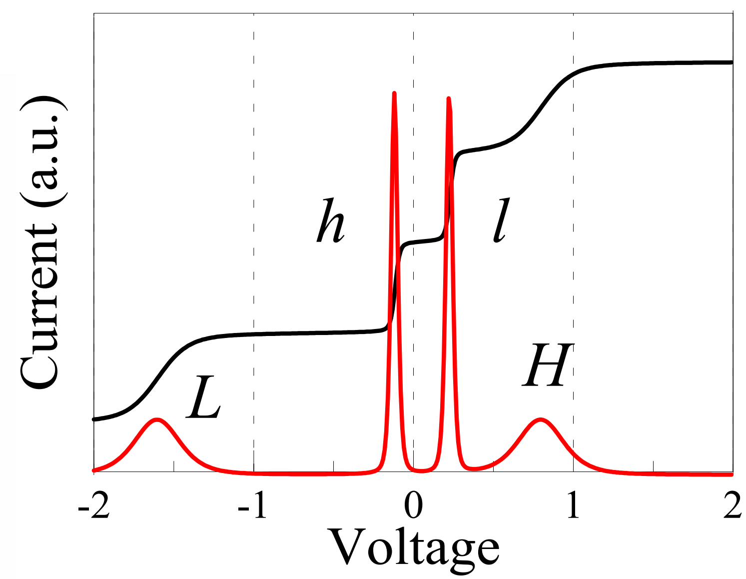
There are some deviations from a noninteracting model.
The experimental *line shape* is not Lorentzian (phonons!).
Negative differential conductance (NDC) is not described.

Pradhan et al., PRL **94**, 076801 (2005)

$$\varepsilon_1 = 0.2,\ \varepsilon_{-1} = -0.1,\ \eta = 0.125,$$
$$\Gamma_L = 0.001,\ \Gamma_R = 0.01$$

Experiment





There are large deviations from a noninteracting model.
Non-Lorentzian line shape & *vibronic satellites*.
Experimental current is very large in *charged states* L & H.

Charging effects

Energy levels are shifted.

$$\varepsilon_\alpha^* = \varepsilon_\alpha + \sum_\beta U_{\alpha\beta}[n_\beta - n_\beta^0]$$

External "polarization"potenial: $U_{\alpha\alpha}[n_\alpha - n_\alpha^0]$

Internal "interaction"potential: $\sum_{\beta\neq\alpha} U_{\alpha\beta}[n_\beta - n_\beta^0]$

Coupling to the leads is changed.

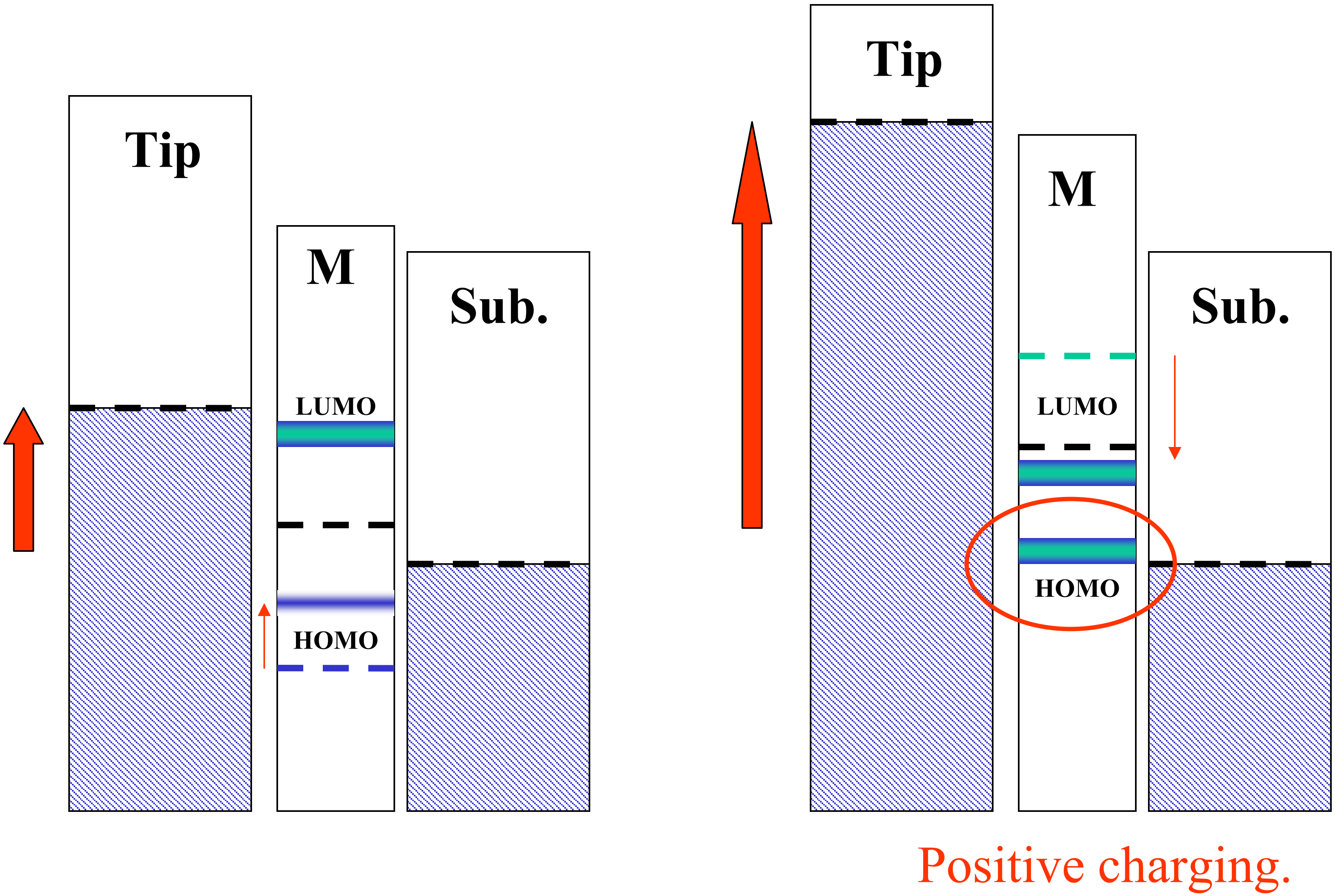
$$\Gamma_{i\alpha} = \Gamma_{i\alpha}^{(0)}(1 + f(n_\alpha - n_\alpha^0))$$

New conduction channels are opened.

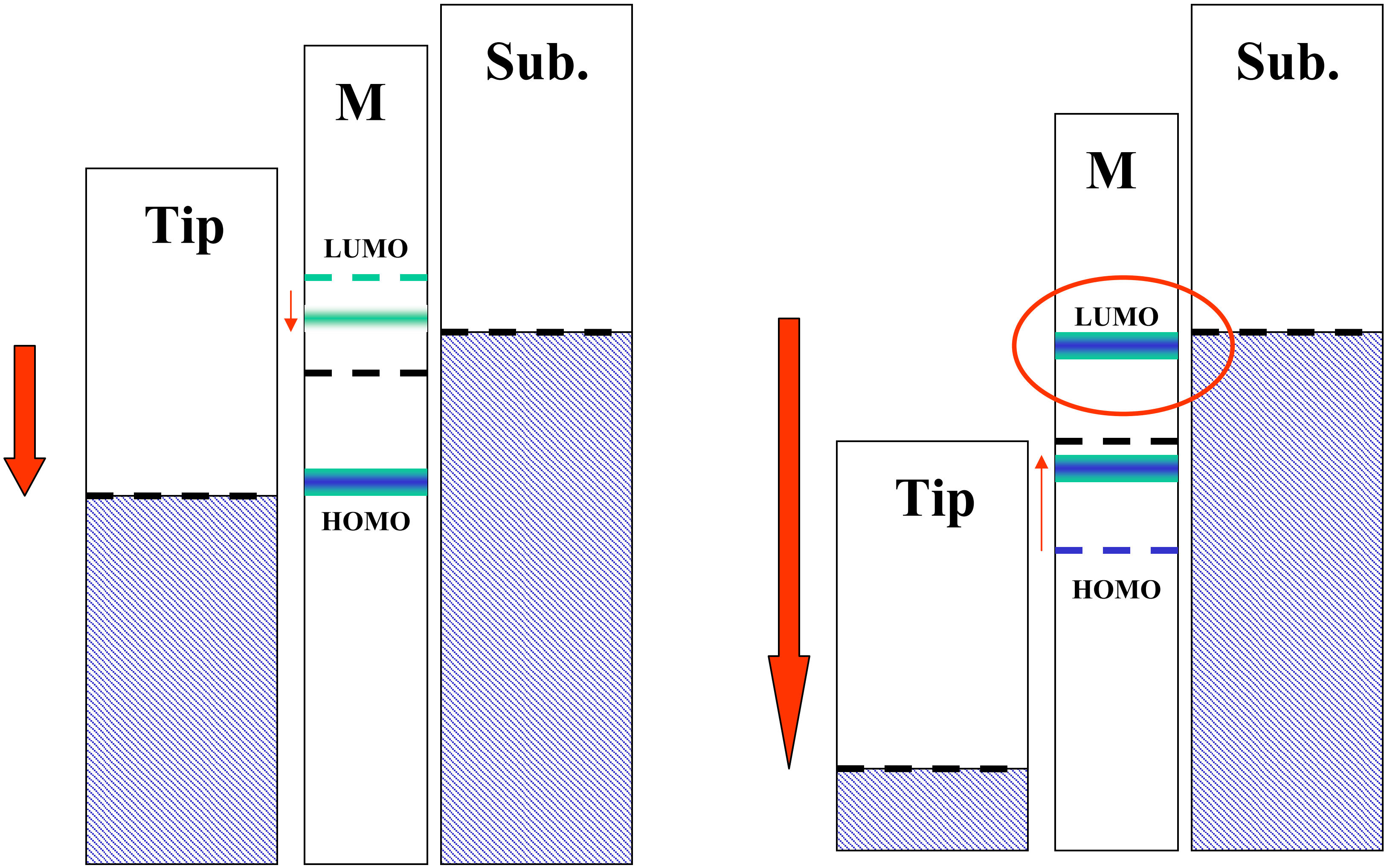
$$\Delta J_i = \sum_\alpha g_{i\alpha}(n_\alpha - n_\alpha^0)$$

Mean field: n_α is the average number of electrons in the state α.

Positive bias



Negative bias



Negative charging.

Equations

$$J_{i=L,R} = \frac{e}{\hbar}\int \frac{d\varepsilon}{2\pi}\sum_{\alpha}\left\{\Gamma_{i\alpha}\left(\varepsilon - e\varphi_i\right)A_{\alpha}\left(\varepsilon\right)\left[f_i^0\left(\varepsilon_{\alpha}^{*} - e\varphi_i\right) - n_{\alpha}\right]\right\}$$

$$A_{\alpha}\left(\varepsilon\right) = \frac{2\Gamma_{\alpha}^{2}}{\left(\varepsilon - \varepsilon_{\alpha}^{*}\right)^{2} + \Gamma_{\alpha}^{2}}$$

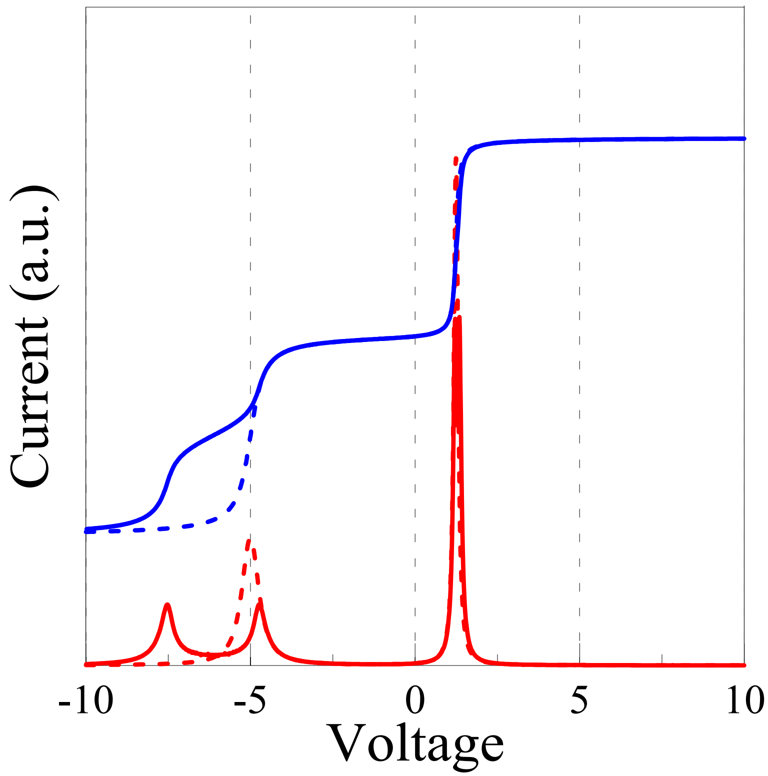
$$n_{\alpha} = \frac{\Gamma_{L\alpha} f_L^0\left(\varepsilon_{\alpha}^{*} - e\varphi_L\right) + \Gamma_{R\alpha} f_R^0\left(\varepsilon_{\alpha}^{*} - e\varphi_R\right)}{\Gamma_{L\alpha} + \Gamma_{R\alpha}}$$

$$\varepsilon_{\alpha}^{*} = \varepsilon_{\alpha} + \sum_{\beta} U_{\alpha\beta}[n_{\beta} - n_{\beta}^{0}]$$

One level with charging

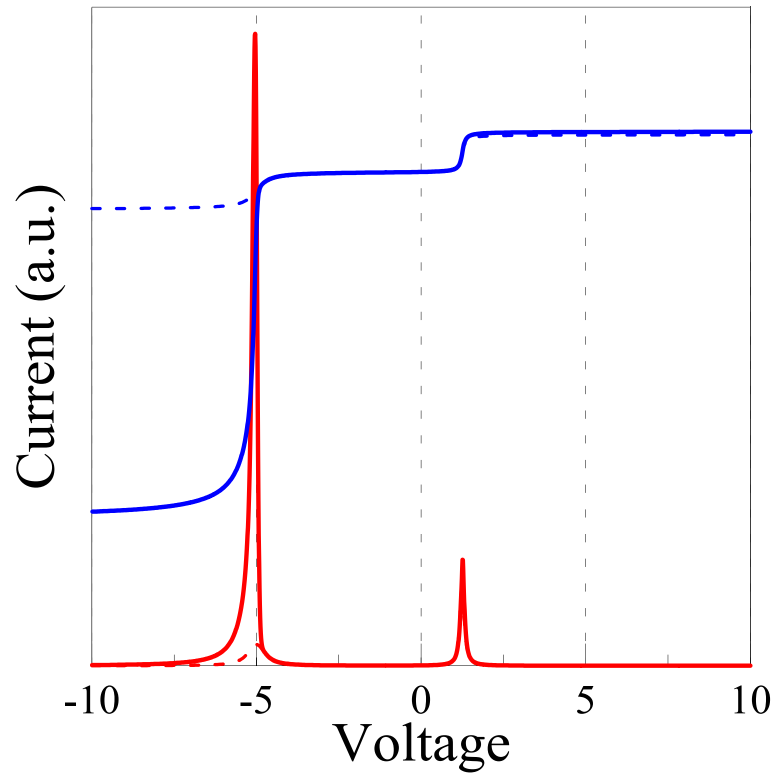
External energy: $\varepsilon_1^* = \varepsilon_1 + U[n_1 - n_1^0]$

$\varepsilon_1 = 1,\ \eta = 0.2,\ U = 0.5$



extra current

$\Gamma_{L(R)} = \Gamma_{L(R)}^{(0)}[1 + \zeta[n_1 - n_1^0]^2]$



LUMO + HOMO

$$\varepsilon_1 = 0.2,\ \varepsilon_{-1} = -0.1,\ \eta = 0.125,$$

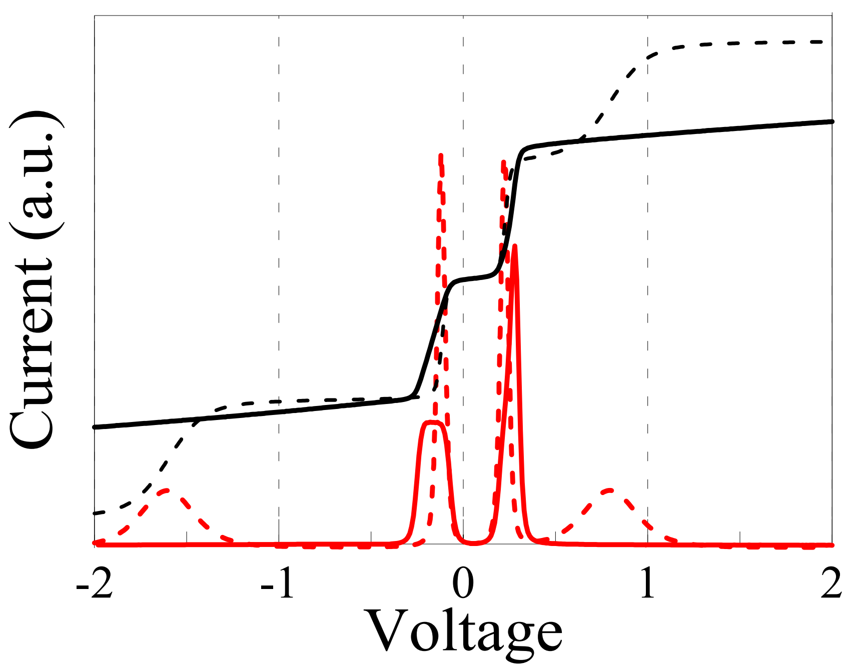
$$\Gamma_L = 0.001,\ \Gamma_R = 0.01,\ U = 1.5$$

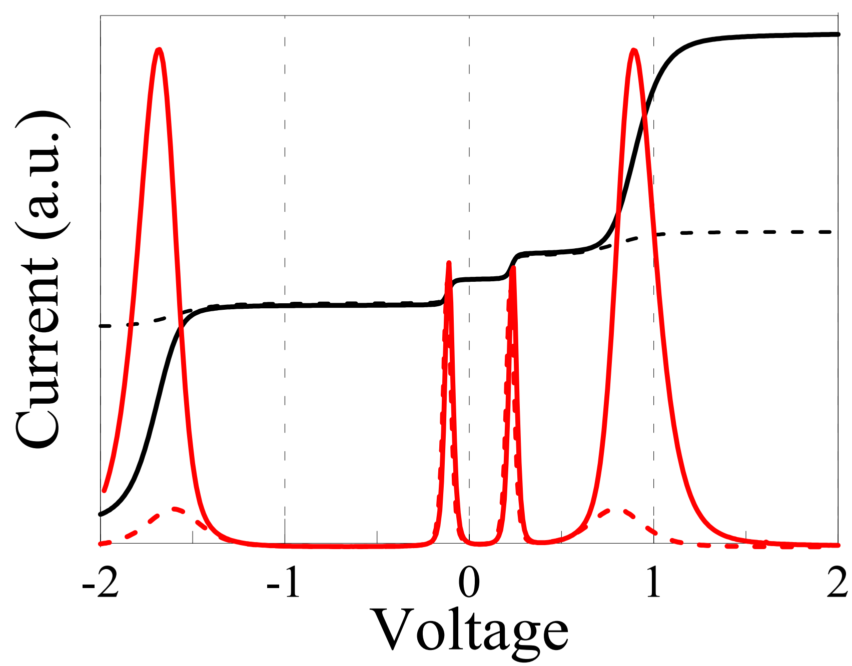
$$\varepsilon_1^* = \varepsilon_1 + U[n_{-1} - n_{-1}^0]$$

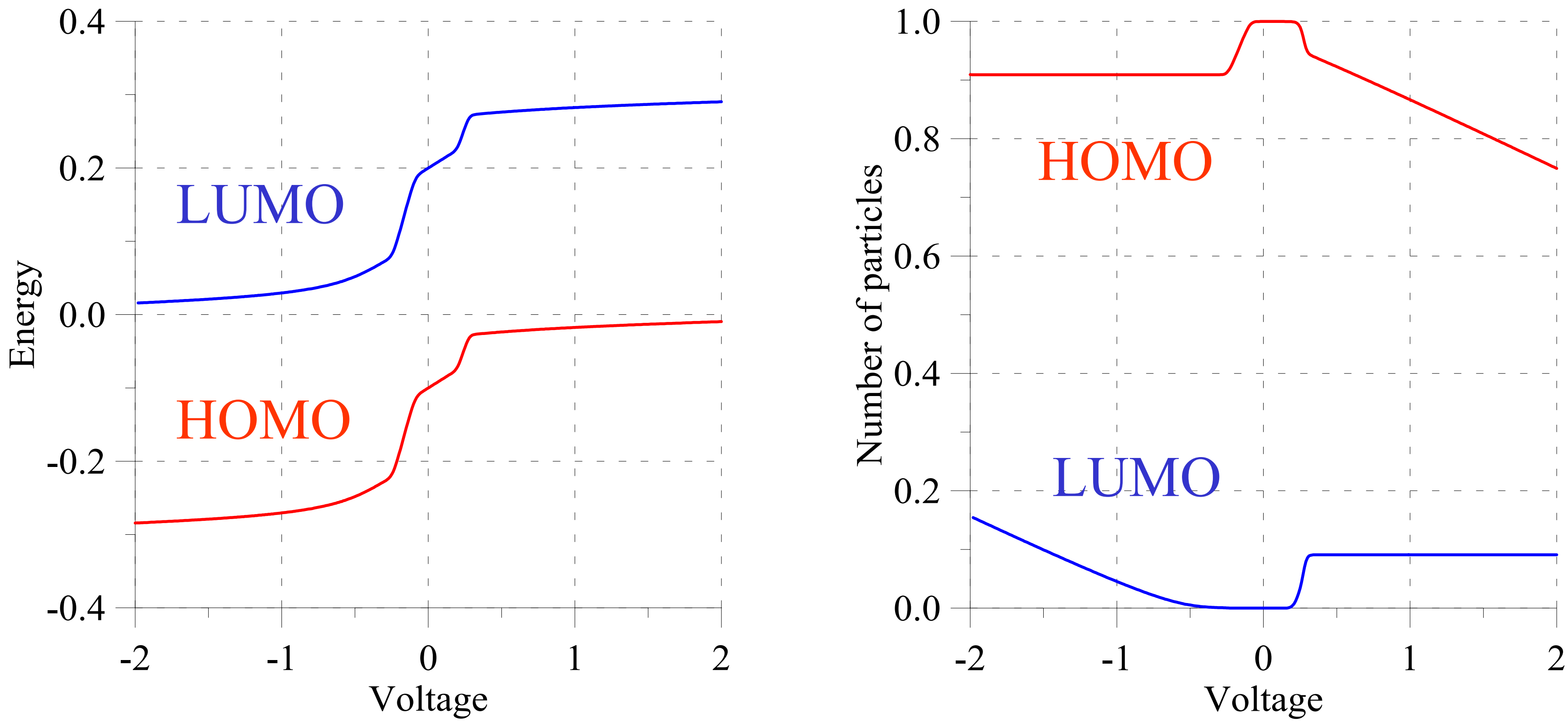
$$\varepsilon_{-1}^* = \varepsilon_{-1} + U[n_1 - n_1^0]$$

extra current

$$\Gamma_{L(R)\alpha} = \Gamma_{L(R)\alpha}^{(0)}[1 + \zeta[n_\alpha - n_\alpha^0]^2]$$

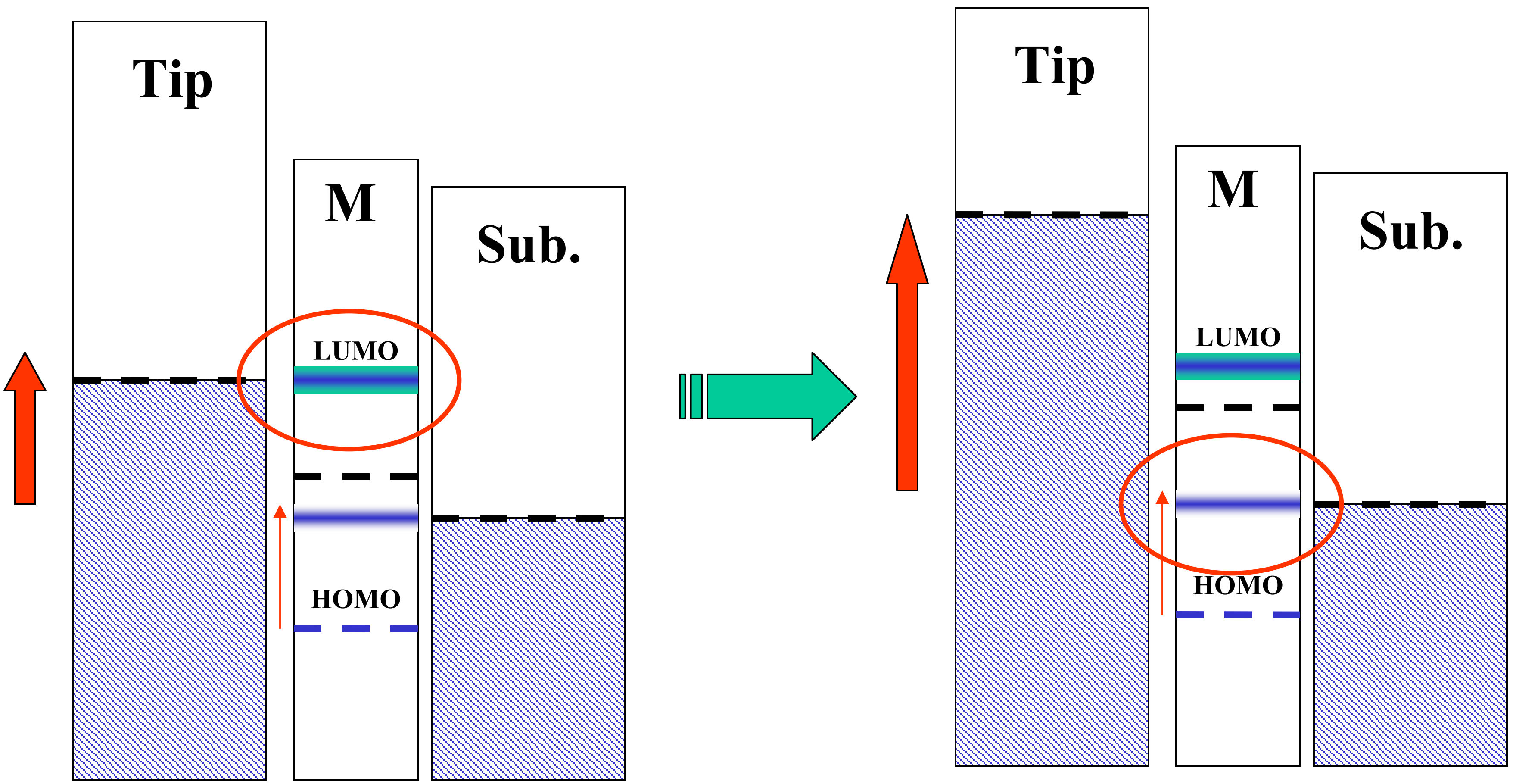




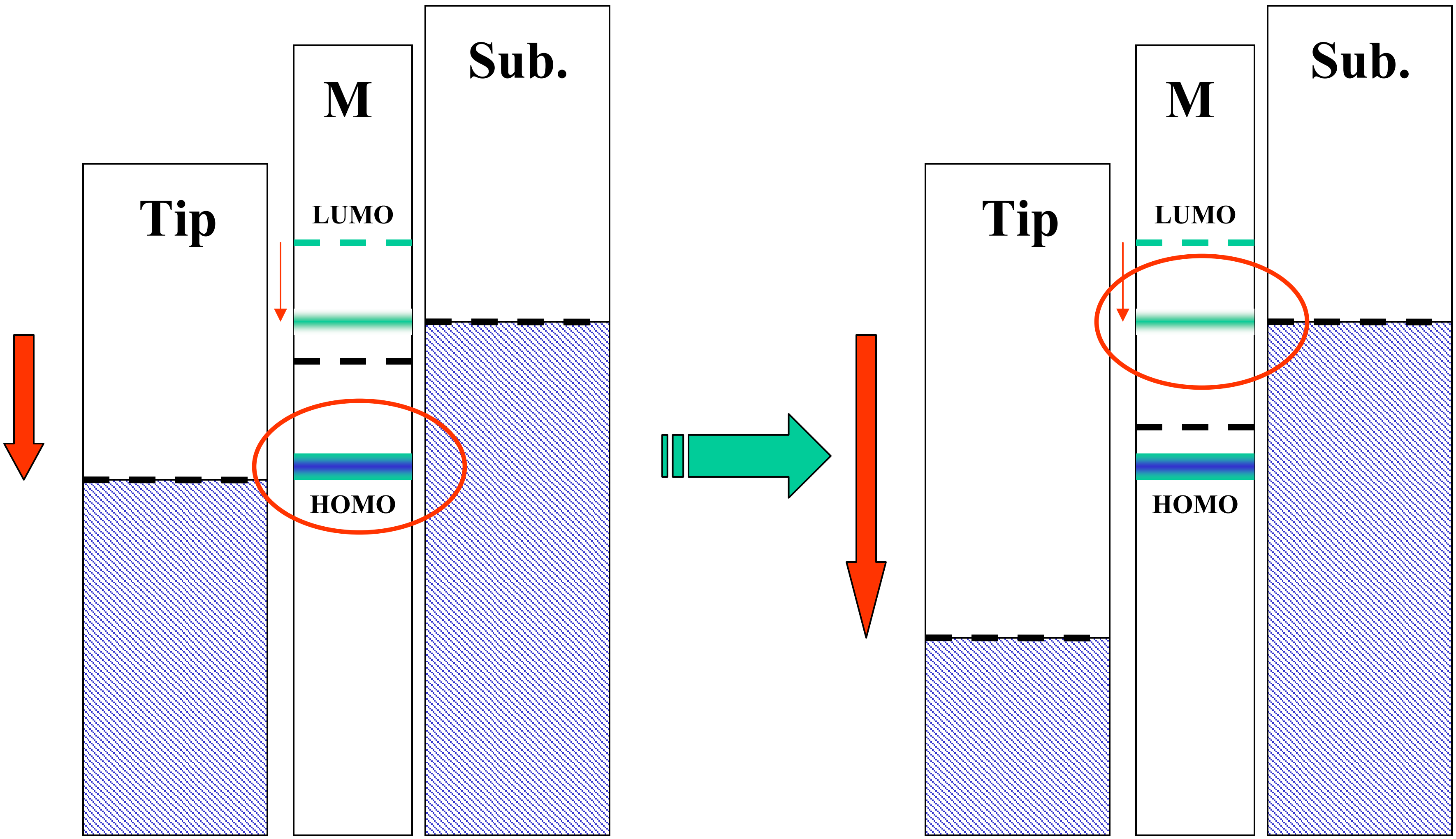


0.4
0.2
0.0
-0.2
-0.4
Energy
LUMO
HOMO
-2
-1
0
1
2
Voltage
1.0
0.8
0.6
0.4
0.2
0.0
Number of particles
HOMO
LUMO
-2
-1
0
1
2
Voltage

Positive bias



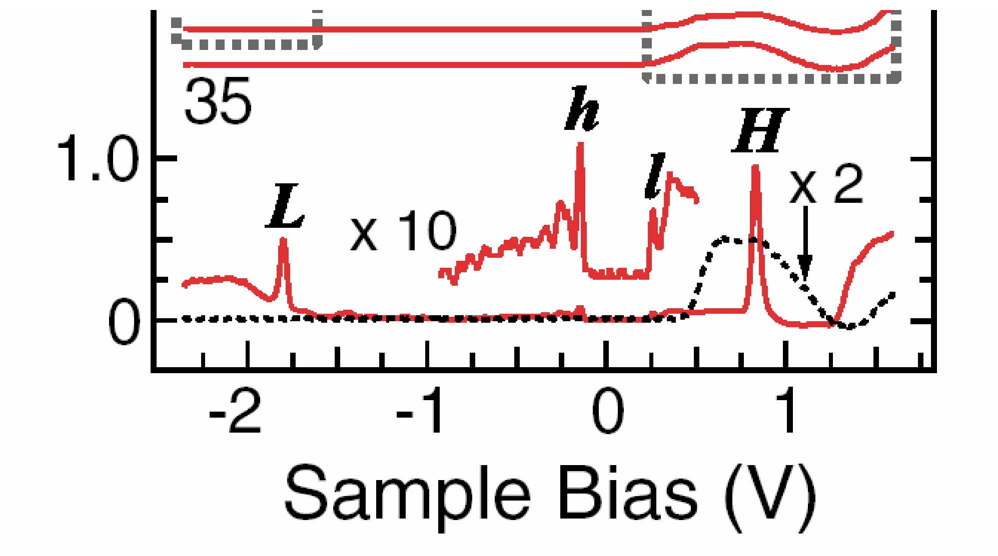
Negative bias

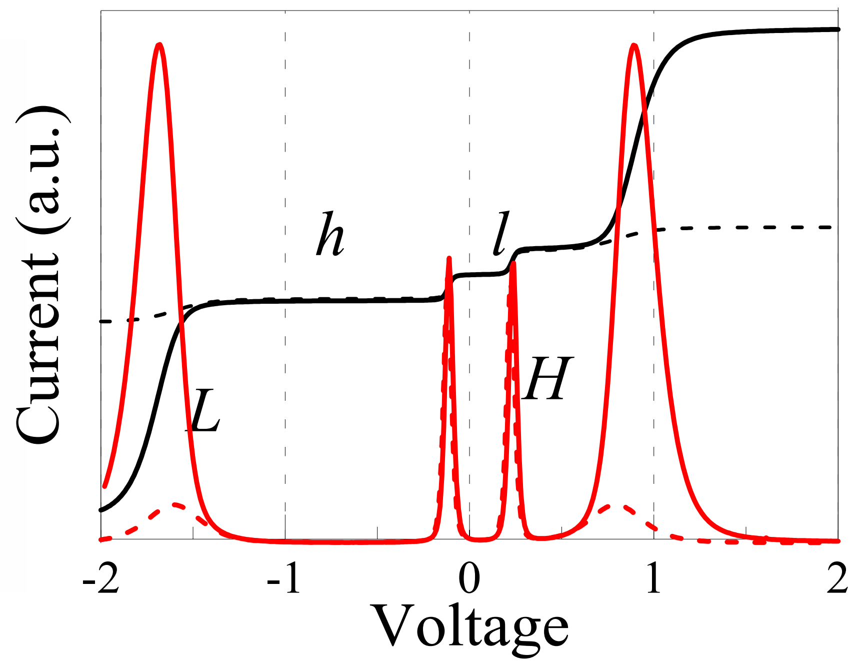


Pradhan et al., PRL **94**, 076801 (2005)

$$\varepsilon_1 = 0.2,\ \varepsilon_{-1} = -0.1,\ \eta = 0.125,$$
$$\Gamma_L = 0.001,\ \Gamma_R = 0.01$$

Experiment





Extra current in the charged states L & H is added.

the end