Molecular electronics - Role of dephasing and electron correlation

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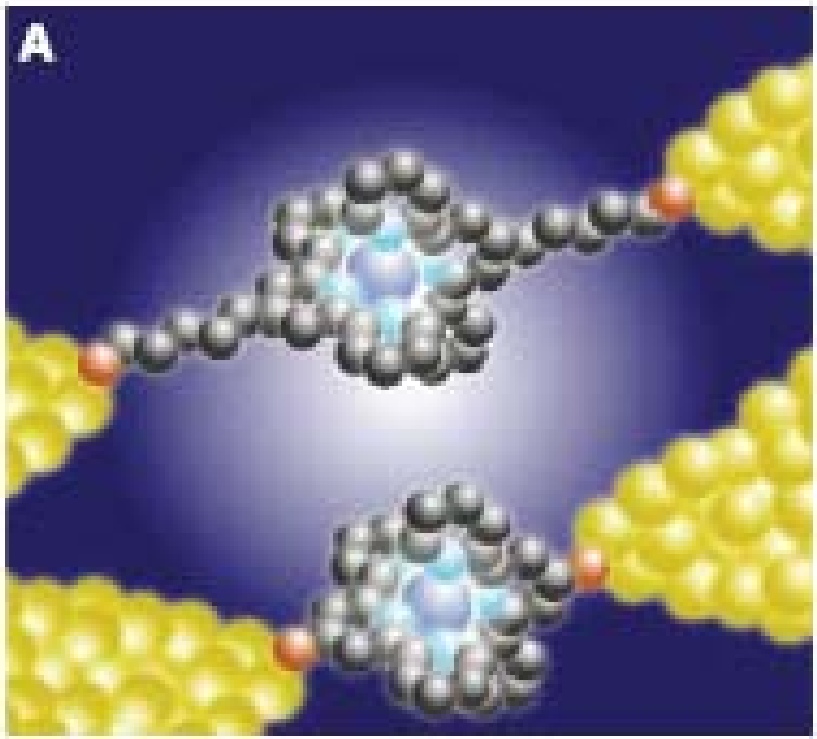
Regensburg, 2005 March - April

Outline of the presentation

- Brief introduction to molecular conduction
- Non-equilibrium Green function (Keldysh) formalism
- Including non-elastic (dephasing) effects
- Including electron-electron interaction – the role of electron correlations

Molecular conduction – an overview



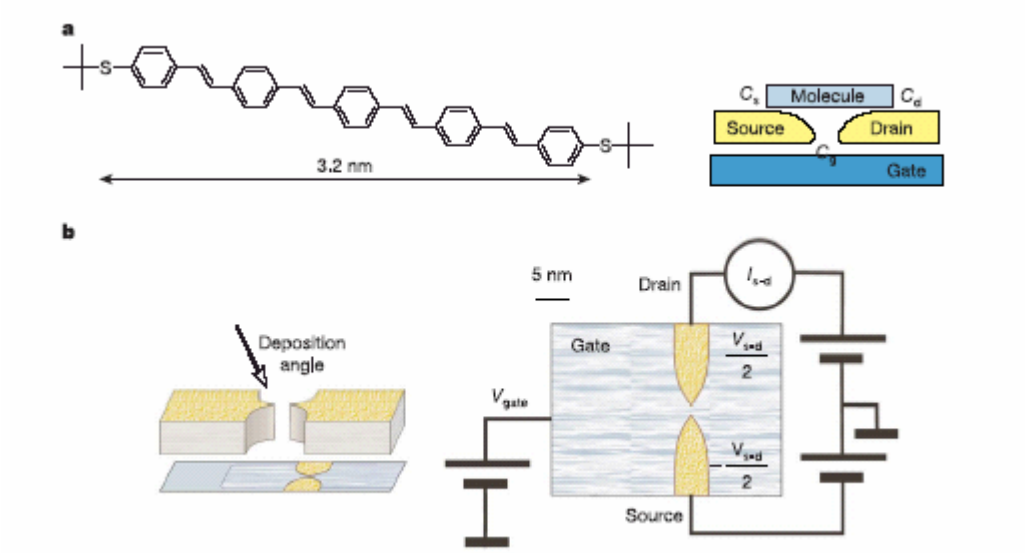
A. Nitzan and M. A. Ratner, Science, 300 (2003)

How do molecules and small clusters conduct electric current ?

How can new features be rationalized and predicted ?

How are these different from macroscopic/ mesoscopic features, and how can we describe both regimes within the same framework ?

Typical experimental set up
What are the knobs?



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

Chemical composition

Chain length

Gate voltage and/ or chemical modification, (“doping”) – control of the Fermi level

Temperature – control of thermal effects

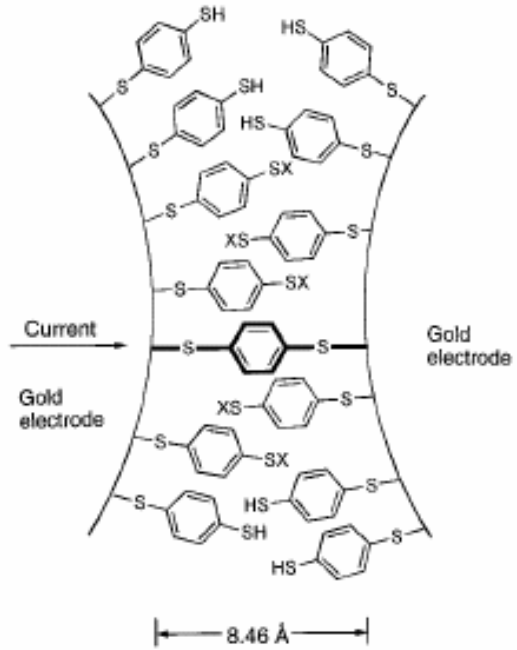
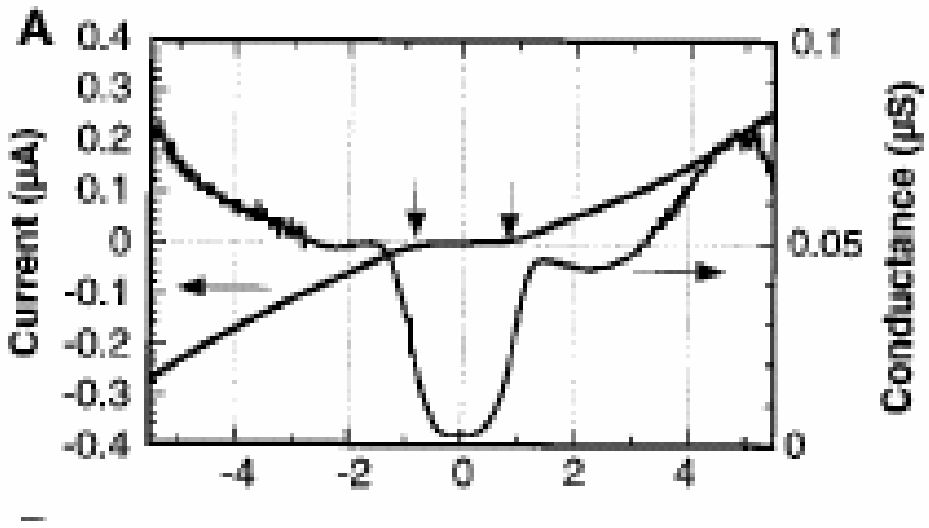


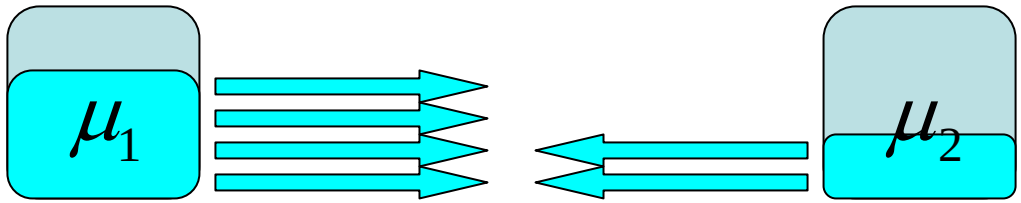
Fig. 3. A schematic of a benzene-1,4-dithiolate SAM between proximal gold electrodes formed in an MCB. The thiolate is normally H-terminated after deposition; end groups denoted as X can be either H or Au, with the Au potentially arising from a previous contact/retraction event. These molecules remain nearly perpendicular to the Au surface, making other molecular orientations unlikely (*21*).

M. A. Reed, et al., Science, 278 (1997)



I(V) characteristics highly non-linear. dI/dV curves show peaks that are related to the electronic structure and/ or to charged states of the molecular system.

Landauer formula



$$I = (2e/h)MT(\mu_1 - \mu_2)$$

$$G = \frac{2e^2}{h}MT$$

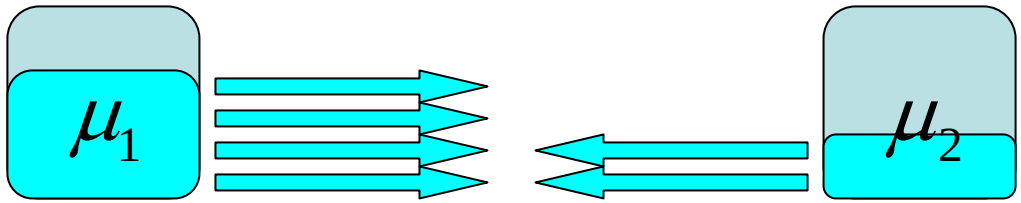
μ_1, μ_2 - chemical potential in contacts

M - number of transverse modes in leads

T - average transmission probability for one mode

G - small bias conductivity

Non-Equilibrium Green's Function method (NEGF)



$$I = \frac{e}{h}\int (f_1 - f_2)\tilde{T}(E)dE$$

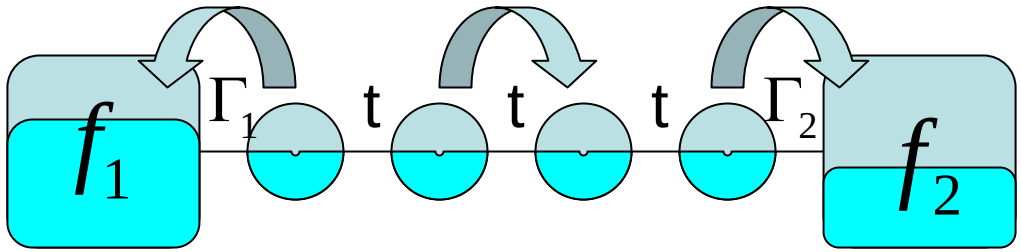
$$G = \frac{2e^2}{h}\tilde{T}$$

Transmission function

Based on the Hamiltonian of the molecular system.
Contacts are taken into account.
Internal interactions (e.g., electron-phonon interaction) can be incorporated in perturbative or phenomenological ways.

Simple model for a molecular chain

$$H = -\begin{pmatrix} 0 & t & 0 & 0 \\ t & 0 & t & 0 \\ 0 & t & 0 & t \\ 0 & 0 & t & 0 \end{pmatrix} \qquad \Gamma_1 = \begin{pmatrix} \Gamma_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \qquad \Gamma_2 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \Gamma_2 \end{pmatrix}$$



$$\Sigma^R = -\frac{i}{2}\Gamma_1 - \frac{i}{2}\Gamma_2 \qquad G^R = (E - H + \frac{i}{2}\Gamma_1 + \frac{i}{2}\Gamma_2)^{-1}$$

Introducing the evolution super-operator:

$$\hat{U}X := G^R X G^A$$

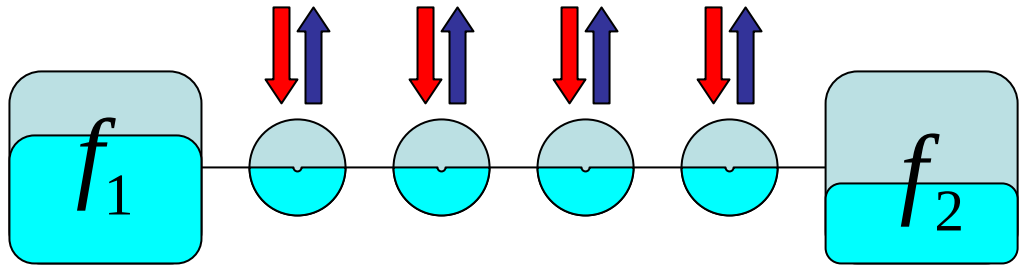
T

$$i(E) = \frac{e}{h}(f_1 - f_2)Tr[\Gamma_1 \hat{U} \Gamma_2] = \frac{e}{h}(f_1 - f_2)\left\langle \Gamma_1 \hat{U} \Gamma_2 \right\rangle$$

Including dephasing

$$\Sigma_{\varphi}^{R} = \hat{D} G^{R}$$

$$\Sigma_{\varphi}^{in} = \hat{D} G^{n}$$



Scattering is proportional with electron-correlations.
Proportionality determined by scattering-center correlations

Non-local model: $(\Sigma_{\varphi}^{in})_{jk} = D(G^{n})_{jk}$

Local model: $(\Sigma_{\varphi}^{in})_{jk} = D\delta_{jk}(G^{n})_{jj}$

Model assumed is local in energy – phonon absorption and emission equally important

Formal results

$$G^R = (E - H + \tfrac{i}{2}\Gamma_1 + \tfrac{i}{2}\Gamma_2 - \hat{D}G^R)^{-1}$$

$$T = \left\langle \Gamma_1 \hat{U}(1 - \hat{D}\hat{U})^{-1}\Gamma_2 \right\rangle =$$

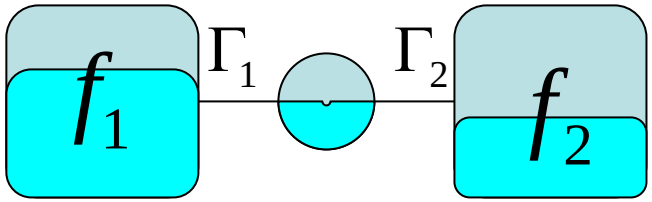
$$\left\langle \Gamma_1 \hat{U}\Gamma_2 \right\rangle + \left\langle \Gamma_1 \hat{U}\hat{D}\hat{U}\Gamma_2 \right\rangle + \left\langle \Gamma_1 \hat{U}\hat{D}\hat{U}\hat{D}\hat{U}\Gamma_2 \right\rangle + \ldots$$

T_{coh} $T_{non-coh}$

Within the local model, the super-operator $\hat{D}\hat{U}$ maps populations to populations, and kills coherences.

Emergence of classical hopping limit.

Analytic results for the one-site model



$$G^R = (E + i\Gamma - DG^R)^{-1}$$

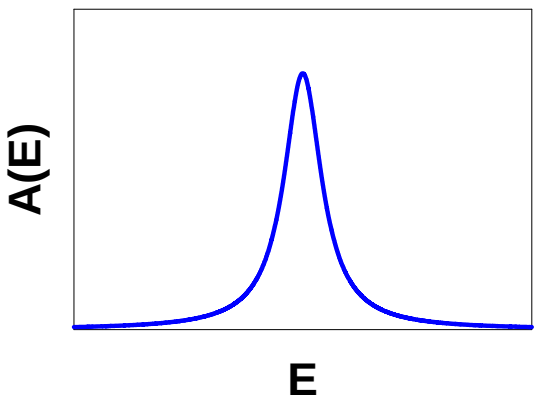
$D \to 0$

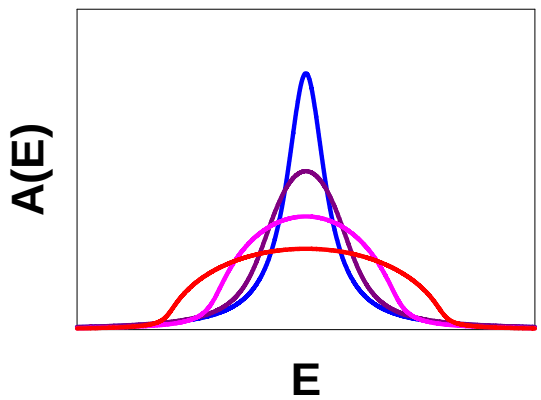
$$A = \frac{2\Gamma}{E^2 + \Gamma^2}$$

$\Gamma_{1,2} \to 0$

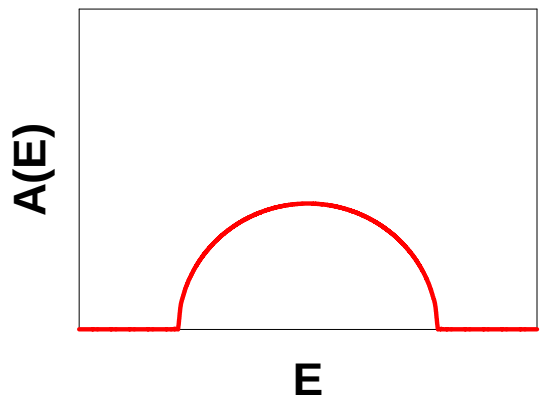
$$A = \frac{\sqrt{4D - E^2}}{D}$$

Lorentzian





Semi-circular



Analytic results for the one-site model

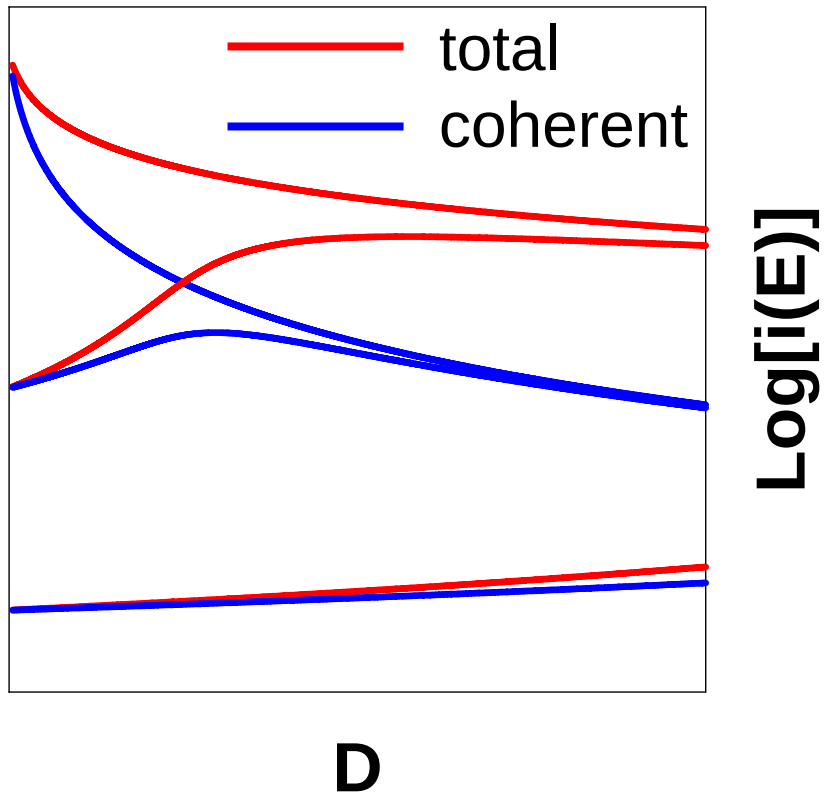
$$T = \frac{\Gamma_1 \Gamma_2}{\Gamma_1 + \Gamma_2} A(E)$$

$$\frac{T_{non-coh}}{T_{coh}} = \frac{DA}{\Gamma_1 + \Gamma_2}$$

resonance – metal?

near resonance – semi-conductor?

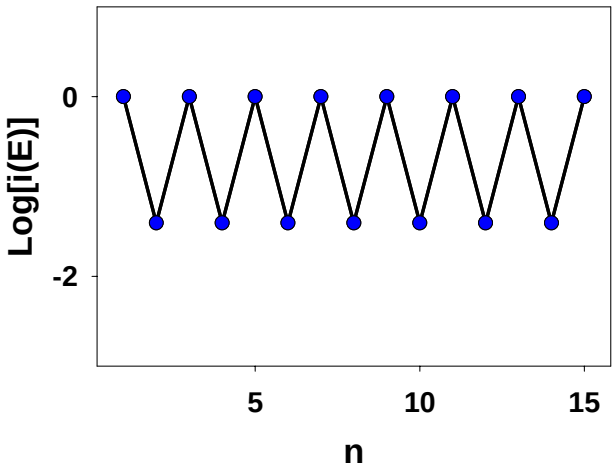
off-resonance – insulator?



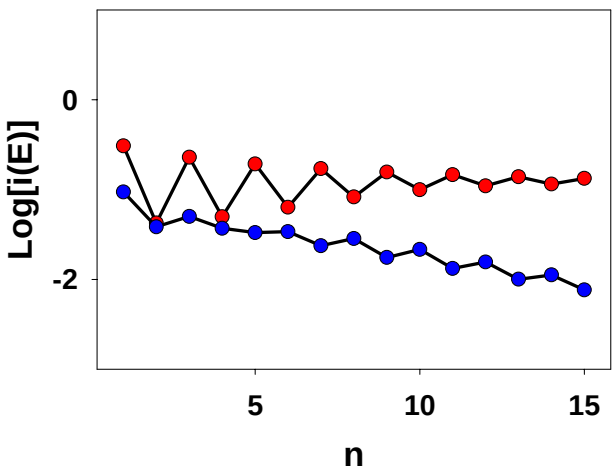
Size effects

half filled band

total current
coherent

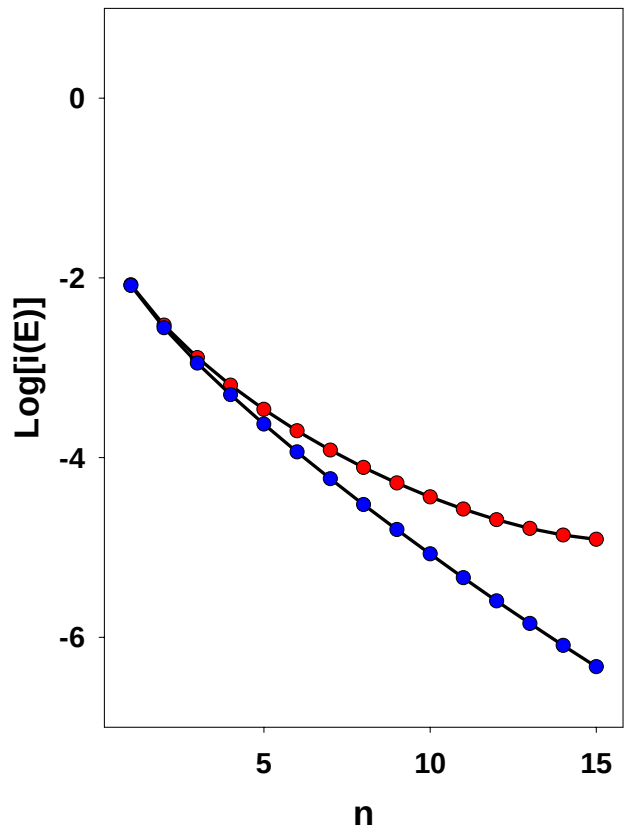


D=0



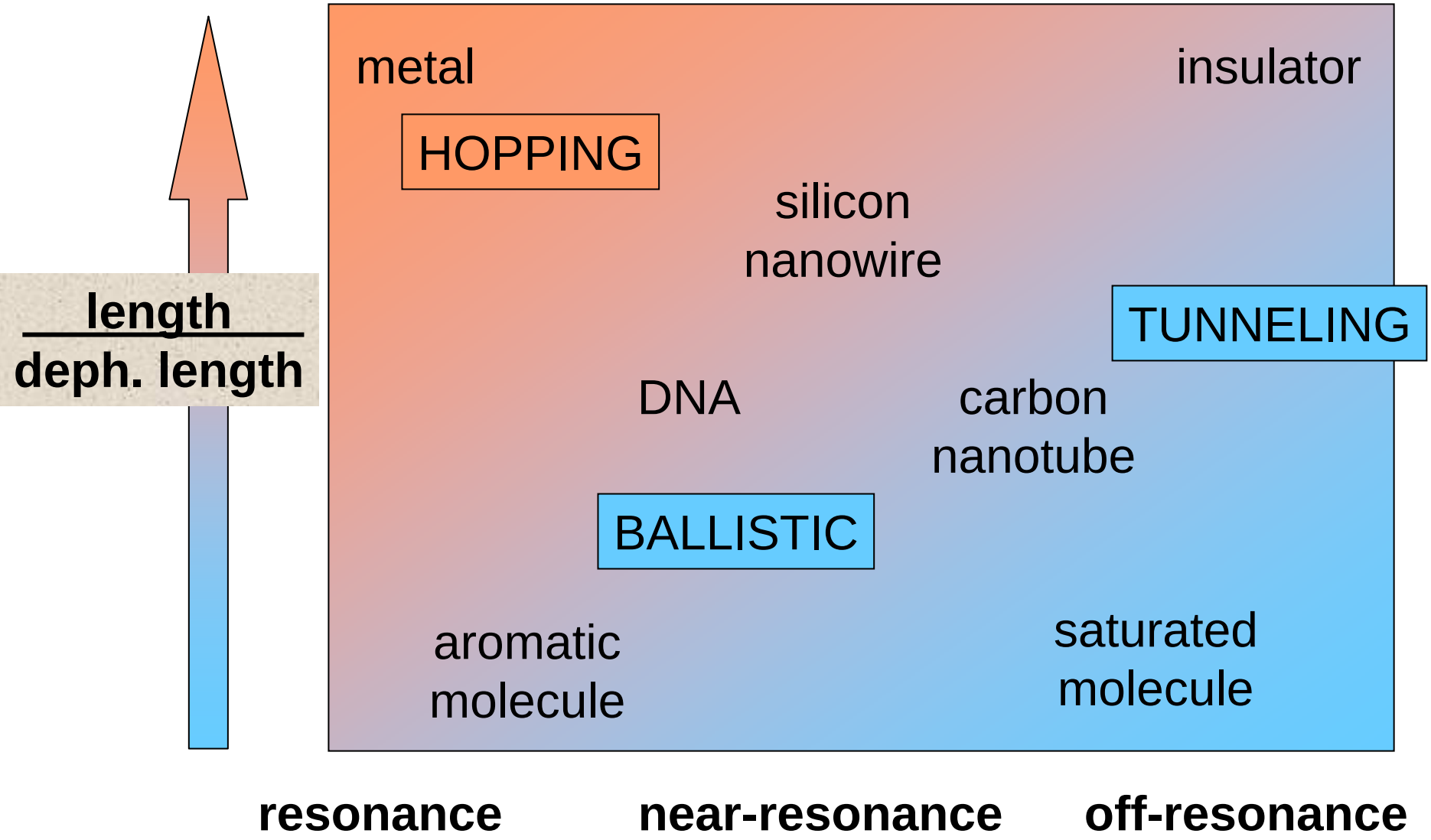
D>0

off-band

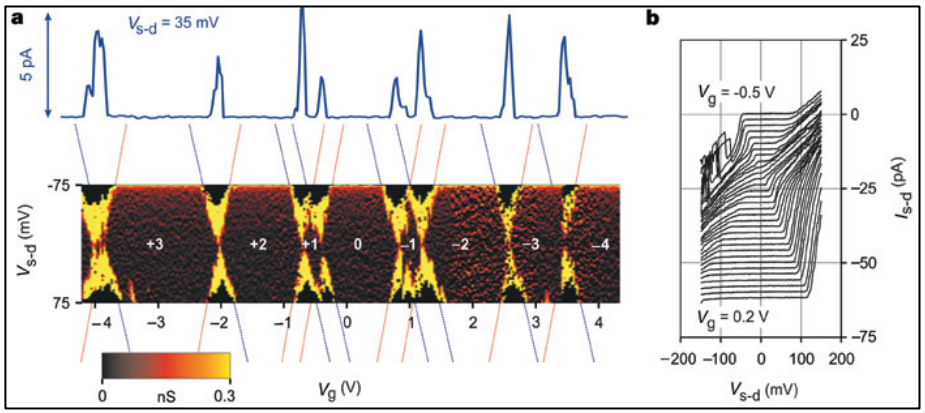


D>0

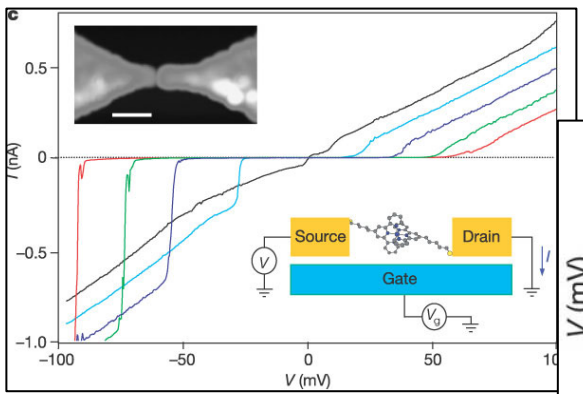
“Phase diagram” of conductors

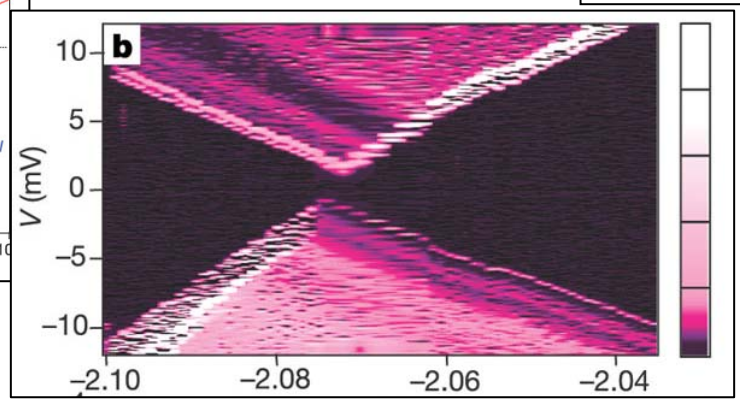


Taking electron – electron interaction into account



S. KUBATKIN et al.,
Nature **425**, 698 (2003).



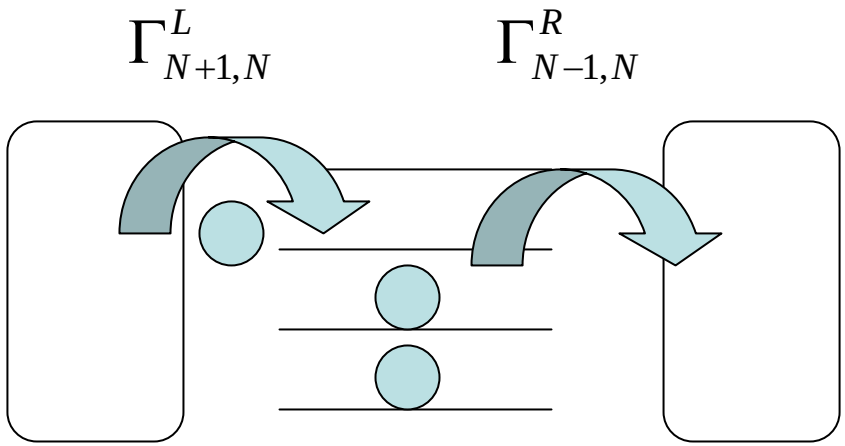


J. PARK et al.,
Nature **417**, 722 (2002).

Taking electron – electron interaction into account

- Experimental results show Coulomb blockade behaviour in single molecule systems
- The “orthodox theory” for Coulomb blockade is semi-classical in nature, does not treat the interacting electrons as quantum-particles
- Quantum-transport methods, although using the full sophistication quantum-chemistry offers, have so far been performed at the mean field (Hartree-Fock) level
- Is there a systematic way to go beyond the mean field approach and develop a more reliable framework for the Coulomb blockade regime ?

Review of the orthodox theory



$$\frac{dP(N)}{dt} = -\left(\Gamma_{N+1,N} + \Gamma_{N-1,N}\right)P(N) + \Gamma_{N,N+1}P(N+1) + \Gamma_{N,N-1}P(N-1) = 0$$

$$\Gamma_{N\pm1,N} = \Gamma^{L}_{N\pm1,N} + \Gamma^{R}_{N\pm1,N}$$

$$\Gamma^{L,R}_{N+1,N} = \gamma^{L,R} f^{*}\left(E(N+1) - E(N) + \varepsilon_0 - \mu_{L,R}\right)$$

$$f^{*}(E) = \frac{E}{e^{\beta E} - 1}$$

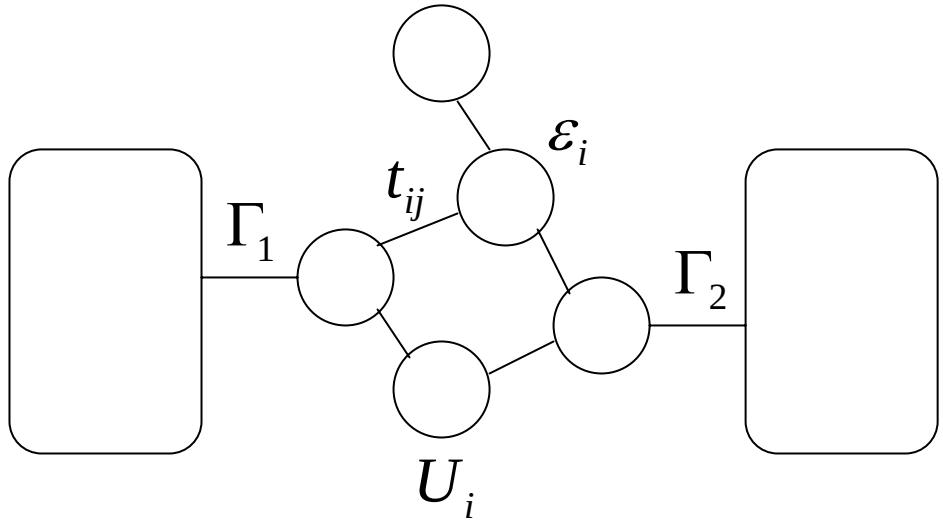
$$I = e\sum_{N} P(N)\left(\Gamma^{L}_{N+1,N} - \Gamma^{L}_{N-1,N}\right)$$

Quantum theory

Green functions:

$$G_{ij} = -i\left\langle d_i ; d_j^+ \right\rangle$$

$$G_{ij}^{(2)} = -i\left\langle \overline{n}_i d_i ; d_j^+ \right\rangle$$



Hubbard Hamiltonian:

site energy

on-site el-el repulsion

$$H = \sum_i \varepsilon_i d_i^+ d_i + \sum_{i,j} t_{ij} d_i^+ d_i + \sum_i U_i n_{i\uparrow} n_{i\downarrow}$$

hopping

Mean Field (MF)

$$(\omega-\varepsilon-t-\Sigma)G = I + UG^{(2)}$$

$$G^{(2)} = \bar{n}G$$

$$G^{r,a} = \left(\omega-\varepsilon-t-U\bar{n}-\Sigma^{r,a}\right)^{-1}$$

$$= \left(\omega - H_{nonin} - U\bar{n} - \Sigma^{r,a}\right)^{-1}$$

$$G^{n} = G^{r}\Sigma^{in}G^{a}$$

Beyond MF

$$(\omega-\varepsilon-t-\Sigma)G = I + UG^{(2)}$$

$$(\omega-\varepsilon-U)G^{(2)} = \bar{n}\left(I + (t+\Sigma)G\right)$$

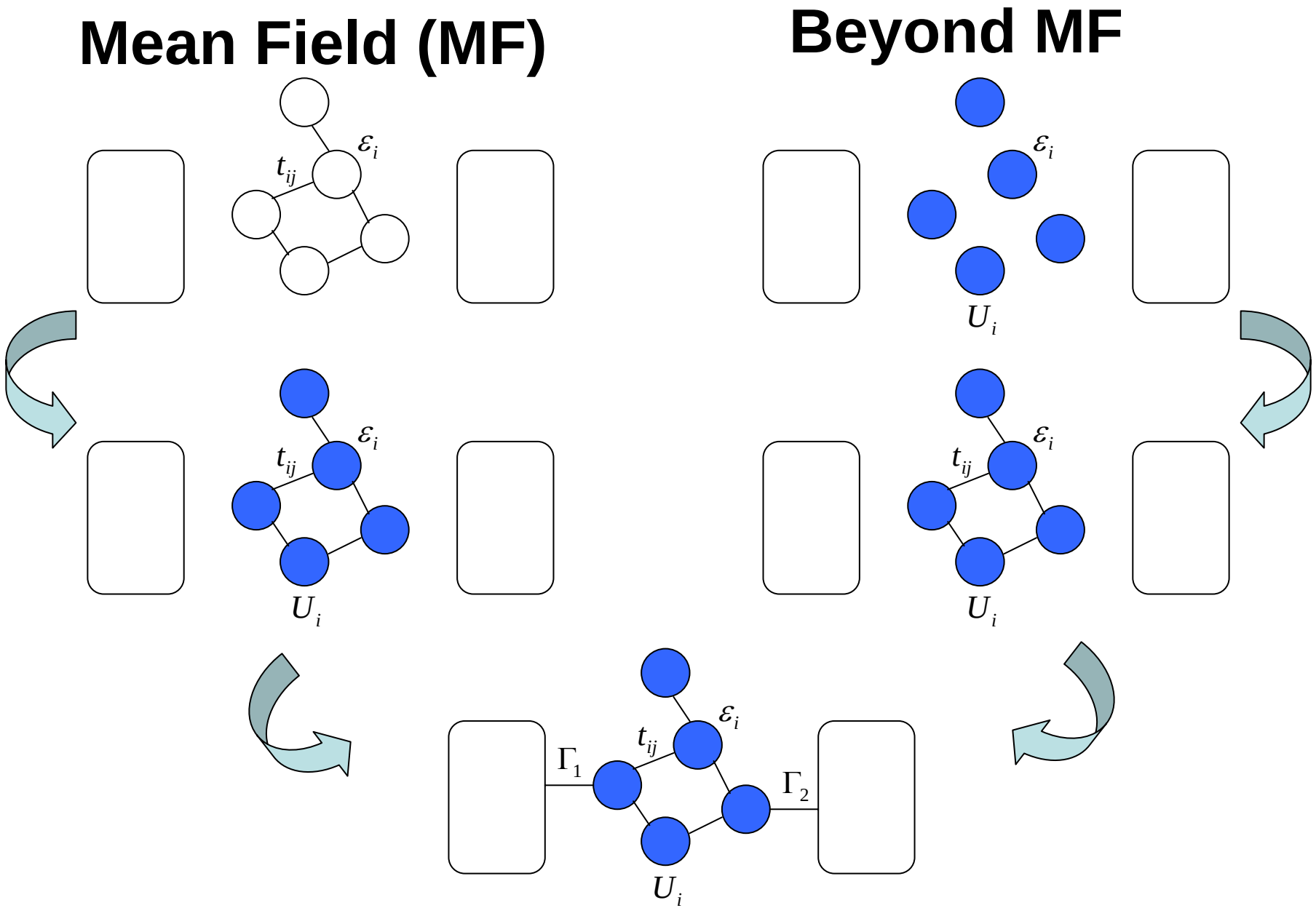
$$\left[G_{atom}\right]_{ii} = \frac{n_i}{\omega-\varepsilon_i-U} + \frac{1-n_i}{\omega-\varepsilon_i}$$

$$G_{free} = \left(G_{atom}^{-1} - t\right)^{-1}$$

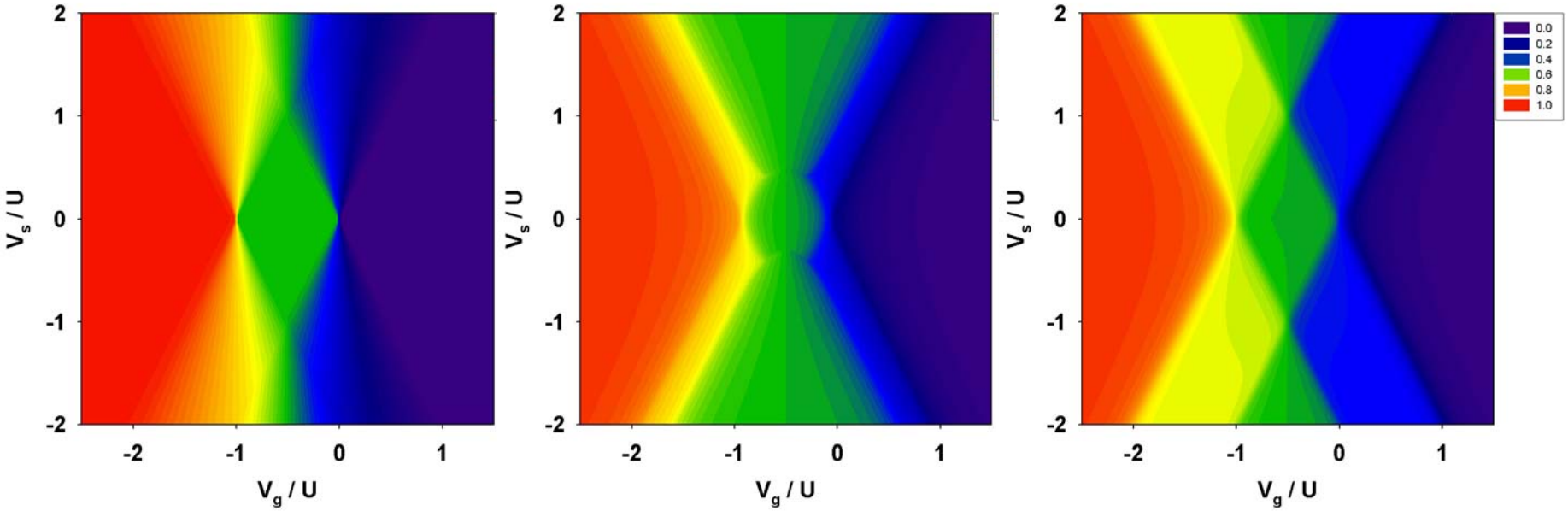
$$G^{r,a} = \left(G_{free}^{-1} - \Sigma^{r,a}\right)^{-1}$$

$$n_i = \int \frac{d\omega}{2\pi} G_{ii}^{n}(\omega)$$

$$I = \frac{e}{h}\int \left(f(\mu_1) - f(\mu_2)\right) Tr\left[\Gamma_1 G^{r}\Gamma_2 G^{a}\right] d\omega$$


Mean Field (MF)
Beyond MF
ε_i
t_{ij}
U_i
Γ_1
Γ_2

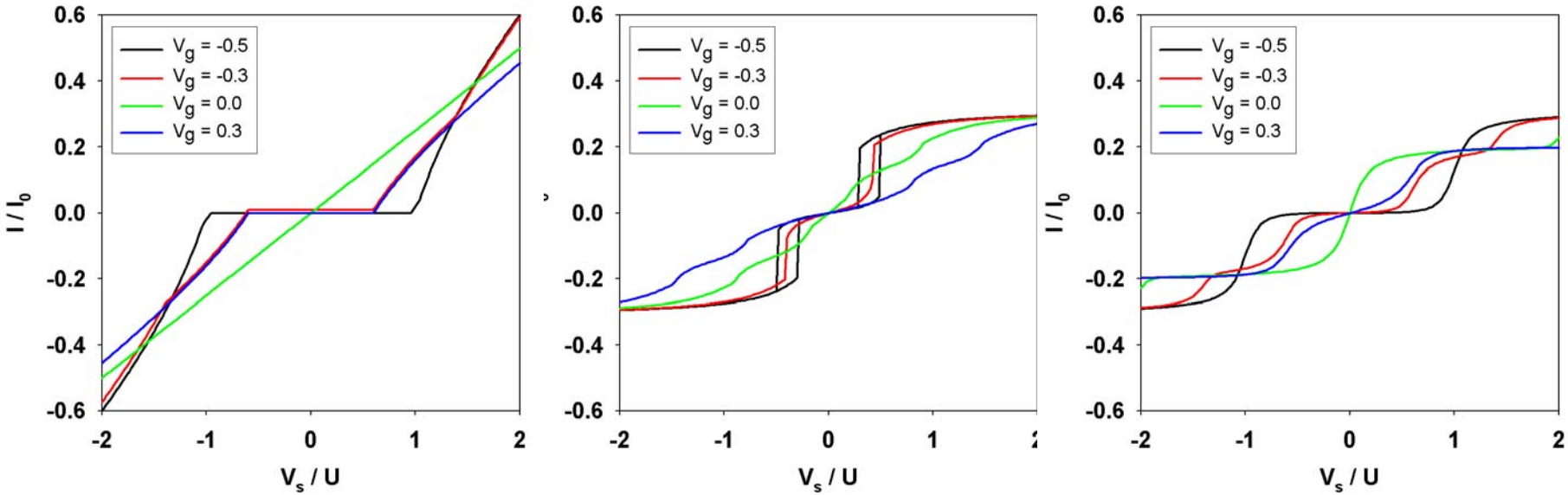
orthodox MF beyond MF



Charge versus gate voltage and bias voltage

The Mean Field approach captures the charging phenomenon, but qualitatively unreliable.
Going beyond Mean Field, the characteristic romboidal plot appears.

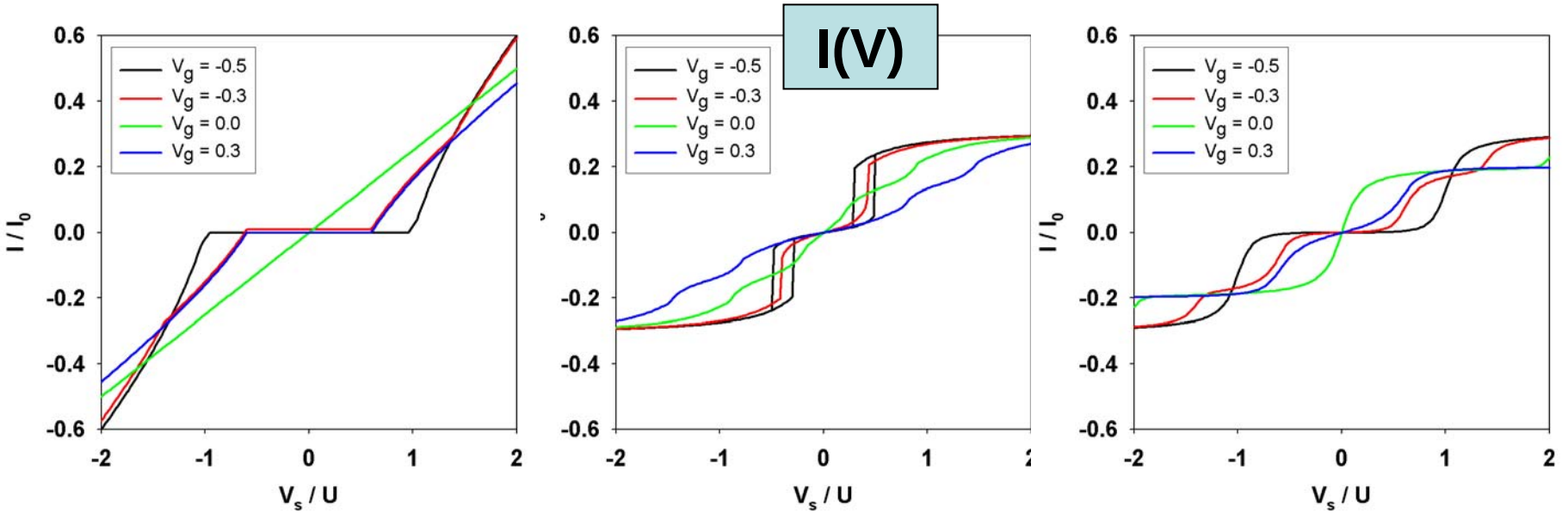
orthodox MF beyond MF

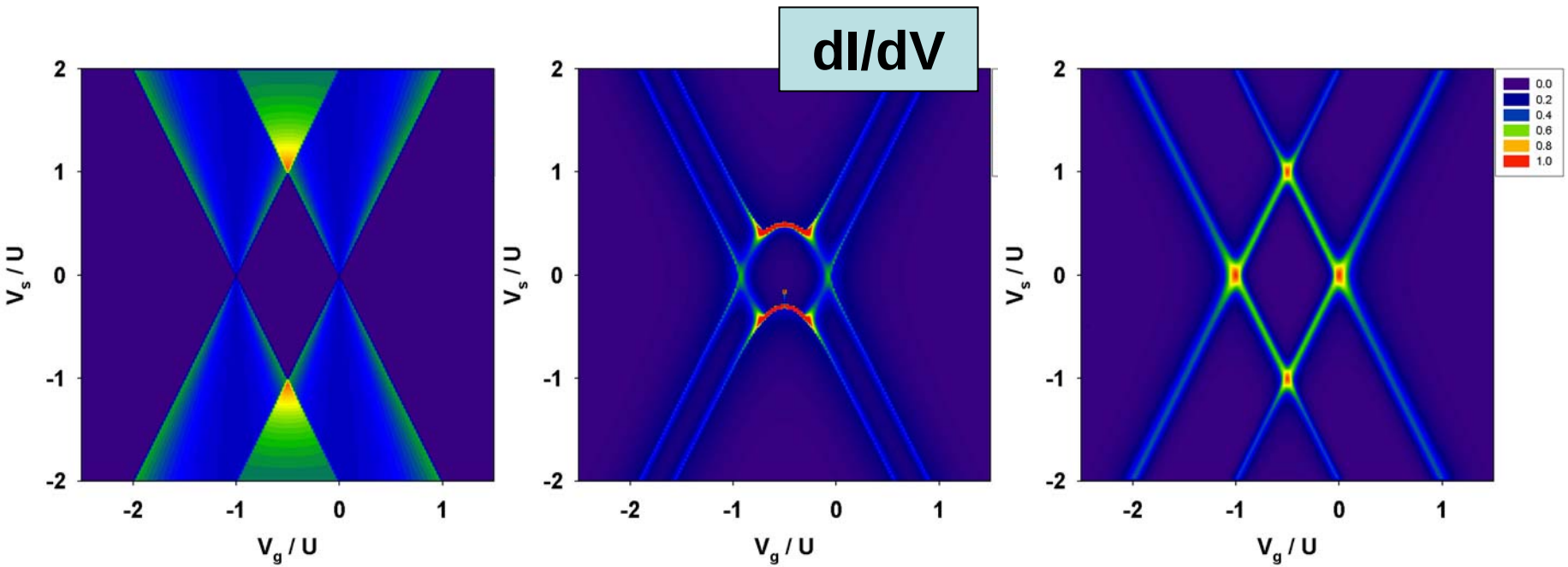


Current versus bias voltage at different gate voltages

The Mean Field approach captures the current staircase phenomenon, but predicts an unphysical hysteresis. Going beyond Mean Field, the staircase clearly emerges, no hysteresis. Current saturates after passing resonance.

orthodox MF beyond MF





Future directions

- Multi-site calculations
- Combine the correlated approach with the modeling of dephasing
- Generalize for extended Hubbard model
- Combine methodology with sophisticated quantum-chemical calculation techniques

Conclusions

- NEGF is a useful technique to describe quantum transport
- Dephasing can be naturally included
- Ballistic, Tunneling and Hopping regimes for conduction can be explored
- It is necessary to go beyond the mean field level when modeling transport in the Coulomb blockade regime