

# Sources, Sinks and Correlation in Electron Transport

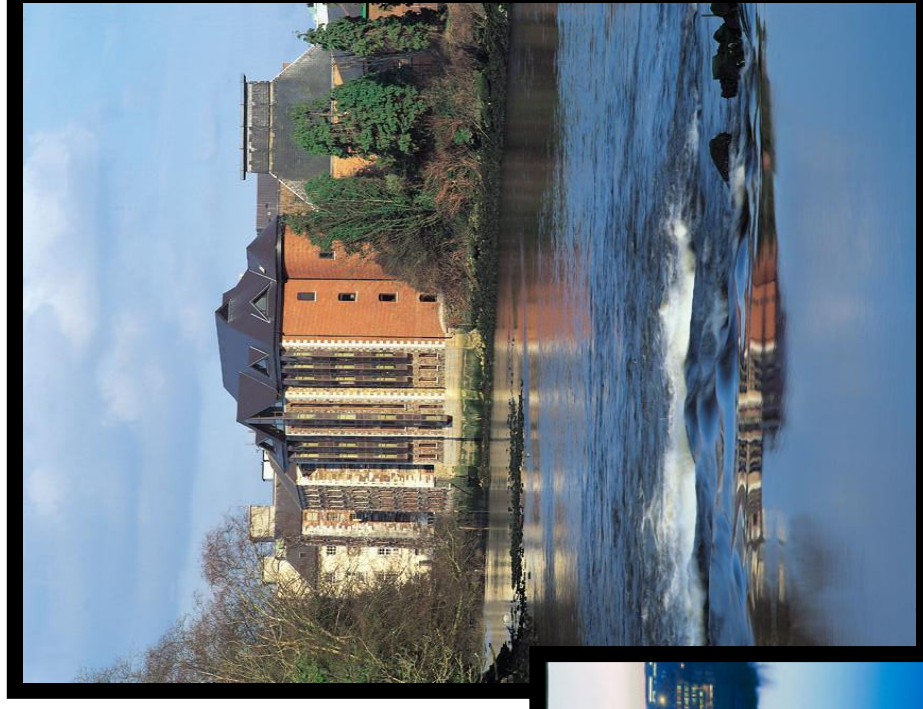
**Jim Greer**

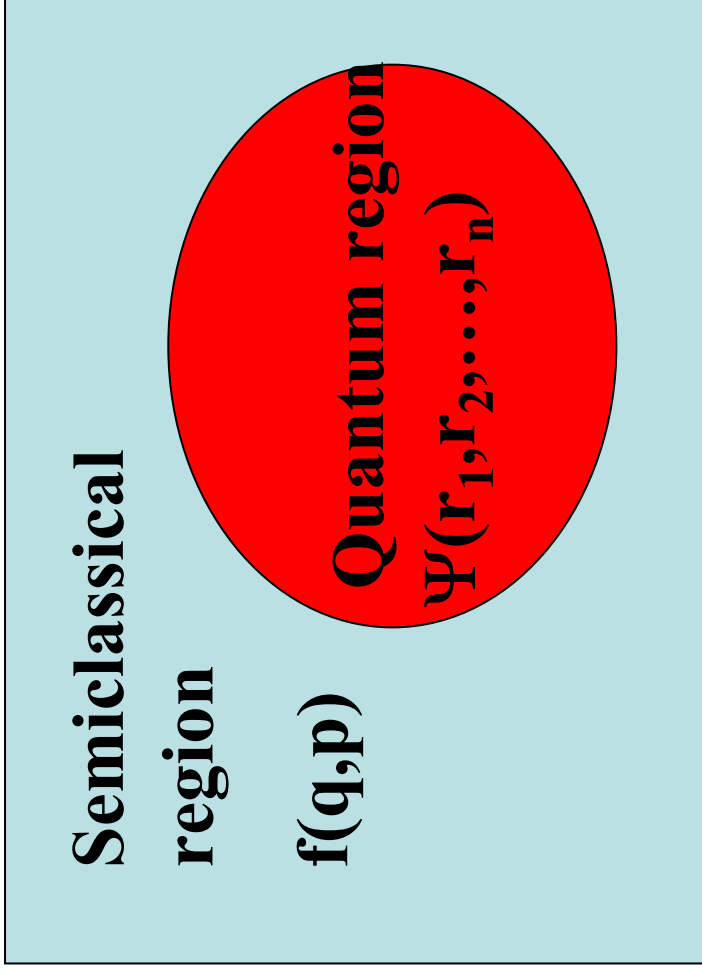
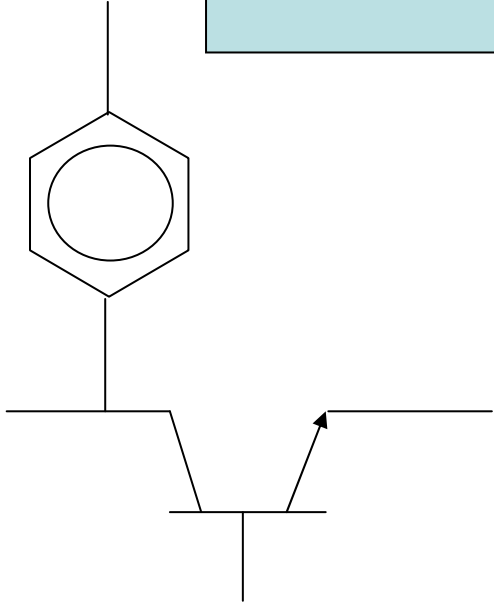
**Giorgos Fagas**

**Tom Henderson**

**Paul Delaney\***

\* now at Queen's University Belfast

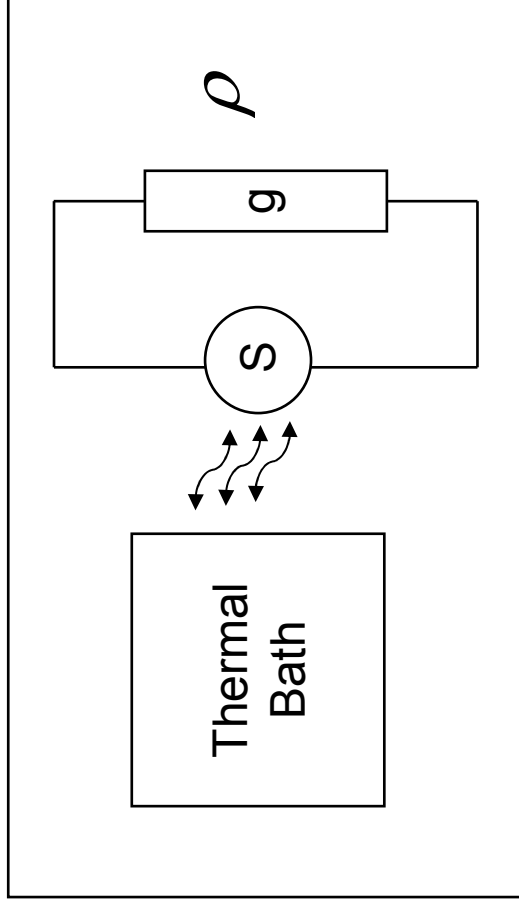




and for technology design, want to describe quantum mechanical degrees of freedom interacting with macroscopic systems  
"READ" "WRITE"

Closed system described by Schrödinger equation

$$H\Psi = i\hbar \frac{\partial}{\partial t} \Psi \approx E\Psi$$



Open system described by reduced density matrix

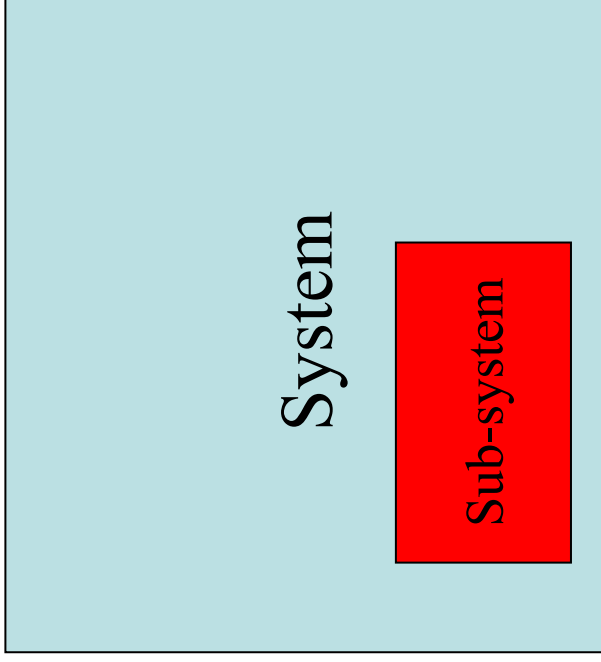
# Quantum Electron Transport

Irreversible



Information Loss

Degrees of freedom within sub-system cannot describe entire system: “irreversible”



System is deterministic: “unitary time evolution”

# Information Loss

- Studying a sub-system implies loss of information
- Formally, introducing information loss may be achieved 2 ways:
  - “removing coherences”
  - “removing correlations”

# Removing Coherences

- Begin with a “fine grain” probability distribution function and “coarse grain”
- Entropy (coarse grain) > Entropy (fine grain)
- Typically implies
  - ignoring off-diagonals of  $\rho$  in energy representation
  - and defining occupation numbers  $n_k$

Leads to rate equation approach  $\frac{dn_k}{dt} = \sum_l (t_{kl}n_l - t_{lk}n_k)$

$$n_i \Leftrightarrow \mathcal{E}_{ij} \quad \mathcal{E}_i \Leftrightarrow n_{ij}$$

but cannot simultaneously diagonalize energy and occupation in a correlated system

## A few comments about rate theories

- Landauer type formulae a special case
- Densities  $\rho(x) = \psi^* \psi$
- But currents determined by density matrix

$$I = \frac{e\hbar}{2im} \psi^* \nabla_x \psi - \psi \nabla_x \psi^*$$

$$I = \frac{e\hbar}{2im} [\nabla_x - \nabla_{x'}] \rho(x', x) \Big|_{x=x'}$$

Off-diagonals of  $\rho$  specify current  
in x-representation

No quantity corresponding to DM in DFT

Possibly better start is DMFT

# Removing Correlation

In practice, implies factorizing density matrix

–  $\rho \approx \rho_1 \bullet \rho_2$     If DM factorizes, no correlation between 1 and 2

– Entropy( $\rho_1 \bullet \rho_2$ ) > Entropy( $\rho$ )

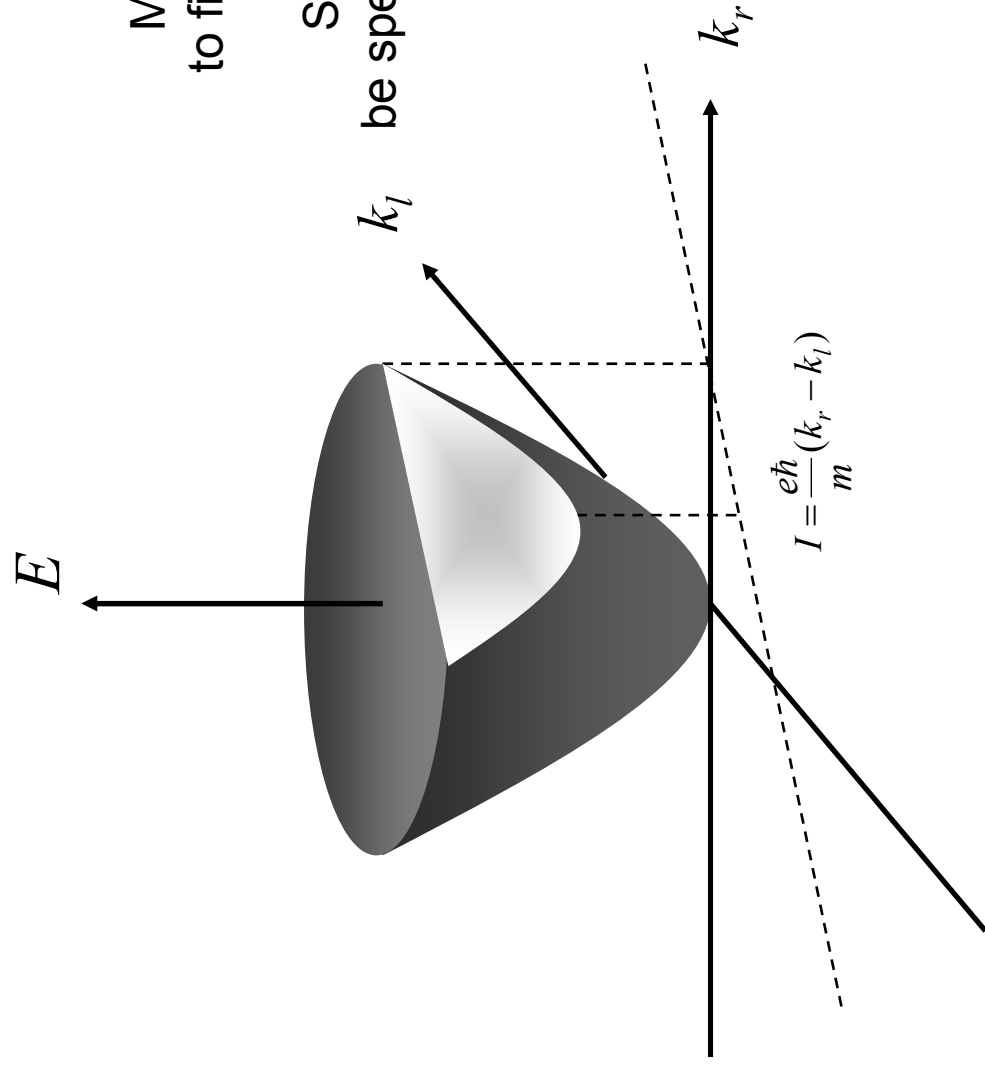
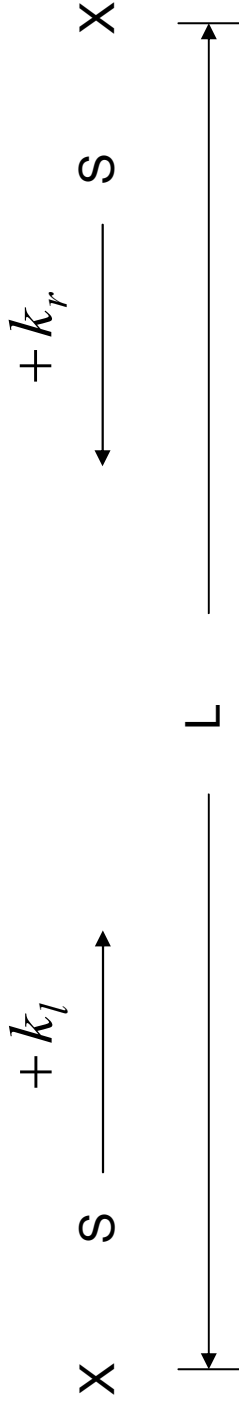
– Removes correlation between 1 and 2

– Keeps correlations on 1 and 2 !

– Problem becomes how to determine  $\rho$  on sub-system:

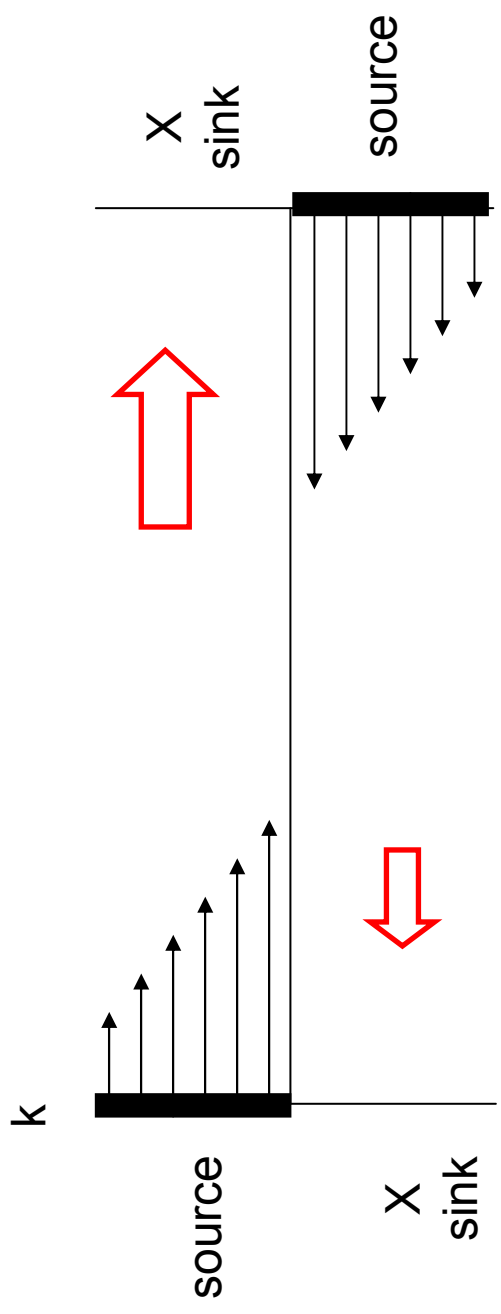
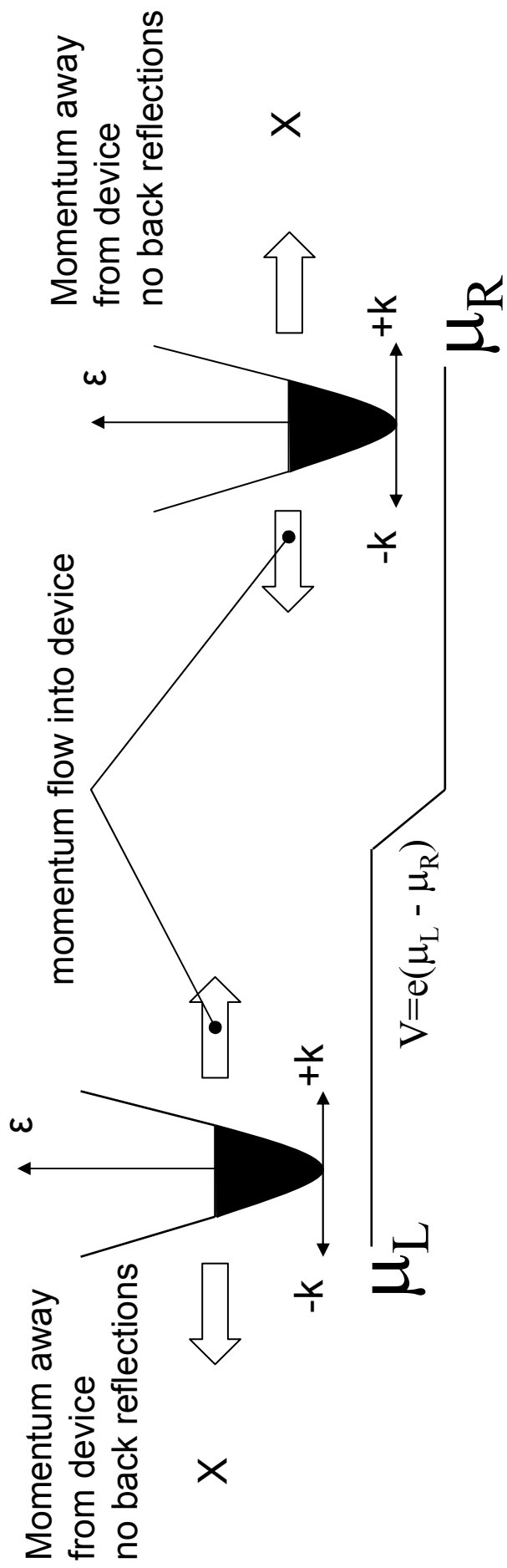
MaxEnt- maximize entropy subject to constraints one option



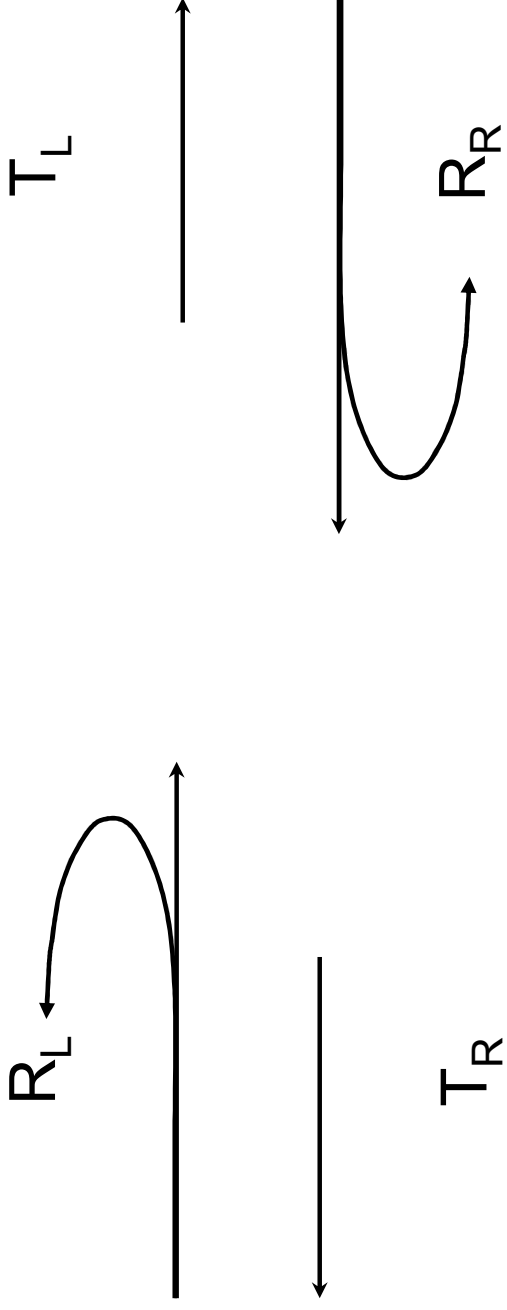


Minimizing energy subject to fixed current is not sufficient

Source properties need to be specified as boundary conditions



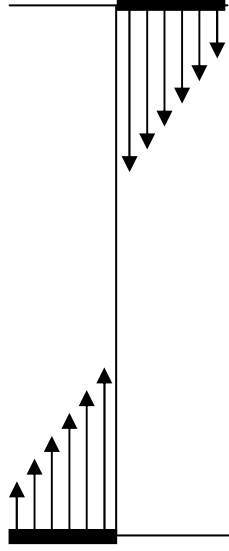
**Left reservoir** | **Device region** | **Right reservoir**



$$I = \frac{e\hbar}{m} \int dk [T_L(k, V_{LR}) - T_R(k, V_{RL})] k$$

# For interacting many-electrons (i.e. molecules)

- we don't have single particle energies
- there is no Fermi-Dirac distribution
- or Fermi energy, etc.
- what is meant by electrons coming from the left or right?



How do we formulate reservoir boundary conditions for many-body physics?

## 1-body reduced density matrix

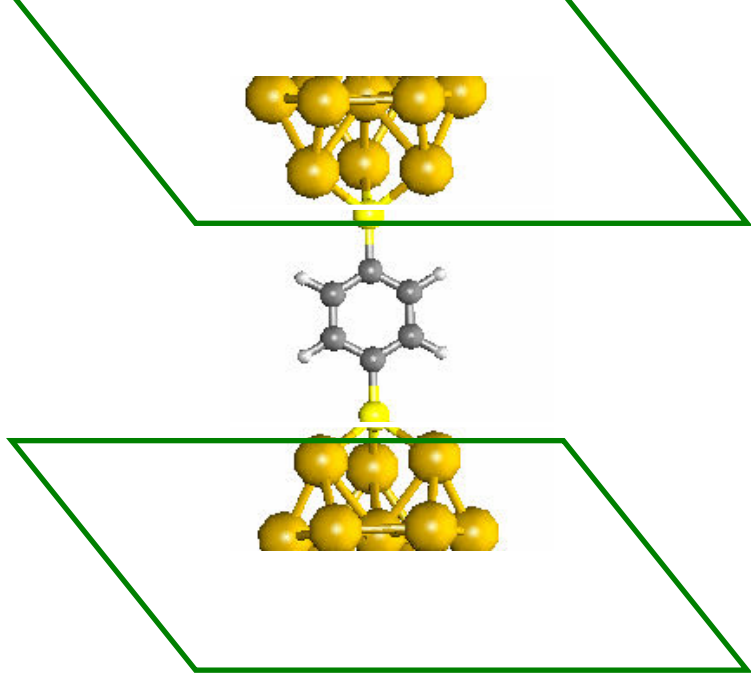
$$\rho(\mathbf{r},\mathbf{r}') = N \int \prod_{i=2}^n d\mathbf{r}_i \Psi^*(\mathbf{r}',\mathbf{r}_2,\dots,\mathbf{r}_n) \Psi(\mathbf{r},\mathbf{r}_2,\dots,\mathbf{r}_n)$$

Apply scattering boundary conditions to Wigner transform

$$f(\mathbf{q},\mathbf{p}) = \int d\mathbf{r} \rho(\mathbf{q}+\mathbf{r}/2,\mathbf{q}-\mathbf{r}/2) \exp(-i\mathbf{p}\mathbf{r})$$

Proposed by Frenksley for 1e transport  
Generalized by us for many-electron transport  
Direct link to Boltzmann transport

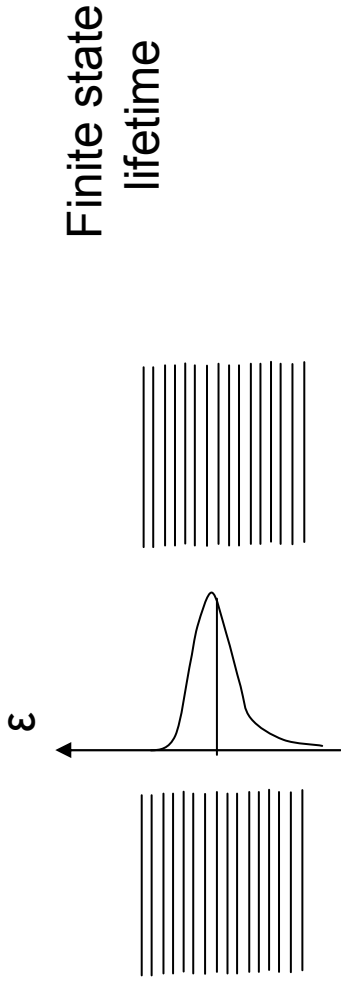
**Idea: constrain the Wigner function  
in the contacts to restrict momentum in-flow  
while allowing out-flow to vary**



Fixed incoming momentum flux acts as  
left and right current sources into the device region

# Defining current sinks

- Want to allow electrons flowing out of device region to ‘equilibrate’ with reservoir (no back reflections)
- Want to describe device state broadening in similar fashion as electron-self energies  $\Sigma(\varepsilon)$ , but without reference to single particle energies!!!



# Determining complex absorbing potentials from electron self energies

$$H_0|\chi_i\rangle = \epsilon_i|\chi_i\rangle$$

$$\langle\chi_j|H_0 = \epsilon_j\langle\chi_j|$$

“device” Hamiltonian

$$[H_0 + \Sigma(\omega_i)]|\psi_i\rangle = \omega_i|\psi_i\rangle$$

$$\langle\phi_i|[H_0 + \Sigma(\omega_i)] = \omega_i\langle\phi_i|$$

Introduce reservoir coupling through electron self energy

$$W = \sum_i |\psi_i\rangle\omega_i'\langle\phi_i| - H_0$$

Construct complex absorbing potential from solutions with the SE



In matrix form

$$\mathbf{H}_0 \mathbf{X} = \mathbf{X} \boldsymbol{\epsilon},$$

$$\mathbf{X}^\dagger \mathbf{H}_0 = \boldsymbol{\epsilon} \mathbf{X}^\dagger$$

$$\mathbf{X}^\dagger \mathbf{X} = \mathbf{1}.$$

“device” Hamiltonian

$$[\mathbf{H}_0 + \boldsymbol{\Sigma}(\omega_i)] \mathbf{U}_i = \omega_i \mathbf{U}_i$$

$$\mathbf{V}_i^\dagger [\mathbf{H}_0 + \boldsymbol{\Sigma}(\omega_i)] = \omega_i \mathbf{V}_i^\dagger$$

Introduce reservoir coupling  
through electron self energy

$$\mathbf{W}_0 = \mathbf{X} \boldsymbol{\omega} \mathbf{X}^\dagger - \mathbf{H}_0,$$

$$\bar{\mathbf{W}}^\psi = \mathbf{U} \boldsymbol{\omega} \mathbf{U}^{-1} - \mathbf{H}_0,$$

$$\bar{\mathbf{W}}^\phi = \mathbf{V}^{-\dagger} \boldsymbol{\omega} \mathbf{V}^\dagger - \mathbf{H}_0,$$

$$\bar{\mathbf{W}} = \frac{\bar{\mathbf{W}}^\psi + \bar{\mathbf{W}}^\phi}{2}.$$

Then we construct several approximations  
to the CAP from the left/right eigenvectors  
of  $\mathbf{H} + \boldsymbol{\Sigma}$

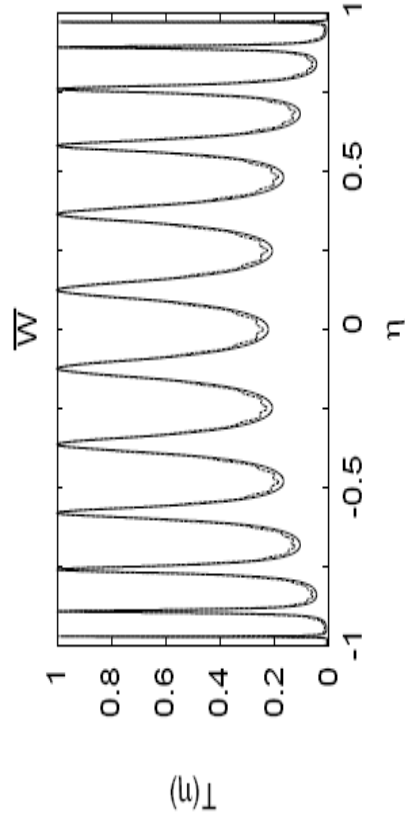
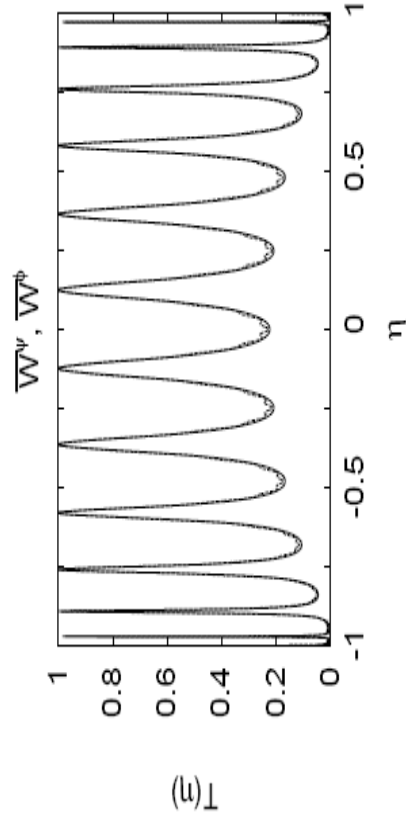
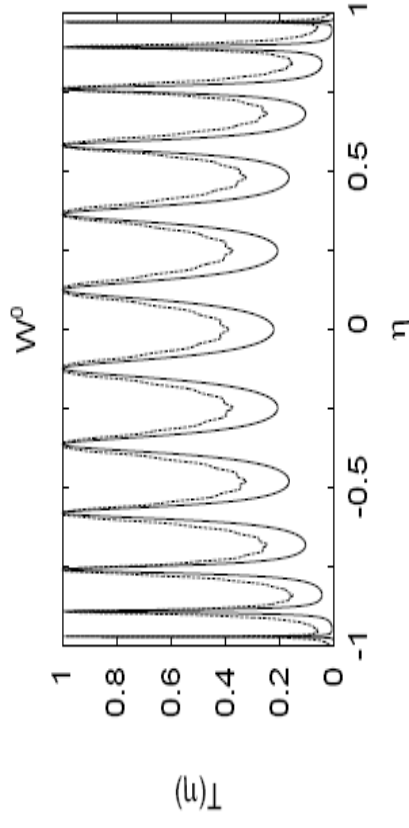
## Exact self-energies for Hückel chain of atoms

A. Kopf and P. Saalfrank, Chem. Phys. Lett. **386**, 17 (2004).

$$H = H_L + H_M + H_R + V$$

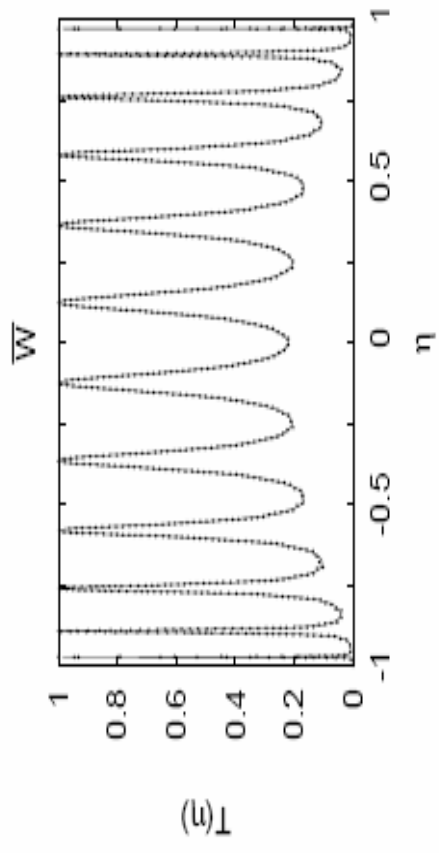
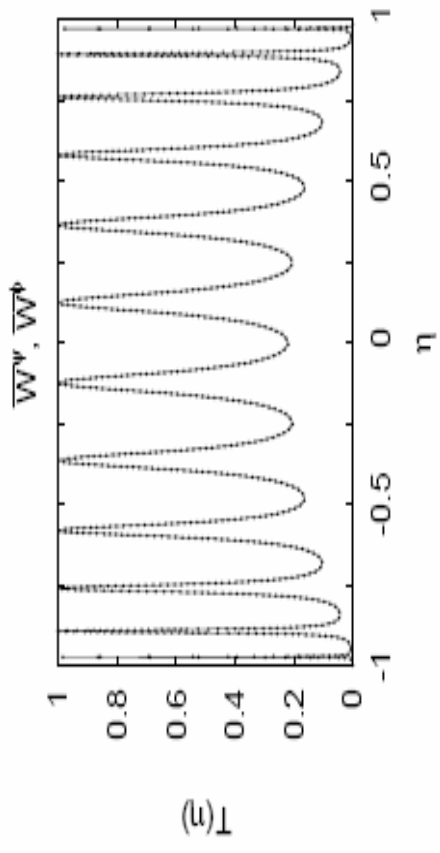
- L left electrode
- M molecule
- R right electrode
- V electrode-molecule coupling

Using same model, we construct CAP and compare



Good agreement  
 But next let's try by  
 splitting the electrodes

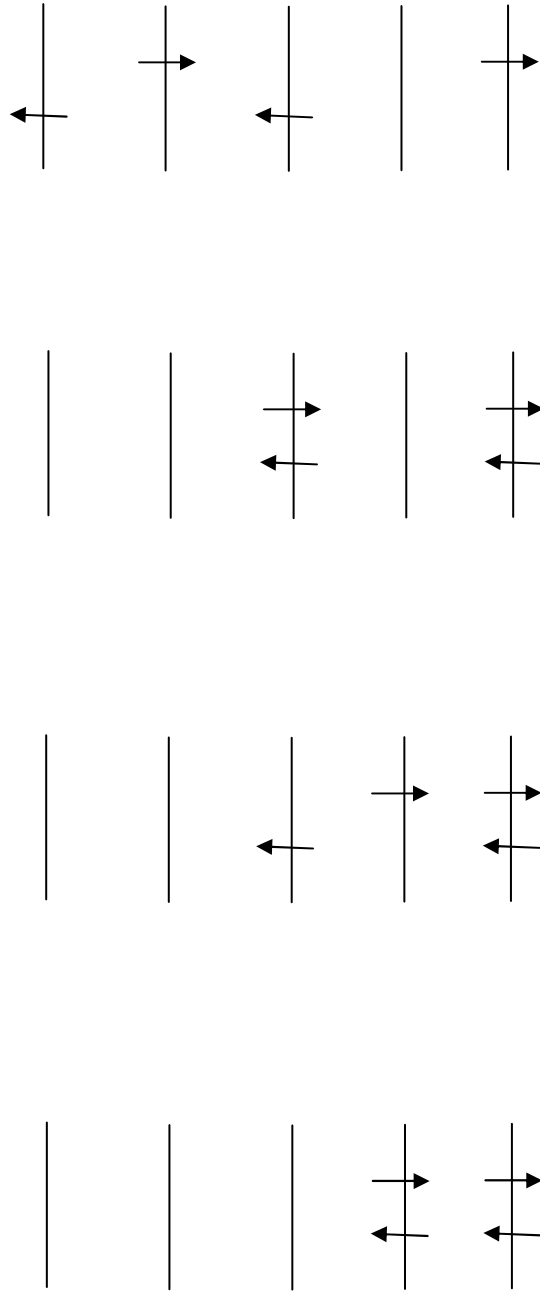




# Our approach to transport

- expand  $|\Psi\rangle = c_0 |\Psi_0\rangle + c_1 |\Psi_1\rangle + c_2 |\Psi_2\rangle + \dots$  as a many electron wave function
- incoming electrons: momentum distribution  $f(p)$  fixed by the nature of the contacts
- molecule reflects/transmits as much as it wants to minimize energy  
 $\langle \Psi | H_0 + e E z | \Psi \rangle$
- keep incoming electron distributions fixed and solve constrained min. problem (Lagrange multipliers)

- Calculate 
$$I = \frac{e\hbar}{2im} [\nabla_x - \nabla_{x'}] \rho(x', x) \Big|_{x=x'}$$



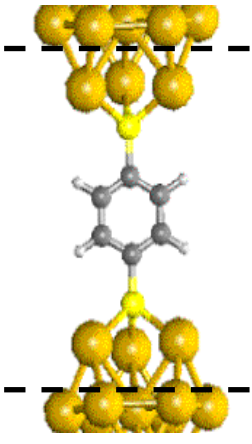
Reference state	Single excitation	Double excitation	Triple excitation
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Approximate number of configurations needed

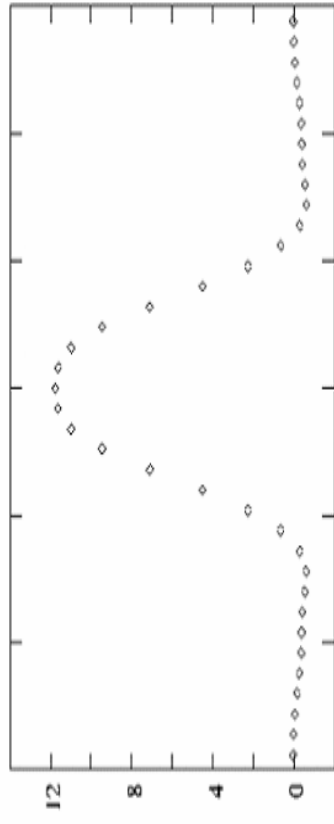
n electrons  
 M spin orbitals  
 N occupied spin orbitals

**We find compact CI expansions by a Monte Carlo search-not excitation limited**

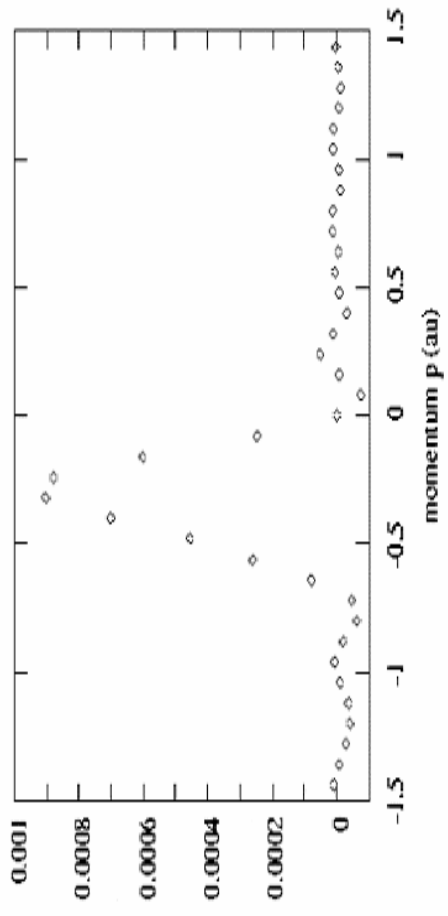
$$\binom{N}{n} \binom{M-N}{n}$$



$q_L$   $q_R$



$f(p)$



$f(p) - f_0(p)$

**Experiment:**

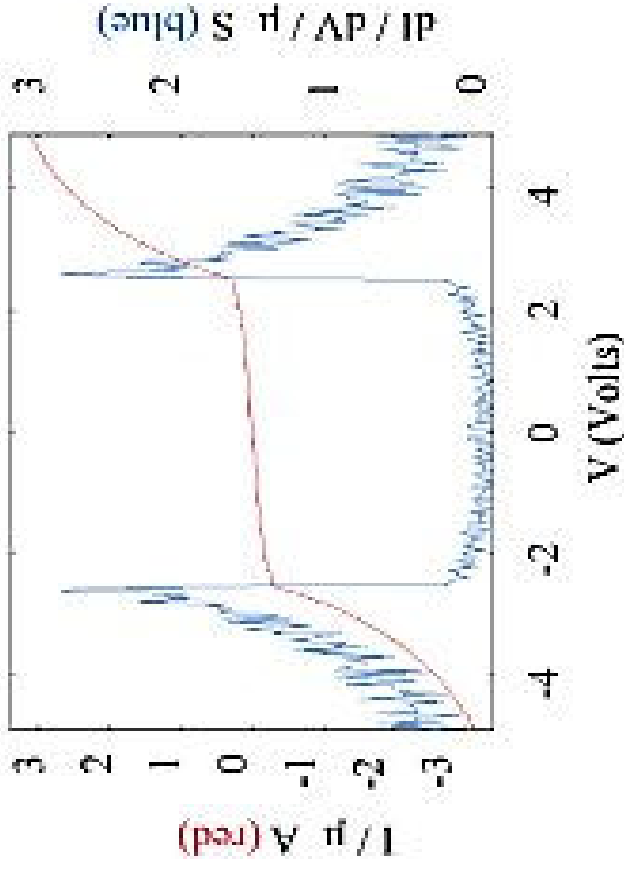
M.A. Reed., C. Zhou, D.J. Muller, T.P. Burgin, and J.M. Tour, Science, 278, 252 (1997)

Onset  $R = 22 \text{ M}\Omega$  followed by  $R = 13 \text{ M}\Omega$

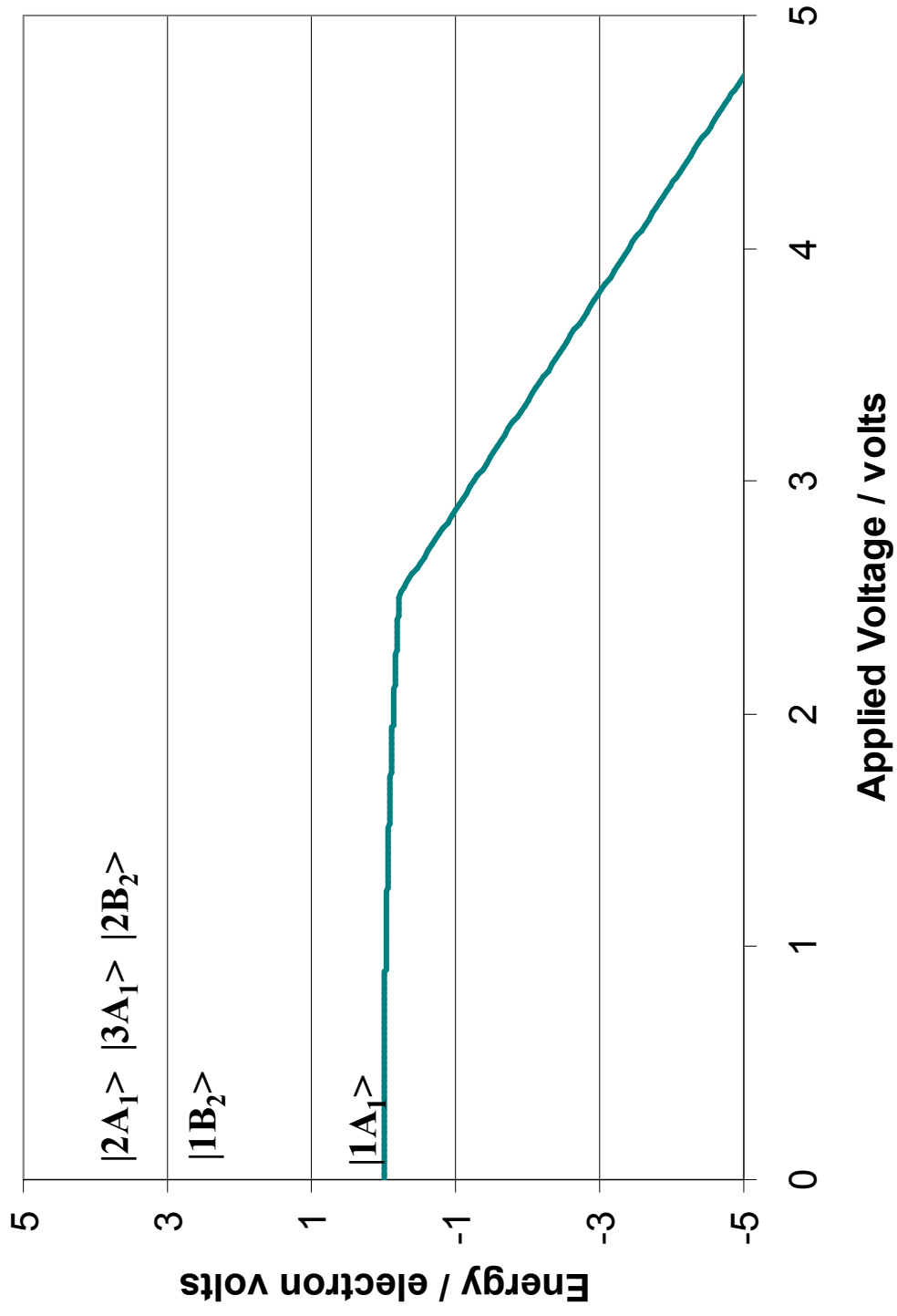
$I|_{2V} = 60 \text{ nAmp}$

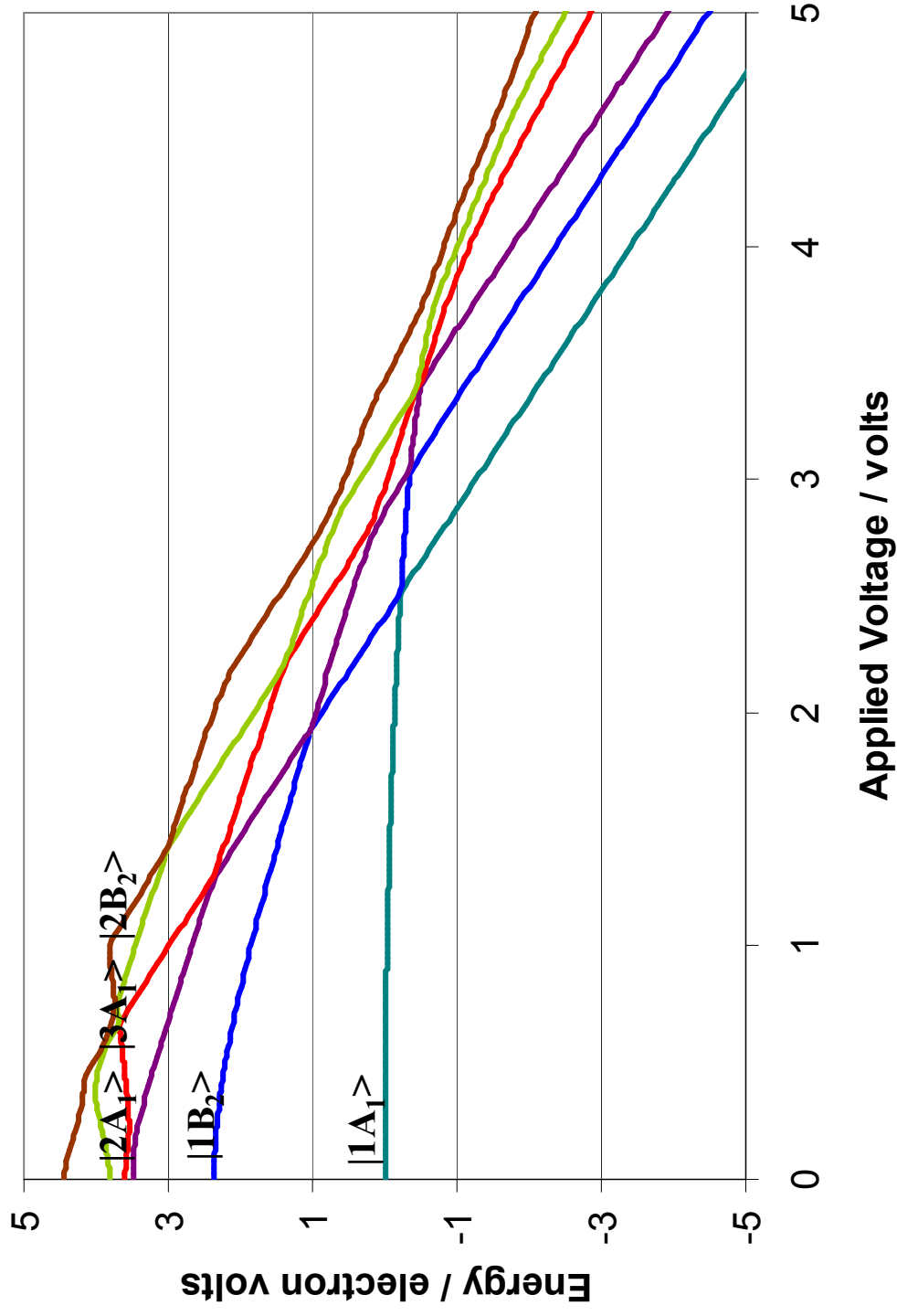
Onset  $R = 18 \text{ M}\Omega$  followed by several  $\text{M}\Omega$   
(dependant where  $\partial V/\partial I$  is calculated)

$I|_{2V} = 160 \text{ nAmp}$





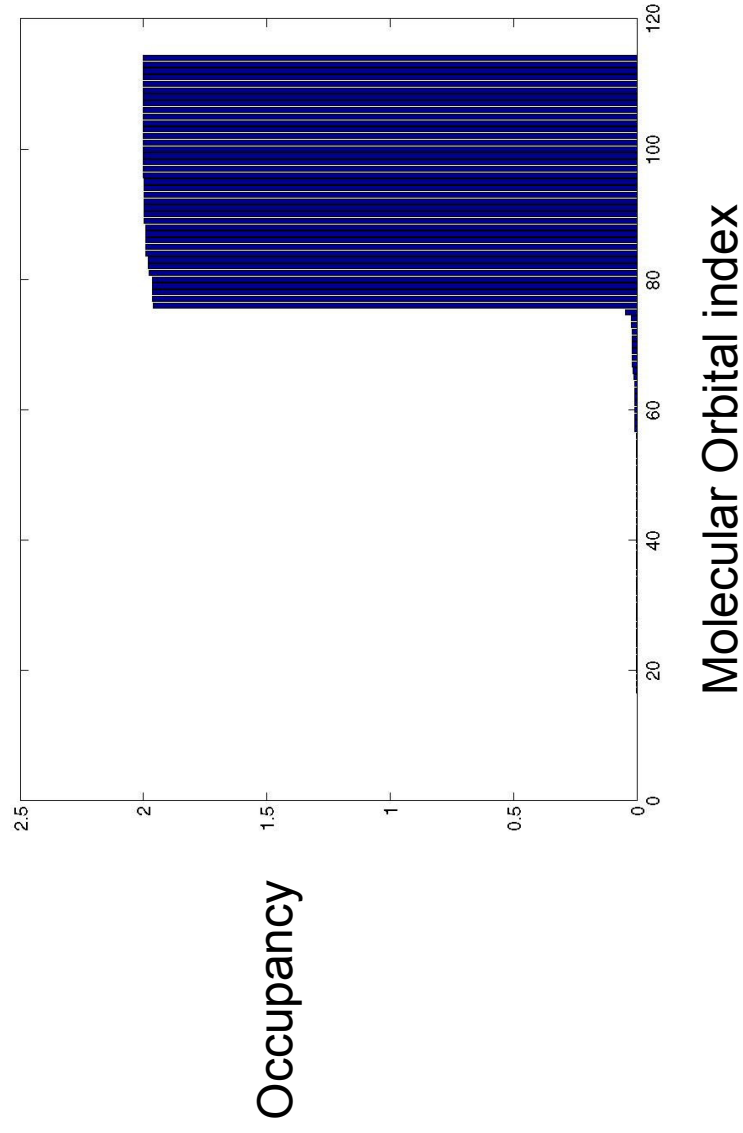




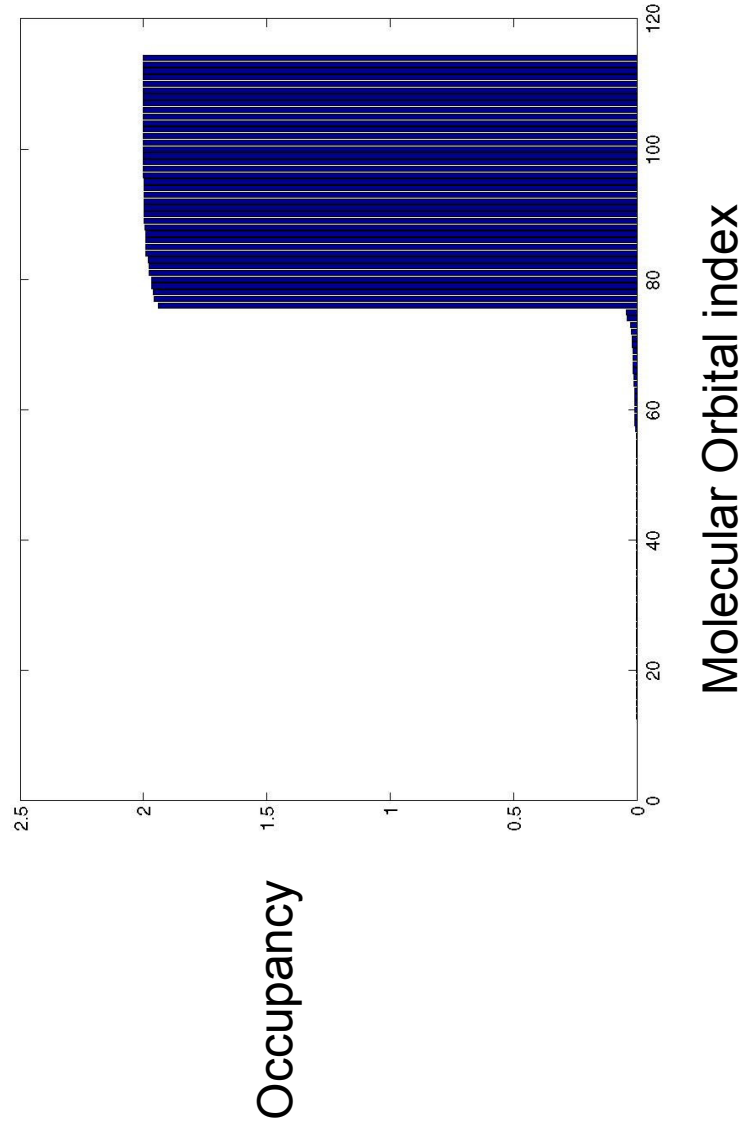
## ***Do we need correlation to describe transport?***

- **Electron correlation:** physics beyond that described by a **single Slater determinant**
- From  $\Psi \rightarrow \rho(r)$  and  $\rho(r,r')$
- Look at the occupations  $n_i$  of  $\rho(r,r')$ 
  - Orbitals diagonalizing  $\rho$ : “natural orbitals”
- If  $\Psi = \text{Det}[\phi_1(r_1s_1), \dots, \phi_N(r_Ns_N)]$  then
  - N eigenvalues  **$n_i = 2$**  (eigenvectors  $\phi_i$ )
  - All the other  **$n_i = 0$**

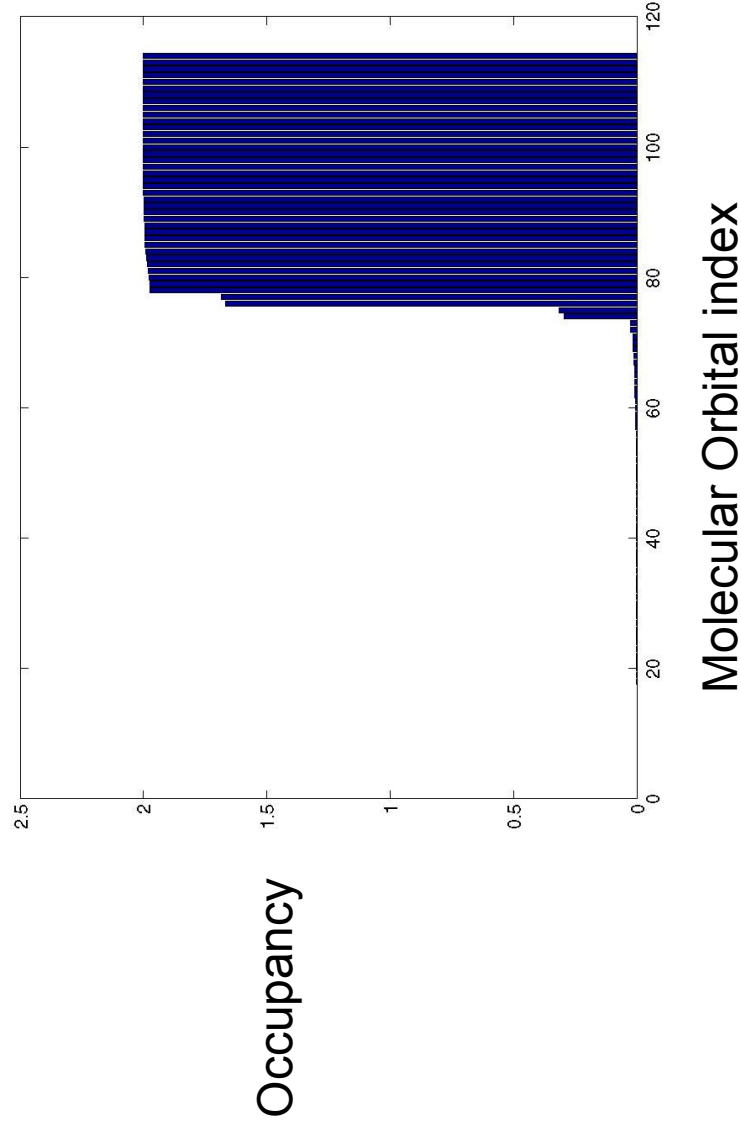
*How important is correlation?*



***How important is correlation?***



**How important is correlation?**



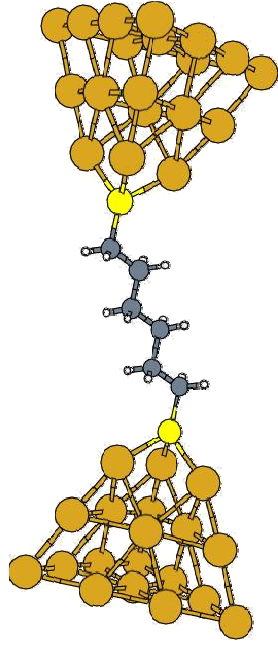
Occupancy

**V>resonance**

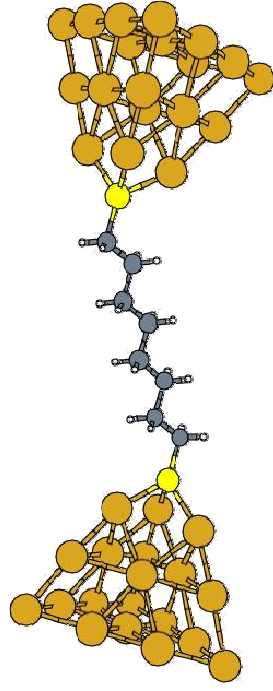
**$\Psi$  can not  
be described  
by a single  
Slater  
determinant**

Molecular Orbital index

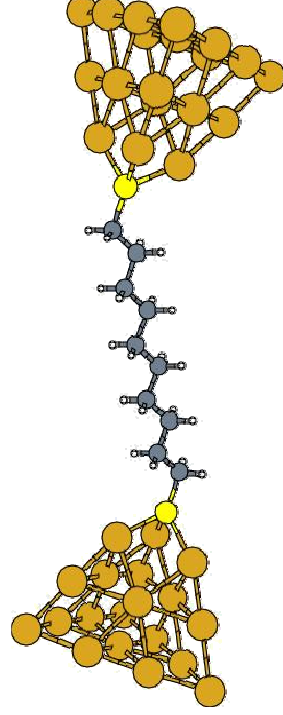
# Alkane-based tunnel junctions



Example of non-resonant transport

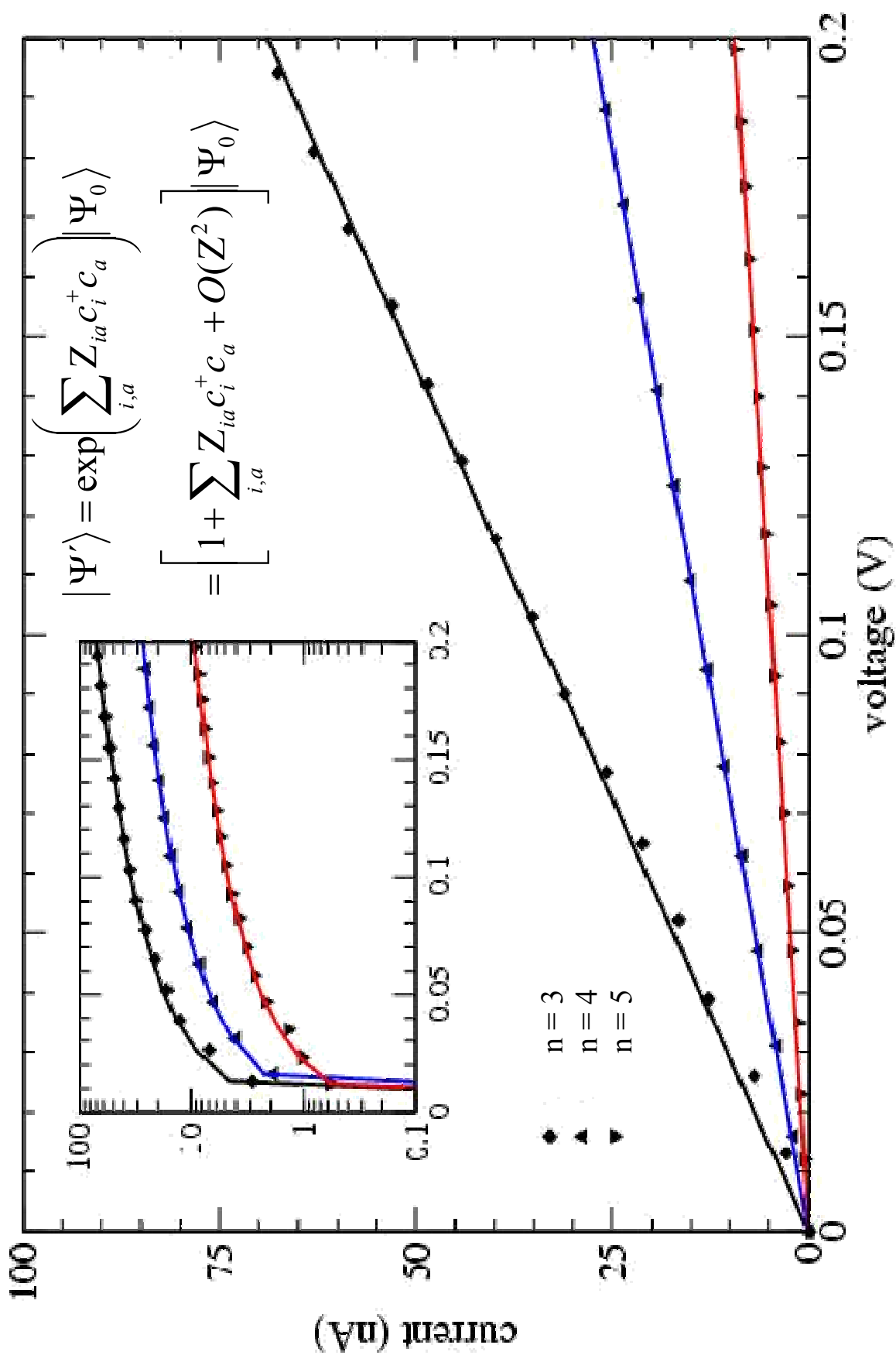


Electronic correlations should not be important



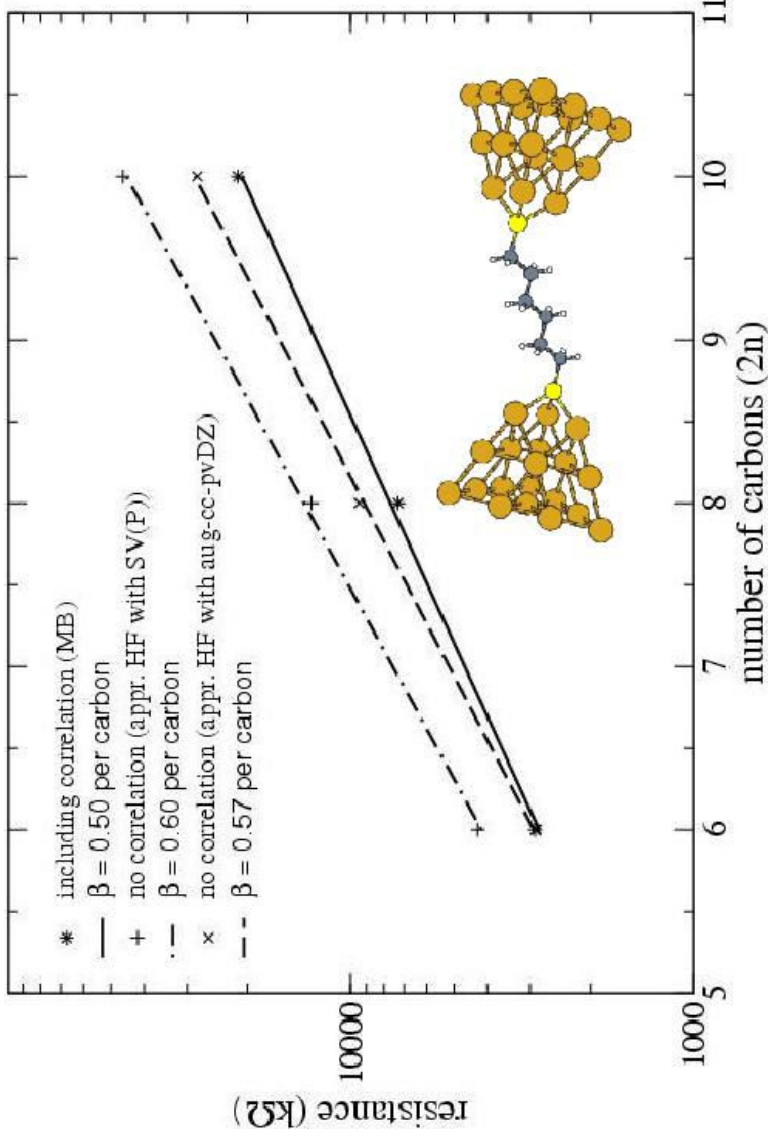
What is the correct 1-electron approximation?

$\text{Au}_{\text{tip}} - \text{S} - (\text{C}_2\text{H}_4)_n - \text{S} - \text{Au}_{\text{tip}}$  molecular junction  
singles-mediated current





## Tunnel resistance exponential law



Agrees well with recent measurements

Cue, Primak, Zarate, Tomfohr, Sankey, Moore, Gust, Nagahara, Lindsay  
*J. Phys. Chem B* **106**, 8609 (2002)  
 $\beta = 0.57 / n$

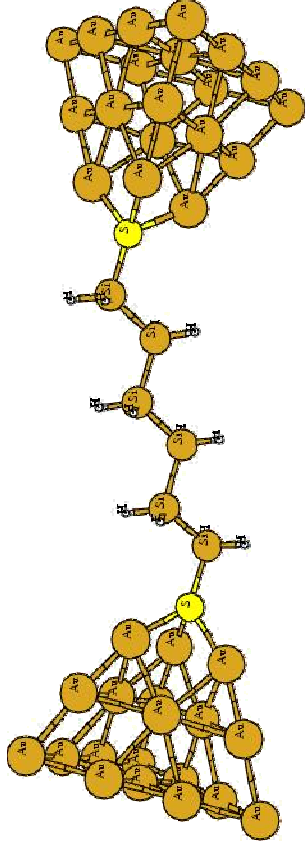
Haiss, Nichols, van Zalinge, Higgins, Bethell, Schiffrin  
*PCCP* **6**, 4330 (2004)  
 $\beta = 0.52 / n$

Akkerman, Blom, de Leeuw, de Boer  
*Nature* **441**, 69 (2006)  
 $\beta = 0.68 - 0.79 / n$

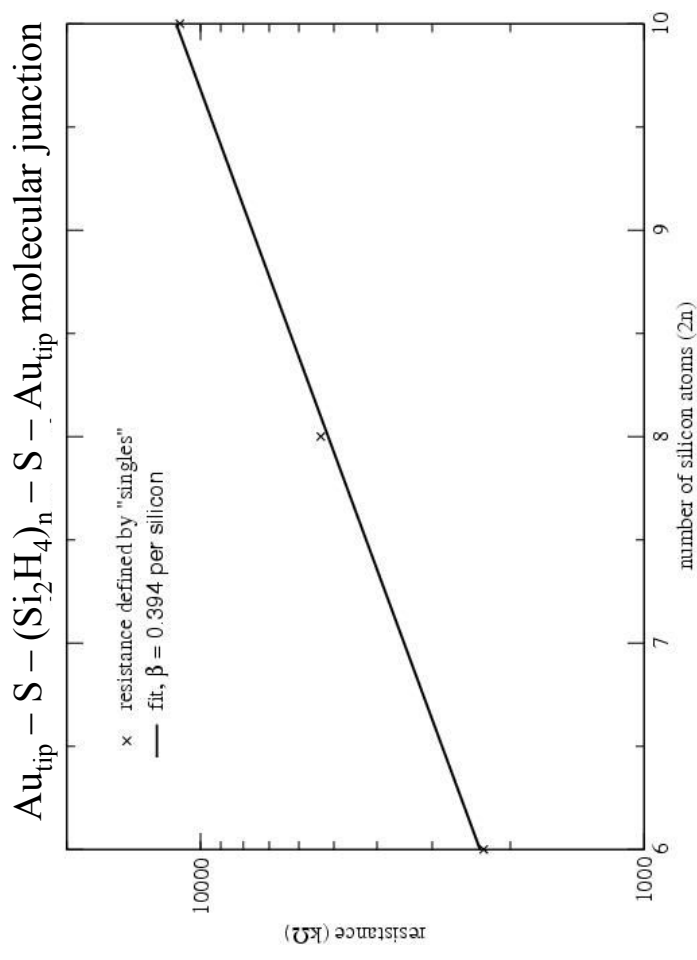
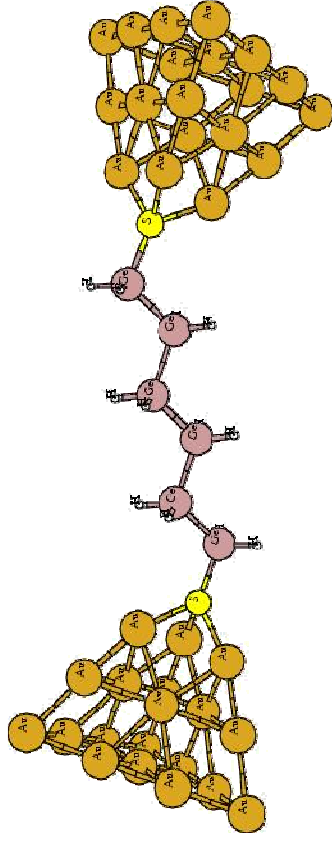
$\beta$  values vary over a range in the literature, our results support the lower end of the range

# Silane/Germane Oligomers

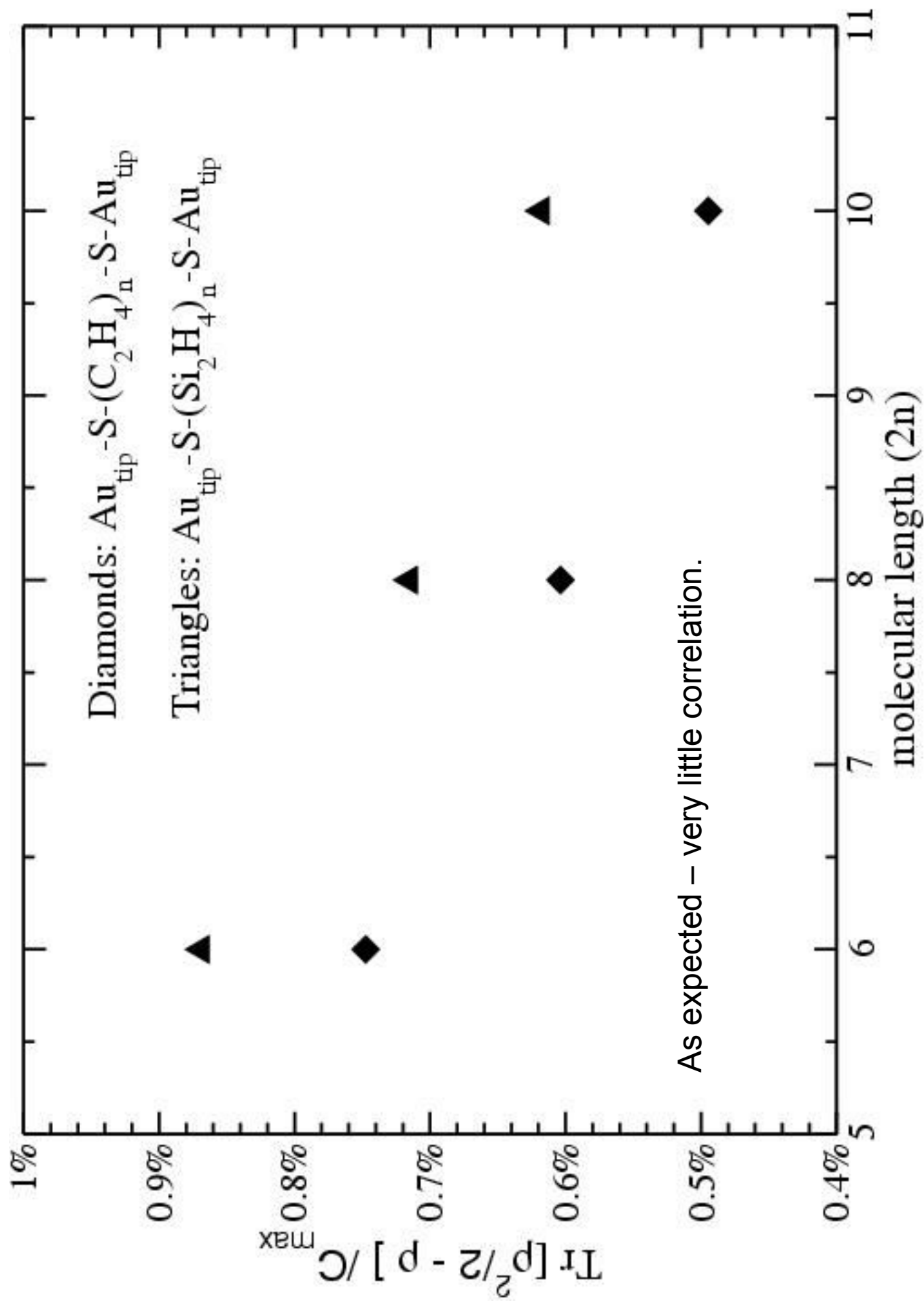
silanes

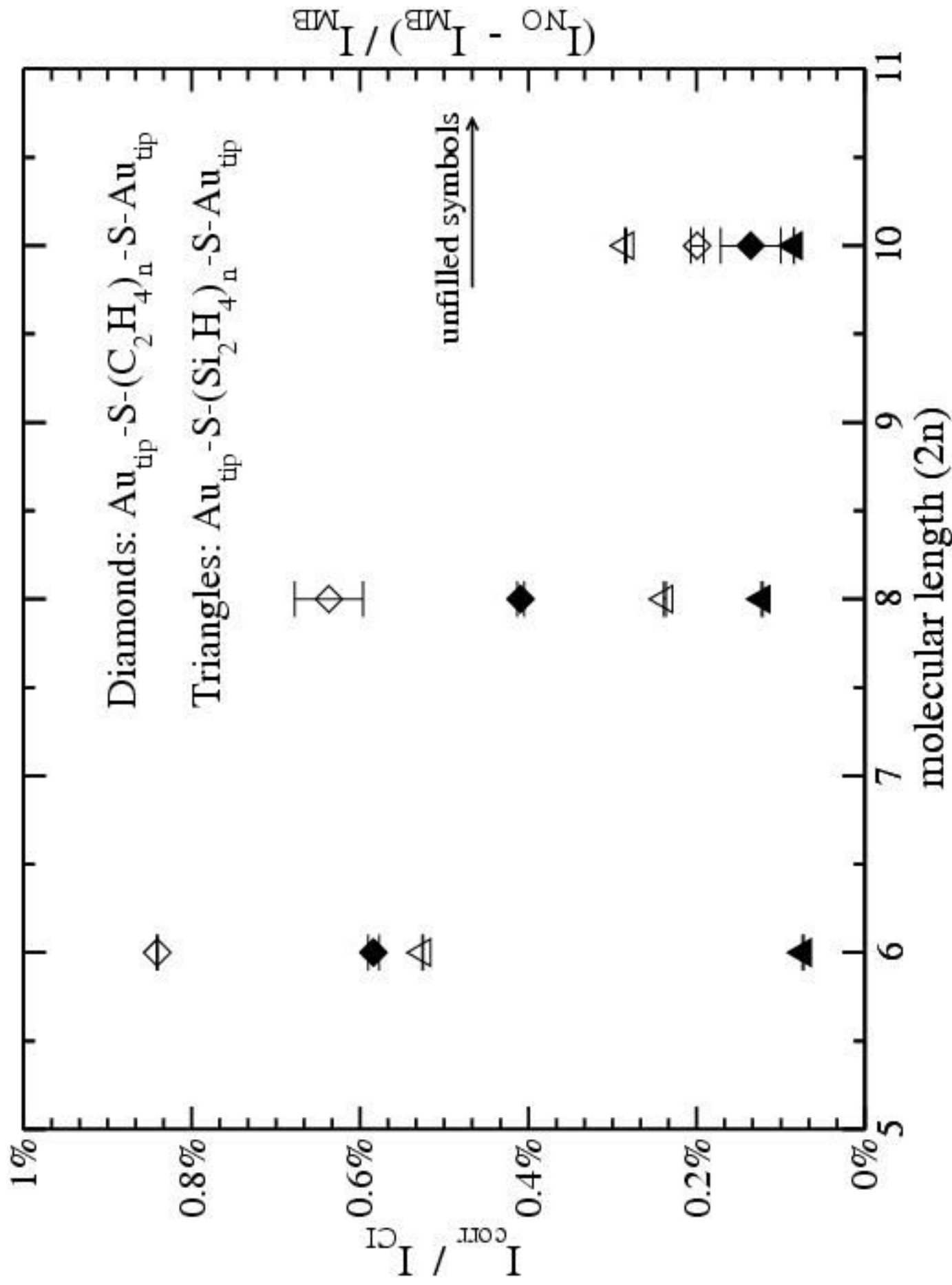


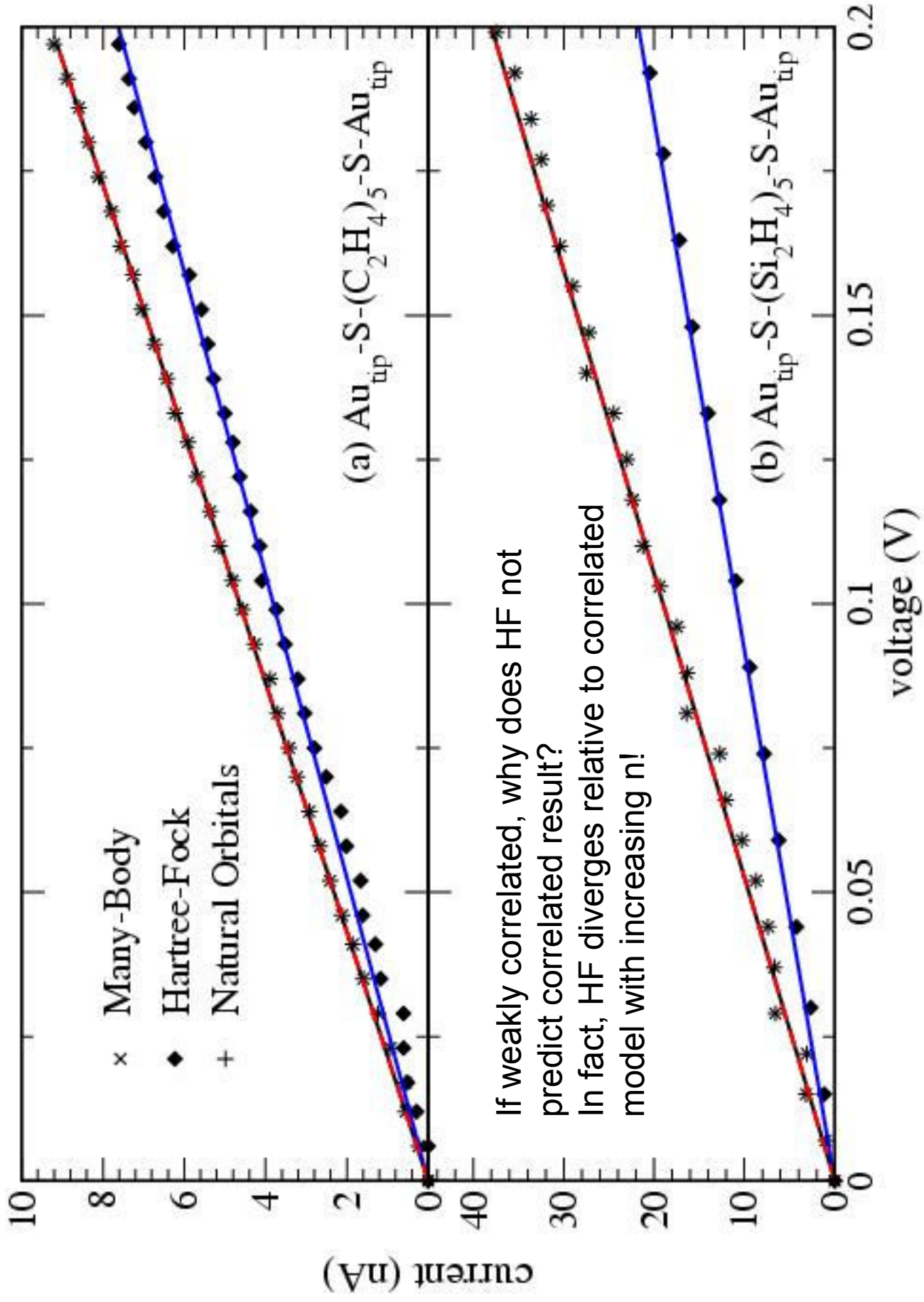
germanes



Note that  $\beta$  ( $\text{\AA}^{-1}$ ) for germanes < silanes < alkanes







# Correlations in alkane-based molecular junctions ...

## What is the best single particle picture?

### ■ Slater determinant made up from:

- single determinant of natural orbitals with highest occupancy (seems to give most of the current contributions)  $\Rightarrow$  “go ahead and turn off  $c$  in  $V_{xc}$ ?”

- Brueckner orbitals ?

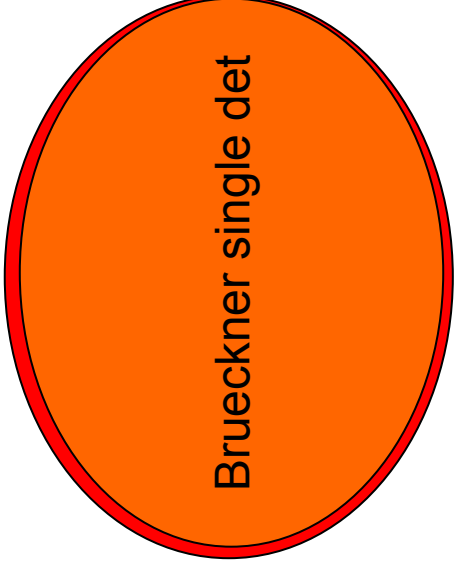
$$\langle \Phi_{1-\text{det}} | \Psi_{\text{exact}} \rangle = \max$$

### ■ Voltage dependence: $C = 1/(N-1) \sum_i [n_i(n_i-2)/2]$

Look at quantity

Note lower bound for  $C$  is  $C_b = (N/N-1)(N/N_T - 1)$

- overall constant with increasing field and same to zero voltage (i.e., ground state) correlations
- $C/C_b$  decreasing with increasing length- system is becoming less correlated!



$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$$

More important to maximize overlap to many-body wavefunction than energy minimization with respect to orbitals or density

# Conclusions

- **Simple formulation of quantum transport, includes many-body effects**
- **Predicted IV curves with reasonable agreement to experiment**
- **Distinction between resonant and non-resonant transport is clarified and the role of correlation in transport may be explored**
- **Allows identification of best single particle Hamiltonian to be used in transport**
- **Allows coupling to conventional device simulation**

**Acknowledgement: [EU Nanotcad](#), [Science Foundation Ireland](#)**

P. Delaney and J. C. Greer, Phys. Rev. Lett. **93**, 036805 (2004)

G. Fagas, P. Delaney and J. C. Greer, Physical Review B, **73**, 241314(R) (2006)

T. M. Henderson, G. Fagas, E. Hyde, and J. C. Greer, Journal of Chemical Physics, in press (2007)