Theoretical Study of Long-ranged Electron Transport in Molecular Junctions Including Dephasing Effects based on D'Amato Pastawski Model

九州大学
KYUSHU UNIVERSITY

野崎　大二郎(Daijiro Nozaki)

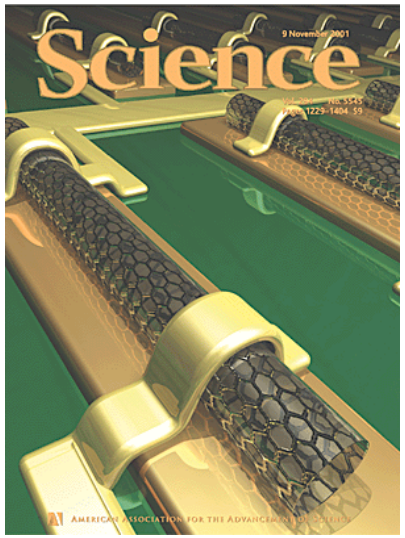
Institute for Materials Chemistry and Engineering(IMCE)
Kyushu Univ., Fukuoka, Japan

Outline

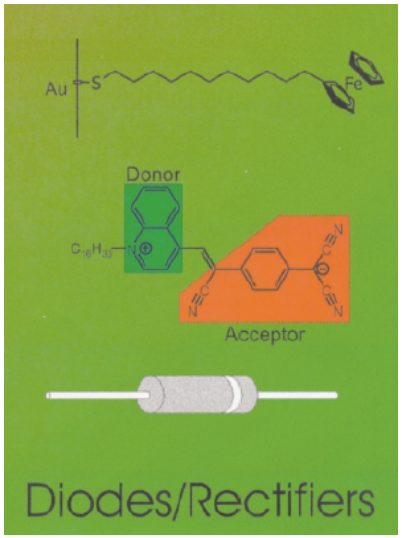
- 1. Generality about molecular wires
- 2. Motivation –Is $G=G_0\exp(-\beta r)$ always true?–
- 3. How to include dephasing effects
  - – D'Amato Pastawski model –
- 4. The flow of the calculations
- 5. Result & Discussion
  - – 1. Coherent transmission spectra –
  - – 2. Length dependence of coherent & incoherent transports –
  - – 3. Does incoherent transports increase with longer wires? –
  - – 4. Odd-even effect of carbon number on coherent transmission –
- 6. Summary
- 7. Acknowledgement

1. Generality about molecular wires
– Si electronics to molecular electronics–

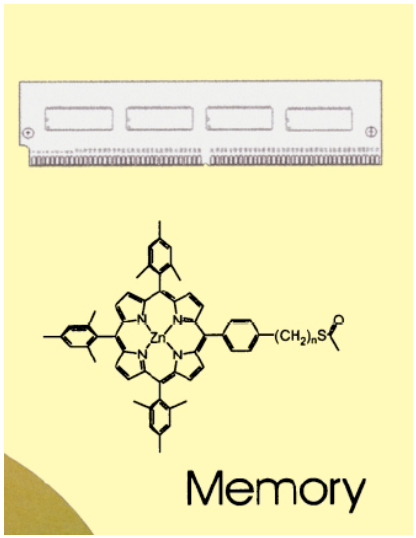
CNT-FET



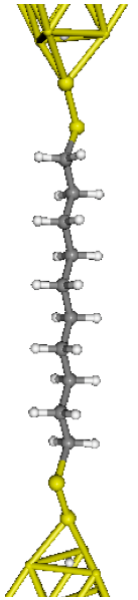
Molecular Diode



Molecular Memory



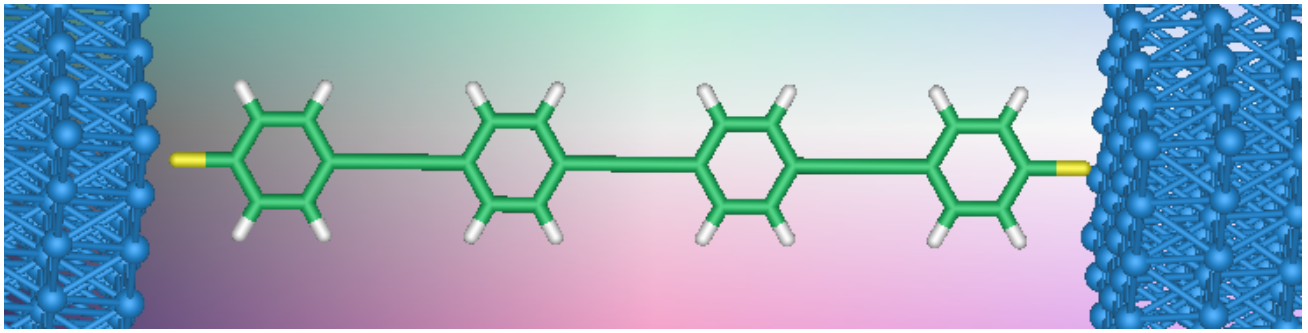
Molecular Wire



Carroll et al. *Angew Chem. Intn. Ed.*, *41*, 4378. (2002)
Bachtold et al. *Science*, *294*, 1317. (2000)

1. Generality about molecular wires
– Role of molecular wires –

- Connect two electrodes or devices
- Transport charges from one side to another

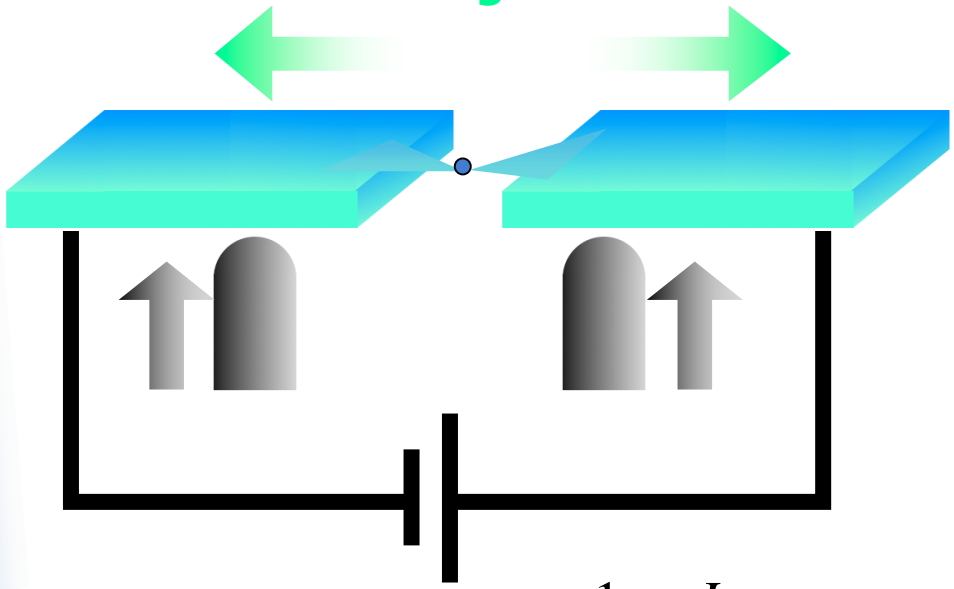


Length v.s. Conductance

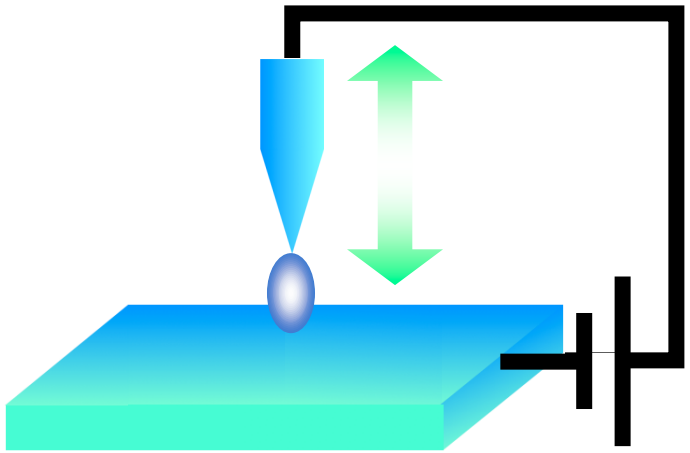
it is important to evaluate the conductivity of molecular wire accurately.

1. Generality about molecular wires
– Definition of conductance –

Mechanically Controlled Break-Junction



Scanning Tunneling Microscopy



conductance $G \equiv \frac{1}{R} = \frac{I}{V}$

Landauer formula $G = \frac{2e^2}{h} T(E,V)$

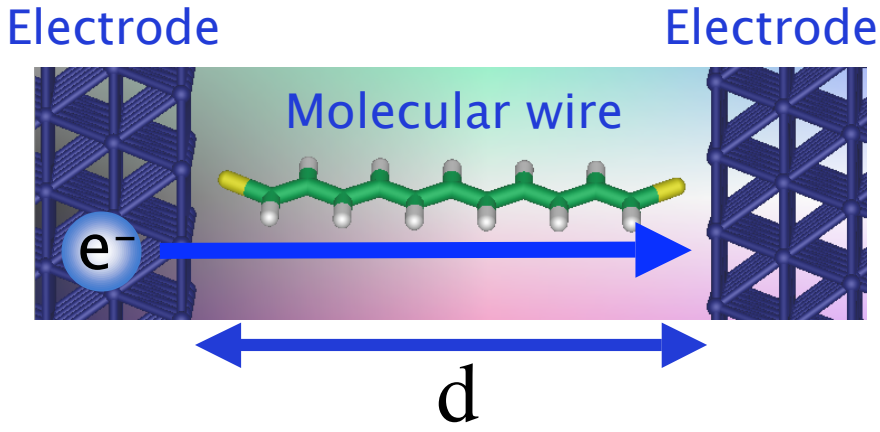
If you can evaluate transmission probability *T(E)*,
you can estimate the condutace of molecules.

R. Landauer, ***IBM J.Res. Dev. 1,*** **223. (1957)**

1. Generality about molecular wires

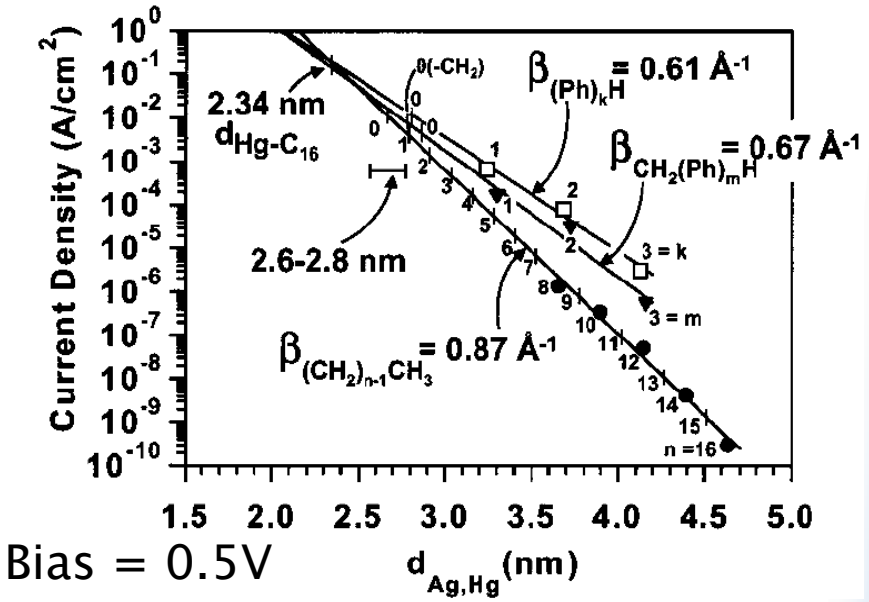
–Exprimental conductance measurements of molecular wires –

Molecular junction



$$G_0 = 2e^2/h$$

Distance dependence of conductance

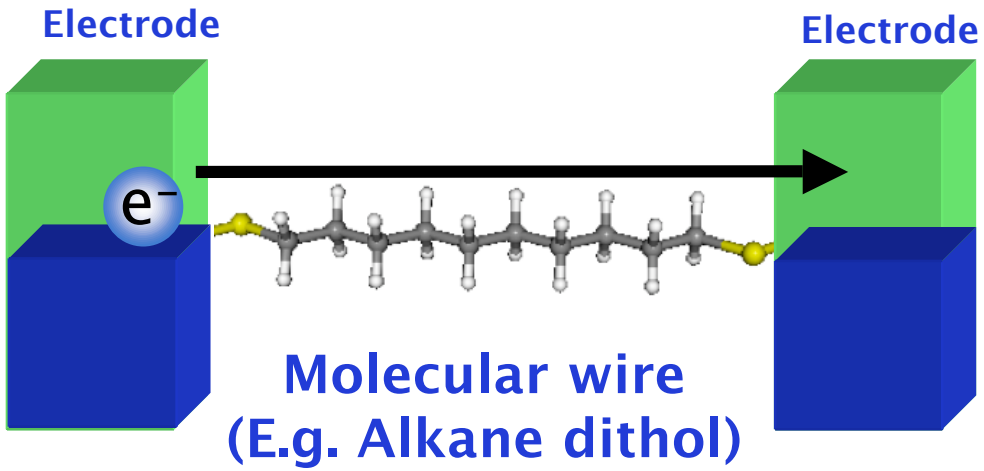


$$G = G_0 \exp(-\beta d)$$ β: Damping factor

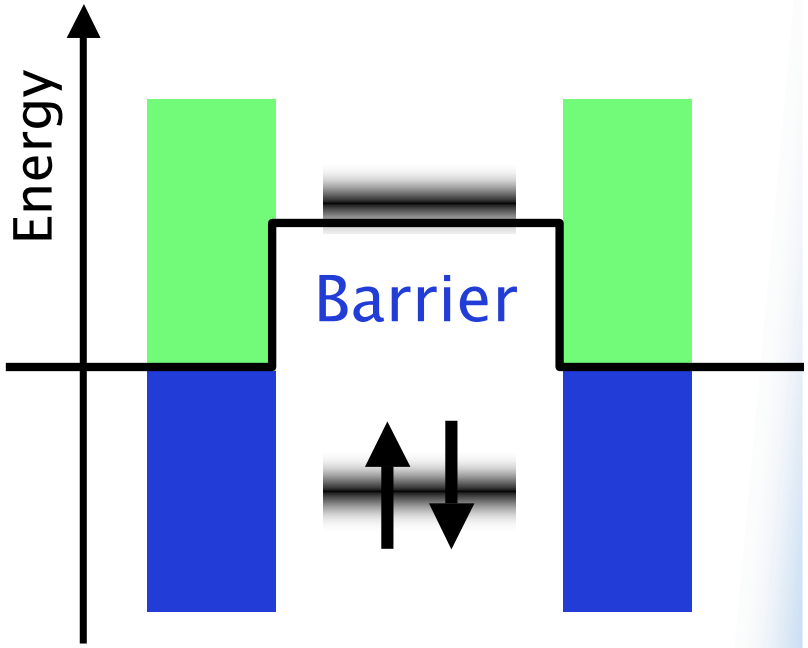
R. E. Holmin, et al. *J. Am. Chem. Soc. 123*, 5075, (2001).

1. Generality about molecular wires
– Energy diagram in molecular junction –

Molecular junction
(After coupling)



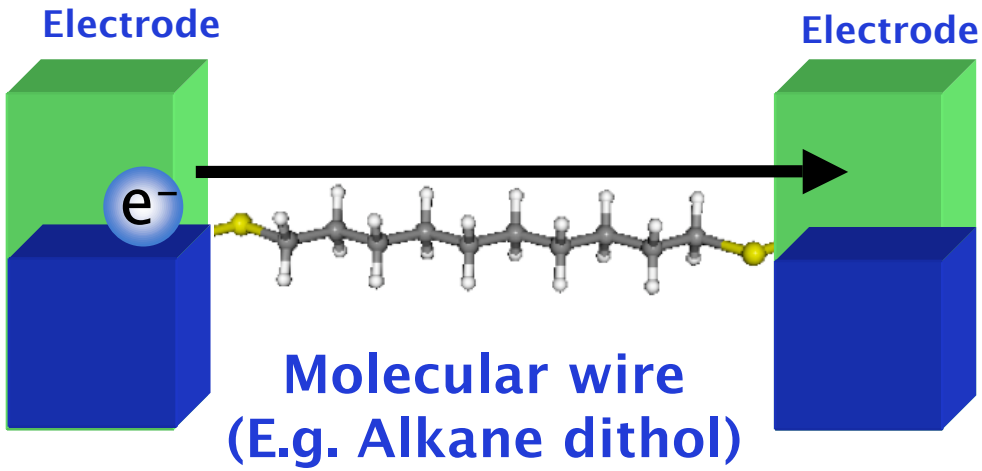
Energy diagram



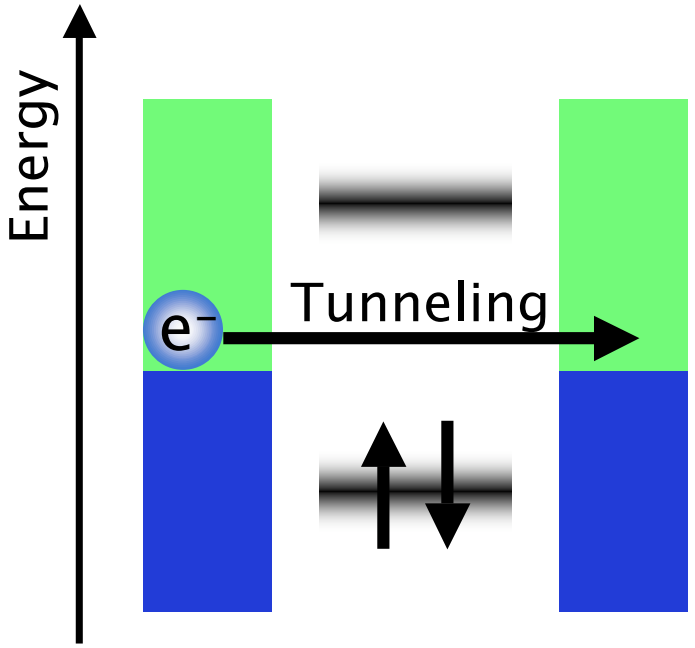
$$G = G_0 \exp(-\beta d)$$

1. Generality about molecular wires
– Energy diagram in molecular junction –

Molecular junction
(After coupling)



Energy diagram

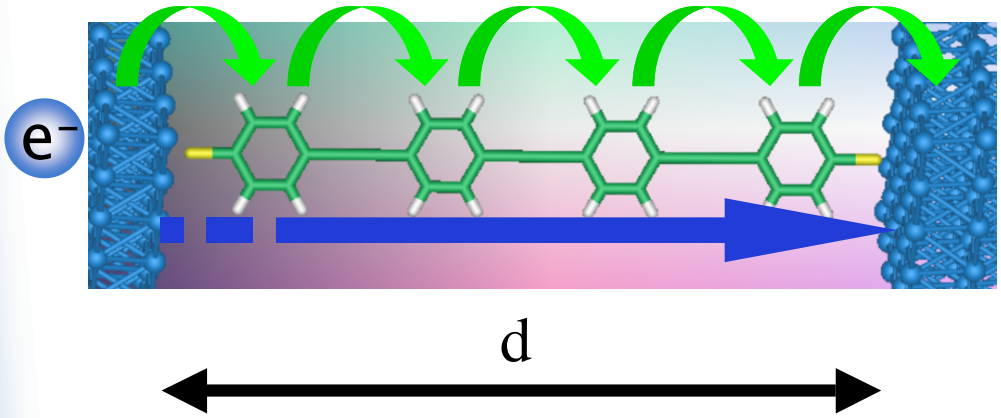


$$G = G_0 \exp(-\beta d)$$

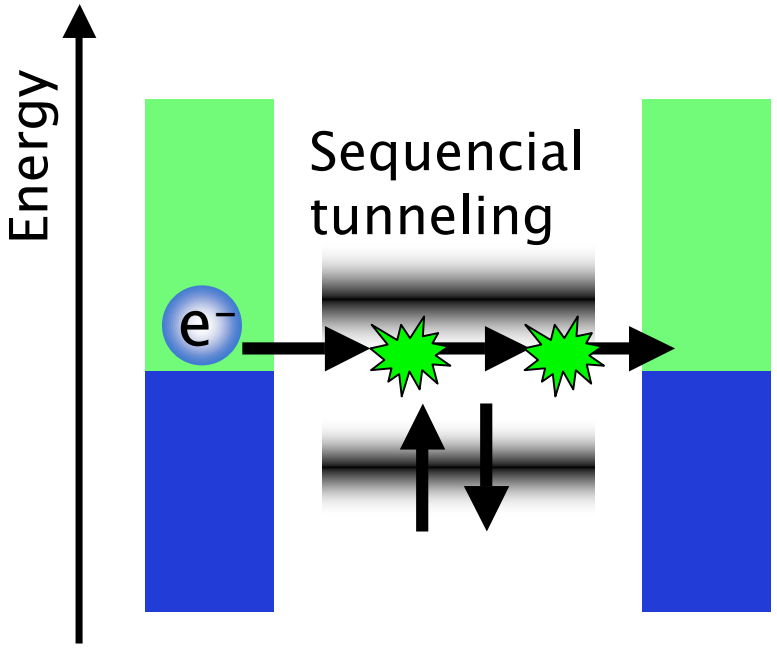
2. Motivation

– Does $G = G_0 \exp(-\beta d)$ always continue ? –

Molecular junction



Energy diagram

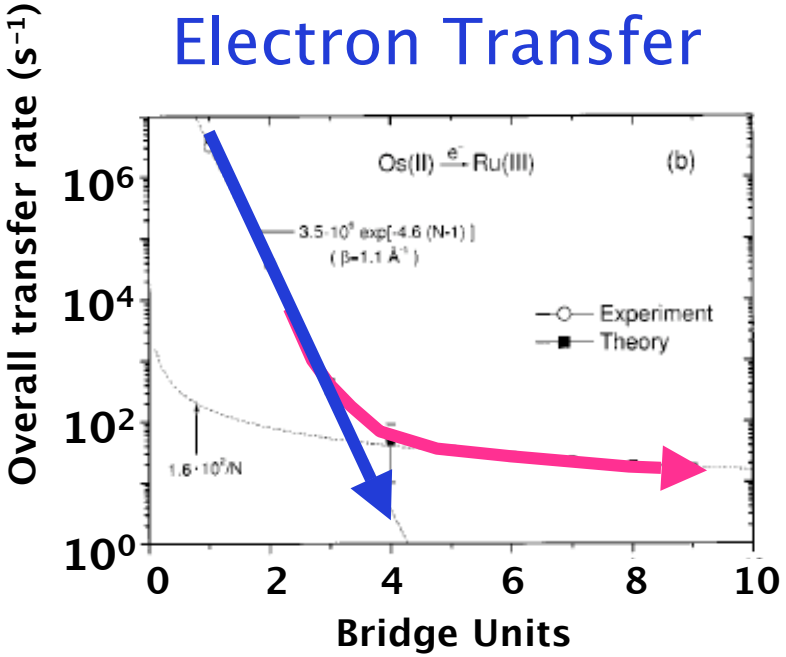


Is $G = G_0 \exp(-\beta d)$ true for long or unsaturated wires?

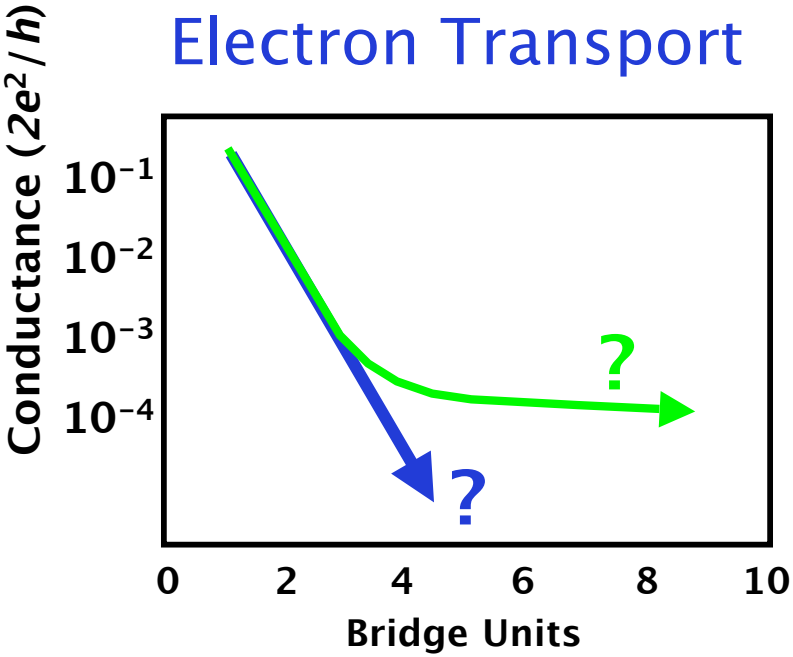
2. Motivation

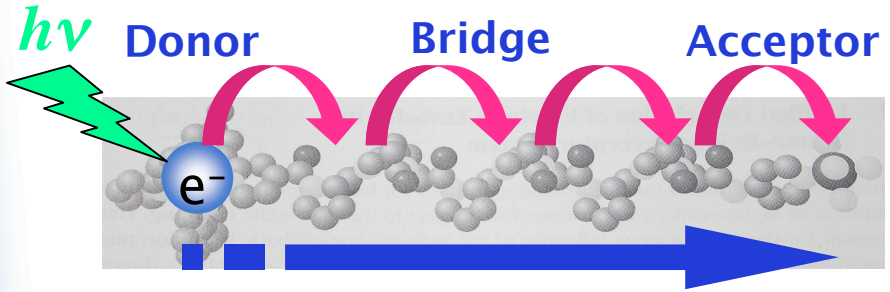
– Does crossover of transport mechanisms occurs? –

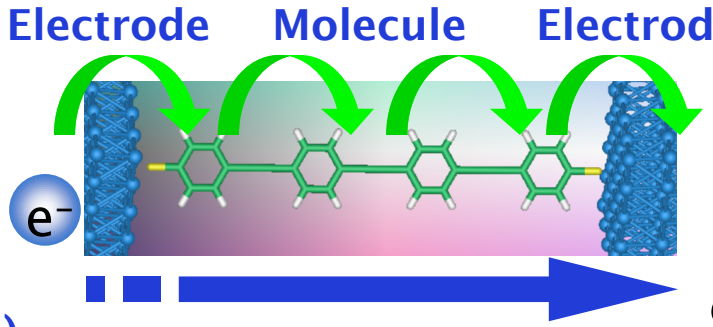
Electron Transfer



Electron Transport



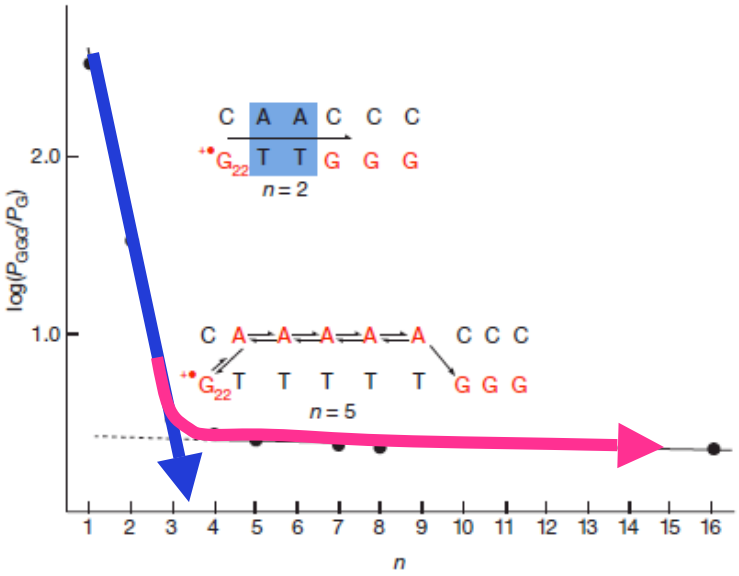


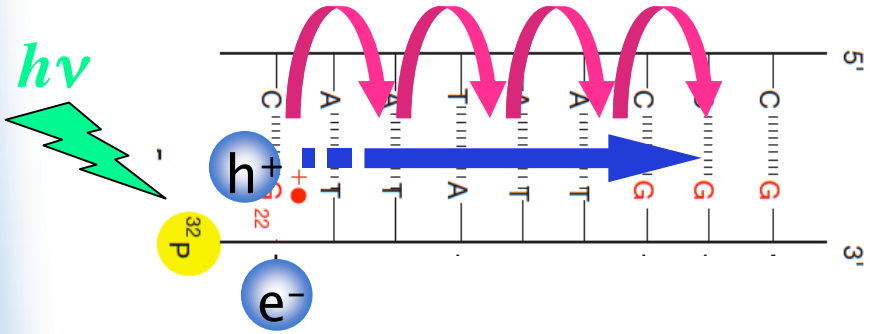


May, V. et al. *J. Phys. Chem. A 105*, 10176 (2001)

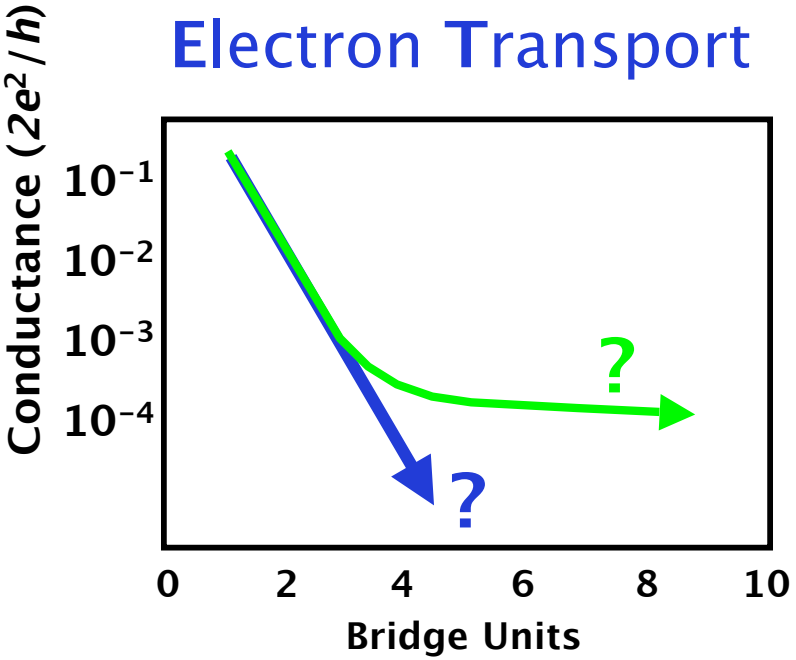
2. Motivation

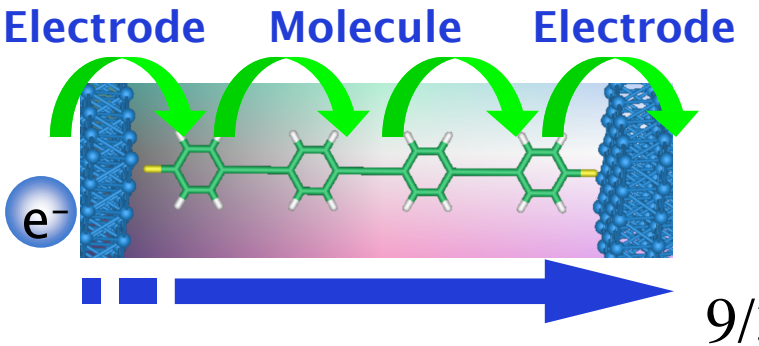
-Does crossover of transport mechanisms occurs?-





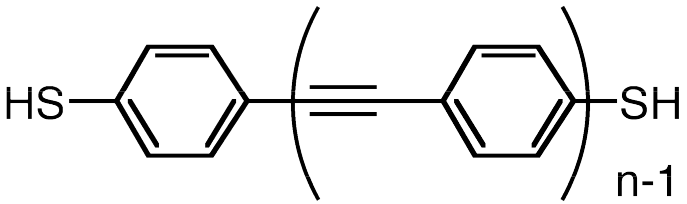
Giese, B. et al. *Nature, 412,* 318 (2001)



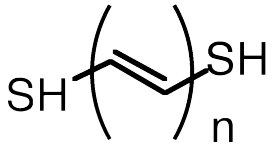


2. Motivation

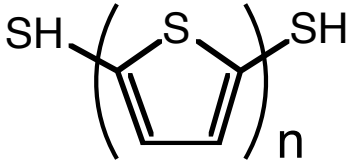
-The molecular wires investigated in this study-



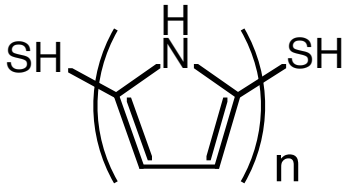
Tour-wire dithiols



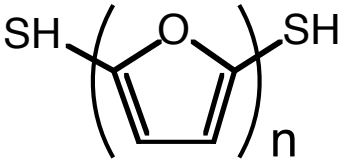
Polyene dithiols



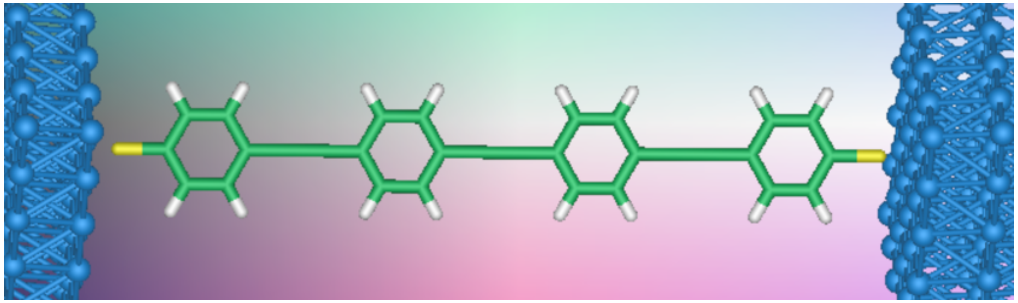
Poly-thiophene dithiols



Poly-pyrole dithiols

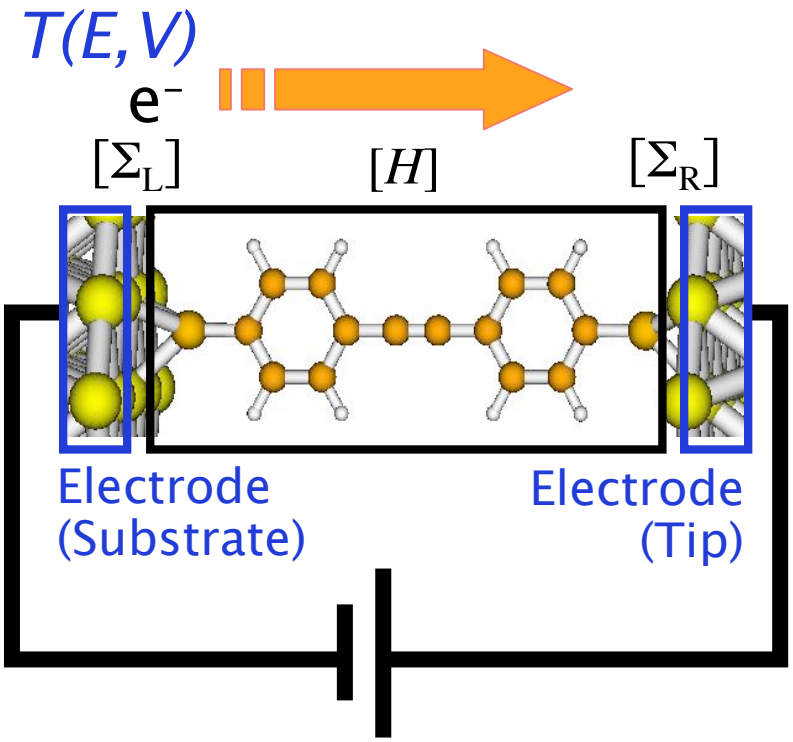


Poly-fran dithiols



3. Method

– How to calculate T(E) with Landauer model –



$$g_L^R(E) = \left[(E + i\delta)I - H_L\right]^{-1}$$

Landauer formula

$$G = \frac{2e^2}{h} T(E)$$

Fisher-Lee relation

$$T(E) = \mathrm{Trace}\left[G^R(E)\Gamma_L(E)G^A(E)\Gamma_R(E)\right]$$

Green's function

$$G^R(E) = \left[(E + i\delta)I - H - \Sigma_L - \Sigma_R\right]^{-1}$$

Self-energy function

$$\Sigma_{L/R}(E) = \tau_{L/R} g_{L/R}(E) \tau_{L/R}^{\dagger}$$

Broadening function

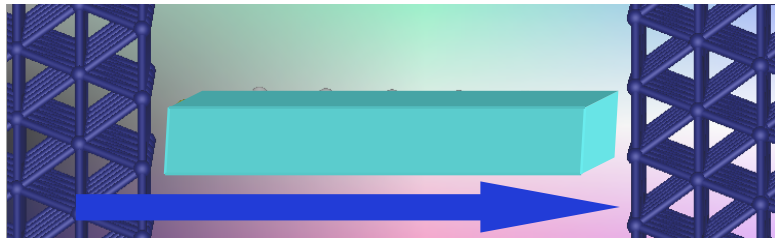
$$\Gamma_{L/R}(E) = i\left[\Sigma_{L/R}(E) - \Sigma_{L/R}^{\dagger}(E)\right]$$

S. Datta "Electronic Transport in Mesoscopic Systems " (1995)
D. S. Fisher and P. A. Lee. *Phys. Rev. B. 23*, R6851. (1981)

3. Method

– Landauer model without Büttiker probes –

$[\Sigma_L]$ $[H]$ $[\Sigma_R]$



Electrode Conductor Electrode

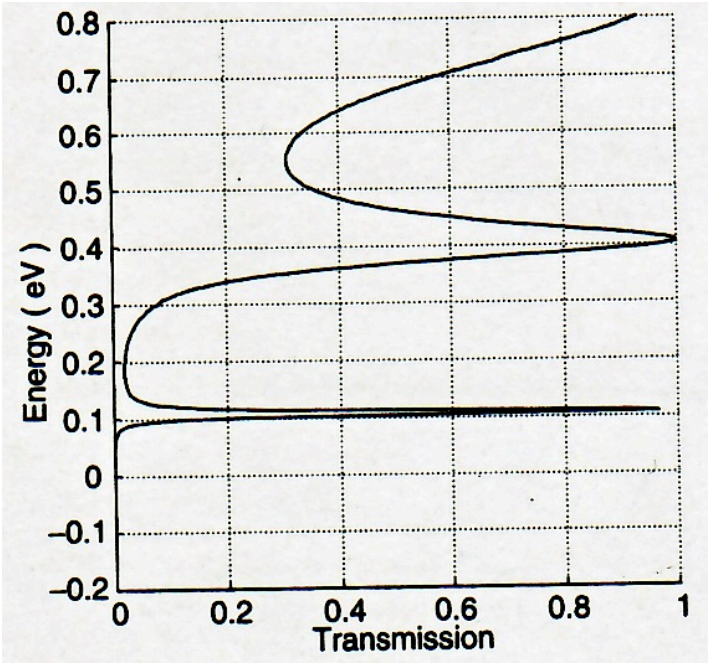
$$T_{LR}(E) = \mathrm{Trace}\left[G^R(E)\Gamma_L(E)G^A(E)\Gamma_R(E)\right]$$

$$G^R(E) = \left[EI - H - \Sigma_L - \Sigma_R\right]^{-1}$$

$$\Sigma_{L/R}(E) = \tau_{L/R} g_{L/R}(E) \tau^{\dagger}_{L/R}$$

$$\Gamma_{L/R}(E) = i\left[\Sigma_{L/R}(E) - \Sigma^{\dagger}_{L/R}(E)\right]$$

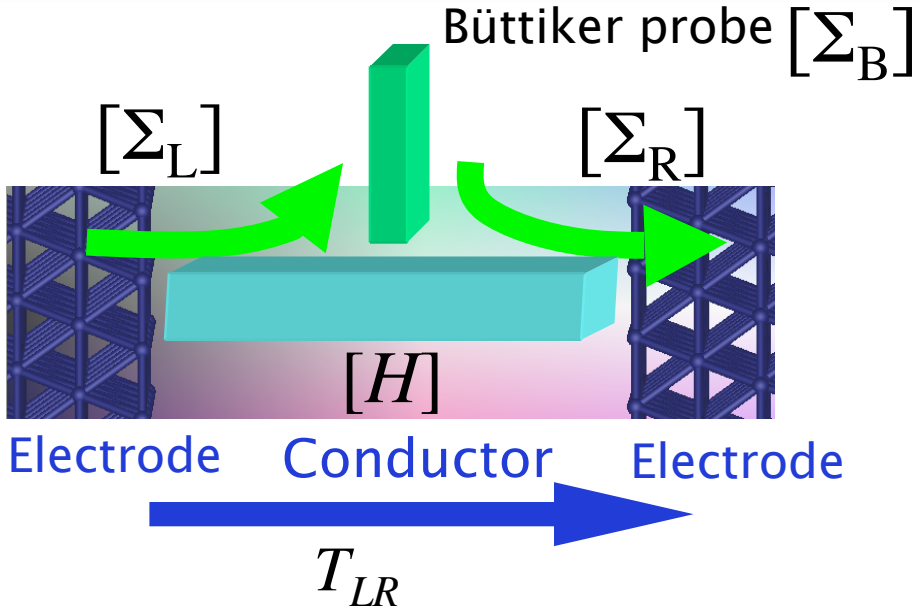
Sharp !



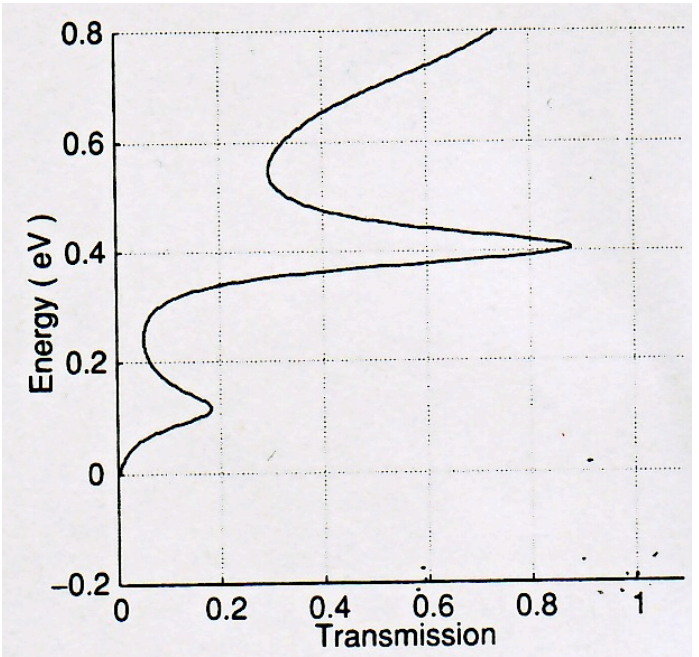
p. 244. of S. Datta "Quantum Transport: Atom to Transistor" (2005)

3. Method

– Landauer model with a Büttiker probe –



Broadened !



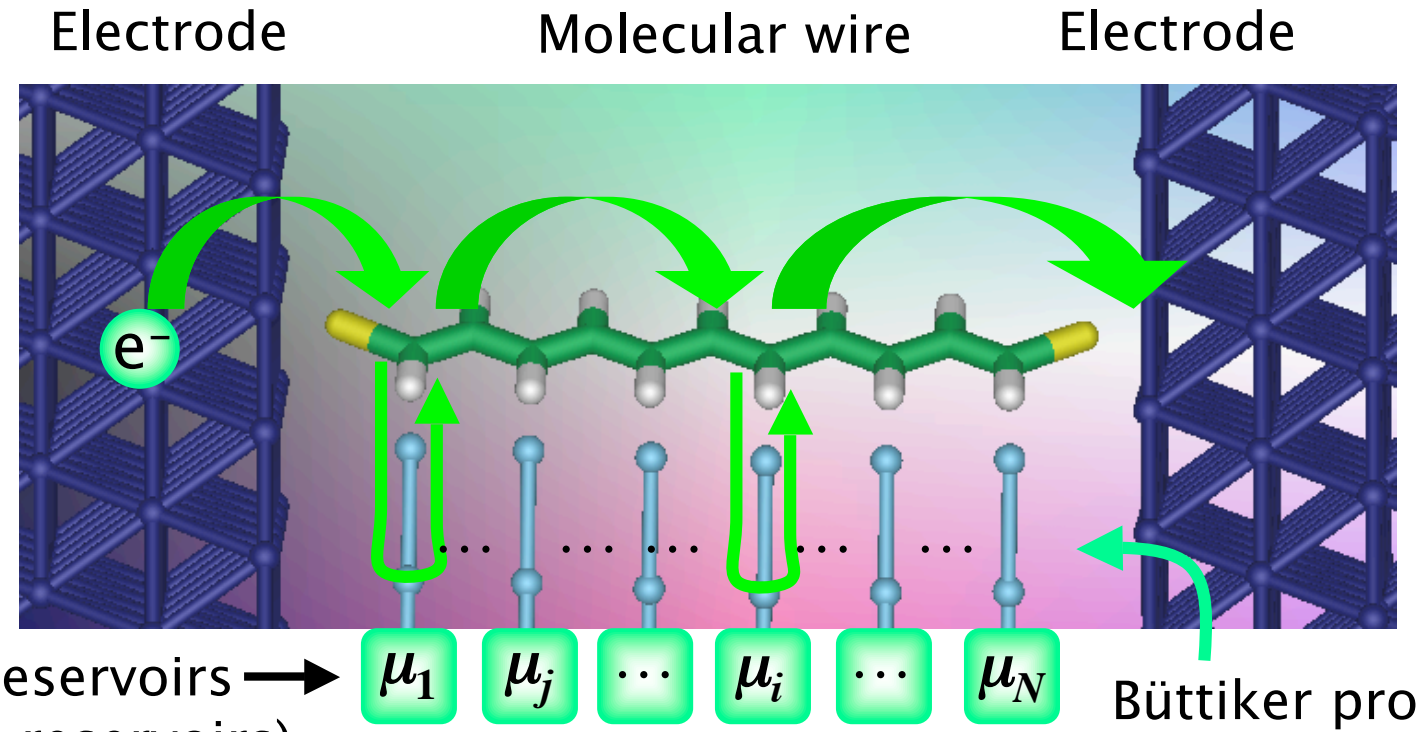
$$G^R(E) = \left[EI - H - \Sigma_L - \Sigma_R - \Sigma_B\right]^{-1}$$

$$T_{tot}(E) = T_{LR}(E) + T_{LB}(E)T_{BR}(E)$$

M. Büttiker, IBM J. Res. Dev. *32*, 317. (1988)
p. 246. of S. Datta "Quantum Transport: Atom to Transistor" (2005)

3. Method

– D'Amato Pastawski model –



Büttiker probes are attached uniformly.

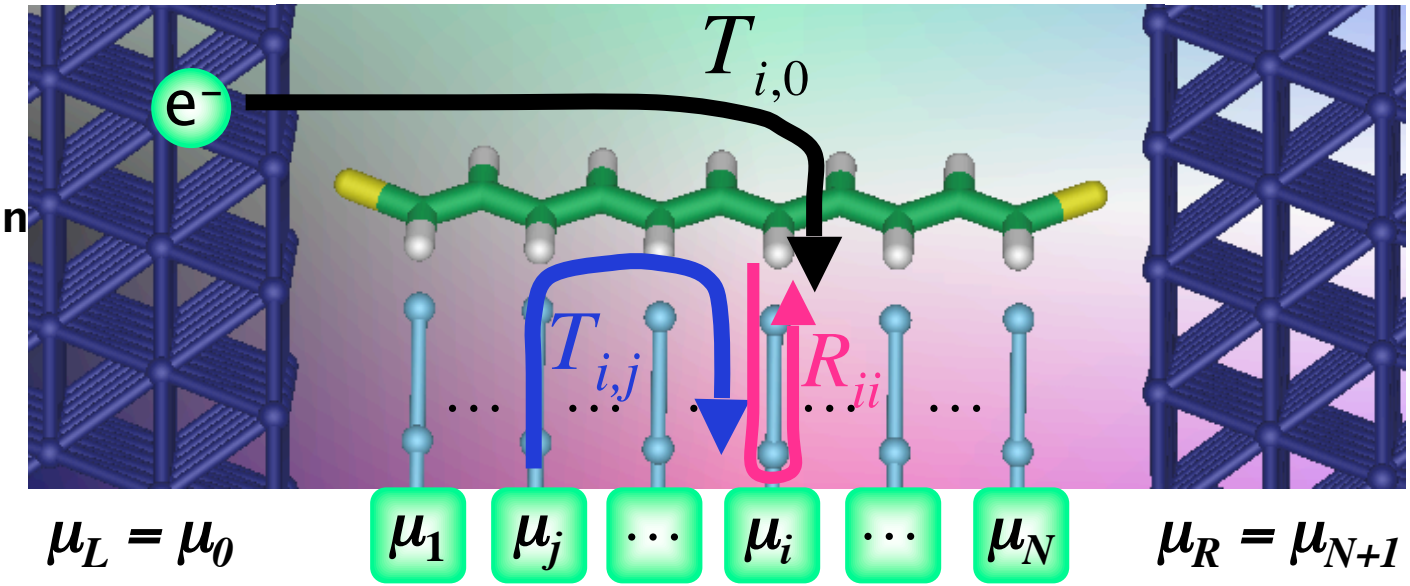
J. L. D'Amato and H. M. Pastawski. *Phys. Rev. B 41*, 7411 (1990)

3. Method

– D'Amato Pastawski model –

Electrode

Electrode



Assumption

$\mu_L > \mu_R$

$\mu_L \approx \mu_R$

$$(1-R_{i,i})(\mu_i-\mu_R) - \sum_{j=1(j\neq i)}^{N} T_{i,j}(\mu_j-\mu_R) - T_{i,0}(\mu_L-\mu_R) = 0, \qquad (1)$$

$$\forall i = 1,2,\ldots,N$$

J. L. D'Amato and H. M. Pastawski. *Phys. Rev. B 41*, 7411 (1990)

3. Method

– D'Amato Pastawski model –

$$(1-R_{i,i})(\mu_i-\mu_R)-\sum_{j=1(j\neq i)}^{N}T_{i,j}(\mu_j-\mu_R)-T_{i,0}(\mu_L-\mu_R)=0, \quad \forall i=1,2,\ldots,N \tag{1}$$

$$\begin{aligned}
(1-R_{1,1})(\mu_1-\mu_R)-\sum_{j=1(j\neq i)}^{N}T_{1,j}(\mu_j-\mu_R)&=T_{1,0}(\mu_L-\mu_R) && i=1\\
(1-R_{2,2})(\mu_2-\mu_R)-\sum_{j=1(j\neq i)}^{N}T_{2,j}(\mu_j-\mu_R)&=T_{2,0}(\mu_L-\mu_R) && i=2\\
&\vdots && \vdots\\
(1-R_{N,N})(\mu_N-\mu_R)-\sum_{j=1(j\neq i)}^{N}T_{N,j}(\mu_j-\mu_R)&=T_{N,0}(\mu_L-\mu_R) && i=N
\end{aligned}$$

$$\begin{bmatrix} 1-R_{1,1} & -T_{1,2} & \cdots & -T_{1,N} \\ -T_{2,1} & 1-R_{2,2} & \cdots & -T_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ -T_{N,1} & -T_{N,2} & \cdots & 1-R_{N,N} \end{bmatrix} \begin{pmatrix} \mu_1-\mu_R \\ \mu_2-\mu_R \\ \vdots \\ \mu_N-\mu_R \end{pmatrix} = \begin{bmatrix} T_{1,0} & 0 & \cdots & 0 \\ 0 & T_{2,0} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & T_{N,0} \end{bmatrix} \begin{pmatrix} \mu_L-\mu_R \\ \mu_L-\mu_R \\ \vdots \\ \mu_L-\mu_R \end{pmatrix} \tag{2}$$

3. Method

– D'Amato Pastawski model –

$$\begin{bmatrix} 1-R_{1,1} & -T_{1,2} & \cdots & -T_{1,N} \\ -T_{2,1} & 1-R_{2,2} & \cdots & -T_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ -T_{N,1} & -T_{N,2} & \cdots & 1-R_{N,N} \end{bmatrix} \begin{pmatrix} \mu_1-\mu_R \\ \mu_2-\mu_R \\ \vdots \\ \mu_N-\mu_R \end{pmatrix} = \begin{bmatrix} T_{1,0} & 0 & \cdots & 0 \\ 0 & T_{2,0} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & T_{N,0} \end{bmatrix} \begin{pmatrix} \mu_L-\mu_R \\ \mu_L-\mu_R \\ \vdots \\ \mu_L-\mu_R \end{pmatrix} \quad (2)$$

W → W^{-1}

Chemical potential of external reservoir

$$\mu_i-\mu_R=\left[\sum_{j=1}^{N} W_{i,j}^{-1}T_{j,0}\right](\mu_L-\mu_R) \quad \forall i=1,2,\ldots,N \quad (3)$$

Total current is obtained from contributions from all reservois.

$$I=\frac{2e}{h}\sum_{i=0}^{N} T_{N+1,i}(\mu_i-\mu_R) \quad (4)$$

L=0; R=N+1

$$I=\frac{2e}{h}T_{\text{eff}}(\mu_L-\mu_R)$$

$$T_{\text{eff}}=T_{N+1,0}+\sum_{i,j=1}^{N} T_{N+1,i}W_{ij}^{-1}T_{j,0}$$

J. L. D'Amato and H. M. Pastawski. *Phys. Rev. B 41*, 7411 (1990)

3. Method

– D'Amato Pastawski model –

Effective transport probability

Coherent Transport

Incoherent Transport

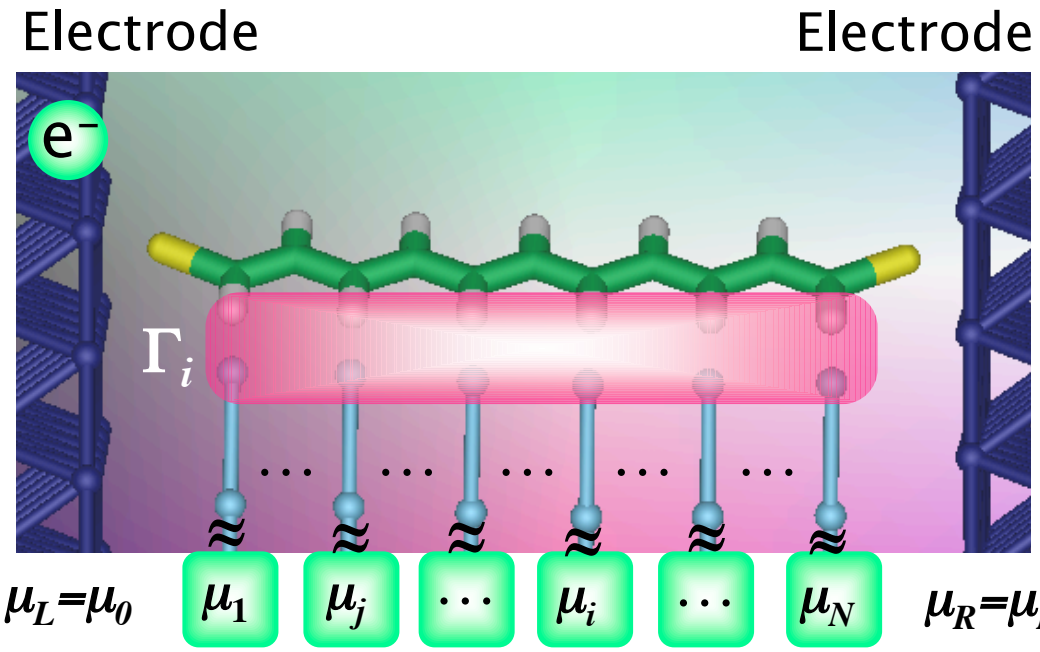
$$T_{\text{eff}} = T_{N+1,0} + \sum_{i,j}^{N} T_{N+1,i} W_{ij}^{-1} T_{j,0}$$

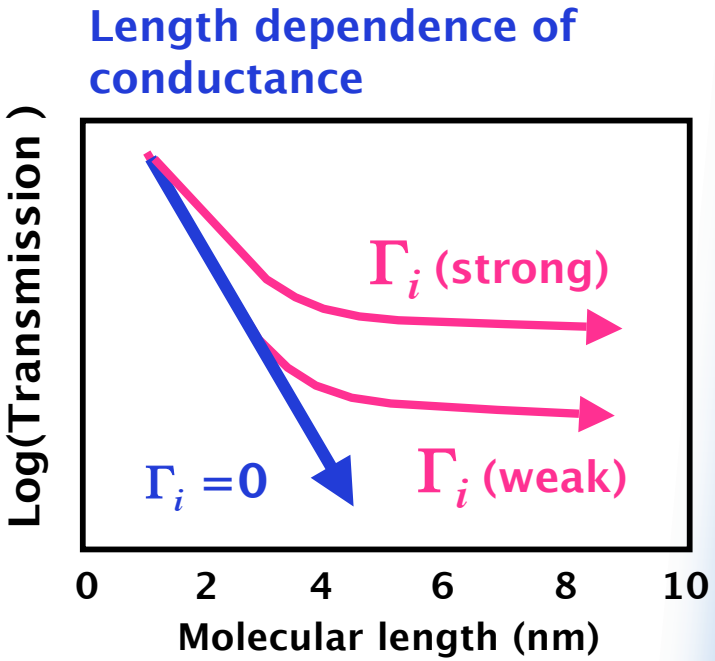
$$W = \begin{bmatrix} 1-R_{1,1} & -T_{1,2} & \cdots & -T_{1,N} \\ -T_{2,1} & 1-R_{2,2} & \cdots & -T_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ -T_{N,1} & -T_{N,2} & \cdots & 1-R_{N,N} \end{bmatrix}$$

J. L. D'Amato and H. M. Pastawski. *Phys. Rev. B 41,* 7411 (1990)

3. Method

– D'Amato Pastawski model –

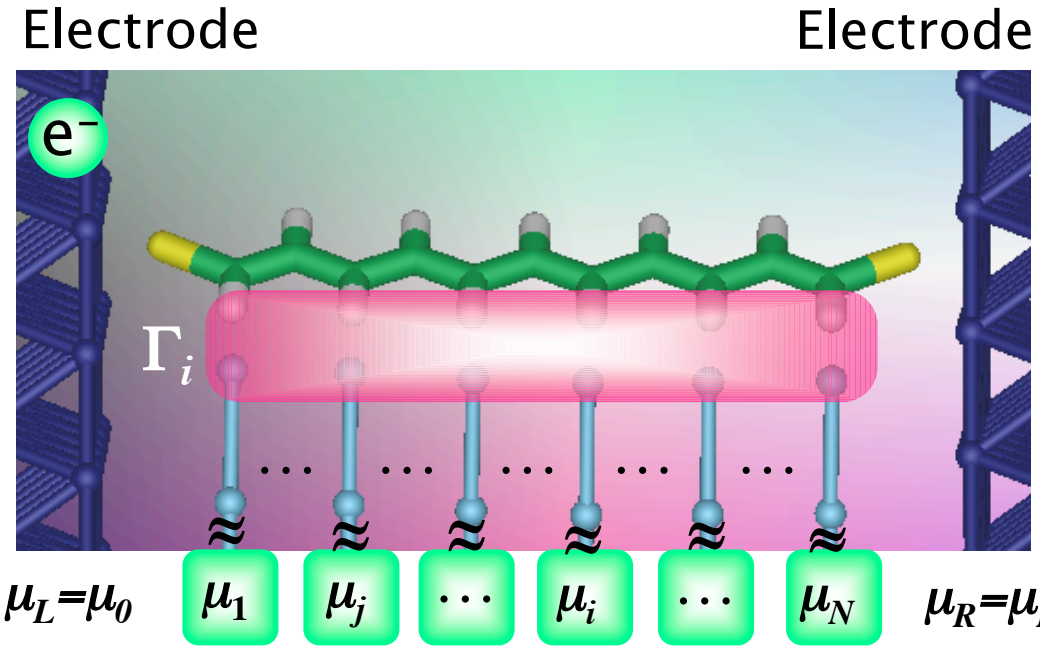


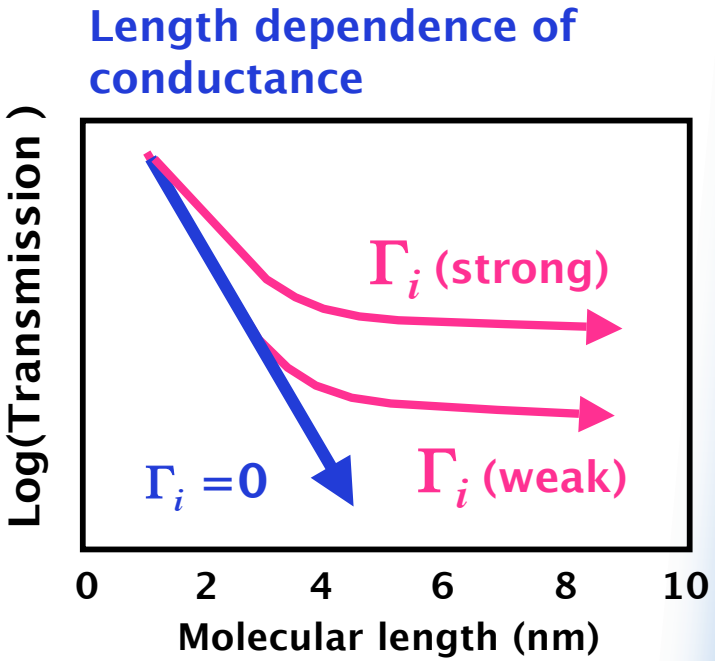


We have calculated the length dependence of incoherent transport through molecular wires changing broadening function Γ_i (scattering rates) as parameter.

3. Method

– D'Amato Pastawski model –





Dephasing strength →

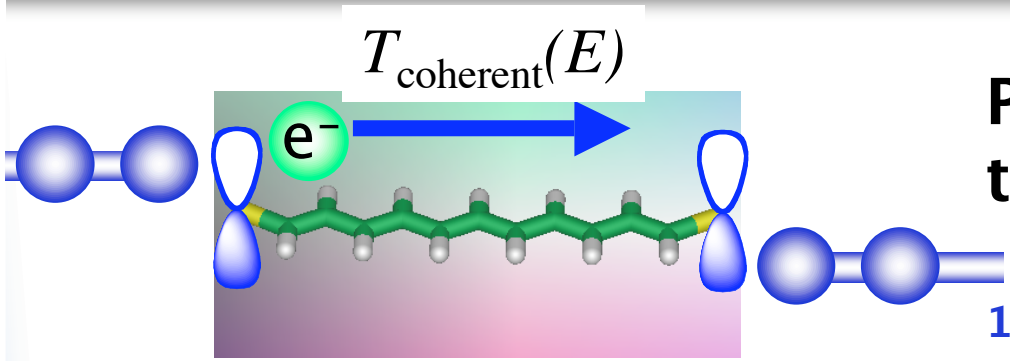
$$\frac{\Gamma_i(\mathrm{eV})}{\hbar(\mathrm{eV}\cdot\mathrm{s})} = k_i(s^{-1}) = \frac{1}{\tau}(s^{-1})$$

Scattering rate

Interval between scattering events

4. Computational details

-Coherent T(E) calculation with Landauer model-



$$T_{LR}(E) = \text{Trace}\left[G^R \Gamma_L G^A \Gamma_R\right]$$

$$G^R(E) = \left[EI - H - \Sigma_L - \Sigma_R\right]^{-1}$$

$$\Gamma_{L/R}(E) = i\left[\Sigma_{L/R}(E) - \Sigma_{L/R}^{\dagger}(E)\right]$$

Newns-Anderson (NA) approximation

$$\Sigma_k(E) = \frac{V_k^2}{E - \alpha_k - \delta_k} = V_k^2 g_k(E)$$

$$\delta_k = \frac{1}{2}\left\{\theta_k - i\sqrt{4\beta_k^2 - \theta_k^2}\right\}; \qquad \theta_k = E - \alpha_k$$

$$k = L, R.$$

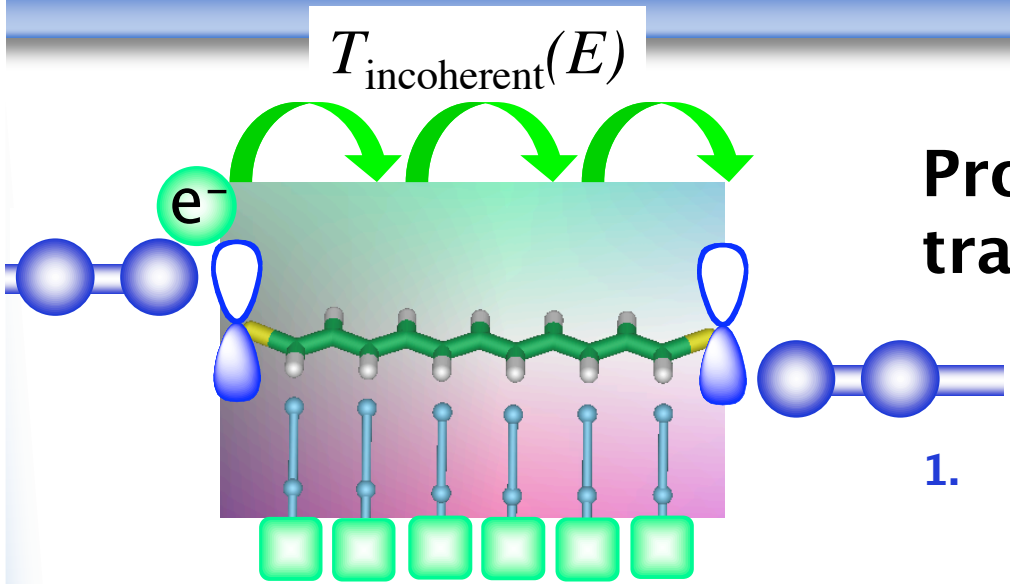
Procedures for coherent transmission calculation

…

1. We have optimized the molecule with Au clusters(B3LYP/LANL2DZ).
2. We have extracted the optimized structure.
3. We have set parameters for coupling between molecule and electrodes using NA approximation.
4. We have calculated transmission probability using Fisher-Lee's relation and Green's function with Extended Hückel parameters.

4. Computational details

–Incoherent $T_{inco}(E)$ calculation with DP model–



$$T_{\text{eff}} = T_{N+1,0} + \sum_{i,j=1}^{N} T_{N+1,i} W_{ij}^{-1} T_{j,0}$$

$$W = \begin{bmatrix} 1-R_{1,1} & -T_{1,2} & \cdots & -T_{1,N} \\ -T_{2,1} & 1-R_{2,2} & \cdots & -T_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ -T_{N,1} & -T_{N,2} & \cdots & 1-R_{N,N} \end{bmatrix}$$

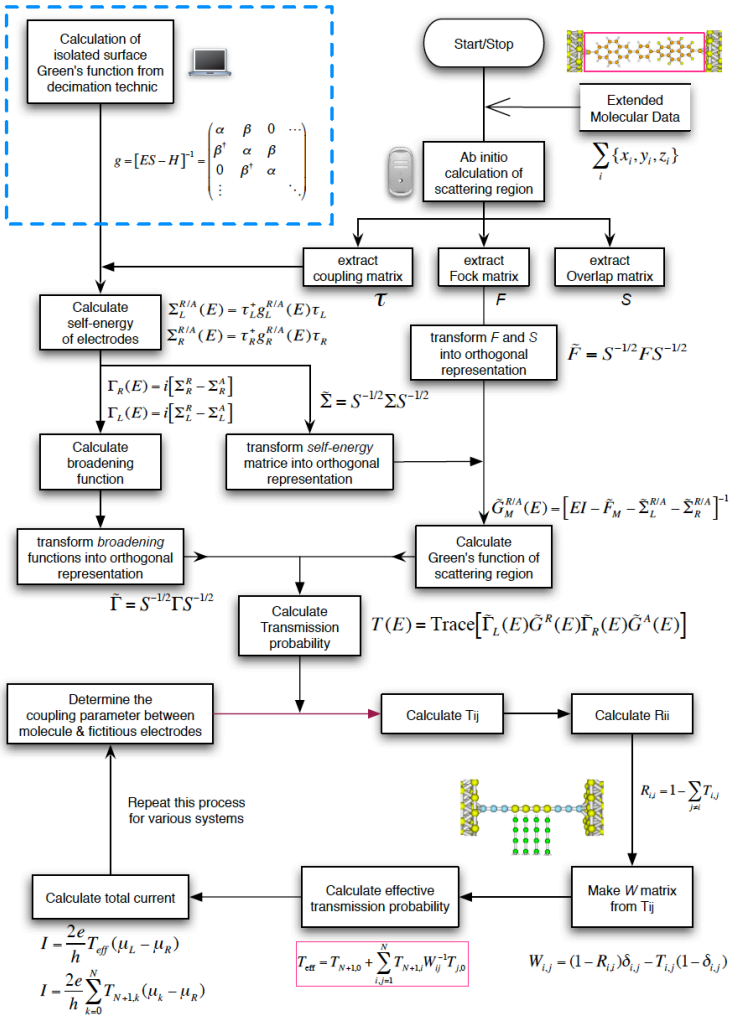
Procedures for incoherent transmission calculation

…

1. We have determined coupling Γ_i between Büttiker probes and atomic orbitals (setting of scattering rate).
2. We have calculate $T_{i,j}$ needed for the calculation of incoherent transport.
3. We have made *W* matrix.
4. We have calculated effective transmission probability using D'Amato Pastawski model.

4. Computational details

-Programing and other conditions-



Coding : MATLAB (OCTAVE)

Optimization : B3LYP/LANL2DZ

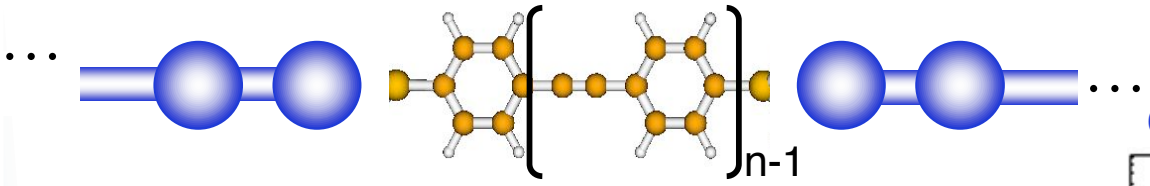
Transmission calculation :
Extended Hückel basis

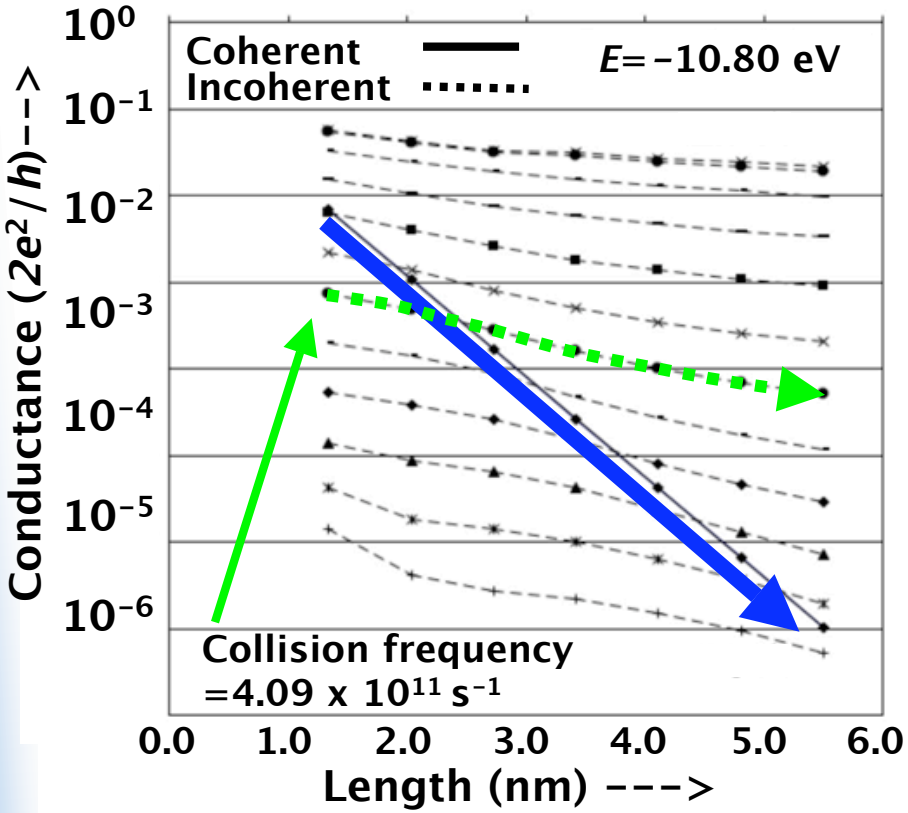
Bias : No bias voltage (0.0 V)

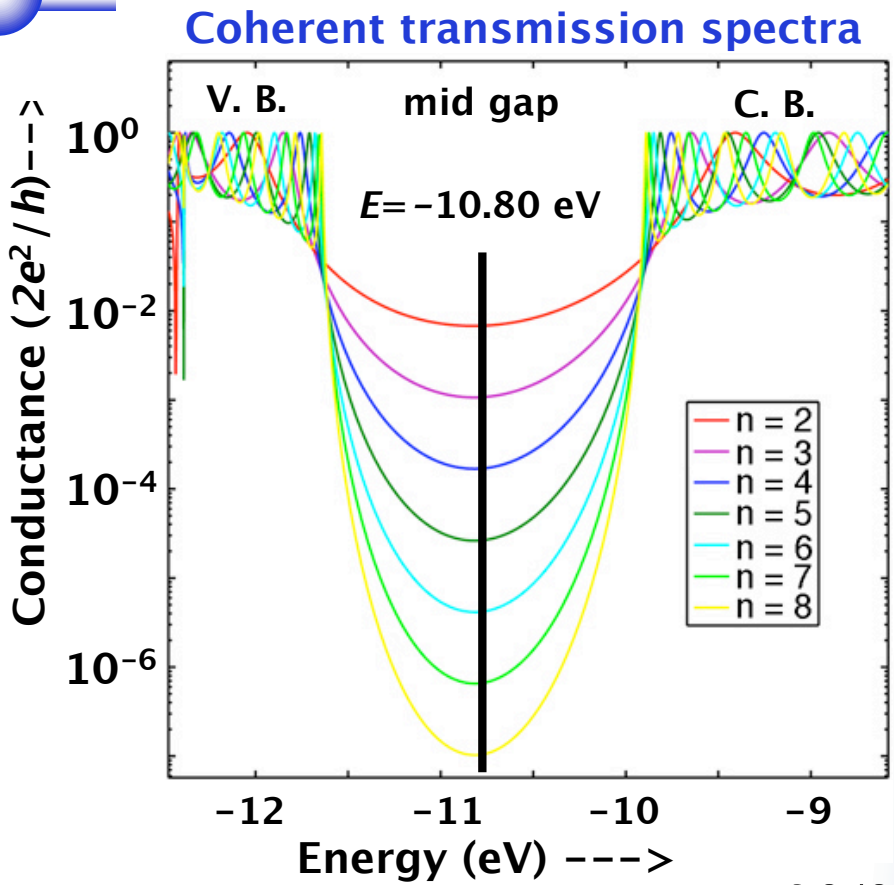
Electrode:
Newns-Anderson approximation

Fermi energy :
We have set Fermi energy in the middle of HOMO-LUMO gap.

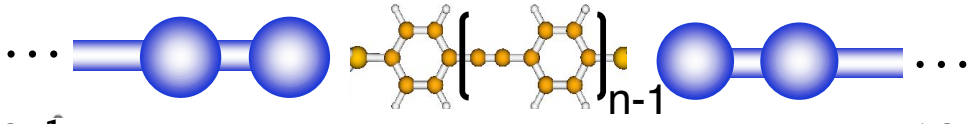
5.1 Coherent transmission spectra through molecular wires

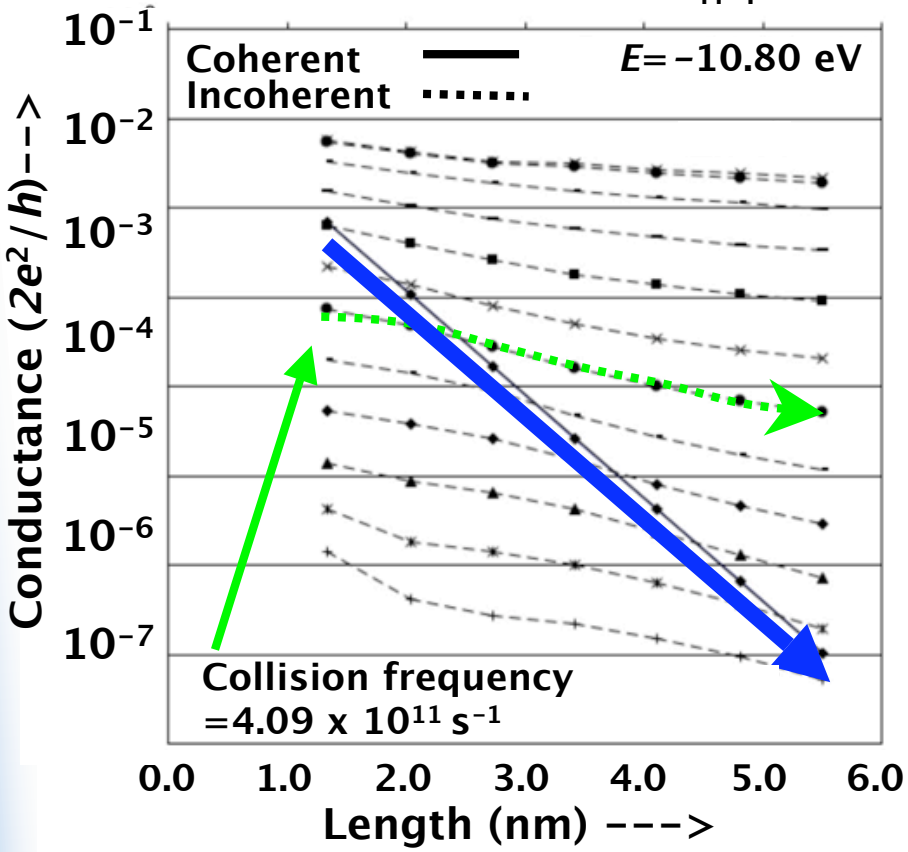


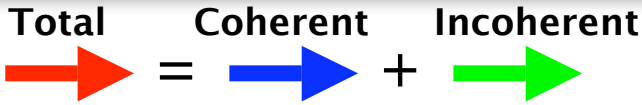


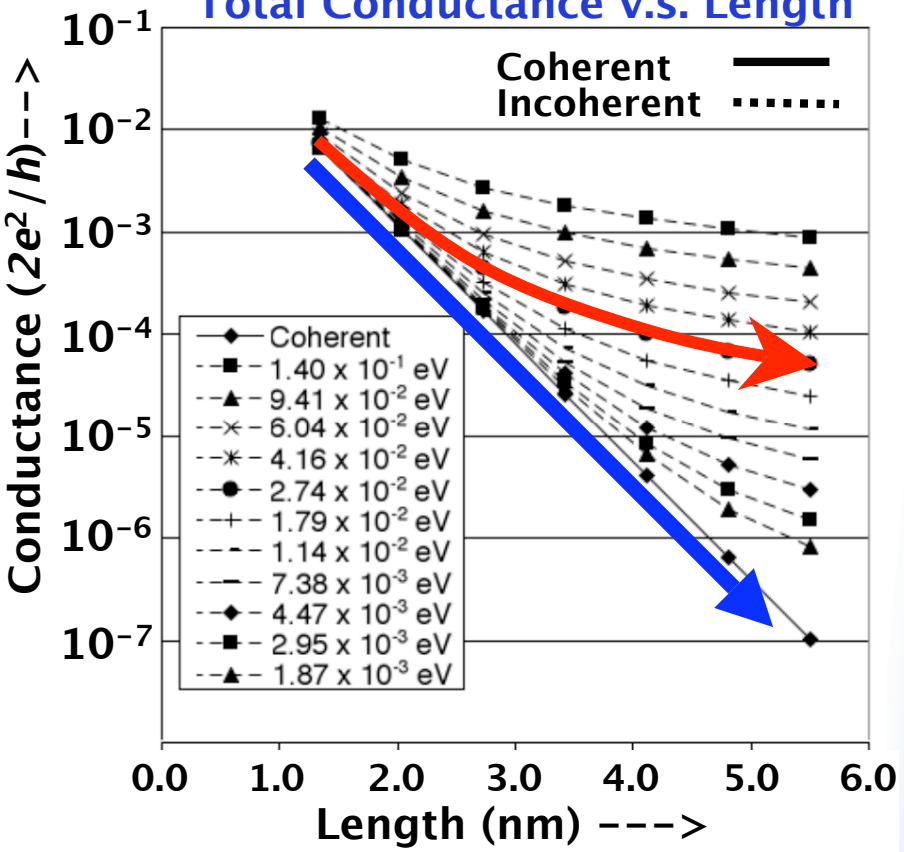


5.2 Length dependence of coherent & incoherent transports

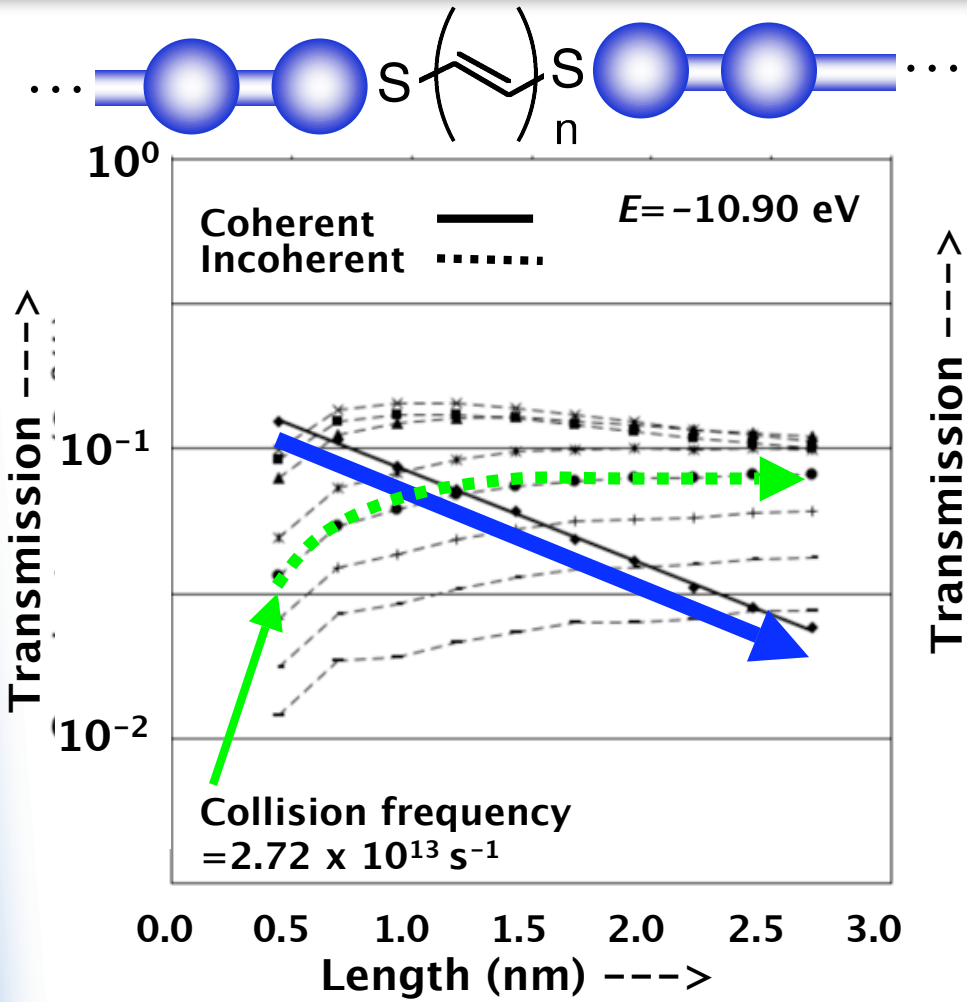


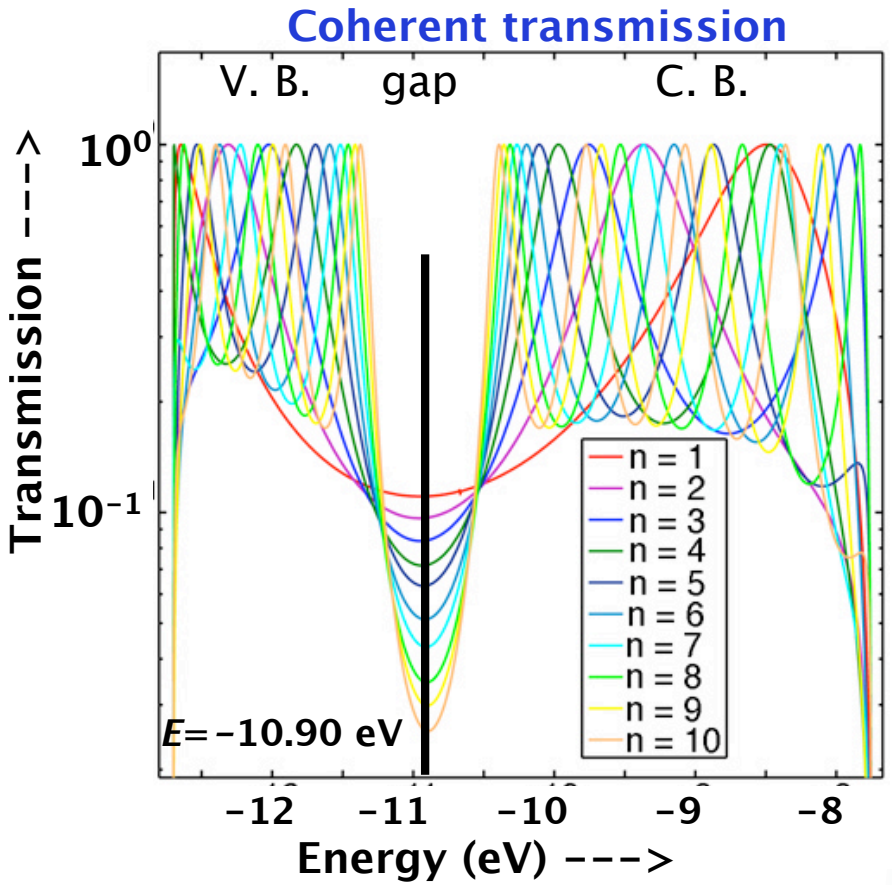




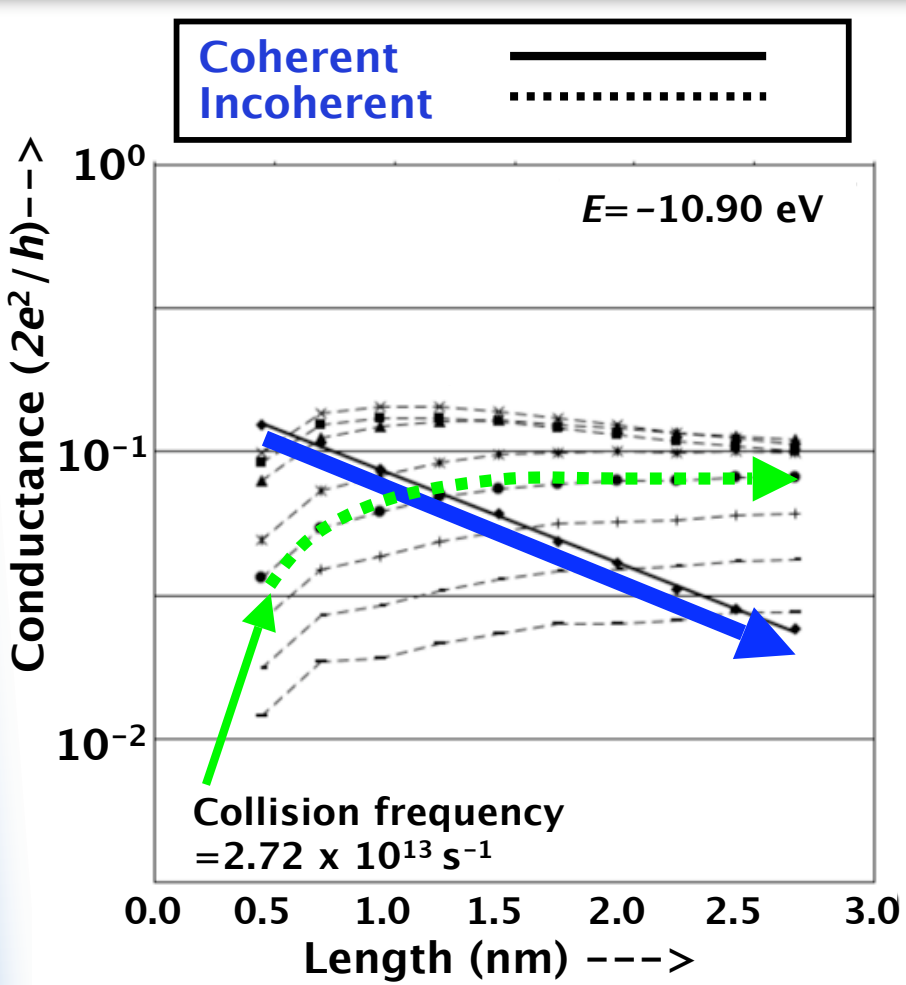


5.1 Coherent transmission spectra through molecular wires

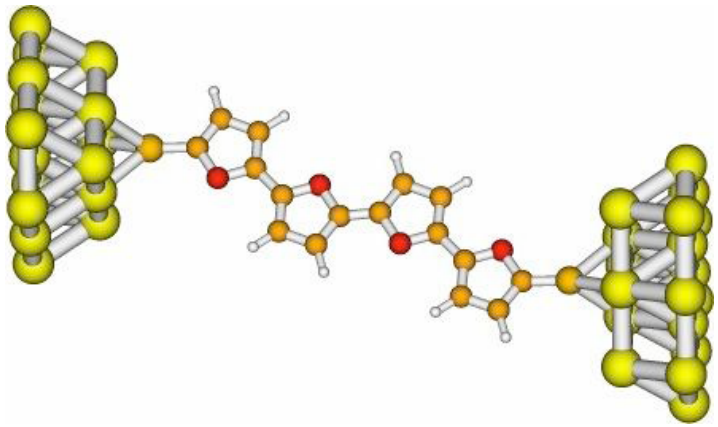


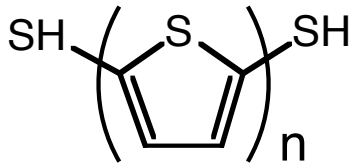


5.2 Length dependence of coherent & incoherent transports

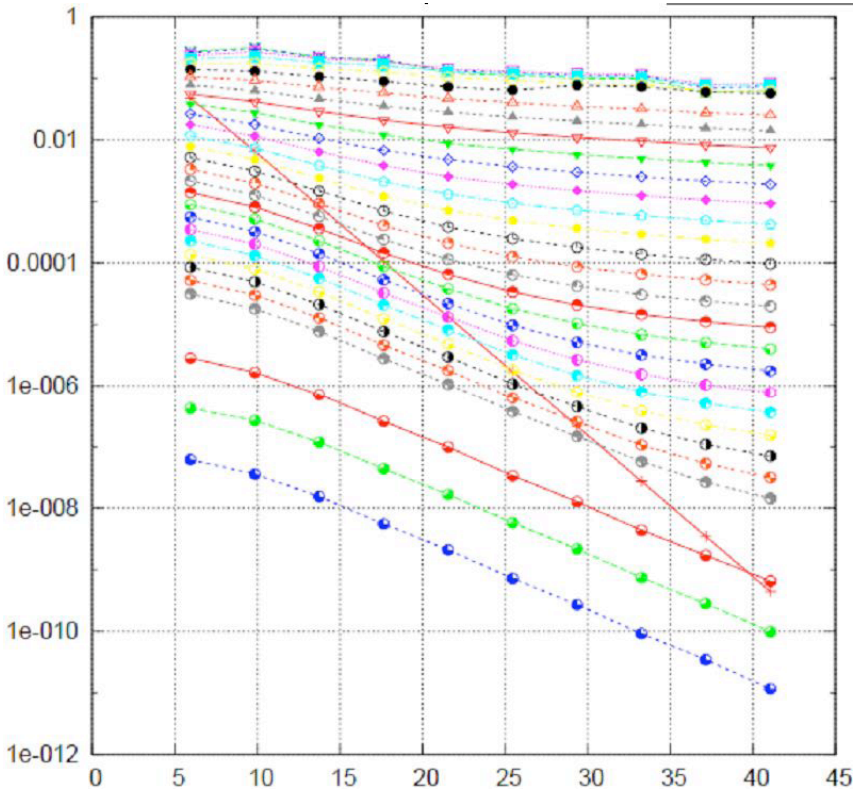


5.2 Poly-thiophene dithiols

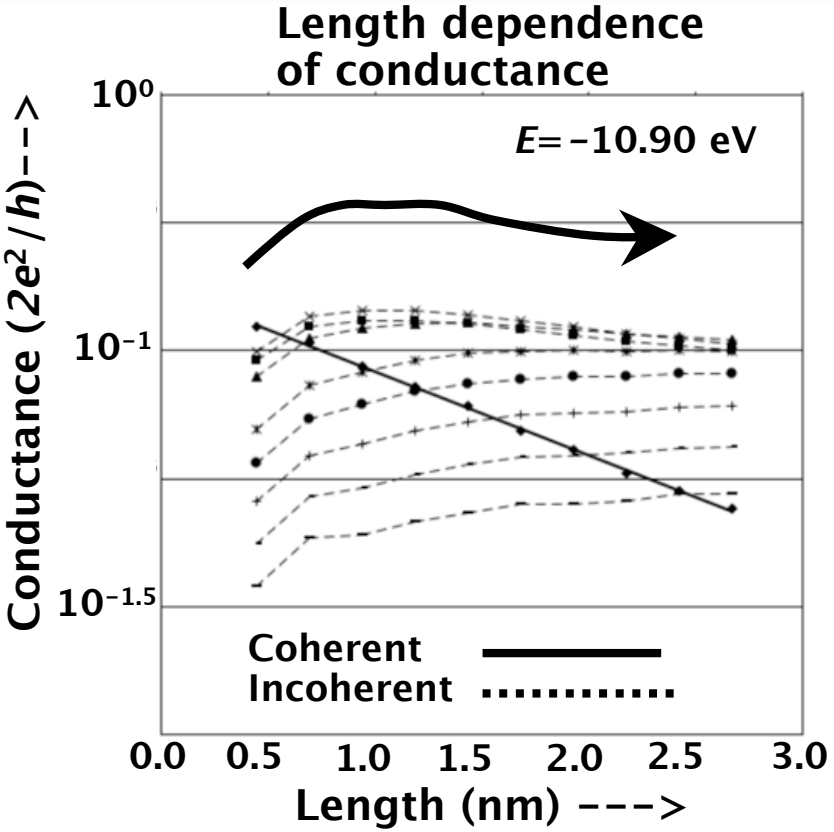




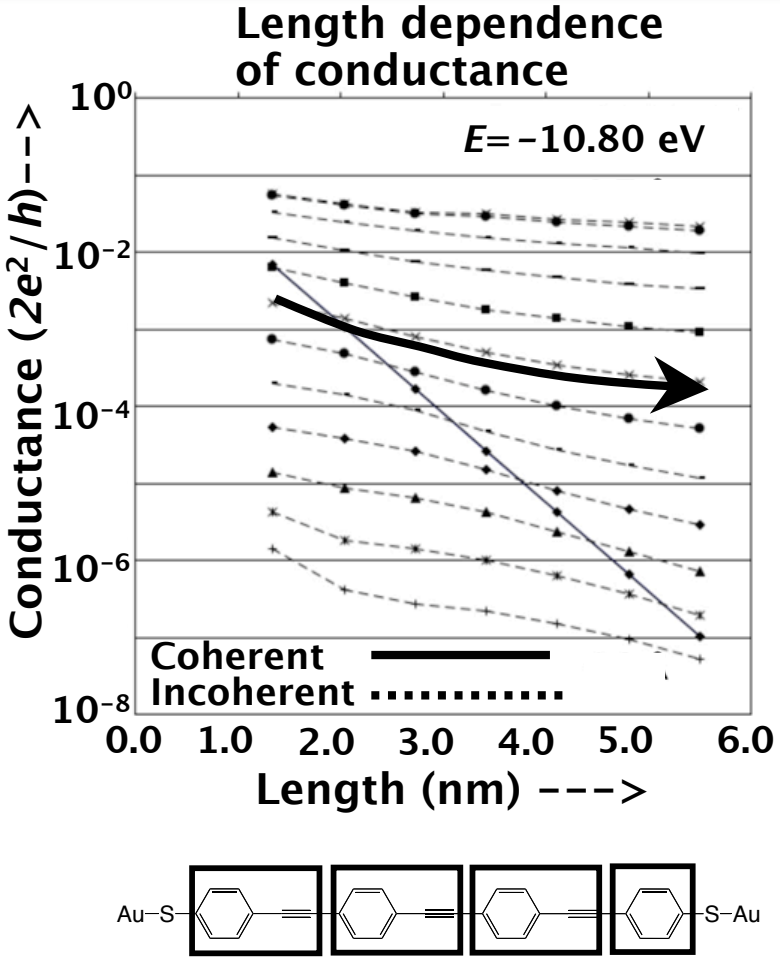
Poly-thiophene dithiols



5.3 Does incoherent transports increase with longer wires?



Polyene wires



Tour wires

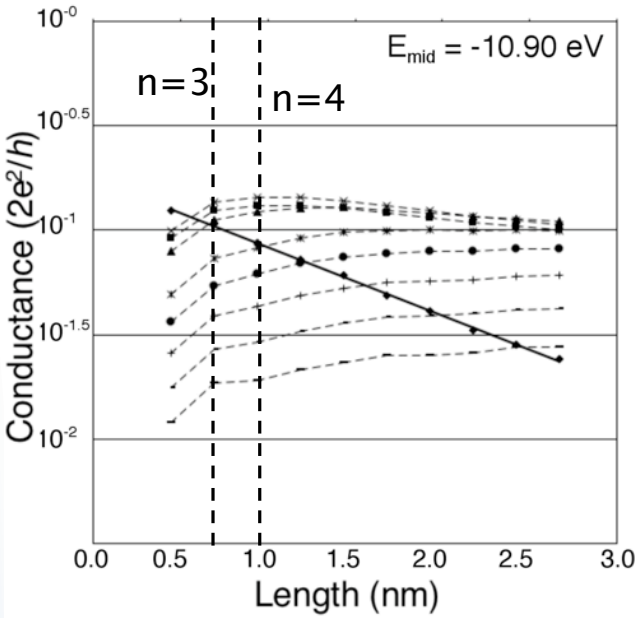
5.3 Explanation to the increase of incoherent transports

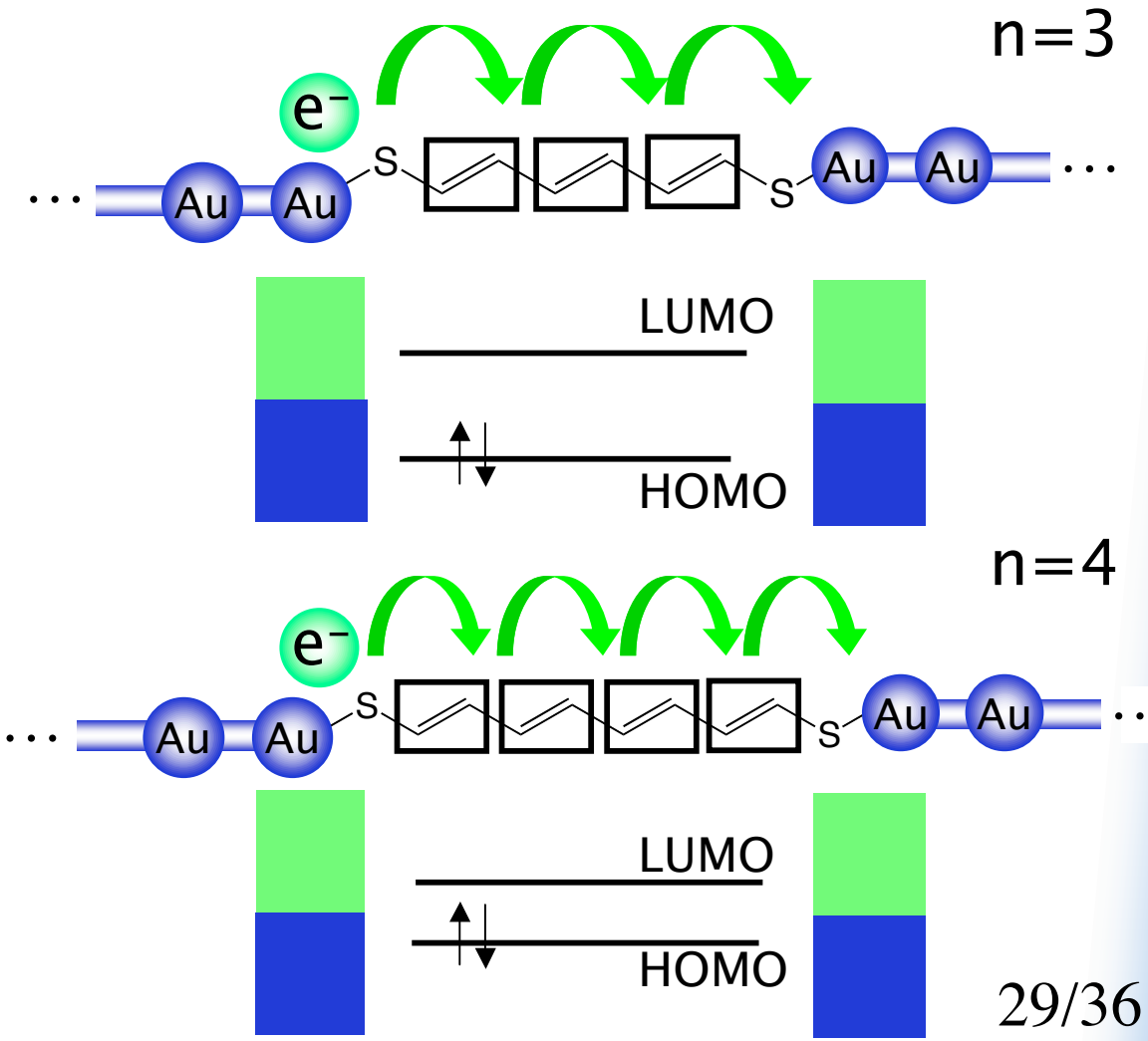
Positive effect

- Orbital interaction between units
- HOMO–LUMO gap decreases

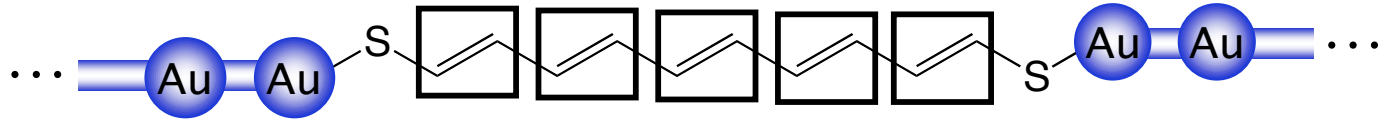
Negative effect

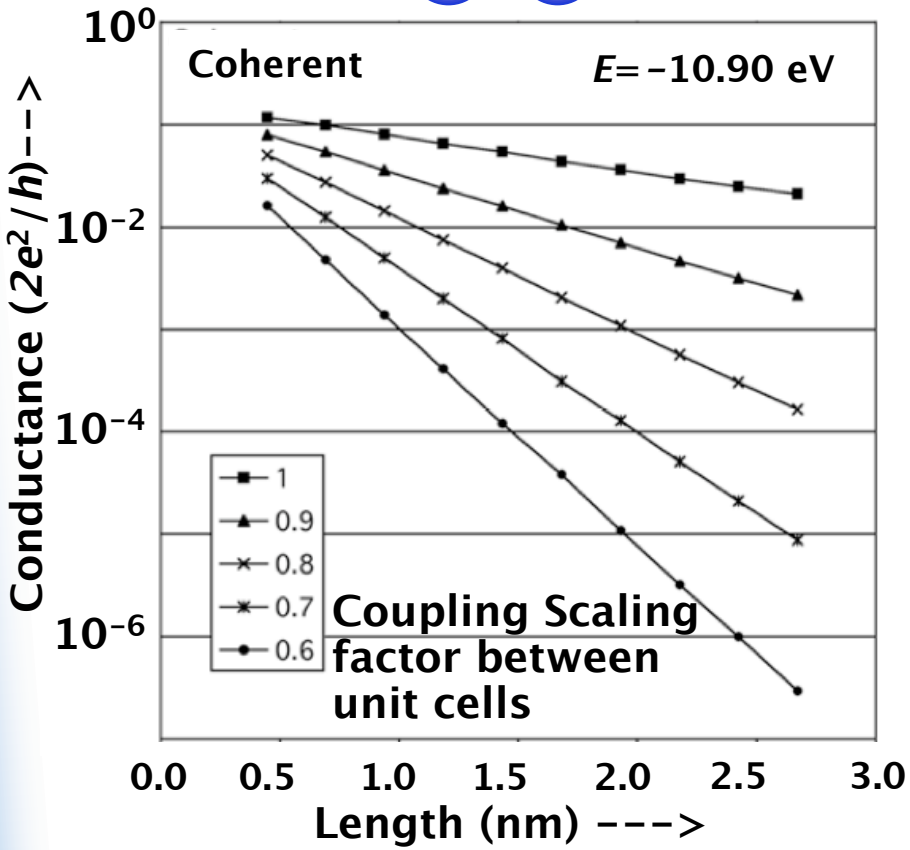
- The path gets longer.



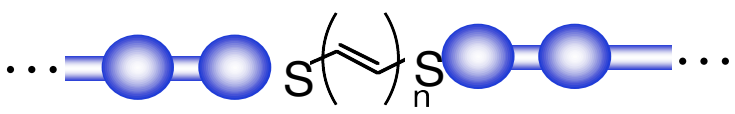


5.3 Explanation to the increase of incoherent transports

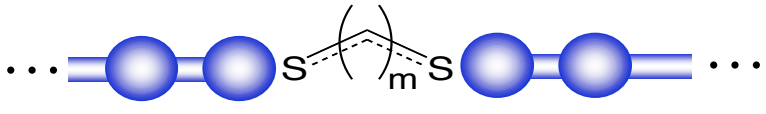




5.4 Odd-even dependence



(even number C atoms)



(odd number C atoms)

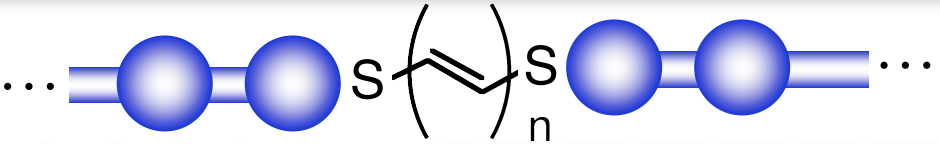
1. Transmission spectra
2. Density of States (DOS)
3. Length dependence of coherent transport

Notations

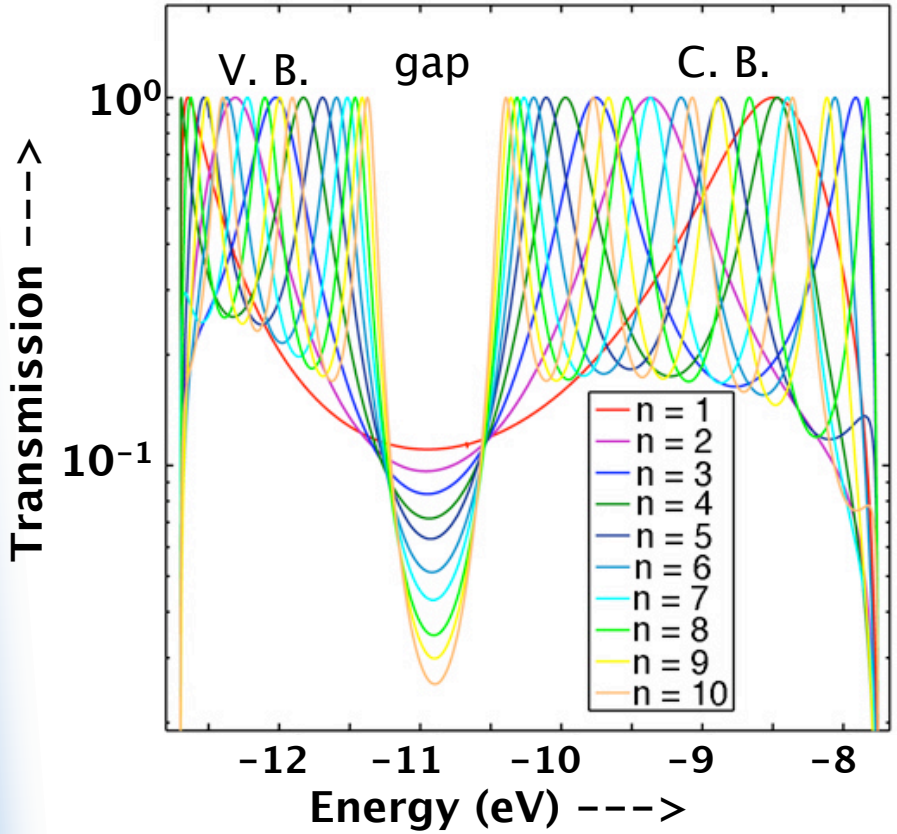
- Length dependence was plotted at the energy of mid gap states.
- Transmission calculations were performed after stucture optimization of isolated molecules with gold clusters
- We used Newns-Anderson approximation for electrodes.

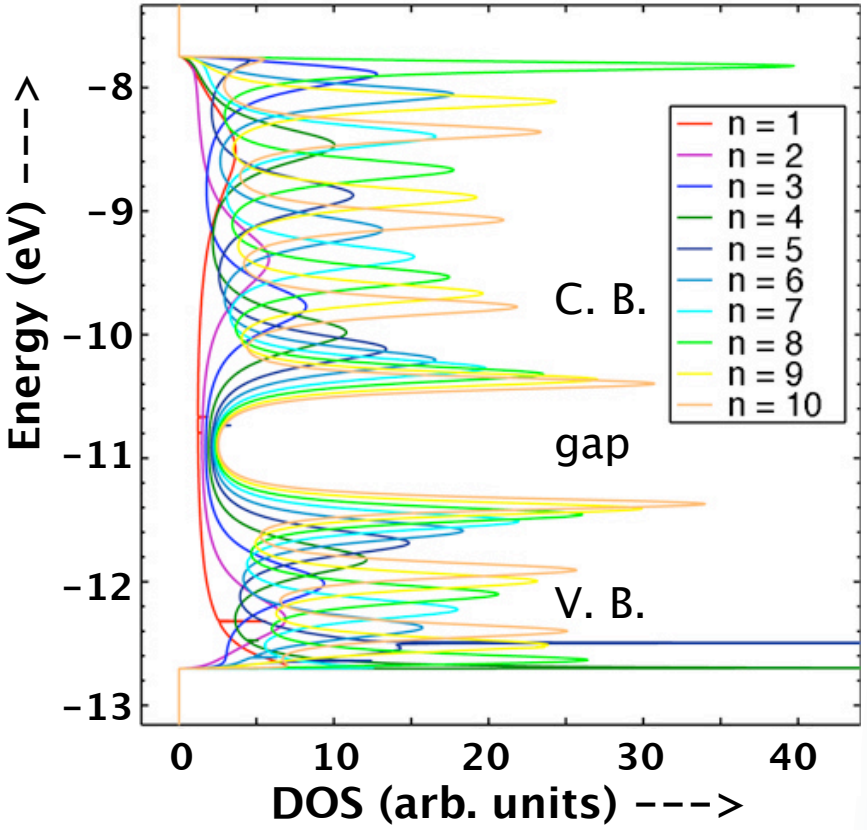
5.4 DOS and T(E) of Polyene-dithiols (even number C atoms)

Coherent T(E)



DOS





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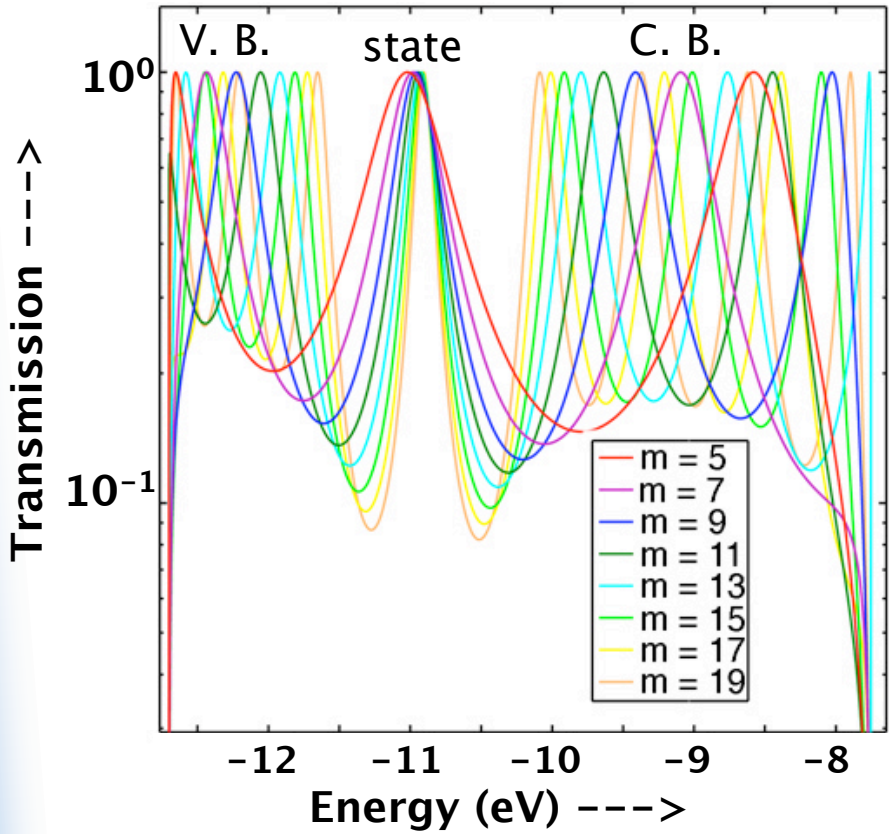
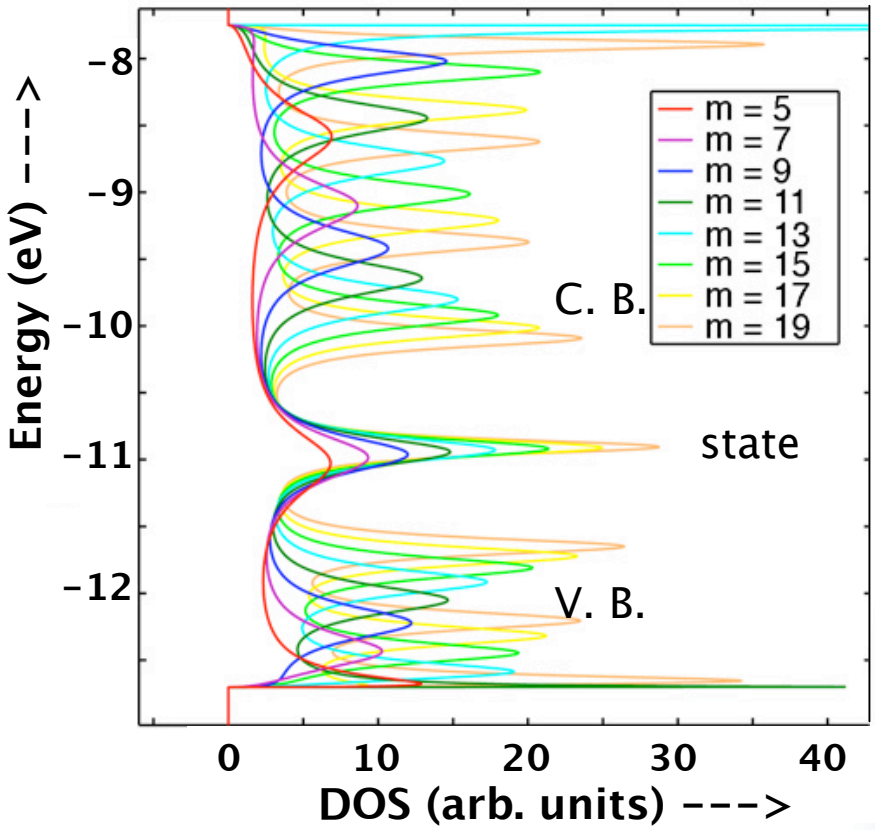
5.4 DOS and T(E) of Polyene-dithiols (odd number C atoms)

Coherent T(E) … S m S … DOS





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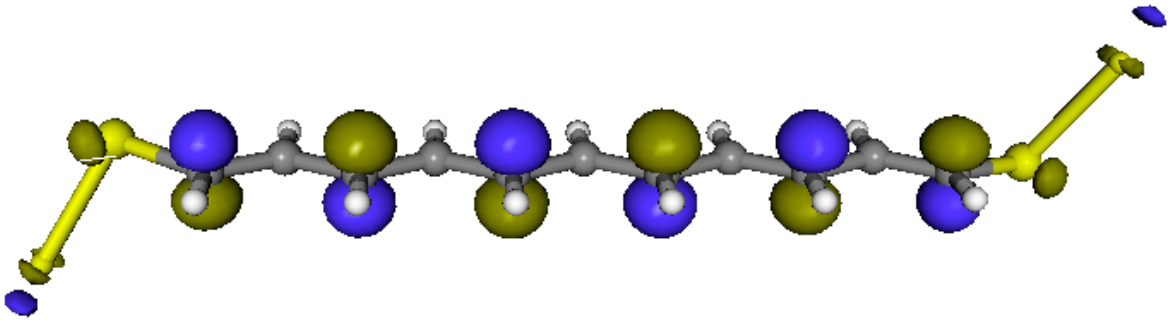
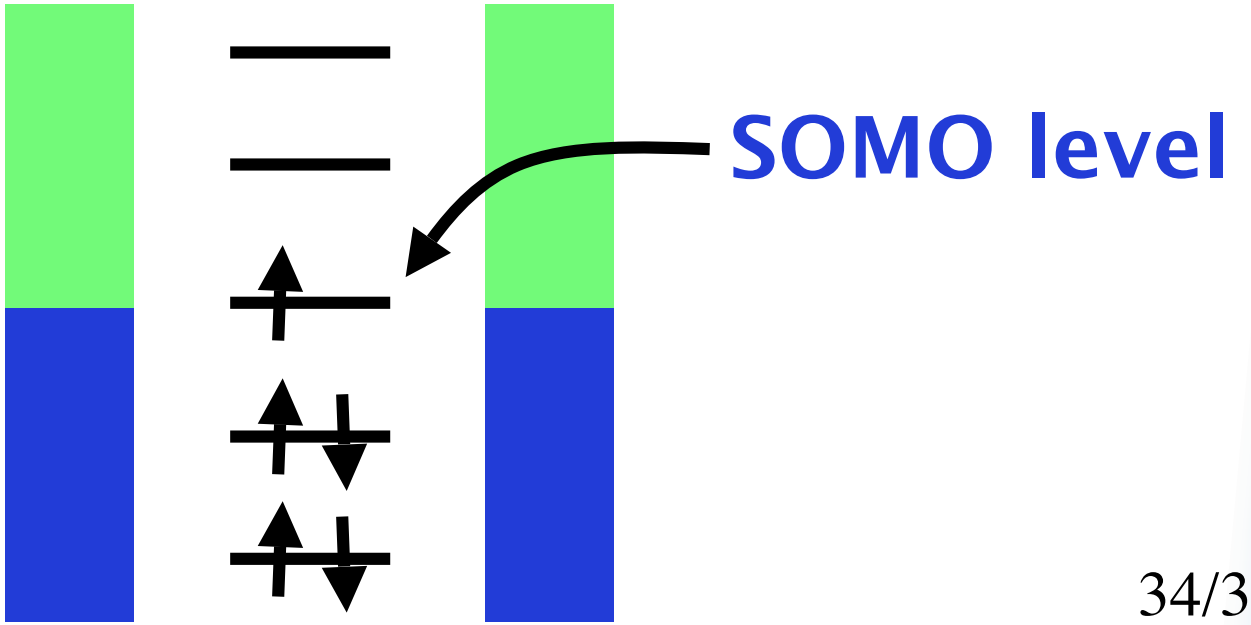
5.4 SOMO of Polyene-dithiole with 2 Au clusters (11 C atoms)





6. Summary

- We have calculated the length dependence of molecular wire including dephasing effect using Büttiekr probes based on the D'Amato-Pastawski model
- The results have shown that the incoherent process becomes dominant transporting mechanism in molecular junctions in long-ranged transport.
- Length dependence of coherent conductance shows quite different features depending on the odd-even number of carbon atoms.

7. Acknowledgement

I express my thanks to
Prof. Yoshizawa
Prof. Kozlowski
Dr. Shoita
Ms. Nishi
Dr. Kamachi
Dr. Staykov
Dr. Girard

And other all members of Yoshizawa's group.

Special thanks to Prof. Gianaurelio Cuniberti for giving me an opportunity for today's presentation!

More accurate description of electrodes is desirable.

$$T(E) = \mathrm{Trace}\left[\Gamma^{L}(E) G(E) \Gamma^{R}(E) G^{\dagger}(E)\right]$$

$$T(E) = \sum_{l \in L, r \in R} T_{l,r}$$

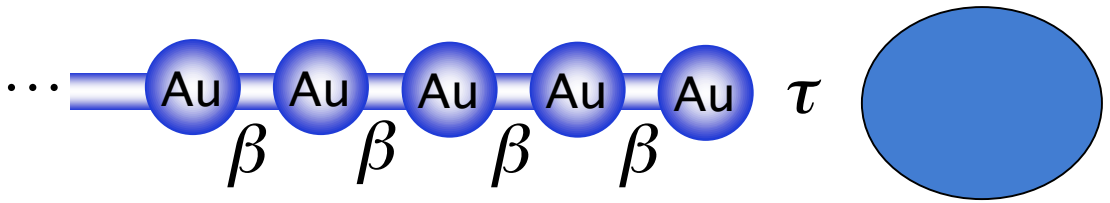
$$T_{lr} = \sum_{i,j} V_{l,i} G_{i,j} V_{j,r}$$

$$\Gamma^{L}_{i,j}(E) = -2\pi \sum_{l} V_{l,i} V^{*}_{l,j} \delta(E_l - E)$$

$$\Gamma^{R}_{i,j}(E) = -2\pi \sum_{r} V_{r,i} V^{*}_{r,j} \delta(E_r - E)$$

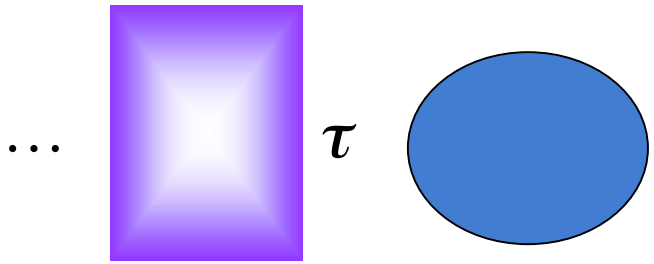
Description of Büttiker probes

Newns-Anderson approximation



$$\Sigma(E) = \tau \frac{\exp(i \cdot ka)}{2\beta} \tau^{\dagger}$$

Wide-band limit

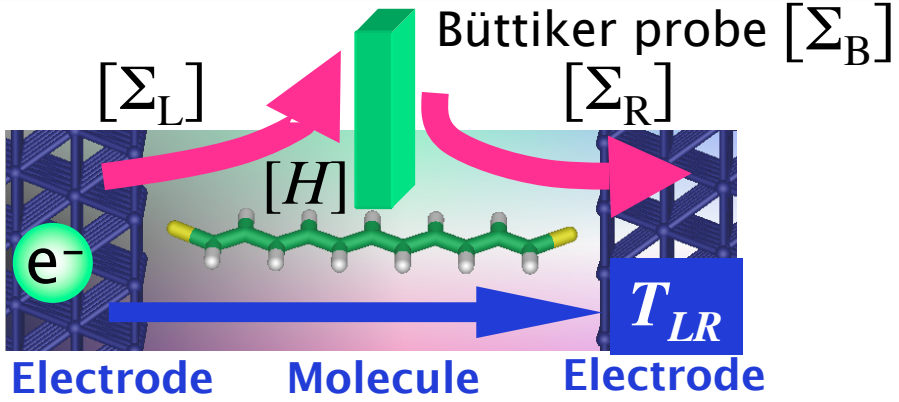


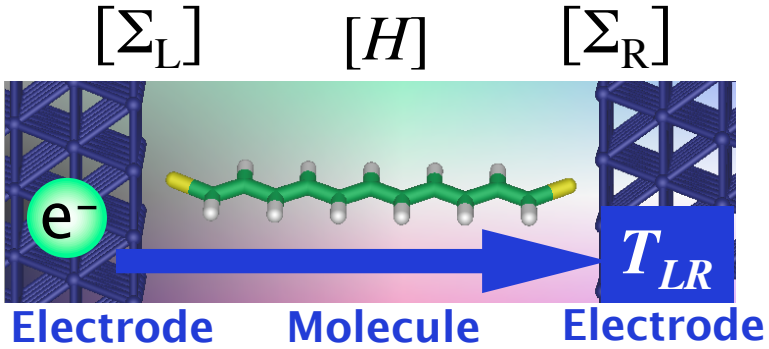
$$\Sigma(E) = i\frac{\eta}{2}$$

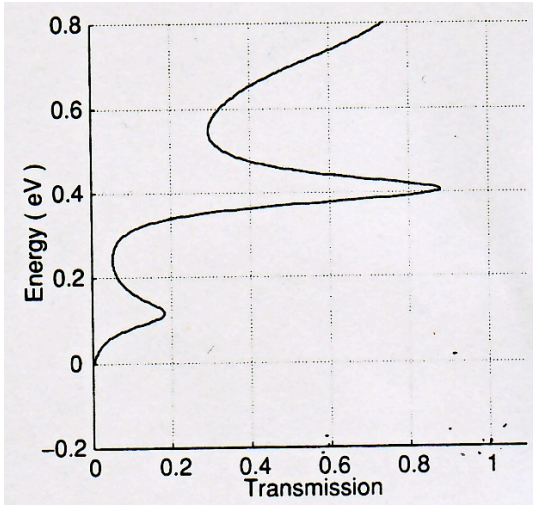
$$\Gamma(E) = \eta$$

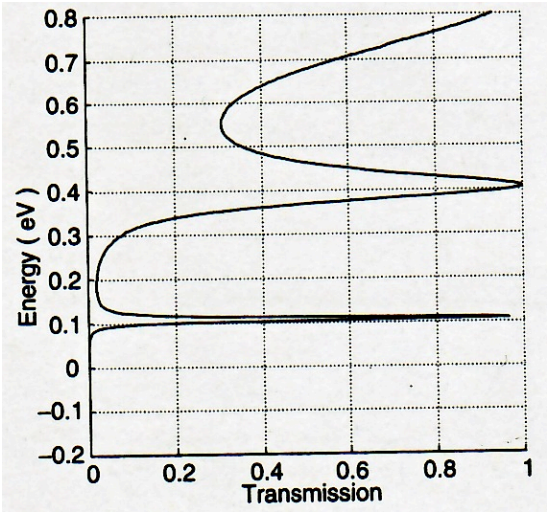
$$\mathrm{Re}[\Sigma(E)] = 0.0$$

2. Landauer model with and witout Büttiker probe





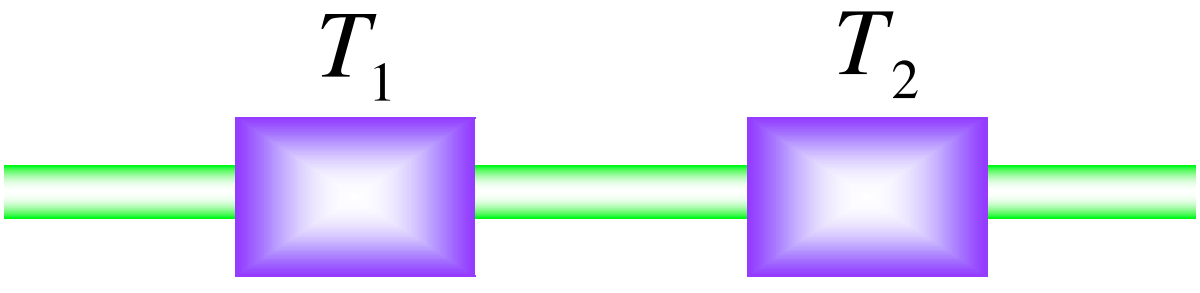




$$T_{tot}(E) = T_{LR}(E) + T_{LB}(E)T_{BR}(E)$$

$$T_{LR}(E) = \mathrm{Trace}\left[G^R(E)\Gamma_L G^A(E)\Gamma_R\right]$$

Convolution of incoherent transport



$T_1 T_2$

$T_1 (R_2 R_1) T_2$

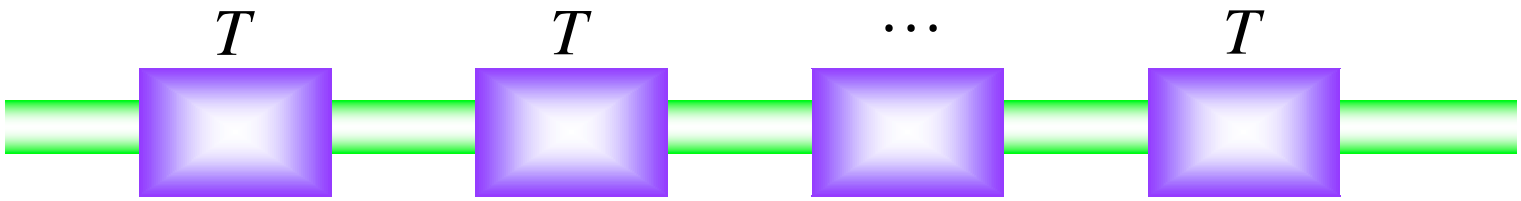
$T_1 (R_2 R_1)^2 T_2$

$T_1 (R_2 R_1)^3 T_2$

$\cdots$ $\cdots$

$$T_{tot} = T_1 T_2 (1 + R_1 R_2 + {R_1}^2 {R_2}^2 + \cdots) = \frac{T_1 T_2}{1 - R_1 R_2} \quad \Leftrightarrow \quad \frac{1 - T_{tot}}{T_{tot}} = \frac{1 - T_1}{T_1} + \frac{1 - T_2}{T_2}$$

$$\frac{1-T_{tot}}{T_{tot}} = \frac{1-T_1}{T_1} + \frac{1-T_2}{T_2}$$



$$\frac{1-T_{tot}}{T_{tot}} = N\frac{1-T}{T}$$

$$T_{tot}(N) = \frac{T}{N(1-T)+T} \qquad T_{tot}(N) \propto \frac{1}{N} \quad \text{(Large N)}$$