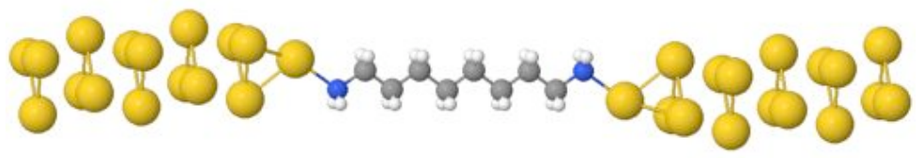
Tunneling conductance of molecular wires



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Work in collaboration with Roberto Car (Dept. of Chemistry, Princeton U)

This work relies heavily on the analytic methods developed during the "Nearsightedness" project coordinated by Walter Kohn

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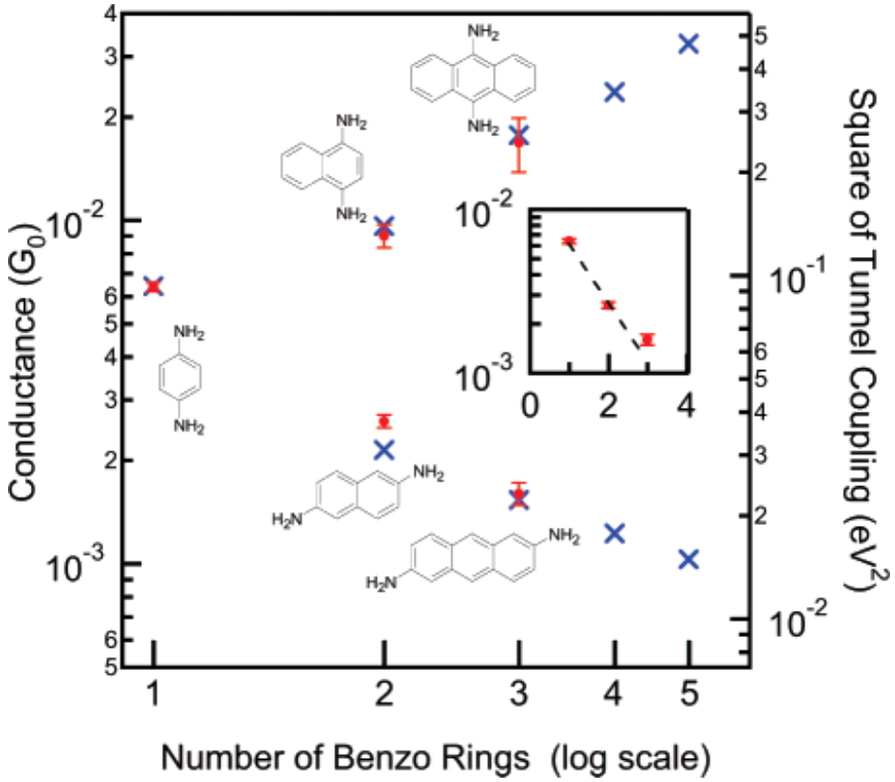
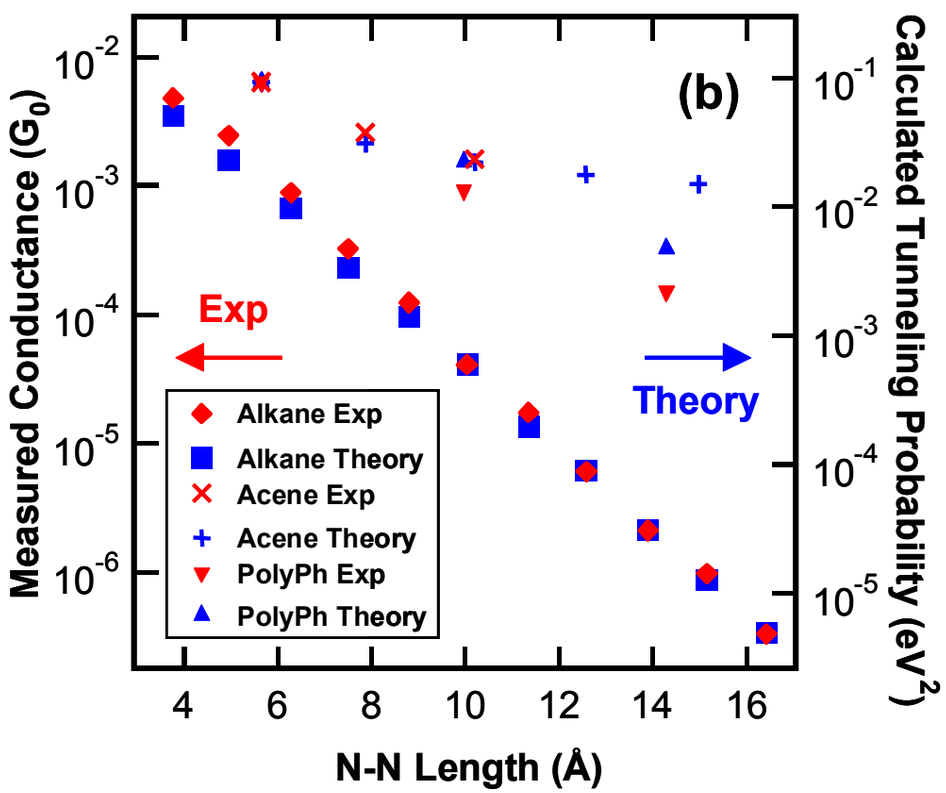
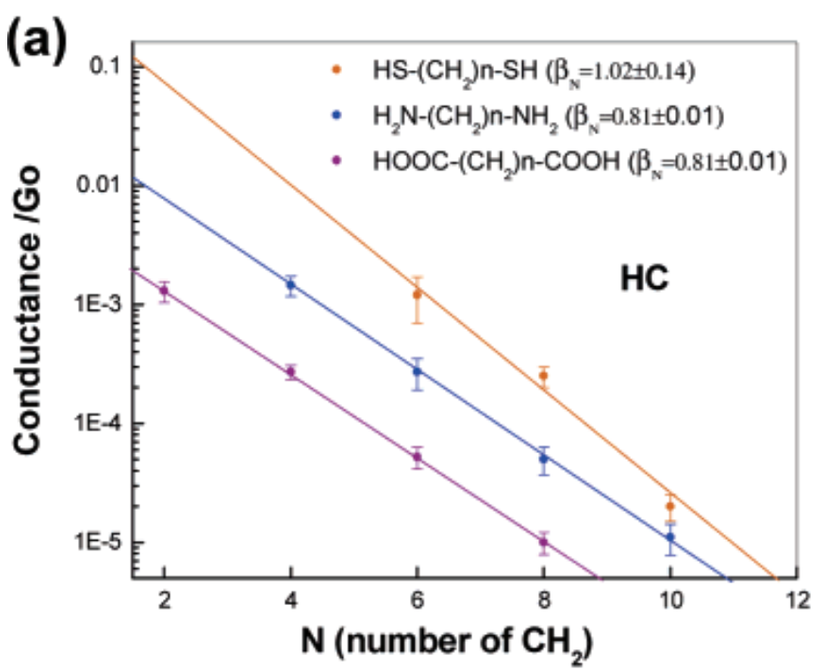
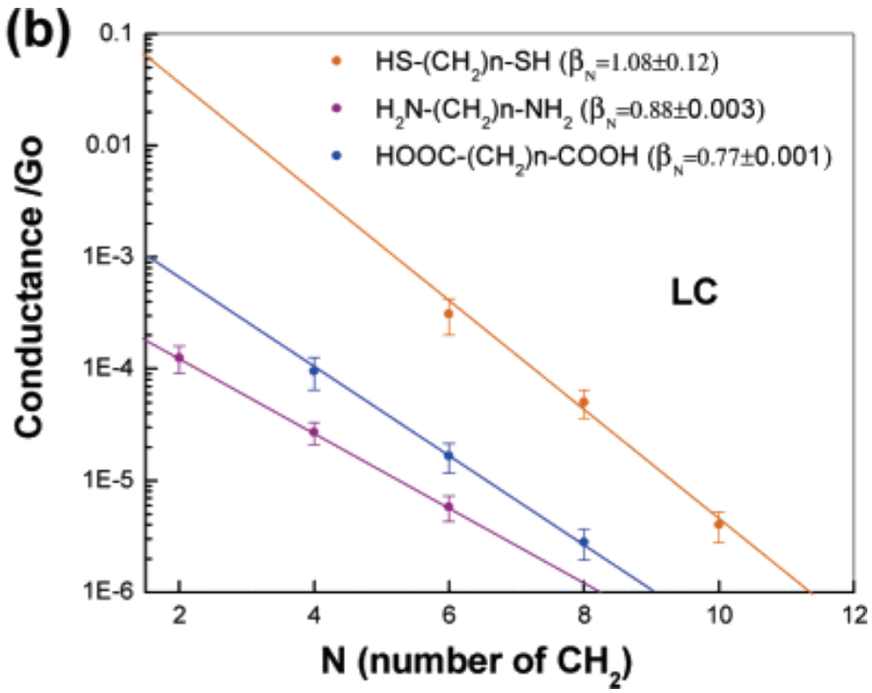
Exciting developments on the experimental side





Latha Venkataram, first highly reproducible results generated in 2006



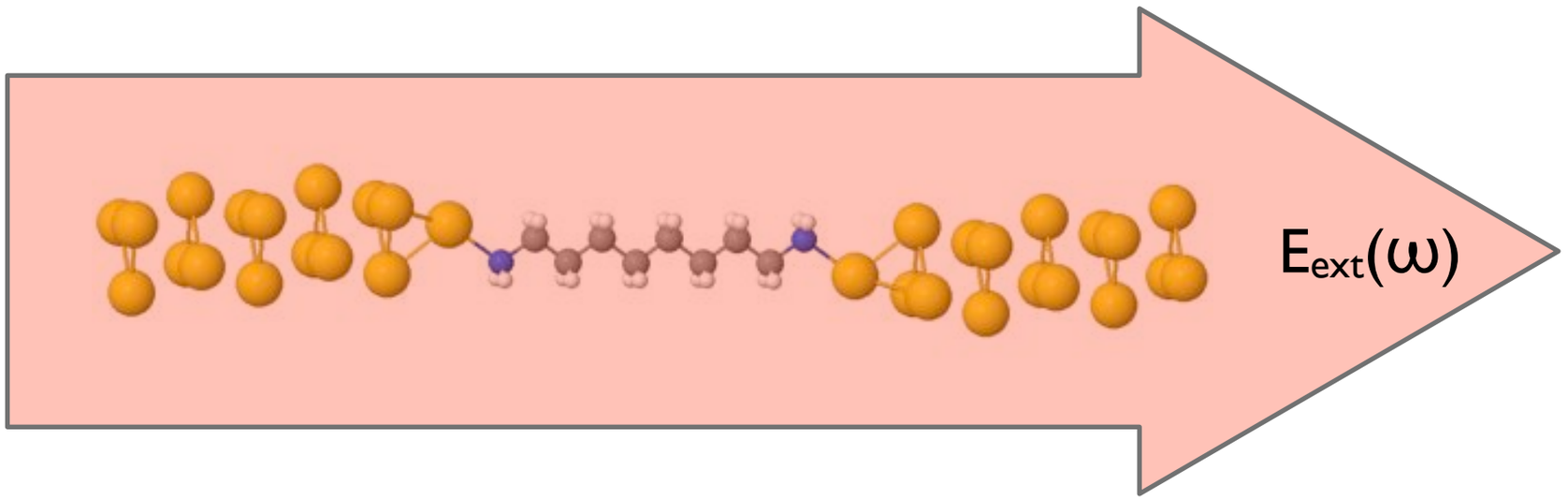


N. Tao et al, JACS 2006

Transport: a Linear Response Approach within Time Dependent Current-Density Functional Theory

Framework: - an equilibrium system that is perturbed by a weak, time oscillating electric field

- DC regime obtained by letting the frequency go to zero

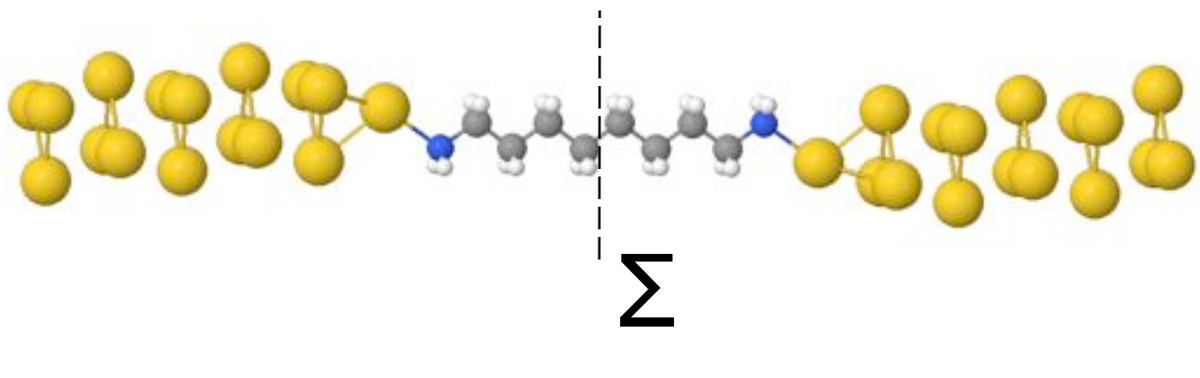


$$\mathbf{j}(\mathbf{r},\omega) = \int \hat{\sigma}^{\mathrm{KS}}(\mathbf{r},\mathbf{r}';\omega)\mathbf{E}_1^{\mathrm{eff}}(\mathbf{r}',\omega)d\mathbf{r}'$$

$$E_1^{\mathrm{eff}}[j] = E_{\mathrm{ext}} + \nabla v_{\mathrm{HXC}}[j] + E_1^{\mathrm{dyn}}[j]$$

We are after the two-point conductance: $g = \dfrac{I}{\Delta\phi_\infty}$

$$\Delta\phi_\infty = \int_\gamma (E^{\mathrm{ext}} + E_1^{\mathrm{H}})dl$$



$$I = \int_\Sigma \mathbf{j}\ d\mathbf{S} \quad \text{with } \mathbf{j} \text{ the self-consistent solution of}$$

$$\mathbf{j}(\mathbf{r},\omega) = \int \hat{\sigma}^{\mathrm{KS}}(\mathbf{r},\mathbf{r}';\omega)\mathbf{E}_1^{\mathrm{eff}}(\mathbf{r}',\omega)d\mathbf{r}' \qquad (\omega \to 0)$$

The exact expression of g within the Linear Response Time Dependent Current-Density Functional Theory

$$g \equiv \frac{I}{\Delta\phi_\infty} = \int d\mathbf{x}_\perp \int d\mathbf{x}'_\perp \, [(1 - \hat{\sigma}^{\mathrm{KS}} * \hat{\mathcal{F}})^{-1} * \hat{\sigma}^{\mathrm{KS}}]_{zz}(\mathbf{x}_\perp, z; \mathbf{x}'_\perp, z')$$

$$\mathcal{F}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \equiv \frac{\delta E_\alpha^{\mathrm{dyn}}(\mathbf{r})}{\delta j_\beta(\mathbf{r}')}$$

Implications:

- the adiabatic v_{HXC} gives no corrections to the 'bare' Kohn-Sham conductance
- the dynamical effects renormalize the Kohn-Sham states
- an exact F matrix will put the resonances at the correct energies and widen to spectral gap to the correct value

The Adiabatic Approximation

$$g \equiv \frac{I}{\Delta\phi_\infty} = \int d\mathbf{x}_\perp \int d\mathbf{x}'_\perp \; [(1 - \hat{\sigma}^{\mathrm{KS}} * \hat{\mathcal{F}})^{-1} * \hat{\sigma}^{\mathrm{KS}}]_{zz}(\mathbf{x}_\perp, z; \mathbf{x}'_\perp, z')$$

Whenever σ^{KS} is small, this part can be neglected and

$$g \equiv \int d\mathbf{r}_\perp \int d\mathbf{r}'_\perp \; \sigma^{\mathrm{KS}}_{zz}(\mathbf{r}_\perp, z, \mathbf{r}'_\perp, z')$$

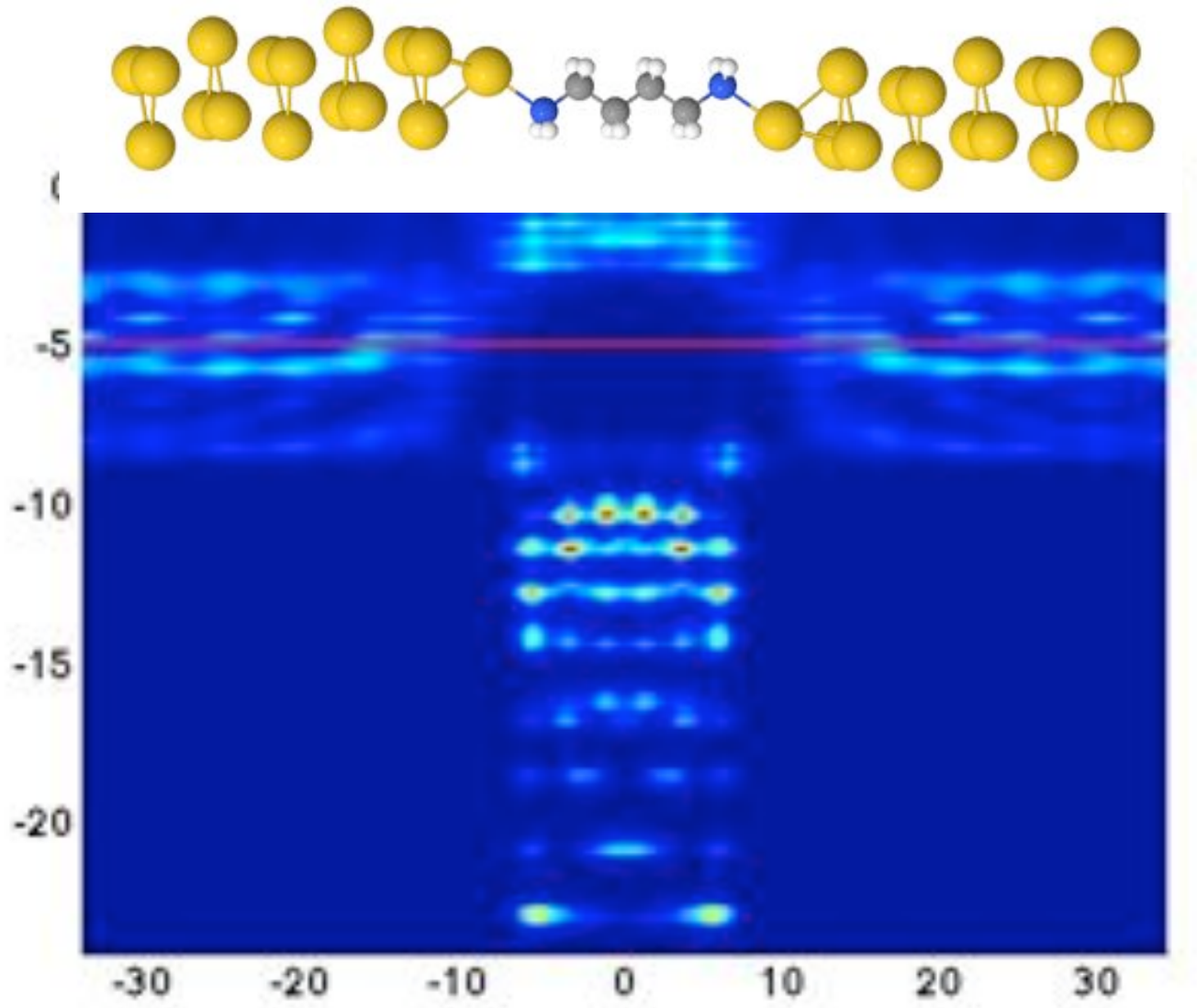
$$\sigma^{\mathrm{KS}}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi} G^{\mathrm{KS}}_{\epsilon_F^+}(\mathbf{r}, \mathbf{r}') \overleftrightarrow{\partial_\alpha} \overleftrightarrow{\partial'_\beta} G^{\mathrm{KS}}_{\epsilon_F^-}(\mathbf{r}', \mathbf{r})$$

(equivalent with Landauer formula)

The problem remains extremely challenging for long molecular chains:

- The super-cells become extremely large
- The conductances become extremely small

Tunneling Transport



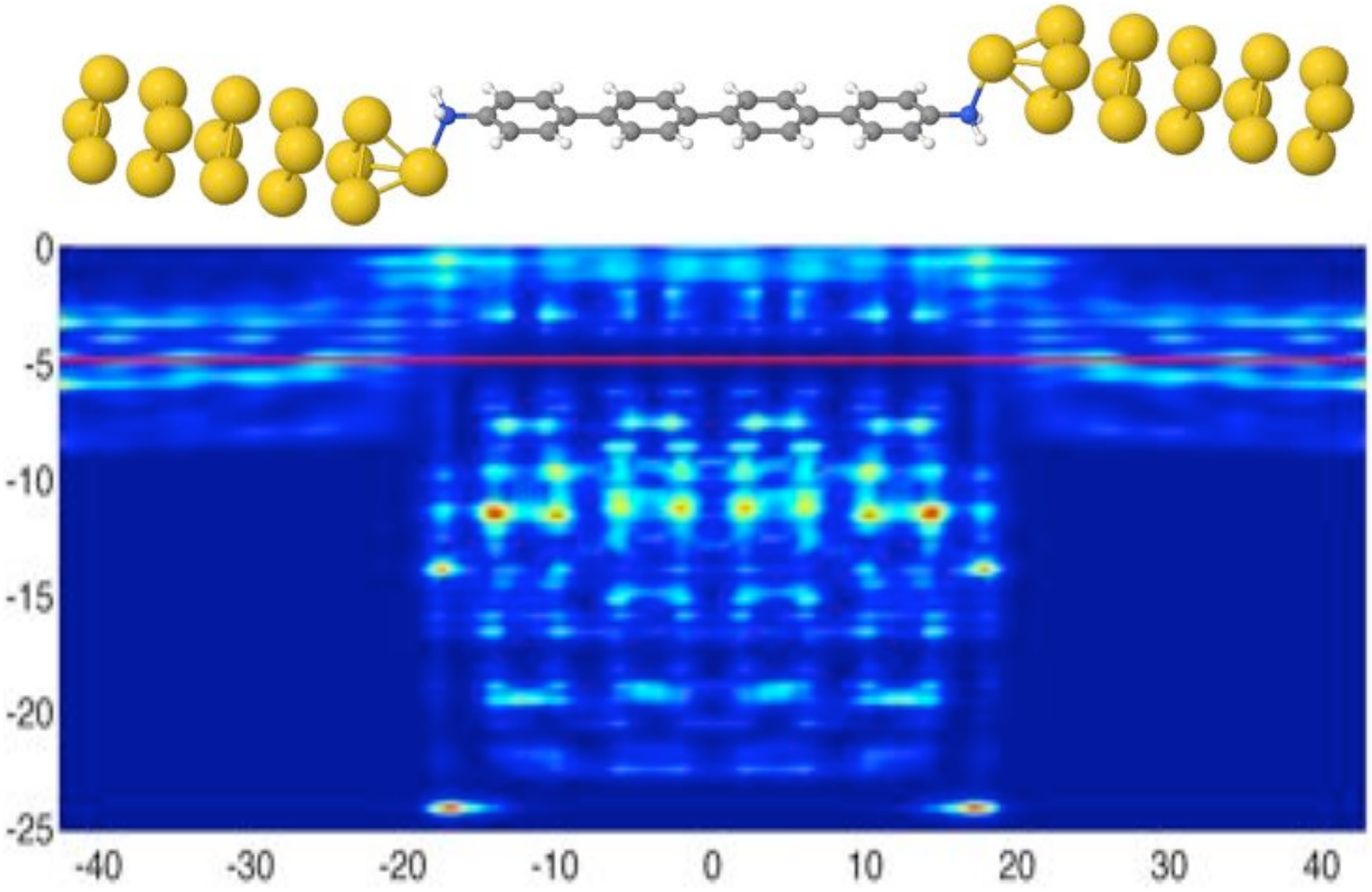
- a crude model will be to consider tunneling through a square barrier

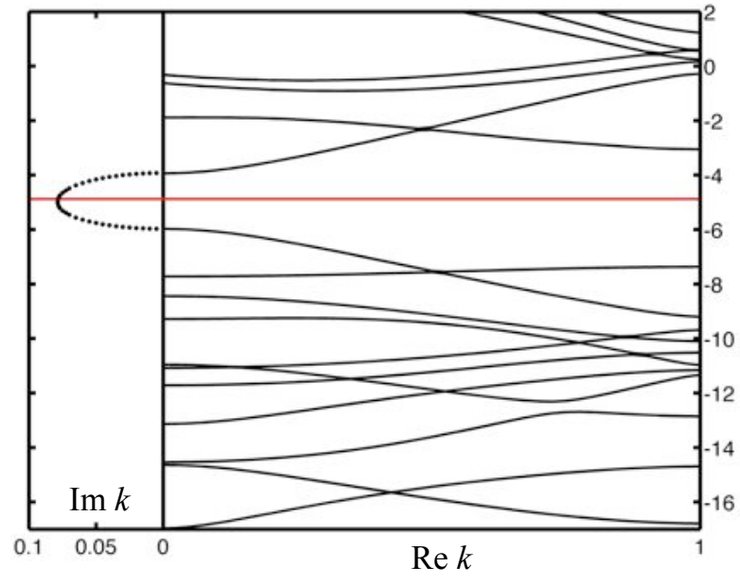
everybody can then understand the typical tunneling behavior:

$g = g_c\, e^{-\beta N}$ (N = number of monomers)

Tunneling Transport in Modern Formulation

P. Mavropoulos, N. Papanikolaou, and P. Dederichs, Phys. Rev. Lett. **85**, 1088 (2000).
J. Tomfohr and O. Sankey, Phys. Rev. B **65**, 245105 (2002).
J. Tomfohr and O. Sankey, J. Chem. Phys. **120**, 1542 (2004).
G. Fagas, A. Kambili, and M. Elstner, Chem. Phys. Lett. **389**, 268 (2004).





- the complex band structure of the infinite chain is aligned with the spectral gap of the device

$$\beta = 2\,\mathrm{Im}\,k_F$$

- the link between the tunneling conductance and complex band structure was established empirically

- no expression for g_c was available

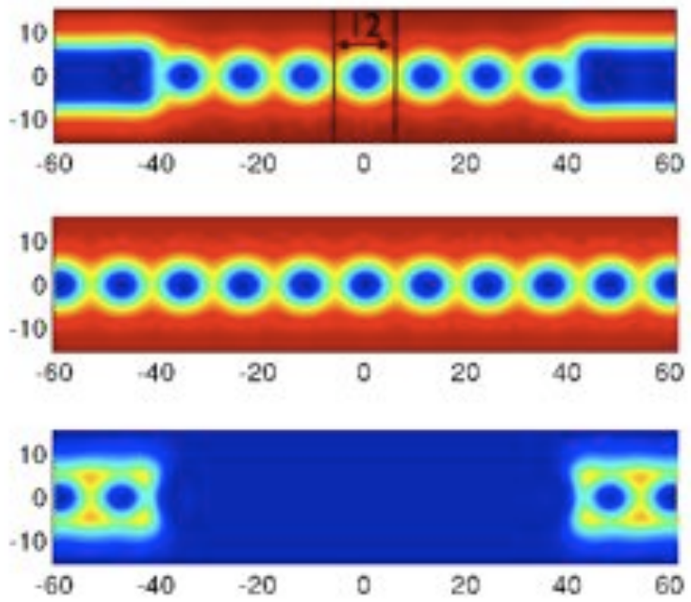
Our contribution

Start from the following decomposition:

V_{eff}

V_0

$\Delta V_{\text{L}} + \Delta V_{\text{R}}$



$$H_{\text{KS}} = -\nabla^2 + V_0 + \Delta V_{\text{L}} + \Delta V_{\text{R}}$$

(Nearsightedness setup: periodic potential perturbed by distant perturbations)

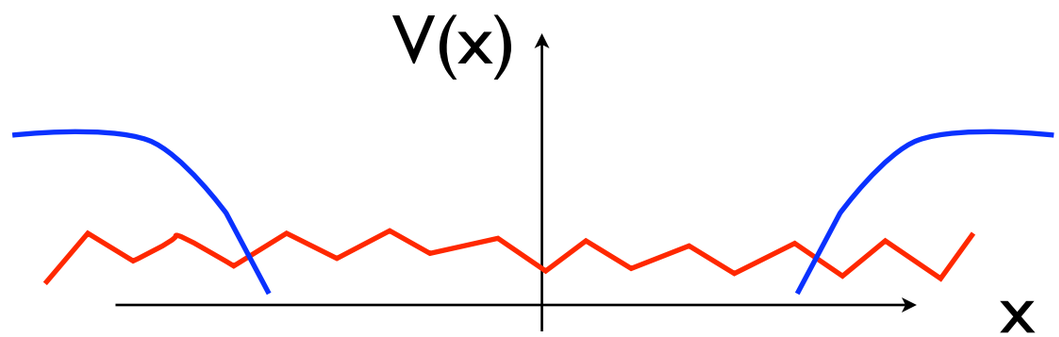
- The reason for decomposition is to use new analytic results on periodic systems (E. P., PRB 2006)

A lesson from a 1 dimensional problem

Remember: we need

$$\sigma^{\rm KS}_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi} G^{\rm KS}_{\epsilon_F^+}(\mathbf{r},\mathbf{r}') \overleftrightarrow{\partial_\alpha}\ \overleftrightarrow{\partial'_\beta}\ G^{\rm KS}_{\epsilon_F^-}(\mathbf{r}',\mathbf{r})$$

$$H = -\frac{d^2}{dx^2} + V(x)$$



Green's function: $G_E(x,x') = (H-E)^{-1} = \sum_n \frac{\psi_n(x)\psi_n^*(x')}{E-\epsilon_n}$ (not very useful)

In 1D, there is an alternative expression

$$G_E(x,x') = \frac{\psi_<(x_<)\psi_>(x_>)}{W(\psi_<,\psi_>)}$$

$(H-E)\psi_< = 0$, with the boundary condition to the left

$(H-E)\psi_> = 0$, with the boundary condition to the right

The expression for the Green's function is so simple that one can compute g analytically!!

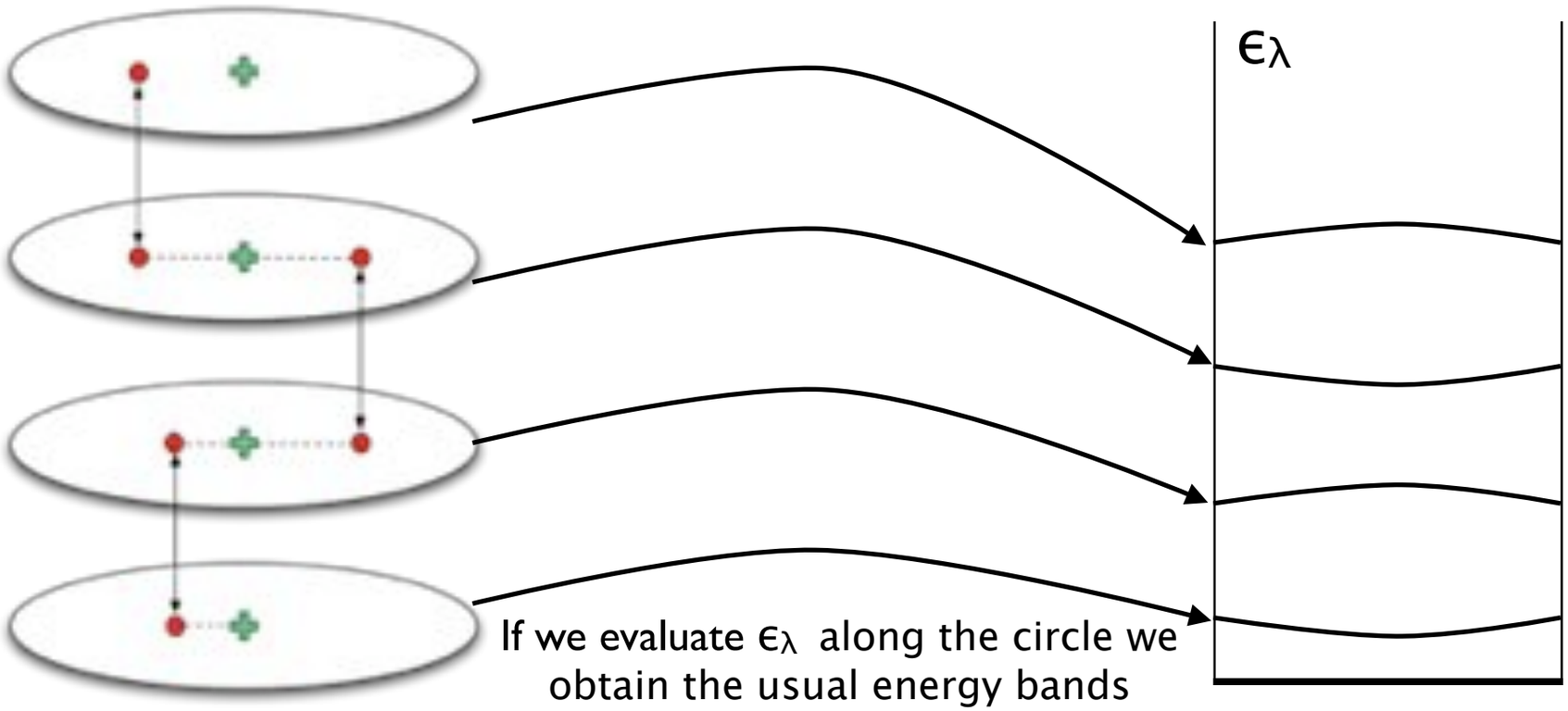
$$g_0(L) = \frac{4}{\pi} \frac{\mathrm{Im}[\mathcal{R}_{\mathrm{L}}(k_F^+)]\mathrm{Im}[\mathcal{R}_{\mathrm{R}}(k_F^+)]e^{-2\beta L}}{|1 - e^{-2\beta L}\mathcal{R}_{\mathrm{L}}(k_F^+)\mathcal{R}_{\mathrm{R}}(k_F^+)|^2}$$

Unfortunately, the textbooks tell that no such expression for the Green's function exists in higher dimensions!

We found the exception, which is the case of periodic potentials!

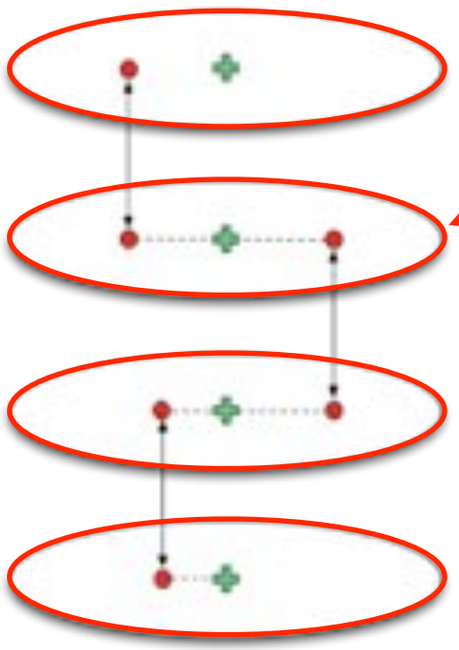
Green's function from the Riemann surface of the bands

Globally defined ϵ_λ, P_λ on a Riemann surface describe the whole band structure ($\lambda=e^{ikb}$).



The Riemann surface of the bands was discovered by Walter Kohn in 1959.

$$G^0_\epsilon(\mathbf{r},\mathbf{r}') = \sum_n \int_{|\lambda|=1} \frac{\psi_{n,1/\lambda}(\mathbf{r})\psi_{n,\lambda}(\mathbf{r}')}{\epsilon-\epsilon_{n,\lambda}} \frac{d\lambda}{2\pi i\lambda} \quad \text{(eigenfunction expansion)}$$



$$G^0_\epsilon(\mathbf{r},\mathbf{r}') = \int_\Gamma \frac{\psi_{1/\lambda}(\mathbf{r}_<)\psi_\lambda(\mathbf{r}'_>)}{\epsilon-\epsilon(\lambda)} \frac{d\lambda}{2\pi i\lambda}$$

But the contour Γ can be deformed to a point:

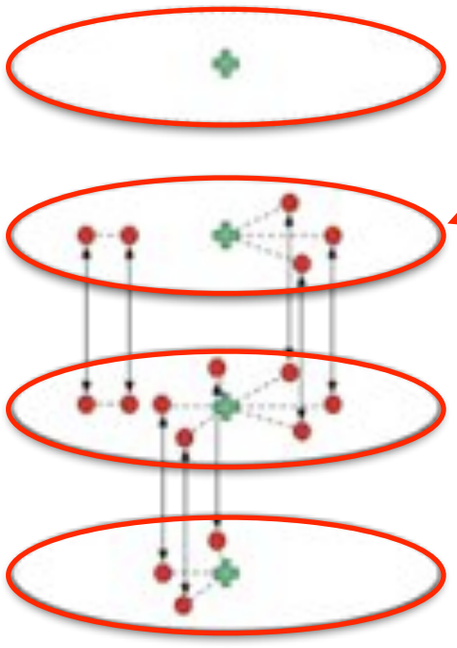
$$\Rightarrow \quad G^0_\epsilon(\mathbf{r},\mathbf{r}') = \frac{\psi_{1/\lambda}(\mathbf{r}_<)\psi_\lambda(\mathbf{r}'_>)}{\lambda\partial_\lambda\epsilon(\lambda)}$$

λ = the point on the Riemann surface so that: $\epsilon = \epsilon(\lambda)$

The existence of the Riemann structure gives the simple expression for the Green's function!

Molecular wires

Existence and characterization of the Riemann surface for molecular wires was given in E. Prodan, PRB 2006



$$G^0_\epsilon(\mathbf{r},\mathbf{r}') = \int_\Gamma \frac{\psi_{1/\lambda}(\mathbf{r}_<)\psi_\lambda(\mathbf{r}'_>)}{\epsilon - \epsilon(\lambda)} \frac{d\lambda}{2\pi i \lambda}$$

But the contour Γ can be deformed to a point:

$$\Rightarrow \quad G^0_\epsilon(\mathbf{r},\mathbf{r}') = \sum_j \frac{\psi_{1/\lambda_j}(\mathbf{r}_<)\psi_{\lambda_j}(\mathbf{r}'_>)}{\lambda_j \partial_\lambda \epsilon(\lambda_j)}$$

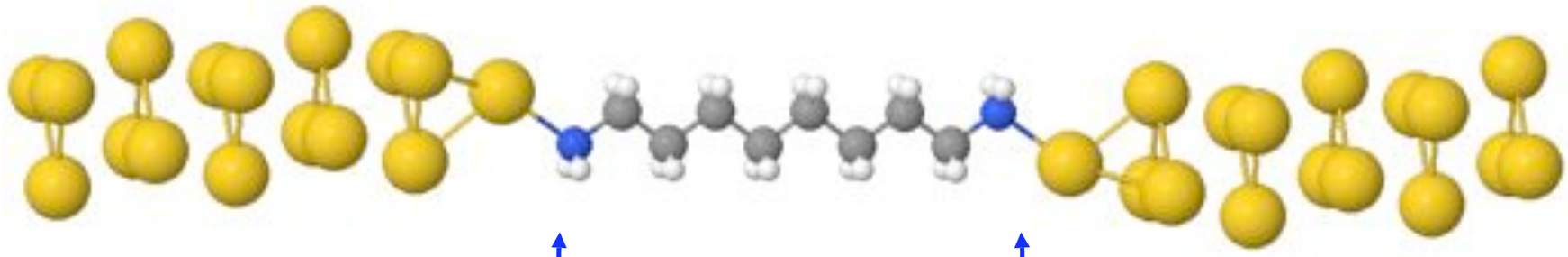
λ_j are all λ on the Riemann surface so that: $\epsilon = \epsilon(\lambda_j)$

Tunneling Conductance

$$g_0(L) = \frac{1}{\pi} \sum_{i,j} \frac{\Theta_{\mathrm{L}}^{ij} \Theta_{\mathrm{R}}^{ij}}{\partial_k \epsilon_{k_i} \partial_k \epsilon_{k_j}} e^{i(k_i + k_j)L}$$

$\varepsilon(k_i) = \varepsilon_F$

E. Prodan & R. Car, PRB 2007



Localized
at the contacts

$$\Theta_{\mathrm{L}}^{ij} = 2\pi i \int d\mathbf{r} \int d\mathbf{r}' \times$$

$$\Delta V_{\mathrm{L}}(\mathbf{r}) e^{-i(k_i z + k_j z')} \Delta V_{\mathrm{L}}(\mathbf{r}') \times$$

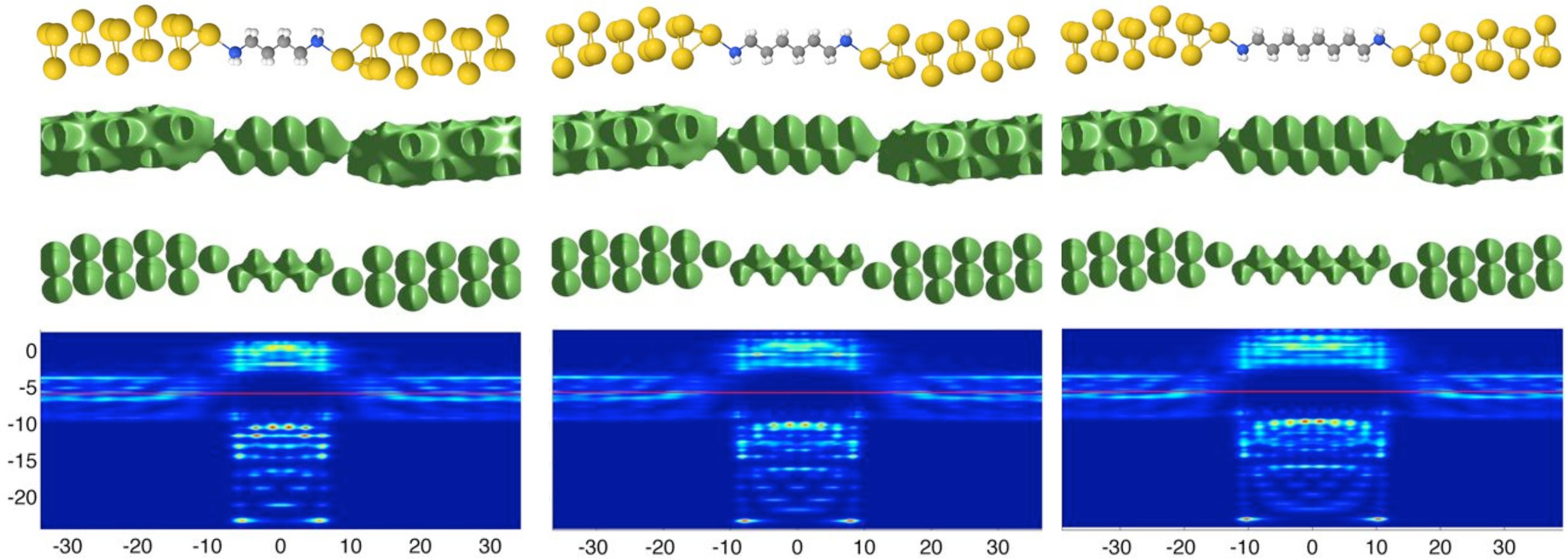
$$u_{-k_i}(\mathbf{r}) \rho_{\epsilon_F}(\mathbf{r}, \mathbf{r}') u_{-k_i}(\mathbf{r}'),$$

$$\Theta_{\mathrm{R}}^{ij} = 2\pi i \int d\mathbf{r} \int d\mathbf{r}' \times$$

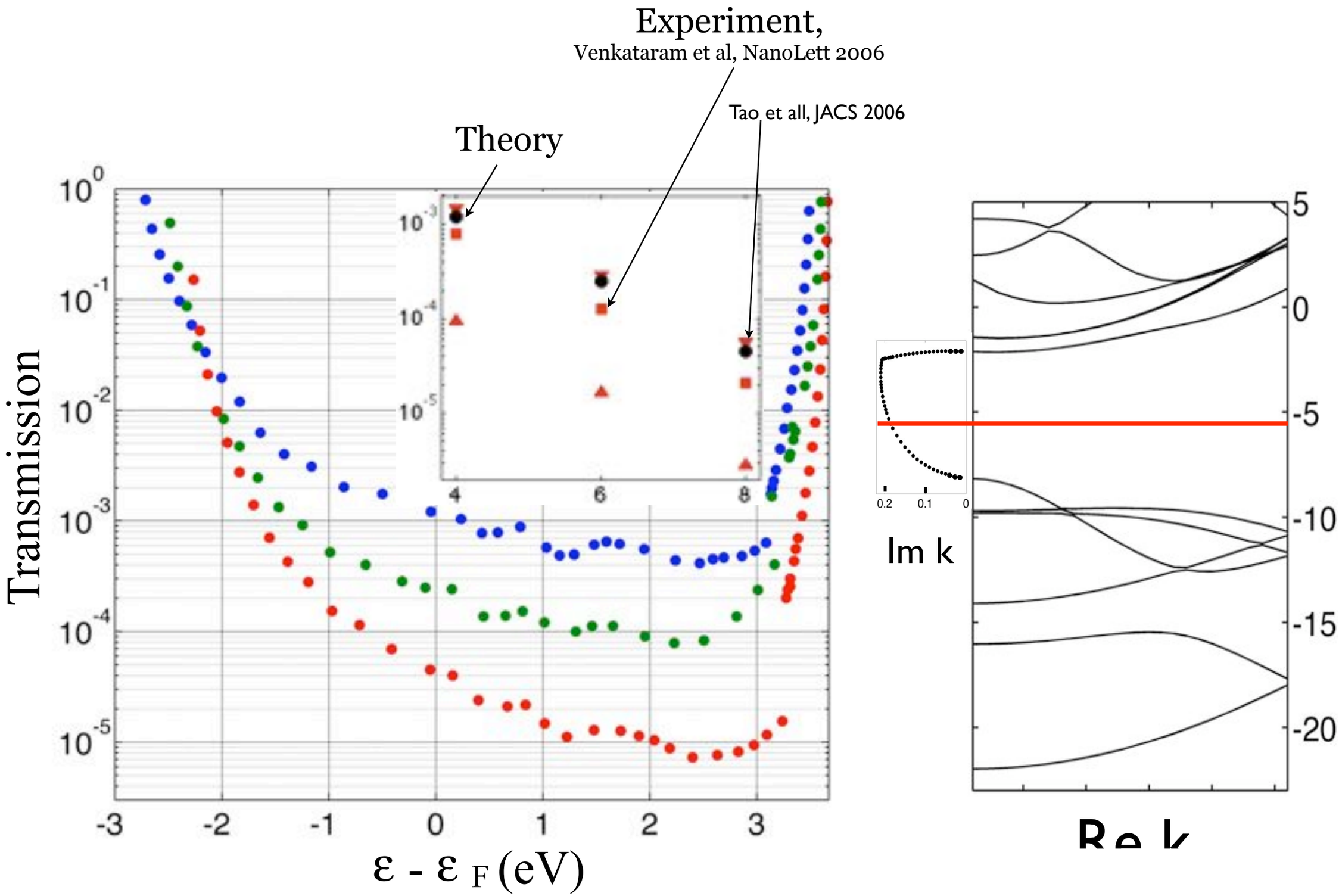
$$\Delta V_{\mathrm{R}}(\mathbf{r}) e^{i(k_i z + k_j z')} \Delta V_{\mathrm{R}}(\mathbf{r}') \times$$

$$u_{k_i}(\mathbf{r}) \rho_{\epsilon_F}(\mathbf{r}, \mathbf{r}') u_{k_i}(\mathbf{r}'),$$

Amine Linked Alkyl Chains (E. P. and R. Car, Nano Lett 2008)



Our Theoretical Predictions



Fermi level shifts lead to small changes in conductance:
band alignment not so important in alkyl chains

New Insight into the Tunneling Transport of the devices

$$g = \frac{1}{\pi} \frac{\Theta_{\mathrm{L}} \Theta_{\mathrm{R}}}{(\partial_k \epsilon_k)^2} e^{2ikL}$$

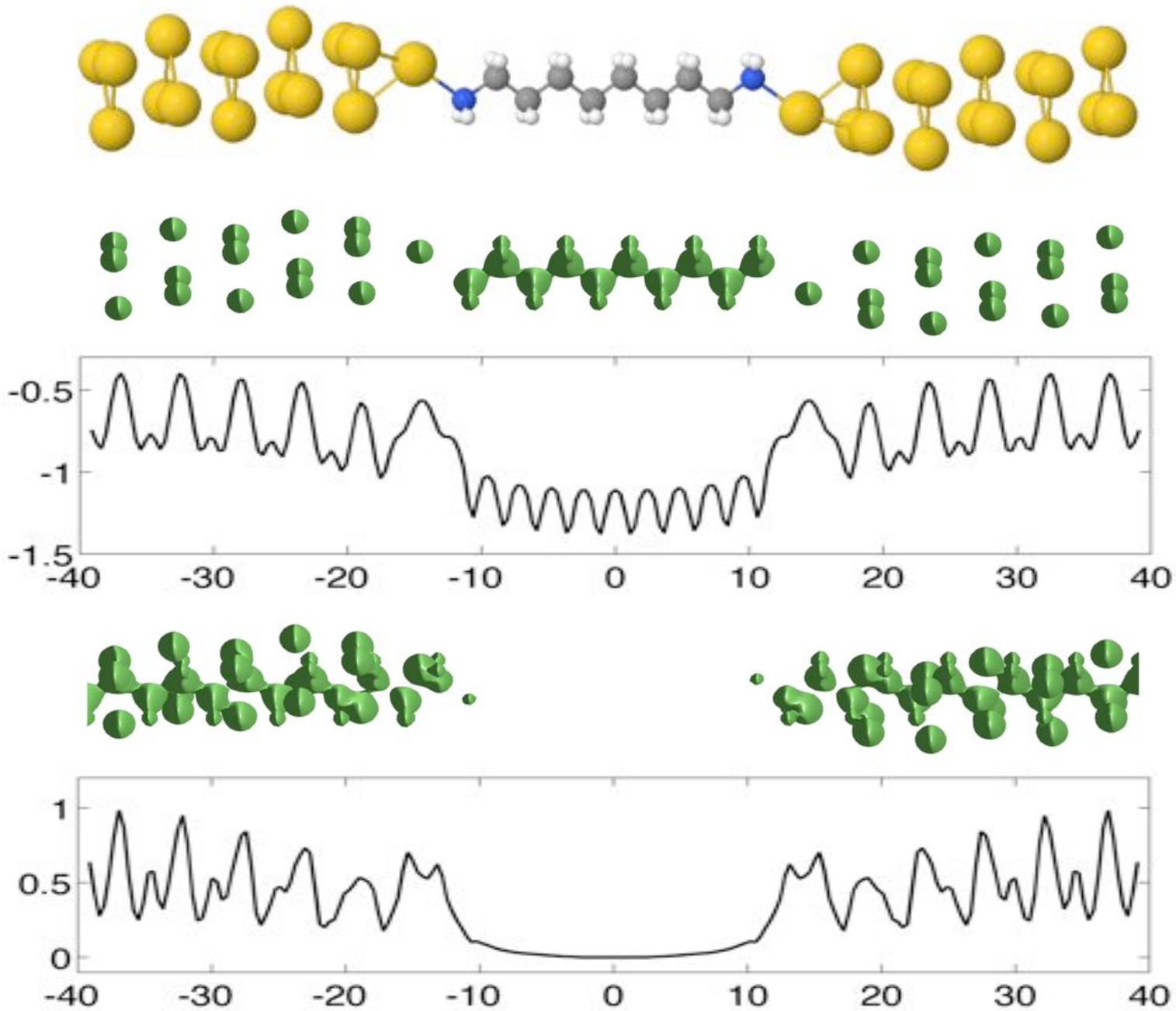
$$\Theta_L = 2\pi i \int d\mathbf{r} \int d\mathbf{r}' \times$$

$$\Delta V_L(\mathbf{r}) \psi_{-k_0}(\mathbf{r}) \rho_{\epsilon_F + e\Phi}(\mathbf{r}, \mathbf{r}'; T) \Delta V_L(\mathbf{r}') \psi_{-k_0}(\mathbf{r}'),$$

$$\Theta_R = 2\pi i \int d\mathbf{r} \int d\mathbf{r}' \times$$

$$\Delta V_R(\mathbf{r}) \psi_{k_0}(\mathbf{r}) \rho_{\epsilon_F + e\Phi}(\mathbf{r}, \mathbf{r}'; T) \Delta V_R(\mathbf{r}') \psi_{k_0}(\mathbf{r}')$$

The self-consistent potential and ΔV



V_{eff}

(isosurface

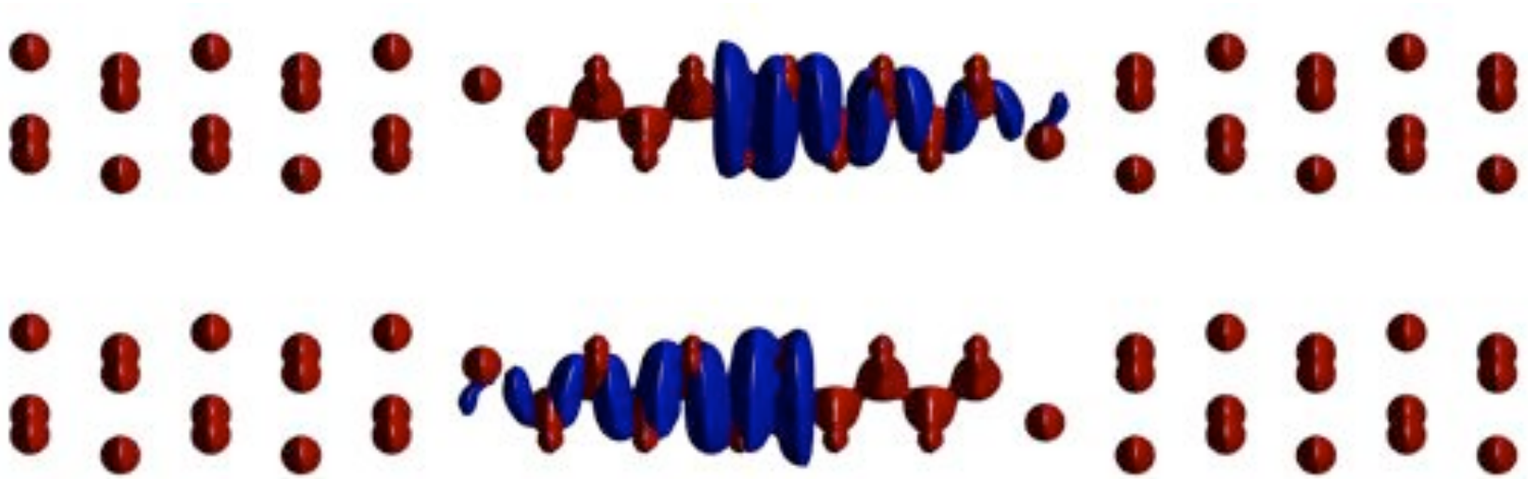
and xy average)

ΔV

(isosurface

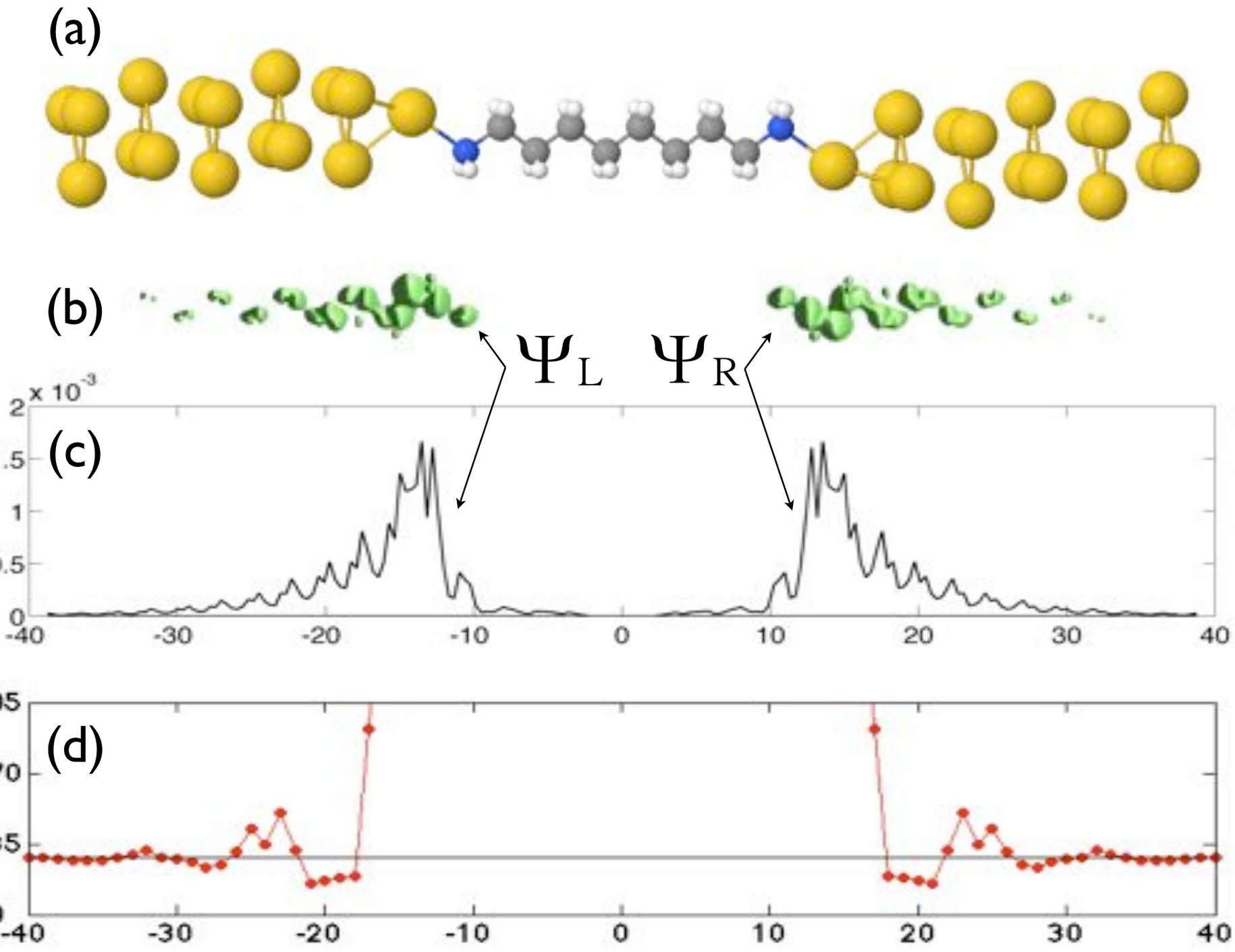
and xy average)

The evanescent Block functions

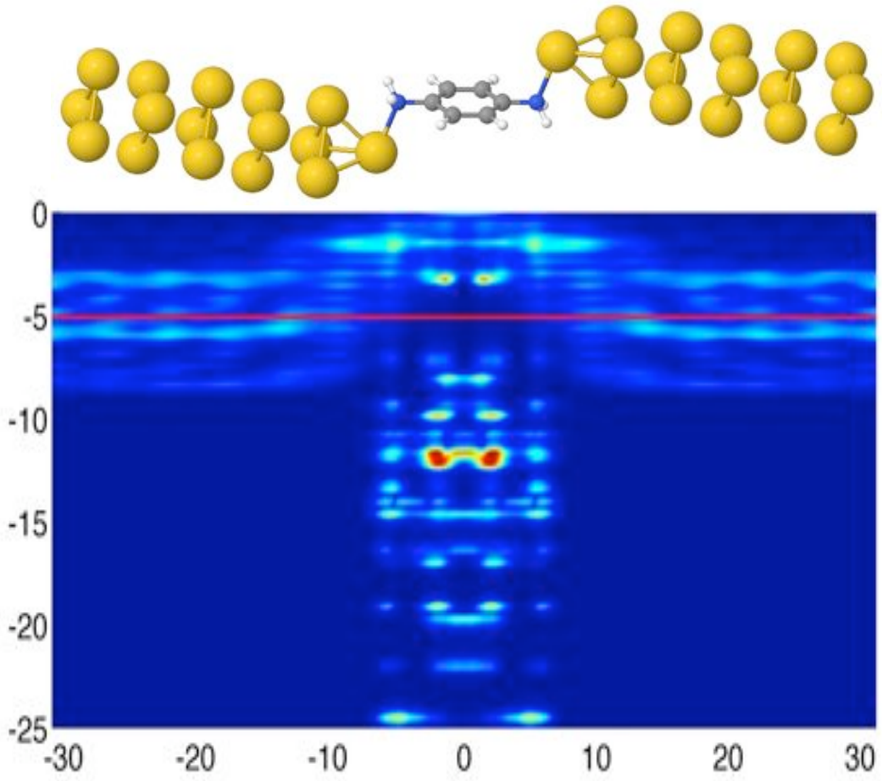


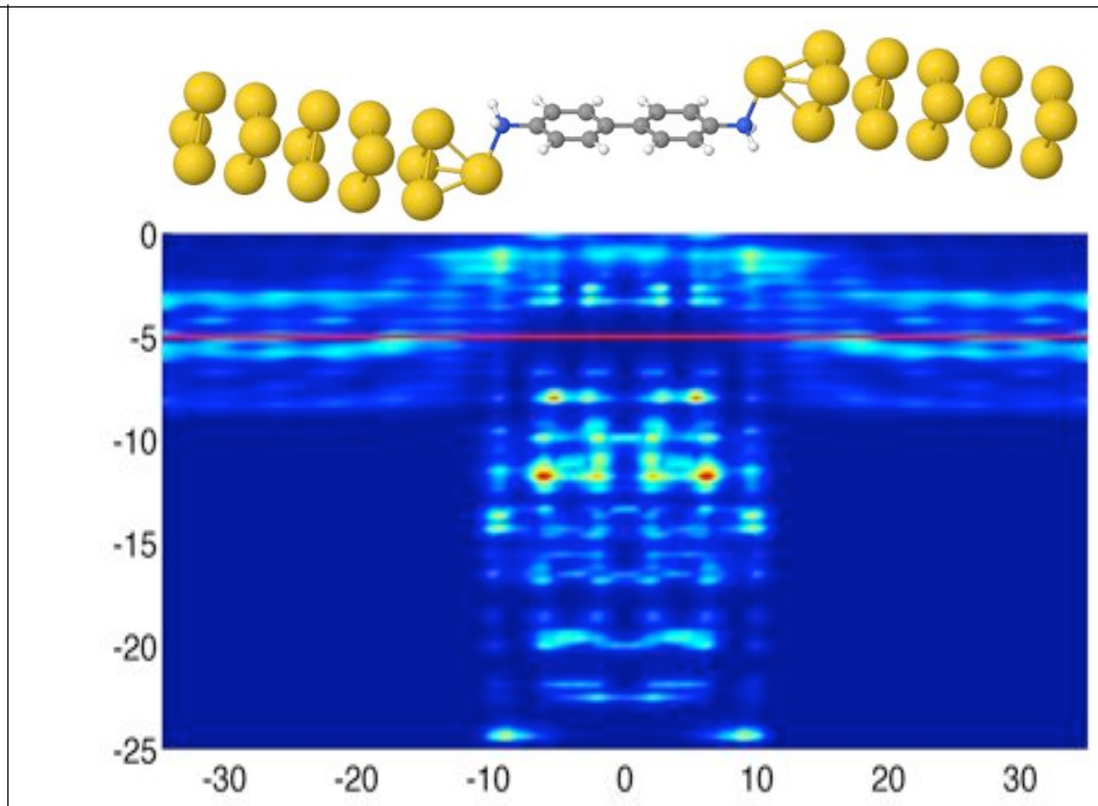
Why contact conductance is a contact conductance

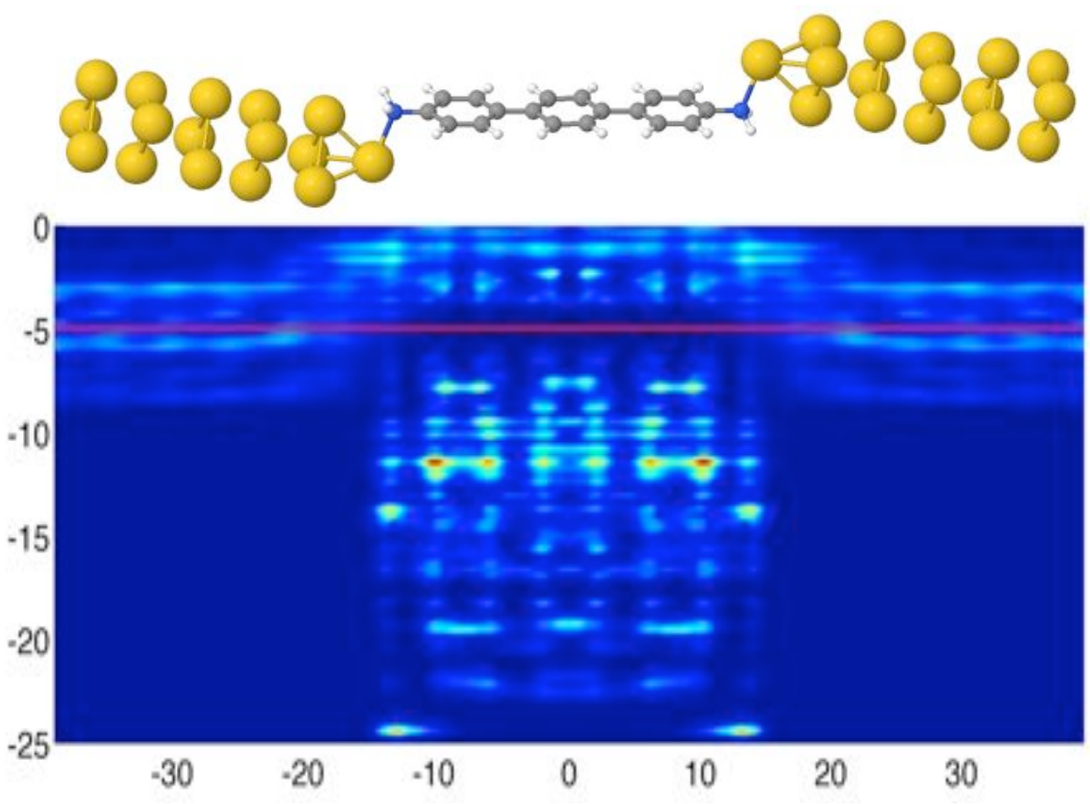
$$\Psi_{\mathrm{L/R}}(\mathbf{r}) = \psi_{\mp k}(\mathbf{r})\Delta V_{\mathrm{L/R}}(\mathbf{r})$$

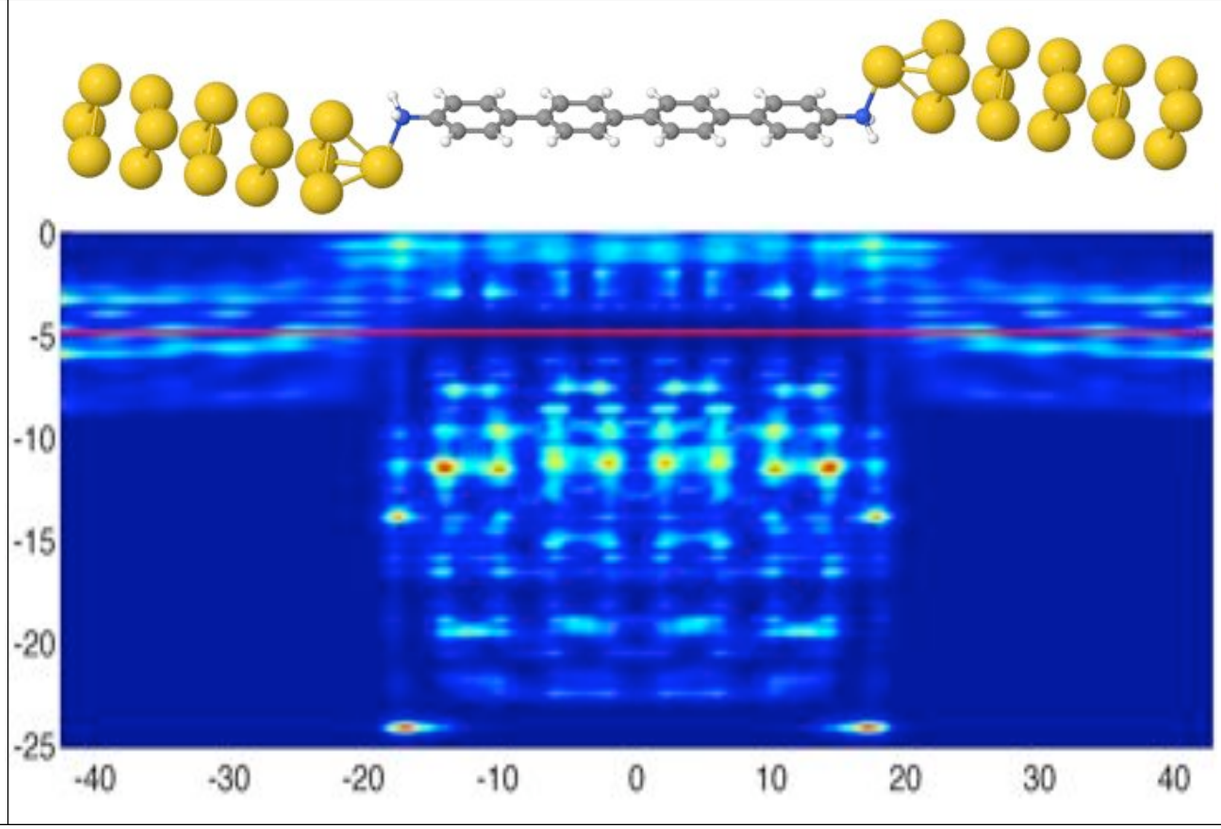


Benzene chains

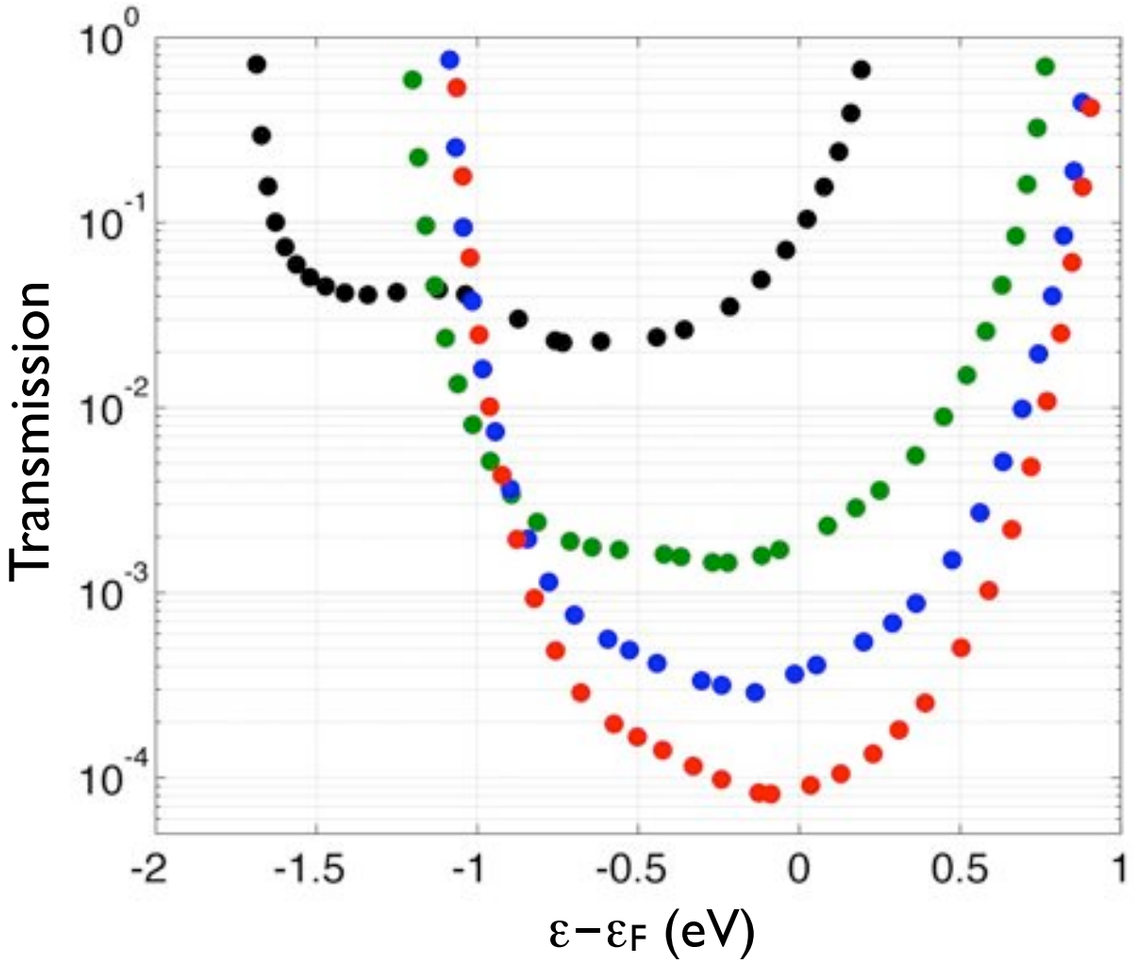


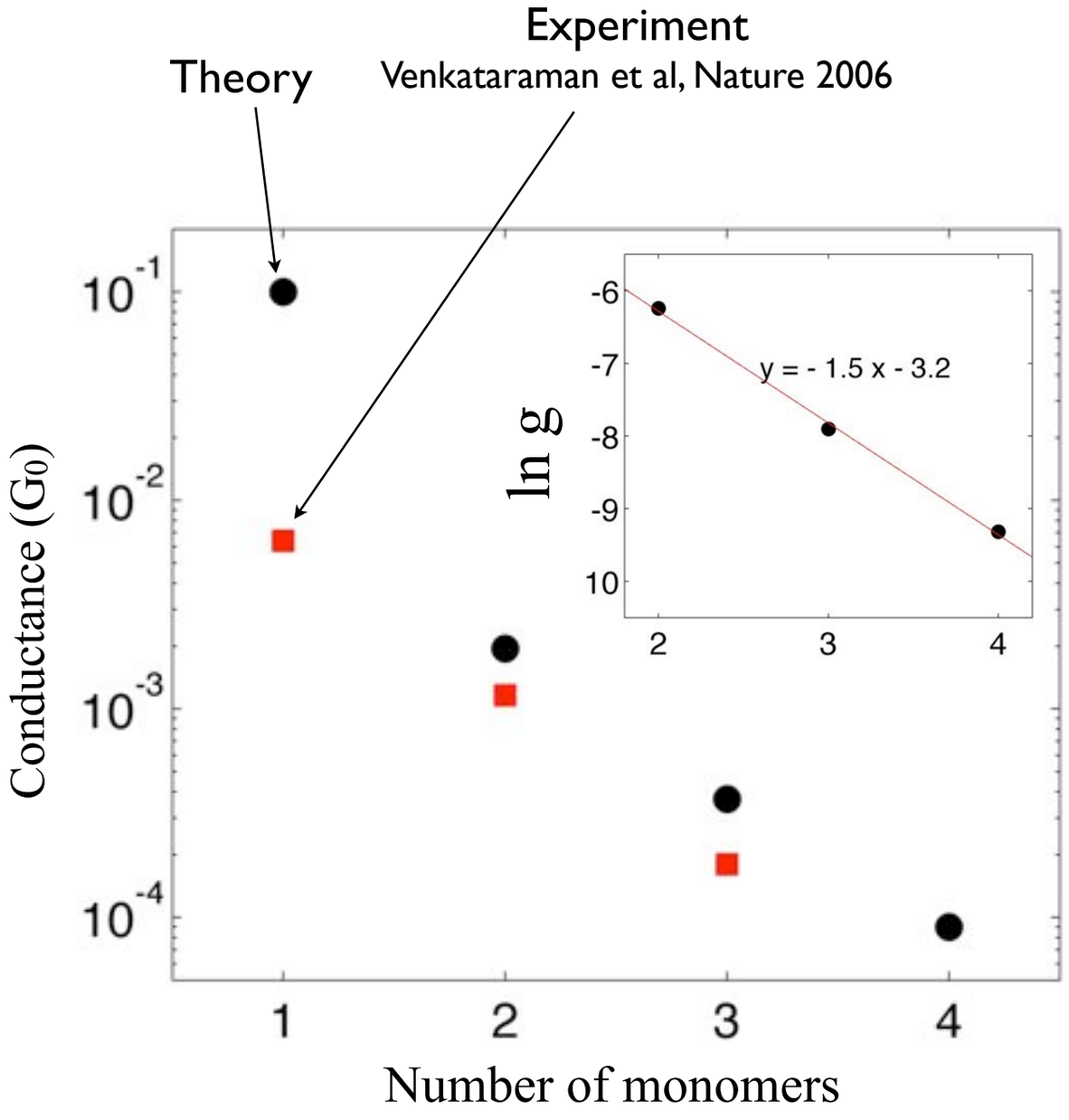






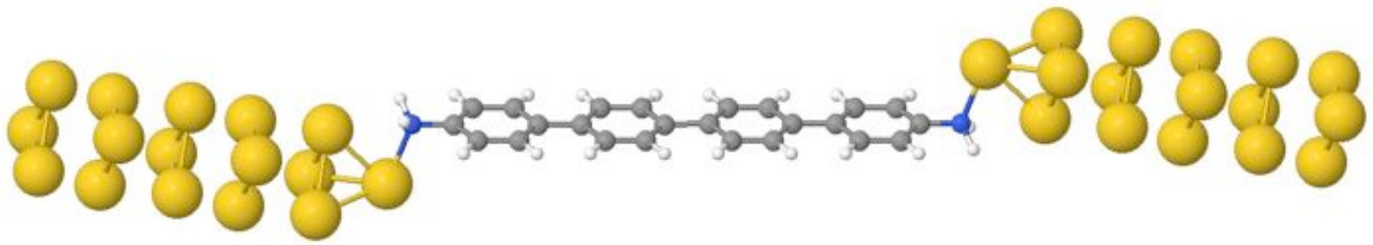
Theory vs Experiment





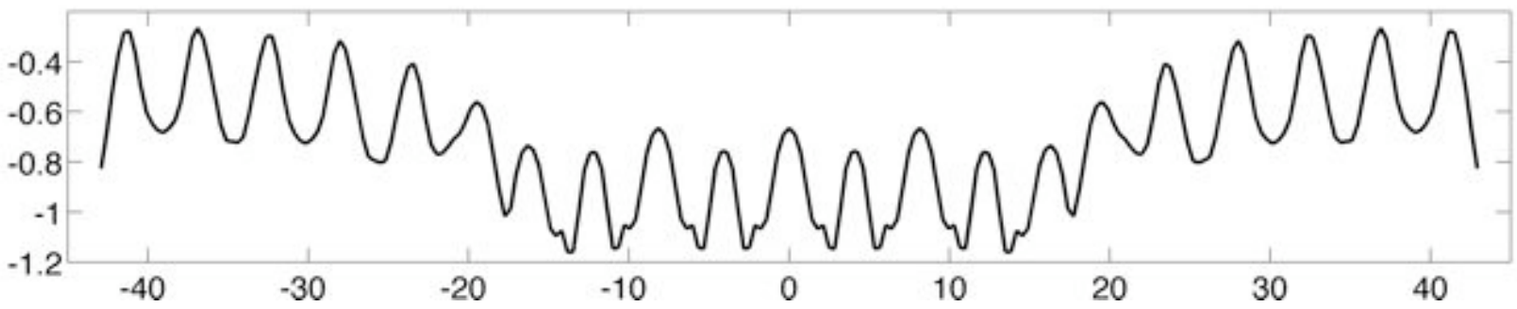
New Insight into the Tunneling Transport of the devices

(a)



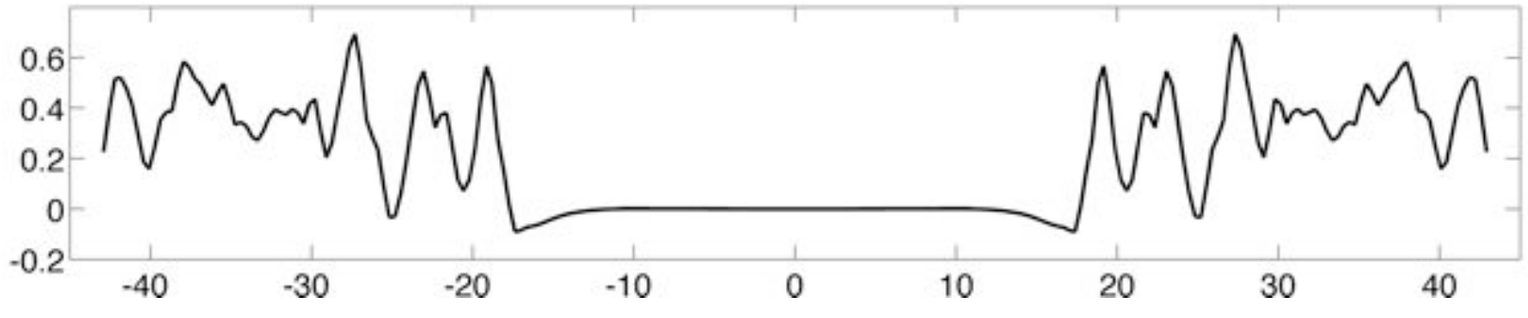
(b)

(c)

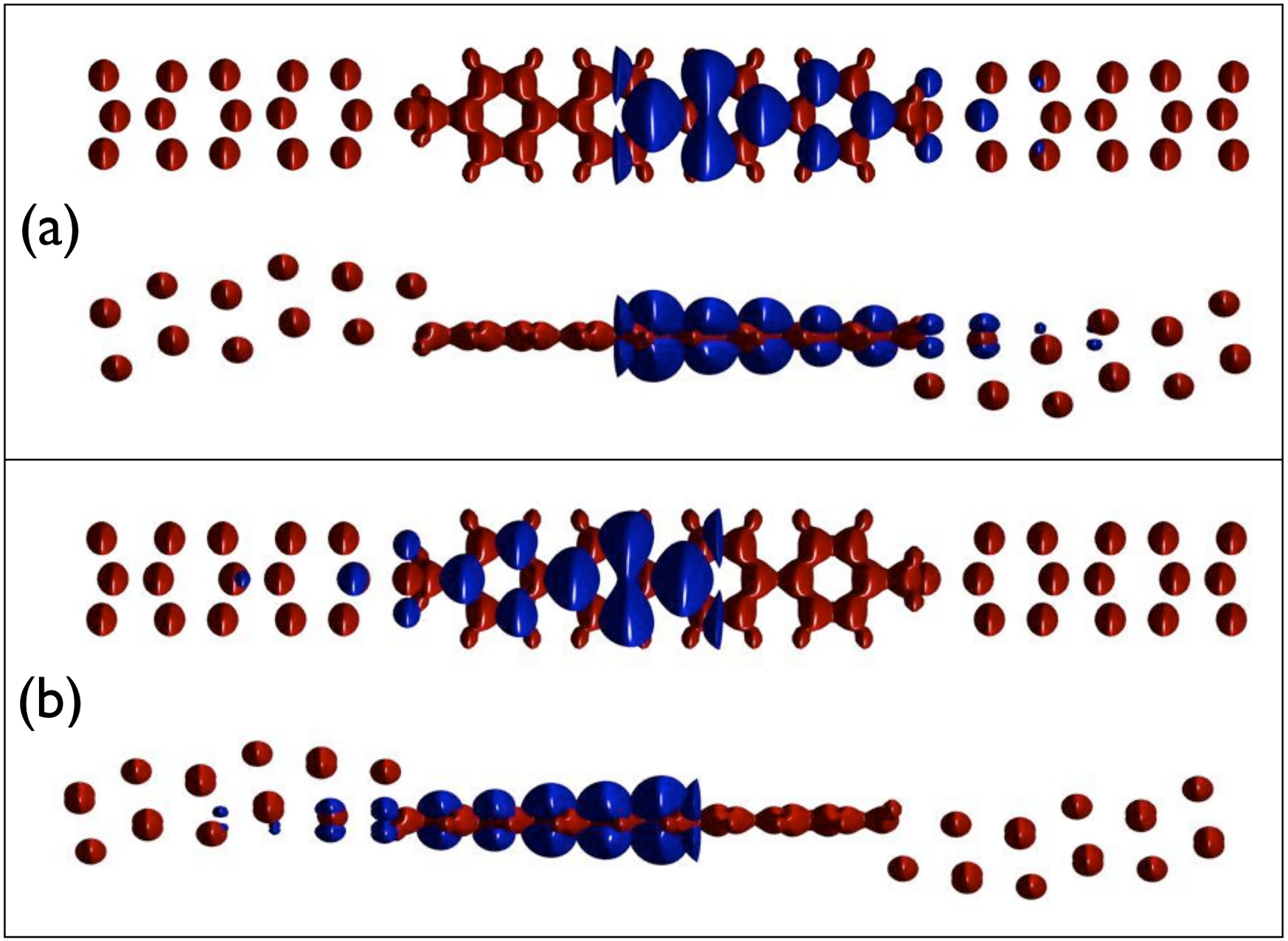


(d)

(e)

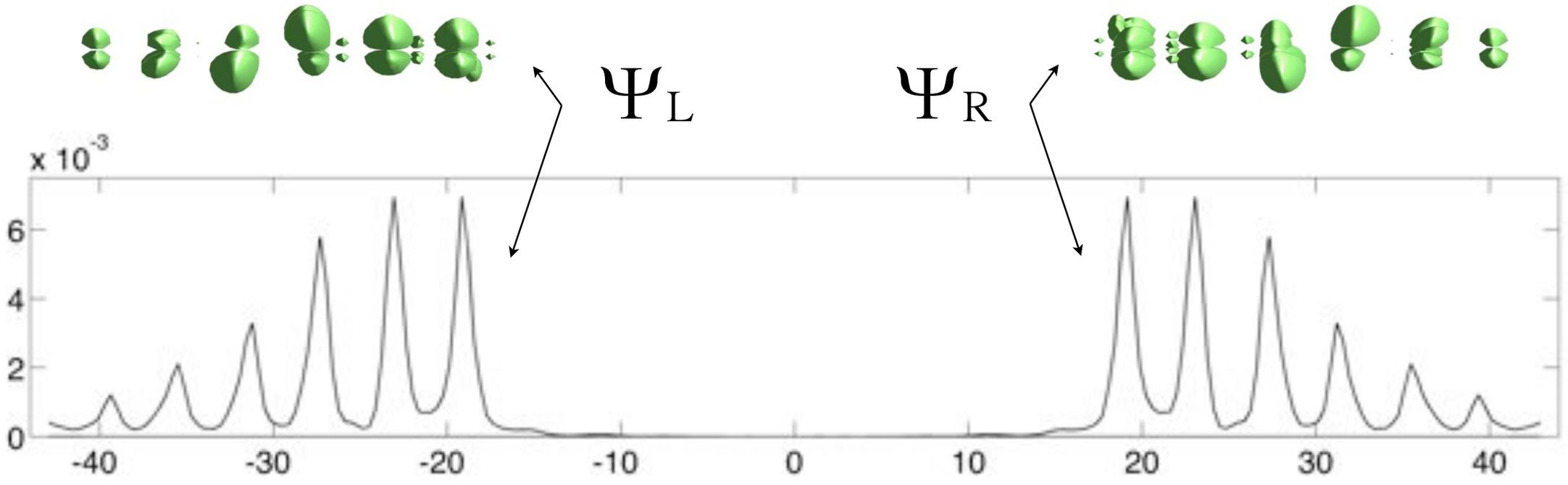


The evanescent Block functions



Again,Why contact conductance is a contact conductance

$$\Psi_{\mathrm{L/R}}(\mathbf{r}) = \psi_{\mp k}(\mathbf{r})\Delta V_{\mathrm{L/R}}(\mathbf{r})$$



Conclusions

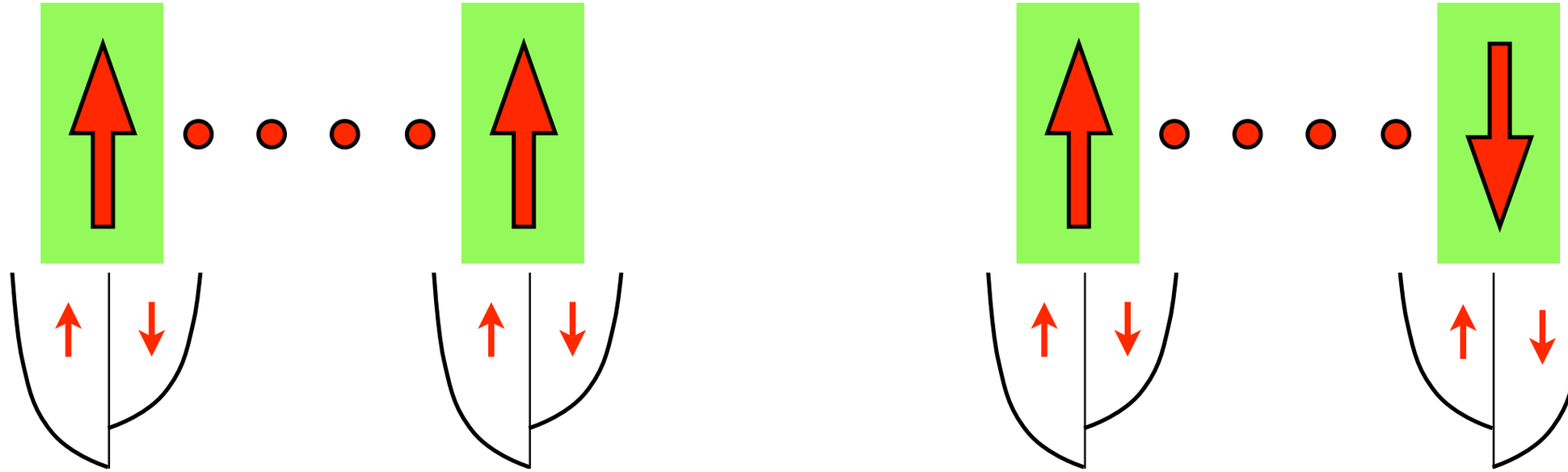
- a newly formulated tunneling transport theory give a rigorous way to compute beta and the contact conductance

- the analytic expression of the contact conductance give insight into the transport characteristics of the devices

- we hope that the formalism will become a useful tool for device design

Further directions

Generalization to the spin polarized case: { Tunneling Magneto-Resistance ; Spin Transport



$$g(L) = \frac{1}{\pi} \frac{\Theta_{\mathrm{maj}}^2 + \Theta_{\mathrm{min}}^2}{(\partial_k \epsilon_{k_0})^2} e^{-\beta L}$$

$$g(L) = \frac{1}{\pi} \frac{2\Theta_{\mathrm{maj}}\Theta_{\mathrm{min}}}{(\partial_k \epsilon_{k_0})^2} e^{-\beta L}$$

$$\frac{G_P - G_A}{G_P + G_A} = \left[\frac{\Theta_{\mathrm{maj}} - \Theta_{\mathrm{min}}}{\Theta_{\mathrm{maj}} + \Theta_{\mathrm{min}}} \right]^2$$