Tunneling conductance of molecular wires

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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

\[
\mathbf{j}(\mathbf{r}, \omega) = \int \hat{\sigma}^{KS}(\mathbf{r}, \mathbf{r}'; \omega) \mathbf{E}_{1}^{\text{eff}}(\mathbf{r}', \omega) d\mathbf{r}'
\]

\[
E_1^{\text{eff}}[j] = E_{\text{ext}} + \nabla v_{\text{HXC}}[j] + E_1^{\text{dyn}}[j]
\]
We are after the two-point conductance: \[ g = \frac{I}{\Delta \phi_\infty} \]

\[ \Delta \phi_\infty = \int_\gamma (E^{\text{ext}} + E^H_1) dl \]

\[ I = \int_\Sigma j \, dS \quad \text{with } j \text{ the self-consistent solution of } \]

\[ j(r, \omega) = \int \hat{\sigma}^{\text{KS}}(r, r'; \omega) E^{\text{eff}}_1(r', \omega) dr' \quad (\omega \to 0) \]
The exact expression of \( g \) within the Linear Response Time Dependent Current-Density Functional Theory

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

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

Implications:

- the adiabatic \( \nu_{\text{HXC}} \) 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

\[ g \equiv \frac{I}{\Delta \phi_\infty} = \int \, dx_\perp \int \, dx'_\perp \left[ (1 - \hat{\sigma}^{KS} \ast \hat{F})^{-1} \ast \hat{\sigma}^{KS} \right]_{zz}(x_\perp, z; x'_\perp, z') \]

Whenever \( \sigma^{KS} \) is small, this part can be neglected and

\[ g \equiv \int \, dr_\perp \int \, dr'_\perp \sigma^{KS}_{zz}(r_\perp, z, r'_\perp, z') \]

\[ \sigma^{KS}_{\alpha\beta}(r, r') = \frac{1}{4\pi} G^{KS}_{\epsilon_+}(r, r') \left( \partial_\alpha \partial'_\beta \right) G^{KS}_{\epsilon_-}(r', r) \]

The problem remains extremely challenging for long molecular chains:

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

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

\[ \beta = 2 \text{Im} \ k_F \]

- 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:

\[ V_{\text{eff}} \]

\[ V_0 \]

\[ \Delta V_L + \Delta V_R \]

\[ H_{\text{KS}} = -\nabla^2 + V_0 + \Delta V_L + \Delta V_R \]

(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

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

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!!

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

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 $\epsilon_{\lambda}, P_{\lambda}$ on a Riemann surface describe the whole band structure ($\lambda = e^{ikb}$).

If we evaluate $\epsilon_{\lambda}$ along the circle we obtain the usual energy bands.

The Riemann surface of the bands was discovered by Walter Kohn in 1959.
\[ G_0^\epsilon(\mathbf{r}, \mathbf{r}') = \sum_n \int_{|\lambda|=1} \frac{\psi_{n,1/\lambda}(\mathbf{r})\psi_{n,\lambda}(\mathbf{r}')}{\epsilon - \epsilon_{n,\lambda}} \frac{d\lambda}{2\pi i \lambda} \]  
(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 \( \Gamma \) can be deformed to a point:

\[ G_0^\epsilon(\mathbf{r}, \mathbf{r}') = \frac{\psi_{1/\lambda}(\mathbf{r}_<)\psi_{\lambda}(\mathbf{r}'_>)}{\lambda \partial_\lambda \epsilon(\lambda)} \]

\( \lambda = \) 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 \( \Gamma \) can be deformed to a point:

\[ G_0^\epsilon (\mathbf{r}, \mathbf{r}') = \sum_j \frac{\psi_{1/\lambda_j} (\mathbf{r}_>) \psi_{\lambda_j} (\mathbf{r}_<')}{\lambda_j \partial_\lambda \epsilon(\lambda_j)} \]

\( \lambda_j \) are all \( \lambda \) on the Riemann surface so that: \( \epsilon = \epsilon(\lambda_j) \)
Tunneling Conductance

\[
g_0(L) = \frac{1}{\pi} \sum_{i,j} \Theta^i_j \Theta^i_j \frac{\Theta^i_L \Theta^i_R}{\partial_k \epsilon_{k_i} \partial_k \epsilon_{k_j}} e^{i(k_i + k_j) L}
\]

\[
\epsilon(k_i) = \epsilon_F
\]

E. Prodan & R. Car, PRB 2007
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

Experiment, Venkataram et al, NanoLett 2006

Theory

Tao et all, JACS 2006
New Insight into the Tunneling Transport of the devices

\[ g = \frac{1}{\pi} \frac{\Theta_L \Theta_R}{(\partial_k \epsilon_k)^2} e^{2ikL} \]

\[ \Theta_L = 2\pi i \int dr \int dr' \times \]
\[ \Delta V_L(r) \psi_{-k_0}(r) \rho_{\epsilon_F + \epsilon}(r, r'; T) \Delta V_L(r') \psi_{-k_0}(r'), \]

\[ \Theta_R = 2\pi i \int dr \int dr' \times \]
\[ \Delta V_R(r) \psi_{k_0}(r) \rho_{\epsilon_F + \epsilon}(r, r'; T) \Delta V_R(r') \psi_{k_0}(r') \]
The self-consistent potential and $\Delta V$

\[ V_{\text{eff}} \]
(isosurface and xy average)

\[ \Delta V \]
(isosurface and xy average)
The evanescent Block functions
Why contact conductance is a contact conductance

\[
\Psi_{L/R}(\mathbf{r}) = \psi_{\pm k}(\mathbf{r}) \Delta V_{L/R}(\mathbf{r})
\]
Benzene chains
Theory vs Experiment

Transmission - F (eV)
Number of monomers

ln g

Theory vs Experiment

Venkataraman et al, Nature 2006

\[ y = -1.5x - 3.2 \]
New Insight into the Tunneling Transport of the devices

(a) [Diagram of molecular structure]

(b) [Diagram of molecular structure]

(c) [Graph showing oscillations]

(d) [Diagram of molecular structure]

(e) [Graph showing oscillations]
The evanescent Block functions

(a)

(b)
Again, why contact conductance is a contact conductance

\[ \Psi_{L/R}(r) = \psi_{\pm k}(r) \Delta V_{L/R}(r) \]
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:

\[ T\text{unneling Magneto-Resistance} \]
\[ \text{Spin Transport} \]

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

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

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