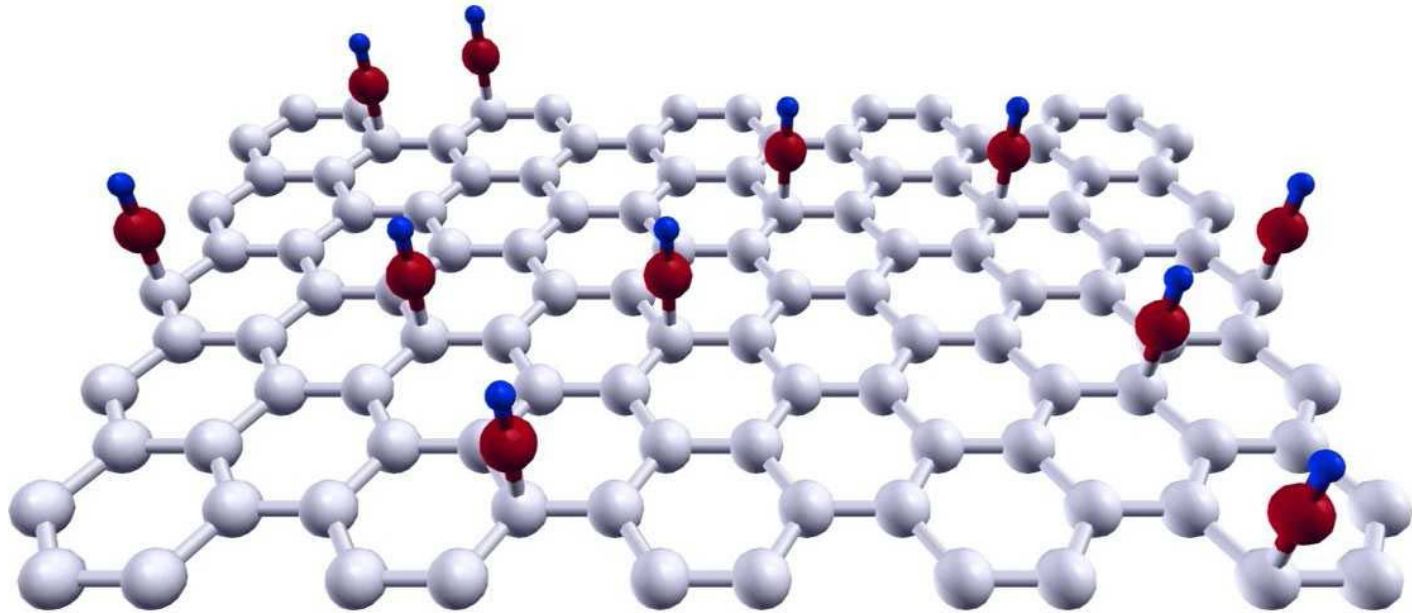


Adsorbate-limited conductivity of graphene



Henning Schomerus (Lancaster)

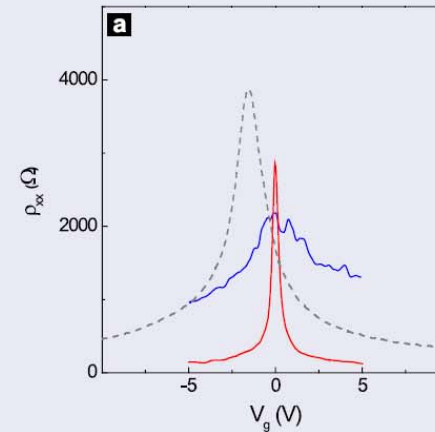
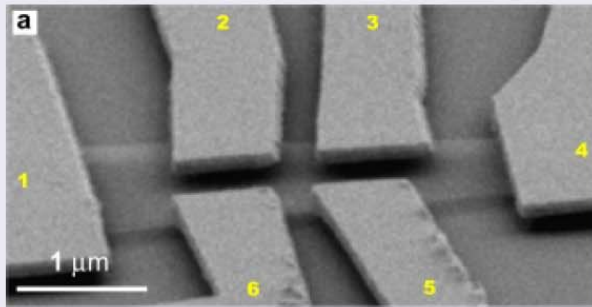
Benasque, 4 August 2009

Outline

- **Chemical disorder –
experimental evidence**
- **Modelling**
- **Transport:**
 - **kinetic theory**
 - **quantum corrections**
 - **localization**

Effects of pollution: experiments

K. I. Bolotin *et al.*, arXiv:0802.2389 (2008)

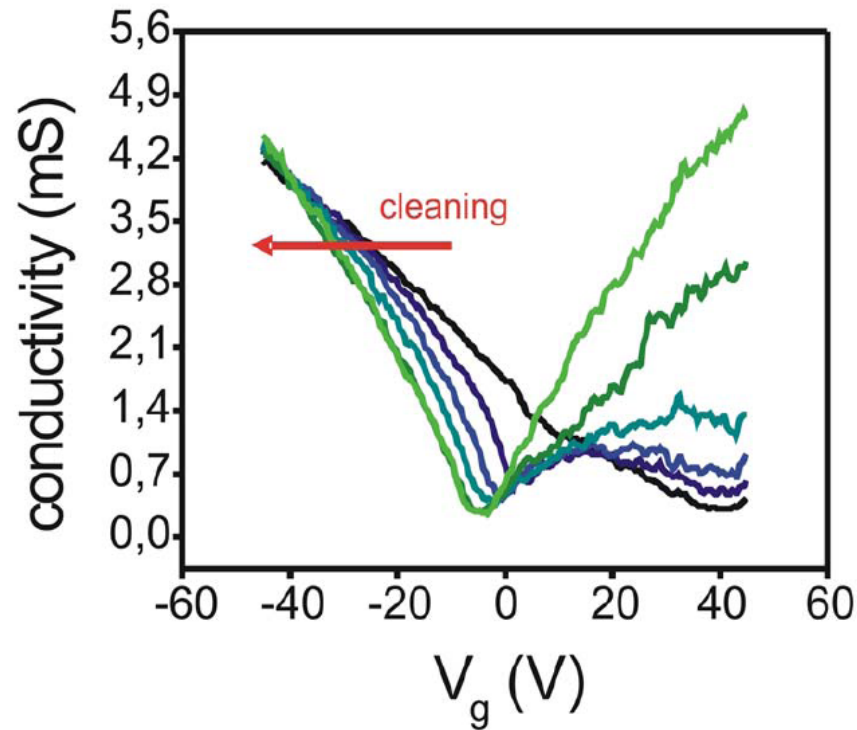


[Solid State Communications 146, 351-355 (2008)]

- Shifted effective Dirac point
- Conductance asymmetric

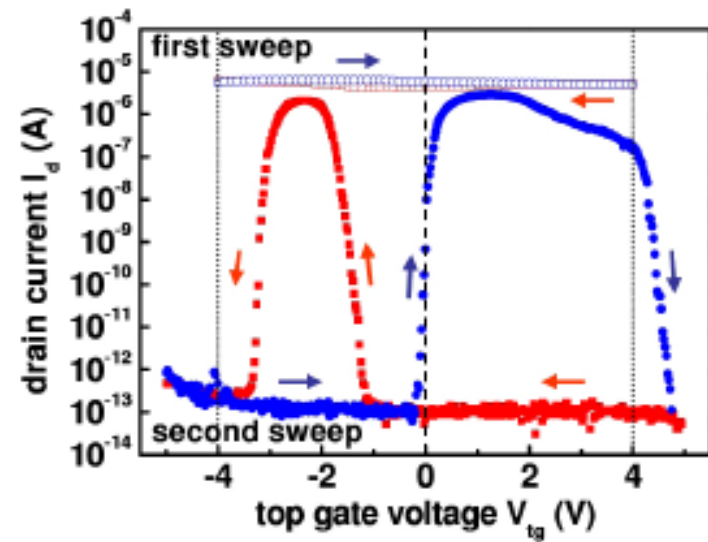
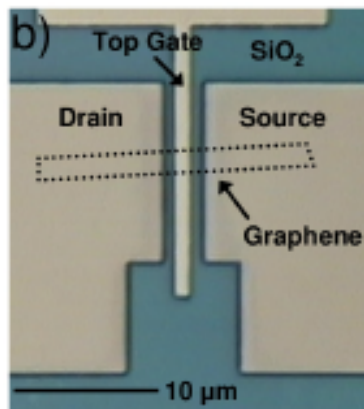
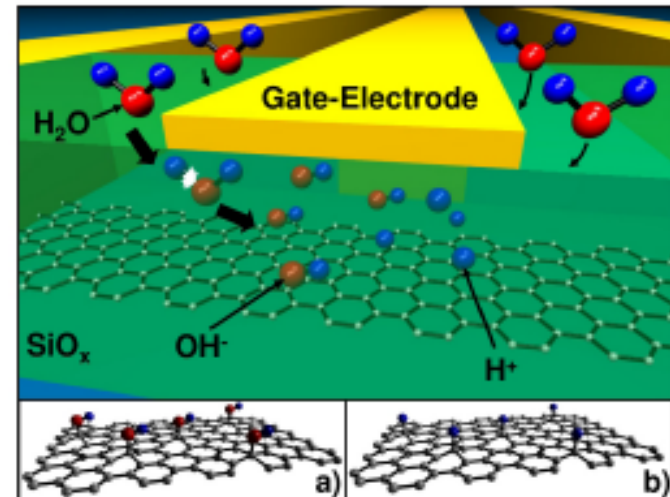
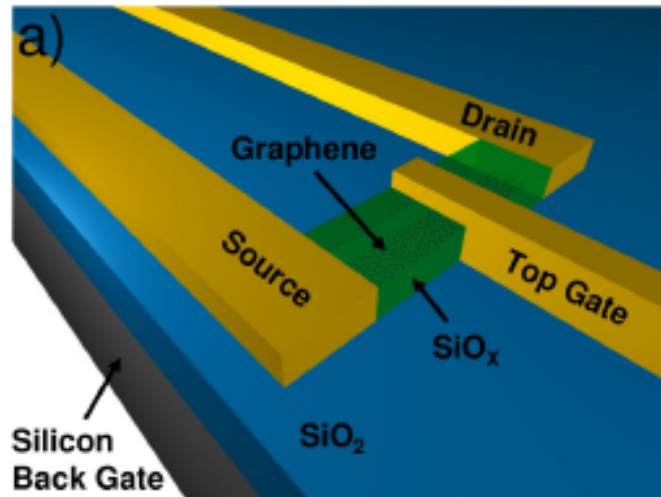
Effects of pollution: experiments

Systematic current annealing

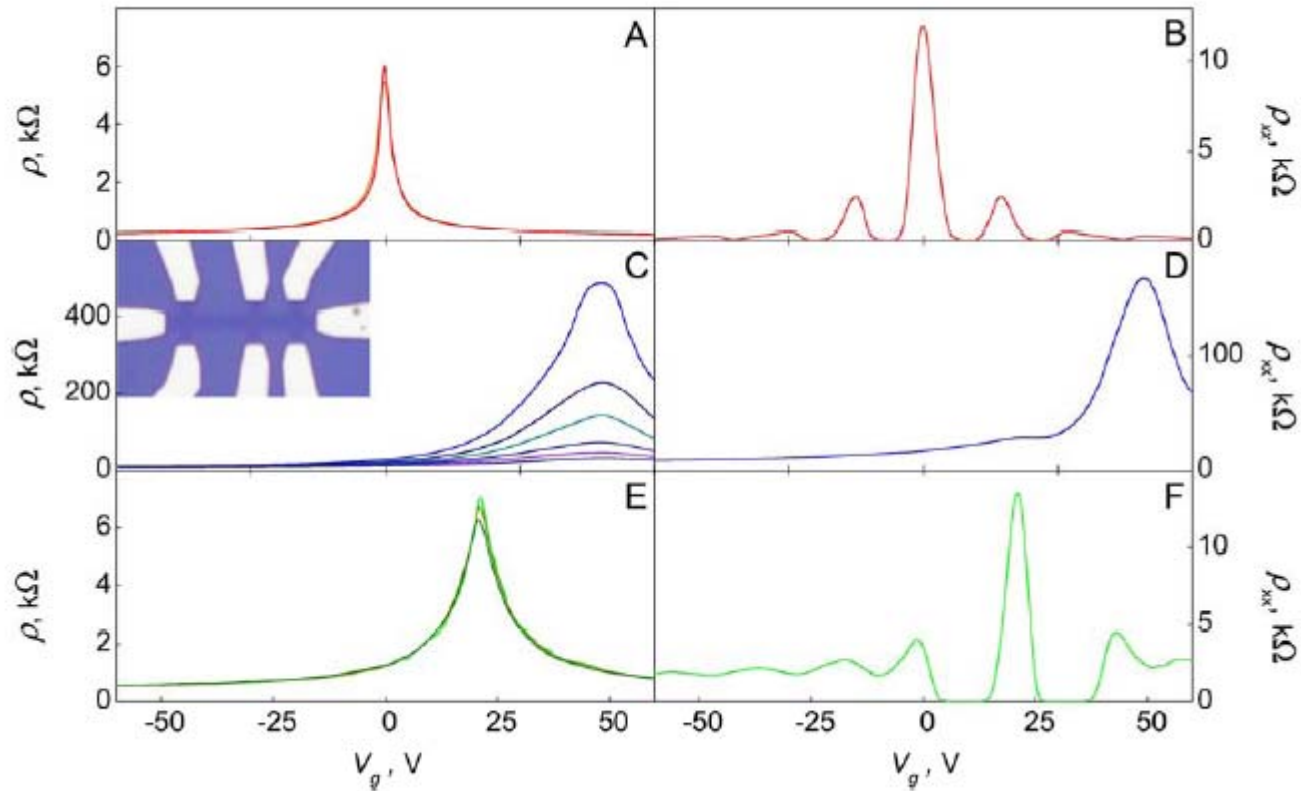


(data courtesy of Amelia Barreiro, Barcelona)

Selective adsorption (T. J. Echtermeyer *et al.* 2007)



Hydrogenated graphene



D. C. Elias et al, Science 323, 610 (2009)

General considerations

Disorder in conventional conductors:

Time reversal symmetry preserved / broken?

Graphene:

Valley index preserved / broken?

Chirality preserved / broken?

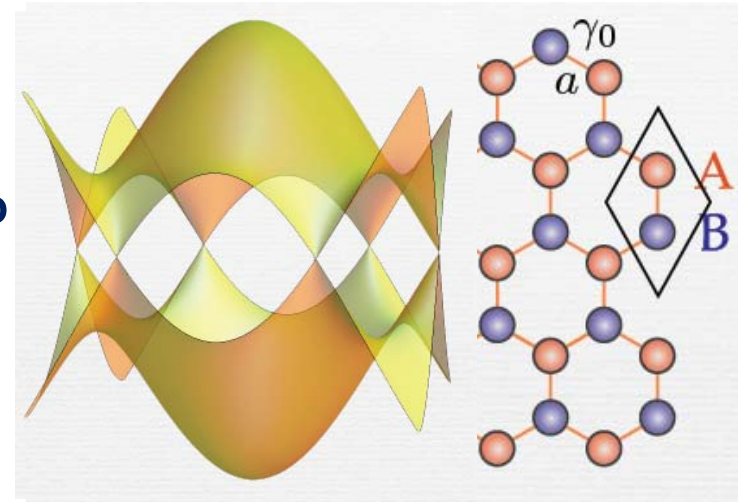
In particular:

Long ranged vs short-ranged

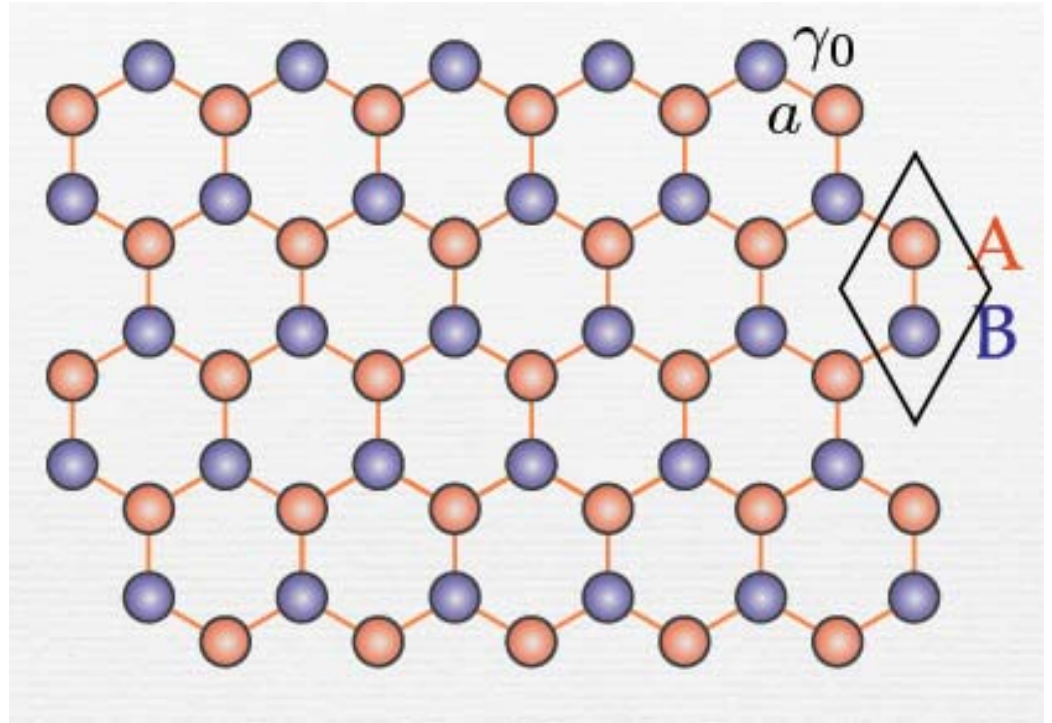
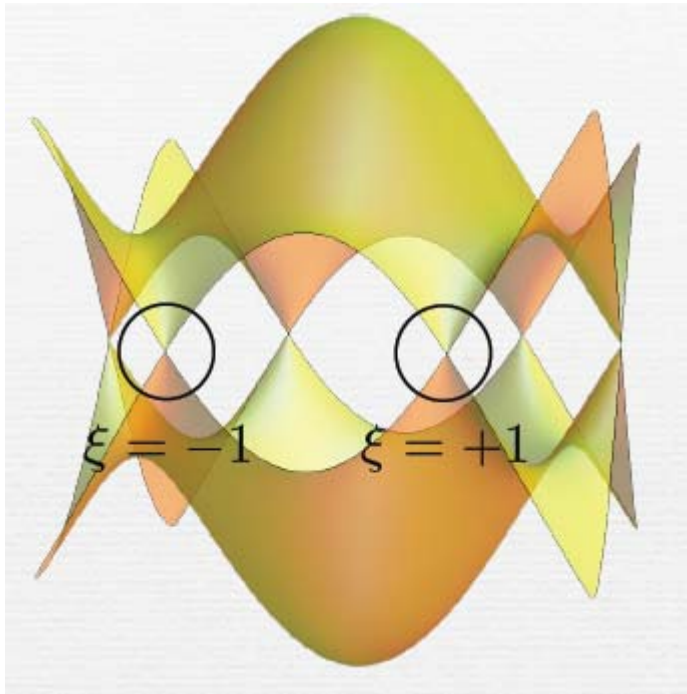
Coulomb vs defect scattering

Ionic vs chemisorbed adsorbates

Aim: Adsorbate-specific theory for chemisorption



Tight-binding description

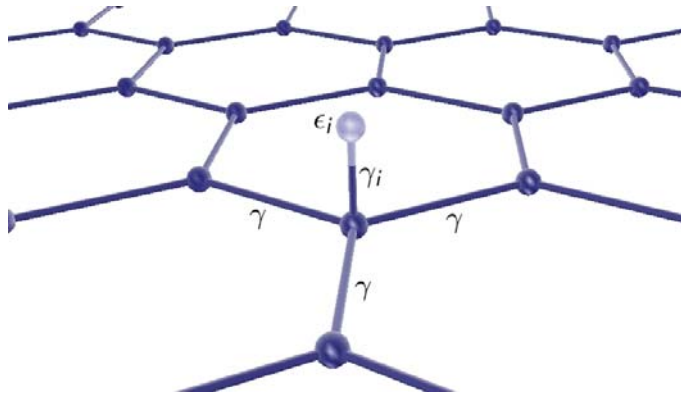


$$H = v_0 (\xi k_x \sigma_x + k_y \sigma_y), \quad v_0 = \frac{3}{2} \gamma_0 a$$

$$H = -\gamma_0 \sum_{\langle nm \rangle} c_m^\dagger c_n$$

Wallace 1946

Tight-binding description



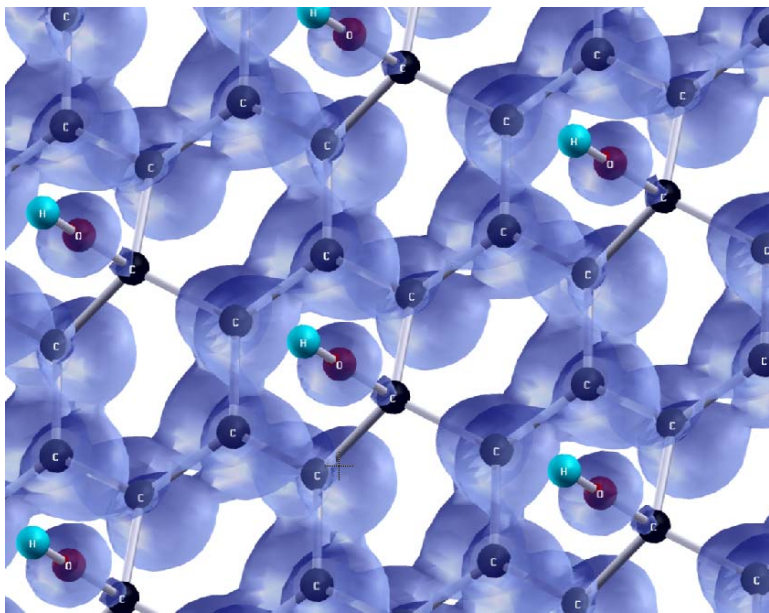
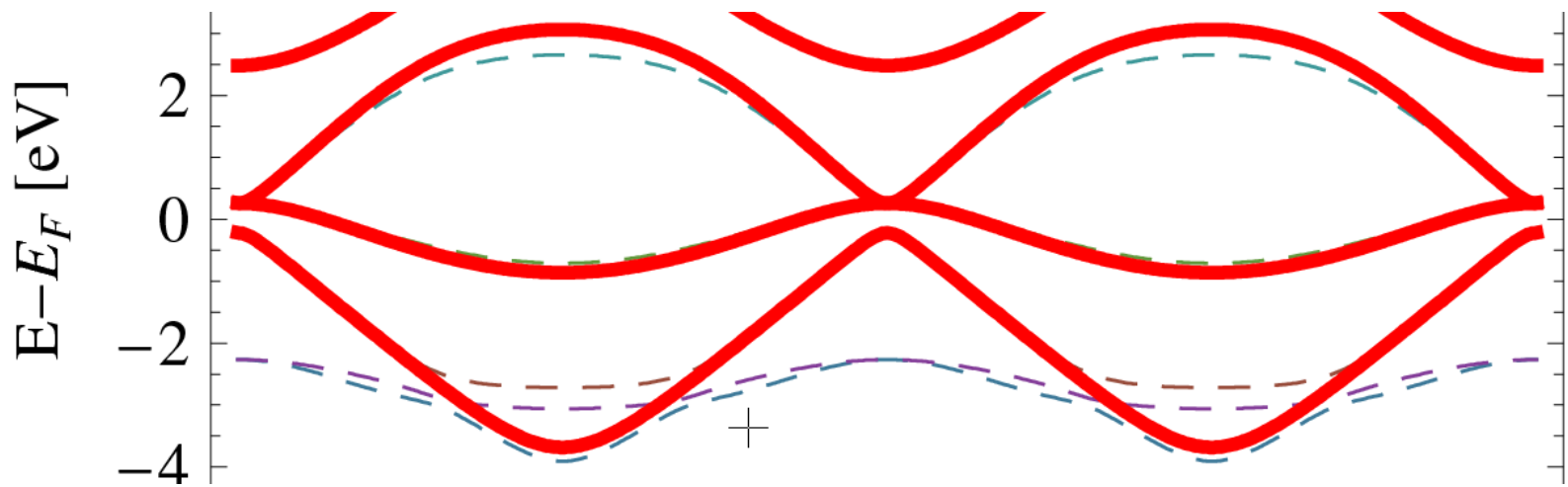
$$H_0 = -\gamma_0 \sum_{\langle nm \rangle} c_m^+ c_n$$

$$H_i = \varepsilon_i d_i^+ d_i - \gamma_i [d_i^+ c_h + c_h^+ d_i]$$

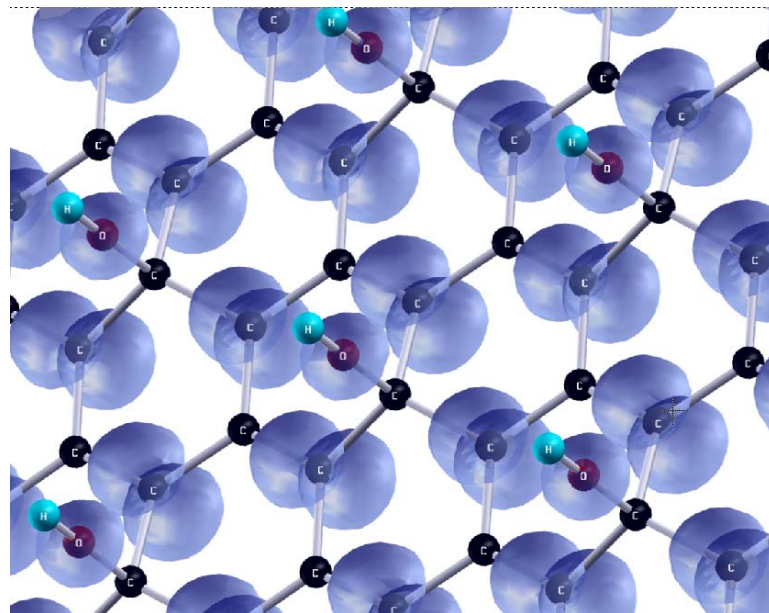
Parameters can be fit from DFT (here: Siesta)

$$\text{H}^+: \quad \varepsilon_i = 0.66 \gamma_0, \quad \gamma_i = 2.2 \gamma_0$$

$$\text{OH}^-: \quad \varepsilon_i = -2.90 \gamma_0, \quad \gamma_i = 2.3 \gamma_0$$



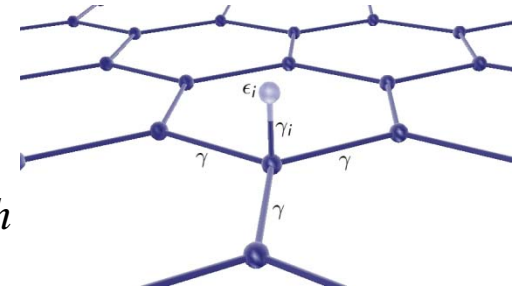
outside the gap



in the gap

Scattering rate off a single adsorbate

Self energy (exact):
$$H_i = \frac{\gamma_i^2}{E - \varepsilon_i} c_h^+ c_h$$



Green's function (exact):
$$G = G_0 + G_0 \underbrace{\frac{\gamma_i^2}{E - \varepsilon_i - g_0}}_{t_i} P_i G_0$$

$$g_0 = P_i G_0 P_i^T = R(E) - i\pi v_0(E)$$

Scattering rate (Fermi golden rule)
$$\tau_k^{-1} = \frac{2\pi}{\hbar} \frac{1}{N} v_0 |t_i|^2$$

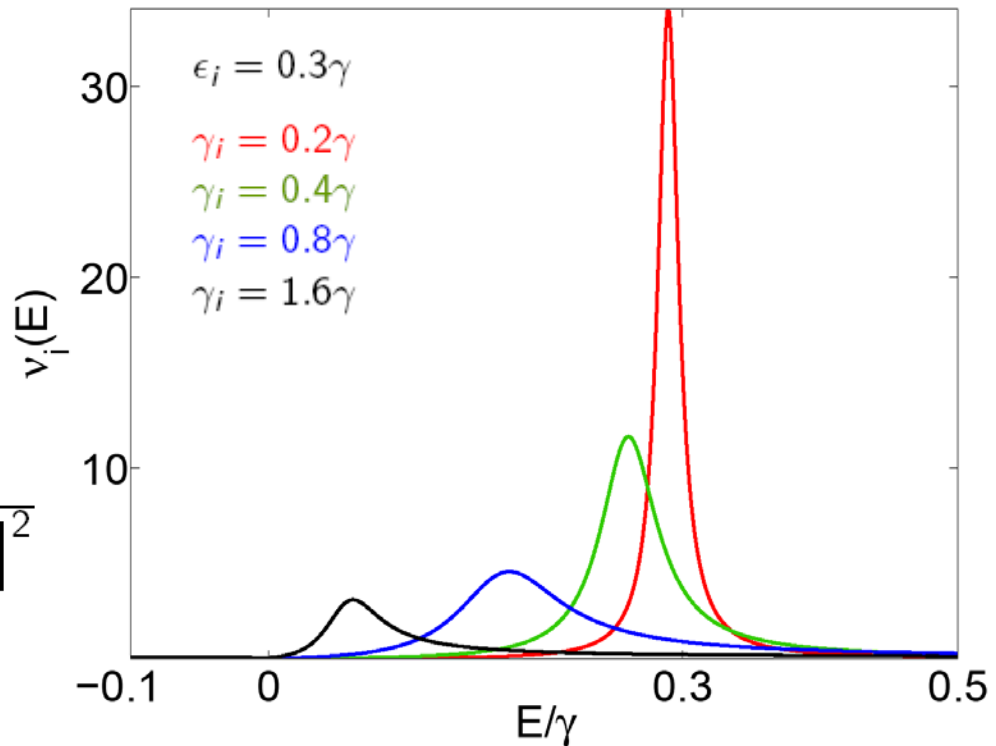
Using dos on adsorbate
$$\tau_k^{-1} = \frac{2\pi}{\hbar} \frac{1}{N} v_i \gamma_i^2$$

Renormalisation of the resonance

$$\tau_k^{-1} = \frac{2\pi}{\hbar} \frac{1}{N} v_i \gamma_i^2$$

dos on adsorbate

$$\frac{\gamma_i^2 \nu_0(E)}{[E - \epsilon_i - \gamma_i^2 \mathcal{R}(E)]^2 + [\pi \gamma_i^2 \nu_0(E)]^2}$$



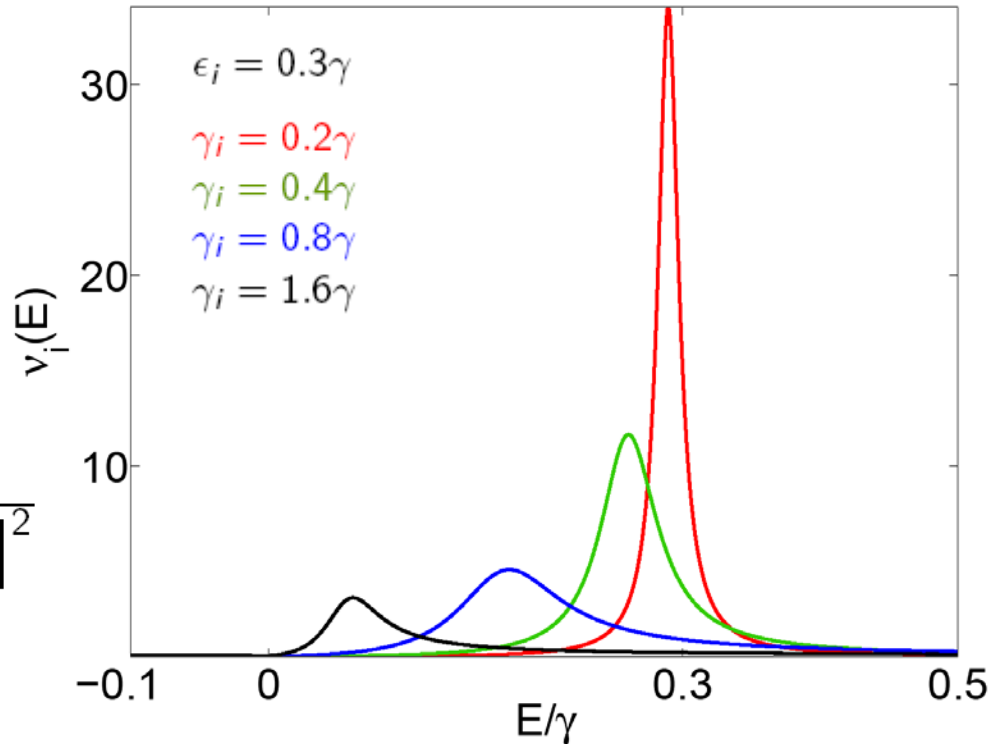
Strong coupling: resonance \rightarrow Dirac point

Renormalisation of the resonance

$$\tau_k^{-1} = \frac{2\pi}{\hbar} \frac{1}{N} v_i \gamma_i^2$$

dos on adsorbate

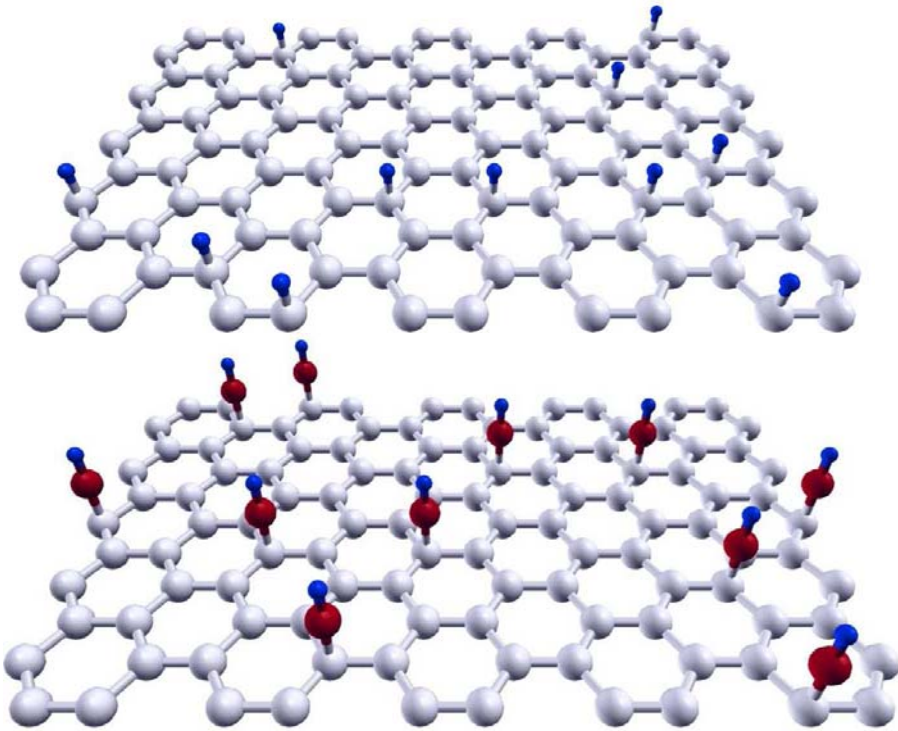
$$\frac{\gamma_i^2 \nu_0(E)}{[E - \epsilon_i - \gamma_i^2 \mathcal{R}(E)]^2 + [\pi \gamma_i^2 \nu_0(E)]^2}$$



Origin: level repulsion

(2nd order perturbation theory : $\frac{\gamma_i^2}{E_i - E}$)

Randomly placed adsorbates



kinetic theory

$$\tau^{-1} = \frac{2\pi}{\hbar} n_i v_0 |t_i|^2$$

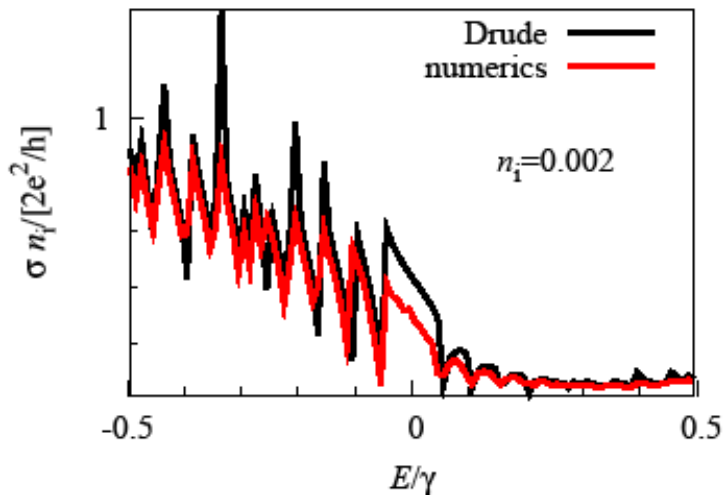
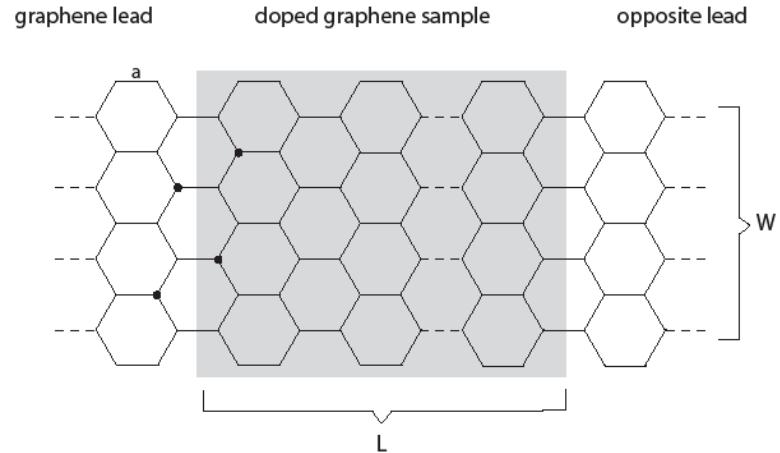
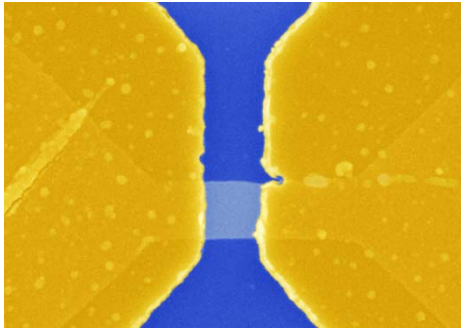
$$\sigma = e^2 D v_0$$

$$D = \frac{\langle v_k \rangle_{E_F}}{2 \langle v_k^{-1} \rangle_{E_F}} \tau$$

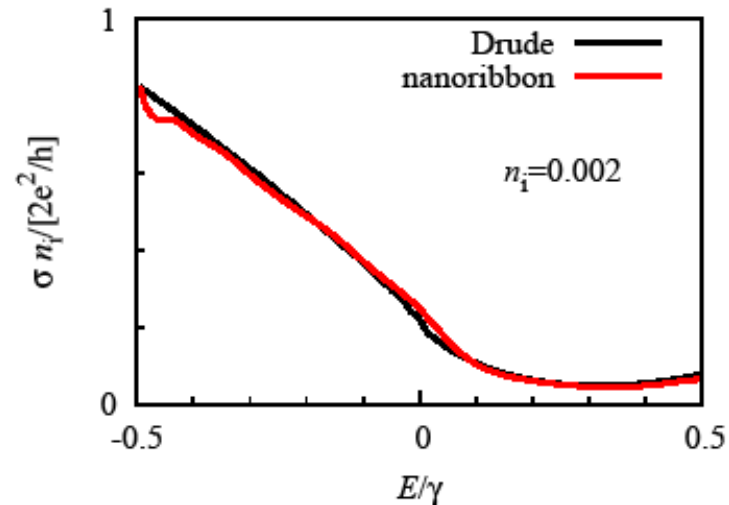
$$A = (3\sqrt{3}/4)a^2$$

$$\sigma = \left(\frac{g_s e^2}{h} \right) \frac{\hbar^2}{A n_i |t_i|^2} \frac{\langle v_k \rangle_{E_F}}{\langle v_k^{-1} \rangle_{E_F}}$$

Comparison to numerics

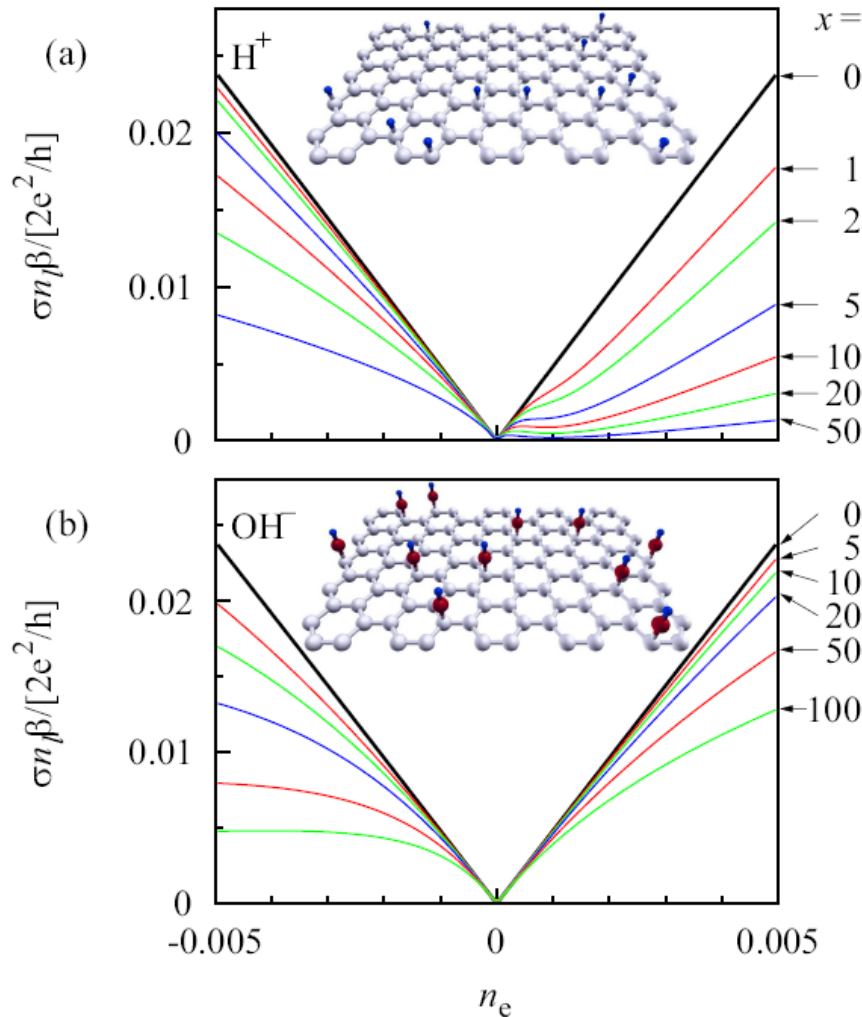


Fixed width nanoribbon



Averaged over width

Additional Coulomb scattering

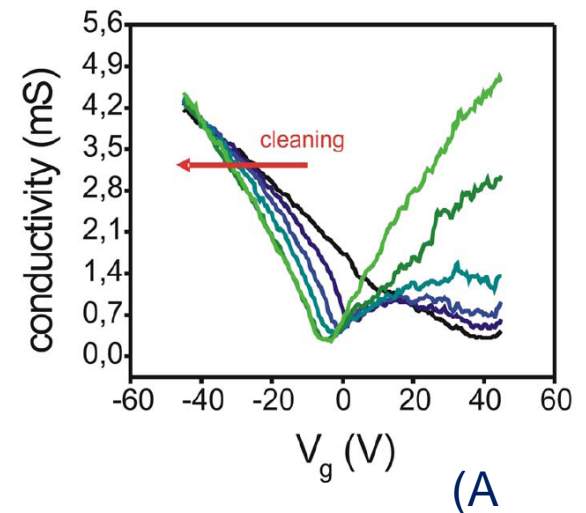


$x = (2\pi/\beta)(n_i/n_l)$: relative amounts of disorder

Additional scattering

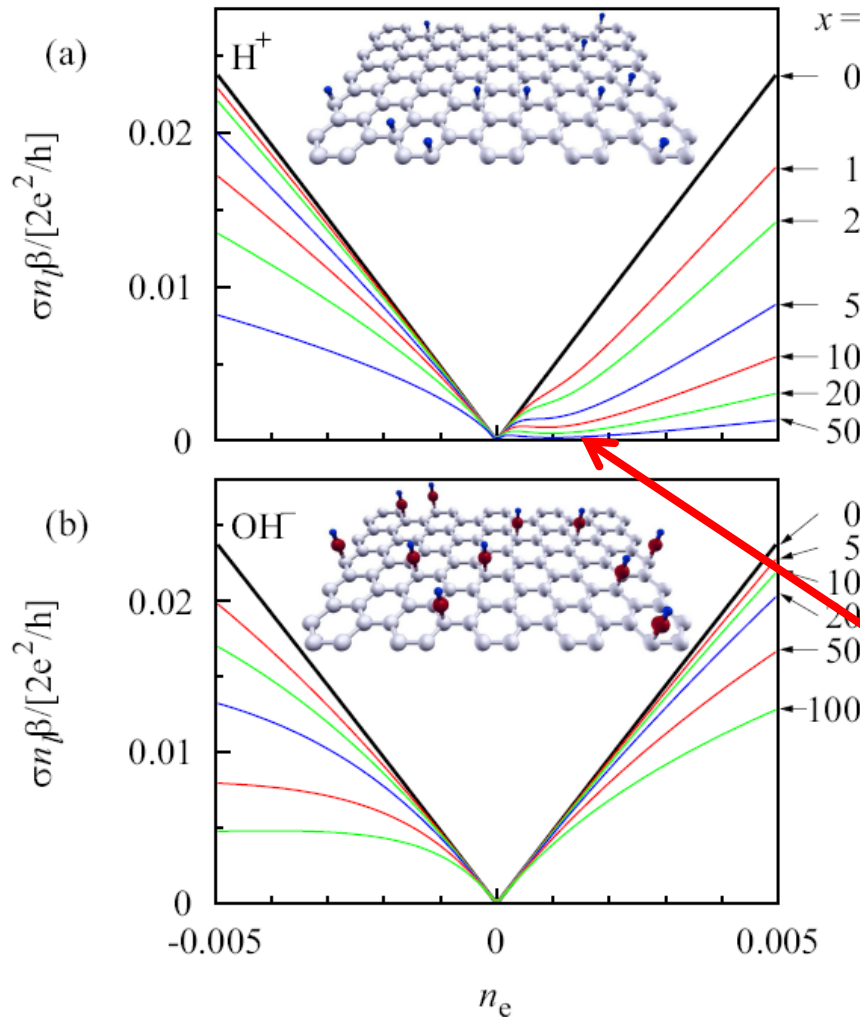
$$\tau_l^{-1} = n_l \beta \frac{\gamma^2}{\hbar |\epsilon|},$$

$$\sigma_l = \frac{2\pi\sqrt{3} g_s e^2}{n_l \beta h} n_e$$



(A)

Additional Coulomb scattering



Additional scattering

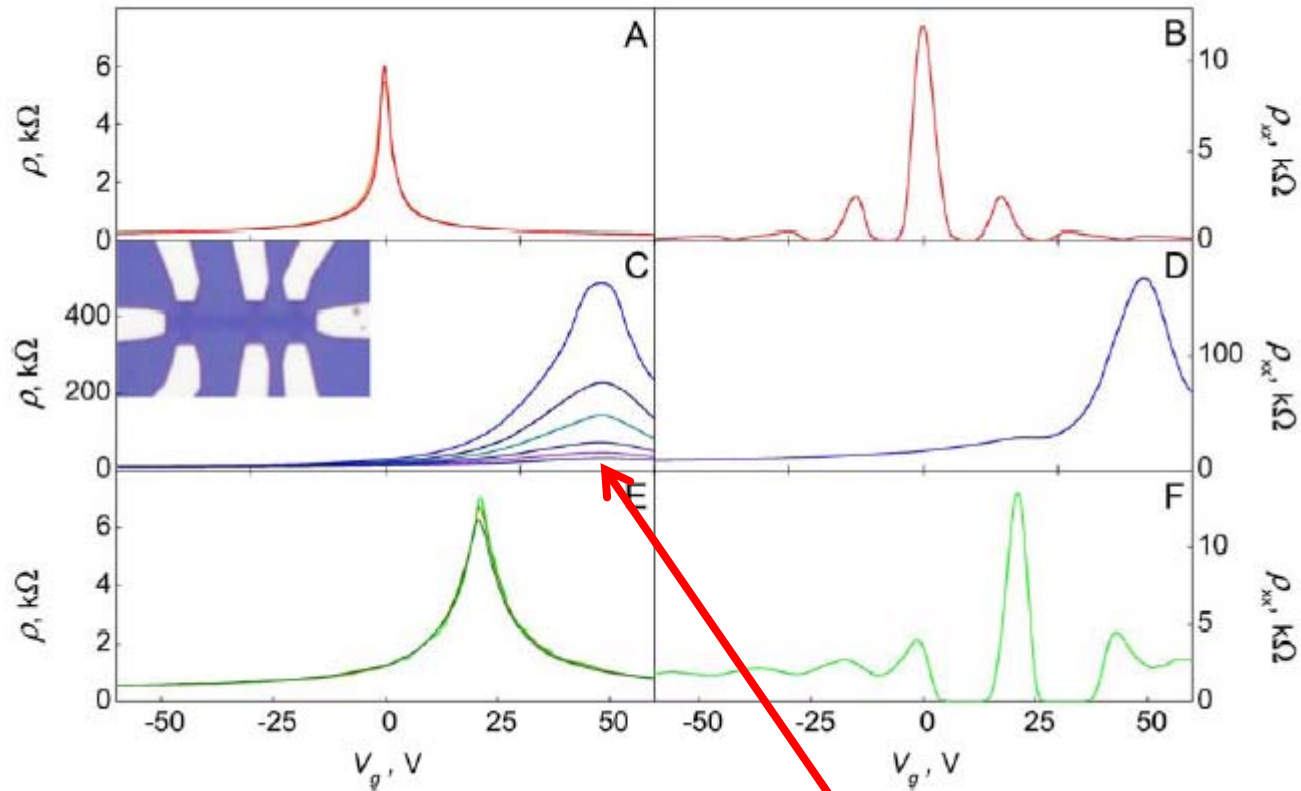
$$\tau_I^{-1} = n_I \beta \frac{\gamma^2}{\hbar |\epsilon|},$$

$$\sigma_I = \frac{2\pi\sqrt{3}}{n_I \beta} \frac{g_s e^2}{h} n_e$$

$4 \times 10^{12} \text{ cm}^{-2}$

$x = (2\pi/\beta)(n_i/n_I)$: relative amounts of disorder

hydrogenated graphene...



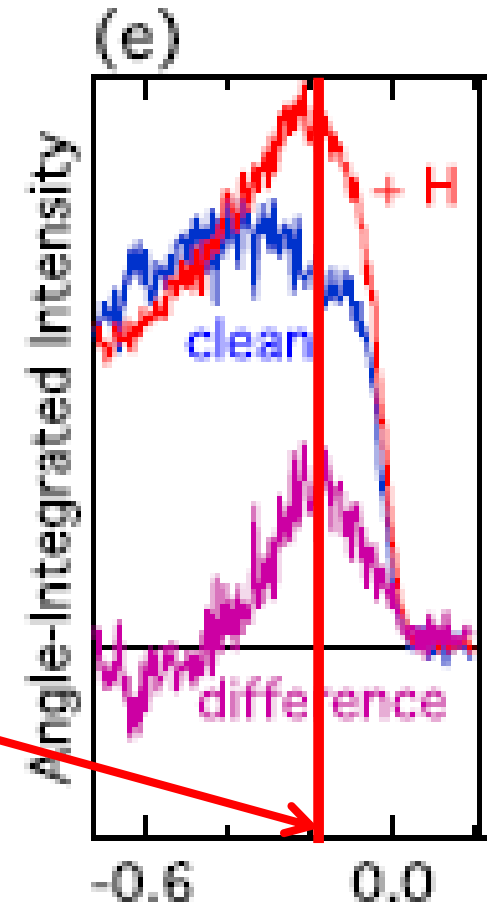
D. C. Elias et al, Science 323, 610 (2009)

$3.8 \times 10^{12} \text{ cm}^{-2}$

hydrogenated graphene II...

ARPES on hydrogenated graphene on SiC(0001),
A Bostwick et al PRL 103, 056404 (2009)

Fundamentally, the asymmetry with respect to E_D arises from the position of a dispersionless hydrogen acceptor level, which is not centered at E_D as for carbon vacancies (in a treatment without second neighbor hopping [16]) but instead ~ 200 meV above E_D [4,9,20]. This state, although weak, is observed by comparing ARPES for the clean and disordered sample obtained far from the π bands [Fig. 2(e)]; it imposes another particle-hole symmetry breaking factor discussed later.



Quantum corrections

Random potential with TRS \rightarrow described by 5 parameters:

[McCann et al,
PRL 97,
146805 (2006)]

- α_0 (preserves all rotation (C_{6v}) symmetries)
- β_z, γ_z (preserve C_{3v} symmetry)
- $\beta_{\perp}, \gamma_{\perp}$ (preserve no symmetry)

$\beta_{z,\perp}$: induce intervalley scattering

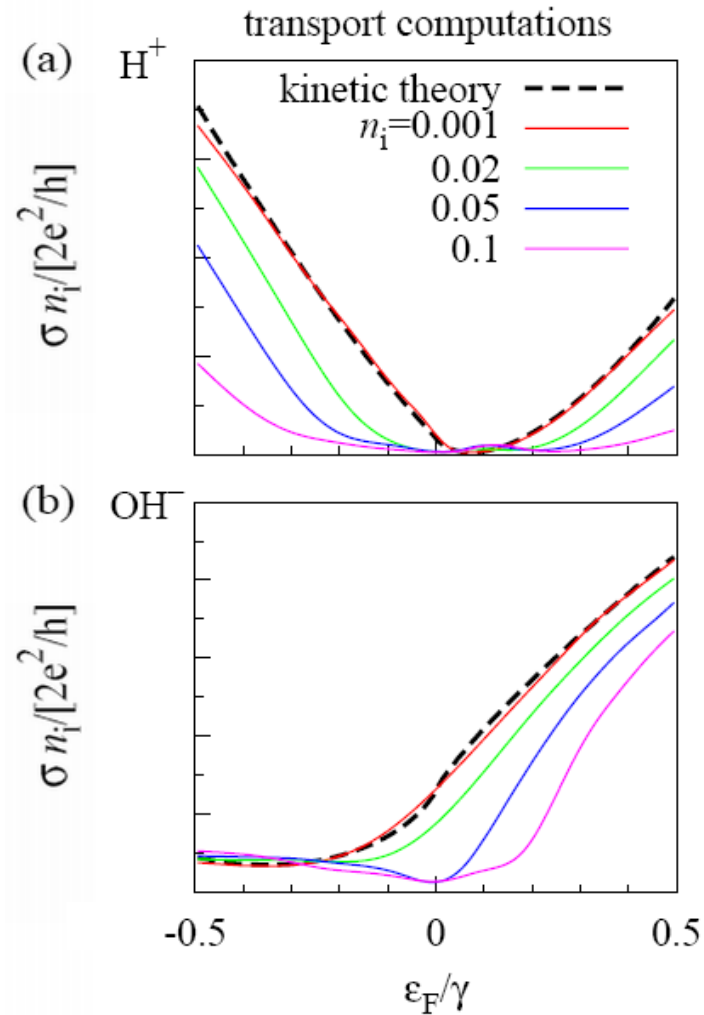
$$\sigma = \frac{g_s e^2}{\hbar \pi^2} \left(\frac{\alpha_0}{2} + \beta_{\perp} + \gamma_{\perp} + \frac{3}{2} \beta_z + \frac{3}{2} \gamma_z \right)^{-1}$$

adsorbate scattering:

$$\alpha_0 = \gamma_z = \beta_{\perp}/2 = \frac{A_c n_i |t_0(\epsilon_F)|^2}{2\pi \langle v_{\mathbf{k}} \rangle_{\epsilon_F} / \langle v_{\mathbf{k}}^{-1} \rangle_{\epsilon_F}}, \quad \beta_z = \gamma_{\perp} = 0$$

- $\beta_{\perp} \gtrsim$ others indicates negative quantum corrections to σ .

Test: increase adsorbate concentration



Renormalization group

- resum corrections into renormalized parameters $\tilde{\alpha}_0$ etc.
- for graphene: Aleiner & Efetov, PRL **97**, 236801 (2006)
- here: follow formulation in abovementioned parameters [Ostrovsky, Gornyi and Mirlin, PRB **74**, 235443 (2006)]
- flow equations

$$\dot{\alpha}_0 = 2\alpha_0(\alpha_0 + \beta_{\perp} + \gamma_{\perp} + \beta_z + \gamma_z) + \beta_{\perp}\beta_z + 2\gamma_{\perp}\gamma_z,$$

$$\dot{\beta}_{\perp} = 4(\alpha_0\beta_z + \beta_{\perp}\gamma_{\perp} + \beta_z\gamma_z),$$

$$\dot{\beta}_z = 2(\alpha_0\beta_{\perp} - \beta_z\alpha_0 + \beta_{\perp}\gamma_z + \beta_z\gamma_z),$$

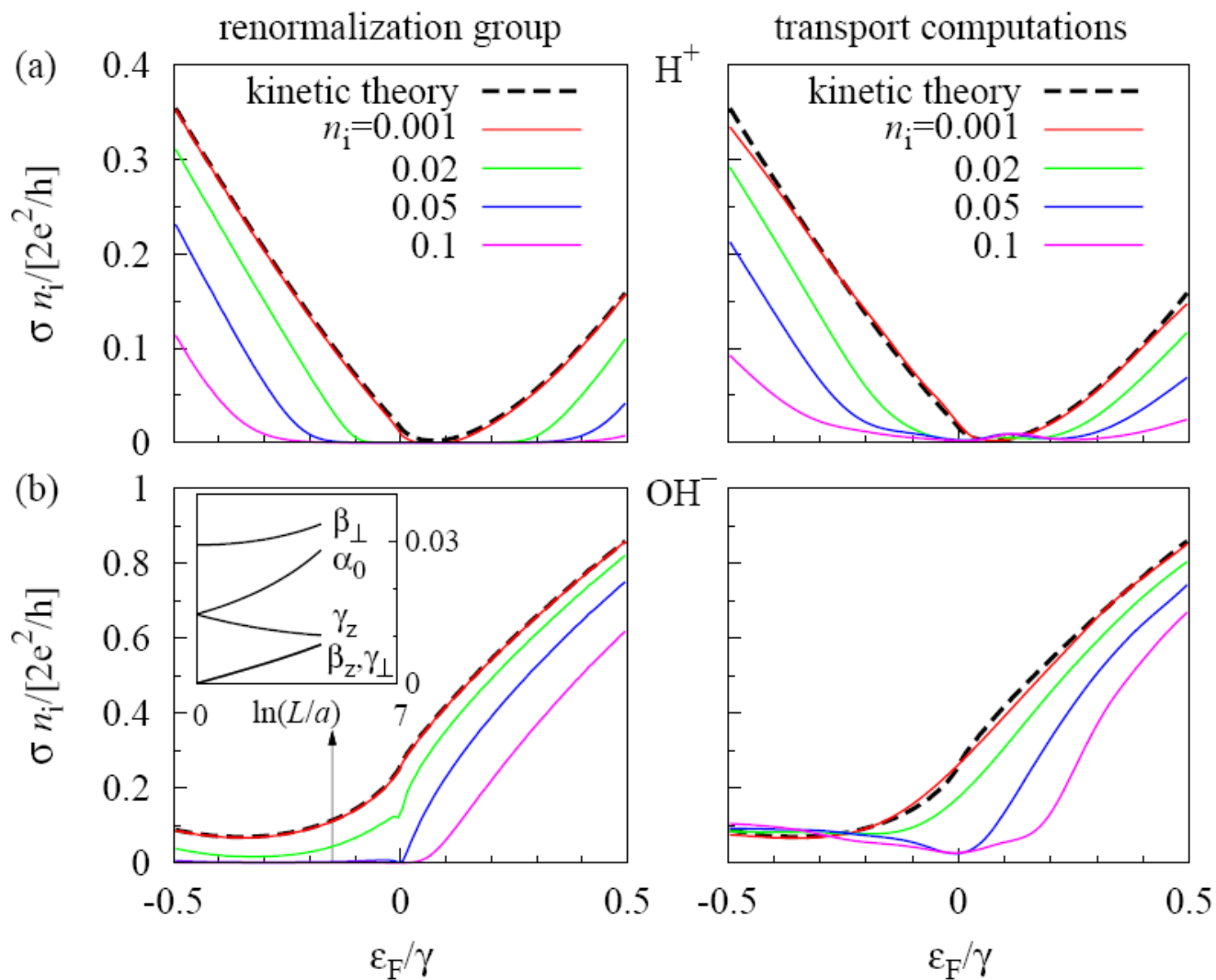
$$\dot{\gamma}_{\perp} = 4\alpha_0\gamma_z + \beta_{\perp}^2 + \beta_z^2,$$

$$\dot{\gamma}_z = 2\gamma_z(-\alpha_0 - \beta_{\perp} + \beta_z + \gamma_{\perp} - \gamma_z) + 2\alpha_0\gamma_{\perp} + \beta_{\perp}\beta_z,$$

$$\dot{\varepsilon} = \varepsilon(1 + \alpha_0 + \beta_{\perp} + \gamma_{\perp} + \beta_z + \gamma_z),$$

- $\dot{X} \equiv dX/d \ln(L/a)$.
- integrate until ε reaches cutoff (bandwidth)
(running length L from a to $\simeq \lambda_F$)

Comparison to numerics

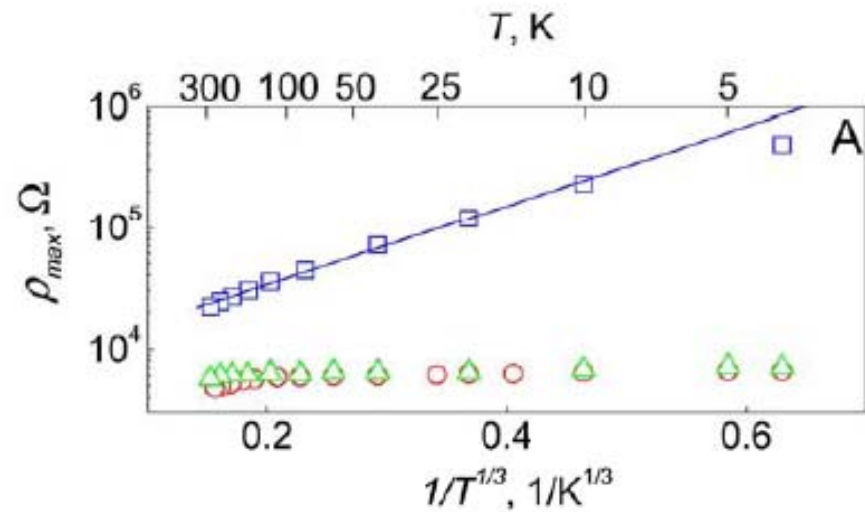


Towards strong localization

Scaling theory: large systems should be insulating

Hydrogenated graphene

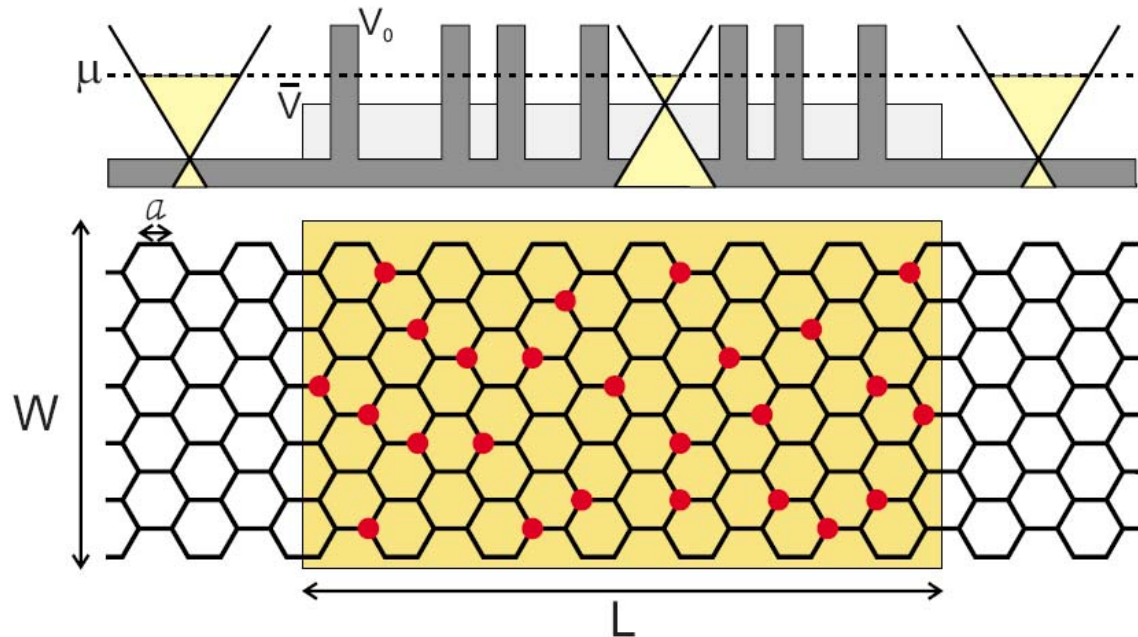
D. C. Elias et al
Science 323, 610 (2009)

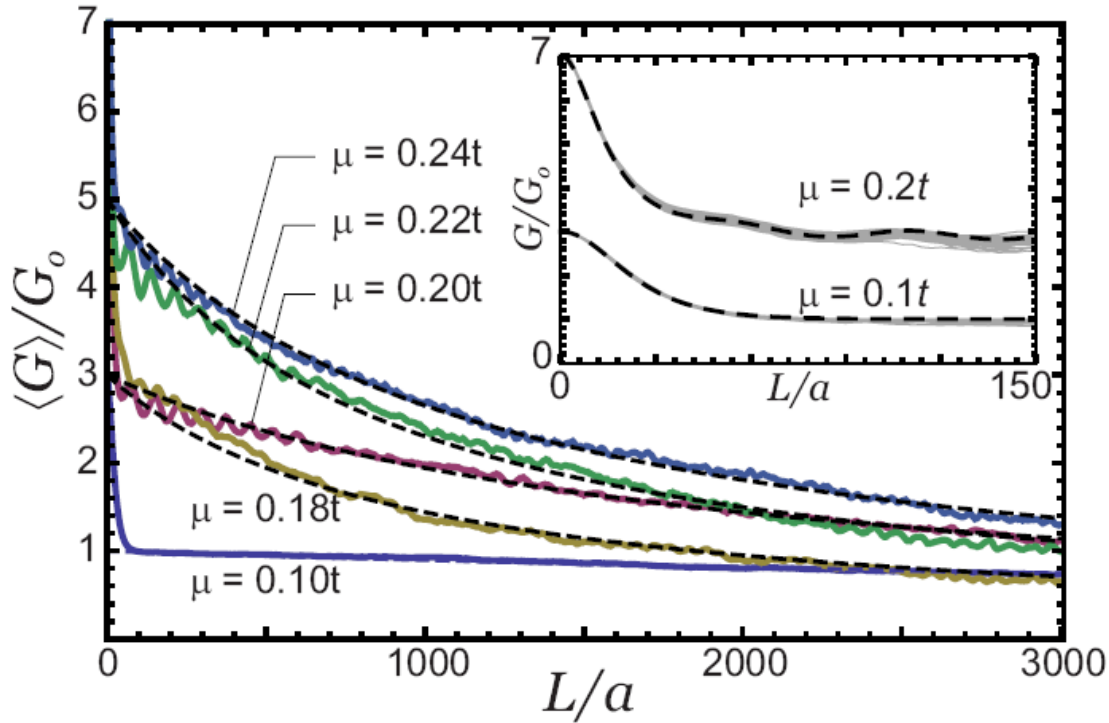


Towards strong localization

Here:
Quasi-1d
Nanoribbon

Onsite
potential V_0 ,
coverage p





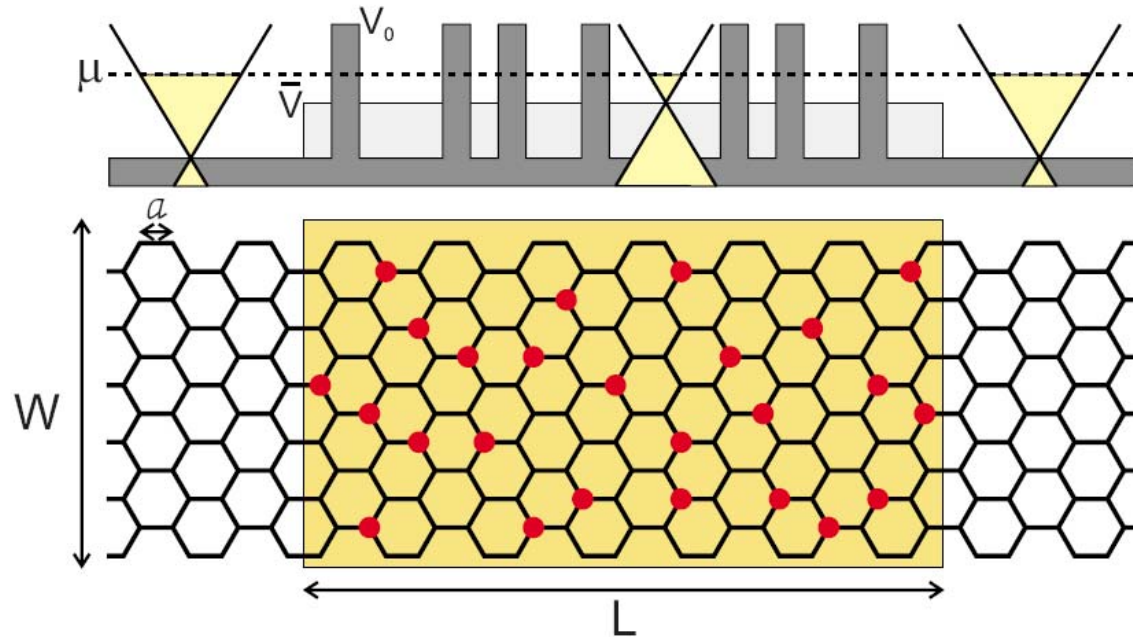
exponential decay of conductance $g \sim \exp(-L/\xi)$

- Localization length ξ can become very large
- Transient regime: ‘ballistic’ minimal conductivity
- Both happens away from the nominal Dirac point

average effect of adsorbates

Effective Dirac point shifted to

$$\bar{V} = V_0 p$$



Localization length diverges at effective Dirac point

$$\xi = \frac{\pi\sqrt{3}}{4} \frac{t^3 W}{p(1-p)V_0^2 \rho^2 (\mu - \bar{V})},$$

Effective potential step induces evanescent modes
 -> intrinsic pseudodiffusive regime

Acknowledgments:

- **Modelling, kinetic theory and quantum corrections:**

JP Robinson, L Oroszlány, VI Fal'ko

- **Localization:**

P Dietl, G Metalidis, D Golubev,
P San-Jose, E Prada, G Schön

Transport in graphene w/adsorbed molecules

- chemistry-dependent energy-dependent scattering
- strong coupling shifts resonance towards Dirac point
- transport asymmetric about Dirac point
- small impurity concentration: kinetic theory
- cumulative effect of many impurities:
quantum corrections towards localization
- RG (quantitative agreement in perturbative regime)
- **disorder-induced pseudodiffusion and localization**

See also: PRL 101, 196803 (2008), PRB 79, 195413 (2009)