Attraction-repulsion transition in the interaction of adatoms and vacancies in graphene

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Outline

1. *Effective coupling of resonant impurities*
2. *Energy spectrum of two impurities*
3. *Effects of chemical potential in a system of many impurities*
4. *Implications for hydrogen transport on graphene*

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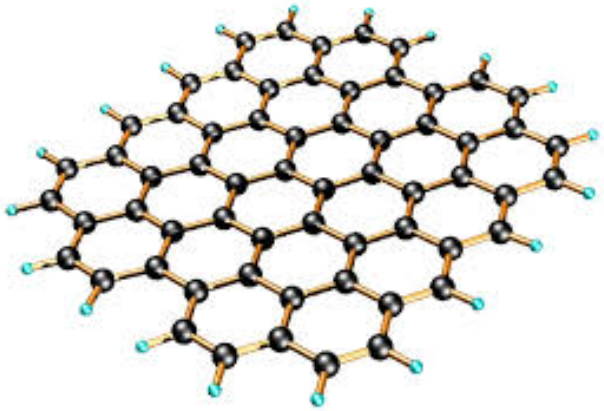
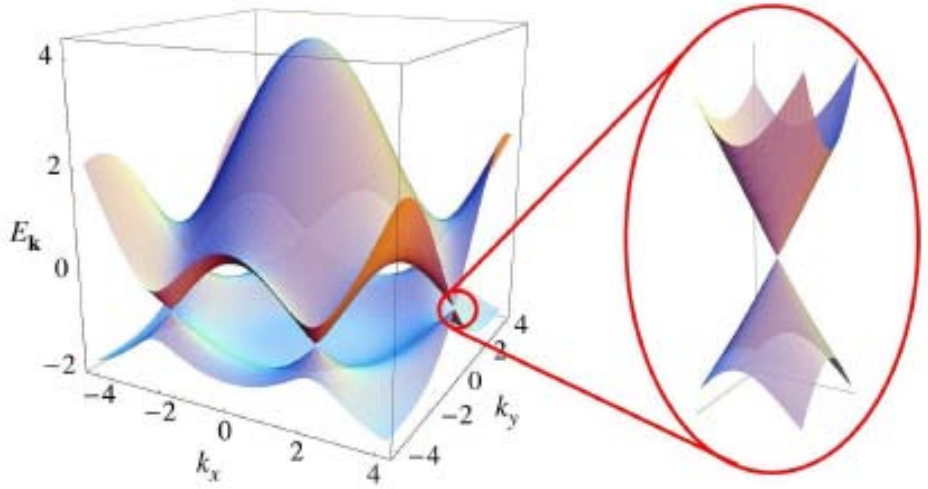
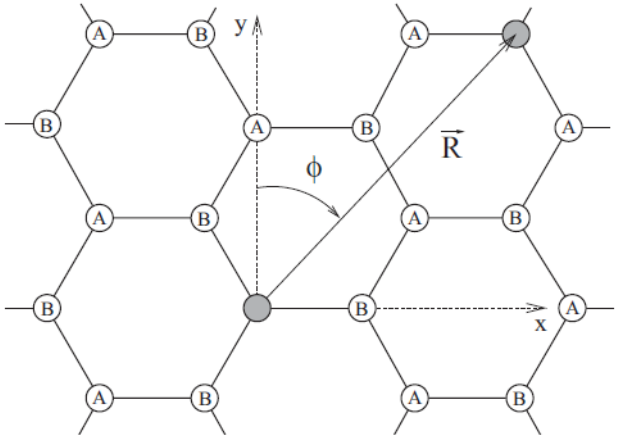
Electron spectrum in graphene

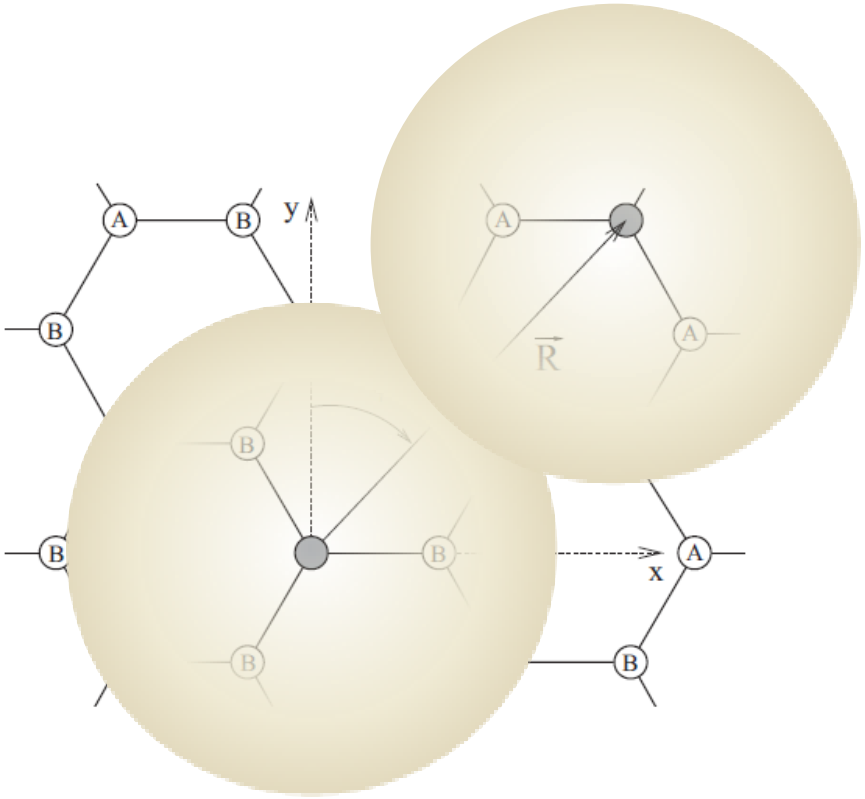




The wave functions near the two Dirac points interfere thus producing patterns on the scale of lattice spacing

Effective coupling of impurities via the modification of conduction electrons' wave functions



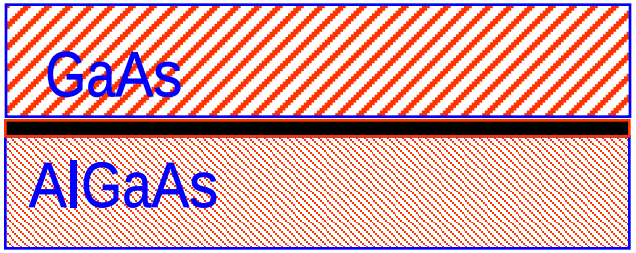


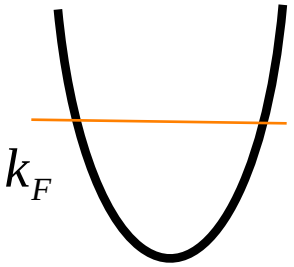
Example: Friedel oscillations in the interaction of impurities in a 3D metal

$$W(R) \sim \frac{\cos(2k_F R)}{R^3}$$

Short-range impurities: 2DEG vs. Graphene

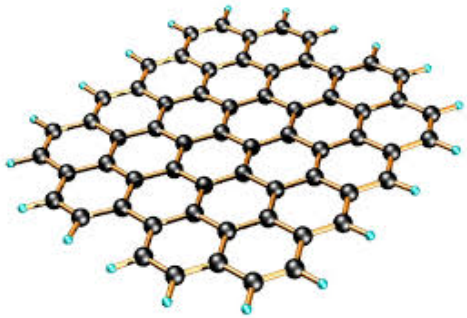
$$U(\vec{R}) = U\delta(\vec{R})$$

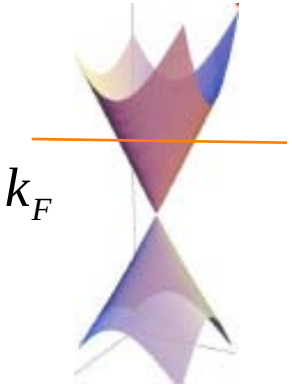




$$W(R) \sim \frac{mU^2}{R^2}\cos(2k_F R)$$

Weak impurity: $mU << 1$





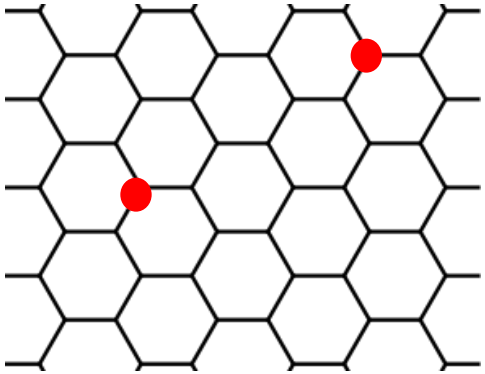
$$m \to \frac{1}{\mathrm{v}R}$$

Weak impurity: $U / R\mathrm{v} << 1$

$$W(R) \sim \frac{U^2}{\mathrm{v}R^3}\cos(2k_F R)$$

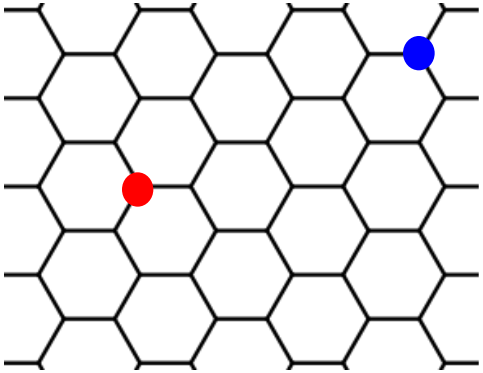
Interaction between weak impurities $V(\vec{r}) = U\delta(\vec{r})$

$$U << Rv$$



Impurities on the same sublattice

$$W_{AA}(\mathbf{R}) = -\frac{1}{16\pi}\frac{U^2A_0^2}{vR^3}\cos^2\theta_{AA}$$

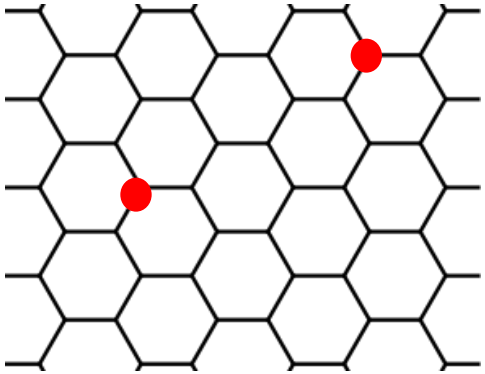


Impurities on opposite sublattices

$$W_{AB}(\mathbf{R}) = \frac{3}{16\pi}\frac{U^2A_0^2}{vR^3}\sin^2\theta_{AB}$$

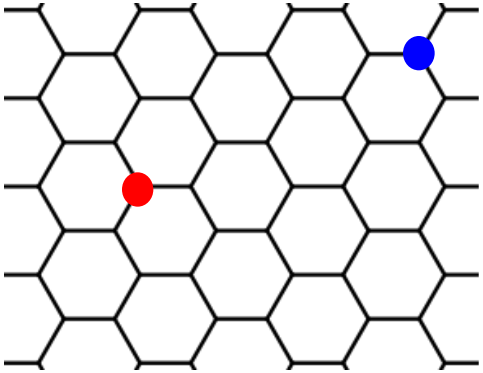
Interaction between strong impurities $V(\vec{r}) = U\delta(\vec{r})$

$$U >> Rv$$



Impurities on the same sublattice

$$W_{AA}(\mathbf{R}) = \frac{\pi v \cos^2\theta_{AA}}{2R\ln^2(R/a)}$$



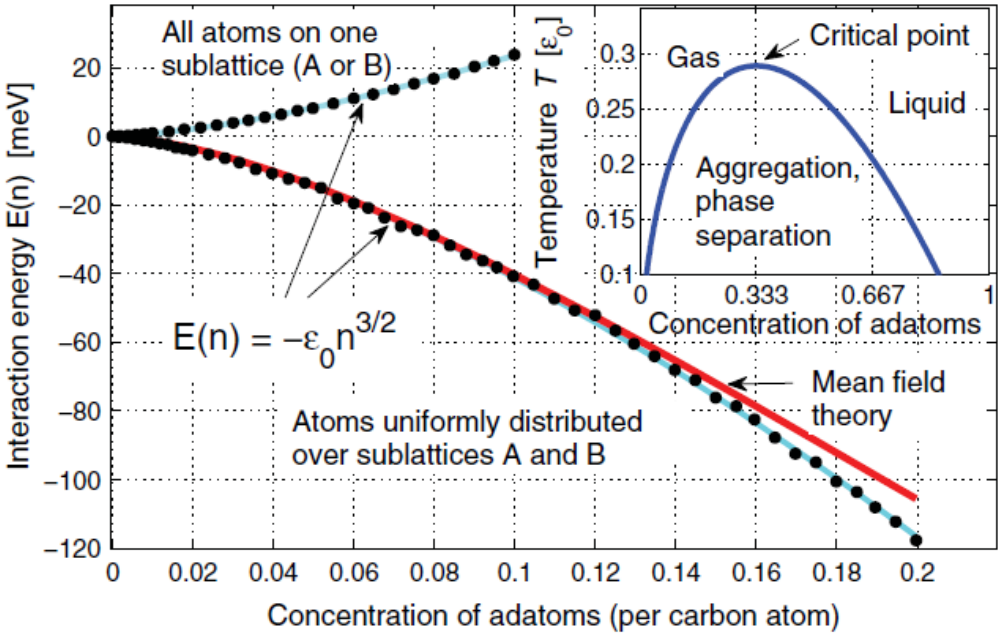
Impurities on opposite sublattices

$$W_{AB}(\mathbf{R}) = -\frac{2v|\sin\theta_{AB}|}{R\ln(R/a)}$$

Shytov, Abanin, Levitov (2009)

Many strong impurities

Shytov, Abanin, Levitov (2009)



Does it matter if doping occurs with the fixed number of electrons or a fixed chemical potential?

The interaction energy does not change appreciably (?)

Our findings

Net interaction in a system of many randomly distributed impurities is indeed attractive when

$$\mu = \text{const}$$

but becomes repulsive when the number of electrons is kept fixed instead

$$N = \text{const}$$

$$W_{AA}(\mathbf{R}) = \frac{\pi v \cos^2\theta_{AA}}{2R \ln^2(R/a)}$$

$$W_{AB}(\mathbf{R}) = -\frac{2v|\sin\theta_{AB}|}{R\ln(R/a)} + \frac{\hbar\pi v \sin^2\theta_{AB}}{2R\ln^2(R/a)}$$

However, the first, attractive, term disappears when the chemical potential is moved away from the Dirac point

How to find interaction energy

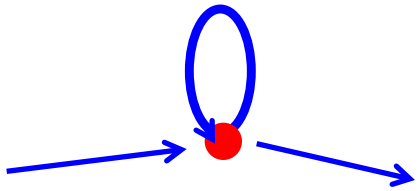
$$\frac{\partial W}{\partial U} = \left\langle \frac{\partial H}{\partial U} \right\rangle$$

$$W(\mathbf{R}) = -2i \int_0^U dU \left[\mathcal{G}(0,0,t=-0) + \mathcal{G}(\mathbf{R},\mathbf{R},t=-0) \right]$$

$$W(\mathbf{R}) = 2i \int_{-\infty}^{\infty} \frac{dE}{2\pi} \ln\left(1 - T_E^2 G_E(\mathbf{R},0) G_E(0,\mathbf{R})\right)$$

Strong impurities on the same sublattice

Non-perturbative multiple scattering



$$U \to U + UG_E(0)U + UG_E(0)UG_E(0)U + \ldots = \frac{U}{1 - UG_E(0)} \to -\frac{1}{G_E(0)}$$

in graphene $G_E(0) = iE \ln|E|$ relevant energies $E \sim \frac{\mathrm{v}}{R}$

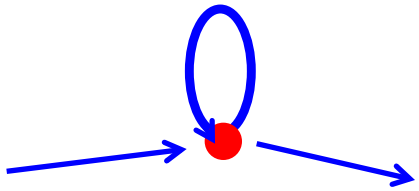
$$U \to \frac{1}{E \ln|E|} = \frac{R}{\mathrm{v} \ln R}$$

$$W_{AA} \sim -\frac{U^2}{\mathrm{v}R^3} \to \frac{\mathrm{v}}{R \ln^2 R}$$

$$W_{AA}(\mathbf{R}) = \frac{\pi v \cos^2\theta_{AA}}{2R \ln^2(R/a)}$$

Strong impurities on different sublattices

Non-perturbative multiple scattering



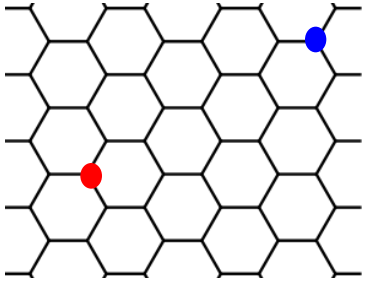
$$U \to U + UG_E(0)U + UG_E(0)UG_E(0)U + \ldots = \frac{U}{1 - UG_E(0)} \to -\frac{1}{G_E(0)}$$

W_{AB} cannot be explained in the same way

$$W_{AB}(\mathbf{R}) = -\frac{2v|\sin\theta_{AB}|}{R\ln(R/a)} + \frac{\hbar\pi v\sin^2\theta_{AB}}{2R\ln^2(R/a)}$$

Exact solution for the energy spectrum of two strong impurities

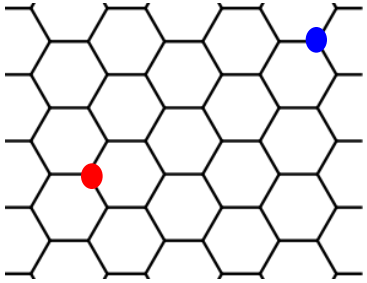
Two impurities:



$$\hat{H} = t \sum_{\mathbf{r}_A} \sum_{i=1,2,3} \hat{a}^\dagger(\mathbf{r}_A)\hat{b}(\mathbf{r}_A + \boldsymbol{a}_i) + \text{h.c.}$$

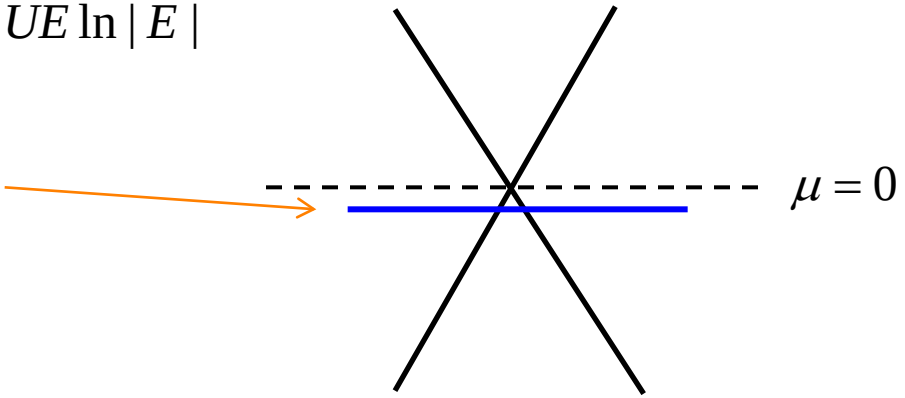
$$+U\hat{a}^\dagger(0)\hat{a}(0) + U\hat{b}^\dagger(\mathbf{R})\hat{b}(\mathbf{R}).$$

Exact solution for the energy spectrum of two strong impurities

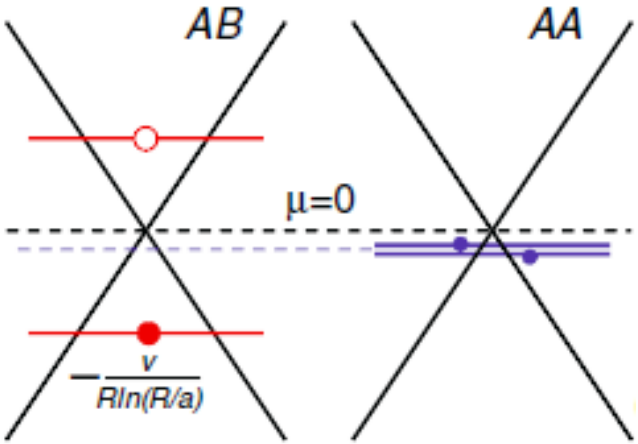


Single impurity $$\frac{U}{1-UG_E(0)} = \frac{U}{1+UE\ln|E|}$$

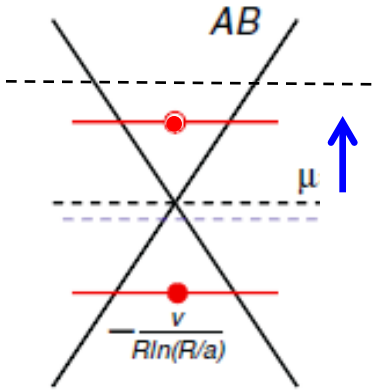
Quasi-bound state $$E \sim -\frac{1}{U\ln U}$$



Two impurities:

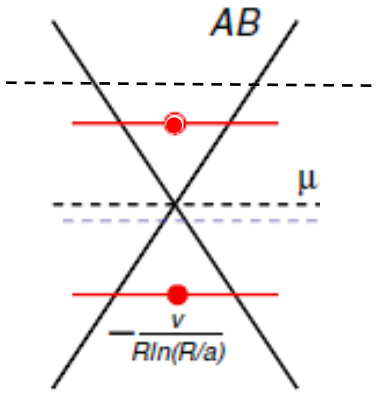


Chemical potential increased



Strong impurities on different sublattices

$$\mathcal{E}_{\mathbf{R}} = \frac{\hbar v |\sin\theta_{AB}|}{R \ln(R/a)}$$

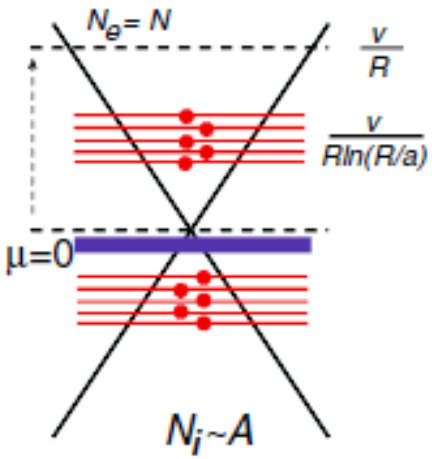


$$W_{AB}(\mathbf{R}) = \frac{\hbar\pi v \sin^2\theta_{AB}}{2R\ln^2(R/a)} - 2\mathcal{E}_{\mathbf{R}}\Theta(\mathcal{E}_{\mathbf{R}} - |\mu|)$$

Renormalization of the energy of all band states

Energy of bound states

Many impurities

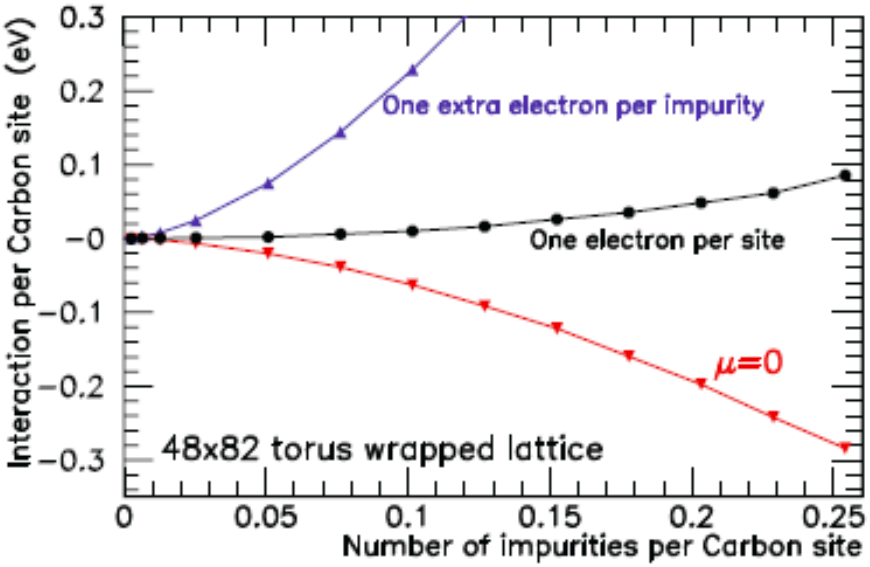


One extra electron per impurity

One electron per site

$\mu=0$

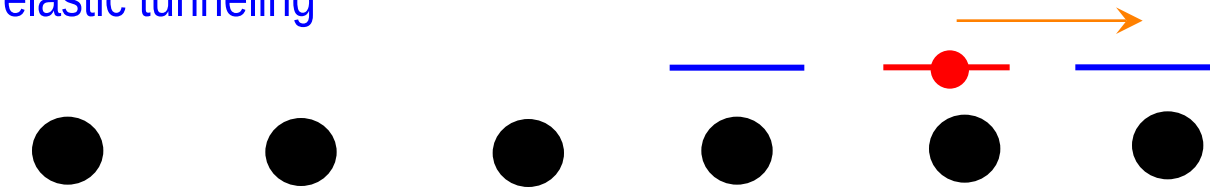
Numerical results



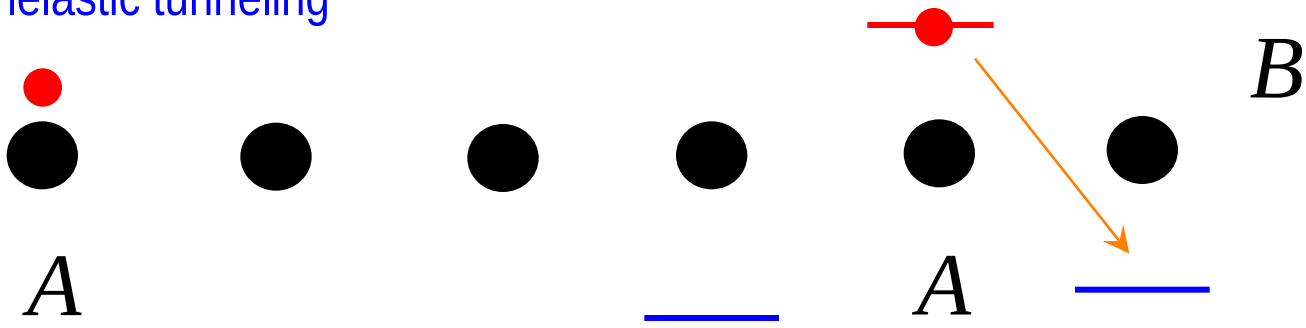
Transport of hydrogen adatoms on graphene

Single H-atom:
elastic tunneling

$t \sim 1\,\mu eV$



Second H-atom present:
inelastic tunneling



$\Delta E \sim 50\,meV$

Transport of hydrogen adatoms on graphene

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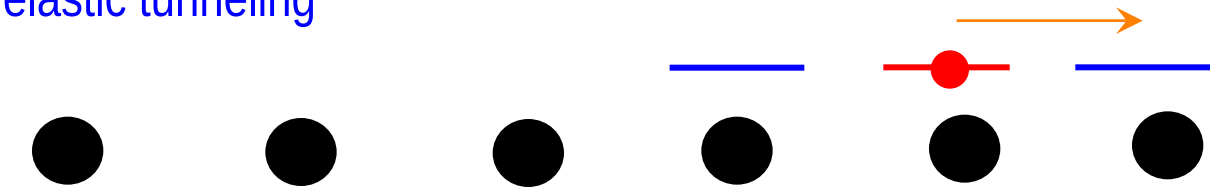

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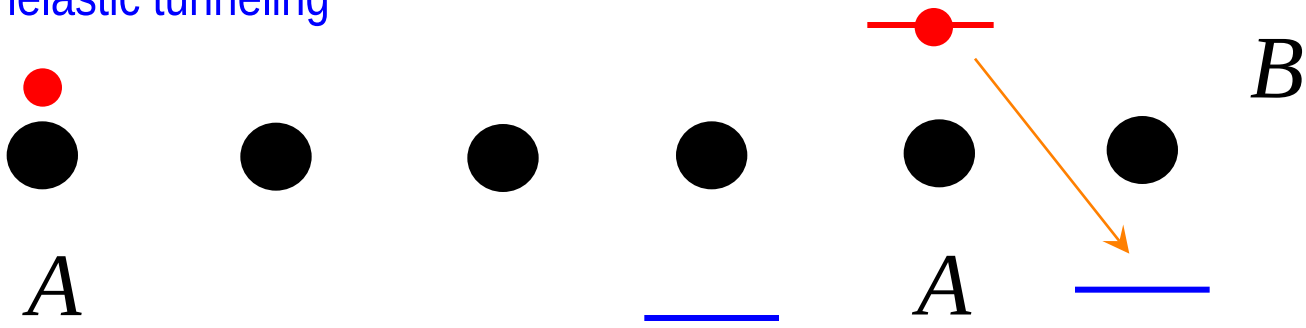
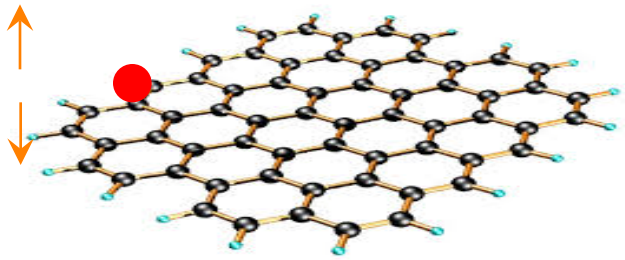


$\Delta E \sim 50\,meV$

Mechanisms of adatom tunneling

Interaction with flexural phonons
(mass defect)

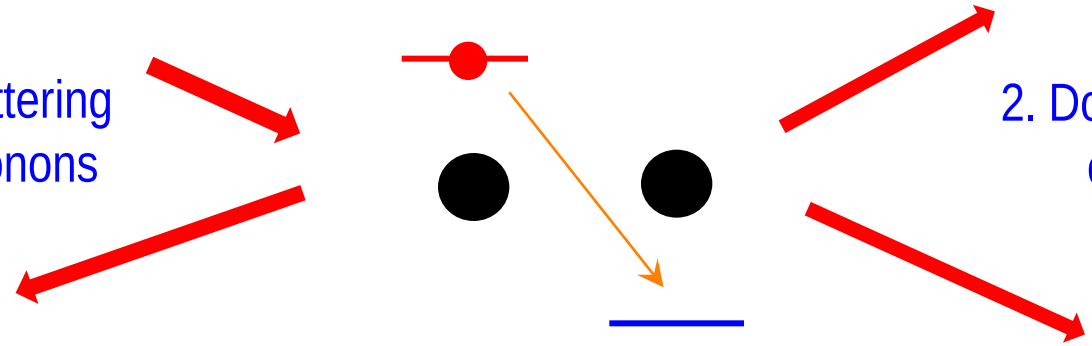


$$V = \frac{1}{2} M \dot{Z}^2$$

$$\mathcal{H}_{sc} = M \sum_{\mathbf{q},\mathbf{k}} A_q A_k a_{\mathbf{q}} a^{\dagger}_{\mathbf{k}} e^{-i(\omega_q - \omega_k)t + i(\mathbf{q}-\mathbf{k})\cdot\mathbf{R}}$$

$$A_q = \sqrt{\hbar\omega_q / 2\rho\mathcal{A}}$$

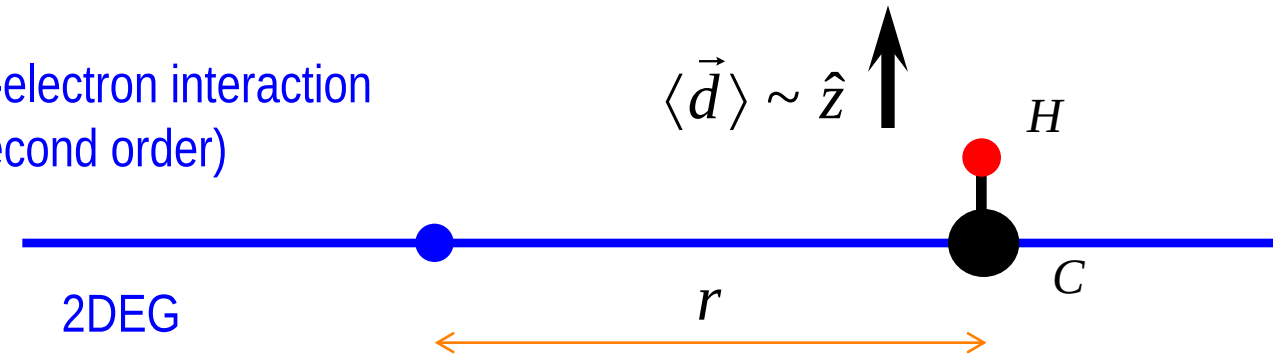
1. Scattering of phonons



2. Double phonon emission

Mechanisms of adatom tunneling

Hydrogen-electron interaction
(second order)



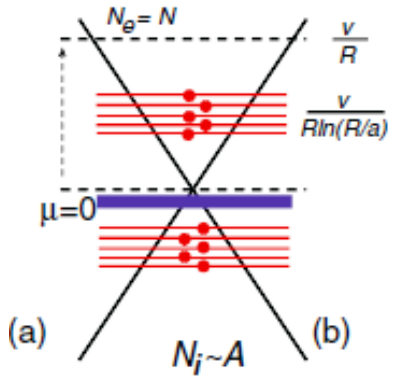
$$V(r) = C\frac{e^2 a_B^3}{r^4} \qquad C \sim 1-5; \quad C \approx 2.9 \text{ (atomic H)}$$

$$\frac{W_{H-e}}{W_{em}} = 24\pi^2 C^2 \left(\frac{e^2}{\hbar\kappa v}\right)^2 \left(\frac{\rho a_B^2}{M}\right)\left(\frac{D}{Mv^2}\right)$$

$$W_{ph} \sim W_{H-e} \sim 1\,\text{Hz} \times (\text{T}/\text{T}_0)^3$$

Conclusions

1. Strong (resonant) impurities (or vacancies) in graphene display long-range interaction whose sign can be controlled with the chemical potential. This phenomenon is due to the formation and population of impurity levels.



2. This long-range interaction suppressed the transport of such impurities on graphene; electron- and phonon-assisted tunneling processes are needed.