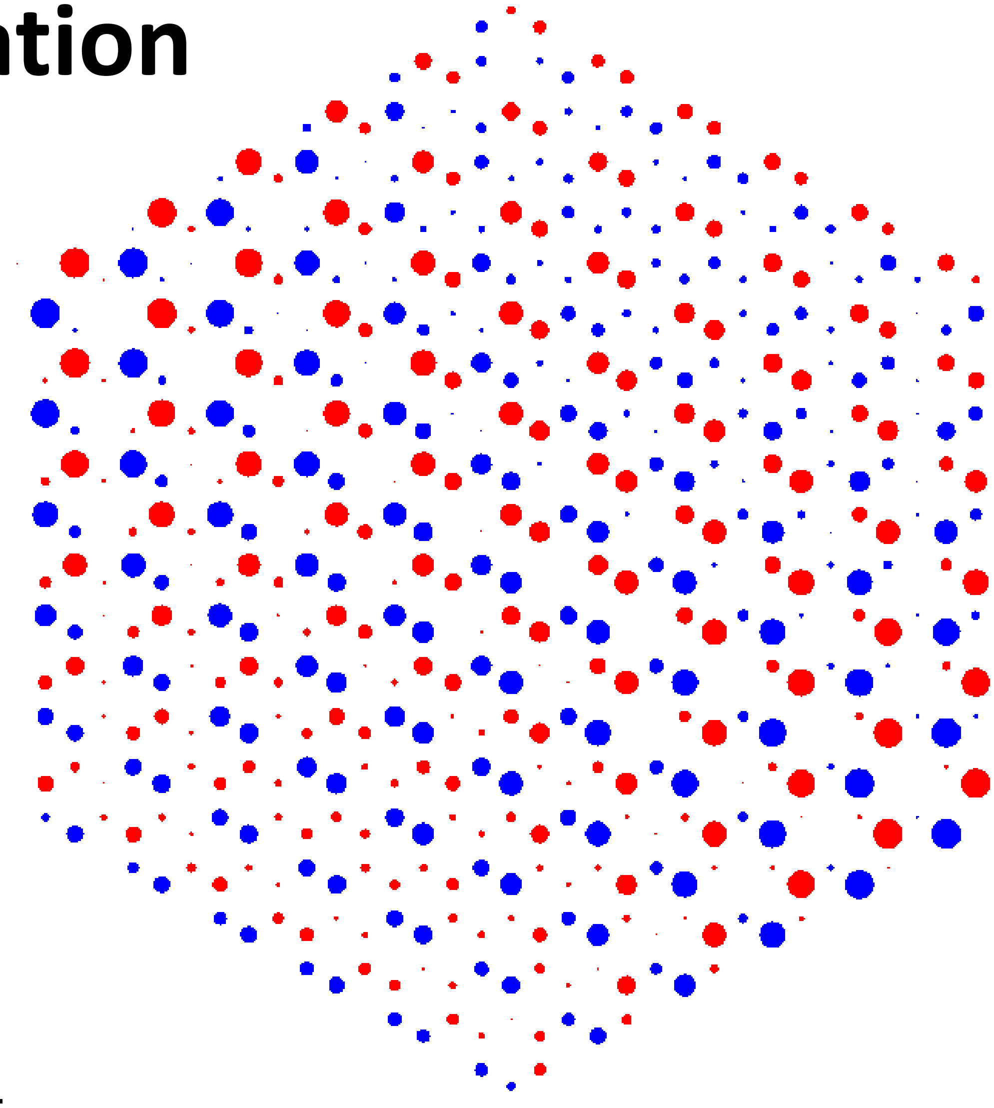
Conjugated molecules described in terms of the Dirac equation



Matthias Ernzerhof

Department of Chemistry, University of Montreal

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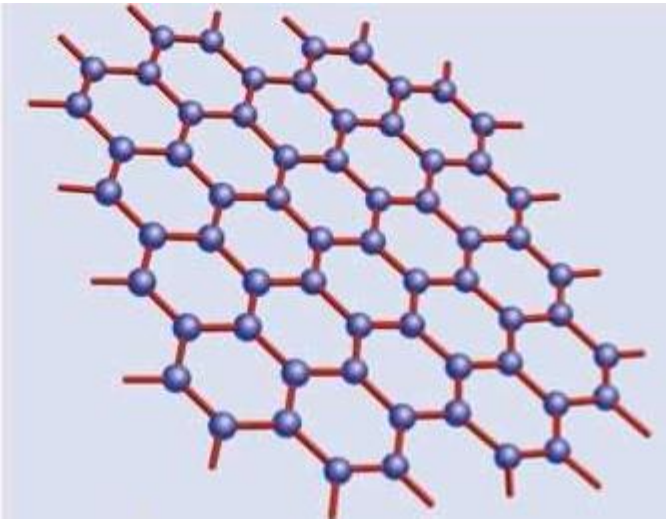
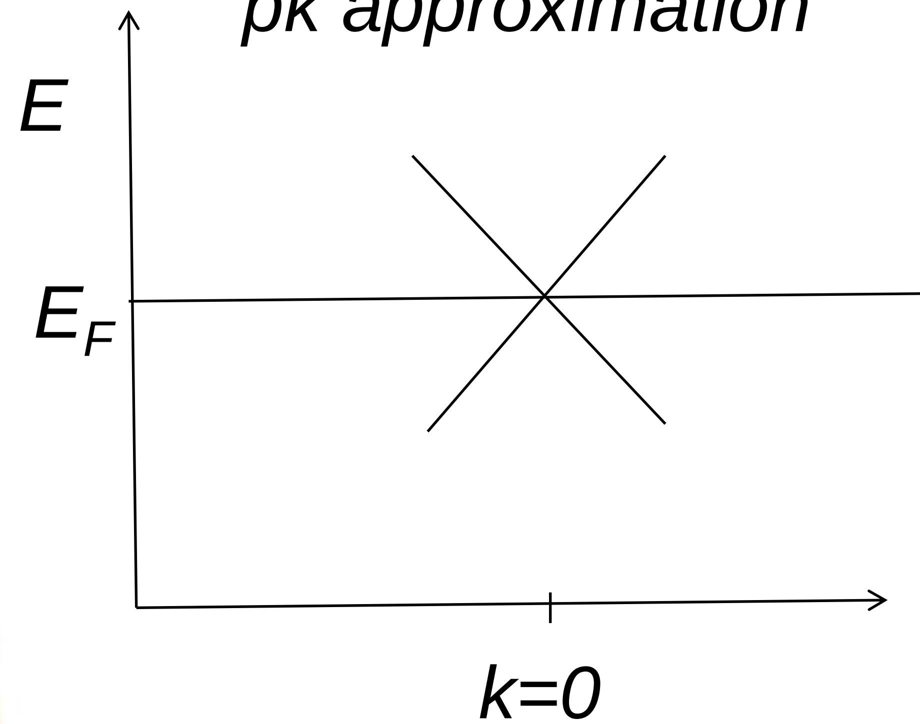
-*Yongxi Zhou*
-*Philippe Rocheleau*
-*Hilke Bahmann*
-*Min Zhuang*
-*Ali Goker*

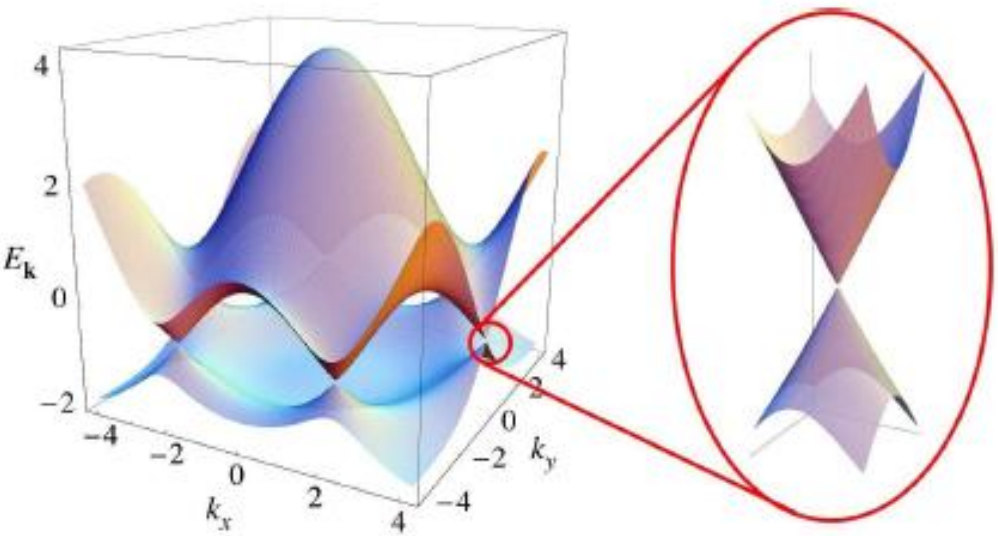
Funding and other support: NSERC, CFI, Gaussian.

Graphene



pk approximation





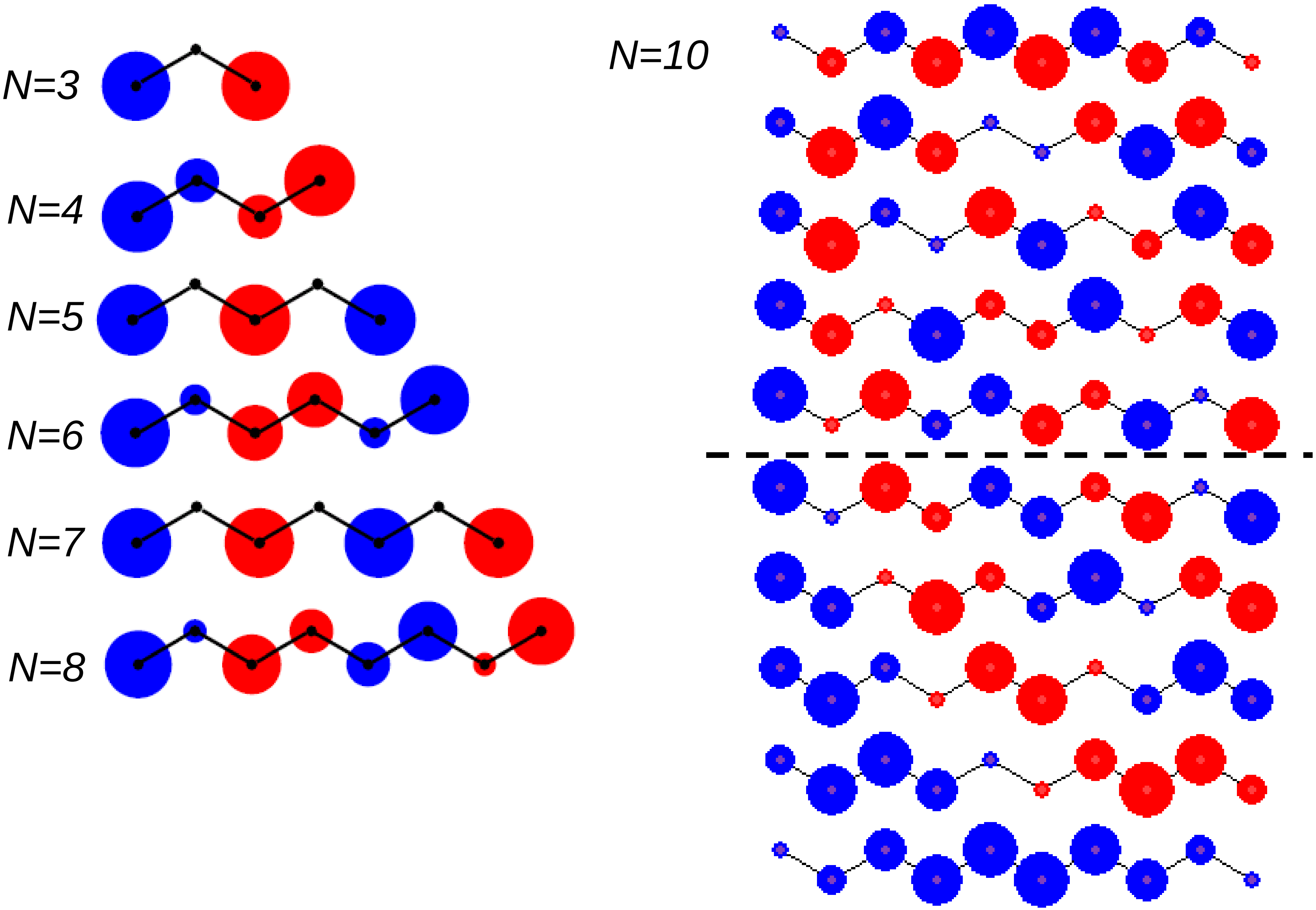
Wallace, PR, 71 622 (1947).

The electronic properties of graphene

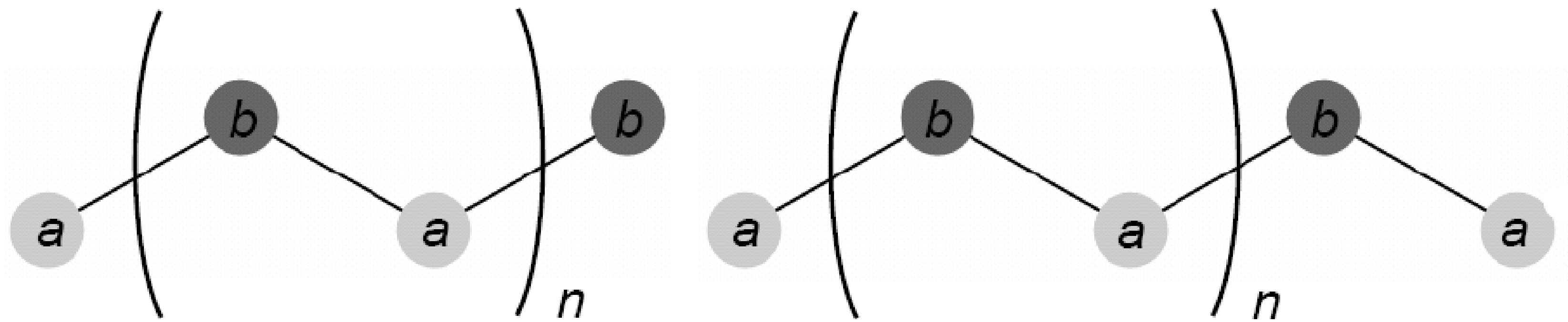
Reviews of Modern Physics, 81, 109 (2009).

A. H. Castro Neto[1], F. Guinea[2], N. M. R. Peres[3], K. S. Novoselov[4], and A. K. Geim[4]

Orbitals in polyenes



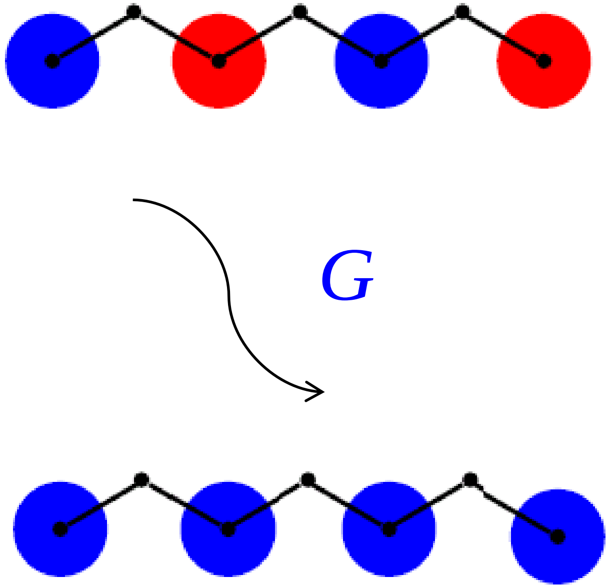
Hückel Hamiltonian



$$
\mathbf{H} = \begin{pmatrix}
\ddots & & & & & & & \\
& a & t & & & & & \\
& t & b & t & & & & \\
& & t & a & t & & & \\
& & & t & b & t & & \\
& & & & t & a & t & \\
& & & & & t & b & \\
& & & & & & & \ddots
\end{pmatrix}.
\quad\longrightarrow\quad
\tilde{\mathbf{H}} = \begin{pmatrix}
\ddots & & & & & \ddots & & & \\
& a & & & & t & t & & \\
& & a & & & & t & t & \\
& & & a & & & & t & \ddots \\
& & & & \ddots & & & & \\
\ddots & t & & & & b & & & \\
& t & t & & & & b & & \\
& & t & t & & & & b & \\
& & & \ddots & & & & & \ddots
\end{pmatrix}.
$$

Applying a gauge transformation

$$
\begin{aligned}
\mathbf{D} &= \mathbf{G}\mathbf{H}\mathbf{G}^{-1} \\
&= \begin{pmatrix}
\ddots & & & & & \ddots & & & \\
& a & & & & -t & t & & \\
& & a & & & & -t & t & \\
& & & a & & & & -t & \ddots \\
& & & & \ddots & & & & \\
\ddots & -t & & & & b & & & \\
& t & -t & & & & b & & \\
& & t & -t & & & & b & \\
& & & \ddots & & & & & \ddots
\end{pmatrix}.
\end{aligned}
$$



$$
2t\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\frac{d}{dx} = 2t\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} i\,\frac{d}{dx}
$$

$$
= -iv_F\sigma\ d
$$

$$
= v_F\sigma\ p
$$

Ernzerhof, Goyer, JCTC, 6, 1818 (2010)

Even-numbered chain

$$-iv_F\sigma\, d\,\phi = \varepsilon\phi$$

$$\phi = \begin{pmatrix}\phi_u \\ \phi_d\end{pmatrix}$$

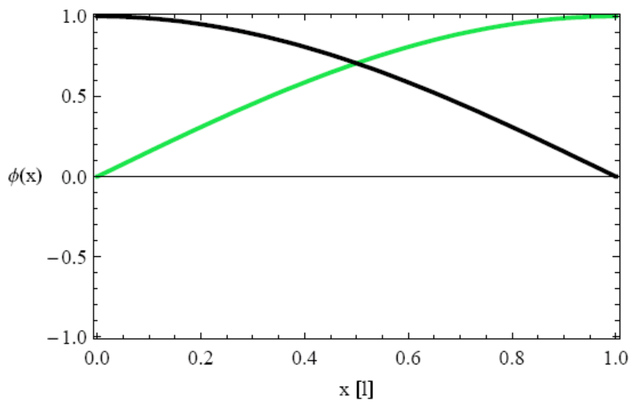
$$\phi^s = \begin{pmatrix}\sin(kx) \\ \cos(kx)\end{pmatrix},$$

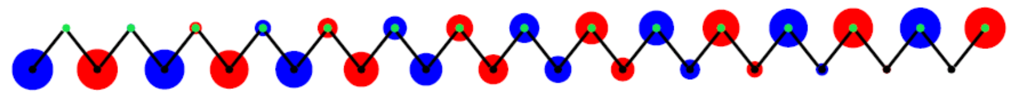
$$\phi^\pm = e^{ikx}\begin{pmatrix}1 \\ \pm i\end{pmatrix}, \quad \varepsilon = \pm v_F k$$

$$k = \frac{(n+1/2)\pi}{l}$$

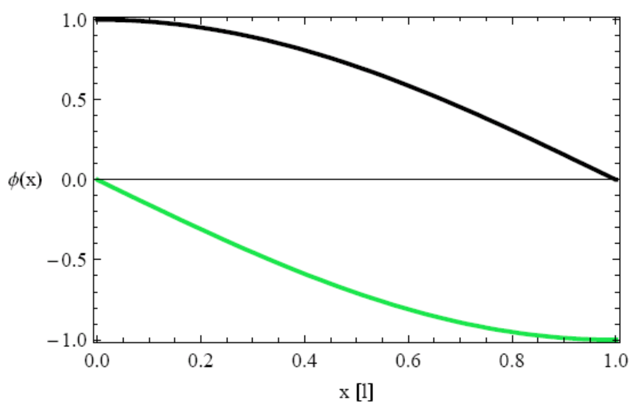
$$\phi^c = \begin{pmatrix}\cos(kx) \\ -\sin(kx)\end{pmatrix}.$$

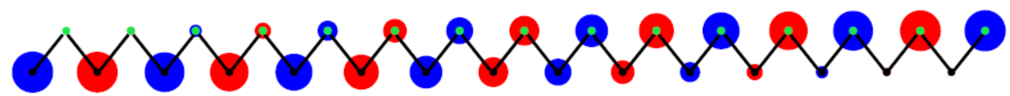
LUMO





HOMO

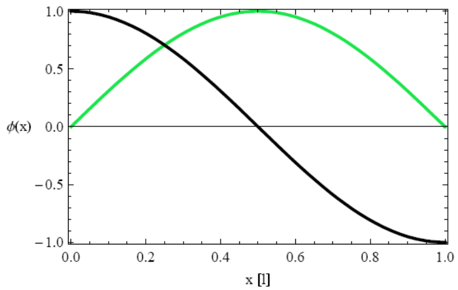


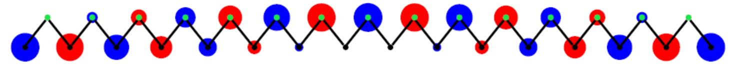


Odd-numbered chain

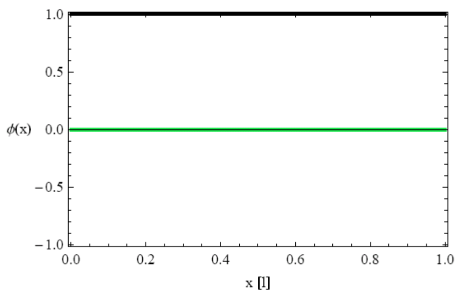
$$k = \frac{n\pi}{l}$$

LUMO

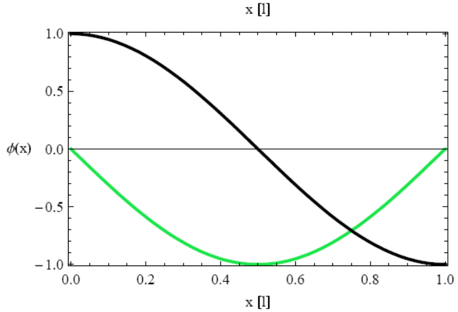


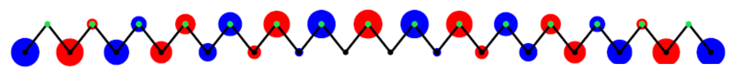


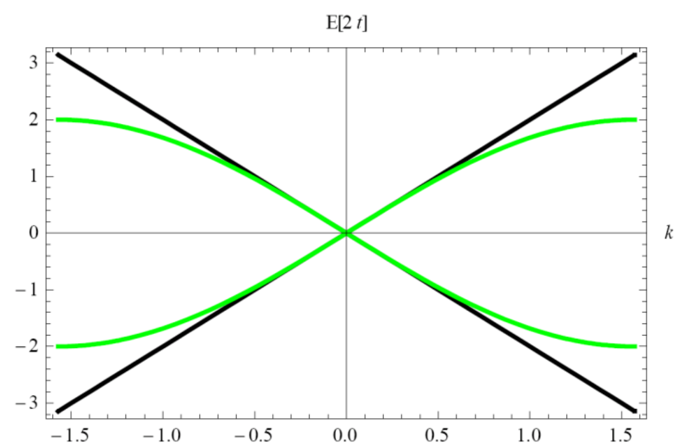
HOMO



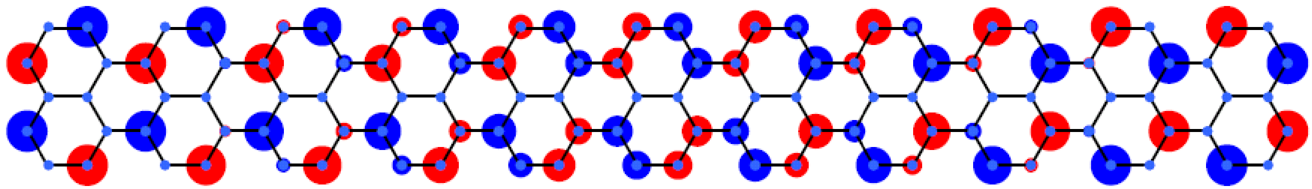
HOMO −1



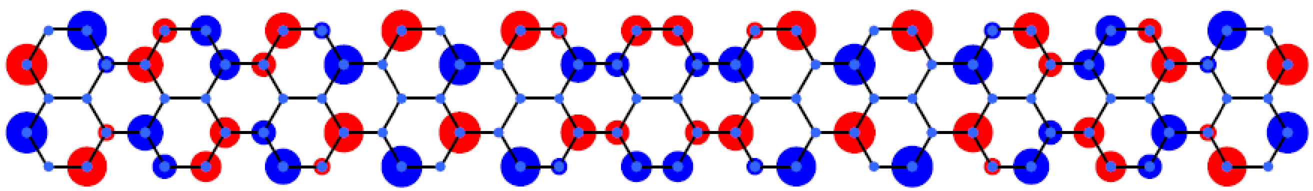




Finite graphene ribbons

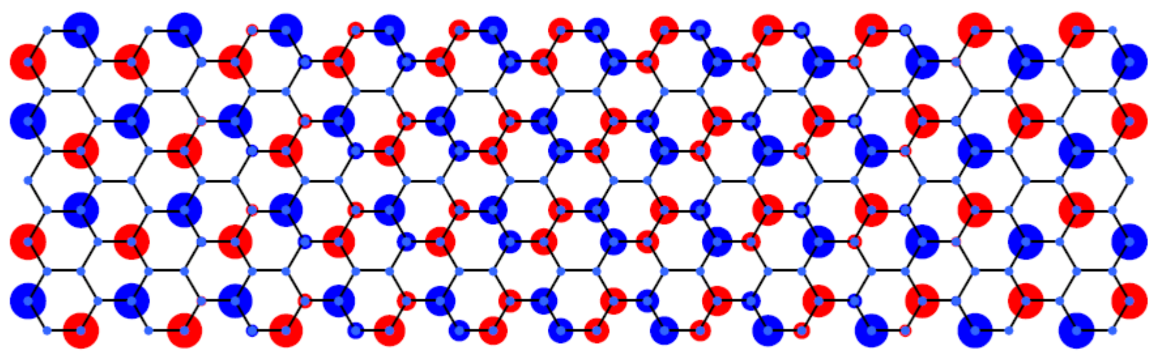


HOMO

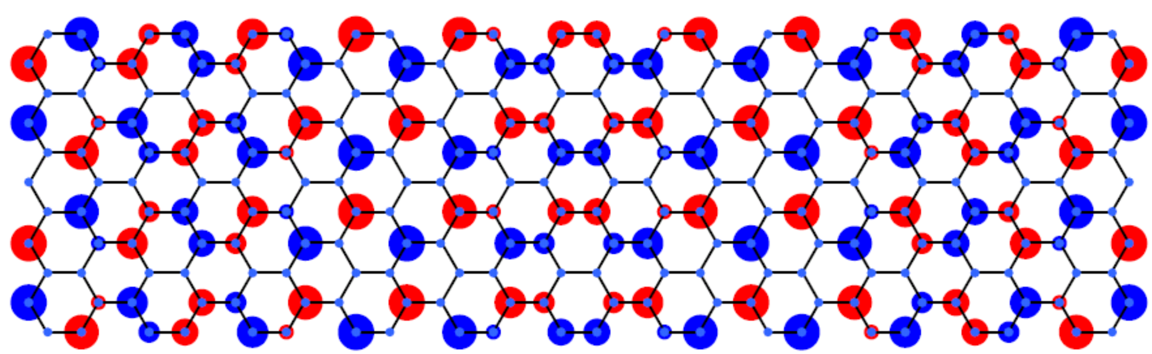


HOMO −1

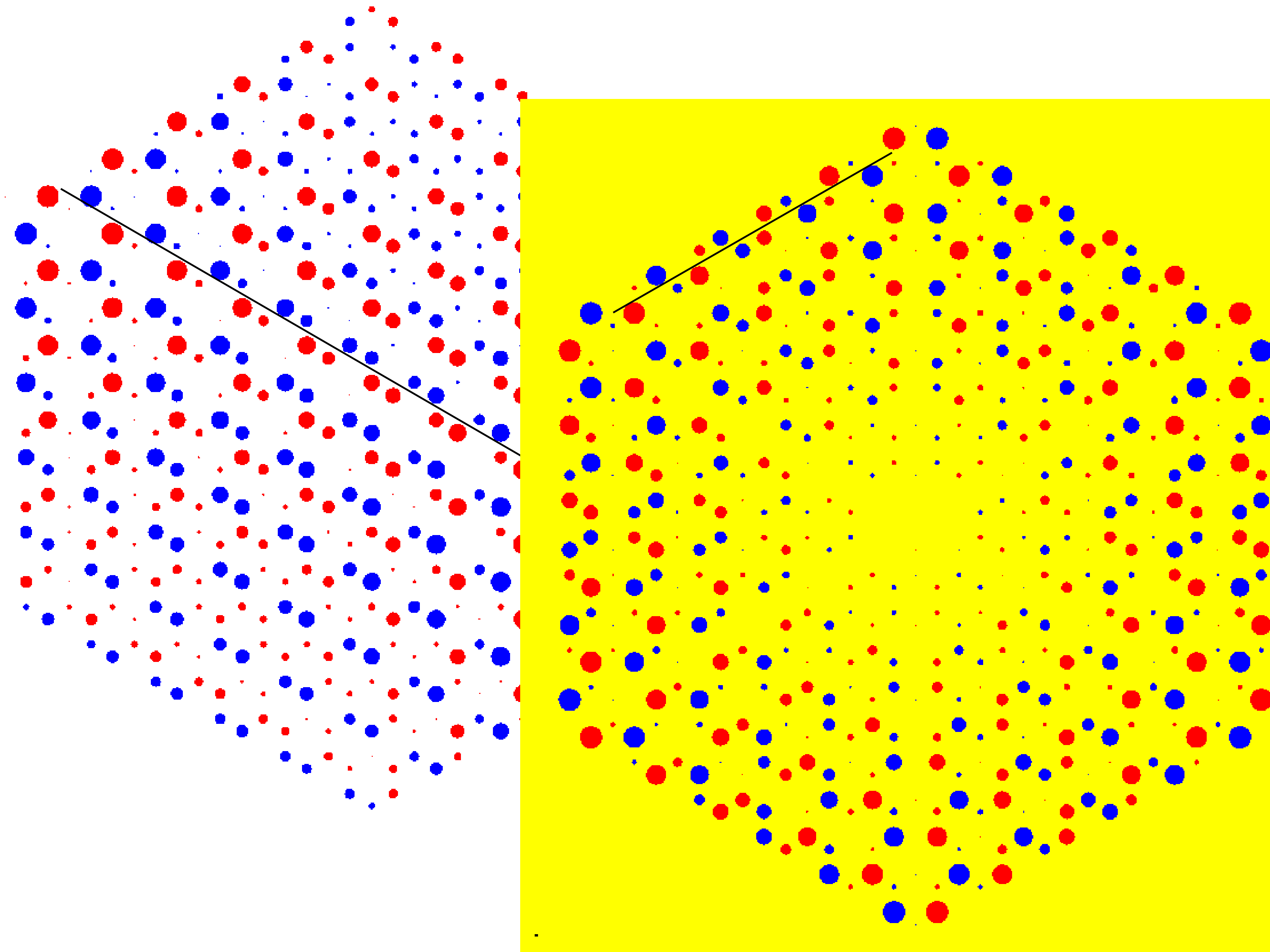
3n+2 benzene rings wide



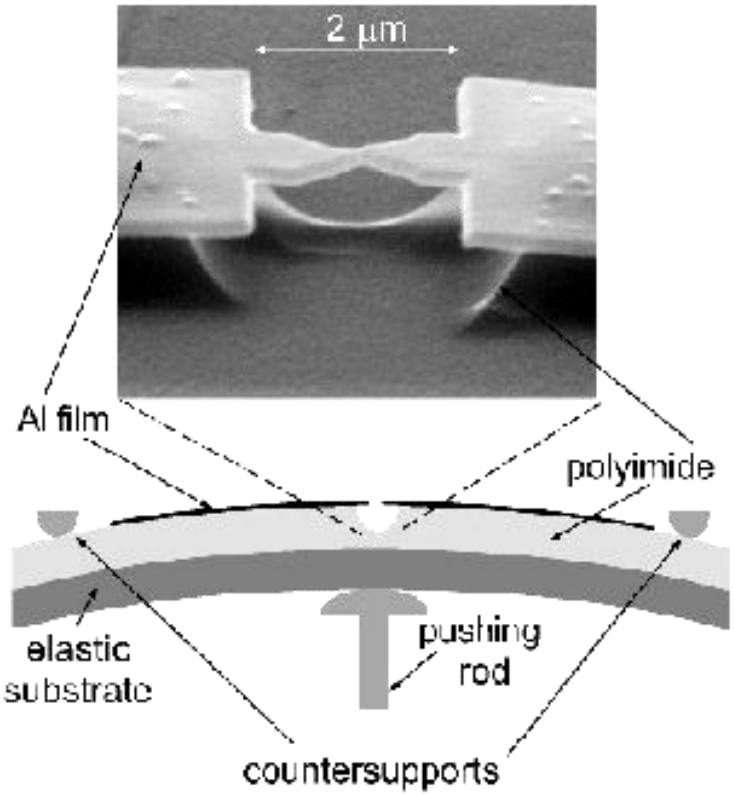
HOMO

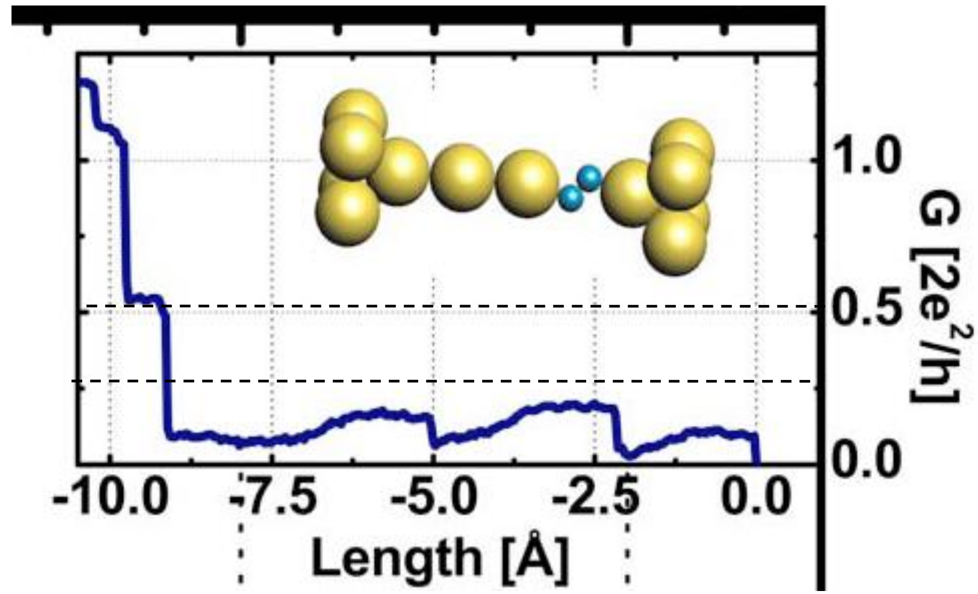


HOMO −1



Experimental molecular electronics



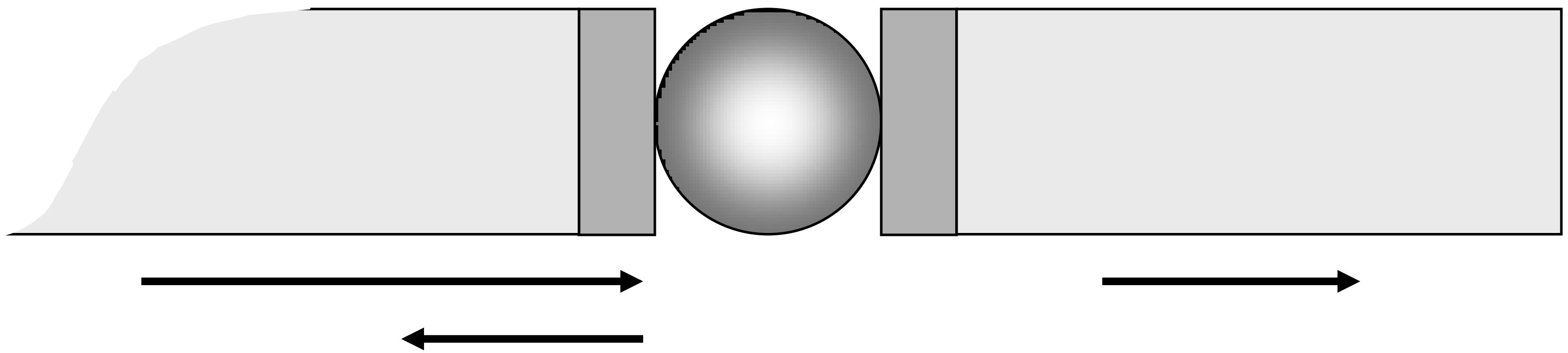


Csonka, Halbritter, Mihály PRB 73, 075405 (2006)

Break junction technique

Reed, Zhou, Muller et al., Science 278, 252 (1997); Reichert, Ochs, Beckman et al., PRL, 88, 176804 (2002)

Scattering wave function obtained from a finite model system: The source-sink potential approach



$$\Psi_L = \varphi^+ + r\,\varphi^-$$

$$\Psi_R = t\,\varphi^+$$

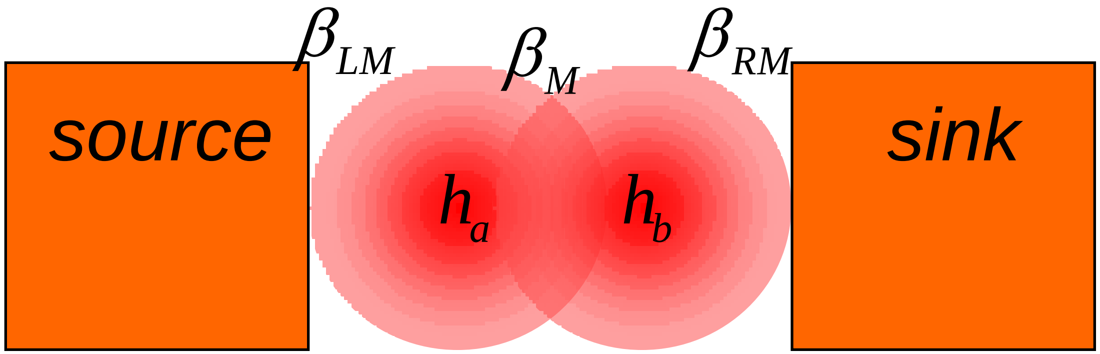
$$\phi_L = \left(\varphi^+ + r\varphi^-\right) f$$

$$\left(-\frac{1}{2}\Delta + v + \Sigma\right)\phi_L = \varepsilon\phi_L$$

$$\frac{\Delta\phi_L}{2\phi_L} - v + \varepsilon = \Sigma(r,\varepsilon)$$

Goyer, Ernzerhof, Zhuang, JCP, 126,144104 (2007).

The source-sink potential approach in tight binding



$$H^{\text{eff}}(r) = \begin{pmatrix} -\beta_{LM}\sigma_L & \beta_M \\ \beta_M & -\beta_{RM}\sigma_R \end{pmatrix}$$

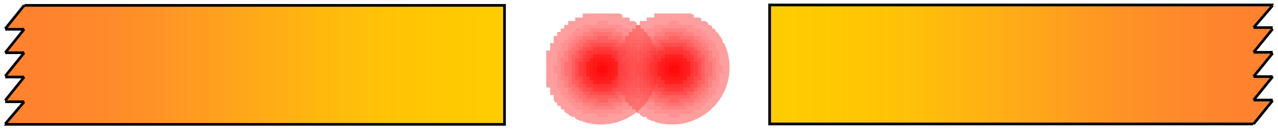
$$\begin{aligned} \sigma_L &= i\frac{1+r}{1-r} \\ \sigma_R &= -i \end{aligned}$$

Source and sink potential

Ernzerhof, JCP 126,144104 (2007).

MED containing a diatomic

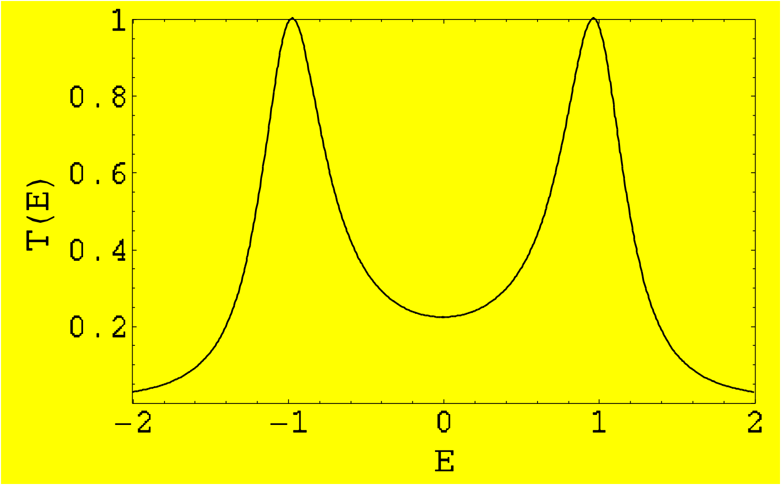
$$H^{\text{eff}}(r)C_M = EC_M \quad \Rightarrow \quad \det\left(H^{\text{eff}}(r) - E\right) = 0$$



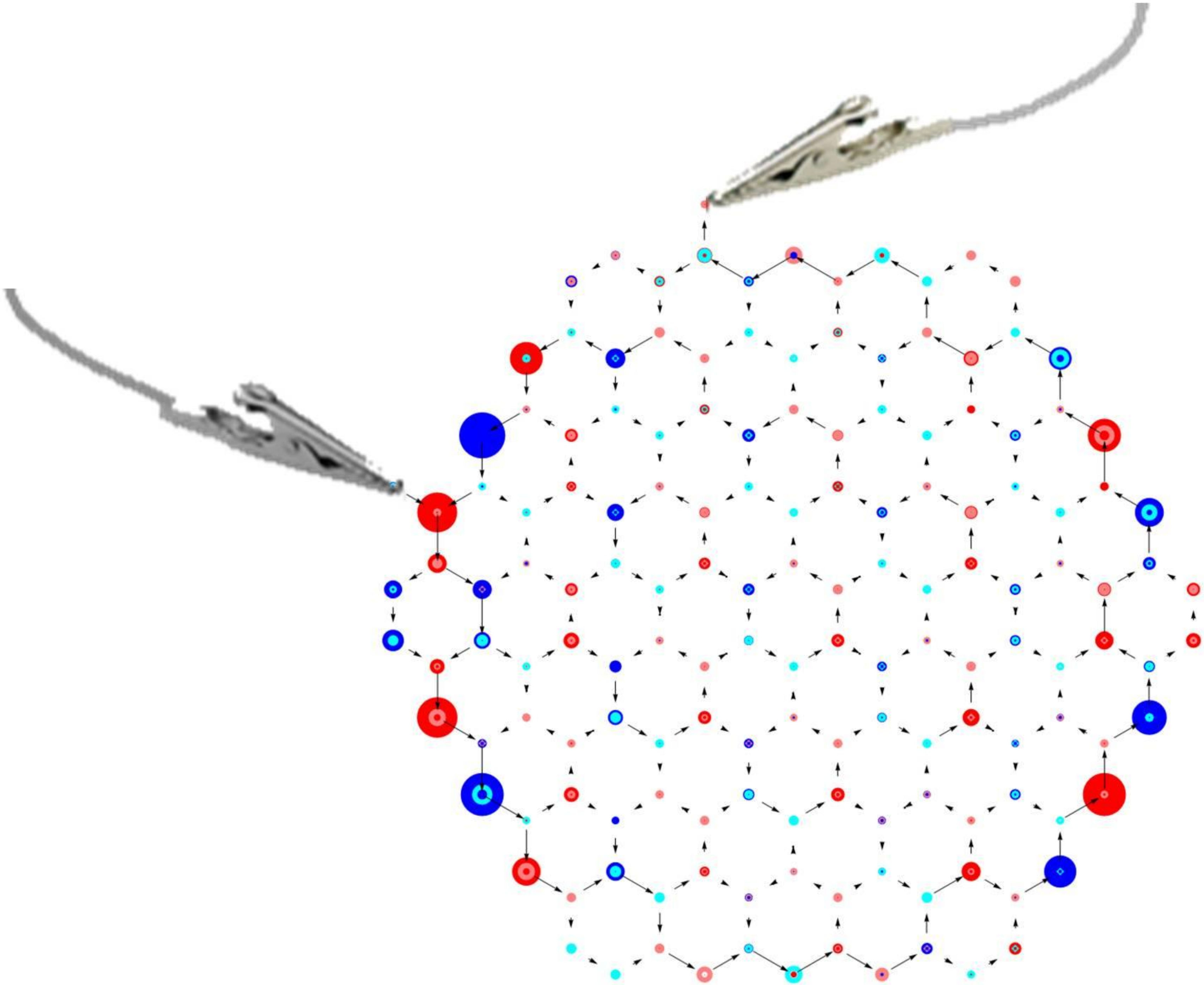
$$r(E) = \frac{(\tilde{E}_1 - E)}{(E_1 - E)} \frac{(\tilde{E}_2 - E)}{(E_2 - E)}$$

$$= \frac{\left(\sqrt{\beta_M^2 - \tilde{\beta}^2} - E\right)\left(-\sqrt{\beta_M^2 - \tilde{\beta}^2} - E\right)}{\left(-\beta_M + i\tilde{\beta} - E\right)\left(\beta_M + i\tilde{\beta} - E\right)}$$

$$\mathrm{T}(E) = |t(E)|^2 = 1 - |r(E)|^2$$



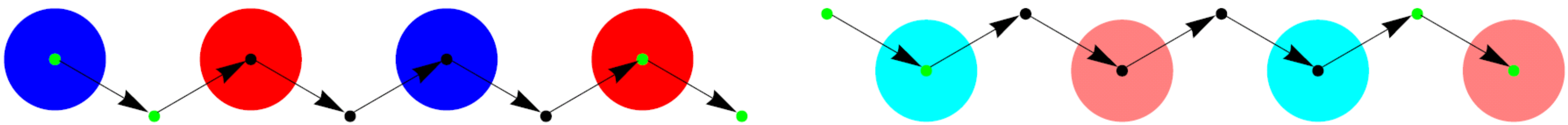
Ernzerhof, JCP 126,144104 (2007);
Rocheleau, Ernzerhof, JCP, 130 (2009).



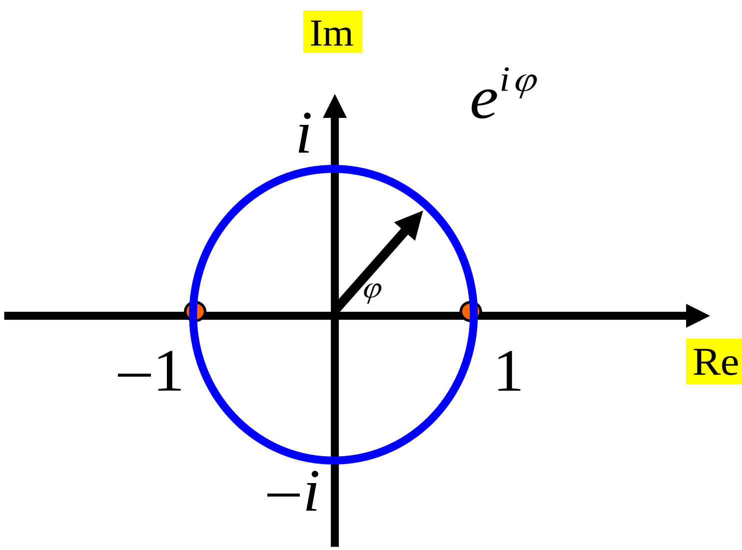
Linear homogeneous conductor

$$H^{\text{eff}} C = EC$$

$$= 0$$



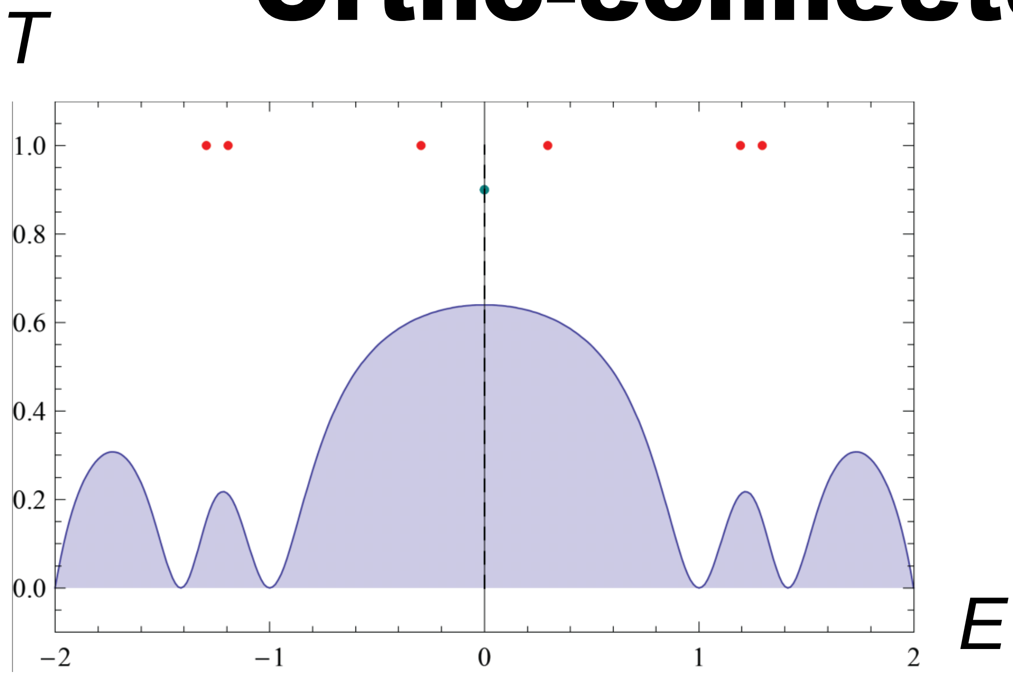
$$\begin{pmatrix} i\frac{1+r}{1-r} & t & 0 & 0 & 0 & \cdots & & & & \\ t & 0 & t & 0 & 0 & \cdots & & & & \\ 0 & t & 0 & t & 0 & \cdots & & & & \\ \vdots & \vdots & & & & & & & \vdots & \vdots \\ & & & & \cdots & 0 & t & 0 & t & 0 \\ & & & & \cdots & 0 & 0 & t & 0 & t \\ & & & & \cdots & 0 & 0 & 0 & t & -i \end{pmatrix} = H^{\text{eff}}$$

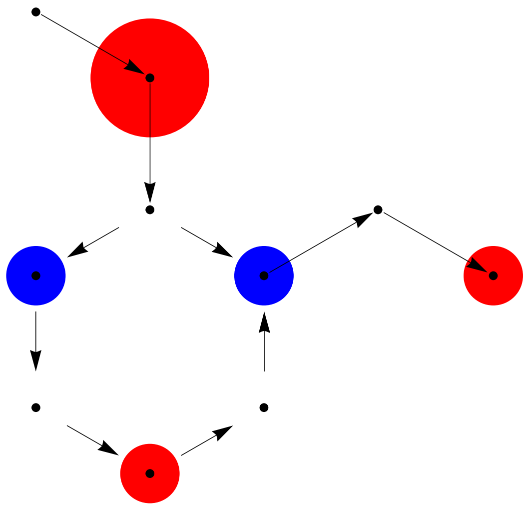


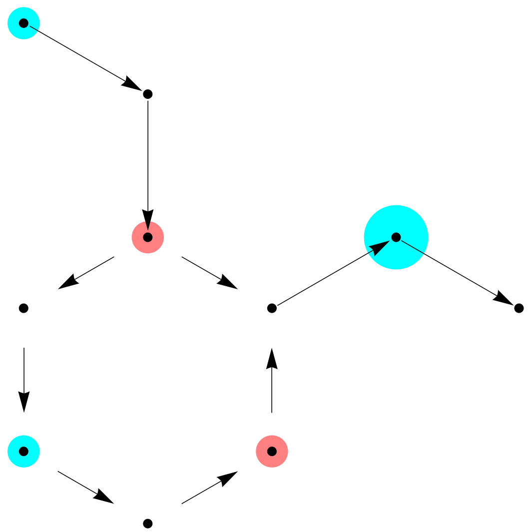
SSP and graph theory

Pickup, Fowler, CPL, 459, 198 (2008);
Fowler, Pickup, Todorova, CPL, 465, 142 (2008);
Fowler, Pickup, Todorova, Pisanski, JCP, 130, 174708 (2009);
Fowler, Pickup, Todorova, Myrvold, JCP, 131, 044104 (2009);
Fowler, Pickup, Todorova, Myrvold, JCP, 131, 244110 (2009).

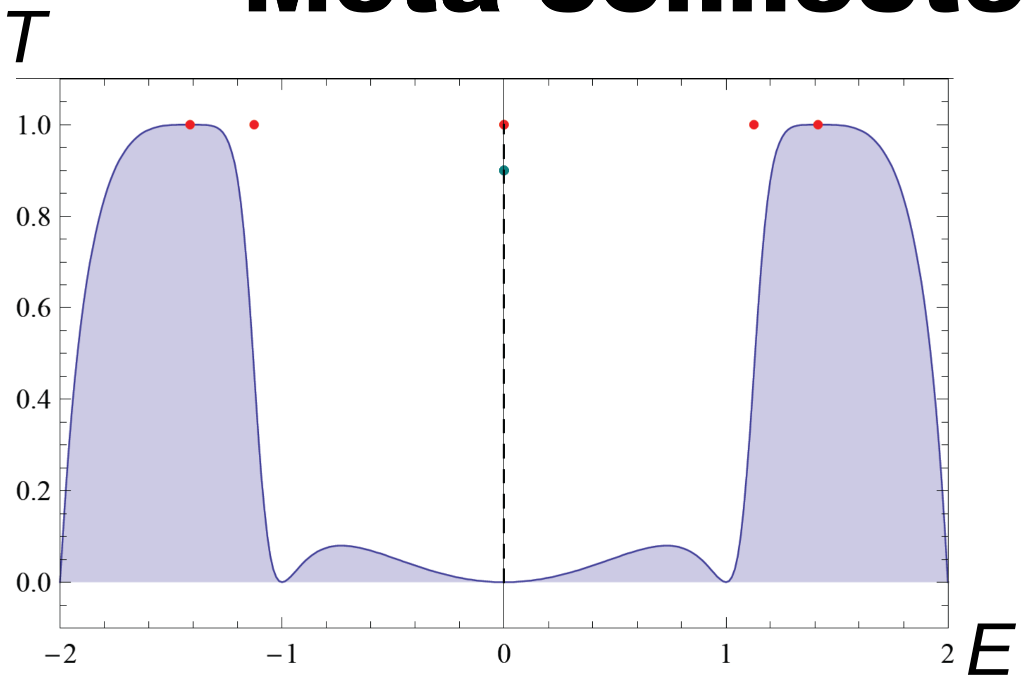
Ortho-connected benzene

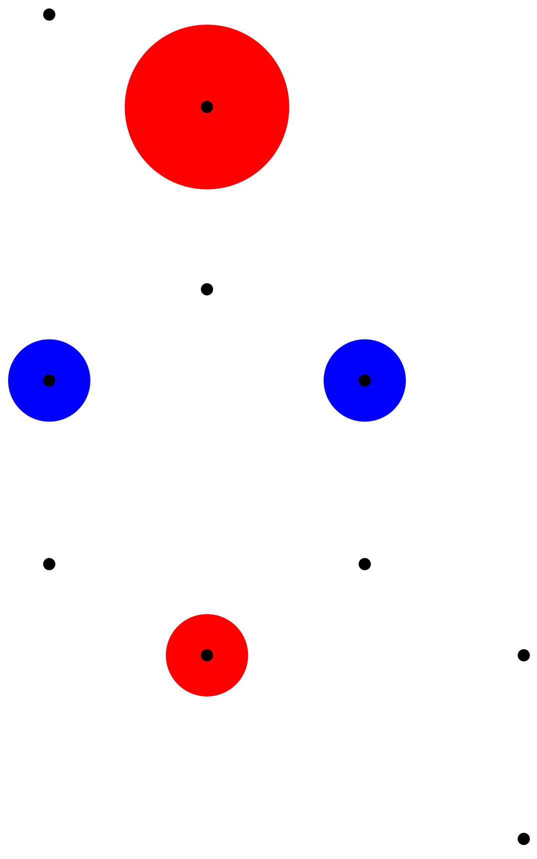






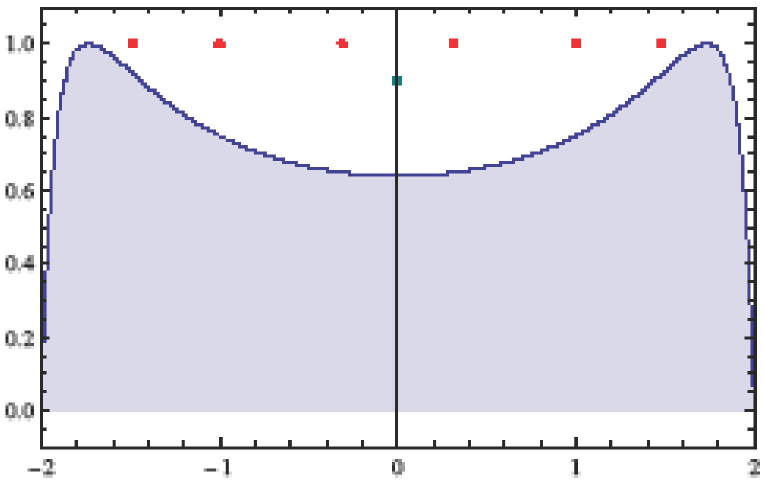
Meta-connected benzene



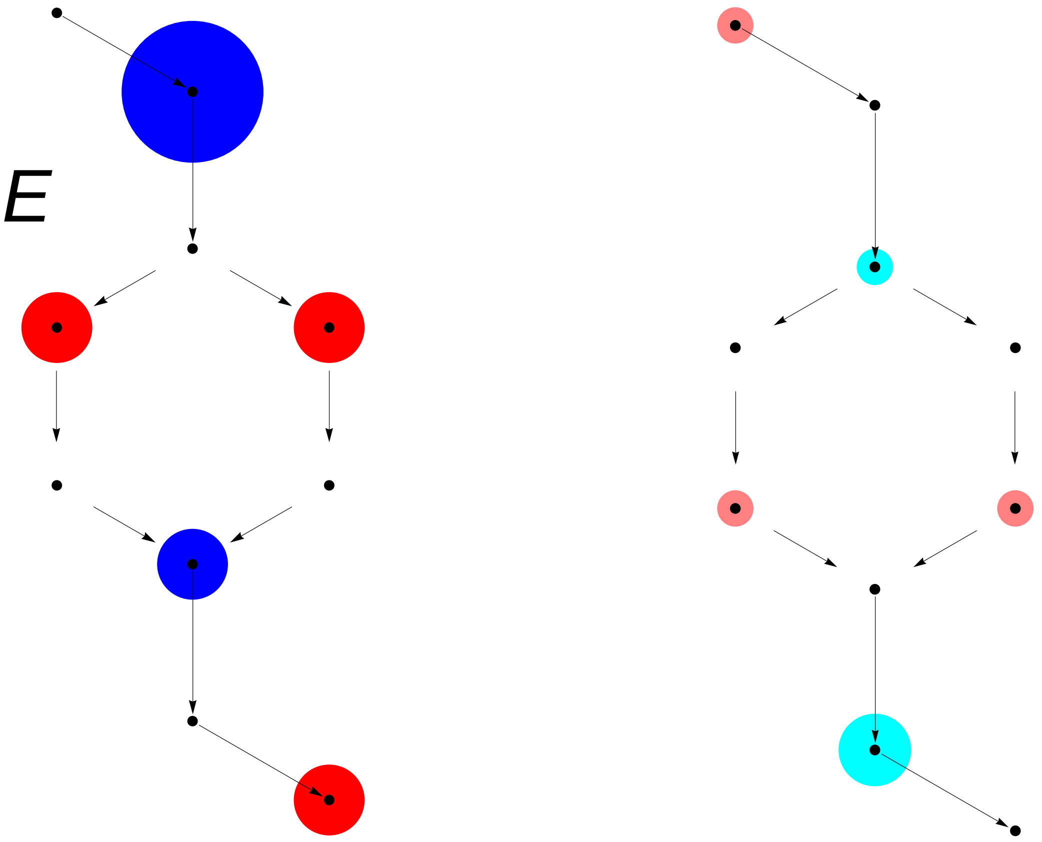


Para-connected benzene

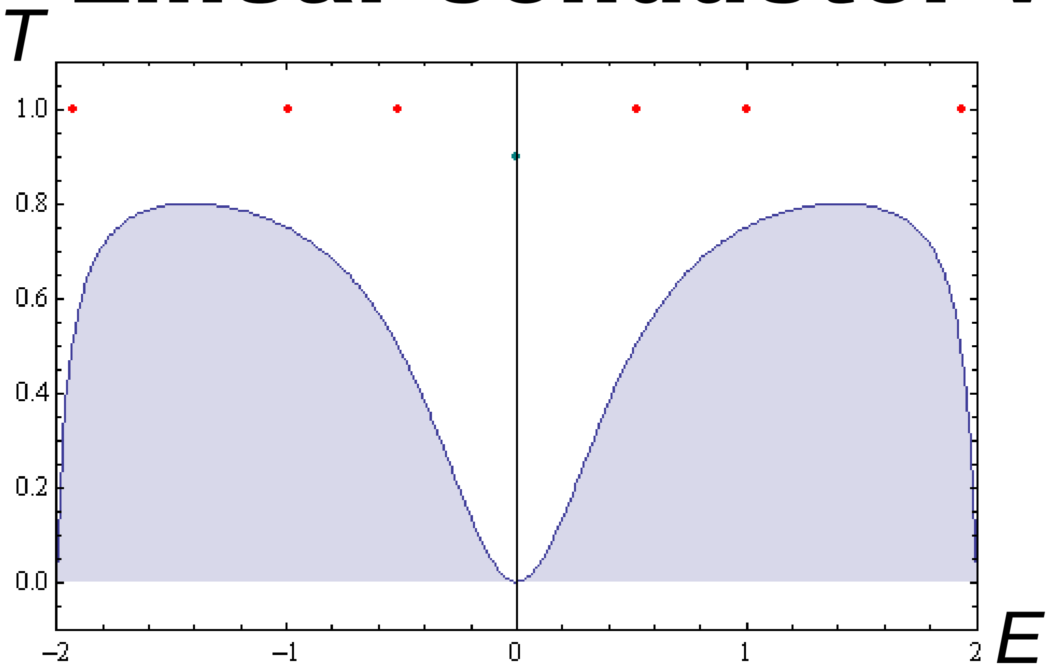
T

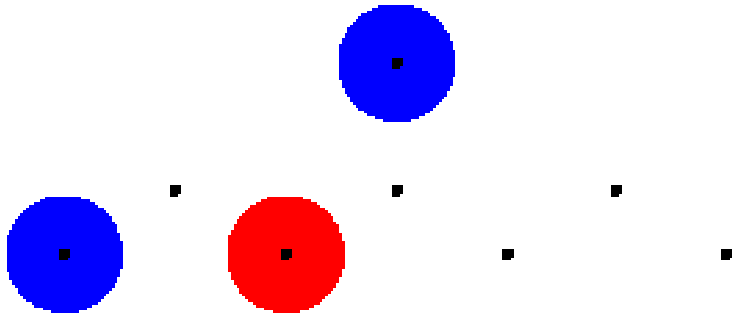


E

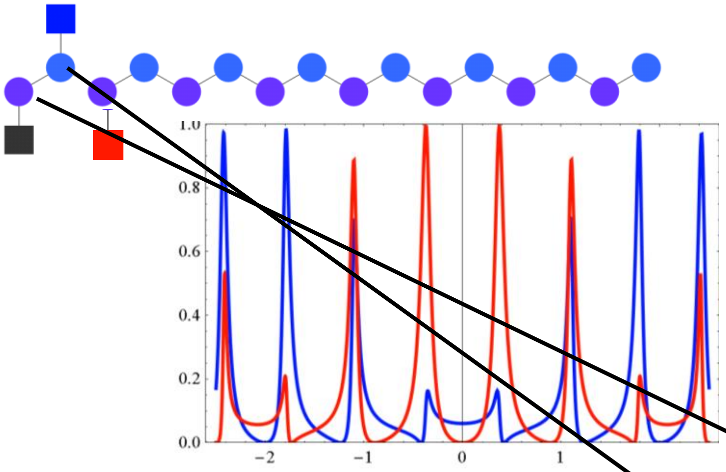


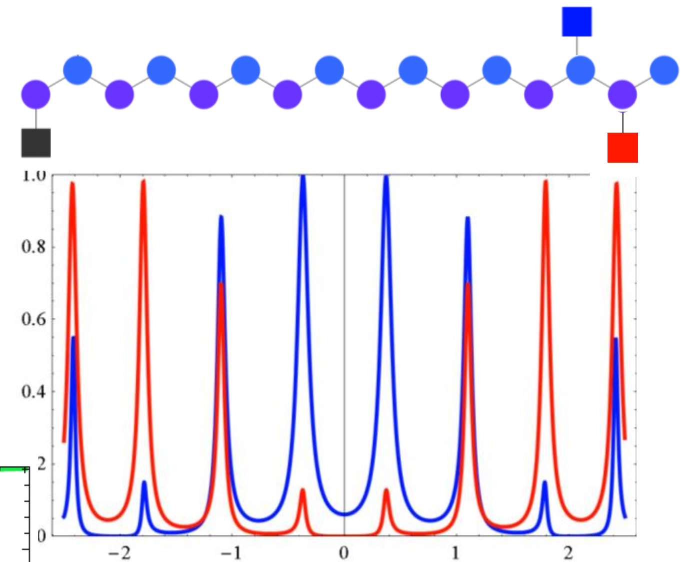
Linear conductor with side chain



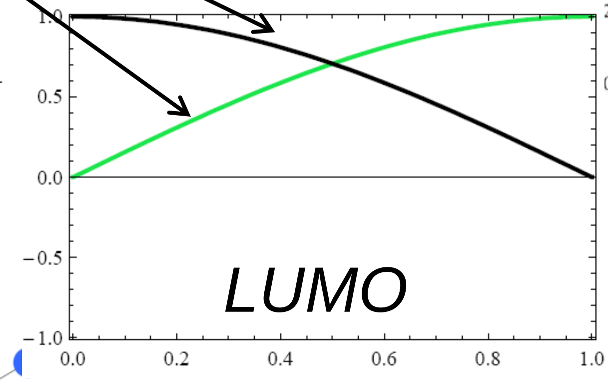


Transmission through linear molecules

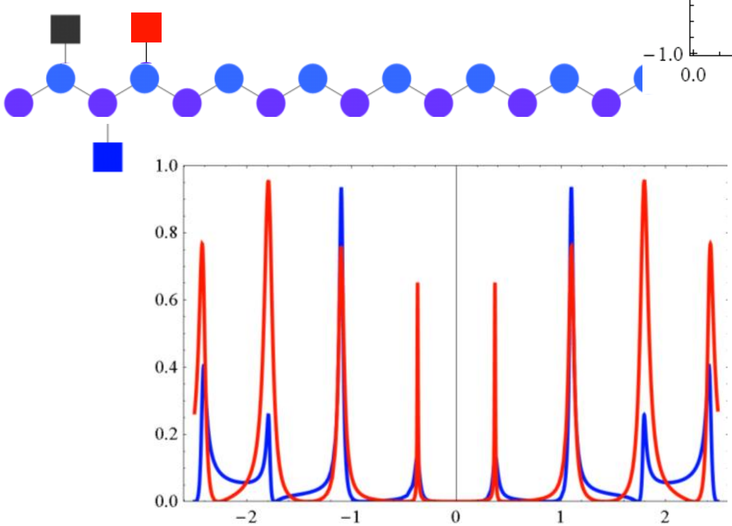


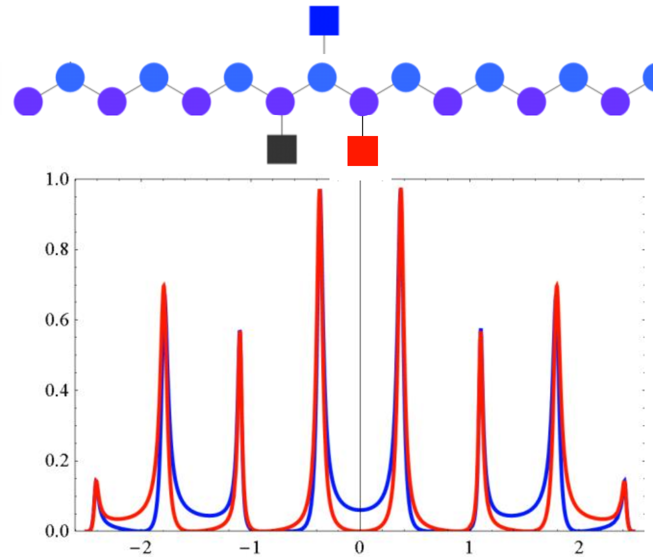


$$T_{\rho_L \rho_R}(E) = \frac{4\tilde{\beta}_{LM}\tilde{\beta}_{RM}\rho_L\rho_R}{(E - E_0)^2 + (\tilde{\beta}_{LM}\rho_L + \tilde{\beta}_{RM}\rho_R)^2}$$

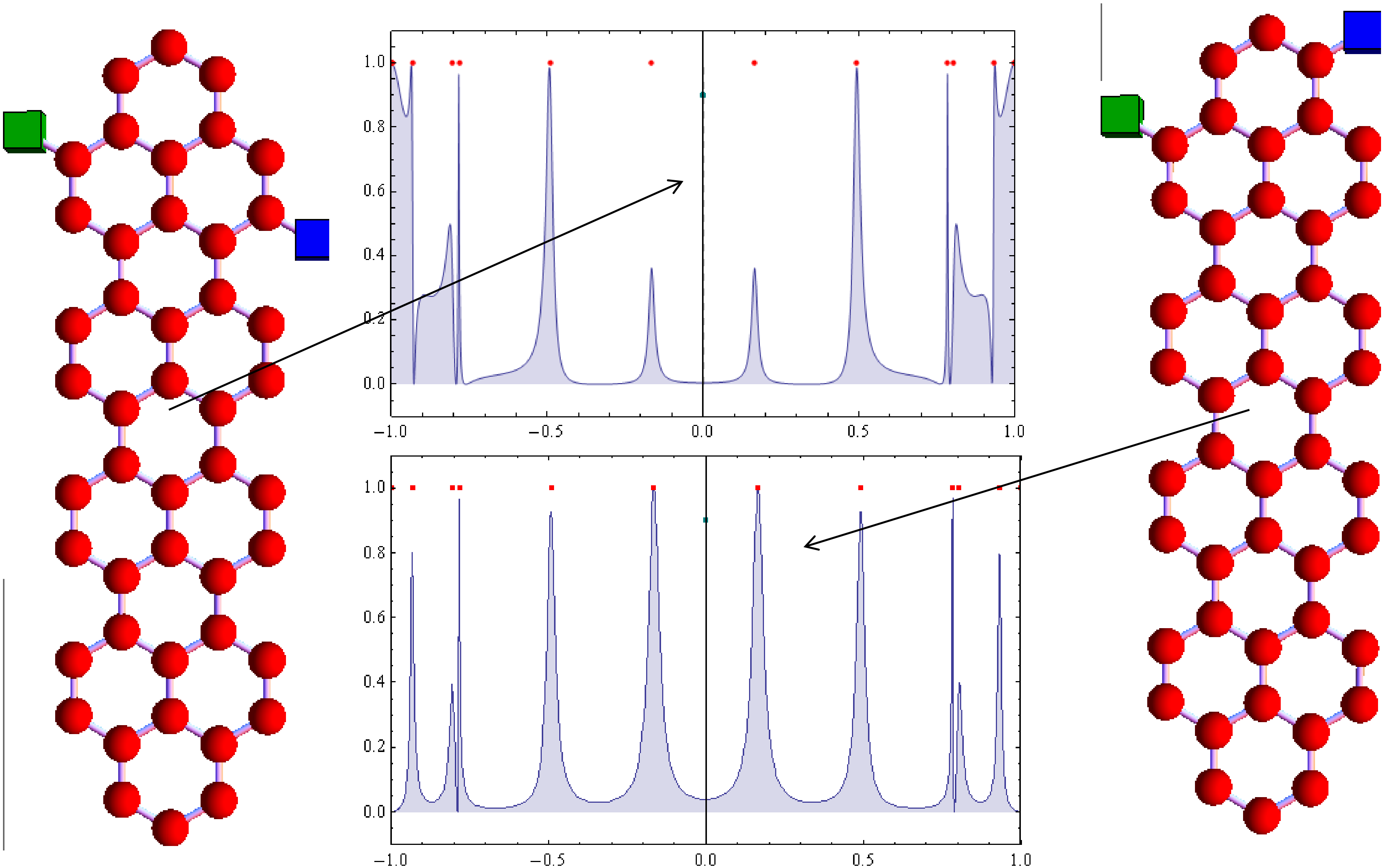


Rocheleau, Ernzerhof, JCP, 130, 184704 2009





Transmission through ribbons



2D Dirac equation

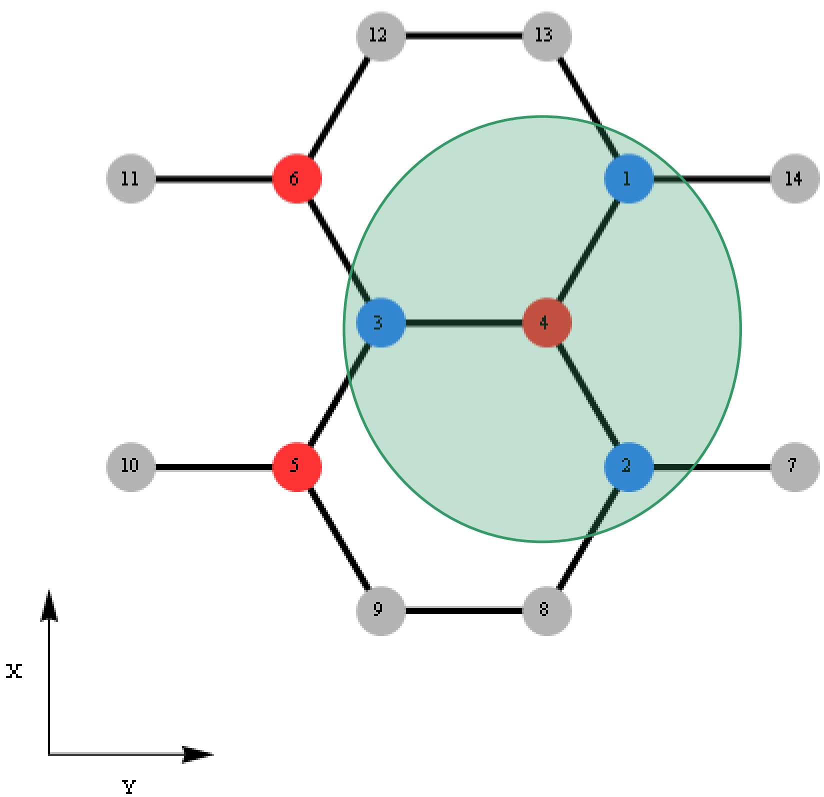
$$v_F(\sigma_x p_x + \sigma_y p_y)\psi = \varepsilon\psi$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \psi = \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix}$$

$$v_F(\sigma_x p_x + \sigma_y p_y)\psi = -v_F \begin{pmatrix} i\dfrac{d\psi_b}{dx} + \dfrac{d\psi_b}{dy} \\ i\dfrac{d\psi_a}{dx} - \dfrac{d\psi_a}{dy} \end{pmatrix}$$

Local solution to Schrödinger's equation

sub lattices are decoupled for E=0

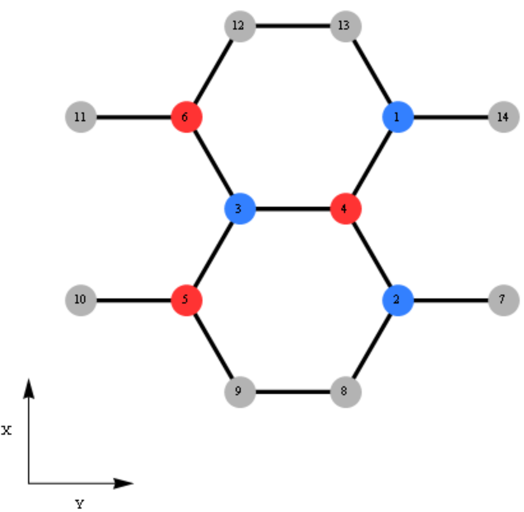


$$\begin{pmatrix} & & \\ & H_{ij} & \\ & & \end{pmatrix} \begin{pmatrix} \\ c_i \\ \\ \end{pmatrix} = 0$$

$$\Rightarrow c_1 + c_2 + c_3 = 0$$

$$\Rightarrow \begin{array}{l} c_1 = 1 \\ c_2 = e^{\frac{2\pi}{3}i} \\ c_3 = e^{-\frac{2\pi}{3}i} \end{array}$$

Gauge transformation of the Hückel matrix

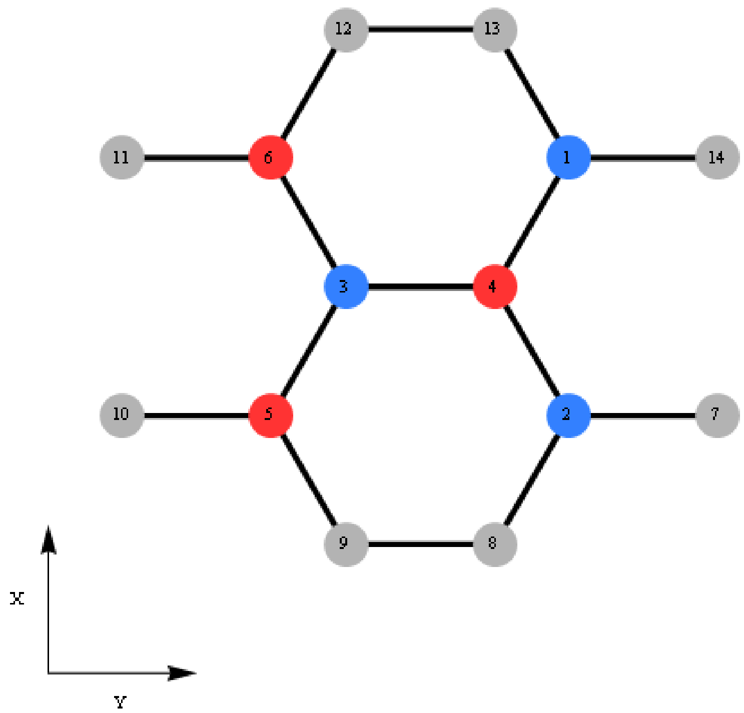


$$\begin{pmatrix} e^{i\frac{2\pi}{3}} & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & e^{-i\frac{2\pi}{3}} & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{-i\frac{2\pi}{3}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & e^{i\frac{2\pi}{3}} \end{pmatrix}$$

$$\begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 1 \\ 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \longrightarrow \begin{pmatrix} 0 & 0 & 0 & e^{\frac{-i2\pi}{3}} & 0 & 0 \\ 0 & 0 & 0 & e^{\frac{i2\pi}{3}} & 0 & 0 \\ 0 & 0 & 0 & 1 & e^{\frac{-i2\pi}{3}} & e^{\frac{i2\pi}{3}} \\ e^{\frac{i2\pi}{3}} & e^{\frac{-i2\pi}{3}} & 1 & 0 & 0 & 0 \\ 0 & 0 & e^{\frac{i2\pi}{3}} & 0 & 0 & 0 \\ 0 & 0 & e^{\frac{-i2\pi}{3}} & 0 & 0 & 0 \end{pmatrix}$$

2D Dirac equation on graphene lattice

$$\frac{d}{dx}\psi(3) = -sin(\frac{2\pi}{3})c5 + sin(\frac{2\pi}{3})c6$$
$$\frac{d}{dy}\psi(3) = c4 + cos(\frac{2\pi}{3})c5 + cos(\frac{2\pi}{3})c6$$



$$\begin{pmatrix} 0 & 0 & 0 & e^{\frac{-i2\pi}{3}} & 0 & 0 \\ 0 & 0 & 0 & e^{\frac{i2\pi}{3}} & 0 & 0 \\ 0 & 0 & 0 & 1 & e^{\frac{-i2\pi}{3}} & e^{\frac{i2\pi}{3}} \\ e^{\frac{i2\pi}{3}} & e^{\frac{-i2\pi}{3}} & 1 & 0 & 0 & 0 \\ 0 & 0 & e^{\frac{i2\pi}{3}} & 0 & 0 & 0 \\ 0 & 0 & e^{\frac{-i2\pi}{3}} & 0 & 0 & 0 \end{pmatrix}$$