The University Of Sheffield.

Why should chemists care about graph theory?

(New applications of graph theory to molecular conductors)

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£££ Thanks to The Royal Society and the University of Sheffield

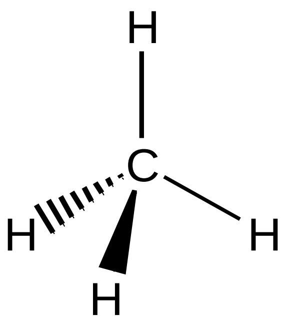
Carbon – the natural element for graph theory

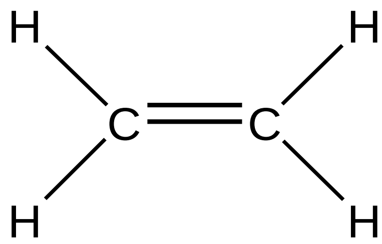
Molecular conductors – a new playground for graph theory

Carbon

Midway between the electropositive metals
and the electronegative halogens

Valency of four, with versatile bonding types and geometries

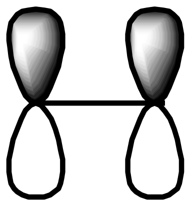


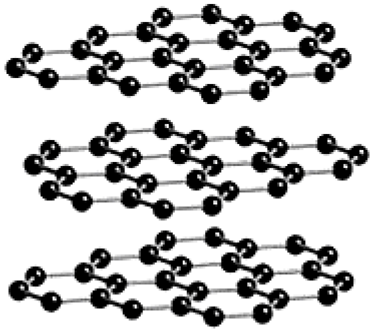


109^o 120^o 180^o

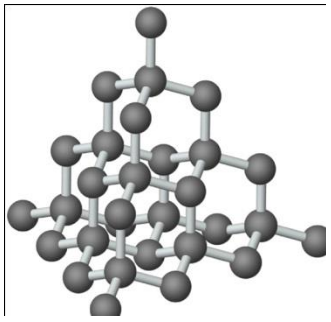
Ability to bond to itself in chains, rings and cages

(small size ⇒good orbital overlap)

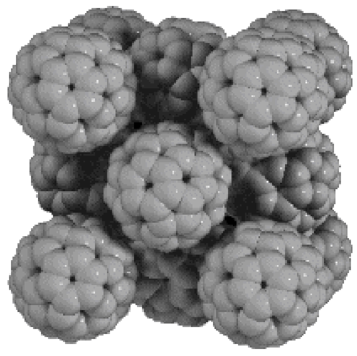




Graphite



Diamond

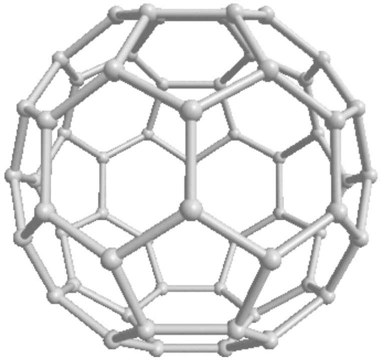


Fullerite

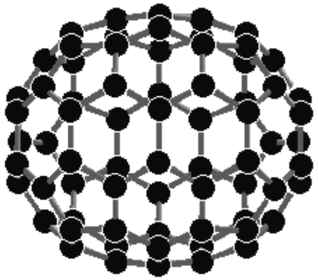
Fullerite (Krätschmer et al, 1990)

A solid made up of C_{60} soccer-ball molecules (fullerenes).

Fullerenes (Kroto et al. 1985)

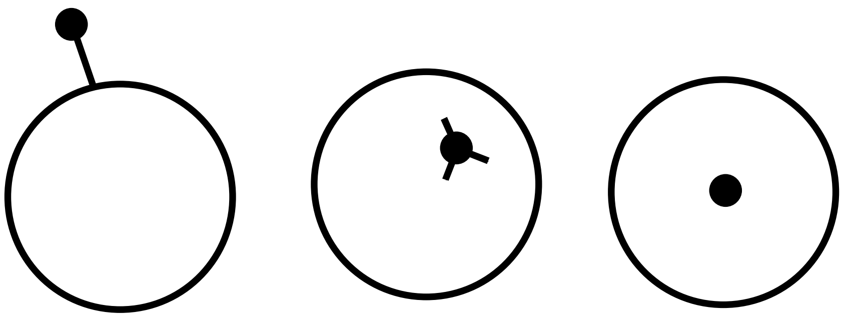


C_{60}



C_{70}

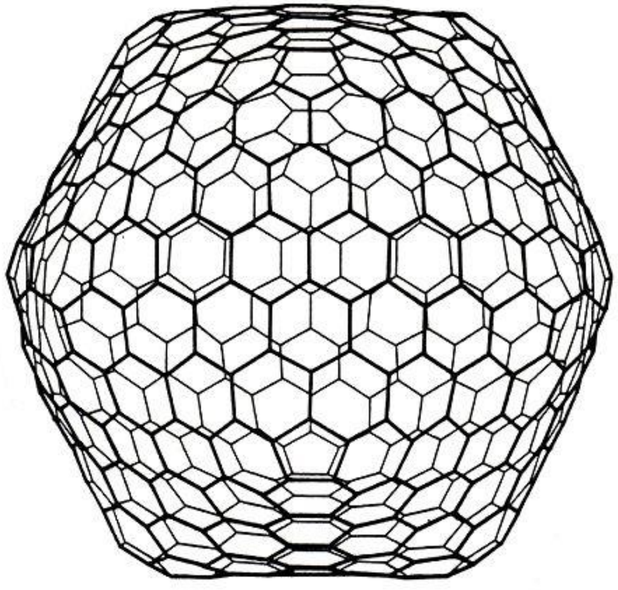
Multiple isomers   New chemistries.



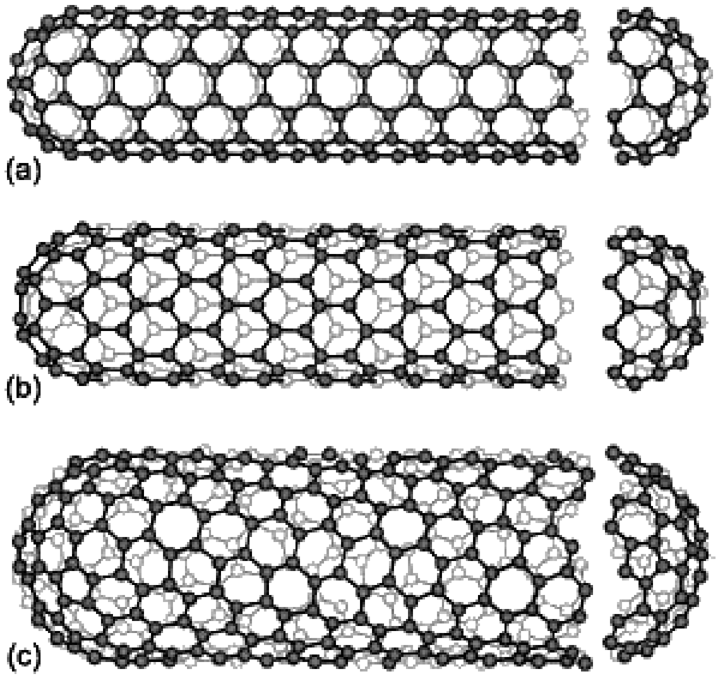
Exohedral   Heterofullerene   Endohedral


Follow
Heart of the City
for
Crucible
Lyceum
Millennium
Galleries
Bramall Lane

Giant fullerenes?

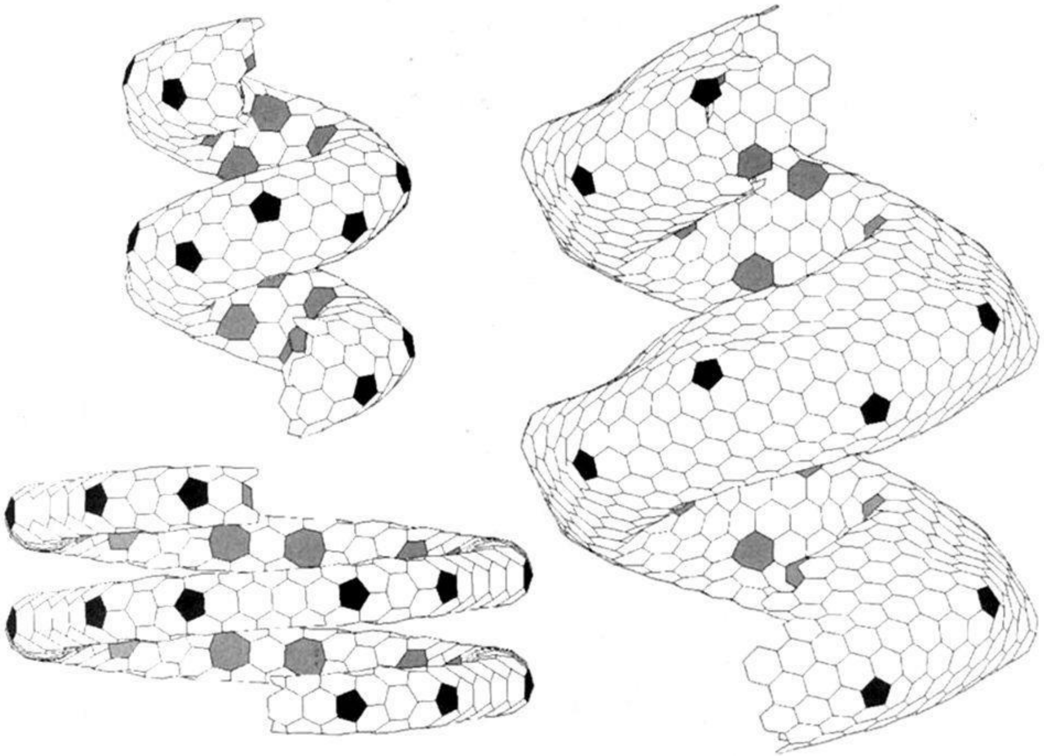


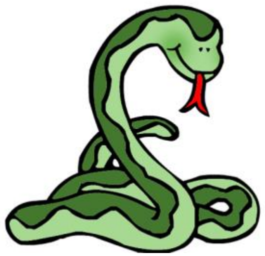
Nanotubes (Iijima, 1991)



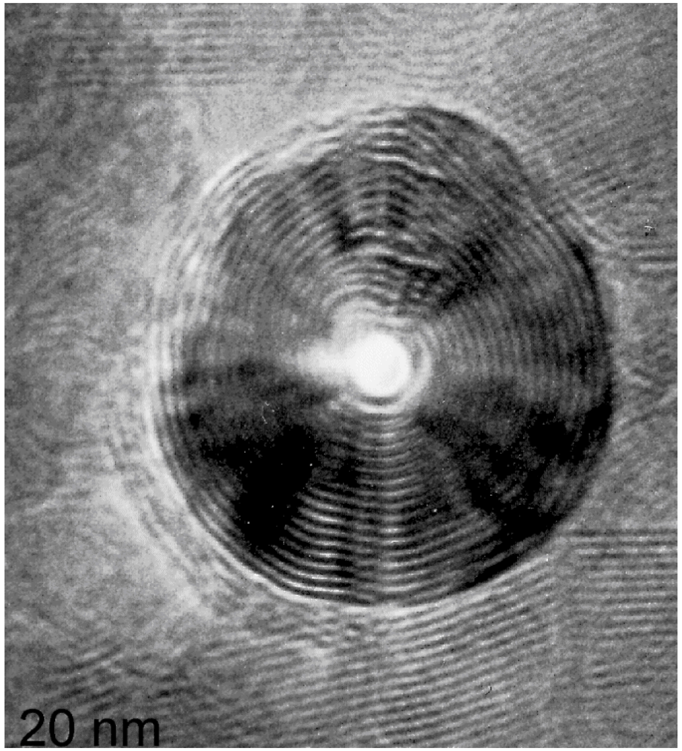
Metallic/insulating depending on radius and twist

Carbon Snakes (Ihara *et al*., 1993)

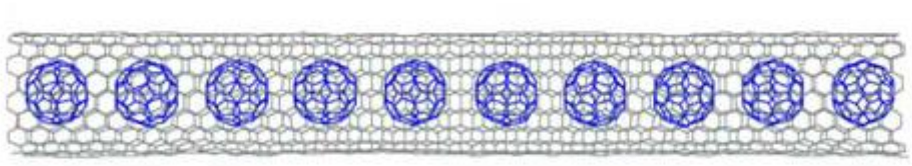




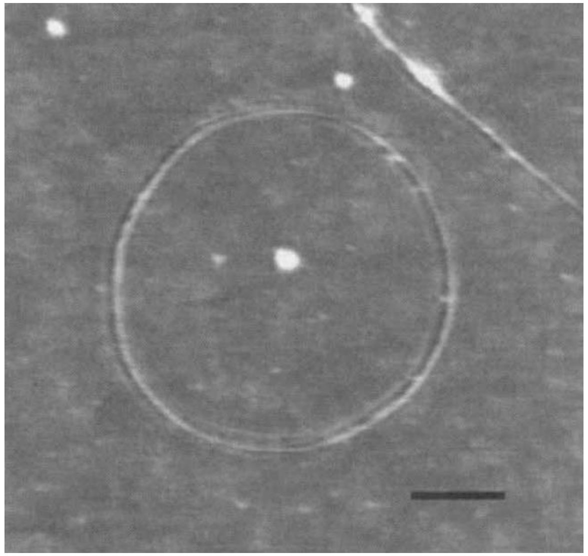
Carbon Onions (Ugarte, 1992)

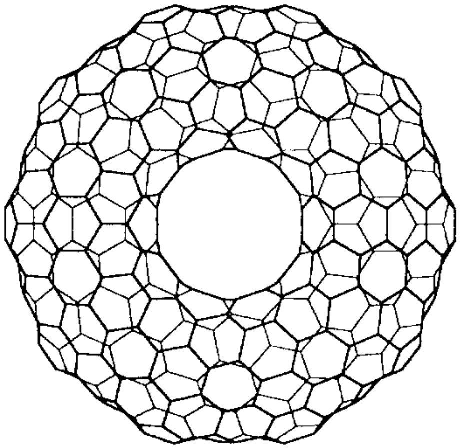


Carbon Peapods (Smith *et al*., 1998)



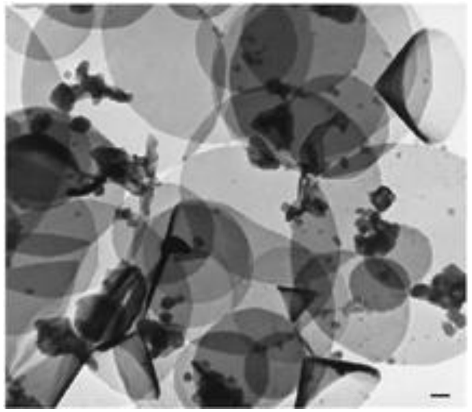
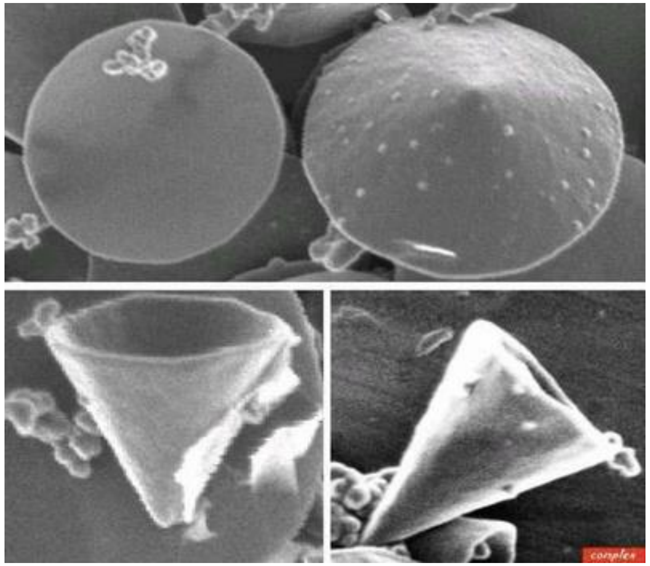
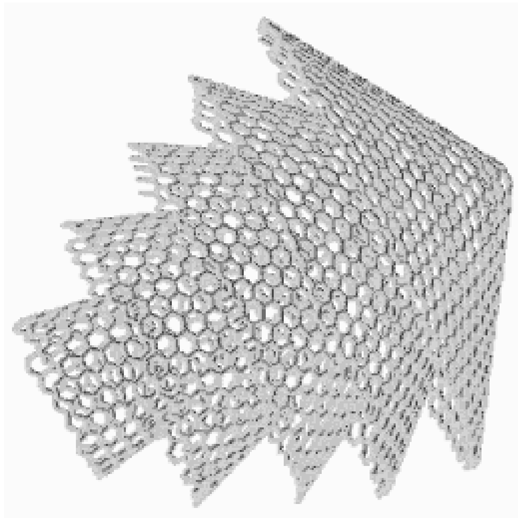
Carbon tori (Liu *et al*, 1997)





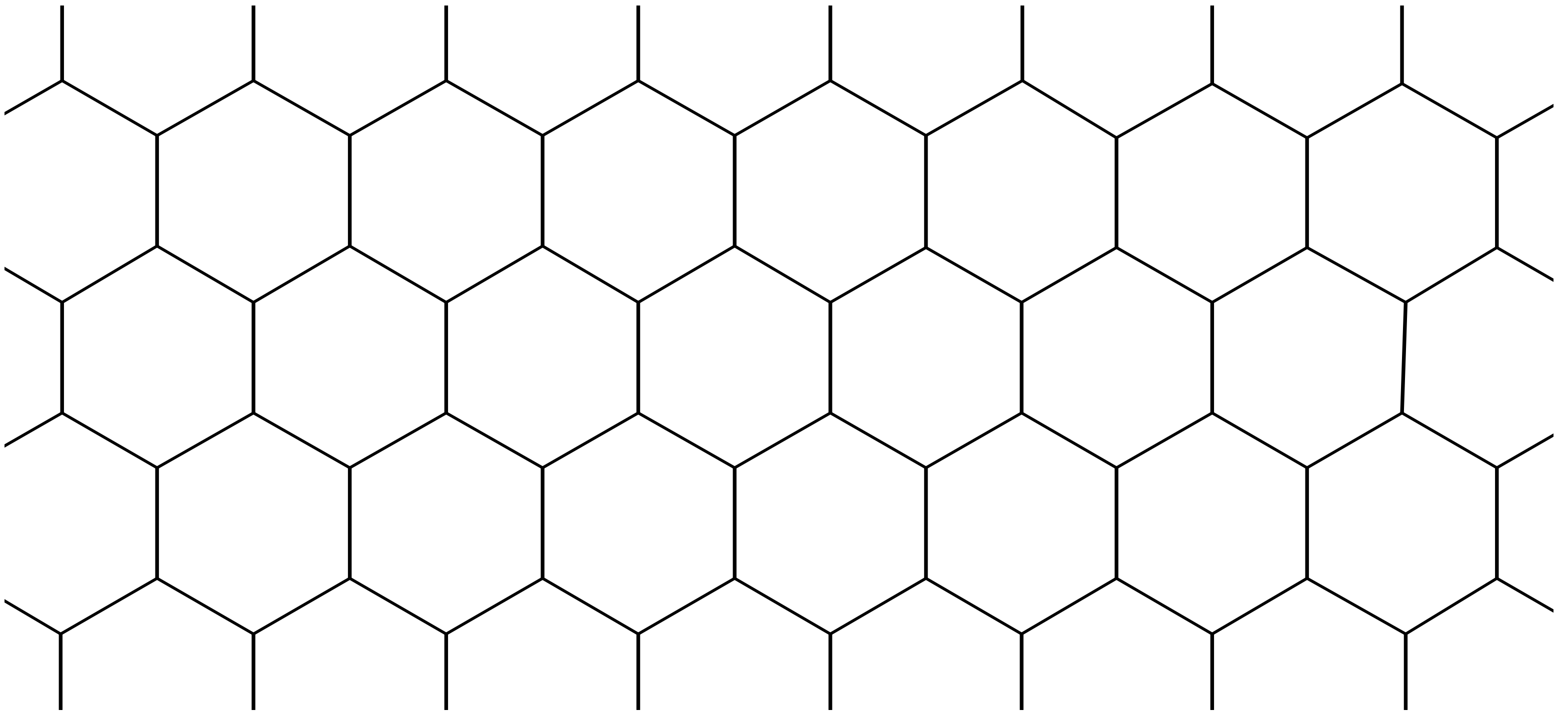
C_{360}
(Itoh, 1993)

Nanocones (Ebbesen, 1997)

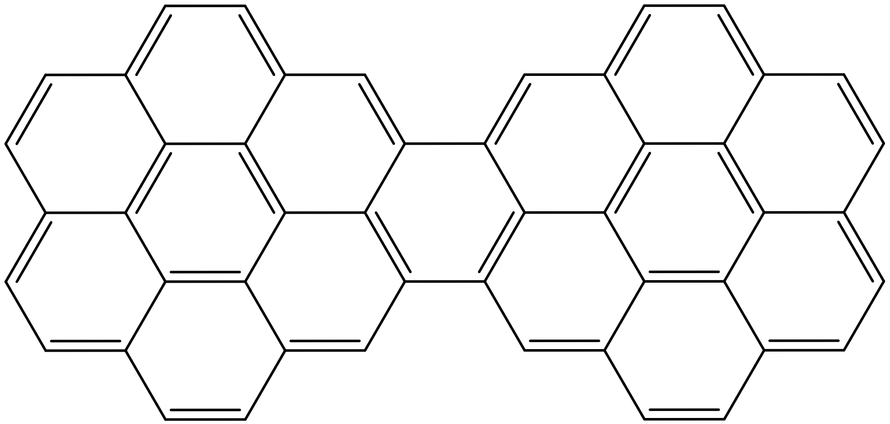
Eight classes of positive-curvature nanocones
(Klein, Balaban, 2006)

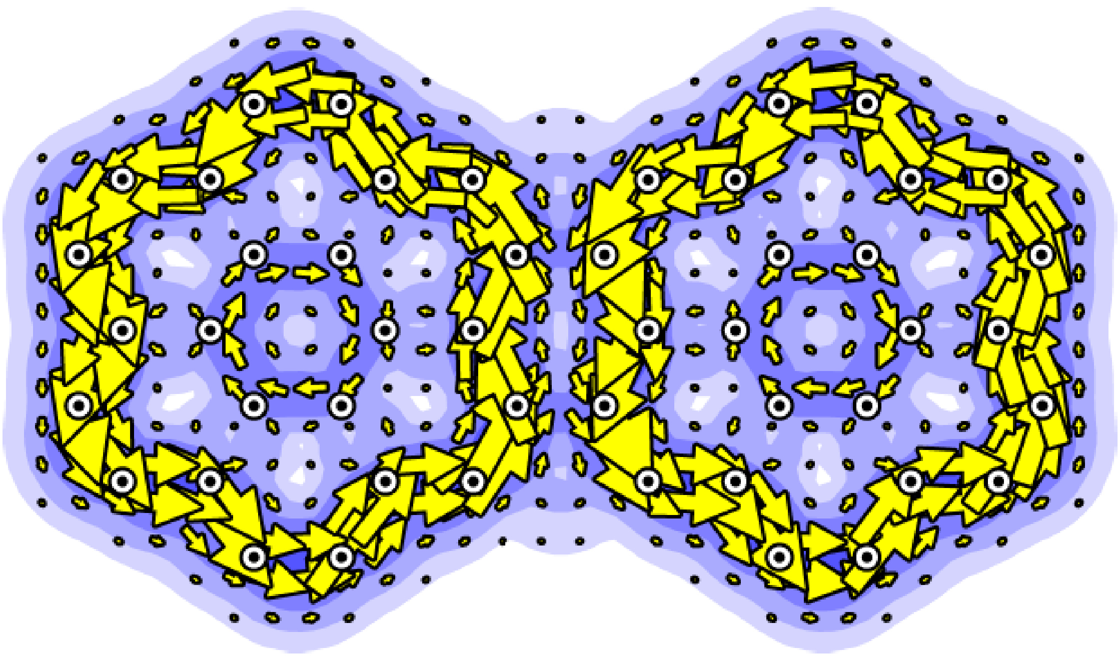
Graphene (Geim et al, 2004)



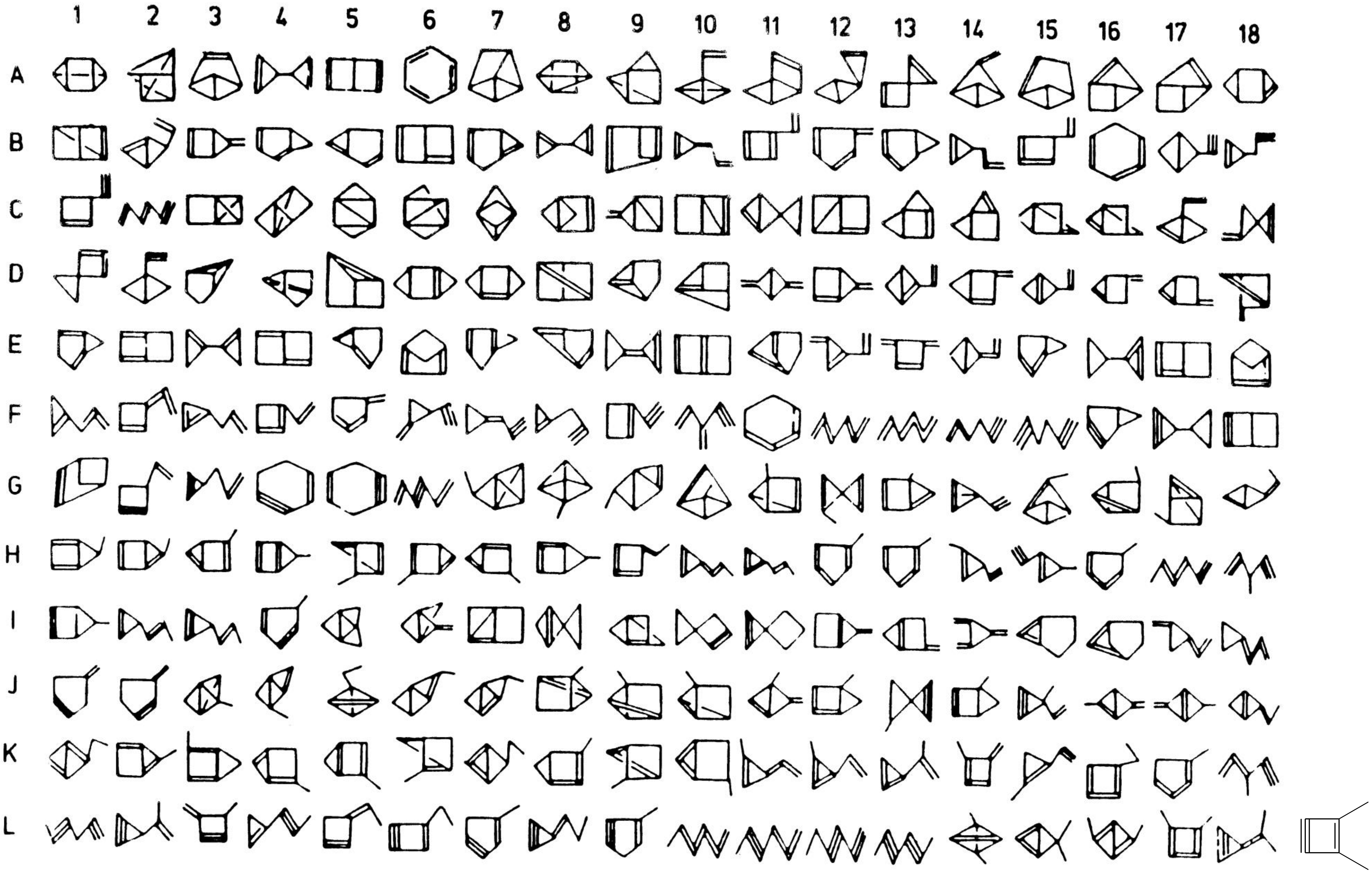
Single-sheet graphite from the ultimate in low-tech synthesis

Plus, the millions of known organic compounds





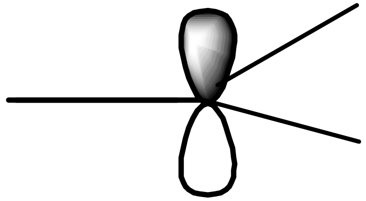
Dicoronylene

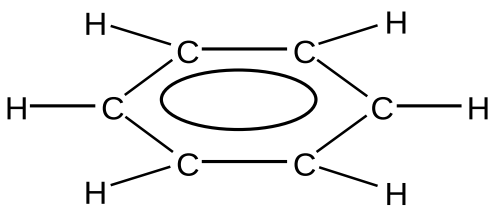


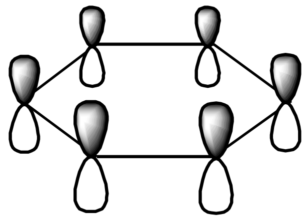
The 217 isomers of benzene – C_6H_6

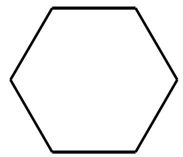
(H. Bock, Angew. Chem. Int. Ed. Engl. ***28****, 1627 (1989).)*

The traditional use of spectral graph theory in chemistry (Hückel Theory)









All-electron Schrödinger equation

Hückel model

Graph

$\hat{H}\,\Psi = E\,\Psi$ after many approximations becomes $\boldsymbol{A}x = \lambda x$

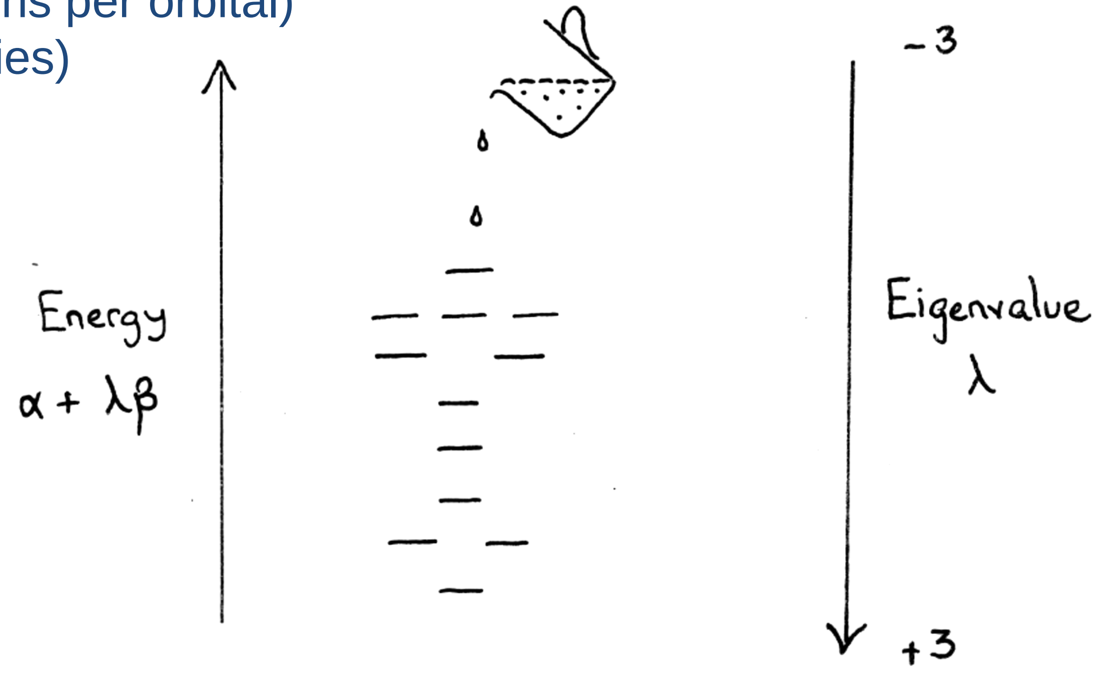
(The eigenvalue equation for the adjacency matrix of the graph)

Electrons in orbitals
(eigenvectors model spatial distribution of the electron)

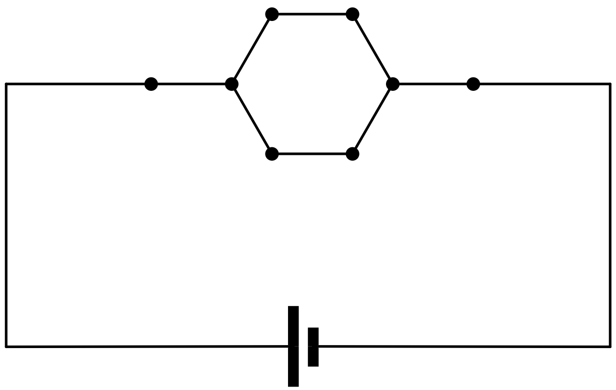
Orbitals have energies
(linear function of adjacency eigenvalue λ)

Graph & spectrum predict electronic configuration and properties

Aufbau	(fill by energy)
Pauli	(no more than two electrons per orbital)
Hund	(spread out at degeneracies)



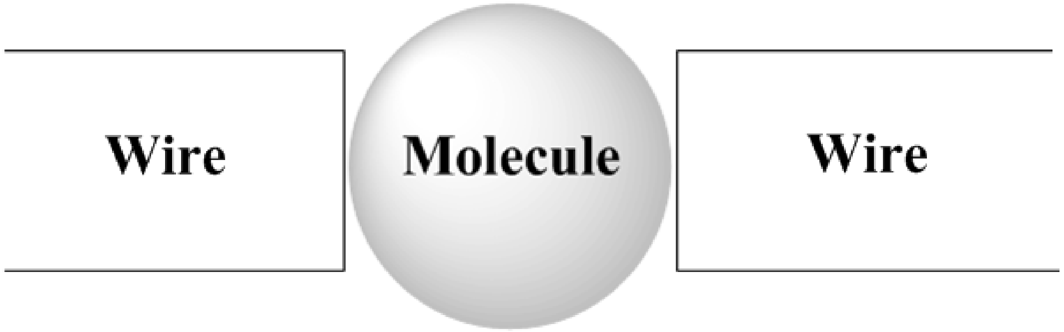
A new application: Molecular Conduction



Scanning Tunnelling Microscopy (STM)

Single-molecule electronic devices (MED)

The physical system:

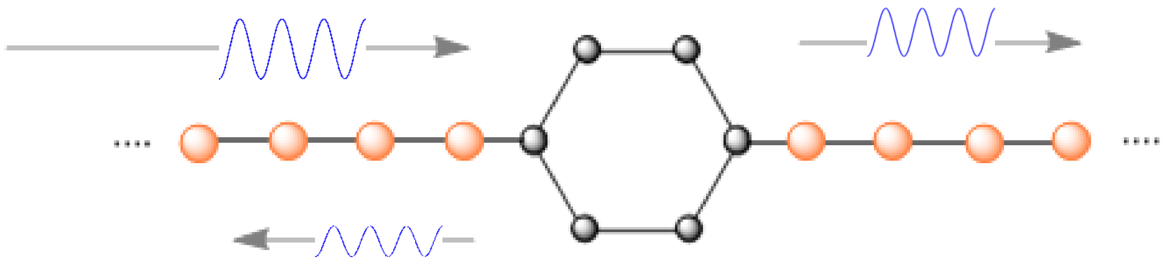


Chemical bonds metal-metal > carbon-carbon

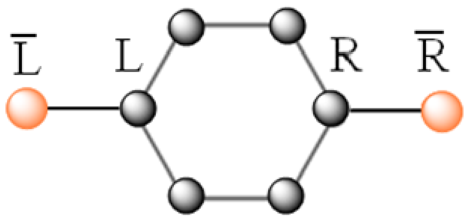
Add a parameter: γ (~ 1.4, say)

Operating at fixed energy, looking for a steady-state current

The source-and-sink model*



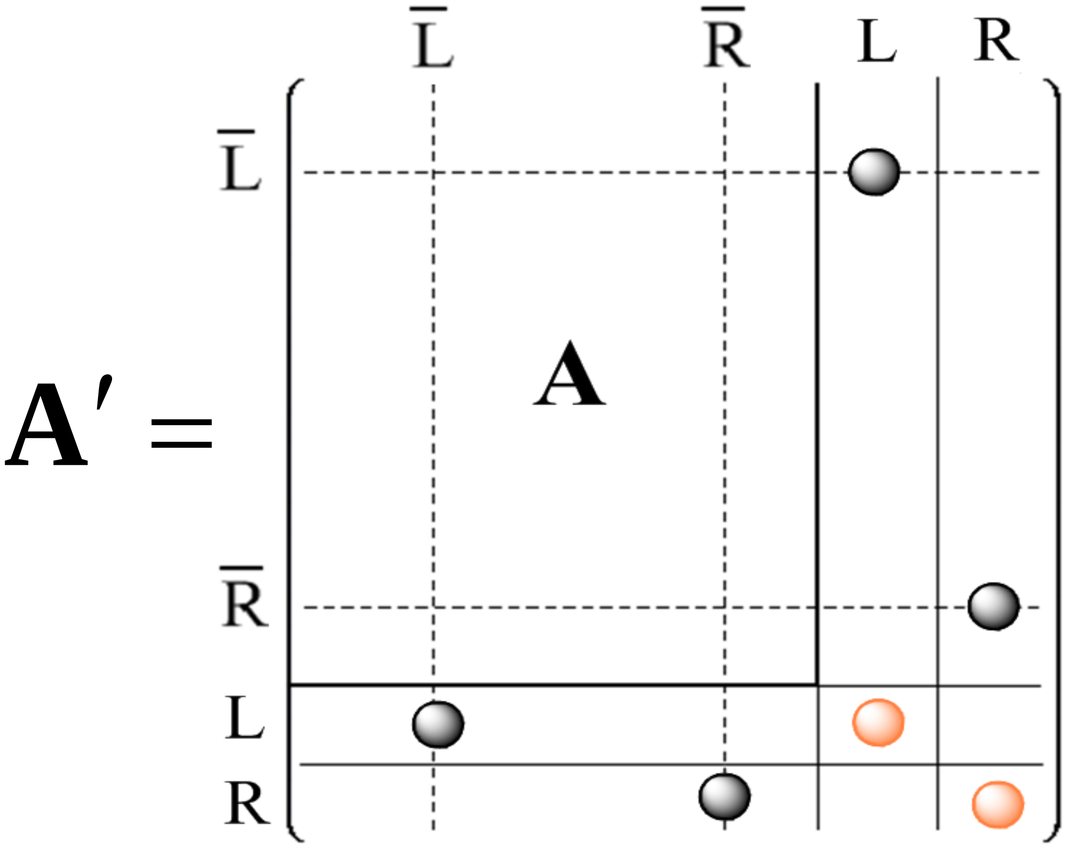
Wire injects fractional electron at source vertex

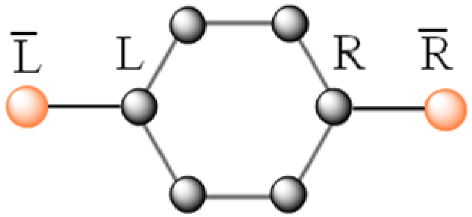


Sink vertex absorbs it

T(*E*) is the fractional transmission per electron injected at energy *E*

*Ernzerhof et al. J Chem Phys 123 (2005); 126 (2006); 127 (2007).





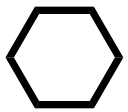
usual edge weights (1)

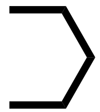
contact vertex weights (complex functions of λ)

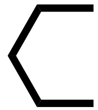
Sparsity of extra rows & columns $\Rightarrow$ simple transmission formula

$$T(E) = \frac{(4\gamma^2 - E^2)(ut - sv)}{\left| \gamma^2 s e^{-2iq} - \gamma(u+t)e^{-iq} + v \right|^2}$$

where *s, t, u, v* are the characteristic polynomials of

s : the molecule ………………………….. 

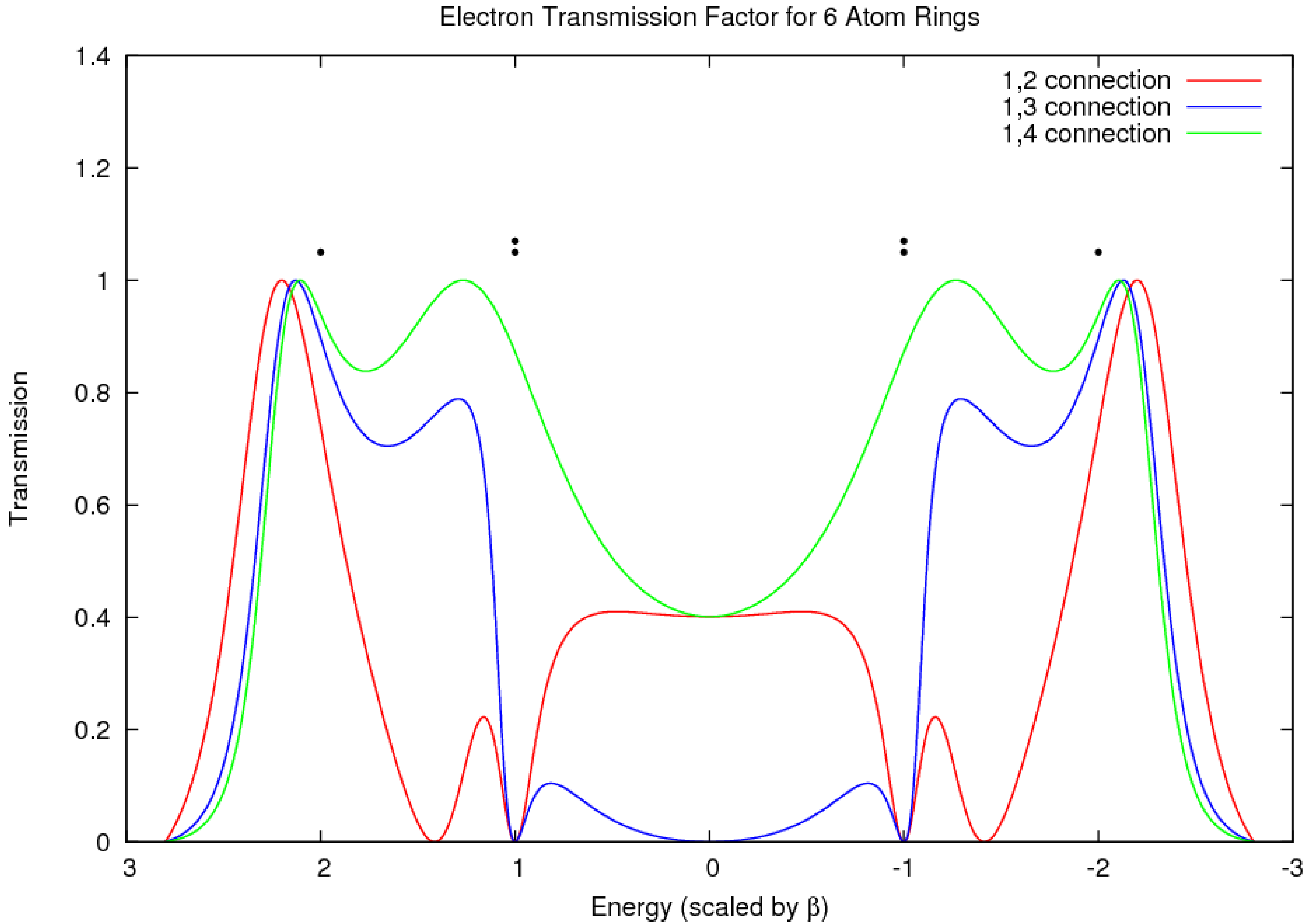
t : the molecule with L deleted …………….... 

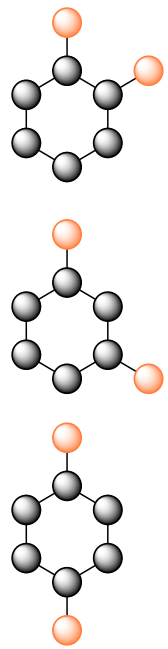
u : the molecule with R deleted . …………… 

v : the molecule with R and L deleted ……... 

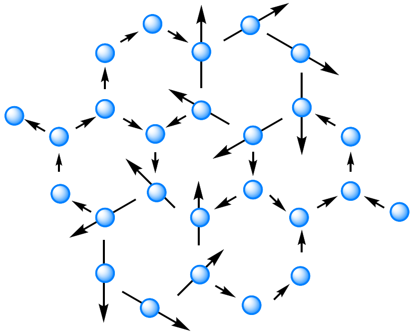
q is the wavevector (electron momentum), a simple function of energy

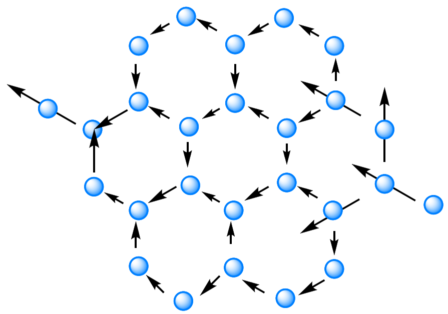
ut–sv is in fact a square (Jacobi's Theorem): the opacity polynomial


Electron Transmission Factor for 6 Atom Rings
1,2 connection
1,3 connection
1,4 connection
Transmission
Energy (scaled by β)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
3
2
1
0
-1
-2
-3



‘Puzzling’ reversals of currents with small energy changes now understood:





Graph theoretical basis allows general deductions

Theorems (!)

Selection rules

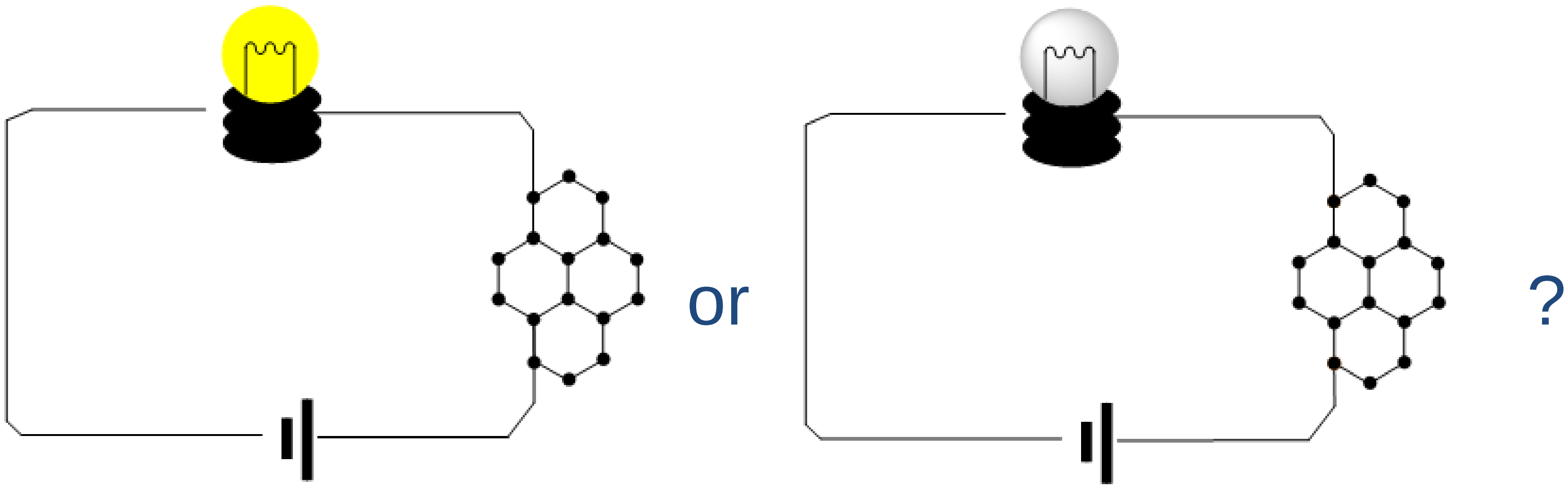
Omni-conductors and omni-insulators

Möbius Conductors

Equi-conductors

Fragment Analysis (‘polymeric’ devices)

Selection Rules:



Conduction at $E = 0$ (the Fermi level) is determined (almost) entirely by the nullities of the molecular graph and vertex deleted subgraphs.

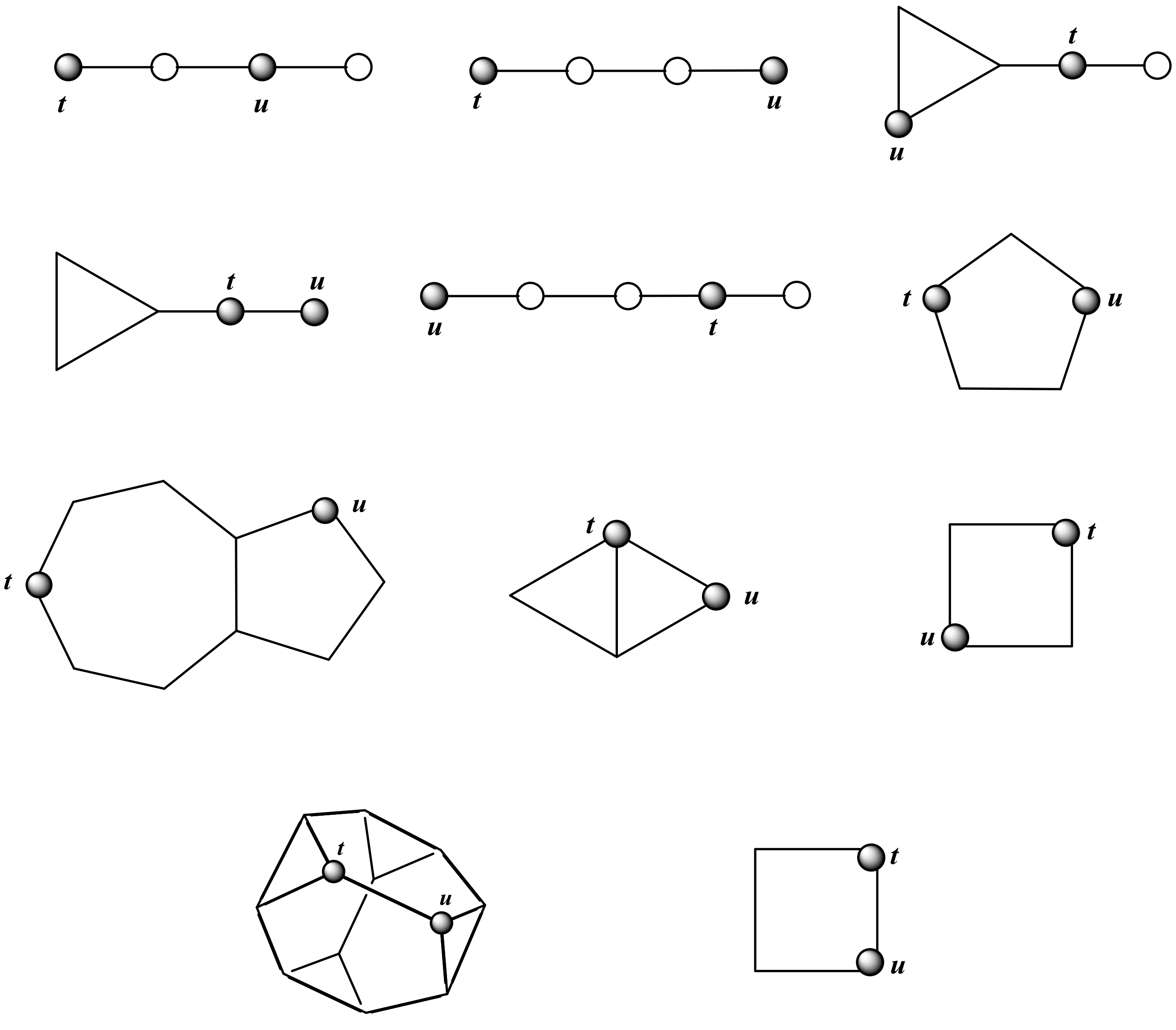
By Interlacing we find 11 cases:

5 conduct, 5 always insulate and one is tricky.

Case	g_s	g_t	g_u	g_v	$T(0)/(4\tilde{\beta}^2)$
1	g	$g+1$	$g+1$	$g+2$	0
2	g	$g+1$	$g+1$	g	$-s'_0v'_0/(s'_0-\tilde{\beta}^2v'_0)^2$
3	g	$g+1$	g	$g+1$	0
4	g	$g+1$	g	g	$-s'_0v'_0/[(s'_0-\tilde{\beta}^2v'_0)^2+(u'_0)^2\tilde{\beta}^2]$
5	g	$g+1$	$g-1$	g	0
6	g	g	g	$g+1$	$u'_0t'_0/[(s'_0)^2+(u'_0+t'_0)^2\tilde{\beta}^2]$
7	g	g	g	g	$(u'_0t'_0-s'_0v'_0)/[(s'_0-\tilde{\beta}^2v'_0)^2+(u'_0+t'_0)^2\tilde{\beta}^2]$
8	g	g	$g-1$	$g-1$	0
9	g	$g-1$	$g-1$	g	$u'_0t'_0/(u'_0+t'_0)^2\tilde{\beta}^2$
10	g	$g-1$	$g-1$	$g-1$	$u'_0t'_0/[(v'_0)^2\tilde{\beta}^2+(u'_0+t'_0)^2]\tilde{\beta}^2$
11	g	$g-1$	$g-1$	$g-2$	0

PWF, BT Pickup, TZ Todorova & W Myrvold, JCP 131 (2009) 044104

All cases exist in molecules



Classes of conductors

Most conjugated systems have a mixture of good and bad pathways

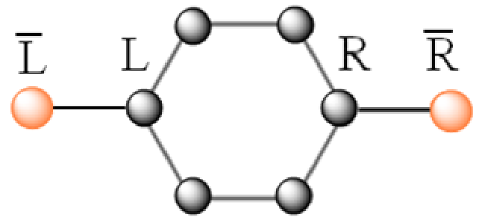
Are there molecular graphs that conduct (at $E = 0$) however we connect them?

‘omni-conductors’

Likewise ‘omni-insulators’ ?

Nullity of the molecular graph (number of non-bonding orbitals) divides the world of conductors:

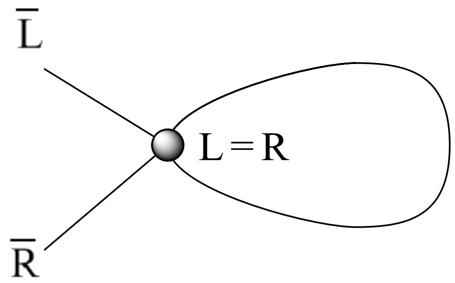
Distinct



omni-conductors exist and have nullity 0 or 1

omni-insulators exist and have nullity 2 or more

Ipso



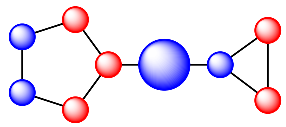
omni-conductors are not constrained by nullity

omni-insulators exist and have nullity 0

Strong (*any* connection, distinct or not)

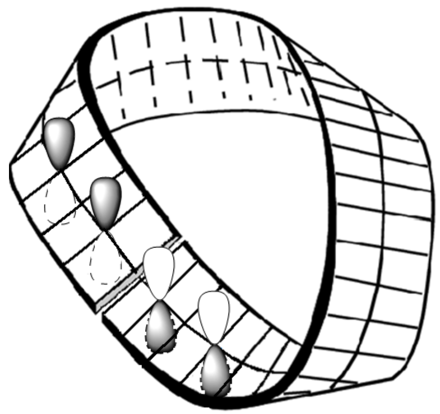
no strong omni-insulators exist

omni-conductors of nullity 1 are exactly the nut graphs



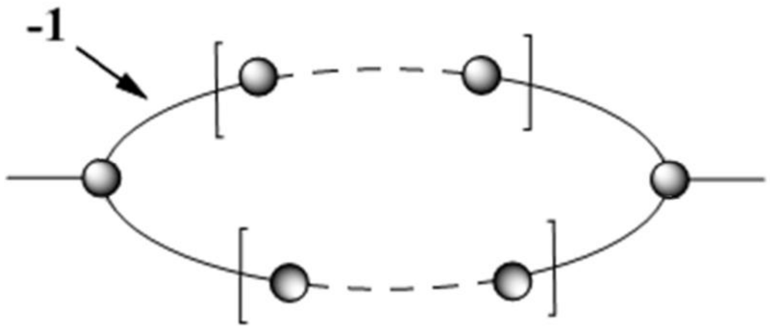
PWF, BT Pickup, TZ Todorova, M Borg, I Sciriha, J Chem Phys 140 (2014) 054115

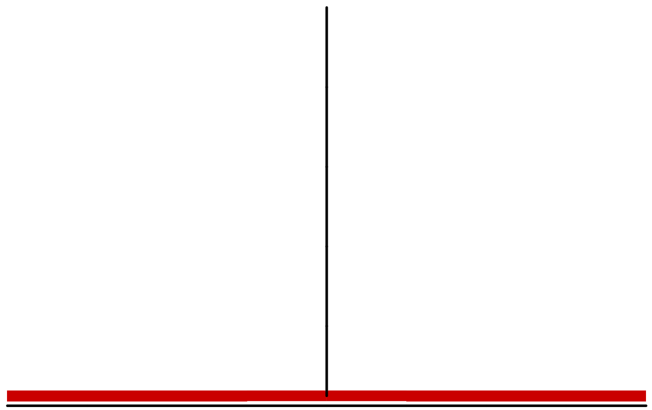
Conduction with a twist



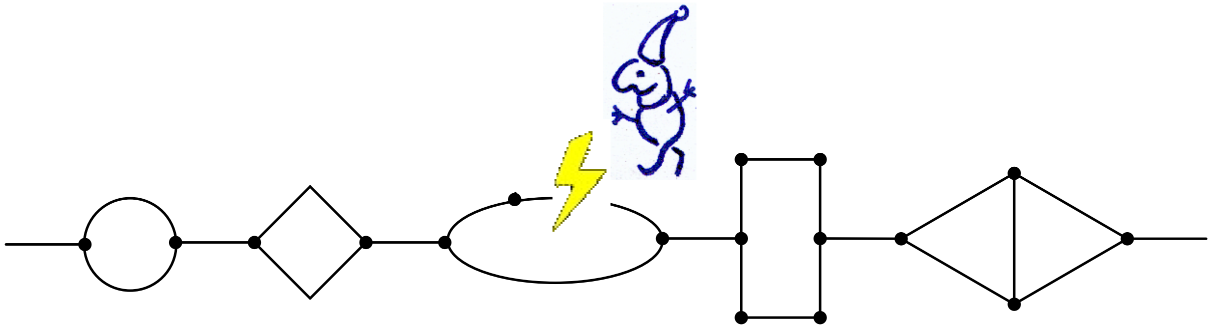
Möbius conductors can be perfect reflectors

e.g. Möbius 2*n*-cycle with antipodal connections





Fragility of serial devices



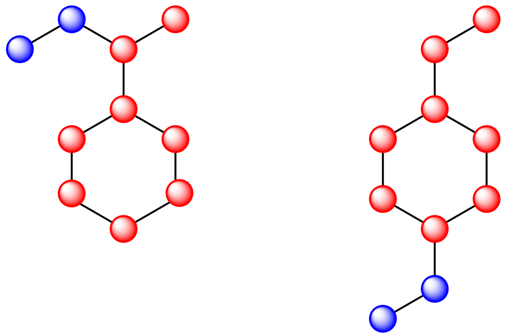
Twisting (not breaking) one bond could kill the whole device

Equi-conductors*

Uses the theory of iso-spectral graphs, vertices and pairs**

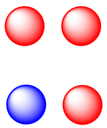
Isospectral chemical graphs:

e.g. the Živković graph pair

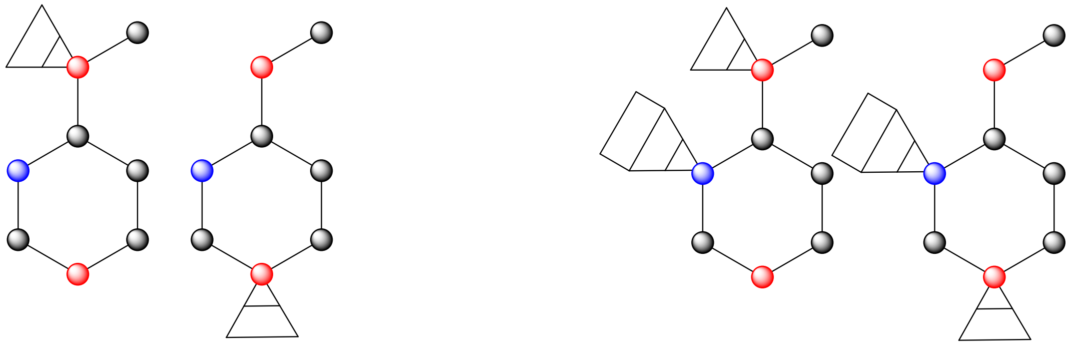


Isospectral vertices

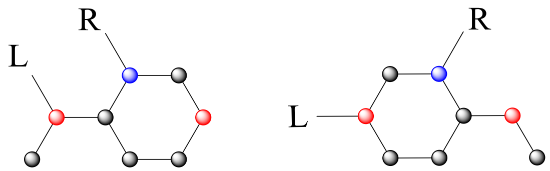
Isospectral pairs



e.g.



Iso-spectral pair gives an equi-conductor (equal $T(E)$ for all E)



*PWF BT Pickup TZ Todorova CPL 465 (2008) 142 ** C & G Rücker J Math Chem 9 (1992) 207

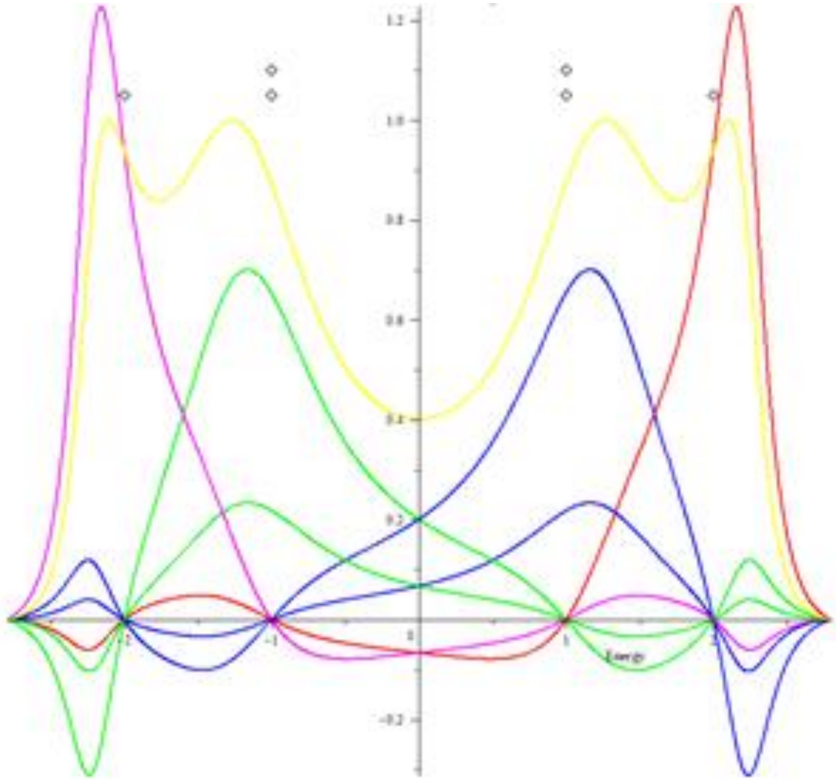
Where next?

(1) Symmetry selection rules

(2) Inclusion of indistinguishability of electrons?

(Pauli principle applies to conduction electrons too)

Both should be straightforward (?) if we use spectral expansion of characteristic polynomials (molecular-orbital partition of total transmission)



THE END!