KEMIJSKI INŠTITUT

Preglov kolokvij

Modern Approaches to Hückel Molecular Orbital Method in Chemistry

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Organisation of this talk

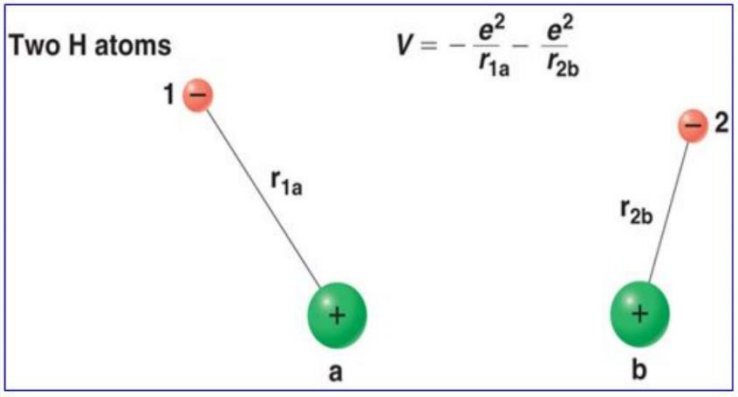
- ✓ *Historic introduction*
- ✓ *HMO in a nutshell*
- ✓ *HMO and molecular stability*
- ✓ *HMO, bipartivity and stability*
- ✓ *What is the HMO energy after all?*
- ✓ *HMO and Spintronics*
- ✓ *HMO and molecular electronics*

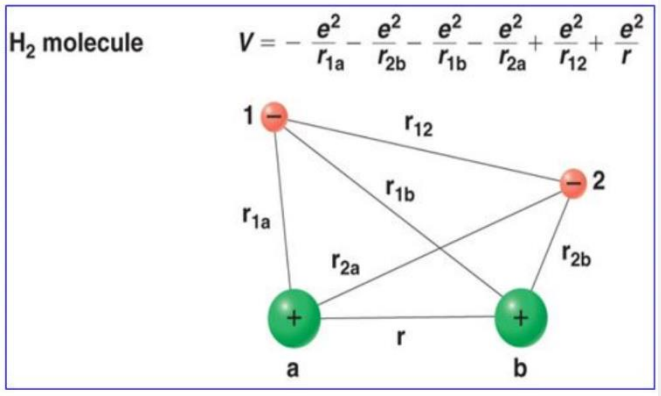
Historic background: 'Influencers'

Walter H. Heitler

Fritz London

1927. W. Heitler and F. London, *"Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik"*,
Zeitschrift für Physik, **44**, 455—472 (1927).





(Taken from Google Images)

H. Hartmann and H. C . Longuet-Higgins, *Biogr. Mems Fell. R. Soc. 28* (**1982**) 153-162.

Historic background: 'Influencers'

1928. Obtains Ph.D. from University of Leipzig. Publishes thesis Uber die Quantenmechanik der Elektronen in Kristallgittern, (On the quantum mechanics of electrons in crystal lattices).

Bloch Theorem

"When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal .... By straight Fourier analysis, I found to my delight that the wave differed from the plane wave of free electron only by a periodic modulation."

--Felix Bloch, *Physics Today* (1976)

Felix Bloch

(Taken from Google Images)

H. Hartmann and H. C . Longuet-Higgins, *Biogr. Mems Fell. R. Soc. 28* (**1982**) 153-162.

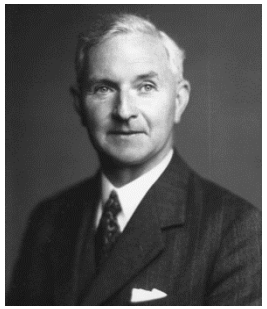
Historic background: 'Influencers'

Fiedrich Hund

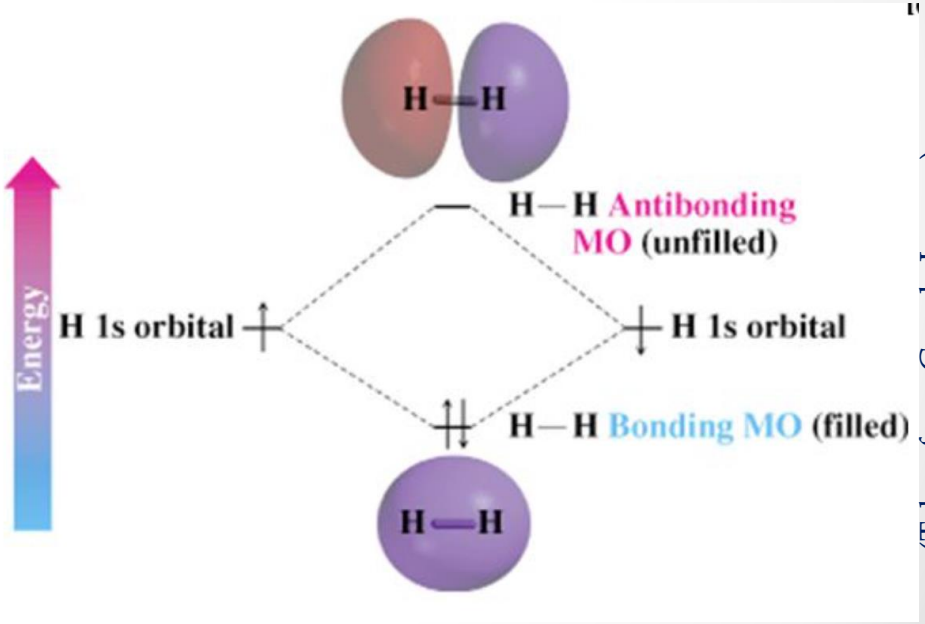
Robert Mulliken

Gerhard Herzberg

John Lennard-Jones



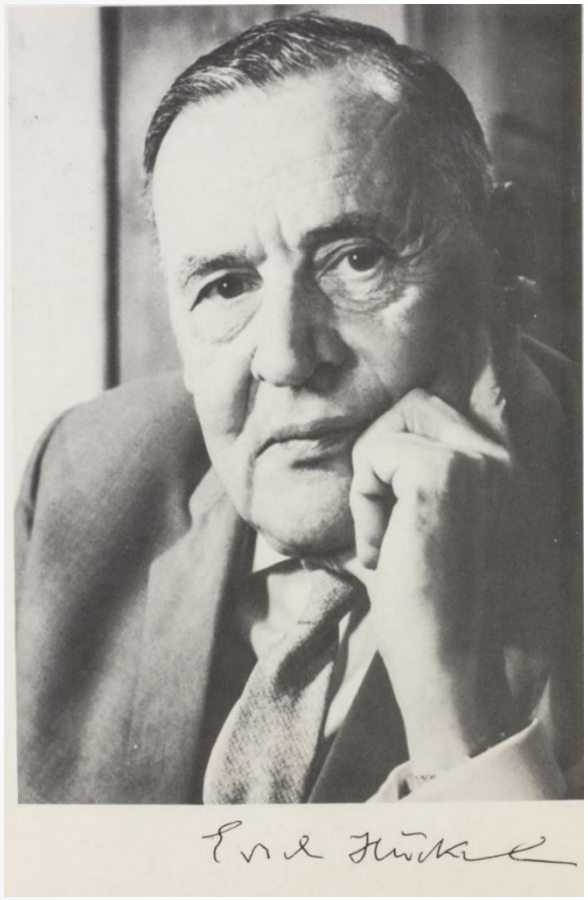
1928-1929: Developed the method of molecular one-electron states.



(Taken from Google Images)

H. Hartmann and H. C . Longuet-Higgins, *Biogr. Mems Fell. R. Soc. 28* (**1982**) 153-162.

Historic background: Erich Hückel



9 August 1896
16 February 1980

Hückel, E. (1930). "Zur Quantentheorie der Doppelbindung" [Quantum theory of double linkings]. *Zeitschrift für Physik*. **60** (7–8): 423–456.

Hückel, E. (1931). "Quantentheoretische Beiträge zum Benzolproblem". *Zeitschrift für Physik*. **70** (3–4): 204–286.

Hückel, E. (1931). "Quantum-theoretical contributions to the benzene problem. I. The electron configuration of benzene and related compounds". *Z. Phys*. **70**: 204–86.

Hückel, E. (1932). "Quantum theoretical contributions to the problem of aromatic and non-saturated compounds". *Z. Phys*. **76**: 628.

Hückel, E. (1937). "The theory of unsaturated and aromatic compounds". *Z. Elektrochem. Angew. Physik. Chem*. **42**: 752 and 827.

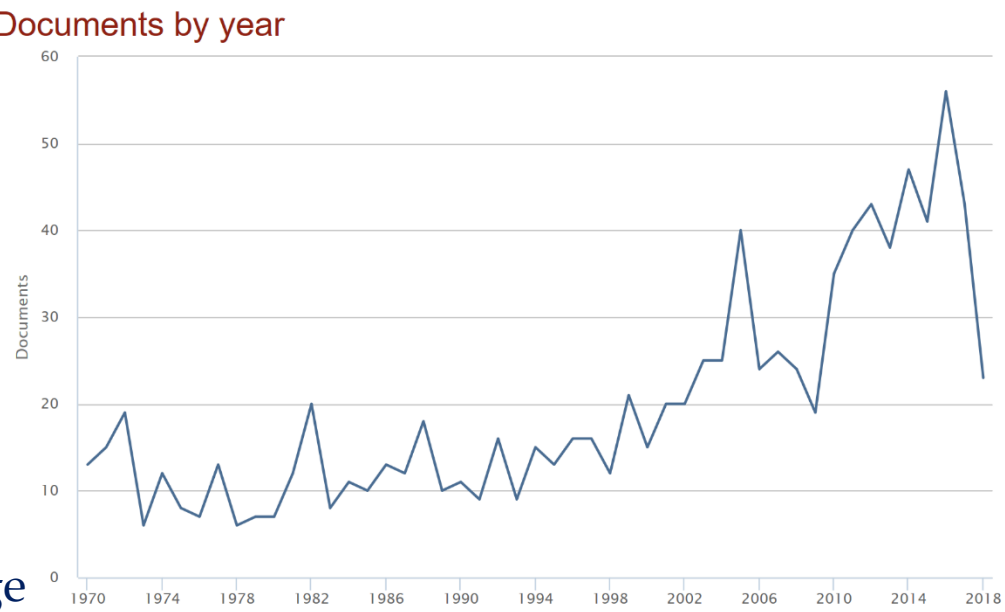
Hückel, E. (1936). "Theory of the magnetism of so-called biradicals". *Z. Phys. Chem*. **B34**: 339.

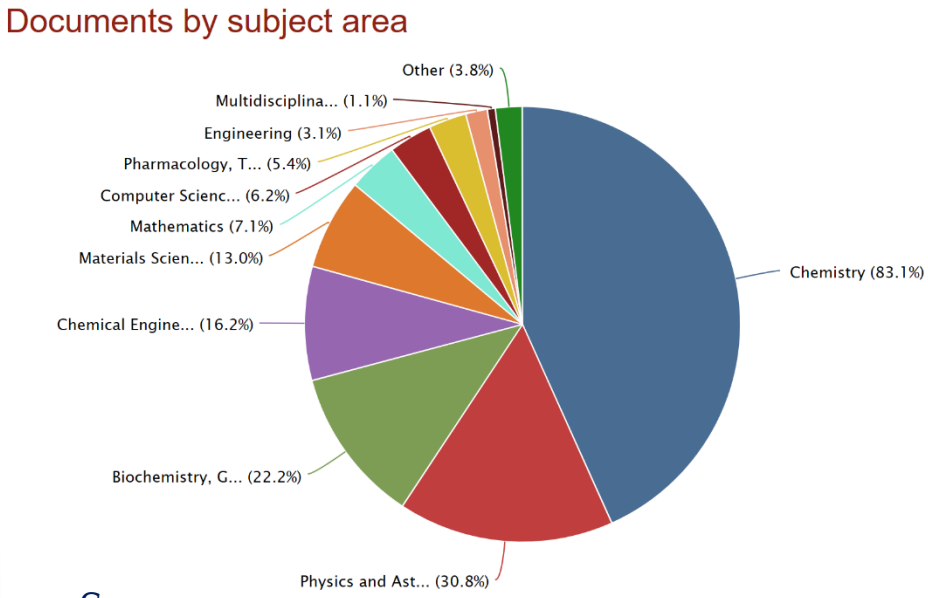
H. Hartmann and H. C . Longuet-Higgins, *Biogr. Mems Fell. R. Soc. 28* (**1982**) 153-162.

Historic background: Erich Hückel

E. Hückel

Quantentheoretische Beiträge zum Benzolproblem - I. Die Elektronenkonfiguration des Benzols und verwandter Verbindungen.
Zeitschrift für Physik, **1931**, (3-4) 204-286

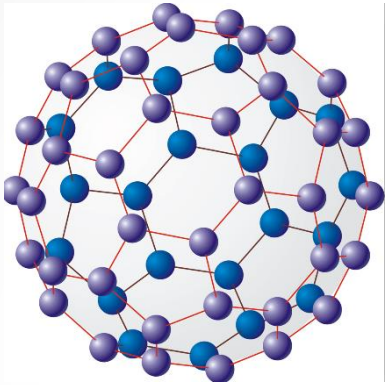




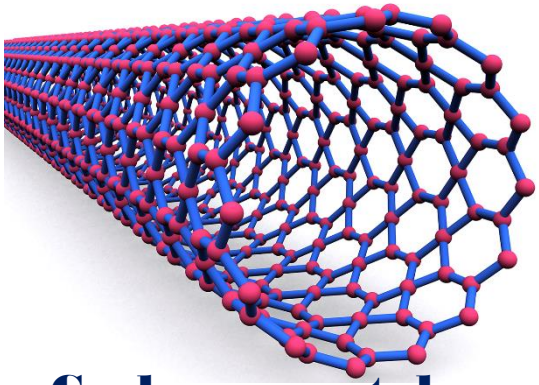
Data from Scopus.

Historic background: Erich Hückel

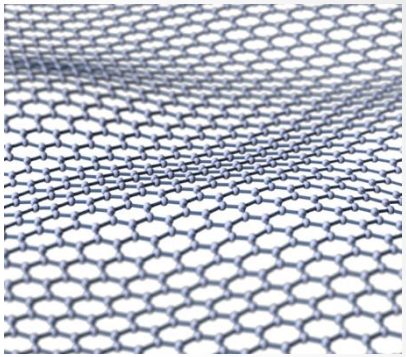
New kids on the block



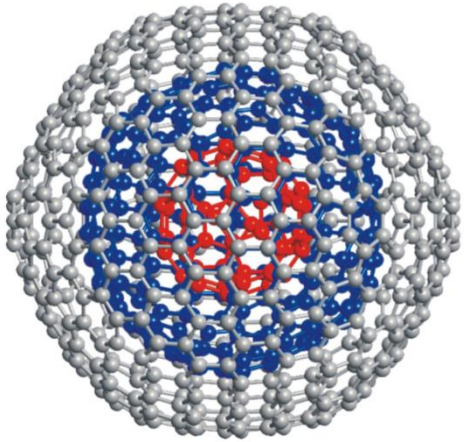
Fullerenes



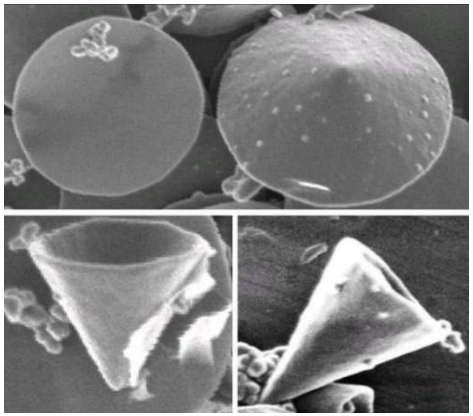
Carbon nanotubes



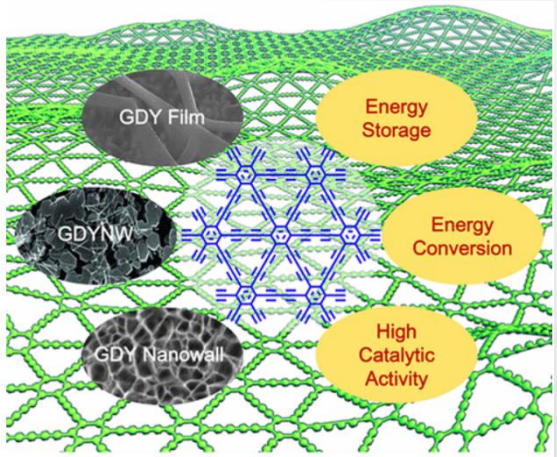
Graphene



Carbon onions



Carbon nanocones



Graphdiyne

(Taken from Google Images)

HMO in a nutshell

E. Hückel

Let us consider a molecule and assume equivalence of all the atoms as well as of their pair-interactions. A molecular orbital is represented as

$$\psi = c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n,$$

then its one-electron energy E and the values of the coefficients are jointly given by the eigenvalue equation

$$\sum_j H_{ij}c_j = Ec_i \qquad i = 1,\ldots,n$$

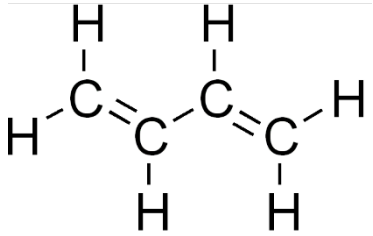
where

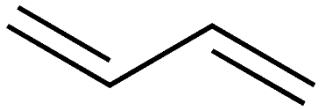
$$H_{ij} = \begin{cases} \tilde{\alpha} & i = j \\ \tilde{\beta} & i \sim j \\ 0 & otherwise. \end{cases}$$

Kutzelnigg W. *J. Comput. Chem.* 28 (**2007**) 25-34.

HMO in a nutshell

Example: 1,3-butadiene





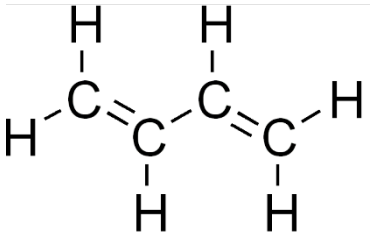
$$\begin{bmatrix} \tilde{\alpha}-E & \tilde{\beta} & 0 & 0 \\ \tilde{\beta} & \tilde{\alpha}-E & \tilde{\beta} & 0 \\ 0 & \tilde{\beta} & \tilde{\alpha}-E & \tilde{\beta} \\ 0 & 0 & \tilde{\beta} & \tilde{\alpha}-E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

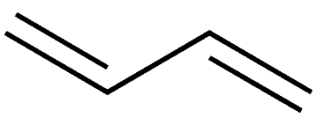
Kutzelnigg W. *J. Comput. Chem.* 28 (**2007**) 25-34.

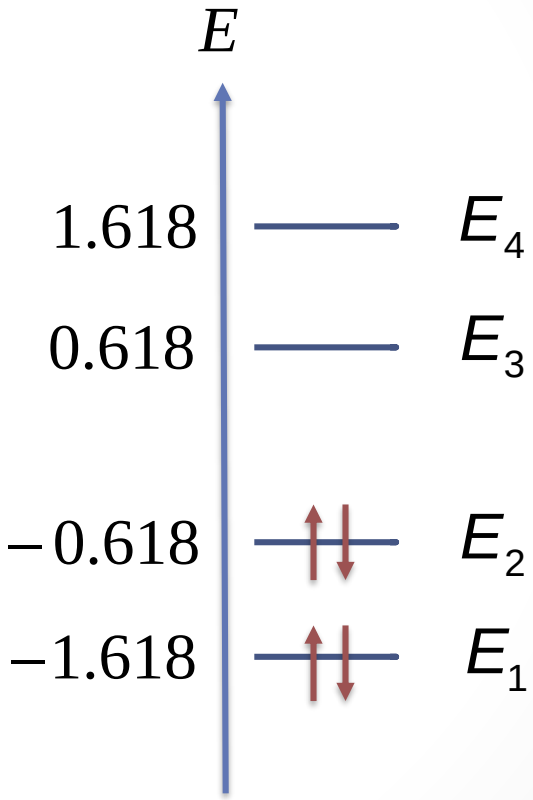
HMO in a nutshell

Further assume that $\tilde{\alpha} = 0$ *and* $\tilde{\beta} = -1$.

Example: 1,3-butadiene





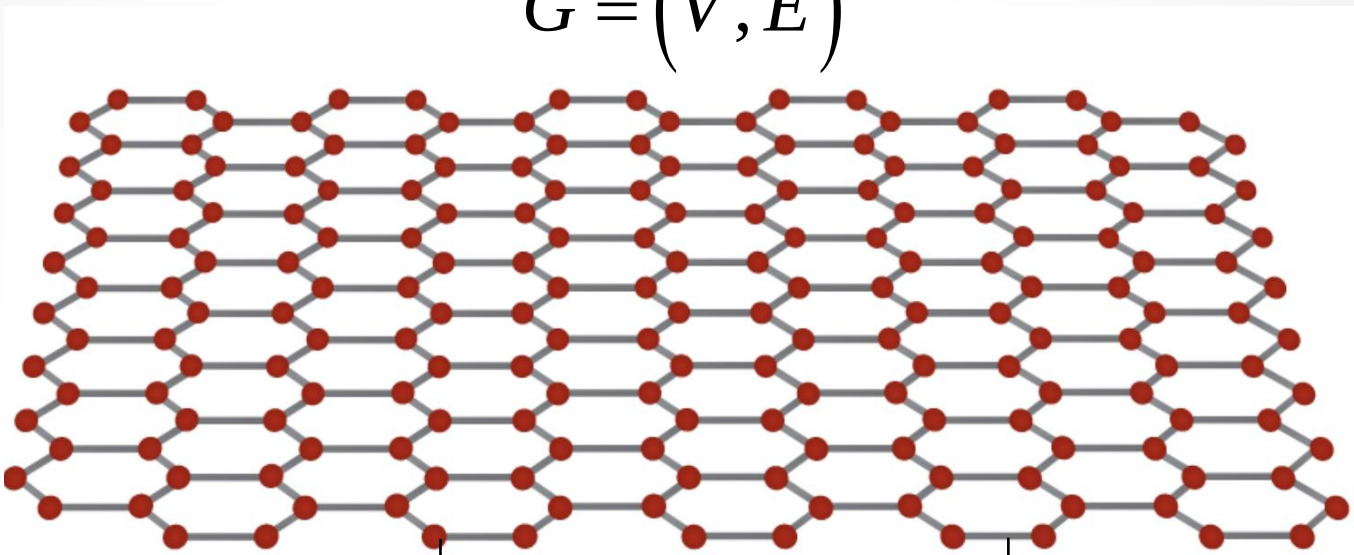


$$E_\pi = \sum_j^{occ} \eta_j E_j = 2\left(E_1 + E_2\right)$$

Kutzelnigg W. *J. Comput. Chem.* 28 (**2007**) 25-34.

Graph connection

$$G = \left(V, E \right)$$



(Taken from Google Images)

nodes or vertices

edges or links

$$V = \left\{ v_1, \cdots, v_n \right\}$$

$$E \subseteq V \times V$$

Adjacency matrix

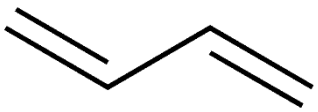
$$A = \left[A_{ij} \right]_{n \times n}$$

$$A_{ij} = \begin{cases} 1 & \left(i, j \right) \in E \\ 0 & \left(i, j \right) \notin E \end{cases}$$

Estrada & Knight: *A First Course on Network Theory*, Oxford Univ. Press, 2015

Graph connection

Example: 1,3-butadiene



$$A = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

Thus, we have that

$$\hat{\mathcal{H}} = \tilde{\alpha} I + \tilde{\beta} A, \qquad \tilde{\beta} < 0$$

and for $\tilde{\alpha} = 0$ *and* $\tilde{\beta} = -1$.

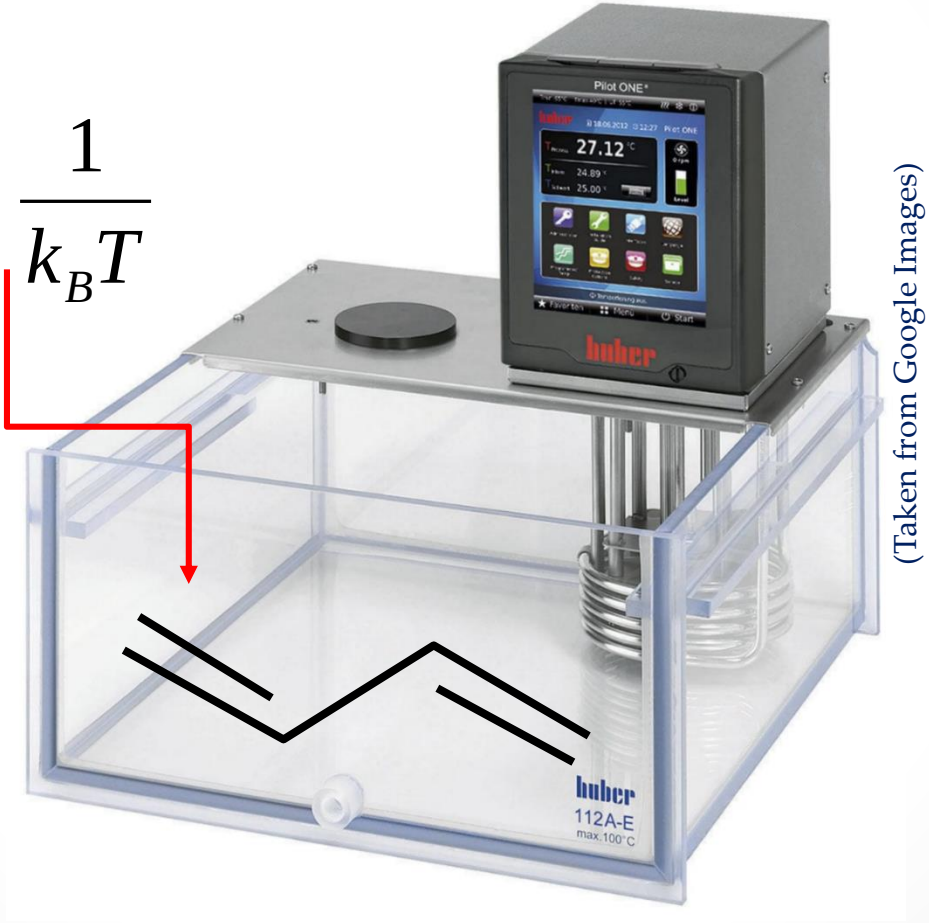
$$\hat{\mathcal{H}} = -A.$$

Estrada & Knight: *A First Course in Network Theory*. Oxford Univ. Press (2015)

HMO & molecular stability

Let us consider that the molecule under study is submerged into a thermal bath of inverse temperature β.

$$\beta = \frac{1}{k_B T}$$

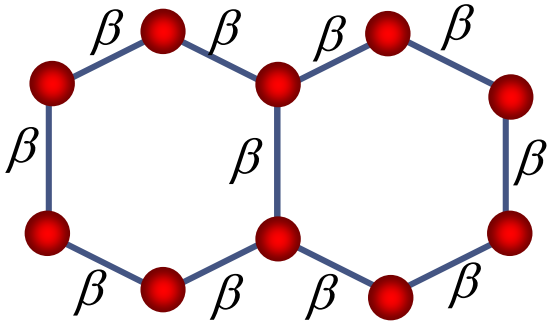


(Taken from Google Images)

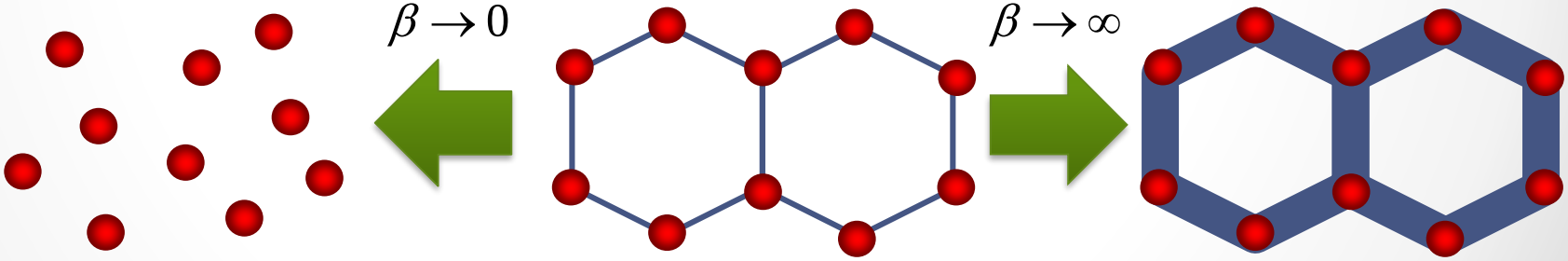
Estrada & Knight: *A First Course in Network Theory*. Oxford Univ. Press (2015)

HMO & molecular stability

At equilibrium we have



And at extremes we get



Estrada & Hatano: *Chem. Phys. Lett.* **439** (2007) 247-251.

HMO & molecular stability

The probability of finding the molecule in a state of energy E_j at the inverse temperature β is

$$p_j = \frac{1}{Z}\exp\left(-\beta E_j\right)$$

L. Bolztmann

where

$$Z = \sum_{j=1}^{n} \exp\left(-\beta E_j\right),$$

such that

$$\sum_{j=1}^{n} p_j = \frac{1}{Z}\sum_{j=1}^{n} \exp\left(-\beta E_j\right) = 1$$

Estrada & Knight: *A First Course in Network Theory*. Oxford Univ. Press (2015)

HMO & molecular stability

Thus, in the context of the HMO method, the partition function is

$$Z = \sum_{j=1}^{\infty} \exp\left(\beta\lambda_j\right) = Tr\exp\left(\beta A\right) = EE\left(G,\beta\right)$$

which is know as the Estrada index of the graph (typically for $\beta = 1$).

The matrix

$$G = I + A + \frac{A^2}{2!} + \cdots = \sum_{k=0}^{\infty} \frac{A^k}{k!} = \exp\left(A\right)$$

is a matrix function of the adjacency matrix of the graph.

Estrada & Higham: *SIAM Rev.* 52 (**2010**) 696-714.

HMO & molecular stability

HMO partition function (Estrada index)

$$Z = EE(G,\beta) = \sum_{j=1}^{\infty} \exp(\beta\lambda_j) = Tr\exp(\beta A)$$

HMO electronic entropy

$$S = -\frac{1}{T}\sum_{j=1}^{n} \lambda_j \frac{\exp(\beta\lambda_j)}{EE} + k_B \ln EE$$

HMO electronic enthalpy

$$H = -\sum_{j=1}^{n} \lambda_j \frac{\exp(\beta\lambda_j)}{EE}$$

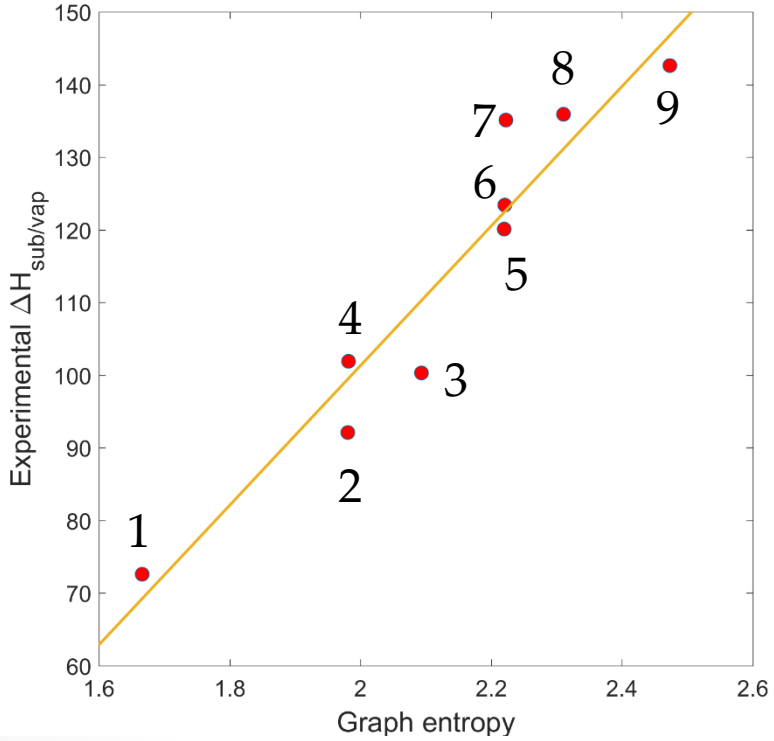
HMO electronic free energy

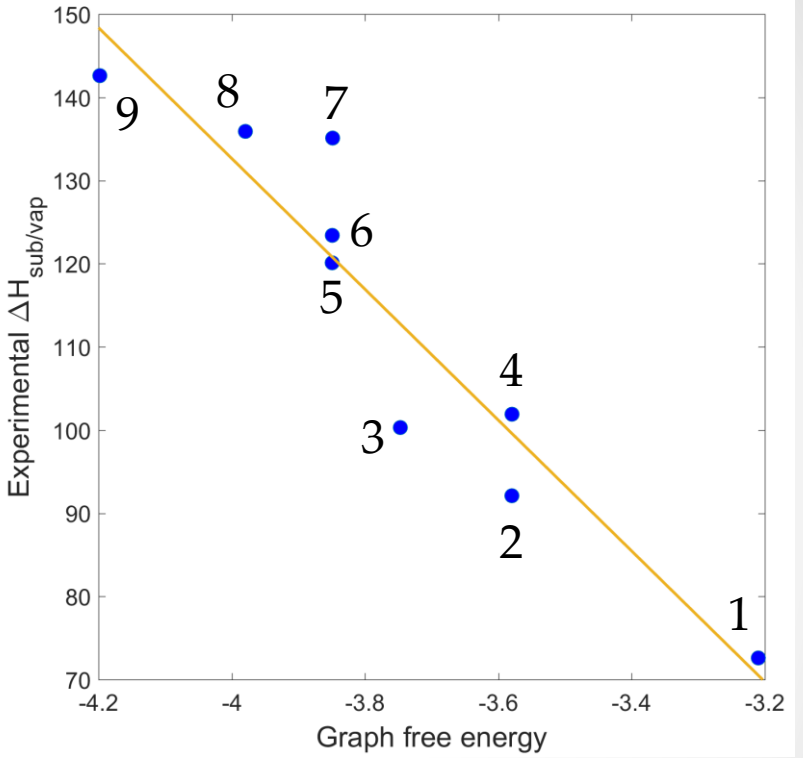
$$F = -\beta^{-1} \ln EE$$

Estrada & Hatano: *Chem. Phys. Lett.* **439** (2007) 247-251.

HMO & molecular stability

Thermodynamic properties of PAHs





1: naphthalene
2: phenanthrene
3: pyrene
4: anthracene
5: triphenylene
6: chrysene
7: naphthacene
8: perylene
9: coronene

Data: Roux *et al*: *J. Phys. Chem. Ref. Data*, **37**, (2008) 1855-1996

A diversion: Matrix Functions

A.-L. Cauchy

Definition. *For* $M \in C^{n\times n}$

$$f(M) := \frac{1}{2\pi i}\int_{\Gamma} f(z)(zI - M)^{-1}\,dz$$

where f is analytic on and inside a closed contour Γ that encloses $\Lambda(M)$.

Remark. *There are two other definitions of a matrix function, using either Hermite polynomials and Jordan canonical forms. All three definitions are equivalent if f is analytic.*

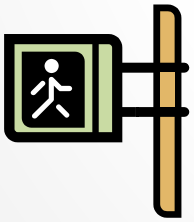
Higham: *Functions of Matrices. Theory and Computations.* SIAM (2008)

A diversion: Matrix Functions

Let f(A) be a function of the adjacency matrix with Taylor series expansion:

$$f(A) = \sum_{k=0}^{\infty} c_k A^k.$$

Definition: A *walk* of length k is any sequence of (not necessarily different) nodes $v_1,\ldots, v_l$ such as for each $i = 1,\ldots,l$ there is a link from v_l to v_{l+1}.



Theorem (Cvetković). *The number of walks of length k between the nodes p and q in a network is equal to:*

$$\left(A^k\right)_{pq}.$$

A diversion: Matrix Functions

Then

$$\exp(A) = I + A + \frac{1}{2}A^2 + \frac{1}{6}A^3 + \cdots$$

and the Estrada index can be written as

$$tr\exp(A) = trI + trA + \frac{1}{2}trA^2 + \frac{1}{6}trA^3 + \cdots$$

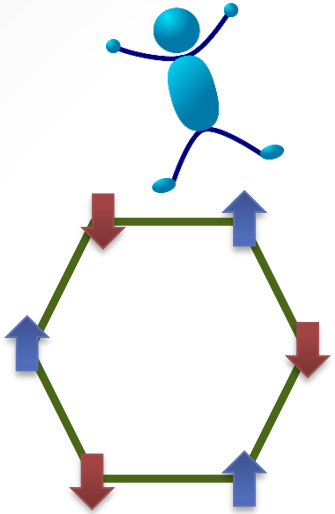
which means that the Estrada index is a weighted sum of subgraphs in the graph:

$$tr\exp(A) = n + \alpha_0 m + \alpha_1 t + \cdots$$

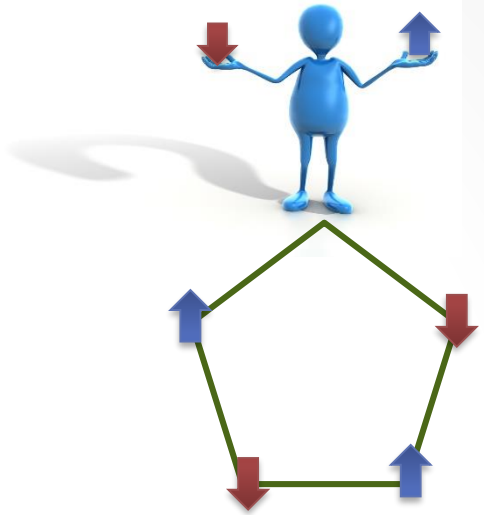
nodes edges triangles

Estrada & Knight: *A First Course in Network Theory*. Oxford Univ. Press (2015)

HMO, bipartivity & stability

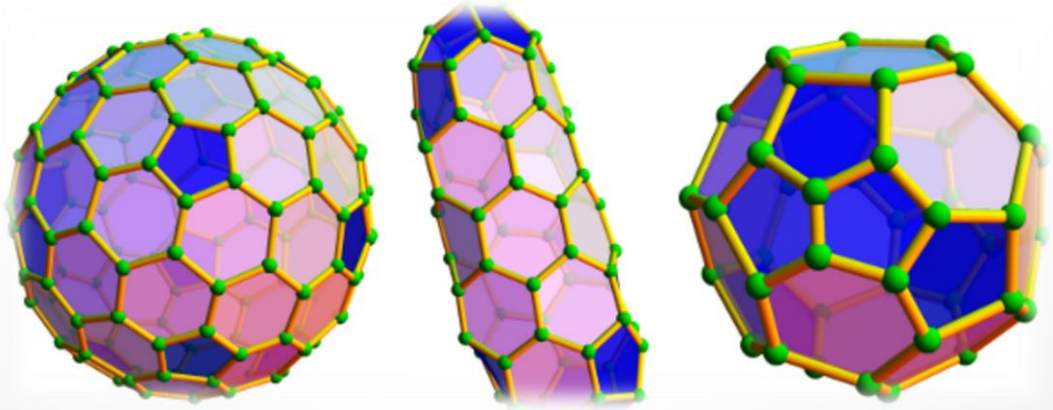


Bipartite system



'Frustrated' system

How much 'frustration' (bipartivity)?



(Taken from Google Images)

HMO, bipartivity & stability

Ising meets Hückel

Hamiltonian

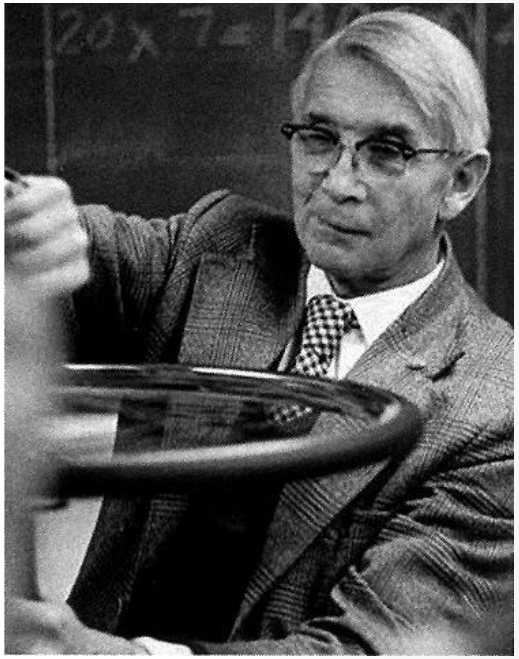
Adjacency matrix

$$\hat{\mathcal{H}}(\sigma) = -\sum_{i<j} A_{ij}\sigma_i\sigma_j$$

Spin at node *i*

$$\sigma_i = \{-1, +1\}$$

$$Z = tr\left(e^{-\beta\hat{\mathcal{H}}(\sigma)}\right)$$

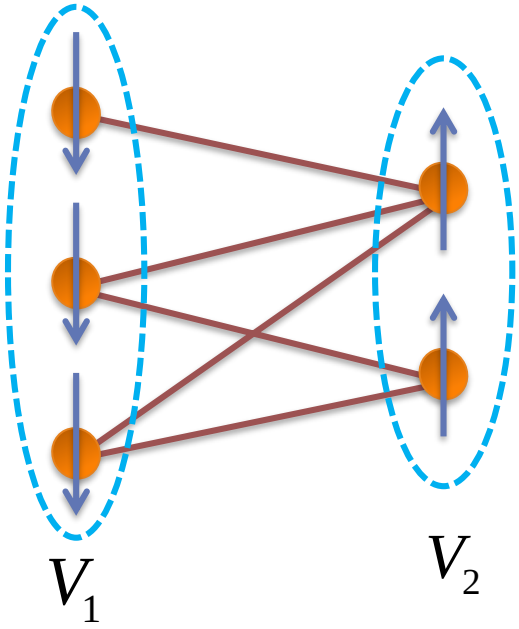


(Taken from Google Images)

Ernst Ising

E. Ising. Beitrag zur Theorie des Ferro- und Paramagnetismus. Dissertation zur Erlangung der Doktorwürde der Mathematisch Naturwissenschaftlichen Fakultät der Hamburgischen Universität vorgelegt von Ernst Ising aus Bochum. Hamburg 1924

HMO, bipartivity & stability



$$V = V_1 \bigcup V_2$$

Characterisation:

(1) $$A = \begin{bmatrix} 0 & B \\ B^T & 0 \end{bmatrix}$$

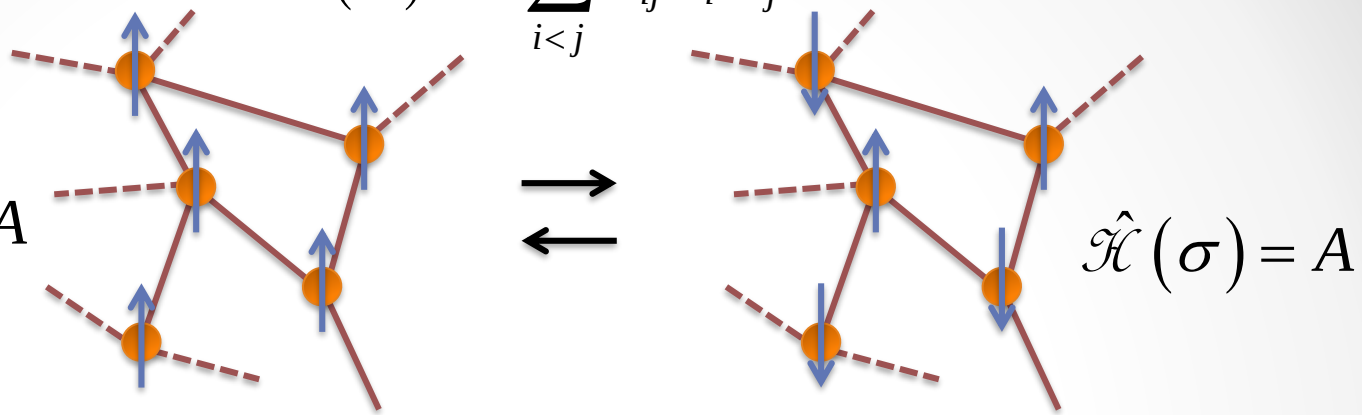
(2) $$\lambda_j = -\lambda_{n-j+1}$$

(3) No cycles of odd length

HMO, bipartivity & stability

$$\hat{\mathcal{H}}(\sigma) = -\sum_{i<j} A_{ij}\sigma_i\sigma_j$$

$\hat{\mathcal{H}}(\sigma) = -A$



$\hat{\mathcal{H}}(\sigma) = A$

Ferromagnetic

Antiferromagnetic

$$\Delta F = F_a - F_f$$

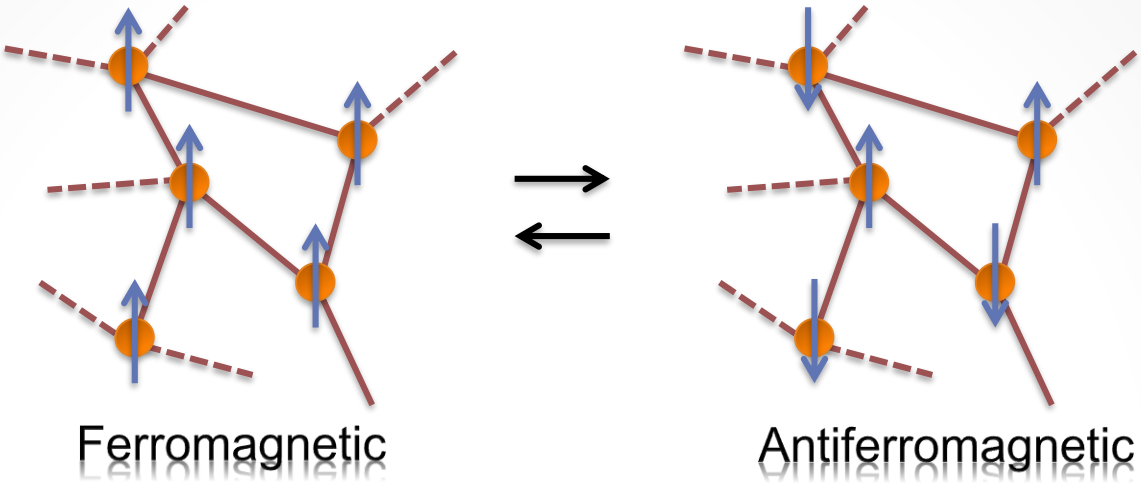
$$F_f = -\beta^{-1}\ln Z_f \qquad F_a = -\beta^{-1}\ln Z_a$$

$$Z_f = tr\left(e^{-\beta\hat{\mathcal{H}}(\sigma)}\right) = tr\left(e^{\beta A}\right) \qquad Z_a = tr\left(e^{-\beta\hat{\mathcal{H}}(\sigma)}\right) = tr\left(e^{-\beta A}\right)$$

$$\Delta F = -\beta^{-1}\ln\left(Z_a / Z_f\right)$$

Estrada & Rodriguez-Velazquez: *Phys. Rev. E* **72** (2005) 046105.
Estrada & Gomez-Gardenes: *Physica D, Nonlinearity* **323-324** (2016) 57-63.

HMO, bipartivity & stability



$$K(G,\beta) = \exp(-\beta \cdot \Delta F) = Z_a / Z_f$$

$$K(G,\beta) = \frac{Tr\left(\exp(-\beta A)\right)}{Tr\left(\exp(\beta A)\right)}$$

$$= \frac{Tr\left(\cosh(\beta A)\right) - Tr\left(\sinh(\beta A)\right)}{Tr\left(\cosh(\beta A)\right) + Tr\left(\sinh(\beta A)\right)}$$

Estrada & Rodriguez-Velazquez: *Phys. Rev. E* **72** (2005) 046105.
Estrada & Gomez-Gardenes: *Physica D, Nonlinearity* **323-324** (2016) 57-63.

HMO, bipartivity & stability

$$Bipartivity \Leftrightarrow No\ odd\ cycles$$

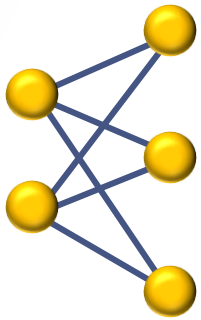
$$No\ odd\ cycles \Leftrightarrow No\ odd\ closed\ walks$$

$$No\ odd\ closed\ walks \Leftrightarrow \left[\sinh\left(A\right)\right]_{ii} = 0$$

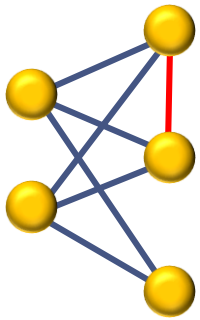
$$Bipartivity \Leftrightarrow K\left(G,\beta\right) = 1$$

HMO, bipartivity & stability

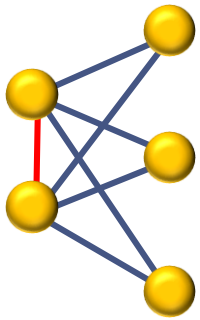
$$0 < b_e = \frac{tr\,\exp(-A)}{tr\,\exp(A)} \leq 1$$



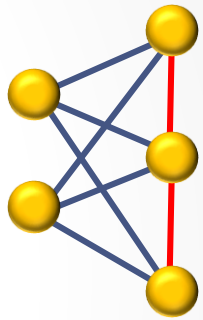
$b_e = 1.000$



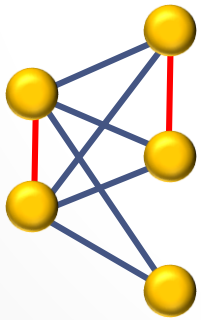
$b_e = 0.658$



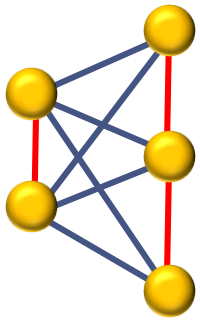
$b_e = 0.538$



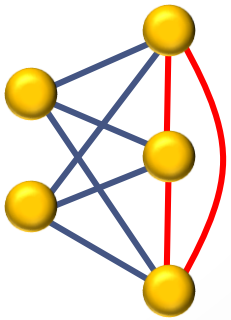
$b_e = 0.462$



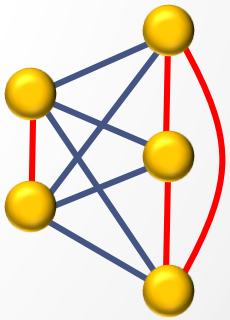
$b_e = 0.383$



$b_e = 0.289$



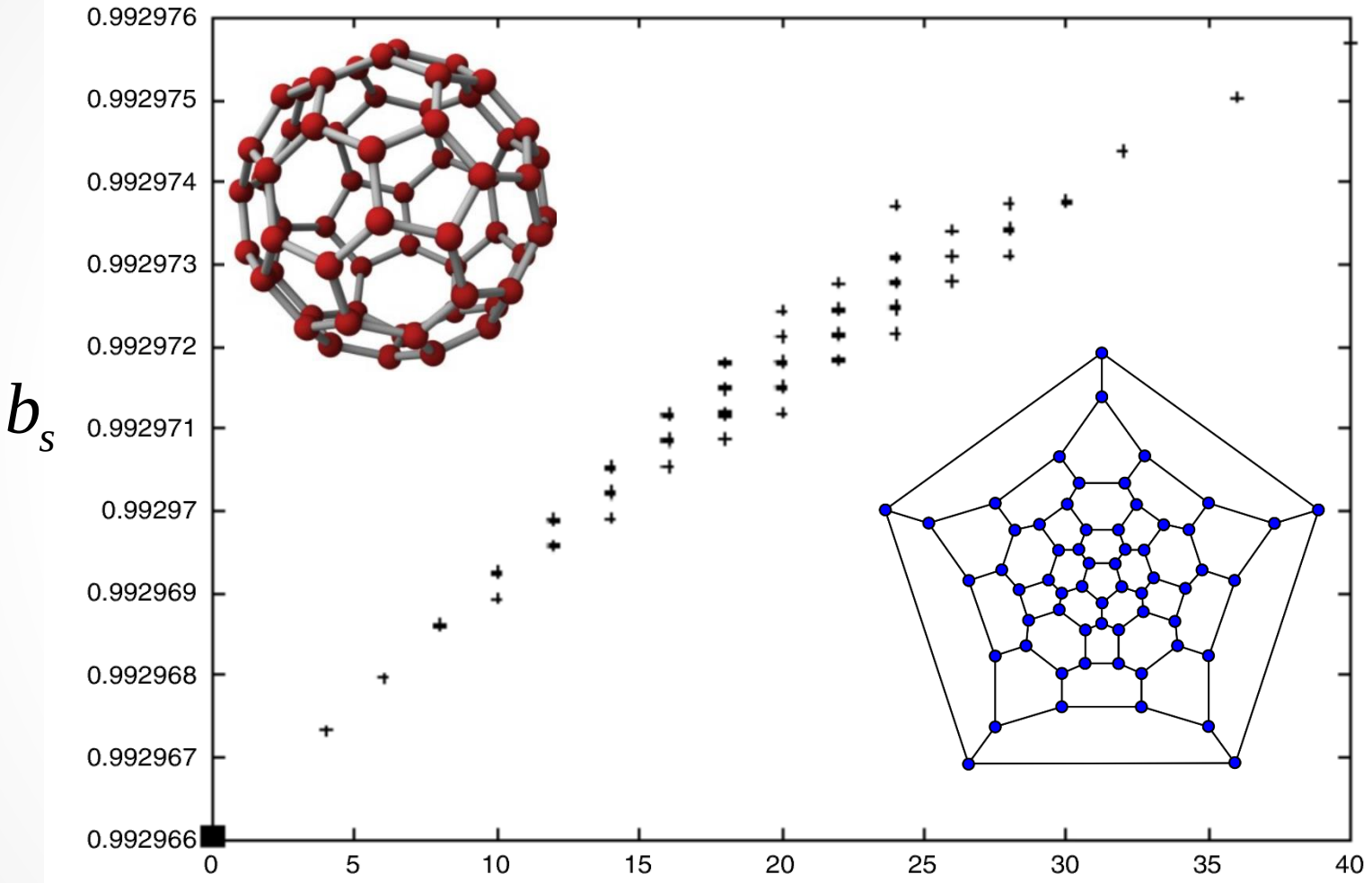
$b_e = 0.289$



$b_e = 0.194$

Estrada & Gomez-Gardenes: *Physica D, Nonlinearity* **323-324** (2016) 57-63.

HMO, bipartivity & stability



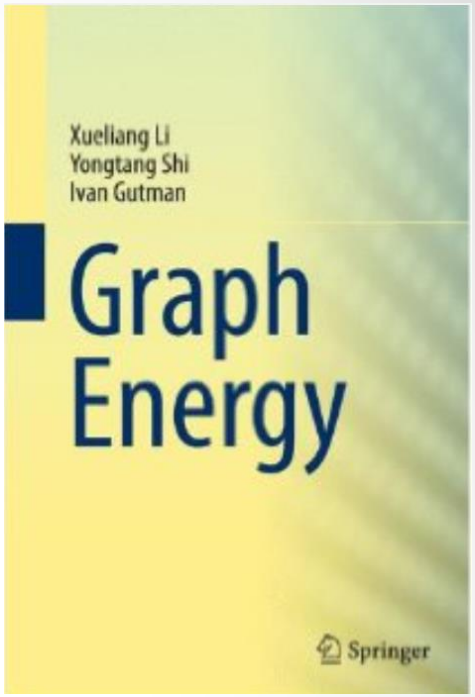
T. Došlić / Chemical Physics Letters 412 (2005) 336–340

Much ado about: Graph Energy

Let:

$$E_j = \tilde{\alpha} + \tilde{\beta}\lambda_j$$

be the energy of the jth level and let us set $\tilde{\alpha} = 0$. *Then,* $E_j = \lambda_j$ *expressed in units of* $\tilde{\beta}$.



The total HMO energy of an alternant conjugated molecule is

$$E = 2\sum_{j}^{occ} \lambda_j = \sum_{j=1}^{n} \left|\lambda_j\right|$$

What is the HMO energy after all?

We can then write the energy as the trace of another matrix function, the absolute matrix function:

$$E = tr|A|$$

where

$$|A| = \sqrt{A^2} \qquad \textit{for} \qquad \|A\| \leq 1$$

In general:

$$\sqrt{M} = \frac{2\sin(\pi/2)}{\pi}\int_0^{\infty}\left(t^2 I + M\right)^{-1} dt$$

Estrada & Benzi: *Discr. Appl. Math*. 230 (**2017**) 307-334.

What is the HMO energy after all?

Let us make the following transformation:

$$|A| = \sqrt{A^2} = \lambda_1 \sqrt{\left(\frac{A}{\lambda_1}\right)^2}$$

Then, we have the following result.

Theorem. *The HMO energy of an alternant conjugated molecule is given by:*

$$E = \lambda_1 \mathrm{tr} \sum_{k=0}^{\infty} \binom{1/2}{k} \sum_{l=0}^{k} (-1)^{k-l} \binom{k}{l} \left(\frac{A}{\lambda_1}\right)^{2l}.$$

Estrada & Benzi: *Discr. Appl. Math.* 230 (**2017**) 307-334.

What is the HMO energy after all?

Example.

$$E = \lambda_1 \mathrm{tr}\left[I + \frac{1}{2}\left(\frac{A^2}{\lambda_1^2} - I \right) - \frac{1}{8}\left(\frac{A^2}{\lambda_1^2} - I \right)^2 + \frac{1}{16}\left(\frac{A^2}{\lambda_1^2} - I \right)^3 - \cdots \right].$$

Estrada & Benzi: *Discr. Appl. Math*. 230 (**2017**) 307-334.

What is the HMO energy after all?

Bounds:

(1) $$E \leq \sqrt{2mn}$$

B. McClelland, Properties of the latent roots of a matrix: The estimation of pi-electron energies. *J. Chem. Phys*. 54, 640-643 (**1971**)

(2) $$E \leq \frac{2m}{n} + \sqrt{(n-1)\left(2m - 4m^2\right)/n^2}$$

J.H. Koolen, V. Moulton, I. Gutman, Improving the McClelland inequality for total -electron energy. *Chem. Phys. Lett*. 320, 213-216 (**2000**)

What is the HMO energy after all?

$$E \leq \left(\frac{\lambda_1}{2}\right)n + \left(\frac{1}{\lambda_1}\right)m \qquad (1^{st}\ Order)$$

$$E \leq \left(\frac{3\lambda_1}{8}\right)n + \left(\frac{6\lambda_1^2 - 1}{4\lambda_1^3}\right)m - \left(\frac{1}{2\lambda_1^3}\right)P_3 - \left(\frac{1}{\lambda_1^3}\right)C_4 \qquad (2^{nd}\ Order)$$

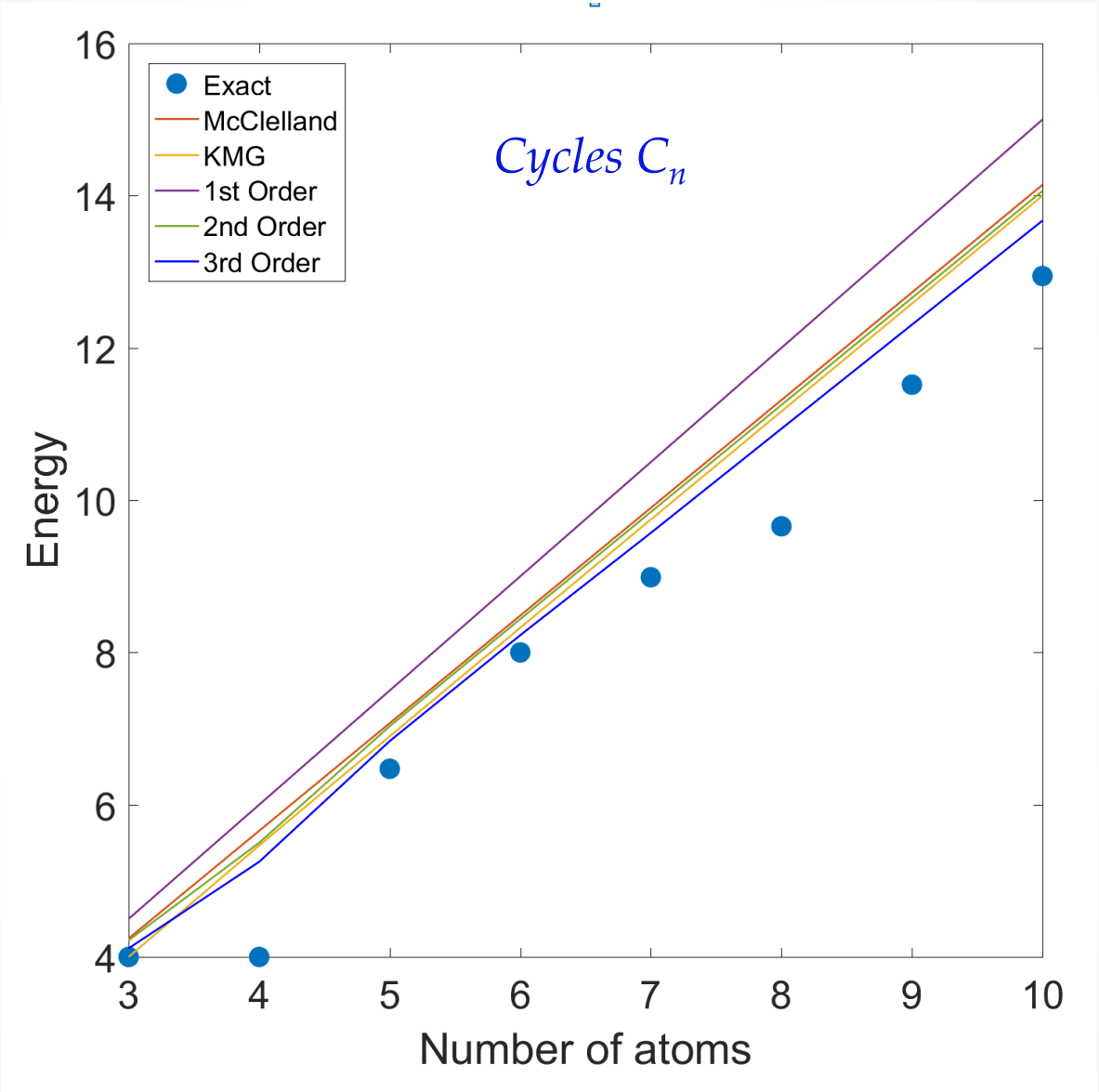
$$E \leq \left(\frac{5\lambda_1}{16}\right)n + \left(\frac{15\lambda_1^4 - 5\lambda_1^2 + 1}{8\lambda_1^5}\right)m - \left(\frac{5\lambda_1^2 - 3}{4\lambda_1^5}\right)P_3 \qquad (3^{rd}\ Order)$$

$$- \left(\frac{5\lambda_1^2 - 6}{2\lambda_1^5}\right)C_4 + \left(\frac{3}{2\lambda_1^5}\right)C_3 + \left(\frac{3}{8\lambda_1^5}\right)P_4 + \left(\frac{3}{4\lambda_1^5}\right)S_{1,3}$$

$$+ \left(\frac{9}{4\lambda_1^5}\right)F + \left(\frac{3}{2\lambda_1^5}\right)H + \left(\frac{3}{4\lambda_1^5}\right)C_6$$

Estrada & Benzi: *Discr. Appl. Math.* 230 (**2017**) 307-334.

What is the HMO energy after all?



Estrada & Benzi: *Discr. Appl. Math*. 230 (**2017**) 307-334.

HMO charge density matrix

The entries of the HMO density matrix are defined by:

$$\rho_{rs} = 2\sum_{j}^{occ} \psi_j(r)\psi_j(s)$$

We have proved that the charge density matrix is expressible as:

$$\rho = I + \frac{A}{\lambda_1}\sum_{k=0}^{\infty}\frac{(2k-1)!!}{(2k)!!}(-B)^k,$$

such that

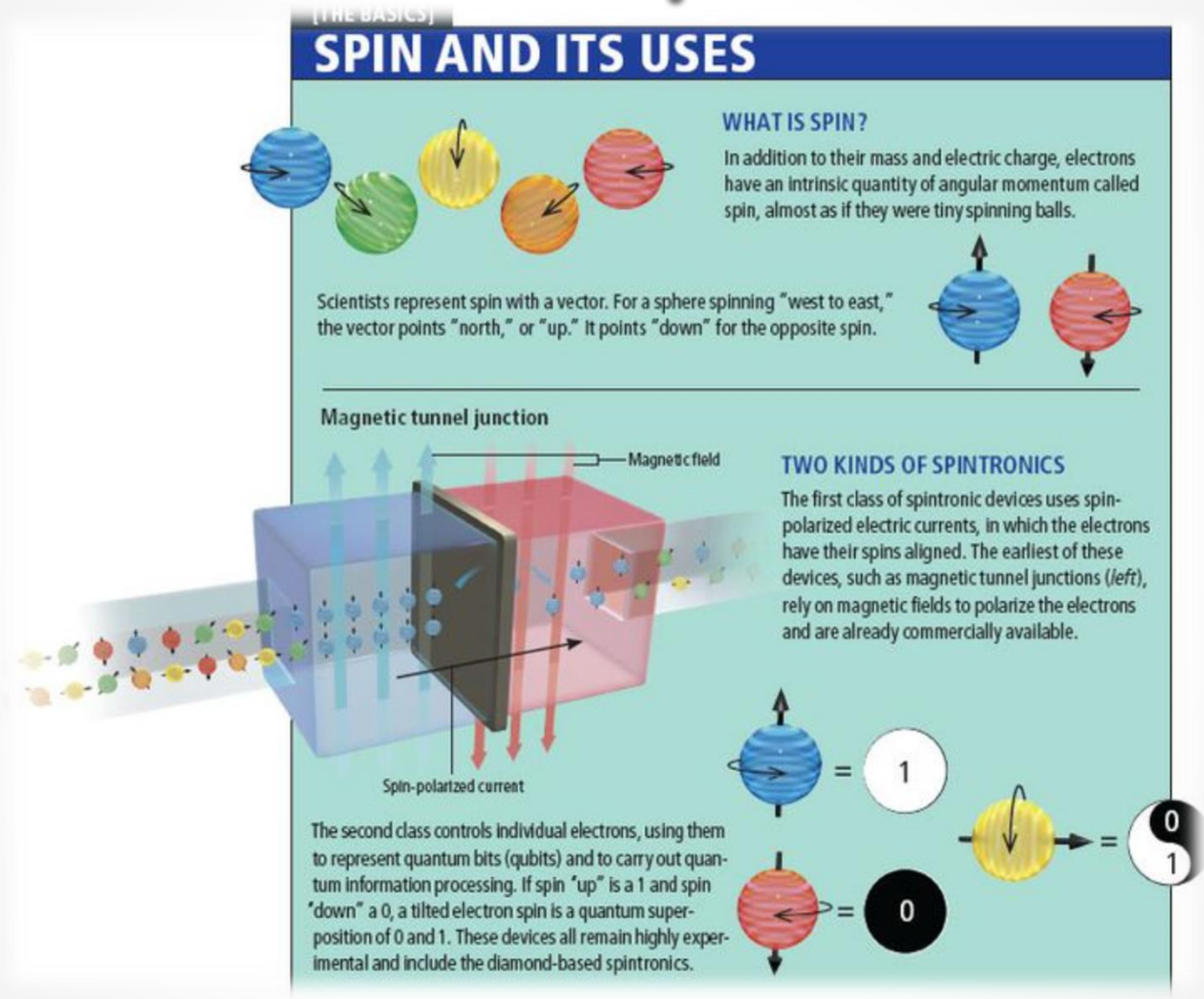
$$\rho = I + \frac{A}{\lambda_1}\left(I - \frac{1}{2}\left(\frac{A^2}{\lambda_1^2} - I\right) + \frac{3}{8}\left(\frac{A^2}{\lambda_1^2} - I\right)^2 - \cdots\right.$$

Example:

$$\rho = I + a_1\frac{A}{\lambda_1} - a_3\frac{A^3}{\lambda_1^3} + a_5\frac{A^5}{\lambda_1^5} - a_7\frac{A^7}{\lambda_1^7} + \cdots$$

Estrada: *Proc. Royal Soc. A* 474 (**2018**) 20170721.

HMO & Spintronics



Awschalom, Epstein & Hanson, *Scientific American* **297**, 84 - 91 (2007)

HMO & Spintronics

Applications

HDD (Hard Disc Drive)
Read head

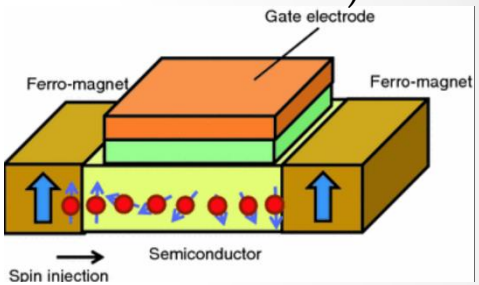
GMR

Large TMR + Low R
Large CPP-GMR

MRAM (Magnetic Random Access Memory)

Huge TMR

Spin-FET (Spin-Field Effect Transistor)



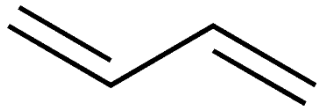
High spin injection efficiency into semiconductor

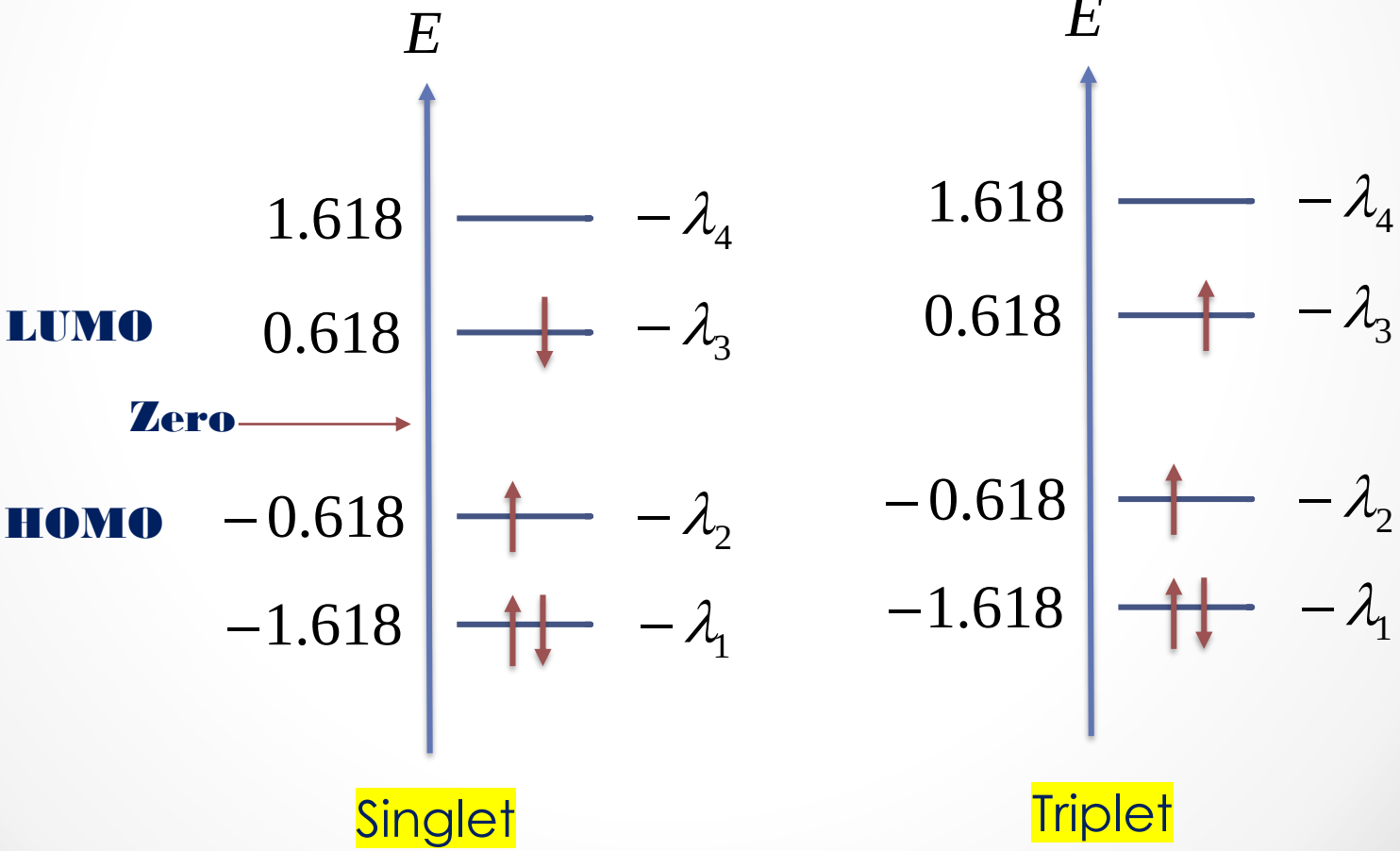
(Taken from Google Images)

TMR: Tunnel Magnetoresistance
CPP-GMR: Current Perpendicular to Plane-Giant Magnetoresistance

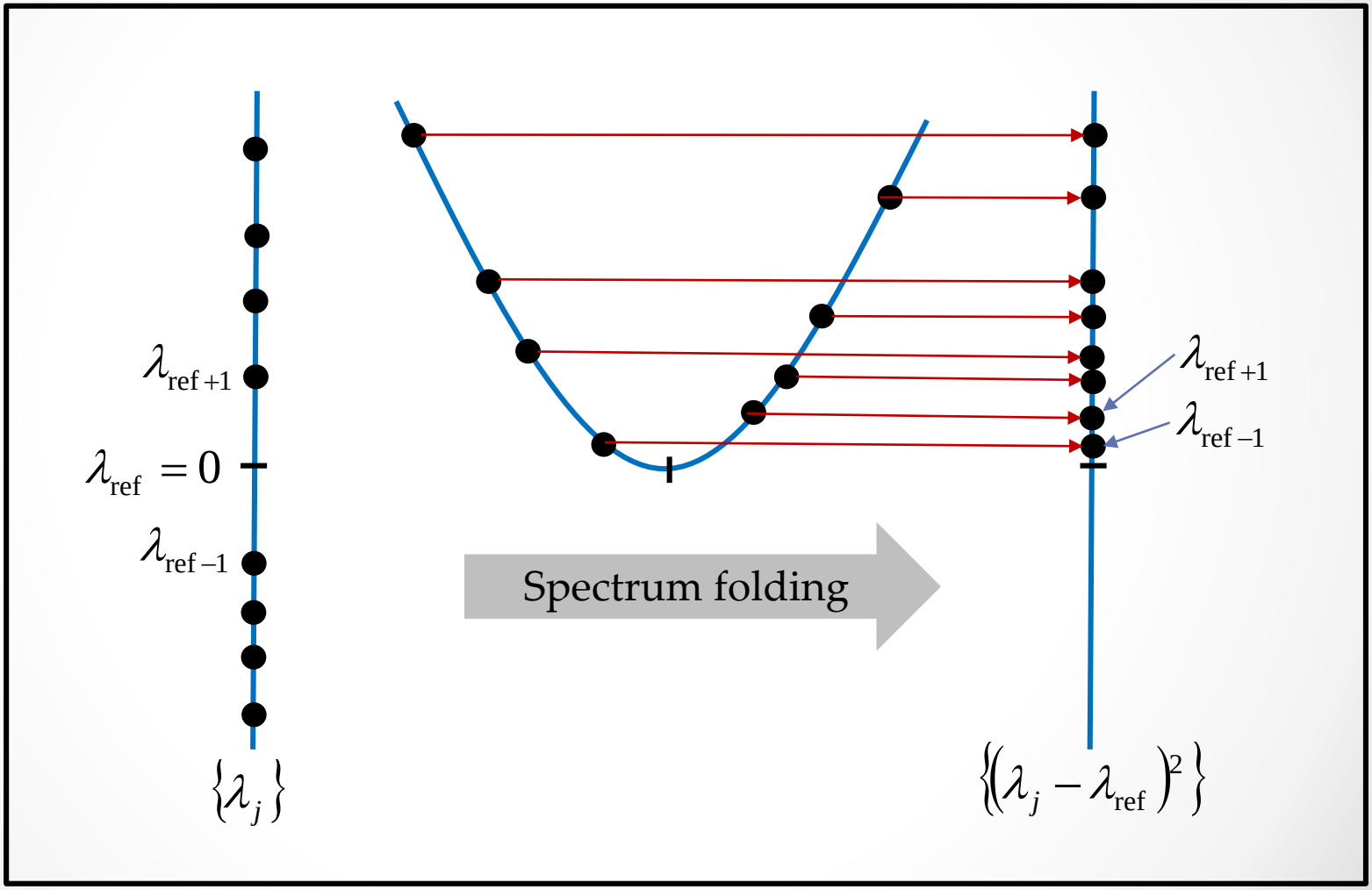
HMO & Spintronics

HOMO-LUMO, and nullity





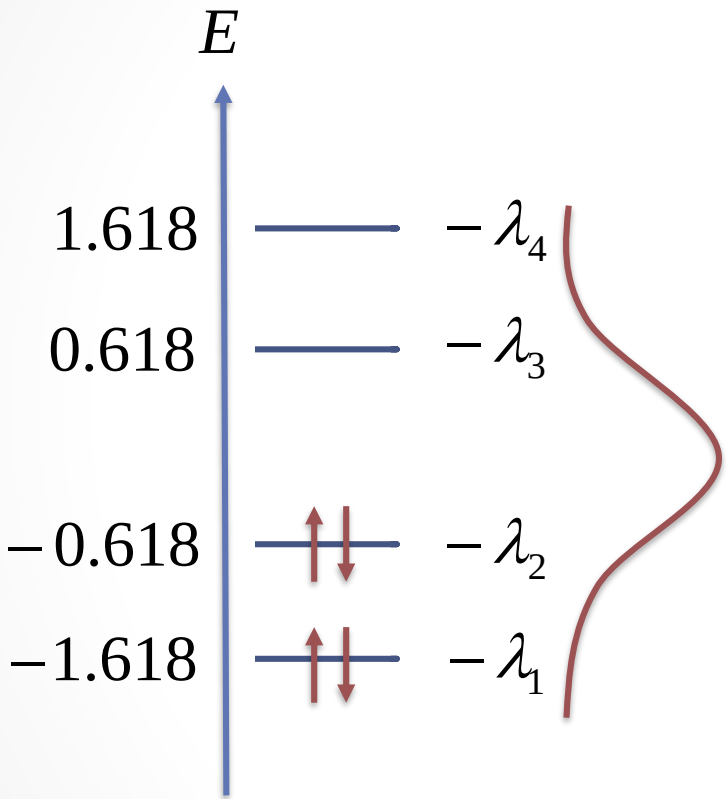
HMO & Spintronics



Barrios-Vargas & Naumis: *J. Phys.: Condens. Matter* **23** (2011) 375501

HMO & Spintronics

Lattice renormalization and a Gaussian matrix function



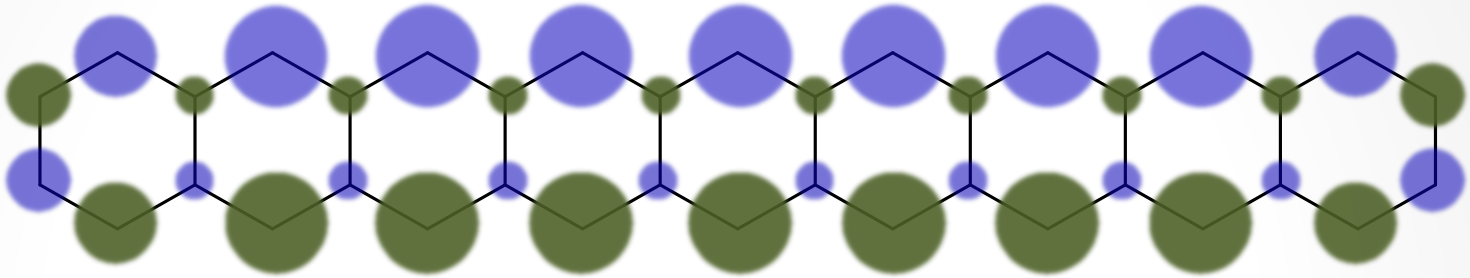
$$\mathbf{H} = \sum_{k=0}^{\infty} \frac{\left(-A^2\right)^k}{k!} = \exp\left(-A^2\right)$$

Estrada & Benzi: *Chem. Phys. Lett.* **568** (2013) 184-189

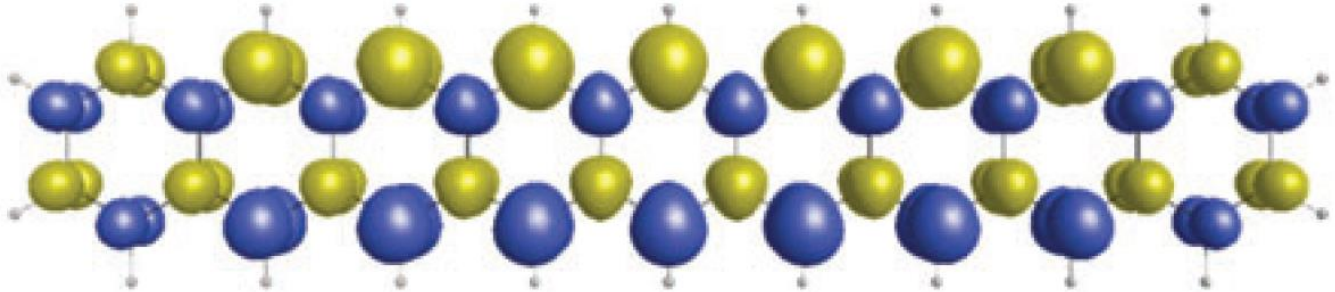
HMO & Spintronics

Spin density of PAHs

$$\mathbf{H}_{ii} = \left(\exp\left(-A^2\right)\right)_{ii}$$



$$LC-(U)BLYP/6-31G^*$$

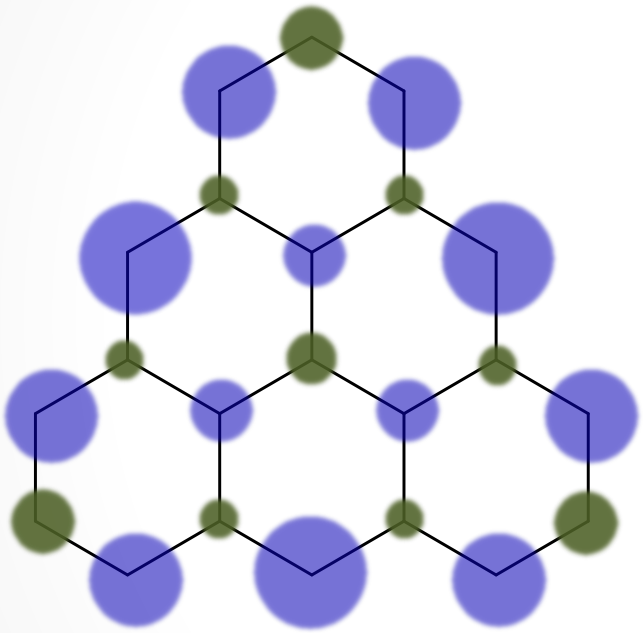


(*Phys. Chem. Chem. Phys.*, 2011, **13**, 20575–20583)

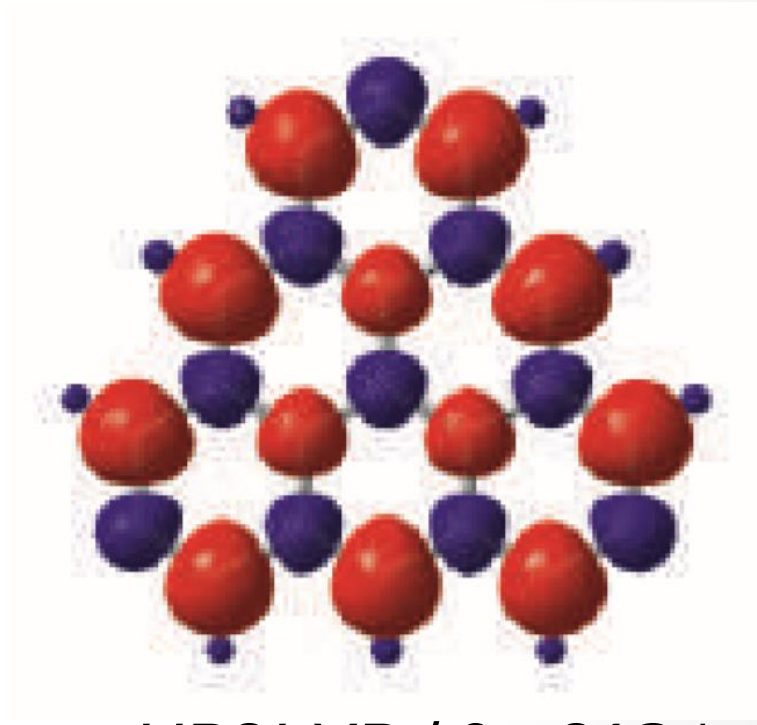
Estrada & Benzi: *Chem. Phys. Lett*. 568 (**2013**) 184-189

HMO & Spintronics

Spin density distribution of triangulenes



$$\mathbf{H}_{ii} = \left(\exp\left(-A^2\right)\right)_{ii}$$



$$UB3LYP/6-31G^*$$

(*Nature Chemistry*, 3, 2011, 197-204)

Estrada & Benzi: *Chem. Phys. Lett.* **568** (2013) 184-189

HMO & Spintronics

CHEMISTRY

Elusive triangulene created by moving atoms one at a time

Researchers used microscope tip to make unstable hydrocarbon with 'molecular surgery'.

BY PHILIP BALL

Researchers at IBM have created an elusive molecule by knocking around atoms using a needle-like microscope tip. The flat, triangular fragment of a mesh of carbon atoms, called triangulene[1], is too unstable to be made by conventional chemical synthesis, and could find use in electronics.

This isn't the first time that atomic manipulation has been used to create unstable molecules that couldn't be made conventionally — but this one is especially desirable. "Triangulene is the first molecule that we've made that chemists have tried hard, and failed, to make already," says Leo Gross, who led the IBM team at the firm's laboratories in Zurich, Switzerland.

The creation of triangulene demonstrates a new type of chemical synthesis, says Philip Moriarty, a nanoscientist who specializes in molecular manipulation at the University of Nottingham, UK. In conventional synthesis, chemists react molecules together to build up larger structures. Here, by contrast, atoms on individual molecules were physically manipulated using a microscope.

But making molecules one at a time will be useful only in particular situations. And the method is unlikely to work for those wit complicated shapes or structures.

Triangulene is similar to a fragment graphene, the atom-thick material in whic carbon atoms are joined in a hexagonal mesh The new molecule is made up of six hexagon of carbon joined along their edges to form triangle, with hydrogen atoms around th sides (see 'Radical triangle'). Two of the outer carbon atoms contain unpaired electrons tha can't pair up to make a stable bond.

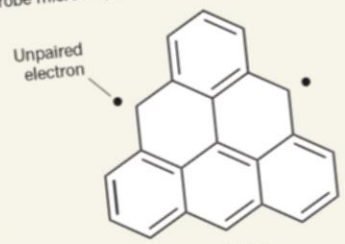
Such a molecule is highly unstable becaus the unpaired electrons tend to react with any thing around them. "As soon as you synthesiz it, it will oxidize," says Niko Pavliček, a membe of the IBM team. So far, the closest conven tional synthesis has come to making molecule of this sort involves buffering the reactiv edges with bulky hydrocarbon appendages[2].

The IBM team turned to a scanning prob microscope, which has a needle-sharp tip tha 'feels' a material's shape. The technique is usuall used to image molecules, by measuring attrac tive forces between the tip and sample, or th electric currents that pass between them. Th IBM team has shown[3] that, if the tip has a sma molecule such as carbon monoxide attached t it, force microscopy can provide images of suc high resolution that they resemble the ball-and stick diagrams of chemistry textbooks.

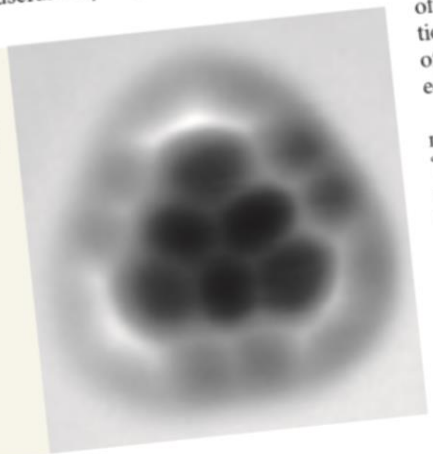
Gross's team has already demonstrated

RADICAL TRIANGLE

Triangulene is a flat molecule made up of a hexagonal mesh of carbon and hydrogen atoms (left). IBM researchers made the molecule by manipulating atoms with a scanning probe microscope, and then imaged it (right).

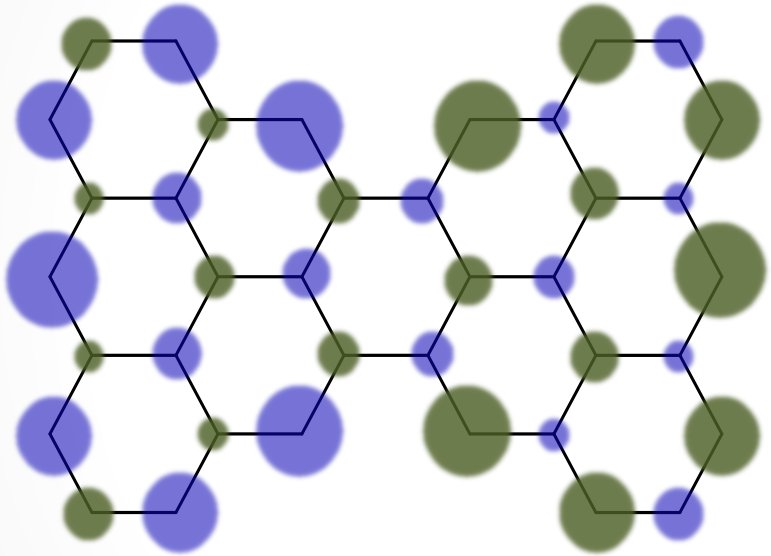


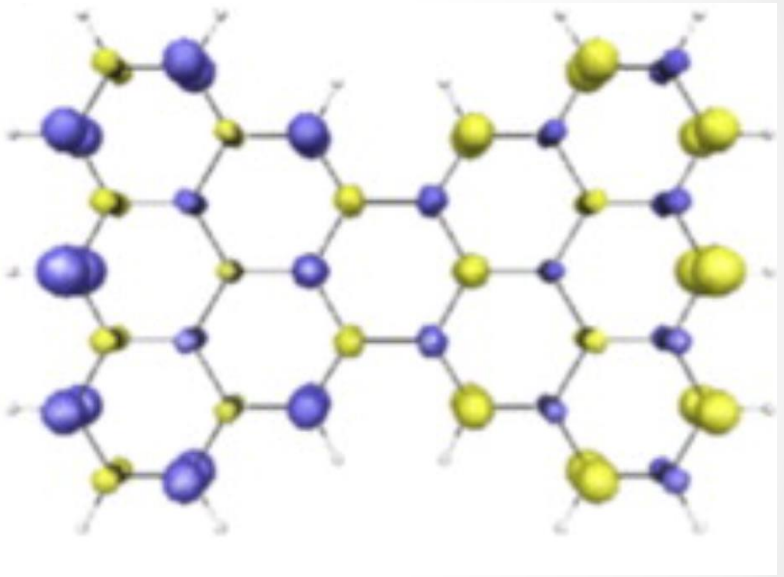
Hydrogen atoms on each corner not shown.



HMO & Spintronics

Spin density distribution of bow-tie PAHs





$$\mathbf{H}_{ii} = \left(\exp\left(-A^2\right)\right)_{ii}$$

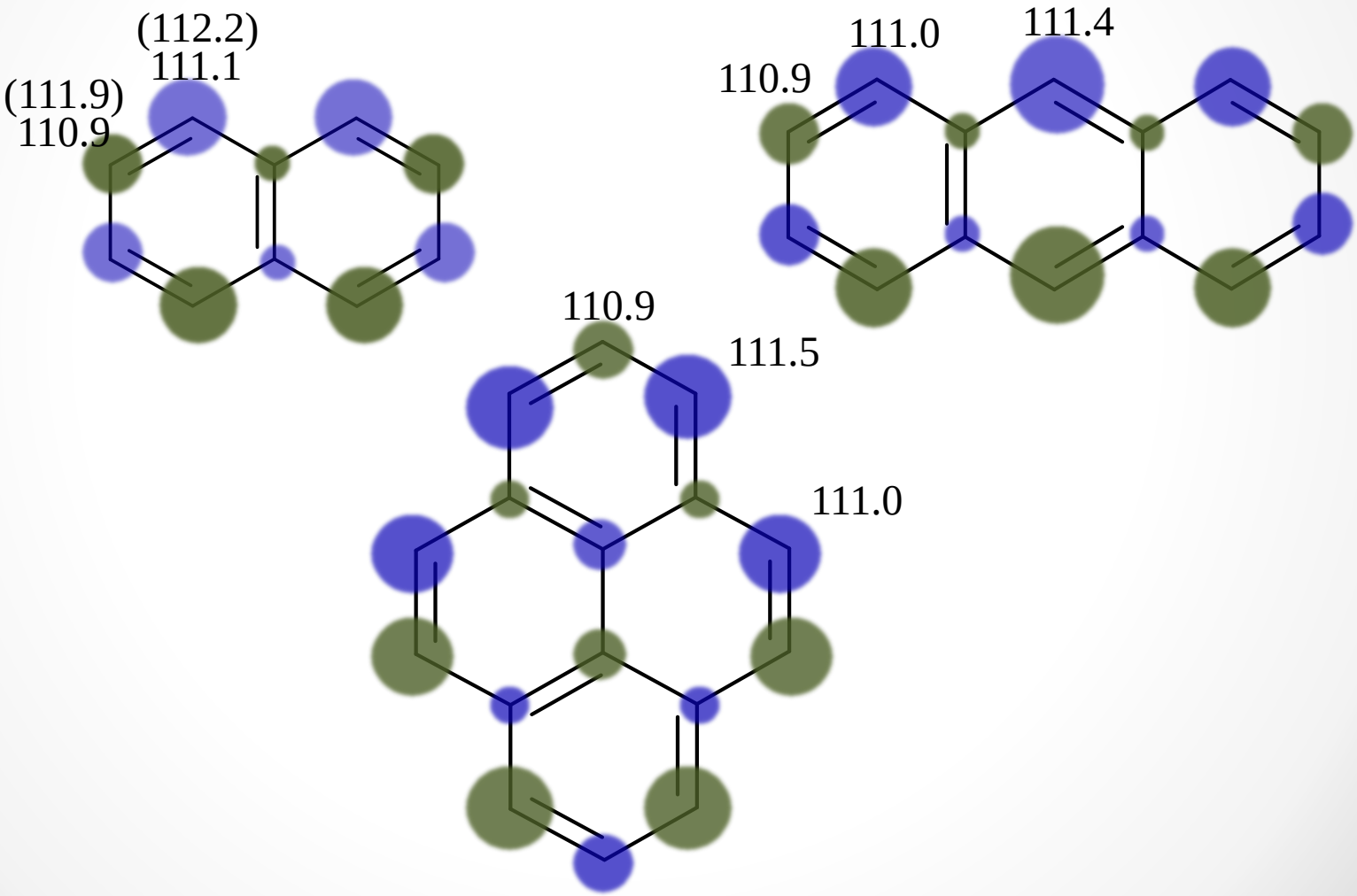
*UBHandHLYP / 6 – 31G **

(*Chem. Phys. Lett.*, 480, 2009, 278-283)

Estrada & Benzi: *Chem. Phys. Lett.* **568** (2013) 184-189

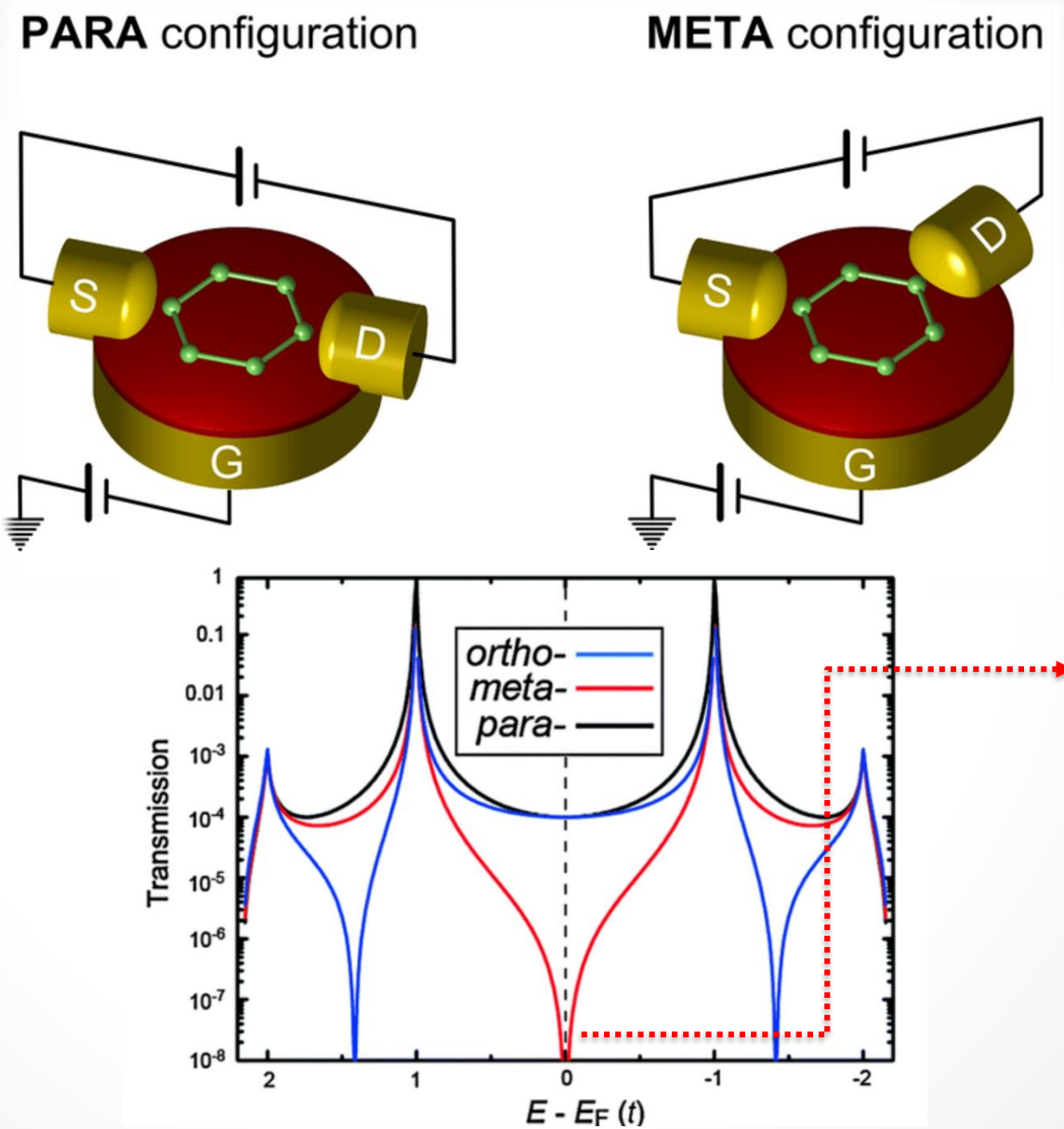
HMO & Spintronics

Bond dissociation enthalpies (kcal/mol at 298K) for the cleavage of the C-H bond



Estrada & Benzi: *Chem. Phys. Lett*. **568** (2013) 184-189

HMO & molecular electronics

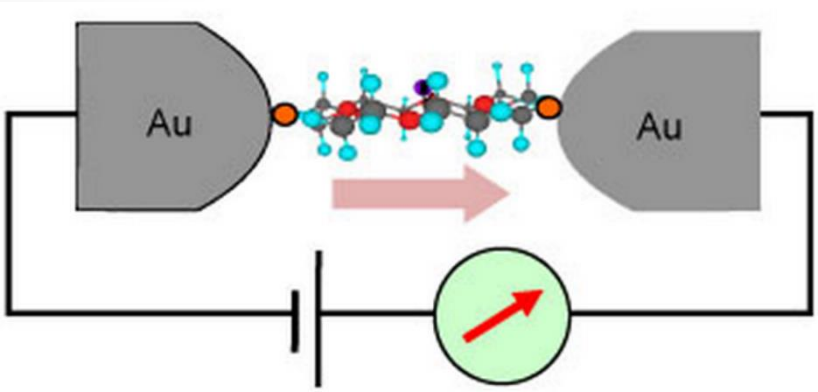


Quantum Interference

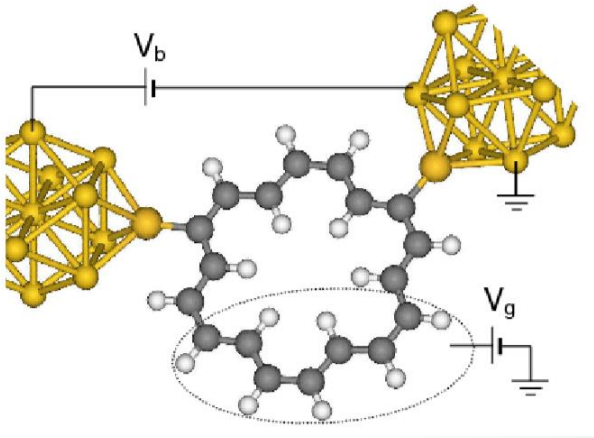
Guédon, et al. *Nature Nanotech 7* (2012) 305-309.

HMO & molecular electronics

Molecular switches

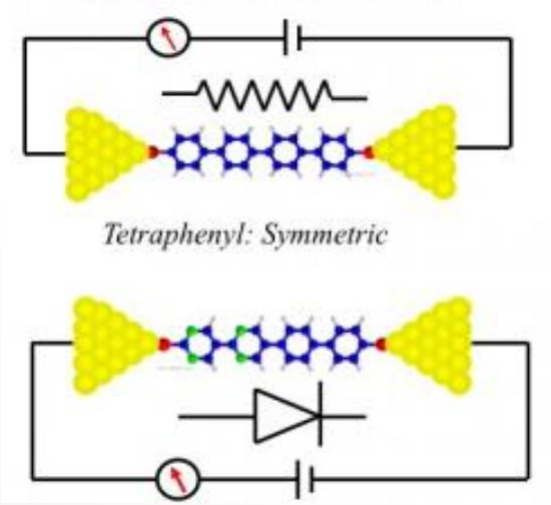


Control currents in molecular electronics

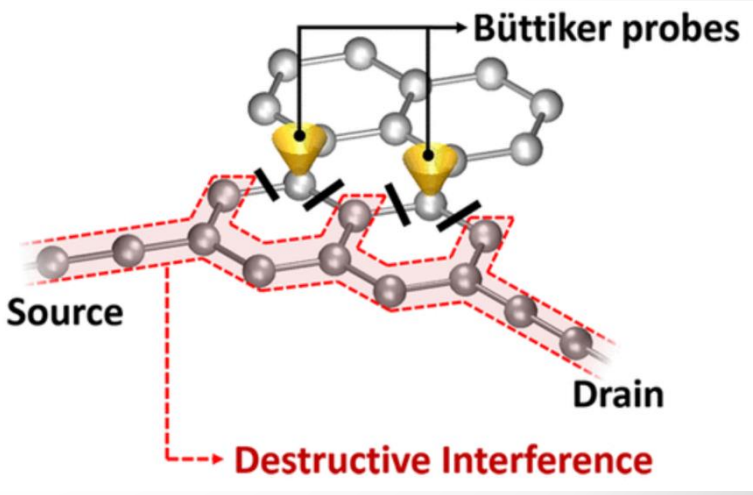


(Taken from Google Images)

Molecular diodes



Effect transistors

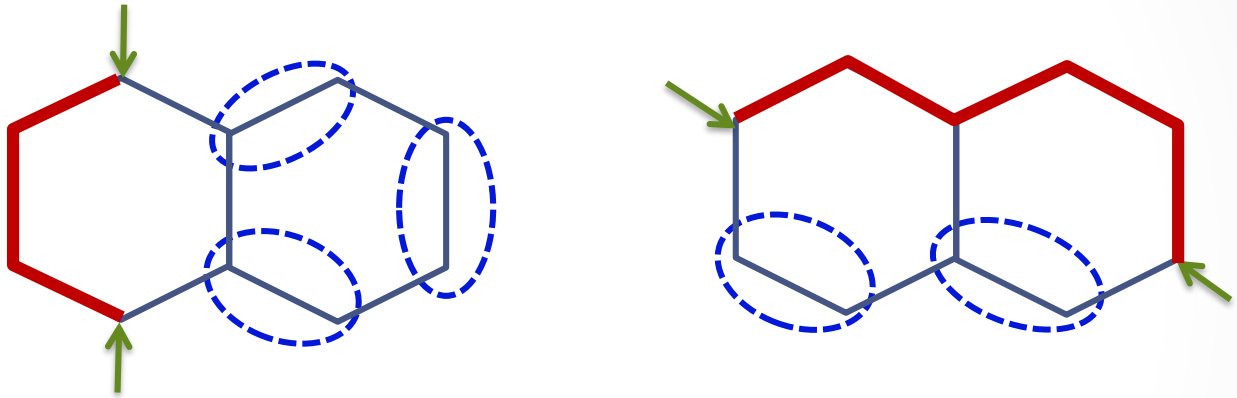


Ratner M. *Nature Nanotech*. 8 (**2013**) 378-381.

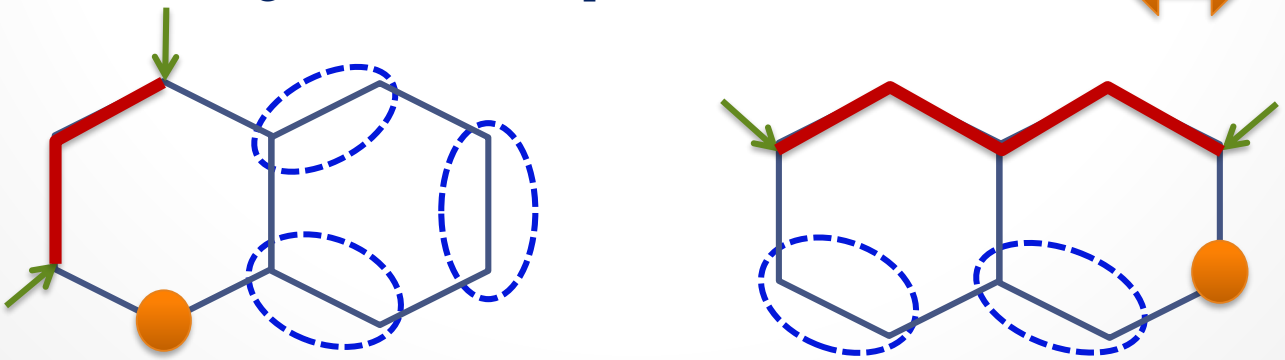
HMO & molecular electronics

Rules for predicting QI

Rule 1: Continuous path between electrodes without remaining atoms, or all of them are paired ⟺ **No QI**



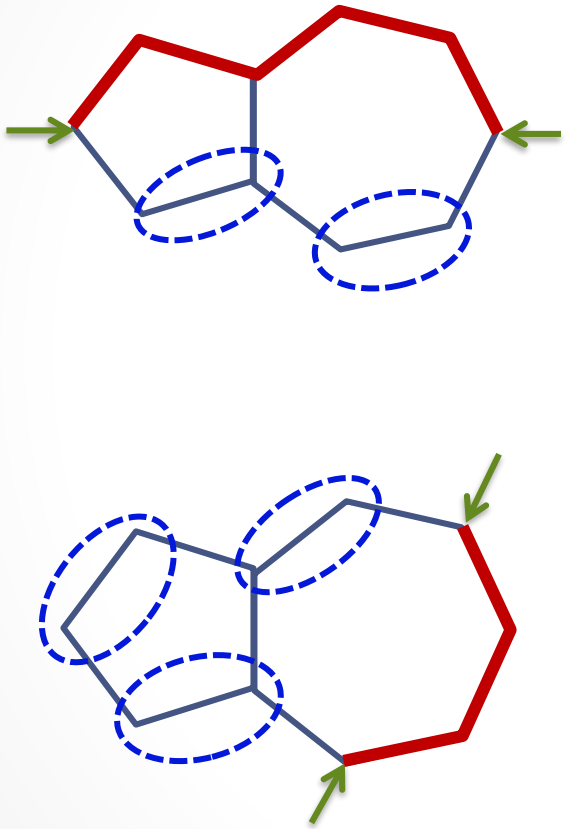
Rule 2: Continuous path between electrodes where not all the remaining atoms can be paired ⟺ **QI**



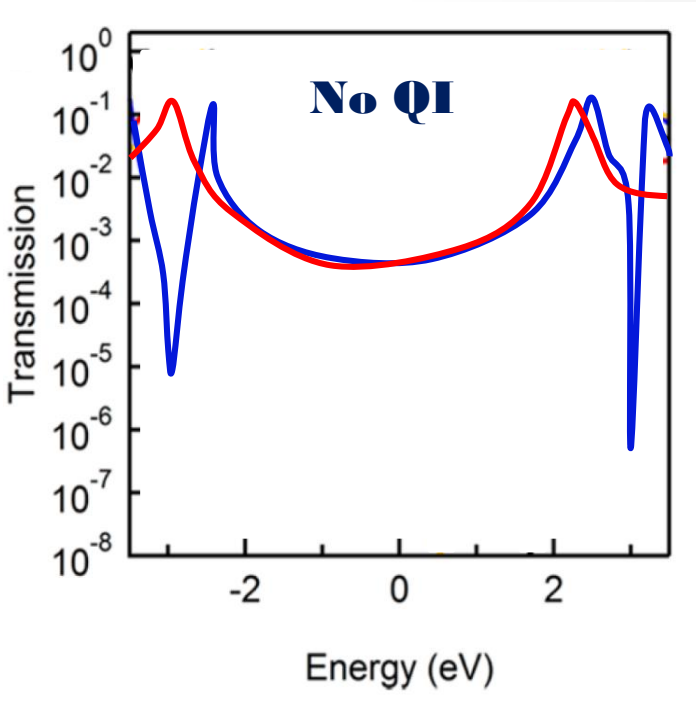
*Markusen et al: Nano Letters 10 (**2010**) 4260-4265*

HMO & molecular electronics

Predicted No QI



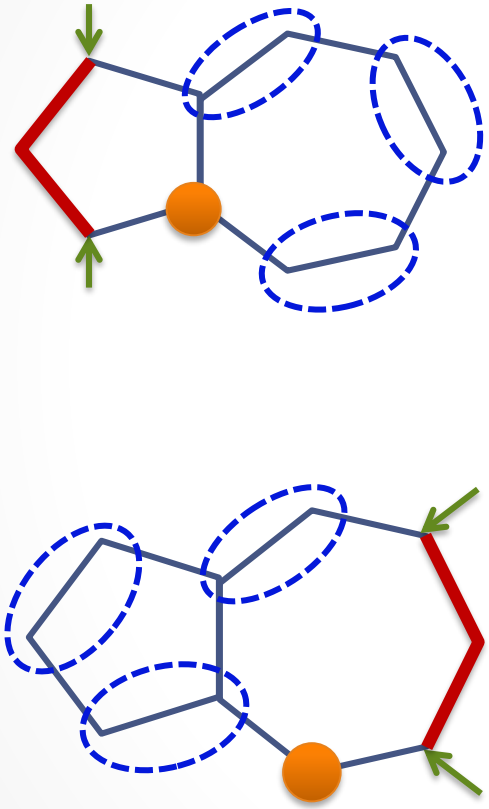
Observed Transmission



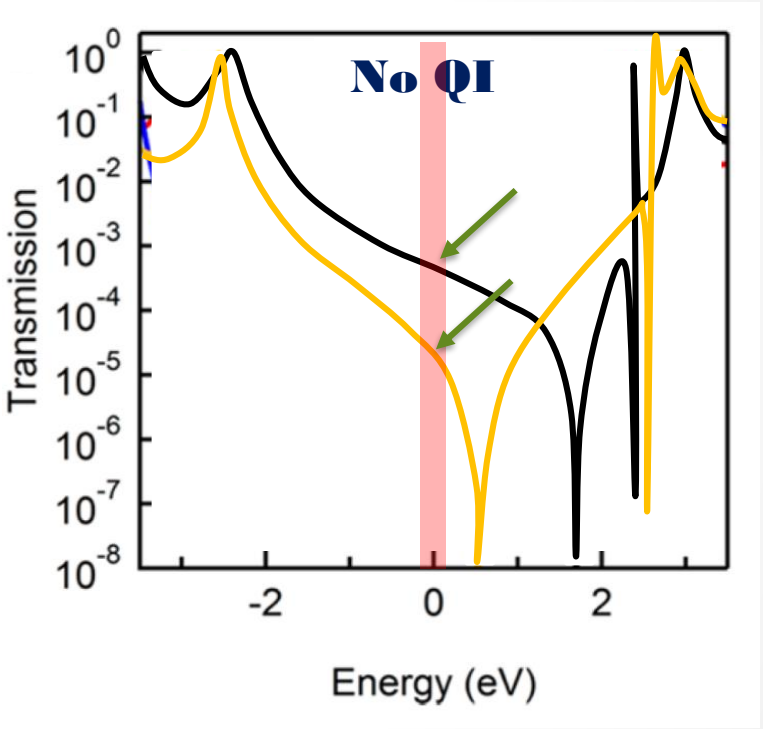
Xia *et al*: *Nano Letters* 14 (**2014**) 2941-2945

HMO & molecular electronics

Predicted QI



Observed Transmission



Xia *et al*: *Nano Letters* 14 (**2014**) 2941-2945

HMO & molecular electronics

The transmission probability of an electron entering a molecular junction with an energy E is given by

$$T(E) = \gamma(E)^2 \left| G(E) \right|^2$$

where

$$\gamma(E) = \left[\Gamma_L(E) \right]_{11} = \left[\Gamma_R(E) \right]_{11}$$

is given by the self-energy matrix due to the left/right lead, and G(E) is the Green function matrix of the contacted molecule.

Datta, S. *Lessons from Nanoelectronics: A New Perspective on Transport* (World Scientific, 2012).

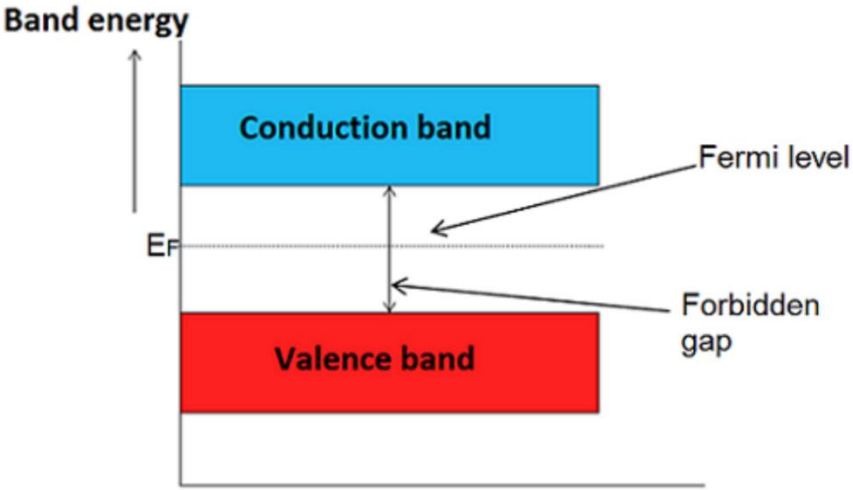
HMO & molecular electronics

In the HMO framework we have that

$$G\left(E\right)=\left(EI-A\right)^{-1},$$

and for the Fermi energy

$$G\left(E_F\right)=-A^{-1}.$$



(Taken from Google Images)

HMO & molecular electronics


Y. Tsuji


R. Movassagh


E. Estrada


R. Hoffmann

We have proved that:

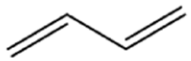
$$G\left(E_F\right)=\frac{\left(-1\right)^{n/2}}{\prod_i^{n/2}\varepsilon_i^2}\left[A^{n-1}-\left(\sum_i^{n/2}\varepsilon_i^2\right)A^{n-3}+\left(\sum_{i\neq j}^{n/2}\varepsilon_i^2\varepsilon_j^2\right)A^{n-5}-\cdots\right]$$

*Tsuji et al.: Chemical Rev. (**2018**) in press.*

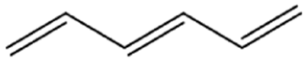
HMO & molecular electronics

Alternant hydrocarbons

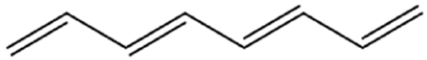
$$G = -A$$



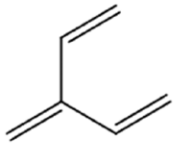
$$G = A^3 - 3A$$



$$G = -A^5 + 5A^3 - 6A$$

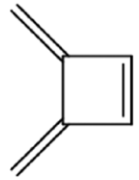


$$G = A^7 - 7A^5 + 15A^3 - 10A$$

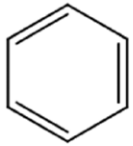


$$G = -A^5 + 5A^3 - 5A$$

$$G = -A^5 + 7A^3 - 7A$$

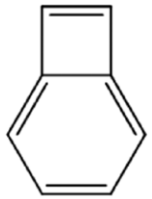


$$G = -A^5 + 6A^3 - 5A$$



$$G = -\frac{1}{4}\left(A^5 - 6A^3 + 9A\right)$$

$$G = A^7 - 8A^5 + 18A^3 - 12A$$



$$G = A^7 - 9A^5 + 22A^3 - 16A$$

*Tsuji et al.: Chemical Rev. (**2018**) in press.*

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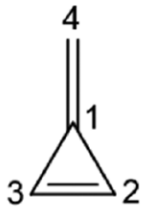
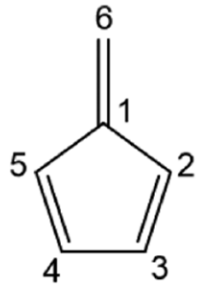
Non-alternant hydrocarbons



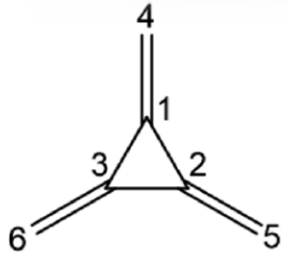
triafulvene

$$\mathbf{G} = \mathbf{A}^3 - 4\mathbf{A} - 2\mathbf{I}$$



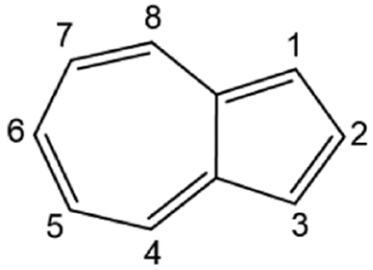
fulvene

$$\mathbf{G} = -\mathbf{A}^5 + 6\mathbf{A}^3 - 8\mathbf{A} + 2\mathbf{I}$$



[3]radialene

$$\mathbf{G} = -\mathbf{A}^5 + 6\mathbf{A}^3 + 2\mathbf{A}^2 - 6\mathbf{A}$$



azulene

$$\mathbf{G} = \frac{1}{4}\left[-\mathbf{A}^9 + 11\mathbf{A}^7 - 41\mathbf{A}^5 + 2\mathbf{A}^4 + 61\mathbf{A}^3 - 6\mathbf{A}^2 - 31\mathbf{A} + 2\mathbf{I}\right]$$

*Tsuji et al.: Chemical Rev. (**2018**) in press.*

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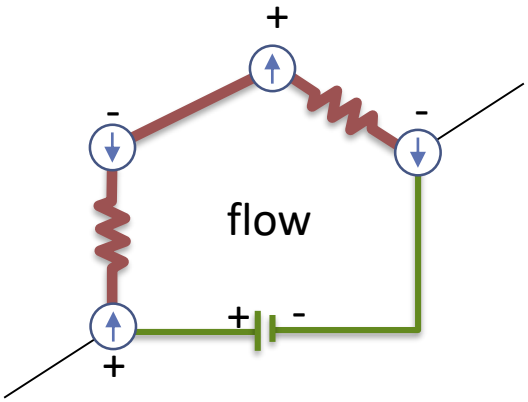
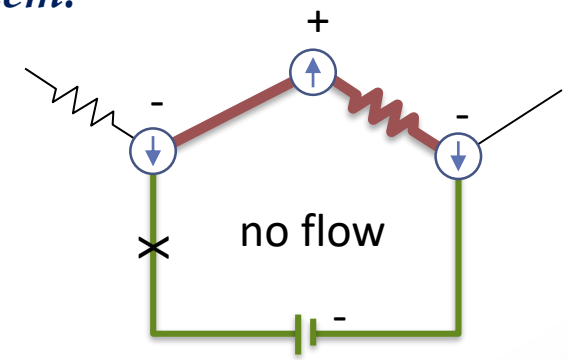
Electron transmission rules

- ***There is transmission between two atoms if and only if there is at least one path of odd length connecting them.***



- ***There is QI between two atoms if and only if there is no path of odd length connecting them.***



Estrada, In *Quantum Chemistry at the Dawn of the 21st Century*; Chakraborty, T., Carbo-Dorca, R., Eds.; Apple Academic Press: Oakville, ON, **2018**; pp 445–468.

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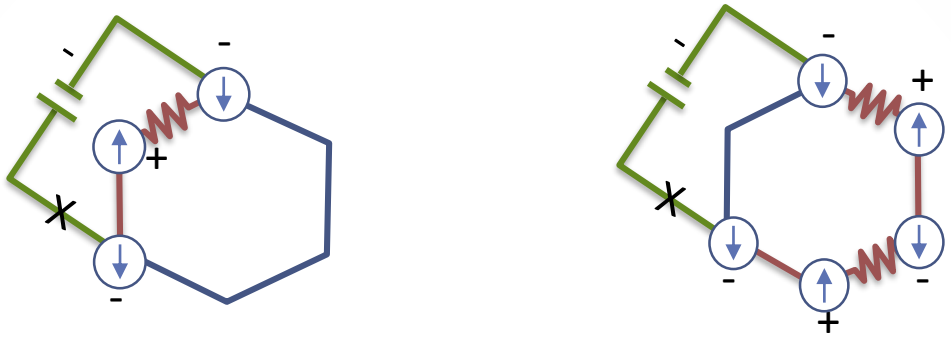
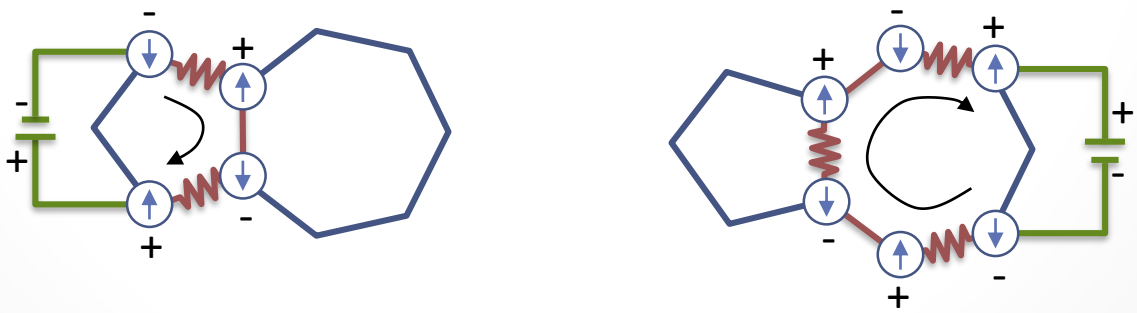
QI in meta position of benzene



Electron transmission in azulene



Estrada, In *Quantum Chemistry at the Dawn of the 21st Century*; Chakraborty, T., Carbo-Dorca, R., Eds.; Apple Academic Press: Oakville, ON, **2018**; pp 445–468.

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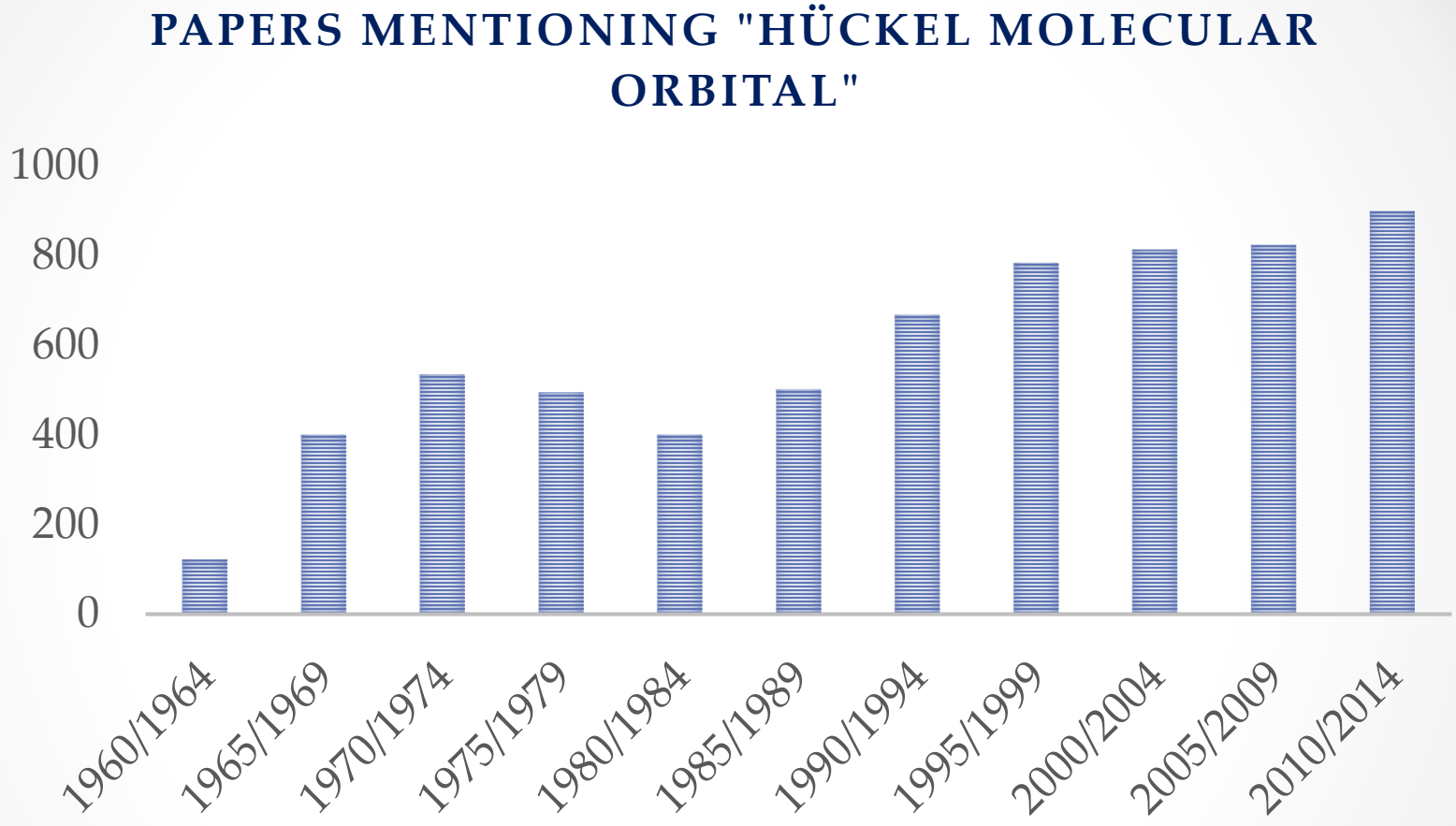

Not that bad for an 87 years old method!

Thank you!
Hvala!