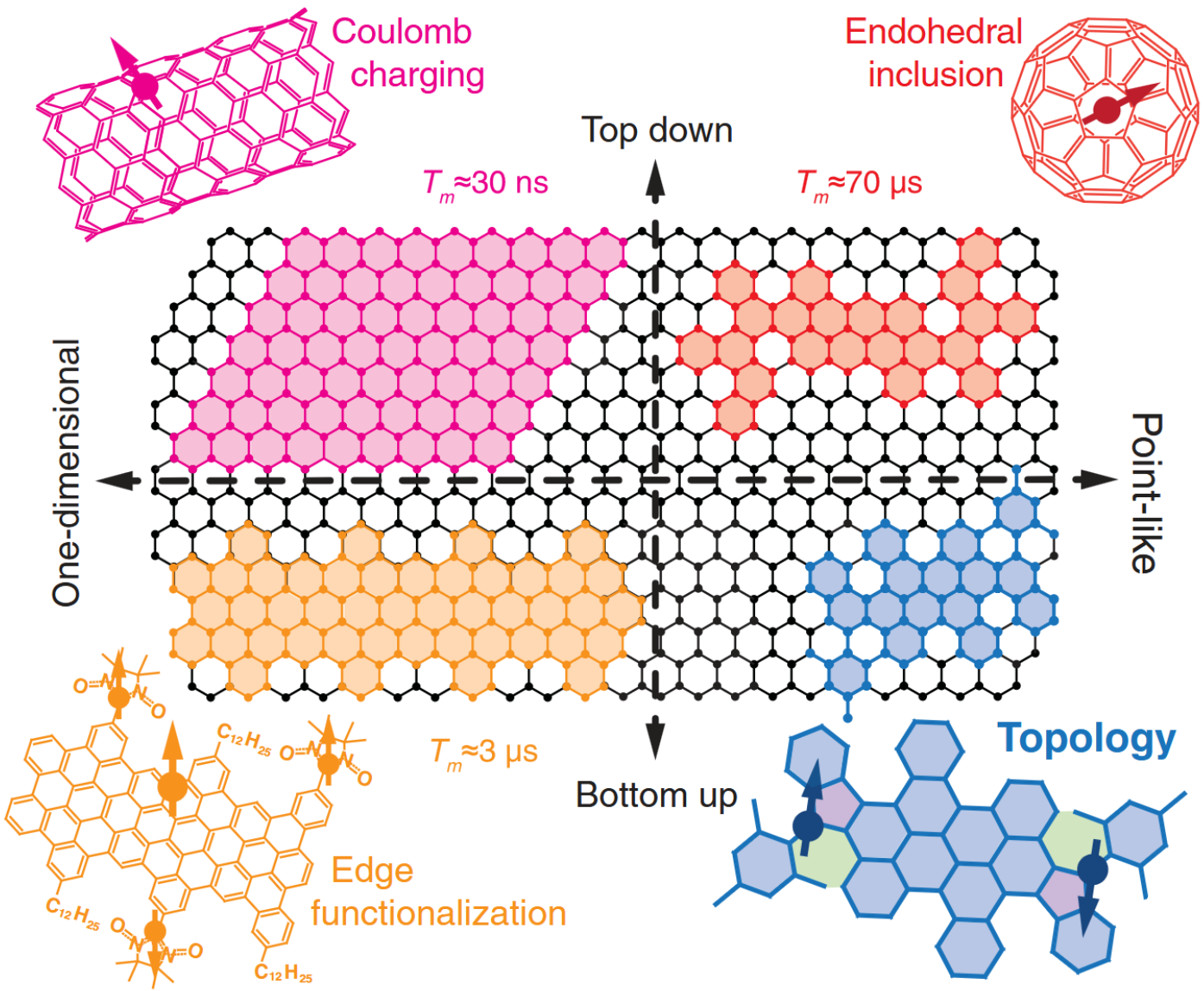
On the Foundations of Aromatic Reactivity

Lapo Bogani

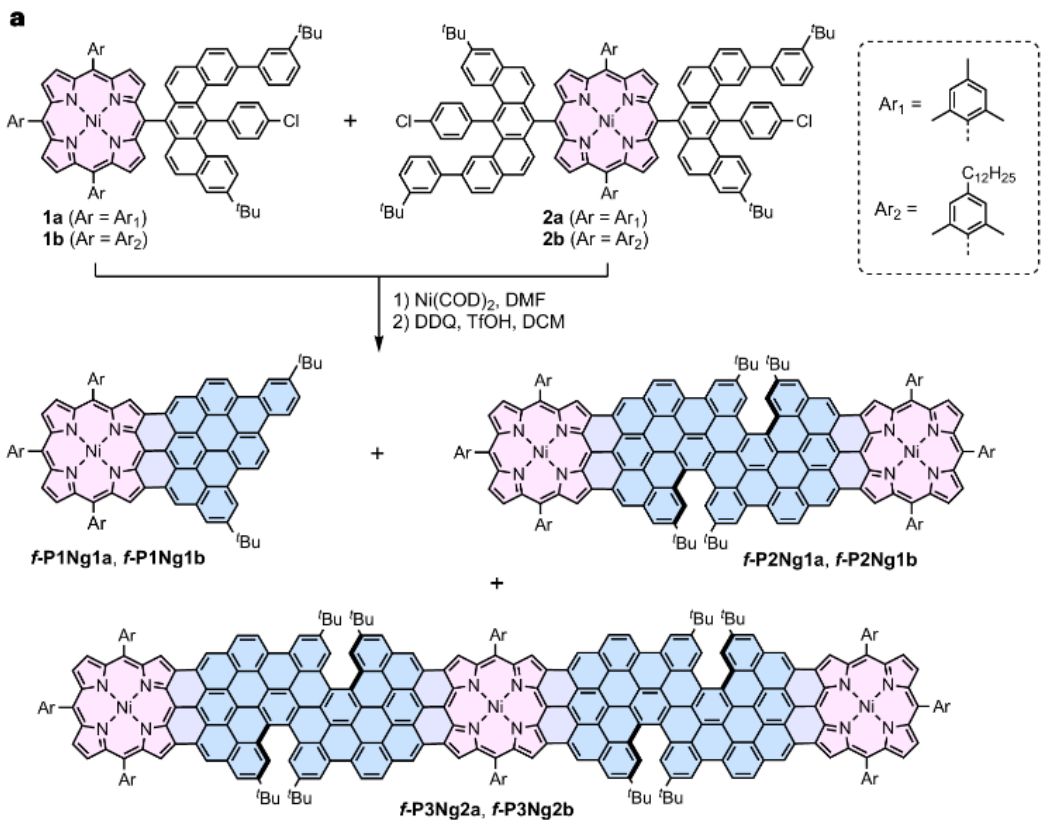
University of Florence – Departments of Chemistry and Physics

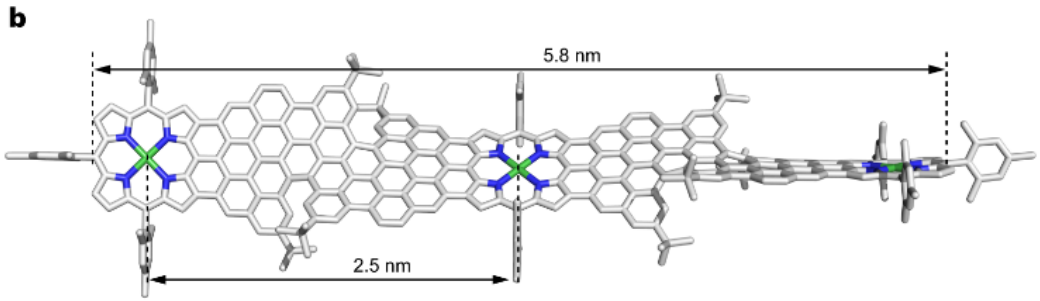
University of Oxford – Department of Materials

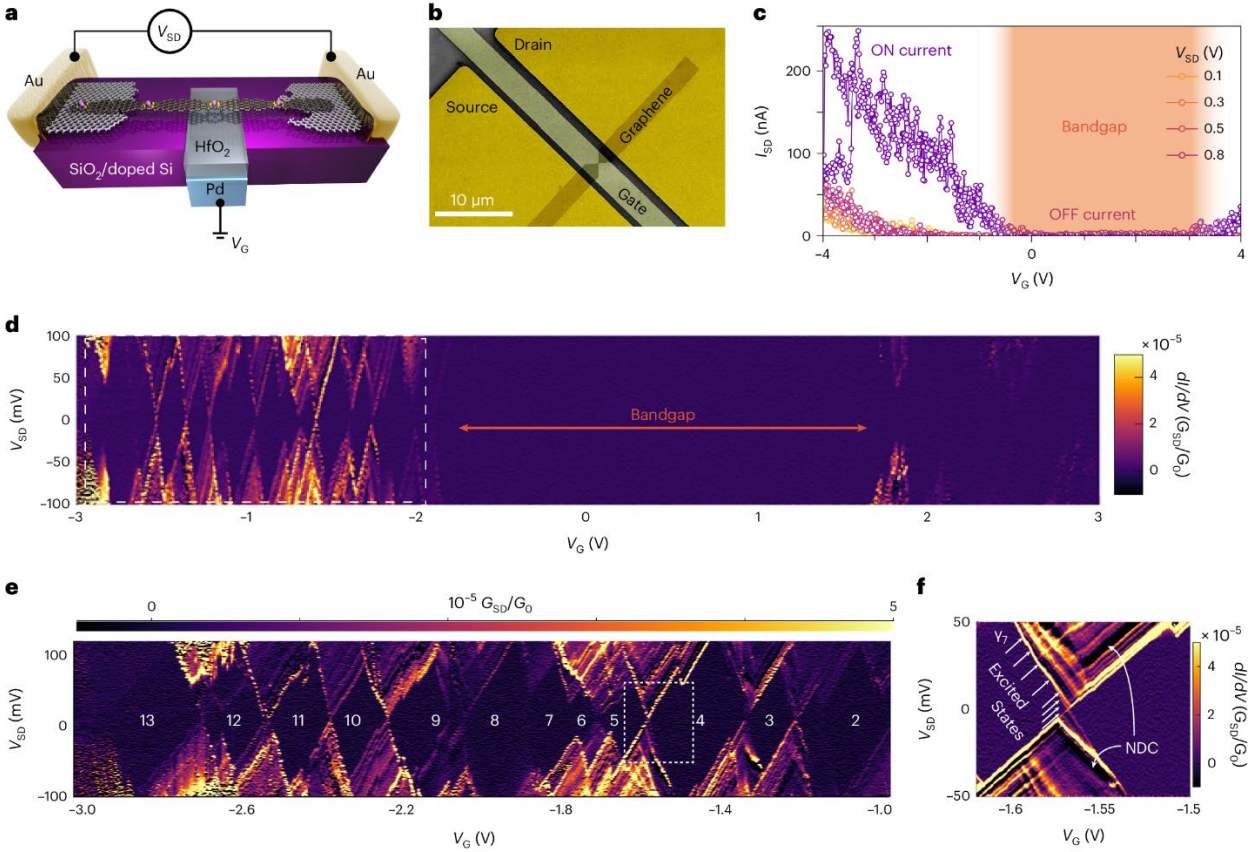
Molecular Graphenoids



Molecular Graphenoids







Nature Chemistry **2024**

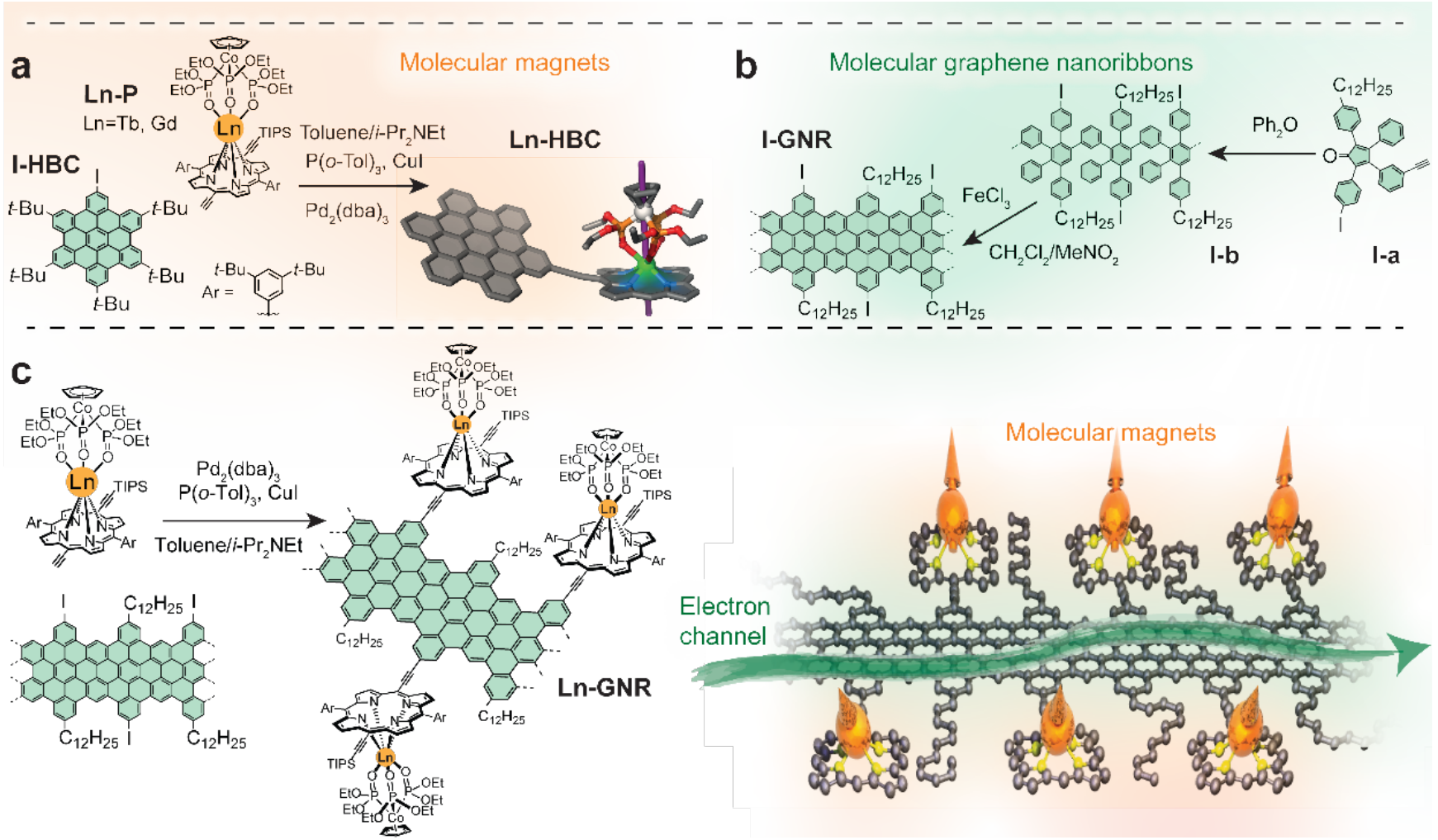
Porphyrin-fused graphene nanoribbons

Qiang Chen ✉, Alessandro Lodi, Heng Zhang, Alex Gee, Hai I. Wang, Fanmiao Kong, Michael Clarke, Matthew Edmondson, Jack Hart, James N. O'Shea, Wojciech Stawski, Jonathan Baugh, Akimitsu Narita, Alex Saywell, Mischa Bonn, Klaus Müllen, Lapo Bogani ✉ & Harry L. Anderson ✉

Molecular Graphenoids

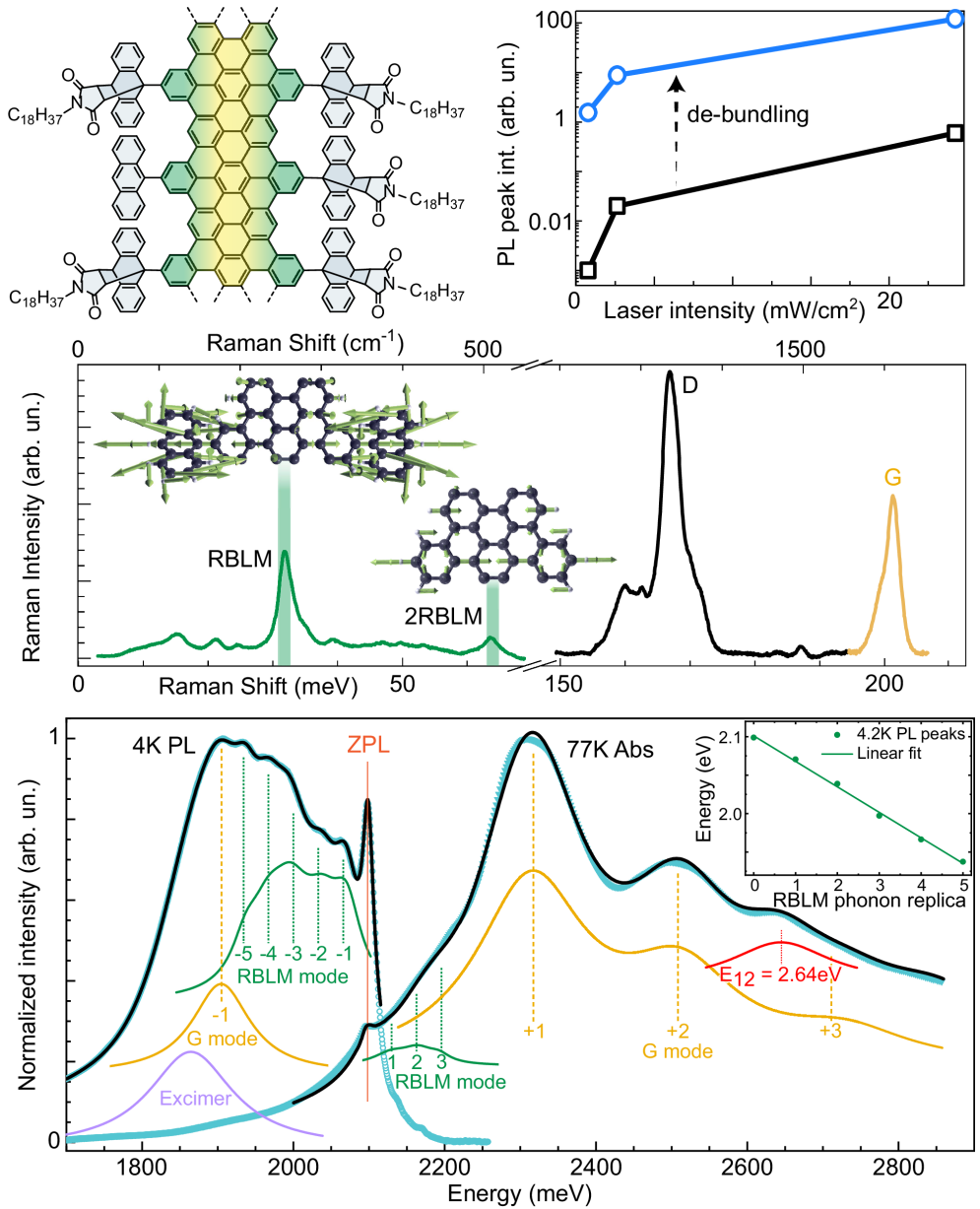
Molecular units

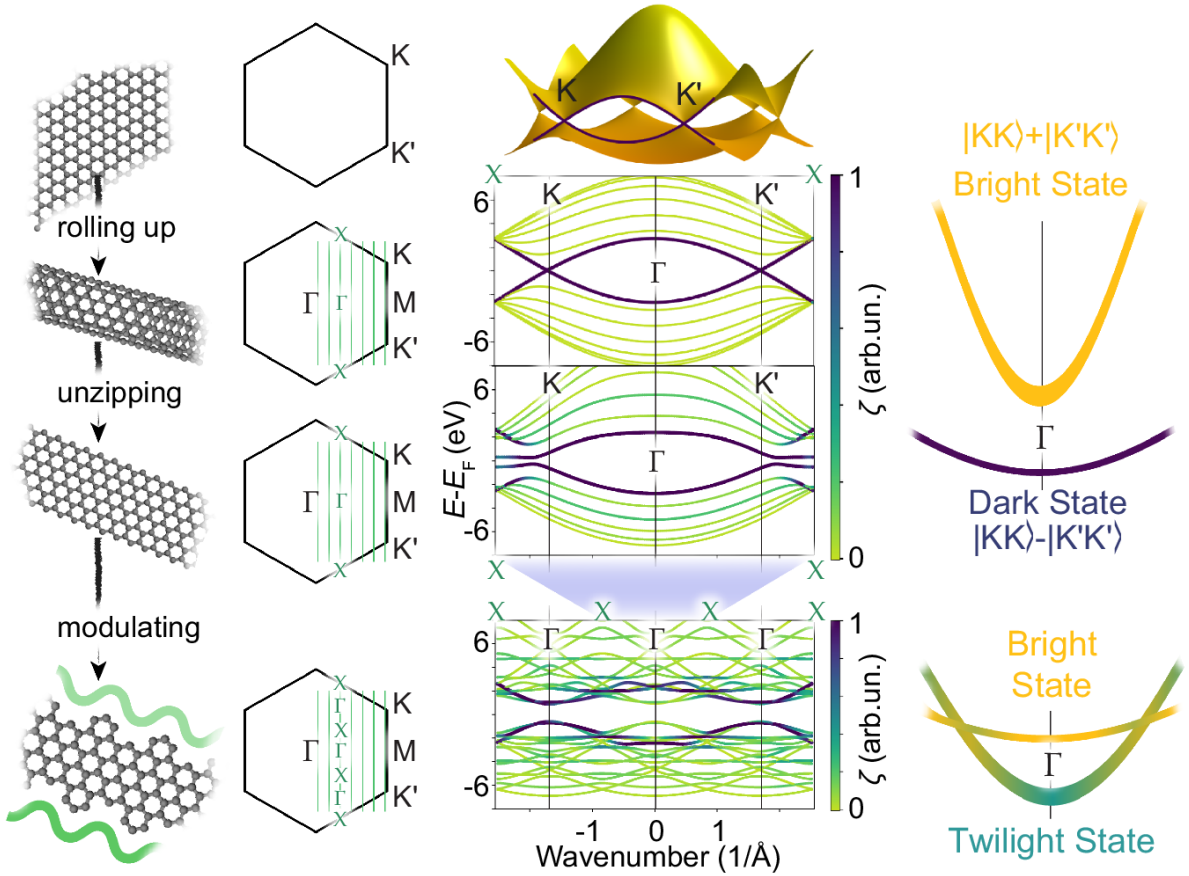
Molecular hybrids



In preparation

Optics





Nature Communications **2024**

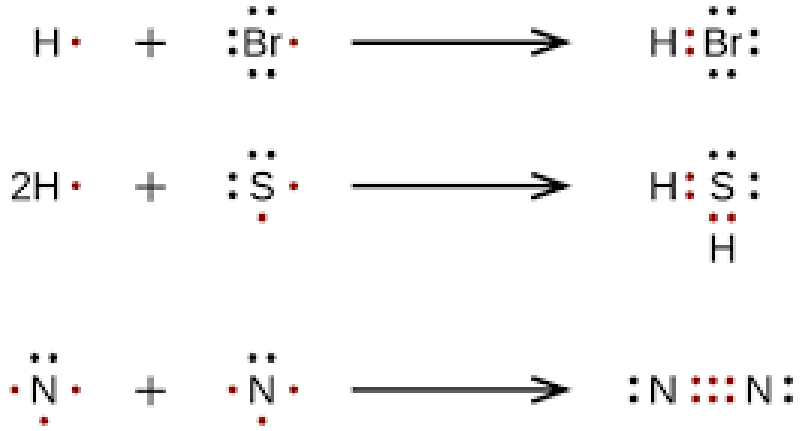
Emissive brightening in molecular graphene nanoribbons by twilight states

Received: 13 December 2023

Accepted: 19 March 2024

Bernd K. Sturdza[1] ✉, Fanmiao Kong[2], Xuelin Yao[2], Wenhui Niu[3,4], Ji Ma[3,4], Xinliang Feng[3,4], Moritz K. Riede[1], Lapo Bogani[2,5] ✉ & Robin J. Nicholas[1] ✉

Something more fundamental?



[Contribution from the Chemical Laboratory of the University of California.]

THE ATOM AND THE MOLECULE.

By Gilbert N. Lewis.

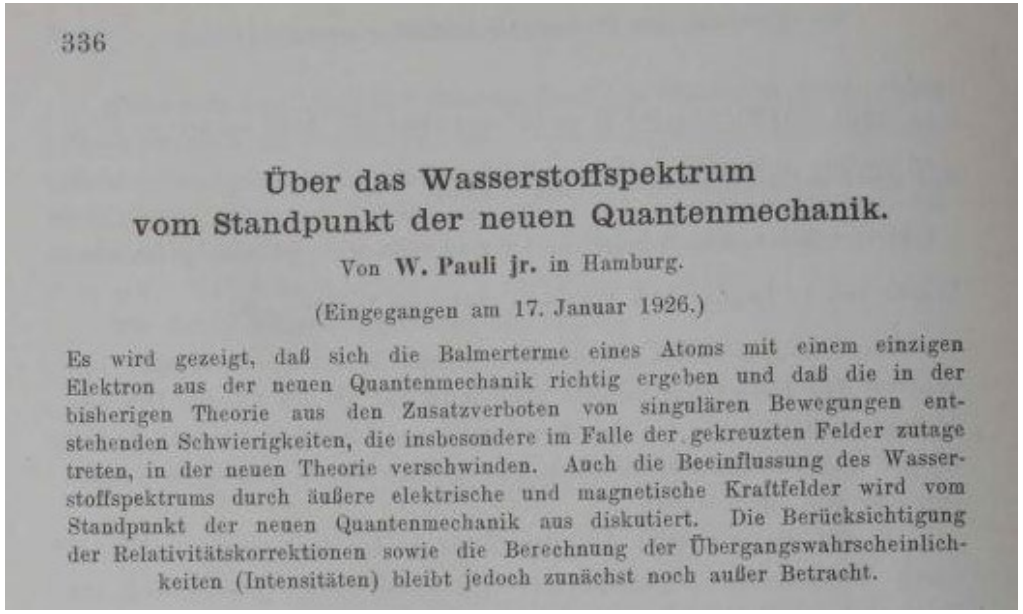
Received January 26, 1916.

In a paper entitled "Valence and Tautomerism"[1] I took occasion

[1] This Journal, **35**, 1448 (1913); see also the important article of Bray and Branch, *Ibid.*, **35**, 1440 (1913).

G. N. Lewis **1916**

W. Pauli **1926**



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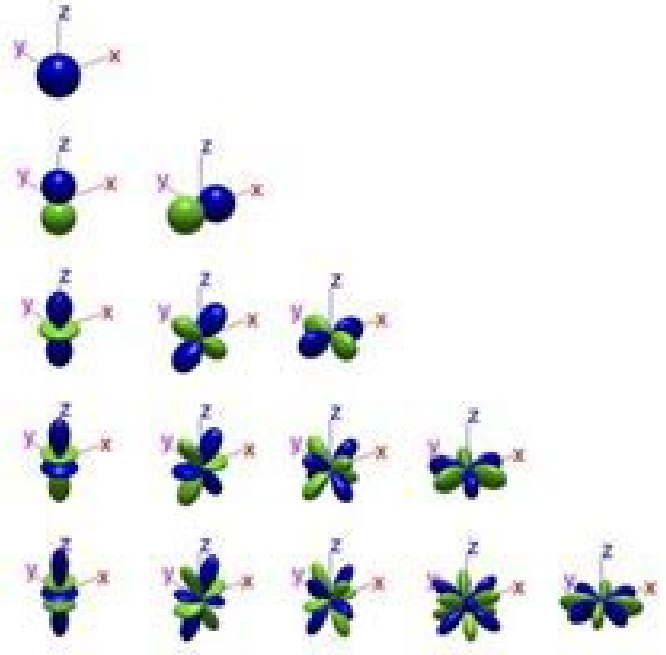
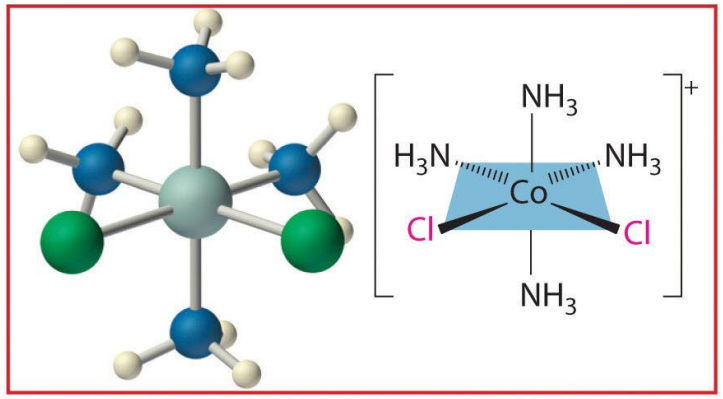
Über das Wasserstoffspektrum
vom Standpunkt der neuen Quantenmechanik.

Von **W. Pauli jr.** in Hamburg.

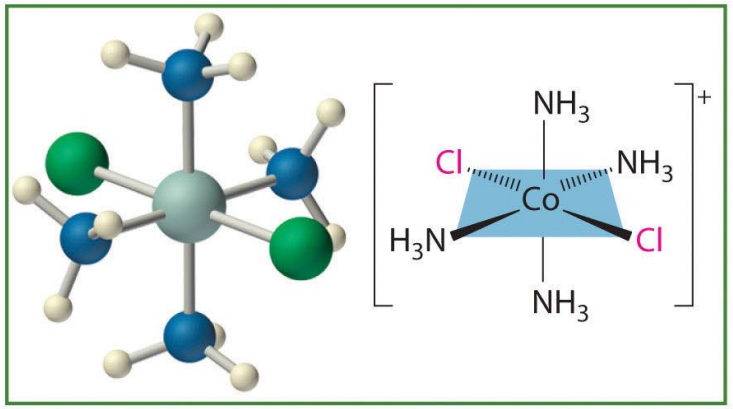
(Eingegangen am 17. Januar 1926.)

Es wird gezeigt, daß sich die Balmerterme eines Atoms mit einem einzigen Elektron aus der neuen Quantenmechanik richtig ergeben und daß die in der bisherigen Theorie aus den Zusatzverboten von singulären Bewegungen entstehenden Schwierigkeiten, die insbesondere im Falle der gekreuzten Felder zutage treten, in der neuen Theorie verschwinden. Auch die Beeinflussung des Wasserstoffspektrums durch äußere elektrische und magnetische Kraftfelder wird vom Standpunkt der neuen Quantenmechanik aus diskutiert. Die Berücksichtigung der Relativitätskorrektionen sowie die Berechnung der Übergangswahrscheinlichkeiten (Intensitäten) bleibt jedoch zunächst noch außer Betracht.

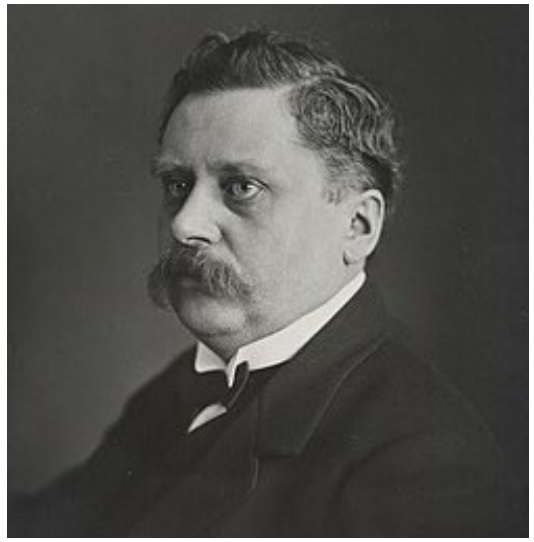




(a) Red form



(b) Green form



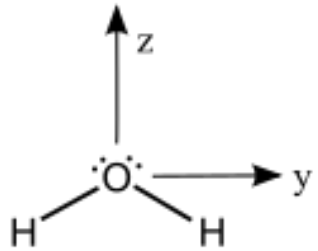
A. Werner **1913**

W. Cotton **1963**

CHEMICAL APPLICATIONS OF GROUP THEORY

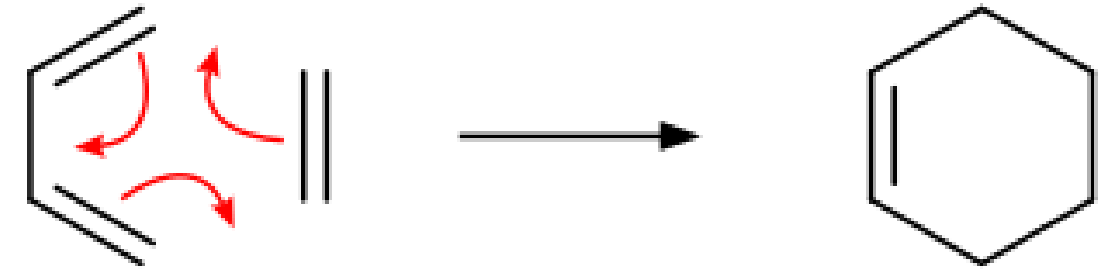
F. Albert Cotton
Department of Chemistry, Texas A&M University
College Station, Texas

THIRD EDITION



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ_σ	2	0	0	2		

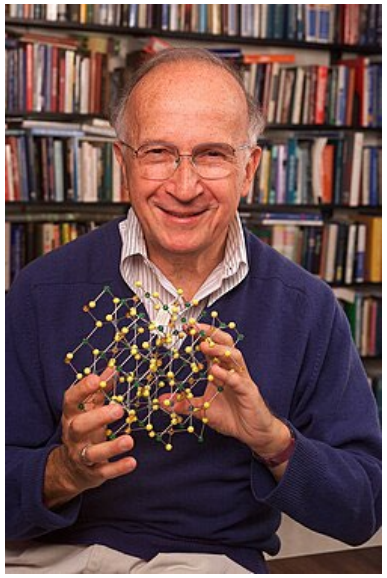
$\Gamma_\sigma = A_1 + B_2$

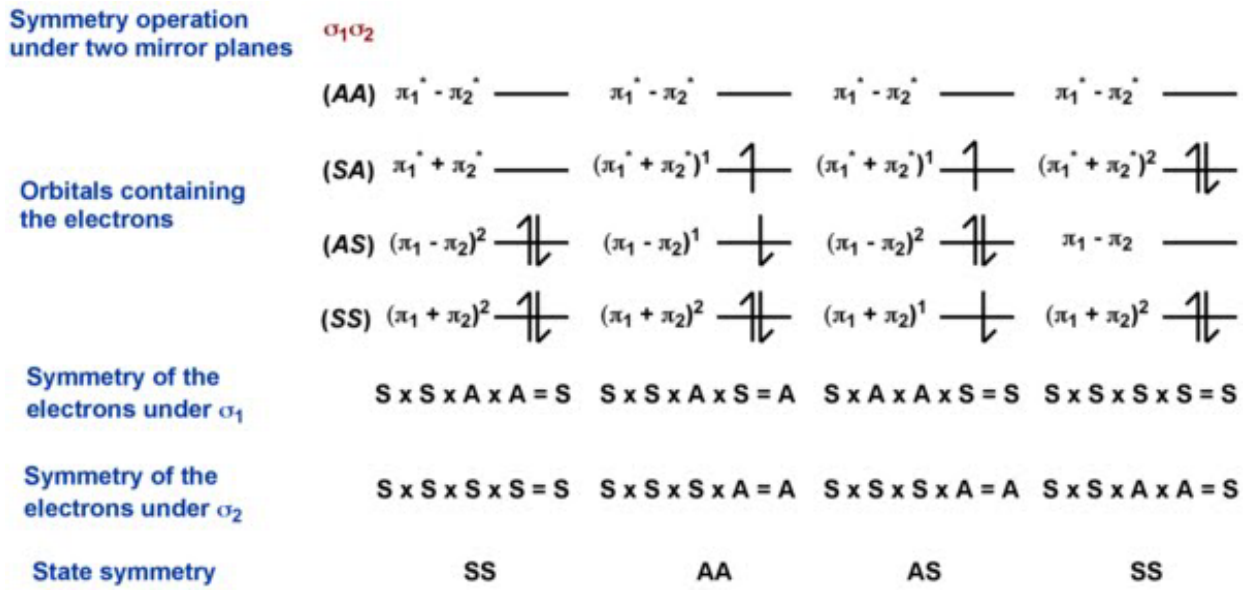


diene dieneophile

O. Diels, K. Alder **1950**

A. Hoffmann, K. Fukui **1983**



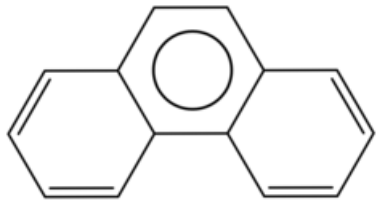


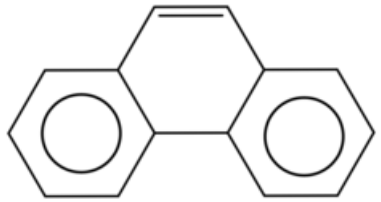
Empiric Lab Rules	Underlying Reason
Draw molecular structures **1910s**	**1930s** Quantum numbers: n, l, m_l
d-orbital reactivity **1900s**	**1960s** Point group symmetry: O_h, E…
pericyclic stereochemistry **1930s**	**1970s** Symmetry-related selection

…more aplenty?

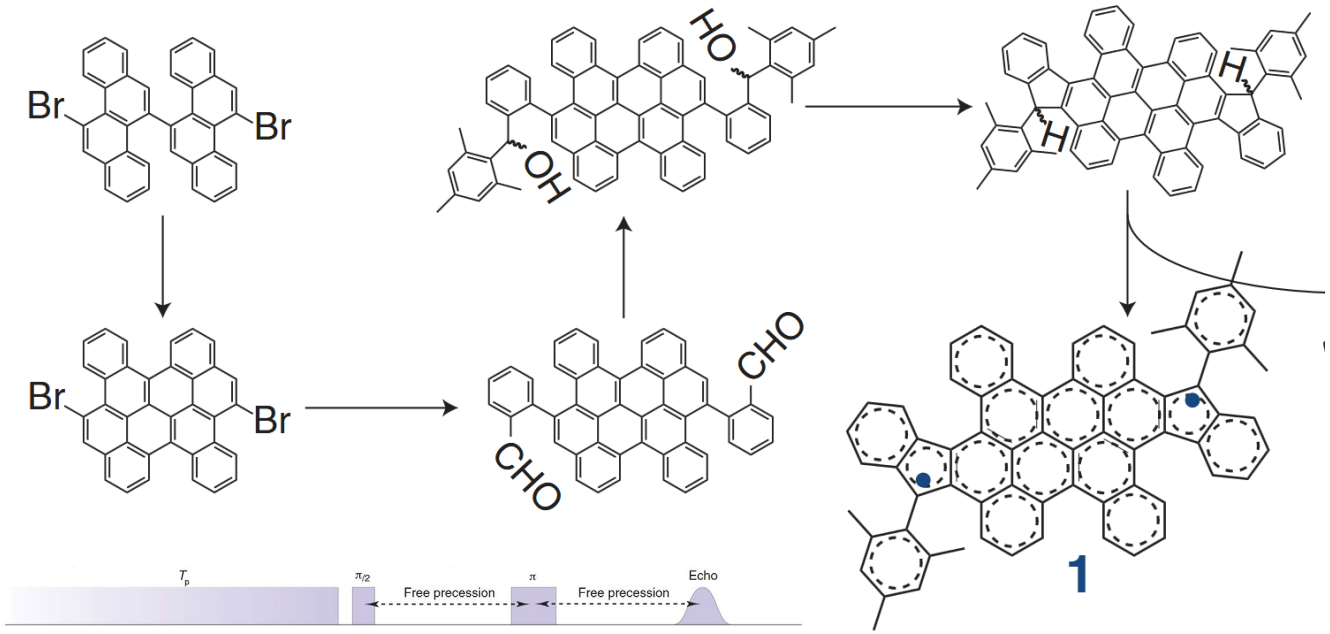
Polycyclic organic compounds

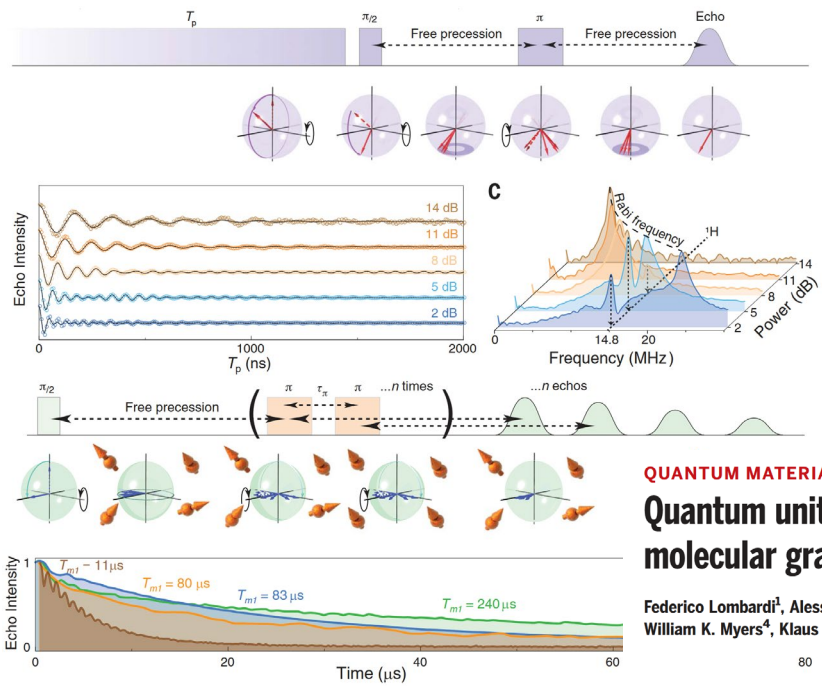
Clar's Sextet Rule **1970s**





The most stable structure is the one with more π sextets (circles).





Science **2019**

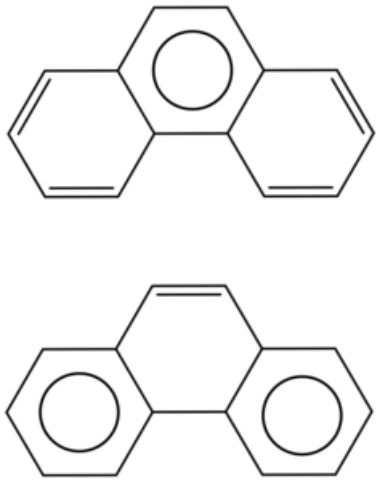
QUANTUM MATERIALS

Quantum units from the topological engineering of molecular graphenoids

Federico Lombardi[1], Alessandro Lodi[1], Ji Ma[2], Junzhi Liu[2]*, Michael Slota[1], Akimitsu Narita[3]†, William K. Myers[4], Klaus Müllen[3]‡, Xinliang Feng[2], Lapo Bogani[1]§

Polycyclic organic compounds

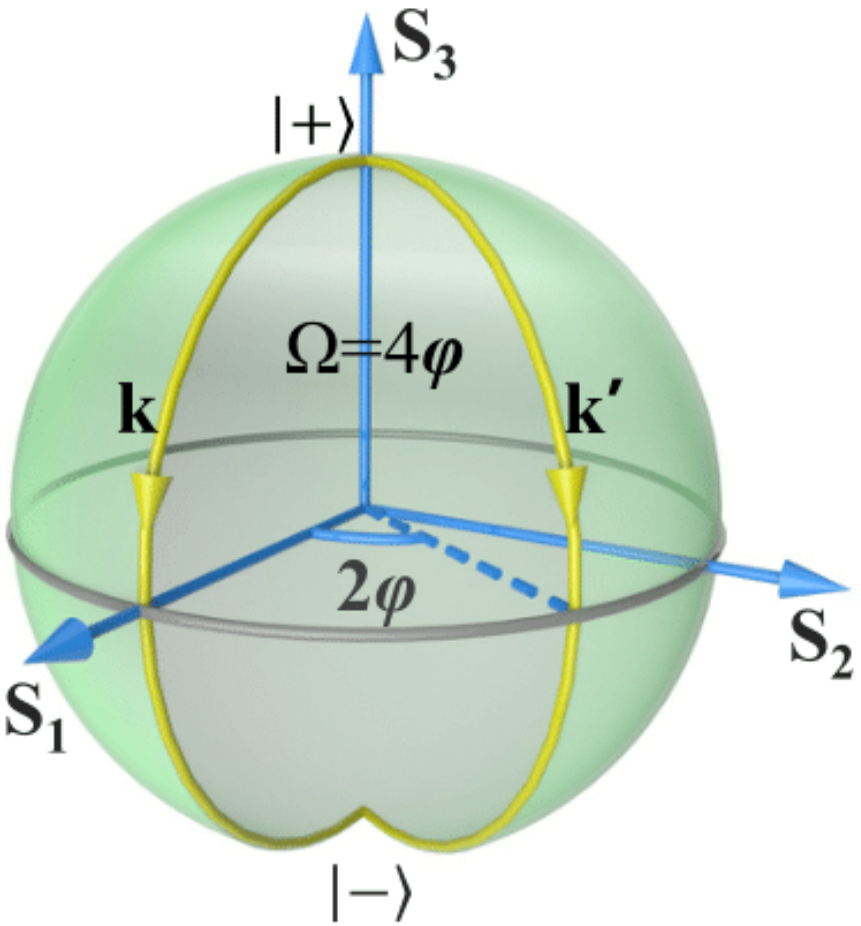
Clar's Sextet Rule **1970s**

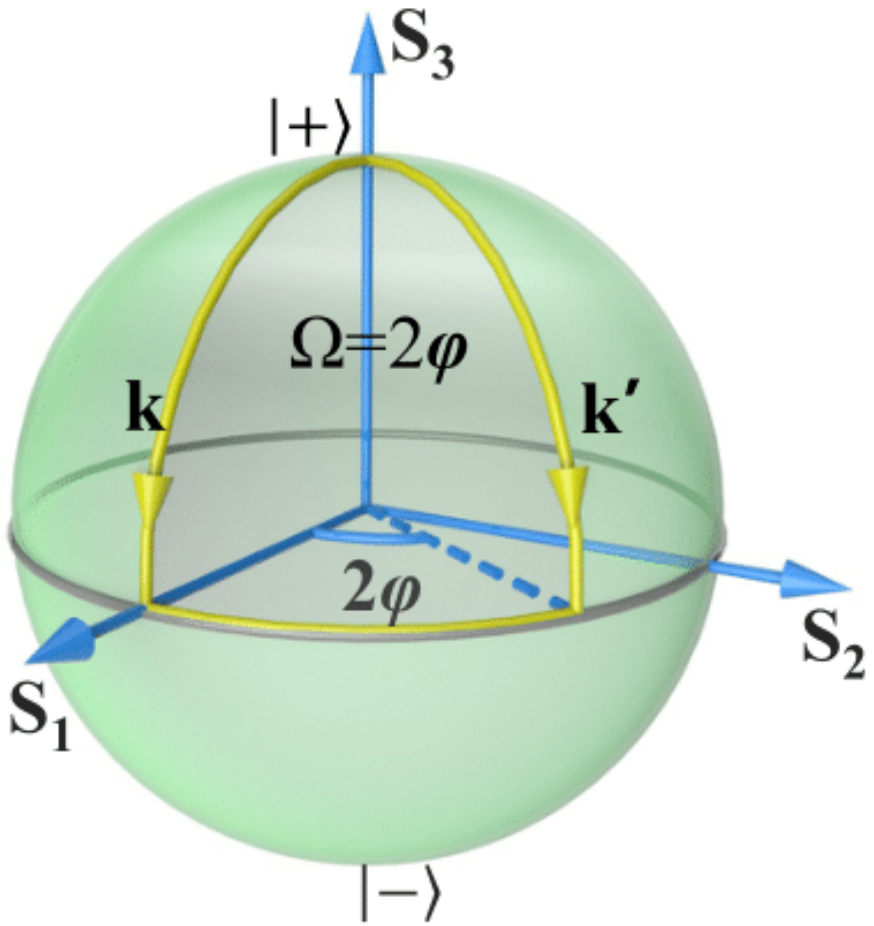


The most stable structure is the one with more π sextets (circles).

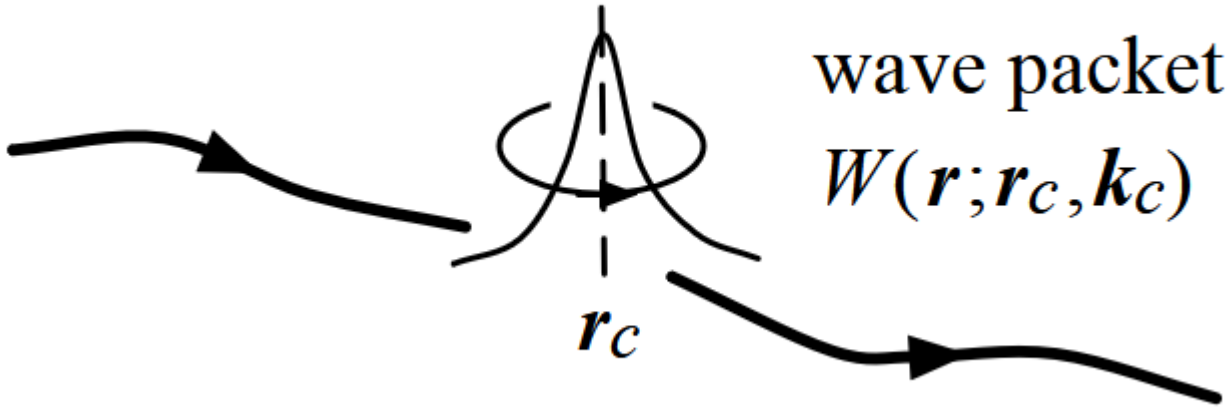
Quantum mechanical reason?

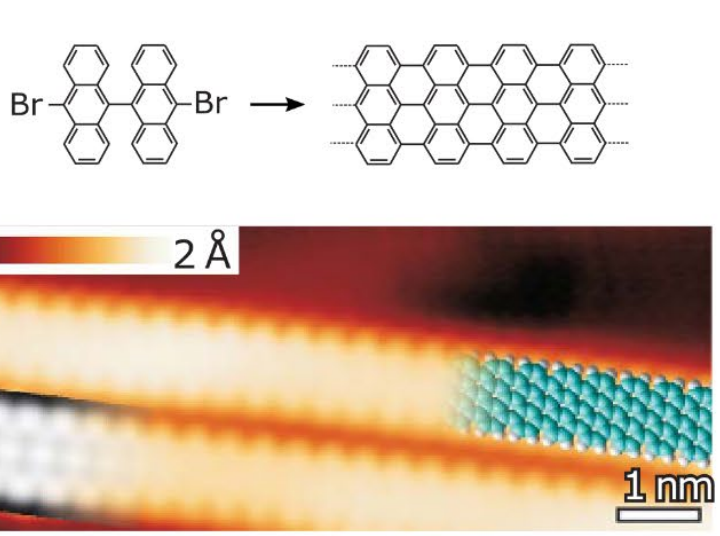
The Berry (Zak) Phase

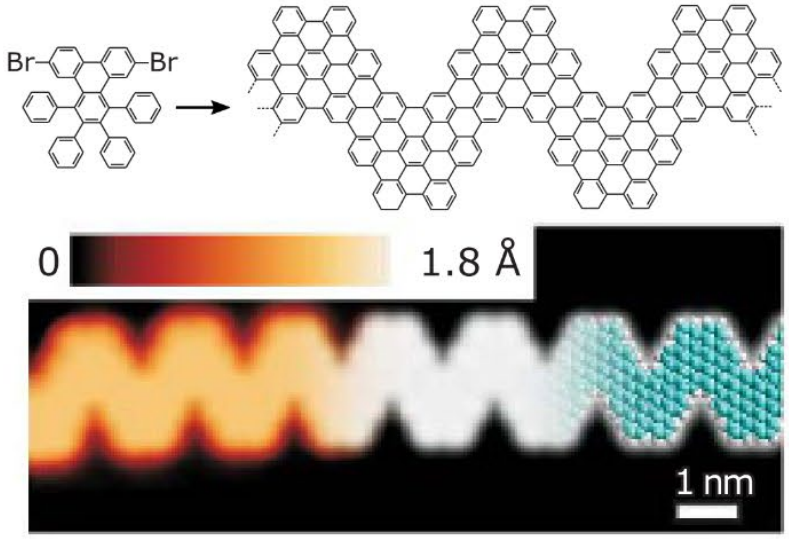


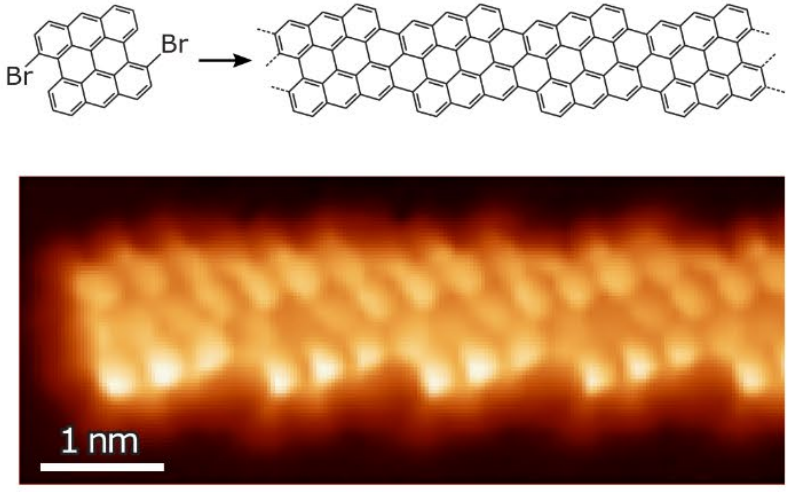


Electrons in Carbon

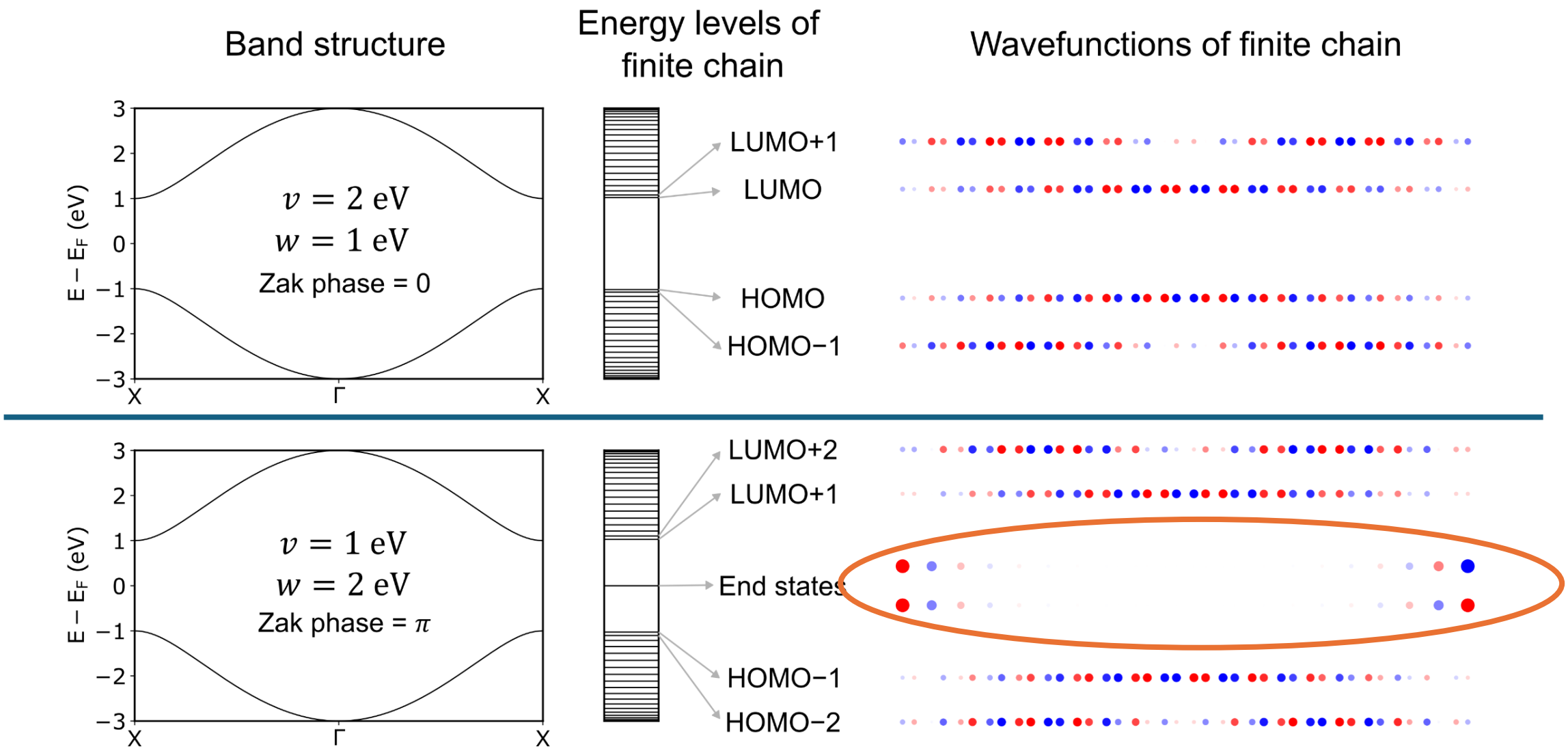








States created by the Zak phase

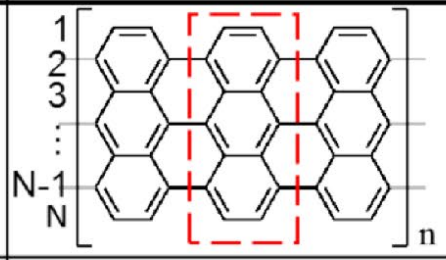
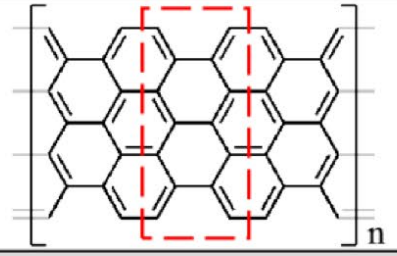
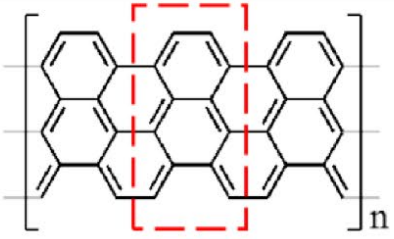
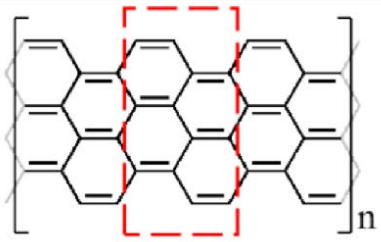


A new number

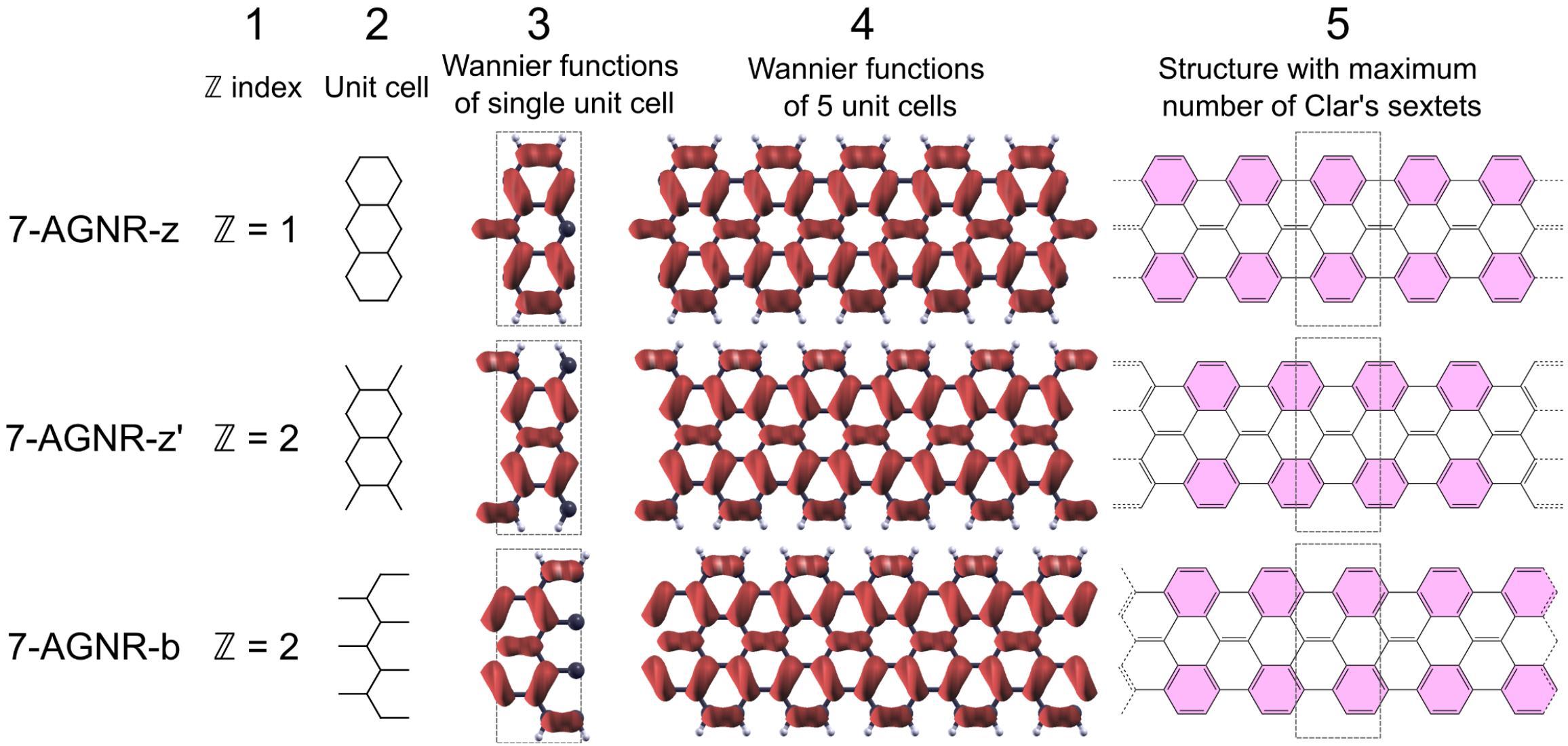
$$\gamma_n = \int_{\mathrm{BZ}} A_n(k)\,\mathrm{d}k \mod 2\pi, \qquad A_n(k) = \mathrm{i}\langle u_n(k)|\nabla_k|u_n(k)\rangle,$$

for all electronic states

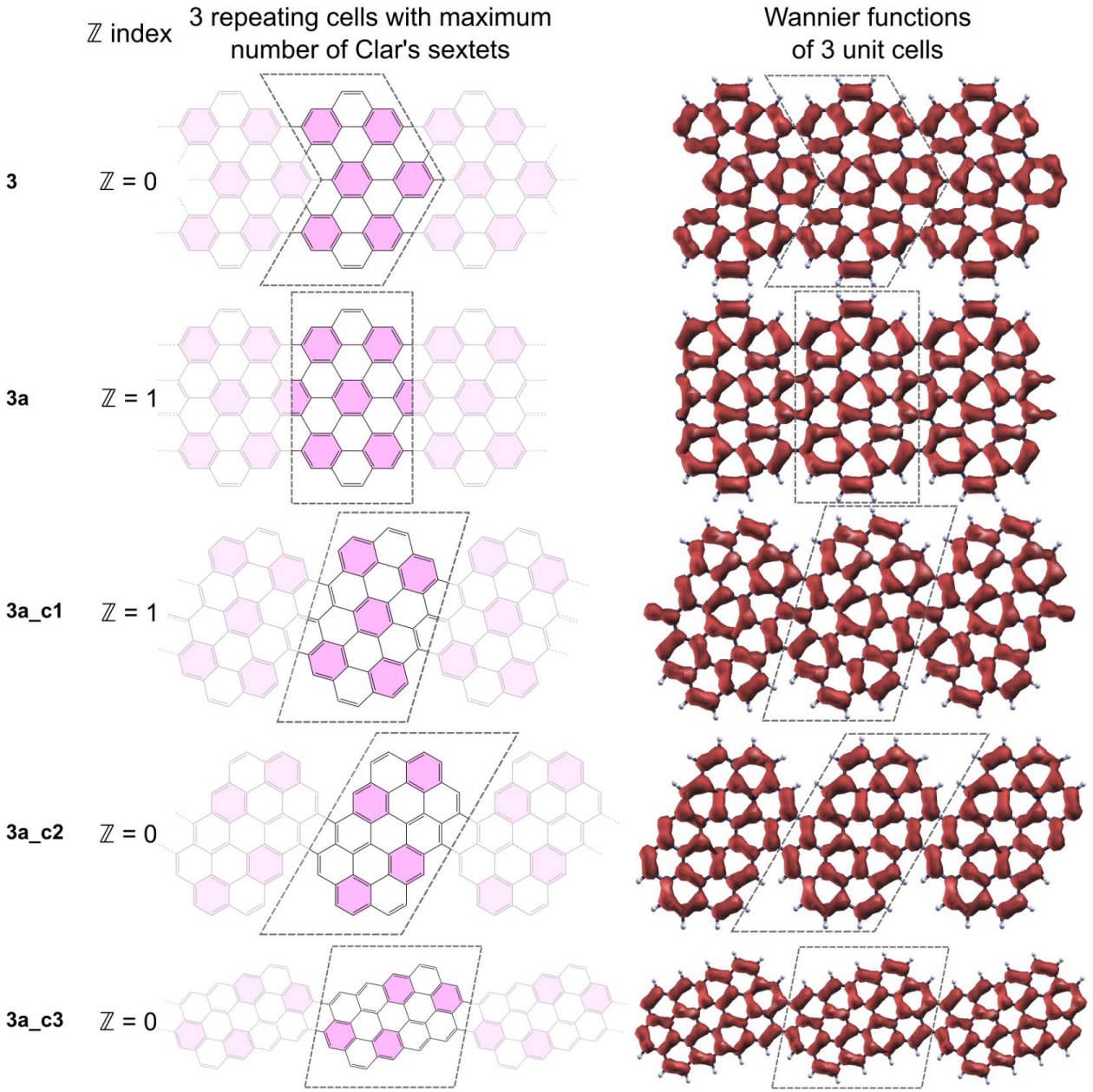
0 = trivial 1 = weird

Termination type	Zigzag (N = Odd)	Zigzag' (N = Odd)	Zigzag (N = Even)	Bearded (N = Even)
Unit cell shape				
Bulk Symmetry	Inversion/mirror	Inversion/mirror	Mirror	Inversion
Z_2	$\frac{1+(-1)^{\left\lfloor\frac{N}{3}\right\rfloor+\left\lfloor\frac{N+1}{2}\right\rfloor}}{2}$	$\frac{1-(-1)^{\left\lfloor\frac{N}{3}\right\rfloor+\left\lfloor\frac{N+1}{2}\right\rfloor}}{2}$		$\frac{1-(-1)^{\left\lfloor\frac{N}{3}\right\rfloor}}{2}$

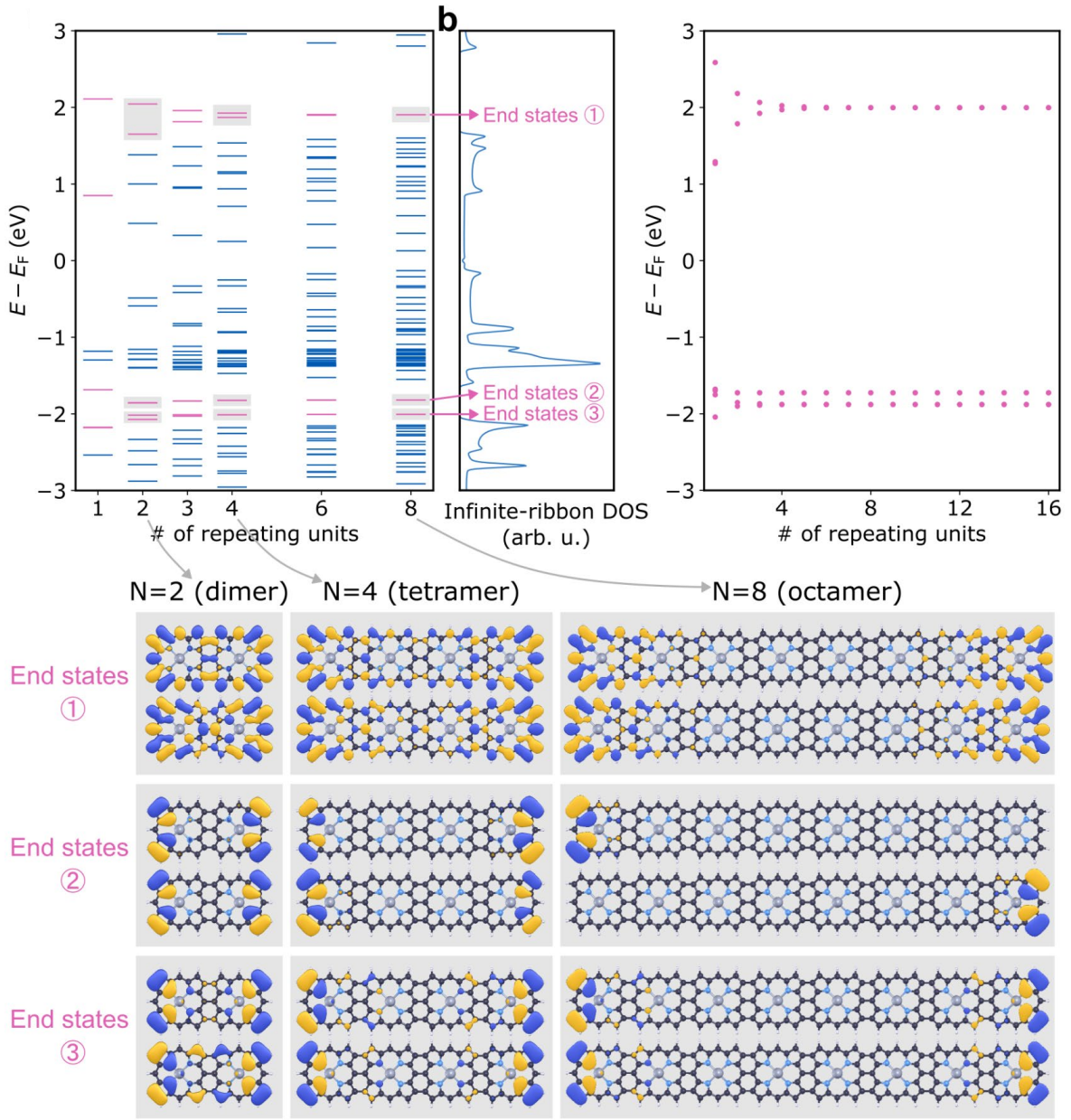
Is this connected to Clar's rule?



Exporting to different compounds



Extending Clar's rules



Different molecules

Different sizes

Something more fundamental?

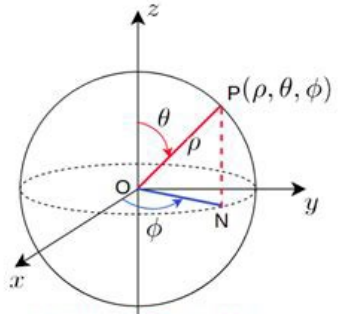
...maybe yes

Draw molecular structures **1910s**

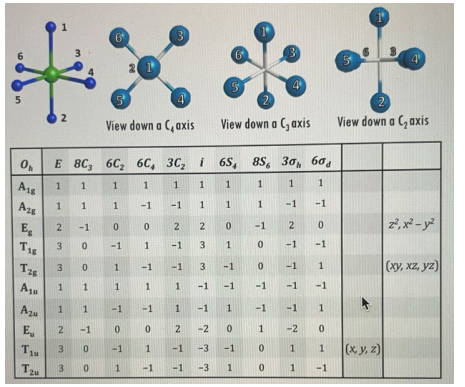
d-orbital reactivity **1900s**

pericyclic stereochemistry **1930s**

1930s Quantum numbers: n, l, m_l

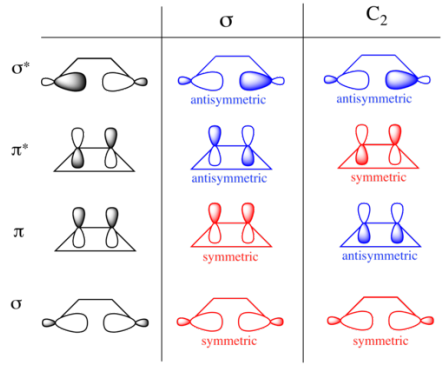


1960s Point group symmetry: O_h, E…



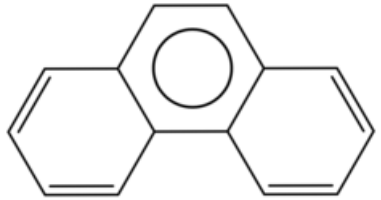
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		z^2, x^2-y^2
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1		
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

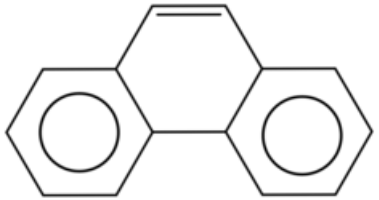
1970s Symmetry-related selection



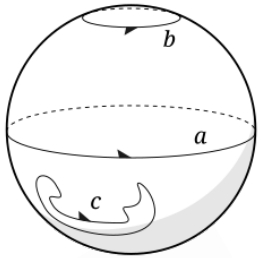
Polycyclic organic compounds

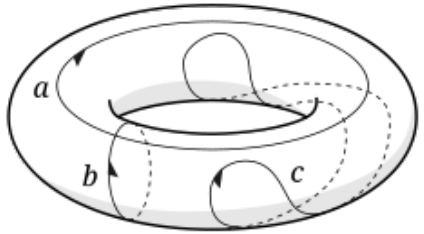
Clar's Sextet Rule **1970s**

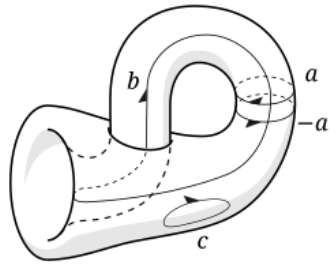


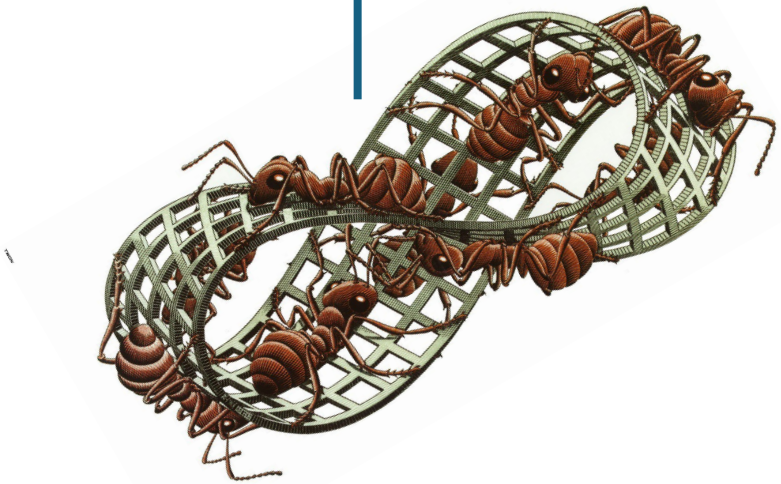


The topology resulting from the reflections of the electronic waves









Thanks

F. Kong, A. Lombardi, S. Sopp, Z. Chen, X. Yao, C. Shen,
H. Chen, A. Lombardi, M. Reavley, R. Torres, M. Slota.

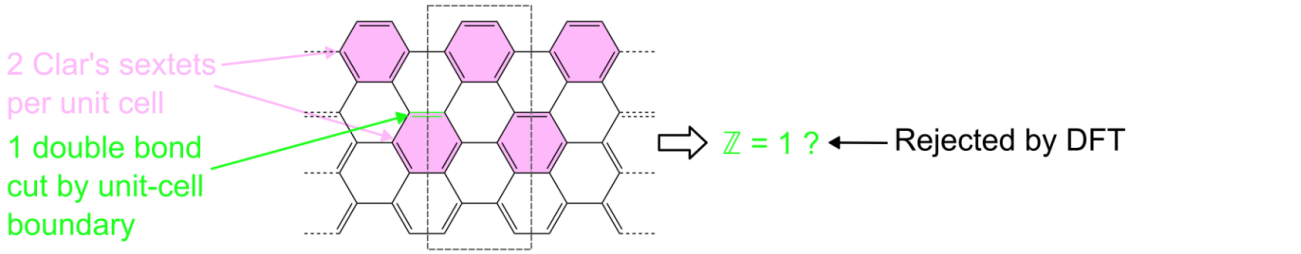
L. Briccolani, L. Chirolli, P. Fu.

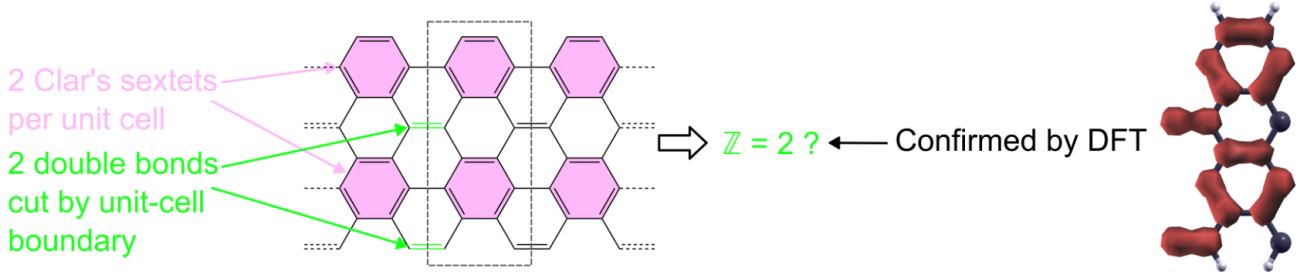
H. L. Anderson, X. Feng, A. Narita, J. Wu, Z. Zhang.

StG-OptoQMol

CoG-MMGNRs

Is this connected to Clar's rule?





Wannier functions