A historic Condensed Matter Problem brought to Life in novel 2D Materials:

Hofstadter's Butterfly in 2D COFs

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TU Dresden

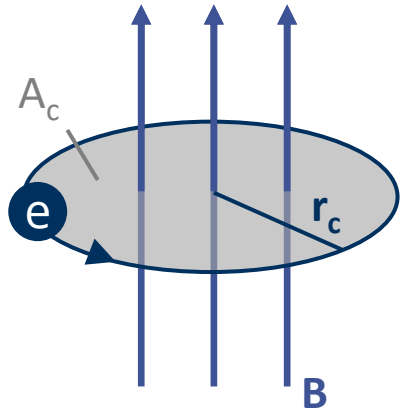
Nano Seminar | 05.08.21

DRESDEN concept

CRC 1415

TECHNISCHE UNIVERSITÄT DRESDEN

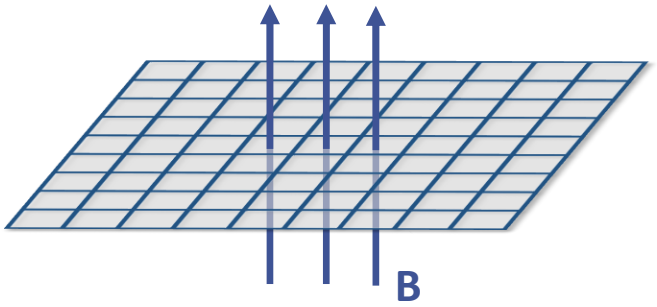
Electrons in a magnetic field



Electron in a magnetic field

$$r_c \propto \frac{1}{B}$$

$$A_c \propto \frac{1}{B}$$



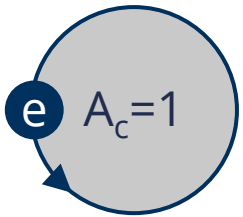
Electrons in a crystal/lattice in a magnetic field

A_c vs lattice

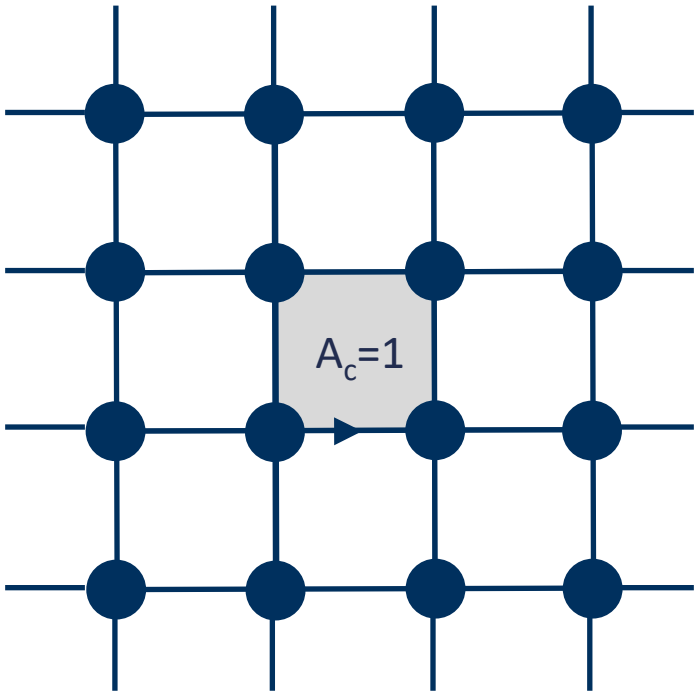
Electrons in a lattice in a magnetic field

$B \rightarrow A_c$

Free electron



Electron in a lattice

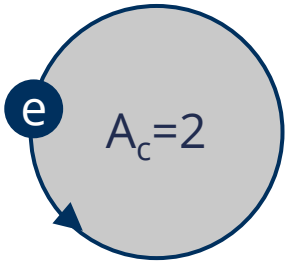


- Applying B results in a cyclotron area A_c
- In lattice: Electrons move from lattice-site to lattice-site

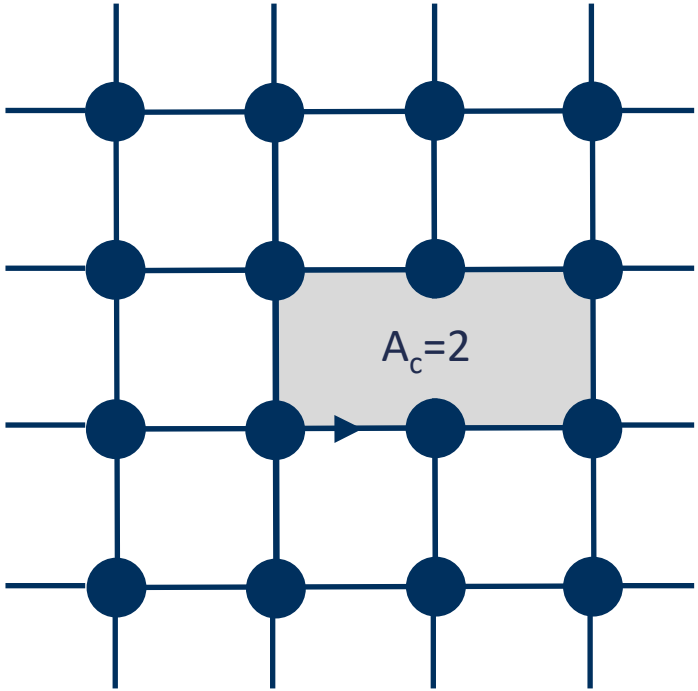
Electrons in a lattice in a magnetic field

$B \rightarrow A_c$

Free electron

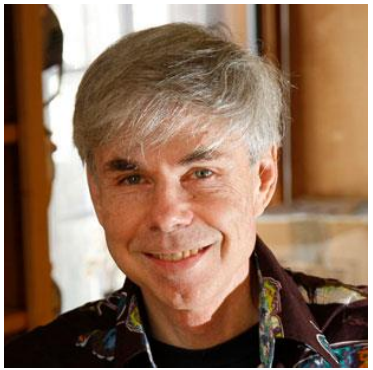


Electron in a lattice

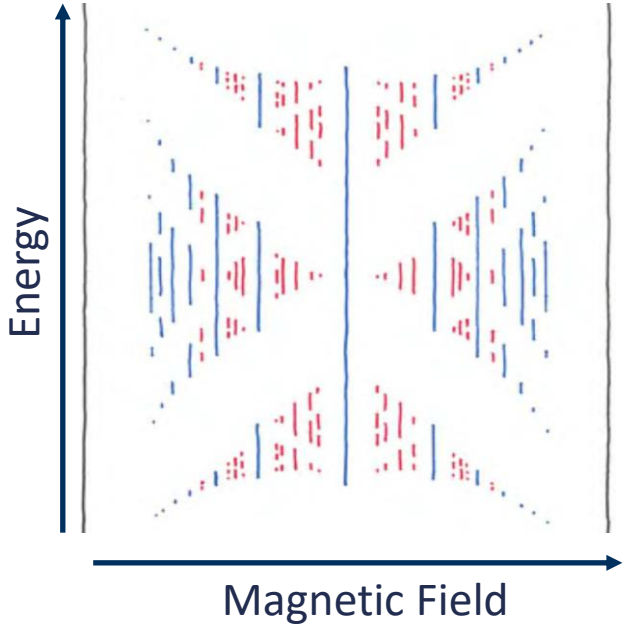


- Only specific values of A_c (and hence B) are allowed because of lattice
- Magnetic field competing with lattice
- Certain number of allowed energy levels for a specific magnetic field

From Pen and Paper to Computational Physics

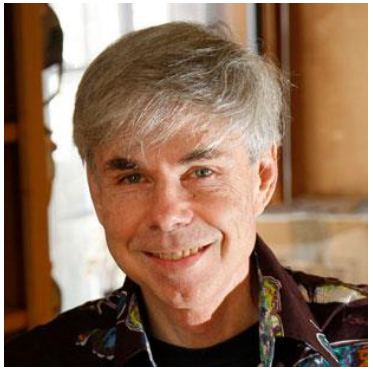


Douglas Hofstadter
1975 at Uni Regensburg



HP 9820A
“Rumpelstilzchen“

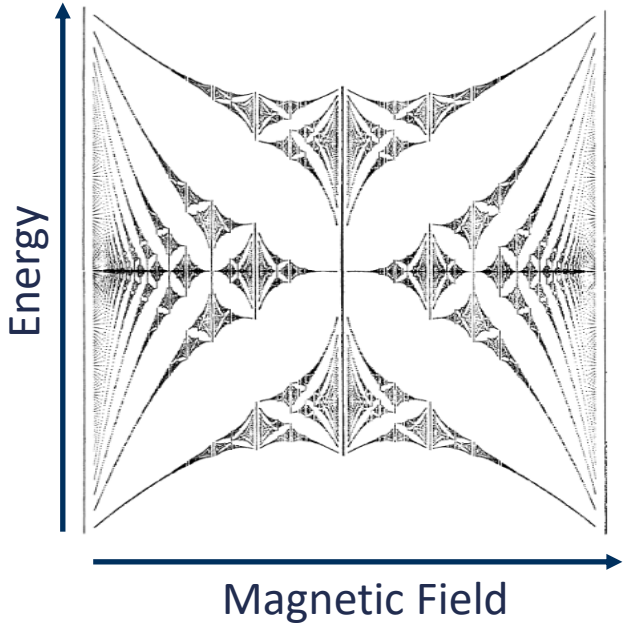
From Pen and Paper to Computational Physics



Douglas Hofstadter
1975 at Uni Regensburg

Hofstadter's Butterfly (HSBF)

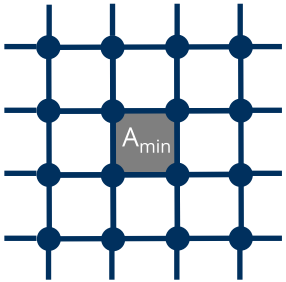
Self-similar, fractal pattern



HP 9820A
"Rumpelstilzchen"

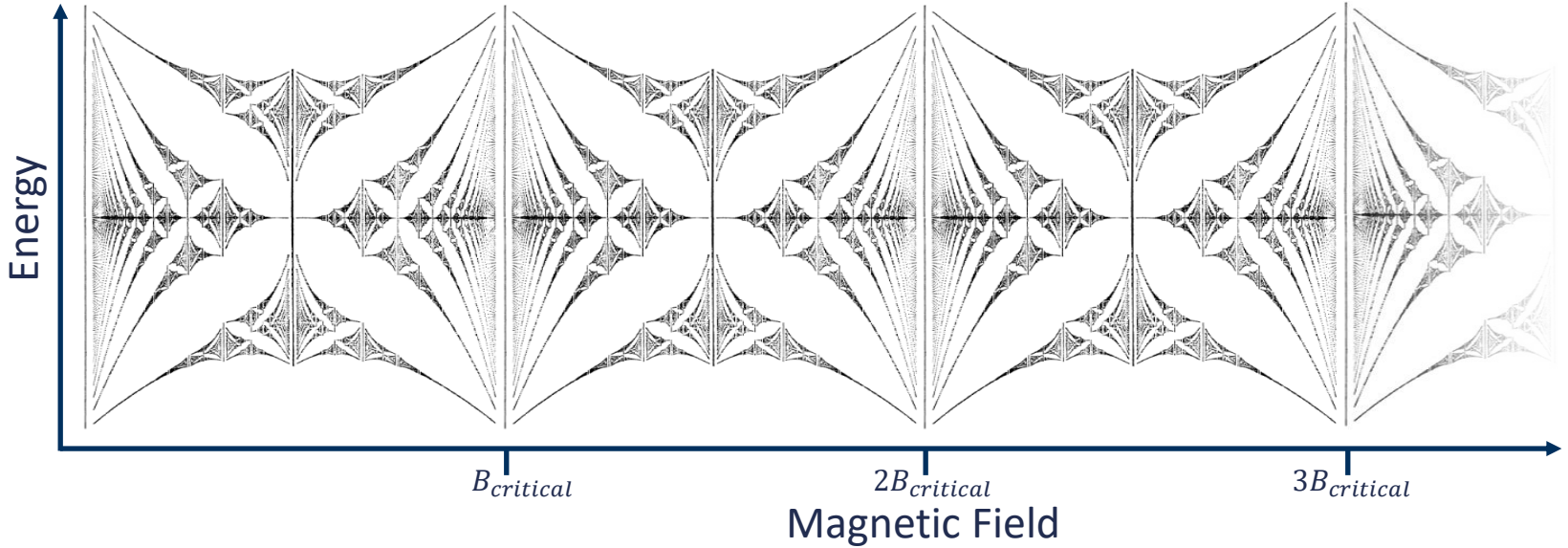
Phys. Rev. B 14, 2239 (1976)

HSBF – A periodic pattern



$$B_{critical} = \frac{\Phi_0}{A_{min}}$$

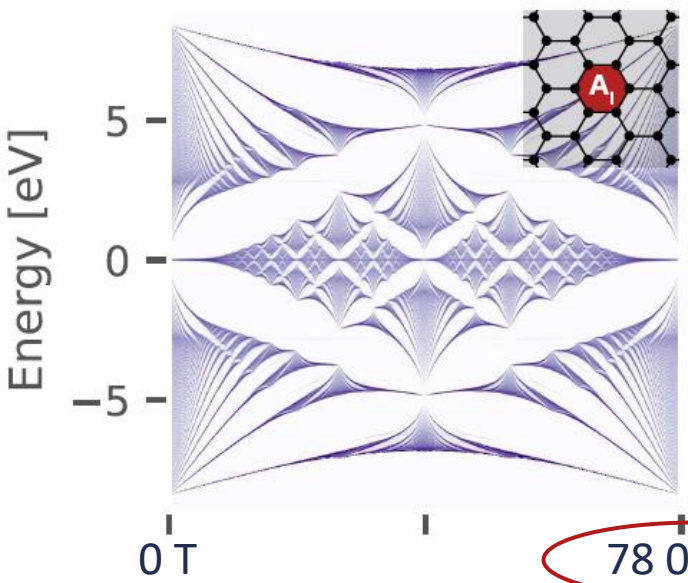
Butterfly spectrum is **periodic in B**



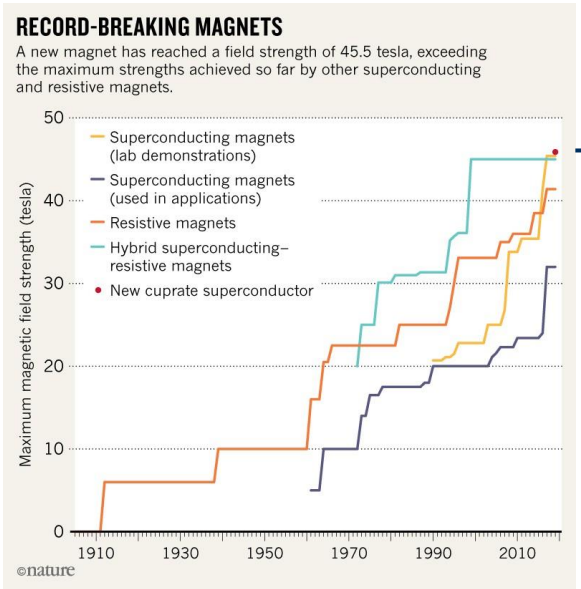
HSBF– Can it be measured?

$$B_{critical} = \frac{\Phi_0}{A_{min}}$$

Graphene



Too high!

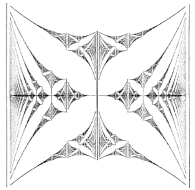


— 45.5 T

→We need big lattices to measure HSBF!

https://www.nature.com/articles/d41586-019-01869-1

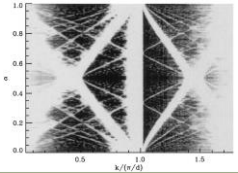
Experimental Validation?



Hofstadter

1976

Microwave scatterers



Kuhl, Stöckmann

1998

2001

Albrecht, Kitzing, et al.

a 2D electron gas

2004

Schweizer et al.

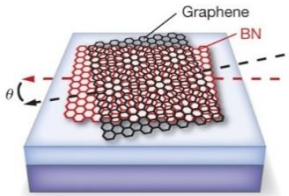
Graphene on h-BN as Moiré superlattices

Geim et al.

Kim et al.

Ashori et al.

2013

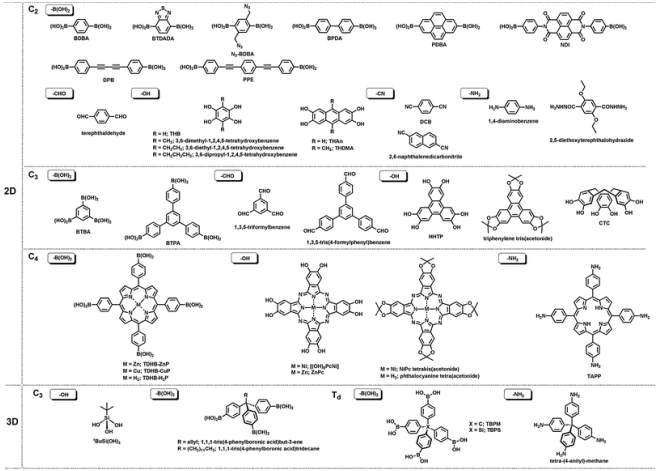


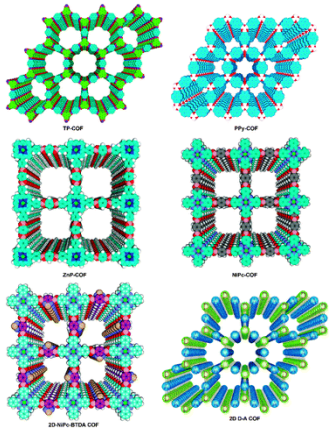
and several more…

All are **artificial lattices**!
HSBF measurable in “pure” materials?

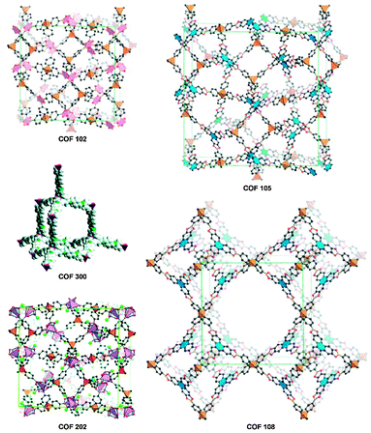
HSBF in Covalent-Organic Frameworks (COFs)?

From building blocks → to crystalline **porous** organic polymers





Stacked 2D COFs

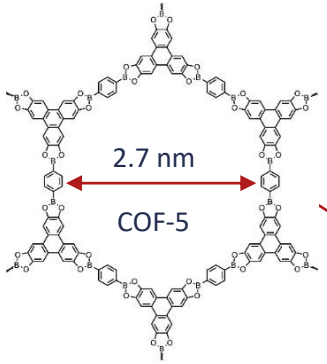


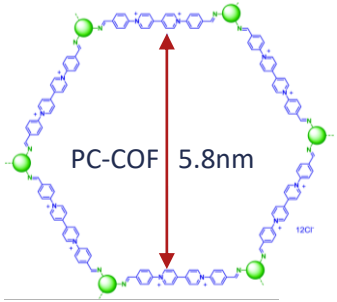
3D COFs

Porous nature makes COFs ideal candidates
Big pores → Small magnetic fields

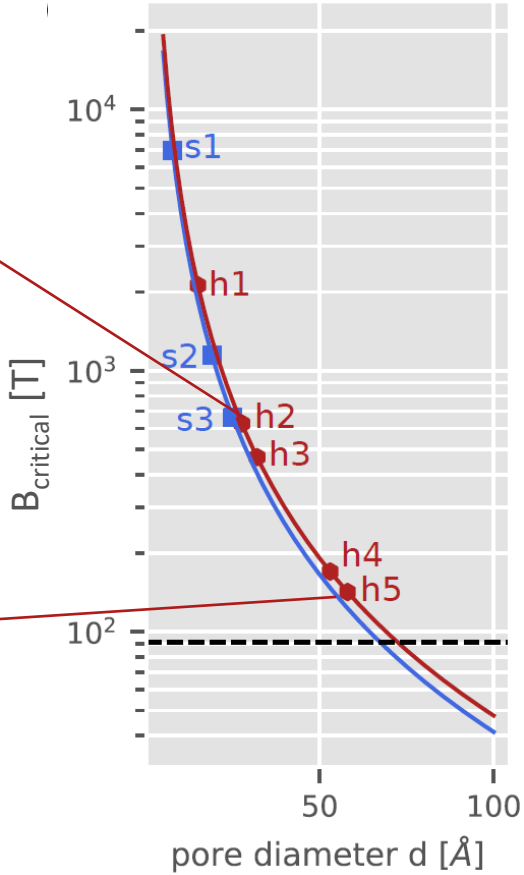
Chem. Soc. Rev., 2012, **41**, 6010-6022

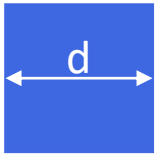
2D COFs with big pores

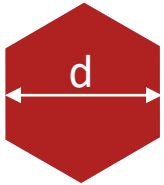




Biggest COF pore





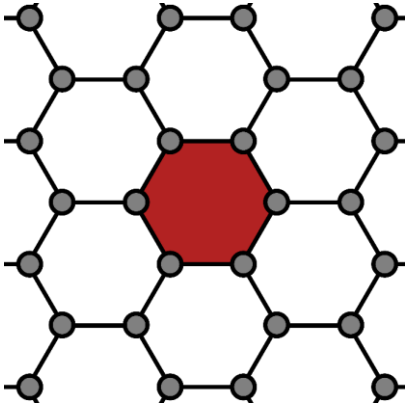


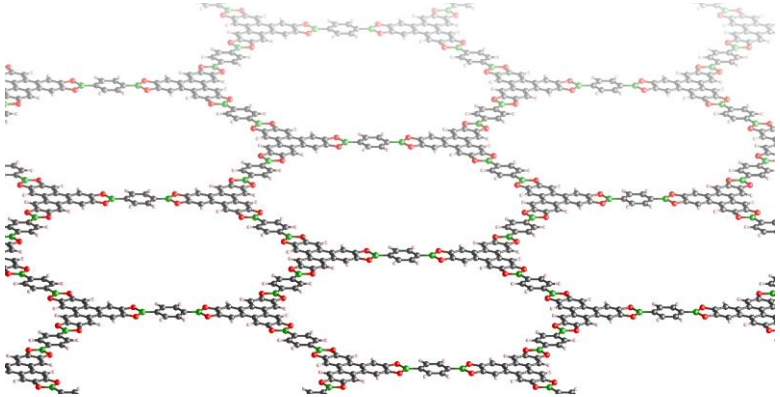
$$B_{critical} = \frac{\Phi_0}{A_{min}}$$

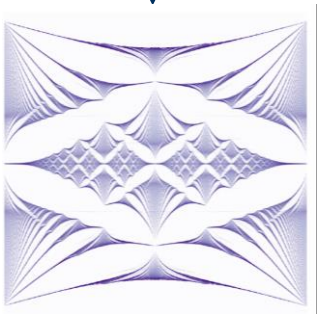
Many COFs with big pores already exist!

2·45.5 T ← 2· Highest achievable magnetic field

2D COFs – Can we find a HSBF in them?



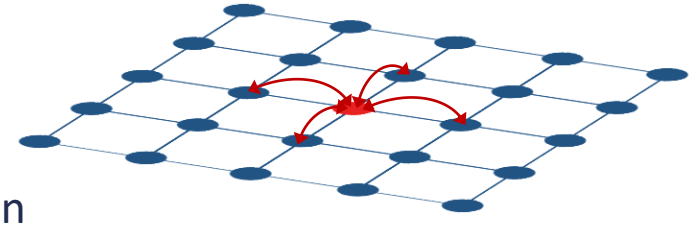




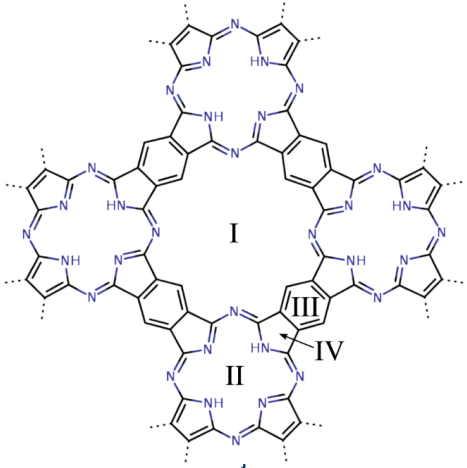
?

Calculating HSBF in COFs – Methods

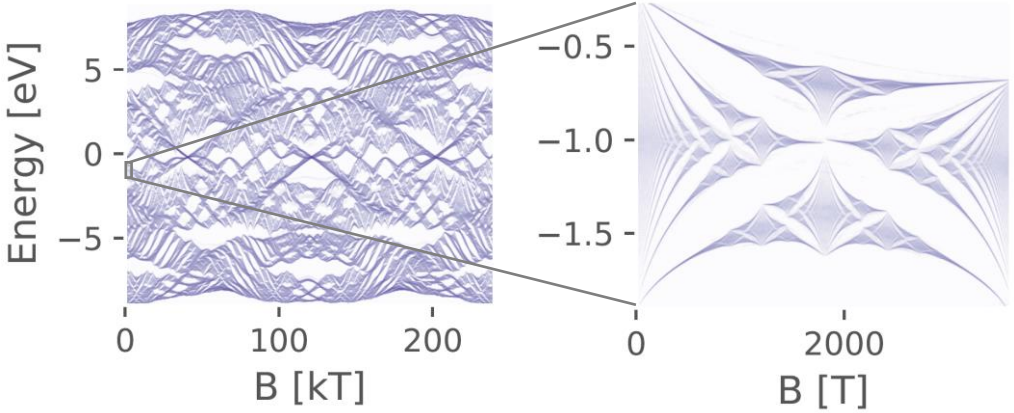
- Tight-Binding model
- On-Site energies E_n and hopping parameters t_{nm} from Slater-Koster files
- Only pp^{π} interactions
- Nearest-Neighbor approximation
- t_{nm} modified by magnetic field via Peierls Subsitution
- Calculating DOS for different magnetic fields
- Using python package *Pybinding*



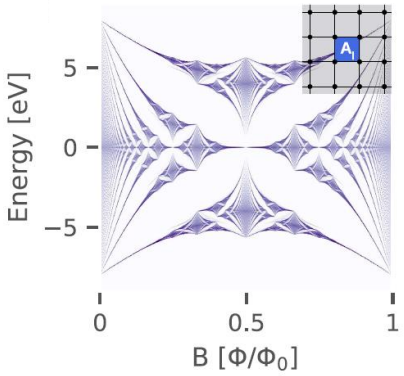
Phthalocyanine-COF (square lattice)



What we see



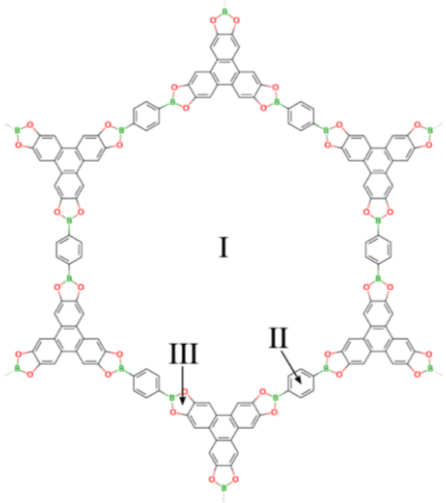
What we expect



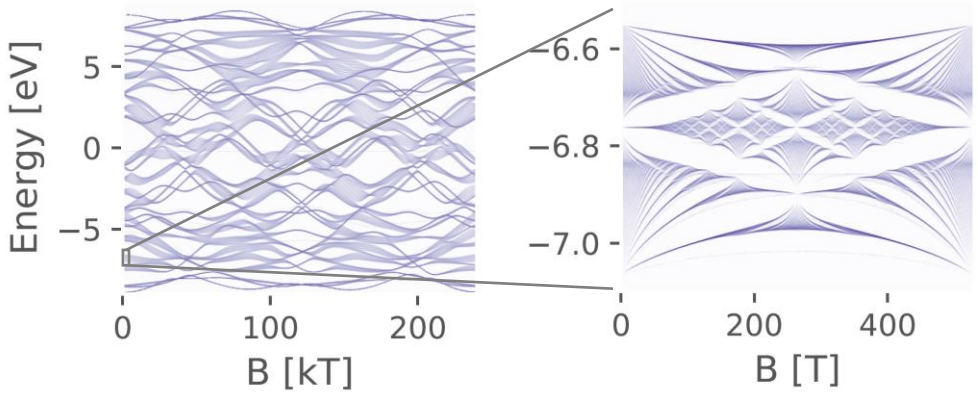
Similarity of HSBF

B too high!

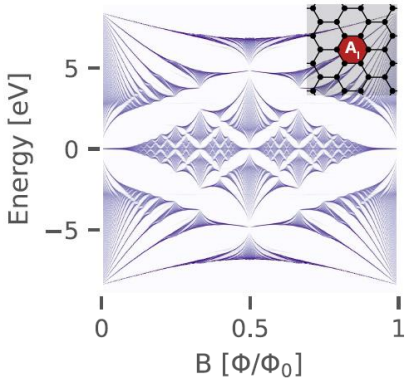
COF-5 (hexagonal lattice)



What we see



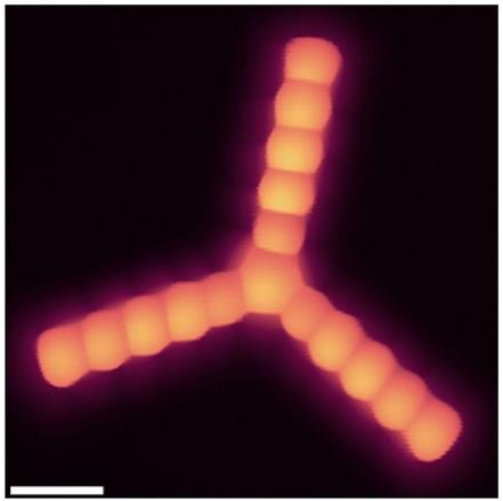
What we expect

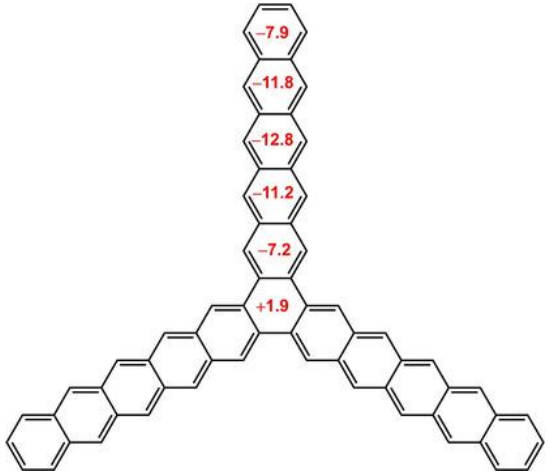


Similarity of HSBF

B still too high!

Starphene Molecules

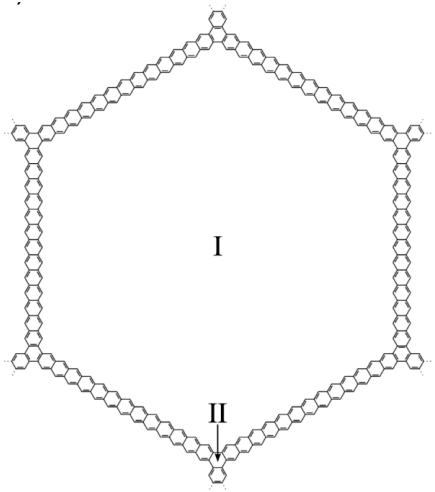




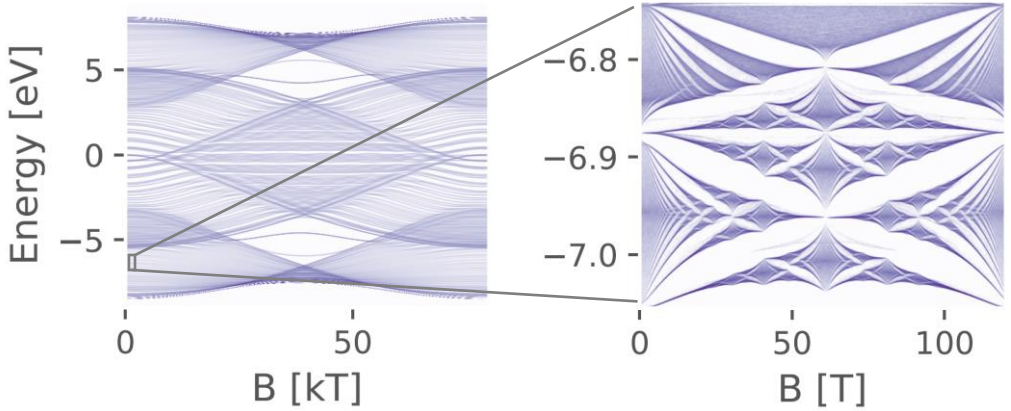
→2D COF based on Starphene Molecules?

Angew. Chem. Int. Ed. **2021**, *60*, 7752

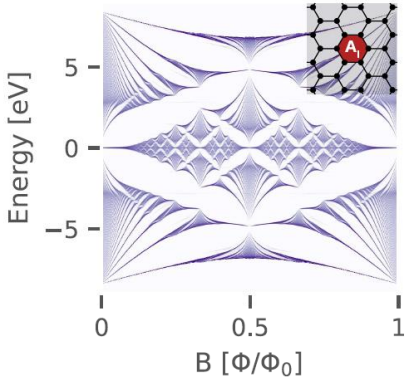
Starphene-COF (hexagonal lattice)



What we see



What we expect



Similarity of HSBF

B small enough!

Summary

- Hofstadter‘s Butterfly has been a purely theoretical matter for a long time
- Validation so far **only in artificial lattices** possible
- **2D COFs** as promising candidates for measuring HSBF
- Calculations show the similarity between simple lattices

  and their COF-counterparts

Thanks for your attention!

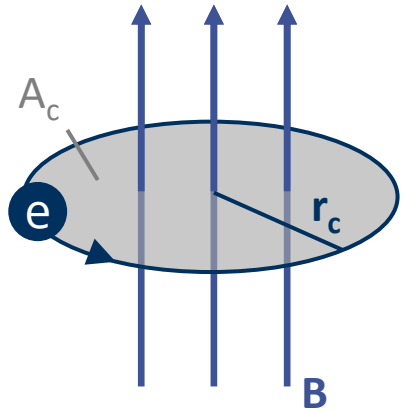
Prof. Gianaurelio Cuniberti

Dr. Robert Biele

David Bodesheim

Appendix

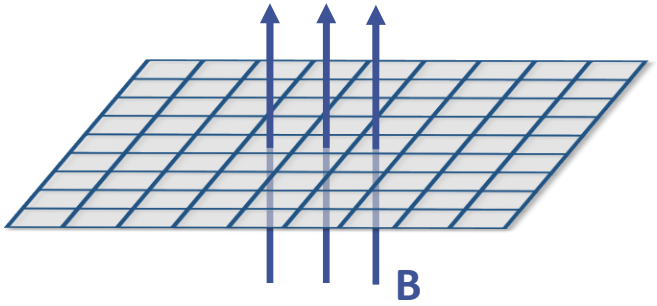
Electrons in a magnetic field



Electron in a magnetic field

$$r_c = \frac{mv}{qB}$$

$$\Phi = A_c B$$



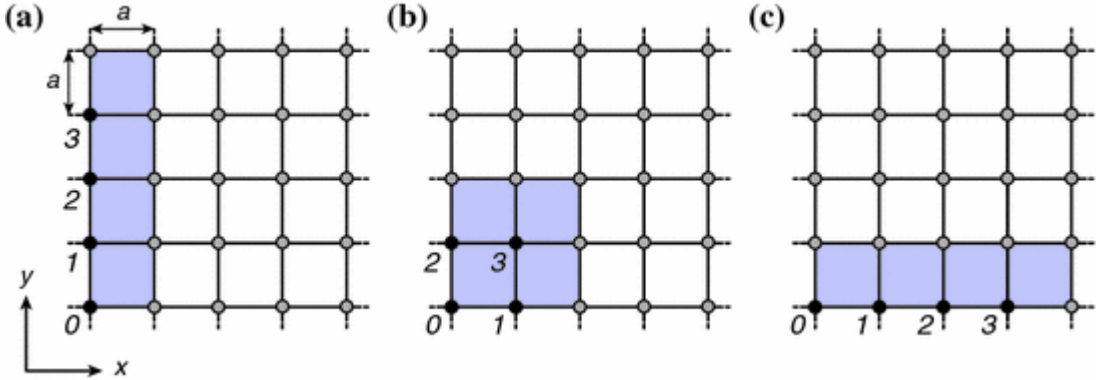
Electrons in a crystal/lattice in a magnetic field

A_c vs lattice

Electrons in a lattice in a magnetic field

$$B_{critical} = \frac{\Phi_0}{A_{min}}$$

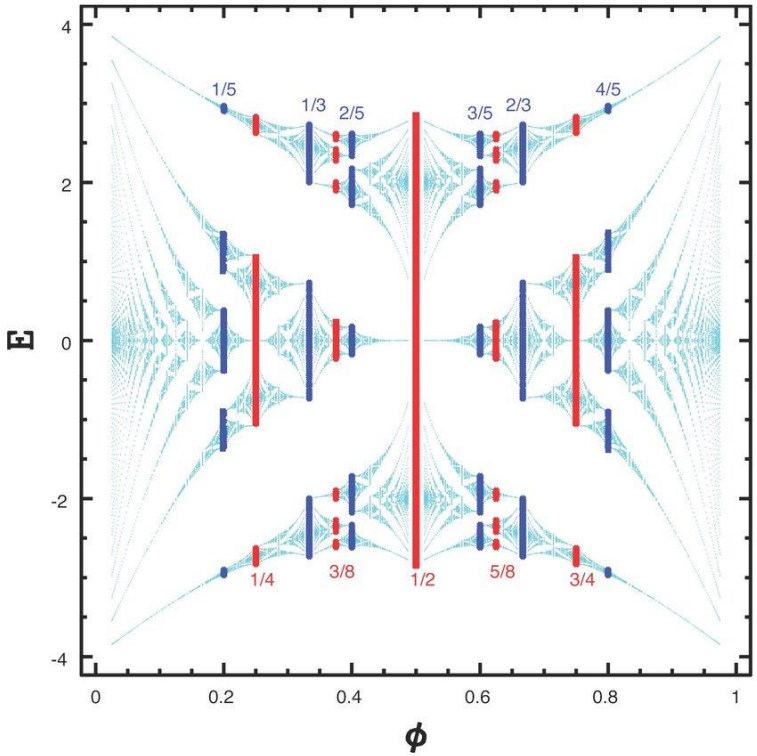
Φ/Φ_0 = *p/q (rational) :* Φ flux through unit cell
p,q: coprimes
q: bloch band breaks up into q distinct energy bands



Example:
Φ/Φ_0 = *1/4 :* ¼ Φ_0 per lattice cell
-> 4 lattice cells=magnetic cell
Shape of the magnetic cell is gauge dependent

Aidelsburger M. (2016) Square Lattice with Magnetic Field. In: Artificial Gauge Fields with Ultracold Atoms in Optical Lattices. Springer, Cham.

Electrons in a lattice in a magnetic field



arXiv:1802.04585

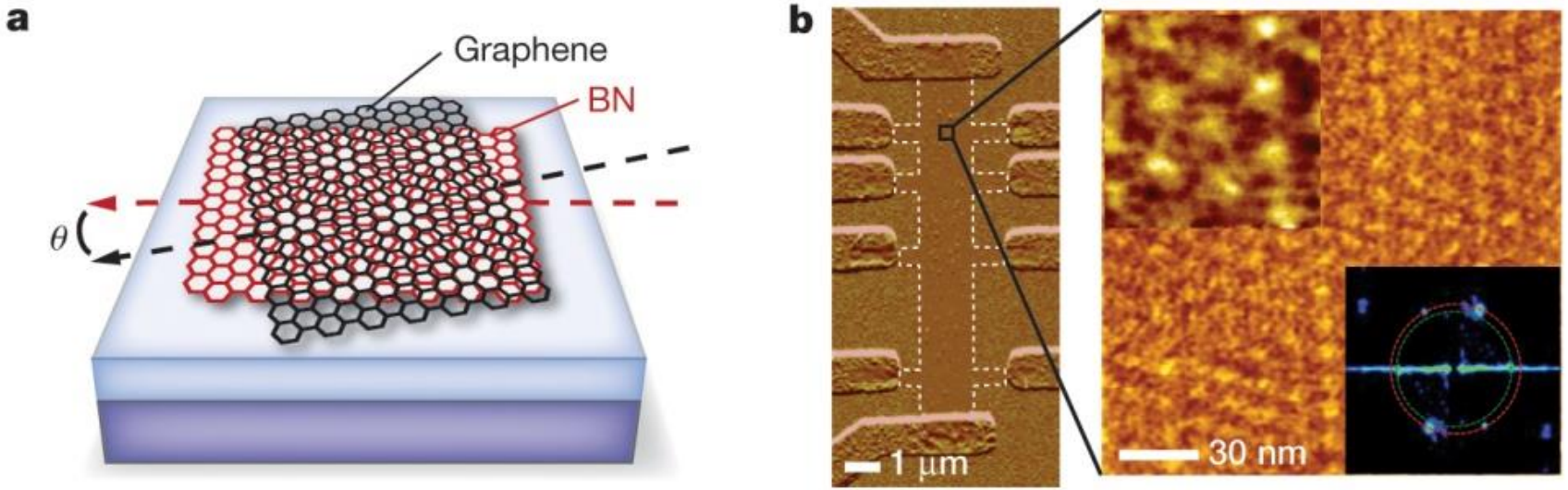
Sketch of derivation of HSBF

1. Tight-Binding Bloch energy function
2. Introducing Peierls Substitution
3. Choose Gauge
4. Make nearest neighbor approximation
5. Make use of lattice geometry and some substitutions to get a one-dimensional Schrödinger equation (Harper‘s equation)

Peierls Substitution

$$t_{nm} \rightarrow t_{nm} e^{i\frac{2\pi}{\Phi_0}\int_n^m \overrightarrow{A_{nm}} d\vec{l}}$$

Measuring HSBF



Via transport measurements with Hall Bars

Nature **497,** 598–602 (2013)

Butterfly in different lattices