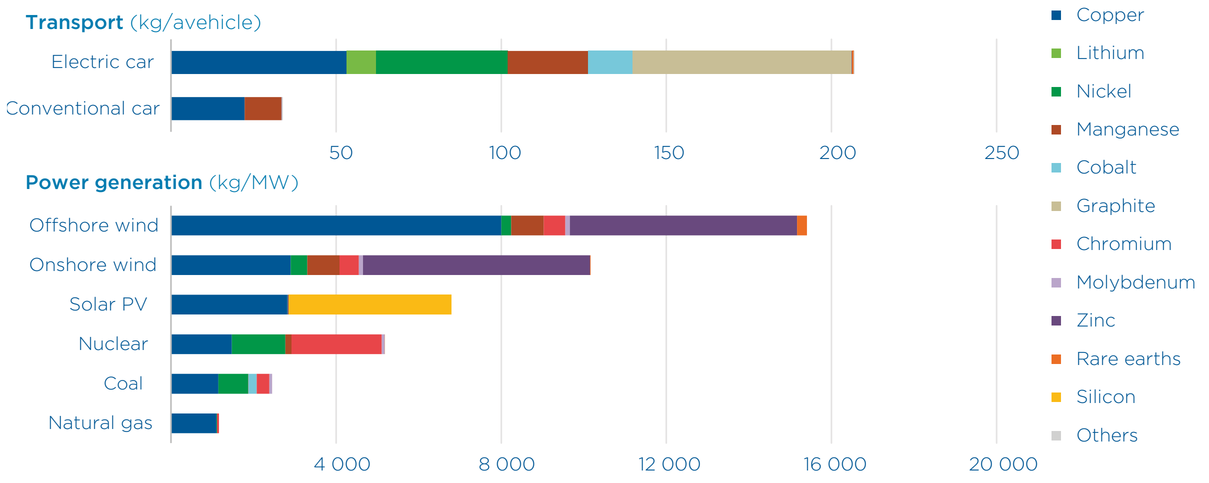
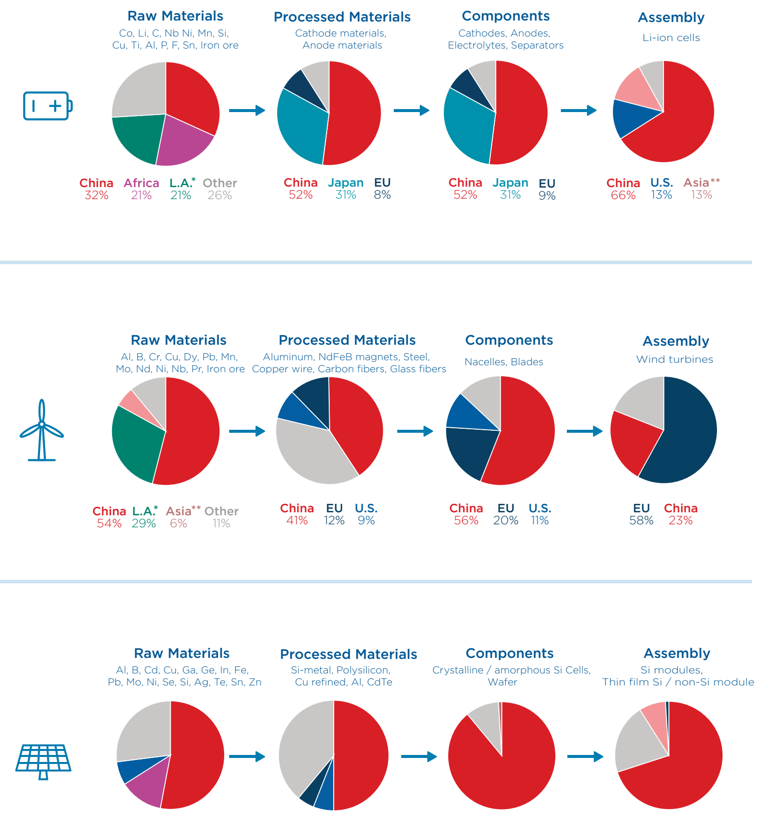
Green Technology Materials & Supply Chains

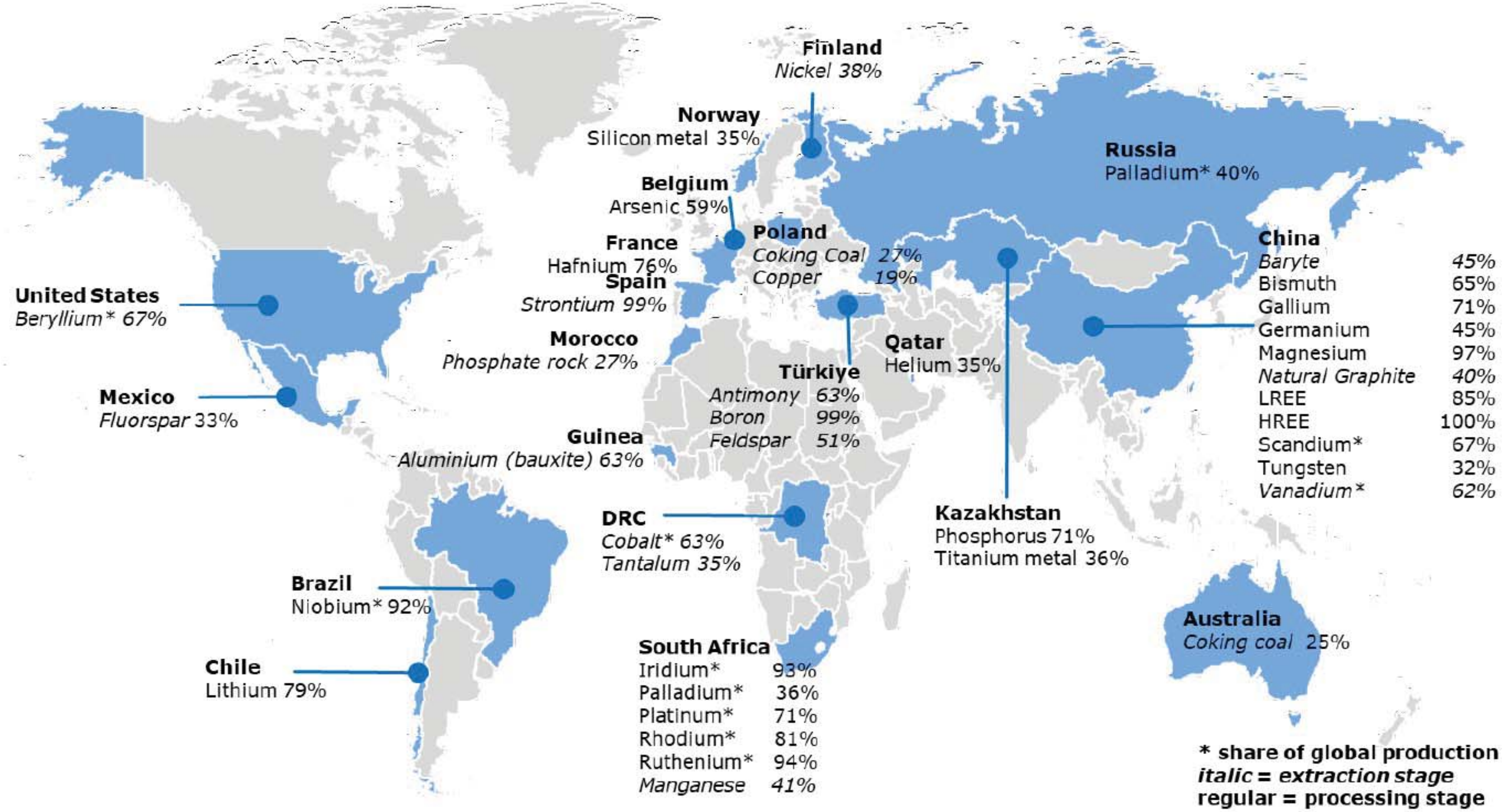
Minerals used in selected clean energy technologies



Geographical concentration of supply chains

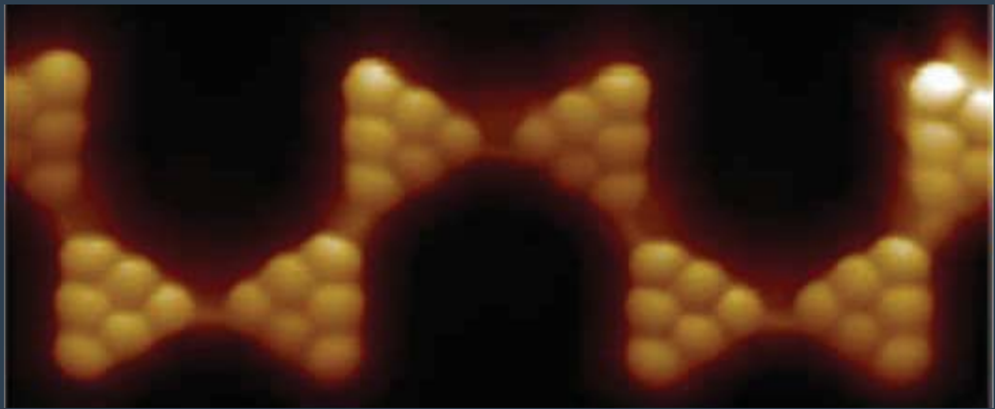


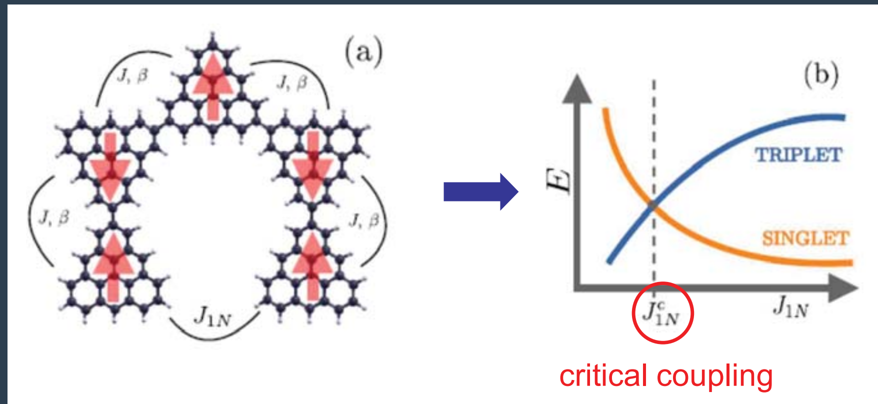
World map of Critical Raw Materials imports to the EU



Source: European Commission, 2023.

Fractionalisation in spin-1 triangulene chains





Universidad de Oviedo

Jaime Ferrer
Department of Physics

cinn

Outline

1. Spin-1 Haldane chains
2. Graphene triangulenes
3. Grogu
4. Triggering a singlet-triplet transition
5. Fractionalisation in Physics

Collaborators & funding

Gabriel Martínez-Carracedo

Laszló Oroszlany

Amador García-Fuente

Laszlo Szunghyo

Grant # PID2022-137078NB-100

AYUD/2021/51185

MINISTERIO DE CIENCIA E INNOVACIÓN

AGENCIA ESTATAL DE INVESTIGACIÓN

UNIÓN EUROPEA
FONDO EUROPEO DE DESARROLLO REGIONAL
"Una manera de hacer Europa"

GOBIERNO DEL PRINCIPADO DE ASTURIAS
CONSEJERÍA DE CIENCIA, INNOVACIÓN Y UNIVERSIDAD

FICYT

What is the angular momentum of a particle?

The angular momentum **L** measures how much angular motion an orbiting particle P has about an origin O

L is a vector perpendicular to the orbit plane, whose length ~ particle mass & speed

Anti-clockwise rotation: **+L**   Clockwise rotation: **-L**

The spin angular momentum **S** measures how much spins a rotating particle P

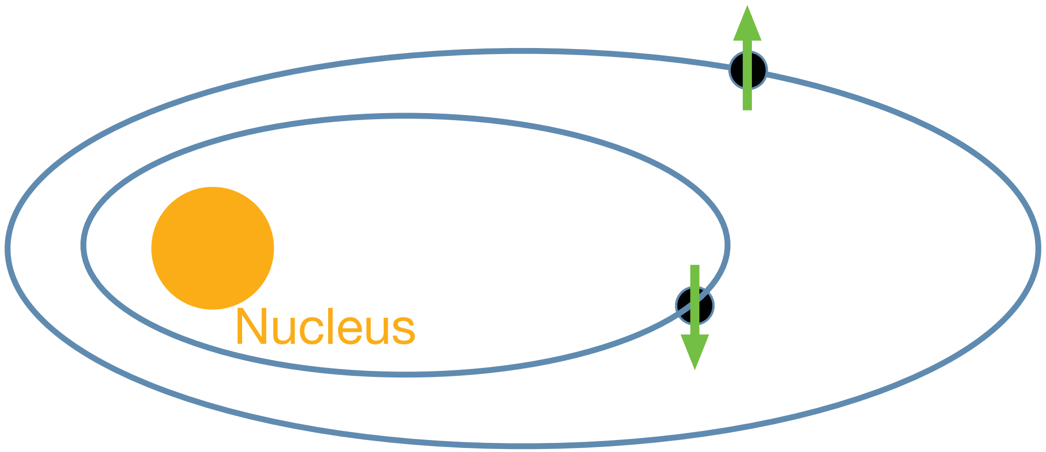
Anti-clockwise rotation: **+S**   Clockwise rotation: **-S**

What are atomic spins S_A ?

Each electron in an atom orbits about its nucleus

Each electron possesses a spin angular moment whose modulus es S = 1/2

We only know its S_z component. S_z can be equal to +1/2 = ↑ or to -1/2 = ↓



Electrons' spins add up (according to Hund's rules) to make up the atomic total spin S_A

What is a quantum spin 1/2 ?

 $= |\uparrow> = |S=1/2, S_z=+1/2> = \begin{pmatrix}1\\0\end{pmatrix}$

 $= |\downarrow> = |S=1/2, S_z=-1/2> = \begin{pmatrix}0\\1\end{pmatrix}$

The spin angular momentum of an electron is

$$\hat{\mathbf{S}} = \left(\hat{S}_x, \hat{S}_y, \hat{S}_z\right) = \frac{\hbar}{2}\left(\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}, \begin{pmatrix}0 & -i\\i & 0\end{pmatrix}, \begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\right)$$

Pauli matrices σ_x σ_y σ_z

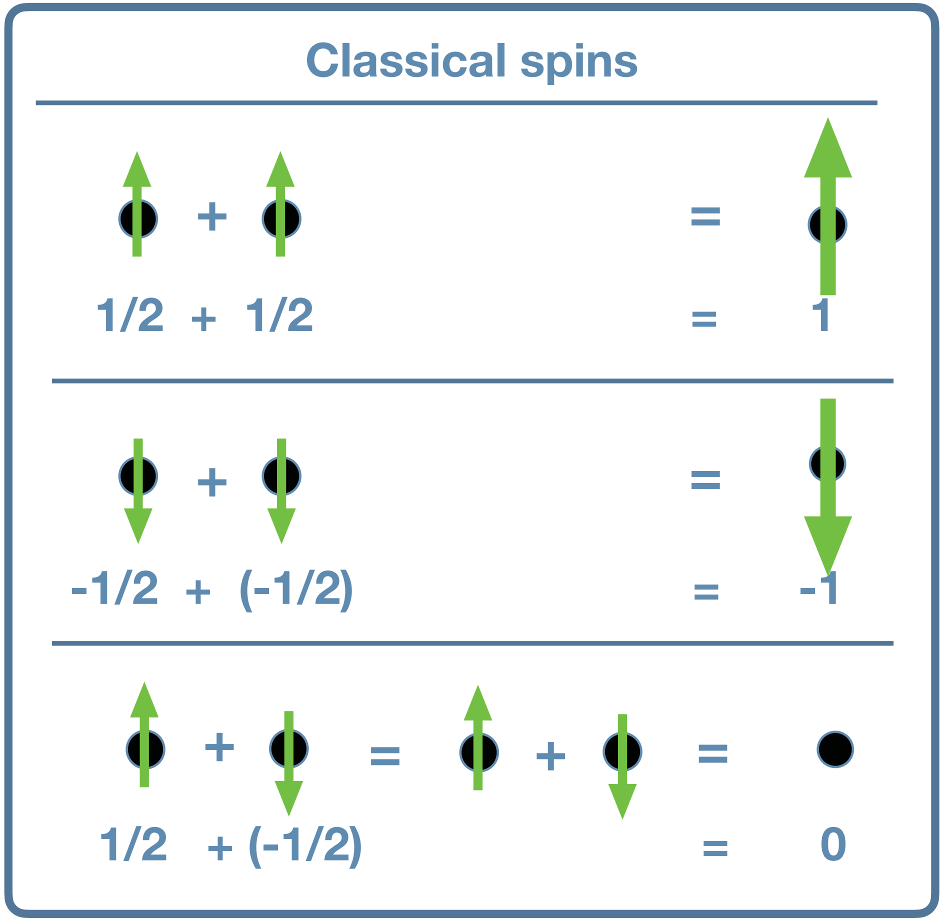
$$\hat{\mathbf{S}}^2 = \frac{3}{4}\hbar^2\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$$

The two eigen-vectors of S_z are precisely $|\uparrow>$ & $|\downarrow>$

Werner Heisenberg

Wolgang Pauli

How do you add two electrons' spins?



Quantum spins

Triplet

$$|\mathbf{T_1}>=|\mathbf{S=1, S_z=+1}>=|\uparrow>\otimes|\uparrow>=|\uparrow\uparrow>$$

$$|\mathbf{T_{-1}}>=|\mathbf{S=1, S_z=-1}>=|\downarrow>\otimes|\downarrow>=|\downarrow\downarrow>$$

$$|\mathbf{T_0}>=|\mathbf{S=1, S_z=0}>=\frac{|\uparrow\downarrow>+|\uparrow\downarrow>}{\sqrt{\mathbf{2}}}$$

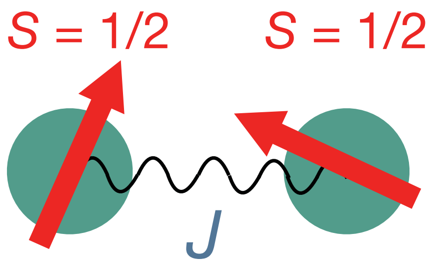
Singlet

$$|\mathbf{S}>=|\mathbf{S=0, S_z=0}>=\frac{|\uparrow\downarrow>-|\uparrow\downarrow>}{\sqrt{\mathbf{2}}}$$

What are interacting atomic spins ?

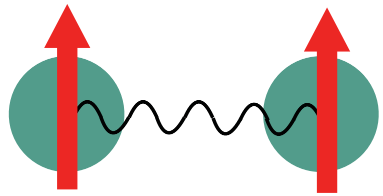
Exchange constant

$$\hat{H} = J\,\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$$

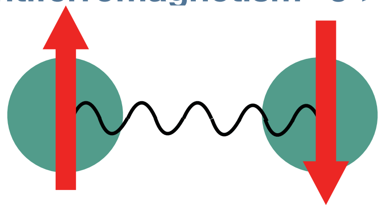


Aligns spins among each other

Ferromagnetism $J < 0$

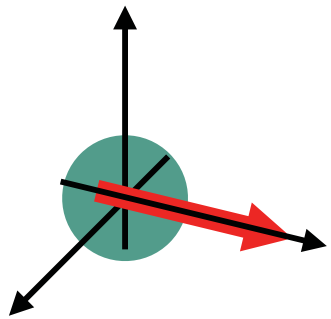


Antiferromagnetism $J > 0$



Intra-atomic anisotropy tensor

$$\hat{H} = \hat{\mathbf{S}}_1\, K\, \hat{\mathbf{S}}_1$$



Aligns spins to axes

Exchange tensor

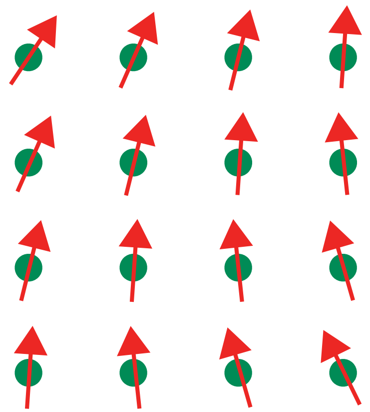
$$\hat{H} = \hat{\mathbf{S}}_1\, J\, \hat{\mathbf{S}}_2 = (\hat{S}_1^x,\, \hat{S}_1^y, \hat{S}_1^z) \begin{pmatrix} J^{xx} & J^{xy} & J^{xz} \\ J^{yx} & J^{yy} & J^{yz} \\ J^{zx} & J^{zy} & J^{zz} \end{pmatrix} \begin{pmatrix} \hat{S}_2^x \\ \hat{S}_2^y \\ \hat{S}_2^z \end{pmatrix}$$

Aligns spins, cants them, etc

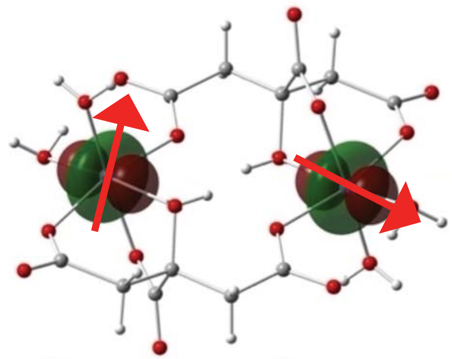
The Heisenberg Hamiltonian

$$\mathcal{H} = \frac{1}{2}\sum_{i,j} \hat{\mathbf{S}}_i\, J_{ij}\, \hat{\mathbf{S}}_j + \sum_{i} \hat{\mathbf{S}}_i\, K_i\, \hat{\mathbf{S}}_i$$

Exchange tensors **Intra-atomic anisotropy tensors**

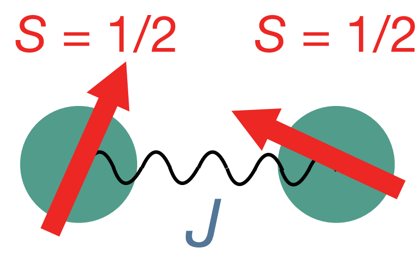


Describes magnetic solids



Describes magnetic molecules

The two-site spin-1/2 Heisenberg Hamiltonian



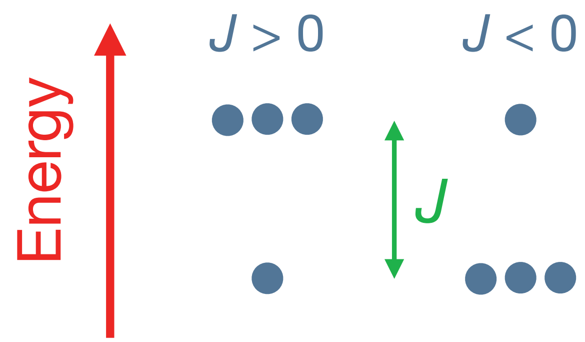
$$\hat{H} = J\,\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \frac{J}{2}\left((\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2)^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_2^2\right) = \frac{J}{2}\left((\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2)^2 - \frac{3}{2}\right)$$

Two spins 1/2 add up as $\left(S = \frac{1}{2}\right) \otimes \left(S = \frac{1}{2}\right) = (S=0) \oplus (S=1) = \text{Singlet} \oplus \text{Triplet}$

Eigen-energies:

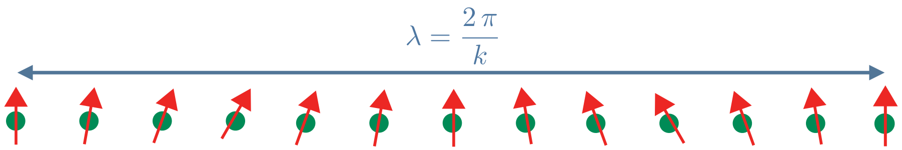
$$E(S=0) = -\frac{3}{4}J$$

$$E(S=1) = +\frac{1}{4}J$$

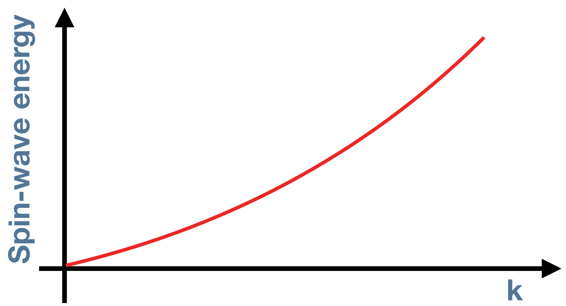


Ordered & disordered spin systems

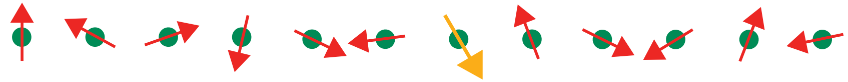
Spins are aligned; the state has a spin stiffness



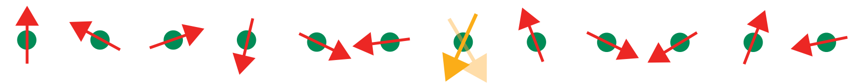
The system supports long-length spin waves



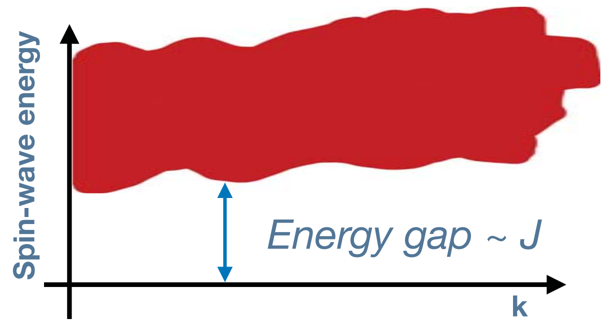
Spin waves cost zero energy when $\lambda \to \infty \; (\mathbf{k} \to 0)$



Spins are not aligned; the state has no spin stiffness



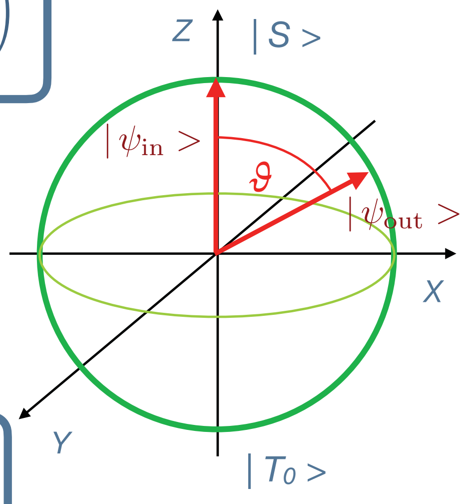
The system supports only short-length spin twists



Spin waves cost always a non-zero energy $> J$

What is a (singlet-triplet) spin qbit ?

It is a linear combination of $|S>=\frac{|\uparrow\downarrow>-|\downarrow\uparrow>}{\sqrt{2}}=\begin{pmatrix}1\\0\end{pmatrix}$ **and** $|T_0>=\frac{|\uparrow\downarrow>+|\downarrow\uparrow>}{\sqrt{2}}=\begin{pmatrix}0\\1\end{pmatrix}$



Initialise qbit in state $|\psi_{\rm in}>=|S>=\begin{pmatrix}1\\0\end{pmatrix}$

Operate on qbit with Hamiltonian $\hat{H}_{\rm qbit}=\cos\frac{\theta}{2}\,\hat{\sigma}_z+\sin\frac{\theta}{2}\,\hat{\sigma}_x=\begin{pmatrix}\cos\frac{\theta}{2} & \sin\frac{\theta}{2}\\ \sin\frac{\theta}{2} & -\cos\frac{\theta}{2}\end{pmatrix}$

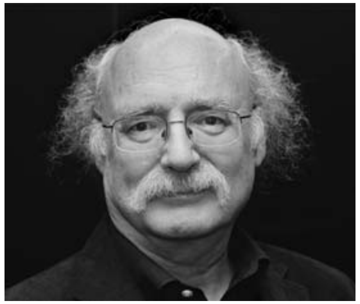
Get output qbit $|\psi_{\rm out}>=\hat{H}\,|\psi_{\rm in}>=\begin{pmatrix}\cos\frac{\theta}{2} & \sin\frac{\theta}{2}\\ \sin\frac{\theta}{2} & -\cos\frac{\theta}{2}\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}=\begin{pmatrix}\cos\frac{\theta}{2}\\ \sin\frac{\theta}{2}\end{pmatrix}=\cos\frac{\theta}{2}\,|S>+\sin\frac{\theta}{2}\,|T_0>$

What is a quantum spin chain ?

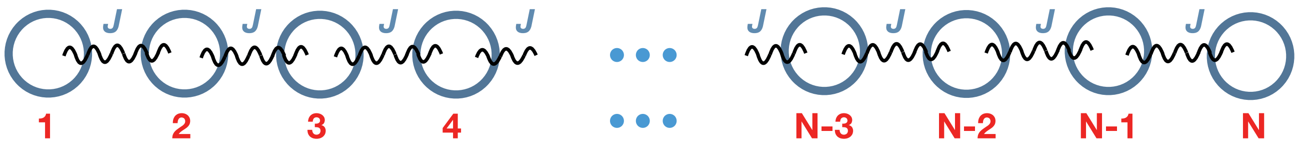
A quantum spin chain has N atoms lined up in a row

Each atom has a spin $\hat{S}$

Atoms interact via the exchange constant J



Duncan Haldane



Finite-length chain having open ends

Quantum chains have always a disordered ground state. Their energy spectrum should have a gap

Spin fractionalisation in the Haldane spin-1 chain

Haldane's conjecture on infinite AFM spin chains

$$\hat{H} = \frac{J}{2}\sum_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \quad (J > 0)$$

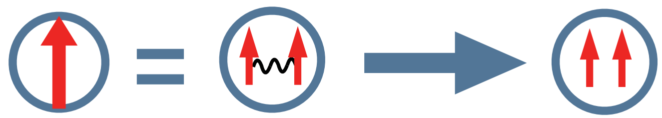
S = integer, then energy spectrum has a gap

S = half-integer, then energy spectrum is gapless

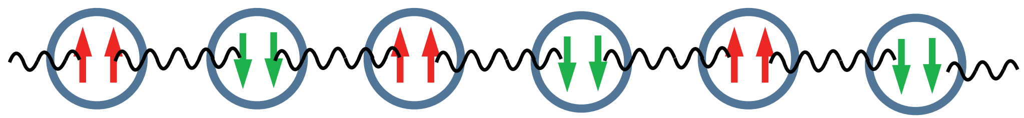
AKLT exactly solvable model on spin-1 infinite AFM chains

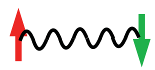
$$\hat{H} = \frac{J}{2}\sum_{ij}\left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + \beta\left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j\right)^2\right) \quad \beta = 1/3$$

Each atomic S=1 spin is fractionalized into two spin-1/2 bits



The chain makes an infinite bond solid





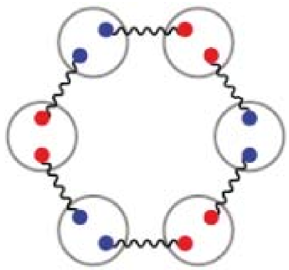
$$= |S> = \frac{|\uparrow\downarrow> - |\downarrow\uparrow>}{\sqrt{2}}$$

Haldane, Physics Letters 93A, 464 (1983)

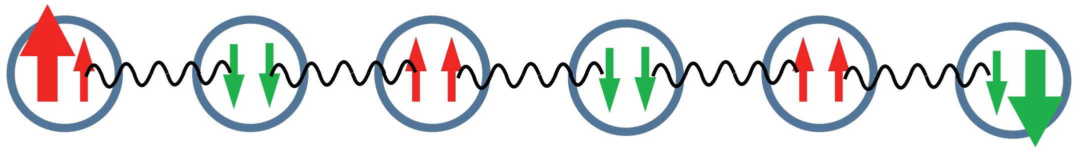
Affleck, Kennedy, Lieb & Tasaki, Phys. Rev. Lett. 59, 799 (1987)

Spin excitations in the Haldane chain

Infinite & circular chains have a singlet ground state



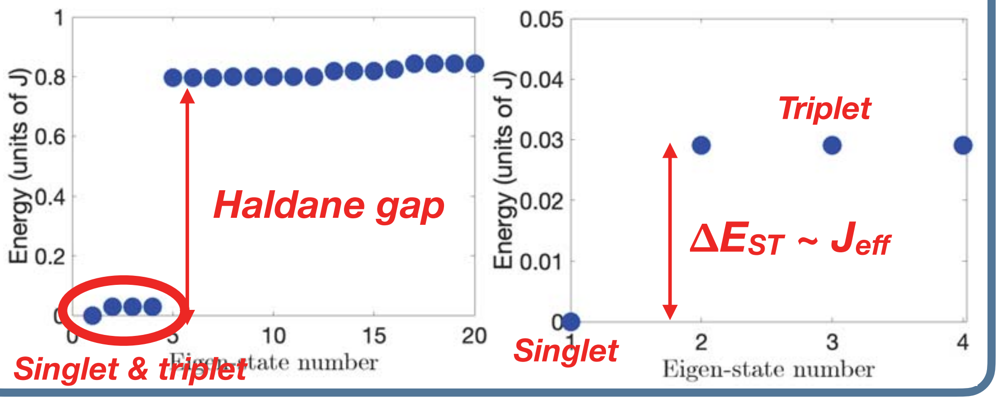
Finite chains have two spin-1/2 edge states because of fractionalization



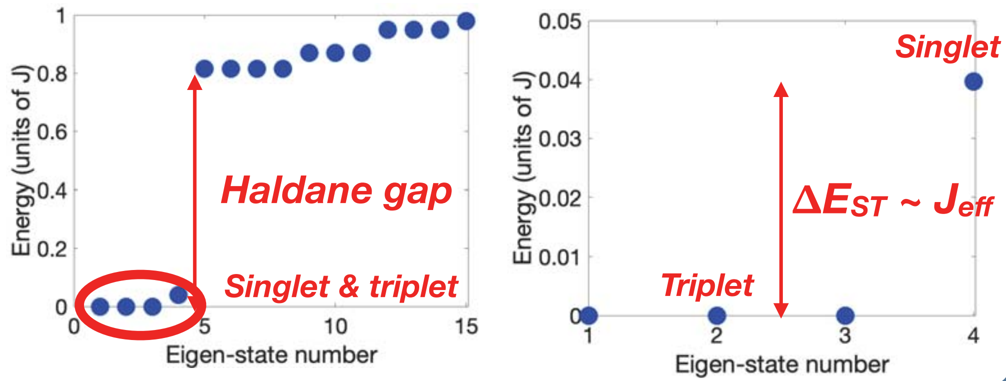
The two spin-1/2 edge states interact via an effective J_{eff}

They add up making a singlet & a triplet

N = even $\Longrightarrow$ $J_{eff} > 0$ $\Longrightarrow$ *singlet ground state*

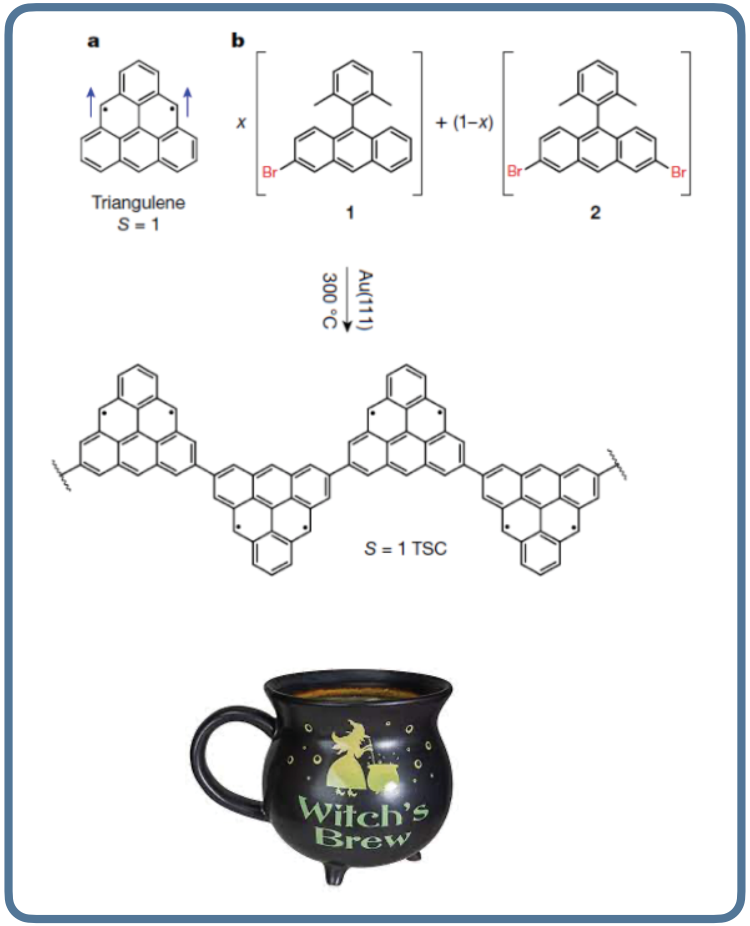


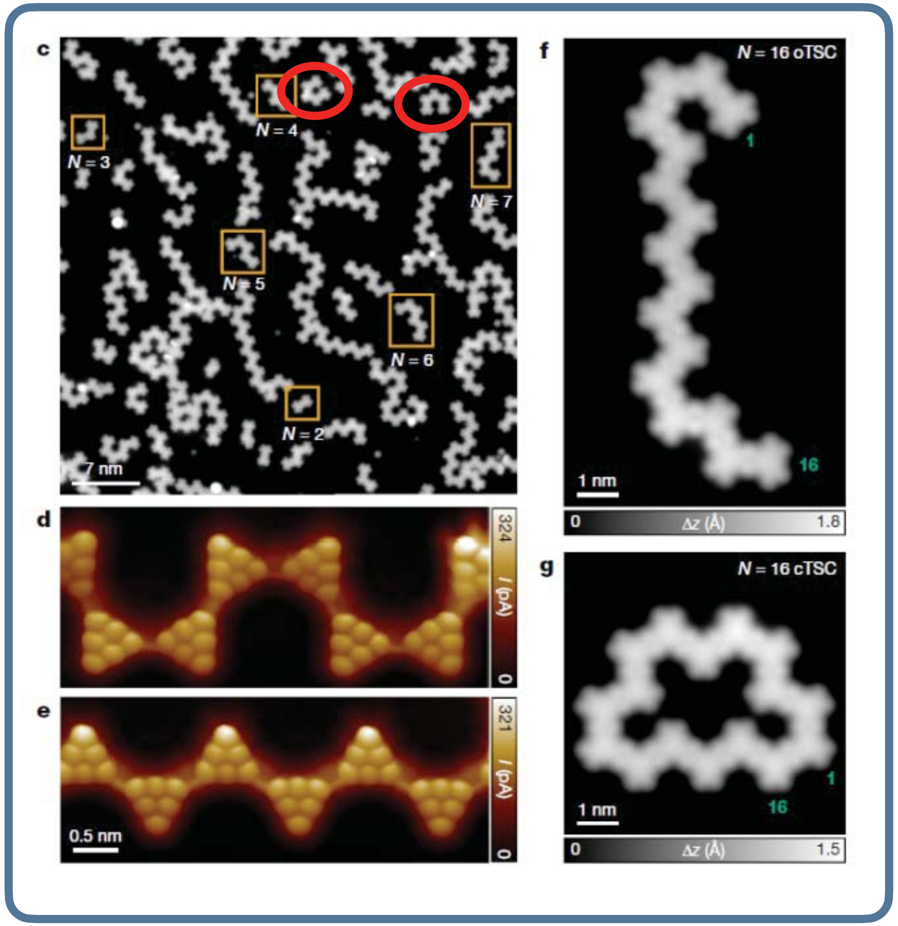
N = odd $\Longrightarrow$ $J_{eff} < 0$ $\Longrightarrow$ *triplet ground state*



White & Huse, Phys. Rev. B 48, 3844 (1993)

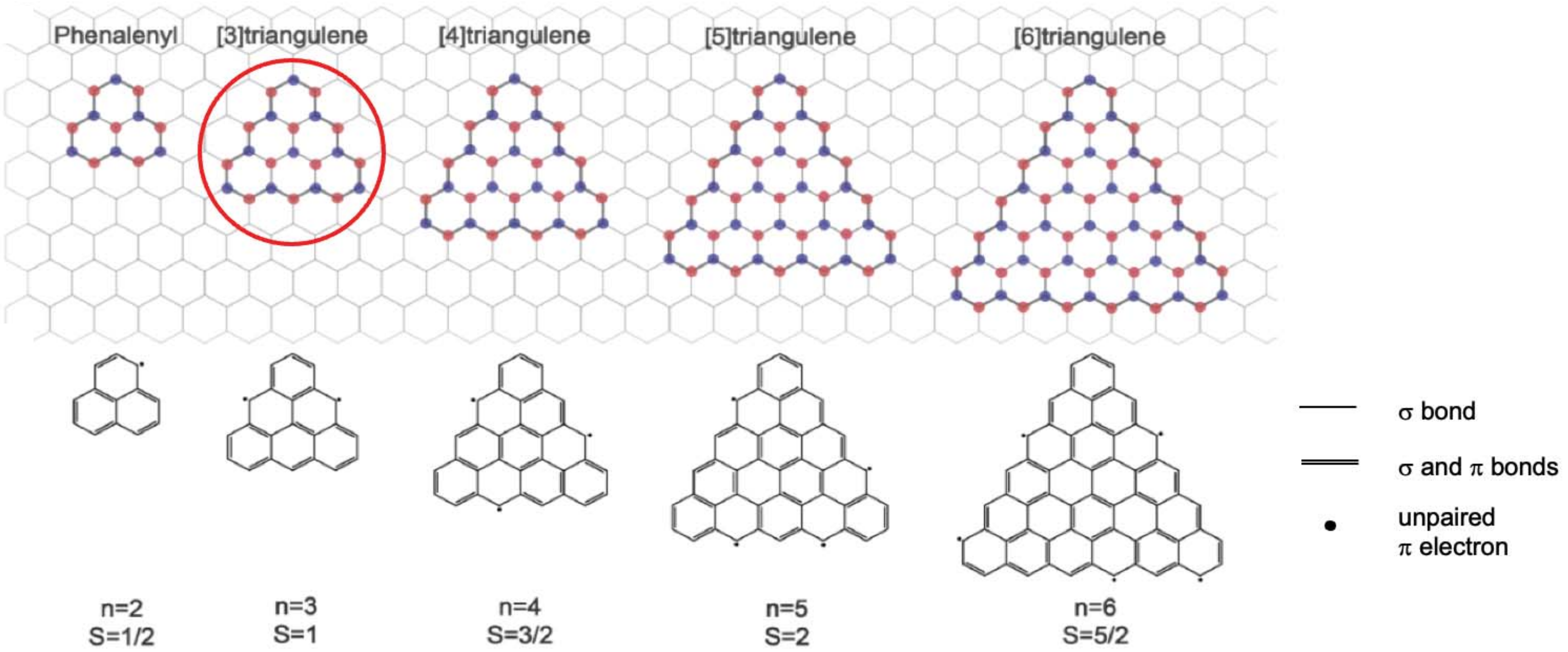
Synthesis of spin-1 graphene triangulene chains





S. Mishra *et al*, Nature 598, 287 (2021)

Graphene triangulenes (GT) are artificial spins

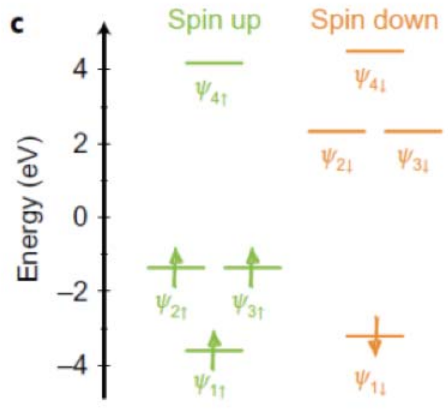


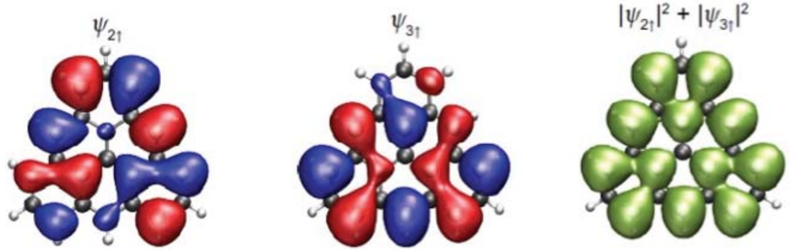
Pavlicek et al., Nat. Nanotech. 12, 308 (2017)

Su et al. Angewandte Chemie 59, 6758 (2020)

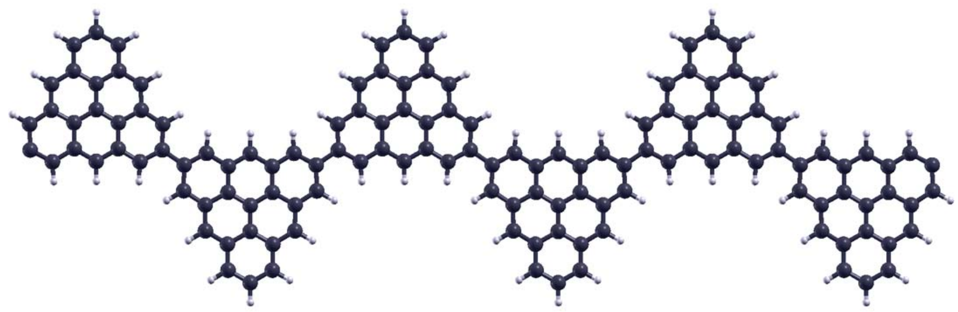
Theory confirms that GT are spin-1 objects

CI & DFT calculations (PBE + GW) find a spin-1 ground-state



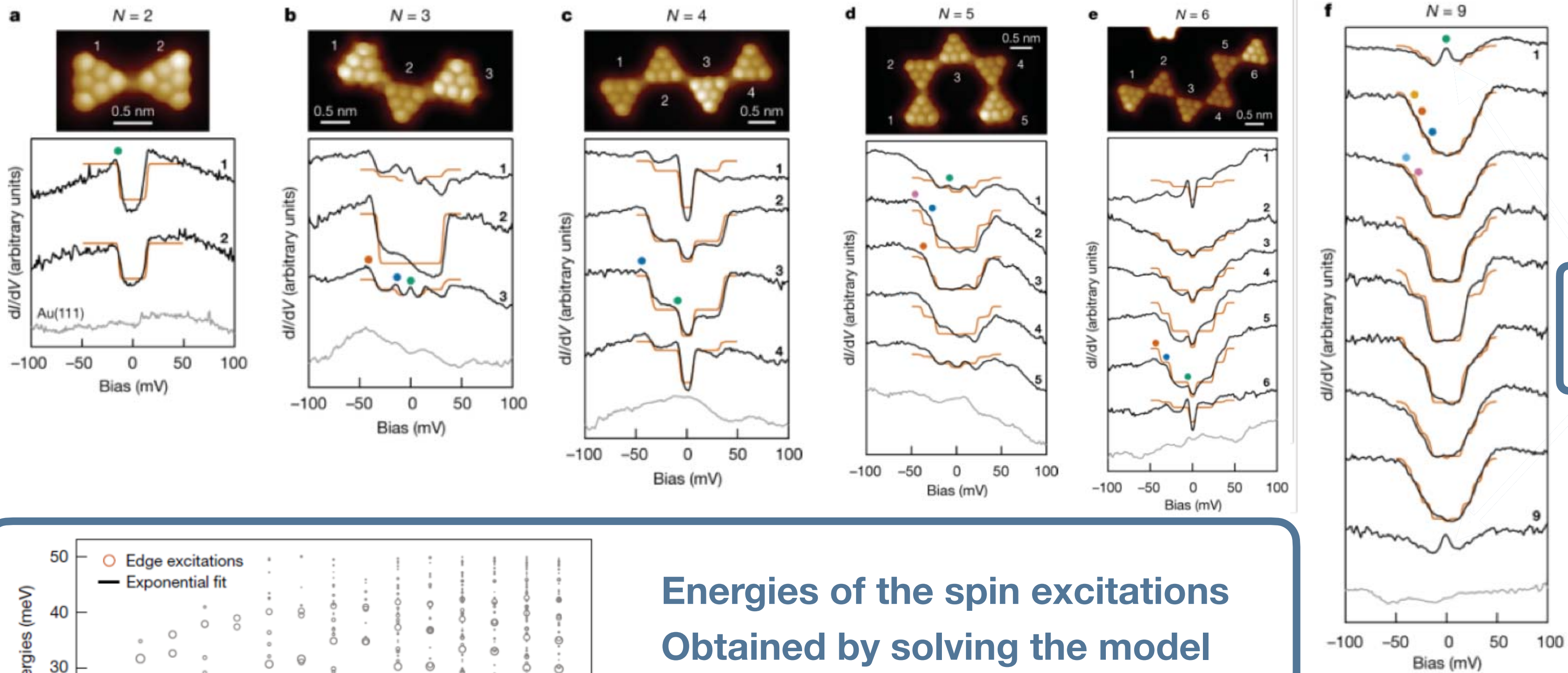


Each GT retains its S=1 spin nature in the chain

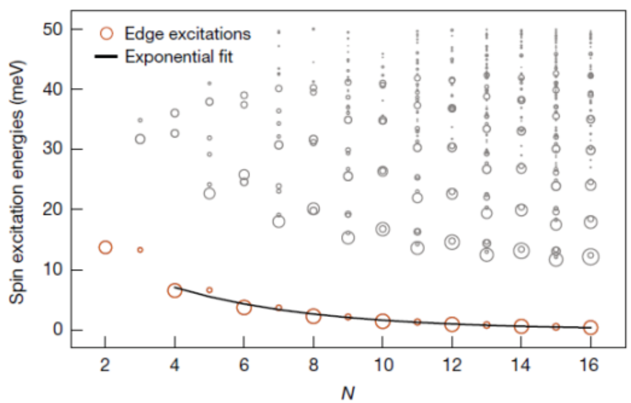


Park, J. Chem. Theor. Comp. 17, 4092 (2021)   Pavlicek et al. Nat. Nanotech. 12, 308 (2017)   Martínez-Carracedo et al., Phys. Rev. B 107, 035432 (2023)

Spin-1 triangulene chains are Haldane spin -1 chains



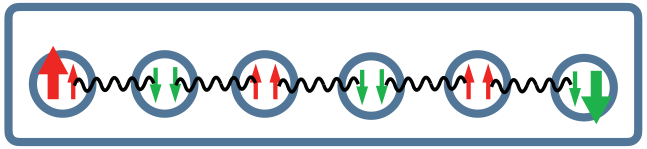
Kondo resonances
Spin-1/2 edge states



Energies of the spin excitations
Obtained by solving the model

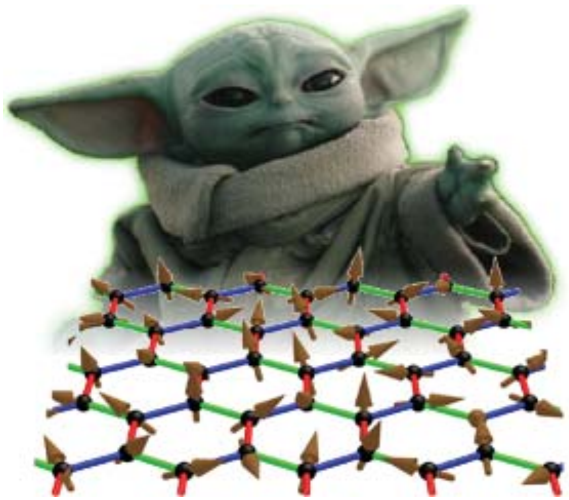
$$\hat{H} = J \sum_i \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} + \beta \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} \right)^2 \right)$$

$J = 18$ meV & $\beta = 0.09$



S. Mishra *et al*, Nature 598, 287 (2021)

Grogu: mastering… the spins !



$$\mathcal{H} = \frac{1}{2}\sum_{i,j} \hat{\mathbf{S}}_i\, J^1_{ij}\, \hat{\mathbf{S}}_j + \sum_i \hat{\mathbf{S}}_i\, K_i\, \hat{\mathbf{S}}_i + \sum_{i,j} \hat{\mathbf{S}}_i\, J^2_{ij}\, \hat{\mathbf{S}}_j \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_J\right) + \sum_{i,j} \hat{\mathbf{S}}_i\, J^2_{ij}\, \hat{\mathbf{S}}_j \left(\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_J\right) + \ldots.$$

Compute any bilinear or biquadratic exchange constant up to any desired neighbour

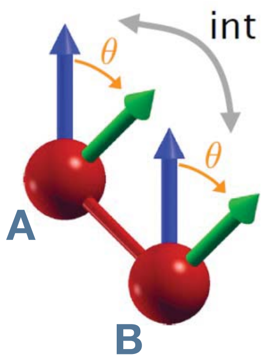
Oroszlany et al., Phys. Rev. B 99, 224412 (2019) G. Martínez-Carracedo et al., arXiv:2309.02558

Our method to extract J and β

Magnet described by the Heisenberg Hamiltonian

$$\hat{H} = \frac{1}{2}\sum_{ij} J_{ij}\, \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$$

Perform infinitesimal rotations on two atoms A & B

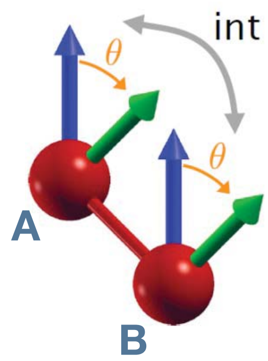


Then the energy variation is $\Delta \mathrm{E}_{\mathrm{rot}} = \mathbf{J_{AB}}\, \delta \mathbf{S_A} \cdot \delta \mathbf{S_B}$

Magnet described by the electron Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}^{XC} + \delta \hat{V}_A^{XC} + \delta \hat{V}_B^{XC}$$

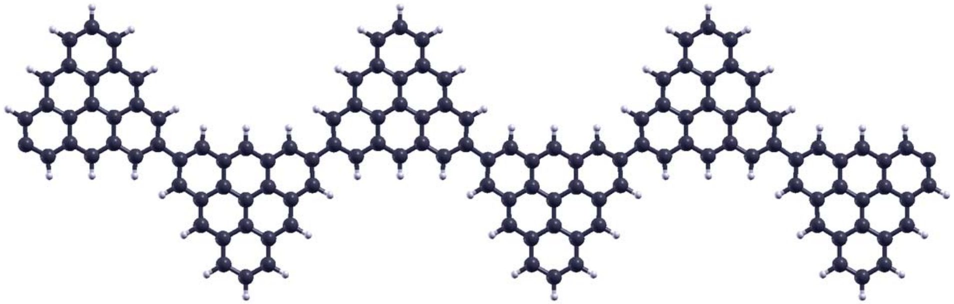
Perform infinitesimal rotations on two atoms A & B



$$J_{AB} = -\frac{1}{\pi}\int_{-\infty}^{\varepsilon_F} \mathrm{d}\varepsilon\, \mathrm{Im}\, Tr\, \left(\delta V_A^{XC}\, G_{AB}\, \delta V_B^{XC}\, G_{BA}\right)$$

Oroszlany et al., Phys. Rev. B 99, 224412 (2019)
G. Martínez-Carracedo et al., arXiv:2309.02558

Our results for *J* and *β*



$$\hat{H} = J \sum_i \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} + \beta \, (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1})^2\right)$$

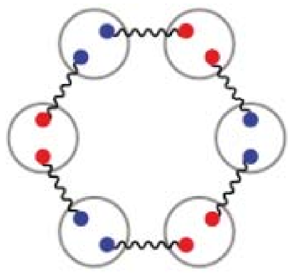
	dimer	infinite chain	Mishra et al.
J	17.7 meV	19.8 meV	18 meV
b	0.03	0.05	0.09

G. Martínez-Carracedo et al., Phys. Rev. B 107, 035432 (2023)

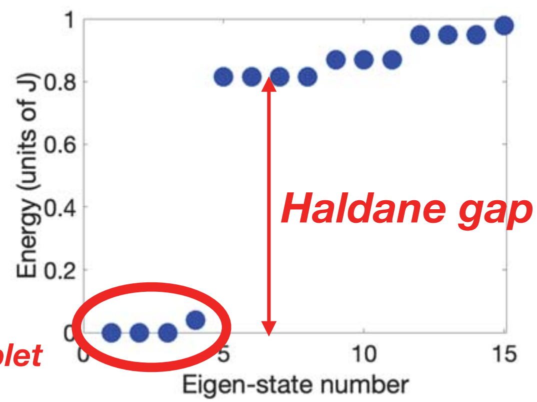
G. Martínez-Carracedo et al., arXiv:2309.02558

What we want to do: control the singlet & triplet states

Circular chains have a singlet ground state

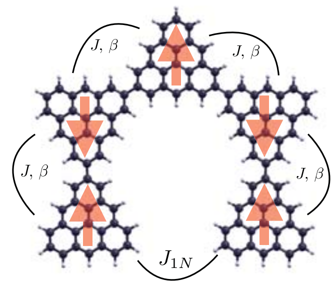


Open odd-chains *have a triplet ground state*



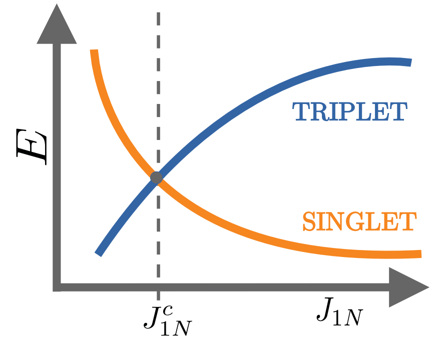
G. Martínez-Carracedo et al., Phys. Rev. B 107, 035432 (2023)

The idea: couple both ends of a horseshoe GT



$$\hat{H} = \sum_{i=1}^{N-1} J \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} + \beta \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} \right)^2 \right) + J_{1N} \hat{\mathbf{S}}_N \cdot \hat{\mathbf{S}}_1$$

Turn on & off J_{1N} *& sweep it through the critical* $J_{1N,c}$

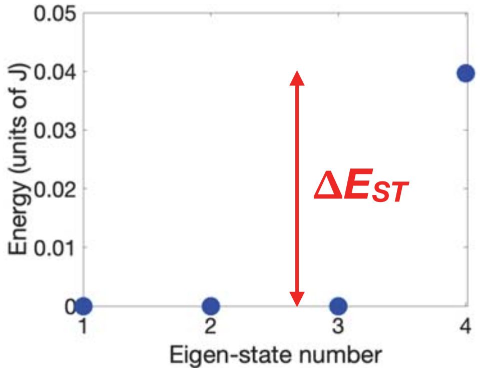


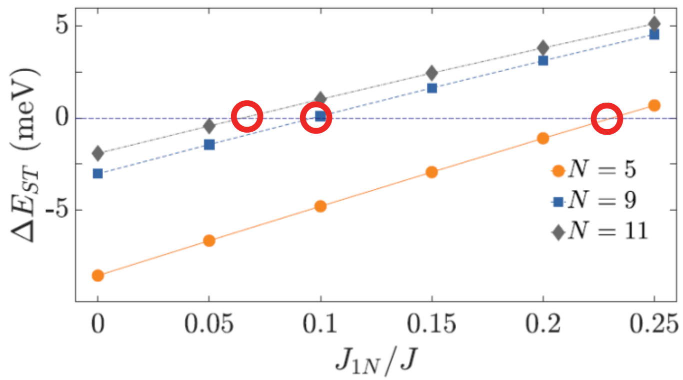
G. Martínez-Carracedo et al., arXiv:2309.02558

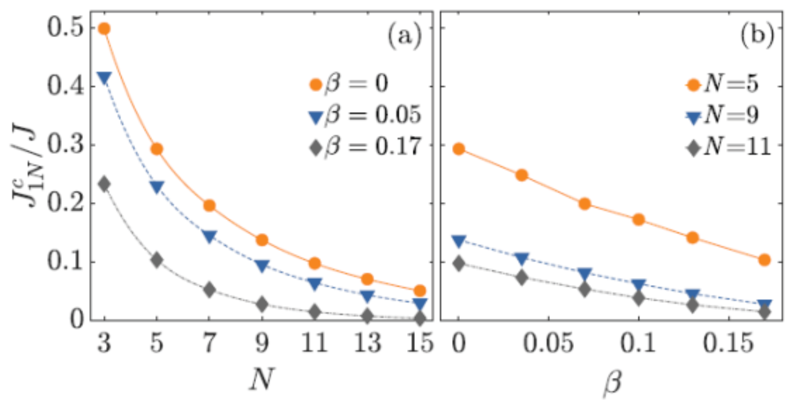
Profiling the idea

Diagonalize exactly the Hamiltonian $\hat{H} = J \sum_i \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} + \beta \left(\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} \right)^2 \right)$

Find the singlet and triplet energies E_S & E_T & determine the splitting $\Delta E_{ST} = E_S - E_T$







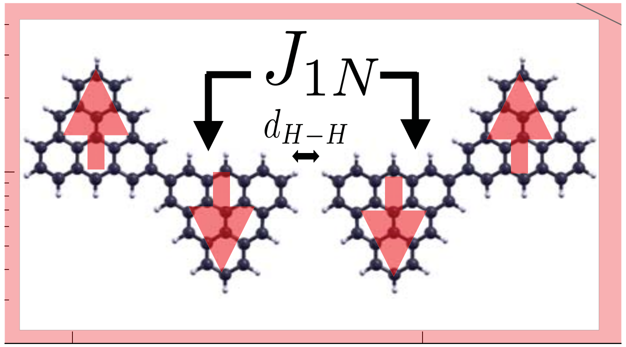
N = 9 chains display a good compromise between sizable enough ΔE_{ST} & small enough critical $J_{1N,c}$

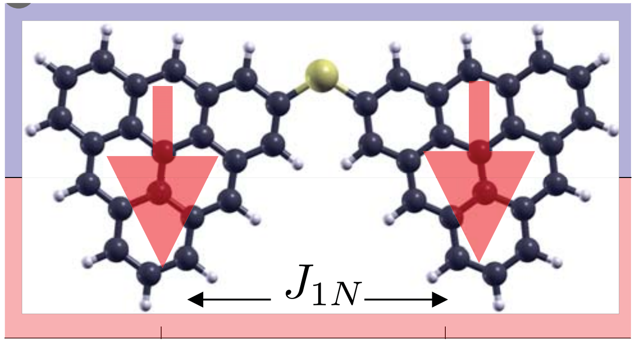
G. Martínez-Carracedo et al., Phys. Rev. B 107, 035432 (2023)

G. Martínez-Carracedo et al., arXiv:2309.02558

Strategies to modify J_{1N}

Make both ends approach each other



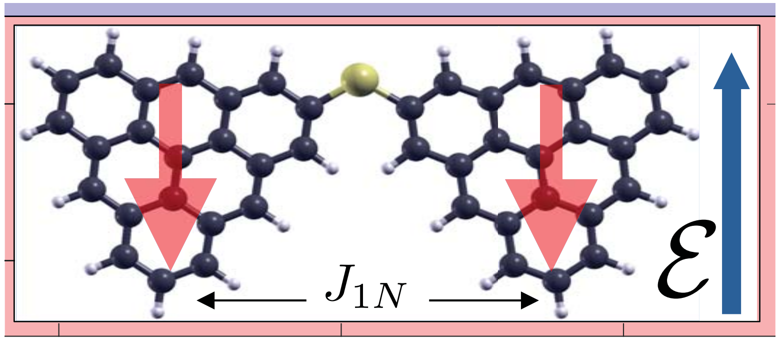


Link ends via a suitable atom (S here)

Make both ends approach each other

Link ends via a suitable atom (S here)

Apply an electric field $\mathcal{E}$

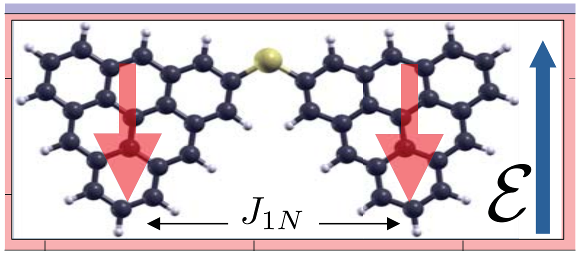


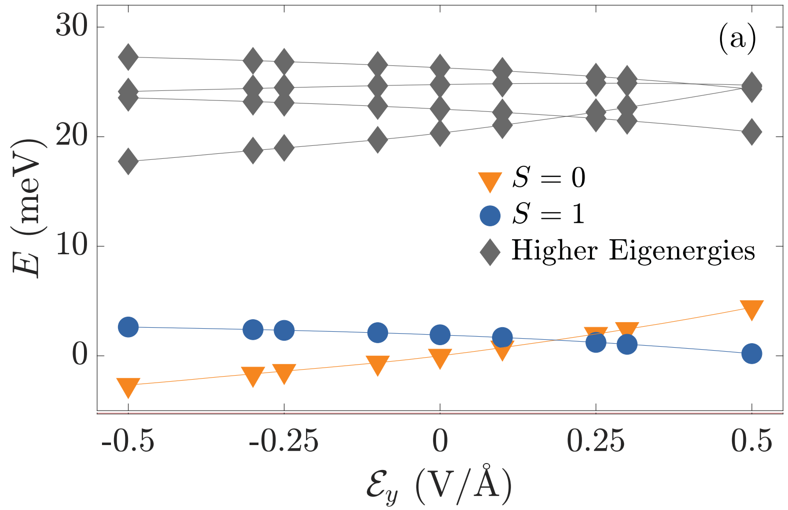
G. Martínez-Carracedo et al., Phys. Rev. B 107, 035432 (2023)

G. Martínez-Carracedo et al., arXiv:2309.02558

Electrically-driven singlet-triplet transition

J_{1N} can be modified by an external in-plane in-axis electric field $\mathcal{E}$





N = 9 GT chain

Singlet-triplet crossing at $\mathcal{E}$ ~ 0.2 V/Å

Computed $J_{1N,c}$ ~ *0.03 J* agrees with exact diagonalization

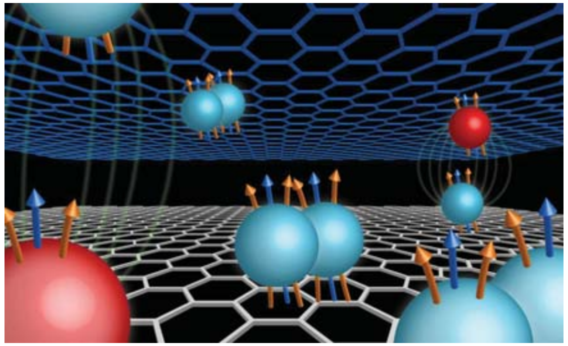
***S*-atom + $\mathcal{E}$ induce a dipole in adjacent triangulenes**

G. Martínez-Carracedo et al., Phys. Rev. B 107, 035432 (2023)

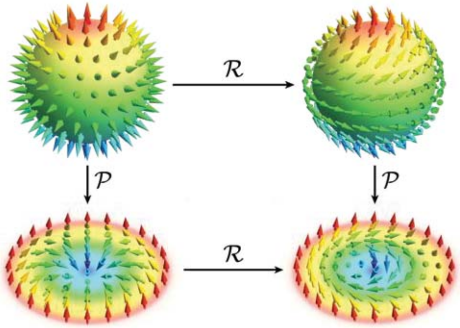
G. Martínez-Carracedo et al., arXiv:2309.02558

Fractionalisation in Physics: what is it ?

Elementary particles cannot be teared apart … or maybe they can ?



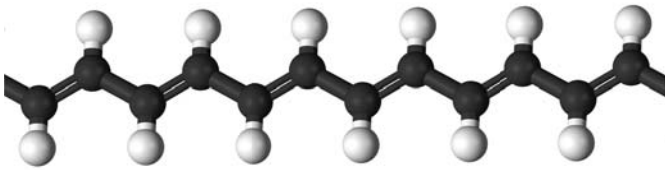
Elementary excitations in the Quantum Hall Effect carry fractional charge

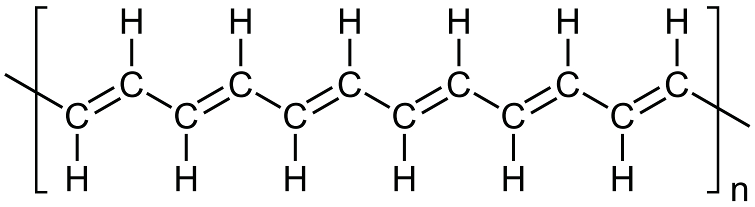


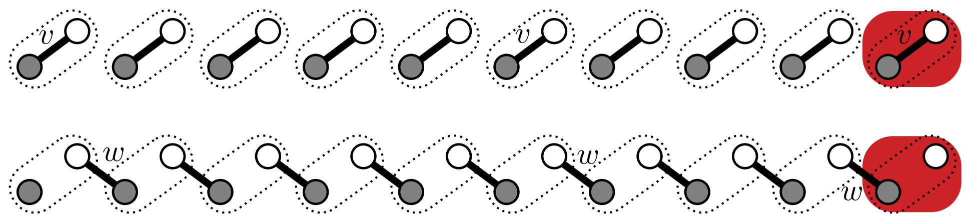
Magnetic monopoles do not exist … but maybe they can be table-top fabricated ?

The Schrieffer - Heeger - Su chain

The SSH chain was introduced to model dimerization in polyacetylene chains







The chain makes intra- or inter-cell bonds depending on the bonding strength ratio *v* - *w*

Alan Heeger

Robert Schrieffer

The chain hosts topologically-protected edge states if *v* > *w*

Su, Schrieffer & Heeger, Phys. Rev. Lett. 42, 1698 (1979)

Jackiw & Schrieffer, Nucl. Phys. B 190, 253 (1981)

The Kitaev chain

Majorana proposed in 1937 that spin-1/2 particles could exist that would be their own antiparticle

These hypothetical Majorana fermions have no charge, therefore hardly interact: they are *hermits*

Majorana fermions do not possibly exist on their own

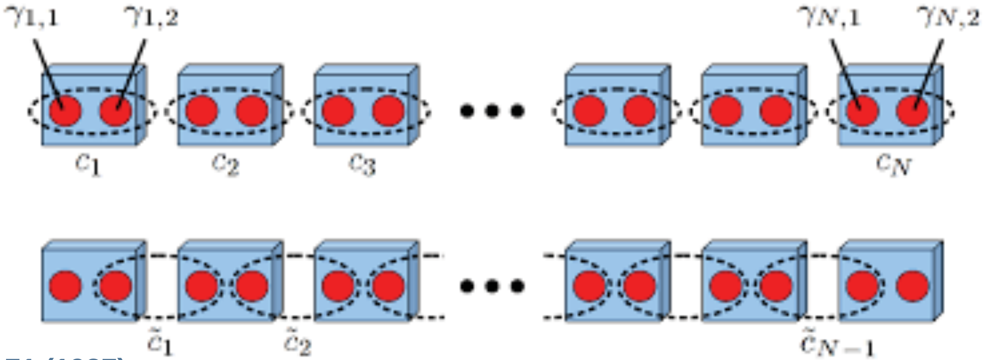
Ettore Majorana

Kitaev proposed in 2000 an atomic chain model where electrons fractionalize into Majorana fermions

Depending on whether they re-bind intra- or inter-atom, unpaired Majorana fermions appear at the chain edges

These edge Majorana fermions are topologically protected & building blocks of *Topological Quantum Computation*

Alexei Kitaev



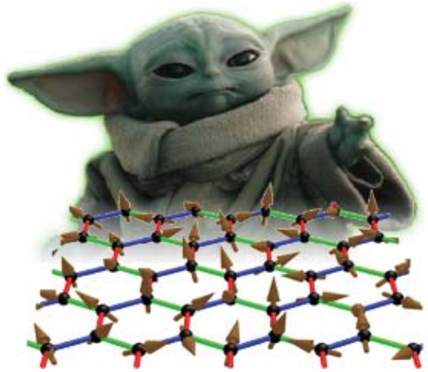
E. Majorana, Nuovo Cimento 14, 171 (1937)

A. Kitaev, Physics Uspekhi 44, 131(2001)

Ad - Ad - Ad FPI PhD grant Ad - Ad - Ad

- **Topic:** theory of 2-dimensional magnets
- **Activities:** modelling, programming & simulation
- **Duration:** 4 years
- **Advisors:** Jaime Ferrer & Amador García-Fuente
- **Place:** Department of Physics, Universidad de Oviedo
- **Gross/net salary:** 1.400 / 1.200 euro-month
- **Other benefits:** social security, exchange visits, etc.
- **Starting date:** december 2023 - february 2024
- **Required education:** physics / quantum chemistry BSc & MSc
- **Contact:** ferrer@uniovi.es

GOBIERNO DE ESPAÑA
MINISTERIO DE CIENCIA E INNOVACIÓN



Conclusions

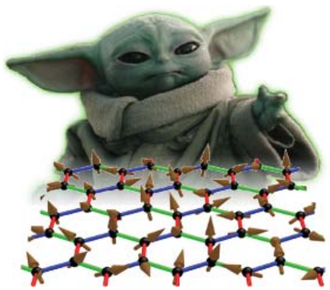
Basic science has endeavored to understand nature in the past

Technology is enabling us to *fabricate* table-top nature

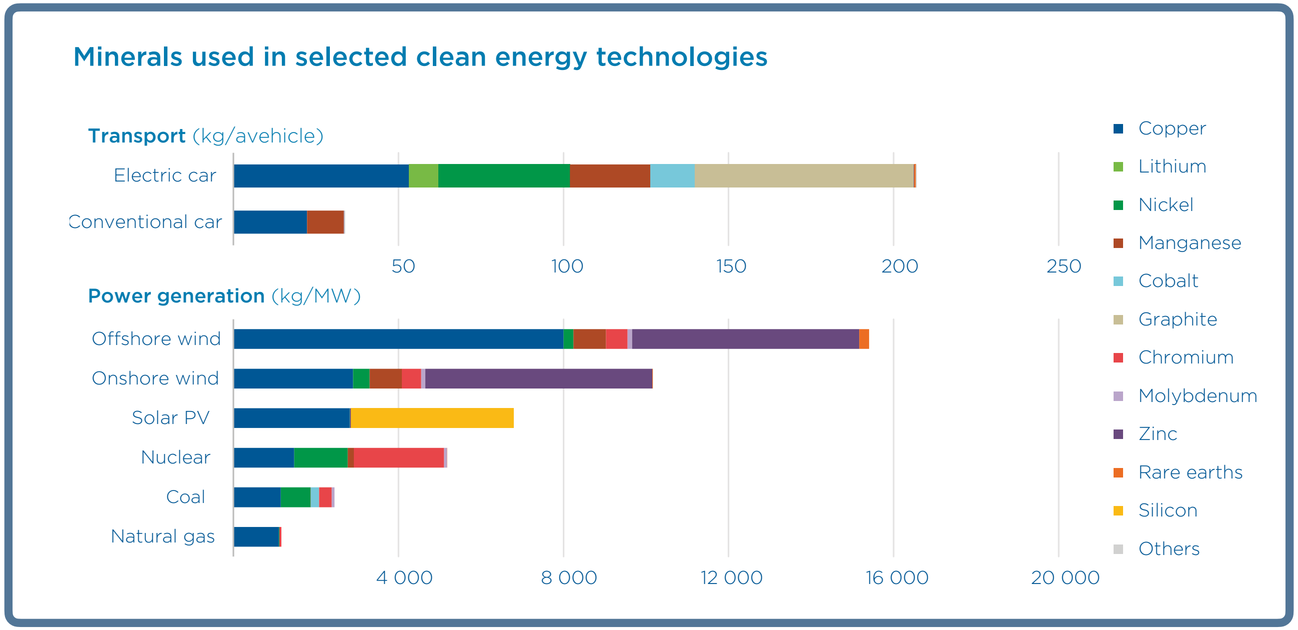
Spin fractionalization occurs in spin-1 chains

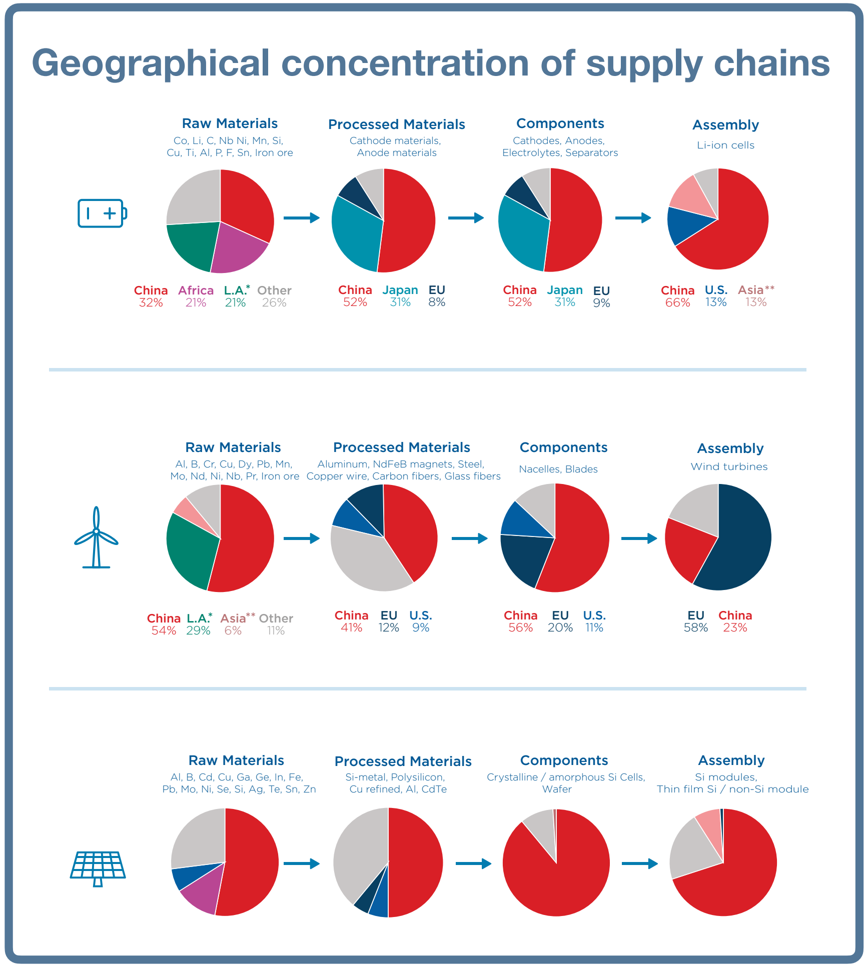
We propose strategies to manipulate spin-qbits in spin-1 chains

We have developed *Grogu*, a tool to master spins

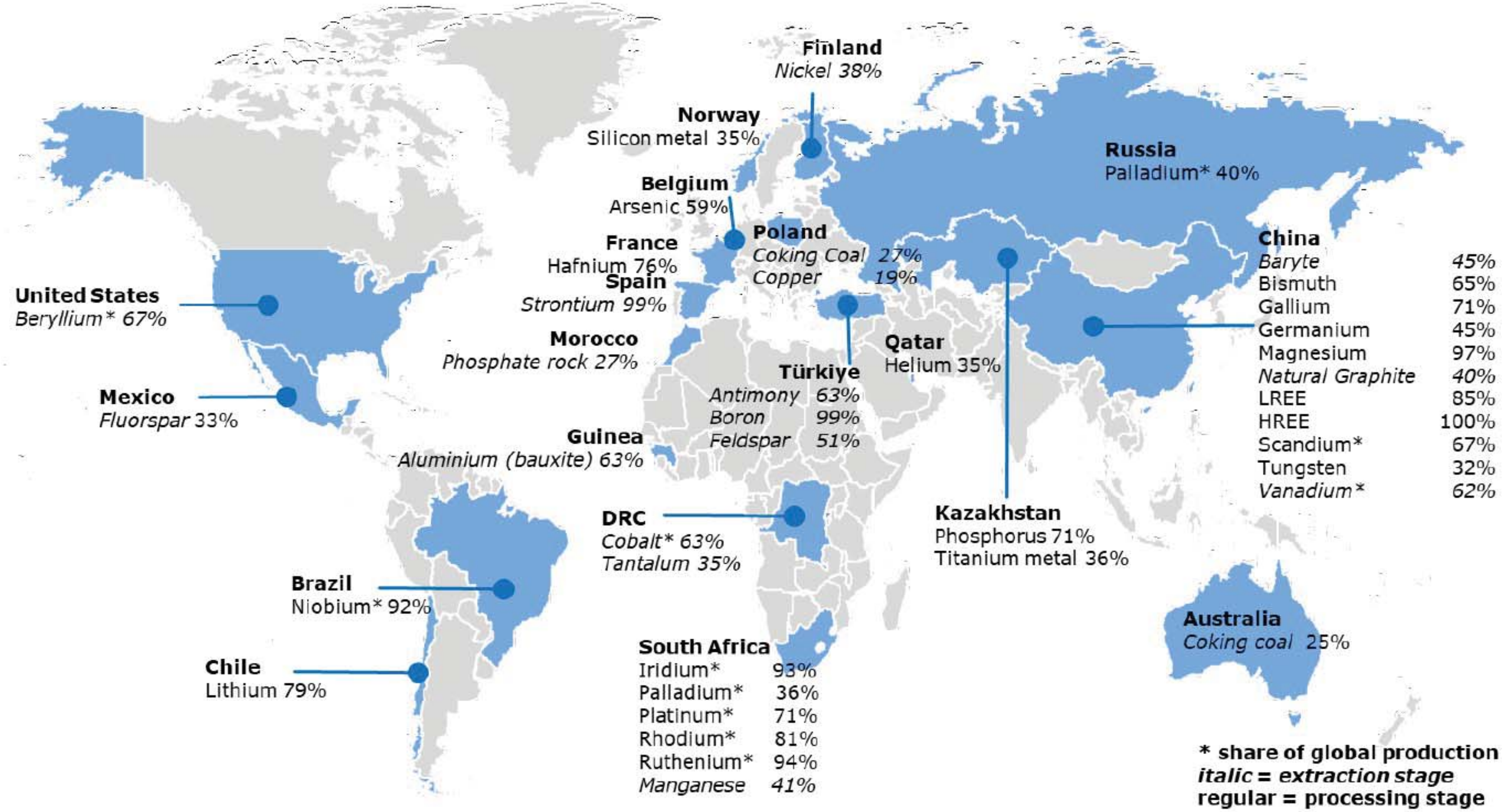


Green Technology Materials & Supply Chains





World map of Critical Raw Materials imports to the EU



Source: European Commission, 2023.