

# CHEM40111/CHEM40121

## Molecular magnetism

### 5 Single-molecule magnets I

The logo of the University of Manchester, featuring the word "MANCHESTER" in white serif font and "1824" in yellow serif font, both on a purple rectangular background.

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# Course Overview

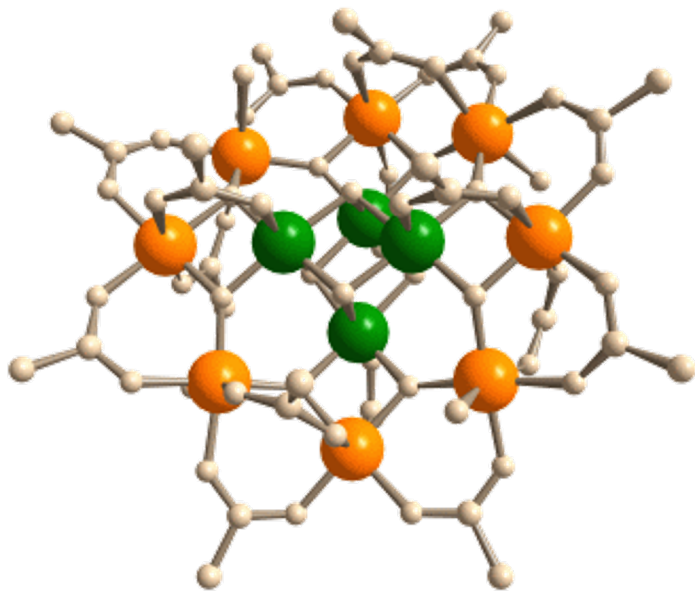
<b>1 Fundamentals</b> <ul style="list-style-type: none"><li>• Motivation</li><li>• Origins of magnetism</li><li>• Bulk magnetism</li></ul>	<b>5 Single-molecule magnets I</b> <ul style="list-style-type: none"><li>• Single-molecule magnets</li><li>• Electrostatic model</li></ul>
<b>2 Quantum mechanics of magnetism</b> <ul style="list-style-type: none"><li>• Zeeman effect</li><li>• Statistical mechanics</li><li>• Magnetisation</li><li>• Magnetic susceptibility</li></ul>	<b>6 Single-molecule magnets II</b> <ul style="list-style-type: none"><li>• Measuring magnetic relaxation</li><li>• Relaxation mechanisms</li><li>• Latest research</li></ul>
<b>3 Magnetic coupling</b> <ul style="list-style-type: none"><li>• Exchange Hamiltonian</li><li>• Experimental measurements</li><li>• Vector coupling</li></ul>	<b>7 Magnetic resonance imaging</b> <ul style="list-style-type: none"><li>• Paramagnetic NMR</li><li>• Magnetic resonance imaging</li><li>• Latest research</li></ul>
<b>4 Magnetic anisotropy</b> <ul style="list-style-type: none"><li>• Zero-field splitting</li><li>• Impact on properties</li><li>• Lanthanides</li><li>• Spin-orbit coupling</li></ul>	<b>8 Quantum information processing</b> <ul style="list-style-type: none"><li>• Quantum information</li><li>• DiVincenzo criteria</li><li>• Latest research</li><li>• <i>Question time</i></li></ul>

# Intended learning outcomes

1. Explain the origin of magnetism arising from electrons in atoms and molecules using formal quantum-mechanical terms
2. Compare and contrast the electronic structure of metal ions in molecules and their magnetic properties, for metals across the periodic table
3. Select and apply appropriate models and methods to calculate molecular magnetic properties such as magnetisation, magnetic susceptibility and paramagnetic NMR shift
4. Deconstruct topical examples of molecular magnetism including single-molecule magnetism, molecular quantum information processing and MRI contrast agents

# Molecular magnets

- What about molecules? Can control properties with chemistry!
  - If we could store information in a molecule, what would the density be?



‘Mn<sub>12</sub>’

~ 2 nanometres square

= 4 nm<sup>2</sup> bit<sup>-1</sup>

= 6.2 × 10<sup>-15</sup> in<sup>2</sup> bit<sup>-1</sup>

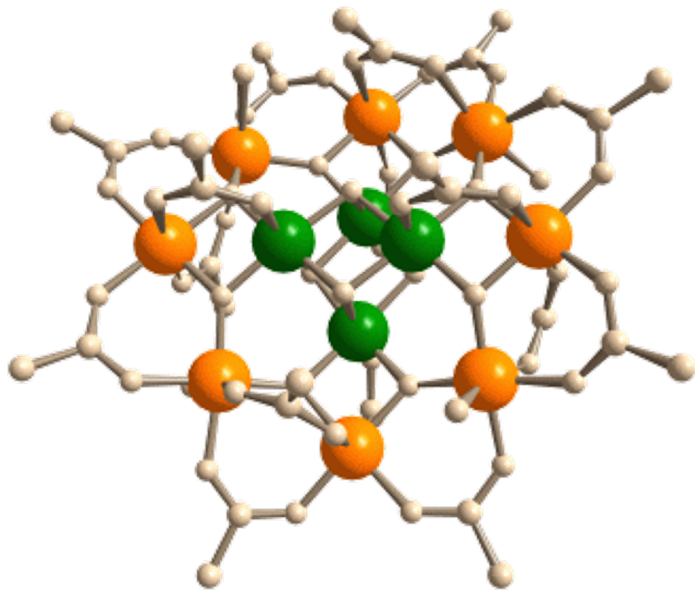
~ **20,120 GB in<sup>-2</sup>**

- *100 times better than current tech!*  
(~ 200 GB in<sup>-2</sup>)
- *Data centres 100 times smaller?*

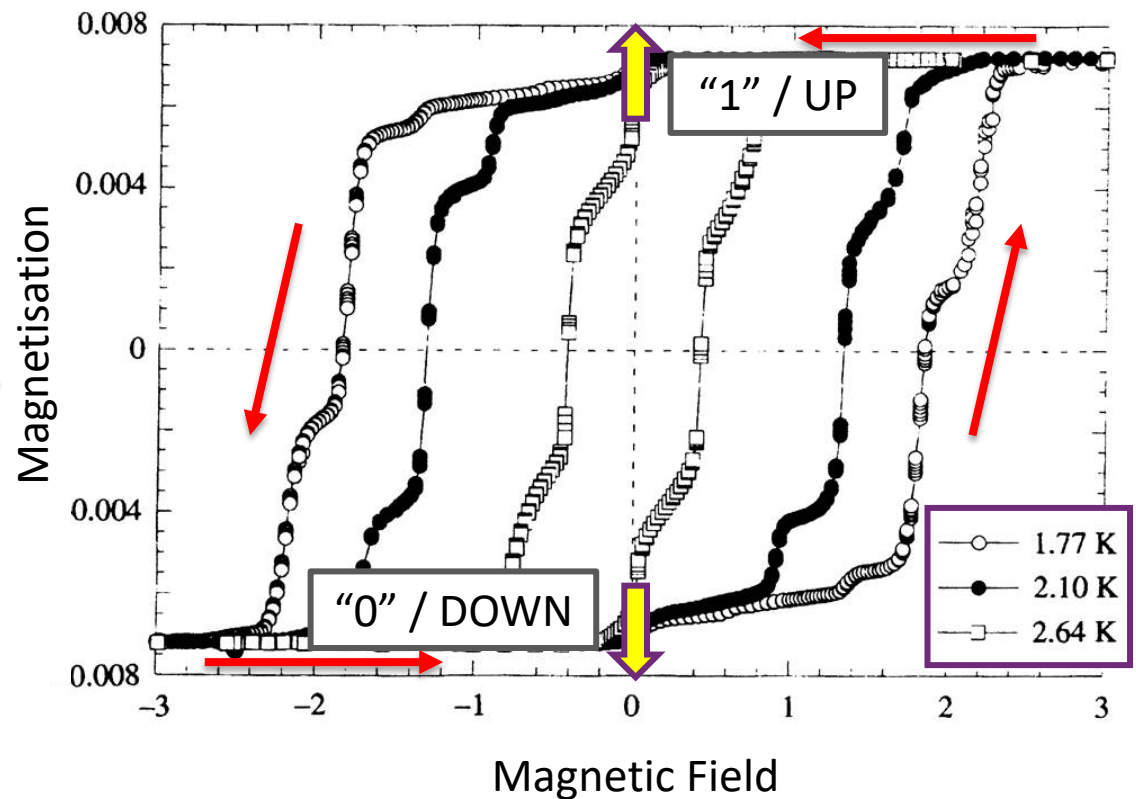


# Molecular magnets

- Definition:
  - Molecules that show magnetic memory effects

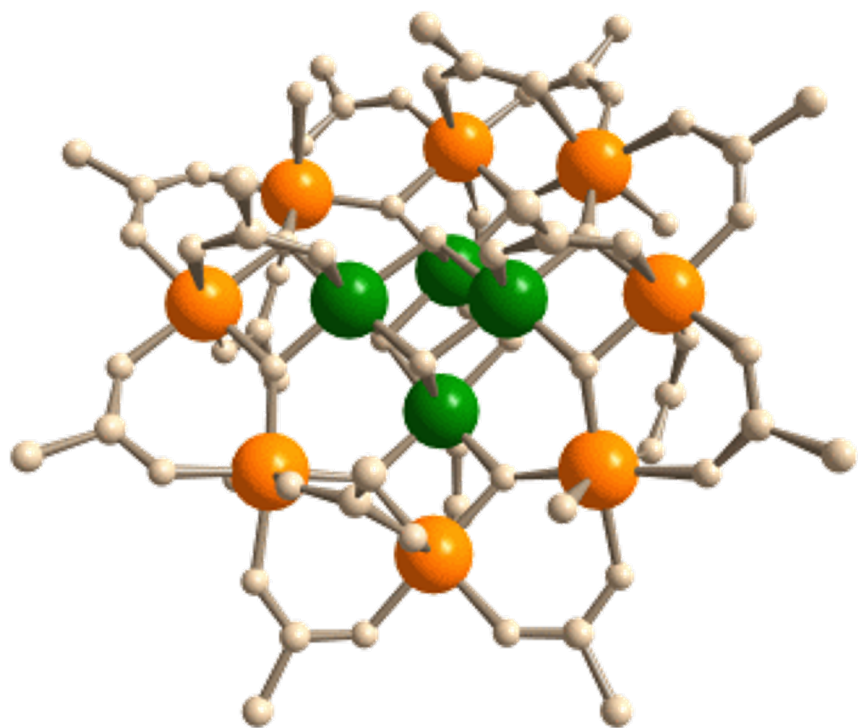


‘Mn<sub>12</sub>’



# How does it work?

- Requirements:
  - **Large spin ground state**
  - Uniaxial magnetic anisotropy (axial zero-field splitting)



‘Mn<sub>12</sub>Ac’

- Magnetic exchange interactions



Mn<sup>III</sup>

$$S = 4/2$$



Mn<sup>IV</sup>

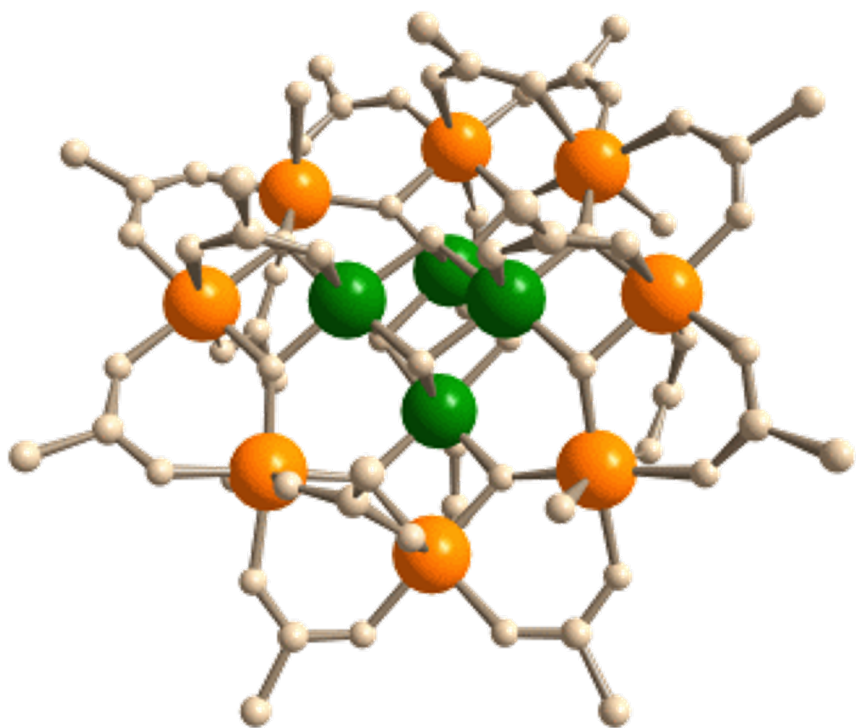
$$S = 3/2$$

$$S = 8 \times \text{orange circle} - 4 \times \text{green circle}$$

$$S = 8 \times 4/2 - 4 \times 3/2 = 20/2 = 10$$

# How does it work?

- Requirements:
  - Large spin ground state
  - **Uniaxial magnetic anisotropy (axial zero-field splitting)**

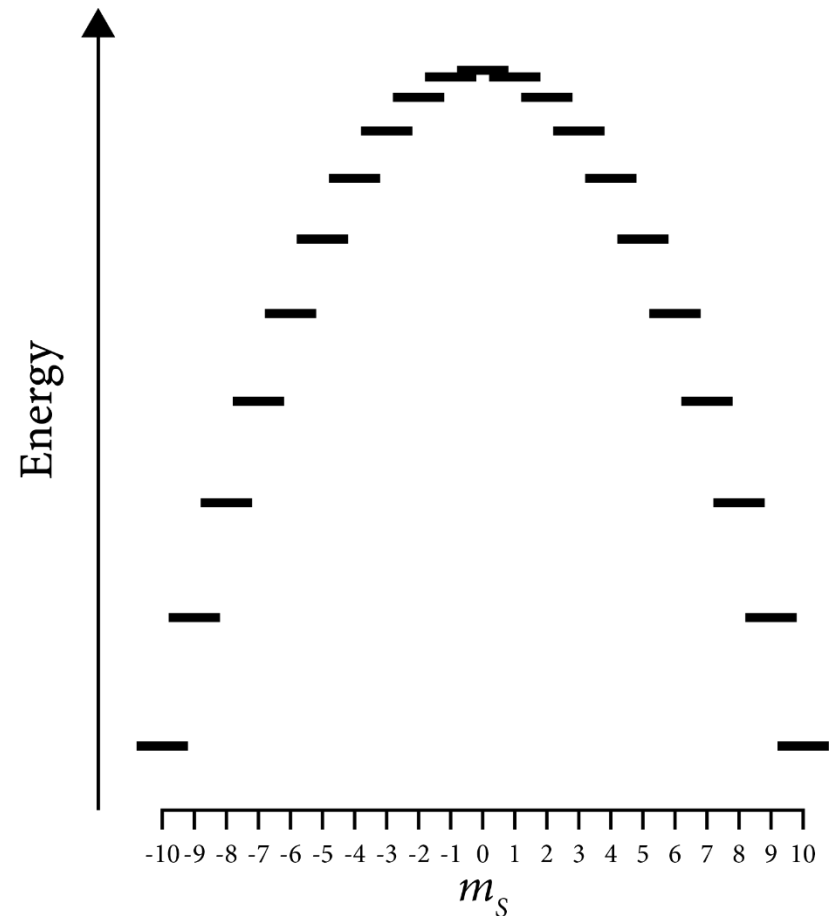
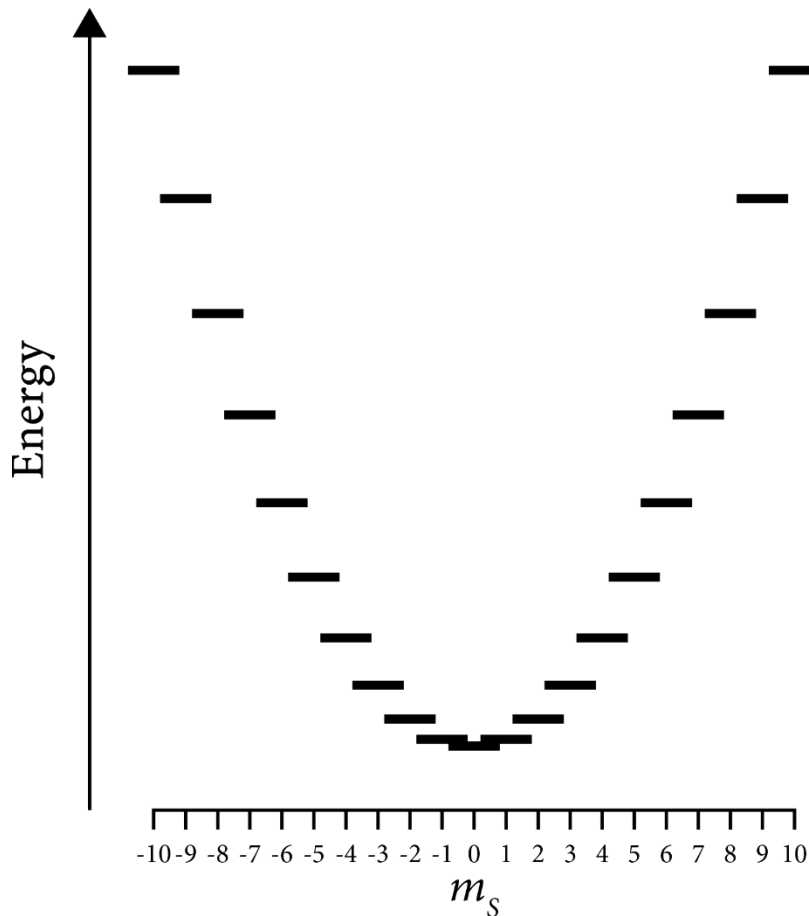


**‘Mn<sub>12</sub>Ac’**

- ‘Mn<sub>12</sub>Ac’ has D<sub>2d</sub> symmetry, giving it an S<sub>4</sub> axis
- There is ZFS of the  $S = 10$  state

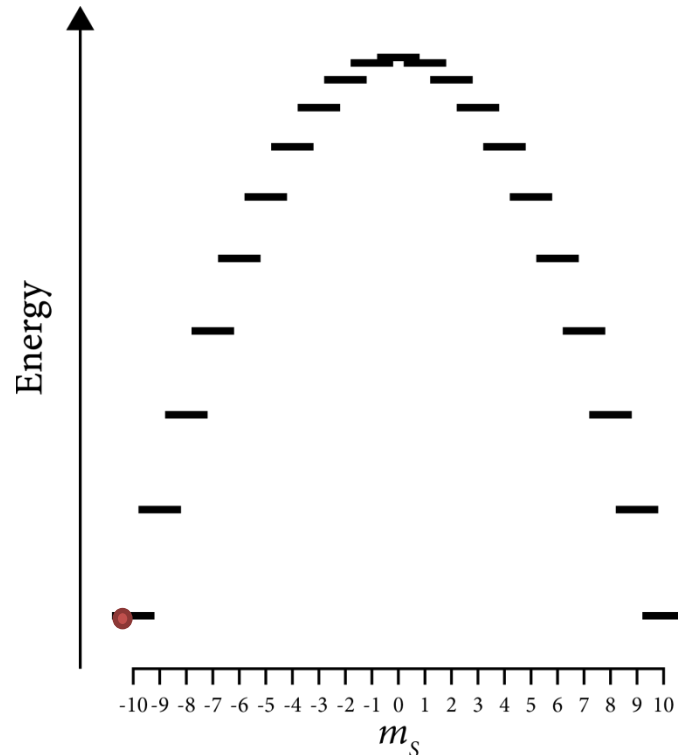
# Zero-field splitting

- $S = 10$  ground state split in the absence of magnetic field
- Two options if axially symmetric:
  - $m_S = 0$  state is most stable
  - $m_S = \pm 10$  states most stable



# Energy barrier to relaxation

- A molecule can be prepared in either the  $m_S = +10$  or  $m_S = -10$  state by cooling in a magnetic field
- The molecule must jump between all the intermediate states to get to the other side – this is the energy barrier to magnetic relaxation

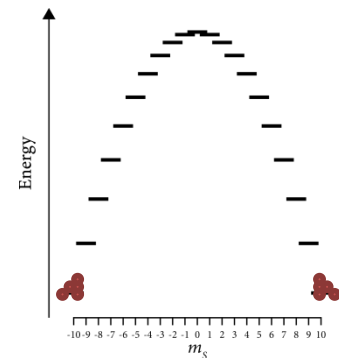
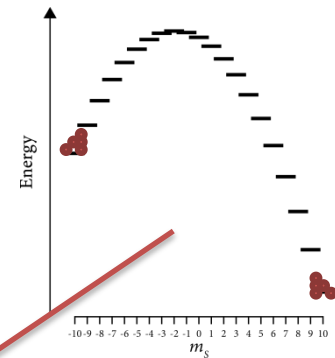
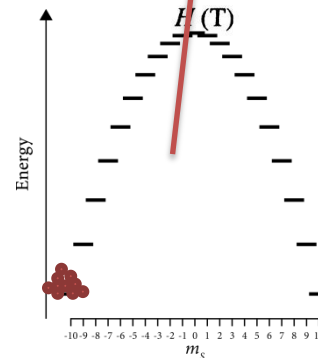
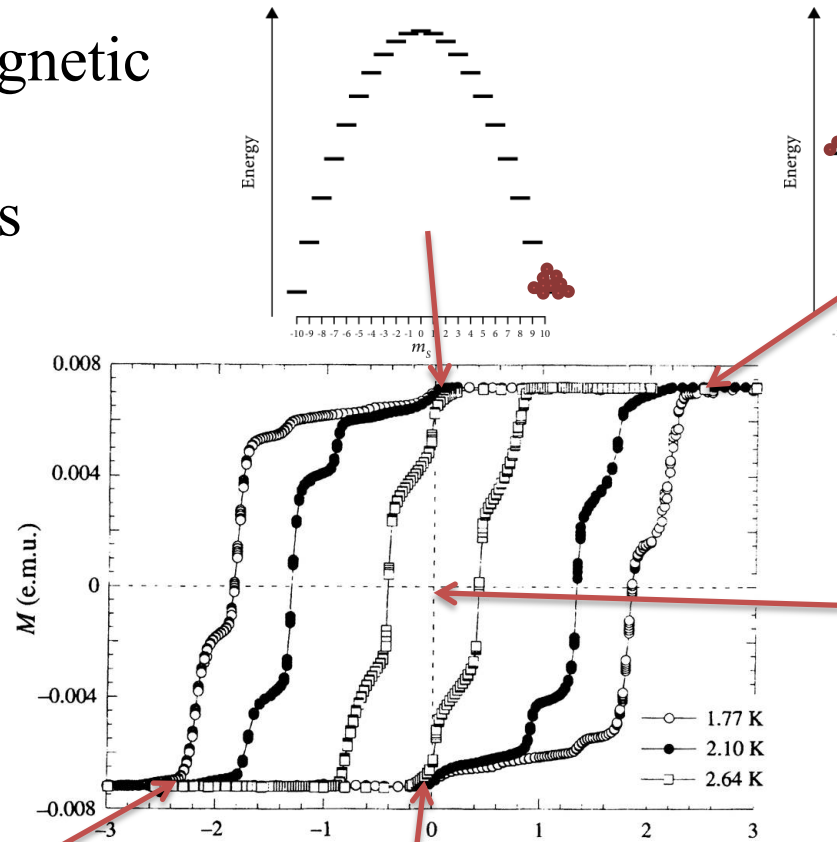
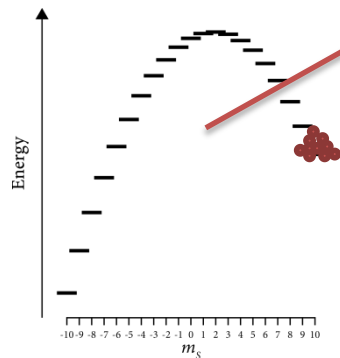


# Hysteresis

- Cooling in a magnetic field can cause a population bias

$$p_i = \frac{1}{Z} \exp \left[ \frac{-E_i}{k_B T} \right]$$

$$Z = \sum_{i=1}^{\dim} \exp \left[ \frac{-E_i}{k_B T} \right]$$



# Relaxation rates

- The characteristic rate for molecules to jump over this barrier is called the *relaxation rate*
- The energy available to a single molecule is determined by the thermal energy (temperature)
- The relaxation rate is therefore dependent on temperature, according to the Arrhenius Law

$$\tau^{-1} = \tau_0^{-1} \exp \left[ \frac{-U_{eff}}{k_B T} \right]$$

- $\text{Mn}_{12}\text{Ac}$   $U_{eff} = 42 \text{ cm}^{-1}$

Height of energy  
barrier

# Recipe for SMMs?

- According to the Arrhenius Law, relaxation rates get slower as the energy barrier  $U_{eff}$  gets bigger:

$$\tau^{-1} = \tau_0^{-1} \exp \left[ \frac{-U_{eff}}{k_B T} \right]$$

- We've seen that  $U_{eff}$  comes from ZFS, for which the Hamiltonian is:

$$\hat{H} = D \hat{S}_z^2$$

- Doing some maths, you can show that:

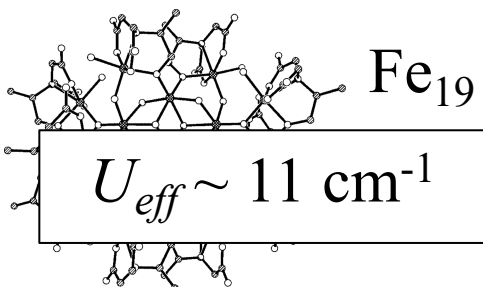
$$U_{eff} = |D| S^2$$

- $U_{eff}$  scales as  $S^2$  so making  $S$  big might be a good idea!



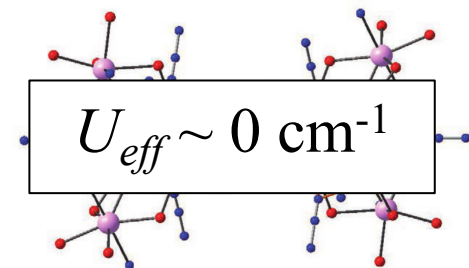
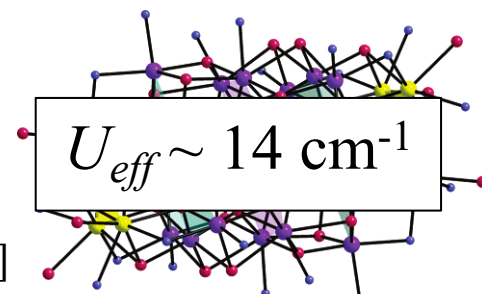
# Brief history of SMMs

- Many HUGE high-spin clusters made:

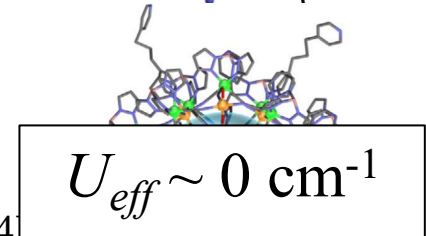


$\text{Fe}_{19} \rightarrow S = 33/2$ , Powell and Heath<sup>[1]</sup>

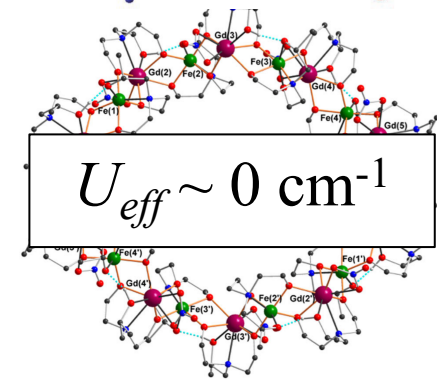
$\text{Mn}_{25} \rightarrow S = 51/2$ , Christou<sup>[2]</sup>



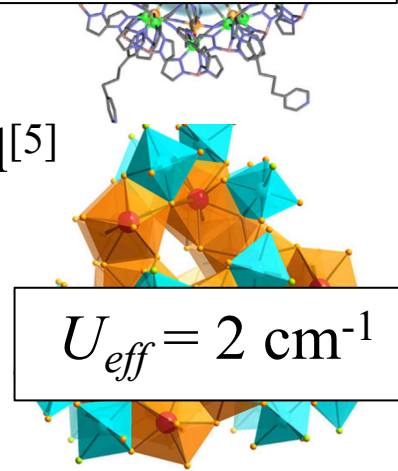
$\text{Mn}_{19} \rightarrow S = 83/2$ , Powell<sup>[3]</sup>



$\text{Fe}_{42} \rightarrow S = 45$ , Sato<sup>[4]</sup>



$\text{Fe}_{10}\text{Gd}_{10} \rightarrow S = 60$ , Schnack and Powell<sup>[5]</sup>

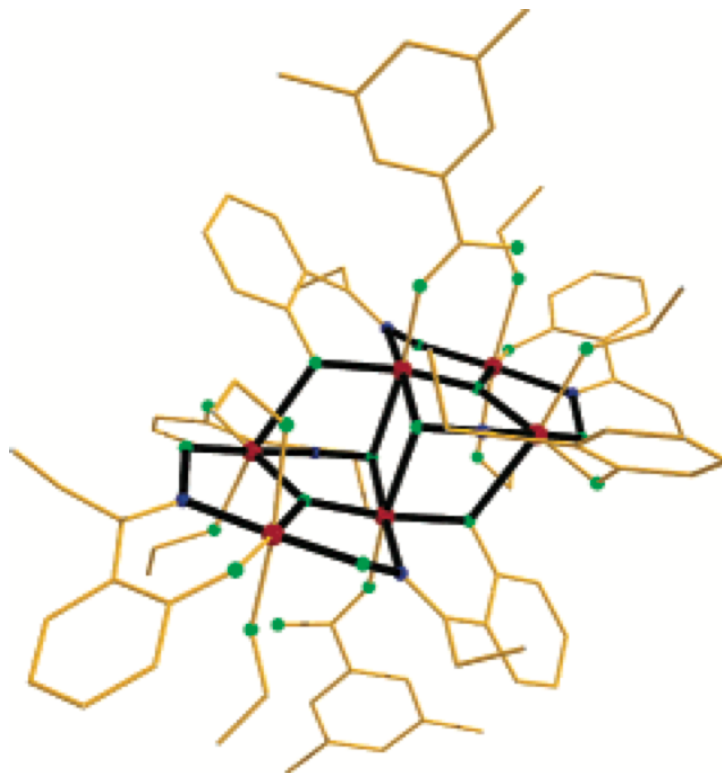


$\text{Ni}_{21}\text{Gd}_{20} \rightarrow S = 91$   
Engelhardt, Winpenny and Zheng<sup>[6]</sup>

[1] Heath *et al.*, *J. Chem. Soc. Dalton Trans.*, 2000, 1835; [2] Christou *et al.*, *J. Am. Chem. Soc.*, 2004, **126**, 4766; [3] Powell *et al.*, *Angew. Chem. Int. Ed.*, 2006, **45**, 4926; [4] Sato *et al.*, *Nature Commun.*, 2015, **6**, 5955; [5] Powell *et al.*, *npj Quant. Mater.*, 2018, **3**, 10; [6] Zheng *et al.*, *Nature Commun.*, 2018, **9**, 2107.

# Brief history of SMMs

- So what was the biggest  $U_{eff}$  for a transition metal SMM?



- $\text{Mn}_6$  by Brechin<sup>[1]</sup> has  $S = 12$ ,  $D = -0.43$  and  $U_{eff} = 60 \text{ cm}^{-1}$   
(so slightly better than  $U_{eff} = 42 \text{ cm}^{-1}$  for  $\text{Mn}_{12}\text{Ac}$ )

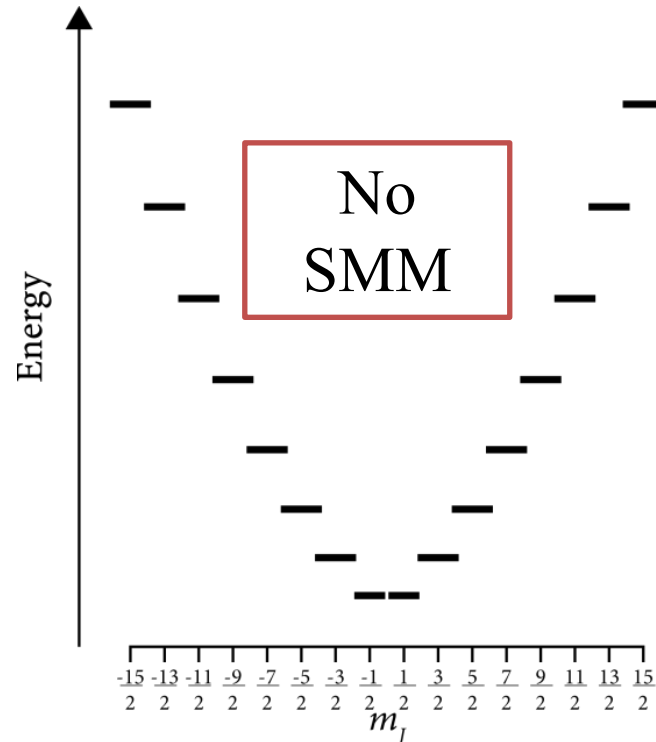
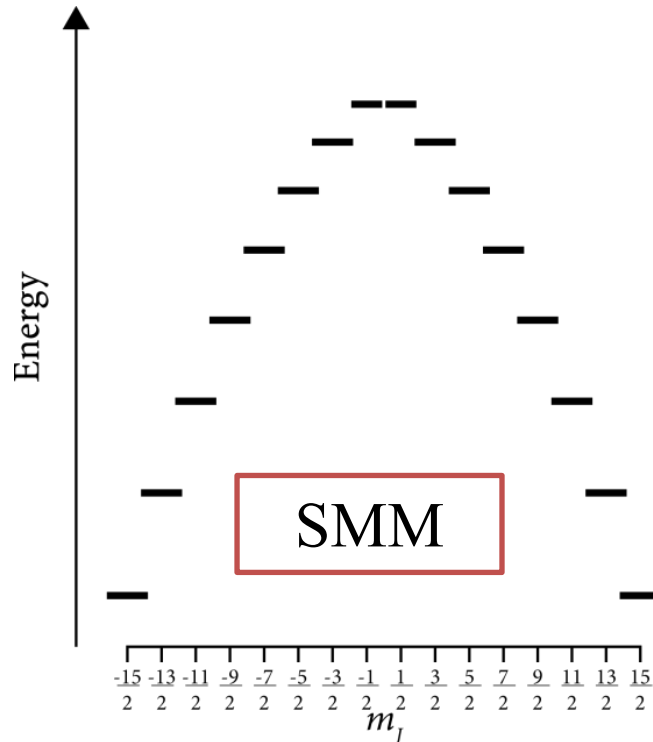
[1] Milios *et al.*, *J. Am. Chem. Soc.*, 2007, **129**, 2754.

# Lanthanide SMMs

- So instead of maximising  $S$ , what about maximising  $D$ ?
- $D$  is the axial magnetic anisotropy
  - Recall that this comes from the *orbital angular momentum*
  - Thus, we should use lanthanides with unquenched orbital angular momentum
- The requirements for lanthanide SMMs become:
  - Large spin ( $S$ )  $\Rightarrow$  ***Large total angular momentum ( $J$ )***
  - Axial zero-field splitting  $\Rightarrow$  ***axial crystal field splitting***

# Lanthanide SMMs

- The magnetic anisotropy of the lanthanides is determined by the crystal field
- Crystal field states provide the barrier to magnetic relaxation and result in SMM behaviour
  - Must have largest  $m_J$  as ground state



# Lanthanide SMMs

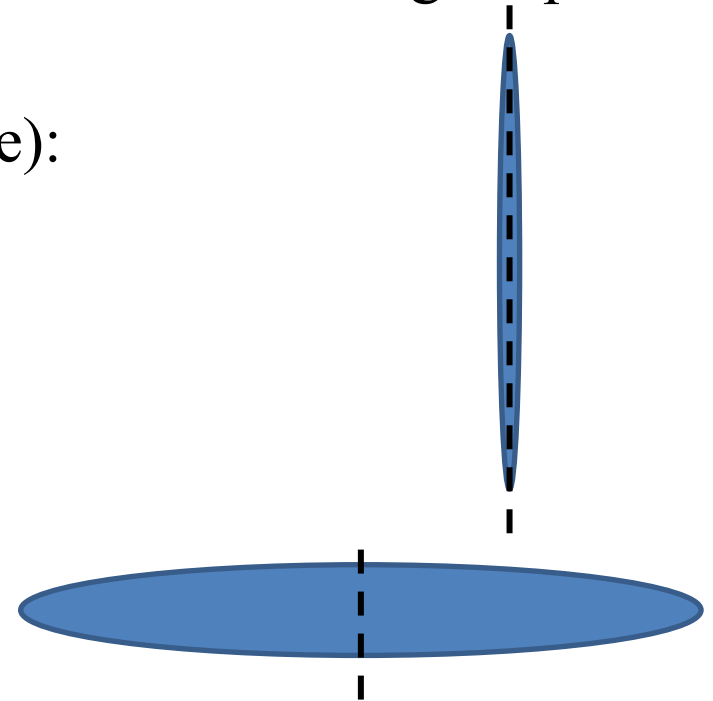
- Two questions:
  - If our molecule is low symmetry, how do we know where the special magnetic axis is?
  - How can we design molecules to be better SMMs?
- There is no single answer to this, open research topic
- One idea is to use classical electrostatics...

# Reminder about electrostatics

- Remember Coulomb's law:
  - Like charges repel each other
  - Unlike charges attract each other

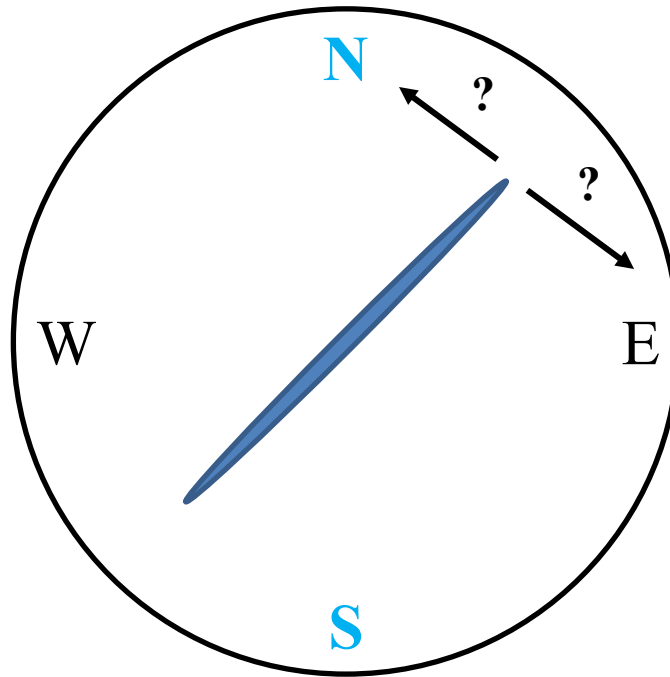
$$F \propto \frac{q_1 q_2}{r^2}$$

- Instead of point charges, let's consider the two limiting shapes with axial symmetry:
  - Long and thin, needle-like (prolate):
  - Flat and round, disk-like (oblate):
  - Both have a  $C_\infty$  axis!



# Reminder about electrostatics

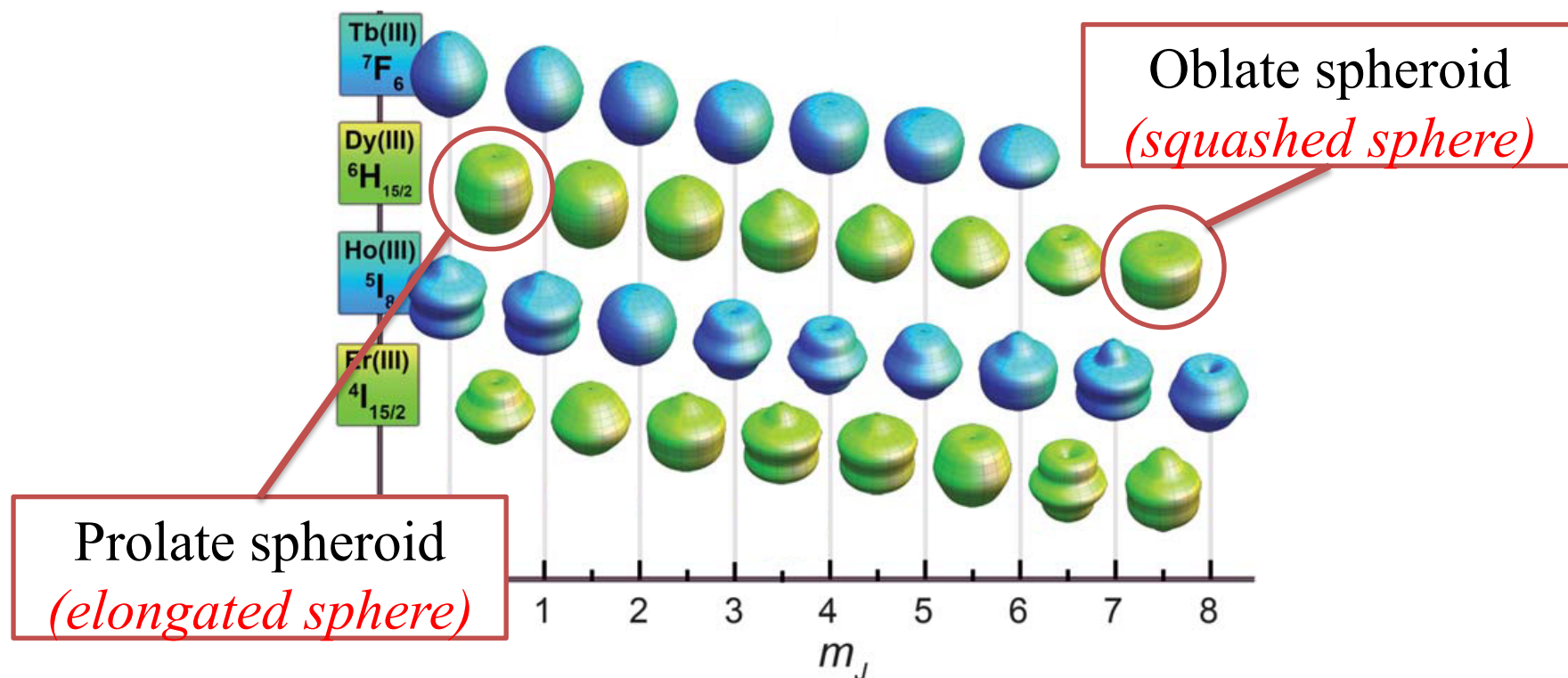
- Imagine a two dimensional compass, where the needle is negatively charged and the North and South poles have negative point charges at them.



- Which way does the needle want point?

# Electrostatic model

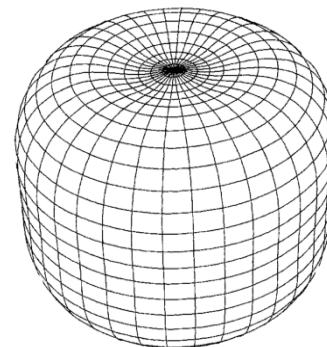
- A free ion has spherical symmetry, but once in a molecule, the  $m_J$  states have *aspherical* electron density distributions.
- Note that all these shapes have a  $C_\infty$  axis! This is called the principal axis, and is the same as the projection axis of  $m_J$ .





# Electrostatic model

- Question 1: how do we know where the special magnetic axis is?
- Most Dy(III) complexes have a crystal field which gives the  $m_J = \pm 15/2$  ground state, hence many Dy(III) complexes are SMMs
  - There is no clear answer why this is the case

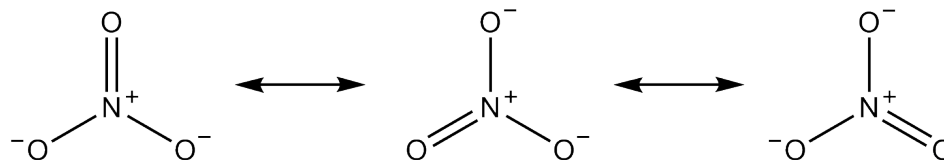


$$\rho_{\pm\frac{15}{2}}$$

- If we make this assumption, can we determine where the magnetic axis is?

# Electrostatic model

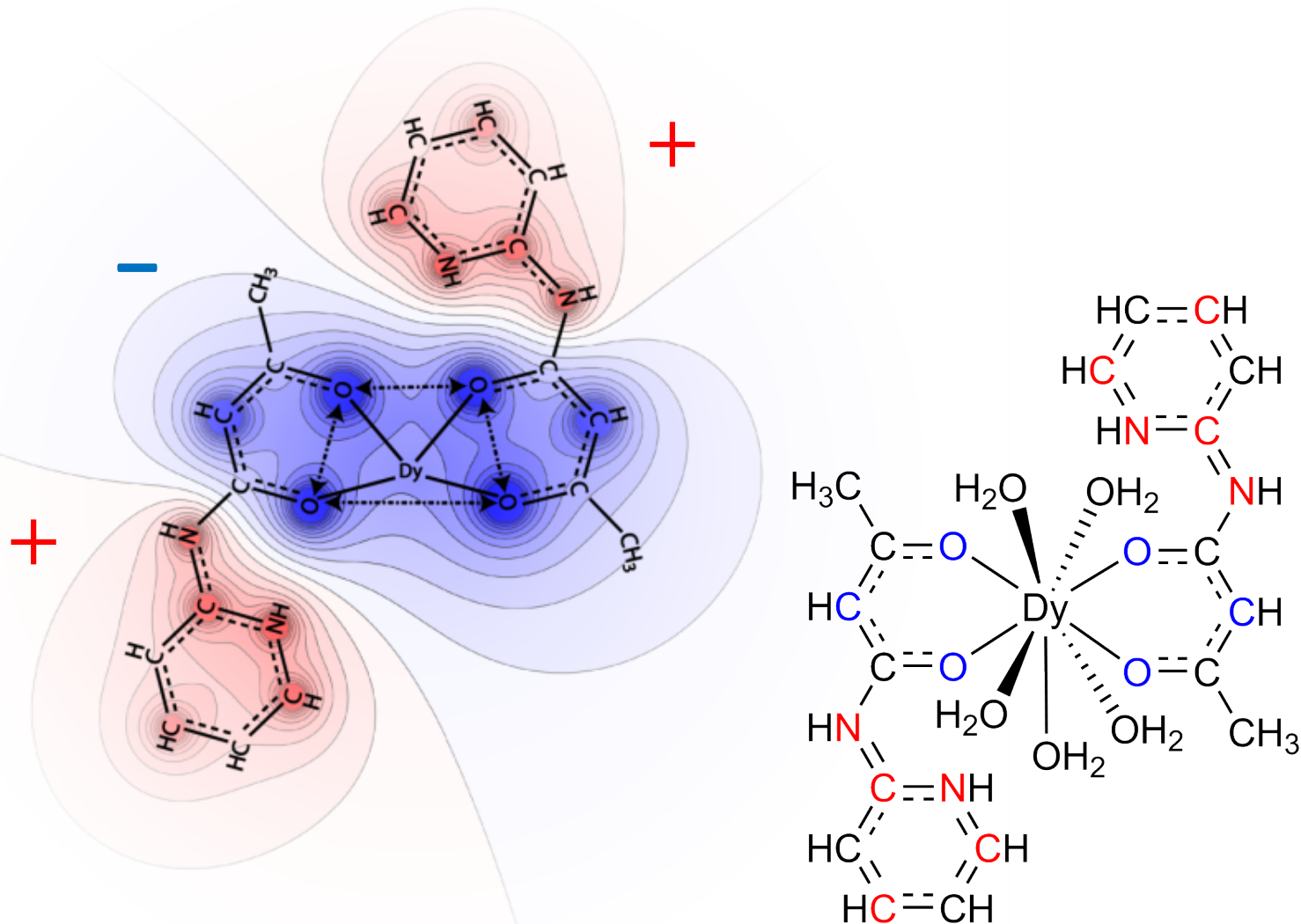
- Let's use electrostatics to see which direction this electron density wants to point
- How do we determine the electrostatic potential of our molecular environment?
  - Let's draw formal charges on our ligands!



- What are the charges for the resonance hybrid?

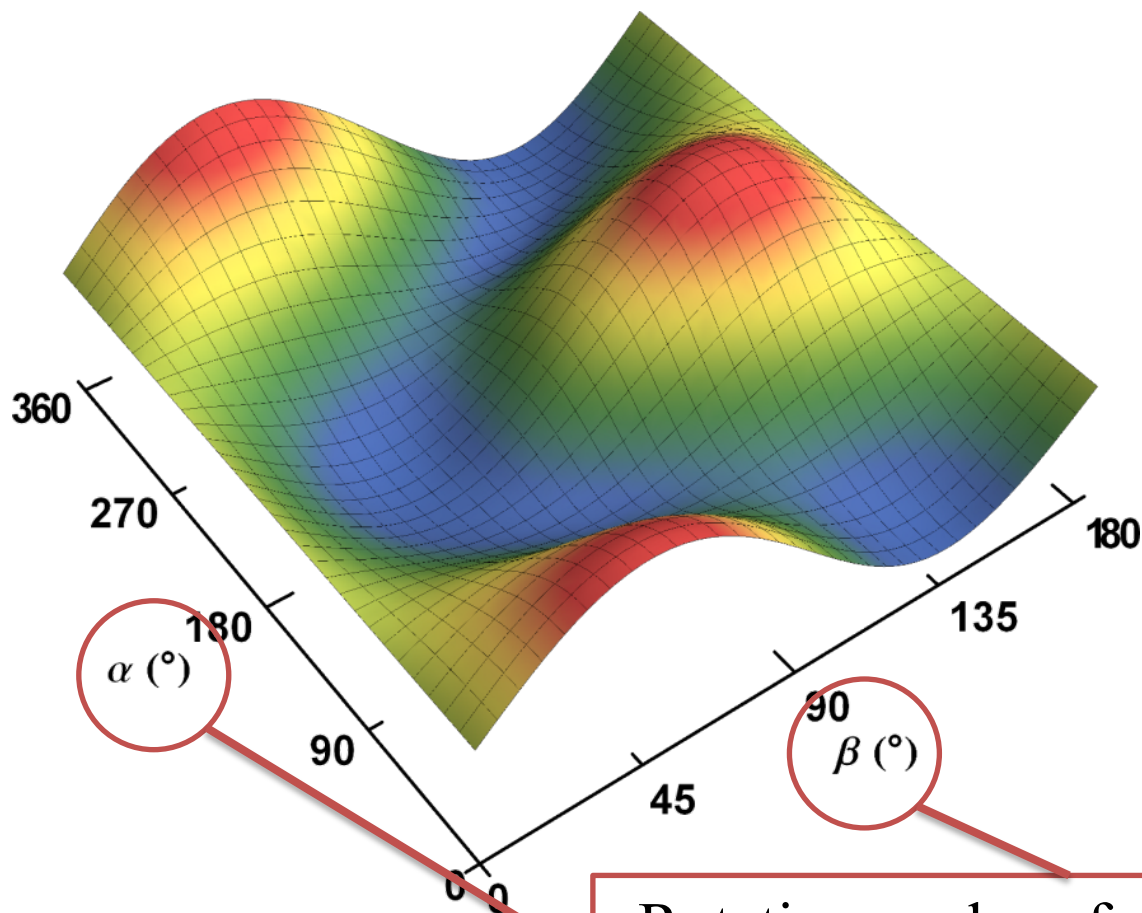
# Electrostatic model

- Superimpose partial point charges on X-Ray crystal structure



# Electrostatic model

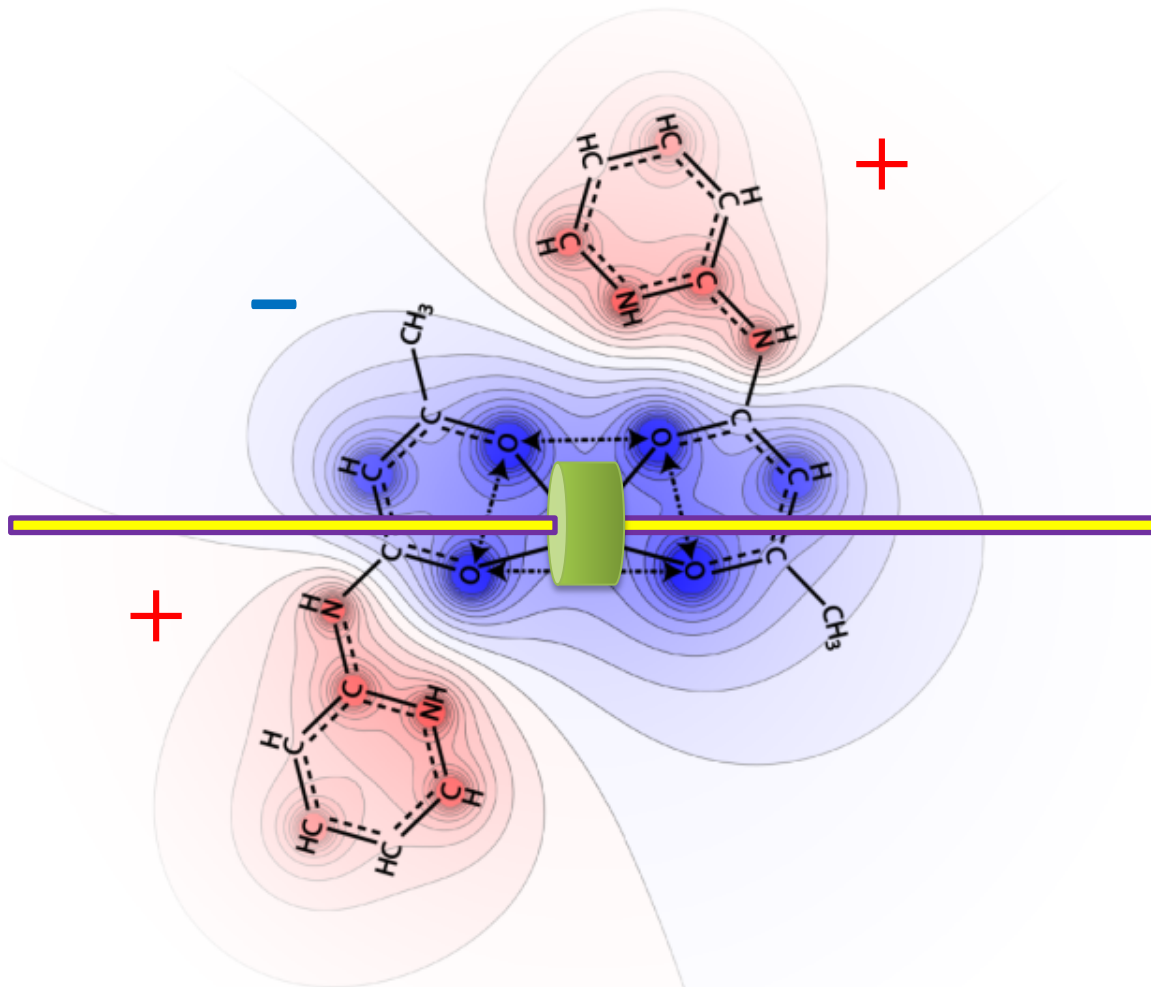
- Rotate the oblate density to find the minimum energy



Rotation angles of oblate electron density with respect to ligands

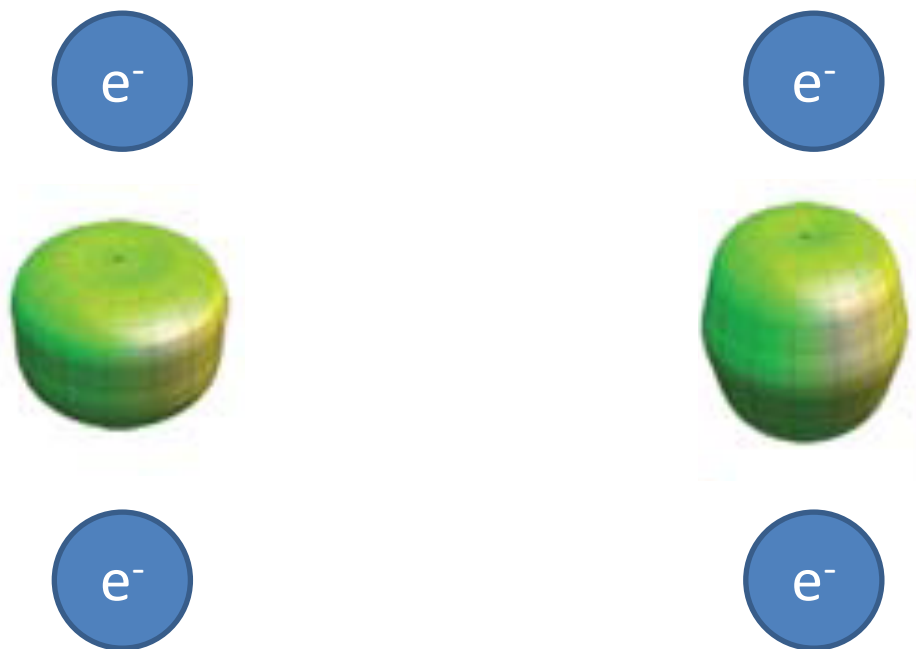
# Electrostatic model

- Rotate the oblate density to find the minimum energy



# Electrostatic model

- Question 2: How can we design better SMMs?
- For Dy(III), *stabilise*  $m_J = \pm 15/2$  and *destabilise*  $m_J = \pm 1/2$ 
  - What charge distribution would accomplish this?



# Problem set:

1. Consider a trigonal planar complex  $[\text{DyCl}_3]$ :
  - a) Sketch a structural diagram of the complex annotating all the proper rotation axes and reflection planes.
  - b) Following the electrostatic model, what would be the ground  $m_J$  state? Explain your answer.
  - c) Draw an energy level diagram (energy vs.  $m_J$ ) showing all  $m_J$  states and their relative energies.
  - d) Would this molecule be a SMM? Explain why or why not.