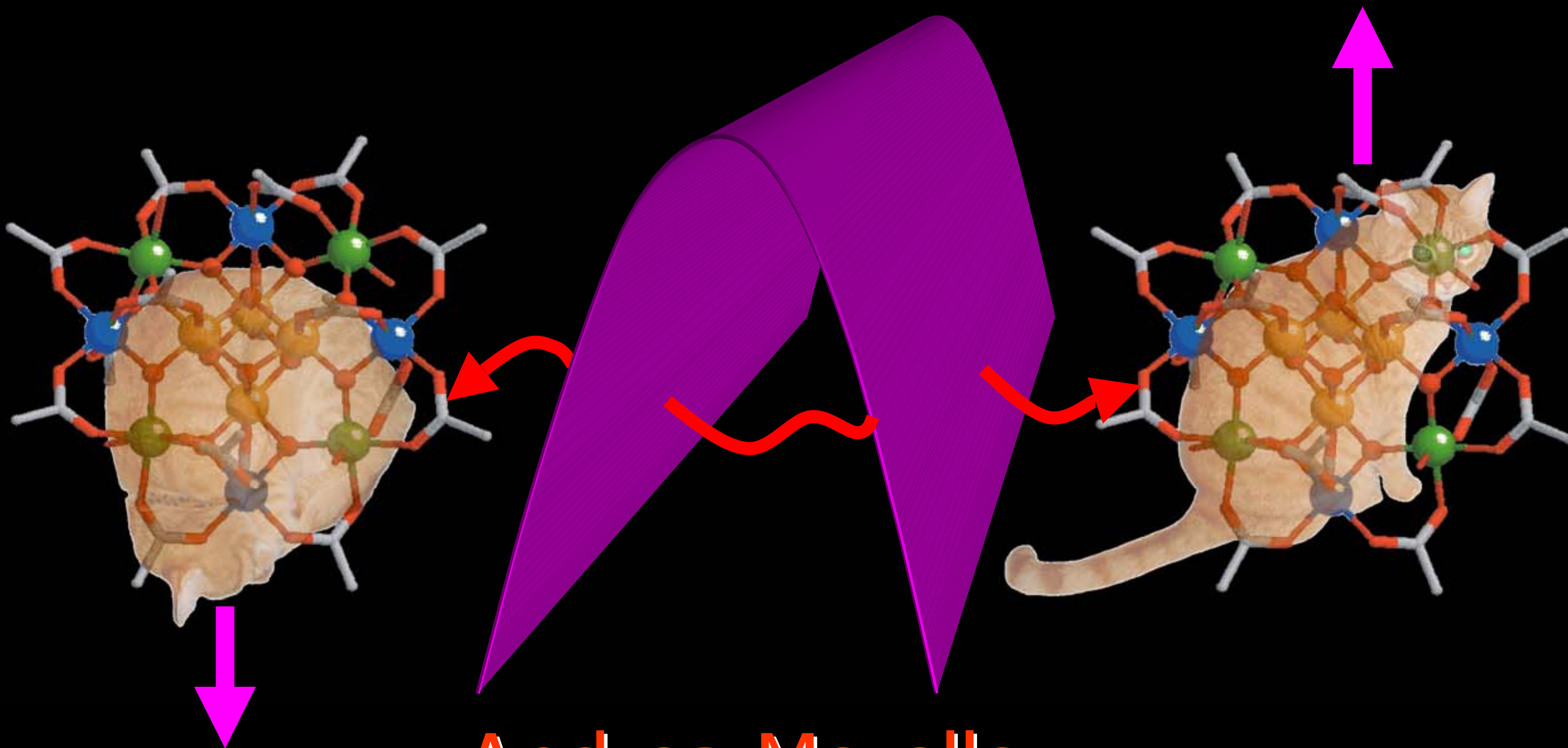
Nuclear spin dynamics in quantum regime of a single-molecule magnet



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Kamerlingh Onnes Laboratory

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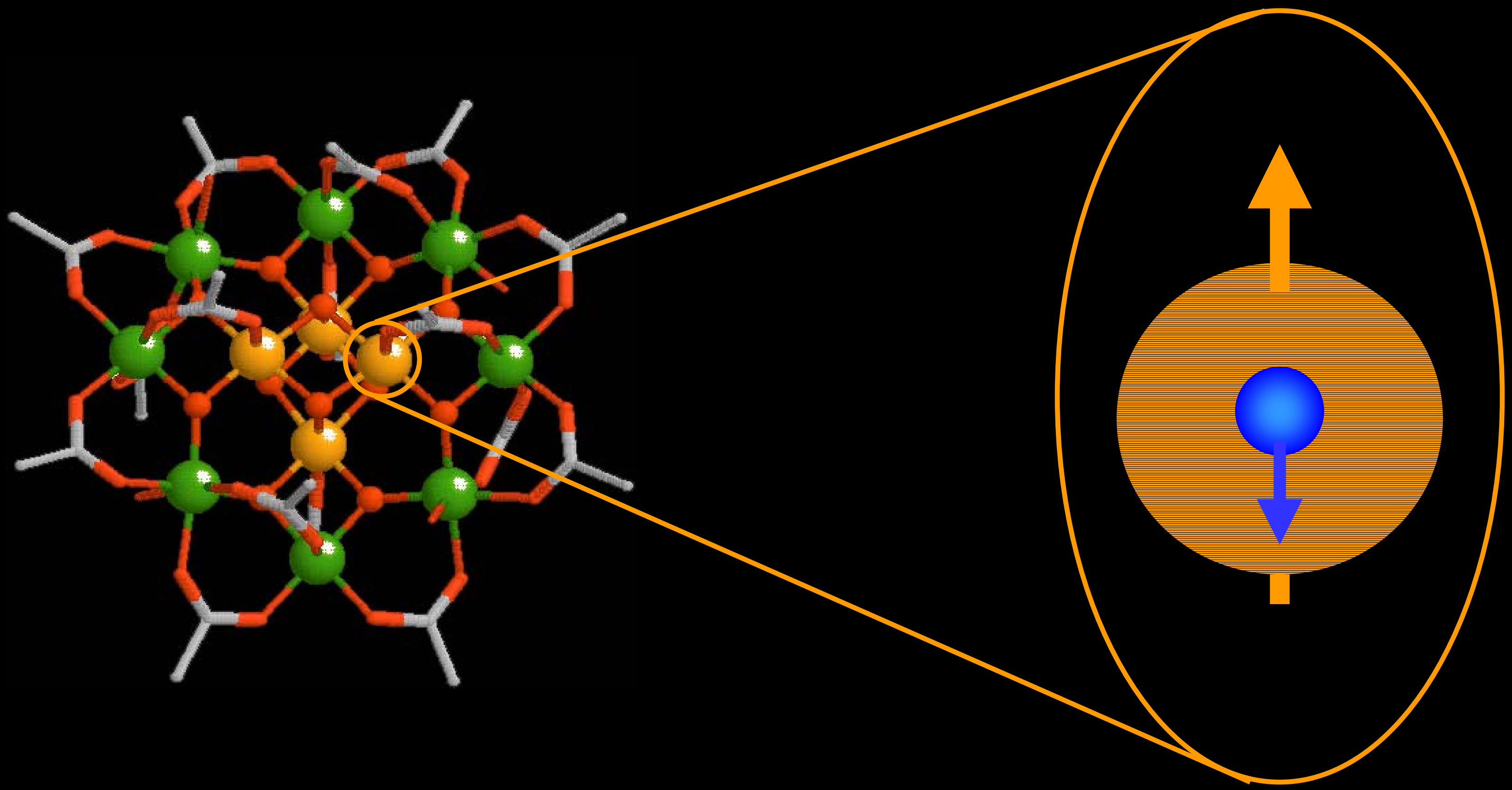
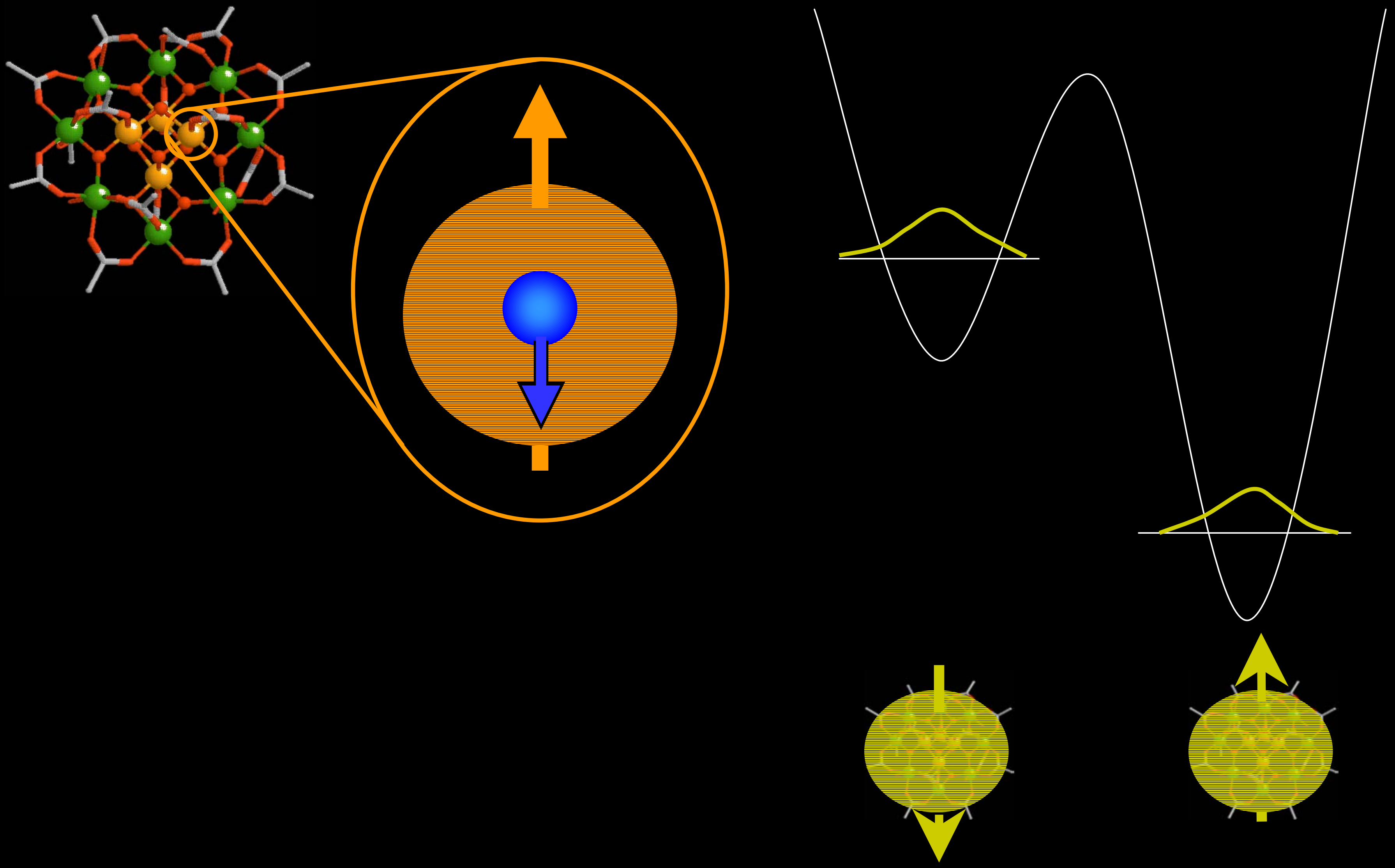
Nuclear spins in SMMs

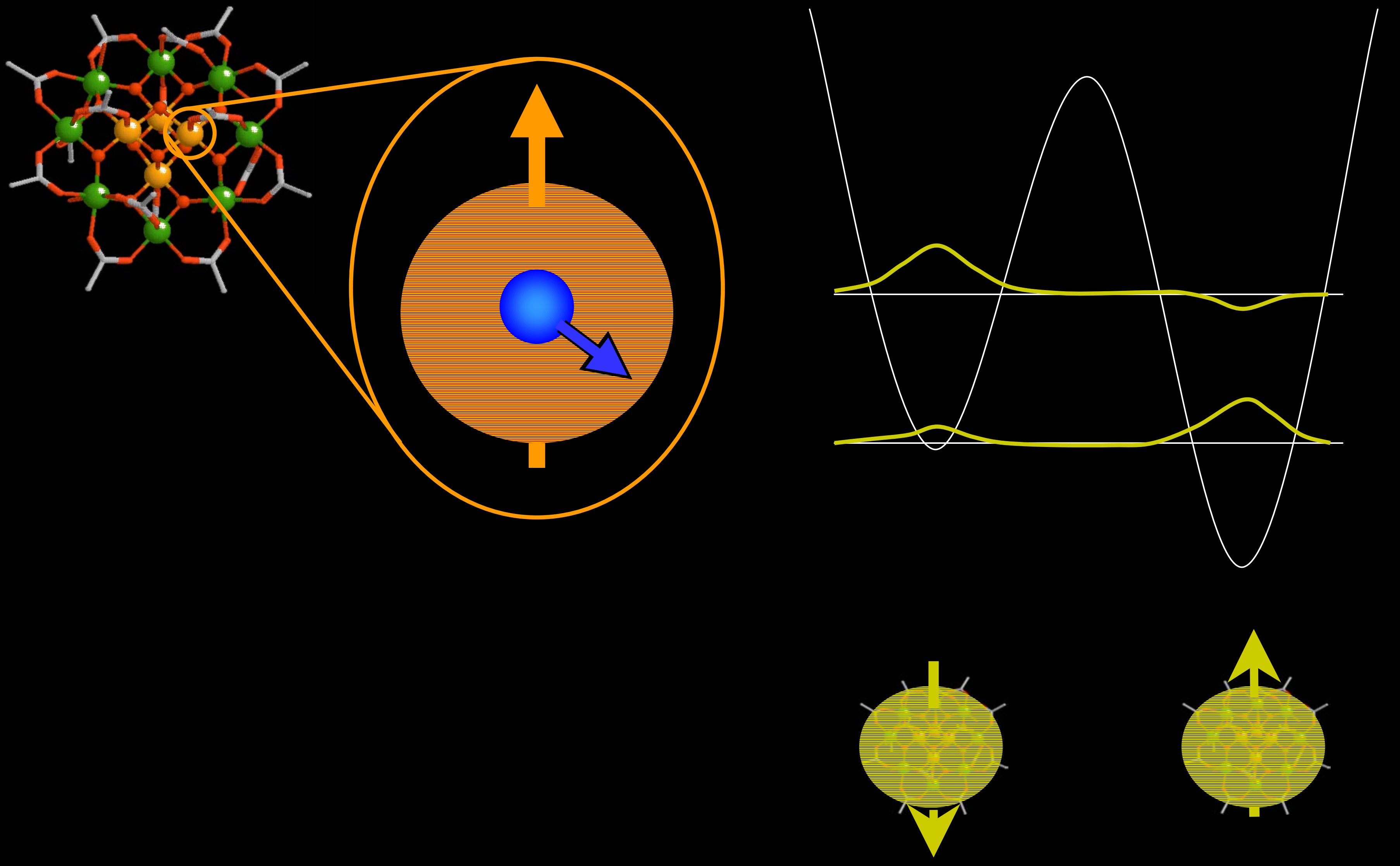


Intrinsic source of decoherence

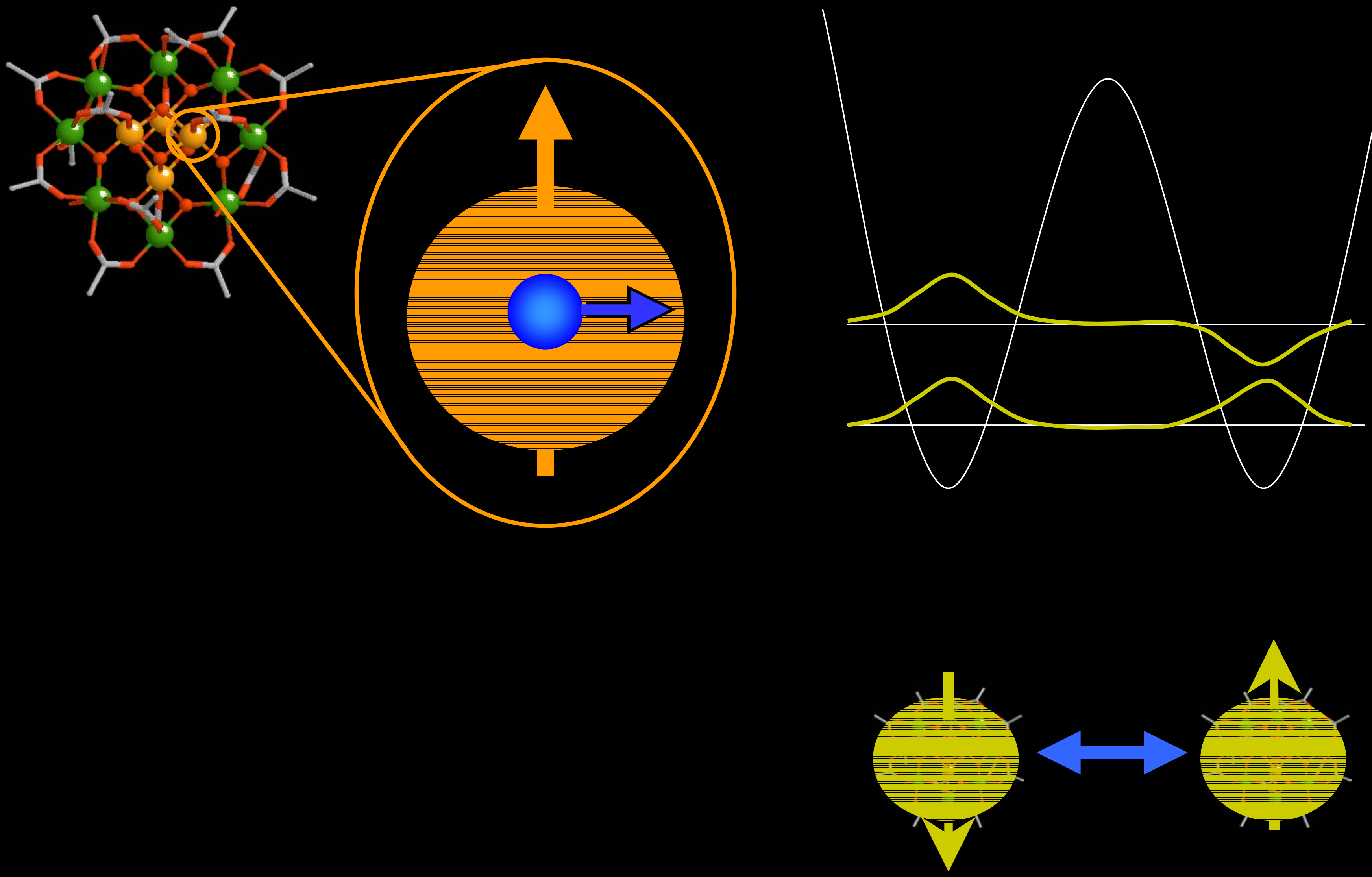
Nuclear bias



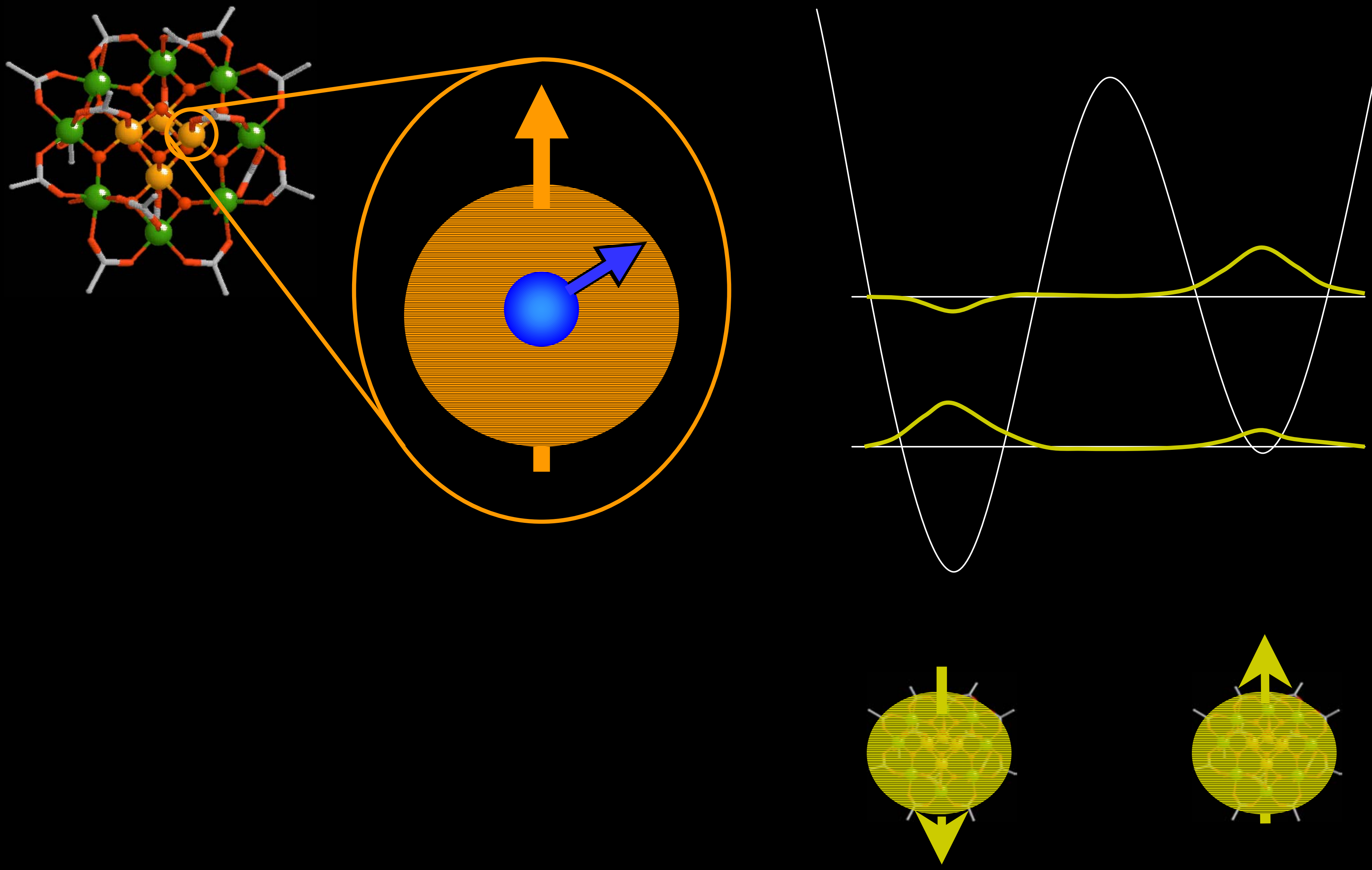
Nuclear bias



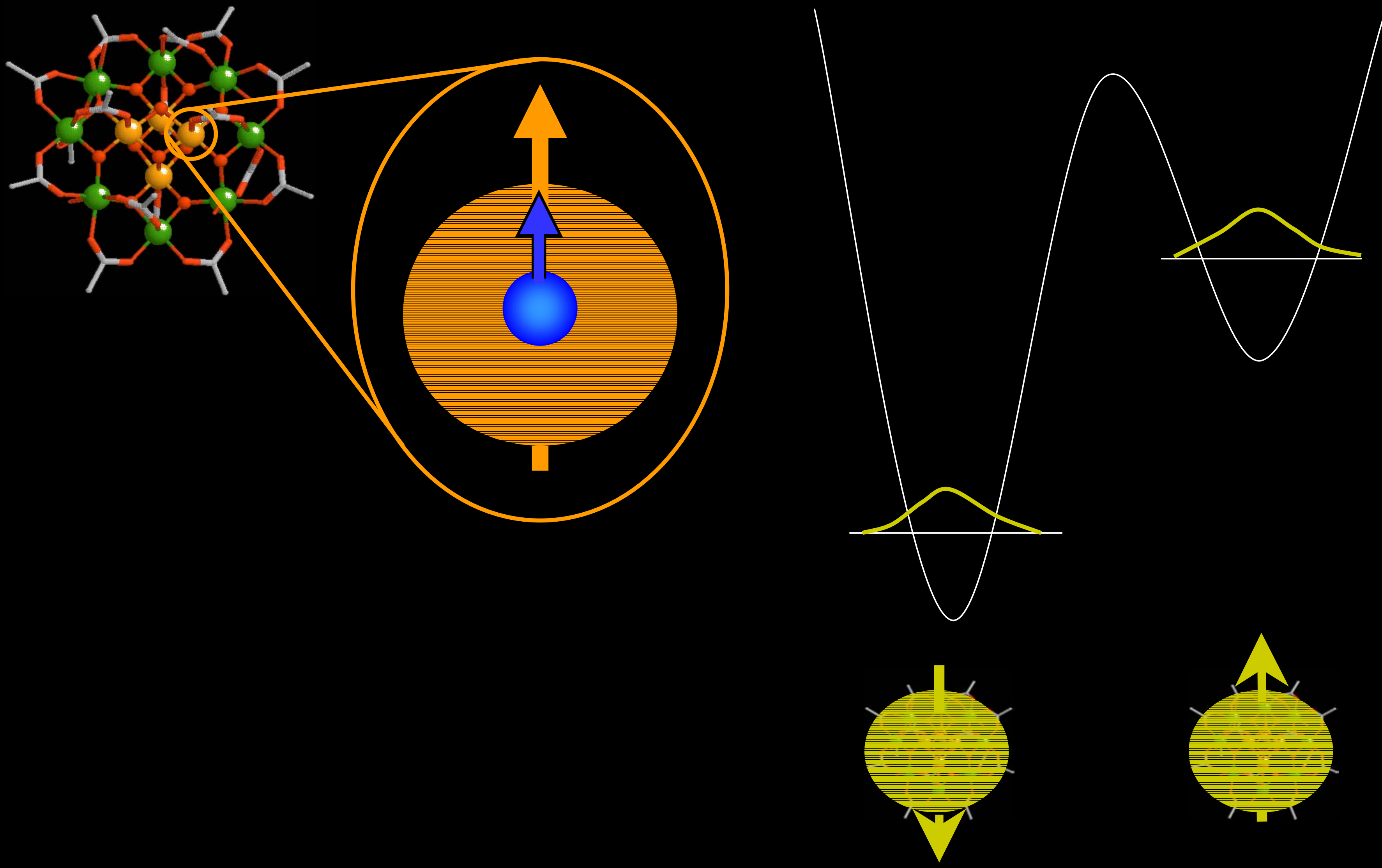
Nuclear bias



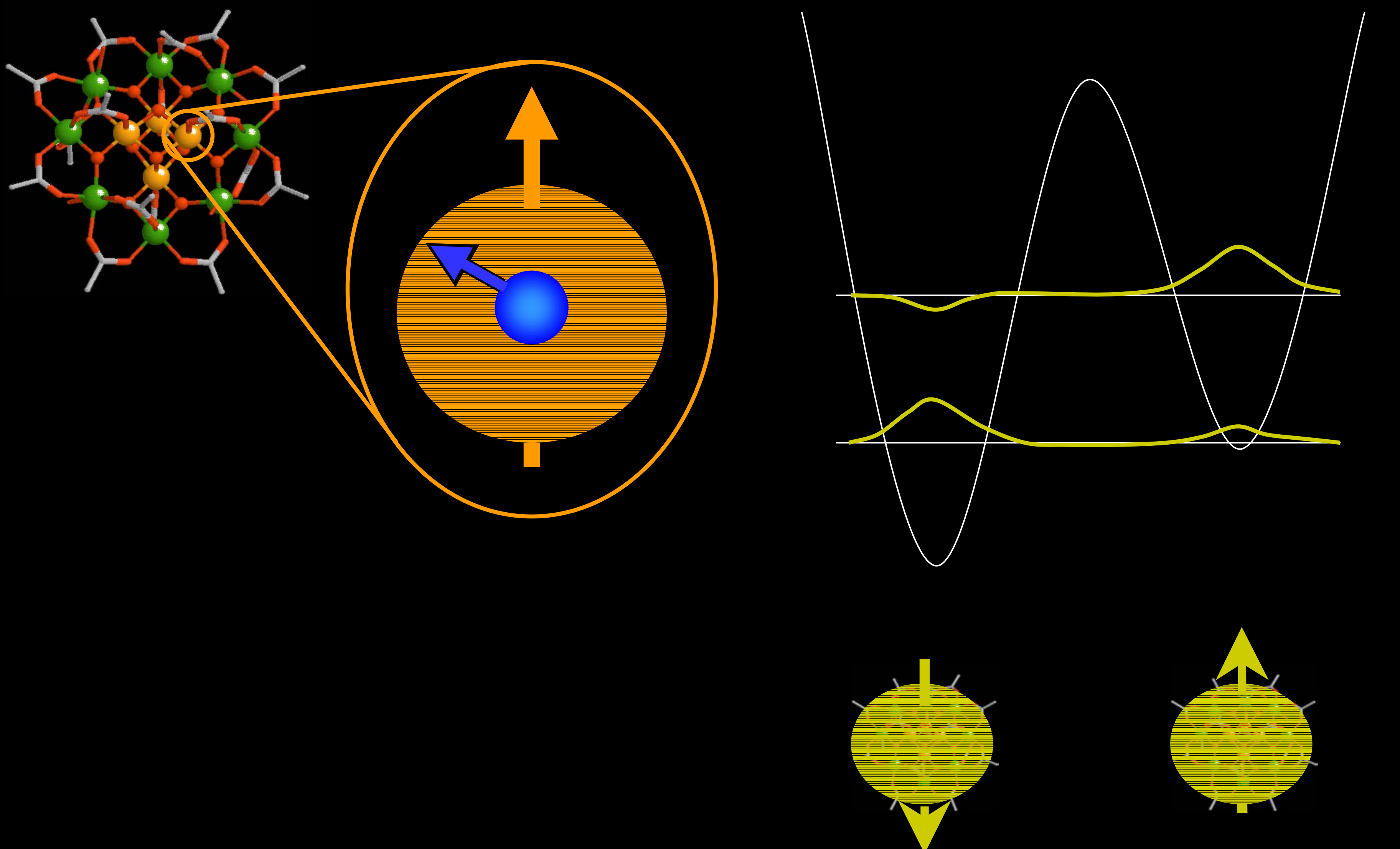
Nuclear bias



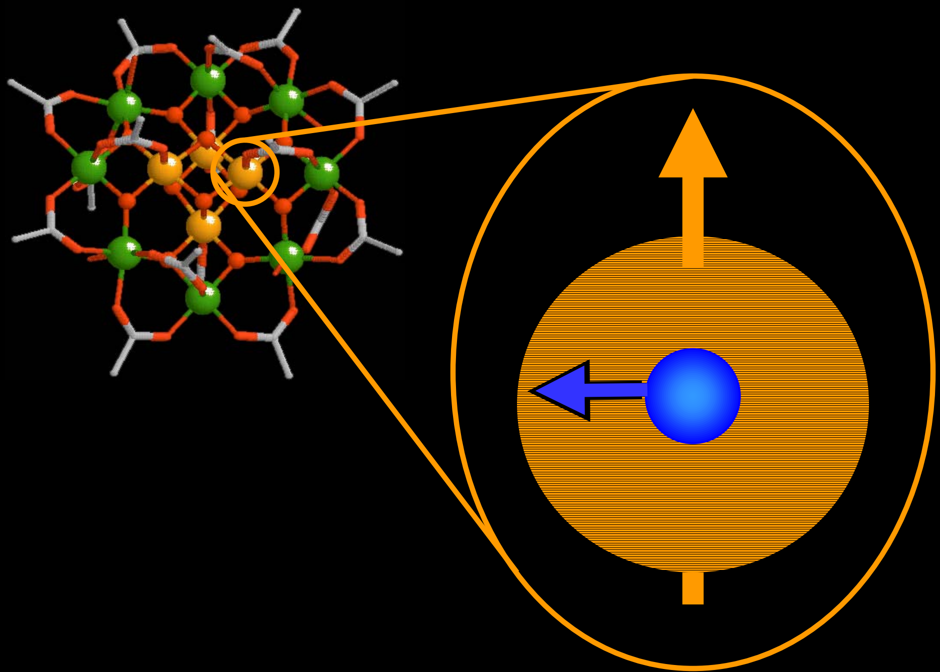
Nuclear bias

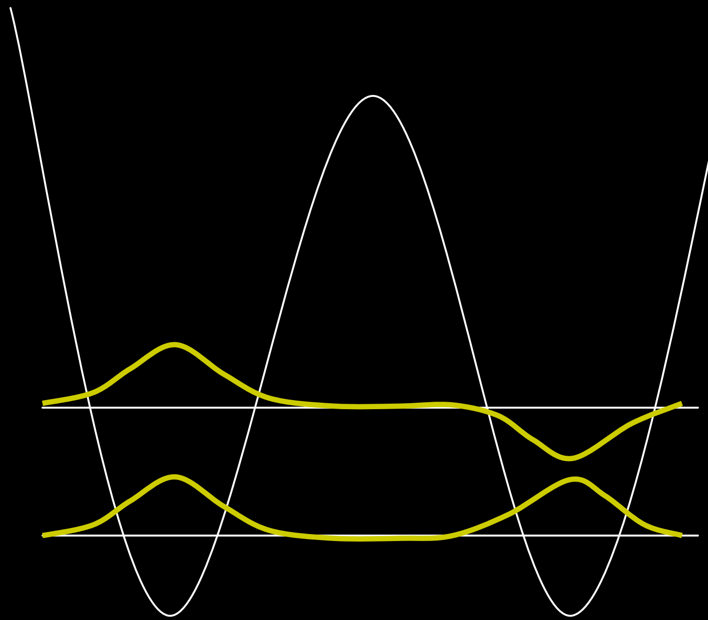


Nuclear bias

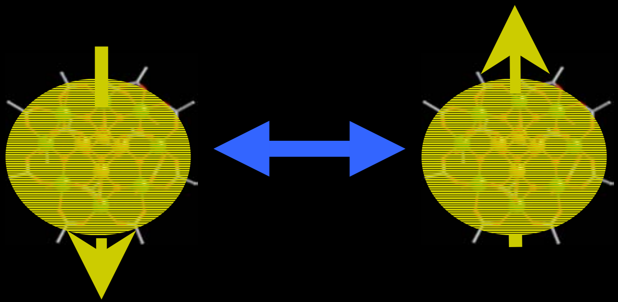


Nuclear bias



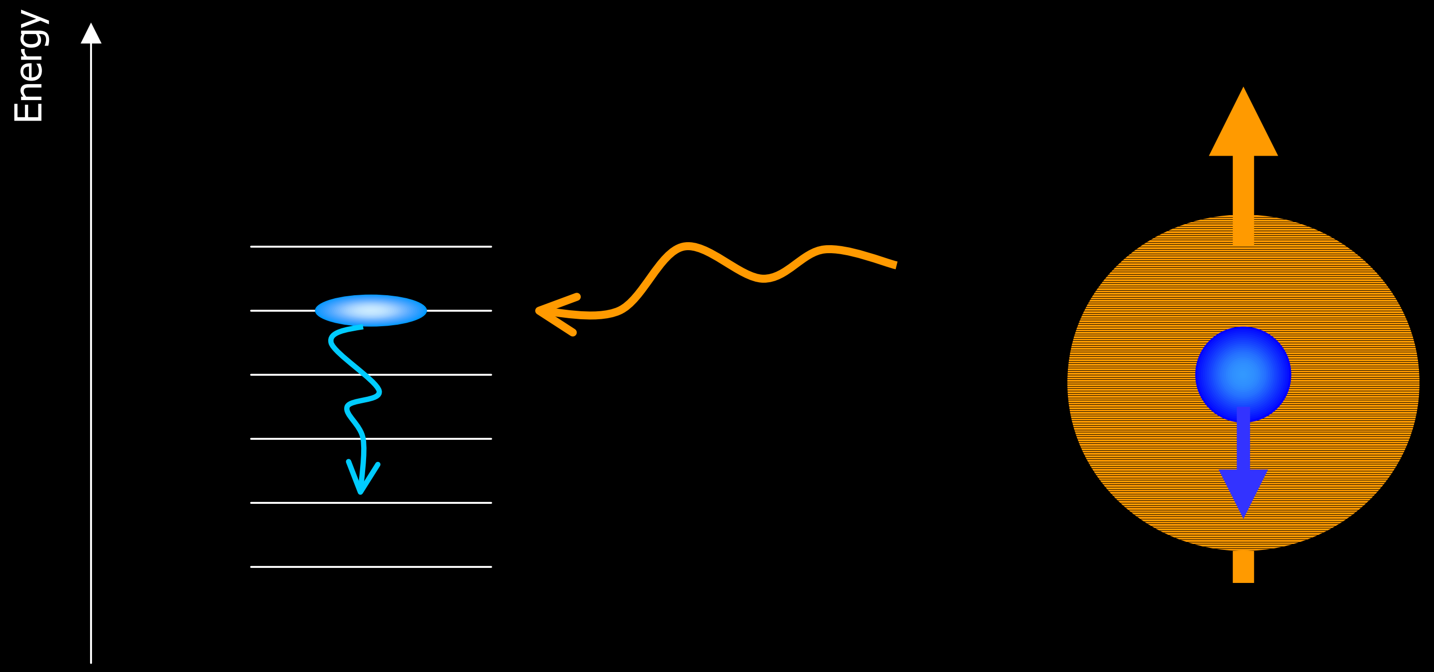


The nuclear spin dynamics can stimulate the quantum tunneling



N.V. Prokof'ev and P.C.E. Stamp,
J. Low Temp. Phys. 104, 143 (1996)

Nuclear relaxation ↔ electron spin fluctuations



At low temperature, the field produced by the electrons on the nuclei is quasi-static → NMR in zero external field

The fluctuations of the electron spins induce nuclear relaxation
→ nuclei are local probes for (quantum?) fluctuations

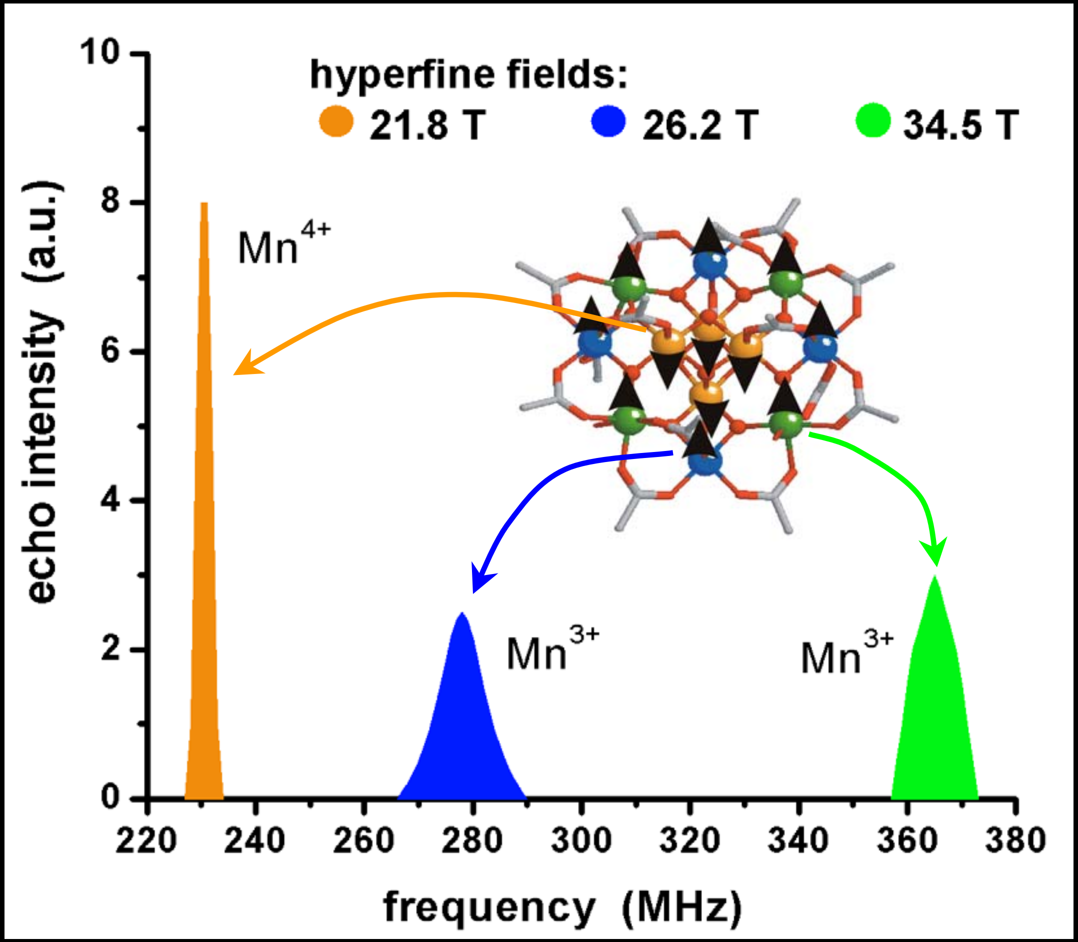
^{55}Mn NMR spectra in zero applied field

$I_{\mathrm{nuclear}} = 5/2$

3 NMR lines corresponding to the 3 inequivalent Mn sites

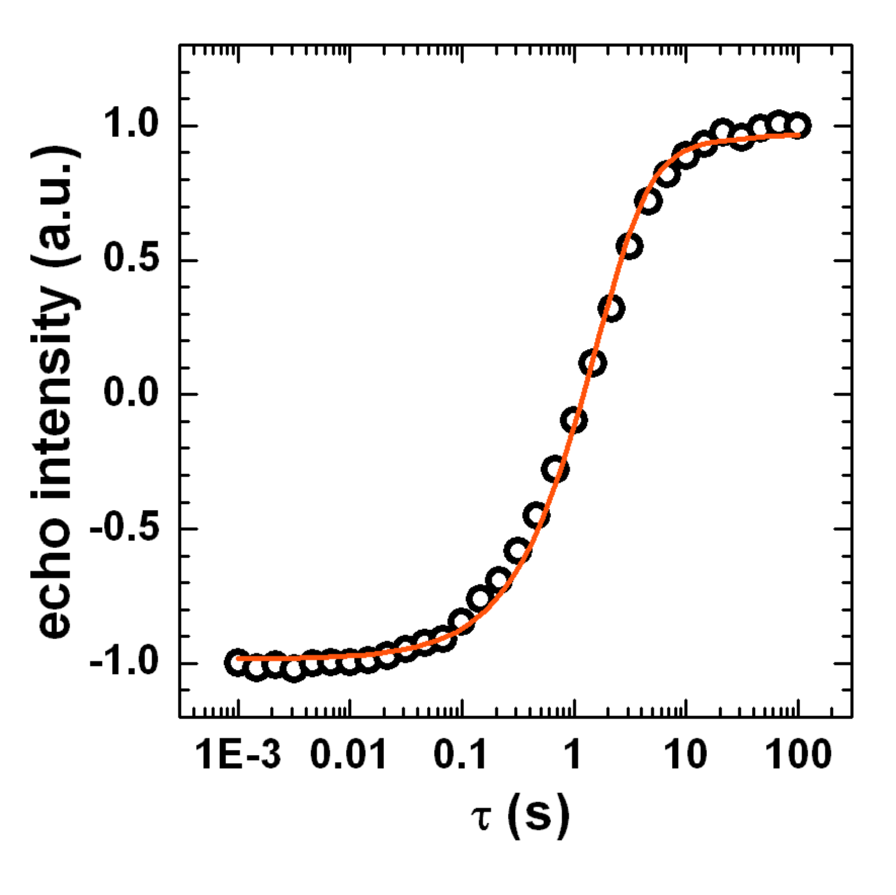
central frequencies:
231, 277, 365 MHz

hyperfine field at the nuclear site parallel to the anisotropy axis for the electron spin



Y. Furukawa *et al.*, PRB 64, 104401 (2001)
T. Kubo *et al.*, PRB 65, 224425 (2002)

Nuclear relaxation: inversion recovery

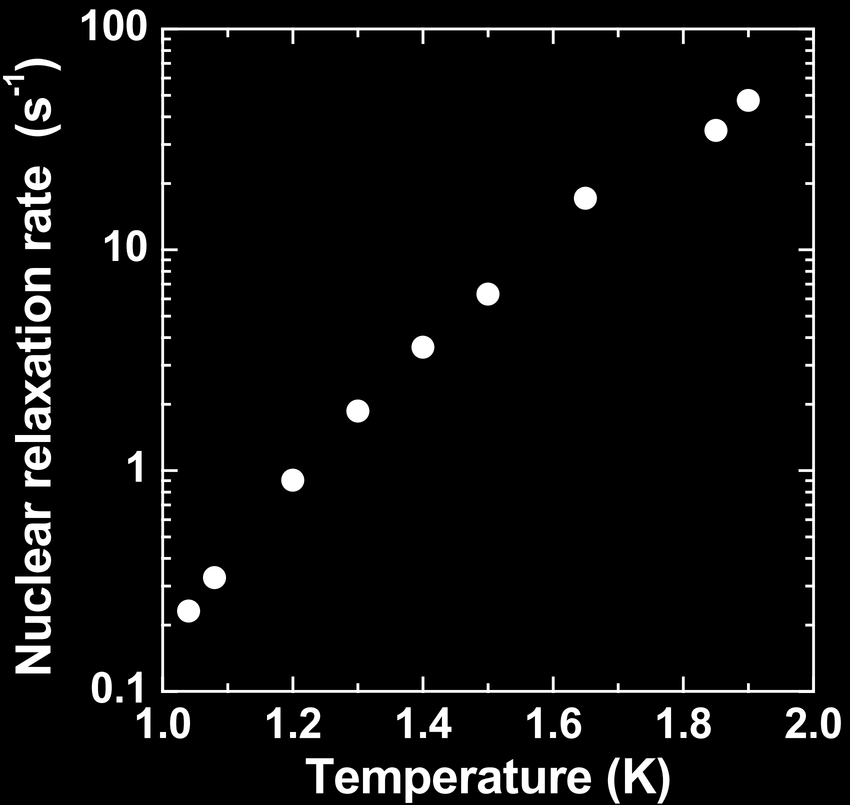


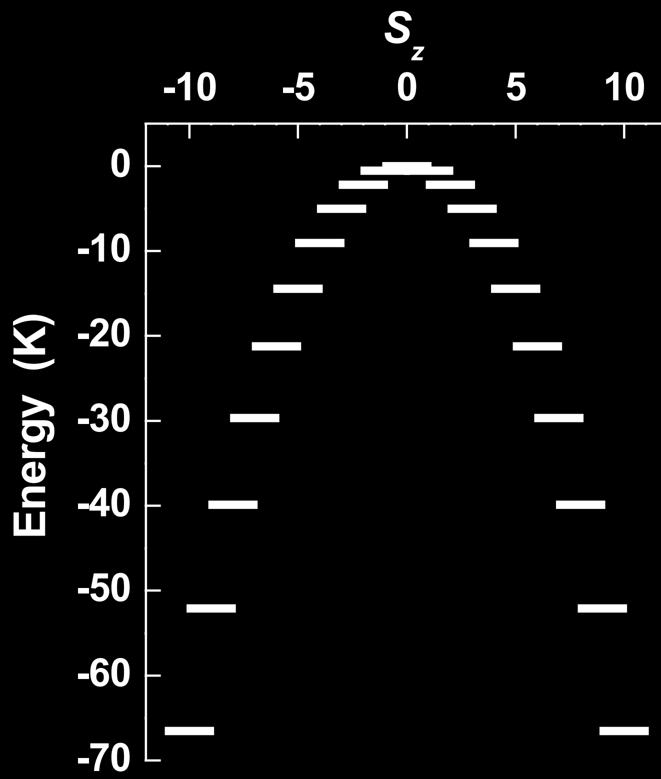
$$M(t) = A\,[\,1 - B\,(100/63\,\exp(-30\,\boldsymbol{W}t) + 16/45\,\exp(-12\,\boldsymbol{W}t) + 2/35\,\exp(-2\,\boldsymbol{W}t)]$$

$\boldsymbol{W}$ = nuclear spin-lattice relaxation rate

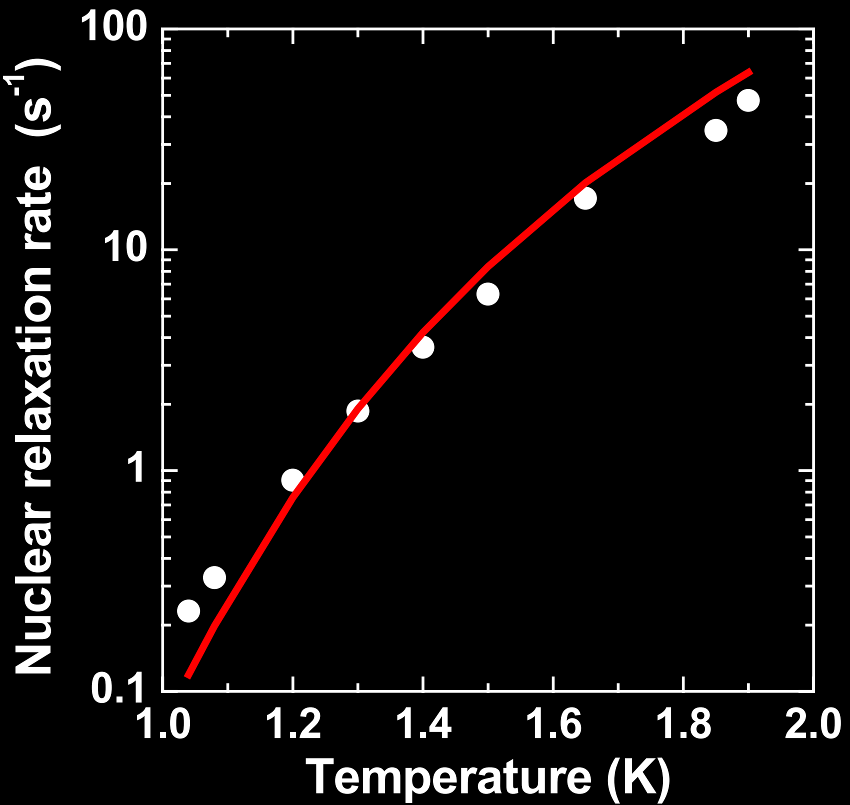
A. Suter et al., J. Phys.: Cond. Matter 10, 5977 (1998)

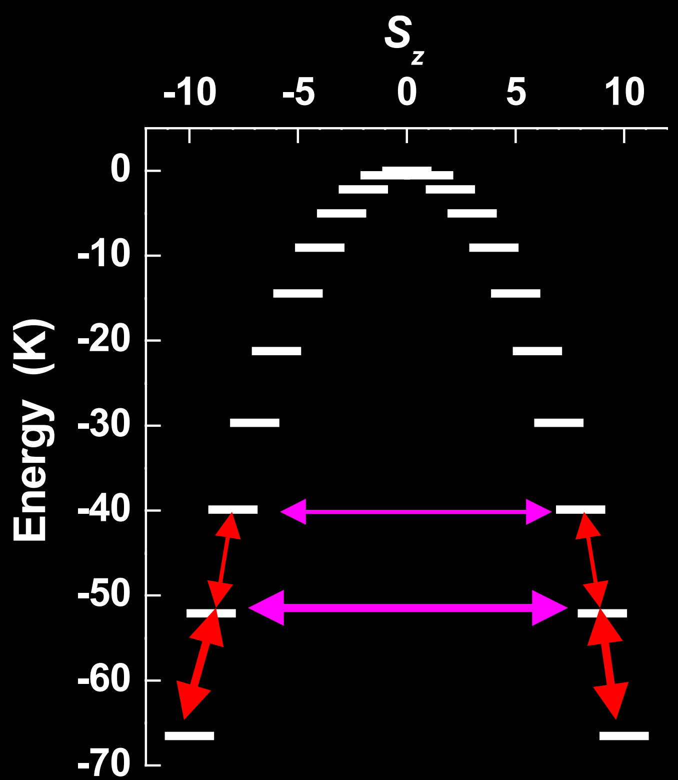
Thermal activation





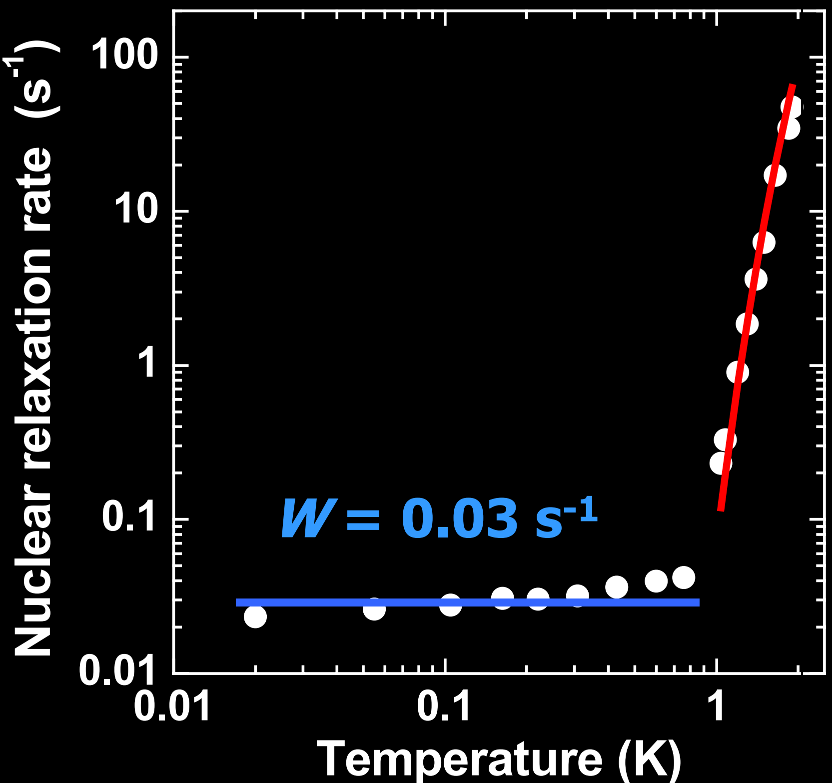
Thermal activation

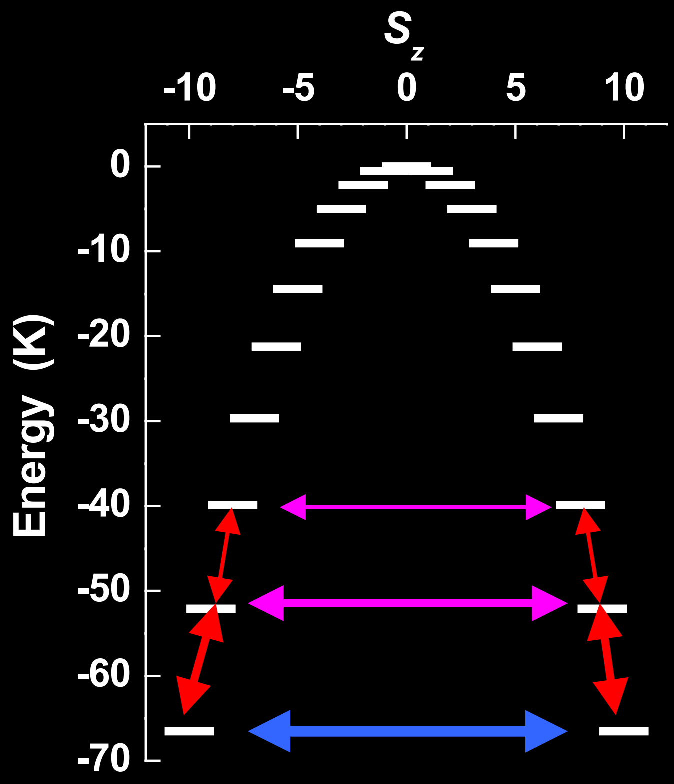




Y. Furukawa *et al*., PRB 64, 104401 (2001)
A. Morello *et al*., Polyhedron 22, 1743 (2003)
see also A. Morello, cond-mat/0404049 (2004)

Quantum tunneling fluctuations





The quantum tunneling fluctuations are able to relax the nuclear spins

A. Morello et al., PRL 93, 197202 (2004)

External field B_z // z

By applying an external field B_z, the resonance condition for tunneling is destroyed

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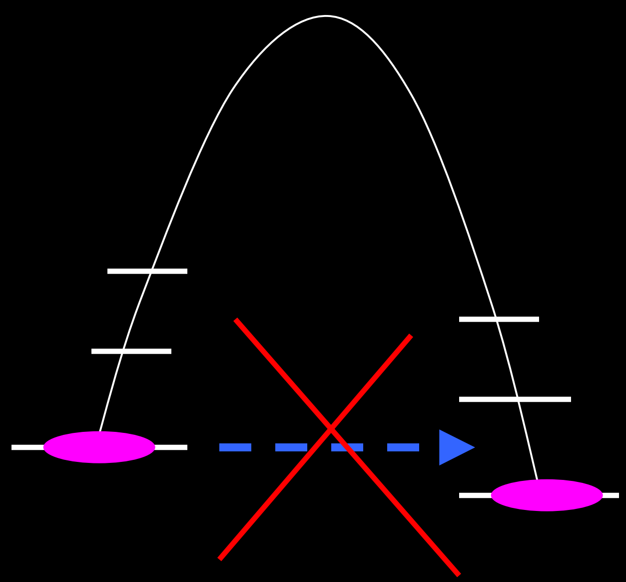
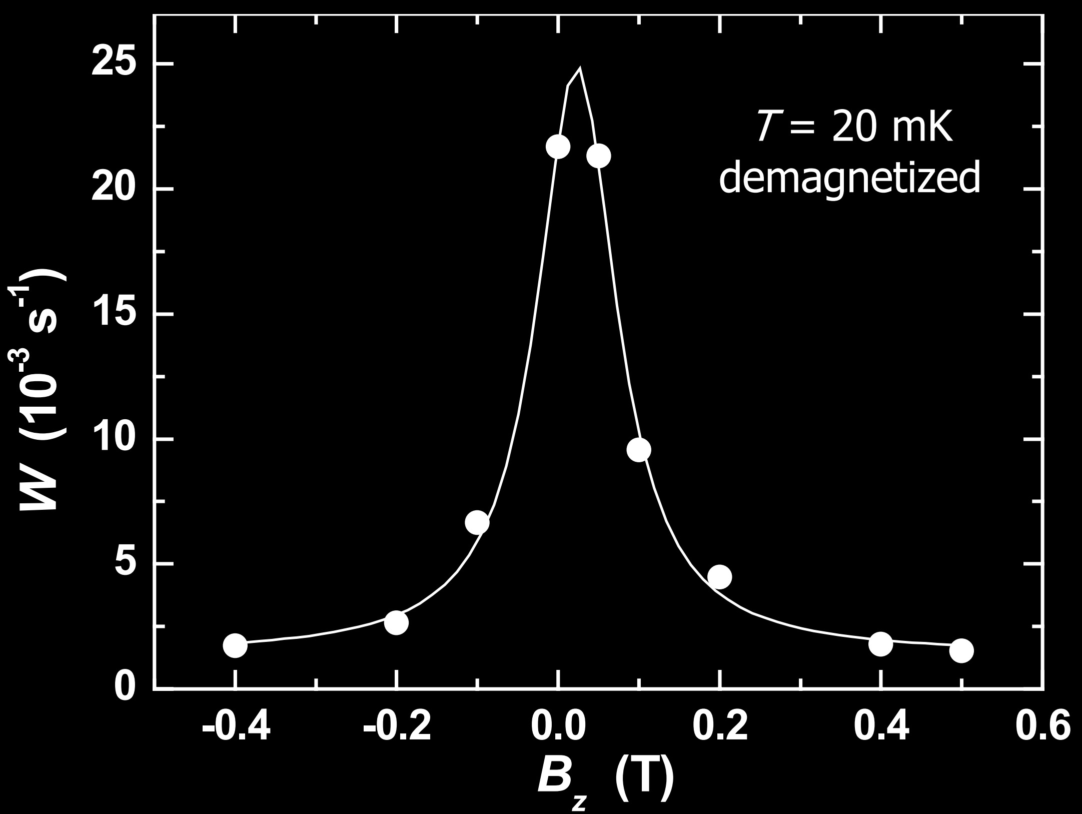
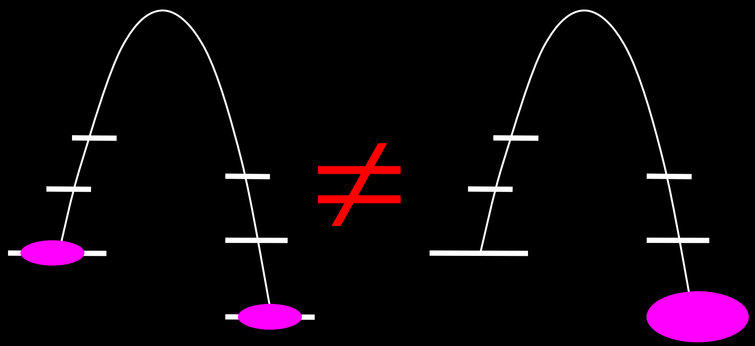
Peak in $W(B_z)$ around zero field

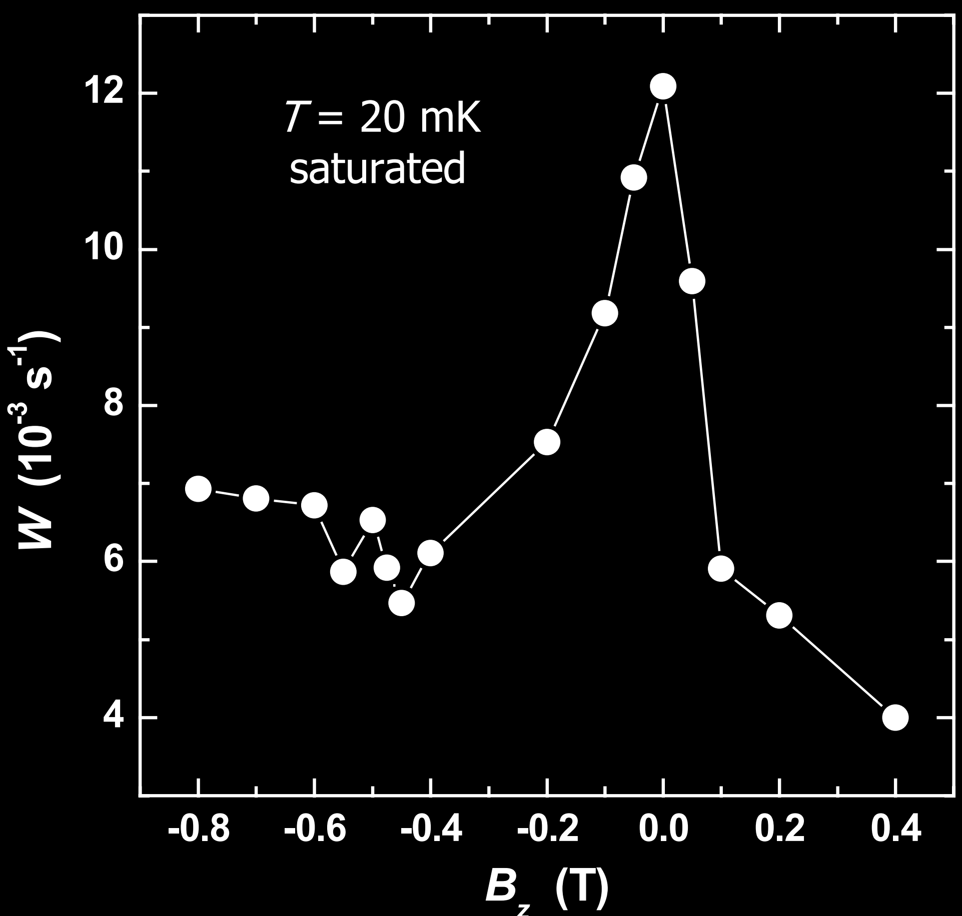




External field B_z // z

Both the zero-field value and the "linewidth" depend on the cluster's magnetization state.





All this does not require any <u>macroscopic</u> change in the magnetization.

Fast-relaxing molecules

Every real sample contains minority species with one or two flipped Jahn-Teller axes

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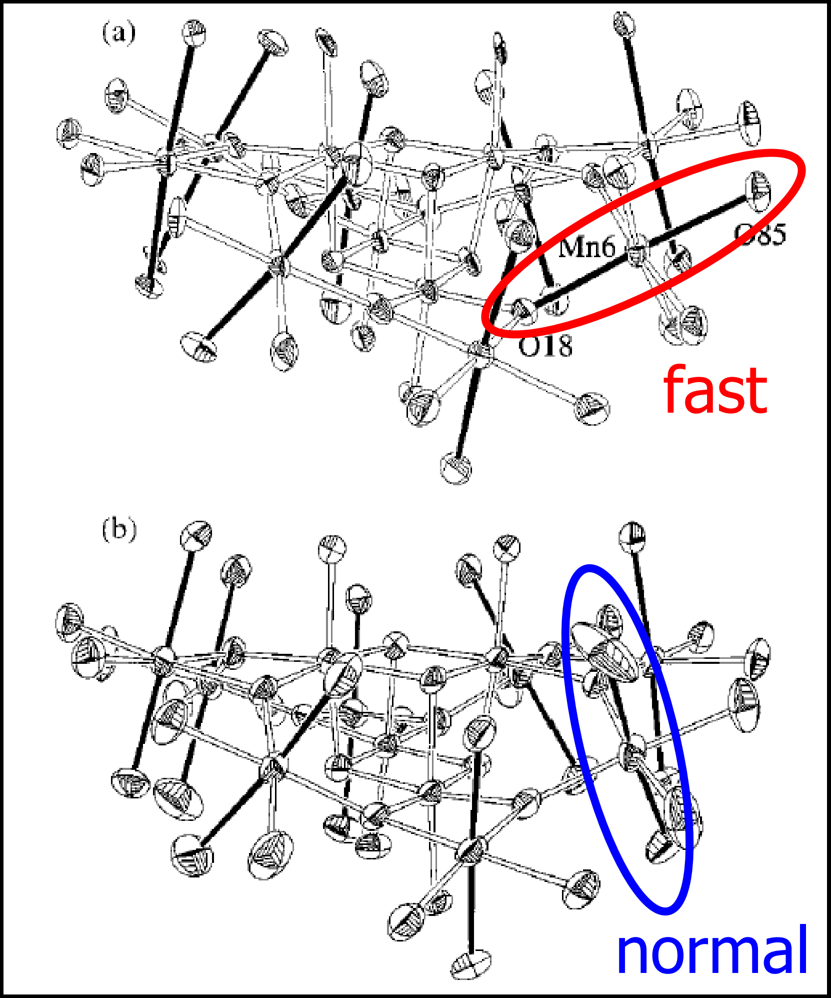
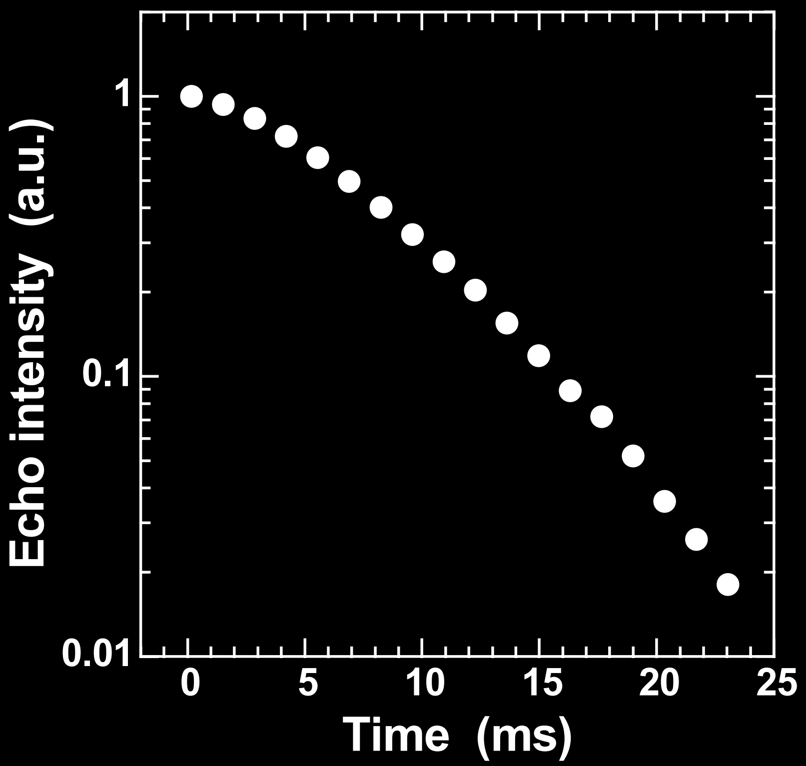
• Smaller anisotropy barrier (15 K or 35 K instead of 65 K)

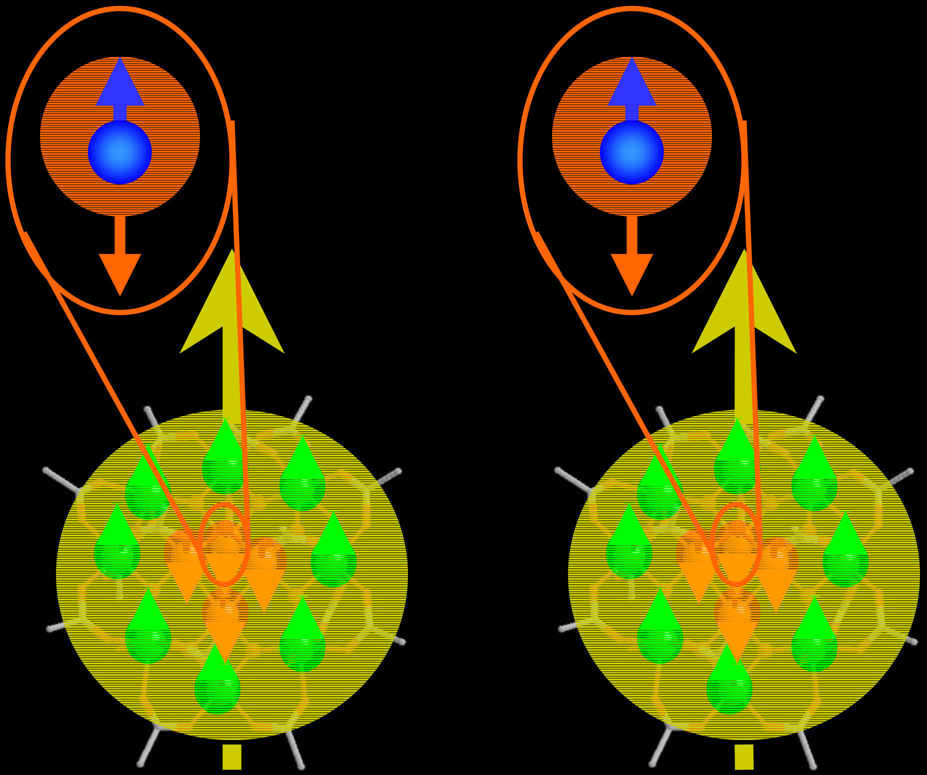
Faster tunneling rate



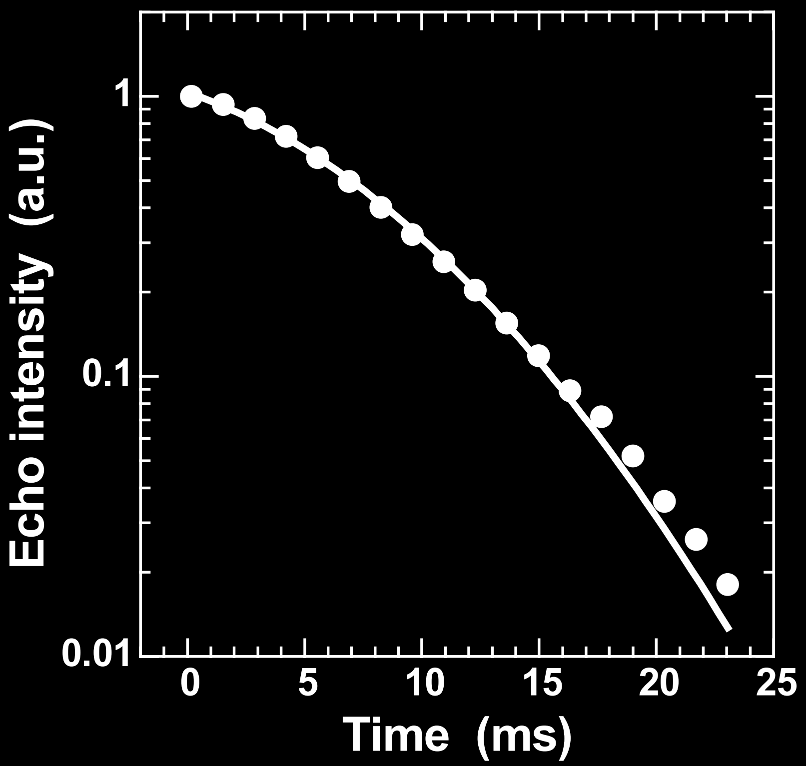
W. Wernsdorfer et al., Europhys. Lett. 47, 254 (1999)
Z. Sun et al., Chem. Comm., 1973 (1999)

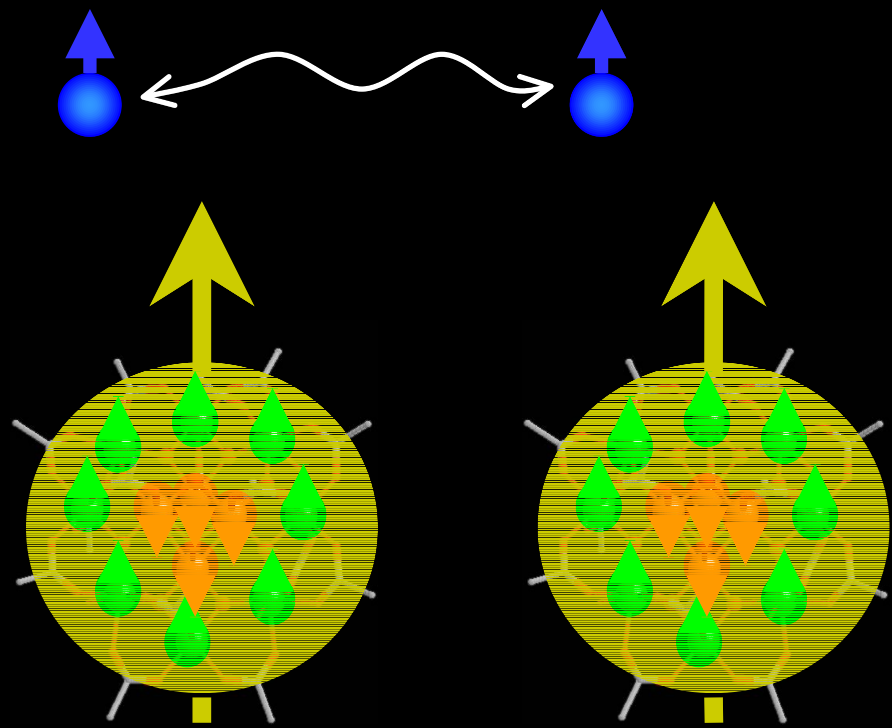
Intercluster nuclear coupling



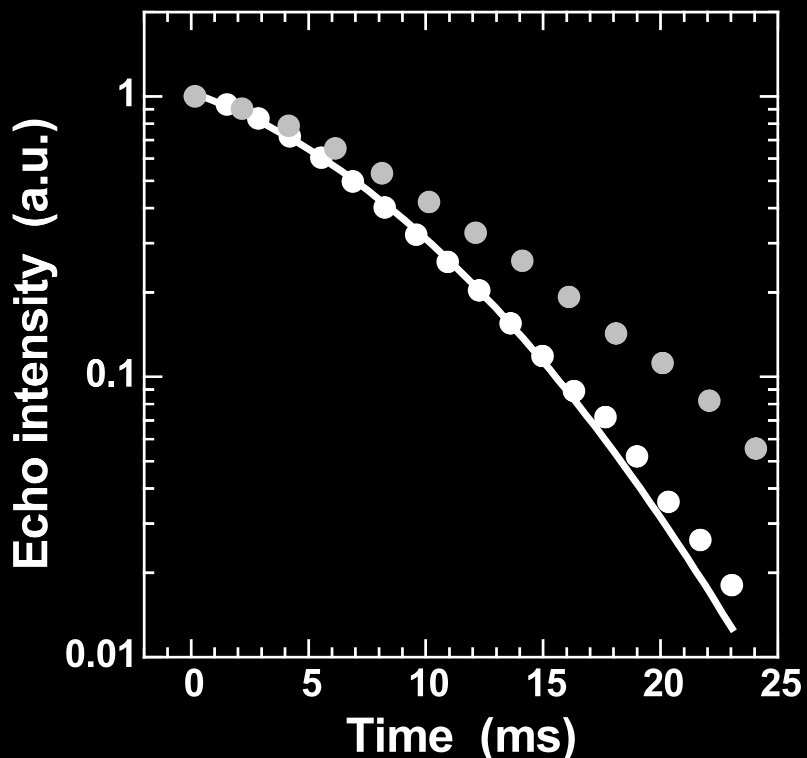


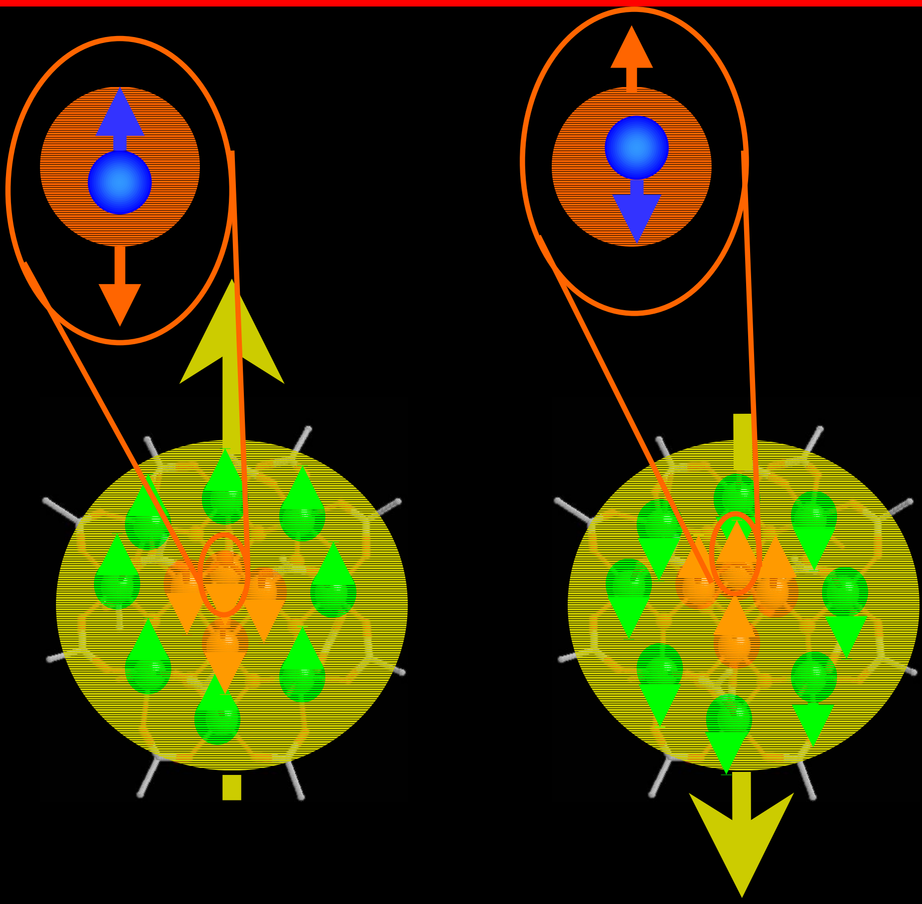
Intercluster nuclear coupling



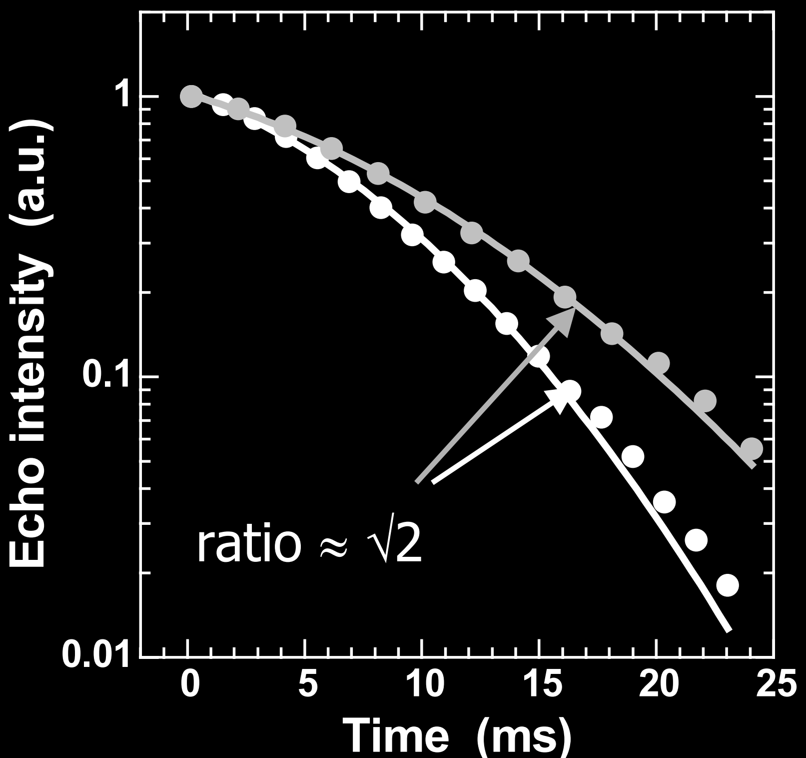


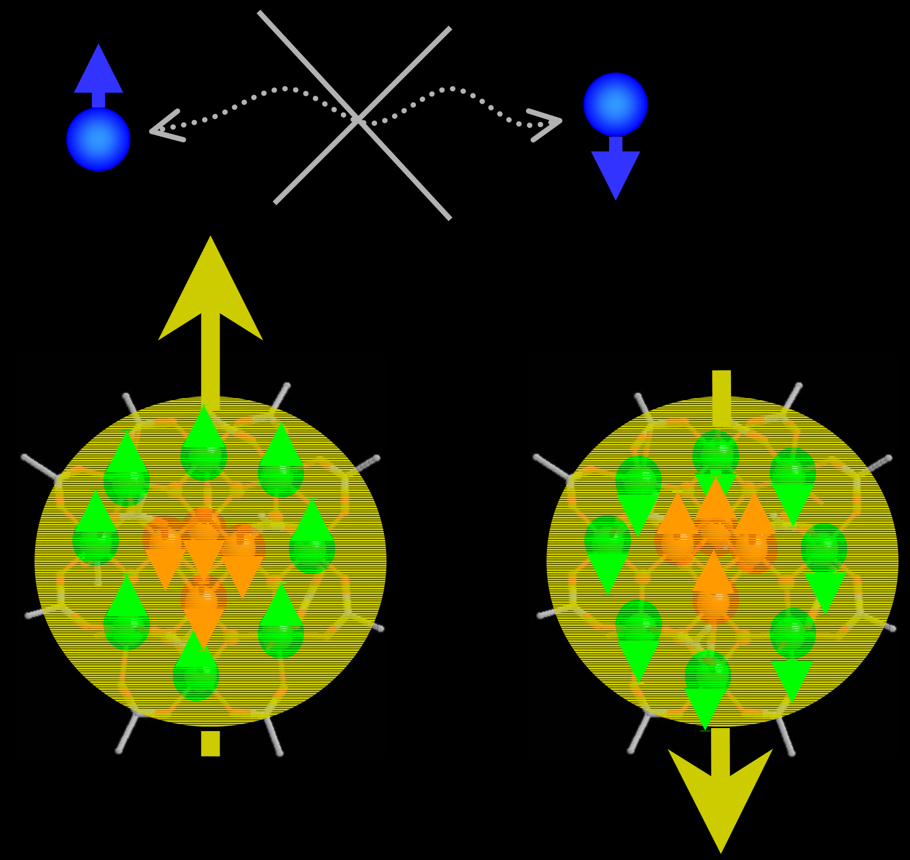
Intercluster nuclear coupling





Intercluster nuclear coupling

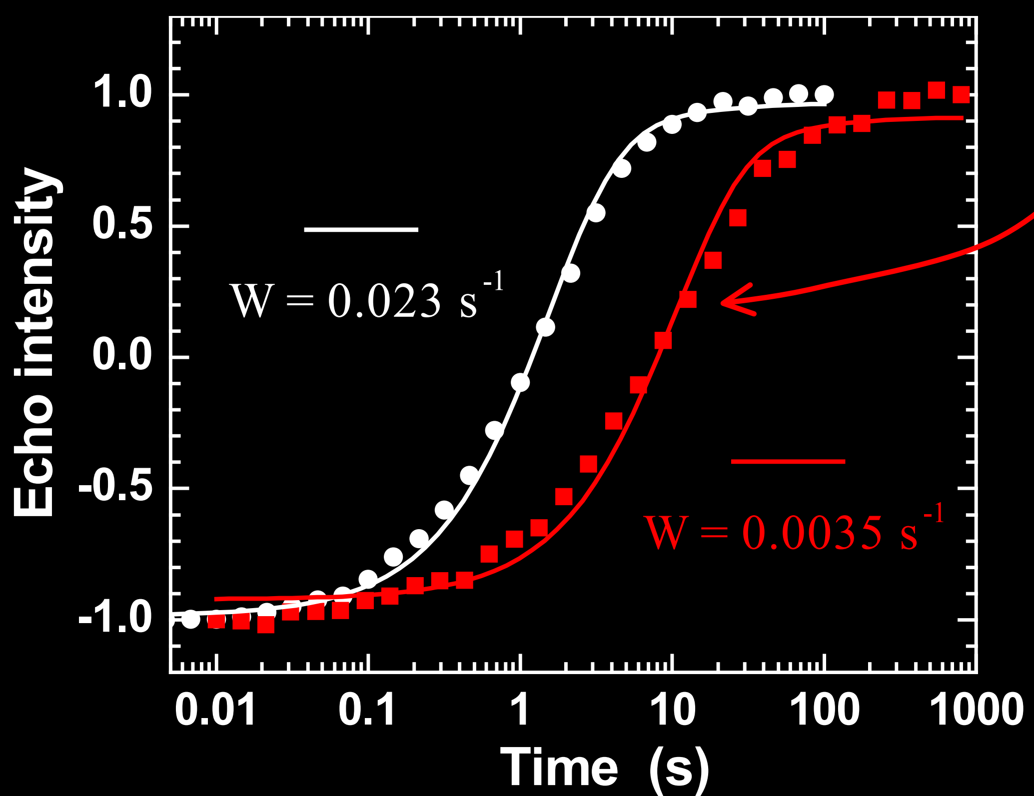




Nuclei in different cluster are mutually coupled → spin diffusion

A. Morello et al., PRL 93, 197202 (2004)

Isotope effect

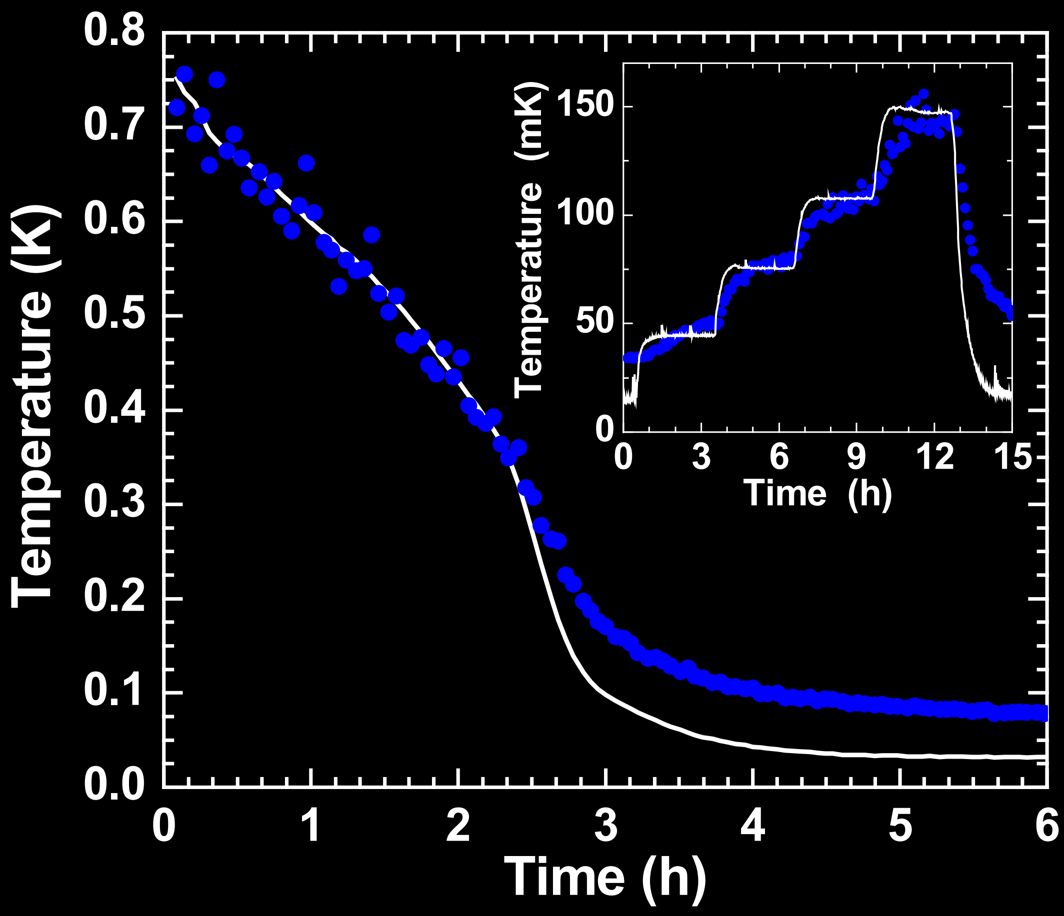


Sample with proton spins substituted by deuterium

$$\frac{\gamma_{proton}}{\gamma_{deuterium}} = 6.5$$

The reduced tunneling rate is directly measured by the ^{55}Mn relaxation rate

Nuclear spin temperature



The nuclear spins follow the lattice temperature

A. Morello et al., PRL 93, 197202 (2004)

Experimental facts: summary

- the nuclear spin-lattice relaxation in the quantum regime is **surprisingly fast** (10 – 100 s)

- the field dependence of W and the isotope effect demonstrate that **tunneling fluctuations** drive the nuclear relaxation

- the intercluster nuclear **spin diffusion is fast** compared to the timescale of spin-lattice relaxation

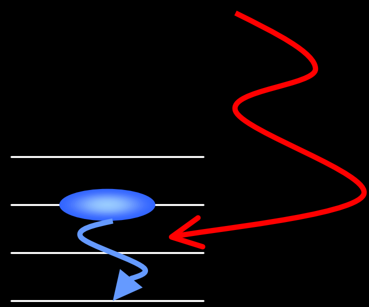
- the **fast-relaxing molecules** are responsible for the tunneling dynamics

- the nuclear spins are in very good contact with the **thermal bath**

Peculiarities of the problem

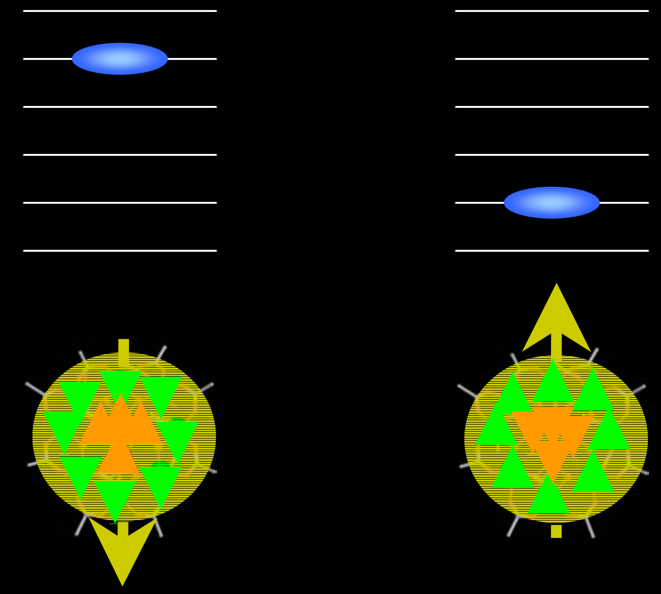
"Standard NMR"

$$H = H_{static} + \color{red}{H_{perturbation}}$$



Tunneling of hyperfine field

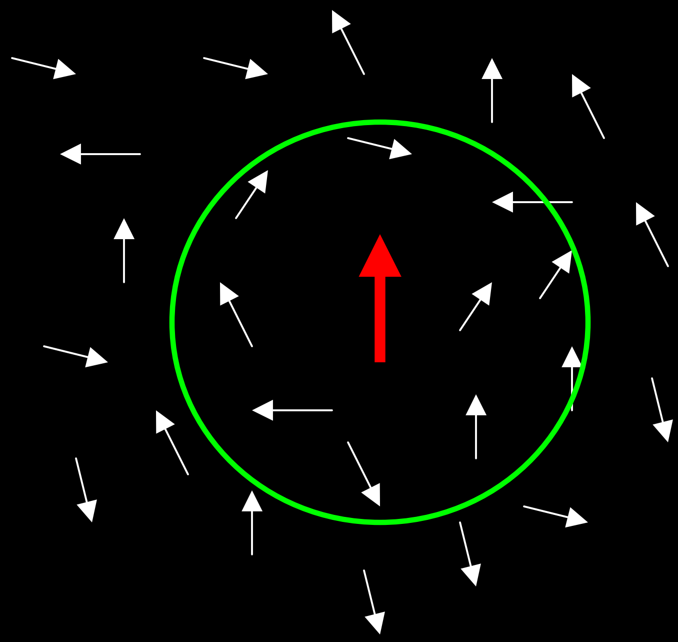
$$H = \begin{cases} H_{\uparrow} \\ H_{\downarrow} \end{cases}$$



Perturbation theory is not applicable

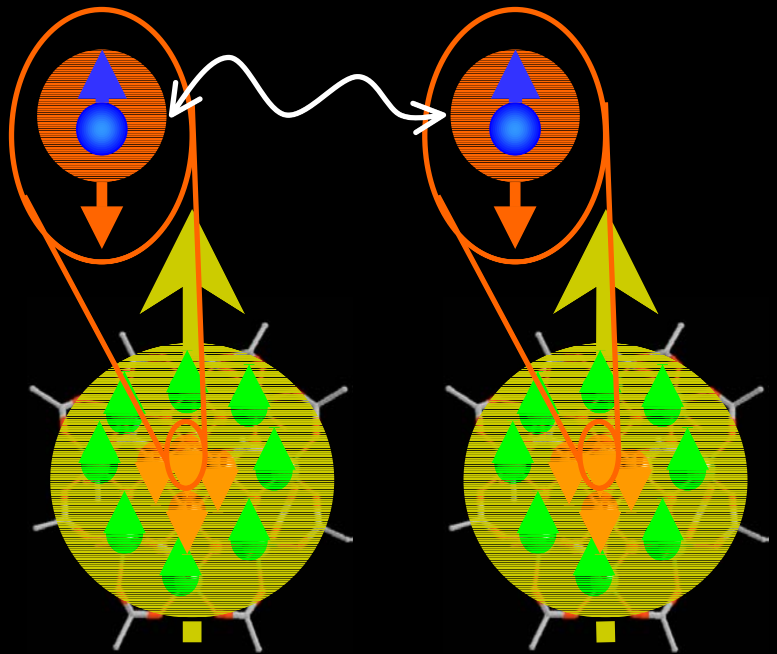
Peculiarities of the problem

Relaxation by
“impurities + spin diffusion”



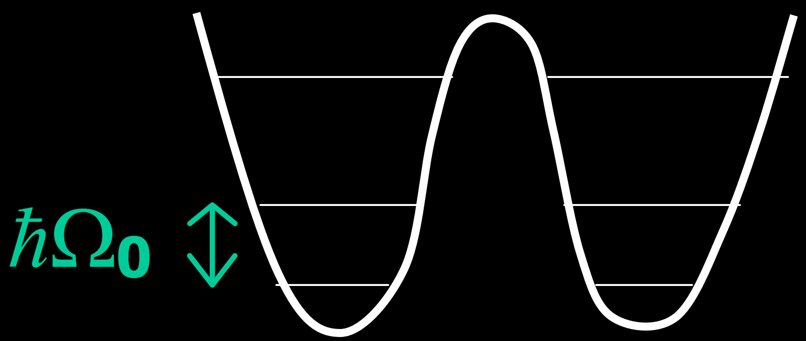
Minimum radius for spin diffusion

Intercluster spin diffusion

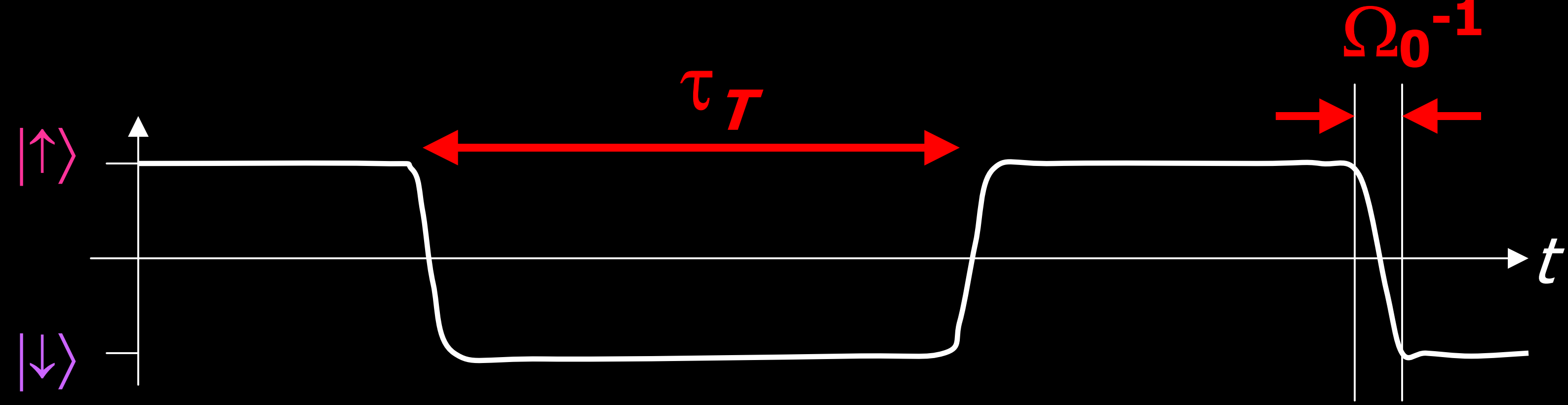


Nuclei in the same sites are
equivalent in all the clusters

Tunneling traversal time



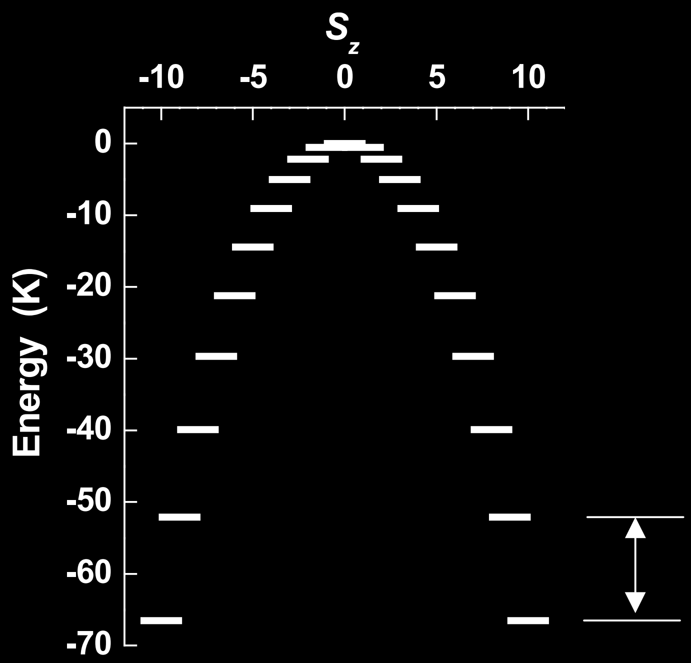
Ω_0 = frequency of the "small oscillations" on the bottom of the well



Ω_0^{-1} is the "tunneling traversal time"

E.H. Hauge et al., Rev. Mod. Phys. 61, 917 (1989)

Coflipping probability



in Mn_{12}-ac:

$\Omega_0^{-1} \sim 10^{-12}$ s

$\Uparrow$

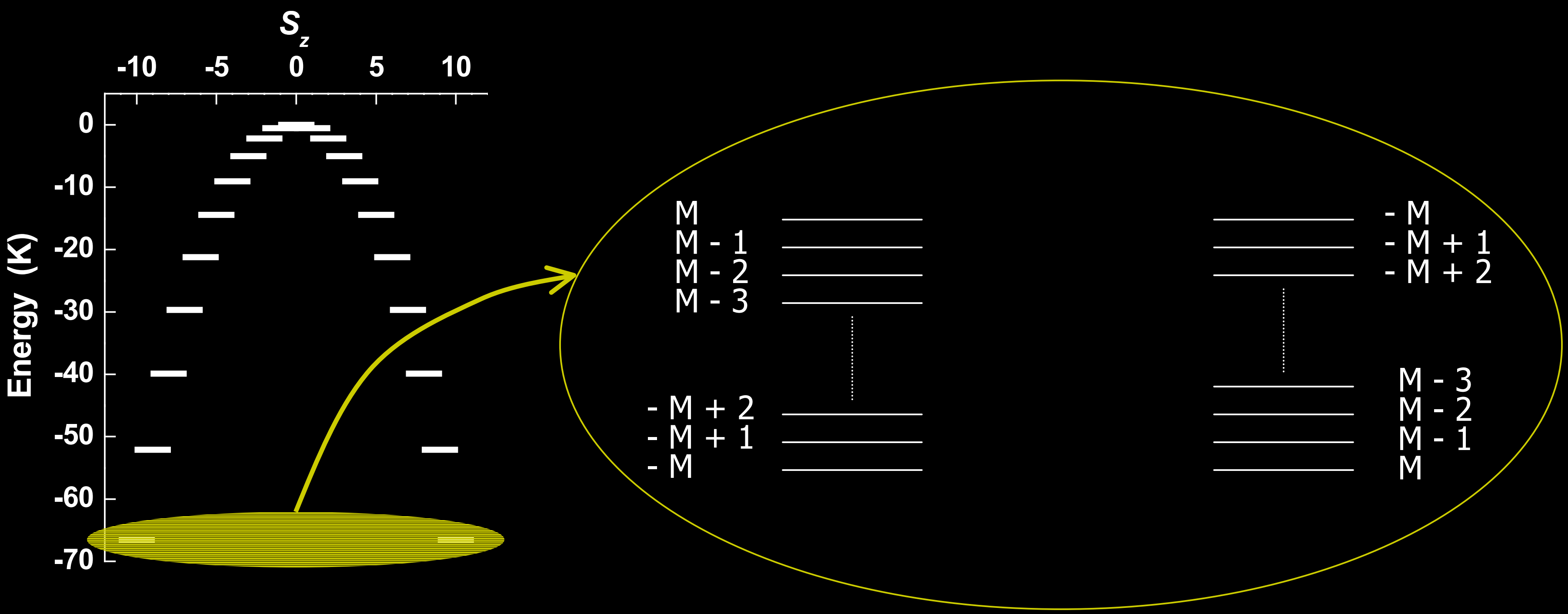
$\hbar\Omega_0 \sim E_9 - E_{10} \approx 3 - 14$ K

The probability for the nuclear spins to "coflip" with the tunneling electron spin is ~ $(\omega_N / \Omega_0)^2 \sim 10^{-6}$

The nuclear spins "inside" a tunneling molecule do not coflip with it

N.V. Prokof'ev and P.C.E. Stamp, cond-mat/9511011 (1995)

Hyperfine-split manifolds



The hyperfine fields before and after tunneling are exactly antiparallel

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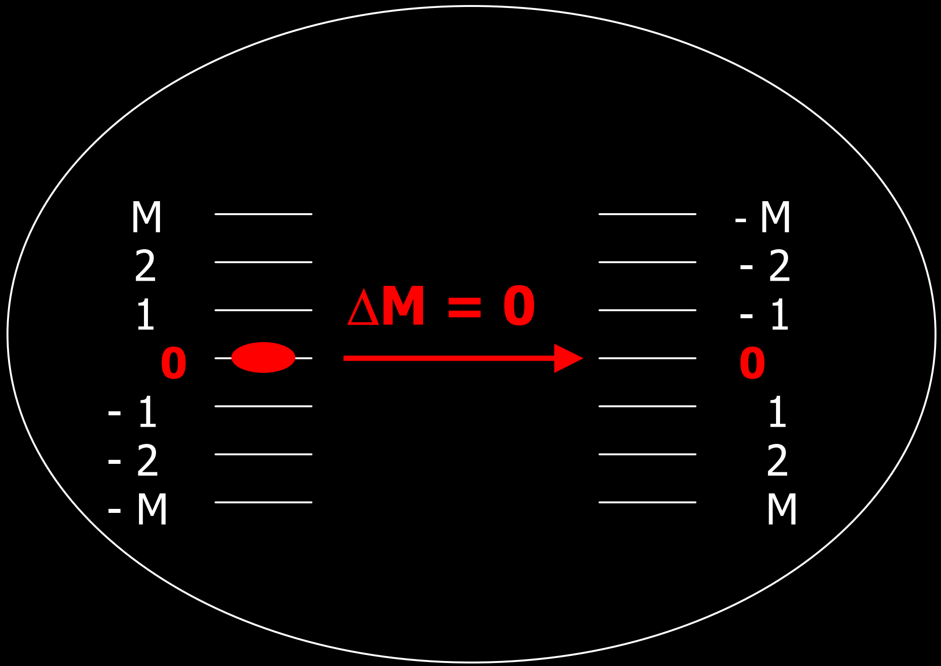
The hyperfine-split manifolds on either sides of the barrier are simply mirrored with respect to the nuclear polarization.

N.V. Prokof'ev and P.C.E. Stamp, cond-mat/9511011 (1995)

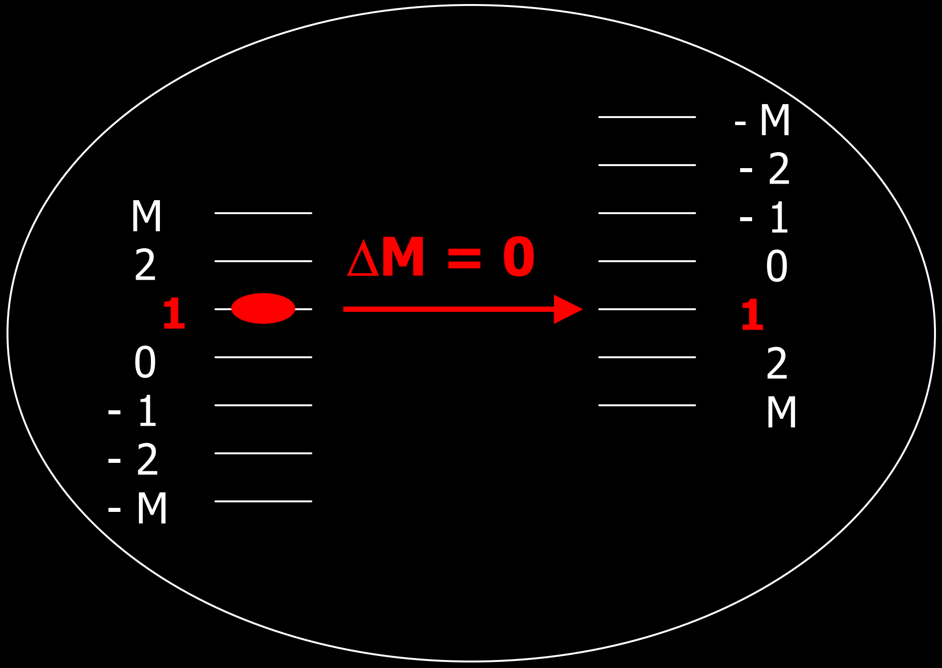
Unbiased case



The most probable tunneling transition (without coflipping nuclei) is between states with zero nuclear polarization.

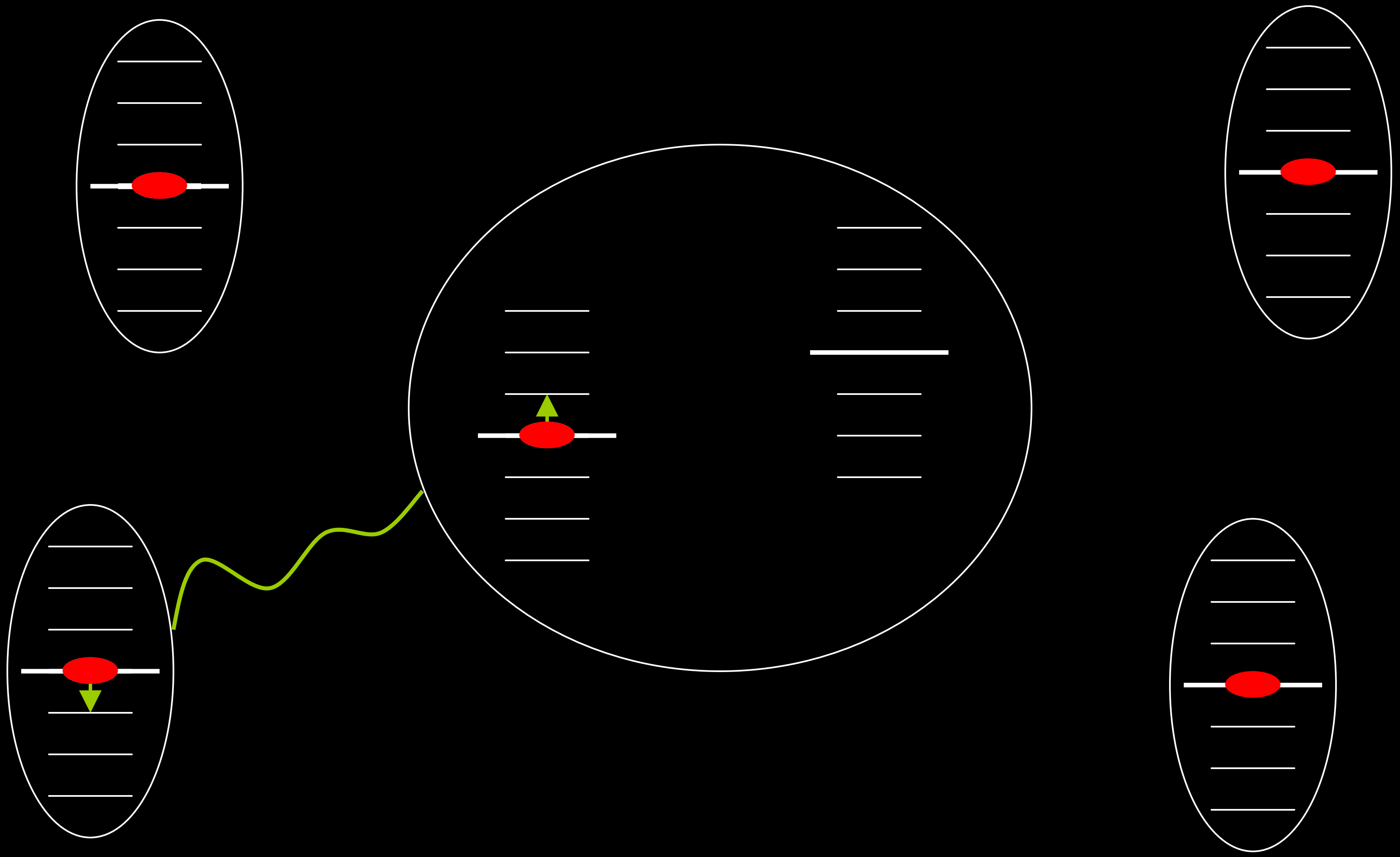
Biased case

e.g. by dipolar coupling with "slow" neighboring clusters

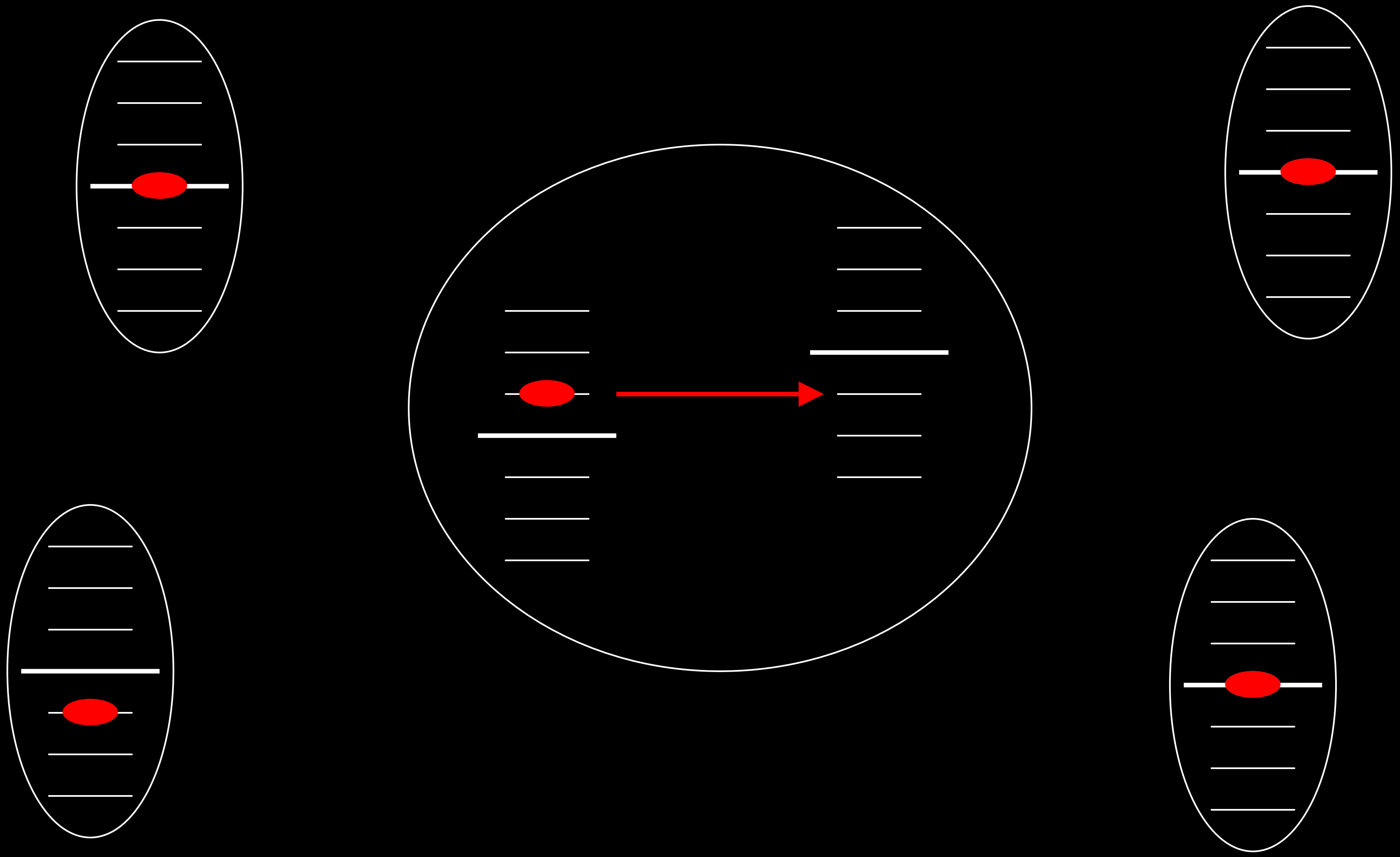


Now the $\Delta M = 0$ transition requires an initial polarization (e.g. $M = 1$ here)

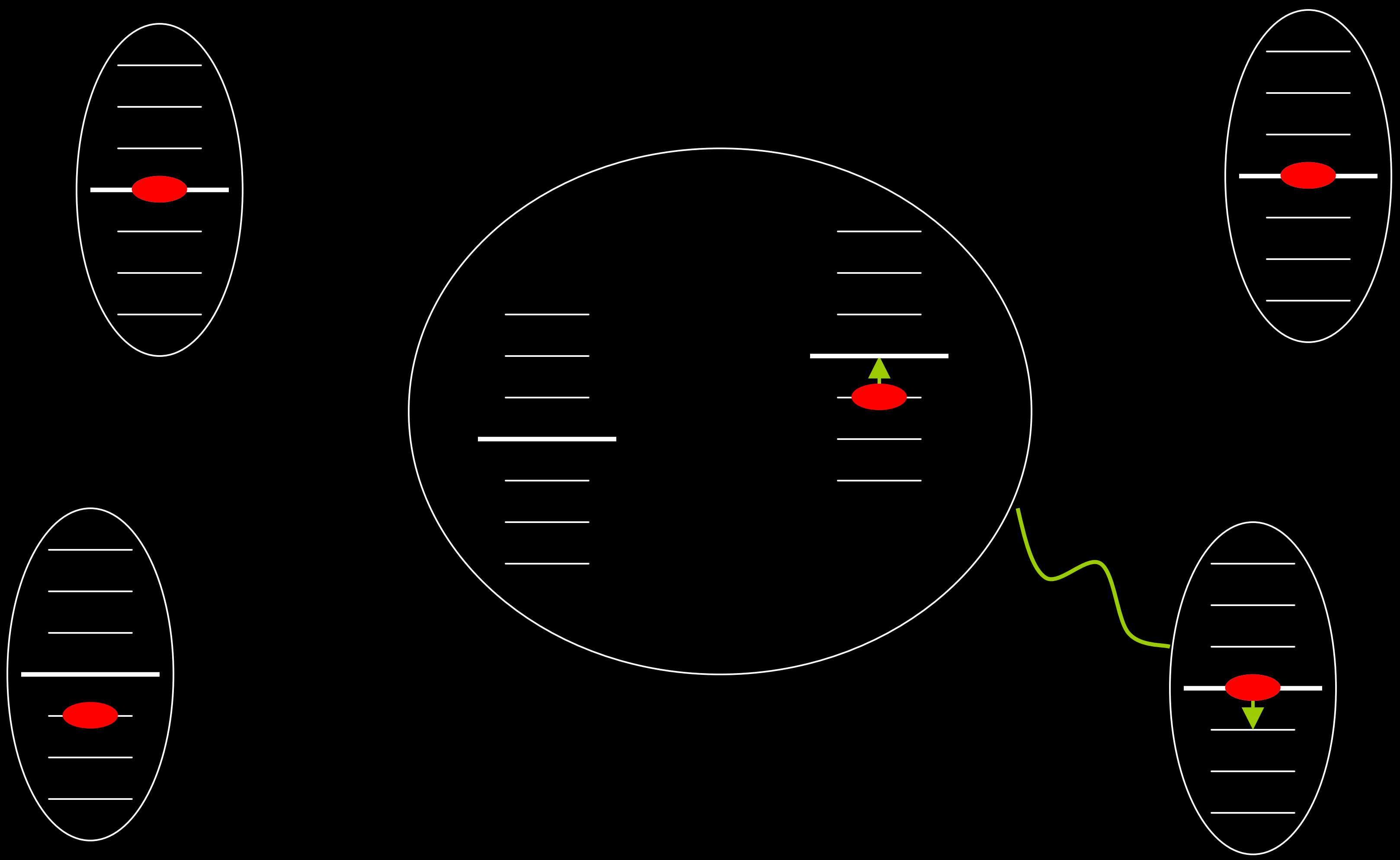
Nuclear flip-flops



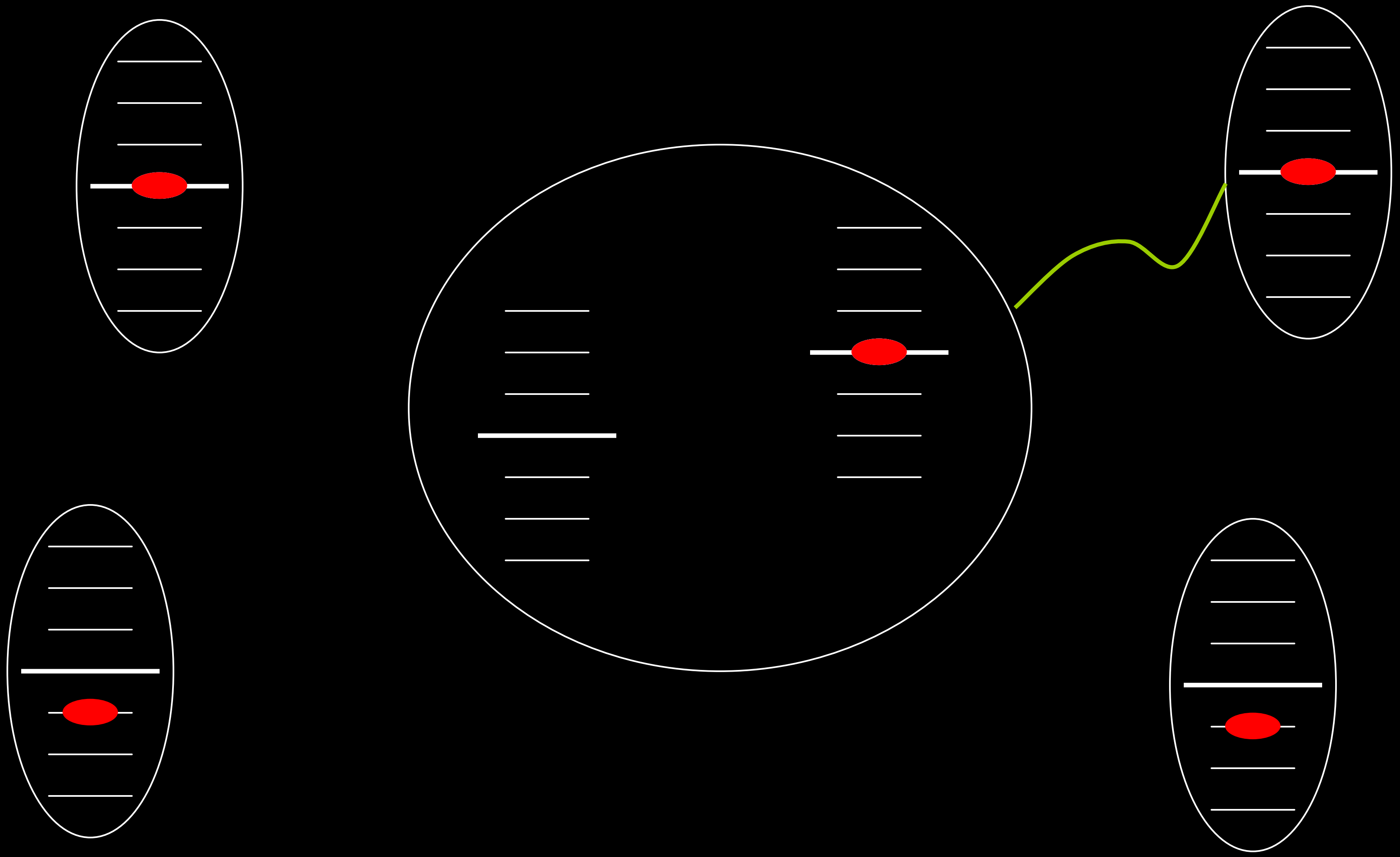
Nuclear flip-flops



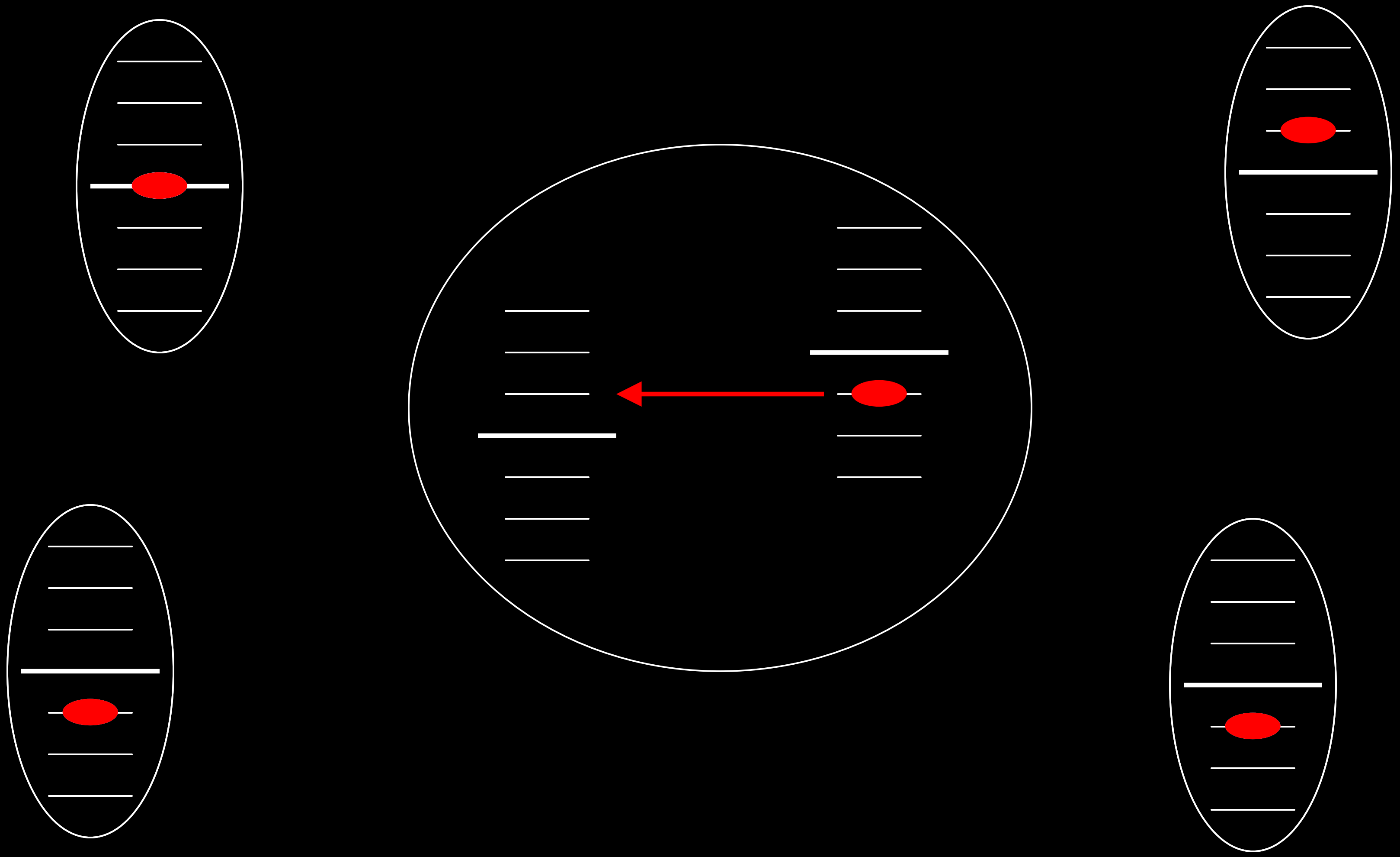
Nuclear flip-flops



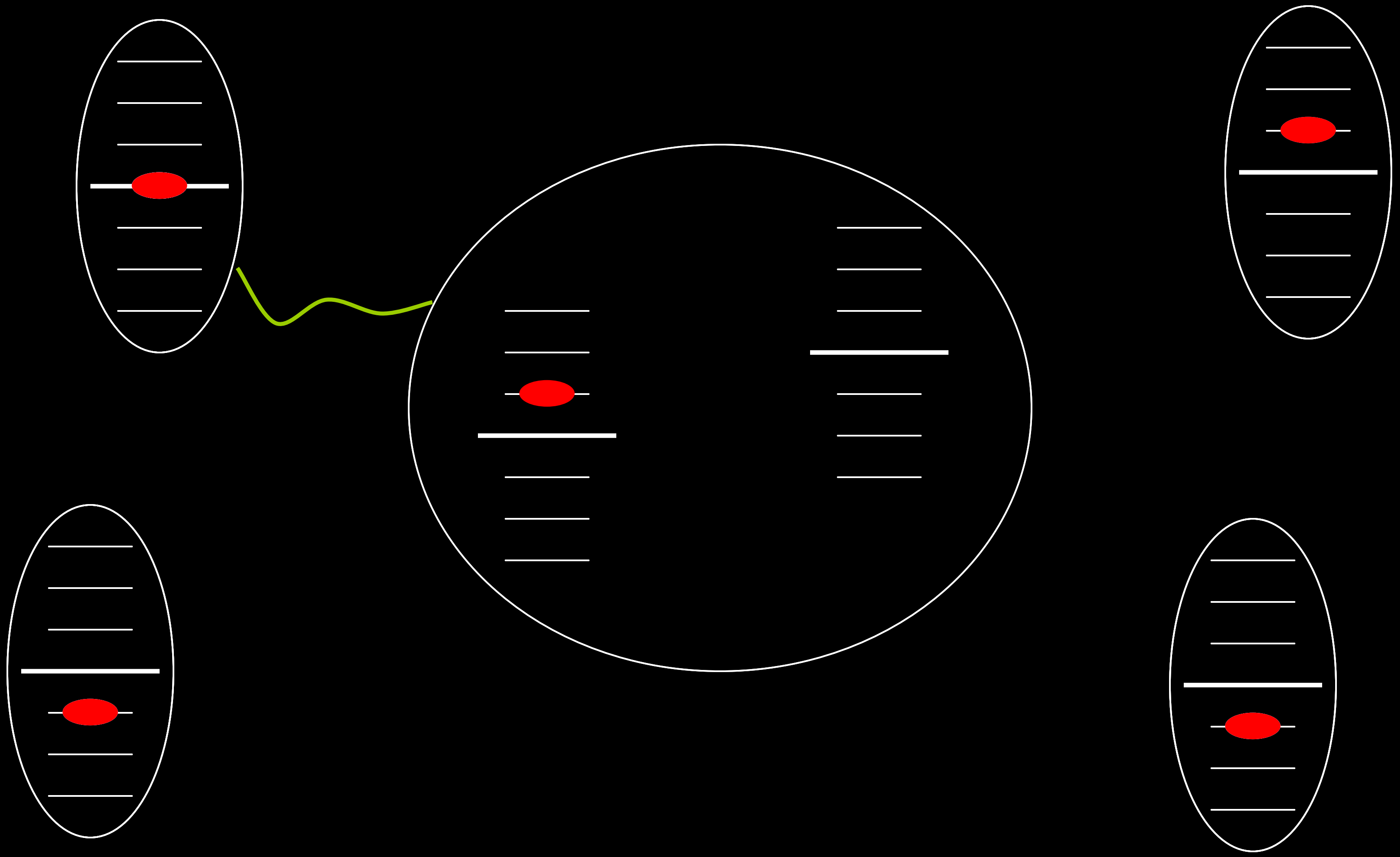
Nuclear flip-flops



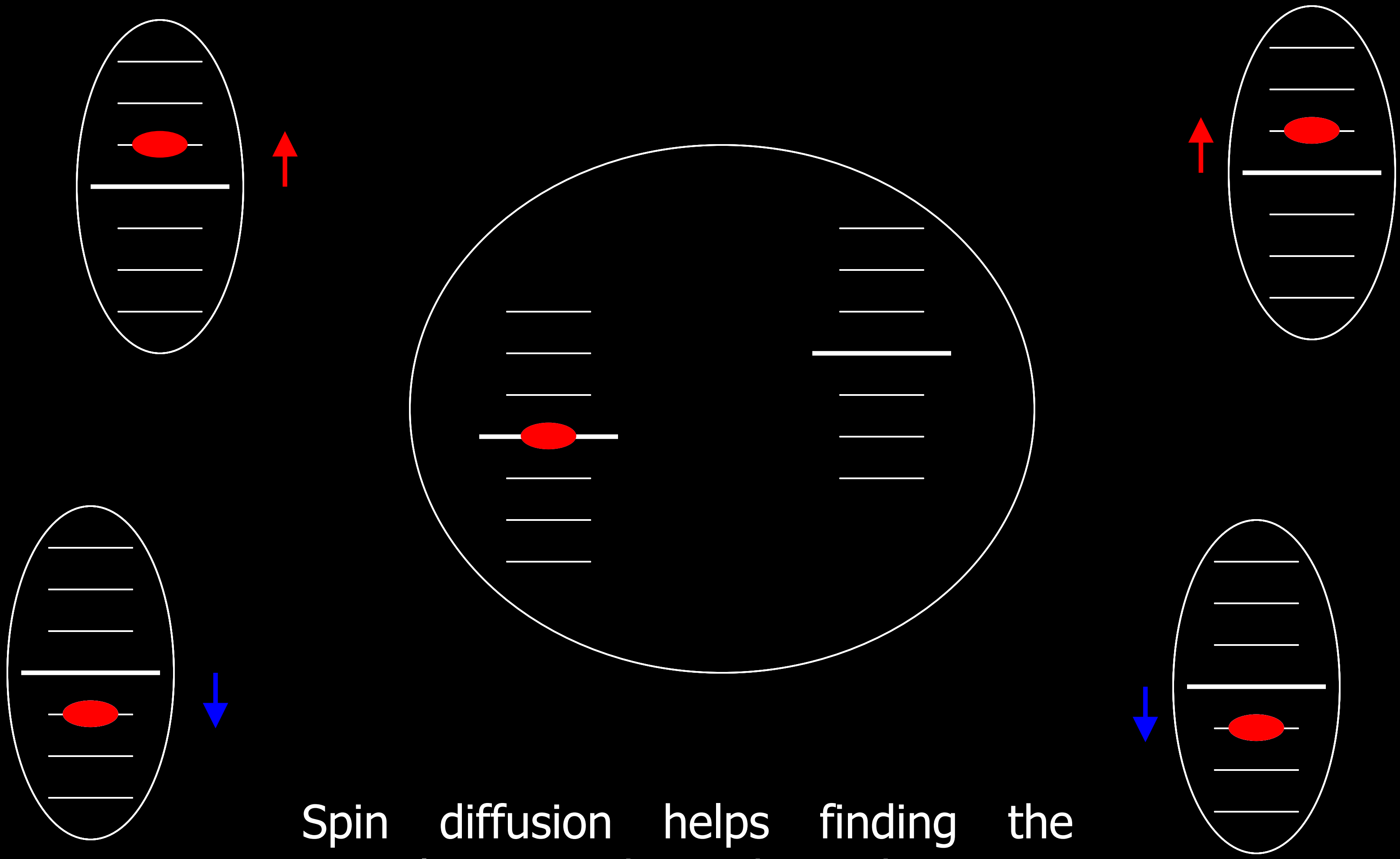
Nuclear flip-flops



Nuclear flip-flops

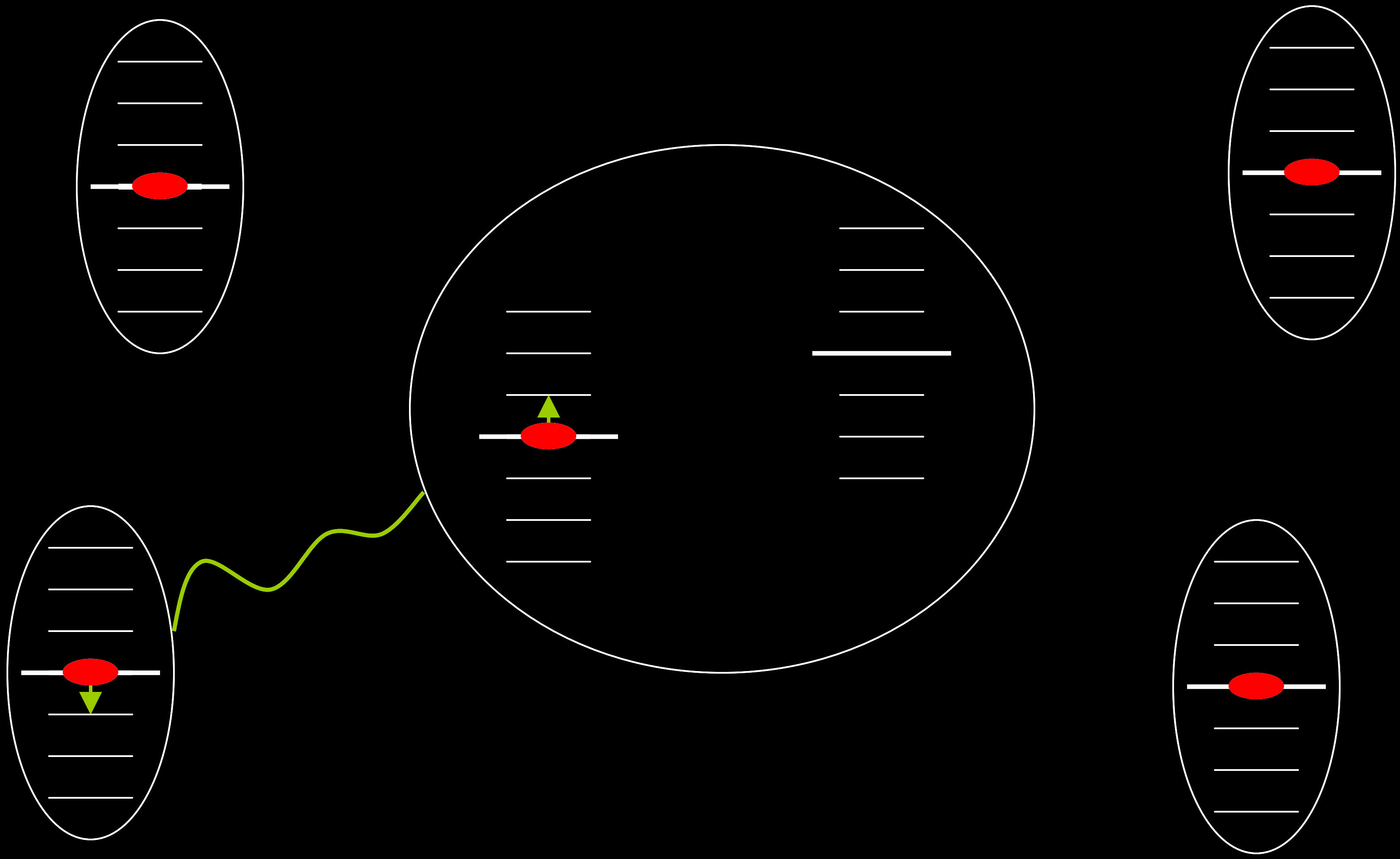


Nuclear flip-flops

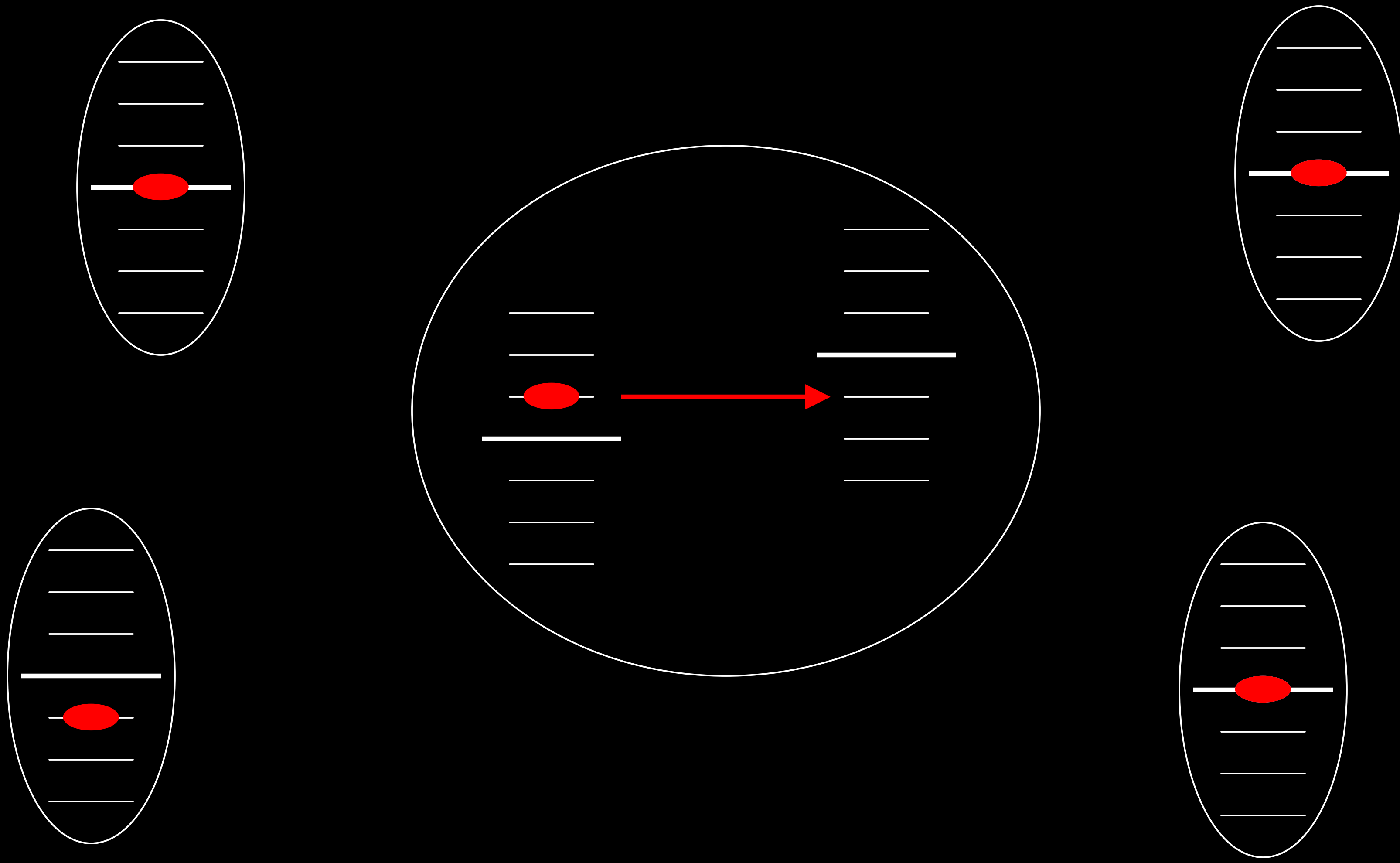


Spin diffusion helps finding the tunneling window, but does not change the total nuclear polarization

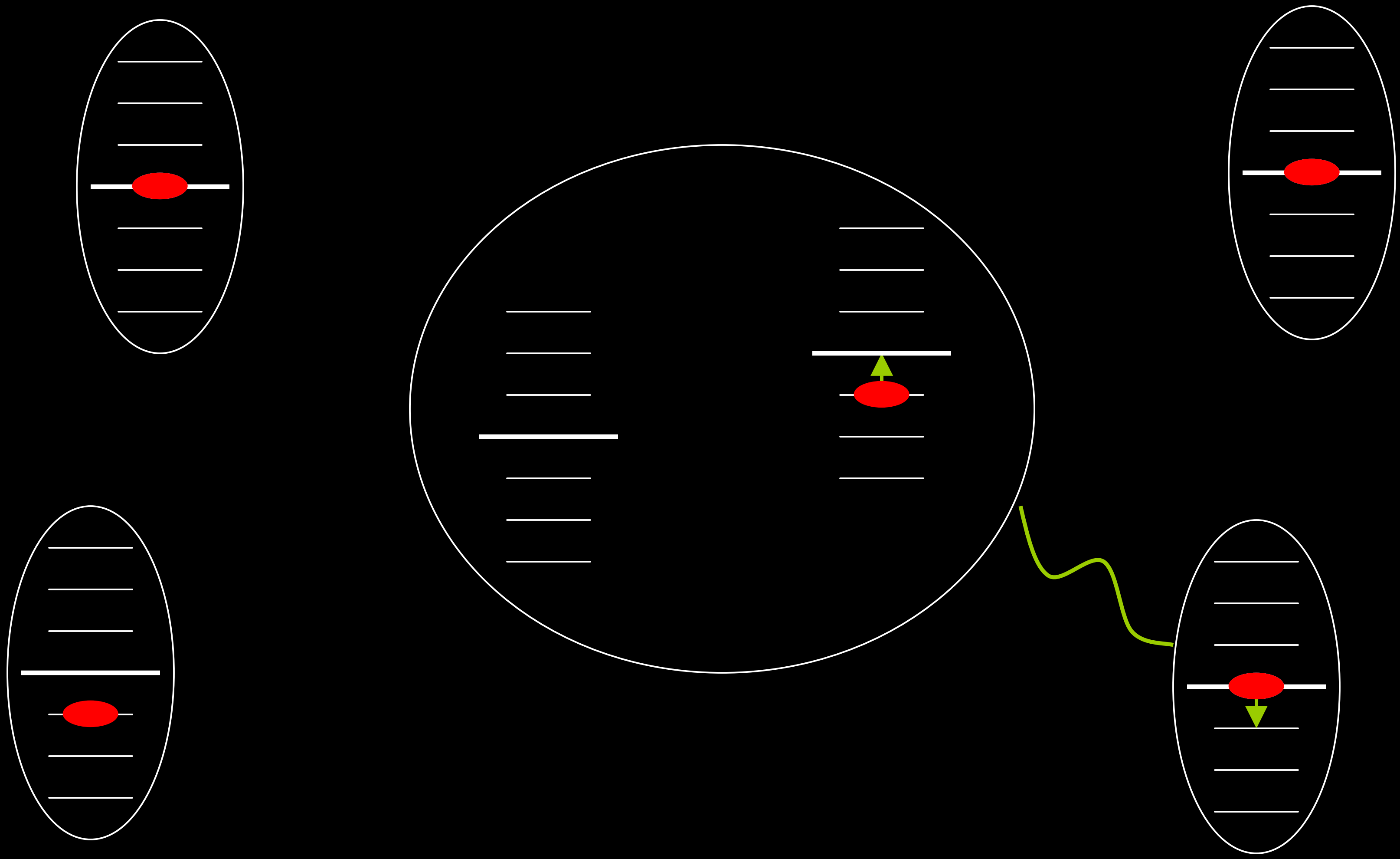
Spin-phonon interaction



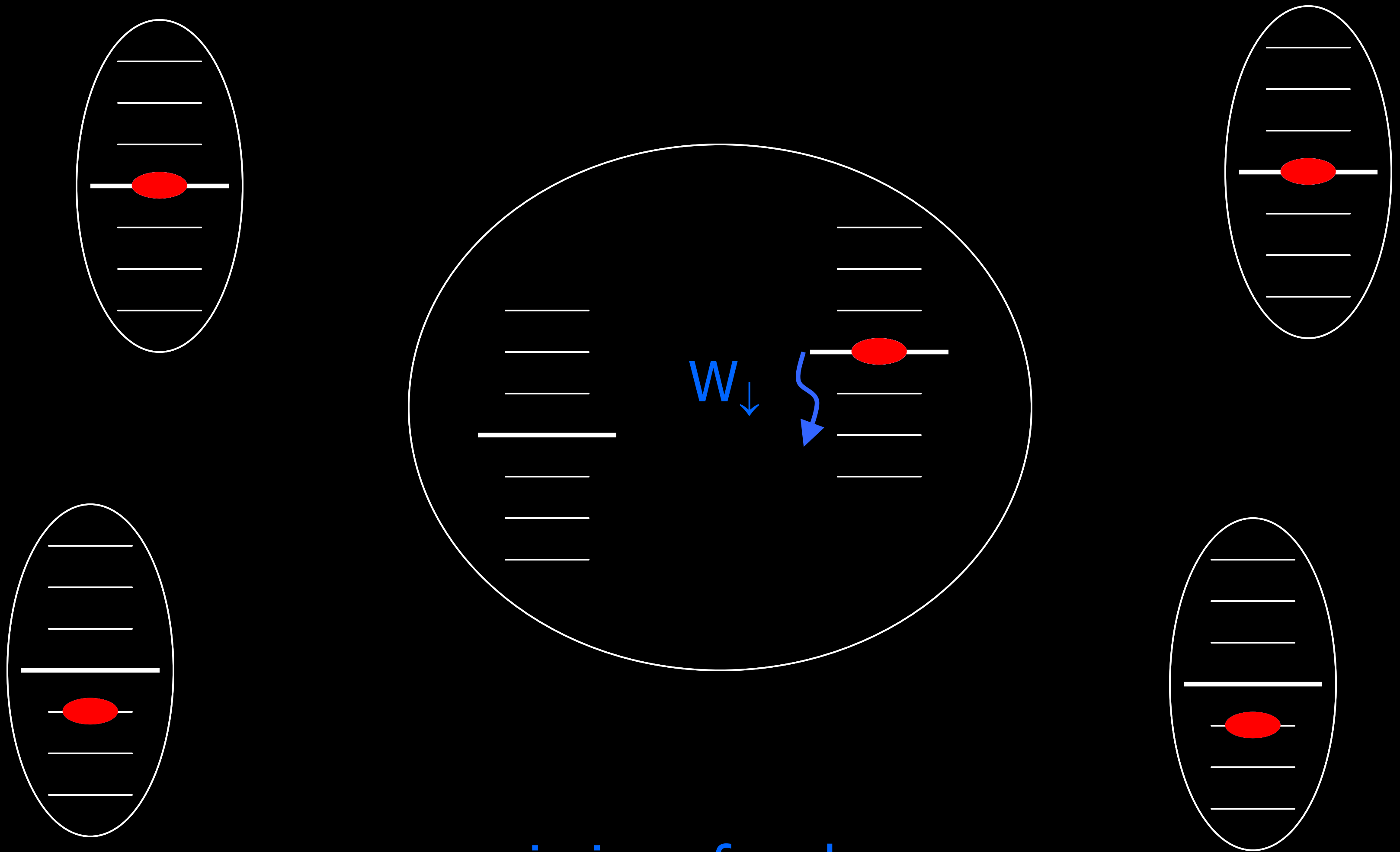
Spin-phonon interaction



Spin-phonon interaction

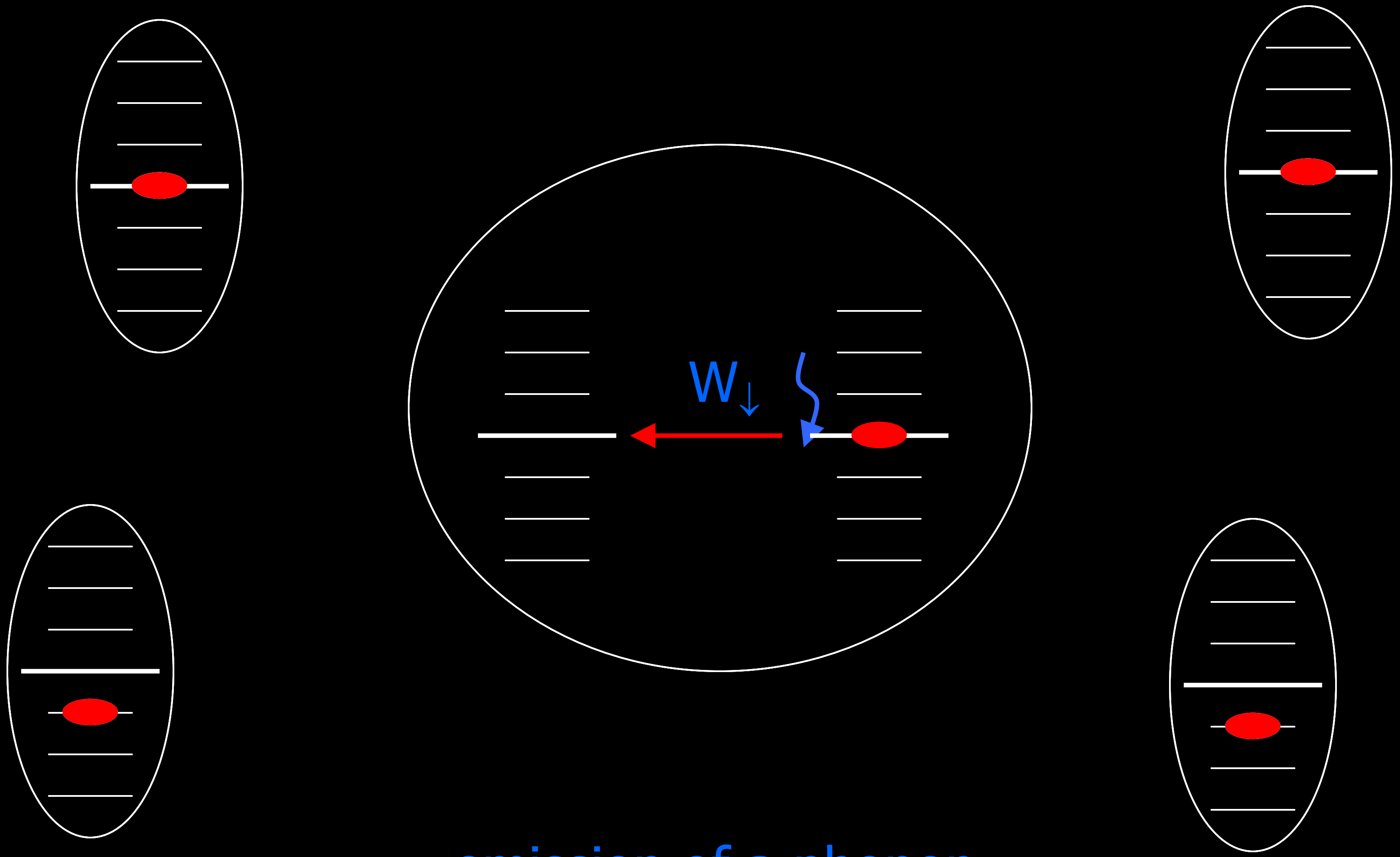


Spin-phonon interaction



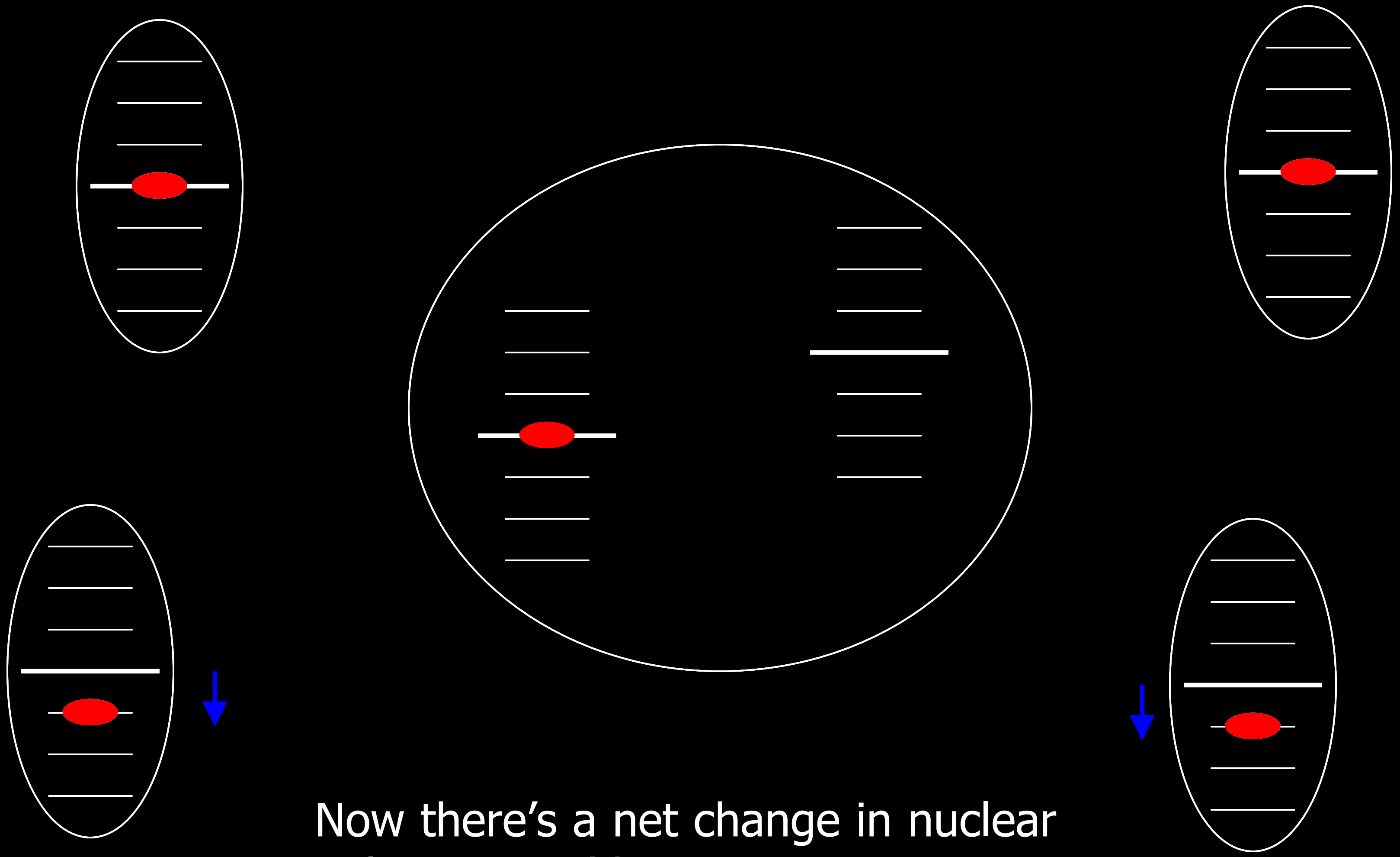
emission of a phonon

Spin-phonon interaction



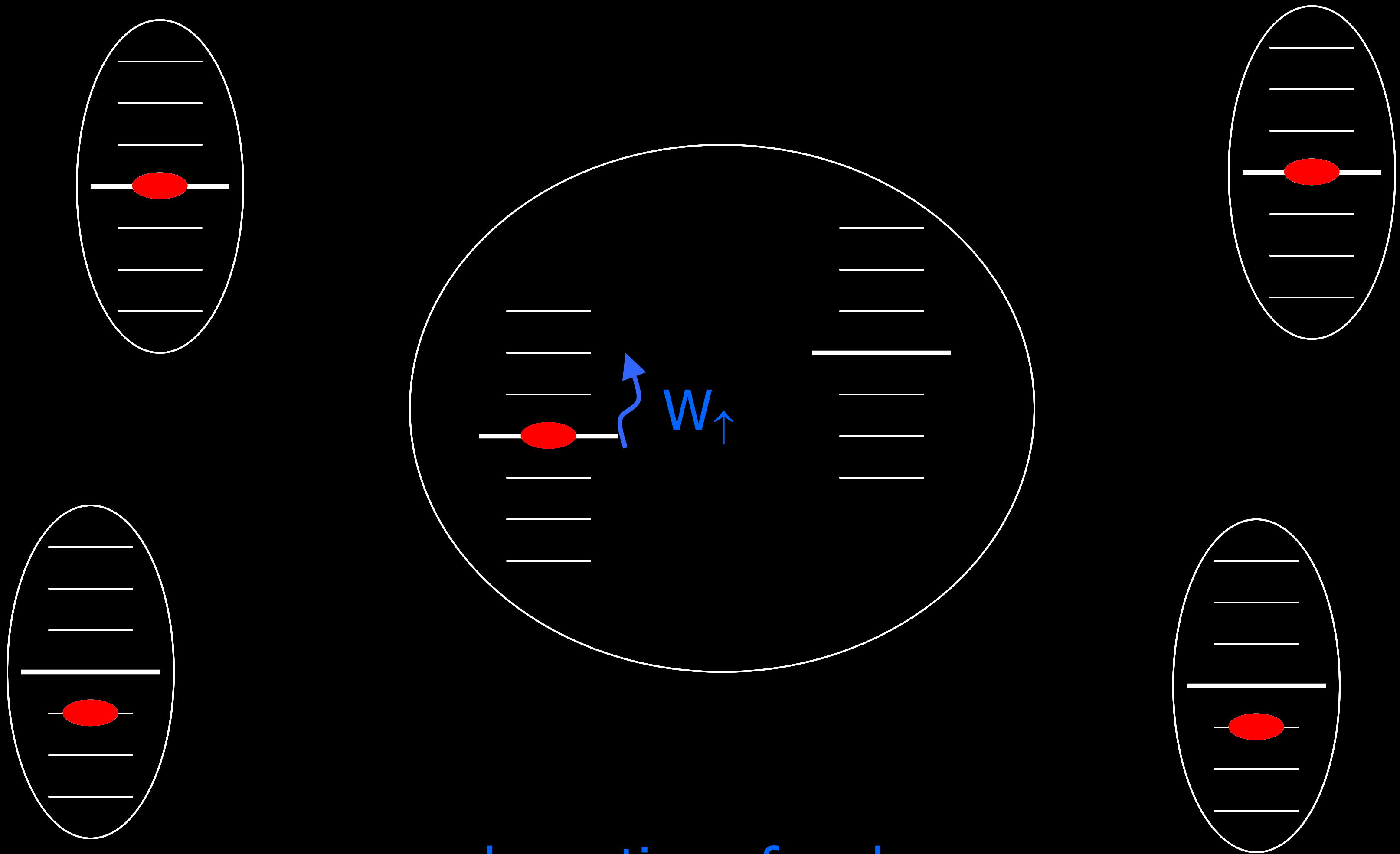
emission of a phonon

Spin-phonon interaction



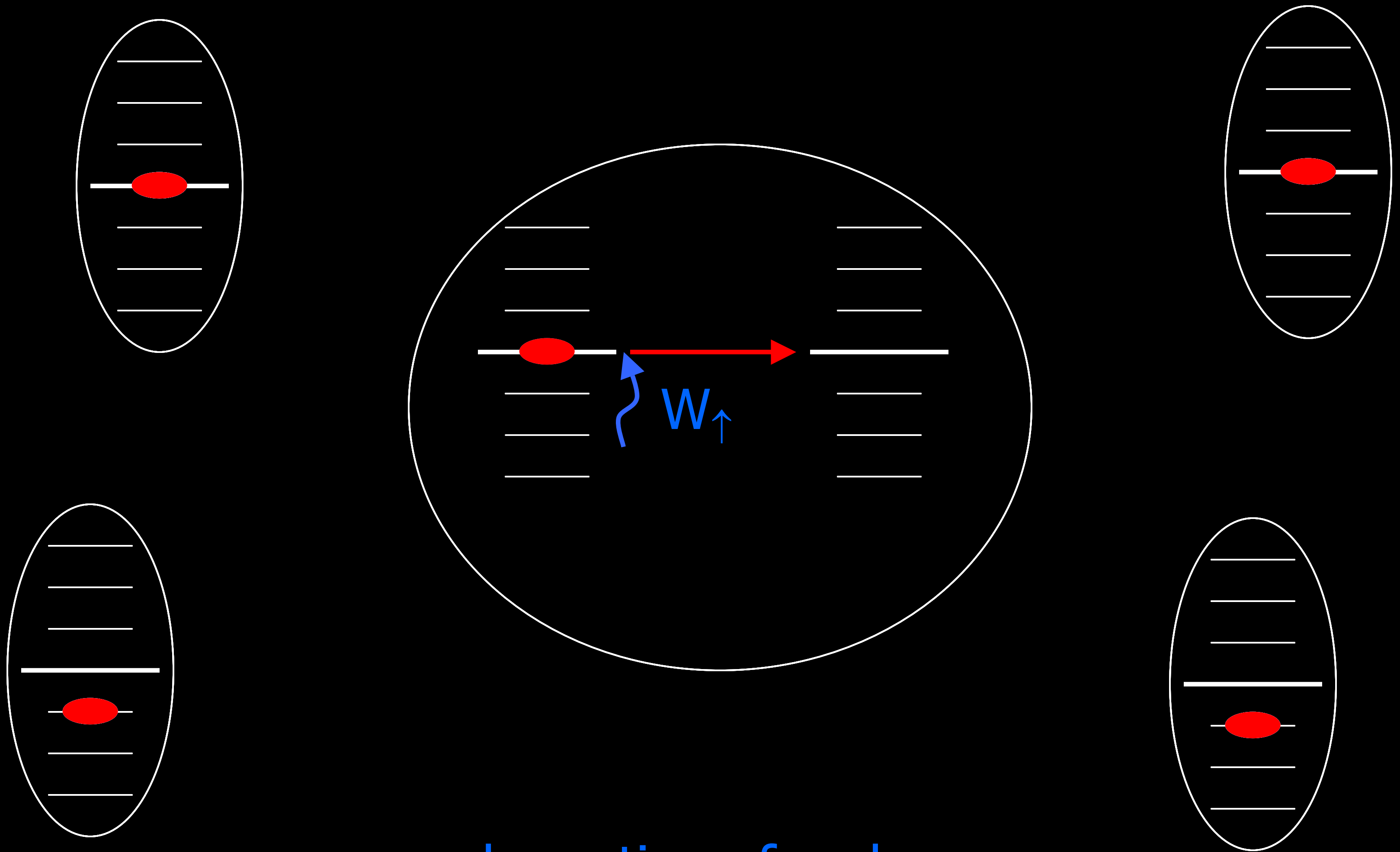
Now there's a net change in nuclear polarization (the spin temperature has been lowered!)

Spin-phonon interaction



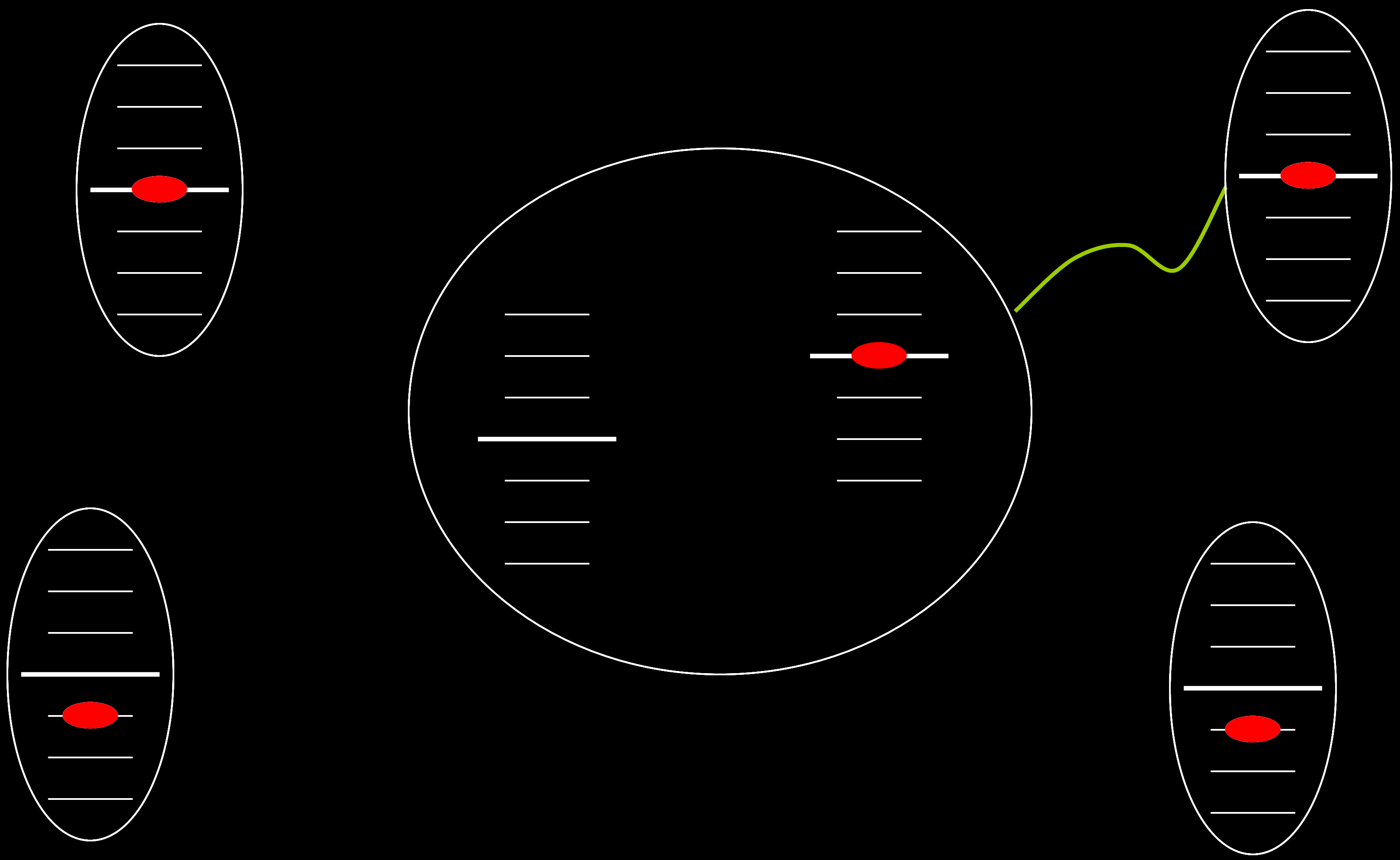
absorption of a phonon

Spin-phonon interaction

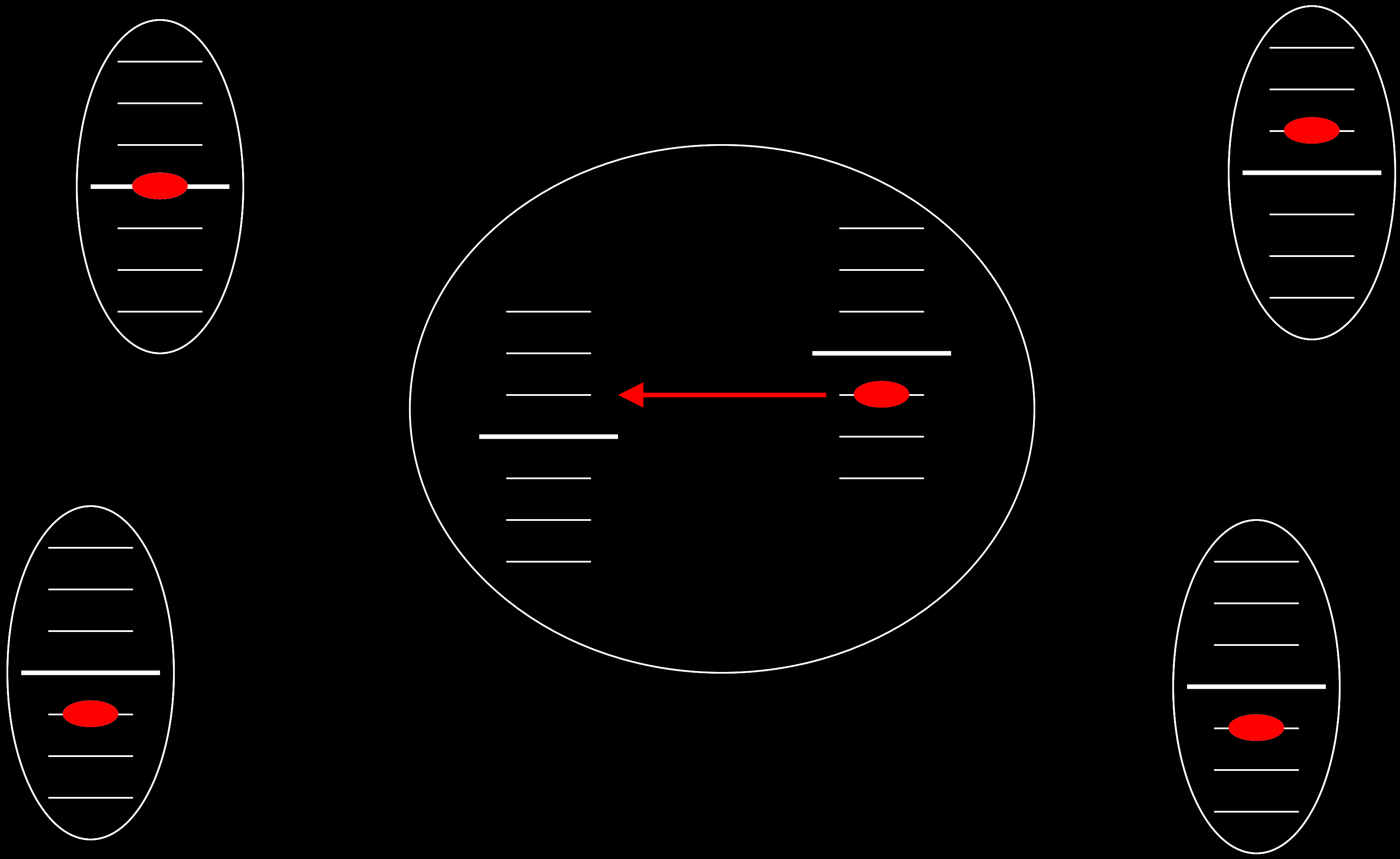


absorption of a phonon

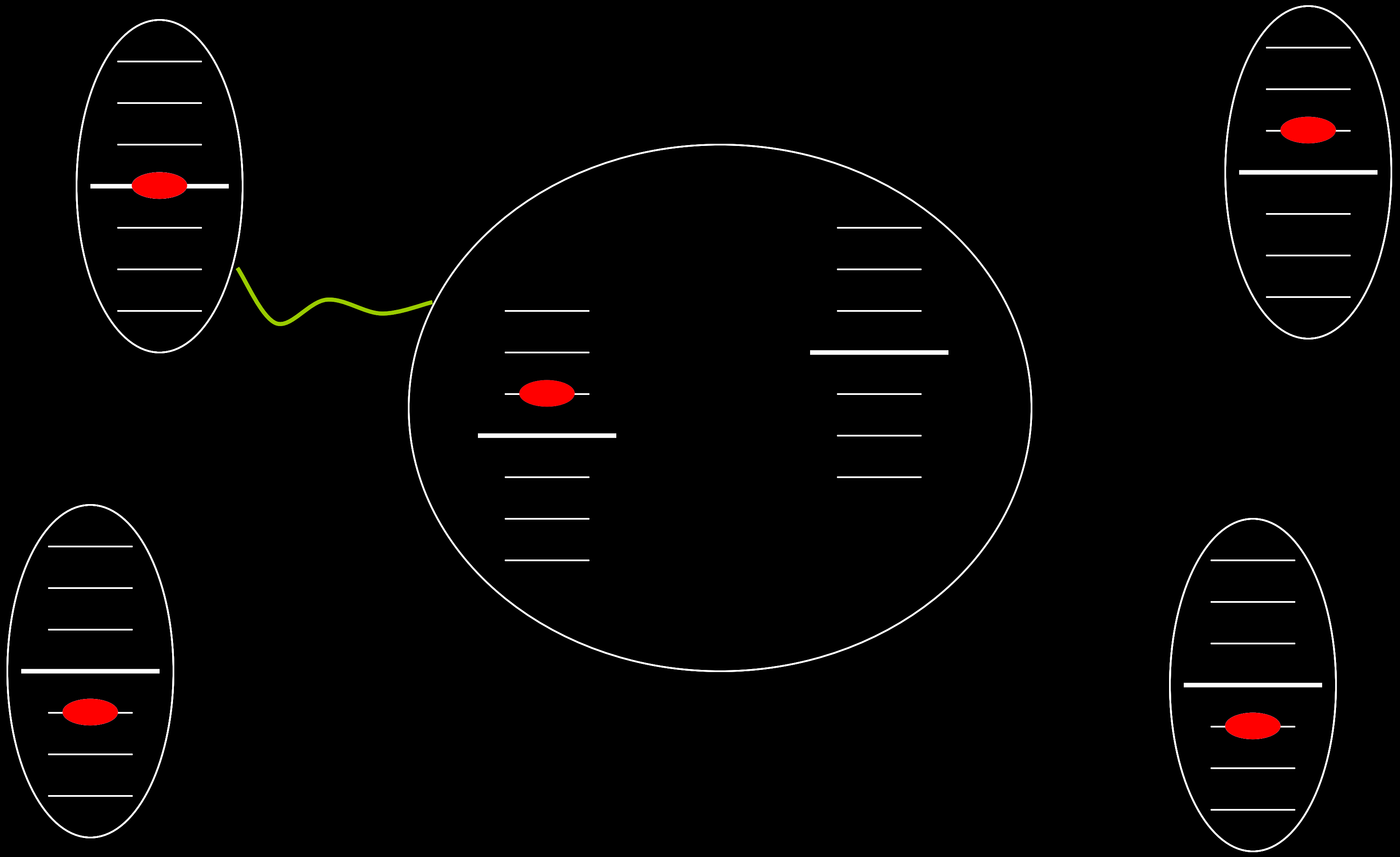
Spin-phonon interaction



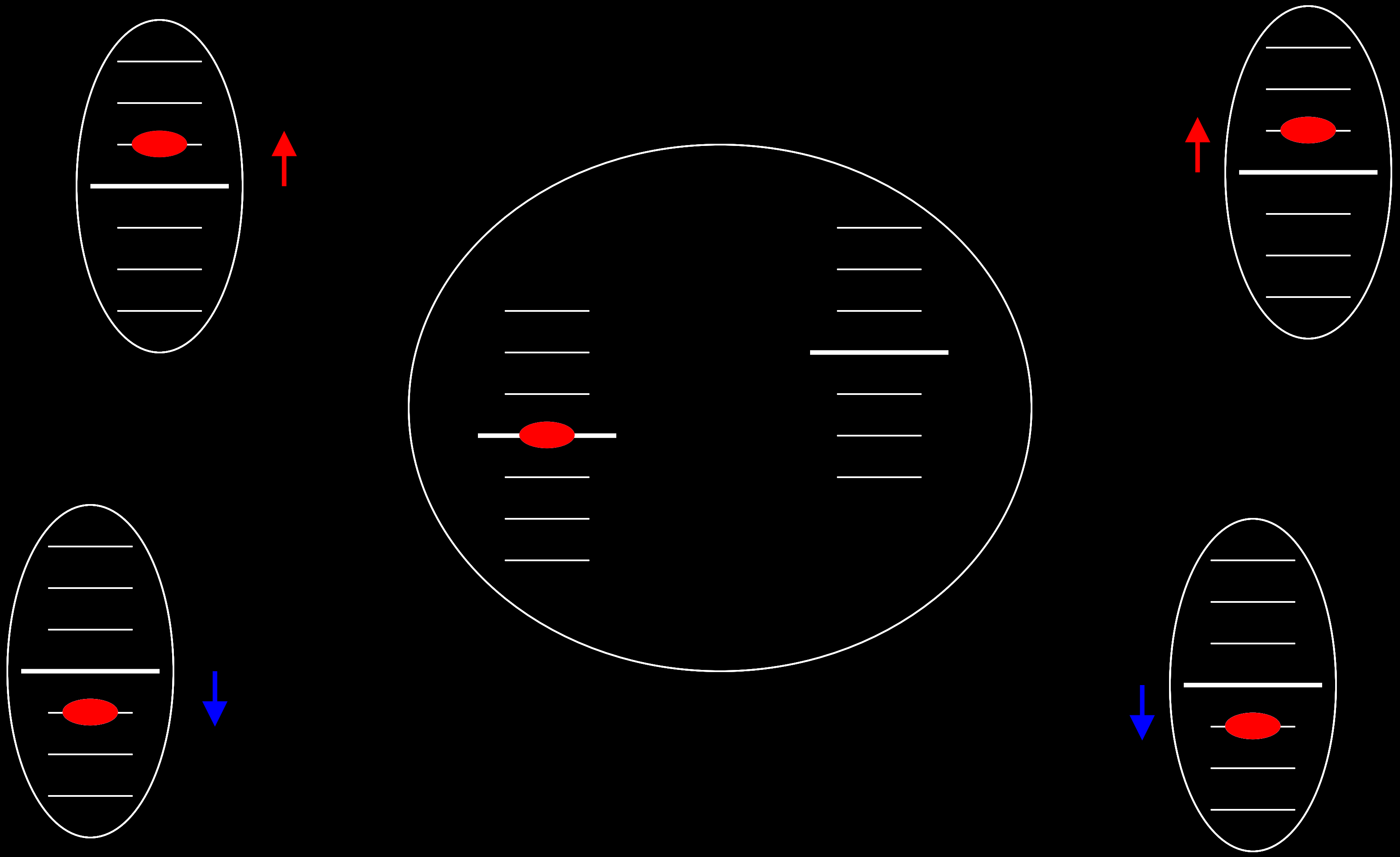
Spin-phonon interaction



Spin-phonon interaction

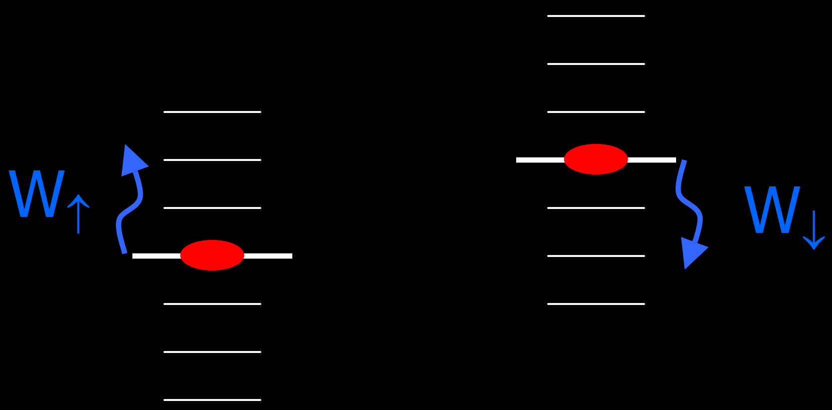


Spin-phonon interaction



Detailed balance

In this picture, it's easy to apply the condition of detailed balance to obtain the equilibrium nuclear polarization

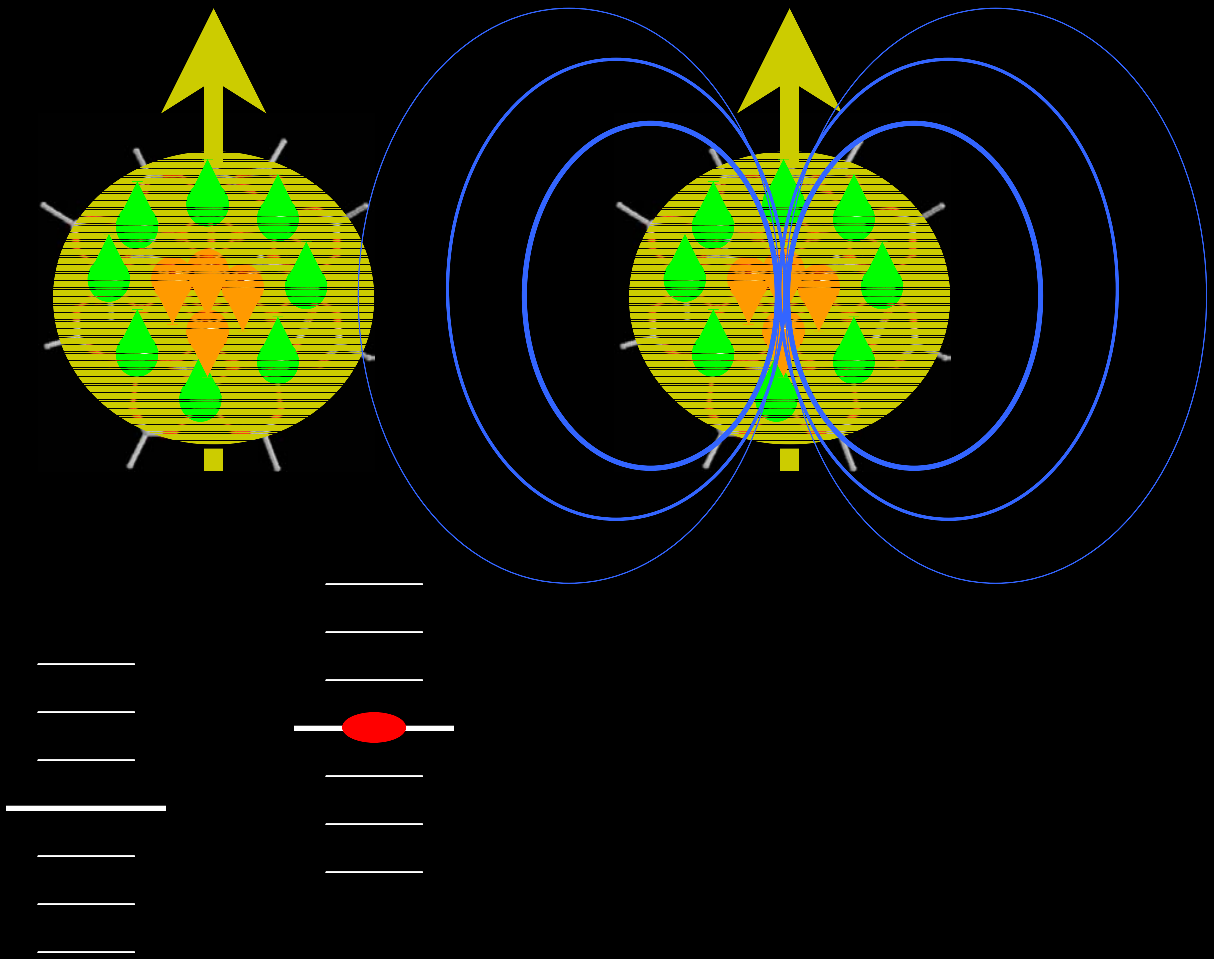


$$\frac{W_\uparrow}{W_\downarrow} = e^{-\Delta E/k_B T}$$

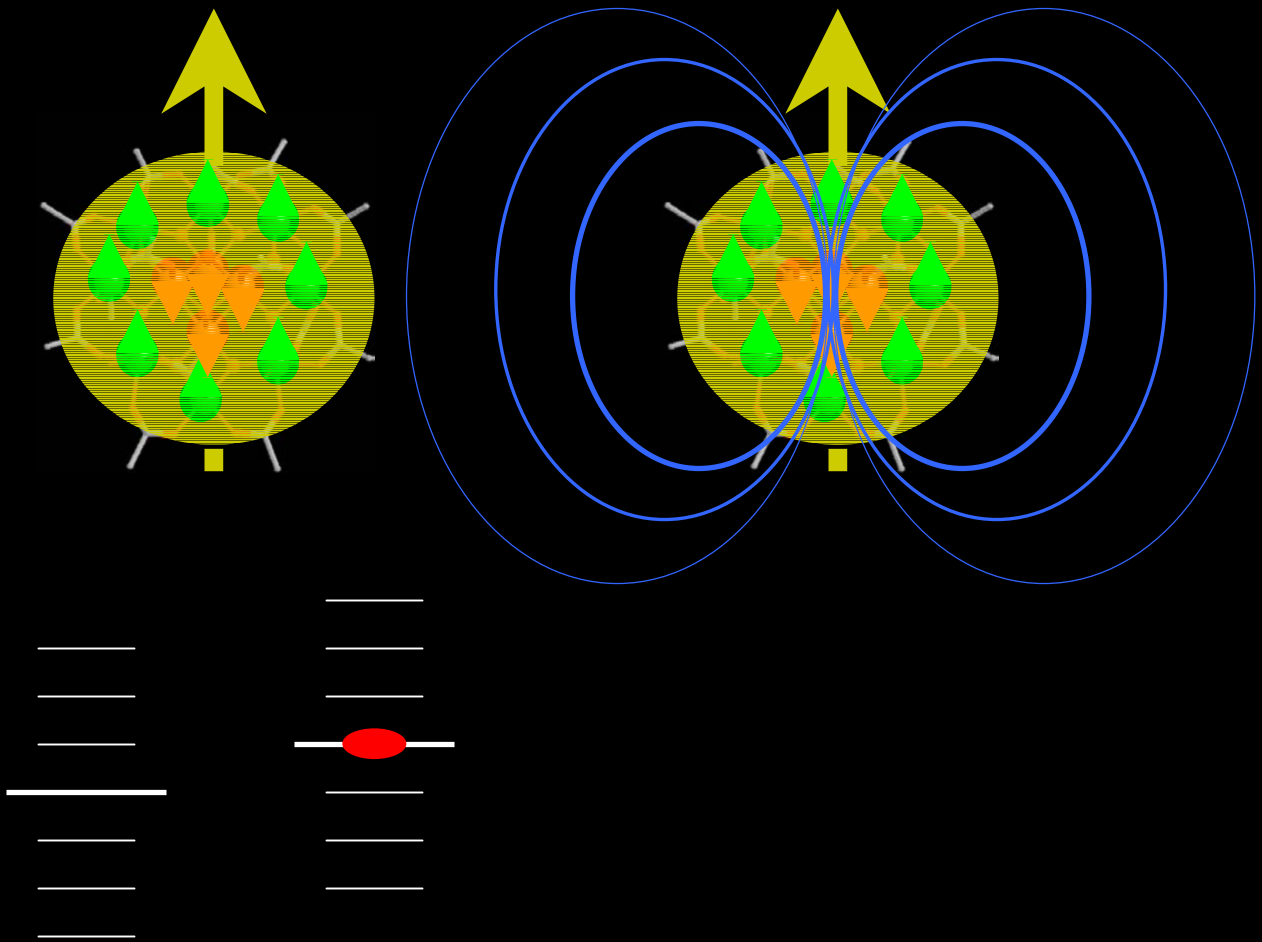
$$\Delta E = \hbar\omega_N \, \Delta M$$

How does the spin-phonon interaction work?
Does the dipolar bias play a special role?

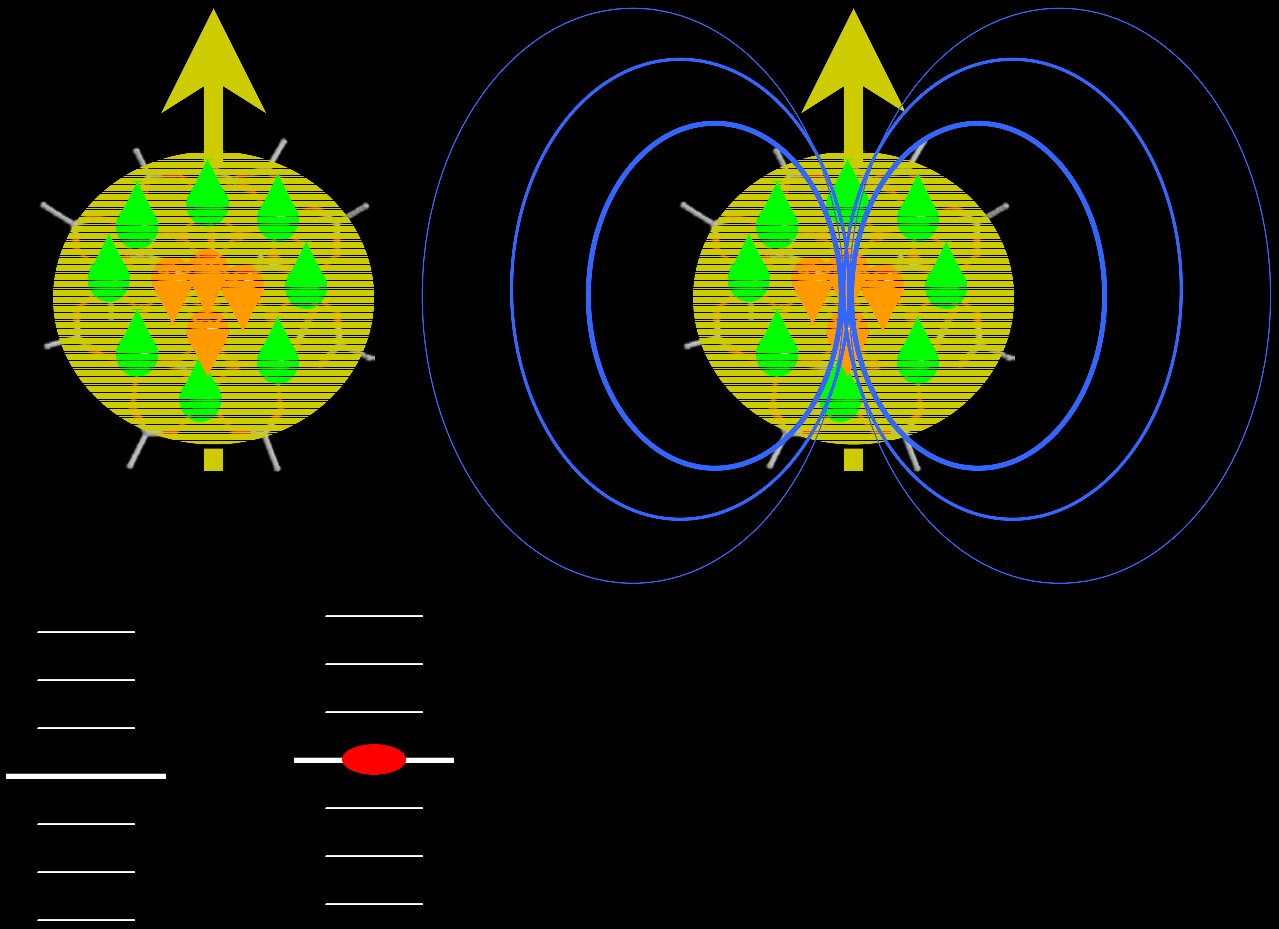
Modulation of dipolar bias



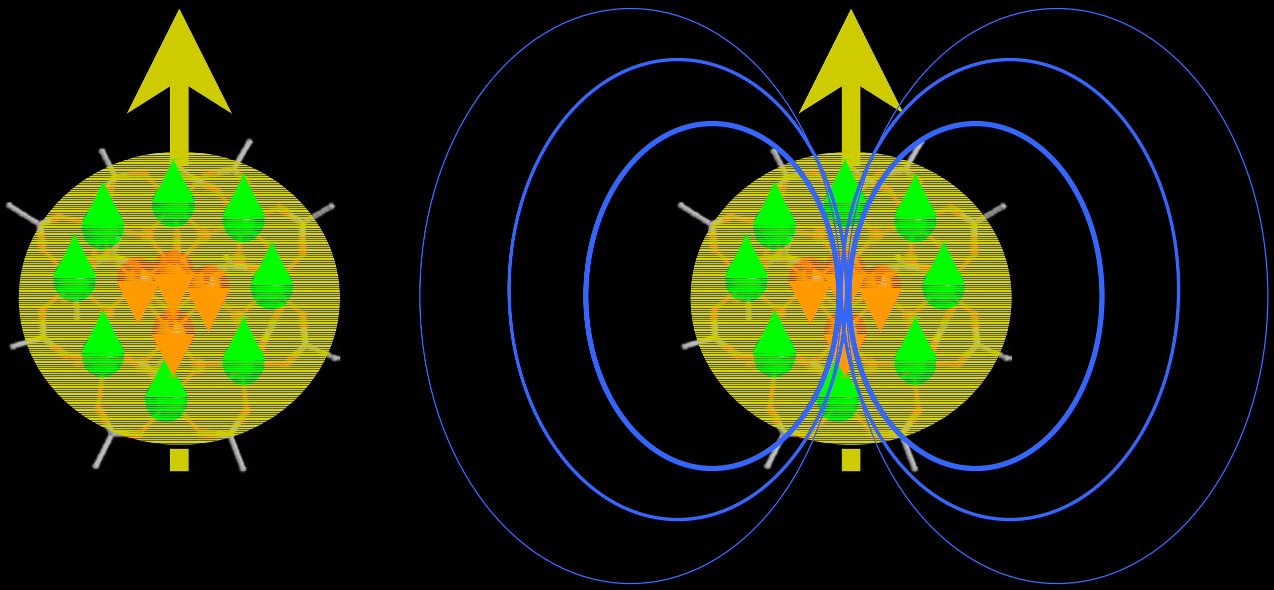
Modulation of dipolar bias

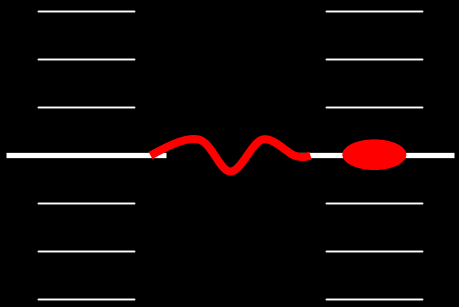


Modulation of dipolar bias

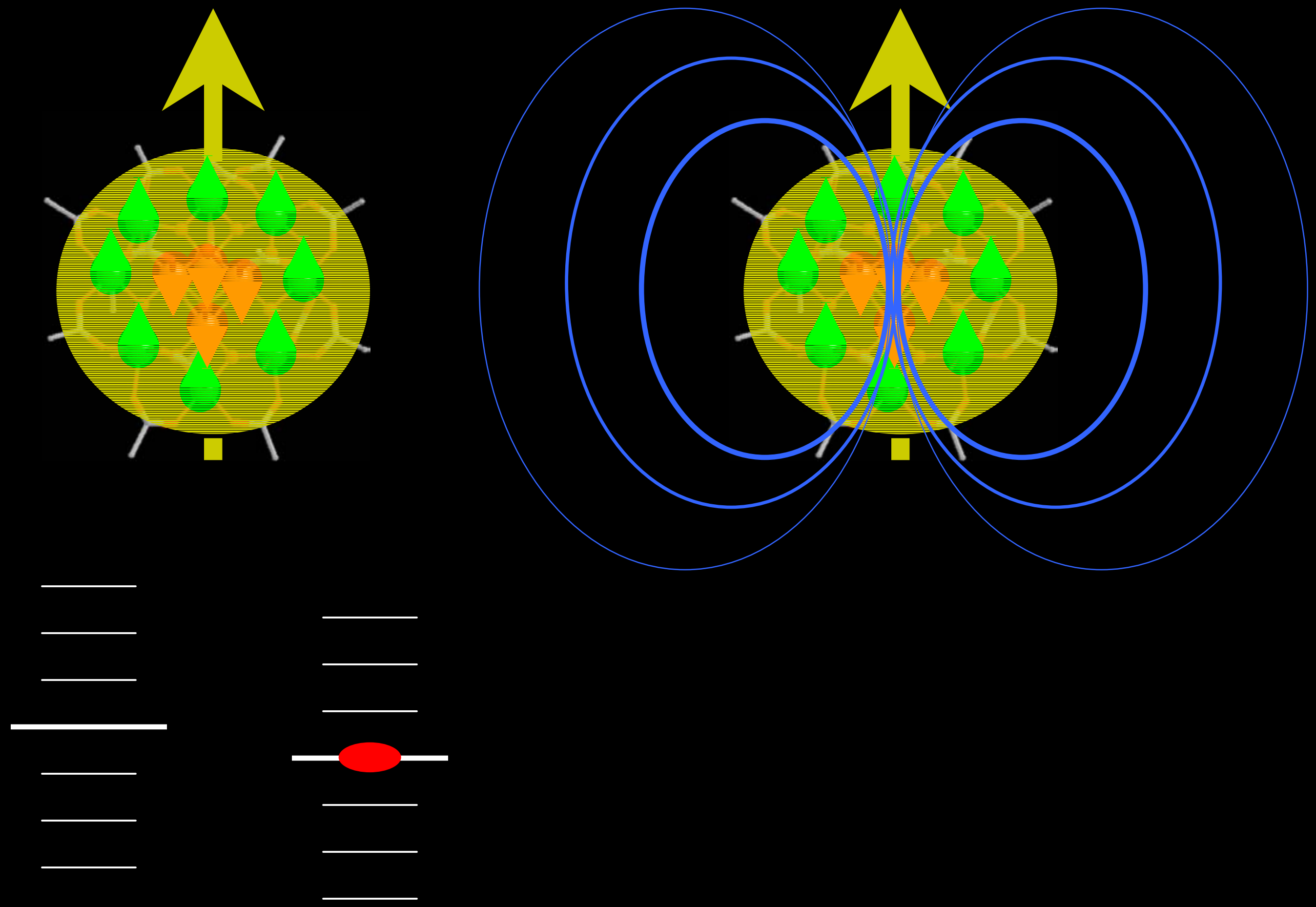


Modulation of dipolar bias

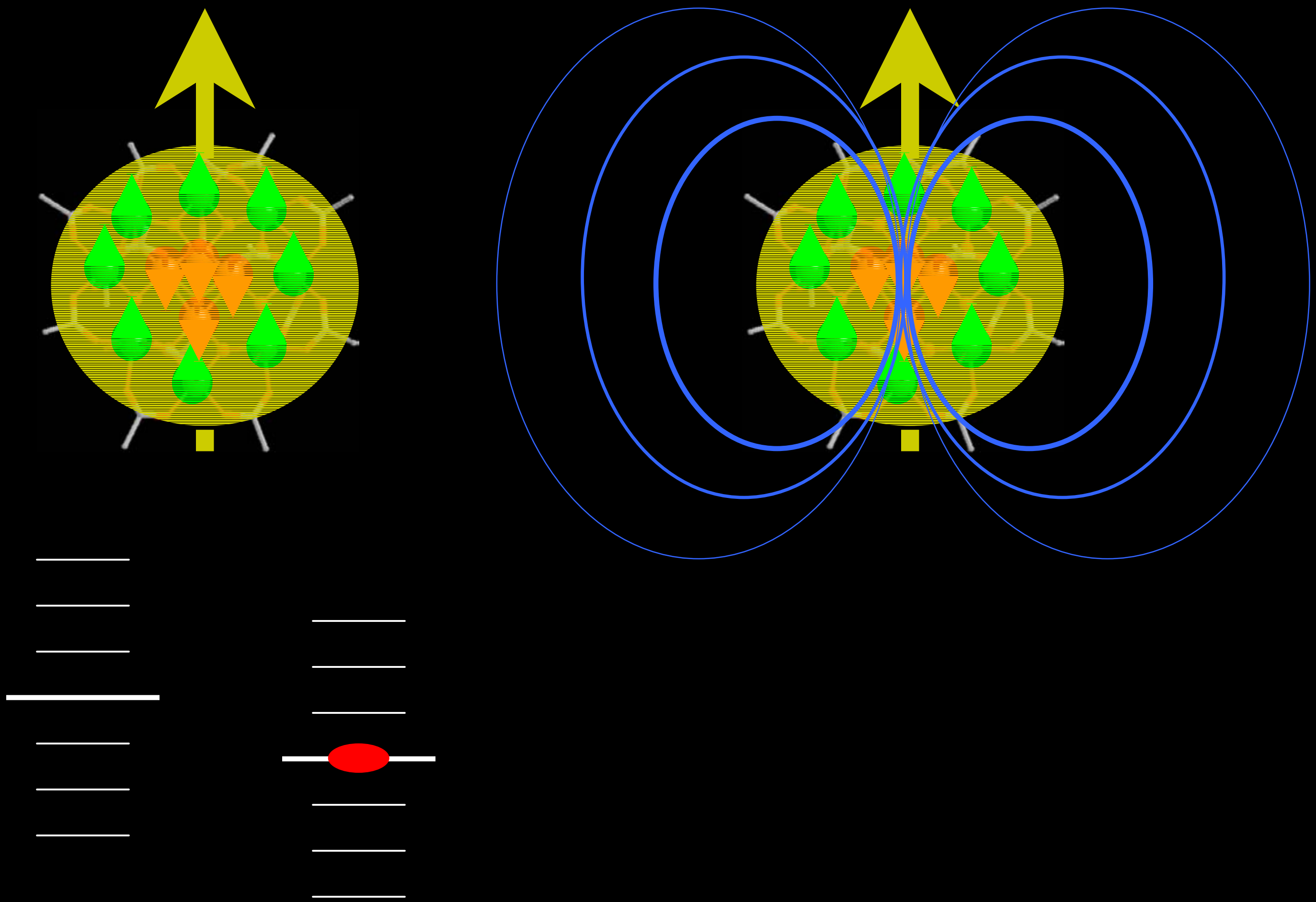




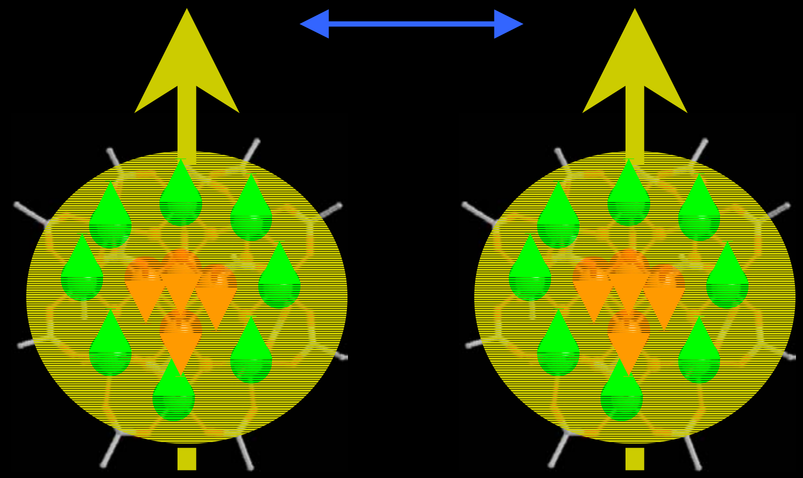
Modulation of dipolar bias



Modulation of dipolar bias

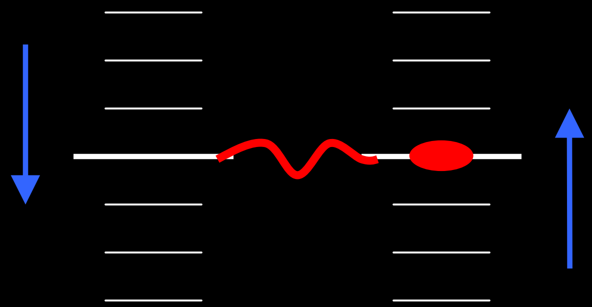


Waller + Landau-Zener



Modulation of dipolar field by phonons:
$\rightarrow$ Waller mechanism

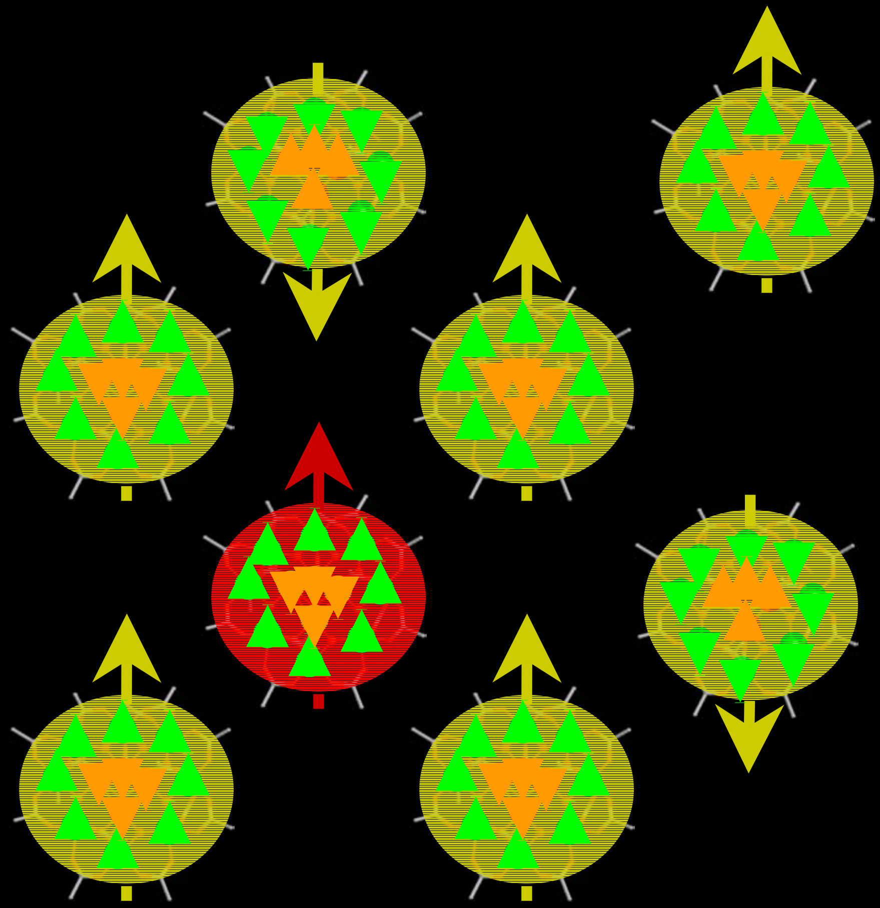
Due to the soft ligands,
$\Theta_D \sim 20$ K intercluster



Incoherent tunneling due to crossing through the resonance:
$\rightarrow$ Landau-Zener process

I. Waller, Z. phys. 79, 370 (1932)
C. Zener, Proc. R. Soc. London A 137, 696 (1932)

Tunneling-driven nuclear relaxation rate



x = fraction of fast-relaxing molecules

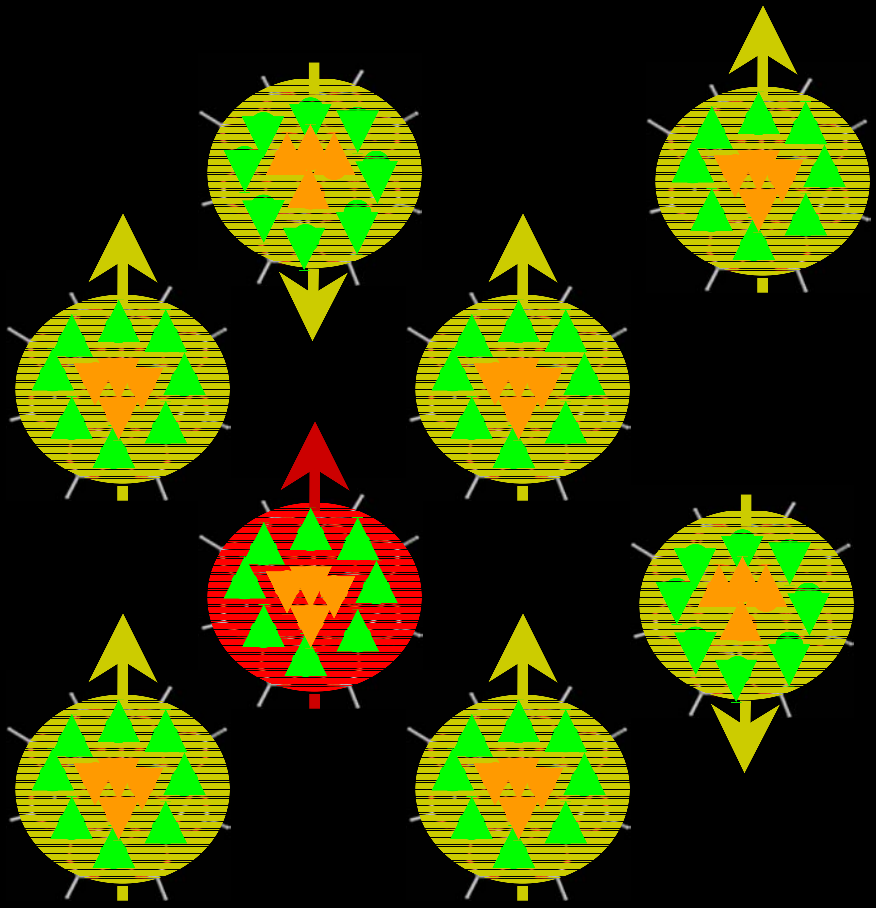
$$W = x\,\tau_T^{-1}$$

e.g.
$x = 0.01$ (1 %)
$W = 0.03\ s^{-1} \Rightarrow \tau_T^{-1} = 3\ s^{-1}$

realistic for the molceules with two flipped J-T axes and 15 K barrier

A. Morello, cond-mat/0404049 (2004)

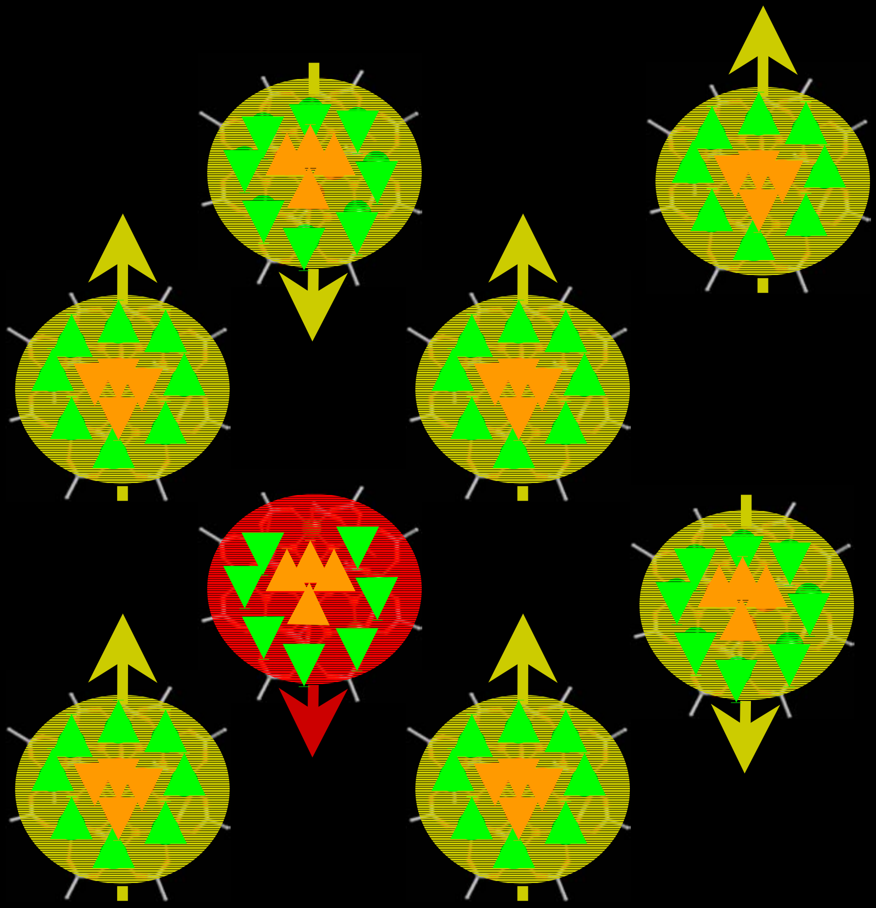
Complete description of the system



Including:

- incoherent tunneling dynamics provided by **fast-relaxing molecules**

Complete description of the system



Including:

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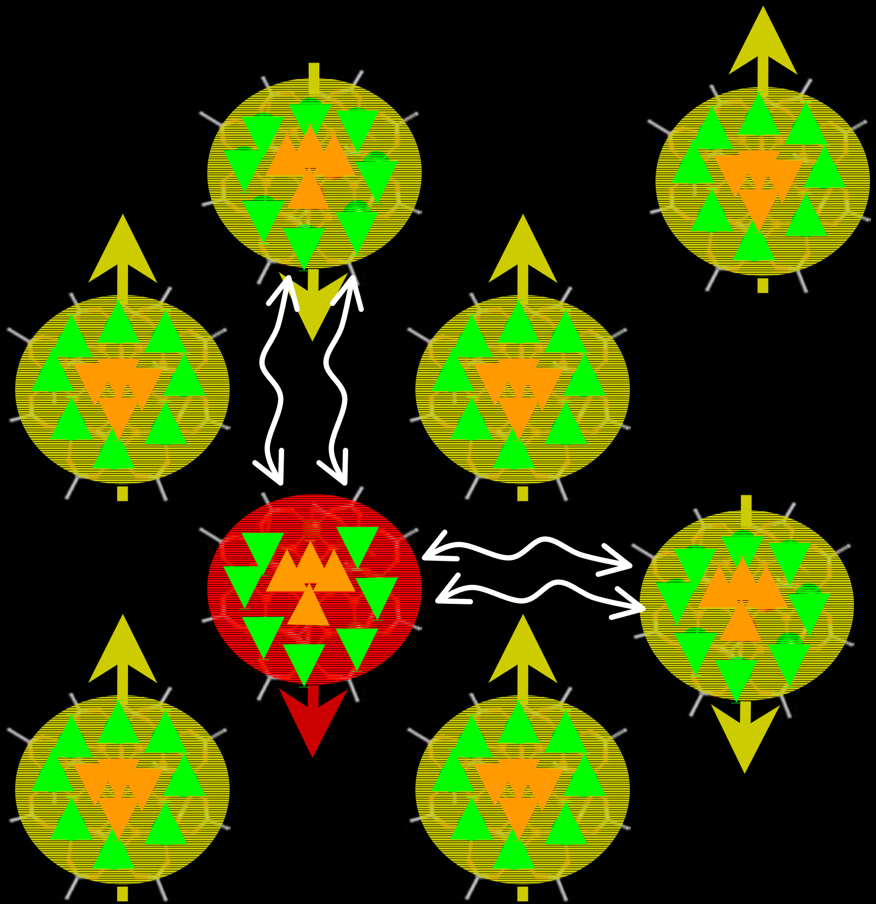
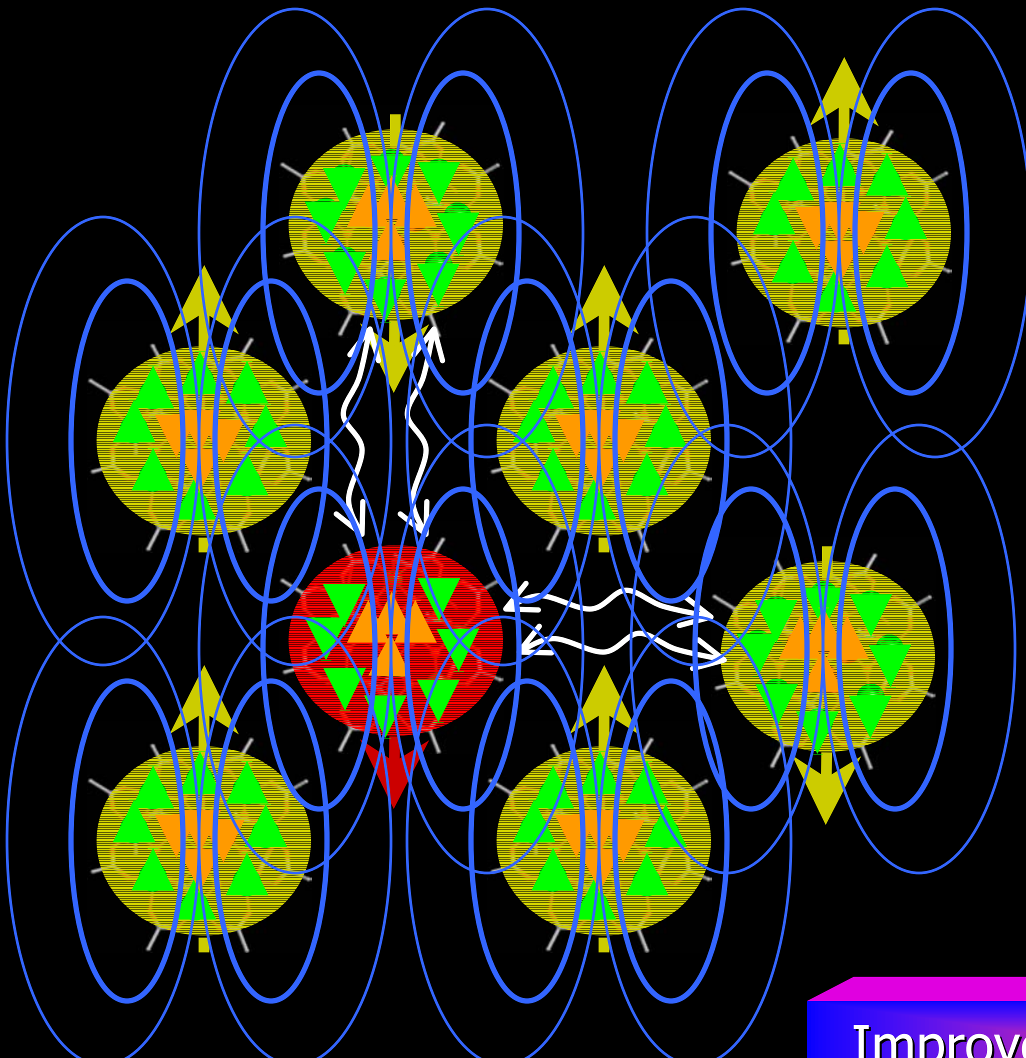
Complete description of the system



Including:

- incoherent tunneling dynamics provided by **fast-relaxing molecules**
- Whole spin system relaxed by **intercluster nuclear spin diffusion**

Complete description of the system



Including:

- incoherent tunneling dynamics provided by **fast-relaxing molecules**
- Whole spin system relaxed by **intercluster nuclear spin diffusion**
- thermal equilibrium with the lattice mediated by **modulation of the dipolar bias due to low-energy phonons**

Improved description of the interaction "quantum spin – spin bath"

A. Morello et al., PRL 93, 197202 (2004)

Conclusions

The nuclear spins in Mn_{12}-ac can be relaxed by quantum tunneling fluctuations of the electron spin

Spin diffusion between nuclei in neighboring molecules is essential, and has been directly observed

The nuclear spin system remains in thermal equilibrium with the lattice

We propose a complete model of the coupled system "quantum spin + spin bath"

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