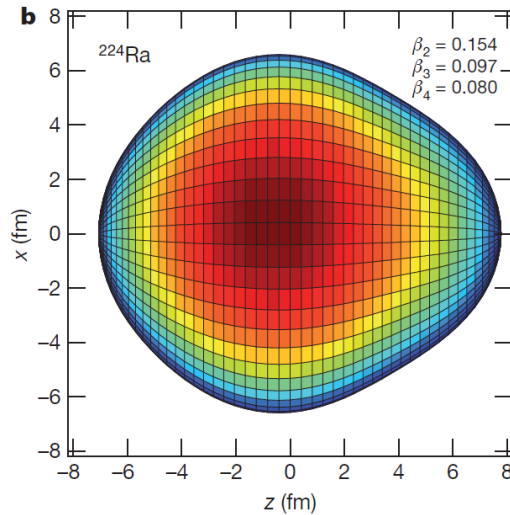
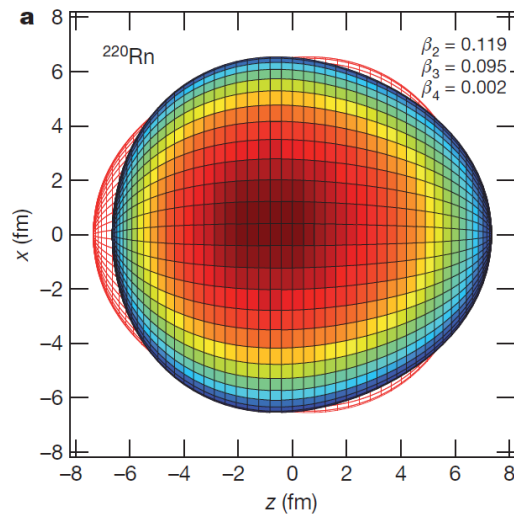
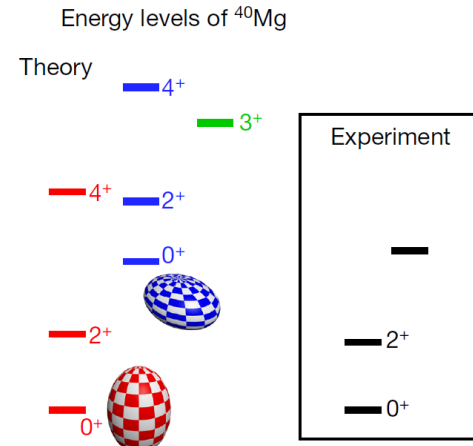




<https://doi.org/10.1038/nature12073>



DOI: 10.1038/s41586-020-2848-x

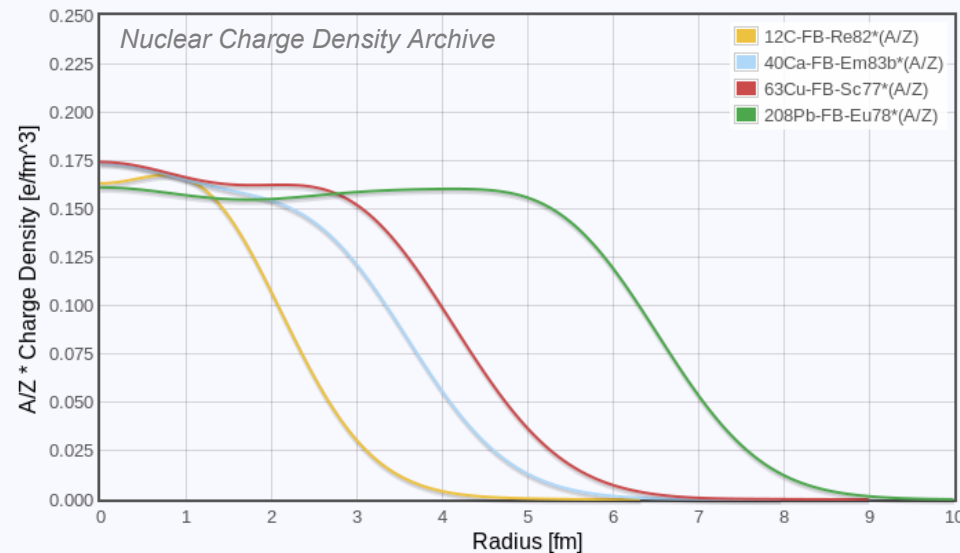
What goes on inside the nucleus?

*origins of nuclear magnetogyric ratio
and nuclear quadrupole moment*

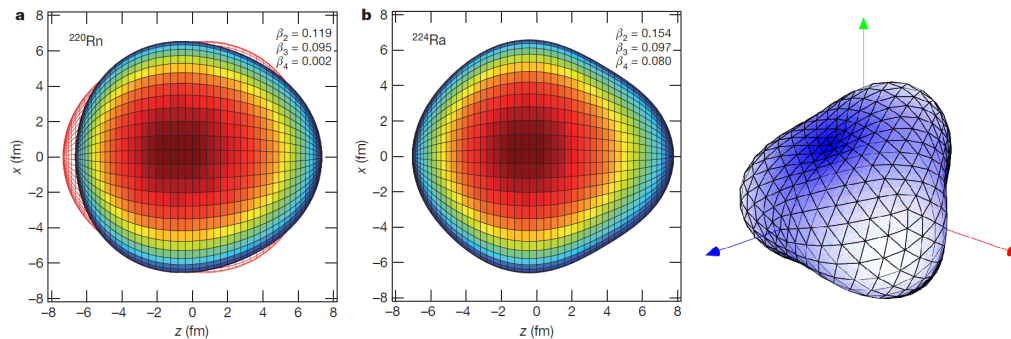
Ilya Kuprov, Weizmann Institute of Science

Wild and wonderful nuclear structure

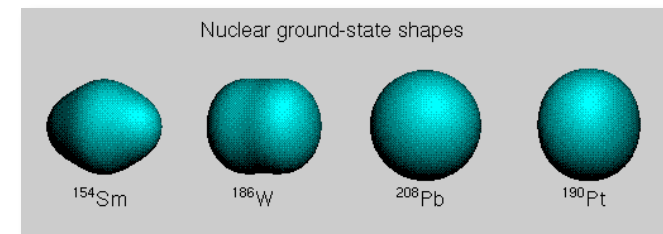
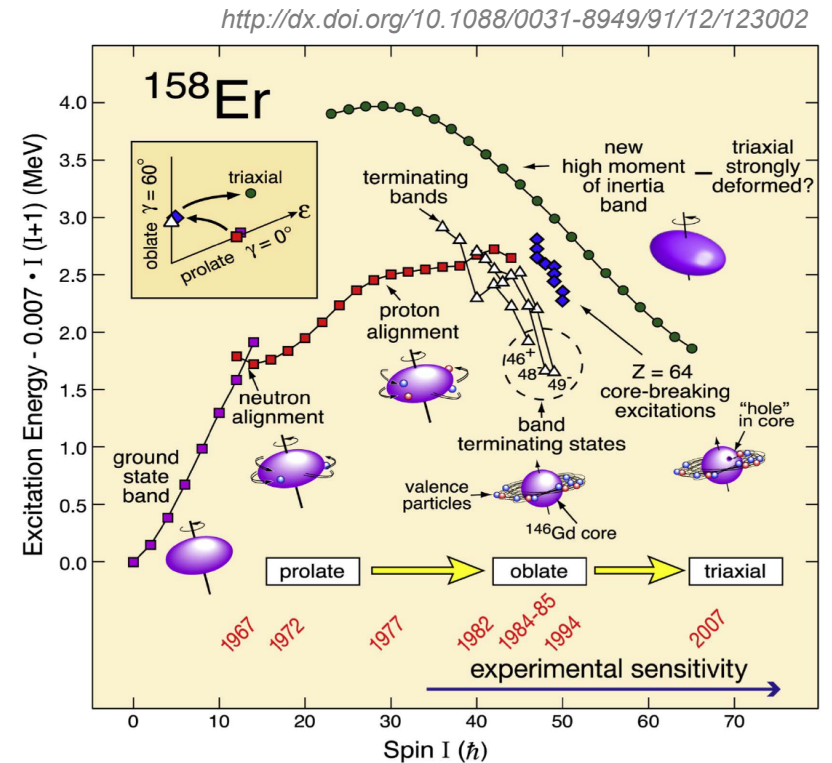
Nuclei have a diffuse surface:



Nuclei come in a variety of shapes:



Nuclei can be spun up and down:



Flashback: electron in a hydrogen atom

Stage 1: centre of mass transformation to expose a centre-symmetric potential

$$\hat{H} = -\frac{\hbar^2}{2m_1}\Delta_{\vec{r}_1} - \frac{\hbar^2}{2m_2}\Delta_{\vec{r}_2} - \frac{e^2}{4\pi\epsilon_0|\vec{r}_2 - \vec{r}_1|} \xrightarrow{\text{centre of mass frame}} \hat{H} = [\dots] - \frac{\hbar^2}{2\mu}\Delta_{\vec{r}} - \frac{e^2}{4\pi\epsilon_0|\vec{r}|}$$

kinetic energy Coulomb potential reduced mass electron position

Stage 2: radial and angular variable separation

$$\psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi)$$

angular part
radial part

$$\Delta = \underbrace{\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)}_{\text{radial part, system-specific}} + \underbrace{\frac{1}{r^2} \left\{ \frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\}}_{\text{angular part, same for all centre symmetric systems}}$$

$$\left\{ \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} R(r) \right) + \frac{2\mu r^2}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R(r) \right\} = a R(r)$$

$$\left\{ \frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} Y_{lm}(\theta, \varphi) = -l(l+1) Y_{lm}(\theta, \varphi)$$

standard orbital classification

► Orbital quantum number (s, p, d, f, ...) classification is a general feature of spherical symmetry.

Strong nuclear force

- Range: ~1 femtometre (10^{-15} m)
- Amplitude: ~100 times stronger than electromagnetic
- Origin: a residuum of the strong force between quarks
- Potential: unknown; mathematically, it must exist
- Symmetry: not unlikely to be centre symmetric

Single-nucleon Schrödinger equation:

$$\hat{H} = \hat{T} + \hat{U} = \frac{\hat{p}^2}{2m} + V_{\text{MF}}(r) = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{MF}}(r)$$

kinetic energy

centre symmetric
mean-field potential

Radial part after variable separation:

orbital quantum number

$$\hat{H}_{\text{R}} = -\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{l(l+1)}{r^2} \right] + V_{\text{MF}}(r)$$

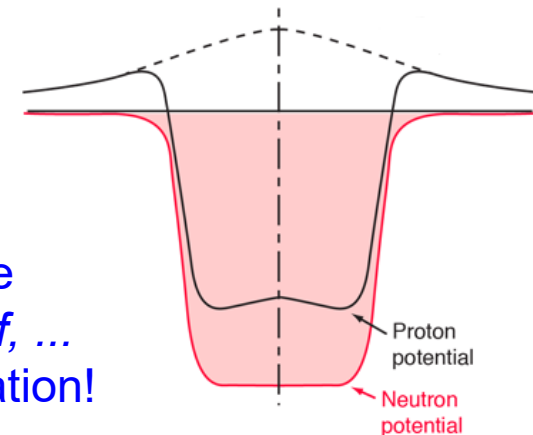
Strategy: postulate a potential and look for “magic” numbers.

The following numbers of protons and / or neutrons yield particularly stable nuclei:

2, 8, 20, 28, 50, 82

Woods-Saxon potential:

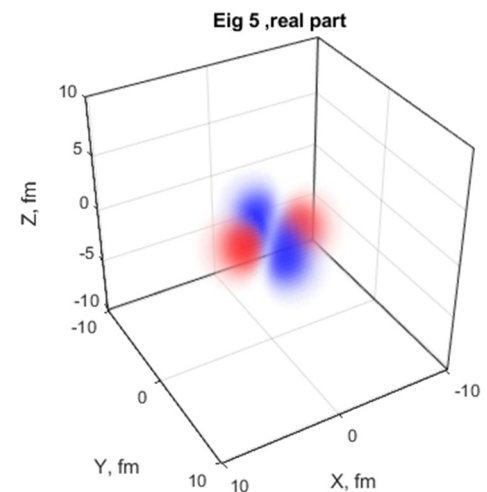
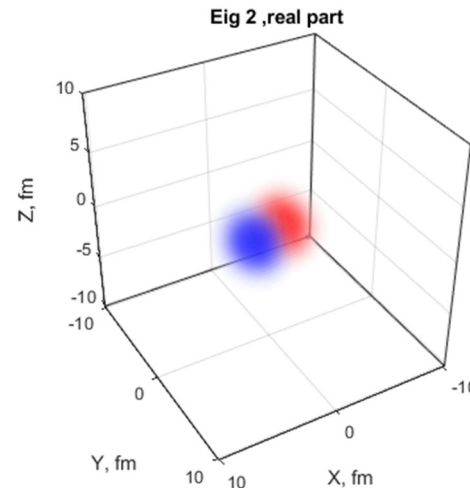
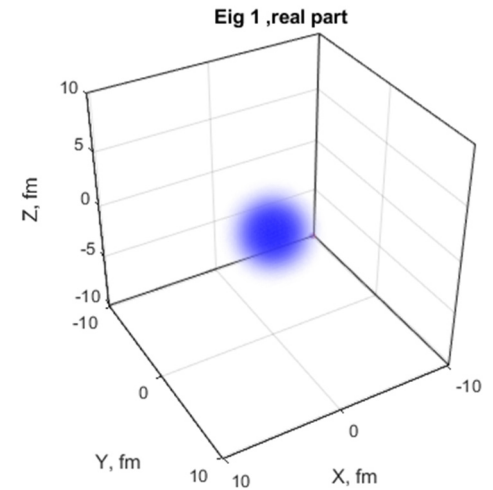
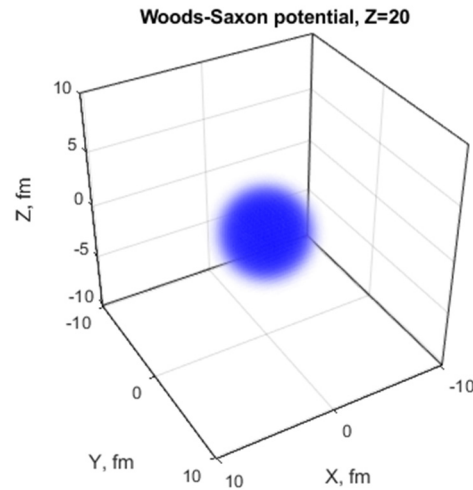
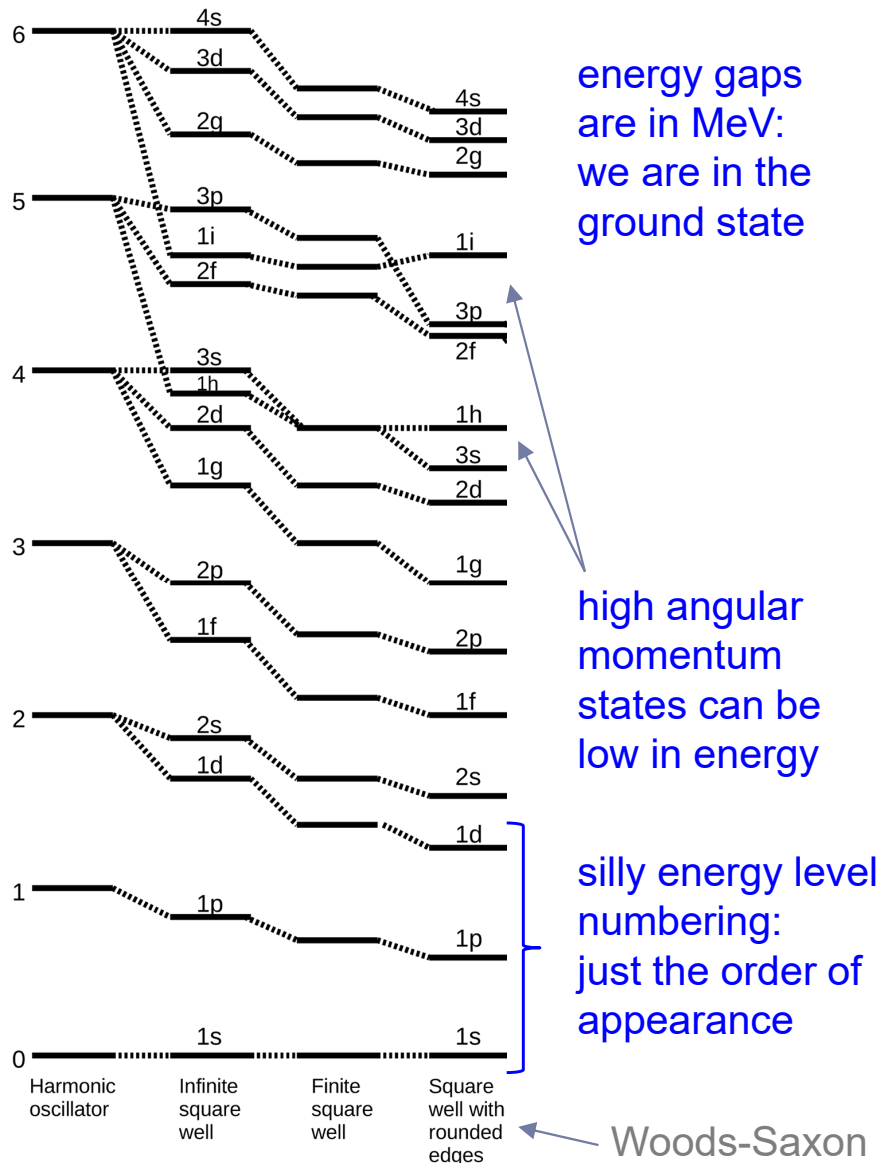
$$V_{\text{MF}}(r) = -\frac{V_0}{1 + e^{(r-r_0)/a}} + \begin{cases} \text{Coulomb} \\ \text{for protons} \end{cases}$$



same
s, p, d, f, ...
classification!

► Mathematically similar to the electron in a hydrogen atom, but with a different radial potential.

Mean-field potential of strong nuclear force



Flashback: electron spin-orbit coupling

Stage 3: spin-orbit coupling

$$\mathbf{H}_{\text{so}} = -\frac{q\hbar}{4m^2c^2} \frac{1}{r} \frac{d\phi}{dr} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{p}) = \xi(r) \mathbf{S} \cdot \mathbf{L}$$

$$\mathbf{S} = \frac{\hbar}{2} \boldsymbol{\sigma}, \quad \mathbf{L} = \mathbf{r} \times \mathbf{p}$$

positive

Pertinent commutators are:

$$[\mathbf{S} \cdot \mathbf{L}, \mathbf{L}^2] = [\mathbf{S} \cdot \mathbf{L}, \mathbf{S}^2] = [\mathbf{S} \cdot \mathbf{L}, (\mathbf{L} + \mathbf{S})^2] = 0$$

good quantum numbers

$\mathbf{S} \cdot \mathbf{L}$ commutes with $\mathbf{J}^2 = (\mathbf{L} + \mathbf{S})^2$, and therefore has the same eigenvectors. Using those with $\mathbf{S} \cdot \mathbf{L}$ yields:

$$\mathbf{S} \cdot \mathbf{L} |j\rangle = \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)] |j\rangle$$

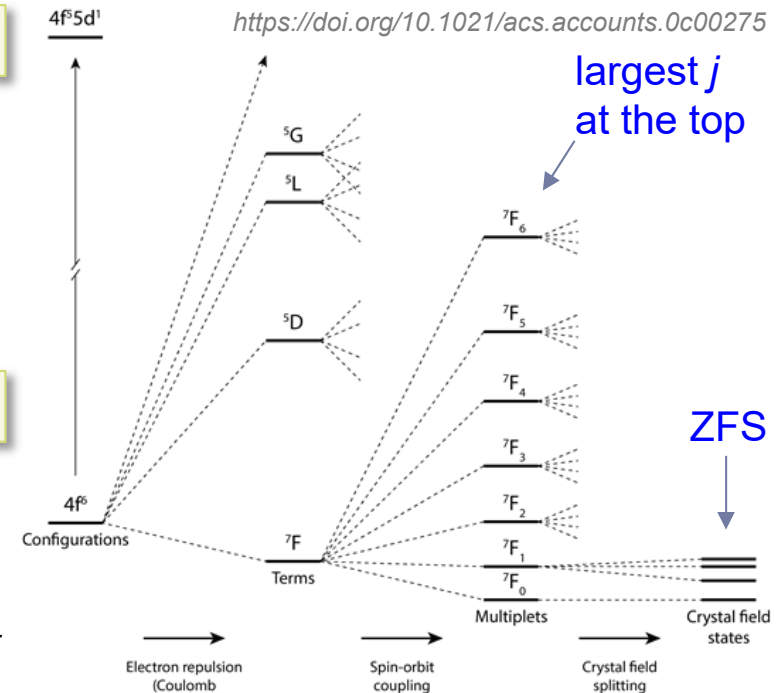
energies

$$j = |l-s|, \dots, (l+s)$$

multiplets

term symbol

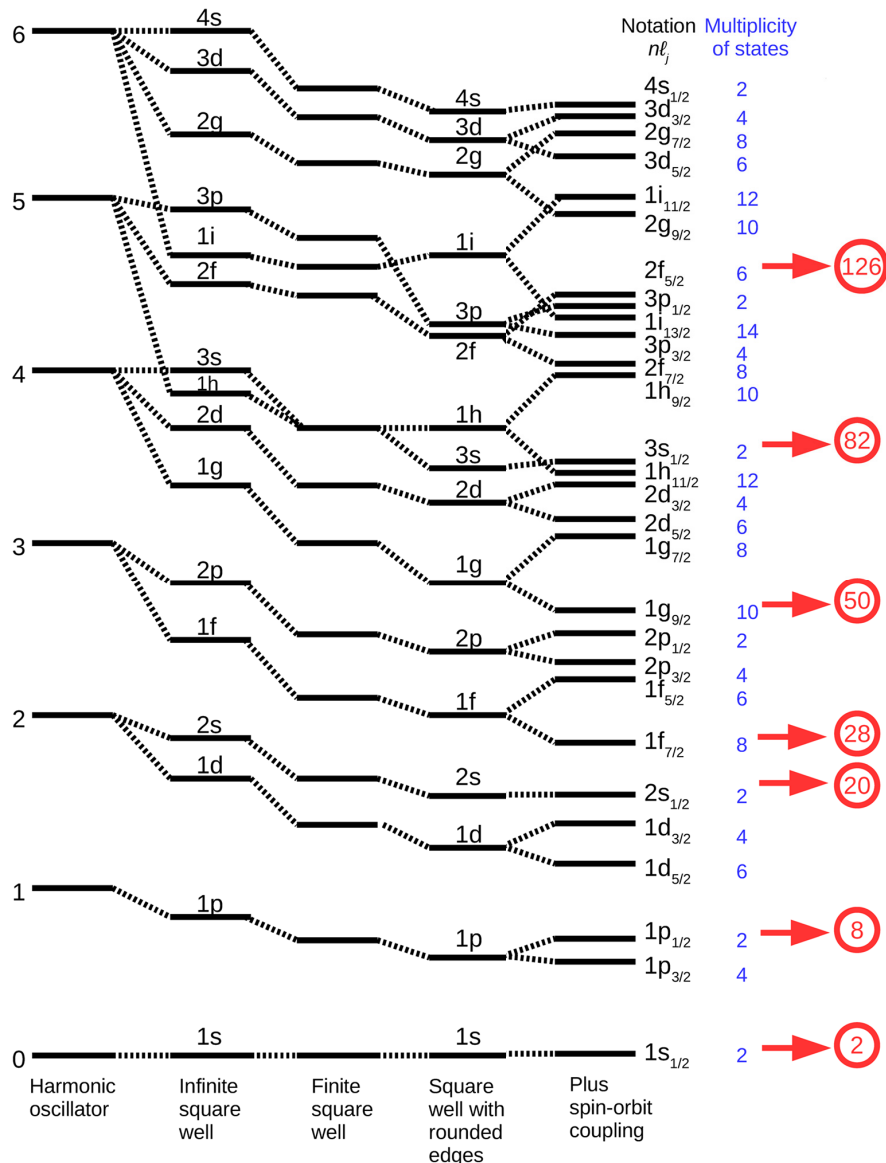
$2S+1 L_J$



Parallel $\mathbf{L}$ and $\mathbf{S}$ orientations are *higher* in energy because $\xi(r)$ is positive.

Zero Field Splitting: $|j, m\rangle$ states with different m have different charge distribution.

Intra-nuclear spin-orbit coupling



Spin-orbit coupling must be present:

non-decreasing

negative

$$\mathbf{H}_{\text{SO}} = -\frac{\hbar}{4m^2c^2} \frac{1}{r} \frac{dV_{\text{MF}}}{dr} \boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{p}) = V_{\text{SO}}(r) \mathbf{S} \cdot \mathbf{L}$$

Parallel $\mathbf{L}$ and $\mathbf{S}$ orientations are *lower* in energy (opposite of hydrogen atom).

$\mathbf{S} \cdot \mathbf{L}$ commutes (and thus has the same eigenvectors) with $\mathbf{J}^2 = (\mathbf{L} + \mathbf{S})^2$:

$$\mathbf{S} \cdot \mathbf{L} = \mathbf{S}_x \otimes \mathbf{L}_x + \mathbf{S}_y \otimes \mathbf{L}_y + \mathbf{S}_z \otimes \mathbf{L}_z$$

⇓ diagonalisation

$$\mathbf{S} \cdot \mathbf{L} |j\rangle = \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)] |j\rangle$$

$$j = |l-s|, \dots, l+s$$

The resulting energy level filling order predicts magic nucleon numbers!

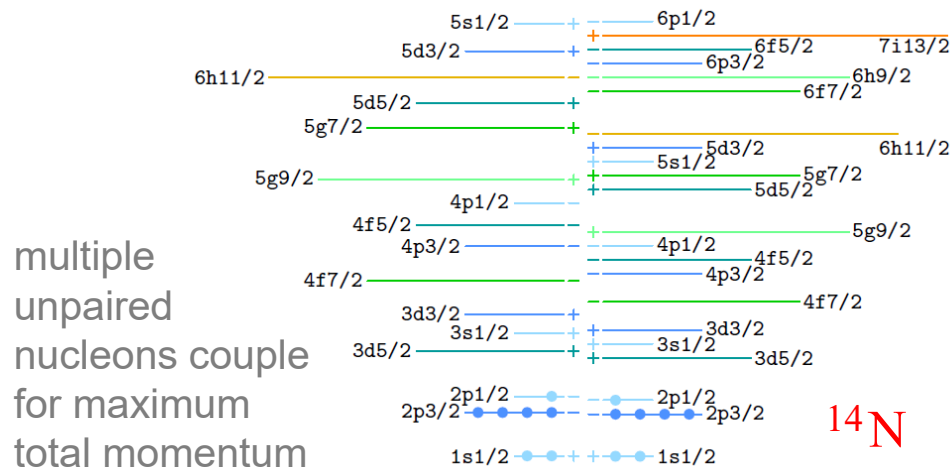
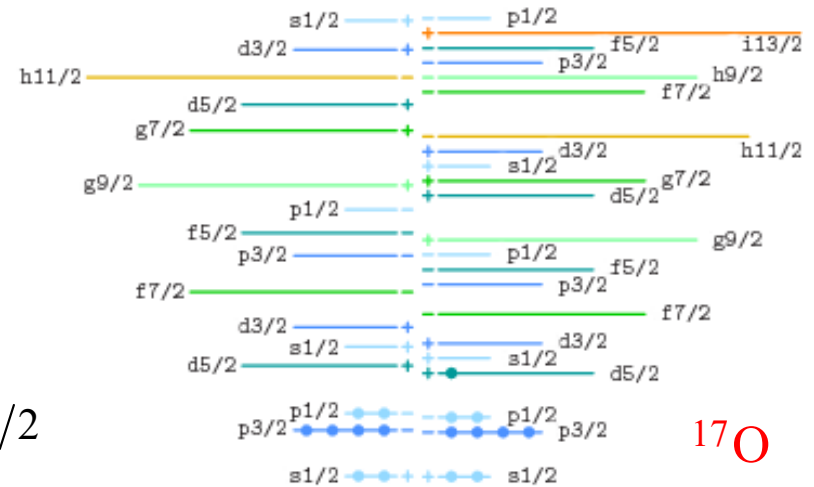
What nuclear spin really is

Nuclear “spin” is actually the total angular momentum j of the ground state:

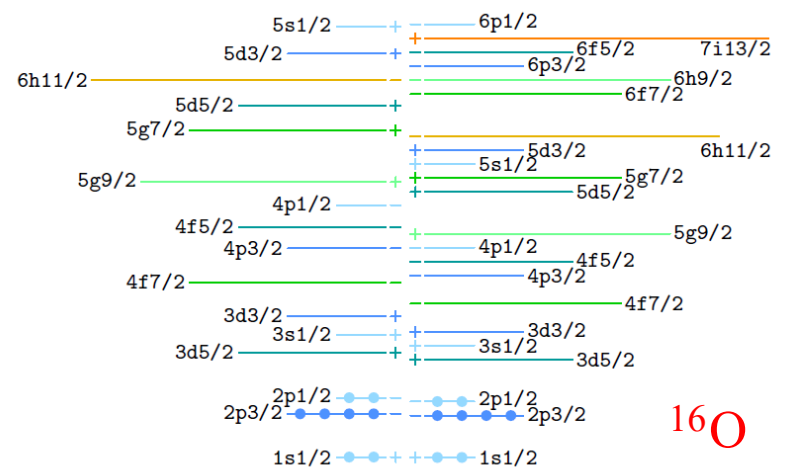
$$^{13}\text{C} \quad \begin{array}{l} \text{protons: } 1s_{1/2}^{(2)}, 1p_{3/2}^{(4)} \\ \text{neutrons: } 1s_{1/2}^{(2)}, 1p_{3/2}^{(4)}, 1p_{1/2}^{(1)} \end{array} \Rightarrow j = 1/2$$

$$^{15}\text{N} \quad \begin{array}{l} \text{protons: } 1s_{1/2}^{(2)}, 1p_{3/2}^{(4)}, 1p_{1/2}^{(1)} \\ \text{neutrons: } 1s_{1/2}^{(2)}, 1p_{3/2}^{(4)}, 1p_{1/2}^{(2)} \end{array} \Rightarrow j = 1/2$$

$$^{17}\text{O} \quad \begin{array}{l} \text{protons: } 1s_{1/2}^{(2)}, 1p_{3/2}^{(4)}, 1p_{1/2}^{(2)} \\ \text{neutrons: } 1s_{1/2}^{(2)}, 1p_{3/2}^{(4)}, 1p_{1/2}^{(2)}, 1d_{5/2}^{(1)} \end{array} \Rightarrow j = 5/2$$

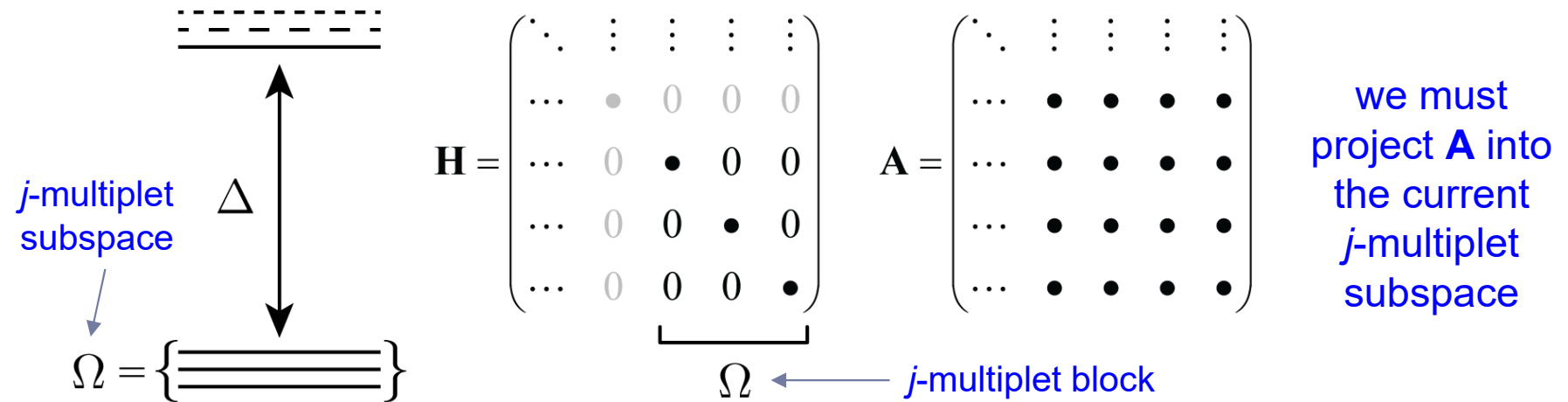


multiple
unpaired
nucleons couple
for maximum
total momentum



Ground j -multiplet projection

Only a small number of nearly degenerate ground levels are populated:



For any vector operator $\mathbf{A}$ in a specific j -multiplet (Wigner-Eckart theorem):

$$\langle j, m | \mathbf{A} | j, m' \rangle = \frac{\langle j, j | \mathbf{A} \cdot \mathbf{J} | j, j \rangle}{j(j+1)} \langle j, m | \mathbf{J} | j, m' \rangle$$

matrix element of $\mathbf{A}$ in j -block

a number

matrix element of $\mathbf{J}$ in j -block

Profound conclusion: any operator, when projected into a particular j -multiplet, becomes a linear combination of angular momentum / spin operators.

► When we project any operator into an algebra, we get a linear combination of the generators.

Flashback: electron g -factor and zero-field splitting

Remember g -factor and magnetic moment in electronic structure theory:

$$\boldsymbol{\mu} = \mu_B (\mathbf{L} + 2\mathbf{S})$$

specific value
of $\mathbf{J}^2 = (\mathbf{L} + \mathbf{S})^2$

use Wigner-Eckart
to project into the
ground j -multiplet

Lande's g -factor

$$\boldsymbol{\mu}_{\text{XYZ}} \rightarrow g_L \mu_B \mathbf{J}_{\text{XYZ}}$$

$$\begin{aligned} \mathbf{S} \cdot \mathbf{L} |j\rangle &= \frac{1}{2} [j(j+1) - l(l+1) - s(s+1)] |j\rangle \\ \mathbf{L}^2 |j\rangle &= l(l+1) |j\rangle, \quad \mathbf{S}^2 |j\rangle = s(s+1) |j\rangle \end{aligned}$$

$$g_L = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}$$

good quantum numbers

$$\frac{\langle j | \boldsymbol{\mu} \cdot \mathbf{J} | j \rangle}{j(j+1)} = \mu_B \frac{\langle j | (\mathbf{L} + 2\mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) | j \rangle}{j(j+1)} = \left(1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \right) \mu_B$$

Wigner-Eckart
prefactor

Likewise for electron zero-field splitting:

ligand field
electrostatics

Wigner-Eckart
theorem

effective spin
interaction

► Wigner-Eckart theorem turns anything that acts on $|j, m\rangle$ into an effective spin interaction.

Nuclear magnetic moment

Nuclear magnetic moment operator is *not* proportional to either **L** or **S**, or even **J**:

orbital g-factor spin g-factor

$$\boldsymbol{\mu} = \mu_N (g_L \mathbf{L} + g_S \mathbf{S})$$

$$\begin{cases} p: & g_L = 1, & g_S = +5.586 \\ n: & g_L = 0, & g_S = -3.826 \end{cases} \leftarrow \text{explains nuclei with negative magnetogyric ratios}$$

nuclear magneton $\mu_N = \frac{e\hbar}{2m_p}$

At room temperature, we are in the ground state of the spin-orbit coupling operator **L**·**S**... a *j*-multiplet!

matrix element of $\boldsymbol{\mu}$ in *j*-block $\langle j, m | \boldsymbol{\mu} | j, m' \rangle = \frac{\langle j, j | \boldsymbol{\mu} \cdot \mathbf{J} | j, j \rangle}{j(j+1)} \langle j, m | \mathbf{J} | j, m' \rangle$ matrix element of **J** in *j*-block

nuclear magnetogyric ratio

$$\frac{\langle j, j | \boldsymbol{\mu} \cdot \mathbf{J} | j, j \rangle}{j(j+1)} = \mu_N \frac{\langle j, j | (g_L \mathbf{L} + g_S \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) | j, j \rangle}{j(j+1)} =$$

$$= \frac{\mu_N}{2j(j+1)} \left\{ g_L [j(j+1) + l(l+1) - s(s+1)] + g_S [j(j+1) - l(l+1) + s(s+1)] \right\} = \gamma$$

$\boldsymbol{\mu} = \gamma \mathbf{J}$

(only simple for nuclei with one unpaired nucleon)

► Qualitative in the same sense as Lande's *g*-factor – other contributions to γ also exist.

Flashback: electric multipole expansion

Taylor series for electrostatic potential:

$$\begin{aligned}\varphi(\mathbf{r}) &= \varphi(0) + \frac{\partial\varphi(0)}{\partial\mathbf{r}} \cdot \mathbf{r} + \frac{1}{2} \mathbf{r}^T \cdot \frac{\partial^2\varphi(0)}{\partial\mathbf{r}^T\partial\mathbf{r}} \cdot \mathbf{r} + \dots = \\ &= \varphi(0) + \frac{\partial\varphi(0)}{\partial\mathbf{r}} \cdot \mathbf{r} + \frac{1}{2} \text{Tr} \left[\frac{\partial^2\varphi(0)}{\partial\mathbf{r}^T\partial\mathbf{r}} \cdot (\mathbf{r}\mathbf{r}^T) \right] + \dots\end{aligned}$$

traceless (Laplace's law)

Charge, dipole, quadrupole, *etc.*:

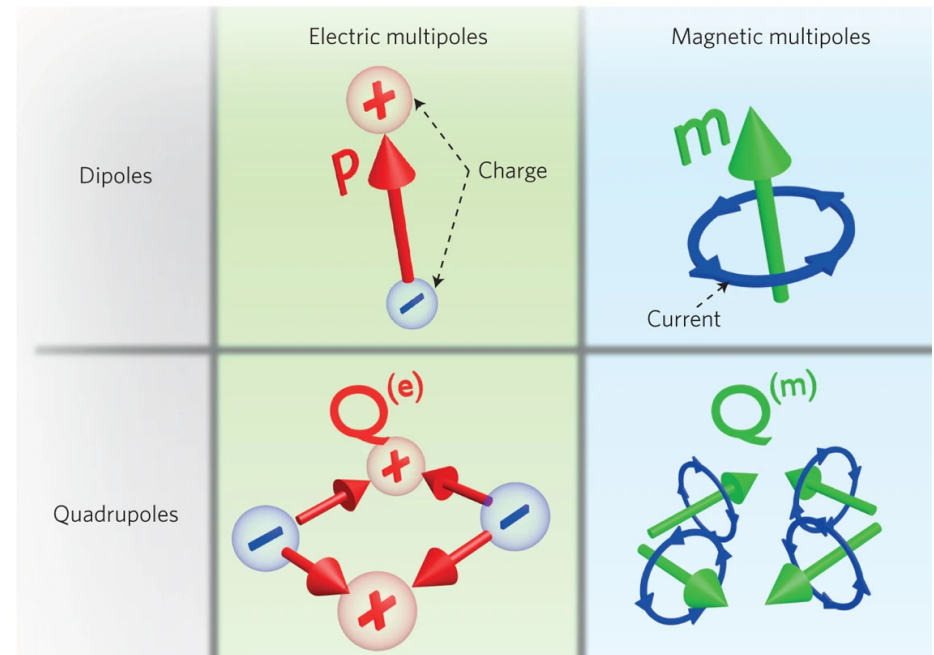
$$E = q\varphi + \frac{\partial\varphi}{\partial\mathbf{r}} \cdot \mathbf{d} + \frac{1}{6} \text{Tr} \left[\frac{\partial^2\varphi}{\partial\mathbf{r}^T\partial\mathbf{r}} \cdot \mathbf{Q} \right] + \dots$$

$$q = \int \rho(\mathbf{r}) d^3\mathbf{r}, \quad \mathbf{d} = \int \mathbf{r} \rho(\mathbf{r}) d^3\mathbf{r}$$

$$\mathbf{Q} = \int \rho(\mathbf{r}) (3\mathbf{r}\mathbf{r}^T - \mathbf{1}r^2) d^3\mathbf{r}$$

Nuclear dipole moment must be zero:

$$\Psi(\mathbf{r}) = \pm \Psi(-\mathbf{r}) \quad \Rightarrow \quad \rho(\mathbf{r}) = \rho(-\mathbf{r})$$



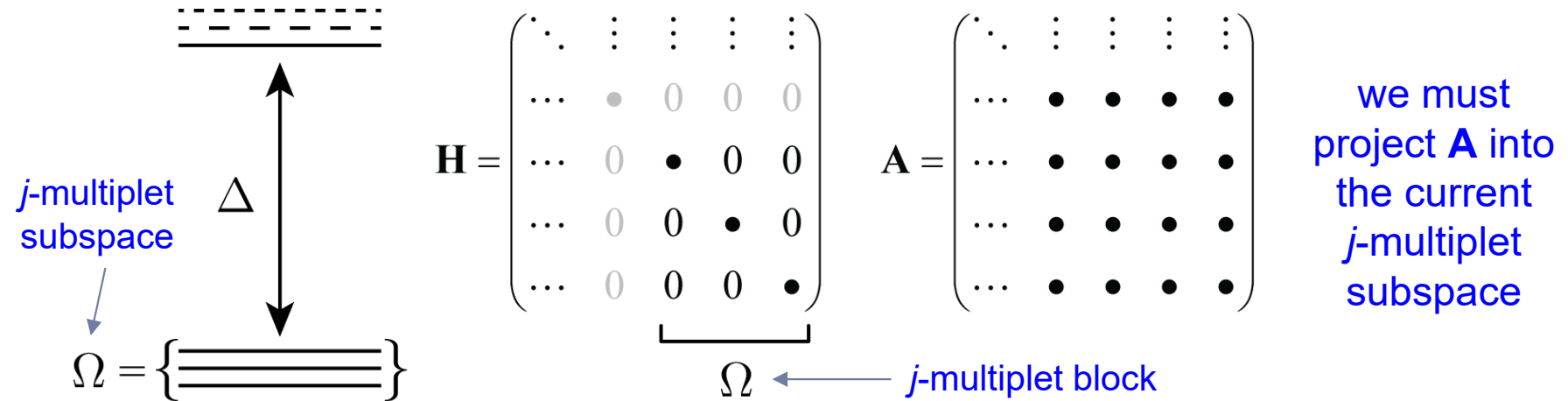
Papasimakis et al., <https://doi.org/10.1038/nmat4563>

$$\begin{aligned}\text{Hamiltonian} &\downarrow \hat{H}_Q = \frac{1}{6} \sum_{nk} \hat{Q}_{nk} V_{nk} \\ \text{quadrupole operator} &\downarrow \mathbf{Q} = 3\mathbf{r}\mathbf{r}^T - \mathbf{r}^T\mathbf{r} \leftarrow \text{coordinate operators} \\ \text{electric field gradient} &\downarrow V_{nk} = \frac{\partial^2\varphi}{\partial r_n \partial r_k}\end{aligned}$$

► Nuclear spin does not appear in this mathematics. But we are in the ground multiplet of $\mathbf{J}^2$...

Multiplet projection of the quadrupole operator

Only a small number of nearly degenerate ground levels are populated:



Wigner-Eckart theorem becomes horrendous:

$$Y_{2,\pm 2} = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \cdot \frac{(x \pm iy)^2}{r^2}$$

$$Y_{2,\pm 1} = \mp \frac{1}{2} \sqrt{\frac{15}{2\pi}} \cdot \frac{(x \pm iy)z}{r^2}$$

$$Y_{2,0} = \frac{1}{4} \sqrt{\frac{5}{\pi}} \cdot \frac{(3z^2 - r^2)}{r^2}$$



$$\hat{T}_{\pm 2}^{(2)} = +\frac{1}{2} \hat{J}_{\pm}^2$$

$$\hat{T}_{\pm 1}^{(2)} = \mp \frac{1}{2} (\hat{J}_z \hat{J}_{\pm} + \hat{J}_{\pm} \hat{J}_z)$$

$$\hat{T}_0^{(2)} = +\sqrt{\frac{2}{3}} \left(\hat{J}_z^2 - \frac{1}{4} (\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+) \right)$$

A simpler approach:

$$|\Psi\rangle = \sum_n a_n |\psi_n(\mathbf{r})\rangle \otimes |j, m_n\rangle$$

spatial part,
integrated away

spin part,
remains



nuclear spin operator

► When we project an operator into an algebra, we get a linear combination of the generators.

How quadrupole moment becomes a spin operator

For the ground multiplet of $\mathbf{J}^2$:

$$|\Psi\rangle = \sum_n a_n |\psi_n(\mathbf{r})\rangle \otimes |j, m_n\rangle$$

spatial part, in the ground state
spin part, dynamic

Another way of looking at it:

$$\langle n, j, m | \left[\frac{1}{6} \sum_{nk} \hat{Q}_{nk} V_{nk} \right] | n, j, m' \rangle = \langle m | \mathbf{H}_Q | m' \rangle$$

n, j fixed by ground state

Similarly, for multiplet Hamiltonian:

$$\hat{H}^{(j)} = \sum_{pq} \hat{H}_{pq}^{(j)} \otimes |j, m_p\rangle \langle j, m_q|$$

spatial parts
spin parts

After taking spatial integrals:

$$\begin{aligned} \langle \Psi | \hat{H} | \Psi \rangle &= \sum_{kn} a_k^* a_n \langle \psi_k(\mathbf{r}) | \hat{H}_{kn} | \psi_n(\mathbf{r}) \rangle = \\ &= \sum_{kn} a_k^* h_{kn} a_n = \langle S | \mathbf{H}_S | S \rangle, \quad |S\rangle = \sum_k a_k |j, m_k\rangle \end{aligned}$$

effective spin Hamiltonian

Coordinate integral is system-dependent, but spin part is universal:

$$\mathbf{H}_Q = \frac{eQ}{6j(2j-1)} \times [V_{xx}(3\mathbf{J}_x^2 - \mathbf{J}^2) + V_{yy}(3\mathbf{J}_y^2 - \mathbf{J}^2) + V_{zz}(3\mathbf{J}_z^2 - \mathbf{J}^2)]$$

electric field gradient
quadrupole constant
“spin”

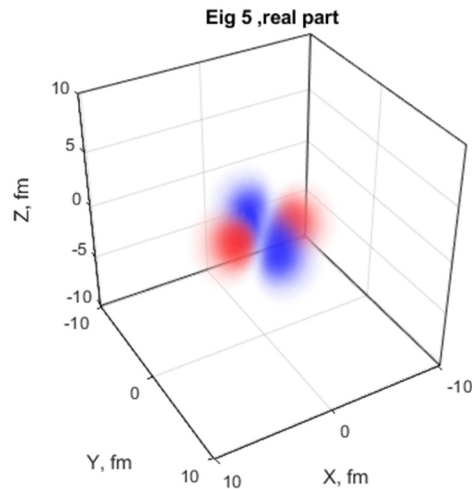
The following parameters are common:

$$C_Q = \frac{eQV_{zz}}{h}, \quad \eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

quadrupolar coupling constant
asymmetry

► Spin states are connected to spatial wavefunctions, and those interact with electric fields.

Summary and further reading

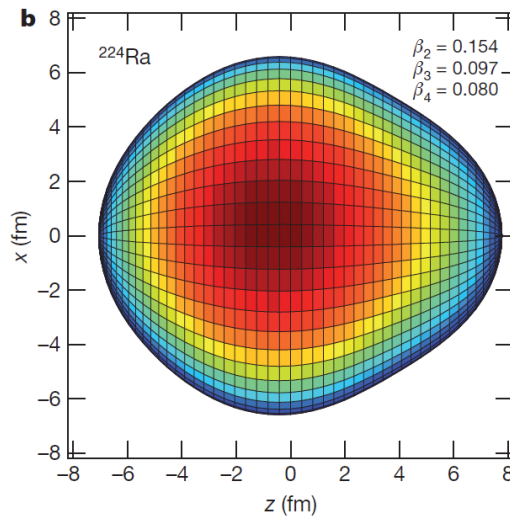


What goes on inside the nucleus:

- The potential for the strong nuclear force is unknown.
- Spin-orbit coupling is stronger than Coulomb interaction.
- Nuclear “spin” is actually total angular momentum.
- Chemists are always in the ground j -multiplet:

Corollary 1: μ becomes proportional to $\mathbf{J}$

Corollary 2: $\mathbf{Q}$ becomes a spin operator



Further reading:

- QNMR: [10.1002/9780470034590.emrstm0429.pub2](https://doi.org/10.1002/9780470034590.emrstm0429.pub2)
- MQMAS: <https://doi.org/10.1021/ja00124a023>
- Overtone NMR: <https://doi.org/10.1063/1.452176>
- Zero-field NQR: <https://doi.org/10.1063/1.449748>
- DOR: [https://doi.org/10.1016/0022-2364\(90\)90236-3](https://doi.org/10.1016/0022-2364(90)90236-3)
- Nuclear shapes: <https://doi.org/10.1038/nature12073>
- Nuclear structure: book by A. Bohr and B.R. Mottelson