NMR Active Isotopes Exist for Nearly Every Element

http://bouman.chem.georgetown.edu/NMRpt/NMRPerTab.html

Select an element by clicking on it:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Ha	Sg	Ns	Hs	Mt									
		*La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		**Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Review of Spin Properties

- NMR active nuclei possess an intrinsic angular momentum, $\vec{\boldsymbol{I}}$, known as the spin angular momentum. The magnitude is

$$\vec{\boldsymbol{I}} = \hbar\,[\,I\,(I+1)\,]^{1/2}$$

- Here I is the nuclear spin quantum number (integral or half-integral). If $I = 0$, no spin angular momentum (not NMR active)

- Associated with $\boldsymbol{I}$ is a magnetic moment, $\boldsymbol{\mu}$

$$\vec{\boldsymbol{\mu}} = \gamma\,\vec{\boldsymbol{I}} = \gamma\,\hbar\,[\,I\,(I+1)\,]^{1/2}$$

- The proportionality constant is the gyromagnetic ratio, γ
- In NMR, larger $\vec{\boldsymbol{\mu}}$ for given $\vec{\boldsymbol{I}}$ (large γ), means more sensitive nucleus

Review of Spin Properties

- In a magnetic field, otherwise degenerate (energetically equivalent) states split into nondegenerate states (known as Zeeman splitting)
- The states are quantized, with the number of states established by the spin quantum number, I

$$\# \text{ levels} = 2I + 1$$

- Each of the $2I+1$ states/levels is associated with a magnetic quantum number, m

$$m = -I, -I+1, \ldots, I-1, \mathrm{I}$$

- The component of $\boldsymbol{I}$ along the z axis, I_z, is defined as follows

$$I_z = m\hbar$$

- Thus

$$\mu_z = \gamma I_z = m\gamma\hbar$$

Review of Spin Properties

- The energies of the states resulting from the interaction of the magnetic moment with a magnetic field, $\vec{\boldsymbol{B}}$ are given by

$$E = -\vec{\mu} \bullet \vec{\boldsymbol{B}}$$

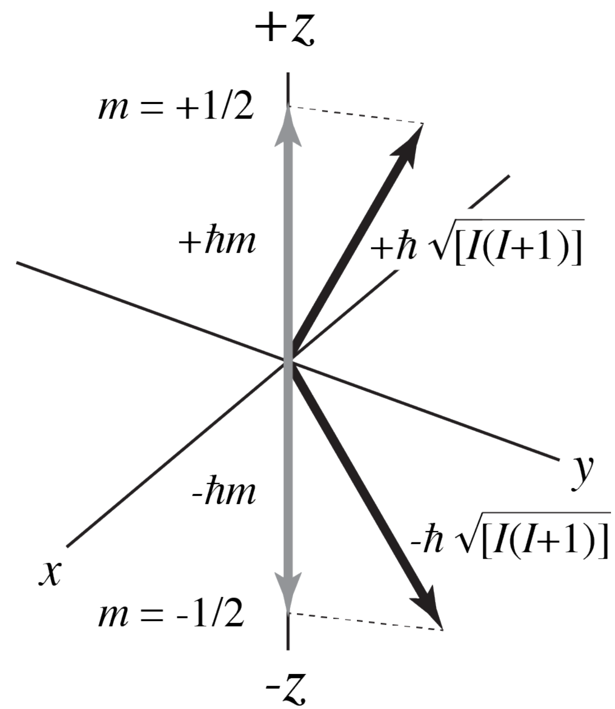
- The energies of the states depend on the orientations of the moments in the magnetic field, hence are proportional to the *scalar* projection of $\vec{\mu}$ on $\vec{\boldsymbol{B}}$ (the dot product), $\boldsymbol{\mu}_z$

$$E = -\,\boldsymbol{\mu}_z B_0 = -\,m\gamma\,\hbar B_0$$

- Here B_0 is the magnetic field strength

- The $2I$+1 energy levels are equally spaced. The energy difference between any two adjacent levels is

$$\Delta E = \gamma\,\hbar B_0$$



classical view of directional quantization for spin ½ nuclei

Review of Spin Properties

- The torque exerted by B_0 on the magnetic moments/dipoles promotes precession about the *z*-axis at a frequency given by

$$\upsilon_L = \gamma B_0 / (2\pi) \quad (\textit{Larmor frequency}, \text{ in Hz})$$

$$\omega_0 = \gamma B_0 \text{ (radians/sec)}$$

- The energy difference between energy (spin) states can then be written as

$$\Delta E = h\upsilon_L$$

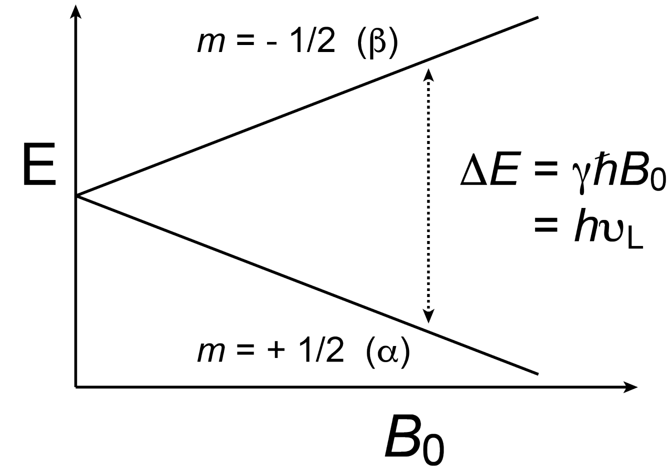
- Transitions between energy (spin) states can be effected by an electromagnetic field with an energy equal to ΔE. This occurs when the frequency of that field, υ_1, is equal to the Larmor frequency (*resonance* condition).

$$\upsilon_1 = \upsilon_L$$

Review of Spin Properties

- For spin 1/2 (I = 1/2), there are $2I+1 = 2$ energy levels, with values of *of m* equal to +1/2 and -1/2, called α and β, with energies

  $E_\alpha = -\tfrac{1}{2}\gamma\hbar B_0 \qquad E_\beta = +\tfrac{1}{2}\gamma\hbar B_0$



- From Boltzman statistics, the population ratio of these states can be estimated

$$\frac{N_\beta}{N_\alpha} = \exp\left(\frac{-\Delta E}{k_B T}\right) \approx 1 - \left(\frac{\Delta E}{k_B T}\right) \approx 1 - \left(\frac{\gamma\hbar B_0}{k_B T}\right)$$

  - example: ^{1}H, 300 °K, 5.875 Tesla (250 MHz)

$$\frac{N_\beta}{N_\alpha} = 1 - \frac{26.7519\times10^{7}\times1.0546\times10^{-27}\times5.875}{1.3805\times10^{-16}\times300} = 0.99996$$

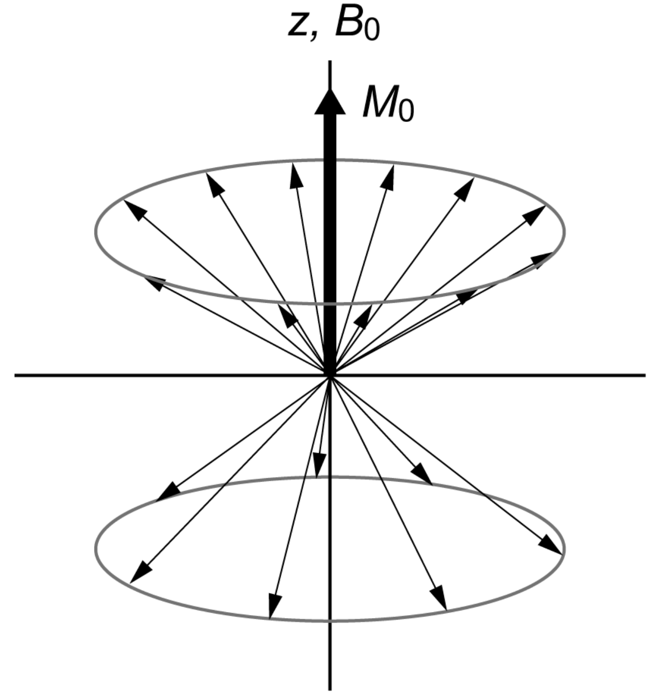
- ΔE is small, so the populations of α and β are nearly equal, and the macroscopic magnetization is small: *NMR is insensitive*

Review of Spin Properties

- The sum of the z-components of the nuclear dipoles in an ensemble gives the macroscopic (bulk) magnetization, M_0

$$M_0 = \gamma\hbar \sum_{m=-I}^{I} m N_m \quad (\text{recall } \mu_z = m\gamma\hbar)$$

$$M_0 \approx \frac{N\gamma^2\hbar^2 B_0}{k_B T(2I+1)} \sum_{m=-I}^{I} m^2 \approx \frac{N\gamma^2\hbar^2 B_0 I(I+1)}{3k_B T}$$

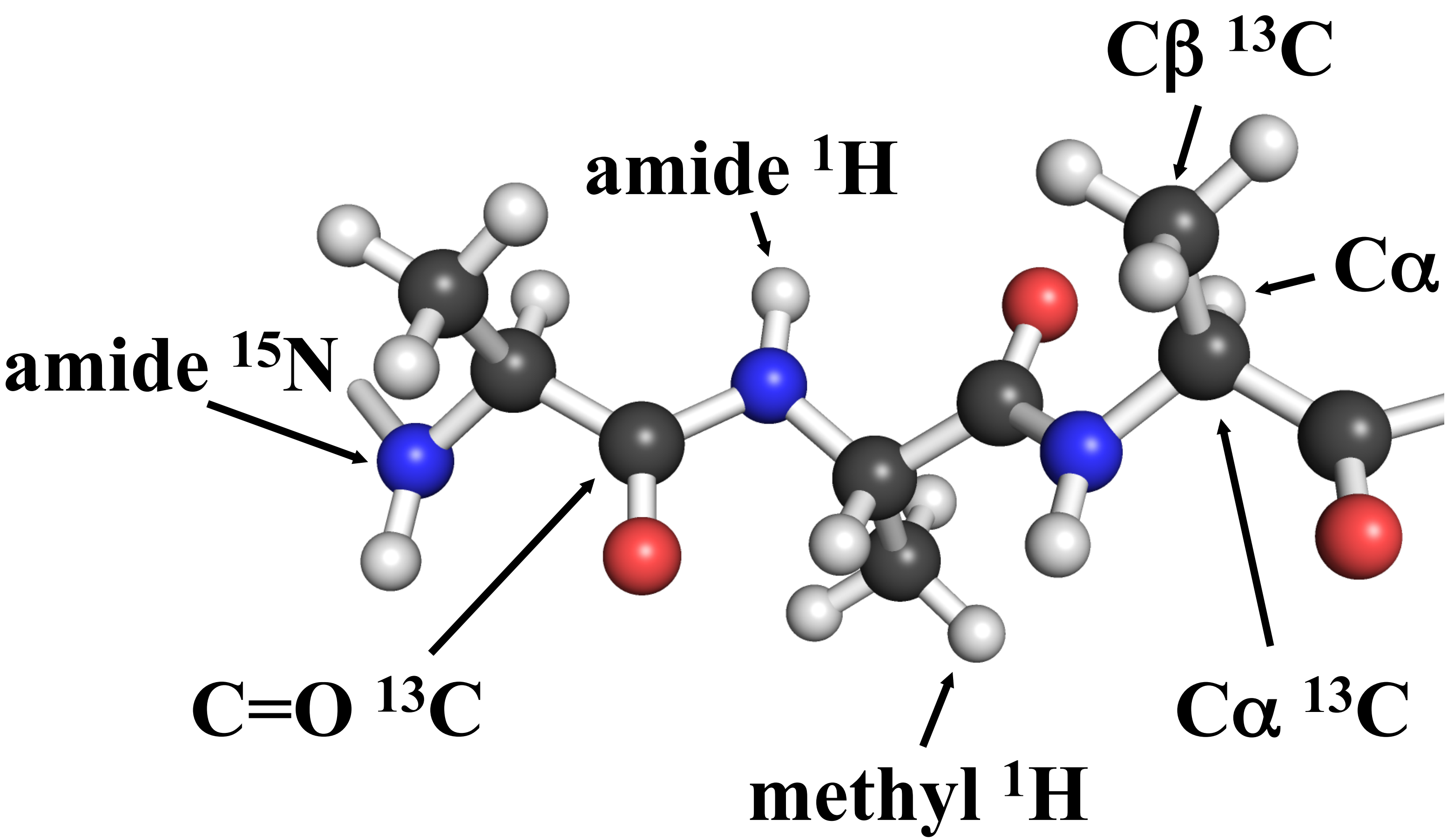


- Note: dependence on γ^2, linear dependence on B_0, dependence on isotopic abundance (N)

Spin ½ Nuclei are Most Useful in Biomolecular NMR

	^{1}H	^{13}C	^{15}N	^{19}F	^{31}P
Spin	1/2	1/2	1/2	1/2	1/2
Natural abundance	99.985%	1.108%	0.37%	100%	100%
Magnetogyric ratio ($\gamma/10^7$, rad T^{-1} s^{-1})	26.7519	6.7283	-2.7126	25.1815	10.8394
Relative sensitivity	1.00	1.59×10^{-2}	1.04×10^{-3}	0.83	6.63×10^{-2}
Relative receptivity	1.00	1.76×10^{-4}	3.85×10^{-6}	0.83	6.63×10^{-2}
Magnetic moment (μ/μ_N)	4.8372	1.2166	-0.4903	4.5532	1.9601
Quadrupole moment	0	0	0	0	0
Resonance frequency (MHz)	100	25.144	10.133	94.077	40.481

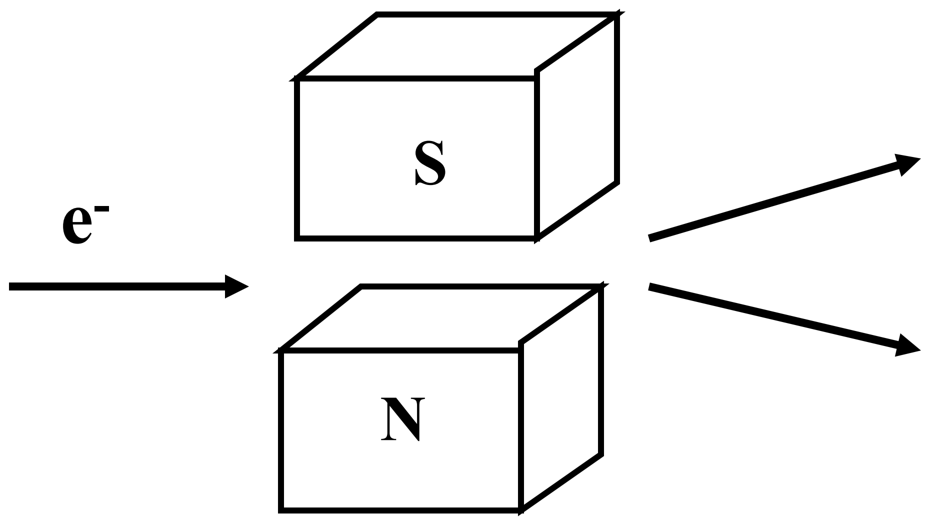
Polypeptides are Rich in NMR Active Nuclei



Nuclear Properties

- Not all nuclei have magnetic moments, Why?
- Not all nuclei are equally abundant, Why?
- Spins vary, Why?
- Magnetogyric ratios vary, Why?

Fundamental Particle Properties



Beam in field gradient

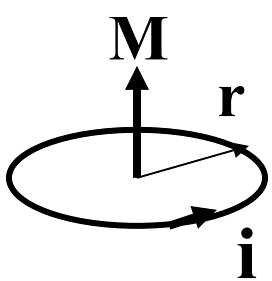
Stern Gerlach experiment:

- demonstrated particles (electrons) possess an intrinsic angular momentum, and it is quantized

- Na atom - 1 unpaired electron
Two spots implies quantized moments: +/- 1/2
protons and neutrons are also spin 1/2 particles

Understanding Magnetic Moments

- Current Loop Model: classical analogy to connect "spin" to magnetic moment
- Can get reasonable estimate of γ for electron



Area, S

$$\vec{M} = i\,\vec{S}$$

i in Coulomb s^{-1}
S in m^2
M in JT^{-1} (Tesla)

Estimates: $i = -ev/(2\pi r)$, $S = \pi r^2$, M (or μ) $= -erv/2$

$$\vec{\mu} = -e(\vec{r} \times \vec{v})/2, \quad \vec{L} = m_e\, \vec{r} \times \vec{v}, \quad \vec{\mu} = -e/(2m_e)\, \vec{L} = \gamma\, \vec{L} = \gamma h/(2\pi) l$$

$\gamma = -g\,(e/(2m_e))$, **g = Lande g factor**

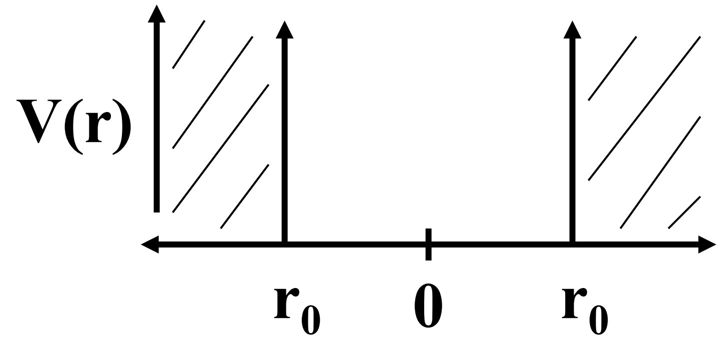
Values of Particle Magnetogyric Ratios

Electron: $g \approx 2$, $\gamma_e = -17.7 \times 10^{10}\ T^{-1}s^{-1}$

Proton: expect $1/m_p$ dependence, 1/2000 and positive
$2.7 \times 10^8\ T^{-1}s^{-1}$

Neutron: similar mass to proton
$-1.8 \times 10^8\ T^{-1}s^{-1}$

Heavier Nuclei: the Shell Model



Analogous to shell model for atomic electrons

Some rules:

a) spherical particle in a box potential

$\psi = R_{nl}(r)\, Y_l^m(\theta,\phi)$, E(n,l)

ladder of energy levels like H atom, but all ls allowed

l=0, 1, 2, 3 for "s", "p", "d", and "f" like atomic case

b) strong coupling of spin and orbit angular momentum

quantized total: $j = l \pm 1/2$ for spin 1/2 particle

larger j, lower energy (usually)

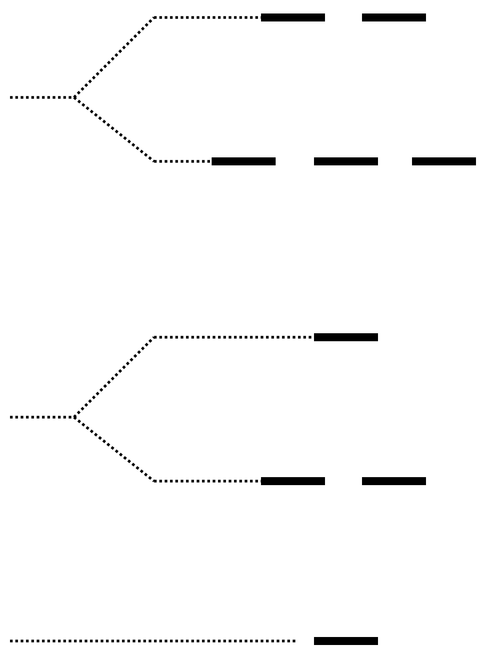
Shell Model Rules Continued

c) Treat protons and neutrons separately and fill from bottom up assuming 2j + 1 degeneracy

d) Assume particle pair strongly within levels: only unpaired spins count - total spin angular momentum given by j of level for unpaired spin

e) sign of moment depends on sign of moment for fundamental particle (+½ for proton, -½ for neutron) but changes sign when moment subtracts instead of adds to l in giving j

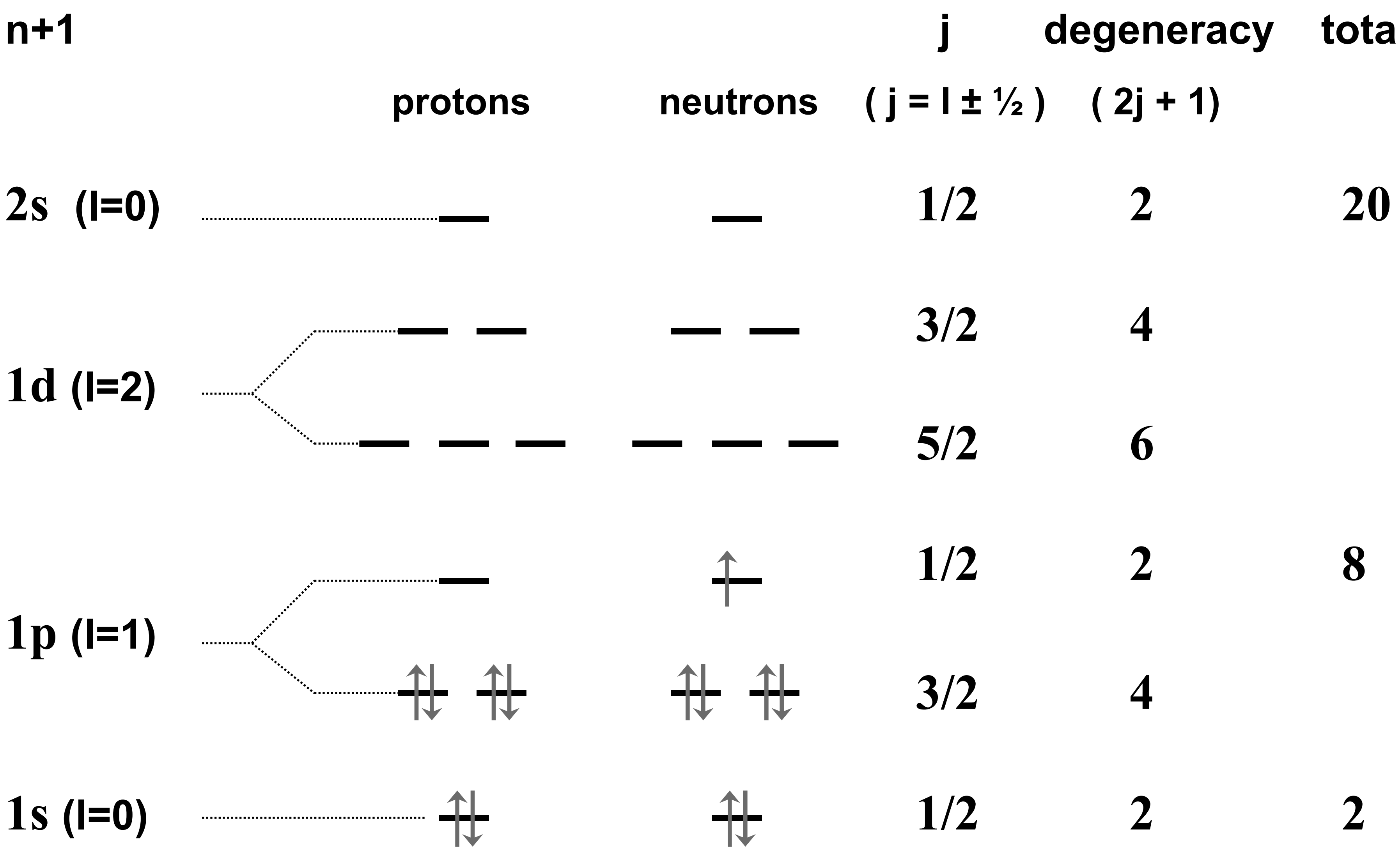
Energy Level Diagram



n+1	j (j = l ± ½)	degeneracy (2j + 1)	total
2s (l=0)	**1/2**	**2**	**20**
	3/2	**4**	
1d (l=2)			
	5/2	**6**	
	1/2	**2**	**8**
1p (l=1)			
	3/2	**4**	
1s (l=0)	**1/2**	**2**	**2**

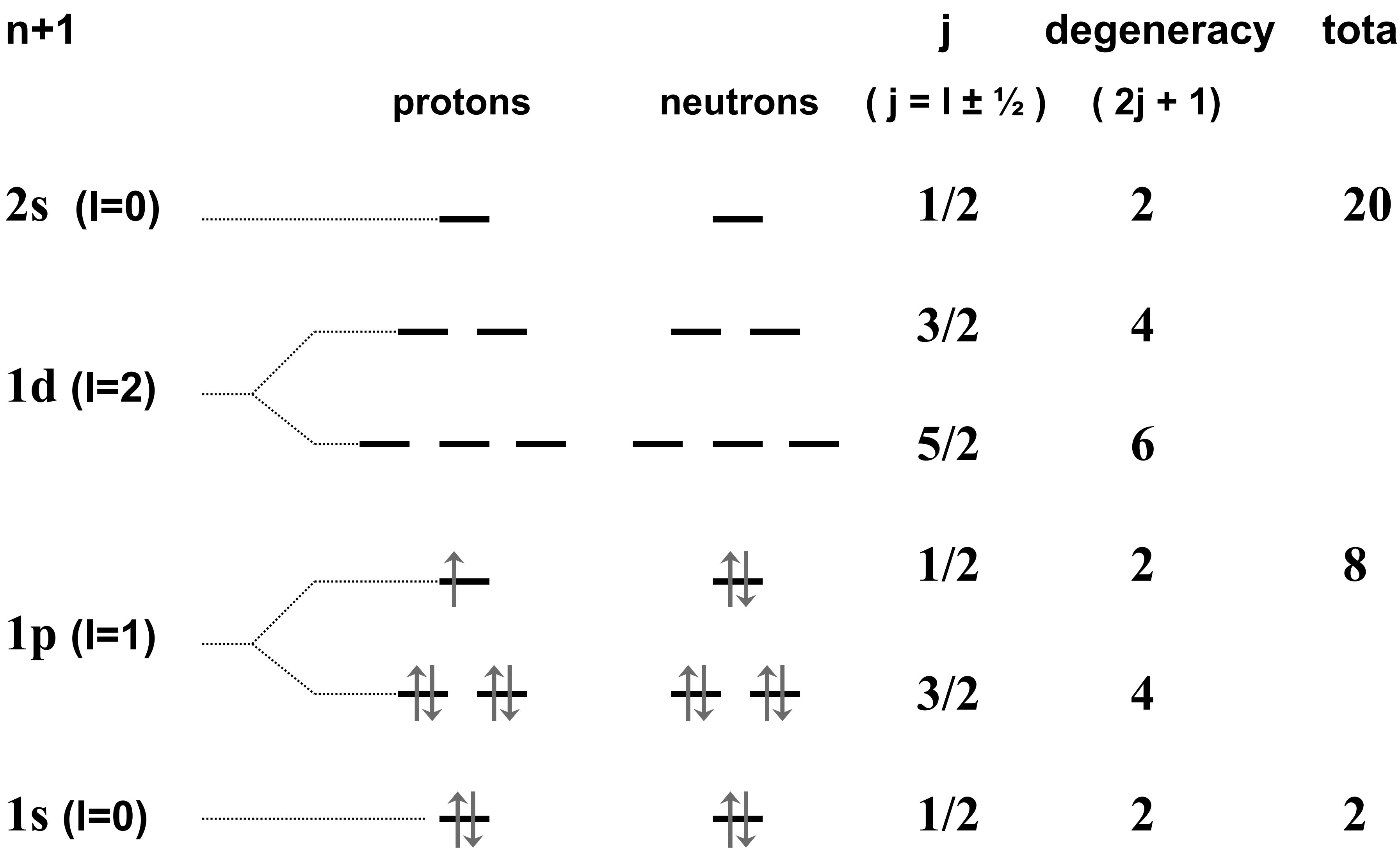
Example: ${}^{13}_{6}C$ (6 protons, 7 neutrons)

- unpaired neutron (-1/2) in $1p_{1/2}$ ($j = 1-1/2 = 1/2$), so spin=1/2, positive γ

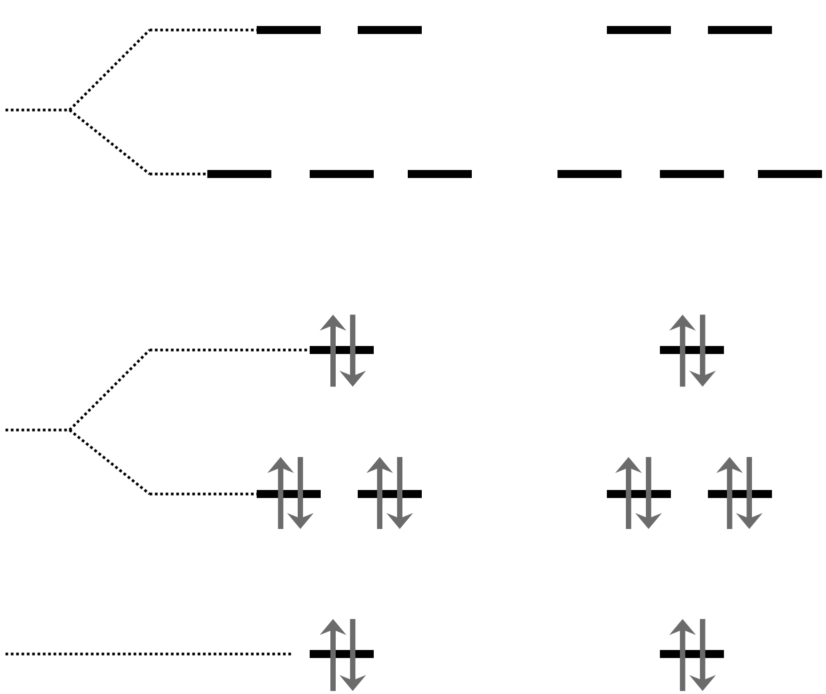


Example: $^{15}_{7}N$ (7 protons, 8 neutrons)

- unpaired proton (+1/2) in $1p_{1/2}$ (j = 1-1/2 = 1/2), so spin=1/2, negative γ



Example: $^{16}_{8}O$ (8 protons, 8 neutrons, two magic numbers), spin = 0
- highly stable (99.76% of all oxygen on Earth)



n+1	protons	neutrons	j (j = l ± ½)	degeneracy (2j + 1)	total
2s (l=0)			1/2	2	20
			3/2	4	
1d (l=2)					
			5/2	6	
			1/2	2	8
1p (l=1)					
			3/2	4	
1s (l=0)			1/2	2	2

Particle Physics / Spin

Proton Spin Mystery Gains a New Clue:

https://www.scientificamerican.com/article/proton-spin-mystery-gains-a-new-clue1/