Solid-state NMR methods

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Outline

- Introduction to NMR:
  - Nuclear properties:
    - Nuclear spin.
    - Magnetic dipole moment.
    - Nuclear shell model.
    - Electric quadrupole moment.
    - Table of nuclides.

Some historical benchmarks of NMR

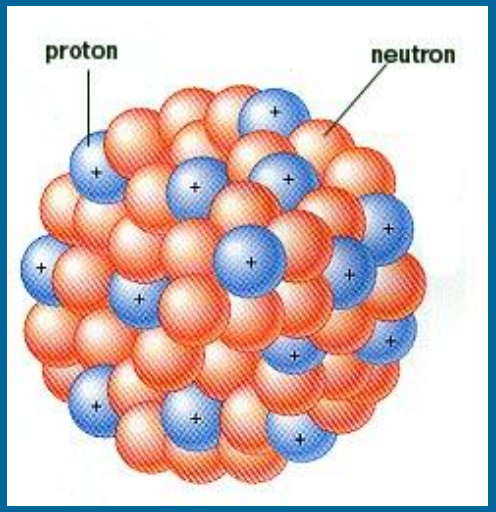
- Rabi (1937): nuclear magnetic resonance in molecular beams.
  - Nobel Prize in Physics - 1944.
- Bloch (1946): radiofrequency absortion in water.
  - Nobel Prize in Physics - 1952.
- Purcell (1946): radiofrequency absortion in paraffin.
  - Nobel Prize in Physics - 1952.
- Hahn (1949): spin echoes.
- Packard (1951): chemical shifts in ethanol.
- Andrew, Lowe (1959): solid-state NMR.
- Ernst (1964): Fourier transform NMR.
  - Nobel Prize in Chemistry - 1991.
- Wüthrich (1968): NMR applied to the study of biological macromolecules.
  - Nobel Prize in Chemistry - 2002.
- Lauterbur, Mansfeld (1973): magnetic resonance imaging (MRI).
  - Nobel Prize in Medicine - 2003.

Nuclear spin and magnetic dipole moment

$$\vec{\mathrm{I}} = \sum_{k=1}^{A} \left(\vec{l}_k + \vec{s}_k \right)$$

***Nuclear spin*:**

- **Quantum number *I*.**
- **Integer or half-integer.**



$$\vec{\mu} = (\mu_N / \hbar)\left[\sum_{k=1}^{Z} \vec{l}_k + \sum_{k=1}^{Z} g_{sp} \vec{s}_k + \sum_{k=Z+1}^{A} g_{sn} \vec{s}_k \right]$$

$g_{sp} = 5.586$

$g_{sn} = -3.826$

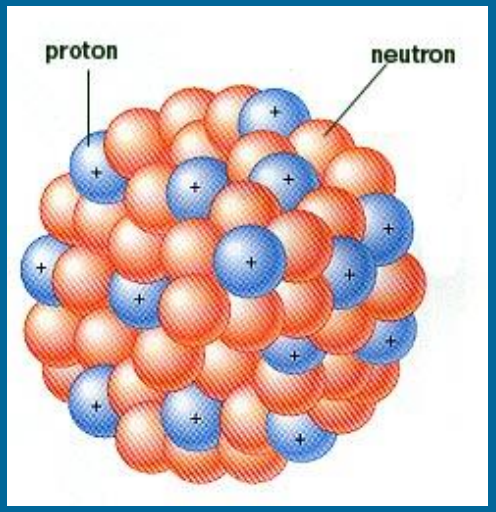
Nuclear magneton: $\mu_N = \dfrac{e\hbar}{2m_p} = 5.051 \times 10^{-27}\ J/T$

Bohr magneton: $\mu_B = \dfrac{e\hbar}{2m_e} = 9.274 \times 10^{-24}\ J/T$

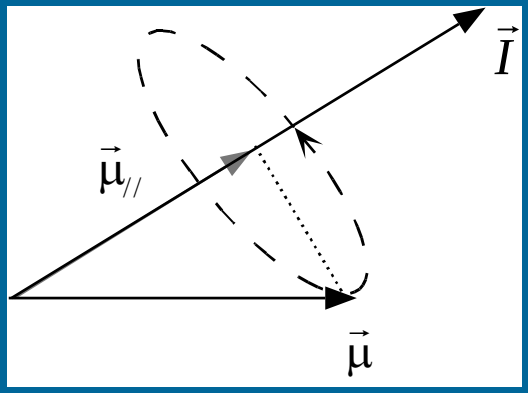
$g_{se} = -2.002$

Nuclear spin and magnetic dipole moment

$$\vec{\mathrm{I}} = \sum_{k=1}^{A} \left(\vec{l}_k + \vec{s}_k \right)$$



$$\vec{\mu} = (\mu_N / \hbar) \left[\sum_{k=1}^{Z} \vec{l}_k + \sum_{k=1}^{Z} g_{sp} \vec{s}_k + \sum_{k=Z+1}^{A} g_{sn} \vec{s}_k \right]$$



$$\vec{\mu}_{effective} = \frac{\left\langle \vec{\mu} \cdot \vec{\mathrm{I}} \right\rangle}{I(I+1)\hbar^2} \vec{\mathrm{I}} = \gamma \vec{\mathrm{I}}$$

Magnetogyric ratio

Nuclear shell model and nuclear spin

Nuclear *magic numbers*:

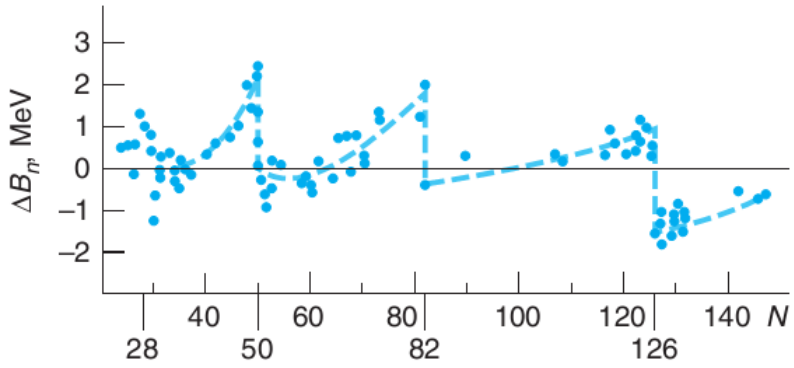


Figure 11-31 Difference in the measured binding energy of the last neutron and that calculated from mass formula versus neutron number. Note the similarity of this curve and the ionization energy of atoms versus Z (Figure 7-20). The neutron numbers 28, 50, 82, and 126 correspond to closed shells. These data show that the neutron with N = magic number +1 is much less tightly bound than that with N = magic number.

Modern Physics, Tipler & Llevellyn, 2014.

Nuclear shell model and nuclear spin

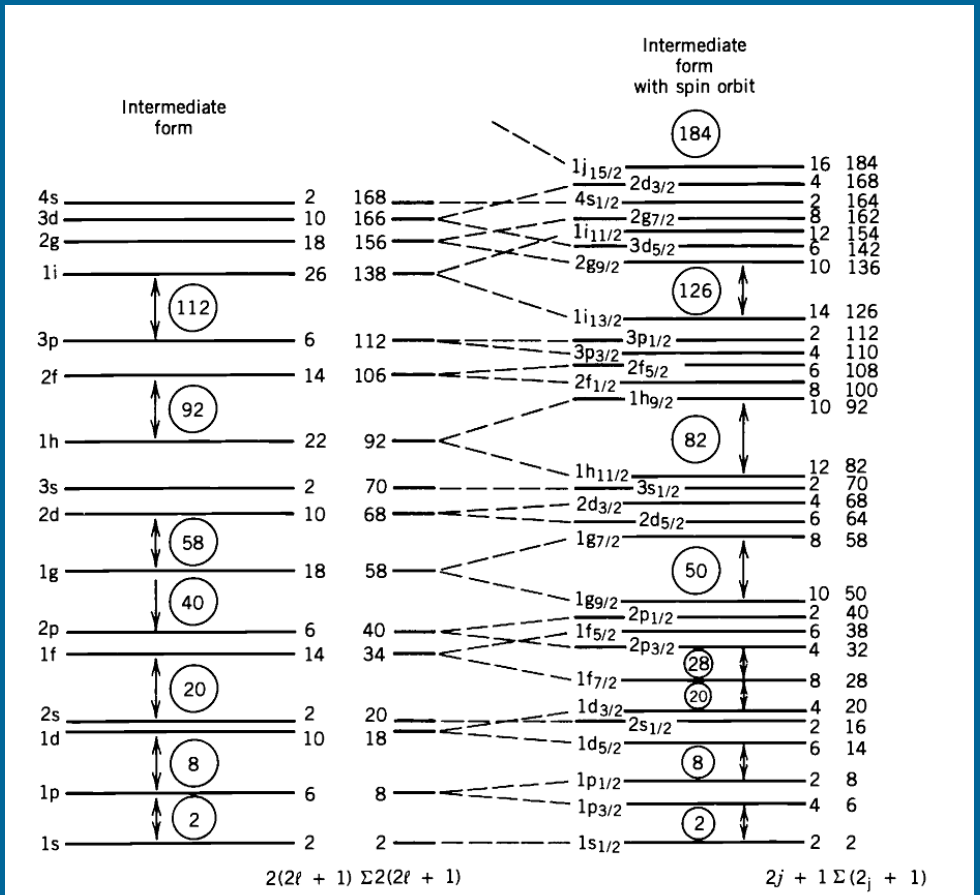


Figure 5.6 At the left are the energy levels calculated with the potential of Figure 5.5. To the right of each level are shown its capacity and the cumulative number of nucleons up to that level. The right side of the figure shows the effect of the spin-orbit interaction, which splits the levels with $\ell > 0$ into two new levels. The shell effect is quite apparent, and the magic numbers are exactly reproduced.

Angular momentum of each nucleon:

$$\vec{j} = \vec{l} + \vec{s}$$

$$j = l \pm 1/2$$

Notation:

$$n\, l_j$$

Multiplicity of each level:

$$2j + 1$$

Introductory Nuclear Physics, Krane, 1988.

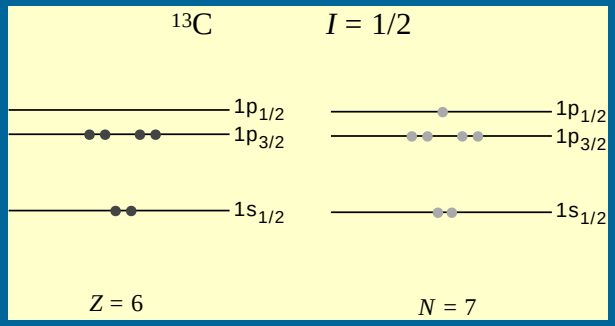
Nuclear shell model and nuclear spin

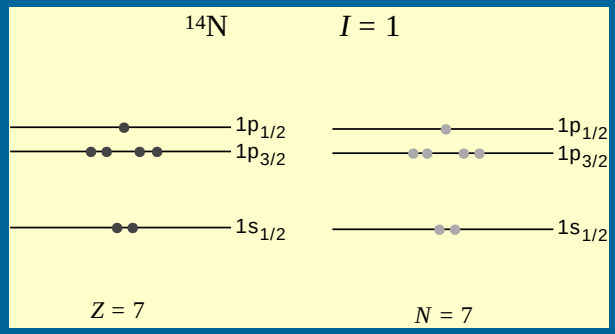
Predictions from the nuclear shell model:

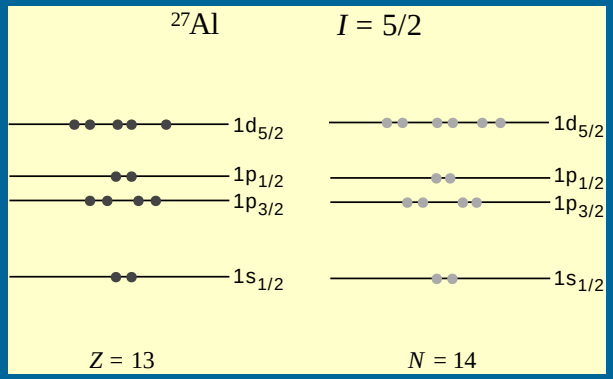
Z	N	A	I	
even	even	even	zero	
even	odd	odd	half-integer	$I = j_n$
odd	even	odd	half-integer	$I = j_p$
odd	odd	even	integer	$\lvert j_n - j_p \rvert \leq I \leq j_n + j_p$

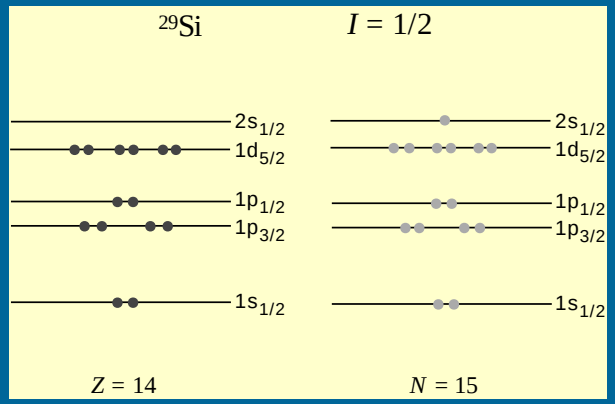
Nuclear shell model and nuclear spin

Predictions from the nuclear shell model:









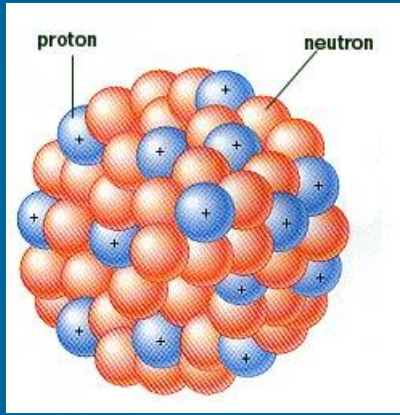
Electric quadrupole moment

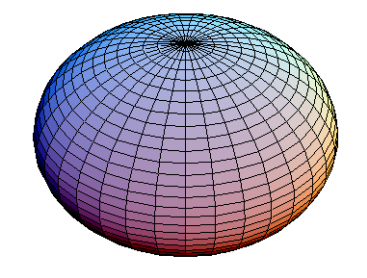
$$\boldsymbol{Q}_{\alpha\beta} = e\sum_{k=1}^{Z}(3\boldsymbol{x}_{\alpha k}\boldsymbol{x}_{\beta k} - \delta_{\alpha\beta}\boldsymbol{r_k}^2)$$

$$\boldsymbol{Q}_{\alpha\beta} = \frac{eQ}{I(2I-1)\hbar^2}\left[\frac{3}{2}\left(\mathbf{I}_\alpha\mathbf{I}_\beta + \mathbf{I}_\beta\mathbf{I}_\alpha\right) - \delta_{\alpha\beta}\mathbf{I}^2\right]$$

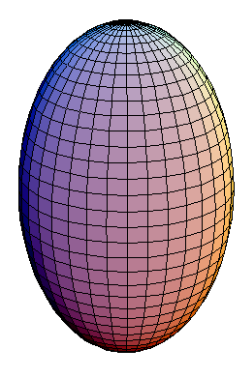
$$eQ = \int(3z'^2 - r'^2)\rho(\vec{r}')d^3r'$$

$$I > 1/2 \Rightarrow Q \neq 0$$





$Q < 0$ (oblate)



$Q > 0$ (prolate)

Table of nuclides – NMR active nuclei

Table 1 The spin properties of spin-$\frac{1}{2}$ nuclei[a].

Isotope[b]	Natural abundance,[c] x/%	Magnetic moment,[d] μ/μ_N	Magnetogyric ratio,[d] $\gamma/10^7$ rad s^{-1} T^{-1}	Frequency ratio,[e] Ξ/%	Reference compound	Sample conditions[f]	Literature for Ξ	Relative receptivity[g] D^p	Relative receptivity[g] D^C
^{1}H	99.9885	4.837 353 570	26.752 2128	100.000 000[h]	Me_4Si	$CDCl_3$, $\varphi = 1\%$	–	1.000	5.87×10^3
^{3}H[i]	–	5.159 714 367	28.534 9779	106.663 974	Me_4Si-t_1	[j]	10	–	–
^{3}He	1.37×10^{-4}	–3.685 154 336	–20.380 1587	76.179 437	He	gas	11	6.06×10^{-7}	3.56×10^{-3}
^{13}C	1.07	1.216 613	6.728 284	25.145 020	Me_4Si	$CDCl_3$, $\varphi = 1\%$	12,13	1.70×10^{-4}	1.00
^{15}N	0.368	–0.490 497 46	–2.712 618 04	10.136 767	$MeNO_2$	neat/$CDCl_3$[k]	9	3.84×10^{-6}	2.25×10^{-2}
^{19}F	100	4.553 333	25.181 48	94.094 011	CCl_3F	[j]	14	0.834	4.90×10^3
^{29}Si	4.6832	–0.961 79	–5.3190	19.867 187	Me_4Si	$CDCl_3$, $\varphi = 1\%$	15	3.68×10^{-4}	2.16
^{31}P	100	1.959 99	10.8394	40.480 742	H_3PO_4	[j]	16	6.65×10^{-2}	3.91×10^2

[a] A complete list for stable nuclei, but excluding the lanthanides, the actinides and most radioactive isotopes.
[b] Nuclei in parentheses are considered to be not the most favorable of the element concerned for NMR.
[c] Data are "representative isotopic compositions", taken from Rosman *et al.* [8], pp. 98–104. For the error limits, see Rosman *et al.* [8].
[d] Data derived from the compilation in Mills *et al.* [6], pp. 98–104, which lists values of $\mu_{max} / \mu_N = \gamma\hbar I / \mu_N$. For the error limits, see Mills *et al.* [6].
[e] Ratios of the resonance frequency of the reference to that of the protons of TMS at infinite dilution (in practice at $\varphi = 1\%$) in $CDCl_3$.
[f] M ≡ molarity in mol dm^{-3} (solution); m ≡ molality in mol kg^{-1} (solvent). Some results from ref. 9 were initially referenced [7] to a TMS concentration of 4.75 m in $CDCl_3$, but the values are corrected to refer to a dilute ($\varphi = 1\%$) solution of TMS in $CDCl_3$.
[g] D^p is the receptivity [5] relative to that of ^{1}H, whereas D^C is relative to ^{13}C.
[h] Value by definition (see the text).
[i] Radioactive (half-life 12 y).
[j] See literature cited.
[k] Small amount of lock substance ($\varphi < 10\%$) in neat liquid.

Harris et al., *Pure Appl. Chem.* 2001;73:1795-1818.

Table of nuclides – NMR active nuclei

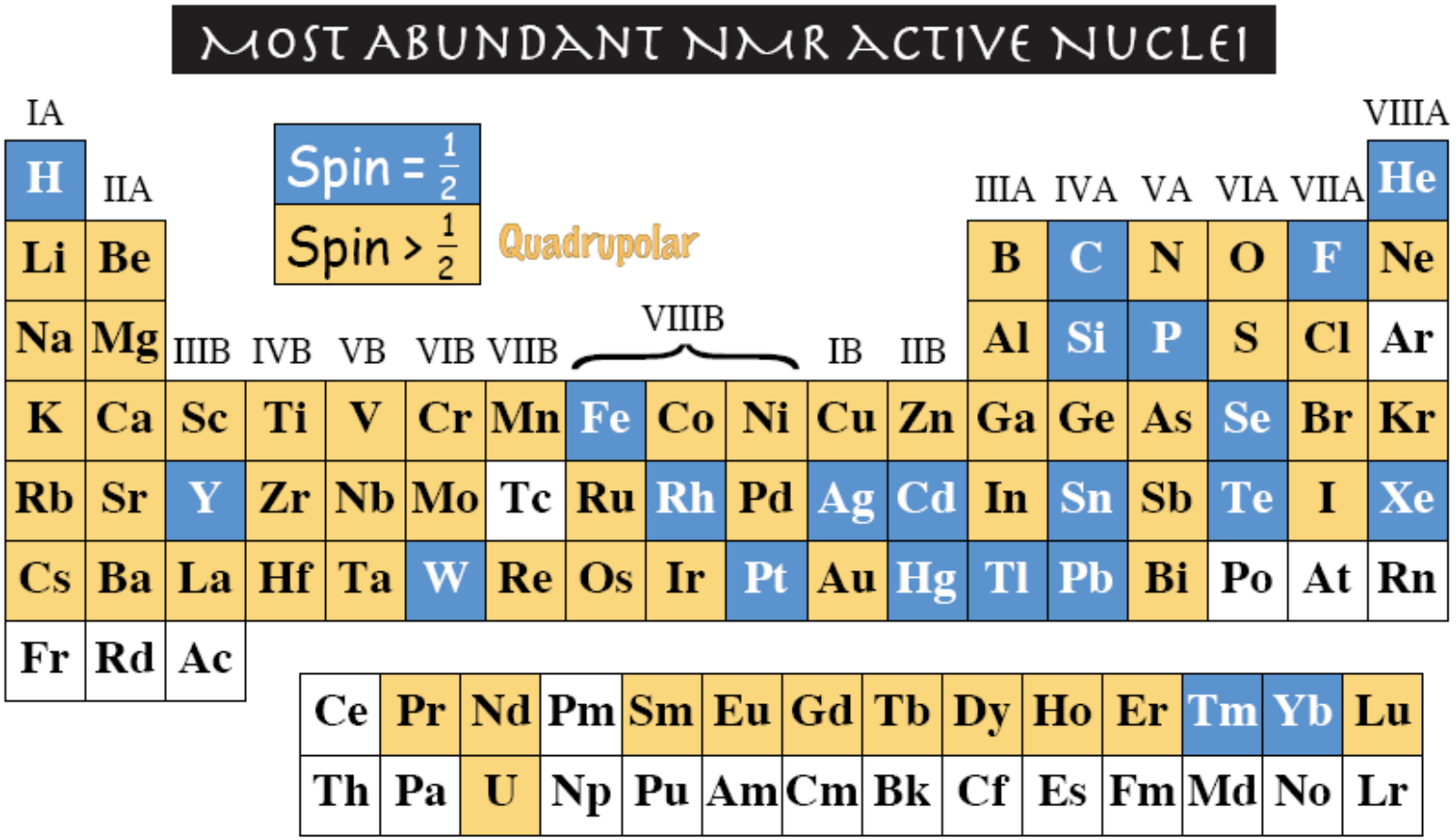
Table 2 The spin properties of quadrupolar nuclei[a].

Isotope[b]	Spin[c]	Natural abundance,[c] x/%	Magnetic moment,[d] μ/μ_N	Magnetogyric ratio,[d] $\gamma/10^7$ rad s^{-1} T^{-1}	Quadrupole moment[e] Q/fm^2	Frequency ratio,[e] Ξ/%	Reference sample	Sample conditions[g]	Literature for Ξ	Line-width factor,[h] ℓ/fm^4	Relative receptivity[i]	
											D^p	D^C
^{2}H[j]	1	0.0115	1.212 600 77	4.106 627 91	0.2860	15.350 609	$(CD_3)_4Si$	neat	15	0.41	1.11×10^{-6}	6.52×10^{-3}
^{6}Li	1	7.59	1.162 5637	3.937 1709	–0.0808	14.716 086	LiCl	D_2O, 9.7 m	9	0.033	6.45×10^{-4}	3.79
^{7}Li	3/2	92.41	4.204 075 05	10.397 7013	–4.01	38.863 797	LiCl	D_2O, 9.7 m	9	21	0.271	1.59×10^3
^{9}Be	3/2	100	–1.520 136	–3.759 666	5.288	14.051 813	$BeSO_4$	D_2O, 0.43 m	9	37	1.39×10^{-2}	81.5
^{10}B	3	19.9	2.079 2055	2.874 6786	8.459	10.743 658	$BF_3.Et_2O$	$CDCl_3$[k]	29	14	3.95×10^{-3}	23.2
^{11}B	3/2	80.1	3.471 0308	8.584 7044	4.059	32.083 974	$BF_3.Et_2O$	$CDCl_3$[k]	29	22	0.132	7.77×10^2
^{14}N[j]	1	99.632	0.571 004 28	1.933 7792	2.044	7.226 317	CH_3NO_2	neat/$CDCl_3$[ℓ]	9	21	1.00×10^{-3}	5.90
^{17}O	5/2	0.038	–2.240 77	–3.628 08	–2.558	13.556 457	D_2O	neat	9	2.1	1.11×10^{-5}	6.50×10^{-2}
^{21}Ne	3/2	0.27	–0.854 376	–2.113 08	10.155	7.894 296[m]	Ne	gas, 1.1 MPa	9	140	6.65×10^{-6}	3.91×10^{-2}
^{23}Na	3/2	100	2.862 9811	7.080 8493	10.4	26.451 900	NaCl	D_2O, 0.1 M	9	140	9.27×10^{-2}	5.45×10^2
^{25}Mg	5/2	10.00	–1.012 20	–1.638 87	19.94	6.121 635	$MgCl_2$	D_2O, 11 M	9	130	2.68×10^{-4}	1.58
^{27}Al	5/2	100	4.308 6865	6.976 2715	14.66	26.056 859	$Al(NO_3)_3$	D_2O, 1.1 m	9	69	0.207	1.22×10^3
^{33}S	3/2	0.76	0.831 1696	2.055 685	–6.78	7.676 000	$(NH_4)_2SO_4$	D_2O, sat.	9	61	1.72×10^{-5}	0.101

[a]Excluding the lanthanides, actinides, and most radioactive isotopes.
[b]Nuclei in parentheses are considered to be not the most favorable of the element concerned for NMR.
[c]Data are "representative isotopic compositions", taken from Rosman *et al.* [8], pp. 98–104. For the error limits on the natural abundances, see Rosman *et al.* [8].
[d]Data derived from the compilation in Mills *et al.*[6] pp. 98–104, which lists values of $\mu_{max} / \mu_N = \gamma\hbar I / \mu_N$. For the error limits, see Mills *et al.* [6].
[e]Data from Mills *et al.* [6], pp. 98–104 (taken mostly from Pyykko [26] and Raghavan [27]) and updated from Pyykko [28]. It should be noted that reported values of Q may be in error by as much as 20–30%. For the error limits, see Pyykko [28].
[f]Ratio of the resonance frequency of the reference to that of the protons of TMS at infinite dilution (in practice at $\varphi = 1\%$) in $CDCl_3$.
[g]M ≡ molarity in mol dm^{-3} (solution); m ≡ molality in mol kg^{-1} (solvent). Some results from ref. 9 were initially referenced [7] to a TMS concentration of 4.75 m in $CDCl_3$, but the values are corrected to refer to a dilute ($\varphi = 1\%$) solution of TMS in $CDCl_3$.
[h]$\ell = (2I+3)Q^2/I^2(2I-1)$ [5]. The values are quoted, arbitrarily, to 2 significant figures.
[i]D^p is the receptivity [5] relative to that of ^{1}H whereas D^C is relative to ^{13}C. The values are given to three significant figures only.
[j]A useful isotope of $I = \frac{1}{2}$ exists.
[k]15% by volume of $BF_3.Et_2O$ in $CDCl_3$.
[ℓ]Small amount of lock substance ($\varphi \leq 10\%$) in neat liquid, except for ^{61}Ni (where φ = ca. 20% of C_6D_6 is involved).
[m]Ξ In reasonable agreement with a value deduced from a ratio given in ref. 30.
[n]Ξ deduced from data in ref. 31.
[o]Ξ deduced from a ratio given in ref. 32.

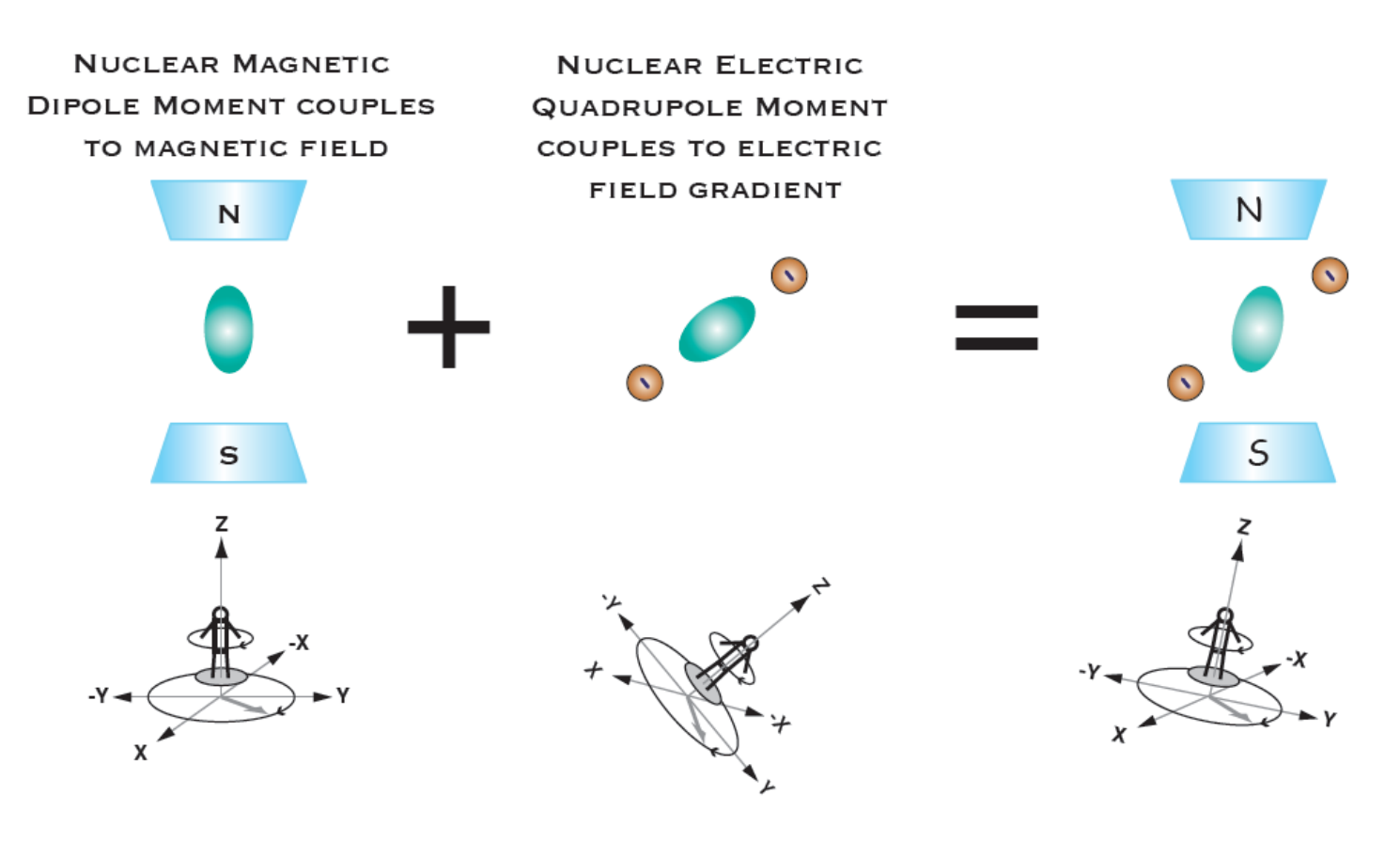
Harris et al., *Pure Appl. Chem.* 2001;73:1795-1818.

NMR periodic table



http://www.grandinetti.org/Research/NMR

Nuclear spin interactions: combined magnetic and electric interactions



http://www.grandinetti.org/Research/NMR

Recommended bibliography

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