

Magnetism I [11n22]

The description of magnetism in matter calls for tools from quantum mechanics and statistical mechanics. This module explores topics that employ such tools – topics traditionally covered (or meant to be covered) in solid-state physics courses.¹

Angular momentum of electrons:

Magnetism in matter is dominated by *orbital* and *spin* angular momenta of electrons, which require a quantum mechanical description.

The net angular momentum of atoms originates in incomplete electronic shells. Many atoms thus carry spin and/or angular momentum.

Conduction electrons, which are free to roam between atoms, leave behind the orbital angular momentum of incomplete shells and carry along their spin angular momentum.

Orbital angular momentum operator: $\mathbf{L} = (L_x, L_y, L_z)$.

Eigenvalue equations for atomic orbital angular momentum:²

$$\begin{aligned} \mathbf{L}^2|l, m\rangle &= l(l+1)|l, m\rangle & : l = 0, 1, 2, \dots \\ L_z|l, m\rangle &= m|l, m\rangle & : m = -l, -l+1, \dots, l. \end{aligned}$$

Atomic orbital magnetic moment:³ $|\boldsymbol{\mu}| = \sqrt{l(l+1)}\mu_B$, $\mu_z = -m\mu_B$.

Eigenvalue equations for atomic spin angular momentum:

$$\begin{aligned} \mathbf{S}^2|s, m_s\rangle &= s(s+1)|s, m_s\rangle & : s = \frac{1}{2}, 1, \frac{3}{2}, \dots \\ S_z|s, m_s\rangle &= m_s|s, m_s\rangle & : m_s = -s, -s+1, \dots, s. \end{aligned}$$

Atomic spin magnetic moment:⁴ $|\boldsymbol{\mu}_s| = \sqrt{s(s+1)}g\mu_B$, $\mu_s^{(z)} = -m_s g\mu_B$.

Zeeman energy-level splitting in a magnetic field $\mathbf{B} = B_z \hat{\mathbf{k}}$:

$$E = E_0 + m_s g \mu_B B_z$$

.

¹To a large extent, this module adapts materials from Blundell 2011.

²All angular momenta are in units of \hbar , which is often suppressed (as here) in the notation.

³All electronic magnetic moments are units of the Bohr magneton $\mu_B \doteq e\hbar/2m_e$.

⁴The g -factor for electrons is $g \simeq 2$.

Two-electron wave function:

Electrons are fermions. The two-electron wave function must be permutation antisymmetric. It can be expressed as the product of a spatial part ψ and a spin part χ .

The spatial part can be written as a linear combination of products of one-electron (spatial) wave functions ϕ_a, ϕ_b, \dots :

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) \pm \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1) \right].$$

The plus (minus) sign makes it symmetric (antisymmetric) under permutation of positions. The function has parity $(-1)^p$ with even or odd p .

The spin part is constructed from the basis, $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$, as linear combinations with a definite parity:

$$\chi(m_1, m_2) = \left\{ |\uparrow\uparrow\rangle, \frac{1}{\sqrt{2}} [|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle], |\downarrow\downarrow\rangle, \frac{1}{\sqrt{2}} [|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle] \right\}.$$

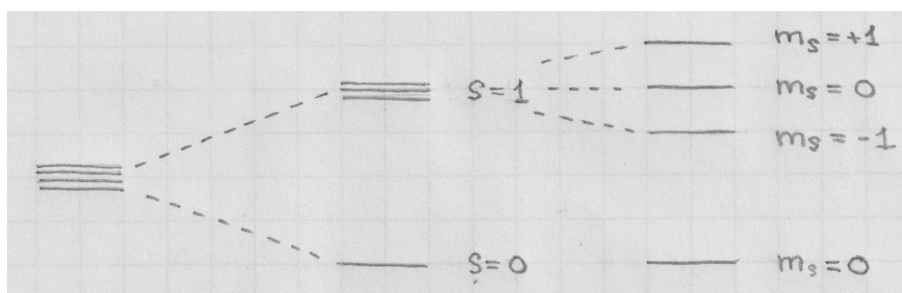
The first three are symmetric (even p) and constitute a triplet ($s = 1$), whereas last is antisymmetric (odd p) and constitutes a singlet ($s = 0$).

To make the two-electron wave function antisymmetric, its spatial and spin parts must have opposite parity.

The Pauli exclusion principle is thus enforced. If both electrons were in the same quantum state, either the spatial part or the spin part of the two-electron wave function would vanish identically, whichever has odd parity.

When two electrons experience an interaction that energetically favors one spatial parity over the other (e.g. Coulomb repulsion), this has the effect that the degeneracy between singlet and triplet is lifted.

When the electron pair is subject to a magnetic field $\mathbf{B} = B_z \hat{\mathbf{k}}$, the triplet splits up energetically, while the singlet is unaffected.



Atomic electrons in a magnetic field:

Consider an atom with Z electrons positioned in a uniform magnetic field \mathbf{B} .

In a semi-classical description each electron is instantaneously at position \mathbf{r}_i moving with instantaneous velocity \mathbf{v}_i .

Vector potential associated with uniform magnetic field [lln12]: $\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}$.

Kinetic momentum of electron: $\mathbf{p}_i = m_e \mathbf{v}_i$.

Canonical momentum of electron (with charge $-e$): $\mathbf{p}_i + e\mathbf{A}(\mathbf{r}_i)$.

Total spin angular momentum: $\hbar \mathbf{S} = \sum_{i=1}^Z \hbar \mathbf{s}_i$.

Total orbital angular momentum: $\hbar \mathbf{L} = \sum_{i=1}^Z \hbar \mathbf{L}_i = \sum_{i=1}^Z \mathbf{r}_i \times \mathbf{p}_i$.

Scalar potential (due to nuclear charge) experienced by electrons: Φ_i .

Hamiltonian:

$$\begin{aligned} \mathcal{H} &= \sum_{i=1}^Z \left[\frac{[\mathbf{p}_i + e\mathbf{A}(\mathbf{r}_i)]^2}{2m_e} + \Phi_i \right] + g\mu_B \mathbf{B} \cdot \mathbf{S} \\ &= \underbrace{\sum_{i=1}^Z \left[\frac{p_i^2}{2m_e} + \Phi_i \right]}_{\mathcal{H}_0} + \mu_B (\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m_e} \sum_{i=1}^Z (\mathbf{B} \times \mathbf{r}_i)^2 \end{aligned}$$

- The first term does not depend on \mathbf{B} . It describes the kinetic energy and potential energy of each electron as it moves in the static electric field of the nucleus, possibly modified summarily by the other electrons.
- The second term is linear in \mathbf{B} . It is the dominant magnetic effect and describes the phenomenon of *paramagnetism*. It is absent for atoms whose total angular momentum vanishes.
- The third term is quadratic in \mathbf{B} . It is present for all atoms and becomes the dominant magnetic effect for atoms that are not paramagnetic. It describes the phenomenon of *diamagnetism*.
- Neglected in this Hamiltonian are the interaction effects between electrons. They give rise to couplings between the total orbital and spin angular momenta (*LS-coupling*) and couplings between the total angular momenta, $\mathbf{J}_i = \mathbf{L}_i + \mathbf{s}_i$, of electrons (*JJ-coupling*).

Diamagnetism:

The diamagnetic response, like the dielectric response, is universal in atomic matter. Diamagnetic materials are those that do not exhibit a stronger magnetic response of any other types.

A classical plausibility argument for diamagnetism invokes Lenz's rule of negative feedback – a consequence for the direction of magnetic fields generated by induced currents as dictated by Faraday's law.

A diamagnetic response can be derived for a single charge carrier moving in a magnetic field [lex121]. However, the effect is wiped out by classical statistical averaging.

The Bohr-van Leeuwen theorem states that on the basis of classical statistical mechanics of charge carriers moving in a magnetic field, neither diamagnetism nor paramagnetism exist. Quantum mechanics is the basis of both.

A quantum theory of diamagnetism starts from the third term of the Hamiltonian constructed on the previous page, rewritten here for an ensemble of N identical electron orbitals in a macroscopic system of volume V :

$$\langle 0 | \mathcal{H}_{\text{dia}} | 0 \rangle = \frac{Ne^2}{8m_e V} \sum_{i=1}^Z \langle 0 | (\mathbf{B} \times \mathbf{r}_i)^2 | 0 \rangle.$$

Diamagnetism is empirically known to be only very weakly T -dependent. Taking a ground-state expectation value ignores any T -dependence in this simple first crack at a theory.

Setting $\mathbf{B} = B \hat{\mathbf{k}}$, we can write $(\mathbf{B} \times \mathbf{r}_i)^2 = B^2(x_i^2 + y_i^2) \simeq \frac{2}{3}B^2r_i^2$.

In a diamagnet, the expectation value $\langle 0 | \mathcal{H}_{\text{dia}} | 0 \rangle$ carries the leading magnetic-field dependence of the Helmholtz free energy F . The diamagnetic response thus follows from a second derivative as follows:

$$\chi \doteq -\mu_0 \frac{\partial^2 F}{\partial B^2} = -\frac{Ne^2 \mu_0}{6m_e V} \sum_{i=1}^Z \langle 0 | r_i^2 | 0 \rangle.$$

Among the first 60 elements, 31 are diamagnetic. A more refined theory of diamagnetism will be presented in a later module.

In solid materials, diamagnetism can be strongly anisotropic.

Paramagnetism:

The dominant form of paramagnetism is caused by unpaired atomic electrons. Magnetic atoms have a total angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, a combination, in general, of orbital and spin angular momentum.

The paramagnetisms of N independent atomic magnetic moments is analyzed in textbook applications of statistical mechanics of canonical ensembles. The canonical partition function factorizes.

Semi-classical theory [tex84]:⁵

- The magnetic moment is treated as a three-component vector $\boldsymbol{\mu}$.
- Energy function for each moment: $\mathcal{H} = -\boldsymbol{\mu} \cdot \mathbf{B}$.
- Partition function evaluated in spherical coordinates:

$$Z_N = 4\pi \left(\frac{\sinh(\beta\mu B)}{\beta\mu B} \right)^N, \quad \beta \doteq \frac{1}{k_B T}.$$

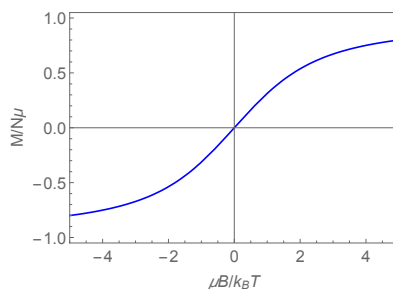
- Gibbs free energy: $G(T, B, N) = -k_B T \ln Z_N$.
- Magnetization: $M \doteq - \left(\frac{\partial G}{\partial B} \right)_{T,N} = N\mu \left[\coth(\beta\mu B) - \frac{1}{\beta\mu B} \right]$.
- Langevin function: $L(y) \doteq \coth(y) - \frac{1}{y} = \frac{y}{3} + O(y^3)$.
- Susceptibility: $\chi \doteq \mu_0 \left(\frac{\partial M}{\partial B} \right)_{T,N} = N\mu_0\mu^2 \left[\frac{1}{\beta\mu^2 B^2} - \frac{\beta}{\sinh^2(\beta\mu B)} \right]$.

Curie's law: $\chi = \frac{N\mu_0\mu^2}{3k_B T} + \dots$ (dominant term at low T).

- Heat capacity: $C_H \doteq k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z_N = Nk_B \left[1 - \frac{\beta^2 \mu^2 B^2}{\sinh^2(\beta\mu B)} \right]$.

Flaw of semi-classical model: $\lim_{T \rightarrow 0} C_H = Nk_B > 0$.

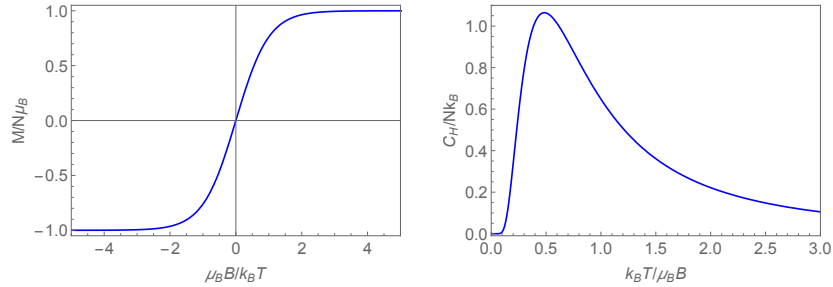
- Universal magnetization curve:



⁵These are exercises of a different course (PHY525: Statistical Physics I).

Two-level system [tex85]:

- Magnetic moment of an electron spin: $S = \frac{1}{2}$, $g = 2$.
- Two energy levels: $E_{\pm} = \pm\mu_B B$.
- Partition function: $Z_N = \left[2 \cosh \left(\frac{\mu_B B}{k_B T} \right) \right]^N$.
- Gibbs free energy: $G(T, B, N) = -k_B T \ln Z_N$.
- Magnetization: $M \doteq - \left(\frac{\partial G}{\partial B} \right)_{T,N} = N\mu_B \tanh \left(\frac{\mu_B B}{k_B T} \right)$.
- Susceptibility: $\chi \doteq \mu_0 \left(\frac{\partial M}{\partial B} \right)_{T,N} = \frac{N\mu_0\mu_B^2}{k_B T} \operatorname{sech}^2 \left(\frac{\mu_B B}{k_B T} \right)$.
- Curie's law: $\chi = \frac{N\mu_0\mu_B^2}{k_B T} + \dots$ (dominant term at low T).
- Heat capacity: $C_H \doteq k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z_N = Nk_B \left(\frac{\mu_B B}{k_B T} \right)^2 \operatorname{sech}^2 \left(\frac{\mu_B B}{k_B T} \right)$.
- Universal magnetization curve and heat capacity:

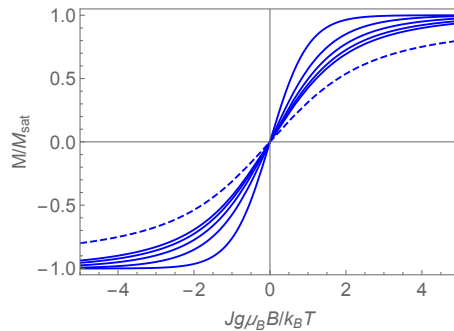


- The magnetization curve is similar in structure but not identical, apart from the different scale.
- The heat capacity of the quantum result is, as expected, consistent with the third law of thermodynamics.
- The broad peak of C_H is known as *Schottky anomaly* – one of several contributions to the heat capacity of a solid magnetic material.

Brillouin paramagnetism [tex86]:

- Atomic angular momentum \mathbf{J} with z -component $m = -J, -J+1, \dots, +J$.
- Energy levels: $E_m = mg\mu_B B$ ($2J + 1$ in number).
- Solution uses geometric sum.

- Partition function: $Z_N = \left[\sum_{m=-J}^{+J} e^{mx} \right]^N = \left[\frac{\sinh \left(\left(J + \frac{1}{2} \right) x \right)}{\sinh \left(\frac{1}{2} x \right)} \right]^N$, $x \doteq \frac{g\mu_B}{k_B T}$.
- Gibbs free energy: $G(T, B, N) = -k_B T \ln Z_N$.
- Magnetization: $M \doteq - \left(\frac{\partial G}{\partial B} \right)_{T, N} = M_{\text{sat}} B_J(y)$, $y = Jx$.
Saturation value: $M_{\text{sat}} = Ng\mu_B J$.
- Brillouin function: $B_J(y) \doteq \frac{2J+1}{2J} \coth \left(\frac{2J+1}{2J} y \right) - \frac{1}{2J} \coth \left(\frac{y}{2J} \right)$.
Quantum limit: $B_{\frac{1}{2}}(y) = \tanh(y)$.
Classical limit: $B_{\infty}(y) = \coth(y) - \frac{1}{y}$.
- One-parameter family of magnetization curves ($J = \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \infty$):



Van Vleck paramagnetism:

If the atomic ground state has $\mathbf{J} = 0$, then the dominant form of paramagnetism is absent. However, excited states with $\mathbf{J} \neq 0$ produce a paramagnetic response as a second-order perturbation:

$$\chi = \frac{N}{V} \left(2\mu_B^2 \sum_n \frac{|\langle 0 | L_z + gS_z | n \rangle|^2}{E_n - E_0} - \frac{e^2 \mu_0}{6m_e} \sum_{i=1}^Z \langle 0 | r_i^2 | 0 \rangle \right).$$

The sum \sum_n is over excited atomic states and the sum \sum_i over electronic orbitals in the ground state.

The van Vleck paramagnetism (first term) is comparable in magnitude to the diamagnetism (second term), but opposite in sign. Both are largely independent of temperature (unlike the dominant form of paramagnetism).

And then there is the Pauli paramagnetism of conduction electrons – a major topic of a later module (see also PHY525: Statistical Physics I) .

Fine structure:

The ground state of an atom with incomplete occupation of electronic shells has either a net orbital angular momentum \mathbf{L} or a net spin angular momentum \mathbf{S} or both.

In the absence of any interactions, such an electronic ground state has a degeneracy $(2L + 1)(2S + 1)$.

In the presence of a spin-orbit coupling, $\mathcal{H}_{LS} = \lambda \mathbf{L} \cdot \mathbf{S}$, \mathbf{L} and \mathbf{S} are not separately conserved. The total angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, remains conserved.

Also conserved remain the magnitudes, $\mathbf{L}^2 = L(L + 1)$ and $\mathbf{S}^2 = S(S + 1)$ (at least nonrelativistically).

States with given L and S exist for a range of J : $|L - S| \leq J \leq L + S$. The spin-orbit coupling reduces the degeneracy to multiplets with fixed J :

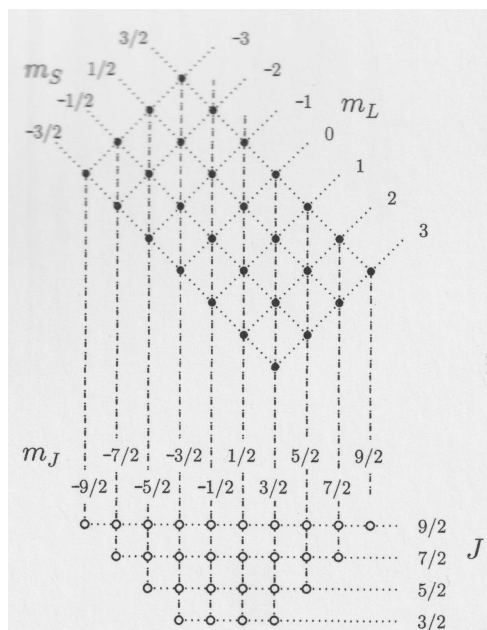
$$\mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L} \cdot \mathbf{S} \Rightarrow \langle \mathcal{H}_{LS} \rangle = \frac{\lambda}{2} [J(J + 1) - L(L + 1) - S(S + 1)].$$

Landé interval rule: $\Delta E_J \doteq E(J) - E(J - 1) = \lambda J$ for fixed L and S .

Visualization of degeneracy reduction due to spin-orbit coupling:

Example with $L = 3$ and $S = \frac{3}{2}$.
 $\Rightarrow J_{\min} = \frac{3}{2}, \quad J_{\max} = \frac{9}{2}$.

[image from Blundell 2011]



Predicting the nature of the electronic ground state of an atom requires knowledge of the values of L , S , and J produced by unpaired electrons.

Hund's rules:

Empirical rules (of limited and ranked scope) regarding the values of L , S , and J of the electronic ground-state configuration in a single incomplete subshell (specified in the periodic table of [lln10]).

#1 Total spin: $S = S_{\max}$.

#2 Total orbital angular momentum: $L = L_{\max}$.

#3 Total angular momentum: $J = \begin{cases} |L - S| & : \text{shell less than half full,} \\ L + S & : \text{shell more than half full.} \end{cases}$

Rule #1 is argued on the fact that electrons with the same spin orientation are forced into different l orbitals, which lowers the Coulomb repulsion.

Rule #2 is argued (more dubiously) on the fact that electrons that maximize L move in the same direction and can thus avoid each other more easily.

Rule #3, supposed to minimize the spin-orbit coupling energy, is the most restricted in scope, given that other couplings or sometimes stronger.

Example: rare-earth ion Dy^{3+} (dysprosium).

- Electronic configuration of atom: $[\text{Xe}]4f^{10}6s^2$.
- Dy^{3+} lacks two 6s electrons and one 4f electrons: $[\text{Xe}]4f^9$.
- The 4f shell has 9 electrons (14 at full capacity).
- Electrons in an f shell have $l = 3$.
- The 4f shell accommodates a maximum $2l + 1 = 7$ electrons with the same spin orientation.
- Two electrons are thus spin-paired, which leaves 5 electrons that are not. Hence $S = \frac{5}{2}$ (rule #1), implying $2S + 1 = 6$.
- The net orbital angular momentum of the 7 electrons with the same spin orientation vanishes.
- The maximum orbital angular momentum of the two remaining electrons (with opposite spin orientation) is $L = 3 + 2 = 5$ (rule #2).
- The 4f shell is more than half full. Hence $J = 5 + \frac{5}{2} = \frac{15}{2}$ (rule #3).
- Symbolic representation: ${}^6\text{H}_{15/2}$.

Hund's rules are applicable to incomplete 3d shells in transition metals (elements 21 to 30) and to incomplete 4f shells in lanthanides (57 to 71). They are more accurate for the latter set for reasons discussed later.

Russell-Saunders coupling:

The coupling between the spin \mathbf{S} and the orbital angular momentum \mathbf{L} of an atom is interpreted as the electron spin alignment with the magnetic field produced by (relative) orbital motion of the nucleus.

- Orbital angular momentum (for a single electron): $\hbar\mathbf{L} = m_e\mathbf{r} \times \mathbf{v}$.
- Nuclear charge: $q = Ze$.
- Electric potential: $\Phi(r) = \frac{q}{4\pi\epsilon_0 r}$.
- Electric field: $\mathbf{E} = -\frac{q}{4\pi\epsilon_0 r^2} \frac{\mathbf{r}}{r} = -\frac{d\Phi}{dr} \frac{\mathbf{r}}{r}$.
- Magnetic field: $\mathbf{B} = \frac{\mu_0}{4\pi} \frac{q\mathbf{v} \times \mathbf{r}}{r^3} = \frac{\mathbf{E} \times \mathbf{v}}{c^2} = -\frac{d\Phi}{dr} \frac{\hbar}{m_e r c^2} \mathbf{L}$.
- Electron spin magnetic moment: $\mathbf{m} = \frac{ge\hbar}{2m_e} \mathbf{S}$.
- Potential energy:⁶ $\mathcal{H}_{LS} = -\frac{1}{2} \mathbf{m} \cdot \mathbf{B} = \frac{e\hbar^2 g}{4m_e^2 c^2} \frac{1}{r} \frac{d\Phi}{dr} \mathbf{S} \cdot \mathbf{L}$.
- If Coulomb potential is applicable: $\frac{1}{r} \frac{d\Phi}{dr} = \frac{Ze}{4\pi\epsilon_0 r^3}$.
- Atomic physics yields estimates of $\langle r^{-3} \rangle$ for estimates of $\langle \mathbf{S} \cdot \mathbf{L} \rangle$.

Landé g-factor:

- Atomic magnetic moment: $\mathbf{m} = \mu_B(g_L\mathbf{L} + g_S\mathbf{S}) = \mu_B g_J \mathbf{J}$
with $g_L = 1$, $g_S = 2$, and g_J to be determined.
- Use $\mathbf{m} \cdot \mathbf{J} = \mu_B g_J \mathbf{J}^2 = \mu_B(g_L\mathbf{L} \cdot \mathbf{J} + g_S\mathbf{S} \cdot \mathbf{J})$.
- Use $\mathbf{L} \cdot \mathbf{J} = \frac{1}{2}(\mathbf{J}^2 + \mathbf{L}^2 - \mathbf{S}^2)$ $\mathbf{S} \cdot \mathbf{J} = \frac{1}{2}(\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2)$.
- Use $\mathbf{J}^2 = J(J+1)$, $\mathbf{L}^2 = L(L+1)$, $\mathbf{S}^2 = S(S+1)$.
$$\Rightarrow 2g_J J(J+1) = g_L [J(J+1) + L(L+1) - S(S+1)]$$
$$+ g_S [J(J+1) - L(L+1) + S(S+1)].$$
- Landé g-factor: $g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$.

⁶The relativistic Thomas factor $\frac{1}{2}$ looks artificial, but appears naturally in a fully relativistic calculation.

Nuclear spins:

Protons and neutrons are fermions with spin $I = \frac{1}{2}$. Their magnetic moments are much smaller than that of the electron.

$$\text{Nuclear magneton: } \mu_N \doteq \frac{e\hbar}{2m_p} = 5.0508 \times 10^{-27} \text{Am}^2 \simeq 5.4 \times 10^{-4} \mu_B.$$

$$\text{Nuclear magnetic moment: } \mu = g_I \mu_N I.$$

The nuclear g-factors g_I are hard to predict, even for the neutron and the proton, due to their complex quark composition.

Some common nuclear spins:

n: neutron

p: proton, ${}^1\text{H}$

d: deuteron, ${}^2\text{H}$

t: triton, ${}^3\text{H}$

N : # of neutrons

Z : atomic number (# of protons)

$A = Z + N$: mass number

X : element in ${}^A X$

I : nuclear spin (in units of \hbar)

μ : nuclear magnetic moment

μ_N : nuclear magneton

g_I : nuclear g-factor

[table from Blundell 2011]

Nucleus	Z	N	I	μ/μ_N	g_I
n	0	1	$\frac{1}{2}$	-1.913	-3.826
p= ${}^1\text{H}$	1	0	$\frac{1}{2}$	2.793	5.586
d= ${}^2\text{H}$	1	1	1	0.857	0.857
t= ${}^3\text{H}$	1	2	$\frac{1}{2}$	-2.128	4.255
${}^{12}\text{C}$	6	6	0	0	0
${}^{13}\text{C}$	6	7	$\frac{1}{2}$	0.702	1.404
${}^{14}\text{N}$	7	7	1	0.404	0.404
${}^{16}\text{O}$	8	8	0	0	0
${}^{17}\text{O}$	8	9	$\frac{5}{2}$	-1.893	-0.757
${}^{19}\text{F}$	9	10	$\frac{1}{2}$	2.628	5.257
${}^{31}\text{P}$	15	16	$\frac{1}{2}$	1.132	2.263
${}^{33}\text{S}$	16	17	$\frac{3}{2}$	0.643	0.429

Identical nucleons tend to form singlet pairs. Nuclei with an odd number of protons and/or an odd number of neutrons have a nonzero nuclear spin.

Hyperfine structure:

The orbital angular momentum \mathbf{L} and spin \mathbf{S} of atomic electrons produce a magnetic field at the nuclear position and thus interact with nuclear spin \mathbf{I} .

Consider a nuclear spin at $\mathbf{r} = 0$ and an electron spin at position \mathbf{r} .

Magnetic dipole field of nuclear spin at position of electron spin [lln12][lex36]:

$$\mathbf{B} = \frac{\mu_0}{4\pi r^3} \left[3(\boldsymbol{\mu}_I \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \boldsymbol{\mu}_I \right].$$

Interaction potential energy of electron spin: $U = -\boldsymbol{\mu}_S \cdot \mathbf{B}$.

Magnetic dipole interaction between electron spin and nuclear spin [lex130]:

$$\begin{aligned}\mathcal{H}_{\text{dip}} &= \frac{\mu_0}{4\pi r^3} \left[\boldsymbol{\mu}_S \cdot \boldsymbol{\mu}_I - 3(\boldsymbol{\mu}_S \cdot \hat{\mathbf{r}})(\boldsymbol{\mu}_I \cdot \hat{\mathbf{r}}) \right] \\ &= \frac{\mu_0 g_S g_I \mu_B \mu_N}{4\pi r^3} \left[\mathbf{S} \cdot \mathbf{I} - 3(\mathbf{S} \cdot \hat{\mathbf{r}})(\mathbf{I} \cdot \hat{\mathbf{r}}) \right].\end{aligned}$$

This dipolar spin-spin interaction averages to zero for electronic s-orbitals.⁷ However, the overlap of the s-orbital wave function with nuclear position produces the Fermi contact interaction:

$$\mathcal{H}_{\text{con}} = \left(\frac{2\mu_0}{3} \right) g_S g_I \mu_B \mu_N \mathbf{S} \cdot \mathbf{I}.$$

There also exists a dipolar interaction between the orbital angular momentum and the nuclear spin. A more complete analysis starts from the Hamiltonian,

$$\begin{aligned}\mathcal{H} &= \frac{1}{2m_e} (\mathbf{p} + e\mathbf{A})^2 + 2\mu_B \mathbf{S} \cdot (\nabla \times \mathbf{A}) + \Phi(r), \\ \mathbf{A} &= \frac{\mu_0}{4\pi r^3} \boldsymbol{\mu} \times \mathbf{r}, \quad \boldsymbol{\mu} = g_I \mu_N \mathbf{I}.\end{aligned}$$

The hyperfine interaction is distilled from this expression in two steps [lex123]:

$$\begin{aligned}\mathcal{H}' &= \frac{\mu_0 g_I \mu_B \mu_N}{2\pi} \left[(\mathbf{S} \cdot \nabla)(\mathbf{I} \cdot \nabla) \frac{1}{r} - (\mathbf{S} \cdot \mathbf{I}) \nabla^2 \frac{1}{r} + \frac{\mathbf{L} \cdot \mathbf{I}}{r^3} \right], \\ &= \frac{\mu_0 g_I \mu_B \mu_N}{2\pi} \mathbf{I} \cdot \left[\frac{\mathbf{L} - \mathbf{S} + 3(\mathbf{S} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}}}{r^3} + \frac{8\pi}{3} \mathbf{S} \delta(\mathbf{r}) \right].\end{aligned}$$

The hyperfine splitting in the ground state of atomic hydrogen with electronic $L = 0, S = \frac{1}{2}$ and nuclear $I = \frac{1}{2}$ involves transitions between a singlet combination and a triplet combination. The singlet state has lower energy.

The transition energy corresponds to the famous 21cm HI emission⁸ detected by astronomers. For comparison, the average wavelength of the cosmic microwave background (CMB) radiation is less than 1cm.

⁷Positional averaging of the electron relative to the nucleus.

⁸H stands for hydrogen and I (Roman 1) for neutral (not ionized).