Magnetic effects and the peculiarity of the electron spin in Atoms

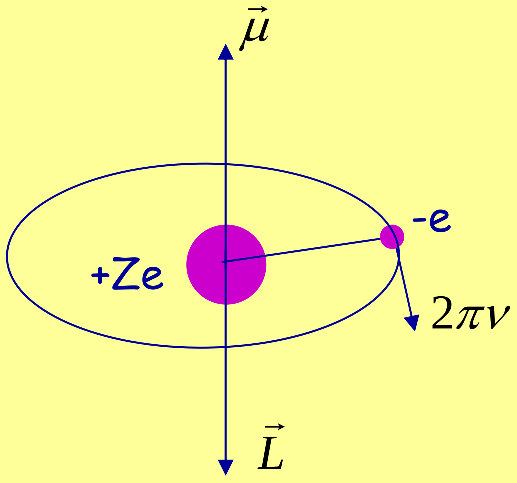

Pieter Zeeman   Hendrik Lorentz
Nobel Prize 1902

Otto Stern
Nobel 1943

Wolfgang Pauli
Nobel 1945

The orbital angular momentum of an electron in orbit

Semiclassical approach



Angular velocity $\omega = 2\pi\nu$

Magnetic moment

$$\mu = IA = \pi r^2 e\nu$$

Angular momentum

$$L = mvr = m\omega r^2 = 2\pi m\nu r^2$$

Hence $\vec{\mu} = -\frac{e}{2m_e}\vec{L}$

Magnetic interaction:

$$V_M = -\vec{\mu}\cdot\vec{B} = -\mu_z B_z$$

From classical electrodynamics:

-A magnetic dipole moment μ undergoes no force in a magnetic field B

-A magnetic dipole undergoes a torque, is oriented in a B field

-A magnetic dipole μ undergoes a force in an inhomogeneous B-field, i.e. a field gradient (Stern-Gerlach experiment)

The energy of a magnetic dipole in an external B-field

Dipole $\vec{\mu} = -\frac{e}{2m_e}\vec{L} = -\mu_B \frac{\vec{L}}{\hbar}$

with: $\mu_B = \frac{e\hbar}{2m_e}$

the "Bohr magneton", the atomic unit for a magnetic dipole moment ~ 5 x 10^{-9} eV/c ~ 9 x 10^{-24} Am^2

This may be generalized for any orbiting charge Q of mass M

$$\vec{\mu} = g\frac{Q}{2M}\vec{L}$$

Where the g-factor for a classical motion $g = 1$

Magnetic interaction:

$$V_M = -\vec{\mu}\cdot\vec{B} = -\mu_z B_z$$

for the magnetic dipole moment: $\vec{\mu} = -g\mu_B \frac{\vec{L}}{\hbar}$

Expectation value:

$$\langle V_M \rangle = -\langle \mu_z \rangle B = \frac{g\mu_B B}{\hbar}\langle L_z \rangle = g\mu_B B m$$

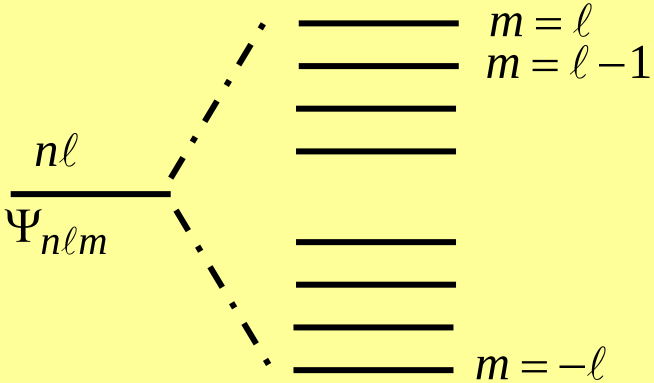
Because: $\langle \Psi_{nlm} | L_z | \Psi_{nlm} \rangle = m\hbar$

for any atomic quantum state

So a B-field breaks the degeneracy for m

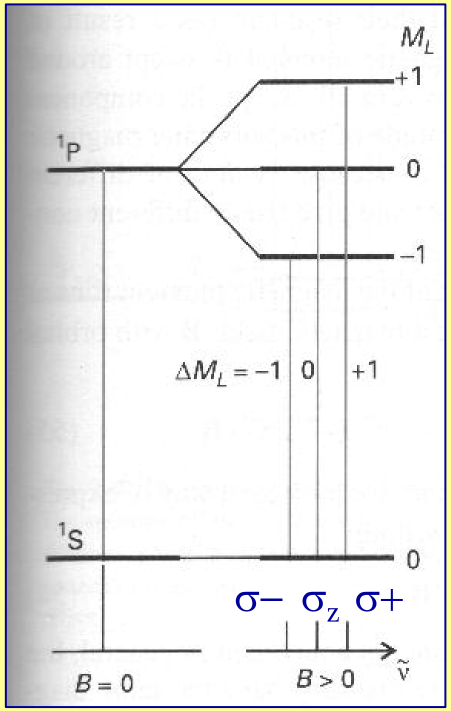
Normal Zeeman effect

Energy splitting for an *nl* state



Energy splitting: $\delta E_m = g\mu_B M$

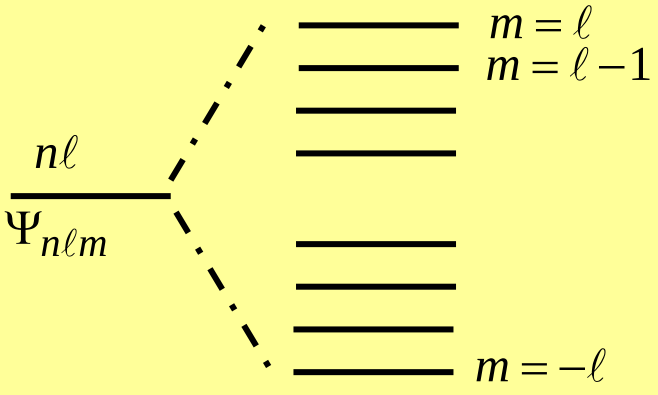
For an $^1S \rightarrow {}^1P$-transition



Recall selection rules for *m* and polarization of light

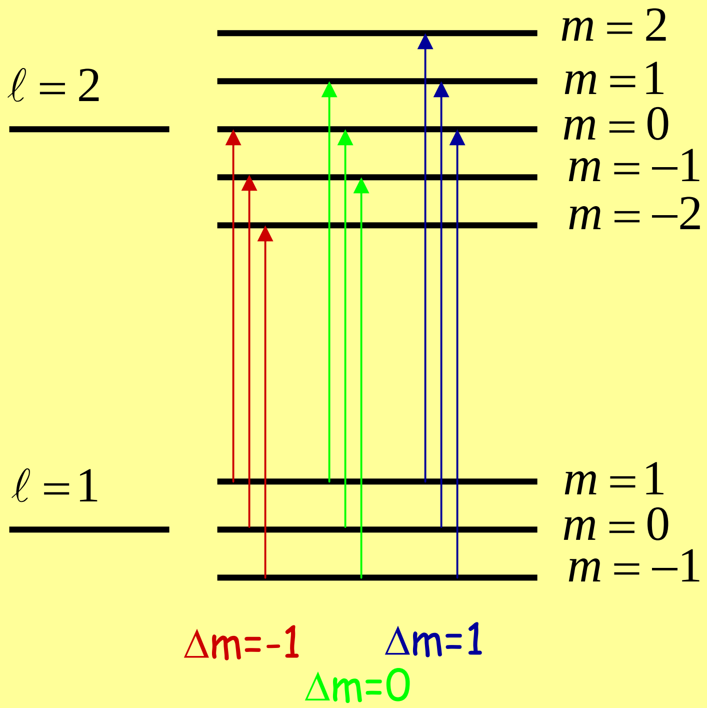
Normal Zeeman effect

Energy splitting for an *nl* state



Energy splitting: $\delta E_m = g\mu_B$

For an $^1P \rightarrow {}^1D$-transition



9 transitions
3 spectral lines (in hydrogen)

Wave functions in a magnetic field

Schrödinger equation;

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V'(r)\right]\Psi_{nlm} = E_n\Psi_{nlm}$$

$$V'(r) = V_{\text{Coulomb}}(r) + V_{\text{Zeeman}}$$

$$= V_C(r) + \frac{g\mu B}{\hbar}L_z = V_C(r) + \frac{g\mu B}{\hbar}\frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

Note: $\Psi_{nlm}(\vec{r},t) = R_{nl}(r)Y_{lm}(\theta,\phi)e^{-iE_n t/\hbar}$

Are simultaneous eigenfunctions of H^0 and L_z

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V_C(r) + \frac{g\mu_B B}{i}\frac{\partial}{\partial\phi}\right]\Psi_{nlm} = \left(E_{nl} + g\mu_B Bm\right)\Psi_{nlm}$$

Eigenvalues of the Zeeman Hamiltonian:

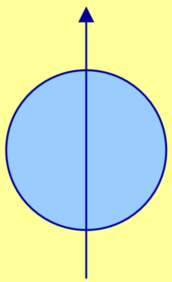
$$E = E_{nl} + g\mu_B Bm$$

Selection rules remain the same

Electron spin

No classical analogue for this phenomenon

$$s = \frac{1}{2}\hbar$$

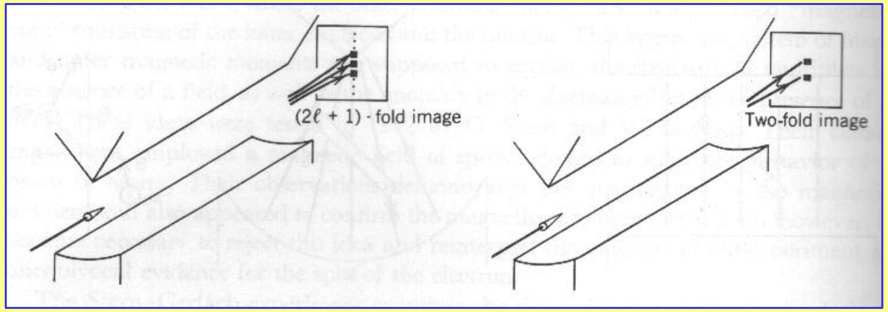


Pauli:
There is an additional "two-valuedness" in the spectra of atoms, behaving like an angular momentum

Goudsmit and Uhlenbeck
This may be interpreted/represented as an angular momentum

Origin of the spin-concept

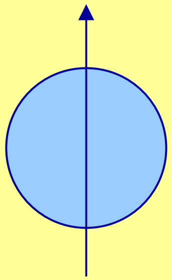
-Stern-Gerlach experiment;
space quantization



-Theory: the periodic system requires an additional two-valuedness

Electron spin

$$s = \frac{1}{2}\hbar$$



Spin is an angular momentum, so it should satisfy

$$S^2|s, m_s\rangle = \hbar^2 s(s+1)|s, m_s\rangle$$

$$S_z|s, m_s\rangle = \hbar m_s|s, m_s\rangle$$

$$s = \frac{1}{2}, m_s = \pm\frac{1}{2}$$

In analogy with the orbital angular momentum of the electron

$$\vec{\mu}_L = -g_L \mu_B \frac{\vec{L}}{\hbar} \qquad g_L = 1$$

A spin (intrinsic) angular momentum can be defined:

$$\vec{\mu}_S = -g_S \mu_B \frac{\vec{S}}{\hbar}$$

a) in relativistic Dirac theory

$$g_S = 2$$

b) in quantum electrodynamics

$$g_S = 2.00232...$$

Note: the spin of the electron cannot be explained from a classically "spinning" electronic charge

Electron spin and the atom

Additional quantum number

$$|nlm\rangle \rightarrow |nlsm_l m_s\rangle$$

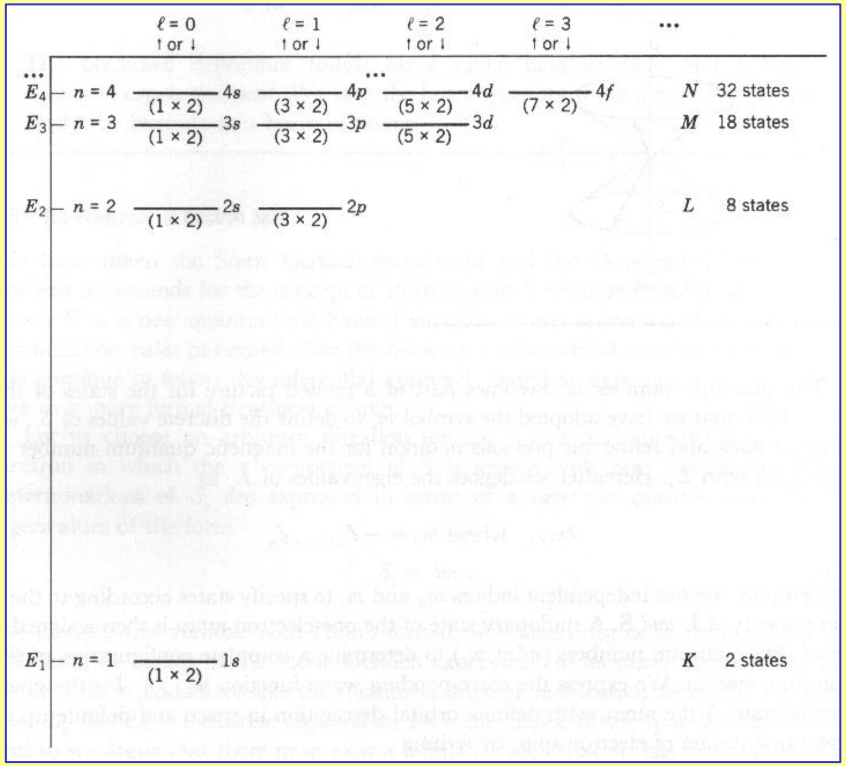
Wave functions

$$\Psi_{nlm}(\vec{r},t) = R_{nl}(r)Y_{lm}(\theta,\phi)e^{-iE_n t/\hbar}|\uparrow,\downarrow\rangle$$

No effect on energy levels,
except for magnetic coupling to
other angular momenta

Degeneracy $\qquad 2(2\ell+1)$

$$2n^2$$



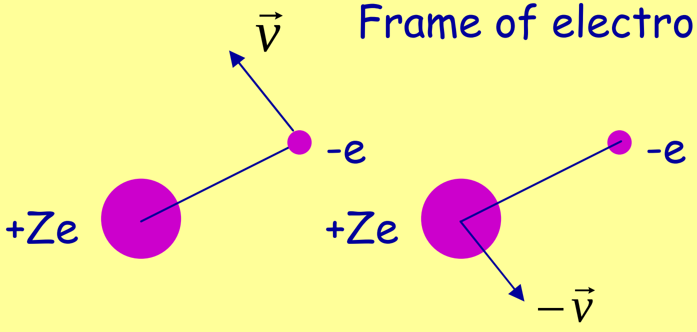
Selection rules

S is not a spatial operator,
so no effect on dipole selection rules

Spin-orbit interaction

Frame of nucleus:

Frame of electron:



The moving charged nucleus induces a magnetic field at the location of the electron, via Biot-Savart's law

$$\vec{B} = \frac{\mu_0}{4\pi} \frac{Ze(-\vec{v}) \times \vec{r}}{r^3}$$

Use $\vec{L} = m\vec{r} \times \vec{v}$; $\mu_0 \varepsilon_0 = \frac{1}{c^2}$

Then $\vec{B}_{\mathrm{int}} = \frac{Ze}{4\pi\varepsilon_0} \frac{\vec{L}}{m_e c^2 r^3}$

Spin of electron is a magnet with dipole

$$\vec{\mu}_S = -g_e \frac{\mu_B}{\hbar} \vec{S}$$

The dipole orients in the B-field with energy

$$V_{LS} = -\vec{\mu}_S \cdot \vec{B} = \frac{Ze^2}{4\pi\varepsilon_0 m_e^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

A fully relativistic derivation (Thomas Precession) yields $V_{LS} = \zeta(r) \vec{S} \cdot \vec{L}$ with

$$\zeta(r) = \frac{Ze^2}{8\pi\varepsilon_0 m_e^2 c^2} \left\langle \frac{1}{r^3} \right\rangle_{nl}$$

Use:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{2}{a^3 n^3 \ell(\ell + 1/2)(\ell + 1)} = \left(\frac{Z\alpha mc}{\hbar n} \right)^3 \frac{2}{n^3 \ell(\ell + 1/2)(\ell + 1)}$$

Fine structure in spectra due to Spin-orbit interaction

In first order correction to energy for state $|lsjm_j\rangle$

$$E_{SO} = \langle lsjm_j | V_{SL} | lsjm_j \rangle$$

$$= \langle lsjm_j | \zeta_{nl} \vec{L} \cdot \vec{S} | lsjm_j \rangle$$

Evaluate the dot-product

$$J^2 = |\vec{L} + \vec{S}|^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S}$$

Then

$$\vec{L} \cdot \vec{S} | \ell sjm_j \rangle = \frac{1}{2}\left(J^2 - L^2 - S^2\right) | \ell sjm_j \rangle$$

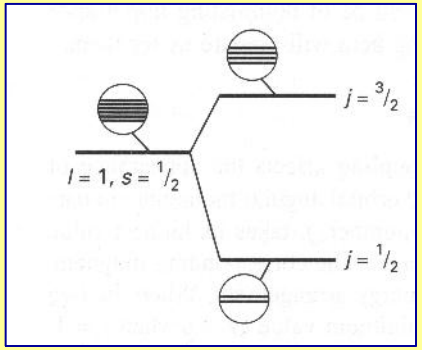
$$= \frac{1}{2}\hbar^2 \{ j(j+1) - \ell(\ell+1) - s(s+1) \} | \ell sjm_j \rangle$$

Then the full interaction energy is:

$$E_{SO} = \alpha^2 Z^4 hcR \left\{ \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{2n^3 \ell(\ell+1/2)(\ell+1)} \right\}$$

S-states $|\ell = 0, j = s\rangle$ $\quad E_{SO} = 0$

P-states $|\ell = 1, j = \ell \pm 1/2\rangle$



$$E_{SO} = \frac{\alpha^2 Z^4 hcR}{2n^3}$$

Show that the "centre-of-gravity" does not shift

Relativistic effects in atomic hydrogen

Relativistic kinetic energy

$$E_{kin}^{rel} = \sqrt{p^2c^2 + m^2c^4} - mc^2 =$$

$$mc^2\sqrt{1 + p^2 / m^2c^2} - mc^2 =$$

$$mc^2\left[1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} + \cdots\right]$$

First relativistic correction term

$$K_{rel} = -\frac{p^4}{8m_e^3c^2}$$

To be used in perturbation analysis:

$$\vec{p} = -\frac{\hbar}{i}\vec{\nabla}$$

operator does not change wave function

$$\left\langle K_{rel}\right\rangle = \left\langle \Psi_{n\ell jm}\left| -\frac{p^4}{8m_e^3c^3}\right|\Psi_{n\ell jm}\right\rangle =$$

$$-\frac{Z^4\alpha^2}{2n^3}(hc)R\left(\frac{1}{2\ell+1} - \frac{3}{8n}\right)$$

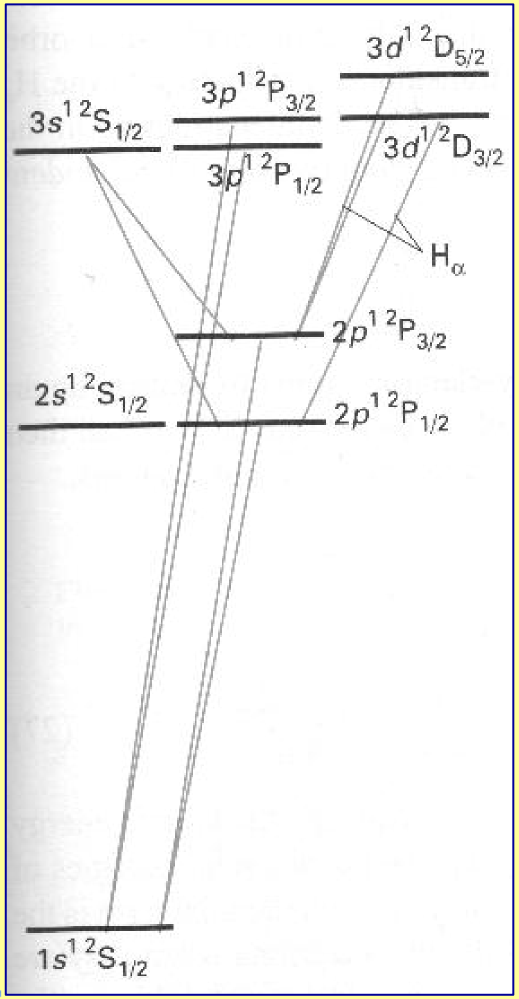
Of the same order as Spin-orbit coupling

Relativistic energy levels:

$$E_{nj} = E_n - \frac{Z^4\alpha^2}{2n^3}(hc)R\left(\frac{2}{2j+1} - \frac{3}{4n}\right)$$

So j=1/2 levels would be degenerate

Relativistic energy diagram for atomic hydrogen



For each configuration (electrons)

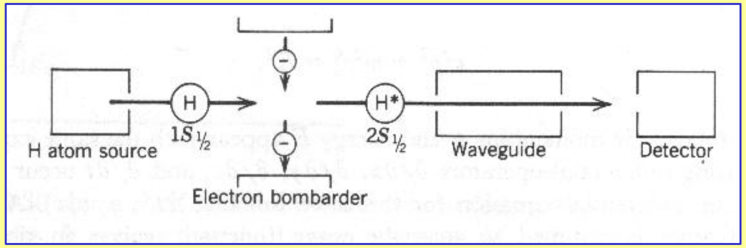
Several terms with term symbols

$$^{2S+1}L_J$$

P.A.M. Dirac
Nobel 1933

Shortcomings of quantum-mechanical model of hydrogen

1. Spontaneous emission from stationary states
2. g-factor of electron $\neq 2$
3. Lamb shift

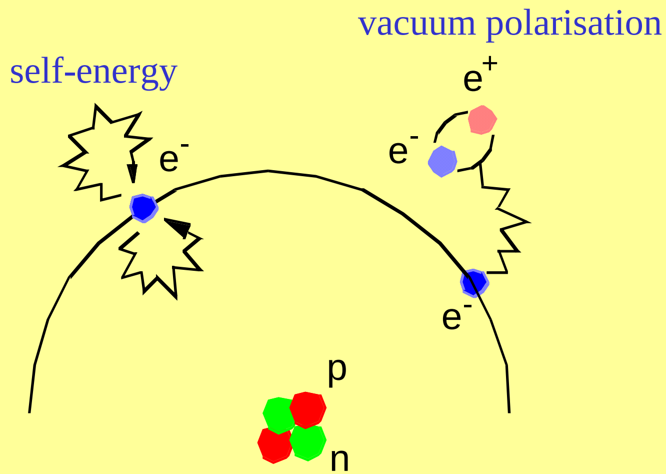


$(n=2)^2S_{1/2}$

Δ = 1060 MHz

$(n=2)^2P_{1/2}$

Quantum Electro Dynamics (QED)



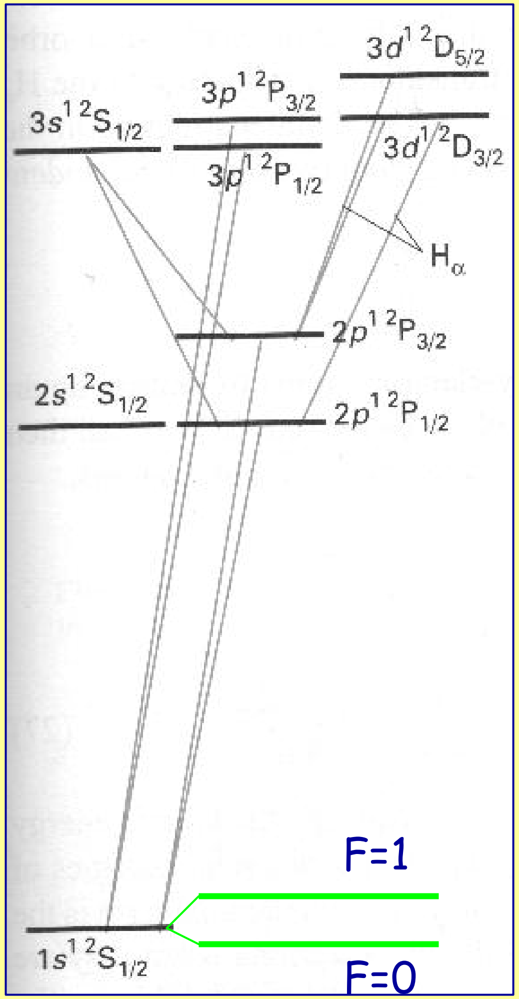
Sin-Itiro Tomonaga

Julian Schwinger

Richard Feynman

Nobel 1965

Hyperfine structure in atomic hydrogen



Nucleus has a spin as well, and therefore a magnetic moment

$$\vec{\mu}_I = g_I \mu_N \frac{\vec{I}}{\hbar} \quad ; \qquad \mu_N = \frac{e\hbar}{2M_p}$$

Interaction with electron spin, that may have density at the site of the nucleus (Fermi contact term)

$$\vec{I} \cdot \vec{S} = \vec{I} \cdot \vec{J} = \frac{1}{2}\left(F^2 - J^2 - I^2\right)$$

Splitting : F=1 ↔ F=0   1.42 GHz

or λ = 21 cm

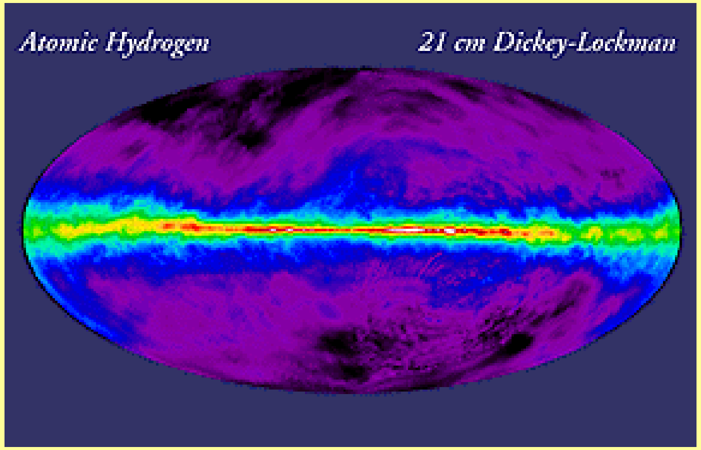
Magnetic dipole transition

Hyperfine structure in atomic hydrogen

Search in space for H-atoms

via 21 cm radiation

Map of the Milky Way in H



Westerbork Telescope Array

Anomalous Zeeman effect

Occurs if S and L play a role

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S = -\frac{\mu_B}{\hbar}(g_L\vec{L} + g_S\vec{S})$$

$$= -\frac{\mu_B}{\hbar}(\vec{L} + 2\vec{S})$$

Approximation: Paschen-Back effect for $V_{Zeeman} >> V_{LS}$

$\Psi_{n\ell m_\ell m_s}$ proper wave functions

$$\langle V_M \rangle = \frac{\mu_B B}{\hbar}\langle L_z + 2S_z \rangle = \mu_B B(m_\ell + 2m_s)$$

But in general:

$\Psi_{n\ell j m_j}$ proper wave functions

At weaker fields:

$$\vec{\mu} = -\frac{\mu_B}{\hbar}(\vec{L} + 2\vec{S}) \quad \text{and} \quad \vec{J} = (\vec{L} + \vec{S})$$

So J and μ non-colinear

Work with projections onto an axis B

$$\langle V_M \rangle = -\vec{\mu} \cdot \vec{B} = \left(-\frac{\vec{\mu} \cdot \vec{J}}{J}\right)\left(\frac{\vec{J} \cdot \vec{B}}{J}\right)$$

$$= \frac{e}{2m} \frac{\left(\vec{L} + 2\vec{S}\right) \cdot \vec{J}}{J} \frac{J_z B}{J}$$

With $\left(\vec{L} + 2\vec{S}\right) \cdot \vec{J} = L^2 + 2S^2 + 3\vec{L} \cdot \vec{S}$

$$3\vec{L} \cdot \vec{S} = \frac{3}{2}\left(J^2 - L^2 - S^2\right)$$

Anomalous Zeeman effect; Lande factor

Result

$$\langle V_Z \rangle = \mu_B B \left(\frac{L^2 + 2S^2 + \frac{3}{2}\left(J^2 - L^2 - S^2\right)}{J^2} \right) \langle J_Z \rangle$$

With the Lande g-factor dependent on J, S, L.

$$g_L = \left(1 + \frac{\left(J(J+1) - L(L+1) + S(S+1)\right)}{2J(J+1)} \right)$$

Zeeman effect

$$\langle V_Z \rangle = \mu_B B g_{\mathrm{Lande}} m_j$$