SPIN

One statement of the Pauli exclusion principle:

Electron wavefunction is antisymmetric w.r.t. interchange of electrons:

$$\Psi(1,2) = -\Psi(2,1)$$

immediately yields the other common statement:

Two electrons cannot have all the same quantum numbers.

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\left[1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2)\right] = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

= 0 if both spatial and spin orbitals are the same. Going to lithium

$$\Psi(1,2,3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

or

$$\Psi(1,2,3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\beta(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\beta(3) \end{vmatrix}$$

(either possible - electron spin up or down) or the general case

$$\Psi(1,2,\ldots,N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} u_1(1) & u_2(1) & \cdots & u_N(1) \\ u_1(2) & u_2(2) & \cdots & u_N(2) \\ \vdots & \vdots & & \vdots \\ u_1(N) & u_2(N) & \cdots & u_N(N) \end{vmatrix}$$

=0 if any two electrons have same total wavefunction $\Rightarrow$ two identical Slater determinant columns

MAGNETIC FIELD EFFECTS on spin states

Spin angular momentum ⇒ magnetic moment

Electron orbital magnetic moment

$$\boldsymbol{\mu}_L = -\frac{e}{2m_e}\mathbf{L}$$

$$\left|\boldsymbol{\mu}_L\right| = -\frac{e\hbar}{2m_e}\sqrt{l\left(l+1\right)} \equiv -\beta_0\sqrt{l\left(l+1\right)}$$

$$\mu_{L_z} = -\frac{e}{2m_e}L_z = -\frac{e\hbar}{2m_e}m = -\beta_0 m$$

Electron spin magnetic moment

$$\boldsymbol{\mu}_s = -\frac{e}{2m_e}g\mathbf{S}$$

$$\left|\boldsymbol{\mu}_s\right| = -\frac{e\hbar}{2m_e}g\sqrt{s\left(s+1\right)} = -\beta_0 g\sqrt{s\left(s+1\right)}$$

$$\mu_{S_z} = -\frac{e}{2m_e}gS_z = -\frac{e\hbar}{2m_e}gm_s = -\beta_0 gm_s \approx \pm\beta_0$$

$$g \equiv \text{"electronic g factor"} = 2.0023$$

MAGNETIC FIELD EFFECTS

Potential energy in magnetic field **B**

$$U = -\boldsymbol{\mu}\bullet\mathbf{B} = -\mu_z B_z = \frac{eB_z}{2m_e}\left(L_z + gS_z\right)$$

Orbital ang. mom. z-comp.

Spin ang. mom. z-comp.

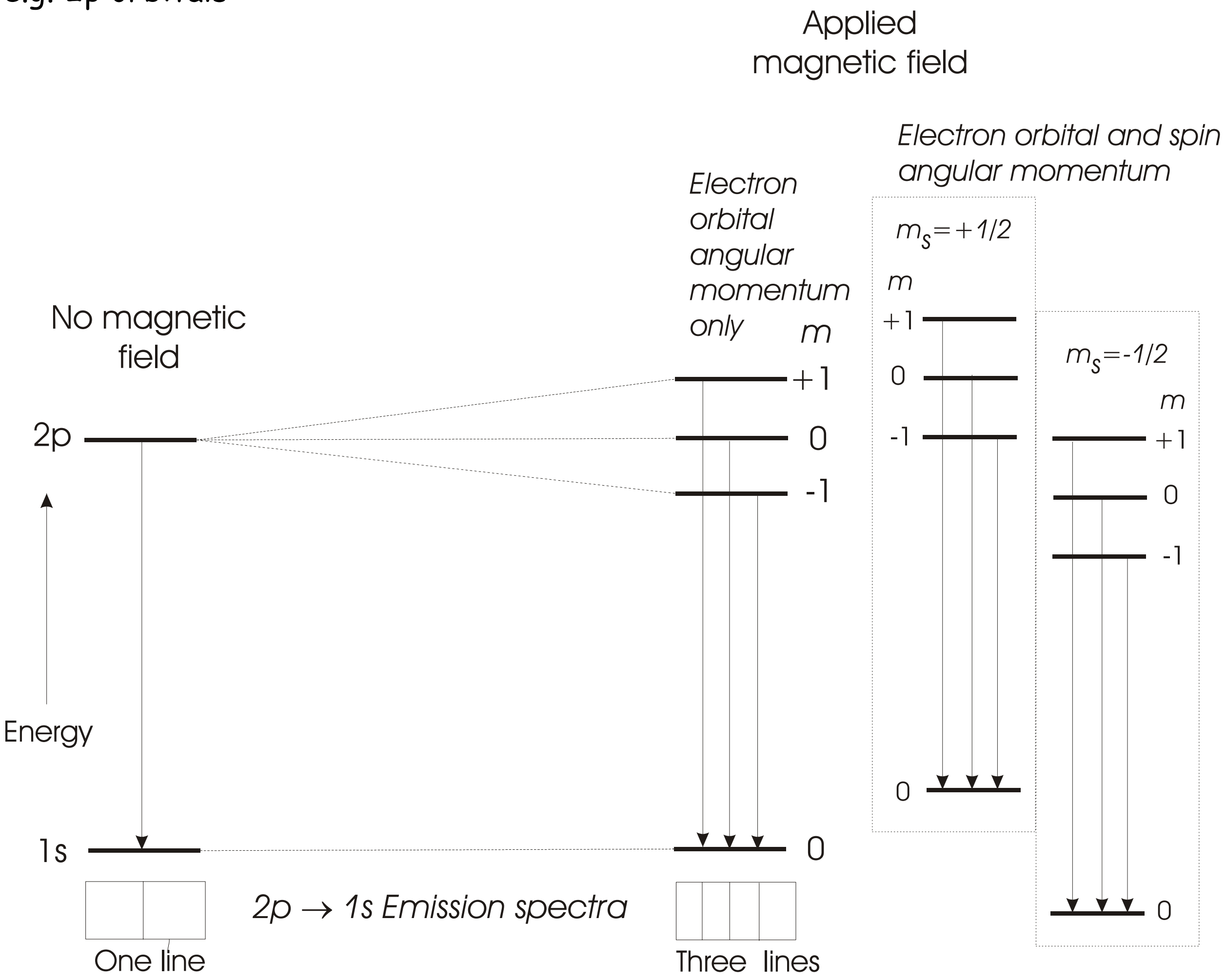
Total Hamiltonian operator: $\hat{H} = \hat{H}_0 + \frac{eB_z}{2m_e}\left(\hat{L}_z + g\hat{S}_z\right)$

$$\hat{H}\Psi_{nlmm_s} = \hat{H}_0\Psi_{nlmm_s} + \frac{eB_z}{2m_e}\left(\hat{L}_z\Psi_{nlmm_s} + g\hat{S}_z\Psi_{nlmm_s}\right) = E\Psi_{nlmm_s}$$

$$E = \frac{-e}{8\pi\varepsilon_0 a_0 n^2} + \frac{eB_z}{2m_e}\hbar\left(m + gm_s\right) = E_n + \beta_0 B\left(m + gm_s\right)$$

E in a magnetic field depends on *m* and m_s as well as *n*.

e.g. 2p orbitals:



Every electron orbital state is split into spin sublevels $m_s = \pm 1/2$

Optical transitions between different electronic levels follow selection rules

$$\Delta m = \pm 1 \qquad \Delta m_s = 0$$

so same three transitions with same splittings (to 1st order)

Small correction due to "*spin-orbit coupling*"
Spin & orbital magnetic moments make tiny magnetic fields which interact

$$E_{SO} \propto \mu_L \bullet \mu_S \propto mm_S \begin{Bmatrix} >0 \text{ for product } mm_S > 0 \\ <0 \text{ for product } mm_S < 0 \end{Bmatrix} \text{ splits 2 of the 3 lines in the spectrum}$$

ELECTRON SPIN RESONANCE

Low-frequency radiation induces transitions between electron spin sublevels

Selection rule $\Delta m_s = \pm 1$

$$\Delta E = g\beta_0 B\left(\tfrac{1}{2} - -\tfrac{1}{2}\right) = g\beta_0 B = h\nu$$

Radiation frequency ν in microwave (GHz) region for usual magnetic fields.

ESR only works for unpaired electron spins!

Useful because precise line positions & splitting patterns depend on coupling between unpaired electron spin and other (nuclear) spins. Tells which nuclei the electron sees most $\Rightarrow$ *electronic orbital structure*

NUCLEAR SPIN

All elementary particles have inherent symmetry w.r.t. interchange among indistinguishable counterparts.

Antisymmetric $\equiv$ fermions, e.g. electron, proton: ½-integral spin $I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$, etc.

Symmetric $\equiv$ bosons, e.g. deuterium ^{2}H or ^{4}He nuclei: integral spin $I = 0, 1, 2,$ etc.

Sublevels: z-component quantum # $m_I = -I,\ -I+1, \ldots, I-1,\ I \quad (2I+1)$ sublevels

MAGNETIC FIELD EFFECTS

$$E = \frac{g_N e B_z}{2m_H}\hbar m_I \equiv g_N \beta_N B m_I, \quad \beta_N = \frac{e\hbar}{2m_H} \equiv \text{ nuclear magneton}$$

"nuclear g-factor" (different for different nuclei) $g_N = 5.6$ for H

$m_H > 1000 m_e \Rightarrow \beta_N < 10^{-3}\beta_0$

NMR

Transitions between nuclear spin sublevels

Selection rule $\Delta m_I = \pm 1$

$$\Delta E = g_N \beta_N B \left(\tfrac{1}{2} - \tfrac{-1}{2} \right) = g_N \beta_N B = h\nu$$

Radiation frequency ν in radiofrequency (MHz) region for usual magnetic fields.

1000x less than ESR frequencies

Useful because precise line positions & splitting patterns depend on coupling between nuclear spin and magnetic moments due to other nuclei (yielding splittings) and to electron spin & orbital angular momentum (yields "shielding", leading to transition frequency shifts)