6.5 Zeeman Effect:

Electron in an atom in the presence of a magnetic field. Before only "spin" **S** in a magnetic field was considered. Now we add the orbital angular momentum **L** because electron is orbiting the proton.

$$H'_Z = -(\boldsymbol{\mu}_l + \boldsymbol{\mu}_s) \cdot \mathbf{B}_{ext}$$

$$\boldsymbol{\mu}_s = -\frac{e}{m}\mathbf{S} \qquad \boldsymbol{\mu}_l = -\frac{e}{2m}\mathbf{L}$$

Missing 2 in spin is due to relativity.

$$H'_Z = \frac{e}{2m}(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}_{ext}$$

$\mathbf{B}_{ext}$ vs $\mathbf{B}_{in} = \frac{1}{4\pi\epsilon_0}\frac{e}{mc^2r^3}\mathbf{L}$

$$B_{ext} \ll B_{int}$$

If magnetic field is very small, then the fine structure constant must be considered as part of the H_0 before adding magnetic field.

$$B_{ext} \gg B_{int}$$

If magnetic field not too small, then the fine structure constant is neglected in H_0 before adding magnetic field.

(1) $B_{\mathrm{ext}} \ll B_{\mathrm{int}}$ Fine structure is important. Good quantum numbers are (n, l, s, j, m_j)

$$E_Z^1 = \langle n l j m_j | H_Z' | n l j m_j \rangle = \frac{e}{2m} \mathbf{B}_{\mathrm{ext}} \cdot \langle \mathbf{L} + 2\mathbf{S} \rangle$$

It can be shown that:

$$\langle \mathbf{L} + 2\mathbf{S} \rangle = \left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right] \langle \mathbf{J} \rangle$$

Lande' g_J factor

Consider magnetic field along z axis:

Then: $$E_Z^1 = \mu_B g_J B_{\mathrm{ext}} m_j$$

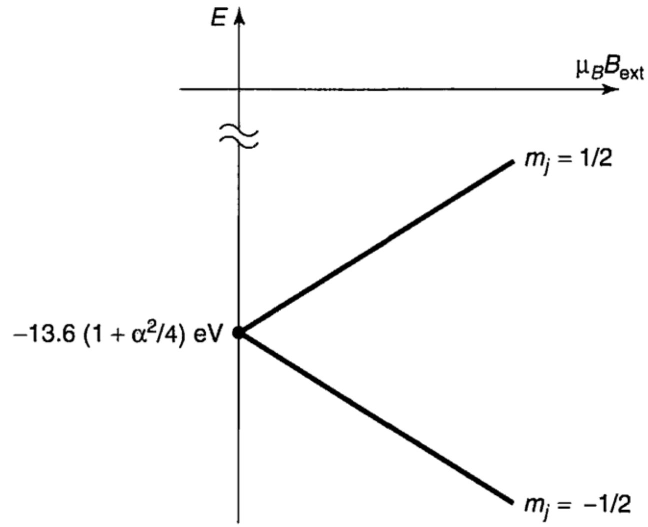
Simple split linear with B_{ext}: some levels up, others down.

where the Bohr magneton is defined as:

$$\mu_B \equiv \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \ \mathrm{eV/T}$$

Example: ground state has n=1, l=0, s=1/2, j=1/2, m_j = ±1/2 (g_J=2)

Egs = $-13.6 \text{ eV}(1+\alpha^2/4) \pm \mu_B B_{ext}$



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(2) $B_{ext} \gg B_{int}$

Magnetic field dominates. Good quantum numbers are (n, l, s, m_l, m_s) because magnetic field is larger than fine structure correction.

$$E_{nm_l m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B_{ext}(m_l + 2m_s)$$

$$E^1_{fs} = \langle n l\, m_l\, m_s | (H'_r + H'_{so}) | n l\, m_l\, m_s \rangle$$

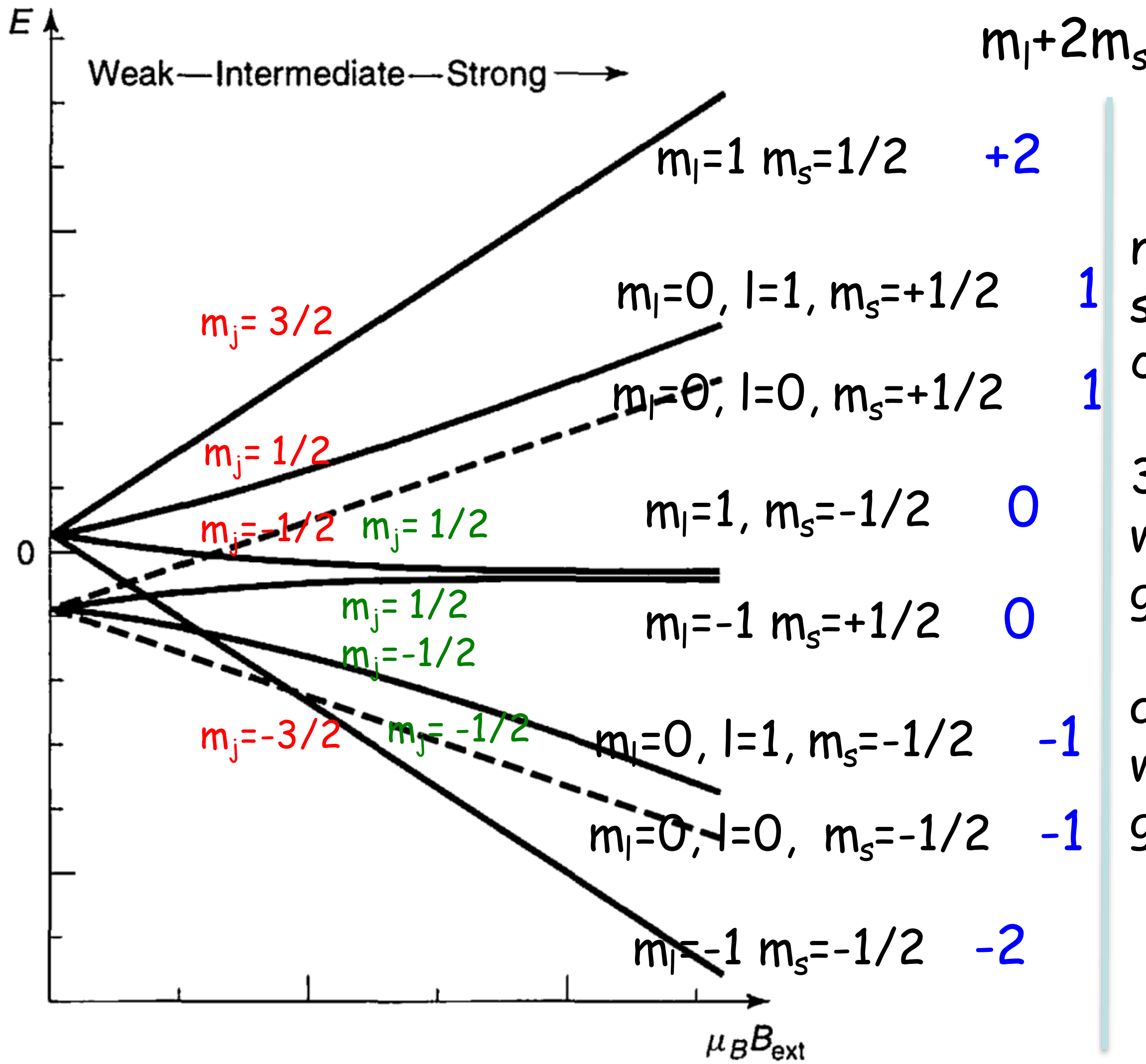
$$E^1_{fs} = \frac{13.6 \text{ eV}}{n^3}\alpha^2 \left\{ \frac{3}{4n} - \left[\frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right] \right\}$$

EXAMPLE:

n=2 states of H atom (8 total)

j=3/2, deg=4,
l=1, s=1/2, j=l+s

j=1/2, deg=2,
l=1, s=1/2, j=l-s
or
l=0 s=1/2



n=2 without fine structure correction has:

3 l=1 states where spin can go up or down

and 1 l=0 state where spin can go up or down

Chapter 7: The variational principle

This is a common occurrence. Suppose you have a Hamiltonian that (i) cannot be solved exactly and (ii) where perturbation theory cannot be applied because there is no simple H_0 and/or because there is no small H'.

Then, what do we do? ☹

One possibility is to use the variational principle: it does not give you the exact answer but gives you an upper bound that is often sufficient.

Select any wave function you wish. Call it Ψ. The claim is that always:

$$E_{gs} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle$$

Although we do not know explicitly the eigenstates of H, because we cannot solve the problem exactly, we know they exist.

$$H\psi_n = E_n\psi_n$$

Then, we can expand our proposed variational wave function in the complete basis of eigenstates:

$$\psi = \sum_n c_n \psi_n$$

If Ψ is normalized, then:

$$1 = \langle\psi|\psi\rangle = \left\langle \sum_m c_m\psi_m \middle| \sum_n c_n\psi_n \right\rangle = \sum_m \sum_n c_m^* c_n \langle\psi_m|\psi_n\rangle = \sum_n |c_n|^2$$

Repeating with *H* included, we find:

$$\langle H \rangle = \left\langle \sum_m c_m \psi_m \middle| H \sum_n c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle \psi_m | \psi_n \rangle = \sum_n E_n |c_n|^2$$

But the ground state has the lowest energy by definition:

$E_{gs} \leq E_n$. Then:

$$\boxed{\langle H \rangle \geq E_{gs} \sum_n |c_n|^2 = E_{gs}}$$

The variational principle is powerful, easy to use, and accurate if you have a good intuition on how the wave function should look like. Problem: you do NOT know how close your result is compared to the exact result. **You only know you are above.**

Example 7.1:

Consider the 1D Harmonic Oscillator with H:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

Here we know the answer exactly, but we pretend we do not.

As a "trial" wave function we will use a Gaussian exponential. Using Gaussians is very common, because the integrals are known.

$$\psi(x) = Ae^{-bx^2}$$

A is the normalization and *b* is called a "variational parameter" that we will optimize by minimizing the energy.

Normalization:

$|\psi(x)|^2$

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\, dx = |A|^2 \sqrt{\frac{\pi}{2b}} \;\Rightarrow\; A = \left(\frac{2b}{\pi}\right)^{1/4}$$

Next we need the expectation value of the Hamiltonian:

$$\langle H \rangle = \langle T \rangle + \langle V \rangle$$

For the kinetic energy:

$$\langle T \rangle = -\frac{\hbar^2}{2m}|A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2}\left(e^{-bx^2}\right) dx = \frac{\hbar^2 b}{2m}$$

For the potential energy:

$$\langle V \rangle = \frac{1}{2} m\omega^2 |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} x^2\, dx = \frac{m\omega^2}{8b}$$

Adding kinetic and potential energy: $\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$

Let us now "optimize" the "variational parameter"

$$\frac{d}{db}\langle H \rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \;\Rightarrow\; b = \frac{m\omega}{2\hbar}$$

If we introduce the "optimal b" into <*H*>, we obtain:

$$\langle H \rangle_{\min} = \frac{1}{2}\hbar\omega$$

which is the exact result, by chance, in this simple example. In the vast majority of cases, you will **not** find the exact result.