

6.5 Behaviour in a magnetic field - expected and unexpected!!

6.5.1 Zeeman effect - expected

For an electron moving in an orbit of radius r with speed v it can be treated as a current loop, with area A and current I

$$\begin{aligned} A &= \pi r^2 \\ I &= -\frac{ev}{2\pi r} \end{aligned}$$

then there is a magnetic moment $\vec{\mu} = I\vec{A}$ and a torque $\vec{\tau} = \vec{\mu} \times \vec{B}$ and a contribution to the potential $U = -\vec{\mu} \cdot \vec{B}$.

so we can get this in a semi classical picture where

$$\mu_l = IA = -\frac{evr}{2} = -\frac{e}{2m_e} m_e vr = -\frac{e}{2m_e} L \quad (1)$$

where L is the orbital angular momentum of the electron. In vector form

$$\boldsymbol{\mu}_l = -\frac{e}{2m_e} \mathbf{L} = -\frac{\mu_B}{\hbar} \mathbf{L} \quad (2)$$

where $\mu_B = e\hbar/2m_e$ is called the Bohr magneton, and is a natural unit of microscopic magnetic moment, with the value $9.27 \times 10^{-24} \text{ J T}^{-1}$ or $5.79 \times 10^{-5} \text{ eV T}^{-1}$.

If we'd kept to the semi-classical Bohr picture of an atom, then the ground state has angular momentum so has a magnetic moment. But in Schrodinger we know that this state ($1s$) has $l = 0$ i.e. has no angular momentum so should have no magnetic moment - which is correct. the energy level of the ground state of hydrogen is not affected by a magnetic field!

so we have to do this for the angular momentum values we have in Schrodinger and here we know the magnitude from the orbital quantum number l and we know direction along ONE axis. so lets use the z -axis!

Hence we also have a component directed along the z axis, $L_z = m_l \hbar$

$$(\mu_l)_z = -\frac{\mu_B}{\hbar} L_z = -\mu_B m_l$$

so possible values of the magnetic moment along the z direction $(\mu_l)_z$ are $-m_l \mu_B$, where m_l is one of the numbers from $-l$ and $+l$ in steps of unity.

Now consider a hydrogen atom in a z -directed magnetic field B_z . A classical model would give the associated magnetic potential energy as

$$U_B = -(\mu_l)_z B_z = m_l \mu_B B_z$$

the magnetic field shifts the energy levels by an amount U_B . when a magnetic field is applied the atom is no longer completely symmetric under rotation - there is a preferred direction in space. by removing the symmetry we remove the degeneracy in m_l .

example YF41.5 An electron in a state with $l = 1$ emits a photon of $\lambda = 600$ nm decays to a state with $l = 0$. What are the shifts that result if this is placed in a magnetic field $B = 2$ T?

$l = 1$ can have $m_l = -1, 0, 1$

$l = 0$ can only have $m_l = 0$ so no splitting

$$E = hc/\lambda = 1240/600 = 2.07 \text{ eV}$$

so the shifts will be $\Delta E = m_l \mu_B B = m_l (5.79 \times 10^{-5} \times 2) = 1.16 \times 10^{-4} m_l \text{ eV}$

this is a very small fraction of the initial energy! $\Delta\lambda \sim 0.034$ nm

6.5.2 and the unexpected!! electron spin

As well as measuring transition energies, there is a very direct way to measure the response to a magnetic field which is to make the atoms move!

The uniform fields above create a torque if there is a magnetic moment, but no translational force. But if the field varies spatially then we get a force $F = -dU/dz$. so the quantum mechanical force on a hydrogen atom to be

$$F_z = (\mu_l)_z \frac{dB_z}{dz} \quad (3)$$

where $(\mu_l)_z$ is equal to one of the discrete values $-m_l \mu_B$.

but if we have the outer electron in the $l = 0$ state e.g silver has its last electron in the $5s$ state - then $m_l = 0$ so there should be no effect.

but the beam IS split in the Stern-Gerlach experiment, showing that there IS a magnetic moment which is NOT associated with orbital angular momentum. And it splits into two - so this can take ONLY 2 potential values rather than the continuum of values you might expect with a randomly aligned spin dipole.

so then we have another magnetic moment which is quantised which is associated with the electron: we'll call it spin angular momentum.

so just like orbital angular momentum, $L^2 = l(l + 1)\hbar^2$ where we can only measure the component in one direction $L_z = m_l\hbar$ where $m_l = -l, (-l + 1) \dots (l - 1), l$, we can define spin angular momentum $S^2 = s(s + 1)\hbar^2$ and we have m_s running from $-s$ to s .

We know from the experiments that we need two states, two different values of m_s . but we know from the maths that m_s as an angular momentum runs from $-s$ to s in integer steps!! this is the trick, just because Δm_s has to be an integer, doesn't mean that s has to be an integer. If I have $s = 1/2$ then $m_s = -1/2, 1/2$ and I get two values which is what I need!!

This is absolutely NOT predicted in the Schroedinger equation. its a property of ALL electrons (and protons and neutrons). ALL electrons have spin $s = 1/2$ in the same way that ALL electrons have charge $-e$ and mass m_e .

beware thinking too classically about this - if the electron was really spinning on its axis as well as orbiting then the spin speed $> c!$

6.6 Summary

The hydrogen atom - 3D electrostatic potential in Schroedinger - gives wavefunctions which depend on 3 quantum numbers. n, l , and m_l , where n is the principle quantum number $n = 1, 2, \dots$, l is orbital quantum number $l = 0, 1, \dots (n - 1)$ and gives the magnitude of the orbital angular momentum $L^2 = l(l + 1)\hbar^2$. we can't know its direction on all three axes, we can only know it along 1. $L_z = m_l\hbar$ where m_l is the magnetic quantum number $m_l = -l, \dots, l$ as it determines the behaviour in a magnetic field.

But this isn't enough to describe EVERYTHING we see. So there is another set of angular momentum quantum numbers associated with electron spin. The magnitude of the spin angular momentum $S^2 = s(s + 1)\hbar^2$ given by the spin quantum number s . THIS DOES NOT RELATE TO ANY OF THE PREVIOUS QUANTUM NUMBERS: we measure it from experimnt and find $s = 1/2$ always - its just a property of the electron. we can't know its direction on all three axes, we can only know it along 1. $S_z = m_s\hbar$ where m_s is the spin magnetic quantum number $m_s = -s, \dots, s = -1/2, 1/2$