The Stern-Gerlach experiment with spin is one of the best to simply show quantum mechanics at its least intuitive! we have atoms with an electrons. If they have angular momentum then this means a current, so there is a magnetic moment and hence a potential if its put in an external field. The field has some direction, so if we put it on the z-axis we get $U = \mu_B m_l B_z$, and the energy levels shift by this amount.

We can go one better and SEE the differerence if we have the magnetic field vary - so now we have dB_z/dz because then there is a force $F_z = dU/dz = \mu_B m_l dB_z/dz$.

Take some atoms in $l = 0$ so $m_l = 0$ so there is no angular momentum, so no current. so they should go straight. They don't. And if there is a smooth distribution of angular momentum then they should have a continuous distribution with z on the screen. They don't. there are only 2 spots. so there is a magnetic moment which is intrinisc to the electrons and NOT part of the orbital angular momentum. and its quantised so that there are only 2 values.

we saw how orbital angular momentum worked - there is a magnitude $L^2 = l(l+1)\hbar^2$ with direction along one axis $L_z = m_l\hbar$ where m_l runs from $-l \ldots l$ in integer steps. BUT THERE IS NO REQUIREMENT FOR l TO BE AN INTEGER. So we can have 2 values of m_s separated by an integer if we make a spin angular momentum with $S^2 = s(s+1)\hbar^2$ and m_s runs from $-s \ldots s$ in integer steps if $s = 1/2$!!

and now we have a way to SEE the effects of quantum mechanics. Take a beam, put it through the varying magnetic field to separate spin states. Take the spin up. put it through ANOTHER magnetic field, this time aligned along the x axis. it splits again into spin up and spin down along this axis. Now put another one on the z-axis. We have already measured spin on this axis, its spin up. but now its NOT. it splits equally into spin-up and spin-down. The measurement of angular momentum along the x direction has disturbed the system and re-randomised it along the z-axis.

6 Many electrons - atoms other than Hydrogen

There is an electron-electron coulomb terms as well as the electron-nucleus coulomb term. This complicates the Schroedinger equation so much that it

can't be solved analytically!

To zeroth order we can ignore it entirely! The nuclear charge is Ze so we could just replace our Hydrogen energy levels $E_n = -13.6/n^2$ eV and put in the electrostatic charge and get $E_n = -13.6Z^2/n^2$ eV. Its a bit drastic, but it'll do to start. And then put electrons in.

We might expect that all the electrons go into the ground state. But they don't! If they did we might see gradual changes of chemical properties with Z. but we see dramatic changes eg $Z = 9, 10, 11$ is fluorine, Neon and sodium. Fluorine forms compounds where it aquires and extra electron, sodium forms ones which lose an electron and Neon doesn't form compounds at all.

Pauli exclusion principle no two electrons can occupy the same state - each electron needs its own distinct set of quantum numbers n, l, m_l, m_s.

the REASON comes out of what happens when we put two electrons into orbitals. the first electron is in state a, the second in state b and we'll assume the wavefunction is separable so $\psi_{system} = \psi_a(1)\psi_b(2)$. But this assumes we can distinguish electron 1 and 2 - but we can't! particles are indistingushable. so lets be more non-committal about which one is in which state by saying it can equally well be electron 1 in state a and 2 in state b or vica versa. and there are two ways to do this - either add or subtract the other possibility so

$$\psi_{system} = A(\psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1))$$

where A is a normalisation factor of $1/\sqrt{2}$ to make the probability work! Remember, its probability $\psi^*_{system}\psi_{system}$ that we can measure, not the wavefunction itself

Whether we add or subtract depends on the fundamental properties of the particle - its SPIN. all particles with $s = 1/2$ (fermions: electrons protons etc) have the -ve sign. All bosons, $s = 1$ eg photons have the +ve sign.

so with the -ve sign, if our two electrons are BOTH in state a, then $\psi_{system} = 0$. So there is NO possibilty for the electrons to exist both in the same state! This is the pauli exclusion principle.

so then when we add more electrons, we progressively fill the orbitals And this actually gives us most of the important features of the periodic table!

But to first order of course the electron-electron potentials make a difference. when we did hydrogen, we looked at the probabilty densities. And in 3D we see something quite fun. The s-states $l = 0$ are spherically symmetric, but the states with $l > 0$ are not - but if we add them together then

Table 41.2 Quantum States of Electrons in the First Four Shells

n	l	m_l	Spectroscopic Notation	Number of States		Shell
1	0	0	$1s$	2		K
2	0	0	$2s$	2	8	L
2	1	$-1, 0, 1$	$2p$	6		
3	0	0	$3s$	2	18	M
3	1	$-1, 0, 1$	$3p$	6		
3	2	$-2, -1, 0, 1, 2$	$3d$	10		
4	0	0	$4s$	2	32	N
4	1	$-1, 0, 1$	$4p$	6		
4	2	$-2, -1, 0, 1, 2$	$4d$	10		
4	3	$-3, -2, -1, 0, 1, 2, 3$	$4f$	14		

Figure 1:

they are! so if we have electrons filling the entire set of available states for a given n then the charge distribution is radially symmetric and shields the nuclear charge - just use Gauss law! so the effective charge Z_{eff} seen by the outer electrons is set by the charge enclosed is Z minus the charge of the filled shells. So the outer electrons can be described by energy levels $-13.6Z_{eff}^2/n^2$.

But its not quite so simple as there is a radial probability distribution for the electrons. so actually even if we have 1 electron outside a filled shell then it spends some of its time INSIDE the filled shell so sees more charge! complexities like these mean that its not straightforward to fill electrons in shells in an orderly way after Argon ($Z = 18$, $1s^2, 2s^2 2p^6, 3s^2 3p^6$)

example YF41.9 potassium has 19 electrons $1s^2, 2s^2 2p^6, 3s^2 3p^6 3, 4s^1$ but we'd have expected $1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^1$!!

what do we expect for the energy levels for the outer electron ? $Z_{eff} = 1$ as there are 18 electrons in the filled shells between the $4s^1$ electron and the nucleus of $Z = 19$ so they shield the charge. This is what we;d get if the $4s^1$ electron NEVER went inside the $n = 3, 2, 1$ charge distribution. but we saw that this isn't true - we saw there was a radial probability distribution. And we might expect that states which had more angular momentum have less probability of being at small radius, so then $4f$ might see the full shielding of the filled shells, while $4s$ sees a bit less shielding.

$E_n = -13.6(1)^2/n^2$. But we are in $n = 4$ so this means $E_4 = -13.6/16 = -0.85$ eV.

So we'd expect this to be about correct for $4f$, then we should have

progressively higher Z_{eff} for $4d$ and $4p$ and $4s$ as they all have progresssively higher probabilities of being found at small radii. and this is what we see - the energy levels are $-0.85, -0.94, -2.73, -4.339$ and this $4s$ level is slightly lower energy than the $3d^1$ level! so up here, where the difference between shells is small, then it gets complicated.