



Spin and Pauli's Principle



The questions

- Why do spectral lines split in a magnetic field?
- What happens in Stern-Gerlach?
- What is Pauli's Principle?
- What is the origin of Hund's rule?
- Why are materials ferromagnetic?



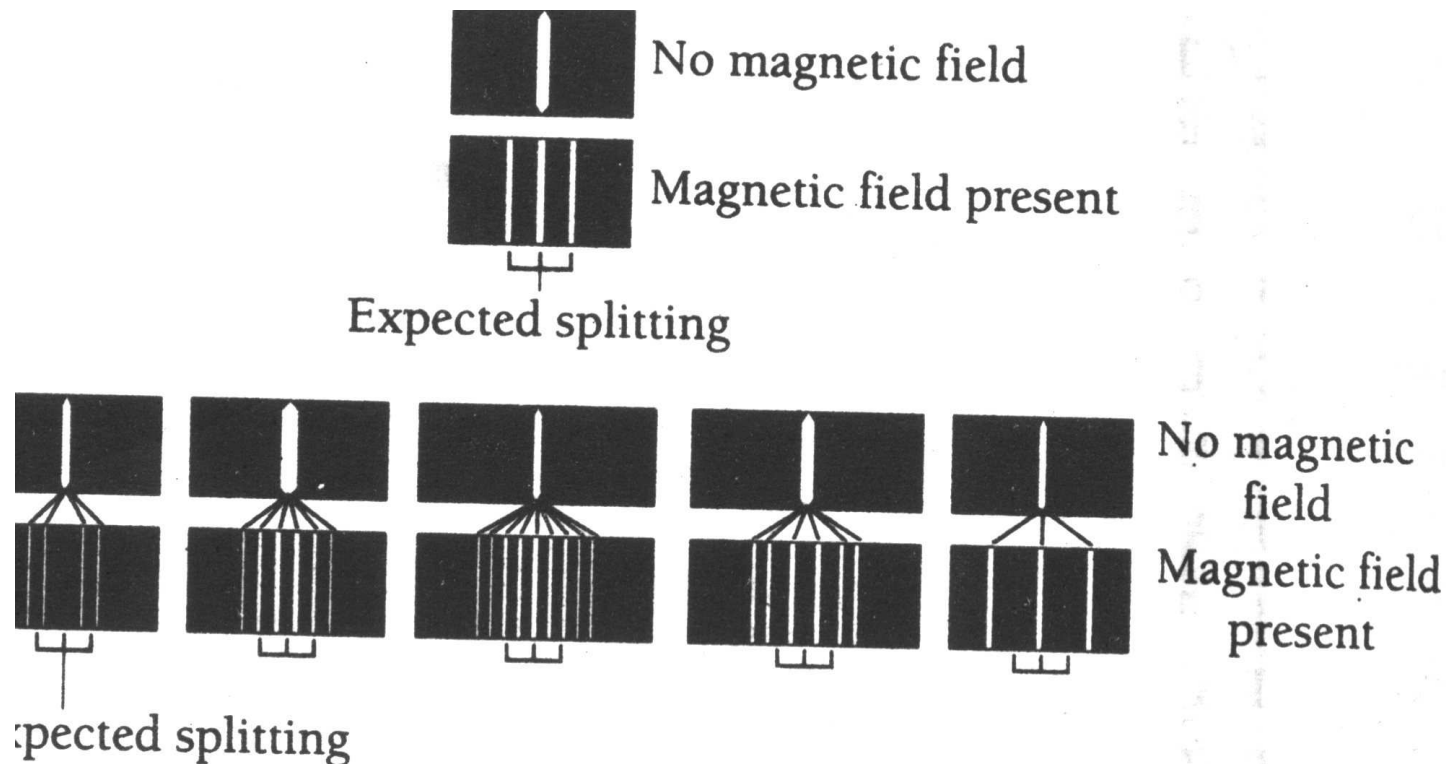
What happens to an atom in a magnetic field?

- The Hamiltonian of interaction is given by $\sim -\frac{e}{2m_e} \mathbf{L} \cdot \mathbf{B}$ where B is the applied magnetic field ($= -\frac{e}{2m_e} B L_z$)
- Thus, the approximate change in the energy levels is
$$\Delta E_{n,l,m} = -\frac{eB}{2m_e} \langle n, l, m | L_z | n, l, m \rangle = -m \frac{e\hbar}{2m_e} B$$
- The quantity $\frac{e\hbar}{2m_e} = \mu_B$ is called Bohr magneton...is equal to $\sim 10^{-23} J/T$ or $\sim 6 \times 10^{-5} eV/T$
- Atoms can undergo transition between these split states, and lines in the absence of magnetic fields will split (Zeeman effect)
- Transitions obey selection rules : $\Delta \ell = \pm 1, \Delta m = \pm 1, 0$



Zeeman Effect – Normal and Anomalous

- A $3d$ to $2p$ transition line will split into three lines...the normal effect



- But it can split into four, even nine !! Anomalous effect!



Stern-Gerlach Surprise

- Atom “feels” a force $\sim \nabla(\mu_{tot} \cdot B)$
- Clearly, total magnetic moment $\mu_{tot} = -\frac{e}{2m}L_{tot}$
- Atomic configuration of silver $4d^{10}5s^1$, i. e., $\mu_{tot} = 0$
- “Quantum-Mechanics-So-Far” tells that there will be NO FORCE on the silver atoms and a single beam will emerge!
- There is something more that sends heads spinning!
Spin!

Spin

- All quantum mechanical objects have a property called spin...which is like an intrinsic angular momentum (as opposed to “orbital”)
- Attempts to think of a “hard round particle” spinning led to purer forms of nonsense...
- Thus in addition to its positional DOFs (x, y, z) or (r, θ, ϕ) , the particle has a fourth one called the spin DOF called σ ...thus the wavefunction will be $\psi(x, y, z, \sigma)$
- It is described by operators S^2, S_x, S_y, S_z ...which act only on the “ σ ” part of the wavefunction
- Of course, $S^2 = S_x^2 + S_y^2 + S_z^2$...physically, expected value of S_z is the observed z component of intrinsic ang. momentum.



Spin

- The main physics $[S_x, S_y] = i\hbar S_z$ (etc.)...Note **THIS IS EXPERIMENTAL FACT...NOT DERIVED** (as in case of L_x etc.)!
- With it we can show that the eigenstates are given by $|s, m_s\rangle$ with $S^2|s, m_s\rangle = s(s+1)\hbar^2|s, m_s\rangle$, $S_z|s, m_s\rangle = m_s\hbar|s, m_s\rangle$ the allowed values of $s = 0, \frac{1}{2}, 1, \frac{3}{2}...$ (note difference with angular momentum!) For a given s , m_s can take values from $-s, \dots, s$
- The main point is for each type of quantum particle s is fixed....is an intrinsic property of the particle...for electrons $s = \frac{1}{2}$



Spin $\frac{1}{2}$

- **Eigenvalues of S^2 is $\frac{3}{4}$**
- **There are two eigenstates for S_z which we call $|z, +\rangle$ and $|z, -\rangle$ such that $S_z|z, \pm\rangle = \pm\frac{\hbar}{2}|z, \pm\rangle$**
- **Note that S_z is a Hermitian operator and hence $|z, \pm\rangle$ form a complete set...and can describe any spin state! (Clearly, $\langle z, \mp|z, \pm\rangle = 0$!)**
- **A general spin state is described by $|\mu\rangle = \alpha|z, +\rangle + \beta|z, -\rangle$, with $\alpha^*\alpha + \beta^*\beta = 1$**
- **Also, $S_x|x, \pm\rangle = \pm\frac{\hbar}{2}|x, \pm\rangle$ and $S_y|y, \pm\rangle = \pm\frac{\hbar}{2}|y, \pm\rangle$**
- **How are $|x, \pm\rangle$ and $|y, \pm\rangle$ related to $|z, \pm\rangle$?**

Spin $\frac{1}{2}$

- It can be shown $|x, \pm\rangle = \frac{|z, +\rangle \pm |z, -\rangle}{\sqrt{2}}$ and $|y, \pm\rangle = \frac{|z, +\rangle \pm i|z, -\rangle}{\sqrt{2}}$! Thus the state of the particle with intrinsic which corresponds to intrinsic angular momentum pointing precisely in the $+x$ -direction is a linear combination of states corresponding to angular momentum pointing precisely in the $+z$ and $-z$ directions!
- This clearly explains all the results of Stern-Gerlach! There is actually quantitative agreement!



Spin $\frac{1}{2}$

- Protons and neutrons are spin $\frac{1}{2}$ particles
- Associated with the spin, there is also an intrinsic magnetic moment...for electron it is μ_B (in fact 1.0015!! QED!), quite unlike $\frac{\mu_B}{2}$ that we would have expected classically!
- Nuclear magnetic moment can be used...NMR (Nuclear Magnetic Resonance) useful to study organic molecules
- ESR(Electron Spin Resonance) is another such technique
- Neutron's magnetic moment can be exploited to study magnetic structure (neutron scattering)



More than one particle!

- We have considered only one particle...what should we do to describe two?
- Stick to 1D
- Two particle wave function $\psi(\{x_1, \sigma_1\}, \{x_2, \sigma_2\}, t)$
- Dropping spin for a minute... $|\psi(x_1, x_2)|^2 dx_1 dx_2$ is the probability that a particle will be found at x_1 and other particle is found at x_2
- The two particle state satisfies the Schrödinger equation $H\psi = i\hbar \frac{\partial \psi}{\partial t}$
- For example, $H = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right)$, for free particles
- If we solve $H\psi = E\psi$, we will get the energy eigenstates



Bosons and Fermions

- What happens if we flip the particles?
- In quantum mechanics particles of same type are indistinguishable
- This indistinguishability is manifested in two ways
- $\psi(\{x_2, \sigma_2\}, \{x_1, \sigma_1\}) = \psi(\{x_1, \sigma_1\}, \{x_2, \sigma_2\})$ – **Bosons**
 $\psi(\{x_2, \sigma_2\}, \{x_1, \sigma_1\}) = -\psi(\{x_1, \sigma_1\}, \{x_2, \sigma_2\})$ – **Fermions**
- **Electrons are fermions**



Two particles in a box

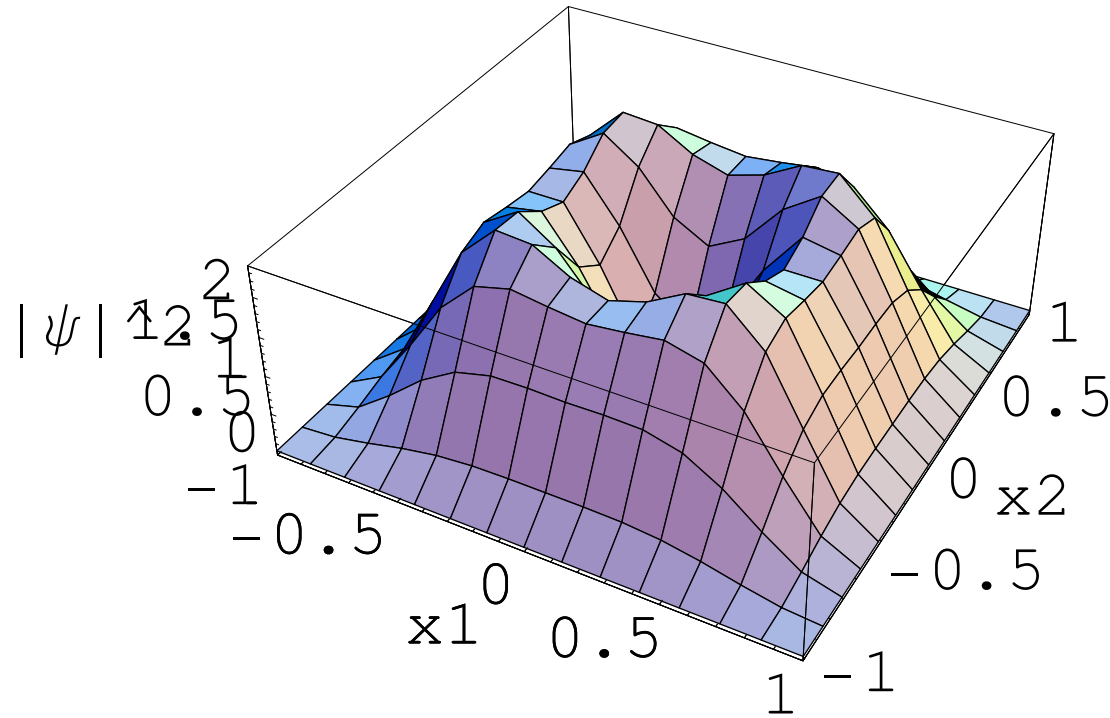
- We have solved single particle states $\phi_n(x)$ in a box
 $E_n \sim n^2$
- Each state is two-fold degenerate due to spin..thus really $\phi_n(x)\chi_{\uparrow}(\sigma)$ and $\phi_n(x)\chi_{\downarrow}(\sigma)$
- We need $\psi(\{x_2, \sigma_2\}, \{x_1, \sigma_1\}) = -\psi(\{x_1, \sigma_1\}, \{x_2, \sigma_2\})$ and how to put two particles
- Consider $\psi(\{x_1, \sigma_1\}, \{x_2, \sigma_2\}) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(x_1)\chi_{\uparrow}(\sigma_1) & \phi_1(x_2)\chi_{\uparrow}(\sigma_2) \\ \phi_1(x_1)\chi_{\downarrow}(\sigma_1) & \phi_1(x_2)\chi_{\downarrow}(\sigma_2) \end{vmatrix}$...called Slater determinant
- This is the ground state with total spin zero and total energy $= 2E_1$



Two particles in a box

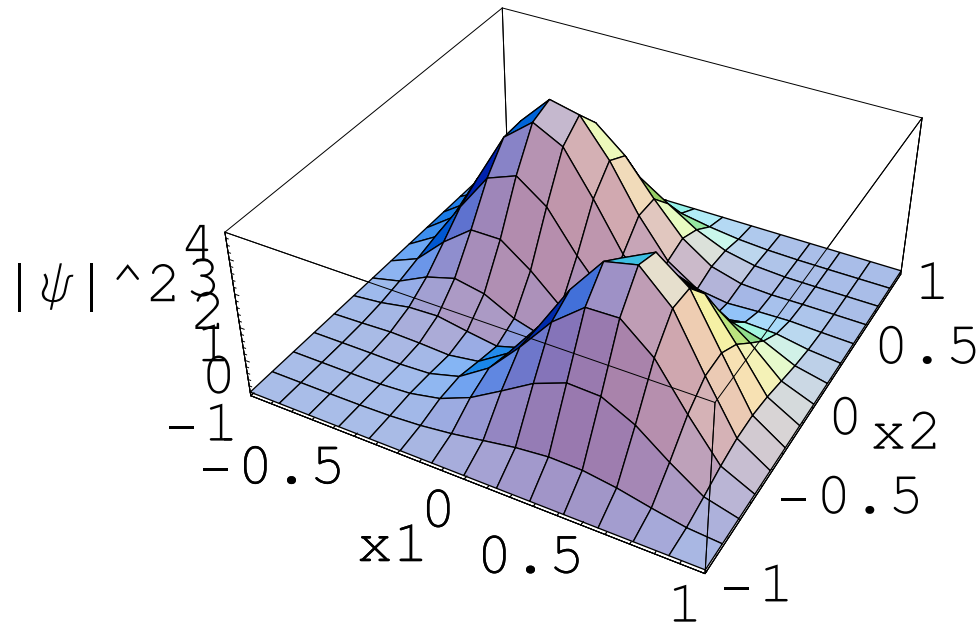
- What happens if you try to put both particles in $\phi_1(x)\chi_\uparrow(\sigma)$?...The Slater determinant vanishes...This is Pauli's principle...no two fermions can be in the same state!
- How about excited states?
- There are four possibilities $|1 \uparrow, 2 \uparrow|$, $|1 \uparrow, 2 \downarrow|$, $|1 \downarrow, 2 \uparrow|$, $|1 \downarrow, 2 \downarrow|$
- The first and last of these will have total spin 1 and the other two will have total spin 0...one is a magnetic state and the other is not!
- All states in the this model have equal energy $E_1 + E_2$?
- But there are crucial differences...

Probability Density (Opposite spins)



- It is likely to find the two electrons near each other

Probability Density(Parallel Spins)



- Electrons avoid each other...seems like there is a repulsive interaction between like spin electrons...called exchange interaction!
- With Coulomb interaction, electrons can “naturally” avoid each other if they occupy up parallel spin states...That's Hund's first rule! Magnetism!



Summary

- **Electrons have spin**
- **Electrons are Fermions, obey Pauli's principle**
- **There is an “exchange interaction” that comes up between two electrons of same spin...they avoid each other...Helps reduce electrostatic energy**
- **Finally, everything that we see is due to mass, spin and charge (Kinetic energy, Coulomb and exchange energies)!**