Lecture 41
(Spatial Quantization & Electron Spin)

Physics 2310-01 Spring 2020

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Quantum States

- So, all of the electron properties are defined by "states", each state determined by the quantum numbers n, ℓ, and m_l.
- These states form the basis states of the differential equation (the Schrödinger's equation), which are then the complete set of solutions.
- Historically, these states have been given names – spectroscopic notation.

Table 41.1 Quantum States of the Hydrogen Atom

n	l	m_l	Spectroscopic Notation	Shell
1	0	0	$1s$	K
2	0	0	$2s$	L
2	1	$-1, 0, 1$	$2p$	
3	0	0	$3s$	
3	1	$-1, 0, 1$	$3p$	M
3	2	$-2, -1, 0, 1, 2$	$3d$	
4	0	0	$4s$	N

and so on

Breaking Symmetry

- Remember that degeneracies were the reflection of symmetries. What if we break some of the symmetry by introducing something that distinguishes one direction from another?
- One way to do that is to introduce a magnetic field.
- To investigate what happens when we do this, we will briefly use the Bohr model in order to calculate the effect of a magnetic field on an orbiting electron.
- In the Bohr model, we can think of an electron causing a current loop.
- This current loop causes a magnetic moment:

$$\vec{\mu} = I\vec{A}$$

- We can calculate the current and the area from a classical picture of the electron in a circular orbit:

$$\left|\vec{\mu}\right| = \mu = IA = \frac{-ev}{2\pi r}\pi r^2 = \frac{-evr}{2}$$

- Where the minus sign just reflects the fact that it is negatively charged, so that the current is in the opposite direction of the electron's motion.

Bohr Magneton

- Now, we use the classical definition of angular momentum to put the magnetic moment in terms of the orbital angular momentum:

$$\mu = \frac{-evr}{2}$$

$$L = mvr \Rightarrow$$

$$\mu = \frac{-e}{2m}L$$

- And now use the Bohr quantization for orbital angular momentum:

$$L = n\hbar$$

$$\mu_B = \frac{-e\hbar}{2m}, \text{ when n=1}$$

- Which is called the Bohr magneton, the magnetic moment of a n=1 electron in Bohr's model.

Back to Breaking Symmetry

- It turns out that the magnetic moment of an electron in the Schrödinger model has the same form as Bohr's model:

$$\mu_z = -\frac{e}{2m}L_z = -m_\ell \frac{e}{2m}\hbar$$

- Now, what happens again when we break a symmetry, say by adding an external magnetic field?

Back to Breaking Symmetry

- Thanks, yes, we should lose degeneracies.

$$\mu_z = -\frac{e}{2m}L_z = -m_\ell \frac{e}{2m}\hbar$$

- But how and why?
- Well, a magnetic moment in a magnetic field feels a torque:

$$\vec{\tau} = \vec{\mu} \times \vec{B}$$

- And thus, it can have a potential energy:

$$U = -\vec{\mu} \cdot \vec{B}$$
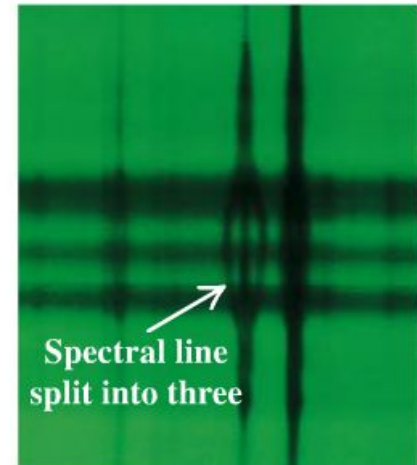
- Or, in our case:

$$U = -\mu_z B = m_\ell \frac{e\hbar}{2m}B = m_\ell \mu_B B$$

Zeeman Effect

- This potential energy breaks the degeneracy and splits the degenerate energy levels into distinct energies.

$$E_{n,m_l} = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{me^4}{2n^2\hbar^2} + m_\ell \frac{e\hbar}{2m}B$$

- This was first seen in 1896 by Pieter Zeeman...

Spectral line split into three

Zeeman Effect

In 1896, three years after submitting his thesis on the Kerr effect, he disobeyed the direct orders of his supervisor and used laboratory equipment to measure the splitting of spectral lines by a strong magnetic field. He was fired for his efforts, but he was later vindicated: he won the 1902 Nobel Prize in Physics for the discovery of what has now become known as the Zeeman effect. As an extension of his thesis research, he began investigating the effect of magnetic fields on a light source. He discovered that a spectral line is split into several components in the presence of a magnetic field. Lorentz first heard about Zeeman's observations on Saturday October 1896 at the meeting of the Royal Netherlands Academy of Arts and Sciences in Amsterdam, where these results were communicated by Kamerlingh Onnes. The next Monday, Lorentz called Zeeman into his office and presented him with an explanation of his observations, based on Lorentz's theory of electromagnetic radiation.

The importance of Zeeman's discovery soon became apparent. It confirmed Lorentz's prediction about the polarization of light emitted in the presence of a magnetic field. Thanks to Zeeman's work it became clear that the oscillating particles that according to Lorentz were the source of light emission were negatively charged, and were a thousand fold lighter than the hydrogen atom. This conclusion was reached well before Thomson's discovery of the electron. The Zeeman effect thus became an important tool for elucidating the structure of the atom.   - Wikipedia

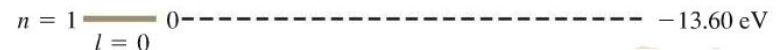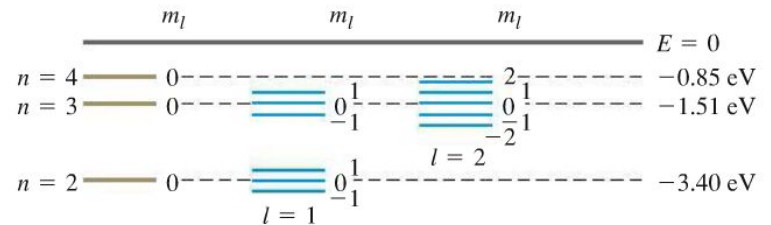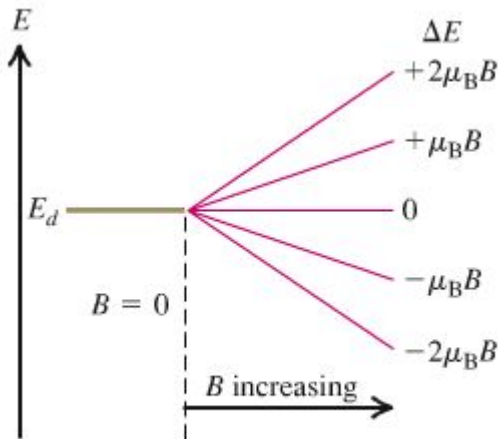# Zeeman Effect

- This energy splitting is a linear function of the strength of the magnetic field, and depends on the value of m_ℓ.

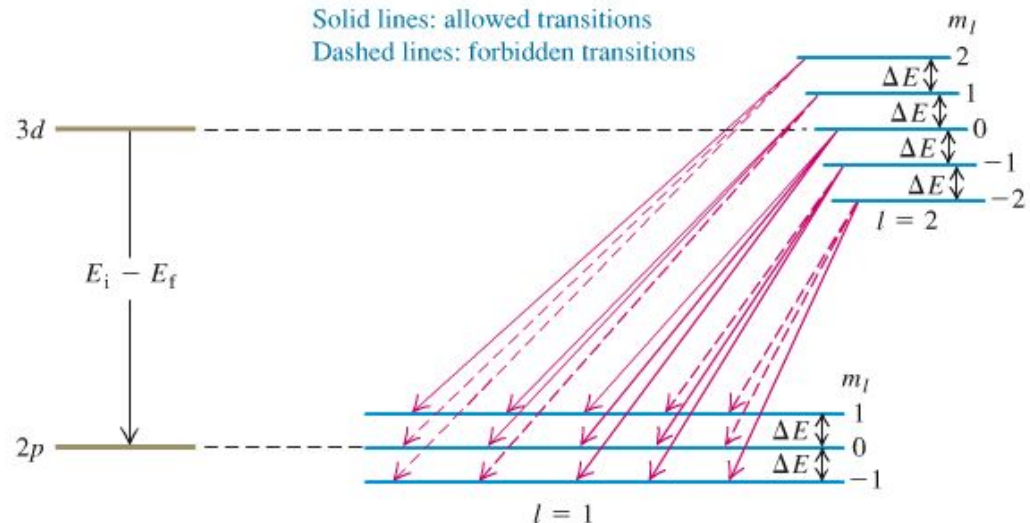$$E_{n,m_\ell} = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{me^4}{2n^2\hbar^2} + m_\ell \frac{e\hbar}{2m}B$$

Selection Rules

- For transitions between energy states, angular momentum must be conserved.
- The photon has an angular momentum of ħ, so the transitions must only be between states with ℓ difference of 1, which then limits difference of the z-projection of angular momentum also to 1 or less.

$$\Delta \ell = 1$$

$$\Delta m_\ell = 0, \pm 1$$

Solid lines: allowed transitions
Dashed lines: forbidden transitions

m_l
2
$\Delta E \updownarrow$
1
$\Delta E \updownarrow$
0
$\Delta E \updownarrow$
-1
$\Delta E \updownarrow$
-2
$l = 2$

3d

$E_i - E_f$

2p

m_l
1
$\Delta E \updownarrow$
0
$\Delta E \updownarrow$
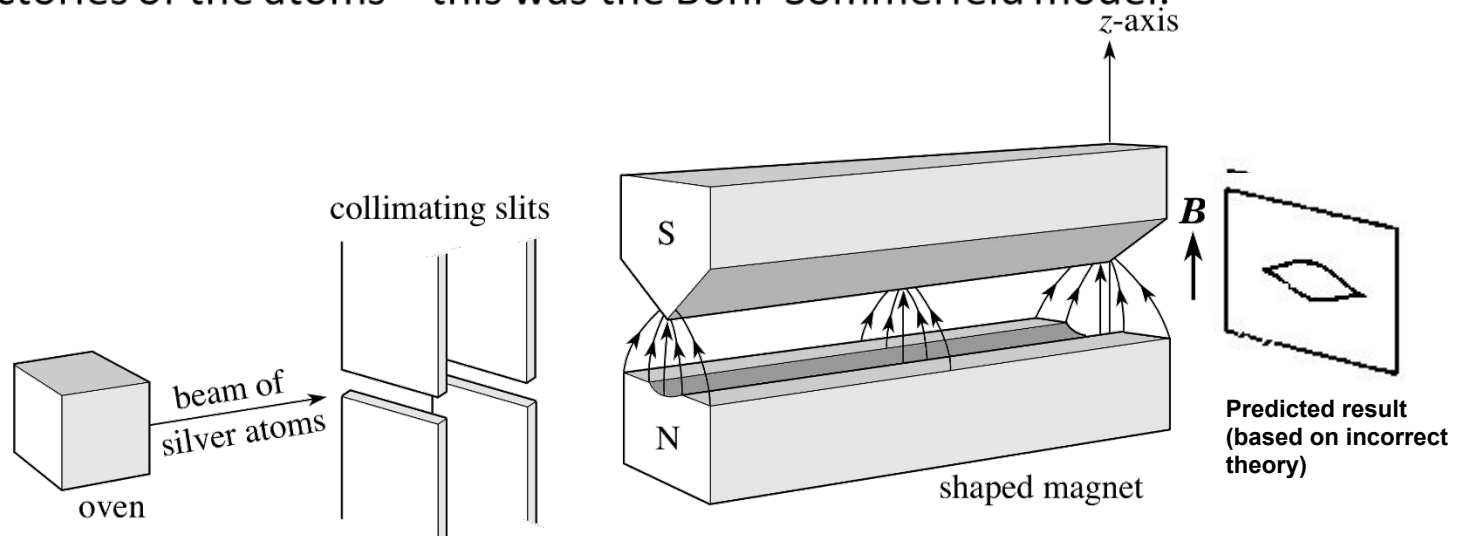-1
$l = 1$

Anomalous Zeeman Splitting

- So, there is one more intricacy of the hydrogen energy levels that must be discussed (there are more, but we're out of time).
- How many different values of m_ℓ are there for a given ℓ?
  - $m_\ell = -\ell, -\ell + 1, \ldots 0, 1, 2, \ldots \ell \Rightarrow$

    $\# m_\ell = 2\ell + 1$
- But if we look carefully at Zeeman splitting, there are cases where the number of lines are even, not odd, and more than the number of allowed m_ℓ values!
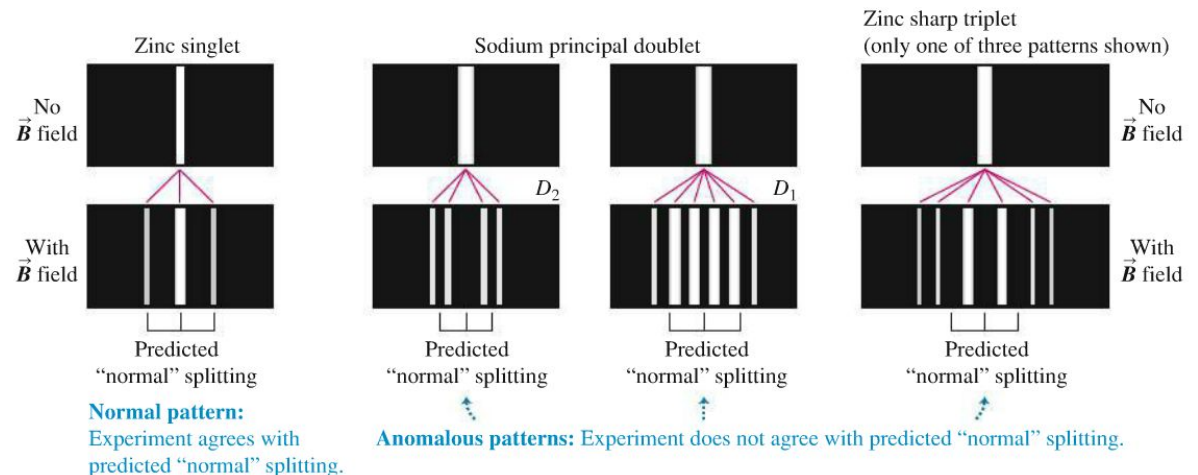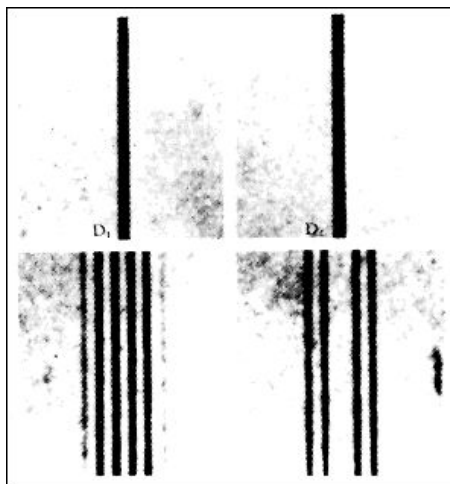
Stern-Gerlach Experiment

- In 1922, two physicists, Otto Stern and Walther Gerlach, performed an experiment to see the splitting (in space) of silver atoms passed through an inhomogeneous magnetic field.

- Classically, a magnetic dipole will feel a force (up or down) in such a field, so that the beam should be split, depending on the value of the magnetic dipole.

- The motivation for the experiment was to see if the orbital angular momentum was quantized in space (quantum theory) as opposed to pointing in just any direction (classical theory).

- However, they used silver atoms and believed that silver was in an $\ell = 1$ state, and also incorrectly believed that for an $\ell = 1$ state, they should see just two separate trajectories of the atoms – this was the Bohr-Sommerfeld model.

z-axis

collimating slits

S

B

beam of
silver atoms

N

oven

shaped magnet

**Predicted result
(based on incorrect
theory)**

Stern-Gerlach Experiment

- They saw the expected results.
- However, silver has completely filled shells up to the 4d shell, plus one electron in the 5s shell – it is in an $\ell = 0$ state, this being determined later by Schrödinger.
- That means that the interpretation of the experiment was wrong – for an $\ell = 1$ state there should be three splittings, and for an $\ell = 0$ state there should be none.
- So why two?
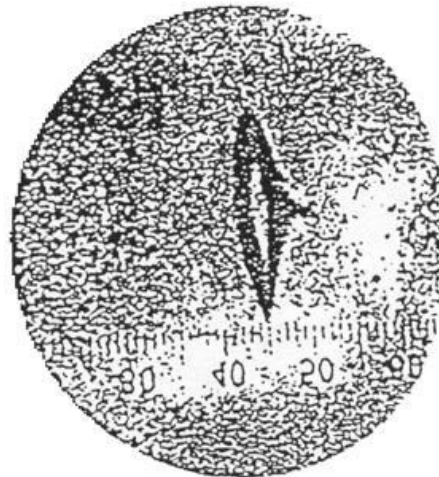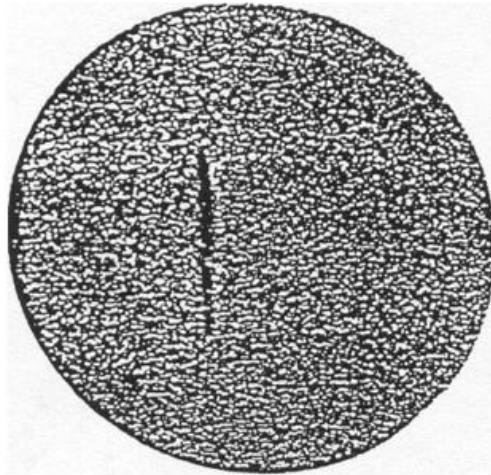
Electron Spin

- Once it was realized that silver was in an $\ell = 0$ state, Schrödinger's theory needed to be modified – something was missing.
- Several years after the experiment, Uhlenbeck and Goudsmit proposed that the electrons themselves had an intrinsic angular momentum, and that the sum of the atoms angular momentum would be the sum of the orbital and the intrinsic spin.
- They proposed that the electron spin would also be quantized and have a value of

$$S_z = m_s \hbar \quad m_s = \pm \frac{1}{2}$$

- This would then give two possibilities for the total angular momentum of an L = 0 state, in agreement with the observation.

$$\vec{J} = \vec{L} + \vec{S} \Rightarrow$$

$$J_z = 0 \pm \frac{1}{2} \hbar$$

Classical Analogy

- But how can we think of the electron having intrinsic angular momentum (or an intrinsic magnetic dipole moment)?
- The classical analogy is useful, but, wrong, as we shall see.
- Think of a sphere of charge, rotating.
- We can divide up the sphere into many loops – current loops, each with a dipole moment and then add them all together (using calculus).
- The problem with this classical calculation, is that the electron is very small, so in order to get the correct amount of magnetic moment, the outer parts must be moving faster than c…
- The intrinsic spin is just a new quantum phenomena!

$\bar{s}$
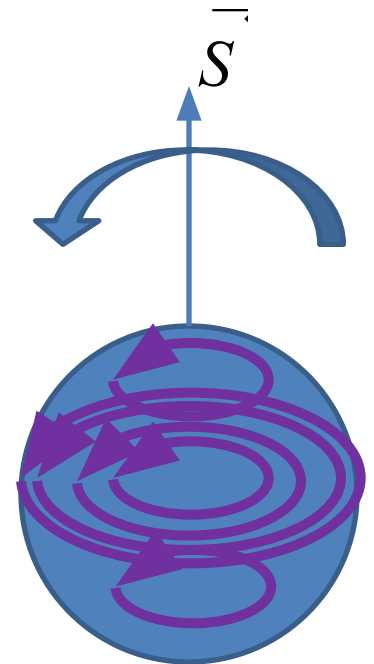
Spin Quantum Numbers

- So, now we have four quantum numbers (n, l, m_l, m_s) with:

$$n = 1, 2, 3, \ldots$$

$$\ell = 0, 1, 2, \ldots, n-1$$

$$m_\ell = -\ell, \ldots, \ell$$

$$m_s = -\frac{1}{2}, +\frac{1}{2}$$

$$L = \sqrt{\ell(\ell+1)}\,\hbar$$

$$S = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\,\hbar = \sqrt{\frac{3}{4}}\,\hbar$$

$$L_z = m_\ell \hbar$$

$$S_z = m_s \hbar$$

- Each state corresponds to a unique set of quantum numbers.

Exclusion Principle

- In 1925, Wolfgang Pauli was looking at the properties of elements and noted that even over a small range in the number of electrons, the properties changed dramatically.
- For example, Fluorine, Neon and Sodium have Z = 9, 10 and 11 respectively, but the properties are very different.
- In particular, it was noted that atoms with 2, 8, and 18 electrons behaved the same.
- If all the electrons were in the lowest energy state, this vast difference in properties wouldn't be seen.
- Pauli solved this puzzle with the following principle:
  - **No two electrons can exist in the same state** – that is no two electrons (in the same atom) can have all four quantum numbers (n, ℓ, m_ℓ, m_s) the same.

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		

Periodic Table

- Dmitri Mendeleev is generally credited with the publication, in 1869, of the first widely recognized periodic table. He developed his table to illustrate periodic trends in the properties of the then-known elements.

Element	Symbol	Atomic Number (Z)	Electron Configuration
Hydrogen	H	1	$1s$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2 2s$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p$
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	Al	13	$1s^2 2s^2 2p^6 3s^2 3p$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^5$
Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

Other Implications

- What the exclusion principle actually states, is that the wavefunction for a system of identical fermions must be antisymmetric – if you exchange any two particles, the new wavefunction should be the negative of the old:

The Pauli exclusion principle with a single-valued many-particle wavefunction is equivalent to requiring the wavefunction to be antisymmetric. An antisymmetric two-particle state is represented as a [sum of states](#) in which one particle is in state $|x\rangle$ and the other in state $|y\rangle$

$$|\psi\rangle = \sum_{x,y} A(x,y)|x,y\rangle,$$

and antisymmetry under exchange means that $A(x,y) = -A(y,x)$. This implies $A(x,y) = 0$ when $x=y$, which is Pauli exclusion.

Fermi Level

- Electrons (and any other spin ½ object) will fill the lowest energy states possible, but cannot exist in the same state with another identical particle…

- Neutron stars…