

**/University of Washington
Department of Chemistry
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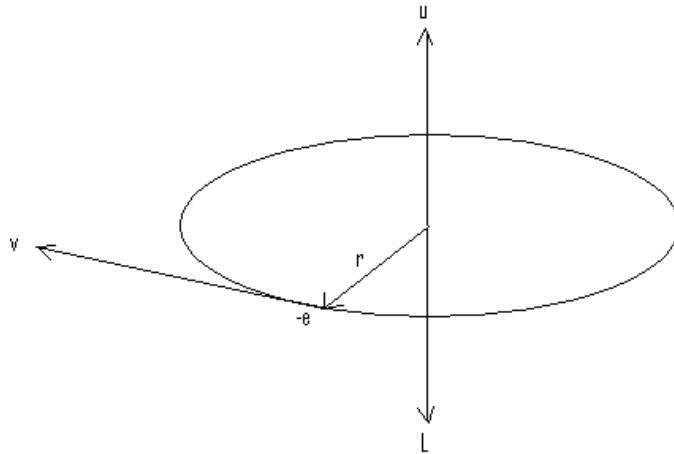
Lecture 10 01/31/11

A. Orbital Magnetic Moments

- Imagine an electron orbiting a nucleus with velocity v . Assume a simple Bohr model picture of this orbit as a circular path with radius r . because the electron is charged we imagine a current exists as the charge moves along this path. The current is (units of Coulombs per second)

$$\vec{i} = -\frac{e}{T} = -\frac{e\vec{v}}{2\pi r} \quad (10.1)$$

- A current circulating in a loop generates a magnetic field, according to classical theories of electricity and magnetism. Associated with this field is a magnetic dipolar moment which is located at the center of the loop and is pointed in a perpendicular direction from the plane of the loop.



- Suppose the area of the area enclosed by the circular loop is $A=\pi r^2$. The magnetic moment is related to the current i and the loop area A by

$$\vec{\mu} = \hat{r} \times \vec{i}A = -\hat{r} \times \frac{e\vec{v}}{2\pi r} \pi r^2 = -\frac{e}{2} \hat{r} r \times \vec{v} = -\frac{e}{2m} \vec{r} \times \vec{p} \quad (10.2)$$

Note that in (10.2) \hat{r} is a unit vector point from the center of the coordinate system (i.e. the nucleus) toward the electron, $\vec{r} = r\hat{r}$ is a vector of length r where r is the distance between the nucleus and the electron.

- As a result of the orbital motion of the electron there is an orbital angular momentum:

$$\vec{L} = \vec{r} \times \vec{p} = \vec{r} \times m\vec{v} \quad (10.3)$$

- Combining (10.2) and (10.3) we get the relationship between the magnetic moment and the orbital angular momentum of the electron.

$$\vec{\mu} = -\frac{e}{2m} \vec{r} \times \vec{p} = -\frac{e}{2m} \vec{L} = -\gamma_e \vec{L} \quad (10.4)$$

where $\gamma_e = \frac{e}{2m}$ is called the magnetogyric ratio. Equation (10.4) means that there is a very simply relationship between the magnetic moment and the orbital angular momentum of the electron. If the total angular momentum is quantized, equation (10.4) also says the magnetic moment must be quantized...

$$\vec{\mu} = -\gamma_e \vec{L} = -\gamma_e \hbar \sqrt{\ell(\ell+1)} \quad (10.5)$$

where $\ell = 0, 1, 2, 3, \dots$

- Because the magnetic moment is a vector we can also quantize the z component:

$$\vec{\mu}_z = -\gamma_e \vec{L}_z = -\gamma_e \hbar m \quad (10.6)$$

where $m = -\ell \dots 0 \dots \ell$

- Physicists in the early 20th century saw equation (10.6) as a great opportunity to confirm Bohr's quantum model for the hydrogen atom. The basis of this model is the quantization of angular momentum, and the connection between the electrons magnetic moment and the quantized angular momentum. The idea was to detect quantization of L_z via the magnetic moment...which can be physically manipulated in space using magnetic fields.

B. The Stern-Gerlach Experiment

- Two scientists Stern and Gerlach proposed to detect Bohr's quantized L_z via equation (10.6). The basis of their idea is that the electron's orbital magnetic moment can be manipulated in space using magnetic fields. If the magnetic moment μ of an orbiting electron is exposed to a uniform magnetic field B a torque τ is exerted on the moment by the field according to

$$\vec{\tau} = \vec{\mu} \times \vec{B} = -\gamma_e \vec{L} \times \vec{B} = \frac{d\vec{L}}{dt} \quad (10.7)$$

- The torque as a cross product depends upon the angle between the magnetic moment and the b field

$$\tau = \frac{dL}{dt} = -\gamma_e |L||B| \sin \theta \quad (10.8)$$

- The torque is the change in the angular momentum direction and the direction of the torque is perpendicular to the plane defined by L and B . This means the magnetic moment will precess like a top with a constant angle θ between L (or μ) and B . This is schematized in the diagram below. This is called Larmor precession and occurs at a frequency

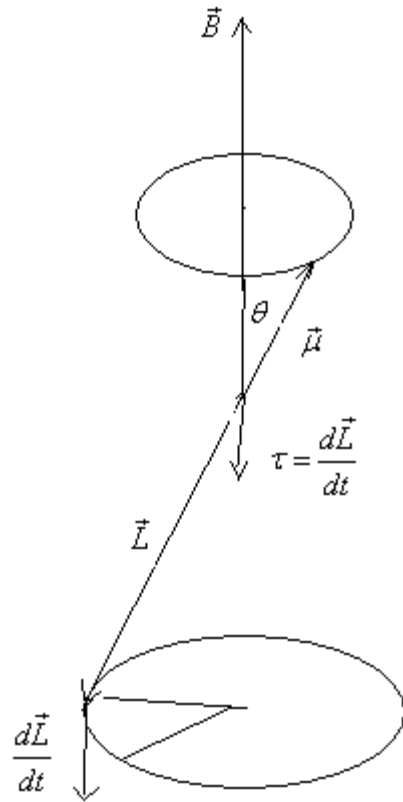
$$\omega = \gamma_e B \quad (10.9)$$

- Classically the magnetic moment m can be oriented at any angle q to the magnetic field to the magnetic field. If the magnetic moemtn is oriented at an angle θ to the magnetic field B , it takes energy to "flip" it to an angle $\pi - \theta$. The energy change ΔE required to flip the magnetic moment in the magnetic field is given by:

$$\Delta E = -\vec{\mu} \cdot \vec{B} = -|\vec{\mu}||\vec{B}| \cos \theta \quad (10.10)$$

where the energy is an inner product between two vectors. The energy and the torque should both be quantized as a result of the quantization of the angular momentum and

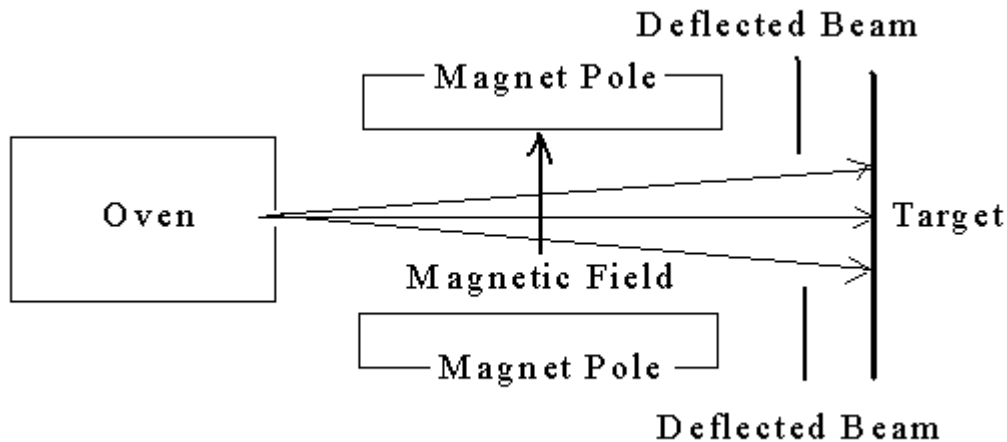
- In principle, the quantization of the magnetic moment (i.e. orbital angular momentum) might be detected either via the precession of the electron magnetic moment in a uniform magnetic field, or from the energy splitting that would be observed if atomic spectra were observed in a uniform magnetic field.



- Both effects were eventually observed but Stern and Gerlach used another detection method. The magnetic moment will precess in a uniform magnetic field, but if the magnetic is not uniform the magnetic moment will actually translate in the direction of the stronger field. Suppose the magnetic field B points in the z direction. The unit increase in the field dB_z per unit change in distance dz is: $\frac{\partial B_z}{\partial z}$. The force that acts to move the magnetic moment in the direction of the stronger field is

$$F_z = \mu_z \frac{\partial B_z}{\partial z}.$$

- S.-G. produced a vapor of silver atoms with an oven. A hole in the oven emitted a beam of silver atoms which passed through a non-uniform magnetic field. This field would deflect the atoms away from a straight path depending on the magnetic moment.



- Classically, any value of μ_z is allowed because any value of L_z is allowed. So the beam of silver atoms should be deflected over a wide angle continuously, forming a smear of silver on the target (see diagram). But S.-G. expected the magnetic moment to be quantized and thus a set of discrete spots should appear on the target corresponding to different values of m where $L_z = \hbar m$.
- According to the Schrodinger treatment of the hydrogen atom the quantum number m must vary as $m = -\ell, -\ell + 1 \dots -1, 0, 1 \dots \ell - 1, \ell$. For example, if $\ell = 1$, the expectation would be the $m = -1, 0, 1$ so there would appear on the target three spots and one spot ($m=0$) should appear at the position of the undeflected beam. In fact what was observed was only two spots one above and one below the $m=0$ position.
- The S.-G. experiment seemed to contradict quantum theory but it was soon realized that the angular momentum possessed by electron spins that caused the deflections observed by S.-G. did not arise from orbital motion.
- To explain the results of the S.-G. experiments m could NOT obey the rule $m = -\ell, -\ell + 1 \dots -1, 0, 1 \dots \ell - 1, \ell$ where $\ell = 0, 1, 2, 3 \dots$ because in such a case there would have to be in general $2\ell + 1$ spots and that means a minimum of three.
- Eventually it was realized that the S.-G. result was due to a second type of angular momentum S for which there is only a single value $S = \hbar \sqrt{s(s+1)}$. But the spin s is confined to a single number i.e. $s=1/2$.
- The z component of this new type of angular momentum obeys the equation $S_z = m_s \hbar$, $m_s = \pm \frac{1}{2} \dots$ and corresponds to the two spots on the target of S.-G.
- Originally it was suggested that this second type of angular momentum was due to the spinning of the electron around its own axis, where the electron was conceived to be a spherical charge. Therefore this new type of angular momentum was called spin. This turns out to be an incorrect interpretation of the origin of spin angular momentum. To generate so much angular momentum by spinning the electron would have to have a mass greater than the proton or a volume greater than the atom. But although there is no simple classical analog for spin, the name has stuck and this type of angular momentum is still called spin.
- The origin of spin angular momentum was eventually explained by correcting the Schrodinger equation for relativistic effects.

- The state of the electron spin angular momentum $S_z = m_s \hbar$, $m_s = \pm \frac{1}{2}$, also called spin “up” or “down” is the fourth quantum number required to express the wave function: ψ_{n,ℓ,m,m_s} .
- Because of the presence of spin angular momentum there is a magnetic moment m_s which arise from the spin. This is the spin magnetic dipole moment and is defined:

$$\vec{\mu}_s = -\frac{e}{m} \vec{S} = -\gamma_e \vec{S} \quad (10.11)$$

- Note the magnetogyric ratio in equation (10.11) $\gamma_e = \frac{e}{m}$ which is a factor of two different from the expression for γ_e given in equation (10.4). The equation (10.4) expression $\gamma_e = \frac{e}{2m}$ is sometimes called the classical magnetogyric ratio because it was derived using a classical picture for electron orbital angular momentum. To avoid confusion an additional term is added to equation (10.11). Referring to spin angular momentum:

$$\vec{\mu}_s = -g_s \gamma_e \vec{S} \quad (10.12)$$

where $\gamma_e = \frac{e}{2m}$ and $g_s=2$.