Spin

CHEM 361B: Introduction to Physical Chemistry

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Lecture 13

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1. The Zeeman Effect
2. Intrinsic Spin

Learning Objectives:

- Calculate energy transitions when hydrogen-like atoms are in magnetic fields
- Discuss the relevance of the fourth quantum number: intrinsic spin

References:

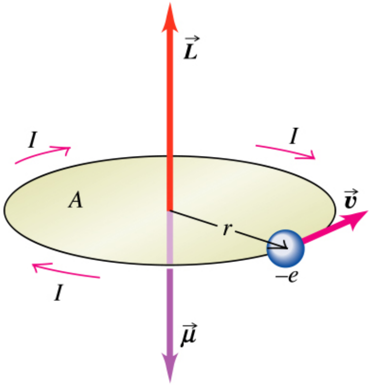
- McQuarrie §7.4 and §7.5

The Zeeman Effect

When an atom (in this case hydrogen) is placed in a magnetic field, the degenerate energy states split. To understand why, first consider that the motion of an electric charge around a closed loop produces a magnetic dipole

$$\mu = iA = \frac{q(r \times v)}{2} = -\frac{|e|}{2m_e}L$$

where i is the current in amperes and A is the area of the loop.



Constructing the Hamiltonian in the Presence of a B-Field

The potential energy due to a magnetic dipole in a magnetic field is

$$U = -\mu \cdot B$$

If the magnetic field is orientated in the z-direction then

$$U = -\mu_z B_z = \frac{|e|B_z}{2m_e} L_z$$

So a Hamiltonian can be constructed as

$$\hat{H} = -\frac{\hbar^2}{2\mu_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + \frac{|e|B_z}{2m_e}\hat{L}_z$$

or

$$\hat{H} = \hat{H}_0 + \frac{|e|B_z}{2m_e}\hat{L}_z$$

where $\hat{H}_0$ is the Hamiltonian in the absence of a magnetic field.

Appling the B-Field Hamiltonian

Applying this Hamiltonian to ψ

$$\hat{H}_0\psi + \frac{|e|B_z}{2m_e}\hat{L}_z\psi = E\psi$$

In particular

$$\hat{H}_0\psi = -\frac{\mu_e e^4}{8\epsilon_0^2 h^2 n^2}\psi$$

and

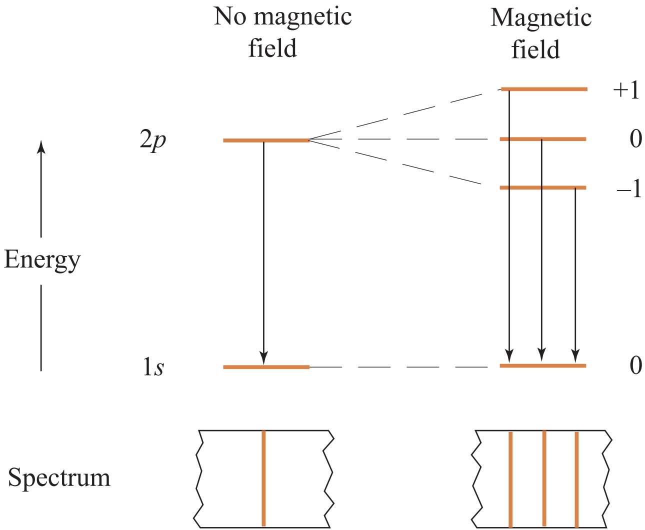
$$\frac{|e|B_z}{2m_e}\hat{L}_z\psi = \frac{|e|B_z}{2m_e}m\hbar\psi$$

which means that the total energy of a given state is

$$E = -\frac{\mu_e e^4}{8\epsilon_0^2 h^2 n^2} + \frac{|e|B_z}{2m_e}m\hbar \qquad \begin{array}{l} n = 1, 2, 3, \ldots \\ m = 0, \pm 1, \pm 2, \ldots, \pm \ell \end{array}$$

and depends on *both* n and m.

The Zeeman Effect



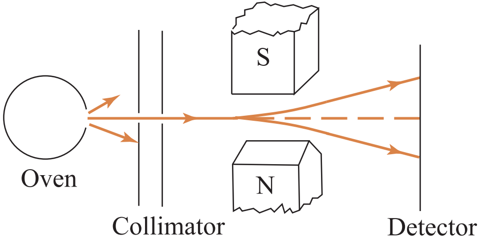
Zeeman Effect Problems

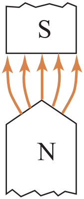
1. Calculate the magnitude of the splitting shown in the $2p$ orbital in the previous slide assmuing that the hydrogen atom is in a 10T magnetic field.
2. Calculate the energy difference between the unperturbed 1s and 2p levels.

Introduction to the Fourth Quantum Number - Spin

- Arthur H. Compton (around 1921) was studying the scattering of x-rays from crystal surfaces.
    - Concluded that "the electron itself, spinning like a tiny gyroscope, is probably the ultimate magnetic particle".
- The analogy of the electron spinning like a top can not be used to literally.
    - An electron is considered to be a structureless point particle described as a wave.
    - It can be said that elementary particles carry extrinsic angular momentum (L) as well as intrinsic angular momentum (S).

Stern-Gerlach Experiment





In 1922, the Stern-Gerlach Experiment showed that $\ell = 1/2$ which is not allowed due to the constraints on the solution to the Legendre differential equation.

The Electron has Intrinsic Spin

- Other irregularities in addition to the Stern-Gerlach result included
  - Why do all electrons in a system not populate the ground state.
  - Doublet spectrums that are observed in alkali spectrum (eg. Na D-line).
- In 1925, Wolfgang Pauli proposed that an electron can exist in two distinct states: $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$
  - This fourth quantum number is called the *spin quantum number*, s.
- This did not appear before in our formulation because relativistic effects were not considered.
  - In the early 1930s, Dirac developed a relativistic extension of quantum mechanics and spin appears naturally.

Spin Notation

Angular Momentum (L)

$$\hat{L}^2 Y_\ell^m(\theta,\phi) = \hbar^2 \ell(\ell+1) Y_\ell^m(\theta,\phi)$$
$$\hat{L}_z Y_\ell^m(\theta,\phi) = m\hbar Y_\ell^m(\theta,\phi)$$

Spin (S)

Spin up

$$\hat{S}^2\alpha = \hbar^2(1/2)(1/2+1)\alpha$$
$$\hat{S}_z\alpha = 1/2\hbar\alpha$$

Spin down

$$\hat{S}^2\beta = \hbar^2(1/2)(1/2+1)\beta$$
$$\hat{S}_z\beta = -1/2\hbar\beta$$

$$\int \alpha^*\alpha d\sigma = \int \beta^*\beta d\sigma = 1$$

Summary

- Because electrons are traveling around the nucleus, if atoms are put into magnetic fields, their magnetic dipoles will change the energy of the state to be

$$E = -\frac{\mu_e e^4}{8\epsilon_0^2 h^2 n^2} + \frac{|e|B_z}{2m_e} m\hbar \qquad \begin{array}{l} n = 1, 2, 3, \ldots \\ m = 0, \pm 1, \pm 2, \ldots, \pm \ell \end{array}$$

- The fourth quantum number, intrinsic spin, has values of $\pm\frac{1}{2}\hbar$
  - Discovered by the Stern-Gerlach experiment
  - Spin naturally falls out of quantum mechanics when relativistic effects are taken into account