PHYS2B22 Quantum Physics
Evening course lecture notes. Set 7.
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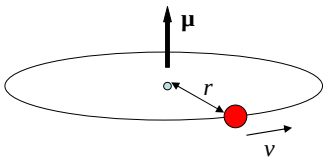
Outline of section 7

- Interaction of atoms with magnetic fields
- Stern-Gerlach experiment
- Electron spin
- Addition of angular momentum
- The 3D infinite square well

Atoms in magnetic fields

Classical theory: Interaction of orbiting electron with magnetic field:

Orbiting electron behaves like a current loop:



$$\text{Loop current} = \frac{-ev}{2\pi r} \quad (\text{- sign because charge} = -e)$$

$$\text{Magnetic moment } \mu = \text{current} \times \text{area}$$

$$= \left(\frac{-ev}{2\pi r}\right) \times \pi r^2 = \frac{-e}{2m_e} \times m_e v r = -\mu_B \frac{L}{\hbar}$$

$$\text{where } \mu_B = \frac{e\hbar}{2m_e} \text{ (the Bohr magneton).}$$

In a magnetic field **B**, classical interaction energy is:

$$H = -\boldsymbol{\mu}.\mathbf{B}$$

Corresponding quantum Hermitian operator is

$$\hat{H} = -\hat{\boldsymbol{\mu}}.\mathbf{B} = \mu_B \hat{\mathbf{L}}.\mathbf{B}/\hbar$$

Splitting of atomic energy levels

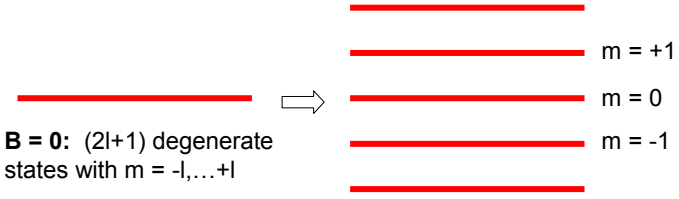
For B-field in the *z* direction, the total Hamiltonian for the atom is

$$\hat{H} = \hat{H}_0 + \frac{\mu_B B_z}{\hbar}\hat{L}_z$$

The energy eigenfunctions of the original atom are eigenfunctions of L_z so they are also eigenfunctions of the new Hamiltonian

$$E = E_0 + m\mu_B B_z \quad -l \le m \le l$$

(Hence the name "magnetic quantum number" for m.)



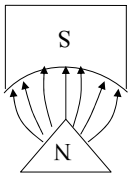
B = 0: (2l+1) degenerate states with m = -l,…+l

B ≠ 0: (2l+1) states with distinct energies

The Stern-Gerlach experiment (1922)

In an inhomogeneous magnetic field there is a force on the atoms which depends on m

$$\mathbf{F} = \nabla(\boldsymbol{\mu}\cdot\mathbf{B}) = -m\mu_B\frac{dB_z}{dz}$$



Direction of force tends to decrease the magnetic potential energy

$$E = E_0 + m\mu_B B_z \quad -l \le m \le l$$

So atoms in different internal angular momentum states will experience different forces and will move apart. So if we pass a beam of atoms through an inhomogeneous B field we should see the beam separate into parts corresponding to the distinct values of m.

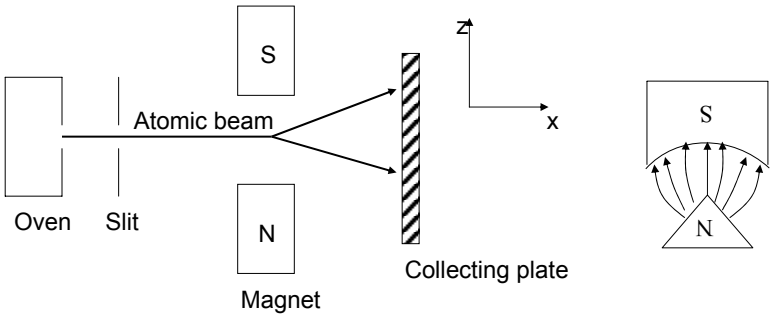
Predictions:

1. Beam should split into an odd number of parts (2l+1)
2. A beam of atoms in an s state (e.g. the ground state of hydrogen, *n* = 1, *l* = 0, *m* = 0) should not be split.

The Stern-Gerlach experiment (2)

Beam of atoms with a single electron in an s state (e.g. silver, hydrogen)

Study deflection in inhomogeneous magnetic field. Force on atoms is $\mathbf{F} = \nabla(\boldsymbol{\mu} \cdot \mathbf{B})$



Results show **two** groups of atoms, deflected in opposite directions, with magnetic moments $\mu = \pm\mu_B$

Consistent neither with classical physics (which would predict a continuous distribution of μ) nor with our quantum mechanics so far (which always predicts an odd number of groups and just one for an s state).

Electron spin

Stern-Gerlach results must be due to some additional internal source of angular momentum that does not require motion of the electron. This is known as "spin" and was suggested in 1925 by Goudsmit and Uhlenbeck building on an idea of Pauli. It is a relativistic effect and actually comes out directly from the Dirac theory (1928).

Introduce Hermitian operators and eigenfunctions for spin by analogy with what we know from orbital angular momentum. We have two new quantum numbers s and m_s

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

$$\hat{\mathbf{S}} = \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix}$$

$$\hat{S}_z \chi_{s,m_s} = m_s \hbar \chi_{s,m_s} = \pm\frac{1}{2}\hbar\chi_{s,m_s}$$
$$\hat{S}^2 \chi_{s,m_s} = s(s+1)\hbar^2 \chi_{s,m_s} = \frac{3}{4}\hbar^2 \chi_{s,m_s}$$

$$s = \frac{1}{2}, \quad -s \le m_s \le s \Rightarrow m_s = \pm\frac{1}{2}$$

Usual form of commutation relations

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z \quad \text{etc. c.f} \quad \left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z$$


Goudsmit


Uhlenbeck


Pauli

A complete set of quantum numbers

Hence the full wavefunction of an electron in the H atom is

$$\psi_{nlmsm_s}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)\chi_{s,m_s}$$

$$\chi_{1/2,1/2} = \begin{pmatrix}1\\0\end{pmatrix}, \quad \chi_{1/2,-1/2} = \begin{pmatrix}0\\1\end{pmatrix}$$

Note that the spin functions χ do not depend on the electron spatial coordinates r,θ,φ; they represent a purely internal degree of freedom.

The **complete** set of quantum numbers is: n,l,m,s,m_s with s = ½ and m_s = +/- ½.

H atom in magnetic field, with spin included:

$$\hat{H} = \hat{H}_0 + \frac{\mu_B}{\hbar}\mathbf{B}\cdot(\hat{\mathbf{L}} + g\hat{\mathbf{S}})$$

$g = 2$ (Dirac's relativistic theory)

$g = 2.00231930437$ (Quantum Electrodynamics)

g = gyromagnetic ratio

Addition of angular momenta

So, an electron in an atom has two sources of angular momentum:

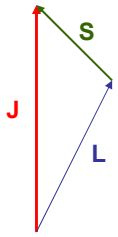
- Orbital angular momentum (from its motion around the nucleus)
- Spin angular momentum (an internal property of its own).

What is the total angular momentum produced by combining the two?

Classically we would just add the vectors to get a resultant

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

$$\big||\mathbf{L}| - |\mathbf{S}|\big| \le |\mathbf{J}| \le |\mathbf{L}| + |\mathbf{S}|$$



In QM we define an operator for the total angular momentum

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

But we have to be careful about the possible eigenvalues for J.
L defines a direction in space and **S** can not be parallel to this because then we would know all three components of **S** simultaneously.

Addition of angular momentum (2)

However, we can certainly add the z-components of angular momentum

Eigenvalues of $\hat{L}_z$ are $m\hbar$ with $-l \le m \le l$
Eigenvalues of $\hat{S}_z$ are $m_s\hbar$ with $m_s = \pm 1/2$
Eigenvalues of $\hat{J}_z$ are $m_j\hbar$ with $m_j = m + m_s$

The possible values for the magnitude of the total angular momentum J^2 are given by the rule

Eigenvalues of $\hat{L}^2$ are $l(l+1)\hbar^2$ with $l = 0,1,2,3...$
Eigenvalue of $\hat{S}^2$ is $s(s+1)\hbar^2$ with $s = 1/2$
Eigenvalues of $\hat{J}^2$ are $j(j+1)\hbar^2$ with $|l-s| \le j \le l+s$ in integer steps

This is like the classical rule but using the *quantum numbers* rather than the angular momentum vector. The total angular momentum quantum number j takes values between the sum and difference of the corresponding quantum numbers for l and s in integer steps. For each j, there are 2j+1 possible values of the quantum number m_j describing the z-component, as usual for angular momentum.

$$j = \left|l - \tfrac{1}{2}\right|, l + \tfrac{1}{2}$$
$$m_j = -j, \ldots, +j$$

Example: the 1s and 2p states of hydrogen

The 1s state:

The 2p state:

Addition of angular momenta (3)

The same rules apply to adding all other angular momenta

Example: 2 electrons in an excited state of the He atom, one in the 1s state and one in the 2p state (defines the 1s2p **configuration** in atomic spectroscopy):

$$l_1 = 0; s_1 = \tfrac{1}{2}; \qquad l_2 = 1; s_2 = \tfrac{1}{2}$$

First construct combined orbital angular momentum *L* of both electrons:

Then construct combined spin *S* of both electrons:

Hence there are two possible **terms** (combinations of *L* and *S*):

…and four **levels** (possible values of total angular momentum J arising from a given *L* and *S*)

Term notation

Spectroscopists use a special term notation to describe terms and levels:

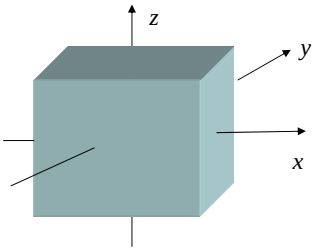
$$^{2S+1}L_J$$

- The first (upper) symbol is a *number* (known as the *multiplicity*) giving the number of spin states corresponding to the total spin *S* of the electrons
- The second (main) symbol is a *letter* encoding the total orbital angular momentum *L* of the electrons:
  - *S* denotes *L* = 0
  - *P* denotes *L* = 1
  - *D* denotes *L* = 2 (and so on);
- The final (lower) symbol is a *number* giving the total angular momentum quantum number *J* obtained from combining L and S.

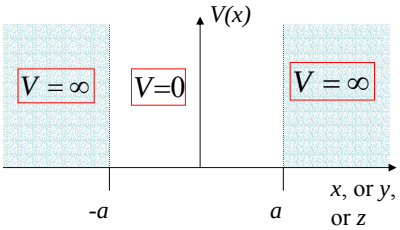
Example: terms and levels from previous examples are:

The 3D infinite square well

Consider a particle which is free to move in *three* dimensions everywhere within a cubic box, which extends from –*a* to +*a* in each direction. The particle is prevented from leaving the box by infinitely high potential barriers.



Time-independent Schrödinger equation within the box is free-particle like:



Separation of variables: take

$$\psi(x,y,z) = X(x)Y(y)Z(z)$$

with boundary conditions $X(\pm a)=Y(\pm a)=Z(\pm a)=0.$

The 3D infinite square well (2)

Substitute in Schrödinger equation:

Divide by *XYZ*:

We obtain three effective *one-dimensional* Schrödinger equations. We've solved these already (cf Sec. 3).

The 3D infinite square well (3)

Wavefunctions and energy eigenvalues are known from solution to one-dimensional square well.

The total energy is

Summary

The electron has spin 1/2

$$\hat{S}_z \chi_{s,m_s} = m_s \hbar \chi_{s,m_s} = \pm \frac{1}{2} \hbar \chi_{s,m_s}$$

$$\hat{S}^2 \chi_{s,m_s} = s(s+1)\hbar^2 \chi_{s,m_s} = \frac{3}{4}\hbar^2 \chi_{s,m_s}$$

Addition of angular momentum with spin

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

$$j = \left| l - \tfrac{1}{2} \right|, l + \tfrac{1}{2}$$

$$m_j = -j, \ldots, +j$$

Eigenvalues of $\hat{J}^2$ are $j(j+1)\hbar^2$

Full atomic wavefunctions are

$$\psi_{nlmsm_s}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta, \phi) \chi_{s,m_s}$$

Interaction with magnetic field

$$\hat{H} = \hat{H}_0 + \frac{\mu_B}{\hbar} \mathbf{B} \cdot (\hat{\mathbf{L}} + g\hat{\mathbf{S}})$$

g = gyromagnetic ratio ≈ 2

Spectroscopic term notation

$$^{2S+1}L_J$$