PHY215-08: Atomic Physics

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April 11, 2025

1 Orbitals

In atomic physics, the number of electrons that can fill each orbital is determined by the Pauli exclusion principle, which states that no two electrons in an atom can have the same set of quantum numbers. Each orbital is defined by the quantum numbers n, l, and m_l, and can hold a maximum of 2 electrons with opposite spins (governed by the spin quantum number $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$).

Key Steps to Determine Orbitals and Electrons for, for example, $n = 3$:

1. Principal Quantum Number (n) Defines the electron shell. For $n = 3$, the possible values of the angular momentum quantum number (l) are $0, 1, 2$ (corresponding to s, p, d subshells).

2. Orbitals per Subshell (l)

- For $l = 0$ (s subshell): Magnetic quantum number $m_l = 0 \rightarrow 1$ orbital.
- For $l = 1$ (p subshell): $m_l = -1, 0, +1 \rightarrow 3$ orbitals.
- For $l = 2$ (d subshell): $m_l = -2, -1, 0, +1, +2 \rightarrow 5$ orbitals.

Total orbitals for $n = 3$: $1 + 3 + 5 = \mathbf{9}$ orbitals.

Note: The total number of orbitals for a given principle value n is n^2.

3. Electrons per Orbital

Each orbital can hold 2 electrons (spin - up and spin - down).

4. Total number of electrons

For $n = 3$: 9 orbitals $\times$ 2 electrons/orbital = **18** electrons.

Common Confusion: Orbitals vs. Electrons

- Orbitals:

Defined by n, l, m_l. For $n = 3$, there are 9 orbitals (not 18).

- Electrons:

Each orbital holds 2 electrons (due to spin), so the $n = 3$ shell can hold 18 electrons in total.

This follows directly from the quantum numbers and the Pauli exclusion principle, which limits each orbital to two electrons with opposite spins.

- The theoretical basis for Pauli exclusion principle is the requirement that the total wavefunction of electrons (spin-$\frac{1}{2}$ fermions) has to be totally antisymmetric under the exchange of any two electrons.

- Consider two electrons in a system. If the two electrons were in the same quantum state (i.e., having the same set of quantum numbers which are n, l, m_l, and m_s), then the spatial part of the wavefunction and the spin part of the wavefunction would be symmetric under the exchange of the two electrons. However, since the total wavefunction (which is a product of the spatial and spin wavefunctions) must be antisymmetric for fermions, this would lead to a contradiction. So, the two electrons cannot be in the same quantum state, which limits each orbital to two electrons with opposite spins.

2 Electron spin

The necessity of an inhomogeneous magnetic field in the Stern-Gerlach experiment arises from the interplay between quantum spin and classical electromagnetism. Here's a detailed mathematical derivation that uncovers the underlying physics:

2.1 Magnetic Moment-Spin Relationship

The electron's intrinsic spin angular momentum $\mathbf{S}$ generates a magnetic dipole moment $\boldsymbol{\mu}$:

$$\boldsymbol{\mu} = -\frac{e}{m_e}\mathbf{S} \quad \text{(classical approximation)}$$

where e is the electron charge and m_e its mass.

2.2 Potential Energy in a Magnetic Field

The interaction energy between $\boldsymbol{\mu}$ and a magnetic field $\mathbf{B}$ is:

$$U = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{e}{m_e}\mathbf{S} \cdot \mathbf{B}$$

In quantum mechanics, $\mathbf{S}$ is an operator. For a spin-1/2 system, the z-component of spin S_z has eigenvalues $\pm\hbar/2$. Substituting S_z, the energy becomes:

$$U = \frac{e}{m_e}\left(\pm\frac{\hbar}{2}\right)B_z = \pm\frac{e\hbar}{2m_e}B_z$$

This predicts two distinct energy states—spin-up (+) and spin-down (−).

2.3 Force from Field Gradient

The force experienced by a magnetic dipole in a nonuniform field is:

$$\mathbf{F} = -\nabla U = \frac{e}{m_e}(\mathbf{S} \cdot \nabla)\mathbf{B}$$

Assuming the magnetic field has a strong gradient in the z-direction ($\nabla B \approx \frac{\partial B_z}{\partial z}\hat{\mathbf{z}}$), the force simplifies to:

$$F_z = \frac{e}{m_e} S_z \frac{\partial B_z}{\partial z}$$

Substituting $S_z = \pm\hbar/2$:

$$F_z = \pm\frac{e\hbar}{2m_e}\frac{\partial B_z}{\partial z}$$

Critical Insight:

- If $\frac{\partial B_z}{\partial z} = 0$ (homogeneous field), $F_z = 0$ —no deflection occurs.
- Only an inhomogeneous field ($\frac{\partial B_z}{\partial z} \neq 0$) creates a net force proportional to spin projection, splitting the beam into two paths.

Classical vs. Quantum Predictions

- **Classical Prediction:** A continuous range of magnetic moment orientations would produce a smeared distribution on the detector.
- **Quantum Prediction:** Only two discrete deflections occur due to quantized spin ($S_z = \pm\hbar/2$).

2.4 Experimental Validation

Silver atoms (^{47}Ag, with the electron configuration [Kr] $4d^{10}5s^1$) with a single unpaired electron in the $5s$ orbital ($L = 0$), have total angular momentum $J = L + S = 1/2$. The force calculation confirms:

$$F_z = \pm\frac{e\hbar}{2m_e}\frac{\partial B_z}{\partial z}$$

This splits the atomic beam into two distinct spots, as observed in the experiment.

The inhomogeneous magnetic field is indispensable because it introduces a position-dependent force proportional to the spin projection. Without this gradient ($\nabla B = 0$), the force vanishes, and quantum spin effects cannot be observed. This experiment fundamentally links classical electromagnetism to quantum spin quantization, cementing the role of spin as an intrinsic particle property.

2.5 Contribution from a closed shell

The contribution of a closed shell (completely filled electron shell) to the total spin angular momentum of an atom is zero. Here's why:

1. Electron Spin in Closed Shells:

- In a closed shell (e.g., a fully occupied s, p, d, or f subshell), electrons are paired in atomic orbitals. Each orbital holds two electrons with opposite spins (spin quantum numbers $m_s = +1/2$ and $m_s = -1/2$).
- The spins of these paired electrons cancel each other out (vector sum of spins for each pair is zero). Since all orbitals in a closed shell are fully occupied and paired, the total spin contribution from the shell is zero.

2. Orbital Angular Momentum in Closed Shells:

- It's worth noting that closed shells also have zero net orbital angular momentum due to symmetry (e.g., in a p^6 shell, the orbital angular momentum vectors from each p orbital cancel out). However, this is a separate property from spin.

3. Atomic Spin Origin:

- The total spin of an atom arises from unpaired electrons in open shells (partially filled subshells). Closed shells, with all electrons paired, do not contribute to the overall spin.

Example:

- For a noble gas like neon (Ne, with electron configuration [He] $2s^2 2p^6$), all shells are closed. The total electron spin angular momentum is zero.

- In contrast, an atom like oxygen (O, with electron configuration [He] $2s^2 2p^4$) has two unpaired electrons in the 2p subshell, so its total spin is non-zero (spin quantum number S = 1).

Conclusion:

A closed electron shell contributes zero to the spin of an atom because all electron spins within it are paired and cancel each other out. The atom's net spin comes exclusively from unpaired electrons in open shells.

3 Derivation of the Magnetic Dipole Moment Generated by the Orbital Angular Momentum of an Electron in a Hydrogen Atom

To derive the magnetic dipole moment $\boldsymbol{\mu}$ generated by the orbital angular momentum of an electron in a hydrogen atom, we first treat the electron's orbital motion as a classical current loop and then transition to the quantum mechanical description. The key steps are as follows:

3.1 Classical Current Loop Model

An electron moving in a circular orbit of radius r with angular velocity ω forms a closed current loop.

- Orbital period: $T = \frac{2\pi}{\omega}$
- Current: $I = \frac{\text{charge}}{\text{period}} = \frac{-e}{T} = \frac{-e\omega}{2\pi}$ (the negative sign is due to the electron charge $-e$)
- Area of the loop: $A = \pi r^2$

The magnetic dipole moment for a current loop is given by:

$$\boldsymbol{\mu} = I \cdot \boldsymbol{A} = I \cdot (A\,\hat{\mathbf{n}})$$

where $\hat{\mathbf{n}}$ is the unit vector perpendicular to the loop (determined by the right - hand rule for the current direction). For an electron, since it is negatively charged, the current direction is opposite to its motion, so $\hat{\mathbf{n}}$ is opposite to the direction of the orbital angular momentum.

3.2 Relation to Orbital Angular Momentum

The classical orbital angular momentum is:

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} = m\boldsymbol{r} \times \boldsymbol{v} = mr^2\omega\,\hat{\mathbf{n}}$$

Solving for ω:

$$\omega = \frac{L}{mr^2}$$

Substituting ω into the expression for the current I:

$$I = \frac{-e}{2\pi} \cdot \frac{L}{mr^2} = \frac{-eL}{2\pi mr^2}$$

The magnetic dipole moment becomes:

$$\boldsymbol{\mu} = I \cdot \pi r^2\,\hat{\mathbf{n}} = \frac{-eL}{2\pi mr^2} \cdot \pi r^2\,\hat{\mathbf{n}} = \frac{-e}{2m}\boldsymbol{L}$$

Since $\boldsymbol{L} = mr^2\omega\,\hat{\mathbf{n}}$, the direction of $\boldsymbol{\mu}$ is opposite to $\boldsymbol{L}$ (due to the negative charge $-e$), so:

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

3.3 Quantum Mechanical Generalization

In quantum mechanics, the orbital angular momentum is an operator $\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}}$, where $\hat{\boldsymbol{p}} = -i\hbar\nabla$ is the momentum operator. The magnetic dipole moment operator becomes:

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

3.3.1 Key Constant: Bohr Magneton

The proportionality constant $\frac{e\hbar}{2m}$ is a fundamental unit of magnetic moment called the Bohr magneton (μ_B):

$$\mu_B = \frac{e\hbar}{2m} \approx 9.274 \times 10^{-24}\,\mathrm{J/T}$$

Using μ_B, the orbital magnetic dipole moment can be written as:

$$\hat{\boldsymbol{\mu}} = -\frac{\mu_B}{\hbar}\hat{\boldsymbol{L}}$$

- The derivation assumes that the electron moves in a circular orbit, and the classical current loop approximation holds.
- This result is valid for any charged particle with orbital angular momentum (not just electrons in a hydrogen atom), but for electrons, the negative sign indicates that the magnetic moment is antiparallel to the angular momentum (due to their negative charge).

4 Summary

The magnetic dipole moment due to the electron's orbital angular momentum in a hydrogen atom is:

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

This relationship connects the classical picture of orbital motion to quantum mechanics, with the Bohr magneton μ_B serving as the natural unit for atomic magnetic moments.