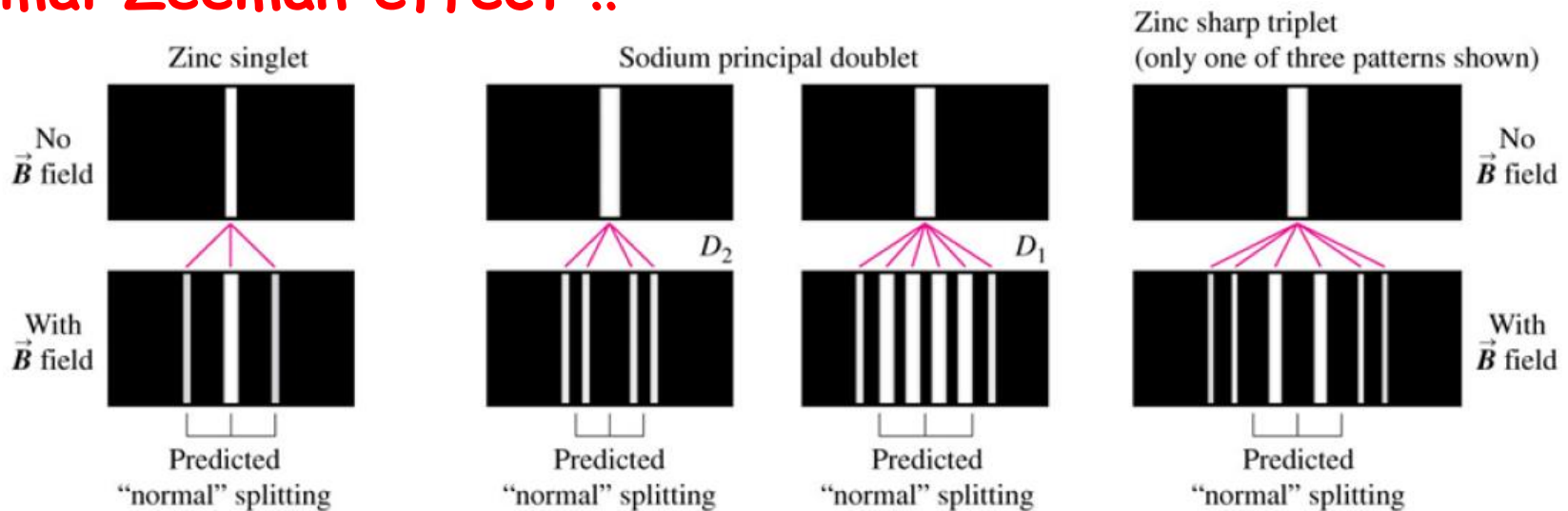


Fine spectral structures of atoms

When an atom is placed in a magnetic field, each of its fine structure lines further splits into a series of equidistant lines with a spacing proportional to the magnetic field strength. The electron has an orbital magnetic moment.

Normal Zeeman effect !!

Anomalous Zeeman effect !!!



The anomalous Zeeman effect shows up particularly for atoms with odd atomic number Z (hydrogen, for example). In such cases, the number of Zeeman sub-levels is actually even rather than odd. This suggests the possible existence of an angular momentum like quantity that can take on half-integer values.

Stern-Gerlach Experiment

W. Gerlach and O. Stern, Z. Physik, 8, 110 (1922); 9, 349 (1922); 9, 353 (1922).

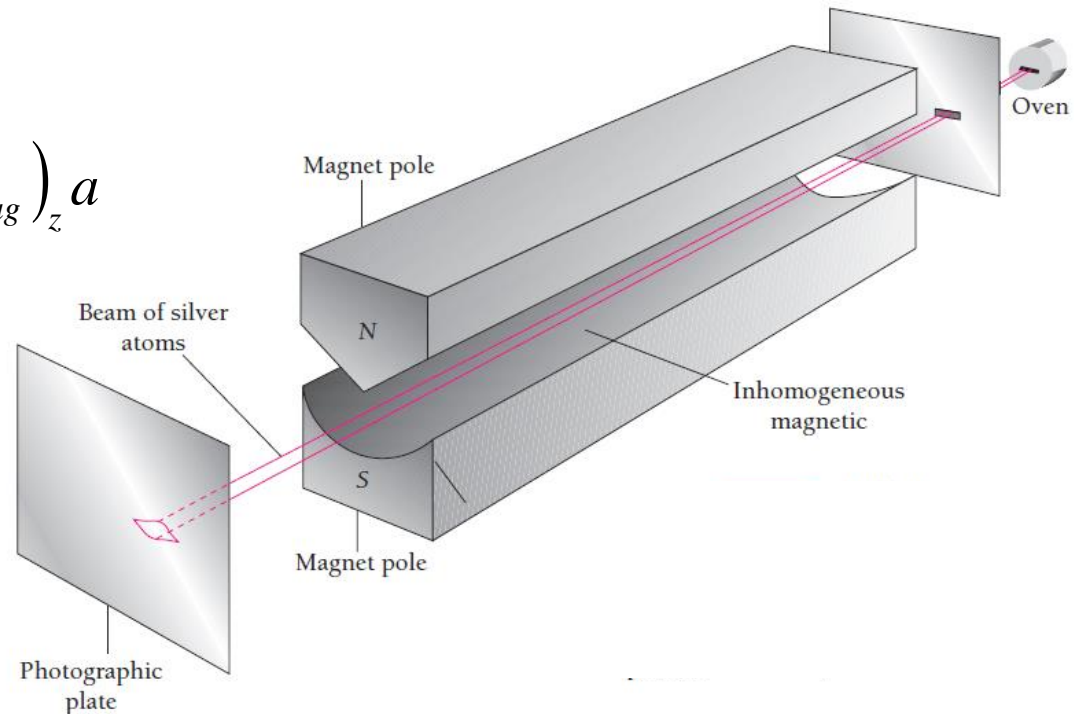
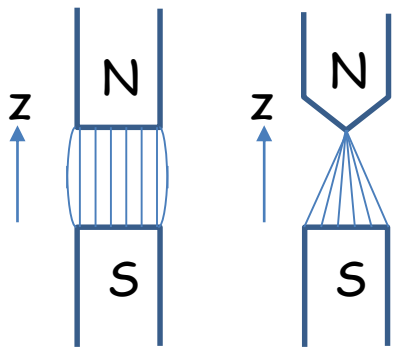
Potential energy in magnetic field:

$$\Delta E_{mag} = -(\mu_{mag})_z (B_0 + az)$$

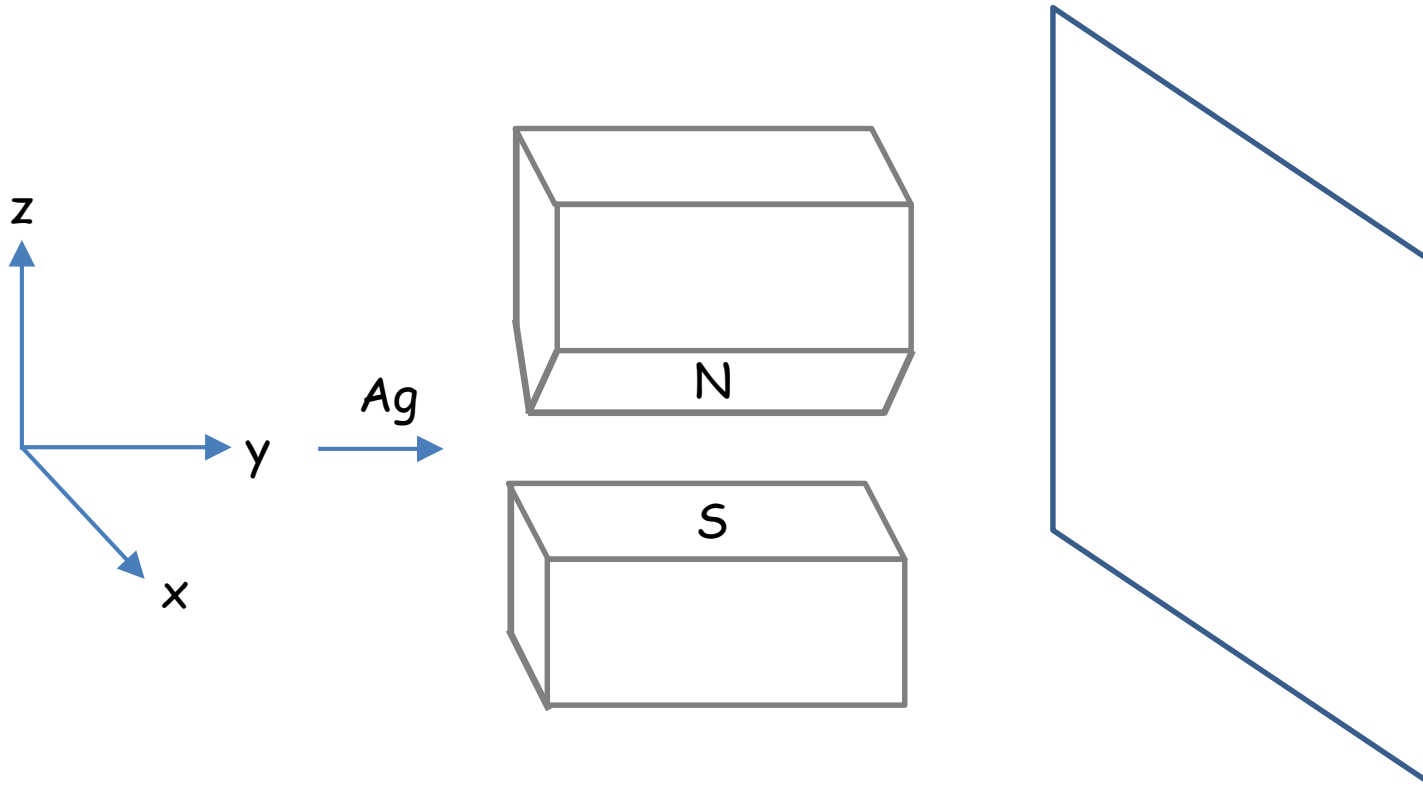
Force to Ag atom:

$$F_{mag} = -\frac{\partial \Delta E_{mag}}{\partial z} = (\mu_{mag})_z a$$

$$B = B_0 + az$$



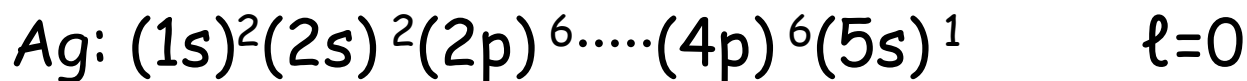
What would be the result?



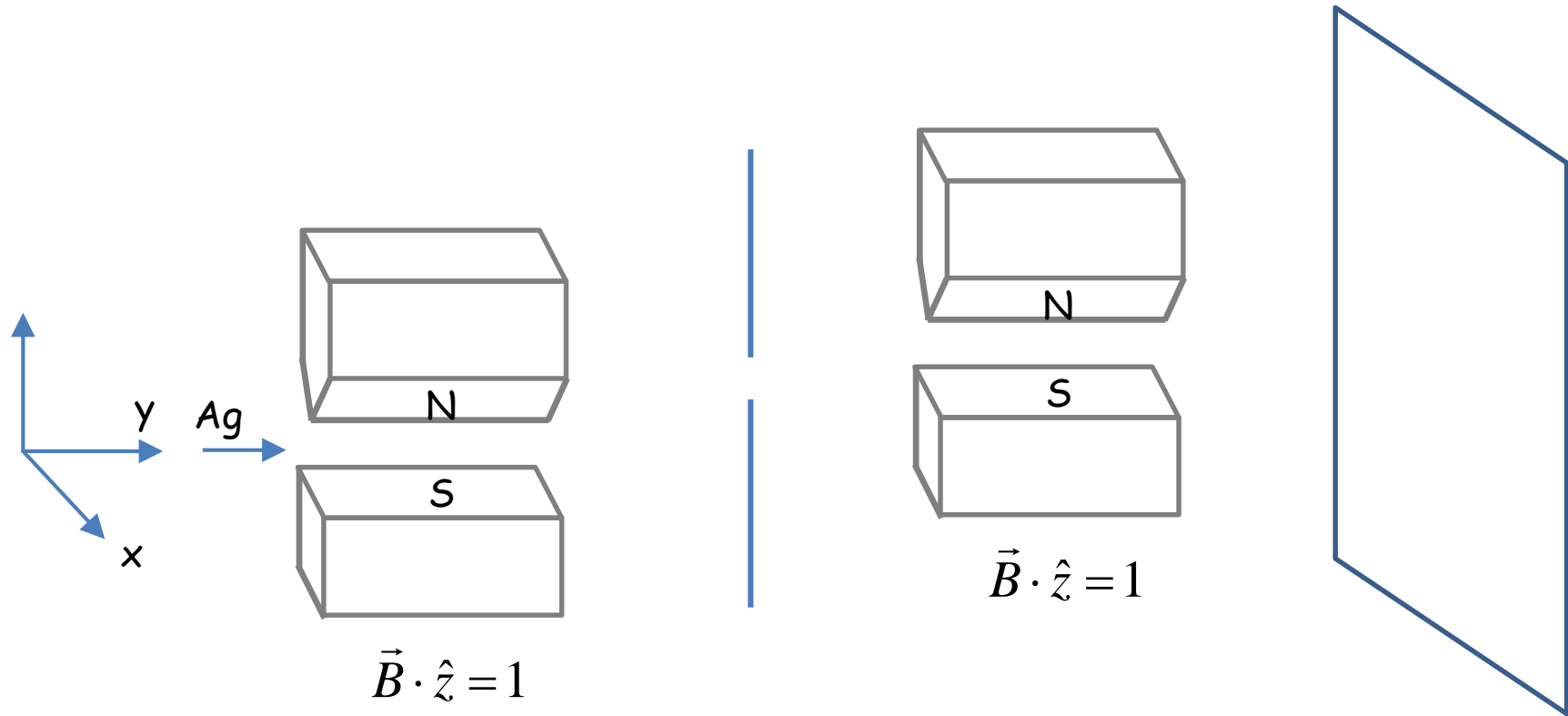
From the Stern-Gerlach Experiment

- ✓ Ag atoms have magnetic moments.
- ✓ Each z component of their magnetic moments just shows one of the two values.
- ✓ The value of $(\mu_{\text{mag}})_z$ can be determined with the velocity of Ag, the distance to the glass plate, the magnitude of inhomogeneous magnetic field and the distance between the two spots on the screen.

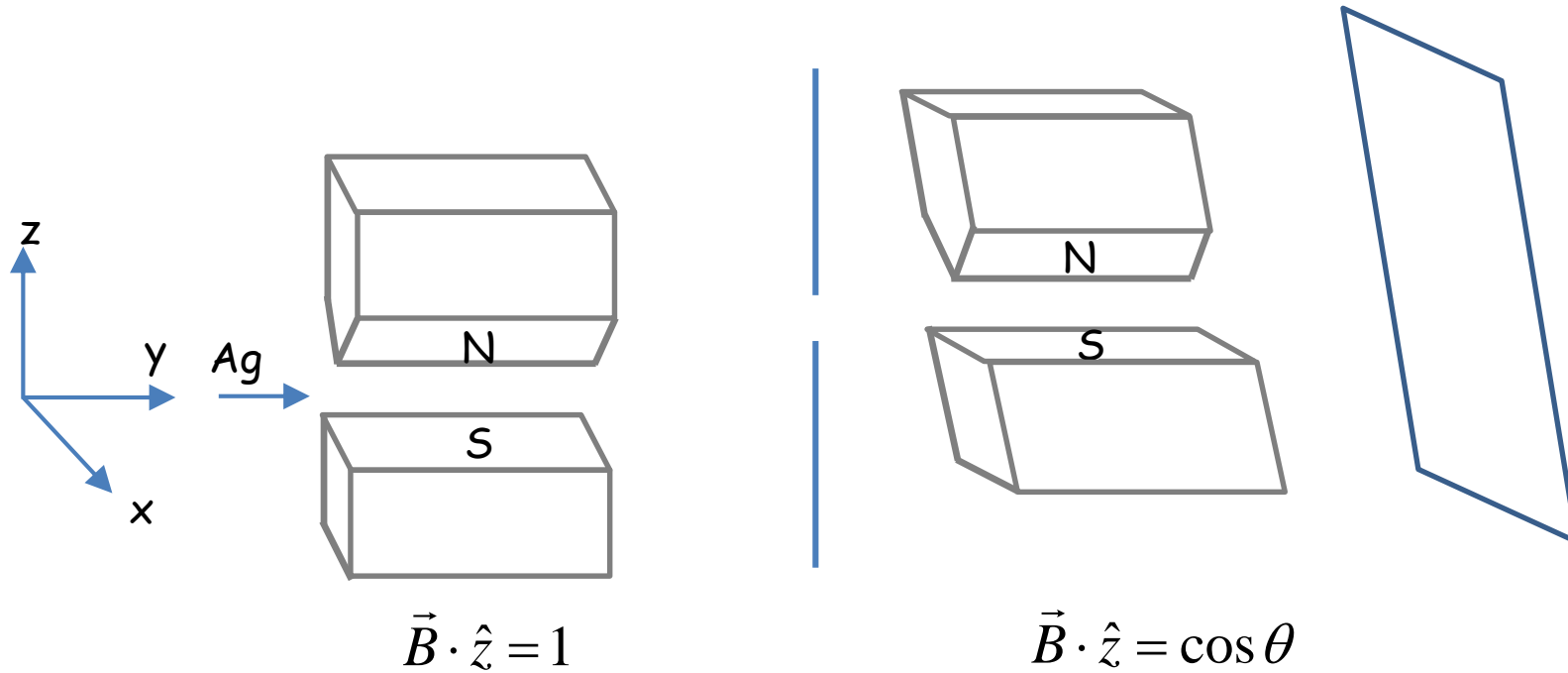
$$(\mu_{\text{mag}})_z = \pm \mu_B \quad \mu_B = \frac{|e|\hbar}{2m_e} = 9.274 \times 10^{-24} \text{ J/T}$$



Double Stern-Gerlach Experiment I



Double Stern-Gerlach Experiment II



Measurement and operator

Physical quantity that can be observed by measurement
: **Observable**

Wave function ψ

Measurement: **Operator \hat{O}**

$$\hat{O}\psi = \lambda\psi$$

$$\text{Average} = \langle \psi | \hat{O} | \psi \rangle = \int \psi^* \hat{O} \psi d\tau$$

Electron spin hypothesis

Year 1925 Uhlenbeck and Goudsmit

1. Electron: spin angular momentum S

Operator S_u ($u=x, y, z$): eigenvalues $+1/2\hbar, -1/2\hbar$

2. Spin magnetic moment $\mu_u^s = -\frac{e}{m_e} \hat{S}_u$

3. Commutation relations

$$[\hat{S}_x, \hat{S}_y] = \hat{S}_x \hat{S}_y - \hat{S}_y \hat{S}_x = i\hbar \hat{S}_z$$

$$[\hat{S}_y, \hat{S}_z] = \hat{S}_y \hat{S}_z - \hat{S}_z \hat{S}_y = i\hbar \hat{S}_x$$

$$[\hat{S}_z, \hat{S}_x] = \hat{S}_z \hat{S}_x - \hat{S}_x \hat{S}_z = i\hbar \hat{S}_y$$

Defining

$$\hat{S}_+ = \hat{S}_x + i \cdot \hat{S}_y$$

$$\hat{S}_- = \hat{S}_x - i \cdot \hat{S}_y$$

$$\hat{S}_\pm |m\rangle = \sqrt{s(s+1) - m_s(m_s \pm 1)} |m_s \pm 1\rangle$$

$$\Rightarrow \hat{S}_+ \alpha = 0 \quad \hat{S}_+ \beta = \hbar \alpha$$

$$\hat{S}_- \alpha = \hbar \beta \quad \hat{S}_- \beta = 0$$

$$\Rightarrow \hat{S}_x \alpha = \frac{\hbar}{2} \beta \quad \hat{S}_x \beta = \frac{\hbar}{2} \alpha$$

$$\hat{S}_y \alpha = \frac{\hbar}{2} i \beta \quad \hat{S}_y \beta = -\frac{\hbar}{2} i \alpha$$

Vector representation:

$$\Rightarrow \hat{S}_x [\alpha \quad \beta] = [\alpha \quad \beta] \begin{bmatrix} 0 & \hbar/2 \\ \hbar/2 & 0 \end{bmatrix}$$

$$\hat{S}_y [\alpha \quad \beta] = [\alpha \quad \beta] \begin{bmatrix} 0 & -i\hbar/2 \\ i\hbar/2 & 0 \end{bmatrix}$$

$$\hat{S}_z [\alpha \quad \beta] = [\alpha \quad \beta] \begin{bmatrix} \hbar/2 & 0 \\ 0 & -\hbar/2 \end{bmatrix}$$

$$\Rightarrow \hat{S}_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\hat{S}_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$\hat{S}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Interpretation of Stern-Gerlach Experiment

Ag atom: α spin and β spin

$$\hat{S}_z \alpha = \frac{1}{2} \hbar \alpha \qquad \hat{S}_z \beta = \frac{1}{2} \hbar \beta$$
$$\mu_u^s = -\frac{e}{m_e} \hat{S}_u \qquad \Rightarrow \qquad \mu_z^s = \pm \frac{e\hbar}{2m_e}$$

Double Stern Gerlach experiment I: $\hat{S}_z \alpha = \frac{1}{2} \hbar \alpha$

Double Stern Gerlach experiment II:

$$(\cos \theta \hat{S}_z + \sin \theta \hat{S}_x) \alpha = \frac{1}{2} \hbar \cos \theta \alpha - \frac{1}{2} \hbar \sin \theta \beta \quad : \text{a is not an eigenfunction}$$

$$\langle \alpha | \cos \theta \hat{S}_z + \sin \theta \hat{S}_x | \alpha \rangle = \frac{1}{2} \hbar \cos \theta \quad : \text{Expectation value}$$

$$- \langle \alpha | \frac{e}{m_e} \cos \theta \hat{S}_z + \frac{e}{m_e} \sin \theta \hat{S}_x | \alpha \rangle = \frac{-e\hbar}{2m_e} \cos \theta = \mu_B \cos \theta$$

: Expectation value of
magnetic moment

The eigen function ψ of operator $\cos \theta \hat{S}_z + \sin \theta \hat{S}_x$

$$\psi = \cos \frac{\theta}{2} \cdot \alpha + \sin \frac{\theta}{2} \cdot \beta$$

Confirmation:

$$(\cos \theta \hat{S}_z + \sin \theta \hat{S}_x) \left(\cos \frac{\theta}{2} \cdot \alpha + \sin \frac{\theta}{2} \cdot \beta \right)$$

$$= \cos \theta \cdot \cos \frac{\theta}{2} \cdot \hat{S}_z \alpha + \cos \theta \cdot \sin \frac{\theta}{2} \cdot \hat{S}_z \beta + \sin \theta \cdot \cos \frac{\theta}{2} \cdot \hat{S}_x \alpha + \sin \theta \cdot \sin \frac{\theta}{2} \cdot \hat{S}_x \beta$$

$$= \frac{\hbar}{2} \left[\left(\cos \theta \cdot \cos \frac{\theta}{2} + \sin \theta \cdot \sin \frac{\theta}{2} \right) \alpha + \left(-\cos \theta \cdot \sin \frac{\theta}{2} + \sin \theta \cdot \cos \frac{\theta}{2} \right) \beta \right]$$

$$= \frac{\hbar}{2} \left(\cos \frac{\theta}{2} \cdot \alpha + \sin \frac{\theta}{2} \cdot \beta \right)$$

: $\psi \rightarrow 100\%$ up by $\cos \theta \hat{S}_z + \sin \theta \hat{S}_x$

$$|\langle \psi | \alpha \rangle|^2 = \left| \langle \cos \frac{\theta}{2} \cdot \alpha + \sin \frac{\theta}{2} \cdot \beta | \alpha \rangle \right|^2 = \cos^2 \frac{\theta}{2}$$

: Probability for a to be up

Eigenvalues and eigenfunctions of a spin operator

How to derive eigen functions and values?

Arbitrary functions are expressed by

$$\psi_i = C_{1i} \cdot \alpha + C_{2i} \cdot \beta$$

$$\hat{S}_u \psi_i = E_i \psi_i \quad \Rightarrow \quad S_u (C_{1i} \cdot \alpha + C_{2i} \cdot \beta) = E_i (C_{1i} \cdot \alpha + C_{2i} \cdot \beta)$$

$$C_{1i} (\langle \alpha | S_u | \alpha \rangle - E_i) + C_{2i} \langle \alpha | S_u | \beta \rangle = 0$$

$$C_{1i} \langle \beta | S_u | \alpha \rangle + C_{2i} (\langle \beta | S_u | \beta \rangle - E_i) = 0$$

$$\Rightarrow \begin{vmatrix} \langle \alpha | S_u | \alpha \rangle - E_i & \langle \alpha | S_u | \beta \rangle \\ \langle \beta | S_u | \alpha \rangle & \langle \beta | S_u | \beta \rangle - E_i \end{vmatrix} = 0 \quad \text{Secular equation}$$

$$\Rightarrow E_i$$

$$|C_{1i}|^2 + |C_{2i}|^2 = 1 \quad \Rightarrow \quad \psi_i$$

Spin angular momentum operator

$$\hat{L}^2 \quad \Leftrightarrow \quad \hat{S}^2 \quad s(s+1)\hbar^2 \quad s = \frac{1}{2}$$

$$\hat{L}_z \quad \Leftrightarrow \quad \hat{S}_z \quad s_m \hbar \quad s_m = \pm \frac{1}{2}$$

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x = i\hbar \hat{L}_z$$

$$[\hat{S}_x, \hat{S}_y] = \hat{S}_x \hat{S}_y - \hat{S}_y \hat{S}_x = i\hbar \hat{S}_z$$

$$[\hat{L}_y, \hat{L}_z] = \hat{L}_y \hat{L}_z - \hat{L}_z \hat{L}_y = i\hbar \hat{L}_x$$

$$[\hat{S}_y, \hat{S}_z] = \hat{S}_y \hat{S}_z - \hat{S}_z \hat{S}_y = i\hbar \hat{S}_x$$

$$[\hat{L}_z, \hat{L}_x] = \hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z = i\hbar \hat{L}_y$$

$$[\hat{S}_z, \hat{S}_x] = \hat{S}_z \hat{S}_x - \hat{S}_x \hat{S}_z = i\hbar \hat{S}_y$$

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$$

$$[\hat{S}^2, \hat{S}_x] = [\hat{S}^2, \hat{S}_y] = [\hat{S}^2, \hat{S}_z] = 0$$

$$[\hat{S}^2, \hat{H}] = [\hat{S}^2, \hat{L}^2] = [\hat{S}^2, \hat{L}_z] = 0$$

$$[\hat{S}_z, \hat{H}] = [\hat{S}_z, \hat{L}^2] = [\hat{S}_z, \hat{L}_z] = 0$$

Atomic wavefunction: determined by n, ℓ, m, s

Anomalous Zeeman effect

Zeeman effect:

Splitting of energy states with the interaction of the resultant angular momentum and magnetic fields. No spin magnetism occurs with pure orbital angular momentum. Only for the states involving several (at least two) electrons.

Anomalous Zeeman effect:

The resultant angular momentum is composed of both spin and orbital angular momentum.

Atomic magnetism

Different g factors

Superposition of orbital and spin magnetism.

Orbital:

$$\mu_L = -\frac{e}{2m_e} L_z = -\frac{e}{2m_e} M_L \hbar = \mu_B M_L$$

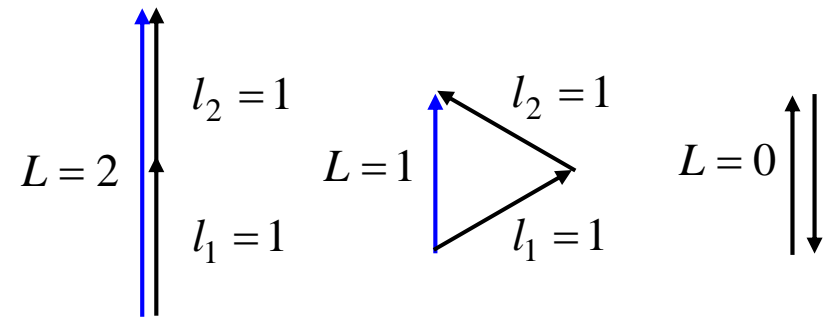
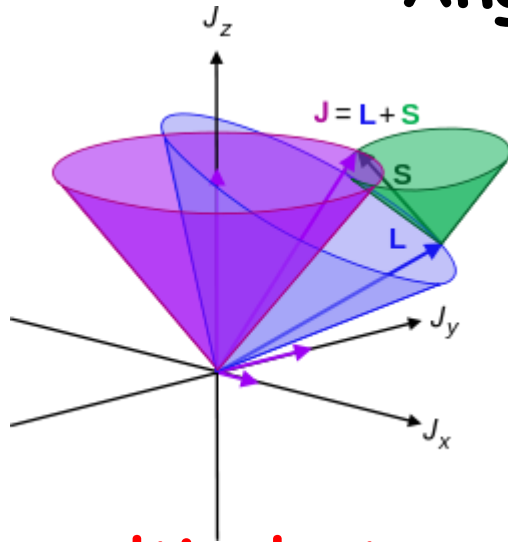
Spin:

$$\mu_S = -\frac{e}{m_e} S_z = -\frac{e}{m_e} M_S \hbar = -g \frac{e}{2m_e} M_S = g \mu_B M_S$$

The g factors are determined by the total angular momentum J.

Angular momentum coupling

These two angular momenta are vectors to "adding" them requires vector addition. That means you cannot simply add magnitudes of the momenta but need to know the direction of the momenta.



In multi-electron atoms,

L: The orbital angular momentum of each electron is vectorially added.
$$\mathbf{L} = \sum_i \mathbf{l}_i$$

S: The spin angular momentum of each electron is vectorially added.
$$\mathbf{S} = \sum_i \mathbf{s}_i$$

J = L + S Total angular momentum

Interaction of the magnetic moment with magnetic fields

Zeeman effect for single-electron system:

$$E = E_0 - \boldsymbol{\mu} \cdot \mathbf{B} = E_0 - \mu_z B = E_0 + \frac{e\hbar}{2m_e} m_\ell B = E_0 + \left(\frac{e}{4\pi m_e} B \right) h m_\ell = h\nu_0 + h \left(\frac{e}{4\pi m_e} B \right) m_\ell$$

For multi-electron system:

$$E = E_0 - \boldsymbol{\mu} \cdot \mathbf{B} = E_0 - \mu_z B = E_0 + \frac{e\hbar}{2m_e} M_L B = E_0 + \left(\frac{e}{4\pi m_e} B \right) h M_L = h\nu_0 + h \left(\frac{e}{4\pi m_e} B \right) M_L$$

Anomalous Zeeman effect: Orbital and spin magnetism

The magnetic moments in the direction of the field are given by

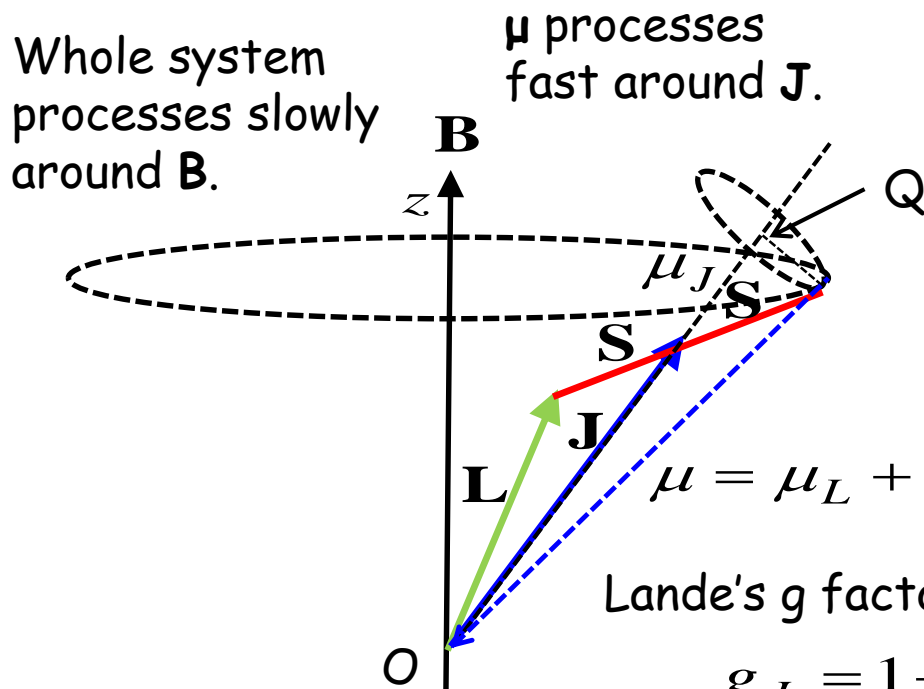
$$\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S = -\frac{e}{2m} \mathbf{L} - \frac{e}{m} \mathbf{S} = -\frac{e}{2m} (\mathbf{L} + 2\mathbf{S})$$

The magnetic energy is given by

$$\Delta E = -\boldsymbol{\mu}_J \cdot \mathbf{B} = -(\boldsymbol{\mu}_J)_z B = \left\langle \hat{L}_z + 2\hat{S}_z \right\rangle \frac{\mu_B}{\hbar} B = g_J M_J \mu_B B$$

Picture of angular momentum coupling

The number of splitting components in the field is given by M_J and is again $2J+1$. The distance b/w the components with different values of M_J depends on the quantum numbers L , S and J .



$$\Delta E = -\mu_J \cdot \mathbf{B} = -(\mu_J)_z B$$

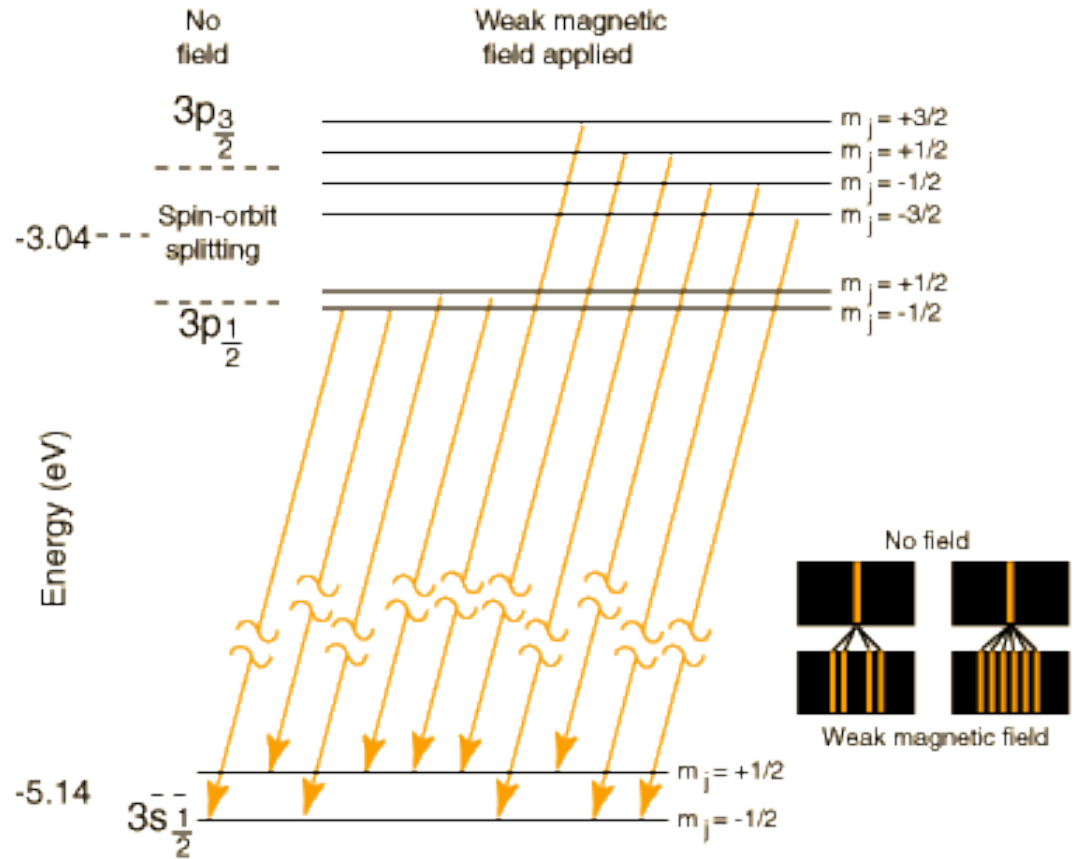
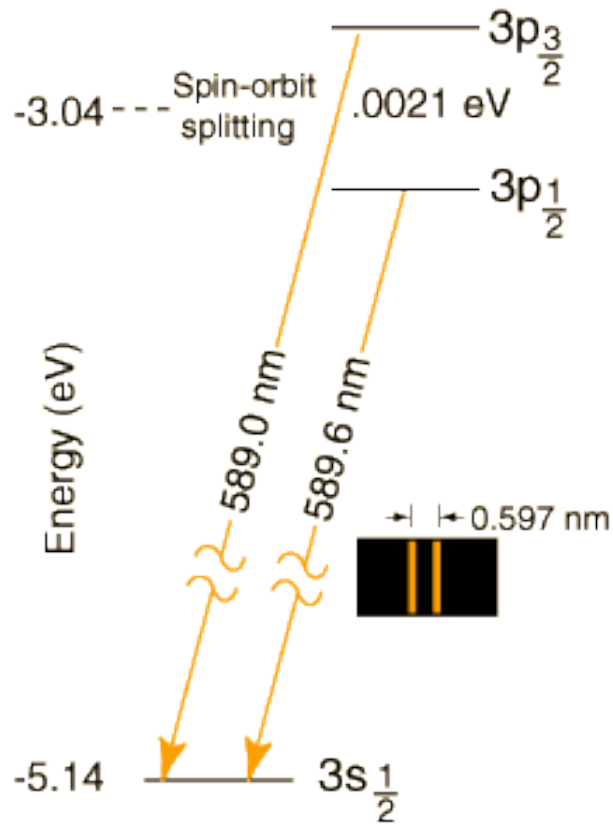
$$= \left\langle \widehat{L}_z + 2\widehat{S}_z \right\rangle \frac{\mu_B}{\hbar} B = g_J M_J \mu_B B$$

$$\mu = \mu_L + \mu_S \quad \mu_J = |OQ| = g_J J$$

Lande's g factor

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Sodium D lines



Recall the hydrogen atom

- ✓ When we solve the Schrödinger Equation using the potential energy for an electron around a proton (hydrogen atom), we get a 3-D solution that gives us **three quantum numbers**: one for energy (n), one for angular momentum (L), and one for the z component of angular momentum (m_L).
- ✓ There is a **fourth** quantum number (recall your chemistry), (**spin**).

Next step:

How do we extend the quantum theory to systems beyond the hydrogen atom?

Extend the theory to two-electron system

- ✓ For systems of **2 electrons**, we simply have a Ψ that depends on time and the coordinates of each of the two electrons:

$$\Psi(x_1, y_1, z_1, x_2, y_2, z_2, t)$$

and the Schrodinger's equation has two kinetic energies instead of one.

$$\Psi(r_1, r_2, t) = \psi_a(r_1)\psi_b(r_2)f(t)$$

- ✓ This is like having electron #1 in state a, and having electron #2 in state b. Note that each state (a or b) has its own particular set of quantum numbers.

Indistinguishable electrons

- ✓ However, from the Heisenberg Uncertainty Principle (i.e., from wave/particle duality), we are not really sure which electron is electron number #1 and which is number #2. This means that the wave function must also reflect this uncertainty.

$$\psi_a(r_1)\psi_b(r_2) \Leftrightarrow \psi_a(r_2)\psi_b(r_1)$$

Indistinguishable!!

$$|\Psi(r_1, r_2, t)|^2 = |\Psi(r_2, r_1, t)|^2$$

$$\Psi(r_1, r_2, t) = \pm \Psi(r_2, r_1, t)$$

Wave functions for indistinguishable two electrons

There are two ways of making the wave functions that reflect the indistinguishability of the two electrons:

$$\Psi_{sym} = \frac{1}{\sqrt{2}} [\psi_a(r_1)\psi_b(r_2) + \psi_a(r_2)\psi_b(r_1)] \quad \text{Symmetric}$$

$$\Psi_{anti} = \frac{1}{\sqrt{2}} [\psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)] \quad \text{Antisymmetric}$$

Which (if either) possibility agrees with experiment?

✓ It turns out that some particles are explained nicely by the **symmetric**, and some are explained by the **antisymmetric**.

Bosons

$$\Psi_{sym} = \frac{1}{\sqrt{2}} [\psi_a(r_1)\psi_b(r_2) + \psi_a(r_2)\psi_b(r_1)]$$

- ✓ Those particles that work with the symmetric form are called **Bosons**. All of these particles have **integer spin as well**. Note that if boson #1 and boson #2 both have the same state ($a=b$), then $\Psi > 0$. This means that both particles CAN be in the same state at the same location at the same time.
- ✓ **Bosons**. **Photons and alpha particles** (2 neutrons + 2 protons) are bosons. These particles can be in the same location with the same energy state at the same time.
- ✓ This occurs in a laser beam, where all the photons are at the same energy (monochromatic).

Fermions

$$\Psi_{anti} = \frac{1}{\sqrt{2}} [\psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)]$$

- ✓ Those particles that work with the anti-symmetric wavefunction are called **Fermions**. All of these particles have **half-integer spin**. Note that if fermion #1 and fermion #2 both have the same state, (a=b), then $\Psi = 0$. This means that **both particles can NOT be in the same state at the same location at the same time**.
- ✓ **Fermions**. Electrons, protons and neutrons are fermions. These particles can NOT be in the same location with the same energy state at the same time.
- ✓ This means that **two electrons going around the same nucleus can NOT both be in the exact same state at the same time!** This is known as **Pauli's Exclusion Principle!**

Pauli's Exclusion Principle

- ✓ Since **no two electrons can be in the same energy state in the same atom at the same time**, the concept of filling shells and valence electrons can be explained and this law of nature makes **chemistry possible** (and so makes biology, psychology, sociology, politics, and religion possible also)!
- ✓ Thus, the possibility of chemistry is explained by the wave/particle duality of light and matter with electrons acting as fermions!

Quantum numbers

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{\ell}^m(\theta, \phi)$$

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

$$\ell = 0, 1, 2, \dots, (n-1)$$

$$m = 0, \pm 1, \pm 2, \pm 3 \dots, \pm \ell$$

Quantum numbers:

- ✓ Principal quantum number: $n=1, 2, 3, \dots$
: Principal energy level of the electron
- ✓ Orbital quantum number: $\ell=0, 1, 2, \dots, (n-1)$
: Values of the angular momentum of the electron
- ✓ Magnetic quantum number: $m_{\ell}=0, \pm 1, \pm 2, \dots, \pm \ell$
: Possible properties of an electron
in a magnetic field
- ✓ Spin quantum number: $m_s = -1/2, +1/2$
: Possible spin vectors or orientations of
an electron in a magnetic field

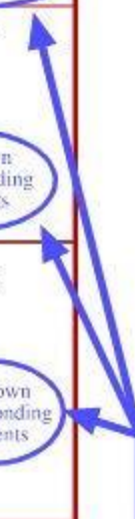
Quantum Numbers

| n | l | m_l | Orbital | Elements | Shell |
|---------|-----|---|---------|----------|-------|
| $n = 1$ | 0 | 0 | 1s | 2 } 2 | K |
| $n = 2$ | 0 | 0 | 2s | 2 } 8 | L |
| | 1 | -1, 0, 1 | 2p | 6 | |
| $n = 3$ | 0 | 0 | 3s | 2 } 18 | M |
| | 1 | -1, 0, 1 | 3p | 6 | |
| | 2 | -2, -1, 0, 1, 2 | 3d | 10 | |
| $n = 4$ | 0 | 0 | 4s | 2 } 32 | N |
| | 1 | -1, 0, 1 | 4p | 6 | |
| | 2 | -2, -1, 0, 1, 2 | 4d | 10 | |
| | 3 | -3, -2, -1, 0, 1, 2, 3 | 4f | 14 | |
| $n = 5$ | 0 | 0 | 5s | 2 } 32 | O |
| | 1 | -1, 0, 1 | 5p | 6 | |
| | 2 | -2, -1, 0, 1, 2 | 5d | 10 | |
| | 3 | -3, -2, -1, 0, 1, 2, 3 | 5f | 14 | |
| | 4 | -4, -3, -2, -1, 0, 1, 2, 3, 4 | 5g | 18 | |
| $n = 6$ | 0 | 0 | 6s | 2 } 18 | P |
| | 1 | -1, 0, 1 | 6p | 6 | |
| | 2 | -2, -1, 0, 1, 2 | 6d | 10 | |
| | 3 | -3, -2, -1, 0, 1, 2, 3 | 6f | 14 | |
| | 4 | -4, -3, -2, -1, 0, 1, 2, 3, 4 | 6g | 18 | |
| | 5 | -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5 | 6h | 22 | |
| $n = 7$ | 0 | 0 | 7s | 2 } 8 | Q |
| | 1 | -1, 0, 1 | 7p | 6 | |
| | 2 | -2, -1, 0, 1, 2 | 7d | 10 | |
| | 3 | -3, -2, -1, 0, 1, 2, 3 | 7f | 14 | |
| | 4 | -4, -3, -2, -1, 0, 1, 2, 3, 4 | 7g | 18 | |
| | 5 | -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5 | 7h | 22 | |
| | 6 | -6, -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5, 6 | 7i | 26 | |

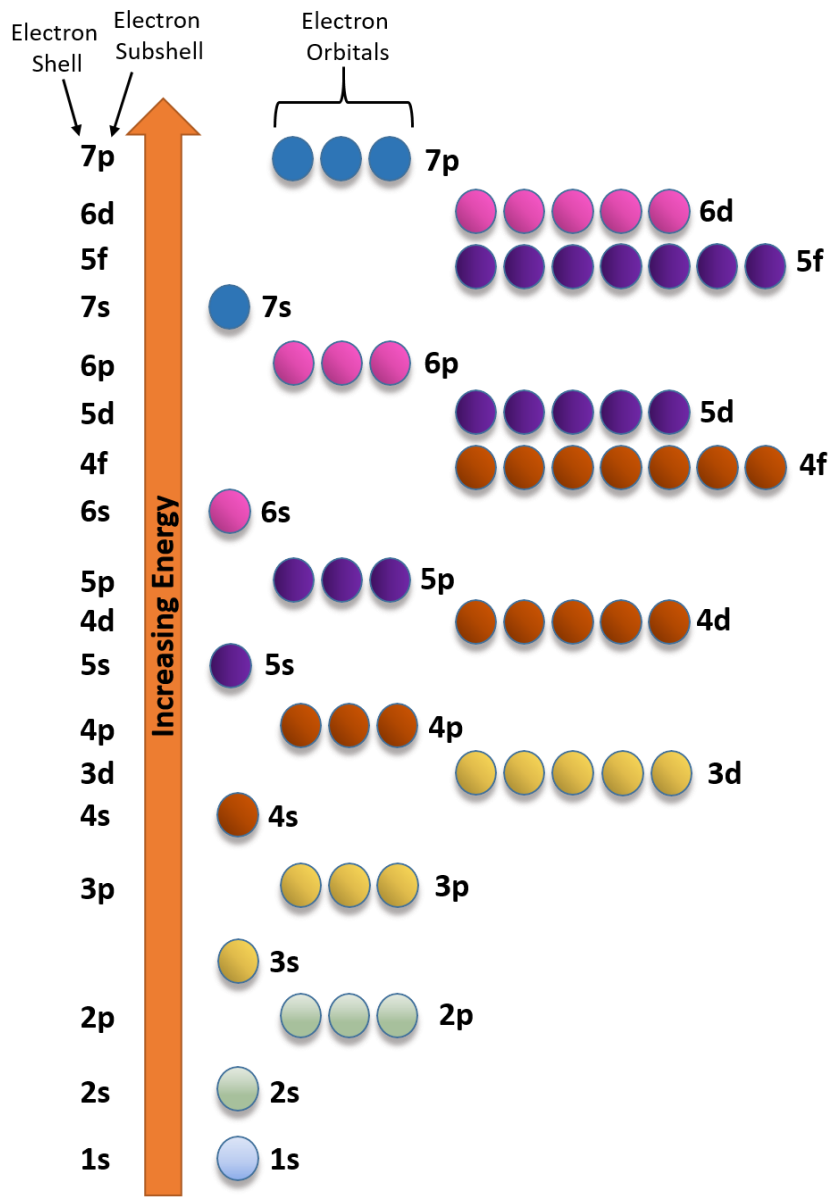
Unknown Corresponding Elements

Unknown Corresponding Elements

Unknown Corresponding Elements



Energy of orbitals



$n = 1$
 $n = 2$
 $n = 3$
 $n = 4$
 $n = 5$
 $n = 6$
 $n = 7$

