

ATOMIC MODELS

QUANTUM ATOMIC MODEL

Due to the fact that classical mechanics, which is valid for large objects, is inadequate to explain the movement of particles that are too small such as electrons, and that its wave property cannot be neglected. A new mechanic was developed in the 1920s. This new mechanic based on the quantized energy concept, Heisenberg uncertainty principle and the de-Broglie hypothesis is called as a quantum mechanics or a wave mechanics. Schrödinger equation is used for the application of quantum mechanics to atom. Schrödinger and Heisenberg said that the Bohr atomic model was wrong and that the electron was moving in three dimensions.

Heisenberg Uncertainty Principle

The calculation of the position and velocity of the electron at the same time was contrary to the uncertainty principle proposed by Heisenberg in 1927. According to Heisenberg, when trying to determine the position of very small particles, such as electrons, there is an uncertainty in their velocity or when trying to determine the velocity of very small particles, such as electrons, there is an uncertainty in their position. To monitor the movement of the electron on the orbital, it is a necessary tool that can interact with the electron. This tool is light. Since the light will be at various wavelengths, a wavelength of magnitude close to the wavelength of the electron should be selected. Considering the electron as a very small sphere, when a light with a wavelength much larger than the diameter of this sphere is used, the light can pass without making any interaction with the electron and there is uncertainty in determining the position of the electron. If the wavelength of light is small, the position of the electron can be determined more precisely. But in this case, the energy of the light will be great and the photon will give energy to the electron and accelerate the electron during the collision. In this case there will be an uncertainty in the velocity of the electron.

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$$\Delta p \cdot \Delta x \geq \frac{h}{4\pi}$$

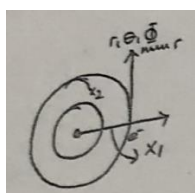
The uncertainty in the momentum Δp or ΔmV

$$\Delta x$$

The uncertainty in the position Δx

the multiplication of two cannot be smaller than $h/4\pi$

Since the velocity and position of the electron cannot be determined at the same time, the specific (certain) orbitals assumption in the Bohr model is not valid. It is possible to mention the possibility that the electron can only be found in a specific (certain) volume. Considered an electron as a particle, possibility of an existence of electron in some regions around the nucleus should be high and should be low in some regions.



$$p = mV$$

$$\Delta p = \Delta(mV)$$

$$(\Delta p)(\Delta x) \geq \frac{h}{2\pi}$$

$$2 \times 10^6 \text{ m/s } [\Delta(mv)] \Delta x = \frac{h}{2\pi}$$

$$(9,1094 \times 10^{-31} \text{ kg} \times 2 \cdot 10^6 \text{ m/s}) \Delta x = \frac{6,63 \times 10^{-34} \text{ J}\cdot\text{s}}{2 \times \frac{2\pi}{7}} \quad \text{J}\cdot\text{s} \rightarrow \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2}$$

$$\Delta x = 5,80 \times 10^{-11} \text{ m} = 0,58 \times 10^{-10} \text{ m} = 0,58 \text{ \AA}$$

According to Bohr

$$r = a_0 = 0,529 \text{ \AA}$$

Bohr said the nucleus had a radius

But $0.58 \text{ \AA} > 0.529 \text{ \AA}$. The error in the calculation is greater than the value found. Heisenberg says to Bohr: If you say you have found the velocity of the electron, you make a mistake on the position of the electron. If you say you have found the position of the electron, you make a mistake on the velocity of the electron. So, quantum physics was born. The value $r = a_0 = 0.529 \text{ \AA}$ is the probability that an electron in the hydrogen is present around the nucleus.

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de-Broglie Wavelength

The photon model is proposed with the assumption that the electromagnetic waves show particle property. de Broglie who was inspired by the wave-particle binary behavior of light, in 1924 he suggested that a moving particle could show wave property and he specified that

the wavelength of such a wave can be found from the equation $\lambda = \frac{h}{mv}$ in a similar manner to that of light. de Broglie combined Einstein's $E = mc^2$ and Planck's $E = h\nu$ equations and he gave an equation referred to his name.

$$mc^2 = h \cdot \frac{c}{\lambda} \Rightarrow \lambda = \frac{h}{mc} \quad \text{If } \nu \text{ is written instead of } c$$

Wavelength of objects with a very large mass and very small velocity is too small to be ignored. But, the wave property of particles such as electrons, whose mass is very small and whose velocity is very big is gaining importance.

Schrödinger Wave Equation

In 1926, Erwing Schrödinger gave an equation that could be applied to the hydrogen atom. The Heisenberg uncertainty principle and the equilibrium of the Broglie equation to be applied to the hydrogen atom. The science that deals with this and similar wave equation is called wave mechanics or quantum mechanics. The Schrödinger wave equation is defined by the wave property, position, mass, total energy and potential energy of the electron. Ψ (psi) wave functions are obtained from the solution of the Schrödinger wave equation. Ψ is essentially an amplitude function and its square gives the possibility of the presence of the electron. The three-dimensional wave function of the electron is expressed by Ψ . In other words, Ψ shows an orbital. Ψ wave function covers all properties of the electron. All information about a particle being examined is found in this wave function depending on location and time.

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The probability of an electron with x, y and z coordinates and being located at a point in space is given by $\Psi^2(x, y, z)$.

$\Psi(x, y, z)$ Cartesian coordinate

$\Psi(r, \theta, \Phi)$ Polar coordinate

\hat{H} Hamilton operator

Other atomic models reveal the particle property of the electron.

The quantum atomic model says that the electron has a wave character.

The quantum atomic model contains the assumptions of quantum physics.

1. HYPOTHESIS: All information about a moving particle is present within a wave function. Ψ is a wave function based on position and time and it is indicated by $\Psi(x, y, z, t)$ if cartesian coordinates are used. Time-independent wave functions $\Psi(x, y, z)$ are used to examine the stable state of the atom.

2. HYPOTHESIS: Square of wave function Ψ^2 gives the probability that the particle is present at any point in space. Since there are no dimensions of the point, it is necessary to accept the existence of the smallest possible volume at that point since this definition has a meaning. In cartesian coordinates, $d\tau = dx \cdot dy \cdot dz$ dir. The possibility of the system in a volume element at a certain point = $\Psi^2 \cdot d\tau$. If the distance is infinite, the probability of the particle being in the volume element $d\tau$ should be 0.

i. The wave function must be normalized. The sum of the possibilities of the electron in any region of space should be 1 at all points of that region.

$$\int \Psi^2 \cdot d\tau = 1 \text{ (Normalization condition)}$$

ii. Wave functions should be orthogonal to each other. The probability of an electron being present in two orbitals of the atom at the same time is 0.

$$\int \Psi_A \cdot \Psi_B \cdot d\tau = 0 \text{ [Orthogonality (perpendicularity) condition]}$$

3. HYPOTHESIS: There is an operator for every observable feature of the system. When this operator is applied to the wave function, a certain feature of the system is obtained. The operator is a symbol that indicates what action to take over the next function. Operators are chosen so that when applied to wave functions they give values about the observable properties of the system. These operators that give real results are called Hamilton operators.

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Quantum theory is applied to very small particles. This is the biggest difference between classical mechanics and quantum theory. There is an energy adoption and a kinetic energy adoption, no acceleration.

basic view of quantum chemistry

$$\hat{H}\Psi = E\Psi$$

total energy operator value (can be a result, contains kinetic energy and potential energy)

$$\hat{H}\Psi(x) = E \cdot \Psi(x)$$

self function

$\hat{H}\Psi(x)$ shows that the \hat{H} operator will be applied to $\Psi(x)$ function

Hydrogen and hydrogenic atoms (He^+ , Li^{2+} , ...) will be examined because they are simple and there is no e-e repulsion propulsion in hydrogen and hydrogenic atoms.

According to classical mechanics $f(x) = \frac{1}{2} g \cdot t^2$ (free fall formula)

1st differentiation of this formula gives the velocity $\frac{df(x)}{dt} = g \cdot t = v$

2nd differentiation of this formula gives the acceleration $\frac{d^2f(x)}{dt^2} = g$ - acceleration of free fall

$$\hat{T} = -\frac{\hbar^2}{2m\pi^2} \cdot \frac{d}{dx^2}$$

kinetic energy operator

$$\hat{P} = -i \cdot \frac{\hbar}{2\pi} \frac{d}{dx}$$

potential energy operator

If the wave function has a function such as $\frac{1}{2} g t^2$, it must give potential energy if we apply Ψ to P . The reason for $-i$ is that the potential energy exists for a particle. It is multiplied by $-i$ to avoid (-) value ($i = \sqrt{-1}$).

1st differentiation of Ψ wave function gives potential energy.

2nd differentiation of Ψ wave function gives kinetic energy.

There are both kinetic energy and potential energy in Ψ . The sum of the two gives the total energy. Because the electron is withdrawn by the nucleus in the hydrogen atom, the electron can only be found in a certain region of the space. This assumption arises that the presence of the hydrogen atom cannot be mentioned in case the distance between the nucleus and the electron is too large or infinite.

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There is a potential energy $V(x,y,z)$ in hydrogen atom due to the Coulomb pulling force between the nucleus and the electron. Hamilton operator for hydrogen atom (electric energy operator)

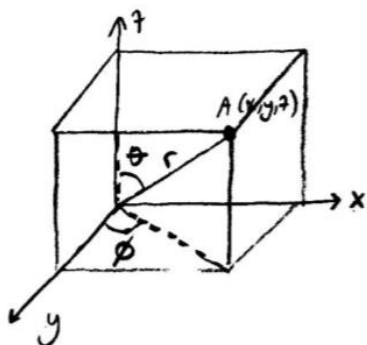
$$\hat{H} = -\frac{\hbar^2}{8m\pi^2} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) + V(x,y,z) \quad \text{An operator working in three dimensions}$$

$$\hat{H}\psi = E\psi$$

$$\left[-\frac{\hbar^2}{8m\pi^2} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) + V(x,y,z) \right] \psi = E\psi$$

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8m\pi^2}{\hbar^2} (E - V)\psi = 0 \quad \text{Schrödinger wave equation}$$

The Schrödinger wave equation is an energy equation. It includes potential energy, kinetic energy and total energy. The Schrödinger equation with Cartesian coordinates can be converted into polar coordinates. Since potential energy is formed by the pulling force between the nucleus and the electron and this pulling force depends on the distance, but not the direction, system can be considered as a sphere with a nucleus in the center. Therefore, it is preferable to define the position of any point in space with spherical polar coordinates (r, θ, Φ) instead of cartesian coordinates (x, y, z) . n is found by one-dimensional solution of the Schrödinger equation. There are many quantum numbers from the solution of the three-dimensional Schrödinger equation, but chemists use three of them (n, l and m_l). When the equation is written in cartesian coordinates, these quantum numbers are of equal weight. When spherical polar coordinates are used, their weight and their contribution to total energy are different.



θ = scans xz space.

Φ = scans xy space.

r = shows the distribution away from the nucleus.

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Calculations related to the solution of wave equation are even simpler when the r, θ and Φ polar coordinates are replaced by the x, y, z vertical coordinates (cartesian coordinates). The coordinates of point A are x, y, z in the vertical coordinate system and r, θ, Φ in the polar coordinate system. These coordinates can be converted into each other using the following equations.

$$\begin{aligned}x &= r \cdot \sin \theta \cdot \sin \phi \\y &= r \cdot \sin \theta \cdot \cos \phi \\z &= r \cdot \cos \theta\end{aligned}$$

In the Schrödinger equation, if the values of x, y and z are put in place and the equation is

$$\Psi(r, \theta, \phi) = \underbrace{R(r)}_{\text{Radial part of the wave function}} \cdot \underbrace{\Theta(\theta) \cdot \Phi(\phi)}_{\text{Angular part of the wave function}}$$

Radial part of the wave function

Angular part of the wave function

Ψ wave function is an orbital function and shows orbitals.

$R(r)$: Function of distance (r) from nucleus and depends on n and l quantum numbers

$\Theta(\theta)$: Function of θ and depends on l and m_l quantum numbers

$\Phi(\phi)$: Function of Φ and depends on m_l quantum number $\Psi_{r, \theta, \phi}^2 = R^2(r) \cdot A^2(\theta, \phi)$

$$\Psi_{(n, l, m_l)} = R(r)_{n, l} \cdot \Theta(\theta)_{l, m_l} \cdot \Phi(\phi)_{m_l}$$

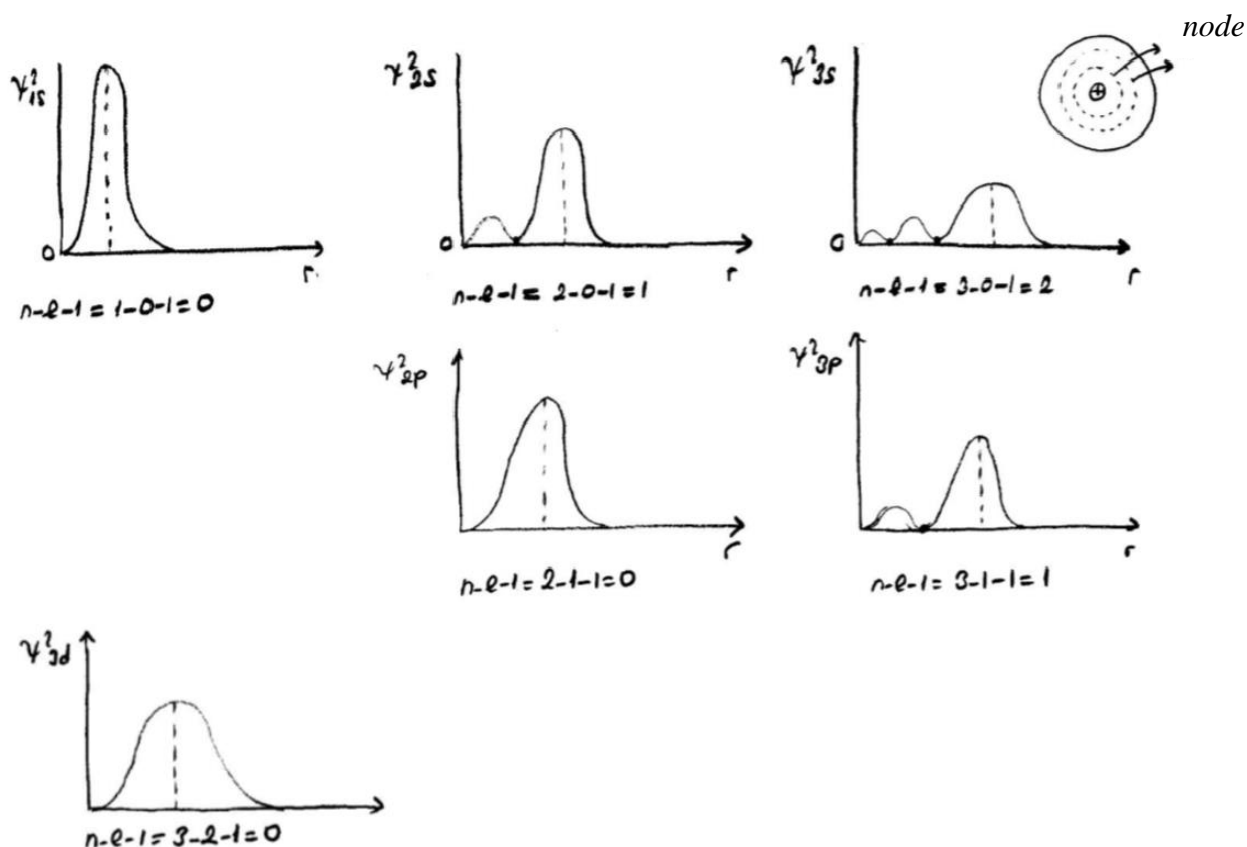
$$\Psi_{(n, l, m_l)} = R(r)_{n, l} \cdot A_{l, m_l} \quad \text{Divides wave function into two parts}$$

The radial part of the wave function says that the probability of the presence of the electron under examination depends not on the direction, but only on the distance to the nucleus. The radial function represents spherical orbitals. Therefore, it is (+). The space fragment (sphere) where the electron density is the minimum is called the node.

The number of radial nodes = $n - l - 1$. Radial node = spherical node R^2 is the probability of the presence of the electron on the sphere with radius r . For the 1s orbital ($n=1, l=0$), the maximum probability is at $r=a_0$. This result is interesting in terms of the comparison of the

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Bohr atomic model with the quantum concept. In the Bohr atomic model, it is assumed that the electron in the hydrogen moves in an orbital with a radius a_0 . According to quantum theory, this orbital is a shell where the electron is most likely to be found. As n increases, the maximum probability shifts away from the nucleus. The small maximums between the maximum probability and the nucleus indicates the penetration effect of an orbital. The probability of the presence of the electron in the nucleus is 0. The electron can be near the nucleus.



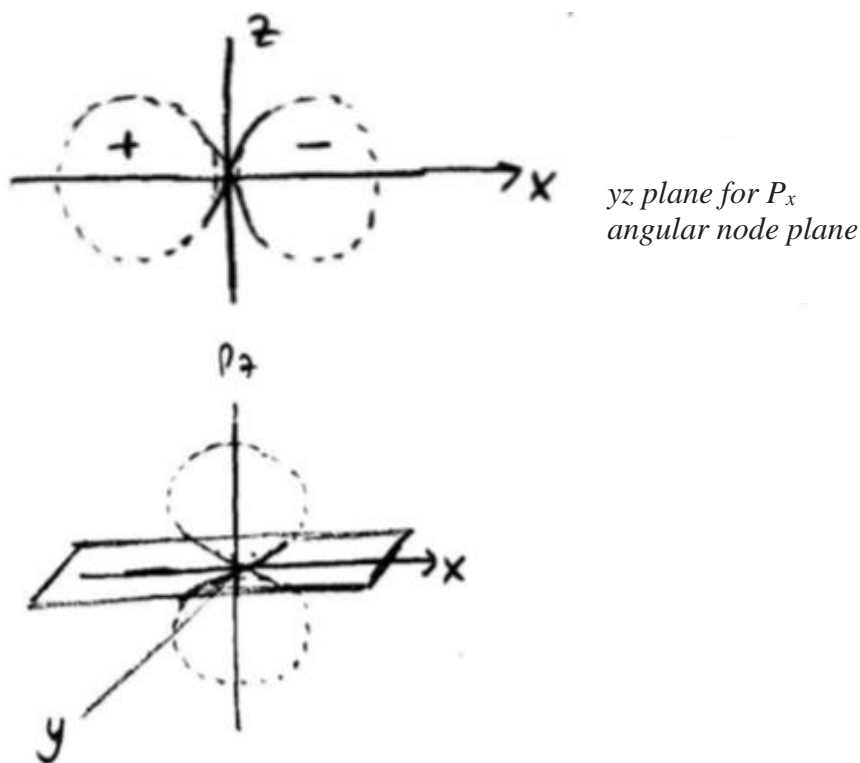
1. The probability of the presence of the electron in the nucleus and infinity is 0. The probability of the presence of the electron being far away from the nucleus is not 0.
2. According to 1s, 2s and 3s curves, the number of $n-l$ is equal to the number of the maximums and radii corresponding to these maximums that is the distance at which the electron is most likely to be, increase as the principal quantum number (n) increases.
3. As the angular quantum number (l) increases, the radius values corresponding to the curve maximums are small.


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Angular part of the wave function gives how the probability of the presence of the electron varies according to the direction or the θ and Φ angles. The number of angular nodes is 0 for s orbital, 1 for p orbital and 2 for d orbital. Only one of the node surfaces of the d_{z^2} orbital is conical.

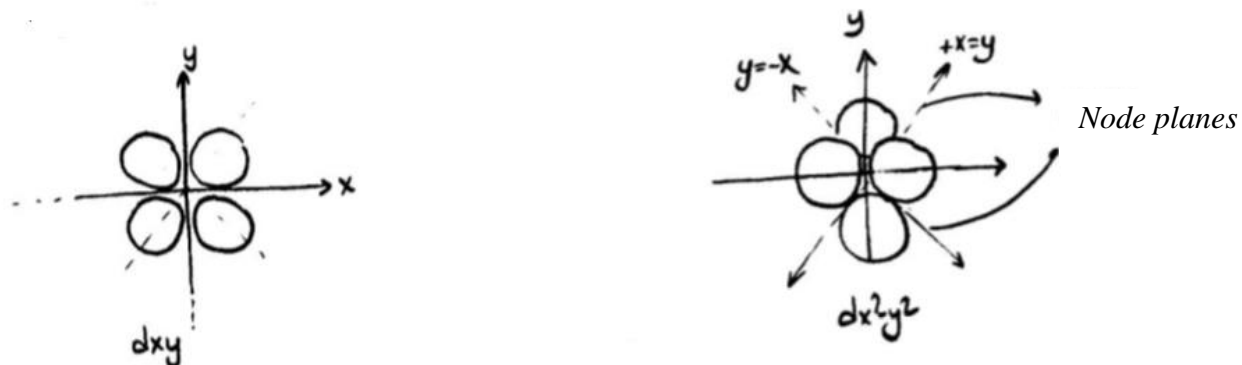


We will think of two basket balls (spheres) scattered around the x-axis. Electron passes from one to the other. This can be thought of as the ant moving between two hands facing each other in punch. But the ant is skipping the nucleus. Therefore, it is shown as follows.

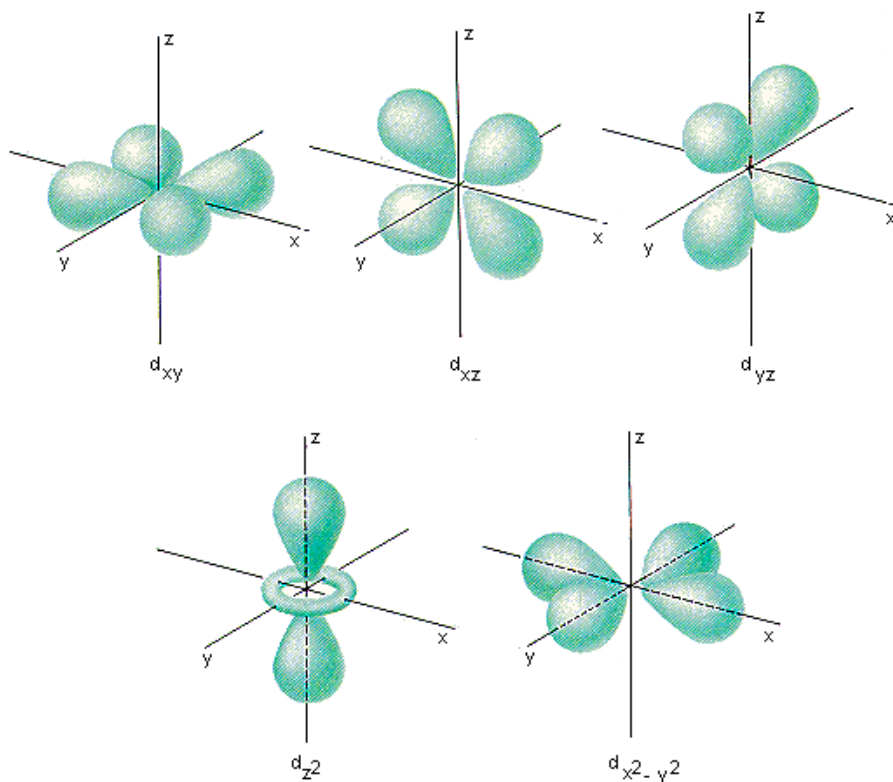
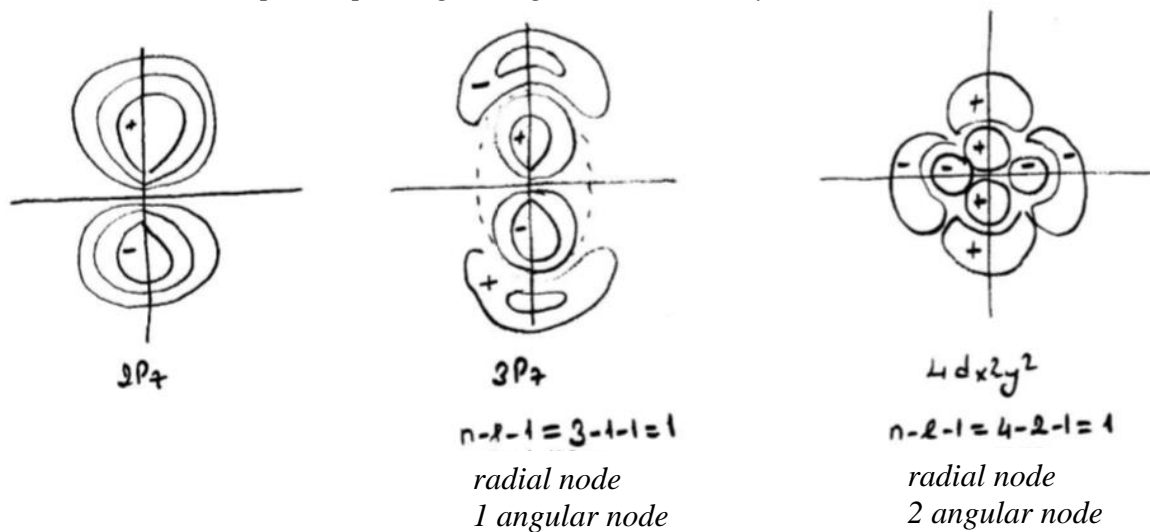


We're going to think of three-dimensional vibration of the electron (combine two hands in the form of punch, switch the electron from one punch to another. Draw  without raising your hand, that is, it makes the three-dimensional vibration movement from our hands. Electron is changing phase from one punch to another. Therefore, there is + and -. There are two angular nodes for d orbitals.

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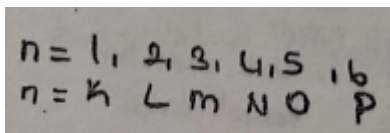


There are two node planes passing through the x-axis and y-axis.



Quantum Numbers

n (The principal quantum number): Used to calculate the energy of the orbital where the electron is present, $n=1,2,3, \dots$



The principal quantum number designates the principal electron shell. Because ***n*** describes the most probable distance of the electrons from the nucleus, the larger the number ***n*** is, the farther the electron is from the nucleus, the larger the size of the orbital, and the larger the atom is. ***n*** can be any positive integer starting at 1, as $n=1$ designates the first principal shell (the innermost shell). The first principal shell is also called the ground state, or lowest energy state. This explains why ***n*** can not be 0 or any negative integer, because there exists no atoms with zero or a negative amount of energy levels/principal shells. When an electron is in an excited state or it gains energy, it may jump to the second principle shell, where $n=2$. This is called absorption because the electron is "absorbing" photons, or energy. Known as emission, electrons can also "emit" energy as they jump to lower principle shells, where ***n*** decreases by whole numbers. As the energy of the electron increases, so does the principal quantum number, e.g., ***n***=3 indicates the third principal shell, ***n***=4 indicates the fourth principal shell, and so on.

l (The angular quantum number or the angular momentum quantum number): Used to determine the geometry of the orbital where the electron is present, $l=0,1,2,3, \dots, n-1$. There are different orbitals for each different value of ***l***. These orbitals are indicated by letters *s, p, d, f*, ... for values 0,1,2,3,...of ***l***, respectively. The orbital angular momentum quantum number ***l*** determines the shape of an orbital, and therefore the angular distribution. The number of angular nodes is equal to the value of the angular momentum quantum number ***l***. Each value of ***l*** indicates a specific *s, p, d, f* subshell (each unique in shape.) The value of ***l*** is dependent on the principal quantum number ***n***. Unlike ***n***, the value of ***l*** can be zero. It can also be a positive integer, but it cannot be larger than one less than the principal quantum number ($n-1$). For example, if $n=3$, $l=0,1,2$. This indicates three subshells in the shell $n=3$. These subshells are 3*s*, 3*p* and 3*d*.

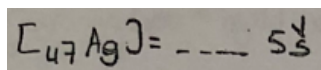
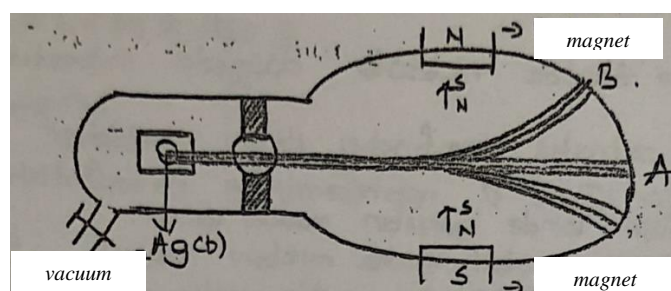
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m_l (The magnetic quantum number): Used to determine the number of orbitals and their orientation within a subshell. Consequently, its value depends on the orbital angular momentum quantum number l . Given a certain l , m_l is an interval ranging from $-l$ to $+l$, so it can be zero, a negative integer, or a positive integer. Each m_l value represents an orbital. There is $2l+1$ orbital in a subshell. For example, there are $(2 \times 2 + 1) = 5$ orbitals in the $3d$ subshell.

$$m_l = -l, (-l+1), (-l+2), \dots, -2, -1, 0, 1, 2, \dots, (l-1), (l-2), +l$$

m_s (The spin quantum number): Used to designate the direction of the electron spin. A fourth quantum number is required to describe some experimental observations, such as the fact that the spectral lines in the alkali metal spectra are paired or alkali metal atom's beam, which is passed through a magnetic field, are divided into two. m_s may have a spin of $+1/2$, represented by \uparrow , $-1/2$, represented by \downarrow or $\pm 1/2$, represented by $\uparrow\downarrow$. This means that when m_s is positive the electron has an upward spin. When it is negative, the electron has a downward spin. The significance of the electron spin quantum number is its determination of an atom's ability to generate a magnetic field or not. m_s was experimentally studied by German scientists (Stern-Gerlach) in 1936. When the magnet is placed, it is seen that silver is divided into 2 parts. After this experiment the spin quantum number is revealed. Paramagnetic property is explained by this experiment.



$$\begin{aligned} & 5s^1 \\ n &= 5 \\ l &= 0 (s) \\ m_l &= 0 \\ m_s &= +\frac{1}{2} (1e) \end{aligned}$$

$$\begin{aligned} m_s &= +1/2 \text{ (rotate clockwise)} \\ m_s &= -1/2 \text{ (rotate counterclockwise)} \end{aligned}$$

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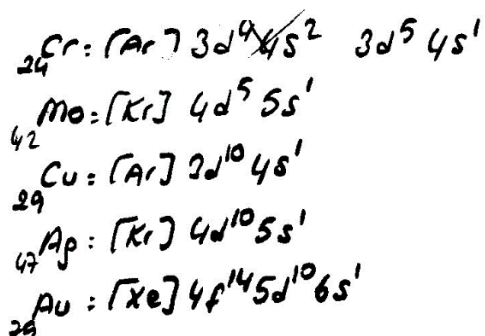
Aufbau Principle

Electrons should be placed in the orbitals in such a way that the energy of the atom is minimal. Since the orbital energy increases while $n+l$ value increases, the orbital, which its $n+l$ value is the smallest, should be filled first.

- The energy of the orbitals increases with the increase of $n+l$.
- Among orbitals with the same $n+l$ value, the energy of orbital having higher n value is bigger.

	1s	<	2s	<	2p	<	3s	<	3p	<	4s	<	3d	<	4p	<	5s	<	4d	<	5p	<	6s	<	4f	<	5d	<	6p	<	7s	..
n=	1		2		2		3		3		4		3		4		5		4		5		6		4		5		6		7	
l=	0		0		1		0		1		0		2		1		0		2		1		0		3		2		1		0	
n+l=	1		2		3		3		4		4		5		5		5		6		6		6		7		7		7		7	

The electron configurations of some elements are not suitable to the Aufbau principle. In these elements, the difference between the energies of the orbitals causing the difference is very small. According to the Aufbau principle, the ns orbital must be filled before the $(n-1)d$ orbital. But, there may be changes due to the stability of filled and fully filled orbitals



The Aufbau principle, which is thoughtfully developed to write the electron configurations in the ground state of the elements, does not apply to the electron configurations of the ions. According to the Aufbau principle, a proton is added to the atomic nucleus and an electron is added to the around nucleus in order to pass from one element to another in writing the electron configuration. In ionization, the number of protons in the nucleus does not change after the electron is removed from the atom. In the ionization event, the order of electron loss does not conform to the Aufbau principle. The first electron removed from the atom is the orbital electron with the highest energy. If the principal quantum numbers n are the same, then the electron is removed from the orbital where the angular momentum quantum number l is the highest.

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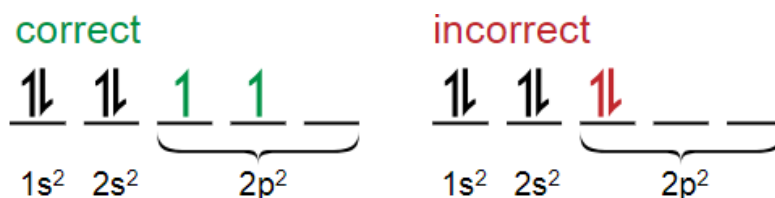
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Pauli Exclusion Principle

Two electrons with the same four quantum numbers can not be found side by side in an atom. The Pauli principle is not a result of the Schrödinger equation but has emerged from the experimental data.

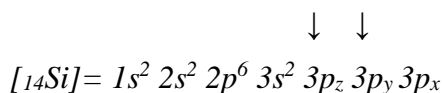
Hund Rule

In the ground state of atoms, electrons are placed one by one to orbitals and their spins are parallel to each other.

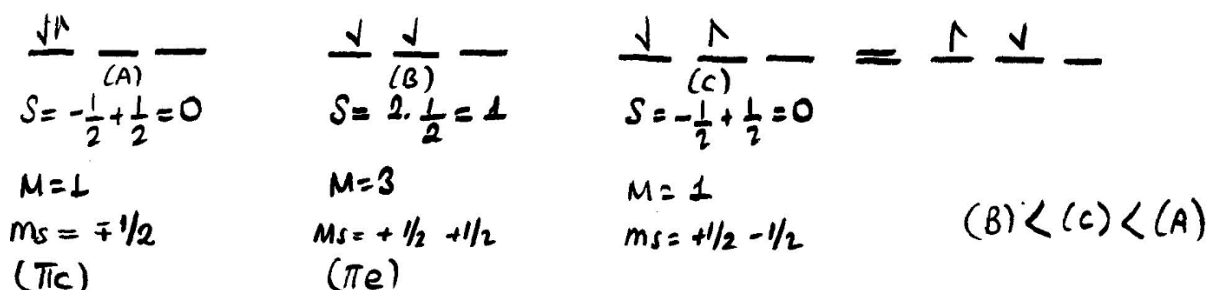


Multiplicity (M)

Probability of settling electrons for a given system. How many values can be taken when the electron is placed in the magnetic field? The answer to this question is multiplicity. Electronic regulation with the greatest multiplicity is at the lowest energy. $M=2S+1$ (S is the total spin). For example,



$n+1=2+1=3$ different settlements (n is the number of unpaired electrons)

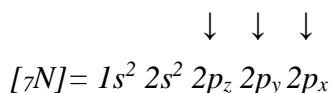


The lowest energy regulation is B.

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Coulomb pushing energy (Π_c) and exchange energy (Π_e) are used to determine the lowest energy regulation. Coulomb pushing energy is the energy that occurs when two electrons in an orbital push each other because of their loads. It increases the energy of the system (+ marked). The exchange energy is the displacement energy of two electrons with the same spins. It decreases the energy of the system (- marked).



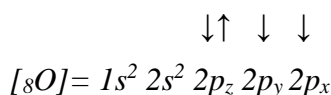
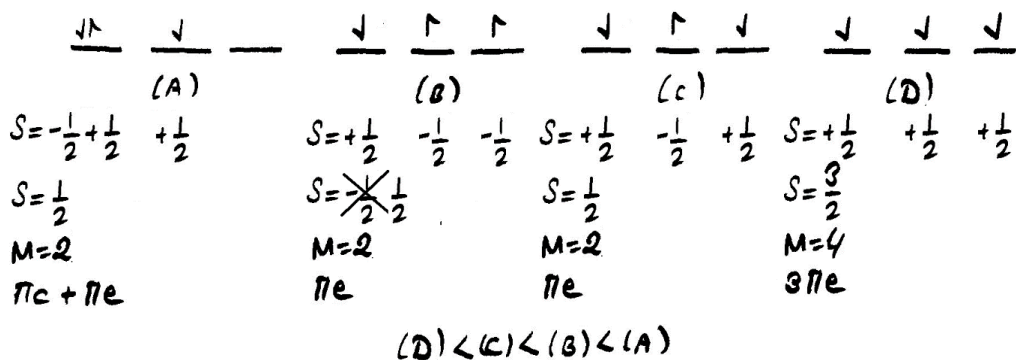
$n+1=3+1=4$ different settlements (n is the number of unpaired electrons)

$$n=2$$

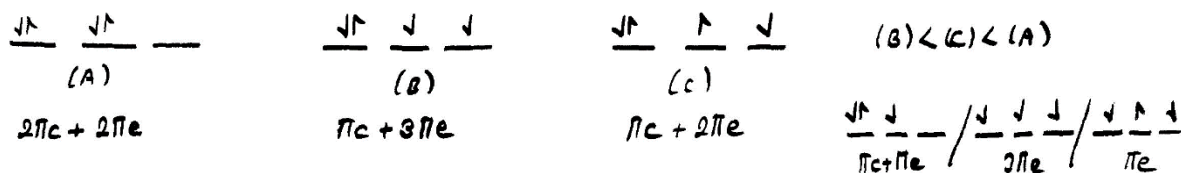
$$l=1 (p)$$

$$m_l = +1, 0, -1$$

$$m_s = +1/2, +1/2, +1/2$$



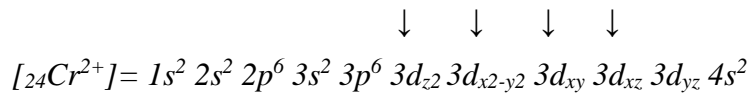
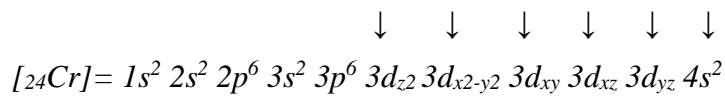
$n+1=2+1=3$ different settlements (n is the number of unpaired electrons)



$$\Pi_c + |\Pi_e| = p \text{ (electron pair energy)}$$

The electron pair energy is the energy required to pair two electrons, which are parallel spins in different orbitals, in one orbital.

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$n+1=4+1=5$ different settlements (n is the number of unpaired electrons)

