The Pauli Exclusion Principle

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लखनऊ विश्वविद्यालय | शताब्दी वर्ष

Pauli’s exclusion principle… 1925 Wolfgang Pauli

The Bohr model of the hydrogen atom MODIFIED the understanding that electrons’ behaviour could be governed by classical mechanics.

Bohr model worked well for explaining the properties of the electron in the hydrogen atom.

This model failed for all other atoms.

In 1926, Erwin Schrödinger proposed the quantum mechanical model.

The Quantum Mechanical Model of the Atom is framed mathematically in terms of a wave equation.

Time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[\frac{-\hbar^2}{2\mathrm{m}}\nabla^2 + V(\mathbf{r},t)\right]\Psi(\mathbf{r},t)$$

Steady State Schrodinger Equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0$$

Solution of wave equation is called wave function

The wave function defines the probability of locating the electron in the volume of space.

This volume in space is called an orbital.

Each orbital is characterized by three quantum numbers.

In the modern view of atoms, the space surrounding the dense nucleus may be thought of as consisting of orbitals, or regions, each of which comprises only two distinct states. The Pauli exclusion principle indicates that, if one of these states is occupied by an electron of spin one-half, the other may be occupied only by an electron of opposite spin, or spin negative one-half. An orbital occupied by a pair of electrons of opposite spin is filled: no more electrons may enter it until one of the pair vacates the orbital.

Pauli’s Exclusion Principle

No two electrons in an atom can exist in the same quantum state. Each electron in an atom must have a different set of quantum numbers n, ℓ, m_ℓ, m_s. Pauli came to the conclusion from a study of atomic spectra, hence the principle is empirical.

The principle governs the electronic configuration of atom having more than one electron.

If in an element the spins of two electrons are in the same direction so that the total spin is 1 then no transitions are observed in the element (except hydrogen) from ground state or vice versa.

If the spins are in opposite direction so that the total spin is 0 the transitions are observed from the ground state and vice versa.

In the missing state the quantum numbers of both electrons would be $n=1$, $\ell=0$, $m_\ell=0$, $m_s=1/2$.

In the state that exists one of the electrons has $m_s=1/2$ and the other $m_s=-1/2$.

Thus, every missing atomic state involves two or more atomic electrons with identical quantum numbers.

Consider that one of the particles is in quantum state **a** and the other is in state **b**.

Since the particles are identical the probability density $|\psi|^2$ of the system remains unaffected if positions are exchanged, with one in state a replacing one in state b, and vice versa.

➡ $|\psi|^{2}(1, 2) = |\psi|^{2}(2, 1)$

Let the wave function $|\psi|(2, 1)$, represent the exchanged particles, it may be expressed as

$|\psi|(2,1)| = |\psi|(1, 2)$ or $|\psi|(2,1) = -|\psi|(1,2)$

Wave functions unchanged by exchange of particles are said to be symmetric, and those reversing sign upon exchange are said to be antisymmetric.

If particle 1 is in state a and particle 2 is in state b, the wave function of the system may be expressed as

$$\psi_{I} = \psi_{a}(1)\, \psi_{b}(2)$$

If particle 2 is in state a and particle 1 is in state b the wave function is

$$\psi_{II} = \psi_{a}(2)\, \psi_{b}(1)$$

The two particles are identical.

Whether ψ_I describes the system or ψ_{II}, we cannot know.

The probability that ψ_I describes the system at any moment is the same as the probability that ψ_{II} does it.

It may be assumed that the system spends half the time in configuration having wave function ψ_I and the other half in the configuration with wave function is ψ_{II}.

Thus, a linear combination of ψ_I and ψ_{II} will describe the system appropriately. There are two such combinations possible.

The symmetric one

$$\psi_s = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]$$

The antisymmetric one

$$\psi_A = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$$

$\sqrt{2}$ factor is required to normalize ψ_S and ψ_A.

Exchanging particles 1 and 2 leave ψ_S unaffected while it reverses the sign of ψ_A.

Two cases

Behaviour of particles in a system whose wave functions are symmetric: both particles 1 and 2 can simultaneously exist in the same state, with a=b.

Behaviour of particles in a systems whose wave functions are antisymmetric, with a=b, $\psi_A=0$; the two particles cannot be in the same quantum state.

Compare above two statements with Pauli’s exclusion principle that no two electrons in an atom can be in the same quantum state.

Conclusion: Systems of electrons described by wave functions that reverse sign upon the exchange of any pair of them obey Pauli Exclusion Principle.

The results of various experiments show that all particles which have a spin of 1/2 have wave functions that are antisymmetric to exchange of any pair of them.

Such particles like proton, neutrons and electrons obey the exchange principle when they are in the same system; i.e. when they move in a common force field each member of the system must be in a different quantum state.

Particles of spin ½ are often referred to as Fermi particles or fermions.

Particles whose spins are 0 or an integer have wave functions that are symmetric on exchange of any pair of them. These particles do not obey the exchange principle. Particles of 0 or integral spins are often referred to as Bose particles or bosons.

Generalized Pauli Exclusion Principle

The Pauli exclusion principle says that no two identical fermions can simultaneously occupy the same quantum state.

All fermions and particles derived from fermions, such as protons and neutrons, obey Fermi-Dirac statistics; this includes obeying the Pauli exclusion principle.

Quarks (up and down) and leptons (electrons, electron neutrinos, muons, muon neutrinos, taus, and tau neutrinos) are all fermions.

Particles obeying the exclusion principle have a characteristic value of spin, or intrinsic angular momentum; their spin is always some odd whole-number multiple of one-half.

The Pauli exclusion principle does not apply to bosons: these are particles that obey Bose-Einstein statistics; they all have integer values of spin. Photons, gluons, gravitons, and the W, Z and Higgs bosons are all bosons.

Quantum numbers should be considered as address of each electron within an atom, each address has four components, and no two electrons can have the exact same address.

This Pauli Exclusion principle states that no two electrons in an atom can have the same four quantum numbers. If two electrons occupy the same orbital, they must have different spins.

Pauli’s Exclusion Principle limits the numbers of electrons that a shell or a subshell may contain.

The four quantum numbers (for electronic wave functions) are:

n	The principal quantum number
ℓ	The angular momentum quantum number
m_ℓ	The magnetic quantum number
m_s	The electron spin quantum number

Principal Quantum Number n

This quantum number describes the electron shell or energy level of an atom.

The value of the principal quantum number can be any integer with a positive value that is equal to or greater than one.

A larger value of the principal quantum number implies a greater distance between the electron and the nucleus (which, in turn, implies a greater atomic size).

The value n=1 denotes the innermost electron shell of an atom, which corresponds to the lowest energy state or the ground state of an electron.

Thus, the principal quantum number, n, cannot have a negative value or be equal to zero because it is not possible for an atom to have a negative value or no value for a principal shell.

When a given electron is given energy and sent to the excited state, the electron jumps from one principle shell to a higher shell, causing an increase in the value of n. Similarly, when electrons lose energy, they jump back into lower shells and the value of n also decreases.

The increase in the value of n for an electron is called absorption, emphasizing the photons or energy being absorbed by the electron. Similarly, the decrease in the value of n for an electron is called emission, where the electrons emit their energy.

Azimuthal Quantum Number ℓ

- The angular or orbital quantum number, describes the sub-shell and gives the magnitude of the orbital angular momentum.
- A value of the azimuthal quantum number can indicate either an s, p, d, or f subshell which vary in shapes. This value depends on (and is capped by) the value of the principal quantum number, i.e. the value of the azimuthal quantum number ranges between 0 and (n-1).
- ℓ = 0 is called an **s** orbital, ℓ = 1 **p** orbital, ℓ = 2 **d** orbital, and ℓ = 3 **f** orbital.

- The value of ℓ ranges from 0 to n − 1 because the first p orbital (ℓ = 1) appears in the second electron shell (n = 2), the first d orbital (ℓ = 2) appears in the third shell (n = 3), and so on.
- This quantum number specifies the shape of an atomic orbital and strongly influences chemical bonds and bond angles.

Magnetic Quantum Number m_ℓ

- m_ℓ is associated with the orbital orientation.
- m_ℓ describes energy levels available within a sub-shell
- m_ℓ yields projection of orbital angular momentum along a specified axis.
- Value of m_ℓ ranges from $-\ell$ to $+\ell$, with integer steps between them.
- The s sub-shell ($\ell=0$) contains one orbital, and therefore the m_ℓ of an electron in an s sub-shell will always be 0.
- p sub-shell ($\ell=1$) contains three orbitals, so m_ℓ of an electron in a p sub-shell will be −1, 0, or 1.
- The d sub-shell ($\ell=2$) contains five orbitals, with m_ℓ values of −2, −1, 0, 1, and 2.

Spin Projection Quantum Number m_s

- Spin quantum number describes the intrinsic angular momentum of the electron within that orbital and gives the projection of the spin angular momentum (s) along the specified axis.
- Value of m_s ranges from −s to +s.
- An electron has spin s = ½, consequently m_s will be ±½, corresponding to spin and opposite spin.
- Each electron in any individual orbital must have different spins because of the Pauli Exclusion Principle. Thus an orbital can never contain more than two electrons.
- The electron spin quantum number is independent of the values of n, ℓ, and m_ℓ. The value of this number gives insight into the direction in which the electron is spinning, and is denoted by the symbol m_s.

Quantum Numbers	**Symbol**	**Possible Values**
Principal Quantum Number	n	1, 2, 3, 4, …..
Angular Momentum Quantum Number	ℓ	0, 1, 2, 3, ….. $n-1$
Magnetic Quantum Number	m_ℓ	$-\ell$ …-1, 0, 1, ….ℓ
Spin Quantum Number	s	+½, -½

Each subshell has a maximum of $2(2\ell + 1)$ electrons

Each shell a maximum of

$$\sum_{\ell=0}^{\ell=n-1} 2(2\ell + 1) \quad \text{electrons}$$

$$= 2n^2$$

For each n, there are n possible values of the quantum number ℓ. For each value of ℓ, there are $2\ell+1$ values of m_ℓ.

An electron has spin $s = ½$, consequently m_s will be $\pm½$, corresponding to spin and opposite spin

n	ℓ	m_ℓ	m_s	Orbital	Electrons	Elements	Shell
1	0	0	+1/2, -1/2	1s	2	2	K
2	0	0	+1/2, -1/2	2s	2	8	L
2	1	-1, 0, 1		2p	6		
3	0	0	+1/2, -1/2	3s	2	18	M
3	1	-1, 0, 1		3p	6		
3	2	-2, -1, 0, 1, 2		3d	10		
4	0	0	+1/2, -1/2	4s	2	32	N
4	1	-1, 0, 1		4p	6		
4	2	-2, -1, 0, 1, 2		4d	10		
4	3	-3, -2, -1, 0, 1, 2, 3		4f	14		
5	0	0	+1/2, -1/2	5s	2	32	O
5	1	-1, 0, 1		5p	6		
5	2	-2, -1, 0, 1, 2		5d	10		
5	3	-3, -2, -1, 0, 1, 2, 3		5f	14		
5	4	-4, -3, -2, -1, 0, 1, 2, 3, 4		5g	18	…………	

n	ℓ	m_ℓ	m_s	Orbital	Electrons	Elements	Shell
6	0	0 -1, 0, 1 -2, -1, 0, 1, 2 -3, -2, -1, 0, 1, 2, 3 -4, -3, -2, -1, 0, 1, 2, 3, 4 -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5	+1/2 -1/2	6s	2	18	P
	1			6p	6		
	2			6d	10		
	3			6f	14	....	
	4			6g	18		
	5			6h	22		
7	0	0 -1, 0, 1 -2, -1, 0, 1, 2 -3, -2, -1, 0, 1, 2, 3 -4, -3, -2, -1, 0, 1, 2, 3, 4 -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5 -6, -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5, 6	+1/2 -1/2	7s	2	8	Q
	1			7p	6		
	2			7d	10	....	
	3			7f	14		
	4			7g	18		
	5			7h	22		
	6			7i	26		

The Periodic Table

The periodic table serves as a guide to both order of increasing electron energies and the order in which electrons fill orbitals.

Electrons occupy the lowest energy orbitals available, and as the number of electrons in an atom increases, the outermost electrons occupy higher and higher energy levels.

In the periodic table, the elements are listed in order of increasing atomic number Z.

A new row or *period* is started when a new electron shell has its first electron.

Columns or *groups* are determined by the electron configuration of the atom. The elements with the same number of electrons in a particular subshell fall into the same columns or groups, e.g. oxygen and selenium are in the same column because they both have four electrons in the outermost p-subshell.

Since 2016, the periodic table has 118 confirmed elements, from element 1 (hydrogen) to 118 (oganesson).

The first 94 elements occur naturally; the remaining 24, americium to oganesson (95–118), occur only when synthesized in laboratories.

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