

Application of Schrödinger Wave Equation



Particle in a 1-dimensional box

The particle in a box problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape.

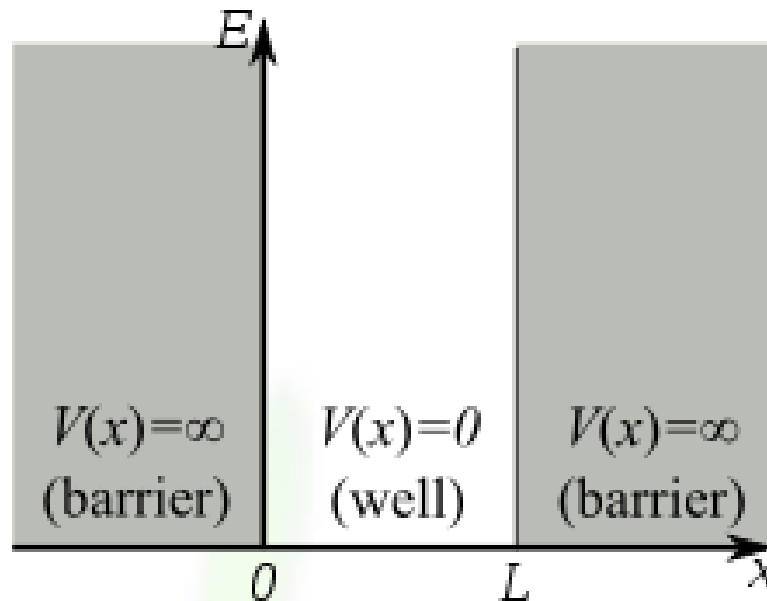
The solutions to the problem give possible values of E and ψ that the particle can possess.

E represents allowed energy values and $\psi(x)$ is a wavefunction, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.

To solve the problem for a particle in a 1-dimensional box, we must,

1. Define the Potential Energy, V
2. Solve the Schrödinger Equation
3. Define the wavefunction
4. Define the allowed energies

Step 1: Define the Potential Energy V



The barriers outside a one-dimensional box have infinitely large potential, while the interior of the box has a constant, zero potential

$$V(x) = \begin{cases} 0, & 0 < x < L, \\ \infty, & \text{otherwise,} \end{cases}$$

where L is the length of the box and x is the position of the particle within the box.

Step 2: Solve the Schrödinger Equation

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

with

- \hbar is the reduced Planck Constant where $\hbar = \frac{h}{2\pi}$
- m is the mass of the particle
- $\psi(x)$ is the stationary time-independent wavefunction
- $V(x)$ is the potential energy as a function of position
- E is the energy, a real number

This means that the observable properties of the particle (such as its energy and position) are related to the mass of the particle and the width of the well by simple mathematical expressions.

This equation has been well studied and gives a general solution of:

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

where A , B , and k are constants.

Step 3: Define the wavefunction

The solution to the Schrödinger equation above is the general solution for a 1-dimensional system.

We now apply **boundary conditions** to find the solution to our particular system.

According to boundary conditions, the probability of finding the particle at $x=0$ or $x=L$ is zero. When $x=0$ $\sin(0)=0$ and $\cos(0)=1$; therefore, *B must equal 0* to fulfill this boundary condition giving:

$$\psi(x)=A\sin(kx)$$

We can now solve for constants (A and k) systematically to define the wavefunction.

$$k = \left(\frac{8\pi^2 m E}{h^2} \right)^{1/2}$$

Substituting k into the wavefunction gives,

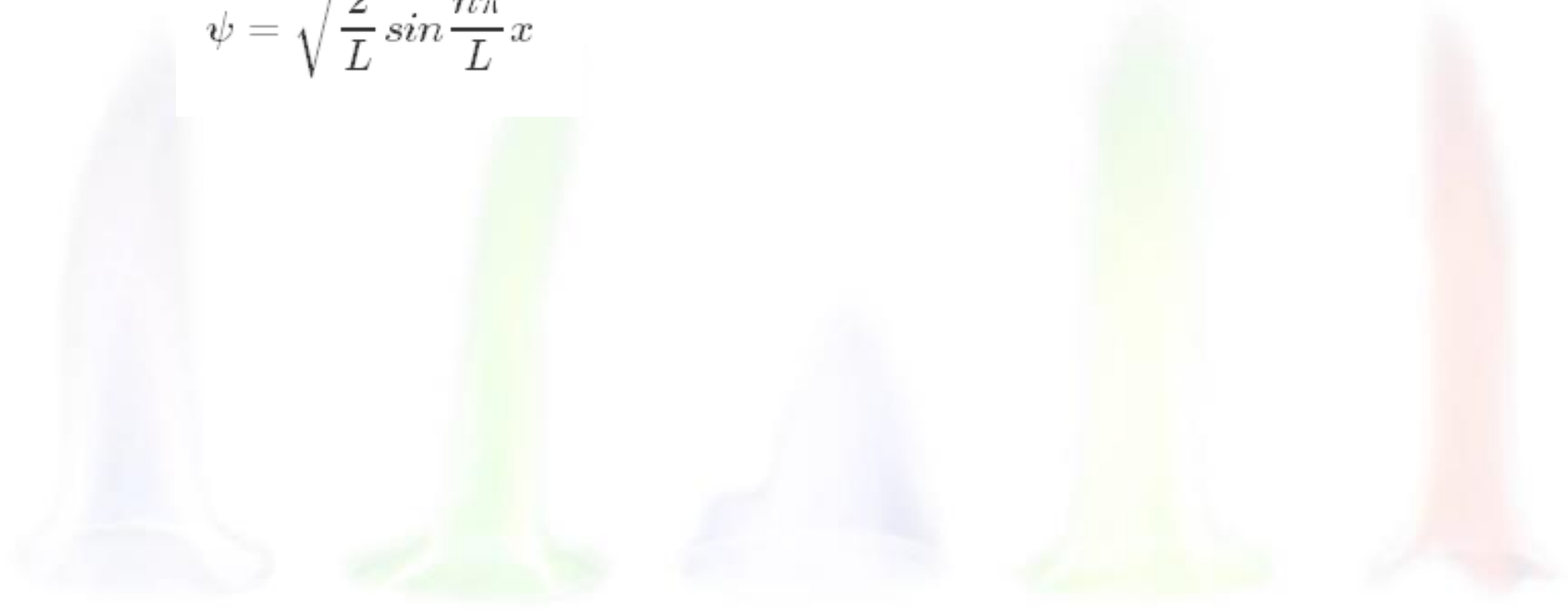
$$\psi = A\sin\left(\left(\frac{8\pi^2 m E}{h^2}\right)^{1/2} x\right)$$

Solving for A gives,

$$A = \sqrt{\frac{2}{L}}$$

Which results in the normalized wavefunction for a particle in a 1-dimensional box:

$$\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$



Step 4: Determine the Allowed Energies

Solving for E results in the allowed energies for a particle in a box:

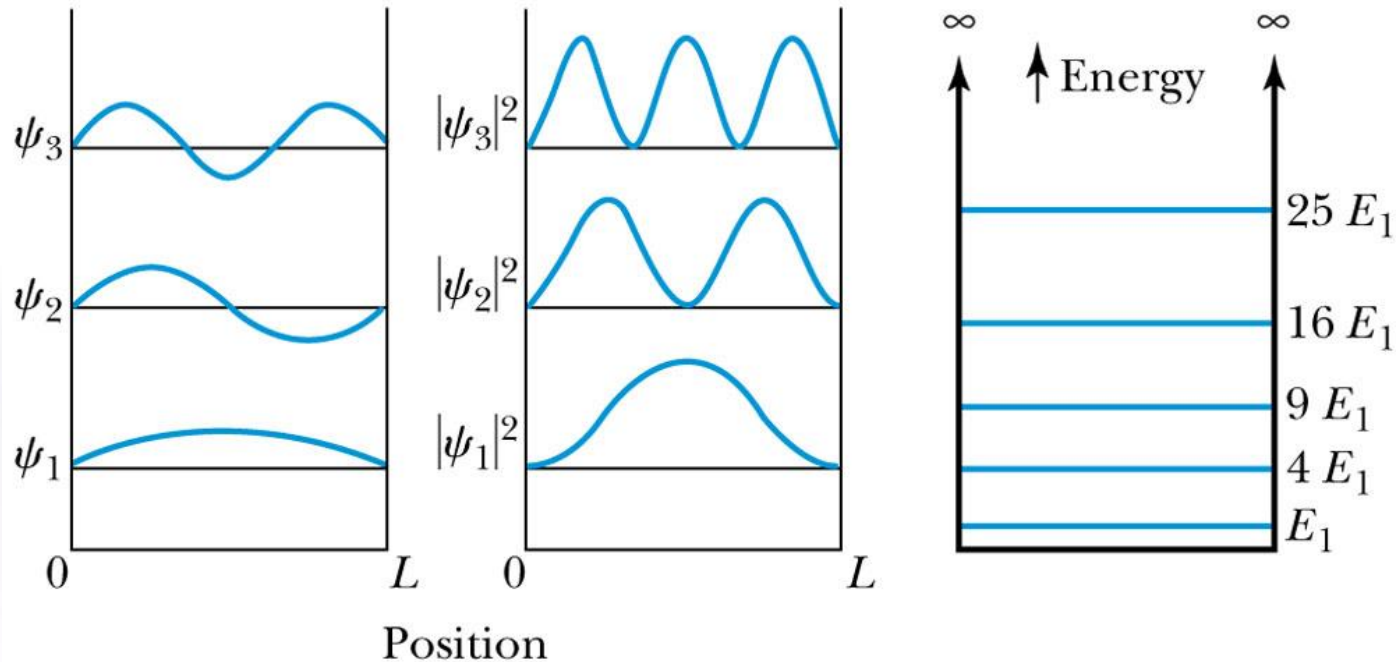
$$E_n = \frac{n^2 h^2}{8mL^2}$$

This is a very important result; it tells us that:

1. The energy of a particle is quantized.
2. The lowest possible energy of a particle is **NOT** zero. This is called the **zero-point energy** and means the particle can never be at rest because it always has some kinetic energy.
3. The energy levels increase with n^2 , meaning that high energy levels are separated from each other by a greater amount than low energy levels are. The lowest possible energy for the particle (its *zero-point energy*) is found in state 1.
4. The minimum kinetic energy of the particle in a box is inversely proportional to the mass and the square of the well width

What does all this mean?

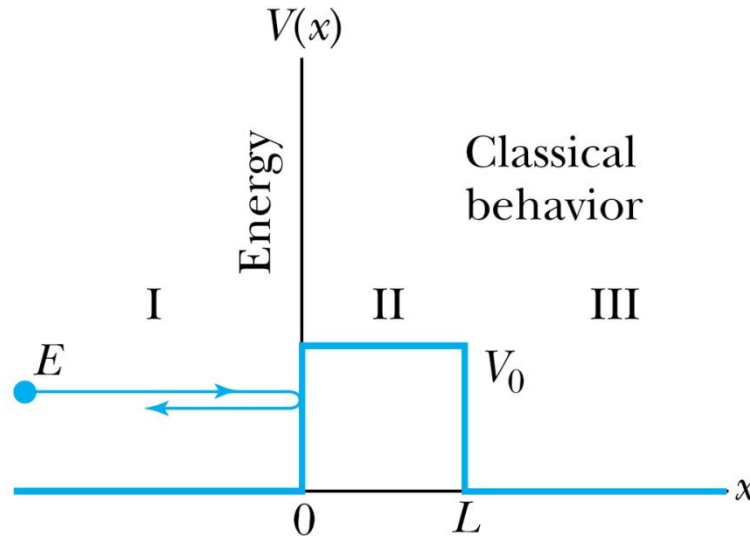
The wavefunction for a particle in a box at $n=1, 2$ and 3 energy levels look like this:



Notice that the number of **nodes** (places where the particle has zero probability of being located) increases with increasing energy n

Tunneling

- Now we consider the situation where classically the particle does not have enough energy to surmount the potential barrier, $E < V_0$.

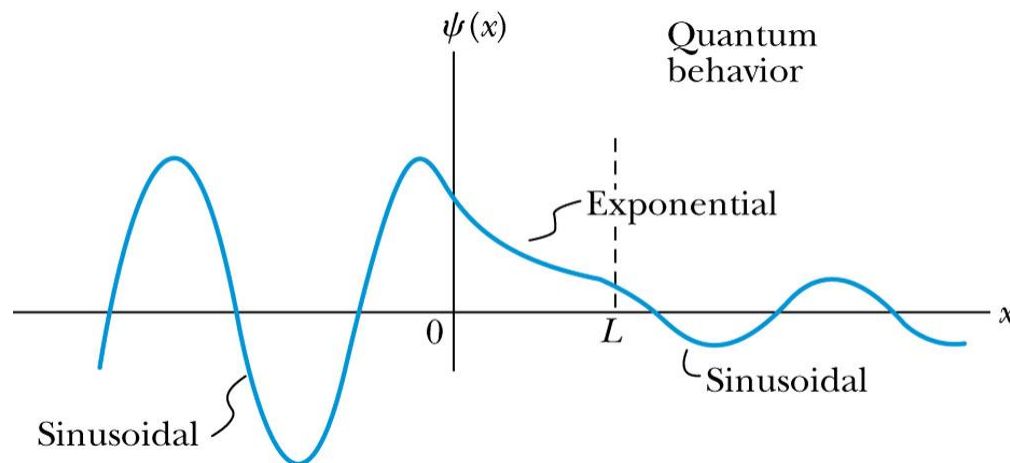


- The quantum mechanical result, however, is one of the most remarkable features of modern physics, and there is ample experimental proof of its existence. There is a small, but finite, probability that the particle can penetrate the barrier and even emerge on the other side.
- The wave function in region II becomes $\psi_{II} = Ce^{\kappa x} + De^{-\kappa x}$ where $\kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$
- The transmission probability that describes the phenomenon of **tunneling** is $T = \left[1 + \frac{V_0^2 \sinh^2(\kappa L)}{4E(V_0 - E)} \right]^{-1}$

Uncertainty Explanation

Consider when $\kappa L \gg 1$ then the transmission probability becomes:

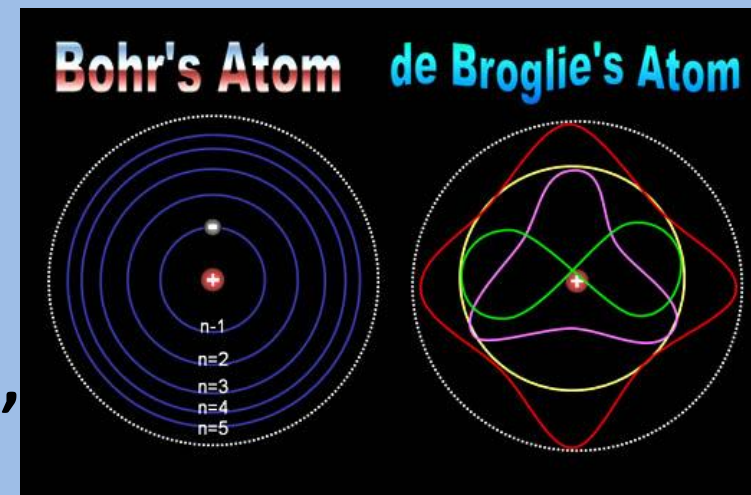
$$T = 16 \frac{E}{V_0} \left(1 - \frac{E}{V_0} \right) e^{-2\kappa L}$$



The above equation implies that there is a finite probability that a particle impinging a potential barrier will penetrate the barrier and will appear in region III. This phenomenon is called tunneling and it, too, contradicts classical mechanics. We will see later how this quantum mechanical tunneling phenomenon can be applied to semiconductor device characteristics, such as in the tunnel diode and SETs.

Quantum Numbers

- Solving the wave equation gives a set of wave functions, or **orbitals**, and their corresponding energies.
- Each orbital describes a spatial distribution of electron density.
- An orbital is described by a set of three **quantum numbers**.
- Quantum numbers can be considered to be “coordinates” (similar to x , y , and z coordinates for a graph) which are related to where an electron will be found in an atom.



Solutions to the Schrodinger Wave Equation

Quantum Numbers of Electrons in Atoms

Name	Symbol	Permitted Values	Property
principal	n	positive integers(1,2,3,...)	Energy level
angular momentum	l	integers from 0 to $n-1$	orbital shape (probability distribution) (The l values 0, 1, 2, and 3 correspond to s, p, d, and f orbitals, respectively.)
magnetic	m_l	integers from $-l$ to 0 to $+l$	orbital orientation
spin	m_s	$+1/2$ or $-1/2$	direction of e^- spin

Looking at Quantum Numbers: The Principal Quantum Number, n

- The principal quantum number, n , describes the **energy level** on which the orbital resides.
- The values of n are integers ≥ 0 .

$$n = 1, 2, 3, \text{ etc.}$$

Looking at Quantum Numbers: The Azimuthal Quantum Number, l

- The azimuthal (or angular momentum) quantum number tells the **electron's angular momentum**.
- Allowed values of l are integers ranging from 0 to $n - 1$.

For example, if $n = 1$, $l = 0$




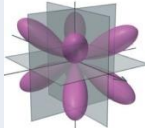
if $n = 2$, l can equal 0 or 1

Value of l	Angular momentum
0	None
1	Linear
2	2-directional
3	3-directional

Looking at Quantum Numbers:

The Azimuthal Quantum Number, l

- The values of l relate to the most probable electron distribution.
- Letter designations are used to designate the different values of l and, therefore, the **shapes of orbitals**.

Value of l	Orbital (subshell) Letter designation	Orbital Shape	Name*
0	s		<i>sharp</i>
1	p		<i>principal</i>
2	d		<i>diffuse</i>
3	f		<i>fine</i>

* From emission spectroscopy terms

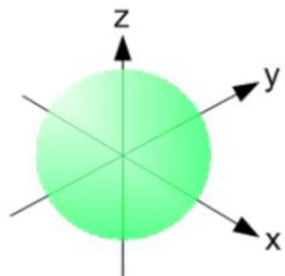
Looking at Quantum Numbers: The Magnetic Quantum Number, m_l

- Describes the orientation of an orbital with respect to a magnetic field
- This translates as the three-dimensional orientation of the orbital.
- Values of m_l are integers ranging from $-l$ to l :

$$-l \leq m_l \leq l.$$

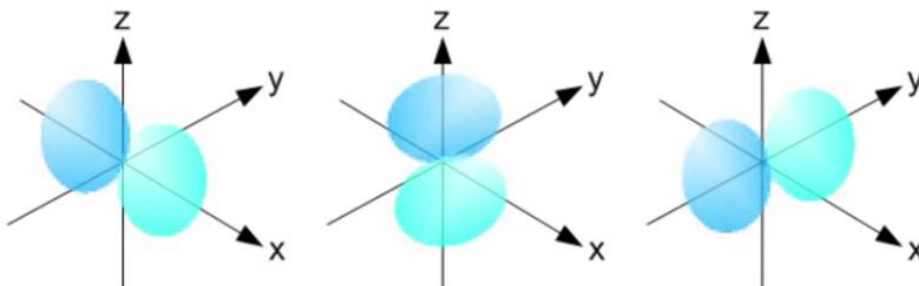
Values of l	Values of m_l	Orbital designation	Number of orbitals
0	0	s	1
1	-1, 0, +1	p	3
2	-2, -1, 0, +1, +2	d	5
3	-3, -2, -1, 0, +1, +2, +3	f	7

$$\ell = 0$$



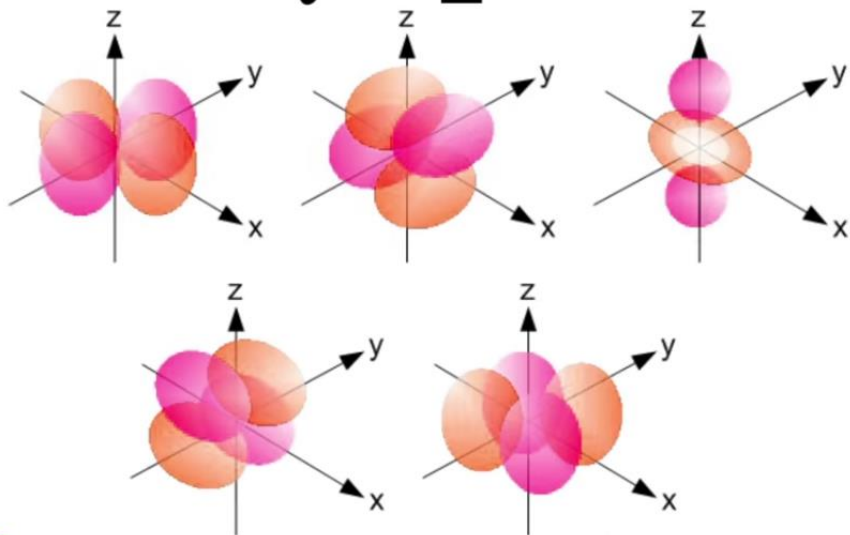
s orbital

$$\ell = 1$$



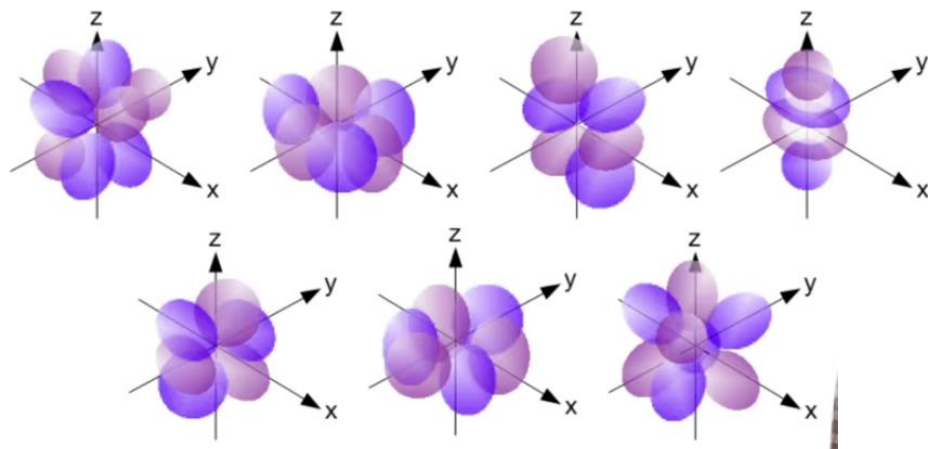
p orbitals

$$\ell = 2$$



d orbitals

$$\ell = 3$$



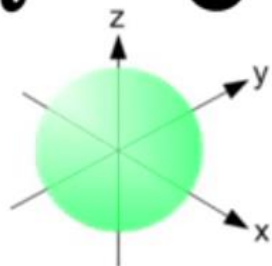
f orbitals

Quantum Numbers and Subshells

- Orbitals with the same value of n form a **shell**
- Different orbital types within a shell are called **subshells**.

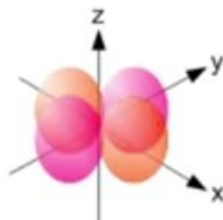
n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	1, 0, -1	3	
3	0	3s	0	1	9
	1	3p	1, 0, -1	3	
	2	3d	2, 1, 0, -1, -2	5	
4	0	4s	0	1	16
	1	4p	1, 0, -1	3	
	2	4d	2, 1, 0, -1, -2	5	
	3	4f	3, 2, 1, 0, -1, -2, -3	7	

$$l = 0$$

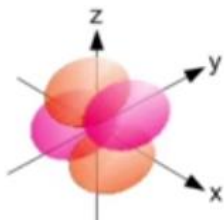


$$m_l: 0$$

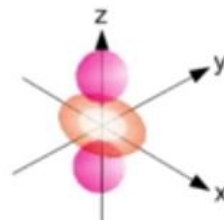
$$l = 2$$



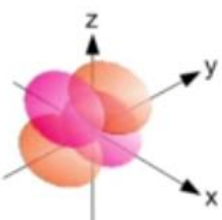
$$m_l: -2$$



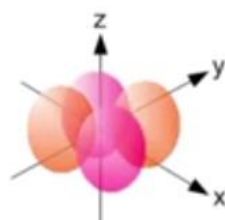
$$-1$$



$$0$$

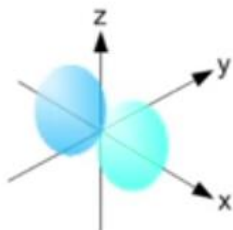


$$1$$

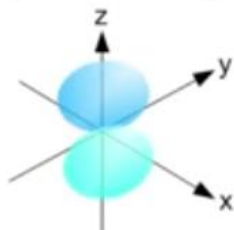


$$2$$

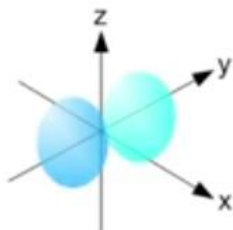
$$l = 1$$



$$m_l: -1$$

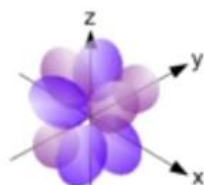


$$0$$

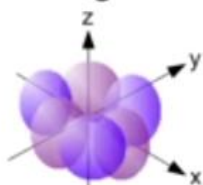


$$1$$

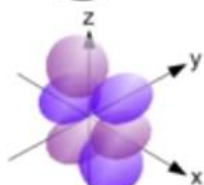
$$l = 3$$



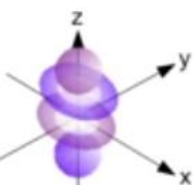
$$m_l: -3$$



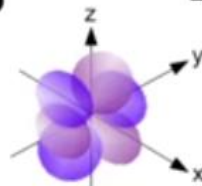
$$-2$$



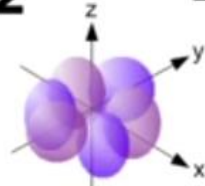
$$-1$$



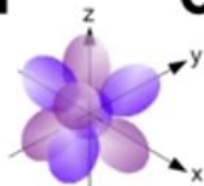
$$0$$



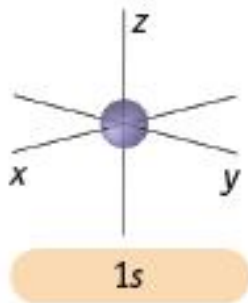
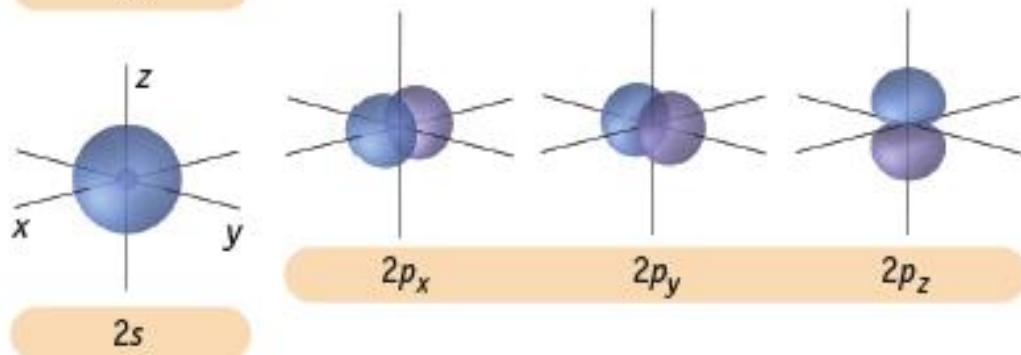
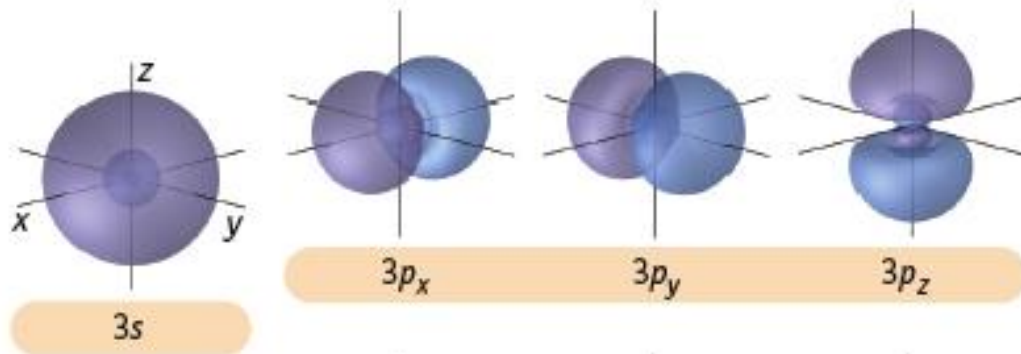
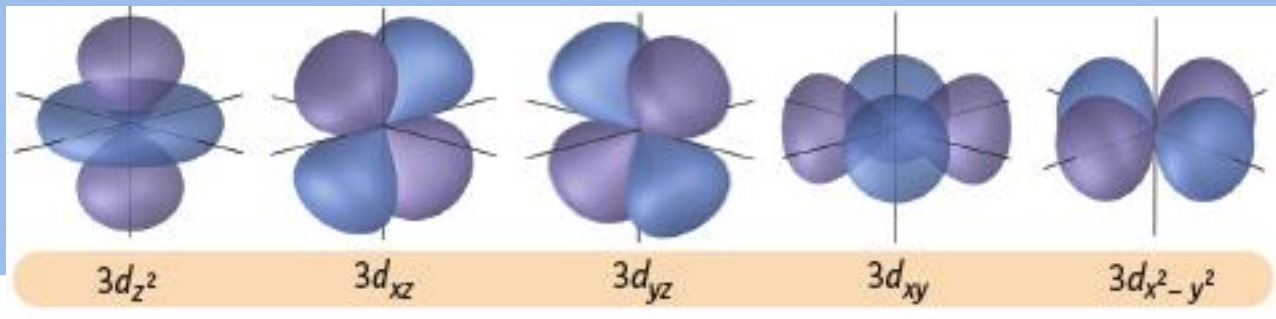
$$1$$



$$2$$



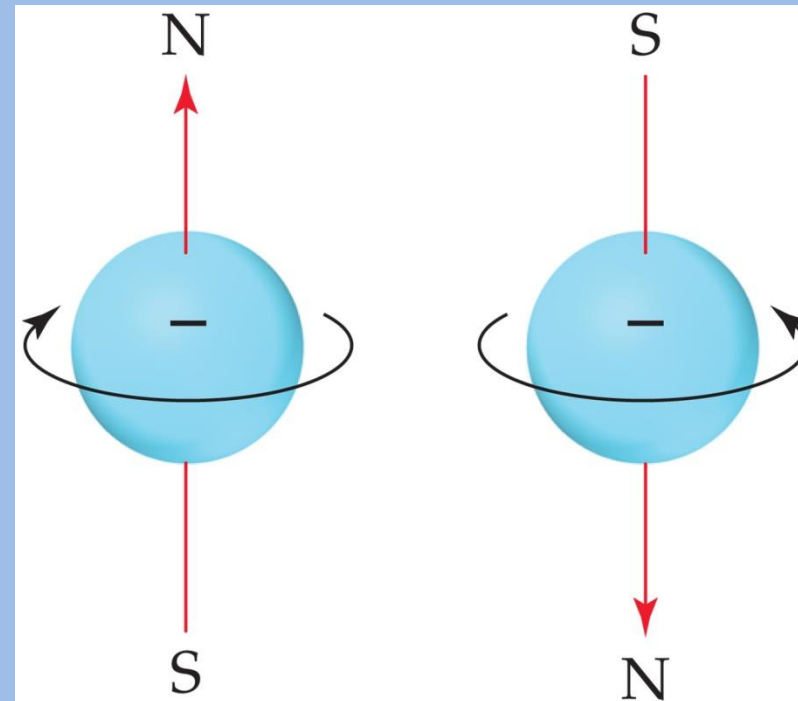
$$3$$



A Summary of Atomic Orbitals from 1s to 3d

The Spin Quantum Number, m_s

- In the 1920s, it was discovered that two electrons in the same orbital do not have exactly the same energy.
- The “spin” of an electron describes its magnetic field, which affects its energy.
- This led to a fourth quantum number, the spin quantum number, m_s .
- The spin quantum number has only 2 allowed values: $+1/2$ and $-1/2$.



- **Wolfgang Pauli (1900-1958)**
 - **Pauli Exclusion Principle, 1925**

“There can never be two or more equivalent electrons in an atom for which in strong fields the values of all quantum numbers n , k_1 , k_2 , m_1 (or, equivalently, n , k_1 , m_1 , m_1) are the same.”

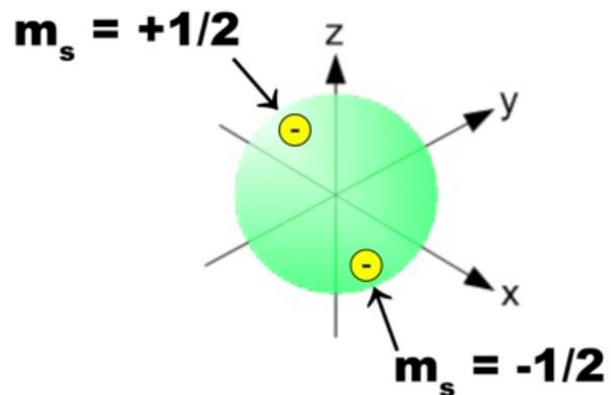


$$n = 1$$

$$\ell = 0$$

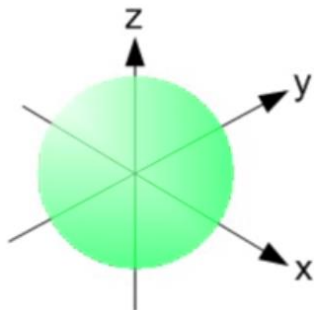
$$m_\ell = 0$$

1s orbital



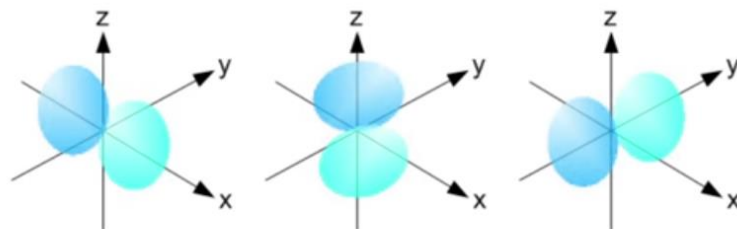
$$n = 2$$

$\ell = 0$ 2s orbital



$$m_\ell = 0$$

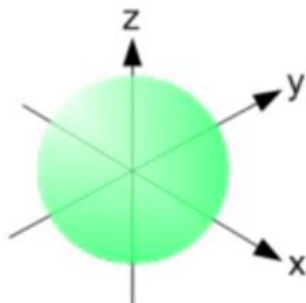
$\ell = 1$ 2p orbitals



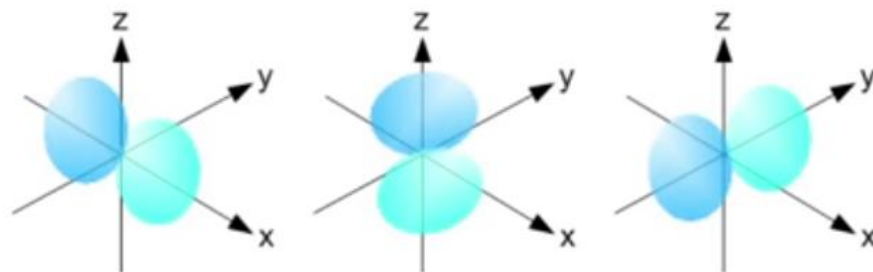
$$m_\ell = -1, 0, 1$$

$n = 3$

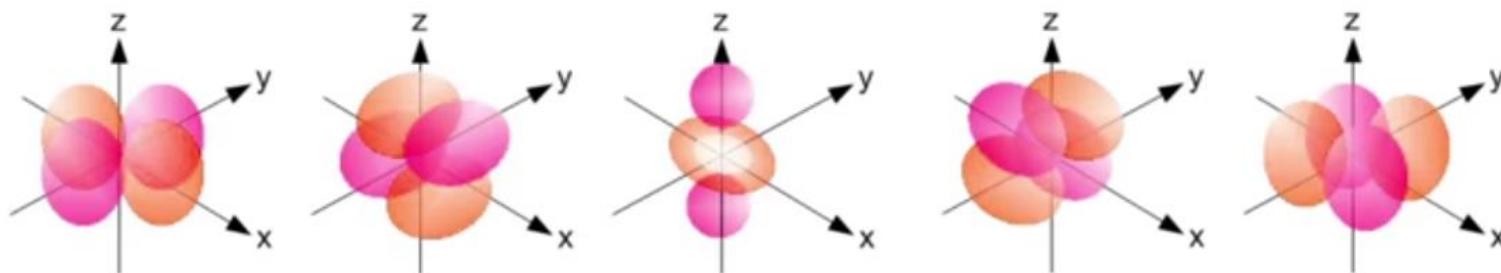
**$\ell = 0$
3s orbital**



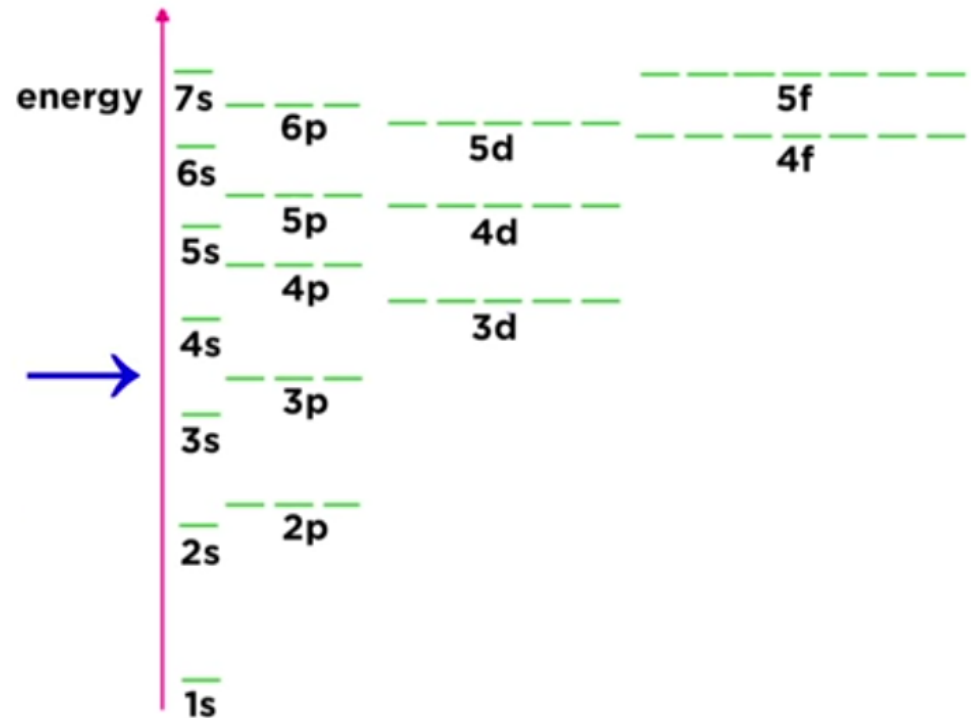
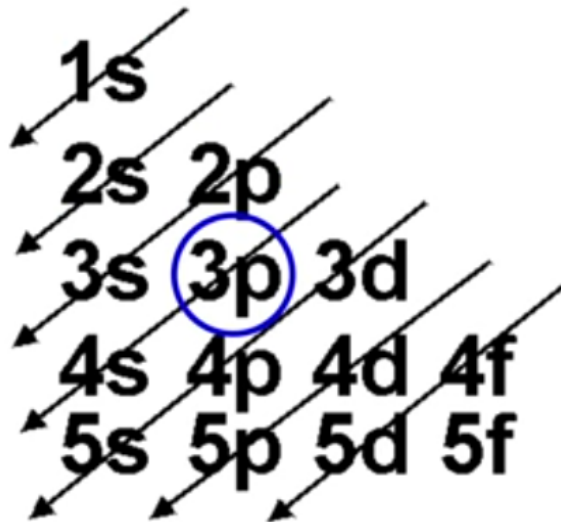
**$\ell = 1$
3p orbitals**



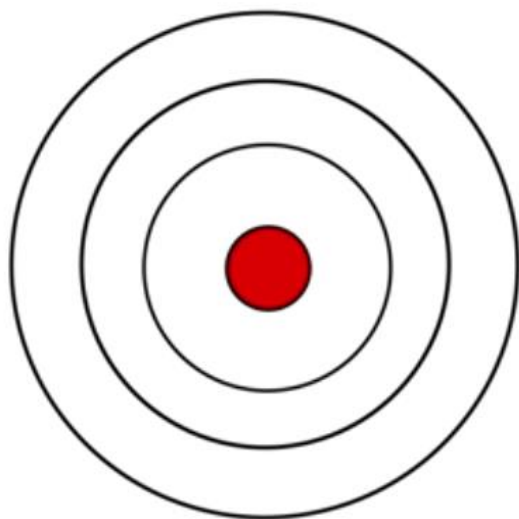
**$\ell = 2$
3d orbitals**



Aufbau Principle



chlorine



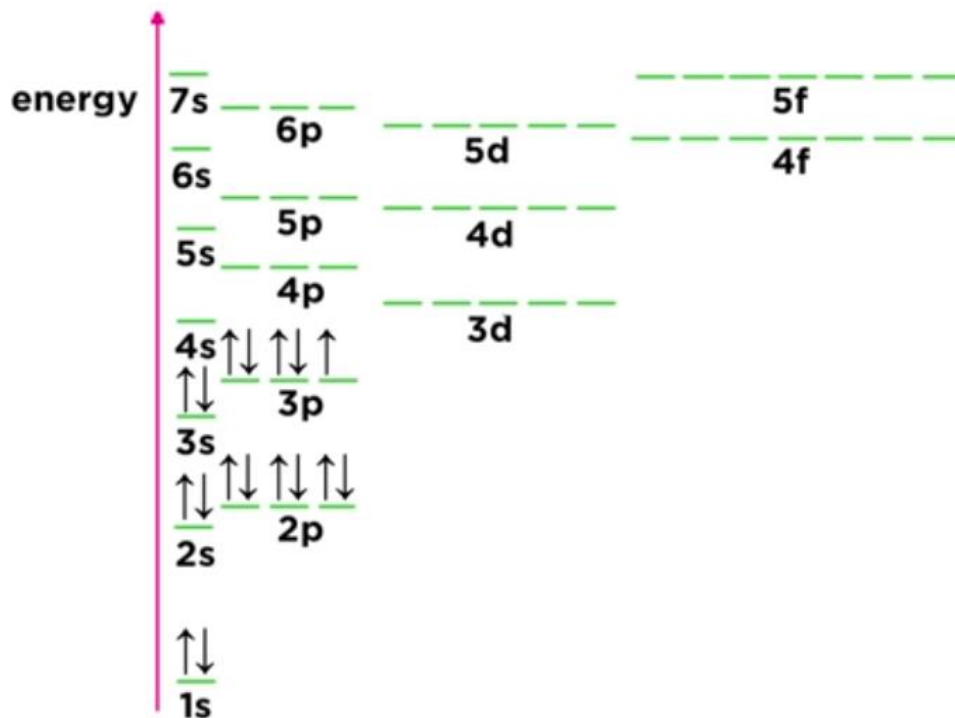
electron configuration

$1s^2 2s^2 2p^6 3s^2 3p^5$

↑
n value

↑
number of
electrons

Hund's Rule



n = 1

n = 2

n = 3



hydrogen 1 H 1.0079	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122
sodium 11 Na 22.990	magnesium 12 Mg 24.305
potassium 19 K 39.098	calcium 20 Ca 40.078
rubidium 37 Rb 85.468	strontium 38 Sr 87.62
cesium 55 Cs 132.91	barium 56 Ba 137.33
francium 87 Fr [223]	radium 88 Ra [226]

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✱ ✱

scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39
yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41
lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59
lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [268]	meitnerium 109 Mt [268]	unnilium 110 Uun [271]	ununium 111 Uuu [272]	unbinium 112 Uub [277]

boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]

* Lanthanide series

** Actinide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

orbital diagram

Lithium	Li	$1s^2 2s^1$	$\uparrow\downarrow$	\uparrow	\square \square \square	←
Beryllium	Be	$1s^2 2s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	\square \square \square	
Boron	B	$1s^2 2s^2 2p^1$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \square \square	←
Carbon	C	$1s^2 2s^2 2p^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow \square	←
Nitrogen	N	$1s^2 2s^2 2p^3$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow \uparrow	←
Oxygen	O	$1s^2 2s^2 2p^4$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ \uparrow \uparrow	←
Fluorine	F	$1s^2 2s^2 2p^5$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow	←
Neon	Ne	$1s^2 2s^2 2p^6$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	

paramagnetic

orbital diagram

Lithium	Li	$1s^2 2s^1$	$\uparrow\downarrow$	\uparrow	\square \square \square	
Beryllium	Be	$1s^2 2s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	\square \square \square	←
Boron	B	$1s^2 2s^2 2p^1$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \square \square	
Carbon	C	$1s^2 2s^2 2p^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow \square	
Nitrogen	N	$1s^2 2s^2 2p^3$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow \uparrow	
Oxygen	O	$1s^2 2s^2 2p^4$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ \uparrow \uparrow	
Fluorine	F	$1s^2 2s^2 2p^5$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow	
Neon	Ne	$1s^2 2s^2 2p^6$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	←

diamagnetic

Diamagnetic materials are slightly repelled by a magnetic field and do not retain the magnetic properties when the external field is removed. Paramagnetic materials are slightly attracted by a magnetic field and do not retain the magnetic properties when the external field is removed.