

**NOTES****MODELS OF THE ATOM*****John Dalton***

- Billiard ball model
  - Limitations

***Thompson (cathode ray experiment)***

- Plum pudding model
  - Limitations

***Rutherford (gold foil experiment)***

- Nuclear model
  - Limitations

***Niels Bohr (electromagnetic spectra)***

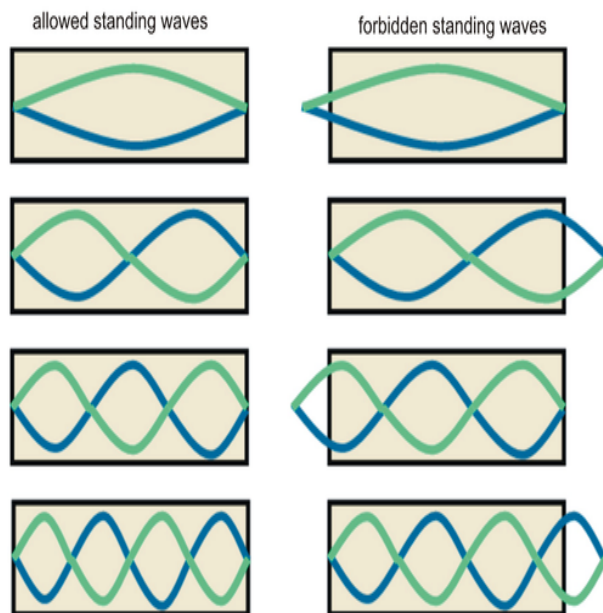
- Bohr model
  - Limitations

***Louis de Broglie (matter waves)***

- Using reason and logic theorized that if light (which was traditionally considered a wave) could have some properties of particles, then particles might have some properties of waves
- His theory was correct and experiments supported it
- Never noticed wave properties of particles because mass of objects studied was too large
  - $\lambda = \frac{h}{mv}$  where  $\lambda$  = wavelength,  $h$  = Planck's constant,  $m$  = mass,  $v$  = speed of particle
- Matter waves applied to radii of allowed orbits for electrons demonstrated the same results as Bohr – this supported Bohr's model
  - Limitation: still cannot explain more complex line spectra of multi-electron atoms

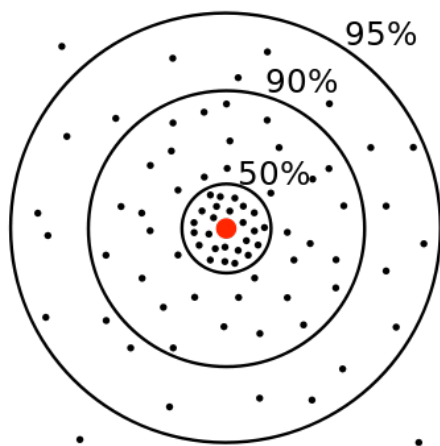
***Erwin Schrödinger (wave functions)***

- Applied idea of electrons behaving as a wave to the problem of electrons in atoms
- Developed the wave equation
- Solution gives a set of math expressions called wave functions  $\Psi$
- Solutions to the Schrödinger wave equation describe the 3D shapes of the atomic orbitals where there is a high probability that electrons are located



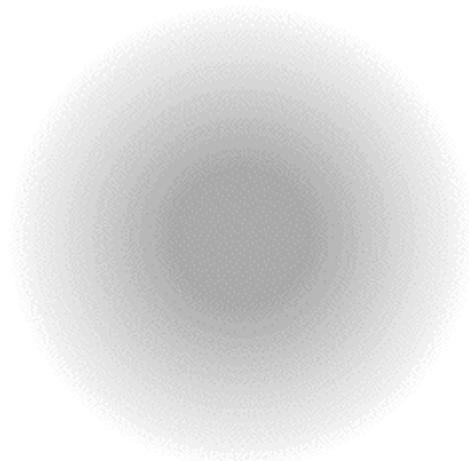
### Werner Heisenberg (uncertainty principle)

- From Schrödinger → electrons behave as both waves and particles
- Determined that it is impossible to know BOTH the exact position and momentum of an electron
- Observed that one cannot simultaneously define the position and momentum an electron
- If defining the energy of an electron precisely, limitation of not knowing the exact position
  - $\Delta x \Delta mv \leq \frac{h}{4\pi}$  where  $\frac{h}{4\pi} = 5.2728 \times 10^{-35} J \cdot s$
- If mass gets too large, then position is so small it cannot be precisely known
- With an electron, mass is so small that speed is large and therefore an electron's position cannot be precisely known
- We can only define the 3D shape (orbital) where we are most likely to find an electron
- Schrödinger merged de Broglie's idea of matter waves with Einstein's idea of quantized energy particles (photons)



- Combined this created the **quantum mechanical model of the atom**
  - Branch of physics that uses mathematical equations to describe wave properties of atomic particles
  - Electrons are described as standing waves
  - Like Bohr's model, energy of an electron is limited to discrete values
- Within this model, the region of space related to a wave function (solution to wave equation) is an **atomic orbital**

### QUANTUM NUMBERS



- **Quantum numbers** are integers arising from the solutions to the wave equation that describe specific properties of electrons in atoms
- Four numbers are needed to describe an electron
  - Principal quantum number = energy level (**shell**)
  - Orbital-shape quantum number = shape of orbital (**sublevel/subshell/suborbital**)
  - Magnetic quantum number = designates a particular subshell
  - Spin quantum number = spin of the electron
- Think of the 4 quantum numbers as the address of an electron...
  - Country > City > Street > Building

### Principal quantum number, $n$

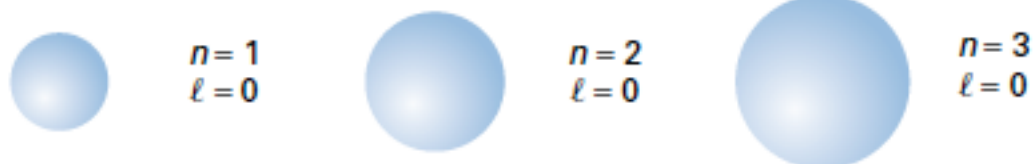
- Each energy level has a principal quantum number
- Currently  $n$  can be any integer from 1-7 because there are 7 periods on the periodic table
- If orbitals have the same value for  $n$  then they are in the same shell

- A higher value of  $n$  means:
  - Higher energy level
  - Larger shell
  - Greater chance of finding an electron farther from the nucleus
- Notice the size of the orbitals (in the diagram below) increase as the energy level does
  - Indicates that if an electron has more energy, it spends more time further from the nucleus
- Squaring  $n$  ( $n^2$ ) gives the total number of orbitals in an energy level
- Multiplying the square of  $n$  by 2 ( $2n^2$ ) gives the total number of electrons an energy level can hold

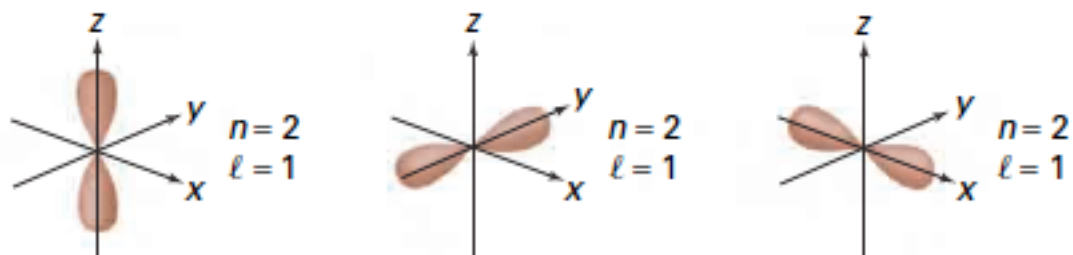
### Orbital-shape quantum number, $l$

- Each energy level (currently) has between 1 and 4 subshells
- Each subshell is associated with a particular shape of probability
- Possible values for  $l$  range from  $l=0$  to  $l=n-1$
- Four shapes for subshells are referred to as **s**, **p**, **d**, and **f** orbitals
  - When  $l=0$ , orbital is called  $s \rightarrow 1$  of these exists
  - When  $l=1$ , orbital is called  $p \rightarrow 3$  of these exist
  - When  $l=2$ , orbital is called  $d \rightarrow 5$  of these exist
  - When  $l=3$ , orbital is called  $f$  (**\*\*\*for the SCH4U course, the shape of the  $f$  orbital will not be covered\*\*\***)
- There is a planar node through the nucleus which is an area of zero probability of finding an electron

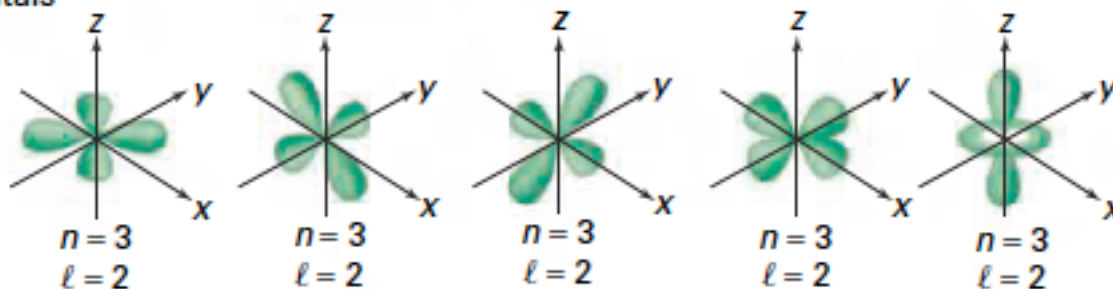
#### s orbitals



#### p orbitals



#### d orbitals



**Adapted from:** Clancy, C., Farrow, K., Finkle, T., Francis, L., Heimbecker, B., Nixon-Ewing, B., Schroder, M., & Thomas, T. (2011). *Chemistry 12*. Canada: McGraw-Hill Ryerson Limited.

**Magnetic quantum number,  $m_l$** 

- Indicates orientation of orbital in space
- Value depends on value of  $l$  and ranges from  $-l$  to  $+l$ 
  - These orbitals have the same shape and energy, but different orientation about the nucleus
- Total number of orbitals for an energy level  $n$  is equal to  $n^2$
- Overall shape of an atom is all orbitals combined which is spherical
  - Ensure to distinguish between spherical shape of  $s$  orbital and overall spherical shape of an atom
- REMINDER: diagrams of orbitals are meant to help visualize the most probable location of an electron
  - Orbitals are NOT containers where electrons are stored

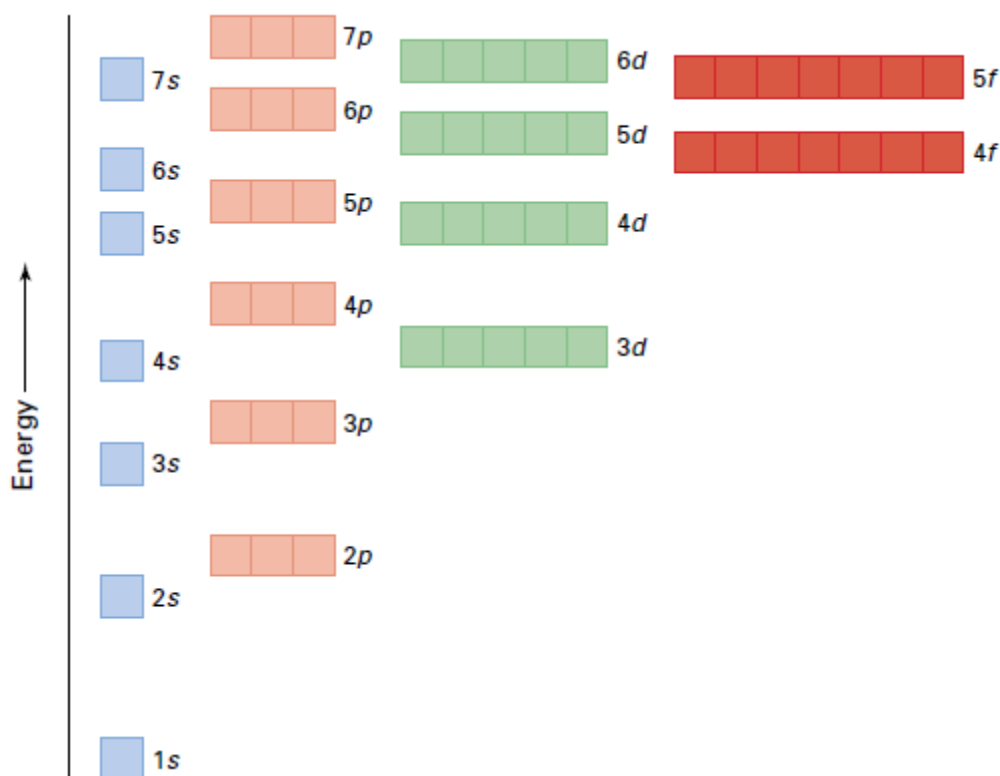
**Spin quantum number,  $m_s$** 

- First 3 quantum numbers provide energy, shape, size, and orientation of orbitals
- Fourth quantum number describes electron spin about its axis
- Any spinning charge generates a magnetic field
- Spin quantum number describes direction of spin which can have only two directions:  $+1/2$  or  $-1/2$ 
  - Generally,  $+1/2$  is used as the first  $m_s$  number
- *Wolfgang Pauli* stated that only two electrons of opposite spin could occupy an orbital (known as the **Pauli exclusion principle**)
  - In other words, if two electrons are in the same energy level, the same subshell, and the same orbital, they must have opposite spins
- Thus, each orbital can hold a maximum of two electrons
  - Orbitals can also hold just one electron or no electrons, but never more than two electrons of opposite spin
- Ultimately, every electron can be described using the four quantum numbers

Name	Symbol	Allowed Values	Property
Principal (shell)	$n$	Positive integers (1, 2, 3, etc.)	Orbital size and energy level
Orbital-shape (subshell)	$l$	Integers from 0 to $n-1$	Orbital shape ( $l$ values 0, 1, 2, and 3 correspond to $s$ , $p$ , $d$ , and $f$ orbitals)
Magnetic	$m_l$	Integers from $-l$ to $+l$	Orbital orientation
Spin	$m_s$	$+1/2$ or $-1/2$	Spin orientation
<b>Adapted from:</b> Clancy, C., Farrow, K., Finkle, T., Francis, L., Heimbecker, B., Nixon-Ewing, B., Schroder, M., & Thomas, T. (2011). <i>Chemistry 12</i> . Canada: McGraw-Hill Ryerson Limited.			

## REPRESENTING ELECTRONS

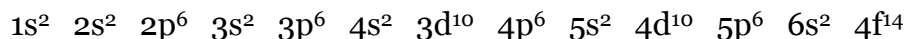
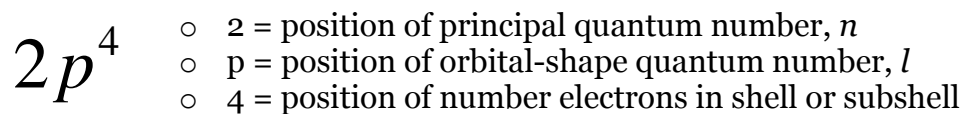
- Use knowledge of orbitals to describe the electronic nature of an element
- Two ways this is done:
  1. **Electron configuration** is a way to describe where the electrons are with respect to energy level and sublevel
  2. **Orbital diagrams** are a visual way to describe where the electrons are with respect to energy level and sublevel



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### Electron configurations

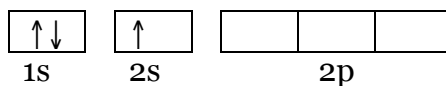
- With Bohr-Rutherford diagrams, the number of electrons in each shell could be indicated
- With electron configurations, not only can the shell electrons are located in be communicated, but also what orbitals the various electrons can be found in as well
- Drawn with atoms in their lowest possible energy levels → ground state



### Orbital diagrams

- Uses a box for each orbital in a given principal energy level
  - An empty box represents no electrons in that orbital
  - A box with a single arrow represents one electron in that orbital
  - A box with two arrows directed in opposite directions represents two electrons of opposite spin in that orbital

#### Orbital diagram for Li

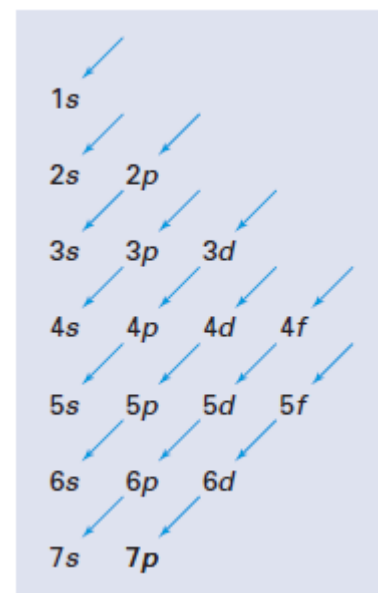


**Rules for writing electron configurations and orbital diagrams**

- Follow the **aufbau principle** which states that each electron occupies the lowest orbital available and that orbitals must be filled from lowest energy to highest energy
- Similar to Bohr-Rutherford diagrams, the first shell is filled before progressing to the second shell (it is more complicated than this)
  - Energy levels of different orbitals in different energy shells are NOT in order
- The diagonal rule is a good way to remember the order of filling orbitals from lowest energy to highest energy
- Guidelines<sup>1</sup>:
  1. Place electrons into the orbitals in order of increasing energy level.
    - a. Energy level of each (group of) orbital(s) increases across periodic table from left to right.
  2. Each set of orbitals of the same energy level must be completely filled before proceeding to the next orbital or series of orbitals.
  3. Whenever electrons are added to orbitals of the same energy sublevel, each orbital receives one electron before any pairing occurs.
    - a. Customary to fill each box from left to right.
  4. When electrons are added singly to separate orbitals of the same energy, the electrons must all have the same spin (arrows in the same direction).
- Steps 3 & 4 summarize **Hund's rule** which specifies that a ground state atom has the maximum number of *unpaired electrons* within an energy sublevel that the Pauli exclusion principle will allow
- *Condensed electron configurations* use the fact that chemical reactivity is based mainly on valence electrons
  - Use the electron configuration of the previous noble gas to summarize the electron configuration up to that point → place the atomic symbol for previous noble gas in square brackets
  - Add in the remainder of the electron configuration as per the guidelines
  - Carbon's electron configuration of  $1s^2 2s^2 2p^2$  becomes  $[\text{He}] 2s^2 2p^2$  where  $[\text{He}]$  represents  $1s^2$
  - Aluminum's electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^1$  becomes  $[\text{Ne}] 3s^2 3p^1$  where  $[\text{Ne}]$  represents  $1s^2 2s^2 2p^6$

<sup>1</sup> **Adapted from:** Clancy, C., Farrow, K., Finkle, T., Francis, L., Heimbecker, B., Nixon-Ewing, B., Schroder, M., & Thomas, T. (2011). *Chemistry 12*. Canada: McGraw-Hill Ryerson Limited.

- For period 1 & 2:
  - Use the guidelines stated above to create electron configurations and orbital diagrams
- For period 3:
  - *d* orbitals have an energy level between the *s* and *p* orbitals of the next energy level
  - No *d* orbitals are filled in period 3
- For period 4:
  - *3d* orbitals are filled after *4s* orbitals are filled, but before *4p* orbitals receive electrons
- *s*-block elements consist of group 1 and 2 elements and spans 2 groups
- *p*-block elements consist of groups 13 to 18 elements and spans 6 groups
- *d*-block elements consist of groups 3 to 12 elements and spans 10 groups
- *f*-block elements consist of inner transition elements (lanthanide and actinide series) and spans 14 groups



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1 (IA)	2 (IIA)											13 (IIIA)	14 (IVA)	15 (VA)	16 (VIA)	17 (VIIA)	18 (VIIIA)				
1 <b>1s</b>																					
2 <b>2s</b>														<b>2p</b>							
3 <b>3s</b>															<b>3p</b>						
4 <b>4s</b>															<b>4p</b>						
5 <b>5s</b>	3 (IIIB)														<b>5p</b>						
6 <b>6s</b>						<b>4f</b>							<b>6p</b>								
7 <b>7s</b>						<b>5f</b>															
<b>s block</b> (main group elements)		<b>f block</b> (inner transition elements)										<b>d block</b> (transition elements)						<b>p block</b> (main elements)			

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### Atomic radii (AR)

- *Half the distance between nuclei of two adjacent atoms*
- Determined by measuring distance between radii of atoms bonded together
- Two factors affect *AR*:
  - Higher  $n$  values equate to larger volumes for orbitals which result a greater chance of finding electrons further from the nucleus and thus a larger  $AR$
  - Effective nuclear charge ( $Z_{\text{eff}}$ ) is the net force of attraction between electrons and nucleus
  - Only sole electron in hydrogen experiences full attraction of its nucleus – all other atoms have electrons that experience shielding from other electrons in the same atom
  - Lower  $Z_{\text{eff}}$  values equate to reduced attraction to nucleus resulting in larger  $AR$

***Ionization energy (IE)***

- *Energy needed to remove an electron from ground-state atom in gaseous state*
- Needed to overcome force of attraction exerted on electron by nucleus
- Can have more than one *IE* for multi-electron atoms
  - Each successive *IE* is greater than the previous *IE* because the electron must be removed from a positively charged ion
- Atoms with low first *IE* tend to form cations
- Atoms with high first *IE* tend to form anions
- As atomic radius increases, distance of valence electrons from nucleus increases, force of attraction exerted by nucleus decreases, less energy needed to remove one electron
- Within a period, first *IE*'s generally increase from left to right because  $Z_{\text{eff}}$  increases from left to right
- Some variations/exceptions to general trends (EX: B, Al, O, S)

***Metallic character***

- Generally, chemical reactivity of metals increases down a group
- Generally, chemical reactivity of metals increases from right to left across a period

***Electron affinity (EA)***

- *Energy change resulting from adding an electron to an atom in the gaseous state*
- Large negative numbers = high *EA*
- Small negative numbers and positive numbers = low *EA*
- Influenced by *AR* and *IE*
- Three general trends:
  - Reactive non-metals: Group 17 (lesser degree Group 16); high *IE*; high *EA*; lots of energy needed to remove electrons; strong attraction for electrons; form negative ions in ionic compounds
  - Reactive metals: Group 1 & 2; low *IE*; low *EA*; give up electrons easily; poor attraction for electrons; form positive ions in ionic compounds
  - Noble gases: Group 18; very high *IE*; very low *EA*; do not give up, gain, or share electrons

[scan images from P. 189-192]

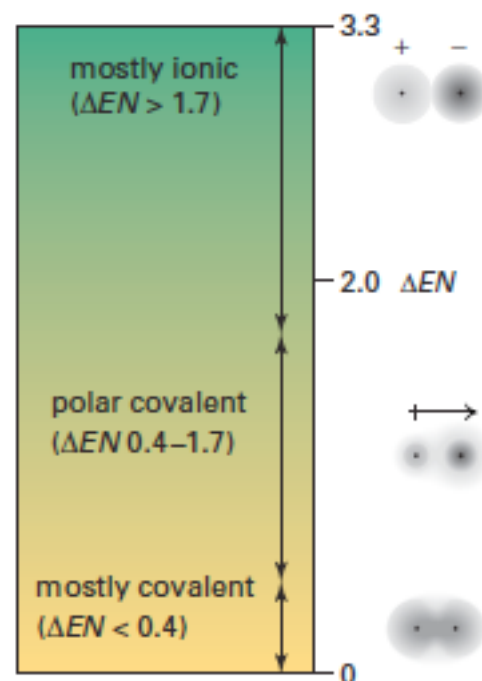
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**CHEMICAL BONDING*****Electronegativity (EN)***

- Relative ability of an atom to attract shared electrons in a bond
- Higher *EN* = greater ability to attract electrons shared in a bond
- *EN* decreases moving down a group
- *EN* increases moving left to right across a period
- These are trends, not rules



- Difference in electronegativity ( $\Delta EN$ ) reveals characteristics of bond formed
  - If  $\Delta EN$  is large, atom with higher  $EN$  will pull electrons away from atom with lower  $EN$  = mostly ionic bond
    - Some sharing of electrons, but generally these compounds behave like ionic compounds
    - **Range of 0.0 – 0.4**
  - If  $\Delta EN$  is (nearly) equal, atoms will share electrons equally = mostly covalent bond
    - Electrons are almost equally shared by two atoms
    - Also referred to as non-polar covalent bond
    - **Range of 1.7 – 3.3**
  - If  $\Delta EN$  is intermediate, atoms will share electrons unequally (atom with high  $EN$  will pull electrons into its space for majority of time) = polar covalent bond
    - Some ionic character
    - Generally behave like molecular compounds
    - Bond is polar = has a positive end and a negative end
    - An arrow is placed with diagrams to indicate slightly negative end (arrow head) and slightly positive end (arrow tail with a plus sign) of a bond
    - A delta sign ( $\delta$ ) with a + or a – is used to indicate that the charge at either end of a polar covalent bond is between 0 and 1
    - **Range of 0.4 – 1.7**
- A “continuum of sharing” exists ranging from equal sharing to minimal sharing of electrons
- No natural cut-off point to distinguish ionic bonding, covalent bonding, and polar covalent bonding
  - Scientists have chosen arbitrary  $\Delta EN$  values that define categories of bond types



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### ***Metallic bonding & properties of metals/alloys***

- Metals attract electrons so weakly that solid and liquid metals have valence electrons that can move freely from one atom to another (not associated with one particular atom) = **delocalized**
- **Electron-sea model** of metals stipulates:
  - Ordered array of cations
  - A “sea” of freely moving electrons
  - Positively charged ions all attracted to many electrons in the “sea” simultaneously
- Made up of aggregates of millions of tiny crystals = **grains**
  - Grains range in size from nanometers to millimeters (depends on metal and conditions of formation)
  - Atoms making up grains are in precise and regular repeating patterns
  - Atoms at boundaries are arranged randomly
- **Melting & boiling points (MP & BP):**
  - Higher MP's & BP's = large amount of kinetic energy needed to pull particles apart

- MP decreases down Group 1
  - Increased distance of valence electrons from nucleus = decrease in attractive forces
- MP increases left to right across a period (for first few metals)
  - Increased positive charge in nucleus + increased electrons in “sea” = increase in attractive forces
- *Electrical & thermal conductivity:*
  - Good electrical conductors
    - Electrons free to move in “sea” = electrons attracted to positive end and repelled from negative end
  - Good thermal conductors
    - Electrons free to move in “sea” = easily pass kinetic energy along from heat source
- *Malleability & ductility:*
  - Metals are malleable (can be hammered into a sheet) and ductile (can be stretched into a wire)
  - Due to electron-sea model – when metals are hammered into a sheet, cations slide past each other because their environment does not change as they are still surrounded by delocalized electrons
- *Alloys:*
  - Solid mixture of two or more different types of metal atoms
  - Electron-sea model → electrons in “sea” can be attracted to any cation so different metals can be held in same “sea”
  - Two types of alloys:
    - If atoms of a second metal take the place of the first metal, result is a **substitutional alloy**
    - If atoms of a second metal fit in space between atoms of first metal, result is an **interstitial alloy**

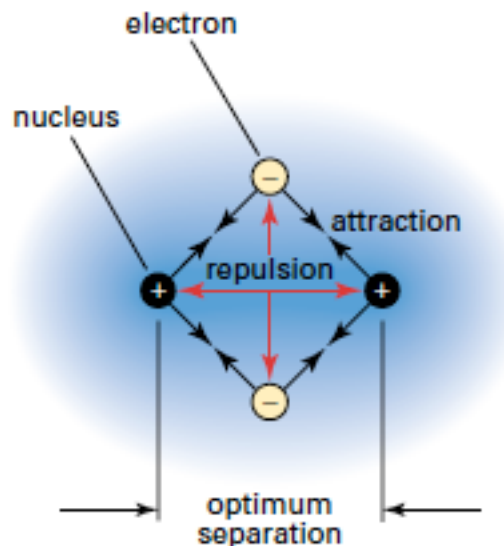
### ***Ionic bonding & properties of ionic compounds***

- Small degree of electron sharing, but essentially one atom loses one or more valence electrons and another atom gains one or more electrons
- Can demonstrate this using:
  - Electron configurations
  - Orbital diagrams
  - Lewis diagrams
- Ionic solids exist in a 3D pattern of alternating positive and negative charges called a **crystal lattice**
- **Lattice energy** is energy released when an ionic crystal forms from gaseous ions of its elements
- Each cation is attracted to multiple anions simultaneously and each anion is attracted to multiple cations simultaneously
- Creates a ratio between two types of atoms
- Smallest whole number ratio of ions in a crystal is a **formula unit**
- Smallest group of ions in a crystal where pattern is repeated is a **unit cell**
- Shape of ionic crystals varies and depends on relative size and charges of ions
- *Melting & boiling points (MP & BP):*
  - Generally high MP's
  - Increase as charge(s) of one or both ions increases

- Larger charges create much stronger attractive forces between ions
  - Increases as radius of one or both ions decreases
    - Ions can pack closer together
- **Solubility:**
  - To be soluble in water, attractive forces between water and ions must be able to overcome attractive forces between ions
- Ionic compounds are generally not malleable or ductile
  - If ions are rearranged, new alignment could cause like charges to be adjacent and thus repel each other
  - Hard but brittle
- **Conductivity:**
  - Ionic solids are poor conductors of electricity and heat
  - When placed in water, ionic solids are good conductors
    - Ions themselves move and carry charge (as opposed to in metals where only electrons carry charge)

### Covalent bonding & types of hybridization

- Involves sharing of pairs of electrons
  - **Shared pair** of electrons helps fill valence shell of TWO atoms simultaneously
  - **Lone pairs** of electrons exist where a pair of electrons from one atom is not involved in bonding
- Balance of nucleus-electron attractions, nucleus-nucleus repulsions, and electron-electron repulsions
  - Results in (1) optimum separation distance, (2) pair of electrons shared, (2) achieving a minimum energy for system, and (4) **creating a new orbital** (by overlapping existing orbitals) with lower energy levels than original orbitals
- Generally atoms want to find a noble gas configuration
- If two atoms share one pair of electrons, a **single bond** is formed
- If two atoms share two pairs of electrons, a **double bond** is formed
- If two atoms share three pairs of electrons, a **triple bond** is formed
- **Bond energy** is energy required to break force of attraction between two atoms in a bond and separate the atoms
- **Properties:**
  - Exist as a soft solid, liquid, or gas at room temperature
  - Low MP's and BP's
  - Poor conductors of electricity (even in solution)
  - Generally not soluble in water (many exceptions like *acetone*)
- An **allotrope** is one of two or more compounds consisting of the same element but having different physical properties



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- Form as a result of a variety of patterns of covalent bonds between atoms
- **Network solids** are substances where all atoms are covalently bonded together in a continuous 2D or 3D array with no natural beginning or end

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## LEWIS STRUCTURES

### ***Octet & duet rule***

- **Octet rule:** observation that atoms of nonmetals tend to form most stable molecules when they are surrounded by eight electrons (to fill their valence orbitals)
- **Duet rule:** similar to octet rule, but for period 1 elements (H & He), valence shell can only hold two electrons
- Some rules for writing Lewis structures<sup>2</sup>:
  - Sum valence electrons from all atoms
    - Which electrons come from which atoms is unimportant
    - *Total* number of electrons is important
  - Use a pair of electrons to form a bond between each pair of bound atoms
  - Arrange remaining electrons to satisfy duet rule for H and octet rule for second-row elements
  - Generally, least EN element is placed in middle
  - Do NOT forget to include *lone pairs of electrons*
- **Co-ordinate covalent bond:** bond where one atom contributes both electrons to shared pair

### ***Exceptions to octet rule***

- Some elements do not obey octet rule
  - EX: BF<sub>3</sub>, SF<sub>6</sub>, PCl<sub>5</sub>
- Elements that do not have full valence shell when forming compounds are highly reactive
- Elements in period 3 and below on periodic table have access to *d* orbitals and can access them if needed giving these atoms more than 8 electrons in their valence shell
- Some additional rules for writing Lewis structures<sup>3</sup>:
  - Second-row elements C, N, O, and F always obey octet rule
  - Second-row elements B and Be often have fewer than eight electrons when found in compounds
    - These compounds are highly reactive
  - Second-row elements never exceed octet rule
    - Their valence orbitals (*2s* and *2p*) can accommodate only eight electrons
  - Third-row (and heavier) elements often satisfy octet rule, BUT can exceed octet rule by using their empty valence *d* orbitals
    - Their valence orbitals (*3s*, *3p* and *3d*) can accommodate more than eight electrons
  - When writing Lewis structures, satisfy octet rule for atoms first
    - If electrons remain after octet rule has been satisfied, place additional (pairs of) electrons on elements having available *d* orbitals

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<sup>2</sup> **Adapted from:** Zumdahl, S., & Zumdahl, A. (2000). *Chemistry*. (5th ed.). Boston: Houghton Mifflin Company.

<sup>3</sup> **Adapted from:** Zumdahl, S., & Zumdahl, A. (2000). *Chemistry*. (5th ed.). Boston: Houghton Mifflin Company.

## Resonance

- Sometimes more than one valid Lewis structure can be drawn for a particular molecule
  - **EX:** SO<sub>2</sub>, NO<sub>3</sub><sup>-</sup>
- Draw all versions of molecule
- Actual structure is an average of the three resonance structures = *resonance hybrid*

## Formal charge (FC)

- Difference between number of valence electrons on free atom and number of valence electrons assigned to atom in molecule
  - **EX:** SO<sub>4</sub><sup>2-</sup>
- **Formal charge = (# of valence electrons on free atom) – (# of valence electrons assigned to atom in molecule)**
  - # of valence electrons assigned to atom in molecule = (# of electrons in lone pairs) + (HALF # of electrons in shared pairs)
    - Lone pair electrons belong entirely to atom in question
    - Shared electrons are *divided equally* between two sharing atoms
- Atoms in molecules try to achieve *FC* as close to zero as possible
- Any negative *FC* are expected to reside on most electronegative atoms
- Some rules for governing<sup>4</sup>:
  - To calculate *FC* on an atom:
    - Sum lone pair electrons and one-half shared electrons = valence electrons assigned to atom in molecule
    - Subtract number of assigned electrons from number of valence electrons on free, neutral atom = formal charge
  - Sum of all *FC*'s in a molecule/ion must equal overall charge on molecule/ion
  - If nonequivalent Lewis structures exist for a species, those with formal charges closest to zero and with any negative *FC*'s on most EN atom are considered to best describe bonding in molecule/ion

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## VSEPR THEORY & HYBRIDIZATION

### VSEPR

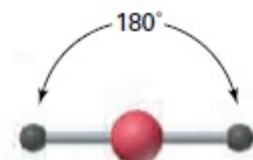
- 3D shapes of molecules affects physical and chemical properties
- A **bond angle** is the angle formed between nuclei of two atoms that surround central atom of a molecule
- **Valence-shell electron-pair repulsion (VSEPR) theory** proposes that particular 3D arrangements of electron group around a central atom is based on repulsions between electron groups and is used to predict molecular shapes
  - First developed in mid-1950's by Ronald Gillespie who was a professor of chemistry at McMaster University in Hamilton, Ontario
- Electron groups around an atom orientate themselves as far apart from each other to minimize repulsion forces
  - Electron group = single bond (SB), double bond (DB), triple bond (TB), or lone pair (LP)

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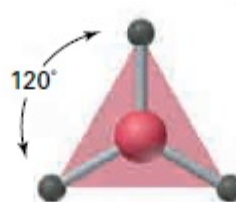
<sup>4</sup> **Adapted from:** Zumdahl, S., & Zumdahl, A. (2000). *Chemistry*. (5th ed.). Boston: Houghton Mifflin Company.

- Five basic geometric arrangements and each bar in these arrangements represents an electron group<sup>5</sup>:

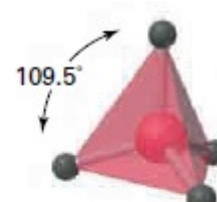
- A = central atom, X = surrounding atoms, E = lone electron pairs
- **Linear** = one central atom and two electron groups



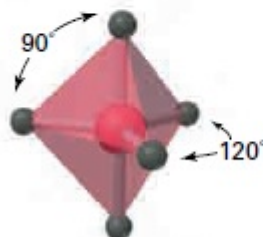
linear



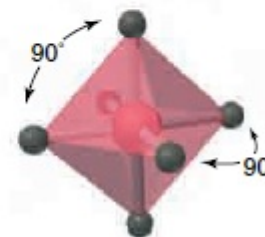
trigonal planar



tetrahedral



trigonal bipyramidal



octahedral

**Adapted from:** Clancy, C., Farrow, K., Finkle, T., Francis, L., Heimbecker, B., Nixon-Ewing, B., Schroder, M., & Thomas, T. (2011). *Chemistry 12*. Canada: McGraw-Hill Ryerson Limited.

- Bonding pairs at opposite ends of a straight line; results in a linear molecule with bond angles of  $180^\circ$
    - $AX_2$
  - **Trigonal planar** = one central atom and three electron groups
    - Three bonds point to corners of an equilateral triangle; atoms are in same plane; bond angles of  $120^\circ$
    - $AX_3, AX_2E$
  - **Tetrahedral** = one central atom and four electron groups
    - Four faces or sides to molecule; form a regular tetrahedron with bond angles of  $109.5^\circ$
    - $AX_4, AX_3E, AX_2E_2$
  - **Trigonal bipyramidal** = one central atom and five electron groups
    - Five bonds extend from central atom generating two three-sided pyramids joined at common triangular base
    - $AX_5, AX_4E, AX_3E_2, AX_2E_3$
  - **Octahedral** = one central atom and six electron groups
    - Central atom is at a common square base; surrounding atoms extend to six corners that generate two square pyramids with a common base
    - $AX_6, AX_5E, AX_4E_2$
- Geometric arrangements are determined by the number of electron groups surrounding central atom
    - Molecular shapes are determined by number of atoms surrounding central atom (a subset of geometric arrangement)
  - Lone pairs of electrons occupy more space than bonding pairs of electrons
    - Replacing a bonding pair of electrons with a lone pair of electrons pushes remaining bonding pairs closer together, decreasing bond angles

<sup>5</sup> **Adapted from:** Clancy, C., Farrow, K., Finkle, T., Francis, L., Heimbecker, B., Nixon-Ewing, B., Schroder, M., & Thomas, T. (2011). *Chemistry 12*. Canada: McGraw-Hill Ryerson Limited.

[scan P. 234 and other images of orbital diagrams]

- Three different types of repulsion forces within a molecule:
  - Between two bonding pairs (BP-BP)
  - Between a bonding pair and a lone pair (LP-BP)
  - Between two lone pairs (LP-LP)
- $LP-LP > LP-BP > BP-BP$
- VSEPR guidelines for predicting molecular shape<sup>6</sup>:
  - Draw Lewis structure of molecule, considering only electron pairs around central atom
  - Count total number of electron groups around central atom
    - Account for any charge for ions
    - Treat double and triple bonds as though they were a single electron group
  - Predict which geometric arrangement best accommodates total number of electron groups
  - Predict shape of molecule based on positions occupied by electron groups and lone pairs
  - Remember that a lone pair of electrons repels another electron group more strongly than a bonding pair
    - Difficult to accurately predict bond angles when central atom possesses one or more lone pairs of electrons

### Hybridization

- **Valence bond theory (VB)** is a quantum mechanically based theory that explains covalent bond formation and molecular shapes based on orbital overlap
- **Molecular orbital theory (MO)** is a quantum mechanically based theory that explains covalent bond formation and molecular shapes based on the formation of new molecular orbitals
- Employ one or the other depending on problem trying to explain
- Three general principles to applying VB:
  - Region of orbital overlap has a maximum of two electrons; electrons have opposite spins
  - Should be maximum orbital overlap
    - Greater orbital overlap = stronger and more stable bond
    - Extent of overlap depends on shapes and directions of orbitals involved
  - To explain observed molecular shapes, concept of atomic orbital hybridization is used
    - Involves combining/mixing atomic orbitals to produce new atomic orbitals
- **Hybrid orbitals** are orbitals formed by combining two or more orbitals in valence shell of an atom
- *Single bonds*:
  - New molecular orbital that forms creates a bond called a **sigma bond ( $\sigma$ )**
  - Can rotate bond around its axis and nothing would change
  - Lower energy than s orbitals involved
  - Single bonds involve one  $\sigma$  bond
  - EX:  $CH_4$

<sup>6</sup> **Adapted from:** Clancy, C., Farrow, K., Finkle, T., Francis, L., Heimbecker, B., Nixon-Ewing, B., Schroder, M., & Thomas, T. (2011). *Chemistry 12*. Canada: McGraw-Hill Ryerson Limited.

- *Double bonds:*
  - Only one sigma bond can form between two atoms
  - If additional bonds are needed between two atoms, a **pi bond ( $\pi$ )** forms
  - A pi bond involves the two lobes of an unhybridized orbital overlapping on opposite sides of a sigma bond
  - Double bonds involve one  $\sigma$  bond and one  $\pi$  bond
  - EX:  $C_2H_4$
- *Triple bonds*
  - Triple bonds involve one  $\sigma$  bond and two  $\pi$  bonds
  - EX:  $C_2H_2$
- Hybridization occurs in many different elements
- Name of hybrid orbitals indicates type and number of atomic orbitals that have combined
- Number of hybrid orbitals that form = number of atomic orbitals that combined to make the hybrid orbitals
- Guidelines for predicting hybridization of central atom<sup>7</sup>:
  - Draw Lewis structure of molecule
  - Predict overall arrangement of electron groups using VSEPR model
  - Deduce hybridization of central atom by matching arrangement of electron pairs with those of hybrid orbitals

[scan P. 237 and other hybridization images]

## POLARITY

- When two atoms bond, sharing of a pair of electrons can be non-polar, polar, or ionic
- When bonding is non-polar, a **bond dipole** is created where the more electronegative atom has a partial negative charge and the less electronegative atom has a partial positive charge
- Polarity of a molecule must consider:
  - Shape of molecule
  - Polarity of all bonds
  - Orientation of all electron groups and atoms
  - EX:  $H_2O$ ,  $CO_2$ ,  $CCl_4$ ,  $CHCl_3$
- Symmetry helps to determine polarity of complex molecules

[scan P. 239, table 4.7]

<sup>7</sup> **Adapted from:** Clancy, C., Farrow, K., Finkle, T., Francis, L., Heimbecker, B., Nixon-Ewing, B., Schroder, M., & Thomas, T. (2011). *Chemistry 12*. Canada: McGraw-Hill Ryerson Limited.



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**INTERMOLECULAR FORCES**

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- **Intramolecular forces** are forces exerted within a molecule or polyatomic ion
  - Influence chemical properties of substances
- **Intermolecular forces** are forces exerted between molecules and/or polyatomic ions
  - Influence physical properties of substances
  - Forces of attraction and repulsion between molecules
- Intermolecular forces are grouped into four categories:
  - Dipole-dipole forces
  - Ion-dipole forces
  - Dipole-induced dipole forces
  - Dispersion forces
- Dipole-dipole, ion-dipole, and dipole-induced dipole forces are collectively referred to as **van der Waals forces**
- *Dipole-dipole forces*
  - Attraction between opposite partial charges of polar molecules
  - Polar molecules are more attracted to each other than similarly-sized non-polar molecules
  - Contribute to higher melting and boiling points in polar molecules
  - **Hydrogen bonding** is a special type of dipole-dipole interactions
    - Involves hydrogen bonding to oxygen or nitrogen
    - Hydrogen when bonded is almost a bare positive nucleus
    - Oxygen and nitrogen have lone pairs of electrons which enhance attractive force
    - Creates dipole-dipole interactions
- *Ion-dipole forces*
  - Attraction between partial charges of polar molecules and ions
  - Can occur between:
    - Polar molecule and cation
    - Polar molecule and anion
  - Cations are usually smaller than anions
  - Generally, cations interact more strongly with dipoles than anions of the same magnitude
  - Hydration involves an ion being surrounded by multiple water molecules arranged in a particular manner
- *Induced dipole forces*
  - *Dipole-induced dipole forces*: attraction between a polar molecule and a temporary dipole of a non-polar molecule
  - *Ion-induced dipole forces*: attraction between an ion and a temporary dipole of a non-polar molecule
  - Electrons in atoms are in constant motion
  - Possible to induce formation of dipoles in non-polar molecules
  - After dipole is induced, two molecules are attracted to each other
- *Dispersion forces (London forces)*
  - Weak attraction between all molecules, including non-polar molecules, due to temporary dipoles
  - Occur because non-polar molecules spontaneously form temporary dipoles
    - For an instant, distribution of electrons can become distorted so that one point in a molecule is very slightly positive and another point is slightly negative

- Two factors influence these forces:
  - Mass: attraction becomes larger as mass of molecules becomes larger
  - Shape: attraction becomes larger as surface area of contact between molecules becomes larger
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**VOCABULARY**

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**Nuclear model**

A model of the atom in which electrons move around an extremely small, positively charged nucleus; also called a *planetary model*

**Electromagnetic radiation**

Oscillating, perpendicular electric and magnetic fields moving through space as waves

**Frequency**

The number of wave cycles that pass a given point in a unit of time

**Photon**

A packet, or quantum, of electromagnetic energy

**Emission spectrum (line spectrum)**

A series of separate lines of different colours of light emitted by atoms of a specific element as they lose excitation energy

**Quantum (plural quanta)**

An indivisible packet of energy that must be absorbed or emitted in an “all or none” manner

**Quantum mechanical model of the atom**

The atomic model in which electrons are treated as having wave characteristics

**Heisenberg uncertainty principle**

A principle stating that it is impossible to simultaneously know the exact position and speed of a particle

**Atomic orbital**

A region in space around a nucleus that is related to a specific wave function

**Quantum numbers**

Integers arising from the solutions to the wave equation that describe specific properties of electrons in atoms

**Principal quantum number,  $n$** 

A positive whole number (integer) that indicates the energy level and relative size of an atomic orbital

**Shell**

The main energy level associated with a given value of  $n$  (the principal quantum number)

**Orbital-shape quantum number,  $l$** 

An integer that describes the shape of atomic orbitals within each principal energy level

**Sublevel**

The energy subshell associated with a given value of  $l$  (the orbital-shape quantum number)

**Magnetic quantum number,  $m_l$** 

An integer that indicates the orientation of an orbital in the space around the nucleus of an atom

**Spin quantum number,  $m_s$** 

The quantum number that specifies the orientation of the axis on which the electron is spinning

**Pauli exclusion principle**

A principle that states that a maximum of two electrons can occupy an orbital, and that the electrons must have opposite signs [spin directions]

**Electron configuration**

A shorthand notation that shows the number and arrangement of electrons in an atom's orbitals

**Orbital diagram**

A diagram that uses a box for each orbital in any given principal energy level

**Aufbau principle**

A principle underlying an imaginary process of building up the electronic structure of the atoms, in order of atomic number

**Hund's rule**

A rule stating that the lowest energy state for an atom has the maximum number of unpaired electrons allowed by the Pauli exclusion principle in a given energy sublevel

**Atomic radius**

Half the distance between the nuclei of two adjacent atoms; for metals, between atoms in a crystal, and for molecules, between atoms chemically bonded together

**Ionization energy**

The energy required to remove an electron from a ground-state atom in the gaseous state

**Electron affinity:**

A change in energy that accompanies the addition of an electron to an atom in the gaseous state

**Electronegativity**

The relative ability of the atoms of an element to attract shared electrons in a chemical bond

**Delocalized**

As applied to the electron-sea model of metals, describes valence electrons that are not associated with a specific atom but move among many metal ions

**Electron-sea model of metals**

A model of metallic bonding that proposes that the valence electrons of metal atoms move freely among the ions, thus forming a "sea" of delocalized electrons that hold the metal ions rigidly in place

**Alloy**

A solid mixture of two or more different types of metal atoms

**Formula unit**

The smallest ratio of ions in a crystal

**Valence bond theory**

A quantum mechanically based theory that explains covalent bond formation and molecular shapes based on orbital overlap

**Molecular orbital theory**

A quantum mechanically based theory that explains covalent bond formation and molecular shapes based on the formation of new molecular orbitals

**Hybrid orbital**

An orbital that is formed by the combination of two or more orbitals in the valence shell of an atom

**Allotrope**

One of two or more compounds consisting of the same element but having different physical properties

**Network solid**

A substance in which all atoms are covalently bonded together in a continuous two- or three-dimensional array; no natural beginning or end exists

**Co-ordinate covalent bond**

A covalent bond in which one atom contributes both electrons to the shared pair of electrons

**Expanded valence (expanded octet)**

A valence energy level of a central atom that has more than eight electrons

**Resonance structure**

One of two or more Lewis structures that show the same relative position of atoms but different positions of electron pairs

**Bond angle**

The angle formed between the nuclei of two atoms that surround the central atom of a molecule

**Valence-shell electron-pair repulsion (VSEPR) theory**

A theory that proposes particular three-dimensional arrangements of electron groups around a central atom based on repulsions between the electron groups; a model used to predict molecular shapes

**Bond dipole**

Polar covalent bonds that have a positive pole and a negative pole

**Intramolecular force**

A force that holds atoms or ions together; in metals, a force between metal cations and free electrons; forms the basis of chemical bonding

**Intermolecular force**

A force that exists between ions and molecules to influence the physical properties of substances

**Dipole-dipole force**

An intermolecular attraction between opposite partial charges of polar molecules

**Ion-dipole force**

An intermolecular attraction between partial charges of polar molecules and ions

**Dipole-induced dipole force**

An intermolecular attraction due to the distortion of electron density of a non-polar molecule by a nearby polar molecule; a force of attraction between a polar molecule and a temporary dipole of a non-polar molecule

**Ion-induced dipole force**

An intermolecular attraction due to the distortion of electron density of a non-polar molecule caused by a nearby ion; a force of attraction between an ion and a temporary dipole of a non-polar molecule

**Dispersion (London) force**

A weak intermolecular attraction between all molecules, including non-polar molecules, due to temporary dipoles