University Physics with Modern Physics - Modern Physics by Young and Freedman Notes

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Contents

17 Temperature and Heat

17.1 Temperature and Thermal Equilibrium

- The **zeroth law of thermodynamics** states: If C is initially in thermal equilibrium with both A and B, then A and B are also in thermal equilibrium with each other.

- Two systems are in thermal equilibrium iff they have the same temperature.

17.2 Thermometers and Temperature Scales

- Water freezes at $0°$C or $32°$F and boils at $100°$C or $212°$F.

- A temperature measurement is denoted $x°$C ("x degrees Celsius") whereas a temperature interval is denoted xC$°$ ("x Celsius degrees").

17.3 Gas Thermometers and the Kelvin Scale

- Under the **Kelvin** temperature scale temperature differences are equal to those of the degrees Celsius scale, but the zero is equal to $-273.15°$C. This is known as **absolute zero** where molecules have their lowest possible kinetic and potential energies.

- The ratio of two temperatures in the Kelvin scale equals the ratio of the corresponding pressures in a constant-volume gas thermometer

$$\frac{T_2}{T_1} = \frac{p_2}{p_1}.$$

17.4 Thermal Expansion

- Materials expand when their temperatures increase.

- Expansion in a single dimension is described by the equation

$$\Delta L = \alpha L_0 \Delta T$$

where ΔL is the change in length, α is the **coefficient of linear expansion**, L_0 is the original length, and ΔT is the change in temperature.

- Expansion in three dimensions (volume expansion) is described by the equation
$$\Delta V = \beta V_0 \Delta T$$

where ΔV is the change in volume, β is the **coefficient of volume expansion** (equal to 3α), V_0 is the original volume, and ΔT is the change in temperature.

- If the ends of a material are fixed in place, changes in temperature can induce **thermal stresses** that can damage the material. The magnitude of these stresses is given by

$$\frac{F}{A} = -Y\alpha\Delta T.$$

17.5   Quantity of Heat

- Energy transferred as a result of a temperature difference is called **heat**.

- The **specific heat** of a material is the amount of energy required to raise the temperature of one unit of mass of the material by one unit of temperature, e.g. $1\,\text{kg}$ by $1\,\text{K}$. It has units like $\text{J}/(\text{kg K})$.

- The specific heat of water is

$$4190\,\text{J}/(\text{kg K}) \text{ or } 1\,\text{cal}/(\text{g C}^\circ).$$

- The energy required to change the temperature of a material is given by

$$Q = mc\Delta T$$

where m is the mass of the material, c is its specific heat, and ΔT is the change in temperature.

- The **molar mass** of a substance is the mass of one mole.

- The total mass of a material m is equal to the mass per mole M times the number of moles n

$$m = nM.$$

- The energy required to change the temperature of a certain number of moles of a substance is

$$Q = nC\Delta T$$

where $C = Mc$ is the **molar heat capacity**.

17.6   Calorimetry and Phase Changes

- A **phase** is a specific state of matter, e.g. solid, liquid, or gas.

- A **phase change** or **phase transition** is a transition from one phase to another.

- For a given pressure, phase change takes places at a definite temperature.

- While a substance is undergoing a phase change, any added or removed energy will affect the progress of the phase change but won't change the temperature.

Phase **of water changes.** During these periods, temperature stays
constant and the phase change proceeds as heat is added: $Q = +mL$.

T (°C)

Ice melts to
liquid water
at 0°C.

Liquid water vaporizes
to steam at 100°C.

f

125

100

d

Boiling
point

75

50

$a \rightarrow b$: Ice initially at −25°C is
warmed to 0°C.

25

$b \rightarrow c$: Temperature remains at 0°C
until all ice melts.

0

b

c

e

Melting
point

$c \rightarrow d$: Water is warmed from 0°C
to 100°C.

−25

a

Time

$d \rightarrow e$: Temperature remains at
100°C until all water vaporizes.

Ice warms.

Liquid water warms.

Steam warms.

$e \rightarrow f$: Steam is warmed to
temperatures above 100°C.

Temperature **of water changes.** During these periods, temperature
rises as heat is added: $Q = mc \Delta T$.

- The heat transfer required for a material to undergo a phase change is
  given by

$$Q = \pm mL$$

where the $\pm$ indicates that heat may need to be added or removed depend-
ing on the direction of the phase change (e.g. energy must be added to
melt ice), m is the mass of the material, and L is the latent heat associated
with the phase change.

- When a material is freezing or melting, $L = L_f$ the **latent heat of fusion**.

- When a material is condensing or vaporising, $L = L_v$ the **latent heat of
  vaporisation**.

- When a material sublimates (changes directly from a solid to a gas, skip-
  ping liquid) or deposits/desublimates (changes directly from a gas to a
  solid, skipping liquid), $L = L_s$ the **latent heat of sublimation**.

- When a material burns, $L = L_c$ the **latent heat of combustion**.

- For any given material at any given pressure, the freezing temperature is
  the same as the melting temperature. This is called **phase equilibrium**.
  Similarly the condensing temperature is the same as the vaporisation tem-
  perature.

17.7   Mechanisms of Heat Transfer

- **Conduction** is a mechanism of heat transfer where the molecules in an
  area of high temperature have greater kinetic energy, they bump neigh-
  boring molecules which increases their kinetic energy, and so on spreading
  the heat through the material.

- The direction of heat flow is always from higher to lower temperature.

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- When a quantity of heat dQ is transferred through a material in time dt we say the rate of heat flow or the **heat current** is

$$H = \frac{dQ}{dt}.$$

- If a rod has cross sectional area A, length L, one end is held at temperature T_H, and the other is held at T_C where $T_H > T_C$, the heat current is

$$H = \frac{dQ}{dT} = kA\frac{T_H - T_C}{L}$$

  where k is the **thermal conductivity** of the material and $(T_H - T_C)/L$ is the temperature difference per unit length or the magnitude of the **temperature gradient**.

- **Convection** is the transfer of heat by mass motion of fluid from one region of space to another, e.g. ducted cooling/heating. If the fluid is circulated by a blower or a pump the process is called **forced convection**; if the flow is caused by differences in density due to thermal expansion, such as hot air rising, the process is called **free convection**.

- **Radiation** is the transfer of heat by electromagnetic waves such as visible light, infrared, and ultraviolet radiation.

- The wavelength of the radiation depends on temperature. At $20\,^\circ$C the radiation is infrared. At $800\,^\circ$C the radiation is red. At $3000\,^\circ$C the radiation is white.

- The **Stefan-Boltzmann law** gives the rate of energy radiation from a surface

$$H = Ae\sigma T^4$$

  where A is its surface area, e is a dimensionless constant between 0 and 1 called the **emissivity** of the surface (1 would be a perfect radiator), σ is the **Stefan-Boltzmann constant**

$$\sigma = 5.670\,374\,42 \times 10^{-8}\,\mathrm{W/(m^2\,K^4)},$$

  and T is the temperature in Kelvin.

- An object's surroundings also emit radiation which is absorbed by the object. The net heat current from the object is this

$$H = Ae\sigma(T^4 - T_s^4)$$

  where T_s is the temperatue of the surroundings. At thermal equilibrium there is no heat flow.

- An object that is a good absorber must also be a good emitter. An ideal radiator with $e = 1$ is also an ideal absorber, absorbing all the raditation that hits it. Such a surface is called an **ideal black body** or a **blackbody**.

18 Thermal Properties of Matter

18.1 Equations of State

- Quantities such as pressure, volume, temperature, and amount of substance are called **state variables**.

- An equation that relates state variables is called an **equation of state**.

- Molar mass (i.e. the mass of one mole of a substance) is sometimes called **molecular weight**.

- The **ideal gas equation** relates the absolute pressure p, volume V, number of moles n, and absolute temperature (in Kelvin) T

$$pV = nRT$$

  or

$$pV = \frac{m_{\text{total}}}{M} RT$$

  or

$$pV = NkT$$

  where R is the gas constant

$$R = 8.314 \, \text{J}/(\text{mol K}).$$

- If the amount of a gas is contant, i.e. nR is constant, then

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} = \text{constant}.$$

- **Standard temperature and pressure** (STP) is defined as $0\,^{\circ}\text{C}$ and $1\,\text{atm}$.

- The **van der Waals** equation extends the ideal gas law to account for the effects of interactions between gas molecules and their finite size

$$\left(p + \frac{an^2}{V^2} \right) (V - nb) = nrT$$

  where a and b are constants that vary between gases, a depends on the strength of attractive forces between the molecules, and b depends on the volume of the molecules.

- A pV-diagram is a two-dimensional diagram plotting pressure as a function of volume. Each line, called an **isotherm**, describes the relationship between pressure and volume at a particular temperature.

- In the pV-diagrams of non-ideal gases, isotherms can have flat areas. These represent periods where the gas is condensing into a liquid.

- The area under a pV-curve represents the work done by the system during a volume change.

18.2 Molecular Properties of Matter

- The force between molecules in a gas varies with r.

- An ideal gas is one whose molecules exert no attractive forces on each other and thus have no potential energy.

- The number of molecules in a mole is given by **Avagadro's number**

$$N_A = 6.022\,140\,76 \times 10^{23} \text{ molecules/mol.}$$

18.3 Kinetic-Molecular Model of an Ideal Gas

- The average translational kinetic energy of an ideal gas is

$$K_\text{tr} = \frac{3}{2} nRT.$$

- The **Boltzmann constant** is

$$k = \frac{R}{N_A} = 1.381 \times 10^{-23} \text{ J/(molecule K).}$$

- The average translational kinetic energy of a gas molecule is

$$\frac{1}{2} m(v^2)_\text{av} = \frac{3}{2} kT$$

and thus the **root-mean-square speed** of a gas molecule is

$$v_\text{rms} = \sqrt{(v^2)_\text{av}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

where m is the mass of a molecule and M is the molar mass.

- The average distance travelled by a particle between collisions is called the **mean free path**

$$\lambda = \frac{V}{4\pi\sqrt{2}r^2 N} = \frac{kT}{4\pi\sqrt{2}r^2 p}$$

where V is the volume of the gas, r is the radius of a gas molecule, N is the number of molecules in the gas, T is its temperature, and p is its volume.

18.4 Heat Capacities

- The **molar heat capacity at constant volume** of a particular gas is determined by its **degrees of freedom**, i.e. the number of ways in which it can store kinetic energy.

- Monatomic gases have three degrees of freedom: one for each translational axis.

- Diatomic gases have five degrees of freedom: one for each translational axis and two for rotational axes (the third is excluded because it's not affected by collisions).

- Polyatomic gases have more than five degrees.

- The **principle of equipartition of energy** states that each degree of freedom contributes $\frac{1}{2}kT$ to the average kinetic energy of the gas, i.e. for monatomic gases the average kinetic energy per molecule is $\frac{3}{2}kT$, for diatomic $\frac{5}{2}kT$, etc.

- The molar heat capacity at constant volume of a gas is equal to

$$C_V = \frac{d}{2}R$$

where d is the number of degrees of freedom.

- Vibrational energy can also contribute to the molar heat capacity at constant volume, but for most diatomic molecules this isn't the case.

- Molar heat capacity at constant volume is temperature dependent, with rotational and vibrational degrees of freedom only coming in to play at higher temperatures.

- Crystalline solids, i.e. solids whose atoms are arranged in a three-dimensional matrix, have six degrees of freedom: three translational and three from the potential energy of intermolecular forces. This results in the **rule of Dulong and Petit** which states that the molar heat capacity at constant volume of an ideal monatomic solid is

$$V_C = 3R.$$

18.5   Molecular Speeds

- In regards to the speeds of molecules in a gas, a **distribution function** $f(v)$ gives the probability per unit speed of finding a particle with a speed near v. That is, the area under the curve between $f(v_1)$ and $f(v_2)$ gives the probability of finding a particle with speed in that range.

- The **Maxwell-Boltzmann distribution** is a particular distribution function

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

where m is the mass of a molecule, T is the absolute temperature of the gas, and v is the molecular speed.

- The peak of the curve and thus the most probable speed occurs at

$$v_{\mathrm{mp}} = \sqrt{\frac{2kT}{m}}.$$

- The average speed is

$$v_{\mathrm{av}} = \sqrt{\frac{8kT}{\pi m}}.$$

- The rms speed is

$$v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m}}.$$

18.6   Phases of Matter

- A pT **phase diagram** is a two-dimensional graph with pressure p on the vertical axis and temperature T on the horizontal axis. The plane is separated into three distinct regions: one for each phase of the material (solid, liquid, and gas).

- The borders between regions represent points of **phase equilibrium** where both phases can coexist at the same pressure and temperature.

- The **fusion curve** separates the solid and liquid regions.

- The **vaporisation curve** separates the liquid and gas regions.

- The **sublimation curve** separates the solid and gas regions.

- The three curves meet at the **triple point** — the only conditions under which all three phases can coexist.

- The vaporisation curve ends at the **critical point**. As the pressure and temperature of a substance approaches those of its critical point the physical differences between the liquid and gas phases decrease. At the critical point there are no differences and a substance whose pressure or temperature is gradually decreased won't undergo a phase transition — instead its properties will continuously change from those of a gas to those of a liquid or vice versa.

19   The First Law of Thermodynamics

19.1   Thermodynamic Systems

- A **thermodynamic system** is any collection of objects that is convenient to regard as a unit, and that may have the potential to exchange energy with its surroundings.

- A process in which there are changes in the state of a thermodynamic system is called a **thermodynamic process**.

- In a termodynamic process, Q represents the heat added to the system (increasing its energy) and W represents work done by the system on its surroundings (decreasing its energy). Both quantities may be negative in which case they represent heat being removed from the system (decreasing its energy) and the surroundings doing work on the system (increasing its energy), respectively.

19.2 Work Done During Volume Changes

- The work done during a volume change is

$$W = \int_{V_1}^{V_2} p \, dV$$

where V_1 is the initial volume, V_2 is the final volume, and p is the pressure.

- In the above equation p is often a function of V, in which case the integral represents the area under the graph of $p = p(V)$. This is the area under the curve of a pV-diagram.

- When volume increases, work is positive. When volume decreases, work is negative.

19.3 Paths Between Thermodynamic States

- When a thermodynamic system changes from an initial state to a final state it passes through a series of intermediate states. This series of states is called a **path**.

- There are an infinite number of paths between any given initial and final states, but the amount of work done by the system on its surroundings can differ between paths.

- The uncontrolled expansion of a gas into vacuum is called **free expansion**. The gas does no work as it expands so its temperature doesn't change.

19.4 Internal Energy and the First Law of Thermodynamics

- The **internal energy** U of a system is the sum of the kinetic energies of all its constituent particles, plus the sum of the potential energies of interactions between these particles.

- The **first law of thermodynamics** states

$$\Delta U = Q - W$$

where ΔU is the change in internal energy of a thermodynamic system, Q is the heat added to the system, and W is the work done by the system on its surroundings.

- The change in internal energy of a thermodynamic system depends only on its initial and final states, not on the path taken.

- A **cyclic process** is on that starts and ends in the same state. In that case $\Delta U = 0$ and thus $Q = W$: if a net amount of work was done by the system during this process, an equal amount of energy must have flowed into the system as heat Q.

- In an **isolated system** that does no work and experiences no heat flow, $Q = W = 0$ and thus $\Delta U = 0$. This means that the inernal energy of an isolated system is constant.

- In a cyclic process, the total work is positive if the process moves clockwise around the pV-diagram and negative if it moves counterclockwise.

- The first law of thermodynamics can also be expressed using infinitesimals

$$dU = dQ - dW = dQ - p\,dV.$$

19.5   Kinds of Thermodynamic Processes

- An **adiabatic process** is one with no heat transfer into or out of the system, i.e. $Q = 0$. This can be achieved by thermally insulating the system or performing the process so quickly that no heat transfer can occur. The path followed by an adiabatic process on a pV-diagram is called an **adiabat**.

- An **isochoric process** is one where the volume of the system doesn't change, i.e. $W = 0$. The path followed by an icochoric process on a pV-diagram is called an **isochor**.

- An **isobaric process** is one where the pressure of the system doesn't change, i.e. $W = p(V_2 - V_1)$. The path followed by an isobaric process on a pV-diagram is called an **isobar**.

- An **isothermal process** is one where the temperature of the system doesn't change. Any heat flowing into or out of the system must occur slowly enough to maintain thermal equilibrium. The path followed by an isothermal process on a pV-diagram is called an **isotherm**.

19.6   Internal Energy of an Ideal Gas

- The internal energy of an ideal gas depends only on its temperature, not on its pressure or volume.

19.7 Heat Capacities of an Ideal Gas

- Gases have two molar heat capacities: one at constant volume C_V, and one at constant pressure C_P.

- When heating a gas at constant pressure, the gas must do work on the container to increase its volume (otherwise pressure would increase). This means not all of the heat is used to increase the temperature of the gas. Thus, the amount of heat required to raise the temperature of a gas at constant pressure is greater than a gas at constant volume, i.e. $C_P > C_V$.

- For ideal gases
$$C_P = C_V + R.$$

- The **ratio of heat capacities** of a substance is denoted
$$\gamma = \frac{C_P}{C_V}.$$

- Because the internal energy of an ideal gas depends only on its temperature, not on its pressure or volume, if $\Delta U = nC_V \Delta T$ is valid for one type of process (an isochoric or constant volume process), it must be valid for all other processes.

19.8 Adiabatic Processes for an Ideal Gas

- An adiabatic expansion results in a drop in temperature and an adiabatic compression results in a rise in temperature.

- For an adiabatic process
$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$$

$$W = nC_V(T_1 - T_2)$$

$$W = \frac{C_V}{R}(p_1 V_1 - p_2 V_2)$$
$$= \frac{1}{\gamma - 1}(p_1 V_1 - p_2 V_2)$$

20 The Second Law of Thermodynamics

20.1 Directions of Thermodynamic Processes

- Thermodynamic processes that occur between objects that aren't in thermodynamic equilibrium are irreversible, e.g. heat flowing from an area of higher to lower temperature, free expansion of gas, etc.

- Thermodynamic processes that occur between objects that are very nearly in thermodynamic equilibrium approach being reversible. They are also called **equilibrium processes**.

20.2   Heat Engines

- Any device that transforms heat into work or mechanical energy is called a **heat engine**.

- Usually a quantity of matter inside the engine undergoes inflow and outflow of heat, expansion and compression, and sometimes change of phase. We call this matter the **working substance** of the engine.

- All heat engines absorb heat from a **hot reservoir** and discard waste heat to a **cold reservoir**.

- The amount of heat absorbed from the hot reservoir is denoted Q_H (positive) and the amount of heat discarded to the cold reservoir is denoted Q_C (negative).

- If a heat engine undergoes a cyclic process $\Delta U = 0$ so

$$W = Q = Q_H + Q_C = |Q_H| - |Q_C|.$$

- The **thermal efficiency** of a heat engine

$$e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \left| \frac{Q_C}{Q_H} \right|$$

  represents the fraction of input energy that's converted into useful work.

20.3   Internal Combustion Engines

- The **Otto cycle** is an idealised version of the thermodynamic process inside a gasoline engine.

- The thermal efficiency of the Otto cycle is

$$e = 1 - \frac{1}{r^{\gamma - 1}}$$

  where r is the compression ratio of the engine.

20.4   Refigerators

- A fridge is like a reverse heat engine — it takes heat from a cold place (the inside of the fridge) to a hot place (the outside of the fridge). However, where a heat engine has a net output of work a fridge has a net input of work.

- When modelling a fridge as a thermodynamic system, Q_C is positive, Q_H is negative, and W is negative.

- A more performant fridge will maximise Q_C (the heat removed from the inside of the fridge) for a given W (the power input to the fridge). This is captured by the **coefficient of performance**

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|}.$$

- Another way of thinking about the performance of an air conditioner or fridge is in terms of the amount of heat removed per unit time, i.e. the heat current H, and the energy input per unit time, i.e. the power P. In terms of these units the coefficient of performance is

$$K = \frac{|Q_C|}{|W|} = \frac{Ht}{Pt} = \frac{H}{P}.$$

20.5 The Second Law of Thermodynamics

- The **second law of thermodynamics** states that it is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which it began.

- An alternative wording is that it is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter object.

20.6 The Carnot Cycle

- The **Carnot cycle** is an ideal thermodynamic process that provides an upper limit on the maximum efficiency of an engine. In it, only reversible thermodynamic processes may be used — namely adiabatic and isothermal processes.

Figure **20.13** The Carnot cycle for an ideal gas. The light blue lines in the *pV*-diagram are isotherms (curves of constant temperature) and the dark blue lines are adiabats (curves of zero heat flow).
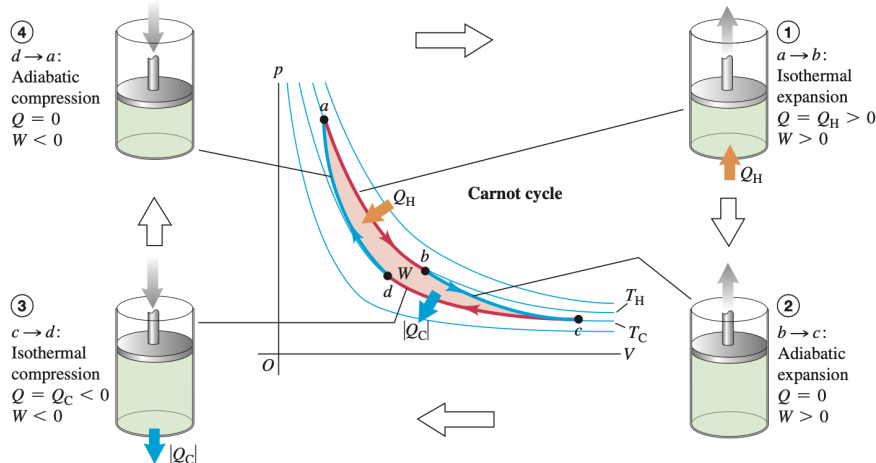
- The amount of heat transferred to/from the reservoirs in a Carnot cycle are related to the temperatures of the reservoirs by

$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H}.$$

- The efficiency of a Carnot engine is

$$e_{\text{Carnot}} = 1 - \frac{T_C}{T_H}.$$

- Because all processes in the Carnot cycle are reversible, the cycle itself can be reversed to make a Carnot fridge.

- The coefficient of performance of a Carnot fridge is

$$K_{\text{Carnot}} = \frac{T_C}{T_H - T_C}.$$

20.7 Entropy

- **Entropy** S is a measure of the randomness in a system. When you add heat to a system the constituent particles gain kinetic energy, there is more randomness to their positions, and thus entropy increases. When you remove heat from a system entropy decreases.

- The units of entropy are J/K.

- The change in entropy during a reversible isothermal process is

$$\Delta S = \frac{Q}{T}.$$

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- The change in entropy during any reversible thermodynamic process can be calculated as

$$\Delta S = \int_1^2 \frac{dQ}{T}$$

  where ΔS is the change in entropy, 1 is the initial state, 2 is the final state, dQ is the infinitesimal heat flow into the system, and T is the absolute temperature of the system.

- Entropy is determined entirely by the state of a system, not how it got there, i.e. entropy is path independent.

- In an adiabatic process $Q = 0$ and thus there is no change in entropy.

- To calculate the change in entropy of an irreversible process, come up with a series of reversible processes that take the system between the same states and calculate the change in entropy of that.

- When a system undergoes a reversible change from state a to state b, the change in entropy is 0. This means that the change in entropy of adiabatic and isothermal processes are 0 (because they are reversible). The Carnot cycle is composed of adiabatic and isothermal processes so its change in entropy is also 0. In general, the change in entropy for any reversible cyclic process is 0.

- An alternative formulation of the second law of thermodynamics is that no process is possible in which total entropy decreases, when all systems that take part in the process are included.

20.8   Microscopic Interpretation of Entropy

- A description of the **macroscopic state** of a system describes the system as a whole rather than individual components of the system, e.g. "50% of the coins are heads, 50% are tails."

- A description of the **microscopic state** of a system describes the individual components, e.g. "Coin 1 is heads, coin 2 is tails, etc."

- Many microscopic states may correspond to a given macroscopic state.

- For any thermodynamic system, the most probable macroscopic state is the one with the greatest number of corresponding microscopic states, which is also the macroscopic state with the greatest randomness and the greatest entropy.

- The entropy of a given macroscopic state is

$$S = k \ln w$$

  where k is the Boltzmann constant and w is the number of microscopic states associated with the macroscopic state.

37 Relativity

37.1 Invariance of Physical Laws

- **Einstein's first postulate** or the **principle of relativity** states that the law of physics are the same in every inertial frame of reference.

- **Einstein's second postulate** states that the speed of light in vacuum is the same in all intertial frames of reference and is independent of the motion of the source.

- It is not possible to travel at the speed of light.

- A **Galilean transformation** transforms between the coordinates of two reference frames that differ only by constant relative motion, e.g.

$$x = x' + vt$$
$$y = y'$$
$$z = z'.$$

37.2 Relativity of Simultaneity

- In a given frame of reference an **event** is an occurence that has a definite position and time.

- In general, two events that are **simultaneous** in one frame of reference are not simultaneous in another frame that is moving relative to the first, even if both are inertial frames.

37.3 Relativity of Time Intervals

- There is only one reference frame in which a given point is at rest and we call it the point's **rest frame**.

- The time interval measured between two events that occur at the same point (and thus in the point's reference frame) is called **proper time** Δt_0.

- The time interval between those two same events in another frame of reference moving at speed u relative to the rest frame is

$$\Delta t = \frac{\Delta t_0}{\sqrt{1 - u^2/c^2}}$$

which is greater than Δt_0. This phenomenon is called **time dilation**.

- The **Lorentz factor** is defined as

$$\gamma = \frac{1}{\sqrt{1 - u^2/c^2}}.$$

- If the relative speed u of a reference frame is large enough that the Lorentz factor γ is appreciably greater than 1, the speed is said to be **relativistic**. Otherwise it's said to be **nonrelativistic**.

37.4   Relativity of Length

- The length of a body as measured in its rest frame is called its **proper length** l_0.

- In a moving reference frame, The length of a body in the direction parellel to motion is
$$l = \frac{l_0}{\gamma}$$
which is less than l_0. This phenomenon is called **length contraction**.

- Length contraction doesn't occur in directions perpendicular to motion.

37.5   The Lorentz Transformations

- If S' is a reference frame moving at speed u along the x-axis relative to reference frame S, then the **Lorentz transformation** can be used to determine the spacetime coordinates x', y', z', and t' in S' from coordinates x, y, z, and t in S

$$x' = \frac{x - ut}{\sqrt{1 - u^2/c^2}} = \gamma(x - ut)$$
$$y' = y$$
$$z' = z$$
$$t' = \frac{t - ux/c^2}{\sqrt{1 - u^2/c^2}} = \gamma(t - ux/c^2).$$

- At relativistic speeds length and time have no meaning independent of a reference frame, so we use **spacetime coordinates** x, y, z, and t.

- The **Lorentz velocity transformation** can be used to determine the velocity in S' in terms of the velocity in S

$$v'_x = \frac{v_x - u}{1 - uv_x/c^2}.$$

37.6   The Doppler Effect For Electromagnetic Waves

- When the source of an electromagnetic wave of proper frequency f_0 is approaching a stationary observer at speed u, the observer measures frequency
$$f = \sqrt{\frac{c + u}{c - u}} f_0.$$
When the source is moving away from the observer the sign of u changes.

37.7 Relativistic Momentum

- The mass of a particle when it is at rest relative to the observer is called its **rest mass**.

- A particle's **relativistic momentum** is

$$\mathbf{p} = \frac{m\mathbf{v}}{\sqrt{1 - v^2/c^2}} = \gamma m\mathbf{v}.$$

  This means that as a particle's speed increases so does its relativistic momentum.

- The expression γm is sometimes called the **relativistic mass**, which increases with a particle's speed.

- Newton's second law must be adjusted at relativistic speeds. For forces parallel to the direction of motion

$$F = \gamma^3 ma$$

  and for forces perpendicular to the direction of motion

$$F = \gamma ma.$$

  This means that, unless the net force on a particle moving at relativistic speeds is either parallel or perpendicular to its direction of motion, the acceleration and force vectors aren't parallel.

37.8 Relativistic Work and Energy

- The kinetic energy of a particle travelling at relativistic speeds is

$$K = (\gamma - 1)mc^2.$$

- The total energy of a particle is

$$E = \gamma mc^2$$

  or

$$E^2 = (mc^2)^2 + (pc)^2.$$

- For a particle at rest $E = mc^2$. This is called the particle's **rest energy**.

38 Photons: Light Waves Behaving as Particles

38.1 Light Absorbed as Photons: The Photoelectric Effect

- To escape from the surface of a material, an electron must absorb enough energy to overcome the attraction of positive ions in the material. The **photoelectric effect** is the phenomenon where light gives the electroncs this energy, producing a current.

- The maximum kinetic energy of an electron emitted via the photoelectric effect is

$$K = \frac{1}{2}mv_{\text{max}}^2 = eV_0$$

where V_0 is the **stopping potential**, i.e. the potential diffreence between the anode and cathode at which electrons no longer flow.

- The energy of a photon is

$$E = hf = \frac{hc}{\lambda}$$

where h is **Planck's constant**

$$h = 6.626\,069\,57 \times 10^{-34}\,\text{J s}.$$

- The maximum kinetic energy of an electron emitted via the photoelectric effect is

$$eV_0 = hf - \phi$$

where ϕ is the material's **work function**, i.e. the amount of energy required for an electron to overcome the attractive foces of ions.

- The momentum of a photon is

$$p = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda}.$$

38.2   Light Emitted as Photons: X-Ray Production

- Accelerated charges produce electromagnetic waves. When an electron is "braked" by a material it is decelerated, producing an electromagnetic wave. The frequency of that wave is determined by the charge's kinetic energy. If the charge is accelerated across a potential difference of V then

$$K = eV = hf = \frac{hc}{\lambda}.$$

38.3   Light Scattered as Photons: Compton Scattering and Pair Production

- When a photon strikes an electron it gives up some of its energy and momentum to the electron and is redirected at an angle ϕ from its original path. The change in wavelength of the photon is given by

$$\lambda' - \lambda = \frac{h}{mc}(1 - \cos\phi)$$

where λ' is the wavelength of the scattered photon, λ is the original wavelength of the photon, h is Planck's constant, m is the mass of the electron, c is the speed of light in vacuum, and ϕ is the scattering angle.

- If a gamma ray photon is fired at a target, it may not scatter. Instead it may disappear and be replaced with an electron / positron pair. A **positron** is a particle with the same mass as an electron but with opposite charge $(+e)$.

38.4 Wave-Particle Duality, Probability, and Uncertainty

- The **Heisenberg uncertainty principle** states that it is impossible to simultaneously determine both the position and momentum of a particle with arbitrarily great precision

$$\Delta x \Delta p_x \geq \hbar/2$$

where Δx is uncertainty in the x coordinate, Δp_x is uncertainty in the x momentum, and $\hbar$ is Planck's constant divided by 2π.

- The Heisenberg uncertainty principle for energy and time is

$$\Delta t \Delta E \geq \hbar/2.$$

39 Particles Behaving as Waves

39.1 Electron Waves

- Like light acting like a particle, particles can act like a wave. The **de Broglie wavelength** of a particle travelling at non-relativistic speed is

$$\lambda = \frac{h}{p} = \frac{h}{mv}.$$

At relativistic speed we replace p with γp

$$\lambda = \frac{h}{\gamma p} = \frac{h}{\gamma m v}.$$

- The energy of a particle is related to its frequency in the same way as light

$$E = hf.$$

- The de Broglie wavelength of an electron accelerated through a potential difference V_{ba} is

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV_{ba}}}.$$

39.2 The Nuclear Atom and Atomic Spectra

- Heated materials emit light and different materials emit different kinds of light. If we pass this light through a prism or diffraction grating we can separate the light into its component wavelengths. This is called an **emission line spectrum** and the lines are called **spectral lines**.

- Solids and liquids have continuous emission line spectrums, i.e. they emit all wavelengths of visible light, while gases only emit a subset of wavelengths.

- The emission line spectrum of each element is constant.

- While a heated gas selectively emits certain wavelengths of light, a cooled gas selectively absorbs the same wavelengths. If we pass white light onto the material and observe the transmitted (i.e. not absorbed) wavelengths we can determine which wavelengths were absorbed. This is called the gas's **absorption line spectrum**.

39.3 Energy Levels and the Bohr Model of the Atom

- An atom's internal energy may be equal to a set of possible **energy levels**, but not to an amount of energy between these levels.

- An atom's lowest energy level is known as its **ground state** and higher energy levels are known as **excited states**.

- When an atom drops from a higher to a lower energy level it emits a photon whose energy is equal to the difference between the energy levels

$$hf = \frac{hc}{\lambda} = E_{\mathrm{i}} - E_{\mathrm{f}}.$$

- An atom can be raised from a lower to a higher energy level via collisions or absorption of photons, however the photon's energy must be equal to the different between the energy levels.

- If an atom is in its ground state there are limited wavelengths of photons it can absorb, i.e. only those whose energy is equal to that of the higher energy levels. However, when the atom is emitting photons it has more options as it can go between different higher energy levels. This means atoms can emit longer wavelengths than they absorb, e.g. absorb infrared and emit visible, a process called **fluorescence**.

- The magnitude of an electron's angular momentum is quantized and must be an integer multiple of $\hbar$, i.e.

$$L_n = mv_n r_n = n\hbar$$

where m is the mass of the electron, v_n is its speed in orbit number n, r_n is its radius in orbit number n, and $n = 1, 2, 3, \ldots$ is called the **principle quantum number** of the orbit.

- Electrons can be considered particles orbiting the nucleus or standing waves at the same radius as the particle. The circumference of the orbit must be equal to an integer multiple of the wavelength of the standing wave.

- Under the Bohr model, the radius of the nth orbit is

$$r_n = \epsilon_0 \frac{n^2 h^2}{\pi m e^2} = n^2 a_0$$

  where a_0 is the **Bohr radius** and the orbital speed of the nth orbit is

$$v_n = \frac{1}{\epsilon_0} \frac{e^2}{2nh}.$$

- The total energy of an electron is

$$E_n = -\frac{hcR}{n^2}$$

  where

$$R = \frac{me^4}{8\epsilon_0^2 h^3 c} = 1.097 \times 10^7 \, \text{m}^{-1}$$

  is called the **Rydberg constant**.

- The energy required to ionise an atom, i.e. remove an electron, is the energy required to move the electron from the ground state ($n = 1$) to an infinitely large orbit radius equal to

$$E_\infty - E_1 = 0 - E_1 = -E_1.$$

  This value is positive because E_1 is negative.

- The Bohr model predicts emission and absorption spectrums with 0.1% accuracy. The discrepancy comes from the assumption that the nucleus doesn't move. It can be made more accurate by using the atom's **reduced mass**

$$m_r = \frac{m_1 m_2}{m_1 + m_2}$$

  instead of the electron's mass.

- The Bohr model can be extended to other one-electron atoms, called **hydrogenlike atoms**. In such atoms the nucleur charge isn't e but Ze where Z is the atomic number, i.e. the number of protons in the nucleus. This means we must replace e^2 with Ze^2 in the formulas above.

39.4   The Laser

- The number of atoms at a given energy level is given by

$$n = Ae^{-E/kT}$$

  where A is a constant determined by the total number of atoms in the gas.

39.5   Continuous Spectra

- A hypothetical material that absorbs all wavelengths of light is called a **blackbody**. Because materials' absorption and emission spectra are equal, the material would also emit all wavelengths of light when heated.

- The **Stefan-Boltzmann law** gives the intensity of radiation per unit area from a blackbody

$$I = \sigma T^4$$

where σ is the Stefan-Boltzmann constant and T is the absolute temperature of the blackbody. This differs from the Stefan-Boltzmann law in section 17.7 in that A isn't included because the intensity is per unit area and e isn't included because it's a blackbody and $e = 1$.

- The intensity of emitted radiation is not equal across all wavelengths and can be described by the intensity per wavelength interval $I(\lambda)$ called the **spectral emittance**. The intensity corresponding to wavelengths in the interval $[\lambda, \lambda + d\lambda]$ is thus given by $I(\lambda)\,d\lambda$.

- The spectral emittance $I(\lambda)$ differs based on temperature T and has a peak wavelength λ_m where the intensity per unit wavelength is the greatest. The **Wien displacement law** relates these two quantities

$$\lambda_m T = 2.90 \times 10^{-3}\,\mathrm{m\,K}.$$

- **Planck's radiation law** gives the spectral emittance (intensity per unit wavelength) of a blackbody

$$I(\lambda) = \frac{2\pi h c^2}{\lambda^5 (e^{hc/\lambda kT} - 1)}.$$

40   Quantum Mechanics I: Wave Functions

40.1   Wave Functions and the One-Dimensional Schrödinger Equation

- A **free particle** is a particle that experiences no force, i.e. its potential energy function is 0 at all locations.

- Thus the energy of a free particle is equal to its kinetic energy

$$E = K = \frac{1}{2}mv^2 = \frac{m^2 v^2}{2m} = \frac{p^2}{2m}.$$

- From the de Broglie relationships we find

$$E = hf = \frac{h}{2\pi} 2\pi f = \hbar\omega$$

$$p = \frac{h}{\lambda} = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k.$$

- Substituting these equations into that of the energy of a free particle we find
$$\hbar\omega = \frac{\hbar^2 k^2}{2m}.$$

- The **one-dimensional Schrödinger equation for a free particle** is
$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} = i\hbar\frac{\partial \Psi(x,t)}{\partial t}$$
the general solution of which is
$$\Psi(x,t) = A[\cos(kx-\omega t) + i\sin(kx-\omega t)] = Ae^{i(kx-\omega t)}.$$

- For a particle that can only move in the x direction, $|\Psi(x,t)|^2$ is called the **probability distribution function** and the value $|\Psi(x,t)|^2\,dx$ is the probability that the particle will be found at time t at a coordinate between x and $x + dx$. This requires that the wave function Ψ be normalized, i.e.
$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = 1.$$

- The probability distribution function can be calculated by multiplying $\Psi(x,t)$ buy its complex conjugate
$$\Psi(x,y)|^2 = \Psi(x,t)\Psi^*(x,t).$$

- A localised wave pulse constructed from multiple superposed waves is called a **wave packet** and it has properties of both a particle and a wave. It can be represented by an expression like
$$\Psi(x,t) = \int_{-\infty}^{\infty} A(k)e^{i(kx-\omega t)}\,dk.$$

- The **general one-dimensional Schrödinger equation**, i.e. for a particle with a nonzero potential energy function $U(x)$, is
$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} + U(x)\Psi(x,t) = i\hbar\frac{\partial \Psi(x,t)}{\partial t}.$$
If $\Psi(x,t) = Ae^{i(kx-\omega t)}$ this reduces to
$$-\frac{\hbar^2}{2m}(-k^2\Psi(x,t)) + U(x)\Psi(x,t) = i\hbar(-i\omega\Psi(x,t))$$
$$\frac{\hbar^2 k^2}{2m}\Psi(x,t) + U(x)\Psi(x,t) = \hbar\omega\Psi(x,t)$$
$$\frac{\hbar^2 k^2}{2m} + U(x) = \hbar\omega$$
$$K + U(x) = E.$$

- If a particle has a known energy E then $\omega = E/\hbar$ and the wave function can be written as

$$\Psi(x,t) = Ae^{i(kx - Et/\hbar)} = Ae^{ikx}e^{-iEt/\hbar} = \psi(x)e^{-iEt/\hbar}.$$

This is known as the **time-dependent wave function for a state of definite energy** or a **stationary state** because

$$
\begin{aligned}
|\Psi(x,t)|^2 &= \Psi(x,t)\Psi(x,t)^* \\
&= (\psi(x)e^{-iEt/\hbar})(\psi^*(x)E^{iEt/\hbar}) \\
&= \psi(x)\psi^*(x) \\
&= |\psi(x)|^2,
\end{aligned}
$$

i.e. the probability distribution function does not depend on time.

- Substituting the stationary state equation into the Schrödinger equation we find the **time-independent one-dimensional Schrödinger equation**

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

40.2   Particle in a Box

- For a particle confined to a potential well, i.e.

$$
U(x) = \begin{cases} \infty & x \leq 0 \\ 0 & 0 < x < L \\ \infty & L \leq x \end{cases}
$$

the stationary state wave function between $x = 0$ and $x = L$ must satisfy the time-indepdendent one-dimensional Schrödinger equation

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

and the boundary conditions $\psi(0) = 0$ and $\psi(L) = 0$.

- The general solution to the above is

$$
\begin{aligned}
\psi(x) &= A_1 e^{ikx} + A_2 e^{-ikx} \\
&= 2iA_1 \sin kx \\
&= C \sin kx
\end{aligned}
$$

where $k = n\pi/L$ and $\lambda = 2\pi/k = 2L/n$ for $n = 1, 2, 3, \ldots$ which is the same as a standing wave one a string.

- For each quantum number n, a particle in a box has a wavelength

$$\lambda_n = \frac{2L}{n}$$

and thus a momentum

$$p_n = \frac{h}{\lambda_n} = \frac{nh}{2L}$$

and an energy

$$E_n = \frac{p_n^2}{2m} = \frac{n^2 h^2}{8mL^2} = \frac{n^2 \pi^2 \hbar^2}{2mL^2}.$$

- Each energy level has an associated wave function

$$\psi_n(x) = C \sin \frac{n\pi x}{L}.$$

- A particle in a box cannot have zero energy because that implies zero uncertainty in momentum and, by Hiesenberg's uncertainty principle, infinite uncertainty in position which potentially places the particle outside the box.

- The normalized time-independent wave function for a particle in a box is

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}.$$

40.3   Potential Wells

- A **potential well** is a potential-energy function $U(x)$ that has a minimum.

- A **finite well** is a potential well that has straight sides but finite height:

$$U(x) = \begin{cases} U_0 & x \leq 0 \\ 0 & 0 < x < L \\ U_0 & L \leq x \end{cases}.$$

- In Newtonian mechanics a particle is trapped in a potential well if its total energy E is less than U_0. In quantum mechanics, such a trapped state is called a **bound state**.

- The wave function for a particle in a finite well of depth U_0 and width L is

$$\psi(x) = \begin{cases} Ce^{\kappa x} & x \leq 0 \\ A\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right) + B\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) & 0 < x < L \\ De^{-\kappa x} & L \leq x \end{cases}$$

where $\kappa = \sqrt{2m(U_0 - E)}/\hbar$.

40.4 Potential Barriers and Tunneling

- A **potential barrier** is a potential ene rgy function with a maximum.

- The **tunneling probability** T is the probability a particle tunnels through a potential barrier and is equal to

$$T = Ge^{-2\kappa L}$$

where

$$G = 16\frac{E}{U_0}\left(1 - \frac{E}{U_0}\right)$$

and

$$\kappa = \frac{\sqrt{2m(U_0 - E)}}{\hbar}.$$

40.5 The Harmonic Oscilator

- The energy levels for a harmonic oscillator are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k'}{m}} = \left(n + \frac{1}{2}\right)\hbar\omega, n = 0, 1, 2, \ldots$$

where n is the quantum number (where $n = 0$ is the ground state), k' is the potential well's force constant, and ω is the oscillator's angular frequency.

41 Quantum Mechanics II: Atomic Structure

41.1 The Schrödinger Equation in Three Dimensions

- The general form of the Schrödinger equation in three dimensions is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \Psi(x, y, z, t)}{\partial x^2} + \frac{\partial^2 \Psi(x, y, z, t)}{\partial y^2} + \frac{\partial^2 \Psi(x, y, z, t)}{\partial z^2}\right)$$
$$+ U(x, y, z)\Psi(x, y, z, t) = i\hbar\frac{\partial \Psi(x, y, z, t)}{\partial t}$$

- As in one dimension, the square of the modulus of the wave function is the probability distribution function of the particle's location, i.e. the probability of finding the particle in a volume V is given by

$$\int_V |\Psi(x, y, z, t)|^2 \, dV.$$

- The normalization condition on the wave function is that the integral of its modulus squared over all space must equal 1, i.e. the probability that the particle is somewhere is 1

$$\int |\Psi(x, y, z, t)|^2 \, dV = 1.$$

- If the wave function represents a state of definite energy E the time component can be dropped leaving the time-independent three-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(x,y,z)}{\partial x^2} + \frac{\partial^2\psi(x,y,z)}{\partial y^2} + \frac{\partial^2\psi(x,y,z)}{\partial z^2}\right)$$
$$+ U(x,y,z)\psi(x,y,z) = E\psi(x,y,z).$$

- The probability distribution function for a stationary state in three dimensions is

$$|\psi(x,y,z)|^2$$

giving the normalization condition

$$\int |\psi(x,y,z)|^2\, dV = 1.$$

41.2   Particle in a Three-Dimensional Box

- The time-independent Schrödinger equation in three dimensions reduces to three independent equations — one for each dimension. These equations are the same as for a particle in a one-dimensional box. The solutions for each dimension are thus

$$X_{n_X}(x) = C_X \sin\frac{n_X\pi x}{L} \qquad (n_X = 1,2,3,\ldots)$$
$$Y_{n_Y}(y) = C_Y \sin\frac{n_Y\pi y}{L} \qquad (n_Y = 1,2,3,\ldots)$$
$$Z_{n_Z}(z) = C_Z \sin\frac{n_Z\pi z}{L} \qquad (n_Z = 1,2,3,\ldots)$$

where C_X, C_Y, and C_Z are constants.

- This means that there are three different quantum numbers — one for each dimension — and the "dead spots" of the wave function are determined by these numbers.

- The energy of the particle is $E = E_X + E_Y + E_Z$ where

$$E_X = \frac{n_X^2\pi^2\hbar^2}{2mL^2}(n_X = 1,2,3,\ldots)$$
$$E_Y = \frac{n_Y^2\pi^2\hbar^2}{2mL^2}(n_Y = 1,2,3,\ldots)$$
$$E_Z = \frac{n_Z^2\pi^2\hbar^2}{2mL^2}(n_Z = 1,2,3,\ldots).$$

Equivalently

$$E_{n_X,n_Y,n_Z} = \frac{(n_X^2 + n_Y^2 + n_Z^2)\pi^2\hbar^2}{2mL^2}.$$

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- For quantum systems in multiple dimensions, two or more sets of quantum numbers (and thus quantum states) can correspond to the same energy level. This is called **degeneracy** and the quantum states are said to be **degenerate**.

- For a particle in a three-dimensional box, degeneracy is a result of the sides of the box having equal lengths. The degeneracy can be removed by making the sides have different lengths.

41.3   The Hydrogen Atom

- The energy levels of a hydrogen atom are given by

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2}\frac{m_r e^4}{2n^2\hbar^2}$$

  where m_r is the reduced mass of the electron/nucleus system and n is the principle quantum number.

- In an energy level E_n with principal quantum number n, the possible values of the magnitude of angular momentum for a hydrogen atom are

$$L = \sqrt{l(l+1)}\hbar,\ l = 0, 1, 2, \ldots, n-1$$

  where l is the **orbital quantum number**. This shows that for principle quantum number n there are n possible magnitude of angular momentum.

- The possible values of the z component of the angular momentum are

$$L_z = m_l\hbar,\ m_l = 0, \pm1, \pm2, \ldots, \pm l$$

  where m_l is called the **orbital magnetic quantum number** or **magnetic quantum number**.

- L_z is always less than L. This can be seen if we maximise L_z and compare it to L

$$L = \sqrt{l(l+1)}\hbar$$
$$L_z = l\hbar.$$

  This means we don't know the x and y components of **L** as is required by the uncertainty principle.

- Like a particle in a three-dimensional box, the wave functions for the hydrogen atom are determined by three quantum numbers n, l, and m_l. The energy E_n is determined by n, the magnitude of the orbital angular momentum L is determined by l, and the z component of the orbital angular momentum **L** is determined by m_l.

- States with various values of the orbital quantum number l are often labelled with letters according to the following scheme:

$$l = 0: \ s \text{ states} \qquad\qquad l = 3: \ f \text{ states}$$
$$l = 1: \ p \text{ states} \qquad\qquad l = 4: \ g \text{ states}$$
$$l = 2: \ d \text{ states} \qquad\qquad l = 5: \ h \text{ states}$$

  an so on alphabetically.

- **Spectroscopic notation** combines the principle quantum number n with the letter associated with the orbital quantum number l as above to describe a state, e.g. $2p$ corresponds to $n = 2$ and $l = 1$.

- The region of space associated with the wave function for a particular value of n is called a **shell**.

- **X-ray notation** is a way of describing the shells associated with various values of n

$$n = 1: \ K \text{ shell}$$
$$n = 2: \ L \text{ shell}$$
$$n = 4: \ M \text{ shell}$$

  and so on.

- For each n, different values of l correspond to different **subshells**.

- If $P(r)$ is the radial probability distribution function for an electron, then the probability the electron will be found in a spherical shell between radii r and $r + dr$ is
$$P(r) \, dr = |\psi|^2 \, dr = |\psi|^2 4\pi r^2 \, dr.$$

41.4   The Zeeman Effect

- The **Zeeman effect** is the splitting of a spectral line into several components in the presence of a magnetic field. This occurs because an orbiting electron has a magnetic moment $\boldsymbol{\mu}$ which has potential energy with the magnetic field $\mathbf{B}$.

- The orbital magnetic interaction energy is given by

$$U = -\mu_z B = -\frac{e}{2m} L_z B = -\frac{e}{2m} m_l \hbar B = m_l \mu_B B$$

  where μ_z is the z component of the magnetic moment, m_l is the magnetic quantum number, and μ_B is the Bohr magneton. Because this depends on m_l which can take on any integer value between $-l$ and l, the potential energy U can be positive or negative which causes the spectral line to "spread out" above and below its usual position.

- **Selection rules** constrain the possible transitions from one quantum state to another. Transitions that obey the rules are called **allowed transitions**; those that don't are called **forbidden transitions**.

41.5   Electron Spin

- **Spin** is an intrinsic form of angular momentum carried by elementary particles. It's like a spinning ball but it's not spinning and it's not a ball.

- The magnitude of the spin angular momentum of an electron is

$$S = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\hbar = \sqrt{\frac{3}{4}}\hbar.$$

- The z-component of the spin angular momentum of an electron is

$$S_z = m_s\hbar$$

where m_s is the **spin magnetic quantum number** with possible values $m_s = -\frac{1}{2}$ ("spin down") and $m_s = \frac{1}{2}$ ("spin up").

- The z-component of the spin magnetic moment is

$$\mu_z = -2.00232\frac{e}{2m}S_z = -2.00232\frac{e}{2m}m_s\hbar = \mp1.00116\mu_B.$$

- The interaction energy between the spin magnetic moment and an external magnetic field is thus

$$U = -\boldsymbol{\mu}\cdot\mathbf{B} = -\mu_z B_z = \pm1.00116\mu_B B_z.$$

- The spin gyromagnetic ratio (the ratio of spin magnetic moment to spin angular momentum) is two times the orbital gyromagnetic ratio.

- Four numbers are needed to describe the state of an electron in a hydrogen atom: n, l, m_l, and m_s.

- Like orbital angular momentum, spin angular momentum causes electron energy levels to split in the presence of a magnetic field (the "anomolous Zeeman effect").

- Electron spin can cause splitting of energy levels in the absense of an external magnetic field. This happens because, from the electron's frame of reference, a magnetic field is generated by the orbiting positively charged nucleus. This is called **spin-orbit coupling**.

- The total angular momentum of an electron is the sum of its orbital and spin angular momenta
$$\mathbf{J} = \mathbf{L} + \mathbf{S}.$$

- The magnitude of its total momentum is

$$J = \sqrt{j(j+1)}\hbar$$

where j is the **total angular momentum quantum number**

$$j = \left| l \pm \frac{1}{2} \right|.$$

- Various combinations of l and j can be expressed in an alternative spectroscopic notation e.g. $^2P_{1/2}$ where the superscript indicates the number of possible spin states (in this case 2), the letter is the capitalised letter associated with the l state (in this case $l = 1$), and the subscript is the value of j.

- In addition to shifts in energy levels due to magnetic effects within the atom, there are also shifts due to relativistic corrections to the kinetic energy of the electron. The term **fine structure** refers to the energy level shifts caused by magnetic and relativistic effects together. Including these effects, the energy levels of the hydrogen atom are

$$E_{n,j} = -\frac{13.60\,\text{eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

where α is the **fine structure constant**.

41.6 Many-Electron Atoms and the Exclusion Principle

- A neutral atom with Z protons also has Z electrons. The wave function of one of these electrons depends on $3Z$ coordinates (3 for each electron), making it very complicated and difficult to solve exactly.

- An approximation that simplifies the above is to assume the atom's charge cloud is spherically symmetric, resulting in a potential energy function $U(r)$. This is called the **central-field approximation**.

- The **Pauli exclusion principle** states that no two electrons in an atom can occupy the same quantum-mechanical state, i.e. they can't have the same values for all four quantum numbers n, l, m_l, and m_s. This determines the number of electrons that can be present in each shell.

TABLE 41.2 Quantum States of Electrons in the First Four Shells

n	l	m_l	Spectroscopic Notation	Number of States	Shell
1	0	0	$1s$	2	K
2	0	0	$2s$	2	
2	1	$-1, 0, 1$	$2p$	6	8 L
3	0	0	$3s$	2	
3	1	$-1, 0, 1$	$3p$	6	18 M
3	2	$-2, -1, 0, 1, 2$	$3d$	10	
4	0	0	$4s$	2	
4	1	$-1, 0, 1$	$4p$	6	
4	2	$-2, -1, 0, 1, 2$	$4d$	10	32 N
4	3	$-3, -2, -1, 0, 1, 2, 3$	$4f$	14	

- The number of electrons permitted in each subshell is given by $2(2l + 1)$.

- The number of electrons permitted in each shell is given by $2n^2$.

- The Pauli exclusion principle can be used to determine the ground state of an element with atomic number Z by filling the lowest energy level electron positions from $1s$ onwards. This can be represented as a sequence

$$1s$$
$$1s^2$$
$$1s^2 2s$$
$$1s^2 2s^2$$
$$1s^2 2s^2 2p$$
$$1s^2 2s^2 2p^2$$
$$1s^2 2s^2 2p^3$$
$$1s^2 2s^2 2p^4$$
$$1s^2 2s^2 2p^5$$
$$1s^2 2s^2 2p^6$$
$$\vdots$$

where superscripts indicate the number of electrons in that position.

- This pattern continues as expected until the M and N shells ($n = 3$ and $n = 4$) where some electrons go into the $4s$ subshell instead of the $3d$ subshell.

- Gauss's law tells us that if the charge distribution within an atom is spherically symmetrical (as in the central-field approximation), the electric field

at radius r is given by $Q_{\mathrm{encl}}/4\pi\epsilon_0 r^2$. As you move from inner to outer shells, Q_{encl} becomes less positive as electrons closer to the nucleus are **screening** some of its positive charge.

- From the view of electrons in outer shells, the atomic number of the atom is effectively reduced. The energy of an electron in shell n is

$$E_n = -\frac{Z_{\mathrm{eff}}^2}{n^2}(13.6\,\mathrm{eV})$$

where Z_{eff} is the **effective atomic number** it experiences as a result of screening.

- An electron's l value determines how many maxima are present in its wave function and how much "time" it spends at various distances from the nucleus. This means it determines Z_{eff} and thus the electron's energy level.

- When electrons strike a metal target, their deceleration results in x-rays being emitted (bremsstrahlung or braking radiation). The type of metal determines the wavelengths that are emitted. There are peaks in radiation intensity at particlar wavelengths that change with the metal.

- The most intense peak is called the K_α line and its frequency is given by **Moseley's law**

$$f = (2.48 \times 10^{15}\,\mathrm{Hz})(Z-1)^2.$$