

Constants to remember

1. Electron and proton mass

$$m_e c^2 = 0.511 \text{ MeV} \quad m_p c^2 = 938. \text{ MeV}$$

2. Speed of sound (\sim typical molecular velocity) and light

$$\text{sound} \sim 300 \text{ m/s} \quad c = 3 \times 10^8 \text{ m/s}$$

3. Typical wavelength of visible light.

$$\lambda_{\text{red}} \sim 600 \text{ nm} \quad \lambda_{\text{blue}} \sim 400 \text{ nm}$$

4. Typical wavelength of X-rays. Energy ~ 50 kilo – Volts

5. 2π is annoying, often use

$$\hbar = \frac{\hbar}{2\pi} \quad \hbar c = 197 \text{ eV nm} = 1970 \text{ eV \AA} \quad (1)$$

6. The fine structure constant is a pure number and is the only dimensionless quantity that can be made out \hbar, c and e

$$\alpha_{\text{EM}} = \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137} \quad (2)$$

The coulomb potential between two objects with $Z_1 e$ charge and $Z_2 e$ charge is

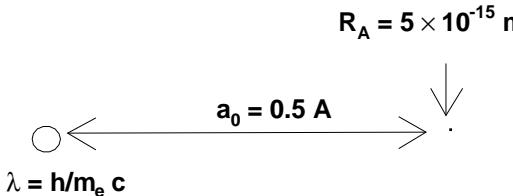
$$U = \frac{1}{4\pi\epsilon_0} \frac{Z_1 e Z_2 e}{r} \quad (3)$$

$$= \alpha_{\text{EM}} \frac{Z_1 Z_2 \hbar c}{r} \quad (4)$$

7. A typical atomic size is

$$1a_o = \frac{\hbar}{m_e c \alpha} = \frac{\hbar^2}{m_e \frac{e^2}{4\pi\epsilon_0}} \sim 0.5 \text{ \AA} \quad 1 \text{ \AA} = 0.1 \text{ nm}$$

8. The picture of the atom is the following (the circle is the electron and the dot is the nucleus)



Solid Angles

1. For a patch on the sphere of area A , the solid angle is defined as

$$\Omega \equiv \frac{A}{r^2} \quad (5)$$

in analogy to $\theta = s/r$. Like radians, the units of solid angle are dimensionless. However, we sometimes use the unit steradians to denote that a given dimensionless number corresponds to a definite solid angle.

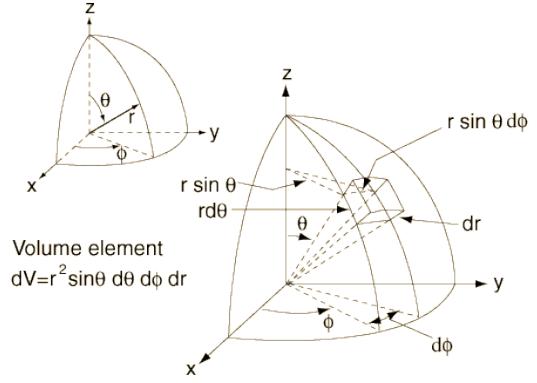


FIG. 1: Figure illustrating spherical coordinates and the concept of solid angle. You should be able to show $d\Omega = \sin(\Theta) d\Theta d\phi$

2. For a small area dA you should be able to show from the picture below that

$$d\Omega = \frac{dA}{r^2} = \sin(\Theta) d\Theta d\phi \quad (6)$$

The area of a little patch of area dA on the sphere is

$$dA = r^2 d\Omega = r^2 \sin(\Theta) d\Theta d\phi \quad (7)$$

The volume of the patch is $dV = r^2 d\Theta d\phi dr$

3. The integral of some quantity over the sphere is

$$\int_{\text{sphere}} d\Omega \dots = \int_0^\pi d\Theta \sin \Theta \int_0^{2\pi} d\phi \dots \quad (8)$$

4. For a small cylindrical strip as shown below you should be able to show that

$$d\Omega = 2\pi \sin(\Theta) d\Theta \quad (9)$$

Rutherford Experiments

The Rutherford experiments shot α particles (${}^4_2 \text{He}$) onto gold nuclei ${}^{197}_{79} \text{Au}$. A schematic of the apparatus is shown in Fig. 3

1. When alpha ($z_\alpha = +2$) particles impinge on a nucleus of charge $+Ze$ the distance of closest approach D is found by equating the initial kinetic energy with the final potential energy

$$K = \frac{1}{2} m_\alpha v_\alpha^2 = \frac{1}{4\pi\epsilon_0} \frac{(Ze)(z_\alpha e)}{D} \quad (10)$$

$$\frac{1}{2} m_\alpha v_\alpha^2 = \alpha_{\text{EM}} \frac{Z z_\alpha \hbar c}{D} \quad (11)$$

i.e.

$$D = \alpha_{\text{EM}} \left(\frac{Z z_\alpha \hbar c}{\frac{1}{2} m_\alpha v_\alpha^2} \right)$$

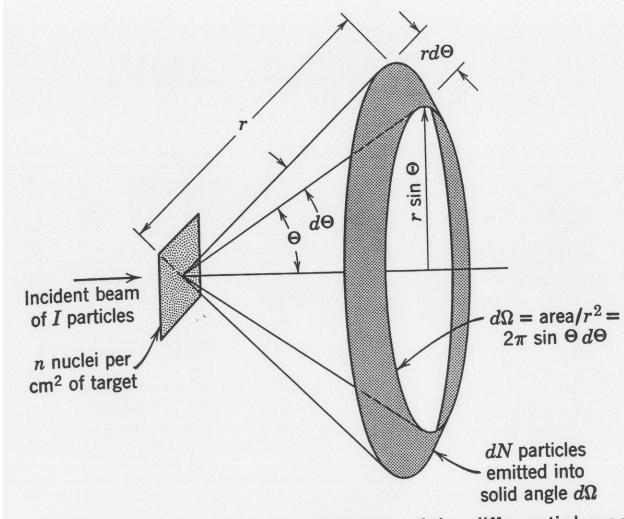


FIG. 2: Figure illustrating the concept of solid angle. You should be able to show that the solid angle subtended by the strip is $2\pi \sin(\Theta)d\Theta$

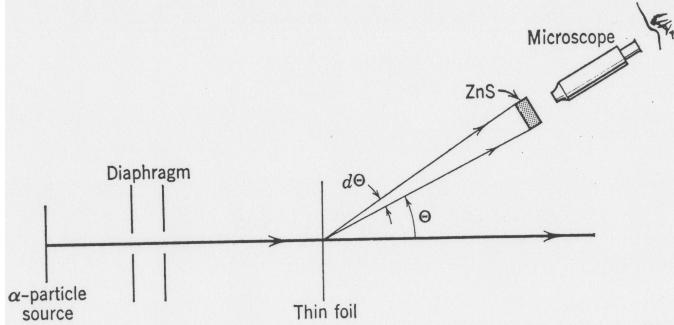


FIG. 3: Schematic of the Rutherford experiment

2. The number of α particles scattered into a given solid angle is

$$dN_{\text{scatt}} = [N_\alpha \rho_{Au} t_{\text{foil}}] \times \frac{D^2}{16} \frac{1}{\sin^4(\Theta/2)} \times d\Omega \quad (12)$$

where

$$N_\alpha = \text{Number of } \alpha's \text{ sent in.} \quad \text{The book calls this } I \quad (13)$$

$$\rho_{Au} = \text{The number of gold nuclei per volume in the foil} \quad (14)$$

$$t_{\text{foil}} = \text{The thickness of the foil} \quad (15)$$

$$d\Omega = \text{the solid angle of the detector} \quad (16)$$

For a ring like detector as shown in Fig. 3 the number scattered into the detector is

$$dN_{\text{scatt}} = [N_\alpha \rho_{Au} t_{\text{foil}}] \times \frac{D^2}{16} \frac{1}{\sin^4(\Theta/2)} \times 2\pi \sin(\Theta) d\Omega$$

Bohr Model

1. Electrons move about the nucleus in circular orbits determined by Newtons Laws

2. Only certain orbits are stable, in these orbits the angular momentum of the electron is

$$L = m_e v r = n\hbar n = 1, 2, 3, \dots \quad (17)$$

3. For these orbits (labelled by n) we have

$$E_n = - \underbrace{\frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_o}}_{\equiv R_\infty} \left[\frac{1}{n^2} \right] \Leftrightarrow \text{Energy} \quad (18)$$

$$= -13.6 \text{ eV} \left[\frac{1}{n^2} \right] \quad (19)$$

where R_∞ is the Rydberg constant $R_\infty = 13.6 \text{ eV}$. For the n -th orbit we also have

$$\frac{v_n}{c} = \alpha \left[\frac{1}{n} \right] \Leftrightarrow \text{velocity} \quad (20)$$

$$r_n = a_0 [n^2] \Leftrightarrow \text{radius} \quad (21)$$

$$(22)$$

4. An extremely important set of relationships is

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_o} = \frac{\hbar^2}{2m_e a_o^2} = \frac{1}{2} m_e c^2 \alpha^2 = 13.6 \text{ eV}$$

5. Light of a given frequency is emitted as the atom makes a transition from one n (say $n = 2$) to another (say $n = 1$). If light is emitted, the change in energy $\Delta E = E_f - E_i$ of the atom is negative sense the atom lowers its energy by emitting light energy which makes up the change. The frequency of the light which is emitted is given by energy conservation.

$$hf = (E_i - E_f) \quad (23)$$

6. The above formulas are for a single electron running around a single proton. When a single electron runs around Z protons the formulas become

$$L = m_e v r = n\hbar \quad n = 1, 2, 3 \dots \quad (24)$$

$$\frac{v_n}{c} = Z\alpha \left[\frac{1}{n} \right] \Leftrightarrow \text{velocity} \quad (25)$$

$$E_n = - \frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_o} Z^2 \left[\frac{1}{n^2} \right] \Leftrightarrow \text{Energy} \quad (26)$$

$$= -13.6 \text{ eV} Z^2 \left[\frac{1}{n^2} \right] \quad (27)$$

$$r_n = \frac{a_0}{Z} [n^2] \Leftrightarrow \text{radius} \quad (28)$$

Basic notions of wave functions

1. DeBroglie says that the momentum is related to the wavelength

$$p = \frac{h}{\lambda} = \hbar \frac{2\pi}{\lambda} = \hbar k \quad (29)$$

2. Similarly the frequency determines energy

$$E = \hbar\omega \quad \omega = 2\pi\nu \quad (30)$$

where ν is the frequency.

3. If the typical size of the wave function is Δx then the typical spread is in the momentum Δp is determined by the uncertainty relation

$$\Delta x \Delta p \gtrsim \hbar/2 \quad (31)$$

4. Similarly if the typical duration of a wave pulse (of e.g. sound, E&M, or electron wave) is Δt then its frequency ω is only determined to within $1/\Delta t$. In quantum mechanics this is written

$$\Delta t \Delta \omega \sim \frac{1}{2} \quad \text{or} \quad \Delta t \Delta E \gtrsim \hbar/2$$

i.e. if something is observed for a short period of time its energy can not be precisely known

5. In general an attractive potential energy tends to localize (make smaller) the particles wave function. As the particle is localized the kinetic energy increases. The balance determines the typical extent of the wave function (or the size of the object).

Wave packets

1. A general wave can be written as a sum of sin's and cos's. For a general wave then there is not one momentum and energy associated with the particle but a range of momenta and energies characterized by $\Delta\omega$ and Δk

2. Consider the addition of two waves

$$\Psi_1(x, t) = \sin(k_1 x - \omega_1 t) \quad \Psi_2(x, t) = \sin(k_2 x - \omega_2 t)$$

The waves have a certain average frequency (energy) $\bar{\omega} = (\omega_1 + \omega_2)/2$ and a frequency spread $\Delta\omega = \omega_1 - \omega_2$. Similarly the two waves have an average wave number (momentum) $\bar{k} = k_1 + k_2$ and $\Delta k = k_1 - k_2$. The sum of the two waves is

$$\Psi_1 + \Psi_2 = \underbrace{2 \sin(\bar{k}x - \bar{\omega}t)}_{\text{Carrier wave}} \underbrace{\cos(\frac{\Delta k}{2}x - \frac{\Delta \omega}{2}t)}_{\text{Envelope Wave}}$$

You should know how to derive this result and the analogous results for cos. When we talk about the energy and momentum of a wave we are really talking about the average momentum (wave number k) and average energy (angular frequency ω).

3. The speed of the envelope is group velocity

$$v_g = \frac{\Delta\omega}{\Delta k} = \frac{d\omega}{dk} = \frac{dE}{dp} \quad (32)$$

4. The spatial extent of the wave packet is of order the wavelength of the envelope

$$\Delta x \sim \frac{1}{\Delta k} \quad \Delta x \Delta k \sim 1 \quad (33)$$

In quantum mechanics this becomes $\Delta x \Delta p \sim \hbar$

5. The temporal extent of the wave packet is of order the period of the envelop

$$\Delta t \sim \frac{1}{\Delta \omega} \quad \Delta t \Delta \omega \sim 1 \quad (34)$$

In quantum mechanics this becomes $\Delta t \Delta E \sim \hbar$

6. The same analysis can be done using complex exponentials. Consider the addition of two waves

$$\Psi(x, t) = e^{-i\omega_1 t + ik_1 x} + e^{-i\omega_2 t + ik_2 x} \quad (35)$$

You should be able to show that

$$\Psi(x, t) = \underbrace{e^{-i\bar{\omega}t + i\bar{k}x}}_{\text{carrier}} \underbrace{2 \cos\left(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x\right)}_{\text{envelope}} \quad (36)$$

Wavefunctions

1. The electron wave function squared $|\Psi(x, t)|^2 = P(x, t)$ is a probability per unit length to find the particle at time t . The the probability $d\mathcal{P}$ to find a particle between x and $x + dx$ at time t

$$d\mathcal{P} = P(x, t)dx = |\Psi(x, t)|^2dx \quad (37)$$

2. The most likely location at time t may be found by maximizing the probability density $P(x, t)$

3. The electron must be somewhere so

$$\int_{-\infty}^{\infty} dx |\Psi(x, t)|^2 = 1 \quad (38)$$

4. The average position at time t

$$\bar{x} = \int_{-\infty}^{\infty} dx x |\Psi(x, t)|^2 \quad (39)$$

5. The average position squared at time t is

$$\bar{x^2} = \int dx x^2 |\Psi(x, t)|^2 \quad (40)$$

6. The uncertainty squared in position $(\Delta x)^2$ is defined to be

$$(\Delta x)^2 \equiv \bar{x}^2 - \bar{x}^2 = \overline{(x - \bar{x})^2} \quad (41)$$

This is also known as the standard deviation squared, or the spread. If the average position is zero \bar{x} then $(\Delta x) \equiv \sqrt{\bar{x}^2}$.

Momentum Averages

1. We use a notation for “Operators”

$$\bar{x} = \int_{-\infty}^{+\infty} dx \Psi^*(x) \mathbb{X} \Psi(x) \quad (42)$$

$$= \int_{-\infty}^{+\infty} dx \Psi^*(x) x \Psi(x) \quad (43)$$

Here \mathbb{X} is simply an “operator” which takes the function $\Psi(x)$ and spits out the new function $x\Psi(x)$. It just gives a notation to things that we already understand, for example $\mathbb{X}^2 \Psi(x) = \mathbb{X} x \Psi(x) = x^2 \Psi(x)$

2. The average momentum is

$$\bar{p} = \int_{-\infty}^{+\infty} dx \Psi^*(x) \mathbb{P} \Psi(x) \quad (44)$$

$$= \int_{-\infty}^{+\infty} dx \Psi^*(x) \left(-i\hbar \frac{d}{dx} \right) \Psi(x) \quad (45)$$

$$= \int_{-\infty}^{+\infty} dx \Psi^*(x) \left(-i\hbar \frac{d\Psi}{dx} \right) \quad (46)$$

Here the momentum operator is

$$\mathbb{P} = -i\hbar \frac{d}{dx}$$

takes the function $\Psi(x)$ and spits out the derivative $-i\hbar \frac{d\Psi}{dx}$.

3. The average momentum squared is

$$\bar{p}^2 = \int_{-\infty}^{+\infty} \Psi^*(x) \mathbb{P}^2 \Psi(x) \quad (47)$$

$$= \int_{-\infty}^{+\infty} \Psi^*(x) \left(-\hbar^2 \frac{d^2}{dx^2} \right) \Psi(x) \quad (48)$$

4. The uncertainty squared in momentum (or standard deviation squared) is defined like for $(\Delta x)^2$

$$(\Delta p)^2 \equiv \bar{p}^2 - \bar{p}^2 \quad (49)$$

Again if \bar{p} is zero then $\Delta p \equiv \sqrt{\bar{p}^2}$ is the “root mean square” momentum.

5. The average kinetic energy is

$$\overline{KE} = \int_{-\infty}^{+\infty} \Psi^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right] \Psi(x) \quad (50)$$

6. The formal statement of the uncertainty principle is

$$(\Delta x)(\Delta p) \geq \frac{\hbar}{2} \quad (51)$$

where the standard deviation in position Δx and momentum Δp are defined as above. (You can see why its a good thing that we know how to use it before we can state it precisely)

Quantum Mechanics

1. As with momentum, the average energy of a particle

$$\bar{E} = \int \Psi^*(x, t) \mathbb{E} \Psi(x, t) \quad (52)$$

$$= \int_{-\infty}^{\infty} dx \Psi^*(x, t) \left[+i\hbar \frac{\partial}{\partial t} \right] \Psi(x, t) \quad (53)$$

and the energy operator

$$\mathbb{E} = +i\hbar \frac{\partial}{\partial t} \quad (54)$$

Note the difference in sign between this and the momentum operator \mathbb{P} which ultimately is a reflection of the fact that waves are written $e^{+i(kx - \omega t)}$ with opposite signs for k and ω

2. The Schrödinger equation can be written

$$\left[\frac{\mathbb{P}^2}{2M} + V(\mathbb{X}) \right] \Psi(x, t) = \mathbb{E} \Psi(x, t) \quad (55)$$

$$\left[-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + V(x) \right] \Psi(x, t) = +i\hbar \frac{\partial \Psi}{\partial t} \quad (56)$$

where $V(x)$ is the potential energy (think $V = 1/2 kx^2$)

3. The stationary wave functions (or eigenfunctions) have the following form

$$\Psi(x, t) = e^{-i\frac{E_n t}{\hbar}} \Psi_n(x) \quad (57)$$

And are called stationary because the square does not depend on time

$$|\Psi(x, t)|^2 = \left| e^{-i\frac{E_n t}{\hbar}} \right|^2 |\Psi_n(x)|^2 \quad (58)$$

$$= |\Psi_n(x)|^2 \quad (59)$$

Since the wave function does not depend on time we can take a long time to determine the energy. So stationary have functions exactly the energy $E = E_n$. There is no uncertainty in the energy.

4. Stationary wave functions (also known as eigenfunctions) obey the time independent Schrödinger equation.

$$\left[-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} + V(x) \right] \Psi_n(x) = E_n \Psi_n(x) \quad (60)$$

Here the E_n are the energy levels (as in the $E_n = -13.6eV/n^2$ in the Bohr Model) are the E_n in the stationary wave functions

Particle in the Box

- For an electron bouncing around in a box of size a the stationary wave functions (eigen-functions) are

$$\Psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right) & n = 1, 3, 5, \dots \\ \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) & n = 2, 4, 6, \dots \end{cases} \quad (61)$$

while the stationary energies are

$$E_n = \frac{\hbar^2 k_n^2}{2M} = \frac{\hbar^2 \pi^2}{2Ma^2} n^2 \quad n = 1, 2, 3, 4, 5, \dots \quad (62)$$

Qualitative Features of Schrödinger Equation

$$\left[\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \Psi_n(x) = E_n \Psi_n(x) \quad (63)$$

- In the classically allowed region the eigen-functions oscillates. In the classically forbidden region the wave function decays exponentially. For a given potential you should be able to roughly sketch the wave functions.
- In the classically allowed region $E > V$, you be able to show (by assuming that the potential V is constant) that the wave function oscillates with wave number $k = 2\pi/\lambda$ as

$$\Psi(k) \propto A \cos(kx) + B \sin(kx) \quad \text{where} \quad k \sim \sqrt{\frac{2m(E-V)}{\hbar^2}} E_n \rightarrow E_n + \delta E_n \quad \overline{\delta V(x)} = \int_{-\infty}^{\infty} \psi_n^*(x) \delta V(x) \psi_n(x) \quad (64)$$

- In the classically forbidden region $E < V$, we say that the particle is “under the barrier” because $E < V$. Assuming that the potential is constant you should be able to show wave function decreases as

$$\Psi \sim C e^{-\kappa x} \quad \text{where} \quad \kappa \sim \sqrt{\frac{2m(V-E)}{\hbar^2}}, \quad (65)$$

as one goes deeper into the classically forbidden region. The length $D \equiv 1/(2\kappa)$ is known as the “penetration” depth. It is the length over which the probability decreases by a factor $1/e$.

- Looking at the Schrödinger equation

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}(E-V)\psi \quad (66)$$

we conclude:

- In the classically allowed region ($E - V > 0$) the wave function is concave down if $\psi > 0$ and concave up if $\psi < 0$. The strength of the curvature (how rapidly it oscillates) is controlled by $2m(E-V)/\hbar^2$.

- In the classically forbidden region ($E - V < 0$) the wave function is concave up if $\psi > 0$ and concave down if $\psi < 0$. The strength of the curvature is controlled by $2m(V-E)/\hbar^2$.

- The energy is determined in the Schrödinger Equation by demanding that the wave function Ψ decreases as $x \rightarrow \infty$. This is why we neglect exponentially increasing solutions $e^{+\kappa x}$ in the preceding item.
- Generally there is one more “half” wavelength in the “box” (or more properly the classically allowed region) each time the particle in the potential is excited from one energy state (i.e. Ψ_n) to the next higher one (i.e. Ψ_{n+1}). Look at Box wave functions or simple harmonic oscillator wave functions for examples.
- The wave function is always continuous and has continuous first derivatives.
- An example of these trends is given by the set of simple harmonic oscillator wave functions handed out in class. You should be able to see these features in the figures handed out in class.

Perturbations

- In the presence of a small additional potential potential $\delta V(x)$ the energy of the n -th state is changed by the average of the additional potential. More specifically, $\delta E_n = \overline{\delta V(x)}$, i.e.

$$\overline{\delta V(x)} = \int_{-\infty}^{\infty} \psi_n^*(x) \delta V(x) \psi_n(x) \quad (67)$$

where $\psi_n(x)$ is the unperturbed wave functions.

2D Shrödinger Equation

- In two dimensions the Schrödinger equations reads

$$\left[\frac{\mathbb{P}_x^2}{2m} + \frac{\mathbb{P}_y^2}{2m} + V(x, y) \right] \Psi(x, y) = E\Psi(x, y) \quad (68)$$

$$\left[\frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + V(x, y) \right] \Psi(x, y) = E\Psi(x, y) \quad (69)$$

- For the particle in the two dimensional box the potential is

$$V = \begin{cases} 0 & \text{inside box } 0 < x, y < L \\ \infty & \text{outside box} \end{cases} \quad (70)$$

We solved this equation using separation of variables making an ansatz $\Psi(x, y) = X(x)Y(y)$ and solving for the functions X and Y

- We will discuss a square box $L_x = L_y = L$ but you should be able to generalize this to a rectangular box and also to three dimensions

- (a) The wave functions are described by two quantum numbers n_x, n_y and are

$$\Psi_{n_x, n_y}(x, y) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n_x}{L} x\right) \times \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n_y}{L} y\right) \quad (71)$$

with

$$n_x = 1, 2, 3, \dots \quad \text{and} \quad n_y = 1, 2, 3, \dots \quad (72)$$

The Energies are

$$E_{n_x, n_y} = KE_x + KE_y \quad (73)$$

$$= \frac{\hbar^2 k_x^2}{2M} + \frac{\hbar^2 k_y^2}{2M} \quad (74)$$

with

$$k_x = \frac{\pi n_x}{L} \quad k_y = \frac{\pi n_y}{L} \quad (75)$$

- (b) Some wave functions can have the same energy which is known as a degeneracy. For instance the following two states are degenerate for a square box

$$E_{21} = E_{12} = \frac{\hbar^2 \pi^2}{2ML^2} 5 \quad (76)$$

This is a consequence of the fact that the x direction is no different from the y . There is a symmetric in the problem

Particle in a Spherical Potential

1. For a particle moving in a Spherically symmetric potential all the forces are in the radial direction

$$F(r) = -\frac{\partial V(r)}{\partial r} \hat{r} \quad (77)$$

We are generally considering an electron moving in the Coulomb field of a proton. In this case the potential and forces are the familiar

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r} \quad F(r) = -\frac{e^2}{4\pi\epsilon_0 r^2} \hat{r} \quad (78)$$

2. The kinetic energy operator is

$$\frac{-\hbar^2}{2m} \nabla^2 \equiv \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \quad (79)$$

$$= \frac{-\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right) \quad (80)$$

$$+ \frac{1}{r^2} \left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \quad (81)$$

Here we have defined the angular momentum squared operator

$$\mathbb{L}^2 = -\hbar^2 \left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \quad (82)$$

3. The Schrödinger equation reads

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_{nlm}(r, \theta, \varphi) = E_{nl} \psi_{nlm}(r, \theta, \varphi) \quad (83)$$

The wave functions depend on the quantum numbers nlm but it turns out that the energies do not depend on m .

4. For *any* radially symmetric potential the wave function is in general written as a product of radial wave function $R_{nl}(r)$ and angular wave functions Θ and Φ

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) \underbrace{\Theta_{lm}(\theta)}_{\equiv Y_{lm}(\theta, \varphi)} \Phi_m(\varphi) \quad (84)$$

Here the labels n, l and m are the quantum numbers. One for each dimension r, θ, φ . Note the labels: for instance $R_{nl}(r)$ depends only on n and l but not m . The product of Θ and Φ is known as a *spherical harmonic* $Y_{lm}(\theta, \varphi) \equiv \Theta_{lm}(\theta)\Phi_m(\varphi)$. For $l = 0$ there is no angular dependence and $Y_{00} = 1$ and $\Theta_{lm} = 1$.

5. Substituting the wave function of $\psi = R(r)Y(\theta, \varphi)$ into the Schrödinger equation we find an equation for R and an equation for Y .

- (a) The equation for R is the radial Schrödinger equation is discussed in the next section

$$\left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r) \right] R_{nl} = E_{nl} R_{nl}(r) \quad (85)$$

The solutions R_{nl} depend on the potential $V(r)$

- (b) The equation for $Y_{lm}(\theta, \varphi)$ is discussed below

$$\mathbb{L}^2 Y_{lm}(\theta, \varphi) = \ell(\ell+1)\hbar^2 Y_{lm}(\theta, \varphi) \quad (86)$$

Only for certain values of the constants E and $\ell(\ell+1)\hbar^2$ will the solutions be bounded. In particular it turns out that ℓ must be an integer. The functions $Y_{lm}(\theta, \varphi) = \Theta_{lm}(\theta)\Phi_m(\varphi)$ are shown in table (II). The angular piece is valid for all spherically symmetric potentials, while the radial piece is specific to hydrogen.

6. In general the wave functions are characterized by the three quantum numbers

- (a) The radial quantum number

$$n = 1, 2, 3, 4, \dots \quad (87)$$

which labels the radial excitation.

- (b) The angular momentum quantum number which must be less than n

$$\ell = 0, 1, \dots, n-1 \quad (88)$$

which labels the total angular momentum of this wave functions. These wave functions have definite angular momentum

$$\bar{L}^2 = \ell(\ell + 1)\hbar^2. \quad (89)$$

These are for $\ell = 0, 1, 2, 3, 4 \dots$ also called by the names

$$\ell = s, p, d, f, g \quad (90)$$

i.e. an “s-wave” is another name for the $\ell = 0$ wave function.

- (c) And a “magnetic” quantum number. These wave functions have definite z component of angular momentum

$$\bar{L}_z = m\hbar Y_{\ell m} \quad (91)$$

with

$$m = -\ell, -\ell + 1, \dots, \ell - 1, \ell \quad (92)$$

- (d) Thus for $n = 2$ (the first excited state) we the following four states

$$\underbrace{(n=2, \ell=0, m=0)}_{\text{s-wave, 2s}} \quad (93)$$

$$\underbrace{(n=2, \ell=1, m=-1)}_{\text{p-wave, 2p}} \quad (94)$$

$$\underbrace{(n=2, \ell=1, m=0)}_{\text{p-wave, 2p}} \quad (95)$$

$$\underbrace{(n=2, \ell=1, m=+1)}_{\text{p-wave, 2p}} \quad (96)$$

For the hydrogen atom these states are listed in Table. II

- (e) When we refer to the $3d$ state, we mean $n = 3$ and $\ell = 2$ and $m = -2, -1, 0, 1, 2$

Radial Part of Schrödinger Equation

1. For $\ell = 0$ $m = 0$ the wave function is independent of angle $\Theta_{00} = \Phi_0 = 1$.

$$\Psi_{n00} = R_{n0}(r) \quad (97)$$

2. The probability $d\mathcal{P}$ is

$$d\mathcal{P} = |\Psi|^2 dV = |R_{nl}(r)|^2 4\pi r^2 dr = P(r)dr \quad (98)$$

where the $4\pi r^2 dr$ is the volume of a spherical shell. Thus:

- (a) The probability to find a particle *per volume* is $|\Psi|^2$

- (b) The probability to find a particle *per unit radius* is:

$$P(r) = |R_{nl}|^2 4\pi r^2 = |u_{nl}(r)|^2 \quad (99)$$

where we have defined the $u_{nl}(r) = \sqrt{4\pi r^2} R_{nl}(r)$

- (c) The functions are normalized so that

$$\int d\mathcal{P} = \int_0^\infty |R_{nl}(r)|^2 4\pi r^2 dr = \int_0^\infty |u_{nl}(r)|^2 dr = 1 \quad (100)$$

3. As in the previous item, it is useful to define the “radial wave function” u_{nl}

$$u_{nl}(r) \equiv \sqrt{4\pi} r R_{nl}(r)$$

This is useful because $P(r)$ is then $|u_{nl}(r)|^2$ as described above. If the wave function of the form given in Eq. (85), then the radial Schrödinger equation for R (Eq. (86)) reduces to the the radial Schrödinger equation for u_{nl}

$$\left[\underbrace{\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial r^2}}_{\text{radial KE}} + \underbrace{\frac{\ell(\ell+1)\hbar^2}{2mr^2}}_{\text{angular KE}} + V(r) \right] u_{nl} = E_{nl} u_{nl} \quad (101)$$

- (a) For $\ell = 0$ (no angular momentum) this reduces to a 1D shrodinger equation in the potential $V(r)$.
(b) For $\ell \neq 0$ there is an extra “potential” which represents the kinetic energy in the angular direction, i.e.

$$V(r) \rightarrow V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} \quad (102)$$

By considering the motion of a particle in a circle you should be able to show classically that

$$KE = \underbrace{\frac{1}{2}mv_r^2}_{\text{radial KE}} + \underbrace{\frac{L^2}{2mr^2}}_{\text{angular KE}} \quad (103)$$

where $L = mv_\perp r$ is the angular momentum. For a wave function with agular quantum number ℓ the angular momentum $\bar{L}^2 = \ell(\ell+1)\hbar^2$ as discussed in Eq. (90). Thus the form of this extra potential is understandable.

- (c) To understand the effect of this this extra potential, we note first that the “centripetal force” for a classical particle moving in a circle is

$$F_C = m \frac{v^2}{r} \hat{r} = \frac{L^2}{mr^3} \hat{r} \quad (104)$$

where $L = mvr$ is the angular momentum. For a state with angular quantum number the angular momentum $\bar{\mathbb{L}}^2 = \ell(\ell + 1)\hbar^2$ as discussed near Eq. (90). Then we note that the “force” due to this extra potential

$$\mathbf{F}_C = -\frac{\partial}{\partial r} \frac{\ell(\ell + 1)\hbar^2}{2mr^2} \hat{\mathbf{r}} = \frac{\bar{\mathbb{L}}^2}{mr^3} \hat{\mathbf{r}} \quad (105)$$

Thus the effect of this extra term is to provide the “centripetal force”. Classically there is no real “centripetal force”. It just summarizes the effect of the circular motion on the radial direction. Similarly there is no extra potential really, it is just the effect of the angular kinetic energy on the radial dynamics.

4. We can average different quantities

$$\overline{PE} = \int_0^\infty \frac{-e^2}{4\pi\epsilon_o r} P(r) dr \quad (106)$$

and

$$\bar{r} = \int_0^\infty r P(r) dr \quad (107)$$

The variance in the radius is

$$(\Delta r)^2 \equiv \bar{r}^2 - \bar{r}^2 \quad (108)$$

5. The average kinetic energy is

$$\overline{KE} = \int_0^\infty u_{nl}^* \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{\ell(\ell + 1)\hbar^2}{2mr^2} \right] u_{nl} d\ell \quad (109)$$

6. You should be able to verify that this or that function satisfies the radial Schrödinger equation. You should be able to describe the qualitative features

Angular Part of the Schrodinger Equation:

1. The wave functions have definite squared angular momentum labeled by the orbital quantum number ℓ and m

$$\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \varphi) \quad (110)$$

so that

$$\bar{\mathbb{L}}^2 Y_{lm} = \ell(\ell + 1)\hbar^2 Y_{lm} \quad (111)$$

The magnetic quantum number m records the angular momentum about the z-axis.

$$\mathbb{L}_z Y_{lm} = m\hbar Y_{lm} \quad (112)$$

where the angular momentum squared operator and are

$$\bar{\mathbb{L}}^2 = -\hbar^2 \left(\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad (113)$$

$$\mathbb{L}_z = -i\hbar \frac{\partial}{\partial \phi} \quad (114)$$

ℓ	m	$\Phi_m(\phi)$	$\Theta_{lm}(\theta)$
0	0	1	1
1	0	1	$\sqrt{3} \cos(\theta)$
1	± 1	$e^{\pm i\phi}$	$\sqrt{\frac{3}{2}} \sin(\theta)$
2	0	1	$\frac{\sqrt{5}}{4} (3 \cos(2\theta) + 1)$
2	± 1	$e^{\pm i\phi}$	$\sqrt{\frac{15}{2}} \sin(\theta) \cos(\theta)$
2	± 2	$e^{\pm i2\phi}$	$\frac{1}{2} \sqrt{\frac{15}{2}} \sin^2(\theta)$

TABLE I: Angular part of the wave functions

n	ℓ	m	$\Phi_m(\phi)$	$\Theta_{lm}(\theta)$	$R_{nl}(r)$
1	0	0	1s	1	$\frac{1}{\sqrt{\pi a_o^3}} e^{-r/a_o}$
2	0	0	2s	1	$\frac{1}{\sqrt{32\pi a_o^3}} \left(2 - \frac{r}{a_o} \right) e^{-r/2a_o}$
2	1	0	2p	$\sqrt{3} \cos(\theta)$	$\frac{1}{\sqrt{96\pi a_o^3}} \frac{r}{a_o} e^{-r/2a_o}$
2	1	± 1	2p	$e^{\pm i\phi}$	$\sqrt{\frac{3}{2}} \sin(\theta)$
					$\frac{1}{\sqrt{96\pi a_o^3}} \frac{r}{a_o} e^{-r/2a_o}$

TABLE II: Hydrogen wave functions

Hydrogen Atom

- For the special case of the hydrogen atom the potential $V(r)$ is just the Coulomb potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_o r} \quad (115)$$

- The energies are

$$E_{n\ell} = -\frac{\hbar^2}{2ma_0^2} \frac{Z^2}{n^2} = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_o a_0} \frac{Z^2}{n^2} \quad (116)$$

We note that the fact that the energies are independent of ℓ for the hydrogen atom is special to the $1/r$ potential.

- The lowest order wave functions are listed in Table II.
- An integral which comes up a lot is

$$\int_0^\infty dx x^n e^{-x} = n! \quad (117)$$

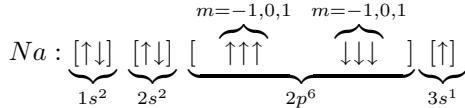
- For $n = 3$ we will quote the R_{nl} only. For the necessary table of Θ_{lm} and Φ_m see Table I. Here

$$\rho \equiv \frac{2r}{3a_o} \quad (118)$$

n	ℓ	R_{nl}
3	0	$\sqrt{\frac{40}{(4\pi)6!}} \left(\frac{2}{3a_o} \right)^{3/2} \frac{1}{2} (6 - 6\rho + \rho^2) e^{-\rho/2}$
3	1	$\sqrt{\frac{5}{(4\pi)6!}} \left(\frac{2}{3a_o} \right)^{3/2} (4 - \rho) \rho e^{-\rho/2}$
3	2	$\sqrt{\frac{1}{(4\pi)6!}} \left(\frac{2}{3a_o} \right)^{3/2} \rho^2 e^{-\rho/2}$

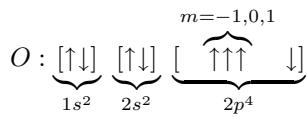
Atoms

- Electrons fill up orbitals one by one. There are some things to know when filling up the shells:
- After filling the $3p$ orbital, one starts filling the $4s$ orbital before filling the $4s$ orbital. This is because the $4s$ state is actually lower than the $3d$ state as shown below. They are very close however.
- For every state of hydrogen the electron can be either spin up or spin down. Thus for example for sodium Na the structure is



where each arrow represents an electron.

- Hunds Rule.* Take filling up the $3p$ orbital for example. When filling up the $2p$ orbital one first fills up the m levels with the same spin, and then one starts the process again for the next spin. Thus the structure of Oxygen is the following



where each arrow represents an electron.

- Atoms with closed shells He, Ne, \dots tend to be chemically inert. This is due to the fact that the sum (over m) of spherical harmonics of is independent of the angle θ

$$\sum_{m=-l,\dots,l} |Y_{lm}|^2 = 2l + 1 \quad (120)$$

Atoms with closed shells can effectively shield the positive nuclear charge.

More about angular dependence in a spherical potential

- The probability to find the particle in a volume dV is

$$d\mathcal{P} = |\Psi|^2 dV = |R_{nl}(r)|^2 |\Theta_{lm}(\theta)|^2 |\Phi_m|^2 \quad (121)$$

$$\times r^2 dr d\Omega \quad (122)$$

$$= |R_{nl}(r)|^2 |\Theta_{lm}(\theta)|^2 |\Phi_m|^2 \quad (123)$$

$$\times r^2 dr \sin(\theta) d\theta d\varphi \quad (124)$$

This is the probability to find the particle between r and $r + dr$, θ and $\theta + d\theta$, φ and $\varphi + d\varphi$. If one integrates over θ and φ one finds the probability to be between r and $r + dr$ without concern for angles is

$$P(r)dr = |R_{nl}|^2 (4\pi r^2)dr \quad (125)$$

i.e. the same as if there were no angular dependence. This is equivalent to saying that the functions Θ and Φ are normalized so that

$$\int d\Omega |\Theta_{lm}(\theta)|^2 |\Phi_m(\varphi)|^2 = 4\pi \quad (126)$$

- The probability to find the electron per unit solid angle (usually what we care about) is

$$P_\Omega(\theta, \varphi) = \frac{|Y_{lm}(\theta, \varphi)|^2}{4\pi} = \frac{|\Theta_{lm}(\theta)|^2}{4\pi} \quad (127)$$

so that the probability to find an electron in a given solid angle (without concern for radius) is $d\mathcal{P} = P_\Omega d\Omega$.