Applications to atomic systems

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Recaptulate

- We have shown how quantum mechanics can be used to explain particle motion in 1-D.
- The instantaneous state of a particle is fully specified by a complex wavefunction $\psi(x, t)$.
- The probability of finding the particle at a time t between x and $x + dx$ is

$$P(x, t)dx = |\psi(x, t)|^2 dx \text{ where } \int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = 1 \text{ at all times.}$$

- Two new features have emerged from the study of 1-D systems:

  1. Quantization of Energy 2. Tunneling Phenomena

We now extend to 3-D systems and explore the predictions of the theory for —
Particle in a box, 3D Oscillator and Hydrogen atom

Learning objectives

By the end of this part, you will be able to:

1. Describe quantum mechanics in higher dimensions.
2. Understand the concept of degeneracy.
3. Applications of model 3-D systems to “real world”.

Quantum mechanics in 3-D

Fundamental concepts in 3-D: Extensions from 1-D

- Generalize $p_x \longrightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$ to 3-D. Cartesian coordinates have no preferential directions

$$p_x \longrightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}, p_y \longrightarrow \frac{\hbar}{i}\frac{\partial}{\partial y}, p_z \longrightarrow \frac{\hbar}{i}\frac{\partial}{\partial z} \qquad \mathbf{p} \longrightarrow \frac{\hbar}{i}\nabla$$

- In 3-D, the instantaneous state of a particle is fully specified by $\psi(x, y, z, t)$.

- By analogy with 1-D systems, the probability to find the particle at time t between x and $x + dx$, between y and $y + dy$, and between z and $z + dz$, is

$$P(x, y, z, t)\, dxdydz = |\psi(x, y, z, t)|^2\, dxdydz \tag{1}$$

- Like in 1-D, this interpretation of the wavefunction only makes sense if the wavefunction is normalized:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x, y, z, t)|^2 dxdydz = 1 \tag{2}$$

- In 3-D, the time-dependent Schroedinger equation is:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(x, y, z)\,\psi \quad \text{where} \quad \bar{\nabla}^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{3}$$

Fundamental concepts in 3-D: Differences from 1-D

- In 1-D, knowing x uniquely determined $\psi(x)$.
  In 3-D, knowing the three quantities x, y, and z can only define the state $\psi(x, y, z)$.
- 1-D bound states: Integer energy level n contains all the information about the particle.
- 3-D bound states: Three quantum numbers are needed to specify the condition. These correspond to the three independent degrees of freedom for a particle in space:

$$\text{1-D: } \{E_n, \psi_n(x)\} \qquad \text{3-D: } \{E_{n,m,l}, \psi_{n,m,l}(x, y, z)\}$$

- Unlike in 1-D, we can have situation where different states have the same energy!

$$E_{n_1,m_1,l_1} = E_{n_2,m_2,l_2} \qquad \psi_{n_1,m_1,l_1} \neq \psi_{n_2,m_2,l_2}$$

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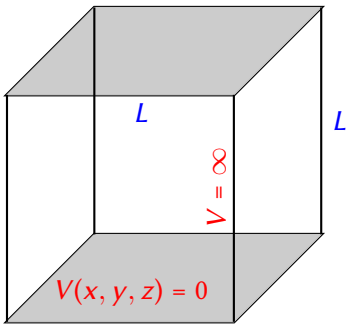
Two or more stationary states of the same quantum-mechanical system may have the same energy even though their wave functions are not the same.

Particle in 3-D box

Particle in 3-D box



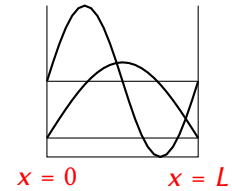
- Consider 3-D version of particle in a box with all sides L.
- Like in 1-D, $\psi(x, y, z)$ must be zero at the walls of the box.
- Following 1-D, we can try the following solution:

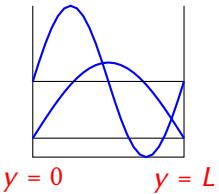
$$\psi(x, y, z) = \phi(x)\,\eta(y)\,\zeta(z)$$

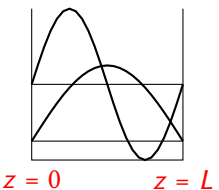
- Inserting this in time-independent Schroedinger equation:

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

Particle in 3-D box







- We have 3 identical equations to solve in three dimensions:

$$-\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dx^2} = E_x\phi(x)$$
$$-\frac{\hbar^2}{2m}\frac{d^2\eta(y)}{dy^2} = E_y\eta(y)$$
$$-\frac{\hbar^2}{2m}\frac{d^2\zeta(z)}{dz^2} = E_z\zeta(z)$$

The solution is

$$\psi_{n_x,n_y,n_z}(x,y,z) = \phi_{n_x}(x)\eta_{n_y}(y)\zeta_{n_z}(z) = A\sin(k_x x)\sin(k_y y)\sin(k_z z)$$

- Applying boundary conditions, we get

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2);\quad k_x = \frac{\pi n_x}{L}, k_y = \frac{\pi n_y}{L}, k_z = \frac{\pi n_z}{L}$$

Particle in 3-D box

n_x	n_y	n_z	n^2	Degeneracy
1	1	1	3	None
1	1	2	6	
1	2	1	6	Threefold
2	1	1	6	
1	2	2	9	
2	1	2	9	Threefold
2	2	1	9	
1	1	3	11	
1	3	1	11	Threefold
3	1	1	11	
2	2	2	12	None

- Energy eigenvalues are

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z \in 1, 2\cdots, \qquad (4)$$

- Wavefunctions are

$$\psi_{n_x,n_y,n_z} = A \sin\left(\frac{\pi n_x}{L}x\right) \sin\left(\frac{\pi n_y}{L}y\right) \sin\left(\frac{\pi n_z}{L}z\right) \qquad (5)$$

- Ground state is $n_x = n_y = n_z = 1$
- First excited state can be obtained in 3 different ways:

$$n_x = n_y = 1, n_z = 2; n_z = n_x = 1, n_y = 2; n_x = 2, n_y = n_z = 1$$

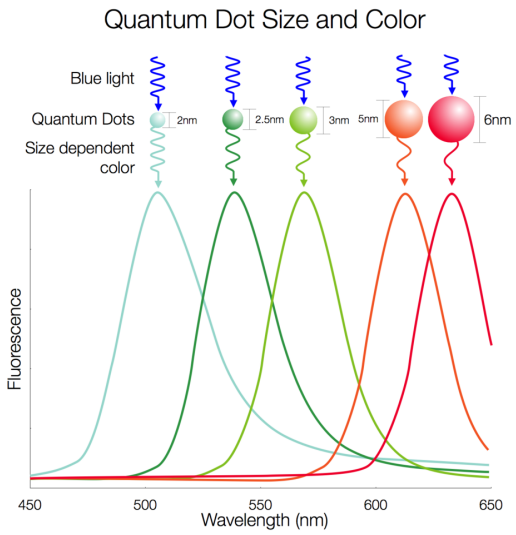
Corresponding ψ's are different $\Longrightarrow$ Degenerate states

“Real world” Particle in 3-D box

Quantum Dots

- A quantum dot is a very small structure, e.g. a semiconductor nanocrystal embedded in another semiconductor material, which can confine electrons or other carriers in all three dimensions.
- The confinement of electron in all three dimensions is like particle in 3-D box!
- Like particle (atom) in a box, an ideal isolated quantum dot has discrete energy levels.
- Quantum dots can be considered as artificial atoms where the energy levels can be adjusted by design, e.g. by controlling the quantum dot dimensions or the material composition
- If the size of the quantum dot is small enough that the quantum confinement effects dominate (typically less than 10 nm), the electronic and optical properties are highly tunable.

Quantum Dots



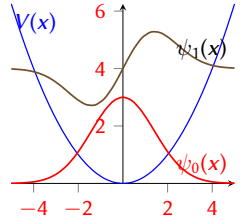
Next generation display (TV) screens will use Quantum dots technology. Several advantages:

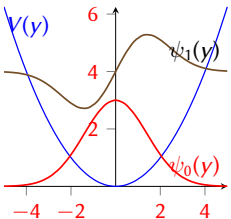
1. The color of light each quantum dot gives is very stable and pure.
2. Quantum dots can show precise colors while the light from LEDs get mixed with adjacent colors.
3. The 3 primary colors are more clearly distinguished in comparison to conventional TVs. Quantum dot display show a wide range of colors more accurately.

Credit: Nanosysinc.com

3-D Isotropic oscillator

3-D Isotropic oscillator





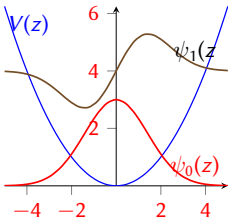
- The potential of the 3-D isotropic oscillator:

$$V(x,y,z) = \frac{1}{2}m\omega^2 r^2 = \frac{1}{2}m\omega^2\left(x^2+y^2+z^2\right)$$
$$= V(x) + V(y) + V(z)$$

- Like particle in a box, we have 3 identical equations to solve in 3-D:

$$-\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dx^2} + V(x)\phi(x) = E_x\phi(x)$$
$$-\frac{\hbar^2}{2m}\frac{d^2\eta(y)}{dy^2} + V(y)\eta(y) = E_y\eta(y)$$
$$-\frac{\hbar^2}{2m}\frac{d^2\zeta(z)}{dz^2} + V(z)\zeta(z) = E_z\zeta(z)$$

3-D Isotropic oscillator



- Energy eigenvalues are

$$E_{n_x,n_y,n_z} = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right) \quad n_x, n_y, n_z \in 0, 1\cdots$$

- Wavefunctions are

$$\psi_{n_x,n_y,n_z}(x, y, z) = \phi_{n_x}(x)\,\eta_{n_y}(y)\,\zeta_{n_z}(z) \tag{6}$$

- Ground state is $n_x = n_y = n_z = 0$

$$\psi_{000}(x, y, z) = \left(\frac{\beta^2}{\pi}\right)^{\frac{3}{4}} e^{-\beta^2\left(x^2+y^2+z^2\right)/2}; \quad \beta^2 = \frac{m\omega}{\hbar}$$

3-D Isotropic oscillator

n_x	n_y	n_z	n	Degeneracy
0	0	0	0	None
0	0	1	1	
0	1	0	1	Threefold
1	0	0	1	
0	0	2	2	
0	2	0	2	
2	0	0	2	Sixfold
1	1	0	2	
0	1	1	2	
0	1	1	2	
			3	Tenfold

- First excited state can be obtained in 3 different ways:

$$n_x = n_y = 0, n_z = 1; n_x = n_z = 0, n_y = 1; n_x = 1, n_y = n_z = 0$$

Like earlier example, corresponding ψ's are different

$$\psi_{100}(x,y,z) = \left(\frac{\beta^2}{\pi}\right)^{\frac{3}{4}} \sqrt{2}(\beta\, x)\, e^{-\beta^2\left(x^2+y^2+z^2\right)/2}$$

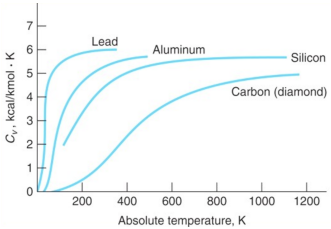
$$\psi_{010}(x,y,z) = \left(\frac{\beta^2}{\pi}\right)^{\frac{3}{4}} \sqrt{2}(\beta\, y)\, e^{-\beta^2\left(x^2+y^2+z^2\right)/2}$$

$$\psi_{001}(x,y,z) = \left(\frac{\beta^2}{\pi}\right)^{\frac{3}{4}} \sqrt{2}(\beta\, z)\, e^{-\beta^2\left(x^2+y^2+z^2\right)/2}$$

- Unlike particle in box, except ground state, all excited states are Degenerate states

“Real world” Isotropic HO

Dulong-Petit law



Dulong-Petit law is not always true, and is never true at low temperatures!

- Heat capacity (C) of a substance is a measure of how much heat is required to raise the temperature of the substance by one degree Kelvin.
- Dulong and Petit law: For a solid, the heat capacity is

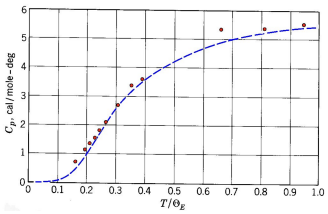
$$C_V = 3k_B \quad \Longrightarrow \quad E = 3\,k_B\,T \tag{6}$$

- Classical Interpretation: From Hooke's law, we can express the proportionality between the deformations of a solid and the counter forces. The energy of an atom in solid

$$E = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + \frac{1}{2}m\omega^2\left(x^2 + y^2 + z^2\right)$$

Suppose each degree of freedom has $\epsilon = k_B T/2$ (Equipartiton law) leads to (6).

Einstein model of solids (1907 before Schroedinger equation)



Comparison of experimental values of C_V for diamond with values calculated for Einstein model.

- Dulong-Petit law uses the classical description of lattice vibrations. They fail to describe at low temperatures.
- Einstein's model takes into account quantum description of lattice vibrations.
- Assumption: Solid is made of N independent 3-D quantum oscillator all with same mass m and frequency ω:

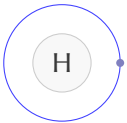
$$E_{\text{total}} = \sum_{i=1}^{N} \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + \frac{1}{2}m\omega^2\left(x^2 + y^2 + z^2\right)$$

- Einstein's model was a good attempt to explain the specific heat of solids. However, it could not explain because it assumed that all the normal modes have the same frequency. Debye model overcame this.

Hydrogen atom

Hydrogen Atom: Classical analysis

- Hydrogen atom is the simplest atom in nature. Consists of a negatively charged electron moving around a positively charged proton.



- In Bohr's model, the electron is pulled around the proton in a perfectly circular orbit by an attractive Coulomb potential:

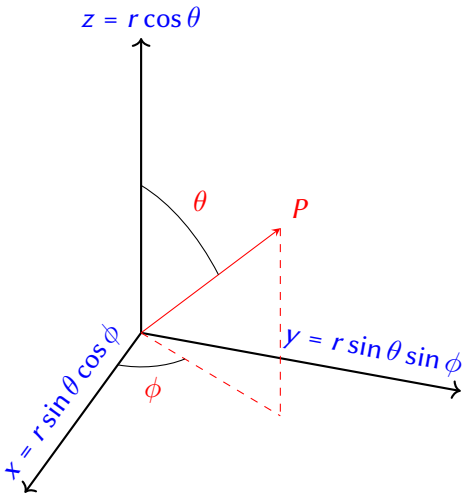
$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{e}{r} \qquad r \text{ is radial distance between proton and electron}$$

- Proton is approximately 1800 times more massive than the electron, so the proton moves very little in response to the force on the proton by the electron. Like Sun-Earth system, Sun moves very little in response to Earth's force.

- We assume Proton to be at rest. Treat Hydrogen as a single particle (electron).

$$T_{\mathrm{e}} = \frac{p^2}{2m_e}; \qquad V(r) = -\frac{1}{4\pi\epsilon_0}\frac{e}{r} \tag{7}$$

A bit on coordinate systems



- Coloumb potential is

$$V(x, y, z) = \frac{C_0}{r} = \frac{C_0}{\sqrt{x^2 + y^2 + z^2}}$$
$$\implies V(x, y, z) \neq V(x) + V(y) + V(z)$$

- For such potentials, Cartesian coordinate (x, y, z) is not useful Spherical polar is better suited.
- Transformation between Cartesian and Polar:

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

Hydrogen Atom: Quantum Analysis

- Since potential depends only on r, ψ can be written as a product of three functions:

$$\psi_{n,l,m}(r,\theta,\phi) = \underbrace{R_{n,l}(r)}_{\text{Radial func}} \underbrace{\Theta_{l,m}(\theta)}_{\text{Polar func}} \underbrace{\Phi_m(\phi)}_{\text{Angular func}} \quad ; \quad E_n = -\left(\frac{m_e e^4}{8h^2\epsilon_0^2}\right)\frac{1}{n^2} = -\frac{E_0}{n^2}$$

- Quantum numbers (n, l, m):

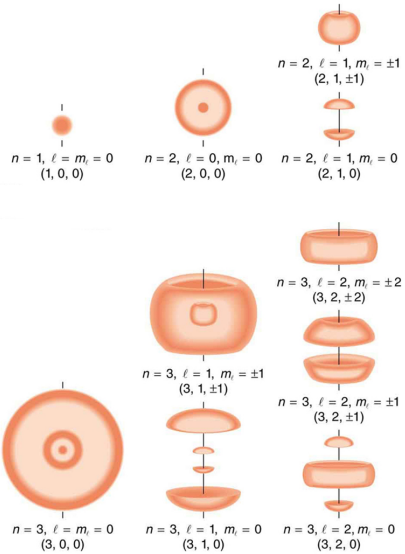
n :	principal quantum number	$1, 2, 3, \cdots$
l :	angular momentum quantum number	$0, 1, 2, \cdots (n-1)$
m :	angular momentum projection quantum number	$-l, -(l+1), \cdots, 0, \cdots (l-1), l$

- Ground state is unique and is given by $n = 1, l = 0, m = 0$.

- First excited state ($n = 2$) can be obtained in 4 (n^2) different ways (4 degenerate states)

$$l = 0, m = 0; l = 1, m = -1, 0, 1$$

Hydrogen Atom: Quantum Analysis



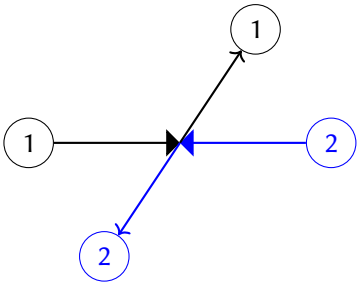
- Probability for the electron in the ground state ($n = 1$) and excited states of hydrogen.
- The probability of finding the electron is indicated by the shade of color; the darker the coloring the greater the chance of finding the electron.
- The nature of these states is determined by their sets of quantum numbers (n, l, m).

Credit: OpenStax

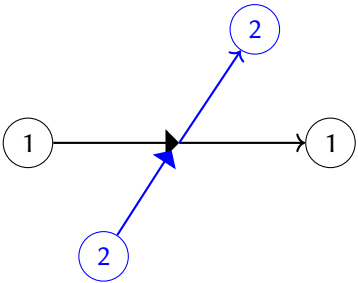
Three types of physical systems

Indistinguishablility and the Quantum

Consider the scattering between two identical particles of gas:

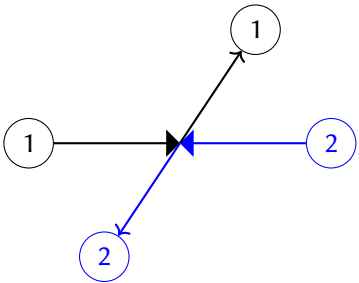


Configuration I of two-particles scattering



Configuration II of two-particles scattering

Indistinguishablility and the Quantum



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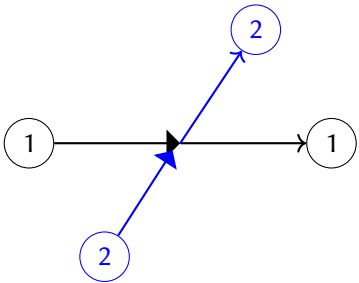
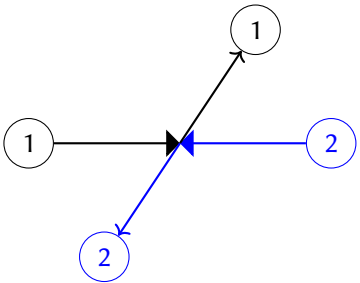


Configuration II of two-particles scattering

We can treat the scattering of the gas particles in two ways:

1. Classical mechanics
2. Quantum mechanics



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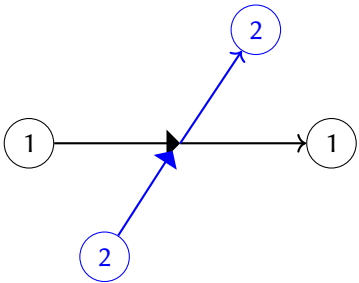


Configuration II of two-particles scattering

Classical mechanics

Even if they are identical, we can track the two particles continuously and can find which one of the scattering processes occurred.

Quantum mechanics

- Due to Uncertainty principle, such a tracking of particles is not possible!
- If we try to watch the trajectories of the particles, at the crucial time when the two atoms are nearby, the uncertainty in the position of the atom is larger, and lose track.
- Since, we can not specify the position and momentum precisely, we will never be able to know precisely which of the two events occur.

Indistinguishablility and the Quantum

- At an instant of time, consider two particles at positions $\mathbf{r}_1$ and $\mathbf{r}_2$. $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ describes the two particle system.

- The wave function for a system of identical particles must reflect the requirement that the particles are indistinguishable from each other.

- The probability density of the two particle wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ must be identical to that of the the wave function $\Psi(\mathbf{r}_2, \mathbf{r}_1)$ where the particles have been interchanged, i. e.

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2 .$$

- Two physical relevant cases in 3D are [when we exchange again the square should be 1.]

  1. Symmetric case: $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1)$
  2. Anti-symmetric case: $\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$

Symmetric and Anti-symmetric case

Symmetric case

- $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1)$
- Such particles are called Bosons
- Such Particles have integral or zero intrinsic spin.
- Example: Photons
- Any number of Bosons can occupy the same quantum state

Anti-symmetric case

- $\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1)$
- Such particles are called Fermions
- Such Particles have half-integral intrinsic spin.
- Example: Electrons, Protons, Neutrons
- No two Fermions can occupy the same state $\Longrightarrow$ Pauli exclusion principle.

Three types of physical systems

Physical systems in the nature can be classified into three categories:

- Distinguishable particles
  1. Treat the particles as classical billiard balls.
  2. Each of the particles are distinguishable from one another
  3. Any number of the particles can occupy a single quantum state.

Three types of physical systems

Physical systems in the nature can be classified into three categories:

- Distinguishable particles
  1. Treat the particles as classical billiard balls.
  2. Each of the particles are distinguishable from one another
  3. Any number of the particles can occupy a single quantum state.
- Indistinguishable particles whose wavefunctions are Anti-symmetric under exchange
  1. Indistinguishable particles (Fermions)
  2. Obey Pauli exclusion principle
  3. Particles with half-integer spins.

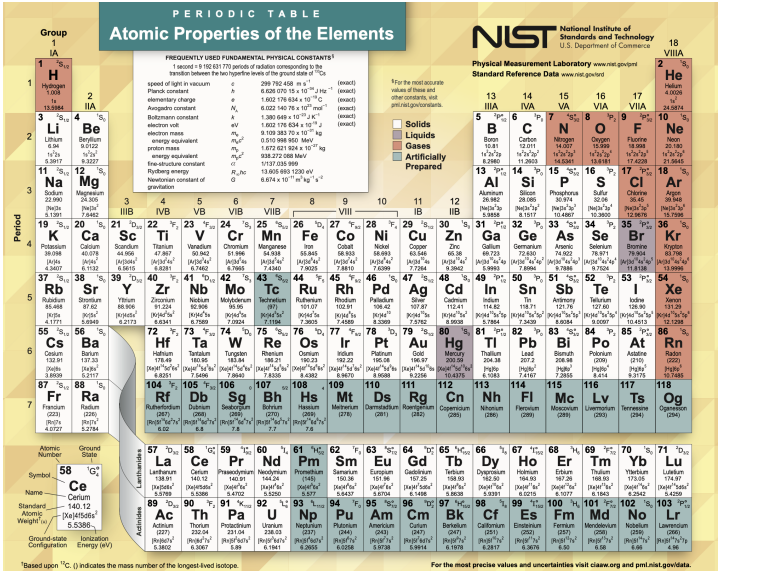
Three types of physical systems

Physical systems in the nature can be classified into three categories:

- Distinguishable particles
  1. Treat the particles as classical billiard balls.
  2. Each of the particles are distinguishable from one another
  3. Any number of the particles can occupy a single quantum state.
- Indistinguishable particles whose wavefunctions are Anti-symmetric under exchange
  1. Indistinguishable particles (Fermions)
  2. Obey Pauli exclusion principle
  3. Particles with half-integer spins.
- Indistinguishable particles whose wavefunctions are Symmetric under exchange
  1. Indistinguishable particles (Bosons)
  2. Do not obey Pauli exclusion principle
  3. Particles with integer spins.

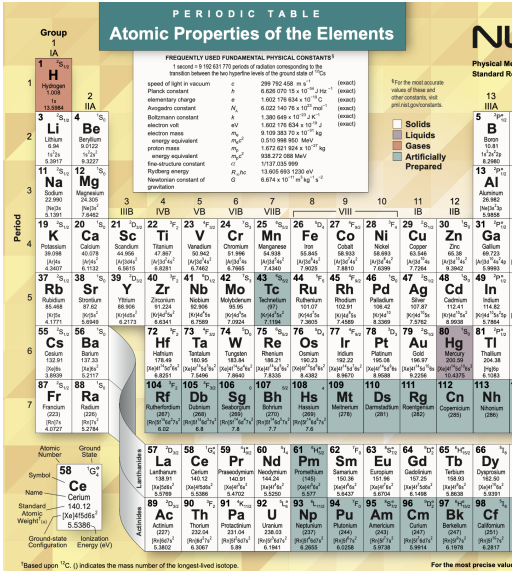
Multi-electron atoms

Periodic table and properties of multi-electron atoms



- All atoms except Hydrogen are multiple-electron atoms.
- The physical and chemical properties of elements are related to the number of electrons a neutral atom has!
- The periodic table of the elements groups elements with similar properties into columns.
- It is also arranged with increasing number of electrons in a neutral atom (atomic number Z).

Periodic table and Properties of multi-electron atoms



- Electrons have intrinsic spin angular momentum.
- As we will show in the next part, no two electrons can occupy the same quantum state. Pauli Exclusion principle
- These two extra ingredients can help to explain the structure and chemical properties of atoms.

Key Take-aways

- In 1-D, particle can move in only forward or backward direction. In 3-D, particles can choose to move in infinite directions!
- Depending on the form of the potential, we can have many quantum states that have the same energy eigenvalue — Degeneracy of states $\Longrightarrow$ Existence of symmetry
- We have explicitly show the degeneracy for particle in 3-D box and isotropic oscillator.
  If box size is not the same, the degeneracy decreases in particle in 3-D box.
- Like in 1-D, the ground state energy is greater than zero. The stationary states (states of definite energy) have non-zero values also in regions beyond classical turning points.
- Looked at application of model 3-D systems to real world!