

Degeneracy & in particular to Hydrogen atom

In quantum mechanics, an energy level is said to be degenerate if it corresponds to two or more different measurable states of a quantum system. Conversely, two or more different states of a quantum mechanical system are said to be **degenerate** if they give the same value of energy upon measurement.

When a wave function is written as a linear combination of two or more linearly independent energy eigenstates (of the same energy level), we can no longer predict with certainty, upon measurement, which energy eigenstate does the measured energy value comes from. Hence the term degenerate which means deteriorate literally.

The number of different states corresponding to a particular energy level is known as the degree of degeneracy of the level. It is represented mathematically by the Hamiltonian for the system having more than one linearly independent eigenstate with the same eigenvalue.

In classical mechanics, this can be understood in terms of different possible trajectories corresponding to the same energy. Take for instance, in projectile motion, we can project the particle in different trajectories each having the same total energy as the particle travel through its parabolic path.



Picture extracted from Wikipedia “Degenerate Energy Level”

In particular, for the degree of degeneracy of Hydrogen atom, we need to calculate how many possible linearly independent energy eigenstates corresponds to energy E_n of the atom. We knew that for hydrogen atom, its energy eigenstates is given by Ψ_{nlm} where:

Principal quantum number $n = 1, 2, 3, \dots$

Azimuthal or Orbital Angular momentum quantum number $l = 0, 1, 2, \dots, n-1$ i.e. n choices of them

Magnetic Quantum number $m = 0, \pm 1, \pm 2, \dots, \pm l$ i.e. $2l + 1$ choices of them.

Hence for a given n , we have n choices for l and for each l , we have $2l + 1$ choices for m . Thus,

Total number of possible energy eigenstates (nlm) =

$$\sum_{l=0}^{n-1} (2l + 1) = 1 + \sum_{l=1}^{n-1} (2l + 1) = 1 + 2 \sum_{l=1}^{n-1} l + \sum_{l=1}^{n-1} 1 = 1 + 2 \left(\frac{(n-1)n}{2} \right) + (n-1) = n^2$$

Therefore

$$\text{The degree of degeneracy of Hydrogen atom} = n^2$$

Pauli exclusion principle states that two identical fermions (particles with half-integer spin) cannot occupy the same quantum state simultaneously. In the case of electrons, it can be stated as follows: it is impossible for two electrons of a poly-electron atom to have the same values of the four quantum numbers: n , the principal quantum number, l , the angular momentum quantum number, m , the magnetic quantum number, and s , the spin quantum number. For two electrons residing in the same orbital, n , l , and m are the same, so s , the spin, must be different. Since electrons have two different type of spins (spin up and spin down), putting that into our degeneracy result, we have

$$\text{The } n\text{th shell of Hydrogen atom can hold up to } 2n^2 \text{ electrons}$$

$n = 1$: The first shell (K) can hold up to two electrons.

$n = 2$: The second shell (L) can hold up to eight 8 electrons.

$n = 3$: The third shell (M) can hold up to 18 electrons

$n = 4$: The fourth shell (N) can hold up to 32 electrons and so on.

Subshells s, p, d, f, g, h, ... & Spectroscopic Notation

For each n , different values of l corresponds to different *subshells*. States with various values of the orbital quantum number l are often labelled with letters, according to the following scheme:

l	0	1	2	3	4	5	...
States	s	p	d	f	g	h	...

This seemingly irrational choice of the letters s, p, d, f , etc originated in the early days of spectroscopy and has no fundamental significance. In *spectroscopic notation*, a state with $n = 2$ and $l = 1$ is called a $2p$ state; a state with $n = 4$ and $l = 0$ is a $4s$ state; and so on.

Table 41.1 Quantum States of the Hydrogen Atom

n	l	m_l	Spectroscopic Notation	Shell
1	0	0	1s	K
2	0	0	2s	L
2	1	-1, 0, 1	2p	
3	0	0	3s	M
3	1	-1, 0, 1	3p	
3	2	-2, -1, 0, 1, 2	3d	
4	0	0	4s	N
and so on				

Spectroscopic Notation

Label	Subshell	s	p	d	f	...
Shell	$n \quad l$	0	1	2	3	...
K	1	1s				
L	2	2s	2p			
M	3	3s	3p	3d		
N	4	4s	4p	4d	4f	
⋮	⋮	⋮	⋮	⋮	⋮	⋮

Refer to last page for a diagram of the subshells.

Example 1 Griffiths Problem 2.45

- (i) The free particle states are doubly degenerate – one solution representing motion to the right, and the other motion to the left.
- (ii) *In one dimension, there are no degenerate bound states.* (Free particles are not in bound states).

Solution

- (i) For free particle, $V = 0$ for all real values of x . Hence the time independent Schrodinger equation becomes

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \implies \frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2} \psi = -k^2\psi \quad \dots\dots (1)$$

where $k = \frac{\sqrt{2mE}}{\hbar}$. This is the harmonic oscillator equation. The auxiliary equation for differential equation (1) with complex function ψ is:

$$m^2 = -k^2 \implies m = \pm ik$$

Thus the general solution to differential equation (1) is:

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad \dots\dots (2)$$

where A and B are complex constants of integration. Notice that k can be complex if $E < 0$. However, by Griffiths Problem 2.2 (see below), a necessary but not sufficient condition for the solution to be normalizable, E must exceed the minimum value of $V(x)$. Thus $E > 0 \Rightarrow k \in \mathbb{R}$ and also free particle is in scattering state. From equation (2), we see that there are two linearly independent solution, namely $e^{\pm ikx}$ for the same energy E . Thus free particle states are doubly degenerate with degree of degeneracy two.

(ii) Suppose there are two solutions, ψ_1 and ψ_2 . Thus

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_1}{dx^2} + V\psi_1 = E\psi_1 \quad \dots\dots (3)$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_2}{dx^2} + V\psi_2 = E\psi_2 \quad \dots\dots (4)$$

$$\psi_2 \times (3): \quad -\frac{\hbar^2}{2m} \frac{d^2\psi_1}{dx^2} \psi_2 + V\psi_1\psi_2 = E\psi_1\psi_2 \quad \dots\dots (5)$$

$$\psi_1 \times (4): \quad -\frac{\hbar^2}{2m} \frac{d^2\psi_2}{dx^2} \psi_1 + V\psi_2\psi_1 = E\psi_2\psi_1 \quad \dots\dots (6)$$

(5) – (6):

$$\frac{d^2\psi_1}{dx^2} \psi_2 - \frac{d^2\psi_2}{dx^2} \psi_1 = 0 \Rightarrow \frac{d}{dx} \left(\psi_2 \frac{d\psi_1}{dx} - \psi_1 \frac{d\psi_2}{dx} \right) = 0 \Rightarrow \psi_2 \frac{d\psi_1}{dx} - \psi_1 \frac{d\psi_2}{dx} = \text{constant}$$

For bound states, the wave functions must be normalizable:

$$\Rightarrow \psi_1, \psi_2, \frac{d\psi_1}{dx} \text{ and } \frac{d\psi_2}{dx} \rightarrow 0 \text{ as } x \rightarrow \pm\infty$$

$$\Rightarrow \psi_2 \frac{d\psi_1}{dx} - \psi_1 \frac{d\psi_2}{dx} = 0 \Rightarrow \int \frac{d\psi_1}{\psi_1} = \int \frac{d\psi_2}{\psi_2} \Rightarrow \ln(\psi_1) = \ln(\psi_2) + \ln(A) \Rightarrow \psi_1 = A\psi_2$$

i.e. ψ_1 and ψ_2 are linearly dependent \Rightarrow no degenerate bound states.

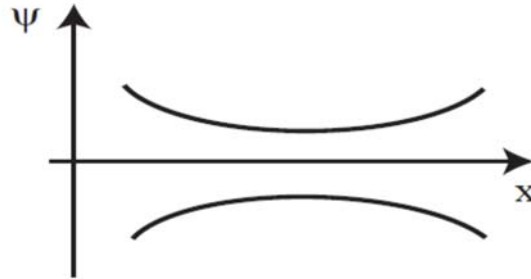
Example 2 Griffiths Problem 2.2

Show that E must exceed the minimum value of $V(x)$ for every normalizable solution to the time-independent Schrodinger equation. What is the classical analogue to this statement?

Solution Rewriting time independent Schrodinger equation we have:

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

If $E < V_{\min} \leq V(x)$ for all x , i.e. $E < V(x)$ then $\frac{d^2\psi}{dx^2}$ and ψ have the same sign *for all real values of x* . Thus $\psi(x)$ will either be concave upwards if $\psi(x) > 0$ or $\psi(x)$ will be concave downwards if $\psi(x) < 0$ as shown in the diagram below:



As a result, $\psi(x)$ is not normalizable. Recall that $\frac{d^2\psi}{dx^2} = \frac{d}{dx} \left(\frac{d\psi}{dx} \right)$, i.e. the rate of change of gradient of $\psi(x)$ at point x and with respect to x .

Similarly, if $E = V_{\min}$, then $V(x) > E$ for all x other than the minimum points. Let x_1, \dots, x_n be the minimum points of $V(x)$. Then $V(x) > E$ for all $x > \max \{x_1, \dots, x_n\}$. From above arguments, $\psi(x) \rightarrow \infty$ or $-\infty$ as $x \rightarrow \infty \Rightarrow \psi(x)$ not normalizable.

Thus, in order for $\psi(x)$ to be normalizable, $E > V_{\min}$ i.e. the constant total energy E must exceed the minimum potential energy.

Classical analogue:

(Constant) Total Energy = $E = V(x) + K(x)$ = Potential Energy at x + Kinetic Energy at x

$$\Rightarrow E = V_{\min} + K_{\max} > V_{\min}$$

as $K_{\max} > 0$. Hence for the quantum system to make sense classically, $E > V_{\min}$.

Note: Some of the materials and diagrams are extracted from:

- (i) https://en.wikipedia.org/wiki/Degenerate_energy_levels
- (ii) https://en.wikipedia.org/wiki/Pauli_exclusion_principle
- (iii) University Physics (Young & Freedman)

