Paper: Quantum Mechanics & Applications (CBCS)

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Problems on Hydrogen Atom

①. Write down the Schrodinger equation for hydrogen atom. What is an orbital?

②. Explain the physical significance of quantum numbers n, l, m in case of hydrogen atom.

③. What are the major differences between the Bohr's description and Quantum Mechanical description of hydrogen atom?

④ The θ-dependent part of the Schrodinger equation for hydrogen atom is

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)\sin^2\theta = m^2$$

What are the permitted values of l, m?

⑤. What is a radial distribution function?

⑥. What are the total number of states for $n = 2$ in case of hydrogen atom?

⑦. What is degeneracy? Find out the degeneracy of energy levels corresponding to nth state.

⑧. How many quantum numbers are needed to solve Schrodinger's equation for hydrogen atom? What are these?

⑨. ~~Consider~~ the ~~hydr~~ normalised wave function for the ground state of hydrogen atom is

$$\Psi_{100} = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

where a_0 is the Bohr radius. Calculate the value of $\langle r\rangle$ and the most probable value of r. Explain why the $\langle r\rangle$ is greater than the most probable r. Also find the probability of finding the electron at $r > a_0$.

⑩. What is the probability of finding an atomic electron (whose radial wave function is $R(r)$) outside a sphere of radius r_0 centered on the nucleus?

If $R = R_{20}$ corresponds to the first excited state of a hydrogen atom, calculate the probability finding the electron in the state at ~~a~~ distance $r > r_0$.

⑪. For H-atom, 1s orbital is given by

$$\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

Find the value of $\langle r \rangle$, $\langle r^2 \rangle$, $\langle \frac{1}{r} \rangle$ • $\langle \frac{1}{r^2} \rangle$ and hence show that (i) $\langle \frac{1}{r} \rangle \neq \frac{1}{\langle r \rangle}$ (ii) $\langle r^2 \rangle > \langle r \rangle^2$.

⑫. Consider the hydrogen atom in its ground state.

(a) With the probability of finding the electron between the radial distance r and r + dr given by P(r)dr, find ~~radial distance~~ P(r) for the ground state of hydrogen atom.

(b) Find the radial distance at which P(r) is maximum.

(c) Find the root mean square radius of the hydrogen atom in its ground state.

(d) What is the probability of finding the electron in the ground state of the hydrogen atom with momentum between $\vec{p}$ and $\vec{p} + d\vec{p}$.

⑬. The probability density for s-orbitals of hydrogen atom is maximum at the nucleus. Does it mean that electron can be found at the nucleus?

⑭. Calculate the average value of $\frac{1}{r}$ for the 1s and 2s electron in H-atom and obtain the average K.E, average P.E. and average total energy. Show that in each case $\langle \frac{1}{r} \rangle \neq \frac{1}{\langle r \rangle}$.

⑮. Calculate the probability an electron in the ground state of a hydrogen atom will be found within one Bohr radius from the nucleus.

⑯. The normalised ground state wave function of a one-electron atom is given by

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{3}{a_0}\right)^{3/2} e^{-3r/a_0}$$

where the notions have their usual meanings. Evaluate the probability of finding the electron in this state at distance greater than $\frac{2a_0}{3}$.

⑰. Hydrogen 1s wavefunction is given by $\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$. Determine the most probable value of r in this state.

⑱. Prove that $\langle V \rangle = 2\langle E \rangle$ and consequently that $\langle T \rangle = -\langle E \rangle$ for a 2s electron of hydrogen atom (T, V, E are the Kinetic energy, potential energy and total energy respectively)

Given

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

where a_0 is the Bohr radius.

⑲. Hydrogen 1s wavefunction is given by

$$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

where a_0 is the Bohr radius. Determine $\langle r \rangle$ and $\left\langle \frac{1}{r} \right\rangle$ in this state, and hence find out the ground state energy for hydrogen atom.

⑳. The unnormalised wave function for the Hydrogen atom in the ground state is

$$\psi = e^{-r/a_0}$$

where a_0 is a constant. Find the expectation value of the coloumb force on an electron in this state.

㉑. Prove that for hydrogen atom the wave functions ψ_{100} and ψ_{200} are orthogonal.

㉒. Consider that for a hydrogen atom whose wave function at $t=0$ is the following super-position of energy eigenfunctions $\psi_{nlm}(\vec{r})$

$$\psi(\vec{r}, t=0) = \frac{1}{\sqrt{14}}\left[2\psi_{100}(\vec{r}) - 3\psi_{200}(\vec{r}) + \psi_{322}(\vec{r})\right].$$

What is the probability of finding the system in the ground state (100), in the state (200) and in the state $\psi(322)$.

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Solutions of Problems on Hydrogen atom

① Schrodinger equation for hydrogen atom in spherical polar co-ordinates is

$$-\frac{\hbar^2}{2\mu r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}\psi$$

$$-\frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi$$

where μ is the reduced mass of the atom, $\psi = \psi(r,\theta,\phi)$.

An orbital in quantum mechanics is actually a wave function (i.e. a mathematical function) depicting the wave nature of an electron or pair of electrons present in an atom. Knowledge of an orbital gives the idea about most likely of an el in an atom.

② The quantum number n called the principal quantum number appears in the expression for total energy of an electron of hydrogen atom $E = -\frac{\mu e^2}{8\epsilon_0^2 n^2 h^2}$. Also, radius of electron orbit is dependent on the quantum number n. The allowed values of n are $n = 1, 2, 3, \text{-----}$ which are discrete. So, energy as well as radius are all discrete.

The Azimuthal or orbital quantum number l arises due to quantization of angular momentum L of the electron according to the expression $L = \sqrt{l(l+1)}\,\hbar$, allowed values of l are $0, 1, 2, \text{-----}, (n-1)$ for a given n.

The magnetic orbital quantum number m arises due to quantization of the component (z-say) of the angular momentum $L_z = m\hbar$, allowed values of m are all integral values from $-l$ through 0 to $+l$, hence there are $(2l+1)$ values of m corresponding to a value of l.

According to wave mechanics, definite values of n, l, m are required to completely define the mode of a wave for a set of these quantum numbers system which corresponds to a particular energy level.

The three integers n, l, m are governed by the condition $|m| < l < n$.

③ The following are the major differences between the Bohr's description and Quantum Mechanical description of hydrogen atom.

Bohr's description	Quantum Mechanical description
1. The electrons are assumed to move in definite orbits round the nucleus.	1. Giving a fixed position in a definite orbit to an electron is no longer correct.
2. The probability density has no meaning in Bohr's orbital context.	2. The probability density is distributed over the whole range of the atom.
3. Total angular momentum of the atom in a state of quantum number l is $l\hbar = \frac{lh}{2\pi}$	3. Total angular momentum of the atom in ~~a~~ state of quantum l is not $l\hbar$ but $\sqrt{l(l+1)}\left(\frac{h}{2\pi}\right)$ and has no fixed direction.
4. It placed the electron at a precise point in a well defined orbit.	4. According to wave mechanics, the chance of finding a moving electron at a given point is governed by a wave equation which necessarily involves a certain degree of uncertainity in its position.

④ l can take values 0, 1, 2, ---- $(n-1)$ corresponding to a particular value of n, the principal quantum number. while m can take values from $-l$ including 0 to $+l$. for a particular value of l.

⑤ Radial distribution function is nothing but radial probability density.

Say ψ_{1s} is a wave function corresponding to 1s orbital then the corresponding radial distribution function is

$$P_{1s}(r) = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} |\psi_{1s}|^2 r^2 \sin\theta \, d\theta \, d\phi .$$

⑥ The total number of states for $n = 2$ is $2 \times 2^2 = 8$.

⑦ The property that two or more quantum states of a particle with different sets of quantum numbers and different eigenfunctions have the same value of energy and momentum is called degeneracy.

The nth state has degeneracy $2n^2$ since the corresponding quantum states have same value of energy, momentum.

⑧ Three quantum numbers (n, l, m) are needed to solve Schrodinger's equation for hydrogen atom.

⑨ For the ground state of hydrogen atom

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$$\therefore \langle r \rangle = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} \psi \, r \, \psi^* \, r^2 \sin\theta \, d\theta \, d\phi \, dr$$

$$= \frac{4}{a_0^3} I \quad \text{where} \quad I = \int_0^\infty r^3 e^{-2r/a_0} dr$$

Let $x = \frac{2r}{a_0} \Rightarrow r = \left(\frac{a_0}{2}\right) x \quad \therefore dr = \left(\frac{a_0}{2}\right) dx$

$$\therefore \langle r \rangle = \left(\frac{4}{a_0^3}\right)\left(\frac{a_0^4}{16}\right) \int_0^\infty x^3 e^{-x} dx$$

$$= \left(\frac{a_0}{4}\right) \Gamma(4) \qquad \left(\because \Gamma(n+1) = \int_0^\infty x^n e^{-x} dx\right)$$

$$\left(\Gamma(n+1) = n!\right)$$

$$= \left(\frac{a_0}{4}\right) 3! = \frac{3}{2} a_0 = 1.5 a_0$$

$$\Rightarrow \langle r \rangle = 1.5 a_0$$

The most probable value of r will be given by the condition

$$\frac{d}{dr}\left(r^2 \psi_{100} \psi_{100}^*\right) = 0$$

$$\Rightarrow \frac{d}{dr}\left(r^2 e^{-2r/a_0}\right) = 0$$

$$\Rightarrow r = a_0$$

$\therefore r = a_0$ is less than $\langle r \rangle$ since the electron will revolve in a orbit where potential energy is minimum.

⑪ $\langle r\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{1s}^{*}\ r\ \psi_{1s}\ r^2 \sin\theta\, d\theta\, d\phi$

$= \frac{4}{a_0^3}\int_0^{\infty} r^3 e^{-2r/a_0} dr$

$= \left(\frac{4}{a_0^3}\right)\left(\frac{a_0}{2}\right)^4 \int_0^{\infty} z^3 e^{-z} dz$ where $z = \frac{2r}{a_0}$

$= \left(\frac{a_0}{4}\right)\Gamma(4) = \left(\frac{a_0}{4}\right)(3!) = 1.5a_0$

$\langle r^2\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{1s}^{*}\ r^2\ \psi_{1s}\ r^2 \sin\theta\, d\theta\, d\phi$

$= \left(\frac{4}{a_0^3}\right)\int_0^{\infty} r^4 e^{-2r/a_0} dr$

$= \left(\frac{4}{a_0^3}\right)\int_0^{\infty}\left(\frac{a_0}{2}\right)^5 z^4 e^{-z} dz$ where $z = \frac{2r}{a_0}$

$= \left(\frac{a_0^2}{8}\right)\Gamma(4) = \frac{a_0^2}{8} \times 4! = 3a_0^2$

$\langle \frac{1}{r}\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{1s}^{*}\left(\frac{1}{r}\right)\psi_{1s}\ r^2 \sin\theta\, d\theta\, d\phi$

$= \left(\frac{1}{a_0}\right)\int_0^{\infty} z e^{-z} dz$ where $z = \frac{2r}{a_0}$

$= \left(\frac{1}{a_0}\right)\Gamma(2) = \frac{1}{a_0}$ $\quad(\Gamma(2) = 1! = 1)$

$\langle \frac{1}{r^2}\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{1s}^{*}\left(\frac{1}{r^2}\right)\psi_{1s}\ r^2 \sin\theta\, d\theta\, d\phi$

$= \left(\frac{4}{a_0^3}\right)\int_0^{\infty} e^{-\frac{2r}{a_0}} dr = \left(\frac{4}{a_0^3}\right)\left[-\left(\frac{a_0}{2}\right)e^{-2r/a_0}\right]_0^{\infty}$

$= \left(\frac{4}{a_0^2}\right)\left(\frac{1}{2}\right)\left[e^0 - e^{-\infty}\right] = \frac{2}{a_0^2}$

∴ (i) $\langle \frac{1}{r}\rangle = \frac{1}{a_0}$, $\frac{1}{\langle r\rangle} = \left(\frac{2}{3}\right)\frac{1}{a_0} \Rightarrow \langle \frac{1}{r}\rangle > \frac{1}{\langle r\rangle}$

(ii) $\langle r^2\rangle = 3a_0^2$, $\langle r\rangle^2 = a_0^2 \Rightarrow \langle r^2\rangle > \langle r\rangle^2$

(12) (a) For the ground state of hydrogen atom, radial probability density P(r) is given by

$$P_{1s}(r) = 4\pi r^2 \left|\psi_{1s}\right|^2$$

$$= 4\pi r^2 \left(\frac{1}{\pi a_0^3}\right) e^{-2r/a_0} \quad \left(\because \psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}\right)$$

(b) For $P_{1s}(r)$ to be maximum,

$$\frac{dP_{1s}(r)}{dr} = 0$$

$$\Rightarrow \frac{d}{dr}\left[r^2 e^{-2r/a_0}\right] = 0$$

$$\Rightarrow e^{-2r/a_0}\left[\left(-\frac{2}{a_0}\right) r^2 + 2r\right] = 0$$

$$\Rightarrow r = a_0$$

(c) We first find $\langle r^2 \rangle$ i.e. mean square radius.

Now, $$\langle r^2 \rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{1s}^* r^2 \psi_{1s} \left(r^2 \sin\theta \, d\theta \, d\phi \, dr\right)$$

$$= \left(\frac{4}{a_0^3}\right)\int_0^{\infty} r^4 e^{-2r/a_0} dr$$

$$= 3a_0^2$$

∴ Root mean square radius $\sqrt{\langle r^2 \rangle} = \sqrt{3}\, a_0 = 1.737\, a_0$

(d) The probability of finding the electron in the ground state of the hydrogen atom with momentum between $\vec{p}$ and $\vec{p} + d\vec{p}$ is $\left|\psi_{1s}\right|^2 \left(4\pi p^2 dp\right)$.

(14) We know $\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$, $\psi_{2s} = \frac{1}{\sqrt{32\pi a_0^3}}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$

$$\therefore \langle r \rangle_{2s} = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{2s}^* \, r \, \psi_{2s} \, r^2 \sin\theta \, d\theta \, d\phi \, dr$$

$$= \frac{1}{8a_0^3}\left[4a_0^4\,\Gamma(4) + a_0^4\,\Gamma(6) - 4a_0^4\,\Gamma(5)\right]$$

$$= \frac{a_0}{8}\left[24 + 120 - 96\right] = 6a_0$$

$$\left\langle \frac{1}{r} \right\rangle_{2s} = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{2s}^* \frac{1}{r} \psi_{2s} \, r^2 \sin\theta \, d\theta \, d\phi = \frac{1}{8a_0^3}\left[4a_0^2\,\Gamma(2) - 4a_0^2\,\Gamma(3) + a_0^2\,\Gamma(4)\right]$$

$$\left\langle \frac{1}{r} \right\rangle_{2s} = \frac{1}{8a_0}\left[4-8+6\right] = \frac{1}{4a_0}$$

$$\therefore \left\langle \frac{1}{r} \right\rangle_{2s} \neq \frac{1}{\langle r \rangle_{2s}}$$

The calculations involved for 1s state can be seen in question no ⑪.

We know,

$$K.E. = T = \frac{e^2}{2(4\pi\epsilon_0)r}, \quad PE = -\frac{e^2}{4\pi\epsilon_0 r}, \quad E = -\frac{e^2}{2(4\pi\epsilon_0)r}$$

$$\therefore \langle T \rangle = \frac{e^2}{2(4\pi\epsilon_0)}\left\langle \frac{1}{r} \right\rangle, \quad \langle PE \rangle = -\frac{e^2}{4\pi\epsilon_0}\left\langle \frac{1}{r} \right\rangle$$

$$\langle E \rangle = -\frac{e^2}{2(4\pi\epsilon_0)}\left\langle \frac{1}{r} \right\rangle$$

$$\therefore \langle T \rangle_{1s} = \frac{e^2}{8\pi\epsilon_0}\left\langle \frac{1}{r} \right\rangle_{1s} = \frac{e^2}{8\pi\epsilon_0 a_0}, \quad \left(\because \left\langle \frac{1}{r} \right\rangle_{1s} = \frac{1}{a_0}\right)$$

$$\langle PE \rangle_{1s} = -\frac{e^2}{4\pi\epsilon_0 a_0}, \quad \langle E \rangle_{1s} = -\frac{e^2}{8\pi\epsilon_0 a_0}$$

$$\langle T \rangle_{2s} = \frac{e^2}{8\pi\epsilon_0}\left\langle \frac{1}{r} \right\rangle_{2s} = \frac{e^2}{64\pi\epsilon_0 a_0}$$

$$\langle PE \rangle_{2s} = -\frac{e^2}{4\pi\epsilon_0}\left\langle \frac{1}{r} \right\rangle_{2s} = -\frac{e^2}{32\pi\epsilon_0 a_0}$$

$$\langle E \rangle_{2s} = -\frac{e^2}{8\pi\epsilon_0}\left\langle \frac{1}{r} \right\rangle_{2s} = -\frac{e^2}{64\pi\epsilon_0 a_0}$$

[**2nd Method**

$$\langle E \rangle_{1s} = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi_{1s}^{*}\, E\, \psi_{1s}\, r^2 \sin\theta \, d\theta\, d\phi\, dr, \quad \psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$$= \frac{4\pi}{\pi a_0^3}\int_0^{\infty}\left(-\frac{e^2}{8\pi\epsilon_0 r}\right) r^2 e^{-2r/a_0} dr$$

$$= -\frac{e^2}{2\pi\epsilon_0 a_0^3}\int_0^{\infty} r e^{-2r/a_0} dr$$

$$= -\frac{e^2}{8\pi\epsilon_0 a_0}$$ (where a_0 is the Bohr radius of the innermost orbit).

Similar steps for other quantities.]

⑯ $$P = 1 - \int_0^{2\pi}\int_0^{\pi}\int_0^{\frac{2a_0}{3}} \psi.\psi^* \, r^2 \sin\theta d\theta d\phi$$

$$= 1 - \frac{1}{2}\int_0^4 t^2 e^{-t} dt \quad \text{where } t = \frac{23r}{a_0}$$

$$= 1 - \frac{1}{2}\left(2 - 26e^{-4}\right)$$

$$= 23.81\%$$

⑰ Most probable value of r in Hydrogen 1S state is given by condition

$$\frac{dP}{dr} = 0$$

$$\Rightarrow \frac{d}{dr}\left(r^2 \psi_{1s}^2\right) = 0$$

$$\Rightarrow \frac{d}{dr}\left(r^2 e^{-2r/a_0}\right) = 0$$

$$\Rightarrow e^{-2r/a_0}\left[2r + r^2\left(-\frac{2}{a_0}\right)\right] = 0$$

$$\Rightarrow r - \frac{r^2}{a_0} = 0$$

$$\Rightarrow r = a_0 ,$$

⑳ At first we need to normalize the wave function for Hydrogen atom following the condition that for (C being normalization constant)

$$\psi = Ce^{-r/a_0},$$

we need to have

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi\psi^* \, r^2 \sin\theta d\theta d\phi dr = 1$$

$$\Rightarrow 4\pi C^2 \int_0^{\infty} r^2 e^{-2r/a_0} dr = 1$$

$$\Rightarrow 4\pi c^2 \left(\frac{a_0}{2}\right)^3 \int_0^{\infty} t^2 e^{-t} dt = 1 \quad \text{where } \frac{2r}{a_0} = t$$

$$\Rightarrow \frac{\pi c^2 a_0^3}{2} \Gamma(3) = 1$$

$$\Rightarrow \pi c^2 a_0^3 = 1$$

$$\Rightarrow c = \frac{1}{\sqrt{\pi a_0^3}}$$

$$\therefore \psi = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

Now, Coulomb force is given by $F = -\frac{e^2}{4\pi\epsilon_0 r^2}$ for Hydrogen atom.

∴ Expectation value of F is

$$\langle F\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi^* F \psi \, r^2 \sin\theta \, d\theta \, d\phi$$

$$= \frac{4\pi(-e^2)}{4\pi\epsilon_0}\int_0^{\infty}\left(\frac{1}{r^2}\right) r^2 \left(\frac{1}{\pi a_0^3}\right) e^{-2r/a_0} \, dr$$

$$= -\frac{e^2}{\pi a_0^3 \epsilon_0}\int_0^{\infty} e^{-2r/a_0} \, dr$$

$$= -\frac{e^2}{\pi a_0^3 \epsilon_0}\left[-\frac{a_0}{2} \times e^{-2r/a_0}\right]_0^{\infty} = -\frac{e^2}{2\pi\epsilon_0 a_0^2}$$

2nd method

$$\langle F\rangle_{1S} = \left\langle -\frac{e^2}{4\pi\epsilon_0 r^2}\right\rangle_{1S} = -\frac{e^2}{4\pi\epsilon_0}\left\langle \frac{1}{r^2}\right\rangle_{1S}$$

$$= -\frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{a_0^2}\right)$$ (Check Problem No. 11)

$$= -\frac{e^2}{2\pi\epsilon_0 a_0^2}.$$

(21) To show that ψ_{100} and ψ_{200} are orthogonal for any hydrogen atom we need to prove

$$I = \int \psi_{100}\psi_{200} \, dv = 0$$

$$\psi_{200} = \frac{1}{4(2\pi a_0^3)^{1/2}}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

We know, $\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$,

$$\therefore I = \frac{1}{4\sqrt{2}(\pi a_0^3)}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\left(2 - \frac{r}{a_0}\right) e^{-\frac{3r}{2a_0}} r^2 \sin\theta \, d\theta \, d\phi \, dr$$

$$= \frac{1}{\sqrt{2}\, a_0^3}\left[\int_0^{\infty} 2r^2 e^{-3r/2a_0} dr - \frac{1}{a_0}\int_0^{\infty} r^3 e^{-3r/2a_0} dr\right]$$

Now, $\int_0^{\infty} r^2 e^{-3r/2a_0} dr = \frac{16 a_0^3}{27}$, $\int_0^{\infty} r^3 e^{-3r/2a_0} dr = \frac{32 a_0^4}{27}$

Actually $\int_0^{\infty} r^2 e^{-3r/2a_0} dr = \left(\frac{2a_0}{3}\right)^3 \int_0^{\infty} t^2 e^{-t} dt$, $t = \frac{3r}{2a_0}$

$$= \frac{8a_0^3}{27}\Gamma(3) = \frac{8a_0^3}{27} \times 2! = \left(\frac{16}{27}\right) a_0^3$$

$$\int_0^{\infty} r^3 e^{-3r/2a_0} dr = \left(\frac{2a_0}{3}\right)^4 \int_0^{\infty} t^3 e^{-t} dt = \frac{16a_0^4}{81} \times \Gamma(4) = \frac{16a_0^4}{81} \times 3! = \frac{32a_0^4}{27}$$

$$\therefore I = \frac{1}{\sqrt{2}\, a_0^3}\left[\frac{32}{27} a_0^3 - \frac{1}{a_0}\left(\frac{32 a_0^4}{27}\right)\right] = 0$$

So, ψ_{100} and ψ_{200} are orthogonal wave functions.

(22). For given ψ,

probability of finding the system in the given state $\psi(\vec{r}, t=0)$

is $P = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi^* \psi \, r^2 \sin\theta \, d\theta \, d\phi \, dr$

$$= \int \psi^* \psi \, dv$$

$$= \left(\frac{1}{\sqrt{14}}\right)\frac{1}{\sqrt{14}} \int \left[2\psi_{100}^* - 3\psi_{200}^* + \psi_{322}^*\right]\left[2\psi_{100} - 3\psi_{200} + \psi_{322}\right] dv$$

$$= \frac{4}{14}\int \psi_{100}^* \psi_{100} \, dv + \frac{9}{14}\int \psi_{200}^* \psi_{200} \, dv + \frac{1}{14}\int \psi_{300}^* \psi_{300} \, dv$$

neglecting other terms following orthoguality condition.

$$= \frac{2}{7} P_{100}(r) + \frac{9}{14} \psi_{200}(r) + \frac{1}{14} \psi_{300}(r)$$

∴ Probability of finding the system in ψ_{100} state is $\frac{2}{7}$

Probability - - - - - - - - - - ψ_{200} state is $\frac{9}{14}$

Probability - - - - - - - - ψ_{300} state is $\frac{1}{14}$.