ROTATIONAL MOTION (RM)

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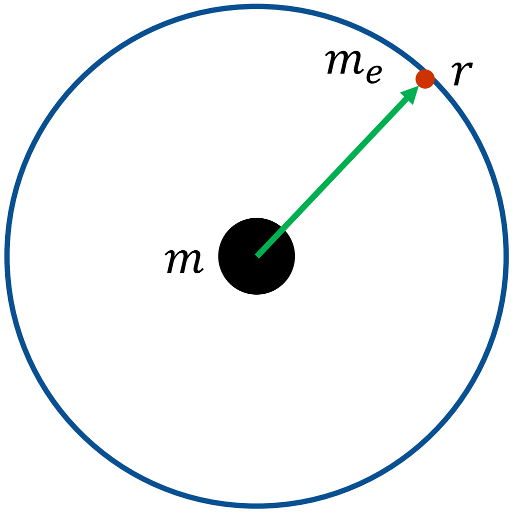
HYDROGEN ATOM



Central force problem:

- ✓ The interacting force between two particles depend on only the separation between them.
- ✓ Independent on the orientation *i.e.* θ and ϕ
- ✓ Potential energy of electron due to nuclear charge

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

- ✓ Since $V(r)$ depends only on the r, hydrogen atom (hydrogen-like) can be treated as central force problems

- ➢ Further, hydrogen atom consists of one electron and nucleus, so it is a two-body problem.

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- From the result of reducing two-body problem to one-body problem, we can write the kinetic energy operator for H

$$\hat{T} = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2$$

Where, $M = m + m_e$, $\mu = \frac{mm_e}{m+m_e}$, R = coordinate of center of mass, and r is relative coordinates of electron with respect to nucleus.

- Hamiltonian operator for H atom

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)$$

- Schrodinger equation for H atom

$$\left[\underset{\nearrow\ \text{Translational motion}}{-\frac{\hbar^2}{2M}}\nabla_R^2 \underbrace{-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)}_{\text{electrical motion}}\right]\psi_T = E_T\psi_T$$

→ This part depends only on coordinates of electron

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Separation of translational and electrical motion

- ✓ Since translation motion does not interfere the electronic part, total wavefunction, ψ_T can be written as

$$\psi_T(R,r) = \phi(R)\cdot\psi(r)$$

- ✓ Double differentiating of ψ_T with respect to R and r gives

$$\nabla_R^2\psi_T = \nabla_R^2\phi(R)\cdot\psi(r)$$

$$\nabla_r^2\psi_T = \phi(R)\cdot\nabla_r^2\psi(r)$$

- ➢ Inserting above derivatives in SE for H gives

$$-\psi(r)\frac{\hbar^2}{2M}\nabla_R^2\phi(R) - \phi(R)\frac{\hbar^2}{2\mu}\nabla_r^2\psi(r) + V(r)\phi(R)\cdot\psi(r) = E_T\phi(R)\cdot\psi(r)$$

- ➢ Dividing both sides by $\phi(R)\cdot\psi(r)$ results

$$-\frac{1}{\phi(R)}\frac{\hbar^2}{2M}\nabla_R^2\phi(R) - \frac{1}{\psi(r)}\frac{\hbar^2}{2\mu}\nabla_r^2\psi(r) + V(r) = E_T$$

$$\Rightarrow -\frac{1}{\phi(R)}\frac{\hbar^2}{2M}\nabla_R^2\phi(R) = E_T - \frac{1}{\psi(r)}\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]\psi(r)$$

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Separation of translational and electrical motion

- ✓ LHS depends on only the center of mass coordinates whereas RHS depends on the relative coordinates, r, hence both sides must equal to the same constant, say W.
- ✓ Thus we obtain two separate equations:

$$-\frac{1}{\phi(R)}\frac{\hbar^2}{2M}\nabla_R^2\phi(R) = W \qquad (1)$$

$$E_T - \frac{1}{\psi(r)}\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]\psi(r) = W \qquad (2)$$

- ✓ Rearranging eq. (2) we get

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]\psi(r) = (E_T - W)\psi(r) = E\psi(r) \qquad (3)$$

- ✓ Eq. (1) leads

$$-\frac{\hbar^2}{2M}\nabla_R^2\phi(R) = W\phi(R) \qquad (4)$$

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Separation of translational and electrical motion

- ✓ Eq. (4) represents the SE for translational motion of hypothetical mass $m + m_e$. This equation is similar to SE of free particle confined in a box.

- ✓ In practical $m \gg m_e$, hence eq. (4) mainly reveals the SE of nucleus.

- ✓ The eq. (3), which contains the potential energy of interaction between electron and nucleus, is actually SE for internal motion of nucleus and electron.

- ✓ In practical, $m \gg m_e$ leads $\mu \sim m_e$, hence eq. (3) becomes

$$\left[-\frac{\hbar^2}{2m_e}\nabla_r^2 + V(r)\right]\psi(r) = E\psi(r) \qquad (5)$$

- ✓ In eq. (5) E represents the energy of electron in the atom.

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Solution of SE for H (hydrogenic atom)

- ✓ In spherical coordinate, Laplacian operator can be written as,

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2\partial}{r\partial r} + \frac{1}{r^2}\Lambda^2 \qquad \text{where,} \quad \Lambda^2 = \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

- ✓ SE in spherical coordinate

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\psi + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

$$\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{1}{\mathrm{r}^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\psi + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi = 0 \qquad (5)$$

- ✓ Note that from particle on sphere or 3D rigid rotator, we have learnt

$$\hat{H}Y_{lm_l}(\theta,\phi) = \frac{l(l+1)\hbar}{2I}Y_{lm_l}(\theta,\phi)$$

$$-\frac{\hbar^2}{2\mu r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y_{lm_l}(\theta,\phi) = \frac{l(l+1)\hbar^2}{2I}Y_{lm_l}(\theta,\phi)$$

$$-\frac{\hbar^2}{2I}\Lambda^2 Y_{lm_l}(\theta,\phi) = \frac{l(l+1)\hbar^2}{2I}Y_{lm_l}(\theta,\phi) \implies \Lambda^2 Y_{lm_l}(\theta,\phi) = -l(l+1)Y_{lm_l}(\theta,\phi)$$

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Solution of SE for H (hydrogenic atom)

- The eq. (5) depends on three variables (r, θ, ϕ). To solve it, it is necessary to separate in independent variable. If it is assumed that r, θ and ϕ does not interfere each other, then ψ can be written as,

$$\psi(r,\theta,\phi) = R(r)\cdot\Theta(\theta)\cdot\Phi(\phi) \quad \text{Or simply,} \qquad \psi = R\Theta\Phi \qquad (6)$$

- From relation (6) we have,

$$\frac{\partial\psi}{\partial r} = \Theta\Phi\frac{\partial R}{\partial r}, \qquad \frac{\partial^2\psi}{\partial r^2} = \Theta\Phi\frac{\partial^2 R}{\partial r^2}, \qquad \frac{\partial\psi}{\partial\theta} = R\Phi\frac{\partial\Theta}{\partial\theta}, \qquad \frac{\partial^2\psi}{\partial\phi^2} = R\Theta\frac{\partial^2\Phi}{\partial\phi^2}$$

- Using these relations in eq. (5) we obtain

$$\Theta\Phi\frac{\partial^2 R}{\partial r^2} + \frac{2\Theta\Phi}{r}\frac{\partial R}{\partial r} + \frac{R\Phi}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta + \frac{R\Theta}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}$$

$$+\frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)R\Theta\Phi = 0 \qquad (7)$$

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Solution of SE for H (hydrogenic atom)

- Multiplying both sides of eq. (7) by $\frac{\mathrm{r}^2 \sin^2\theta}{R\Theta\Phi}$ results

$$\frac{r^2\sin^2\theta}{R}\frac{\partial^2 R}{\partial r^2}+\frac{2r\sin^2\theta}{R}\frac{\partial R}{\partial r}+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta+$$

$$\frac{2\mu r^2\sin^2\theta}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad (8)$$

- LSH of eq. (8) depends on r and θ, while RHS on ϕ only. This equality is only hold if both sides is equal to the same constant, say m_l^2, which gives two equations,

$$\frac{\partial^2\Phi}{\partial\phi^2}=-m_l^2\Phi \qquad (9)$$

$$\frac{r^2\sin^2\theta}{R}\frac{\partial^2 R}{\partial r^2}+\frac{2r\sin^2\theta}{R}\frac{\partial R}{\partial r}+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta+\frac{2\mu r^2\sin^2\theta}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)=m_l^2$$

.............(10)

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Solution of SE for H (hydrogenic atom)

- Dividing eq. (10) by $\sin^2\theta$ and rearranging r dependent terms on LHS and θ dependent on RHS,

$$\frac{r^2}{R}\frac{\partial^2 R}{\partial r^2}+\frac{2r}{R}\frac{\partial R}{\partial r}+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)=\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta \qquad (11)$$

- Again LSH of eq. (11) depends on r, while RHS on θ only. This equality is only hold if both sides is equal to the same constant, say $l(l+1)$, which gives two equations,

$$\frac{r^2}{R}\frac{\partial^2 R}{\partial r^2}+\frac{2r}{R}\frac{\partial R}{\partial r}+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)=l(l+1) \qquad (12)$$

$$\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta=l(l+1) \qquad (13)$$

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Solution of SE for H (hydrogenic atom)

- For the sake of convenience, we rewrite eq. (9), (12) and (13) together

$$\frac{\partial^2 \Phi}{\partial \phi^2} + m_l^2 \Phi = 0 \tag{14}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta = 0 \tag{15}$$

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{l(l+1)\,\hbar^2}{2\mu r^2}\right)R = 0 \tag{16}$$

- Solutions of eq. (14) and (15) have been shown in particle on sphere or 3D rigid rotator. The combined solution is spherical harmonics $Y_{lm_l}(\theta,\phi)$.
- The eq. (16) is called radial equation and is new. Now we try to solve this equation.

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Solution of SE for H (hydrogenic atom)

ϕ equation:

- The eq. (14) is similar to particle on ring or 2D rotator. Its normalized solution is

$$\Phi_{m_l} = \frac{1}{\sqrt{2\pi}} e^{im_l\phi}, \qquad m_l = 0, \pm1, \pm2, \cdots$$

θ equation:

- The eq. (15) is similar to the θ part of particle on sphere or 3D rotator. Its solution is associated Legendre polynomial

$$P_{lm_l}(\theta) = NP_l^{|m_l|}(\cos\theta)$$

Where N is normalization constant and is given by

$$N = \sqrt{\frac{2l+1}{2}\frac{(l-|m_l|)!}{(l+|m_l|)!}}, \qquad l = 0, 1, 2, \cdots \quad \text{and} \quad |m_l| \le l$$

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Solution of SE for H (hydrogenic atom)

Spherical Harmonics

The product of $\Theta(\theta)$ and $\Phi(\phi)$ is denoted by $Y_{lm_l}(\theta,\phi)$.

For a given values of l and m_l,the normalized wave functions, $Y_{lm_l}(\theta,\phi)$ are called the **spherical harmonics** and given by

$$Y_{lm_l}(\theta,\phi)=\frac{(-1)^{l+|m_l|}}{2^l l!}\sqrt{\frac{2l+1}{4\pi}\cdot\frac{(l-|m_l|)!}{(l+|m_l|)!}}\times$$

$$\left[\sin^{|m_l|}\theta\frac{d^{l+|m_l|}}{d(\cos\theta)^{l+|m_l|}}\sin^{2l}\theta\right]e^{im_l\phi}$$

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Solution of SE for H (hydrogenic atom)

Spherical Harmonics

Example: Evaluate $Y_{2,\pm 2}$

Soln: If $l = 2$ then $m_l = 0, \pm 1, \pm 2$

For $l = 2$ and $m_l = \pm 2$

$$N = \frac{(-1)^{2+2}}{2^2 \cdot 2!}\sqrt{\frac{2\cdot 2+1}{4\pi}\cdot\frac{(2-2)!}{(2+2)!}} = \frac{1}{32}\sqrt{\frac{5}{6\pi}}$$

$$\begin{aligned} x &= \cos\theta \\ y &= \sin^4\theta \\ \Rightarrow y &= (1-x^2)^2 \\ \Rightarrow y &= 1 - 2x^2 + x^4 \\ y_1 &= -4x + 4x^3 \\ y_2 &= -4 + 12x^2 \\ y_3 &= 24x \\ y_4 &= 24 \end{aligned}$$

$$P_2^2(\cos\theta) = \sin^2\theta \boxed{\frac{d^4}{d(\cos\theta)^4}\sin^4\theta} = 24\sin^2\theta$$

$$Y_{2,\pm 2} = \frac{1}{32}\sqrt{\frac{5}{6\pi}}\cdot 24\sin^2\theta\, e^{\pm 2i\phi} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\phi}$$

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Solution of SE for H (hydrogenic atom)

Spherical Harmonics

The $Y_{lm_l}(\theta,\phi)$ for some l and m_l are given in Table1.

$$Y_{lm_l}(\theta,\phi)=\frac{(-1)^{l+|m_l|}}{2^l l!}\sqrt{\frac{2l+1}{4\pi}\cdot\frac{(l-|m_l|)!}{(l+|m_l|)!}}\left[\sin^{|m_l|}\theta\,\frac{d^{l+|m_l|}}{d(\cos\theta)^{l+|m_l|}}\sin^{2l}\theta\right]e^{im_l\phi}$$

$\boldsymbol{l}$	$\boldsymbol{m_l}$	$P_l(\cos\theta)$	N	$P_l^{\|m_l\}}(\cos\theta)$	$e^{im_l\phi}$	$\boldsymbol{Y_{lm_l}(\theta,\phi)}$
0	0	1	$\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$	1	1	$\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$
1	0	$-\cos\theta$	$\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}$	$\cos\theta$	1	$\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta$
	±1					
2	0					
	±1					
	±2					

BACKGROUND 1

Laguerre Polynomial:

Let $y = x^k e^{-x}$

Differentiating gives

$$\frac{dy}{dx} = \left(kx^{k-1} - x^k\right)e^{-x}$$

$$\frac{d^2y}{dx^2} = \left(k(k-1)x^{k-2} - kx^{k-1} - kx^{k-1} + x^k\right)e^{-x}$$

Generally, $$\frac{d^ky}{dx^k} = e^{-x}L_k(x)$$

$$\Rightarrow L_k(x) = e^x \frac{d^ky}{dx^k} = e^x \frac{d^k}{dx^k}\left(x^k e^{-x}\right)$$

e.g., $$L_1(x) = e^x \frac{d}{dx}\left(xe^{-x}\right) = e^x(1-x)e^{-x} = 1 - x$$

$$L_2(x) = e^x \frac{d^2}{dx^2}\left(x^2e^{-x}\right) = e^x \frac{d}{dx}\left[\left(2x - x^2\right)e^{-x}\right]$$

$$= e^x\left(2 - 2x - 2x + x^2\right)e^{-x} = 2 - 4x + x^2$$

BACKGROUND 1

Associated Laguerre Polynomial:

- ✓ Pth derivative of Laguerre polynomial $L_k^p(x) = \frac{d^p}{dx^p}[L_k(x)] = \frac{d^p}{dx^p}\left[e^x \frac{d^k}{dx^k}\left(x^k e^{-x}\right)\right]$ is known as Associated Laguerre polynomial, which is the solution of following differential equation, called associated Laguerre differential equation.

$$x\frac{d^2L_k^p(x)}{dx^2} + (p+1-x)\frac{dL_k^p(x)}{dx} + (k-p)L_k^p(x) = 0$$

- ➢ The associated Laguerre polynomial is of degree $k-p$ and order p, where $p \leq k$. Replacing x by ρ, k by $n+l$ and p by $2l+1$, where $n+l \geq 2l+1$ Or, $n \geq l+1$

$$\rho\frac{d^2L_{n+l}^{2l+1}(\rho)}{d\rho^2} + (2l+1+1-\rho)\frac{dL_{n+l}^{2l+1}(\rho)}{d\rho} + (n+l-2l-1)L_{n+l}^{2l+1}(\rho) = 0$$

$$\Rightarrow \rho\frac{d^2L_{n+l}^{2l+1}(\rho)}{d\rho^2} + [2(l+1)-\rho]\frac{dL_{n+l}^{2l+1}(\rho)}{d\rho} + (n-l-1)L_{n+l}^{2l+1}(\rho) = 0$$

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Solution of SE for H (hydrogenic atom)

The r equation:

$$\frac{\partial^2 R}{\partial r^2}+\frac{2}{r}\frac{\partial R}{\partial r}+\frac{2\mu}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{l(l+1)\hbar^2}{2\mu r^2}\right)R=0 \qquad (17)$$

- Note that third term in bracket adds an additional terms to the potential energy. Previously, it was shown that $L^2 = l(l+1)\hbar^2$. So it is obvious that third term comes from the angular momentum and counts the centrifugal force that acts against the coulombic force. Thus, effective potential energy V_{eff} is given by

$$V_{eff} = -\frac{Ze^2}{4\pi\varepsilon_0 r}+\frac{l(l+1)\hbar^2}{2\mu r^2}$$

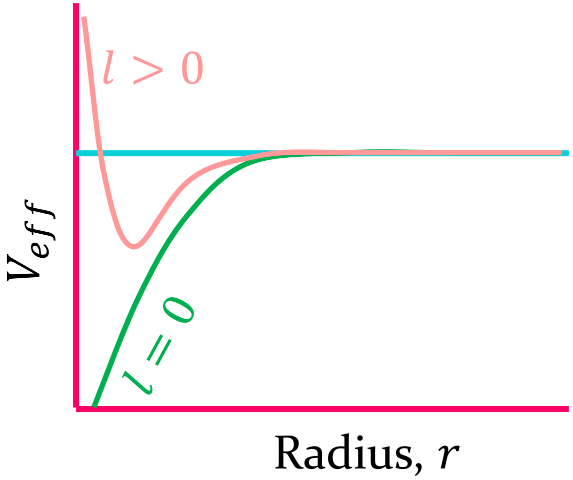

Fig. The effective potential experienced by an electron in a hydrogen atom. When *l* > 0 centrifugal contribution prevents the close approach of the electron to the nucleus, as it increases more rapidly (as $1/r^2$) than the Coulomb attraction (which varies as $-1/r$).

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Solution of SE for H (hydrogenic atom)

The r equation:

- To simplify eq. (17), put dimensionless variable, $\rho = \alpha r$, where α is constant and its dimension is reciprocal to r

$$\frac{dR}{dr} = \frac{dR}{d\rho}\frac{d\rho}{dr} = \frac{dR}{d\rho}\alpha, \qquad \frac{d^2R}{dr^2} = \frac{d}{dr}\left(\frac{dR}{d\rho}\alpha\right) = \frac{d}{d\rho}\left(\frac{dR}{d\rho}\alpha\right)\frac{d\rho}{dr} = \alpha^2\frac{d^2R}{d\rho^2}$$

- Now eq. (17) becomes

$$\alpha^2\frac{d^2R}{d\rho^2} + \frac{2\alpha}{r}\frac{dR}{d\rho} + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R = 0$$

$$\frac{d^2R}{d\rho^2} + \frac{2}{\alpha r}\frac{dR}{d\rho} + \left[\frac{2\mu E}{\alpha^2\hbar^2} + \frac{2\mu Ze^2}{4\pi\varepsilon_0\hbar^2\alpha^2 r} - \frac{l(l+1)}{\alpha^2 r^2}\right]R = 0$$

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\frac{2\mu E}{\alpha^2\hbar^2} + \frac{2\mu Ze^2}{4\pi\varepsilon_0\hbar^2\alpha\rho} - \frac{l(l+1)}{\rho^2}\right]R = 0 \qquad (18)$$

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Solution of SE for H (hydrogenic atom)

The r equation:

- For convenient, α is chosen so that first term in bracket becomes $-\frac{1}{4}$ and coefficient of $\frac{1}{\rho}$ is defined by n, i.e.,

$$\frac{2\mu E}{\alpha^2\hbar^2} = -\frac{1}{4} \quad \Rightarrow \alpha = \sqrt{-\frac{8\mu E}{\hbar^2}}$$

$$n = \frac{2\mu Z e^2}{4\pi\varepsilon_0\hbar^2\alpha} \Rightarrow \alpha = \frac{2Z}{n a_0}, \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

- Now eq. (18) becomes

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right]R = 0 \qquad (19)$$

- For large ρ, $\frac{1}{\rho}$ becomes infinitesimal and eq. (19) becomes

$$\frac{d^2R}{d\rho^2} - \frac{1}{4}R = 0 \qquad (20)$$

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Solution of SE for H (hydrogenic atom)

The r equation:

- Solution of eq. (20)

$$R = Ae^{\pm\frac{\rho}{2}}$$

- The positive exponent makes R infinite and is not acceptable. The acceptable function is

$$R = Ae^{-\frac{\rho}{2}}$$

- For small ρ, $\frac{l(l+1)}{\rho^2} \gg \frac{n}{p}$ and $\frac{1}{4}$ then eq. (19) reduces to

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2}R = 0 \qquad (21)$$

- Let assume the solution of eq. (21) is

$$R = \rho^k$$

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Solution of SE for H (hydrogenic atom)

The r equation:

- Inserting this function in eq. (21) gives

$$k(k-1)+2k-l(l+1)=0$$
$$(k-l)(k+l)+(k-l)=0$$
$$k=l \quad or \quad -(l+1)$$

- Function may be

$$R=\rho^{l} \qquad or \;\; R=\rho^{-(l+1)}$$

- The latter solution approaches to infinity as ρ increases and is not acceptable. The acceptable solution is

$$R=\rho^{l}$$

- For intermediate values of ρ, the solution of eq. (19) is given by

$$R=\rho^{l}L(\rho)e^{-\frac{\rho}{2}} \tag{22}$$

Where $L(\rho)$ is a polynomial of power series in ρ. $L(\rho)$ is to be determined.

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Solution of SE for H (hydrogenic atom)

The r equation:

- Inserting eq. (22) in eq. (19) gives

$$\rho\frac{d^2L}{d\rho^2}+[2(l+1)-\rho]\frac{dL}{d\rho}+(n-l-1)L=0 \tag{23}$$

- The solution of eq. (23) is the associated Laguerre polynomial (see background 1), which is given as

$$L_{n+l}^{2l+1}(\rho)=\frac{d^{2l+1}}{d\rho^{2l+1}}\left[e^{\rho}\frac{d^{n+l}}{d\rho^{n+l}}\left(\rho^{n+l}e^{-\rho}\right)\right]$$

- The degree of polynomial is $n-l-1$ and order $2l+1$ with the condition $2l+1\leq n+l$ or $n\geq l+1$.

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Nature of n and l

- From $L_{n+l}^{2l+1}(\rho)$ it is concluded that
- The minimum degree is zero, i.e., $n-l-1=0 \;\Rightarrow n=l+1$
- Since lowest value of n is 1, above condition says that the lowest value of l is zero.
- Further, the degrees of polynomial are integers, hence acceptable values of n and l are integers.
- Therefore, acceptable values of n are 1, 2, 3, ⋯ and l are 0, 1,2, ⋯
- For $n \geq l+1$, $L_{n+l}^{2l+1}(\rho)$ exists
- However, for $n < l+1$ or $n=l$, $L_{n+l}^{2l+1}(\rho)$ does not exist.
- For example, let $n \;=1$ and $l \;=1$

$$L_2^3(\rho) = \frac{d^3}{d\rho^3}\left[e^\rho \frac{d^2}{d\rho^2}(\rho^2 e^{-\rho})\right] = \frac{d^3}{d\rho^3}\left[e^\rho \frac{d}{d\rho}\{(2\rho-\rho^2)e^{-\rho}\}\right]$$

$$= \frac{d^3}{d\rho^3}[e^\rho(2-4\rho+\rho^2)e^{-\rho}] = 0$$

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Atomic Units (au)

- ✓ The units used for macroscopic scale are not convenient in quantum mechanics. Further, quantum mechanical equations in terms of fundamental constants are very cumbersome to handle.
- ✓ The units that are designed to simplify the form of the fundamental equations of quantum mechanics by eliminating from them fundamental constants are atomic unit (au).
- ✓ The advantage of atomic units is that if all calculations are directly expressed in such units, the results do not vary with any revision of the numerical values of the fundamental constants.
- ✓ If we introduce a set of units such that $\hbar = 1, m_e = 1, |e| = 1$ and $\kappa_0 = 4\pi\epsilon_0 = 1$

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = \frac{1\cdot 1^2}{1\cdot 1^2} = 1 \text{ Bohr}, \qquad E = -\frac{m_e Z^2 e^4}{2n^2\hbar^2(4\pi\varepsilon_0)^2} = -\frac{1}{2n^2} \text{ Hartree}$$

HYDROGEN ATOM

Some fundamental constants in atomic units (au)

Quantity	Atomic Unit	SI equivalent
Mass	$m_e = 1$ (electron mass)	9.1091×10^{-31} kg
Charge	$\lvert e \rvert = 1$ (electronic charge)	1.6021×10^{-19} C
Angular momentum	$\hbar = 1$	1.0545×10^{-34} J·s
Permitivity	$\kappa_0 = 4\pi\epsilon_0 = 1$	$1.1126 \times 10^{-10} \ C^2 \cdot J^{-1} \cdot m^{-1}$
Length	$\frac{\kappa_0 \hbar^2}{m_e e^2} = a_0 = 1$ (bohr) (Bohr radius)	5.29167×10^{-11} m
Energy	$\frac{m_e e^4}{\kappa_0^2 \hbar^2} = \frac{e^2}{\kappa_0 a_0} = 1$ (hartree) (twice the ionization energy of atomic hydrogen)	4.35944×10^{-18} J
Time	$\frac{\kappa_0^2 \hbar^2}{m_e e^4} = 1$ (period of an electron in the first Bohr orbit)	2.41889×10^{-17} s
Speed	$\frac{e^2}{\kappa_0 \hbar} = 1$ (speed of an electron in the first Bohr orbit)	$2.18764 \times 10^{6} \ m \cdot s^{-1}$
Electric potential	$\frac{m_e e^3}{\kappa_0^2 \hbar^2} = \frac{e}{\kappa_0 a_0} = 1$ (potential energy of an electron in the first Bohr orbit)	27.211 V
Magnetic dipole moment	$\frac{e\hbar}{m_e} = 1$ (twice a Bohr magneton)	$1.85464 \times 10^{-23} \ J \cdot T^{-1}$

HYDROGEN ATOM

Ex. One hartree, the unit of energy in atomic units, is given by $hartree = \frac{me^4}{\kappa_0^2 \hbar^2}$

Express one hartree in units of joules (J), kilojoules per mole ($kJ \cdot mol^{-1}$), wave numbers (cm^{-1}) and electron volts (eV).

Solution: To find one $hartree$ expressed in joules, we substitute the SI values of m, e, κ_0 and $\hbar$ into the above equation.

$$one\ hartree = \frac{(9.1091 \times 10^{-31}\ kg)(1.6021 \times 10^{-19}\ C)^4}{(1.1126 \times 10^{-10}\ C^2 \cdot J^{-1} \cdot m^{-1})^2 (1.0545 \times 10^{-34}\ J \cdot s)^2}$$

$$= 4.3595 \times 10^{-18}\ J$$

If we multiply this result by Avogadro's number, we obtain

$$one\ hartree = 2625\ kJ \cdot mol^{-1}$$

To express one $hartree$ in wave numbers (cm^{-1}), we use the equation

$$\bar{\nu} = \frac{1}{\lambda} = \frac{E}{ch} = \frac{(4.3595 \times 10^{-18}\ J)}{(2.9979 \times 10^8\ m \cdot s^{-1})(6.6262 \times 10^{-34}\ J \cdot s)} = 2.195 \times 10^7\ m^{-1}$$

$$= 2.195 \times 10^5\ cm^{-1}$$

Lastly, to express one $hartree$ in terms of electron volts, we use the conversion factor

$$1eV = 1.602 \times 10^{-19}\ J$$

$$one\ hartree = (4.3595 \times 10^{-18}\ J)\left(\frac{1\ eV}{1.602 \times 10^{-19}\ J}\right) = 27.21\ eV$$

HYDROGEN ATOM

Eigenvalues

- ✓ To simplify the r-equation, 2 constants, α and n were introduced

$$\alpha = \sqrt{-\frac{8\mu E}{\hbar^2}} \qquad (1) \qquad\qquad n = \frac{2\mu Z e^2}{4\pi\varepsilon_0\hbar^2\alpha} \qquad (2)$$

- ✓ Eliminating α from eq. (1) and (2)

$$n^2 = \frac{4\mu^2 Z^2 e^4}{16\pi^2\varepsilon_0^2\hbar^4} \times \left(-\frac{\hbar^2}{8\mu E}\right)$$

$$E = -\frac{4\mu Z^2 e^4 \times 4\pi^2}{n^2(4\pi\varepsilon_0)^2 h^2 \times 8} = -\frac{2\pi^2\mu Z^2 e^4}{n^2(4\pi\varepsilon_0)^2 h^2}$$

- ✓ Nucleus mass of H atom $m \gg m_e$ leads $\mu \rightarrow m_e$

$$E = -\frac{2\pi^2 m_e Z^2 e^4}{n^2 h^2 (4\pi\varepsilon_0)^2} = -\frac{m_e Z^2 e^4}{2n^2\hbar^2(4\pi\varepsilon_0)^2}, \qquad n = 1, 2, 3, \cdots$$

- ✓ Eigenvalue of H atom in ground state (au)

$$E = -\frac{m_e Z^2 e^4}{2n^2\hbar^2(4\pi\varepsilon_0)^2} = -\frac{1\cdot 1^2\cdot 1^4}{2\cdot 1^2\cdot 1^2\cdot 1^2} = -\frac{1}{2}\ Hartree$$

HYDROGEN ATOM

Radial wavefunctions

- The radial wavefunction is written as

$$R_{nl}(\rho) = N_{nl}\rho^{l} L_{n+l}^{2l+1}(\rho)\mathrm{e}^{-\frac{\rho}{2}}$$

$$\text{where,}\qquad N_{nl} = -\sqrt{\left(\frac{\rho}{r}\right)^{3}\frac{(n-l-1)!}{2n\left\{(n+l)!\right\}^{3}}} = -\left(\frac{2Z}{na_0}\right)^{\frac{3}{2}}\left[\frac{(n-l-1)!}{2n\left\{(n+l)!\right\}^{3}}\right]^{\frac{1}{2}}$$

- In terms of r

$$R_{nl}\left(\frac{2Zr}{na_0}\right) = N_{nl}\left(\frac{2Zr}{na_0}\right)^{l} L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)\mathrm{e}^{-\frac{Zr}{na_0}}$$

$$\text{where,}\qquad N_{nl} = -\left(\frac{2Z}{na_0}\right)^{\frac{3}{2}}\left[\frac{(n-l-1)!}{2n\left\{(n+l)!\right\}^{3}}\right]^{\frac{1}{2}}$$

$$R_{nl}\left(\frac{2Zr}{n}\right) = N_{nl}\left(\frac{2Zr}{n}\right)^{l} L_{n+l}^{2l+1}\left(\frac{2Zr}{n}\right)\mathrm{e}^{-\frac{Zr}{n}}\quad \text{(in au)}$$

HYDROGEN ATOM

Some examples of radial wavefunctions

- For $n = 1$ and $l = 0$

$$R_{10}(\rho) = N_{10}\rho^0 L_1^1(\rho)\mathrm{e}^{-\frac{\rho}{2}}$$

$$N_{10} = -\sqrt{\left(\frac{2Z}{a_0}\right)^3 \frac{(1-0-1)!}{2\times 1\,\{(1+0)!\}^3}} = -\left(\frac{2Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{0!}{2\times(1!)^3}\right)^{\frac{1}{2}} = -2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}$$

$$L_1^1(\rho) = \frac{d}{d\rho}\left[e^{\rho}\frac{d}{d\rho}(\rho e^{-\rho})\right] = \frac{d}{d\rho}[e^{\rho}(1-\rho)e^{-\rho}] = -1$$

$$e^{-\frac{\rho}{2}} = e^{-\frac{1}{2}\left(\frac{2Zr}{a_0}\right)} = e^{-\frac{zr}{a_0}}$$

$$R_{10}(r) = -2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}(-1)e^{-\frac{zr}{a_0}} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}e^{-\frac{zr}{a_0}}$$

$$\Rightarrow R_{10}(r) = 2(Z)^{\frac{3}{2}}e^{-Zr} \qquad \text{(in au)}$$

HYDROGEN ATOM

Some examples of radial wavefunctions

- For $n = 2$ and $l = 0,\ 1$

$$R_{20}(\rho) = N_{20}\rho^{0}L_{2}^{1}(\rho)\mathrm{e}^{-\frac{\rho}{2}}$$

$$N_{20} = -\sqrt{\left(\frac{2Z}{2a_0}\right)^{3}\frac{(2-0-1)!}{2\times 2\left\{(2+0)!\right\}^{3}}} = -\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{1!}{4\times(2!)^{3}}\right)^{\frac{1}{2}} = -\frac{1}{4\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}$$

$$L_{2}^{1}(\rho) = \frac{d}{d\rho}\left[e^{\rho}\frac{d^{2}}{d\rho^{2}}\left(\rho^{2}e^{-\rho}\right)\right] = \frac{d}{d\rho}\left(2-4\rho+\rho^{2}\right) = 2\rho-4 = \frac{2Zr}{a_0}-4$$

$$e^{-\frac{\rho}{2}} = e^{-\frac{1}{2}\left(\frac{2Zr}{2a_0}\right)} = e^{-\frac{zr}{2a_0}}$$

$$R_{20}(r) = -\frac{1}{4\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{2Zr}{a_0}-4\right)e^{-\frac{zr}{2a_0}} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{Zr}{a_0}\right)e^{-\frac{zr}{2a_0}}$$

$$\Rightarrow R_{20}(r) = \frac{1}{2\sqrt{2}}(Z)^{\frac{3}{2}}(2-Zr)e^{-\frac{zr}{2}} \quad \text{(in au)}$$

HYDROGEN ATOM

Some examples of radial wavefunctions

- For $n = 2$ and $l = 0,\ 1$

$$R_{21}(\rho) = N_{21}\rho^{1}L_3^3(\rho)\mathrm{e}^{-\frac{\rho}{2}}$$

$$N_{21} = -\sqrt{\left(\frac{2Z}{2a_0}\right)^3 \frac{(2-1-1)!}{2\times 2\,\{(2+1)!\}^3}} = -\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{0!}{4\times(3!)^3}\right)^{\frac{1}{2}} = -\frac{1}{12\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}$$

$$L_3^3(\rho) = \frac{d^3}{d\rho^3}\left[e^{\rho}\frac{d^3}{d\rho^3}\left(\rho^3 e^{-\rho}\right)\right] = \frac{d^3}{d\rho^3}\left(6-18\rho+9\rho^2-\rho^3\right) = -6$$

$$e^{-\frac{\rho}{2}} = e^{-\frac{1}{2}\left(\frac{2Zr}{2a_0}\right)} = e^{-\frac{zr}{2a_0}}$$

$$R_{21}(r) = -\frac{1}{12\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{2Zr}{2a_0}\right)(-6)e^{-\frac{zr}{2a_0}} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} re^{-\frac{zr}{2a_0}}$$

$$\Rightarrow R_{21}(r = \frac{1}{2\sqrt{6}}(Z)^{\frac{5}{2}}re^{-\frac{zr}{2}} \qquad \text{(in au)}$$

HYDROGEN ATOM

Complete wave functions or atomic orbitals of hydrogenic atoms

- ✓ It is product of r, θ and ϕ dependent wavefunctions

$$\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)\cdot P_l^{|m_l|}\cdot\Phi(\phi) = R_{nl}(r)\cdot Y_{lm_l}(\theta,\phi)$$

where n, l and m_l are the three quantum number used to characterize the wave function.

- ✓ For example, for $n = 1$, $l = 0$, $m_l = 0$, the wave function is

$$\psi_{100} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\exp\left(-\frac{Zr}{a_0}\right)\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2\pi}}\right) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\exp\left(-\frac{Zr}{a_0}\right)$$

- ✓ In atomic unit, $a_0 = 1$

$$\psi_{100} = \frac{1}{\sqrt{\pi}}(Z)^{\frac{3}{2}}\exp(-Zr)$$

- ✓ For hydrogen atom, $Z = 1$

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\exp(-r)$$

HYDROGEN ATOM

Complete wave functions or atomic orbitals of hydrogenic atoms

- ✓ The wave functions for hydrogenic atoms are also called atomic orbitals.
- ✓ Prior to the development of quantum mechanics, the atomic orbitals are denoted as $s, p, d, f, \cdots$ for $l = 0, 1, 2, 3, \cdots$ respectively. The letters being preceded by numbers representing principle quantum numbers. Thus we have $1s$, $2s$, $2p$ atomic orbitals corresponding to $(n = 1, l = 0)$, $(n = 2, l = 0)$, $(n = 2, l = 1)$ respectively
- ✓ Since the energy of hydrogenic atoms depends only on n and independent of l and m_l, orbitals having same n and different l and m_l are degenerate. Thus we have the following hierarchy of energy states of hydrogenic atoms:

$$[1s] < [2s, 2p] < [3s, 3p, 3d], \cdots$$

- ✓ Wherein the degenerate states are bracketed. To specify magnetic quantum numbers, we may add the subscripts as follows:

$$[1s_0] < [2s_0, 2p_{+1}, 2p_0\,, 2p_{-1}] < \cdots$$

HYDROGEN ATOM

Significance of the quantum numbers n, l and m_l

- ✓ State of an electron can be represented by ψ from which the following three important quantities can be extracted:

$$E = -\frac{1}{2n^2}$$

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

$$L_z = m_l\hbar$$

where n is principal quantum number

l is angular momentum (azimuthal) quantum number

m_l is magnetic quantum number

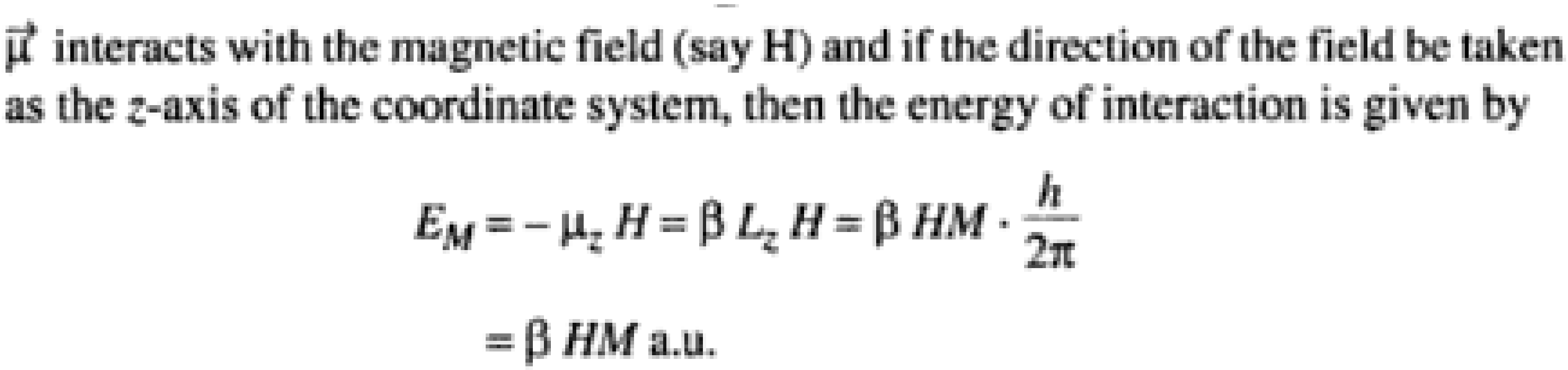
- ✓ With increase in n, E increases. Thus, n is related to size of atom which increases with increase in n.
- ✓ l determines the angular momentum of electron. Since the angular momentum vector always points an electron with respect to nucleus . Thus, l describes the orientation of electron in atom.

HYDROGEN ATOM

Significance of the quantum numbers n, l and m_l

- ✓ m_l arises from the fact that when H atom is placed in a magnetic field, the degenerate states split up into $2l+1$ different states, each state is characterized by its m_l value (Zeeman effect)
- ✓ The electron rotating round the nucleus has also magnetic moment (μ) vector colinear with the vector $\vec{L}$ and is proportional to it.

$$\mu = -\beta L \quad \text{where } \beta \text{ is called Borh magneton}$$

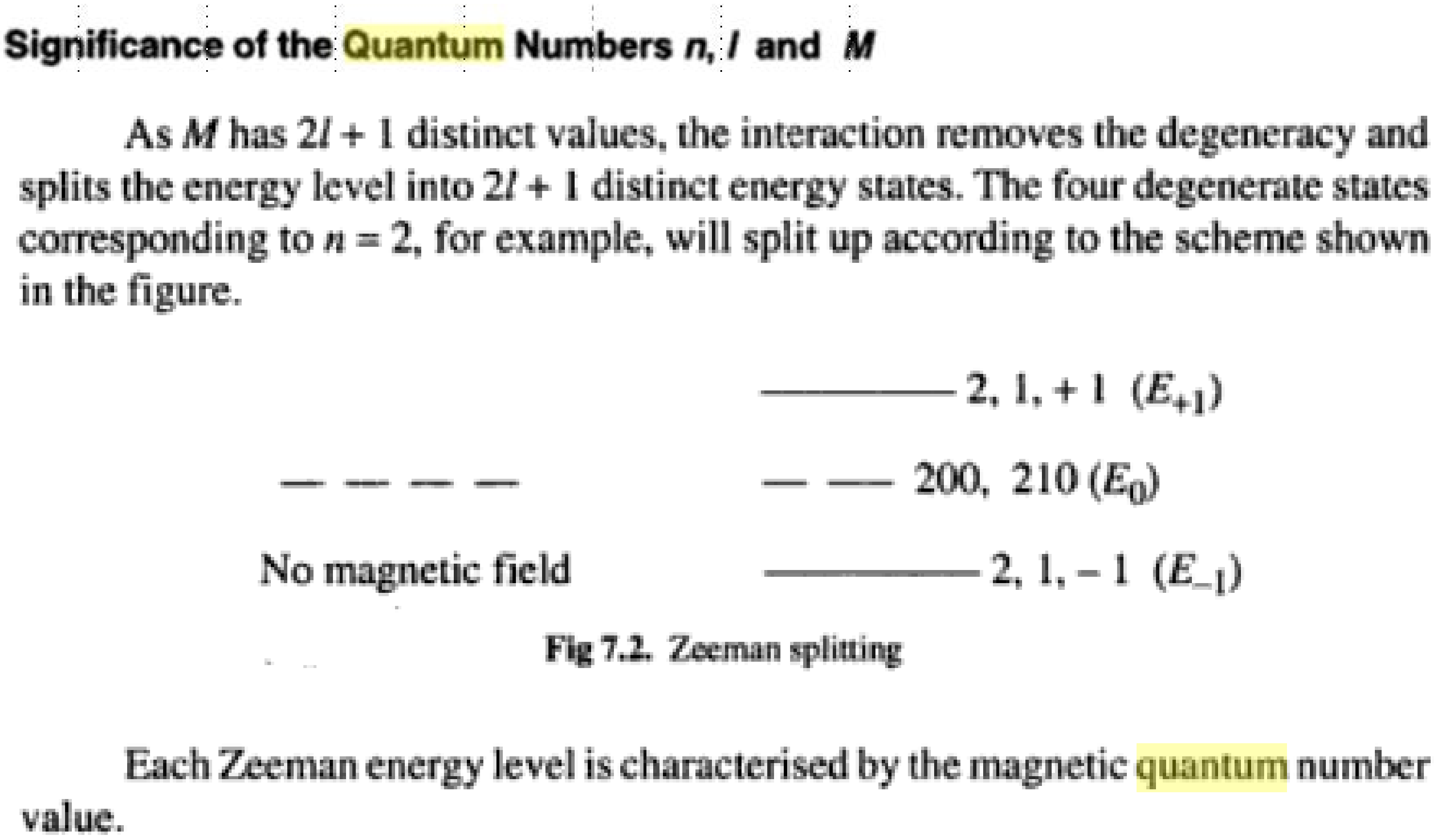


$\vec{\mu}$ interacts with the magnetic field (say H) and if the direction of the field be taken as the z-axis of the coordinate system, then the energy of interaction is given by

$$E_M = -\mu_z H = \beta L_z H = \beta HM \cdot \frac{h}{2\pi}$$

$$= \beta HM \text{ a.u.}$$

HYDROGEN ATOM



Significance of the Quantum Numbers *n*, *l* and *M*

As M has $2l + 1$ distinct values, the interaction removes the degeneracy and splits the energy level into $2l + 1$ distinct energy states. The four degenerate states corresponding to $n = 2$, for example, will split up according to the scheme shown in the figure.

2, 1, + 1 (E_{+1})

200, 210 (E_0)

No magnetic field

2, 1, – 1 (E_{-1})

Fig 7.2. Zeeman splitting

Each Zeeman energy level is characterised by the magnetic quantum number value.

HYDROGEN ATOM

Significance of the quantum numbers n, l and m_l

1.Principal quantum number (n): The principal quantum number explains about the size and energy of shells (or) orbitals.

As “n” increases, the orbitals become larger and the electrons in those orbitals are farther from the nucleus.

It take values 1, 2, 3, 4 for that the shells are represented by letters K, L, M, N.

2.Orbital quantum number (l) : It defines the shape of the orbital occupied by the electron and the orbital angular momentum of the electron is in motion. So it is also called as Angular momentum quantum number.

l has integer values between 0 to n - 1 for these values the orbitals are designated by letters s, p, d, f, etc.

l also governs the degree with which the electron is attached to nucleus. The larger the value of l, smaller is the bond with which it is maintained with the nucleus.

3.Magnetic orbital quantum number : The orientation of orbital with external magnetic field determines magnetic orbital quantum number.

m; has integer values between -1 and l including zero. The number of values for m are 2l + 1, which give the number of orbitals per sub-shell.

The maximum number of electrons in orbitals in the sub-shell is 2(2l + 1).

HYDROGEN ATOM

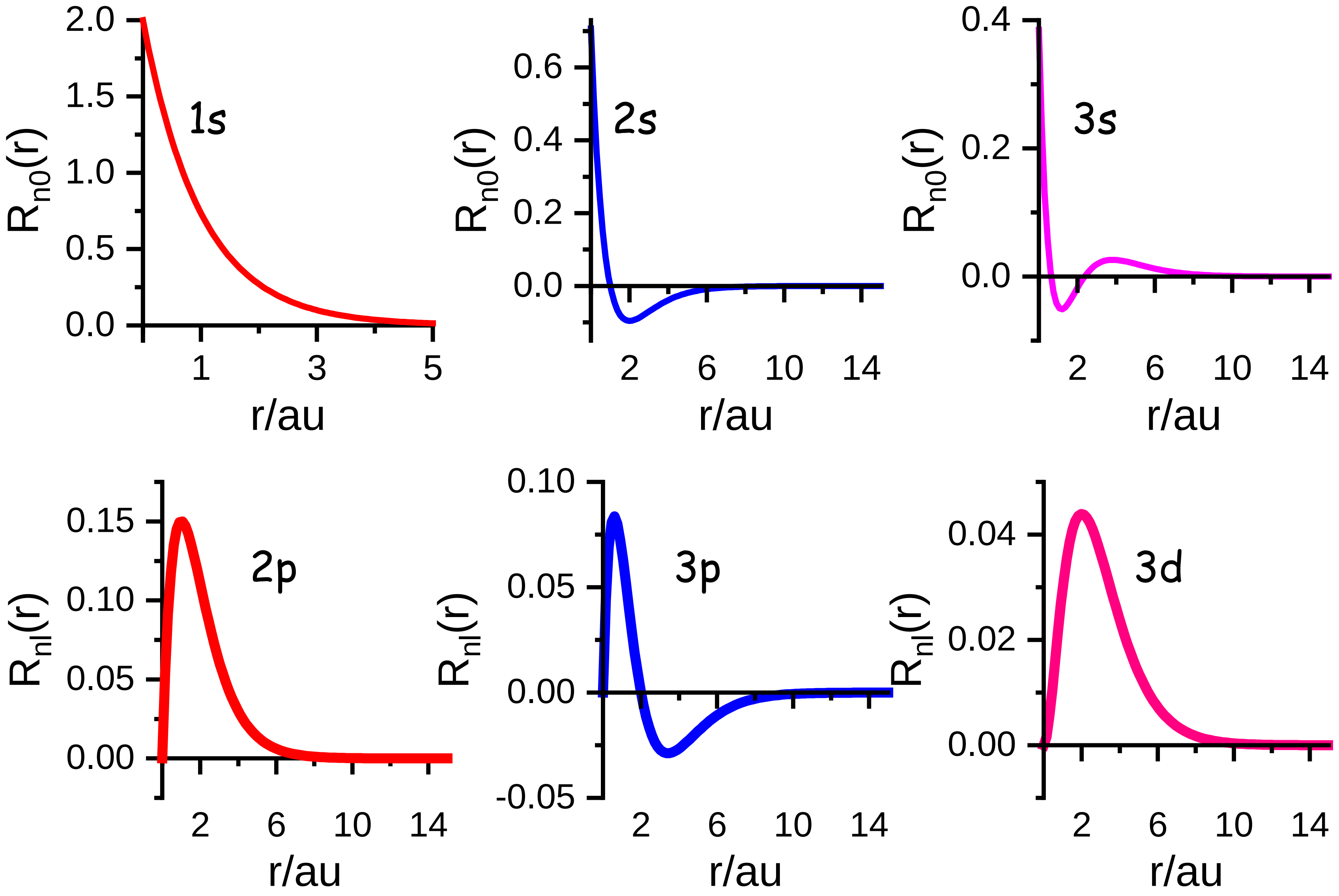
Significance of the quantum numbers n, l and m_l

The principal quantum number, nn, describes the energy of an electron and the most probable distance of the electron from the nucleus. In other words, it refers to the size of the orbital and the energy level an electron is placed in.

The principal quantum number, nn, designates the principal electron shell. Because n describes the most probable distance of the electrons from the nucleus, the larger the number n is, the farther the electron is from the nucleus, the larger the size of the orbital, and the larger the atom is.

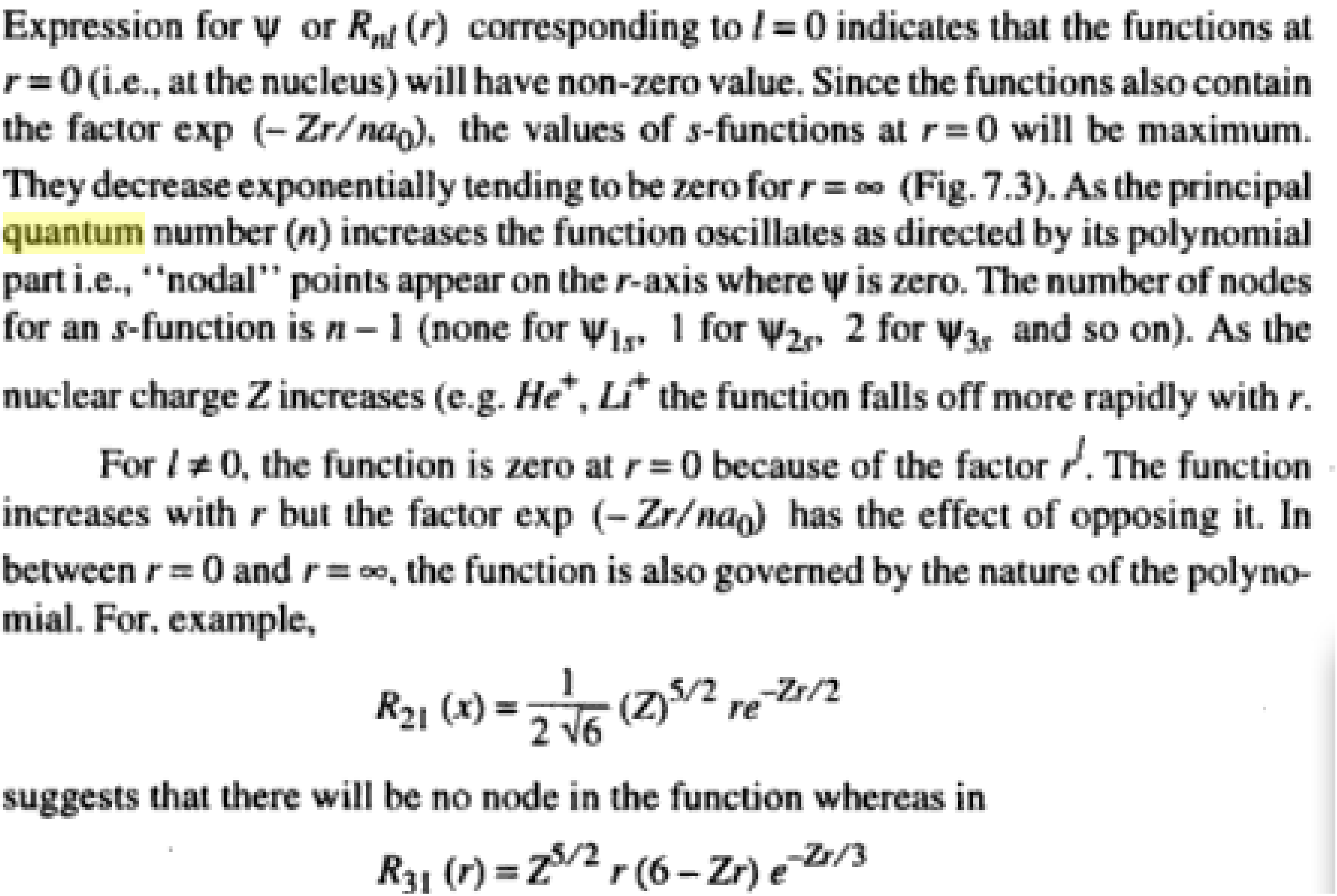
HYDROGEN ATOM

Graphical representations of radial wavefunctions



HYDROGEN ATOM

Graphical representations of radial wavefunctions



Expression for ψ or $R_{nl}(r)$ corresponding to $l = 0$ indicates that the functions at $r = 0$ (i.e., at the nucleus) will have non-zero value. Since the functions also contain the factor exp $(-Zr/na_0)$, the values of *s*-functions at $r = 0$ will be maximum. They decrease exponentially tending to be zero for $r = \infty$ (Fig. 7.3). As the principal quantum number (n) increases the function oscillates as directed by its polynomial part i.e., ''nodal'' points appear on the r-axis where ψ is zero. The number of nodes for an *s*-function is $n - 1$ (none for ψ_{1s}, 1 for ψ_{2s}, 2 for ψ_{3s} and so on). As the nuclear charge Z increases (e.g. He^+, Li^+ the function falls off more rapidly with r.

For $l \neq 0$, the function is zero at $r = 0$ because of the factor r^l. The function increases with r but the factor exp $(-Zr/na_0)$ has the effect of opposing it. In between $r = 0$ and $r = \infty$, the function is also governed by the nature of the polynomial. For, example,

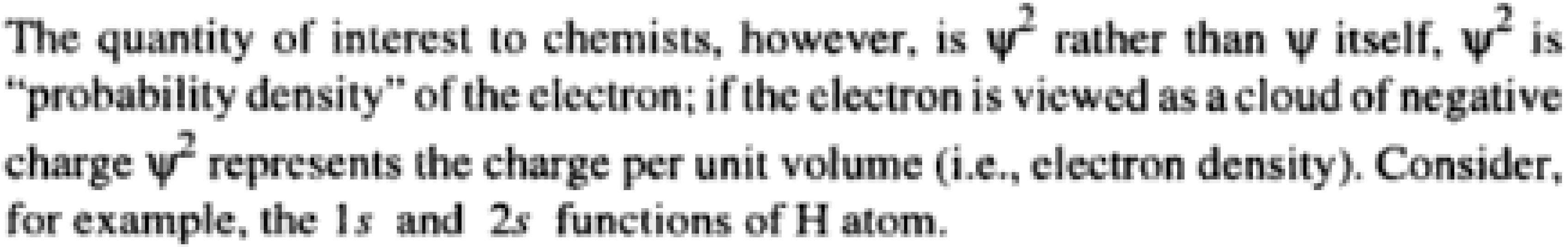
$$R_{21}(x) = \frac{1}{2\sqrt{6}}(Z)^{5/2}\, re^{-Zr/2}$$

suggests that there will be no node in the function whereas in

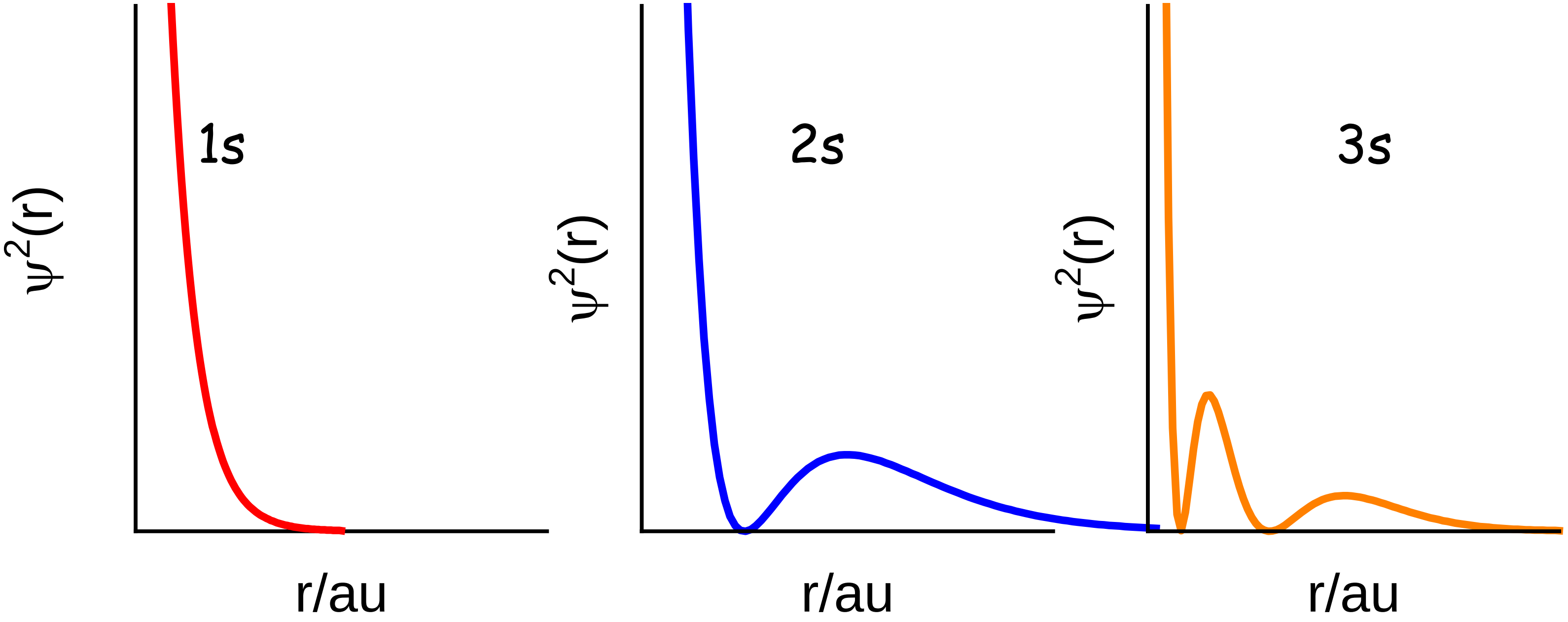
$$R_{31}(r) = Z^{5/2}\, r\,(6 - Zr)\, e^{-Zr/3}$$

HYDROGEN ATOM

Probability density



The quantity of interest to chemists, however, is ψ^2 rather than ψ itself. ψ^2 is "probability density" of the electron; if the electron is viewed as a cloud of negative charge ψ^2 represents the charge per unit volume (i.e., electron density). Consider, for example, the 1*s* and 2*s* functions of H atom.



- ✓ The plot show that electron density is maximum at $r = 0$ in case of $l = 0$ and decays exponentially.
- ✓ It contradicts to Bohr atomic structure. Since ψ^2 is the probability per volume and not actual probability of finding electron as a point.

HYDROGEN ATOM

Probabilities and the radial distribution function

The actual probability of finding the electron at any point is given by $\psi^2\, d\tau$ where $d\tau = r^2\, dr \sin\theta\, d\theta\, d\varphi$. Since it depends on both radial distance (r) and direction (θ, φ) it is more convenient to determine separately the probability distributions at various values of r irrespective of direction (the radial probability distribution) and along the various directions irrespective of distance (the angular probability distribution).

- ✓ A radial distribution function, $P(r)$ is obtained by integrating $\psi^2 d\tau$ over all angles θ and ϕ but not over r.

$$P(r)dr = \int_0^{\pi}\int_0^{2\pi} |\psi(r,\theta,\phi)|^2 r^2 dr sin\,\theta d\theta d\phi$$

$$= R_{nl}^2(r) r^2 dr \int_0^{\pi}\int_0^{2\pi} \left|Y_{lm_l}(\theta,\phi)\right|^2 sin\,\theta d\theta d\phi$$

$$= R_{nl}^2(r) r^2 dr \qquad \text{[Since } Y_{lm_l}(\theta,\phi) \text{ is normalized]}$$

$$\Rightarrow P(r) = R_{nl}^2(r) r^2 \qquad \text{Radial probability density}$$

- ✓ It gives the probability of finding electron at distance r from the nucleus.

HYDROGEN ATOM

Probabilities and the radial distribution function

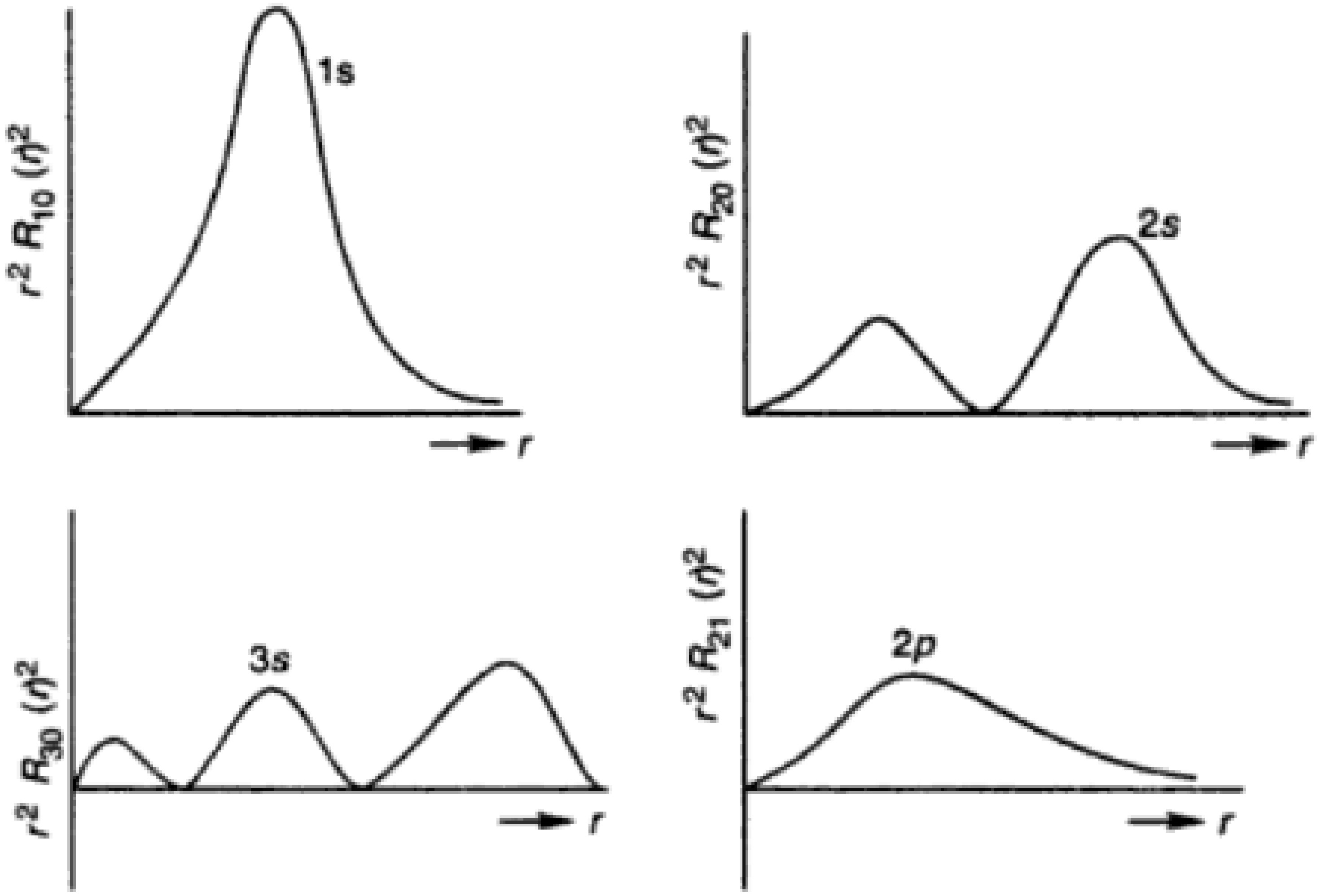
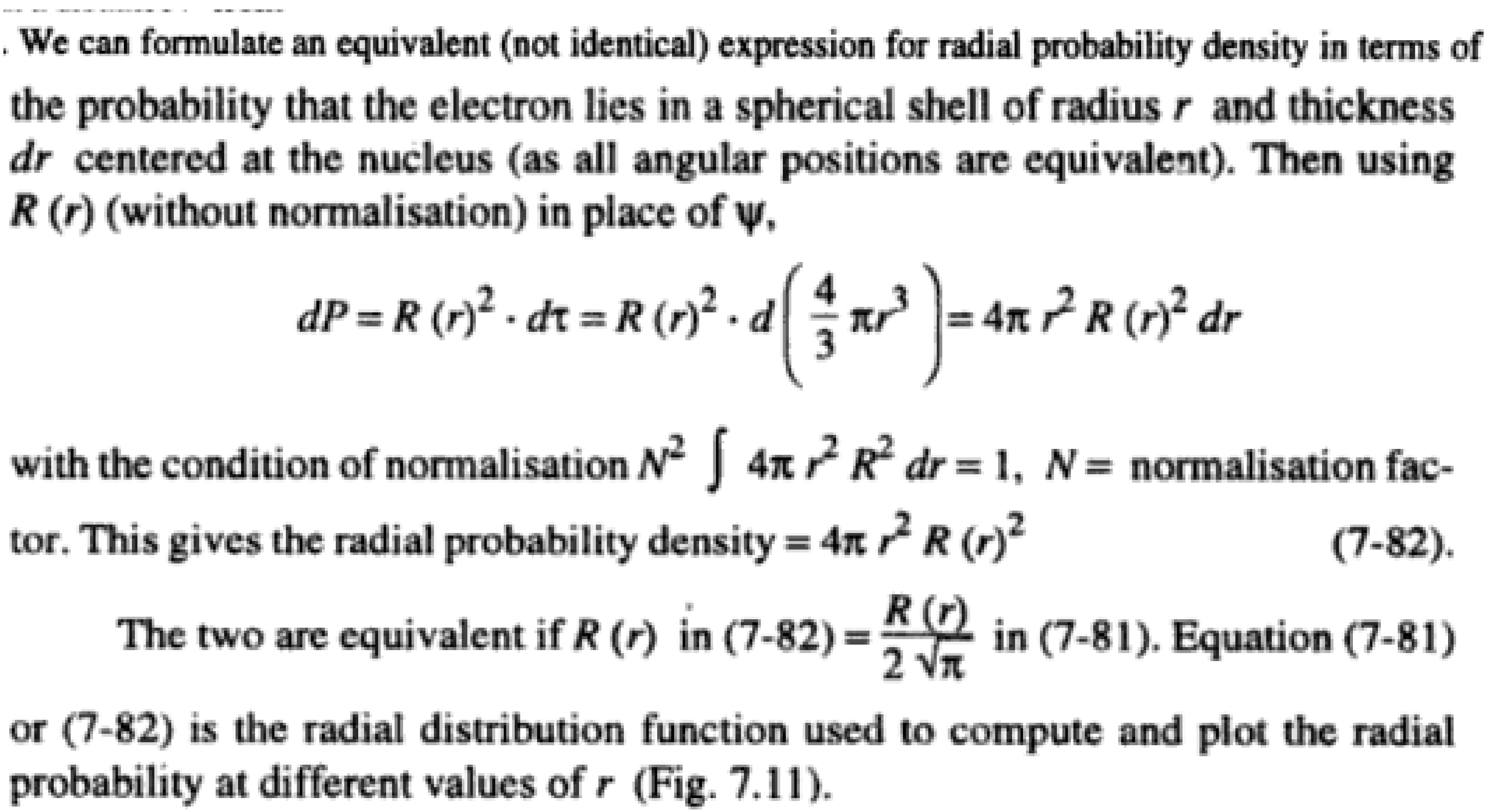


Fig. 7.11

HYDROGEN ATOM

Probabilities and the radial distribution function



We can formulate an equivalent (not identical) expression for radial probability density in terms of the probability that the electron lies in a spherical shell of radius r and thickness dr centered at the nucleus (as all angular positions are equivalent). Then using $R(r)$ (without normalisation) in place of ψ,

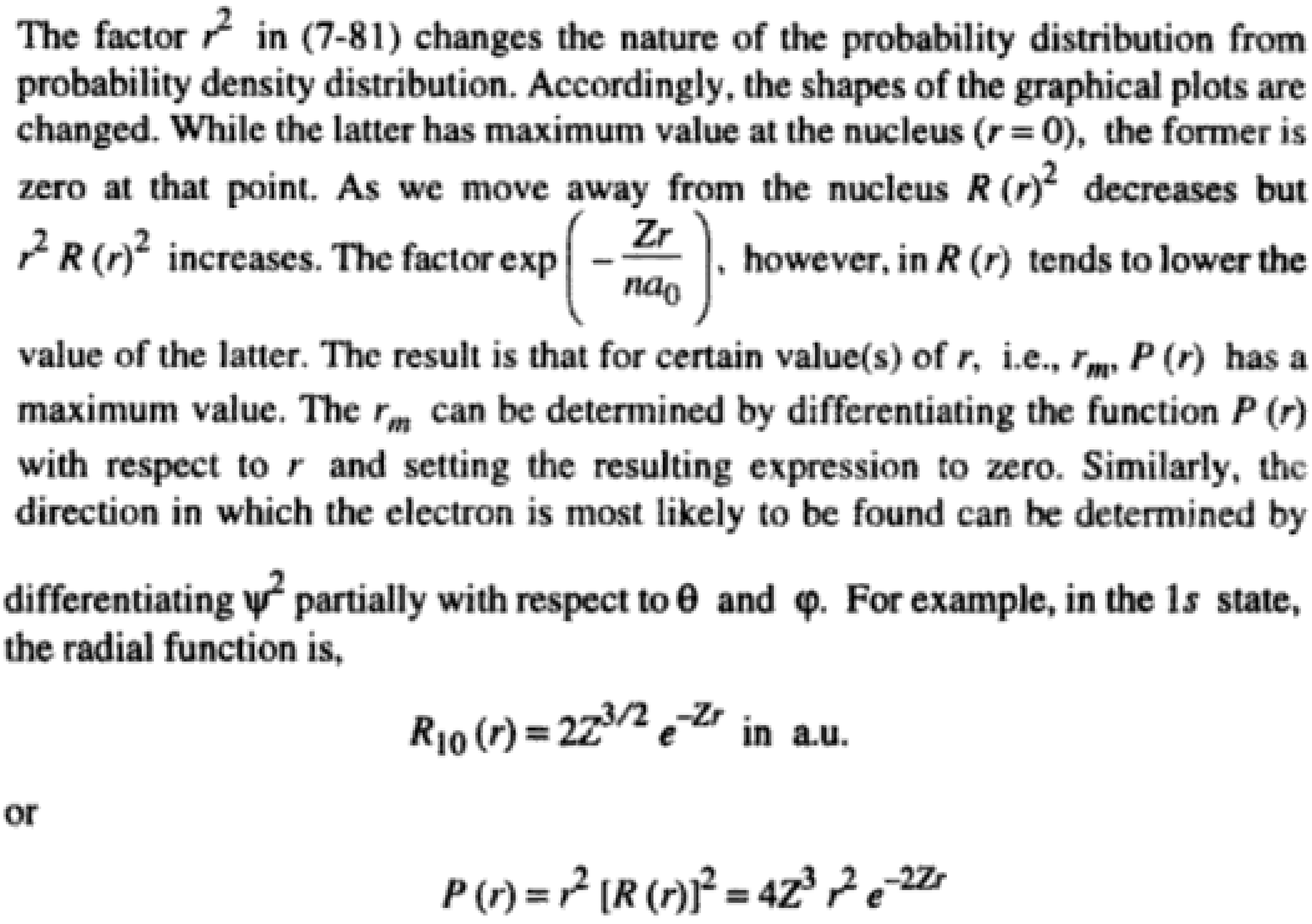
$$dP = R(r)^2 \cdot d\tau = R(r)^2 \cdot d\left(\frac{4}{3}\pi r^3\right) = 4\pi r^2 R(r)^2\, dr$$

with the condition of normalisation $N^2 \int 4\pi r^2 R^2\, dr = 1$, $N =$ normalisation factor. This gives the radial probability density $= 4\pi r^2 R(r)^2$ (7-82).

The two are equivalent if $R(r)$ in (7-82) $= \dfrac{R(r)}{2\sqrt{\pi}}$ in (7-81). Equation (7-81) or (7-82) is the radial distribution function used to compute and plot the radial probability at different values of r (Fig. 7.11).

HYDROGEN ATOM

Points of maximum probability



The factor r^2 in (7-81) changes the nature of the probability distribution from probability density distribution. Accordingly, the shapes of the graphical plots are changed. While the latter has maximum value at the nucleus $(r = 0)$, the former is zero at that point. As we move away from the nucleus $R(r)^2$ decreases but $r^2 R(r)^2$ increases. The factor $\exp\left(-\frac{Zr}{na_0}\right)$, however, in $R(r)$ tends to lower the value of the latter. The result is that for certain value(s) of r, i.e., r_m, $P(r)$ has a maximum value. The r_m can be determined by differentiating the function $P(r)$ with respect to r and setting the resulting expression to zero. Similarly, the direction in which the electron is most likely to be found can be determined by differentiating ψ^2 partially with respect to θ and φ. For example, in the $1s$ state, the radial function is,

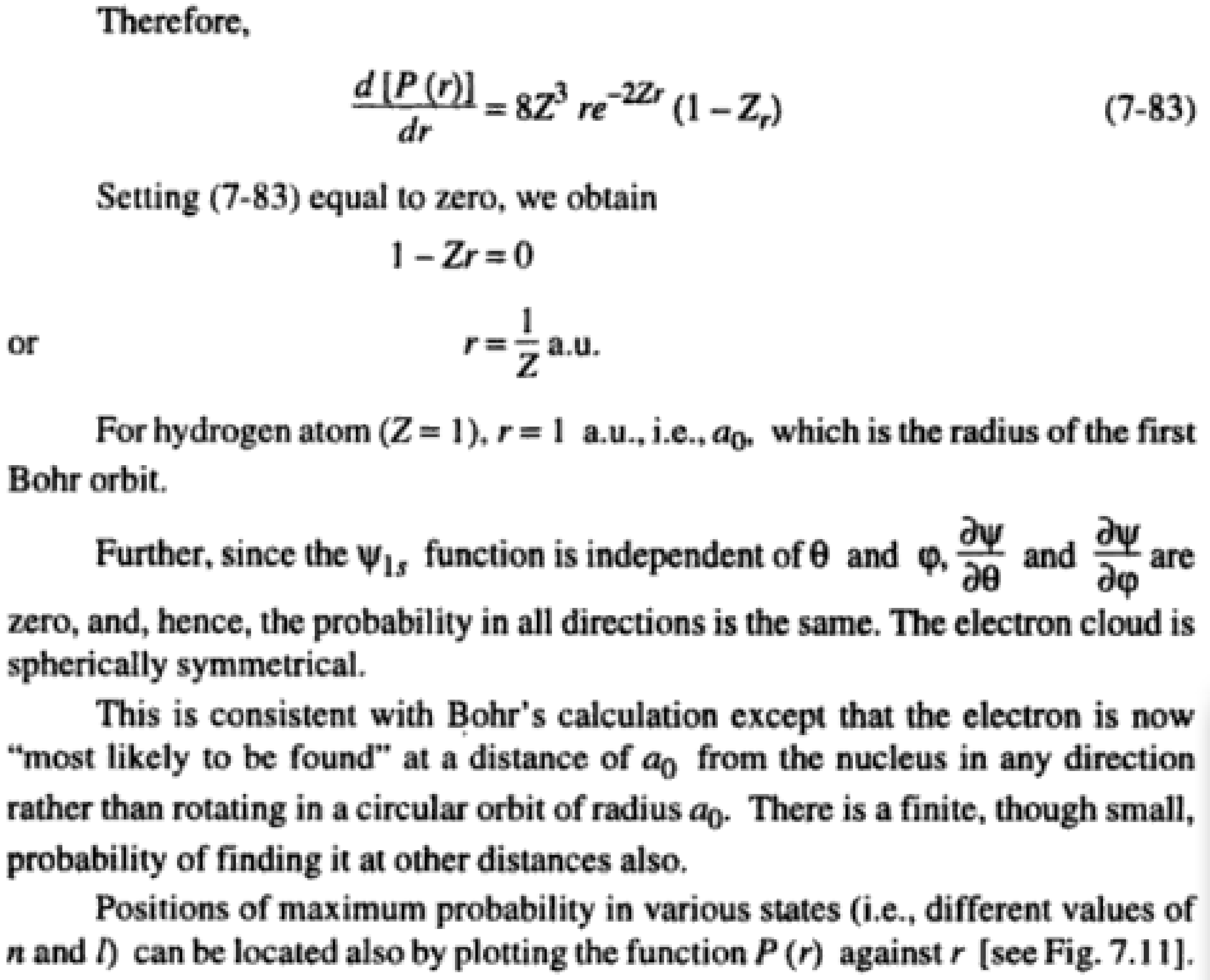
$$R_{10}(r) = 2Z^{3/2} e^{-Zr} \text{ in a.u.}$$

or

$$P(r) = r^2 [R(r)]^2 = 4Z^3 r^2 e^{-2Zr}$$

HYDROGEN ATOM

Points of maximum probability



Therefore,

$$\frac{d\,[P\,(r)]}{dr} = 8Z^3\, re^{-2Zr}\,(1 - Z_r) \qquad (7\text{-}83)$$

Setting (7-83) equal to zero, we obtain

$$1 - Zr = 0$$

or

$$r = \frac{1}{Z}\ \text{a.u.}$$

For hydrogen atom ($Z = 1$), $r = 1$ a.u., i.e., a_0, which is the radius of the first Bohr orbit.

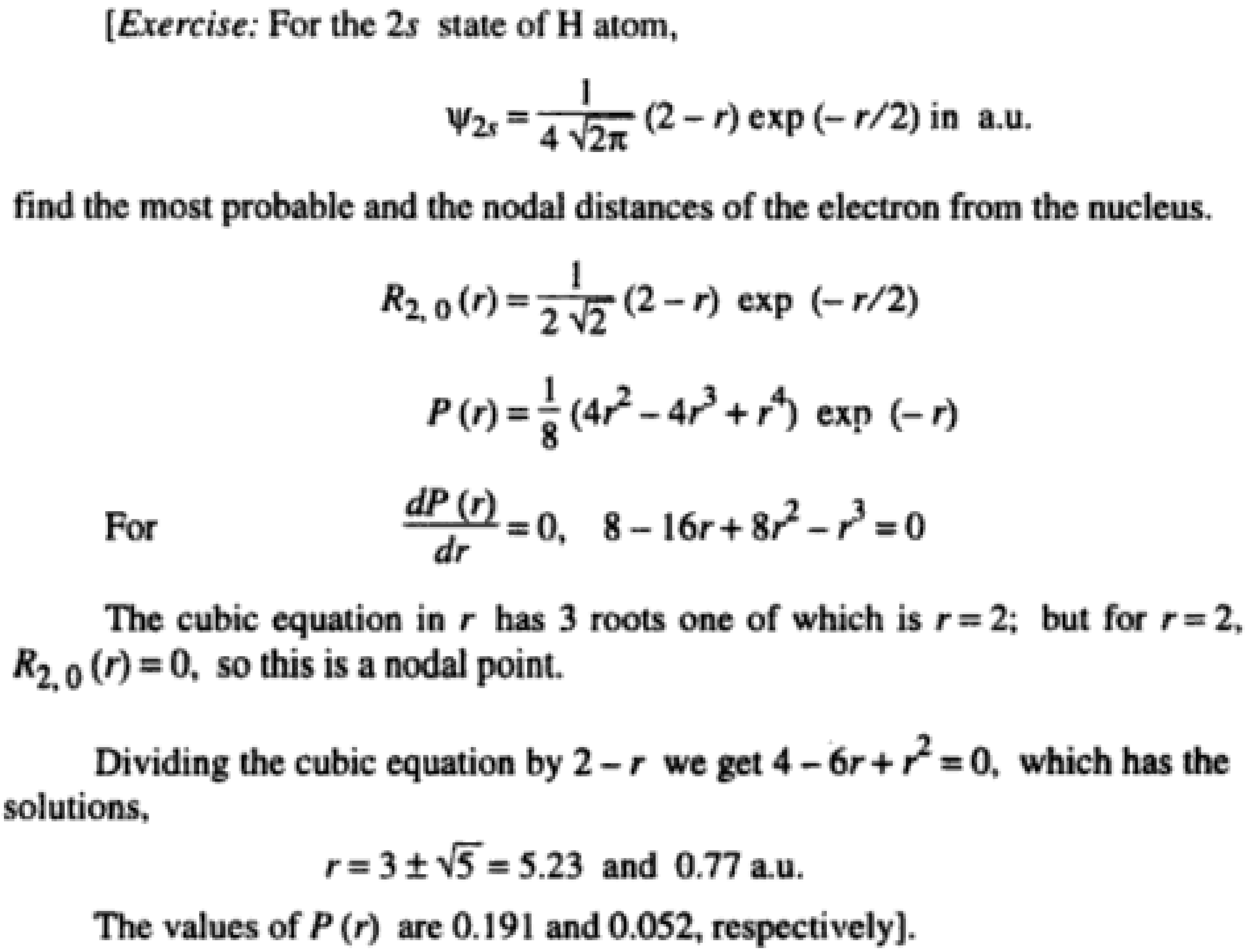
Further, since the ψ_{1s} function is independent of θ and φ, $\frac{\partial\psi}{\partial\theta}$ and $\frac{\partial\psi}{\partial\varphi}$ are zero, and, hence, the probability in all directions is the same. The electron cloud is spherically symmetrical.

This is consistent with Bohr's calculation except that the electron is now "most likely to be found" at a distance of a_0 from the nucleus in any direction rather than rotating in a circular orbit of radius a_0. There is a finite, though small, probability of finding it at other distances also.

Positions of maximum probability in various states (i.e., different values of n and l) can be located also by plotting the function $P\,(r)$ against r [see Fig. 7.11].

HYDROGEN ATOM

Points of maximum probability



[*Exercise:* For the 2s state of H atom,

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}(2-r)\exp(-r/2) \text{ in a.u.}$$

find the most probable and the nodal distances of the electron from the nucleus.

$$R_{2,0}(r) = \frac{1}{2\sqrt{2}}(2-r)\ \exp\ (-r/2)$$

$$P(r) = \frac{1}{8}(4r^2 - 4r^3 + r^4)\ \exp\ (-r)$$

For $\frac{dP(r)}{dr} = 0, \quad 8 - 16r + 8r^2 - r^3 = 0$

The cubic equation in r has 3 roots one of which is $r = 2$; but for $r = 2$, $R_{2,0}(r) = 0$, so this is a nodal point.

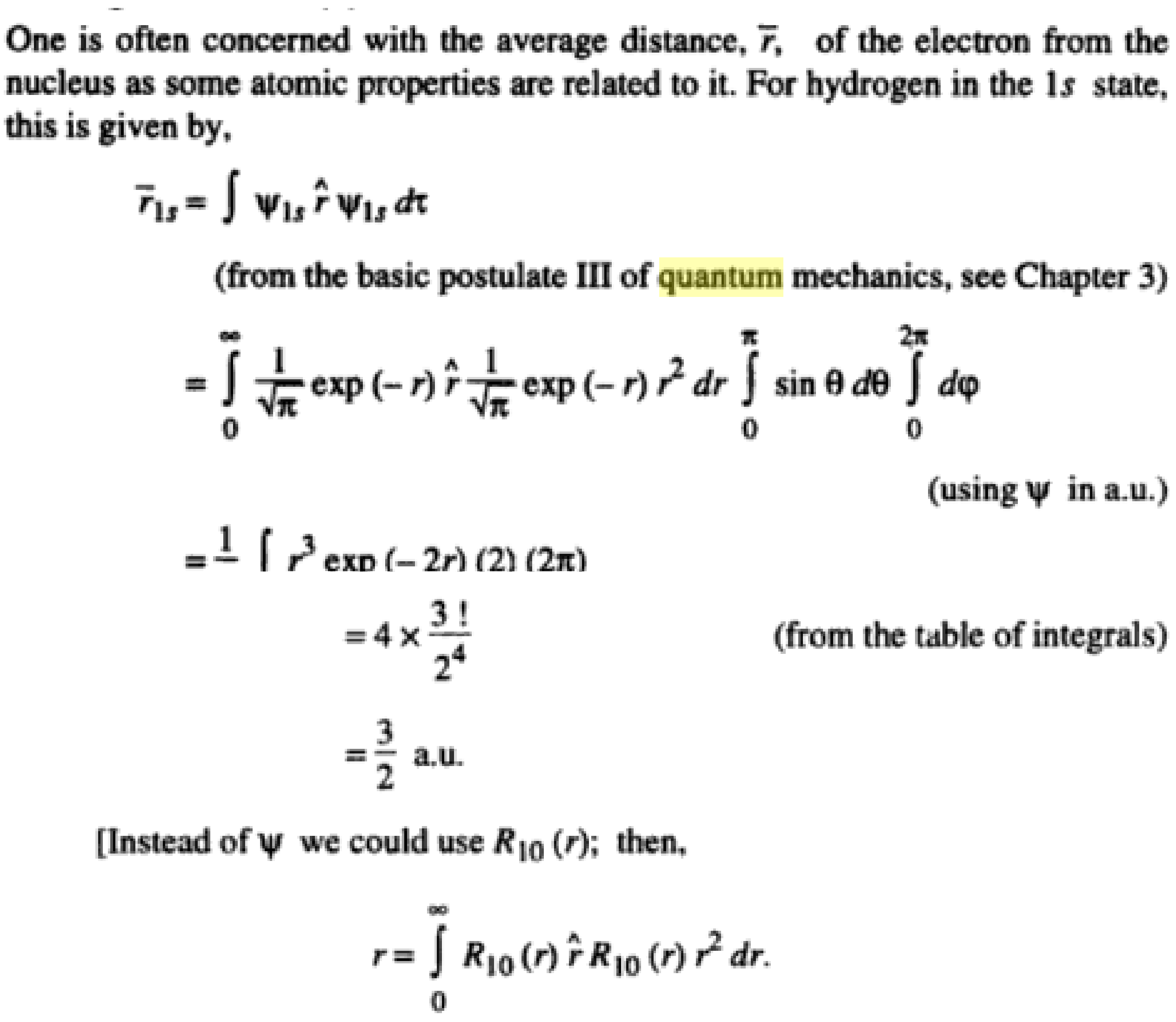
Dividing the cubic equation by $2 - r$ we get $4 - 6r + r^2 = 0$, which has the solutions,

$$r = 3 \pm \sqrt{5} = 5.23 \text{ and } 0.77 \text{ a.u.}$$

The values of $P(r)$ are 0.191 and 0.052, respectively].

HYDROGEN ATOM

Average distance of the electron from nucleus



One is often concerned with the average distance, $\bar{r}$, of the electron from the nucleus as some atomic properties are related to it. For hydrogen in the $1s$ state, this is given by,

$$\bar{r}_{1s} = \int \psi_{1s}\, \hat{r}\, \psi_{1s}\, d\tau$$

(from the basic postulate III of quantum mechanics, see Chapter 3)

$$= \int_0^\infty \frac{1}{\sqrt{\pi}} \exp(-r)\, \hat{r}\, \frac{1}{\sqrt{\pi}} \exp(-r)\, r^2\, dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\varphi$$

(using ψ in a.u.)

$$= \frac{1}{\;} \int r^3 \exp(-2r)\,(2)\,(2\pi)$$

$$= 4 \times \frac{3\,!}{2^4}$$

(from the table of integrals)

$$= \frac{3}{2} \text{ a.u.}$$

[Instead of ψ we could use $R_{10}(r)$; then,

$$r = \int_0^\infty R_{10}(r)\, \hat{r}\, R_{10}(r)\, r^2\, dr.$$

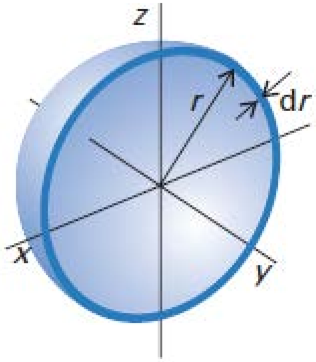
HYDROGEN ATOM

Probabilities and the radial distribution function

- ✓ The probability of finding an electron in a volume element $d\tau = \mathrm{r}^2 \sin\theta \, d\theta d\phi dr$ at a point specified by the spherical polar coordinates (r, θ, ϕ) when the state of the electron is described by the wavefunction ψ_{nlm_l} is given by

$$\left|\psi_{nlm_l}\right|^2 d\tau$$

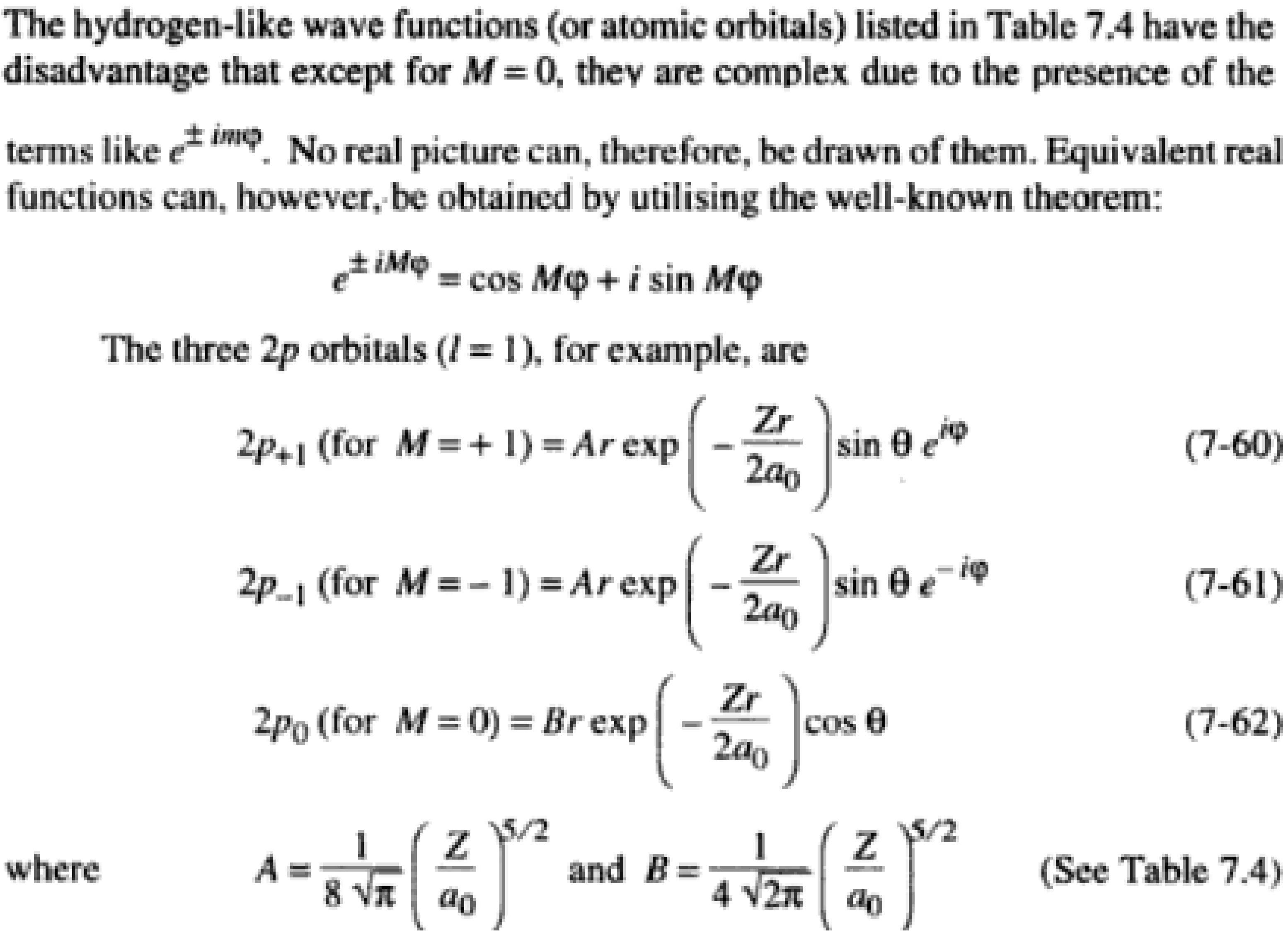
- ✓ Although the wavefunction gives the probability of finding an electron at a specified location, it is sometimes more helpful to know the probability of finding the particle at a given radius regardless of the direction. This probability is obtained by integration over the volume contained between two concentric spheres of radii r and $r + dr$



The radial distribution function gives the probability that an electron will be found anywhere between two concentric spheres with radii that differ by dr.

HYDROGEN ATOM

Presentation of Atomic orbitals



The hydrogen-like wave functions (or atomic orbitals) listed in Table 7.4 have the disadvantage that except for $M = 0$, they are complex due to the presence of the terms like $e^{\pm im\varphi}$. No real picture can, therefore, be drawn of them. Equivalent real functions can, however, be obtained by utilising the well-known theorem:

$$e^{\pm iM\varphi} = \cos M\varphi + i \sin M\varphi$$

The three $2p$ orbitals ($l = 1$), for example, are

$$2p_{+1} \text{ (for } M = +1) = Ar \exp\left(-\frac{Zr}{2a_0}\right) \sin\theta \, e^{i\varphi} \tag{7-60}$$

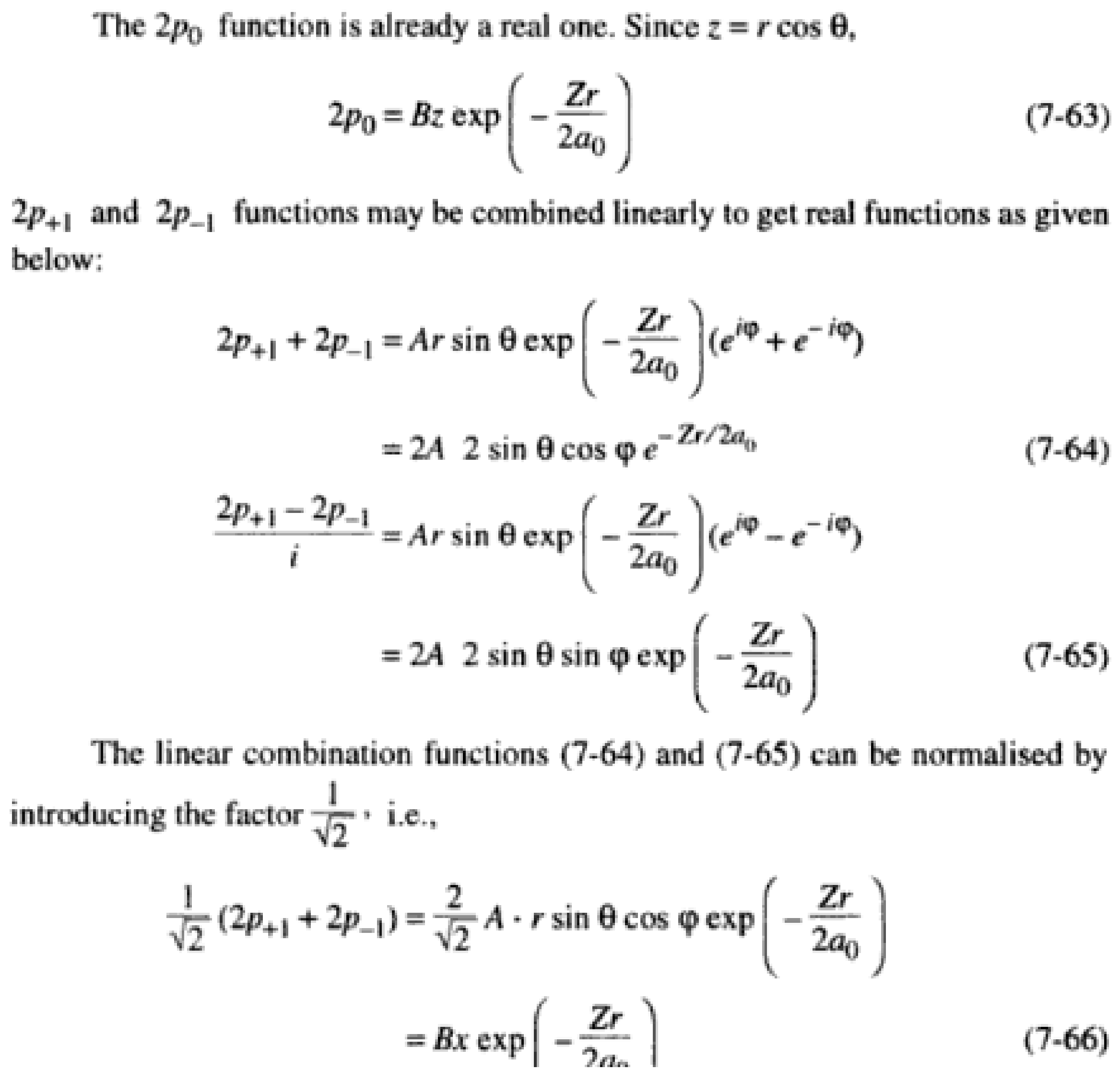
$$2p_{-1} \text{ (for } M = -1) = Ar \exp\left(-\frac{Zr}{2a_0}\right) \sin\theta \, e^{-i\varphi} \tag{7-61}$$

$$2p_{0} \text{ (for } M = 0) = Br \exp\left(-\frac{Zr}{2a_0}\right) \cos\theta \tag{7-62}$$

where $A = \dfrac{1}{8\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{5/2}$ and $B = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{5/2}$ (See Table 7.4)

HYDROGEN ATOM

Presentation of Atomic orbitals



The $2p_0$ function is already a real one. Since $z = r\cos\theta$,

$$2p_0 = Bz\exp\left(-\frac{Zr}{2a_0}\right) \tag{7-63}$$

$2p_{+1}$ and $2p_{-1}$ functions may be combined linearly to get real functions as given below:

$$2p_{+1} + 2p_{-1} = Ar\sin\theta\exp\left(-\frac{Zr}{2a_0}\right)(e^{i\varphi} + e^{-i\varphi})$$

$$= 2A\ \ 2\sin\theta\cos\varphi\, e^{-Zr/2a_0} \tag{7-64}$$

$$\frac{2p_{+1} - 2p_{-1}}{i} = Ar\sin\theta\exp\left(-\frac{Zr}{2a_0}\right)(e^{i\varphi} - e^{-i\varphi})$$

$$= 2A\ \ 2\sin\theta\sin\varphi\exp\left(-\frac{Zr}{2a_0}\right) \tag{7-65}$$

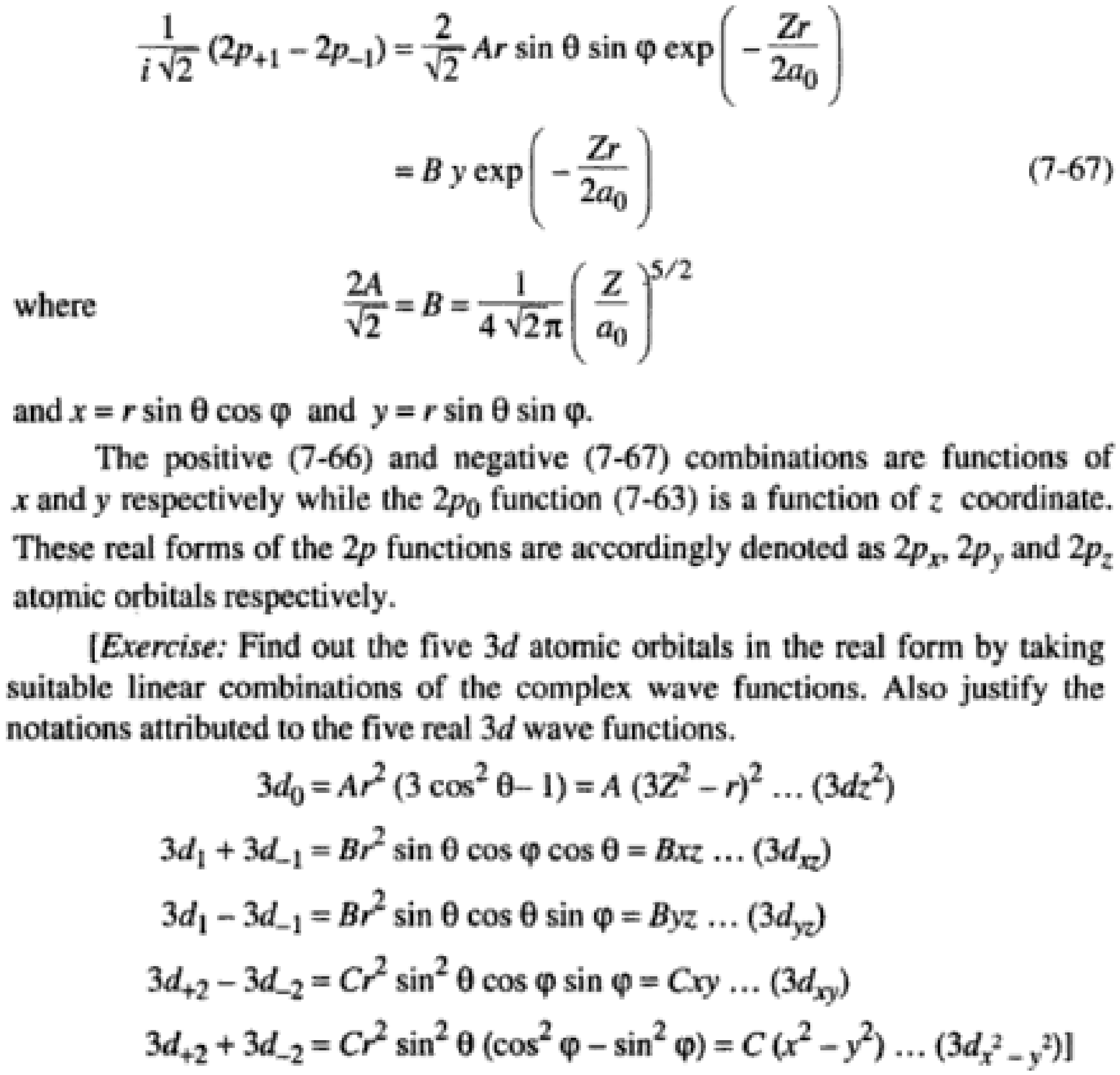
The linear combination functions (7-64) and (7-65) can be normalised by introducing the factor $\frac{1}{\sqrt{2}}$, i.e.,

$$\frac{1}{\sqrt{2}}(2p_{+1} + 2p_{-1}) = \frac{2}{\sqrt{2}}A \cdot r\sin\theta\cos\varphi\exp\left(-\frac{Zr}{2a_0}\right)$$

$$= Bx\exp\left(-\frac{Zr}{2a_0}\right) \tag{7-66}$$

HYDROGEN ATOM

Presentation of Atomic orbitals



$$\frac{1}{i\sqrt{2}}(2p_{+1}-2p_{-1}) = \frac{2}{\sqrt{2}}\, Ar \sin\theta \sin\varphi \exp\left(-\frac{Zr}{2a_0}\right)$$

$$= B\, y \exp\left(-\frac{Zr}{2a_0}\right) \qquad (7\text{-}67)$$

where $$\frac{2A}{\sqrt{2}} = B = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2}$$

and $x = r\sin\theta\cos\varphi$ and $y = r\sin\theta\sin\varphi$.

The positive (7-66) and negative (7-67) combinations are functions of x and y respectively while the $2p_0$ function (7-63) is a function of z coordinate. These real forms of the $2p$ functions are accordingly denoted as $2p_x$, $2p_y$ and $2p_z$ atomic orbitals respectively.

[*Exercise:* Find out the five 3*d* atomic orbitals in the real form by taking suitable linear combinations of the complex wave functions. Also justify the notations attributed to the five real 3*d* wave functions.

$$3d_0 = Ar^2(3\cos^2\theta - 1) = A(3Z^2 - r)^2 \ldots (3dz^2)$$

$$3d_1 + 3d_{-1} = Br^2 \sin\theta\cos\varphi\cos\theta = Bxz \ldots (3d_{xz})$$

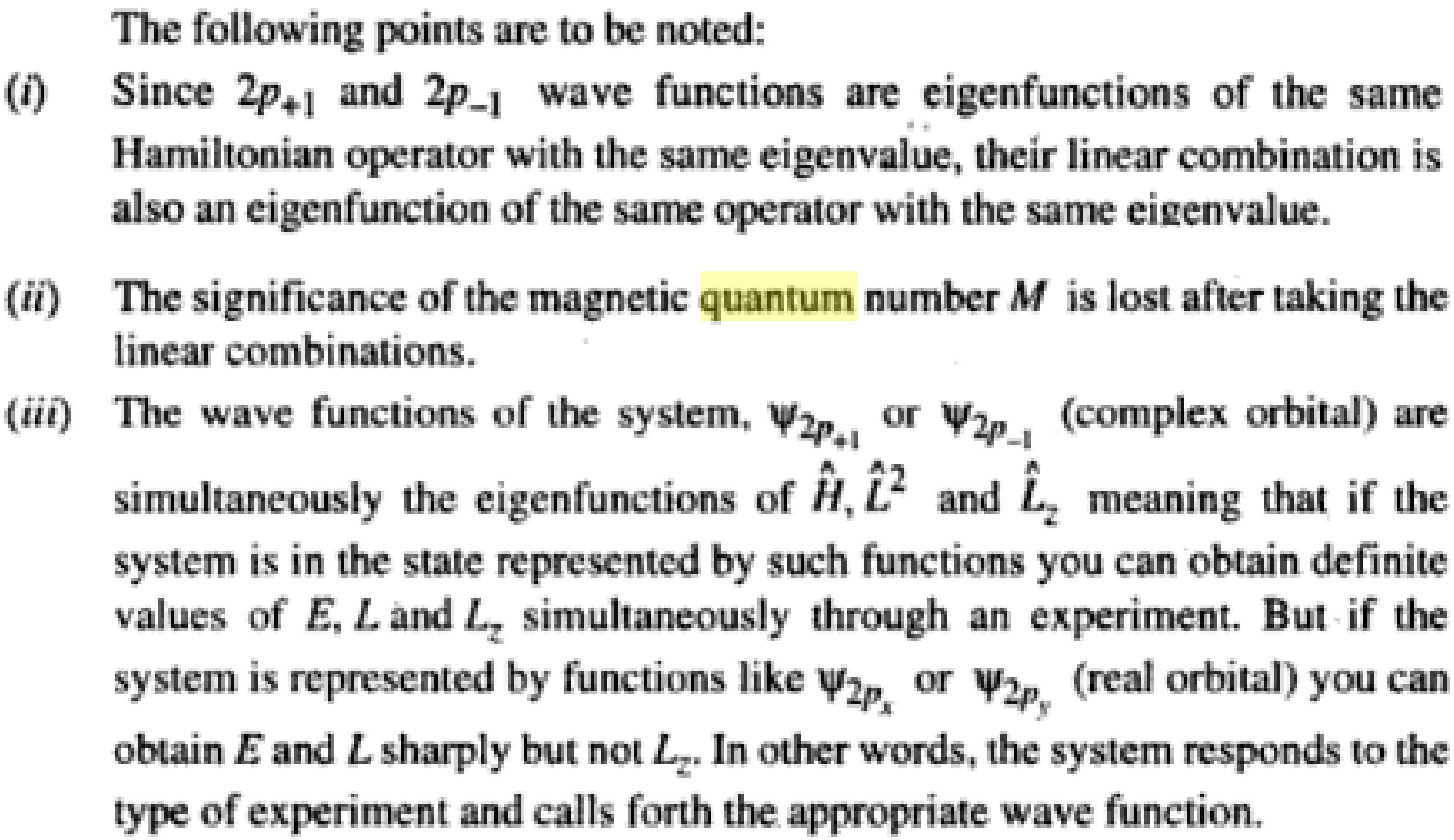
$$3d_1 - 3d_{-1} = Br^2 \sin\theta\cos\theta\sin\varphi = Byz \ldots (3d_{yz})$$

$$3d_{+2} - 3d_{-2} = Cr^2 \sin^2\theta\cos\varphi\sin\varphi = Cxy \ldots (3d_{xy})$$

$$3d_{+2} + 3d_{-2} = Cr^2 \sin^2\theta(\cos^2\varphi - \sin^2\varphi) = C(x^2 - y^2) \ldots (3d_{x^2-y^2})]$$

HYDROGEN ATOM

Presentation of Atomic orbitals



The following points are to be noted:

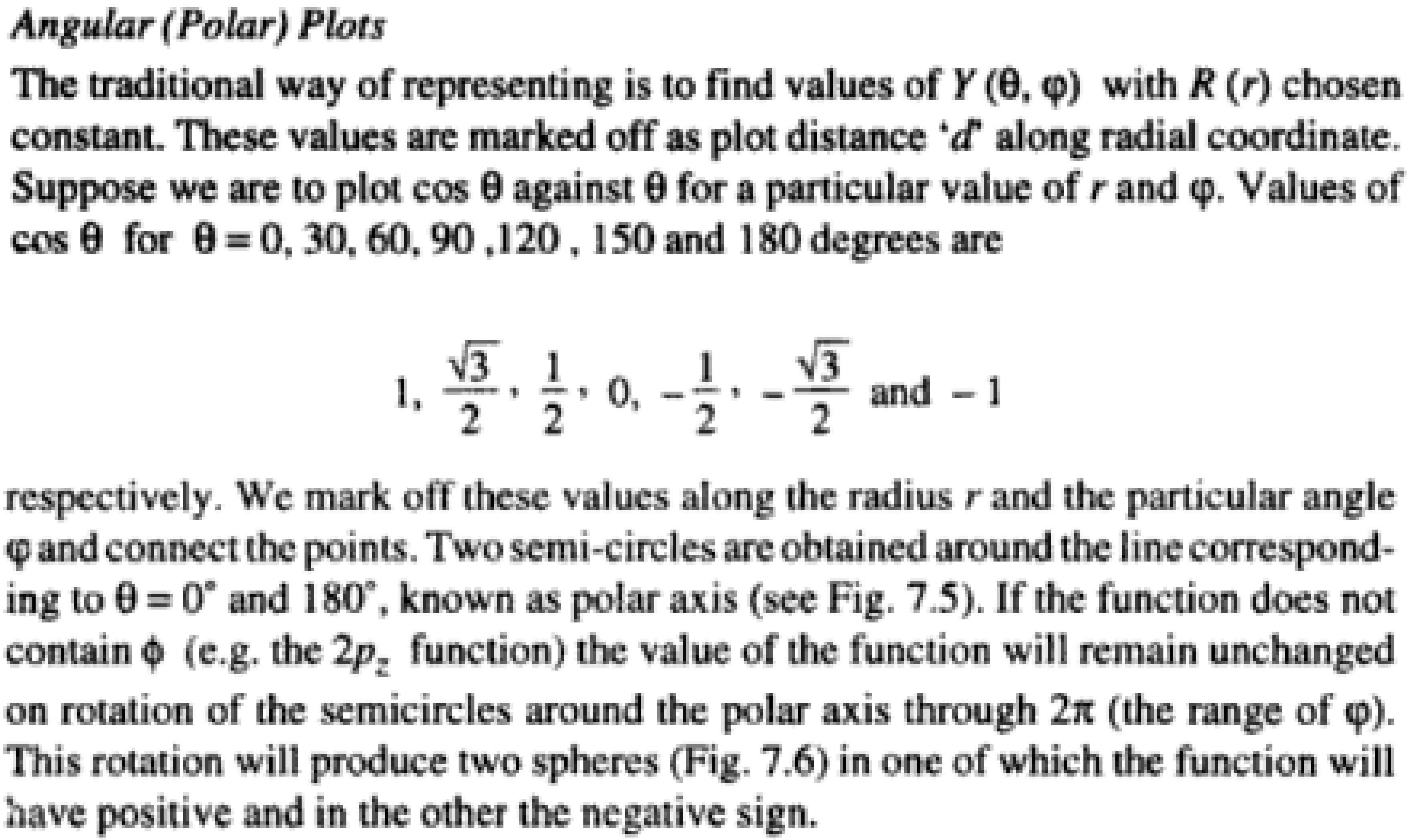
(*i*) Since $2p_{+1}$ and $2p_{-1}$ wave functions are eigenfunctions of the same Hamiltonian operator with the same eigenvalue, their linear combination is also an eigenfunction of the same operator with the same eigenvalue.

(*ii*) The significance of the magnetic quantum number M is lost after taking the linear combinations.

(*iii*) The wave functions of the system, $\psi_{2p_{+1}}$ or $\psi_{2p_{-1}}$ (complex orbital) are simultaneously the eigenfunctions of $\hat{H}, \hat{L}^2$ and $\hat{L}_z$ meaning that if the system is in the state represented by such functions you can obtain definite values of E, L and L_z simultaneously through an experiment. But if the system is represented by functions like ψ_{2p_x} or ψ_{2p_y} (real orbital) you can obtain E and L sharply but not L_z. In other words, the system responds to the type of experiment and calls forth the appropriate wave function.

HYDROGEN ATOM

Presentation of Atomic orbitals



Angular (Polar) Plots

The traditional way of representing is to find values of $Y(\theta, \varphi)$ with $R(r)$ chosen constant. These values are marked off as plot distance ‘*d*’ along radial coordinate. Suppose we are to plot cos θ against θ for a particular value of r and φ. Values of cos θ for θ = 0, 30, 60, 90 ,120 , 150 and 180 degrees are

$$1,\ \frac{\sqrt{3}}{2},\ \frac{1}{2},\ 0,\ -\frac{1}{2},\ -\frac{\sqrt{3}}{2}\ \text{and}\ -1$$

respectively. We mark off these values along the radius r and the particular angle φ and connect the points. Two semi-circles are obtained around the line corresponding to $\theta = 0^\circ$ and 180°, known as polar axis (see Fig. 7.5). If the function does not contain ϕ (e.g. the $2p_z$ function) the value of the function will remain unchanged on rotation of the semicircles around the polar axis through 2π (the range of φ). This rotation will produce two spheres (Fig. 7.6) in one of which the function will have positive and in the other the negative sign.

HYDROGEN ATOM

Presentation of Atomic orbitals

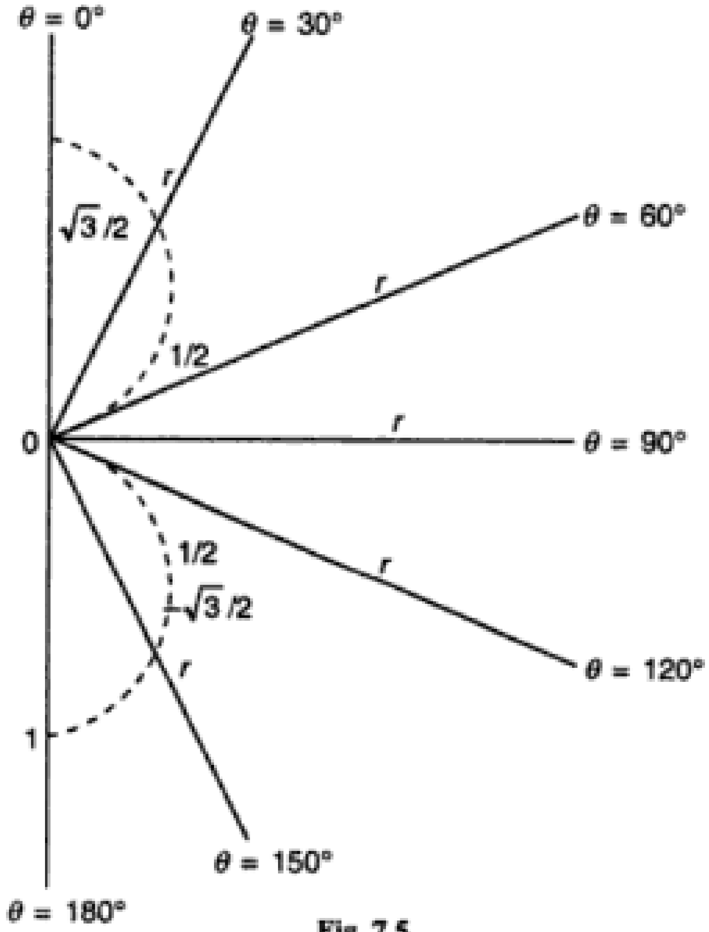


Fig. 7.5

The value of cos θ in any direction (i.e., for any value of θ and φ) can then be read off the polar plot by drawing a straight line in that direction from the origin upto the point where it meets the sphere.

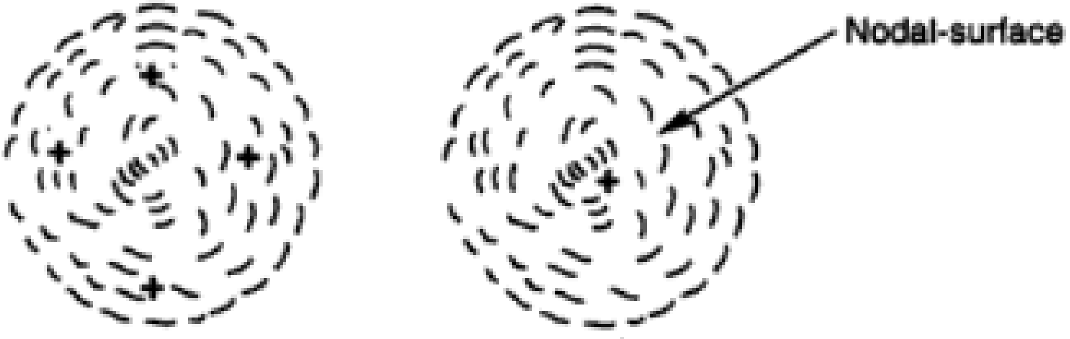
HYDROGEN ATOM

Presentation of Atomic orbitals

A polar plot presents a physical shape of the orbital in question. Such plots can be easily drawn for *s*, *p* and *d* orbitals; for others (*f*, *g*... orbitals) it is difficult (not impossible) to derive the shapes.

The polar plot for an *s*-orbital (which is independent of θ and φ) is spherical. 1*s* orbital is a single sphere, 2*s* orbital has two concentric spheres, and so on, with nucleus at the centre. (Fig. 7.7).

The $2p_z$-function is independent of φ; hence, it is symmetric with respect to the polar (z) axis. For any value of r, the function has the largest positive value in the $+z$ and the largest negative value in the $-z$ direction; xy-plane is the nodal plane (see Fig. 7.6).



(a) (b)

Fig. 7.7

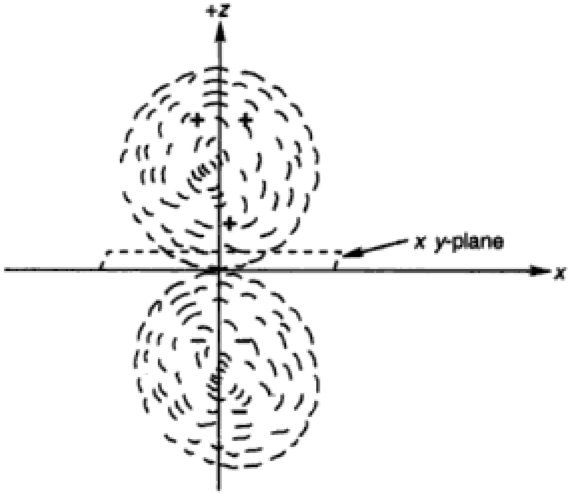


Fig. 7.6

HYDROGEN ATOM

Presentation of Atomic orbitals

The $2p_x$ function contains $\sin\theta\cos\varphi$. First, plot the $\sin\theta$ for $\varphi = 0$ (i.e., along the $+x$ direction). This function goes through $0, \frac{1}{2}, \frac{\sqrt{3}}{2}, 1, \frac{\sqrt{3}}{2}, \frac{1}{2}$ and 0 as θ moves through 0, 30°, 60°, 90°, 120°, 150° and 180° respectively. The polar plot is a circle (Fig. 7.8). We have another circle for $\varphi = 180^{\circ}$ (i.e., along $-x$-direction) in which the function is negative. As φ goes from 0 to π and then π to 2π the function changes continuously vanishing for $\varphi = 90^{\circ}$ and 270°. As φ increases, the value of $\sin\theta\cos\varphi$, for any value of θ, decreases because of the factor $\cos\varphi$. The complete polar plot of the p_x function consists of two spheres along the x-axis (Fig. 7.9) in one of which the function is positive and in the other negative; yz-plane is the nodal plane.

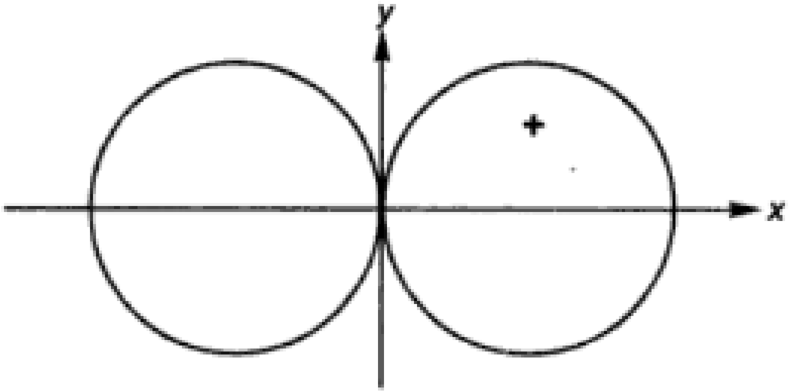


Fig. 7.8

HYDROGEN ATOM

Presentation of Atomic orbitals

The polar plot of $2p_y$ function (or $\sin\theta \sin\varphi$) can likewise be shown to consist of two spheres along the y-axis with xz-plane as the nodal plane.

The three $2p$ functions ($2p_x$, $2p_y$ and $2p_z$) differ only in their orientation.

Polar plots for higher values of n differ only in the size of the spheres.

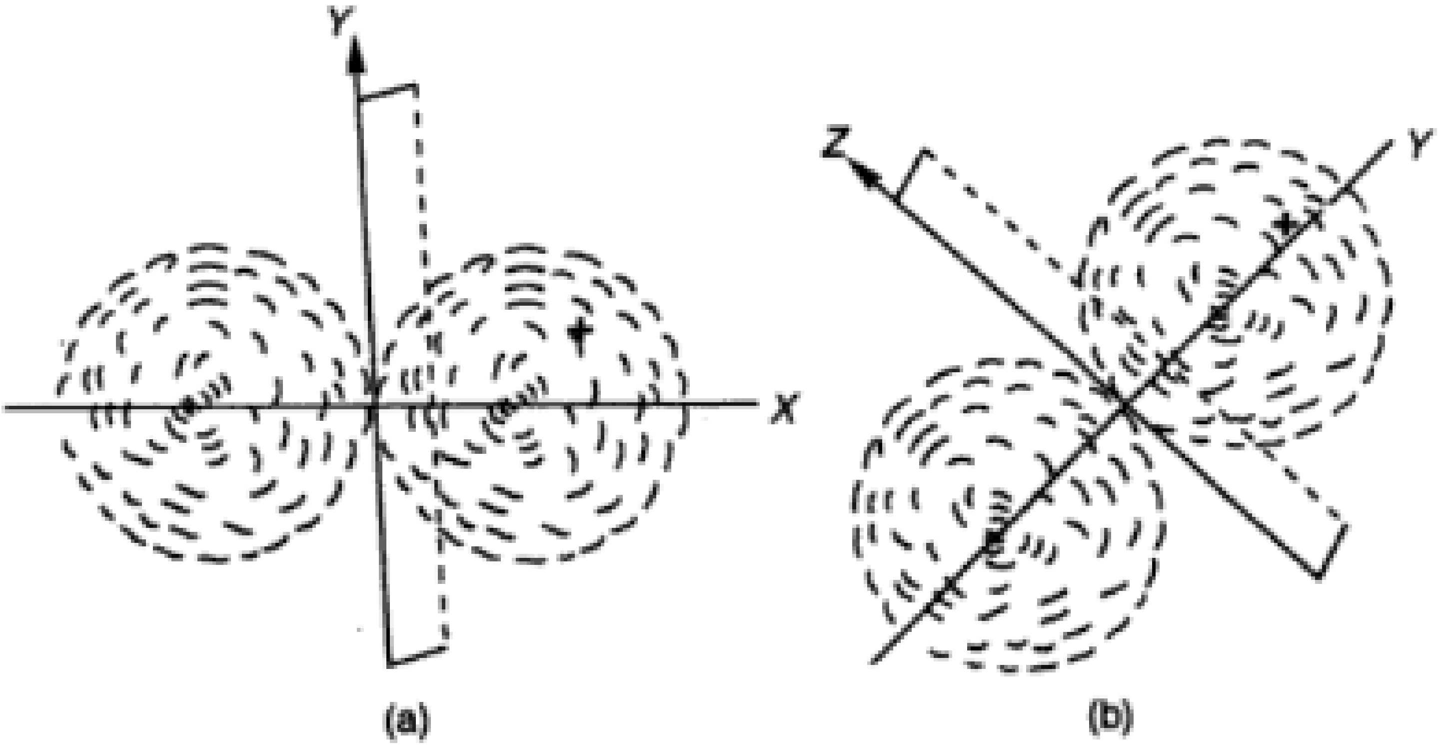
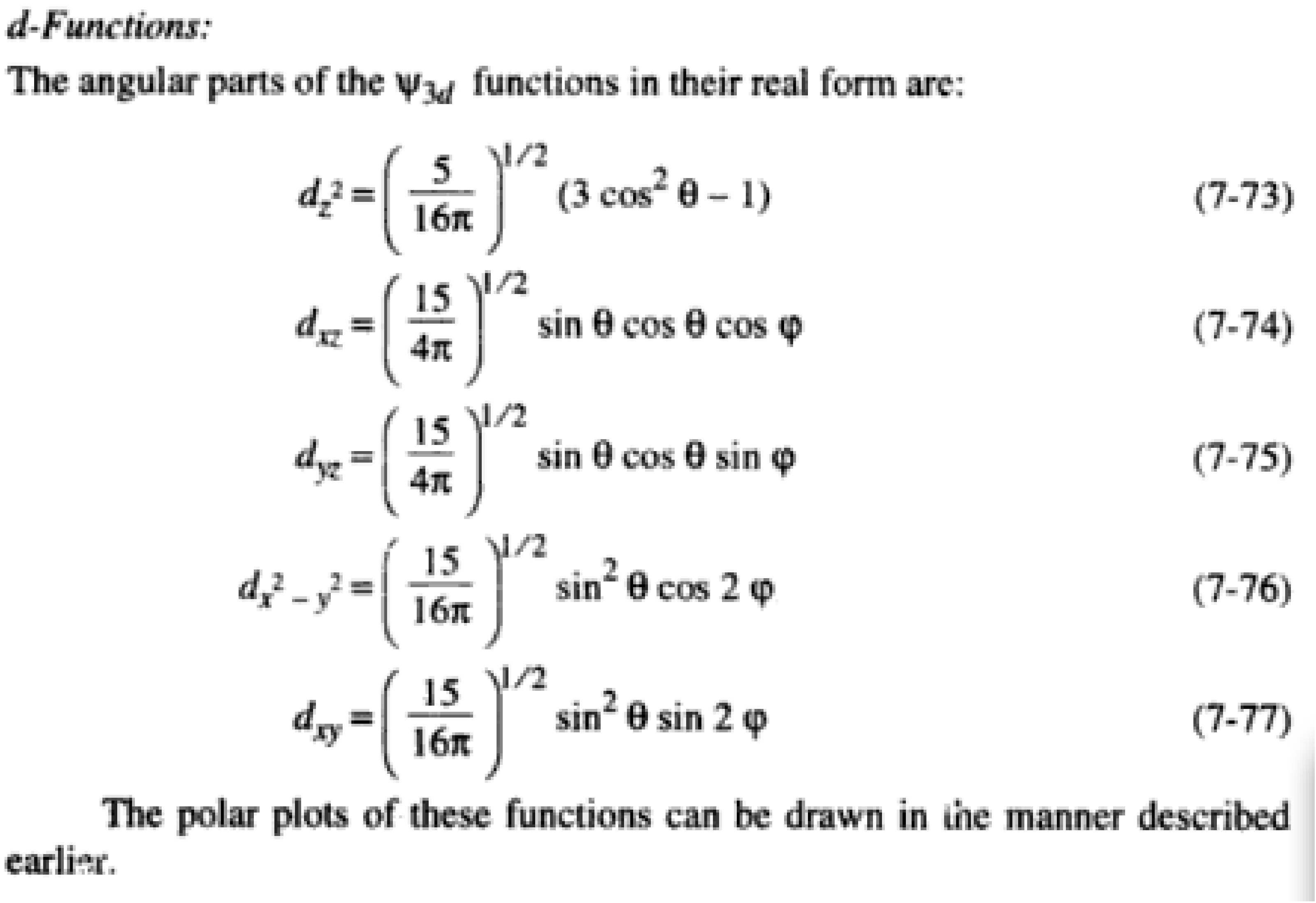


Fig. 7.9

HYDROGEN ATOM

Presentation of Atomic orbitals



d-Functions:

The angular parts of the ψ_{3d} functions in their real form are:

$$d_{z^2} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \qquad (7\text{-}73)$$

$$d_{xz} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\varphi \qquad (7\text{-}74)$$

$$d_{yz} = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\varphi \qquad (7\text{-}75)$$

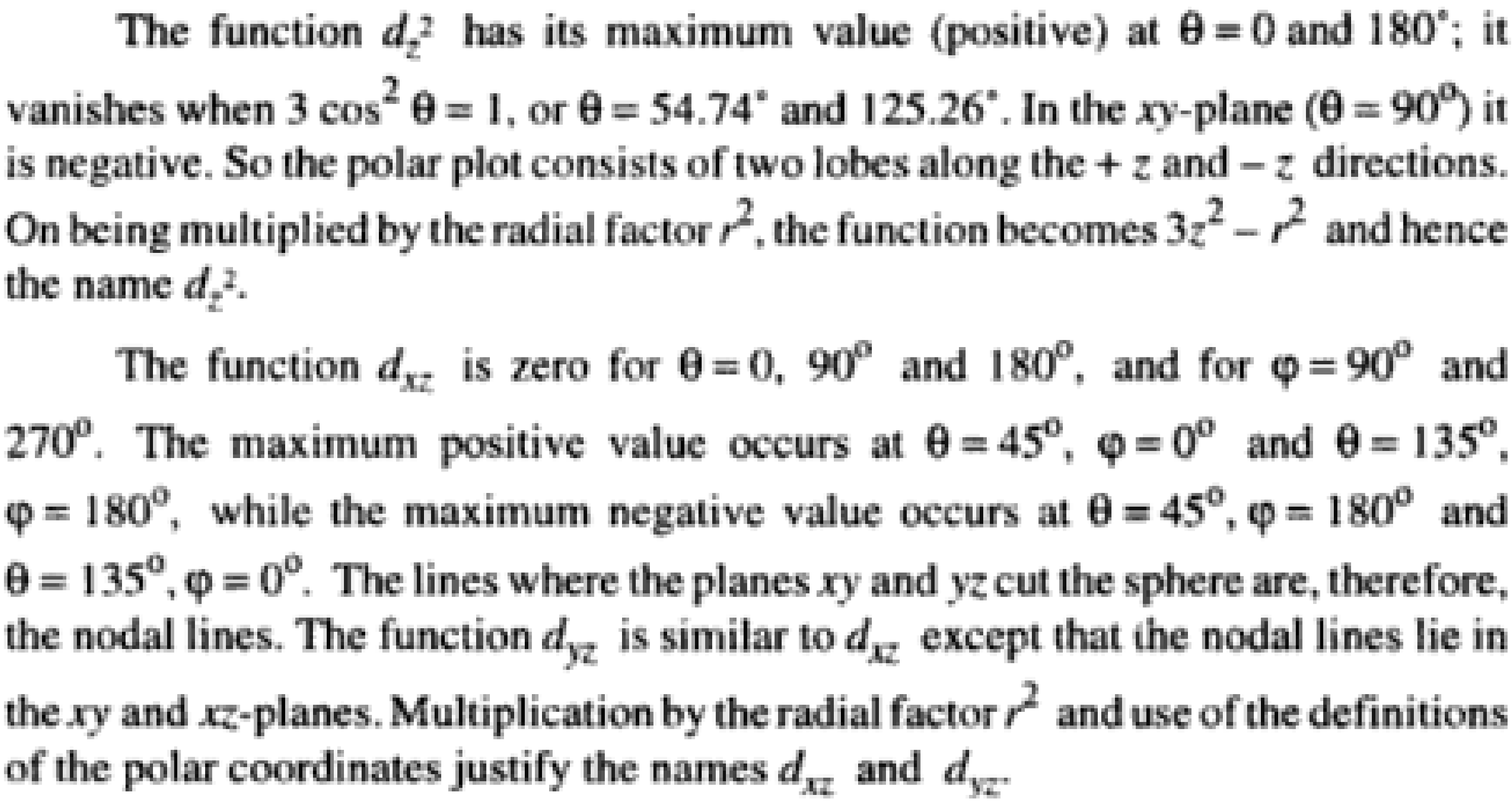
$$d_{x^2-y^2} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\varphi \qquad (7\text{-}76)$$

$$d_{xy} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\varphi \qquad (7\text{-}77)$$

The polar plots of these functions can be drawn in the manner described earlier.

HYDROGEN ATOM

Presentation of Atomic orbitals

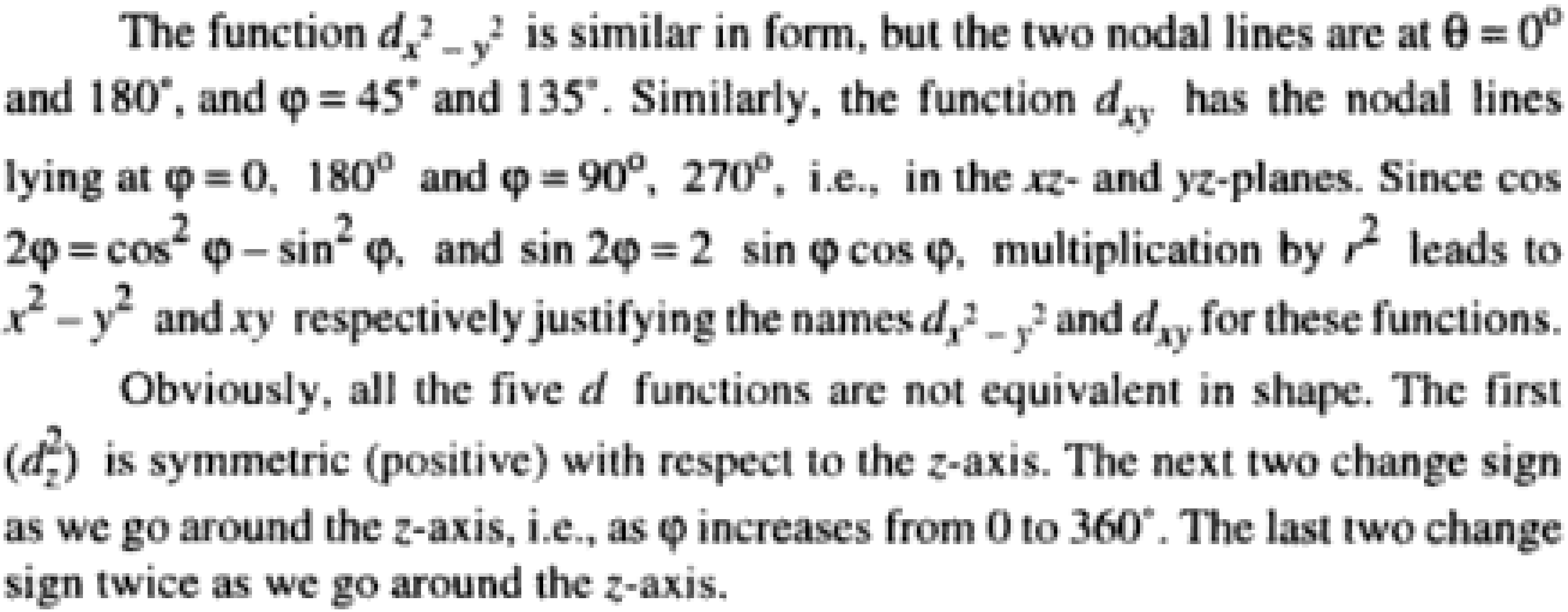


The function d_{z^2} has its maximum value (positive) at $\theta = 0$ and 180°; it vanishes when $3\cos^2\theta = 1$, or $\theta = 54.74°$ and 125.26°. In the xy-plane ($\theta = 90^o$) it is negative. So the polar plot consists of two lobes along the $+z$ and $-z$ directions. On being multiplied by the radial factor r^2, the function becomes $3z^2 - r^2$ and hence the name d_{z^2}.

The function d_{xz} is zero for $\theta = 0$, 90^o and 180^o, and for $\varphi = 90^o$ and 270^o. The maximum positive value occurs at $\theta = 45^o$, $\varphi = 0^o$ and $\theta = 135^o$, $\varphi = 180^o$, while the maximum negative value occurs at $\theta = 45^o$, $\varphi = 180^o$ and $\theta = 135^o$, $\varphi = 0^o$. The lines where the planes xy and yz cut the sphere are, therefore, the nodal lines. The function d_{yz} is similar to d_{xz} except that the nodal lines lie in the xy and xz-planes. Multiplication by the radial factor r^2 and use of the definitions of the polar coordinates justify the names d_{xz} and d_{yz}.

HYDROGEN ATOM

Presentation of Atomic orbitals

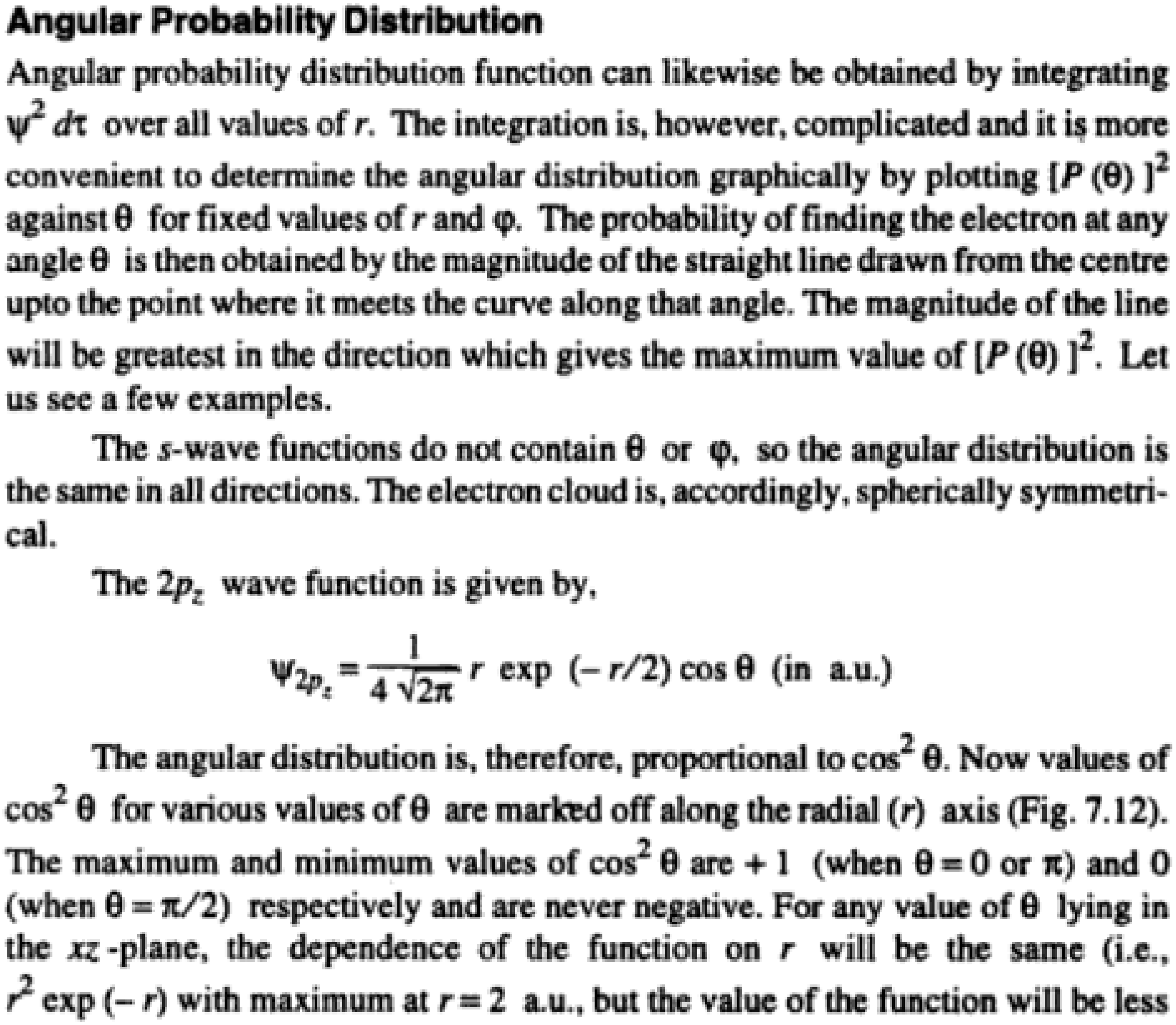


The function $d_{x^2-y^2}$ is similar in form, but the two nodal lines are at $\theta = 0^o$ and 180°, and $\varphi = 45^\circ$ and 135°. Similarly, the function d_{xy} has the nodal lines lying at $\varphi = 0,\ 180^0$ and $\varphi = 90^0,\ 270^0$, i.e., in the xz- and yz-planes. Since cos $2\varphi = \cos^2\varphi - \sin^2\varphi$, and $\sin 2\varphi = 2\ \sin\varphi\cos\varphi$, multiplication by r^2 leads to $x^2 - y^2$ and xy respectively justifying the names $d_{x^2-y^2}$ and d_{xy} for these functions.

Obviously, all the five d functions are not equivalent in shape. The first (d_z^2) is symmetric (positive) with respect to the z-axis. The next two change sign as we go around the z-axis, i.e., as φ increases from 0 to 360°. The last two change sign twice as we go around the z-axis.

HYDROGEN ATOM

Angular probability functions



Angular Probability Distribution

Angular probability distribution function can likewise be obtained by integrating $\psi^2 \, d\tau$ over all values of r. The integration is, however, complicated and it is more convenient to determine the angular distribution graphically by plotting $[P(\theta)]^2$ against θ for fixed values of r and φ. The probability of finding the electron at any angle θ is then obtained by the magnitude of the straight line drawn from the centre upto the point where it meets the curve along that angle. The magnitude of the line will be greatest in the direction which gives the maximum value of $[P(\theta)]^2$. Let us see a few examples.

The s-wave functions do not contain θ or φ, so the angular distribution is the same in all directions. The electron cloud is, accordingly, spherically symmetrical.

The $2p_z$ wave function is given by,

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \, r \ \exp \ (-r/2) \cos\theta \ \ (\text{in a.u.})$$

The angular distribution is, therefore, proportional to $\cos^2\theta$. Now values of $\cos^2\theta$ for various values of θ are marked off along the radial (r) axis (Fig. 7.12). The maximum and minimum values of $\cos^2\theta$ are $+1$ (when $\theta = 0$ or π) and 0 (when $\theta = \pi/2$) respectively and are never negative. For any value of θ lying in the xz-plane, the dependence of the function on r will be the same (i.e., $r^2 \exp(-r)$ with maximum at $r = 2$ a.u., but the value of the function will be less

HYDROGEN ATOM

Angular probability functions

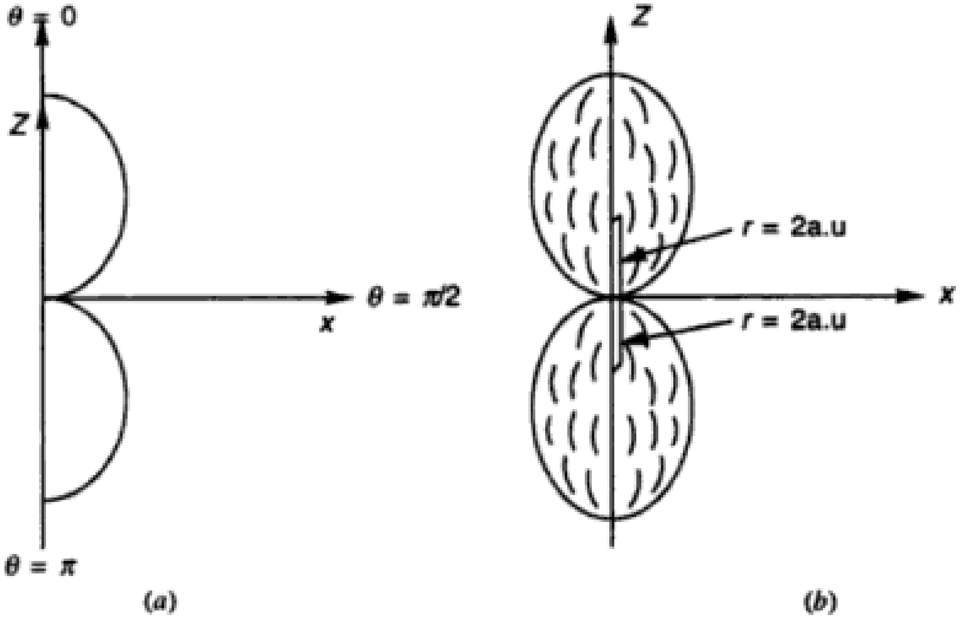
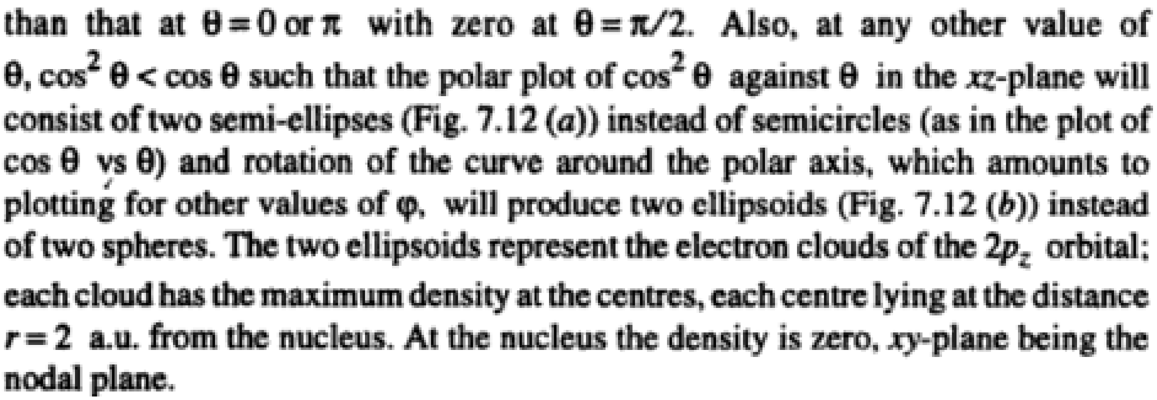


Fig. 7.12

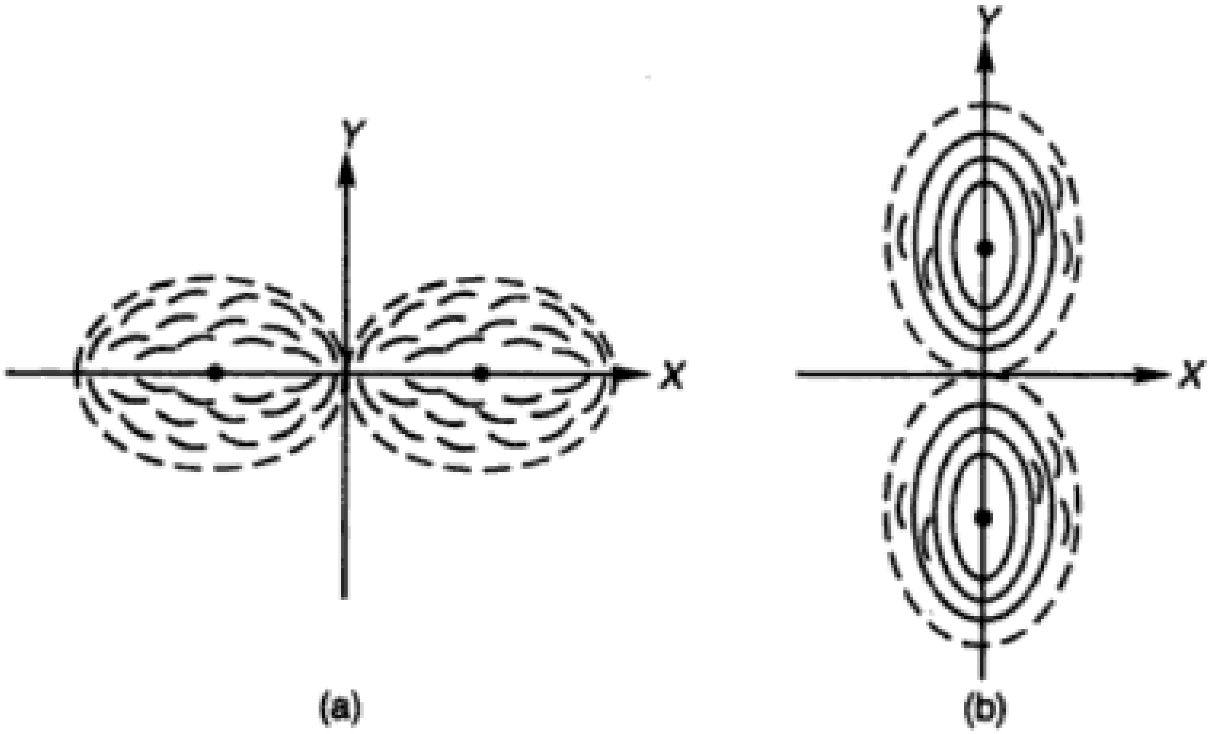


than that at $\theta = 0$ or π with zero at $\theta = \pi/2$. Also, at any other value of θ, $\cos^2\theta < \cos\theta$ such that the polar plot of $\cos^2\theta$ against θ in the *xz*-plane will consist of two semi-ellipses (Fig. 7.12 (*a*)) instead of semicircles (as in the plot of $\cos\theta$ vs θ) and rotation of the curve around the polar axis, which amounts to plotting for other values of φ, will produce two ellipsoids (Fig. 7.12 (*b*)) instead of two spheres. The two ellipsoids represent the electron clouds of the $2p_z$ orbital; each cloud has the maximum density at the centres, each centre lying at the distance $r = 2$ a.u. from the nucleus. At the nucleus the density is zero, *xy*-plane being the nodal plane.

HYDROGEN ATOM

Angular probability functions

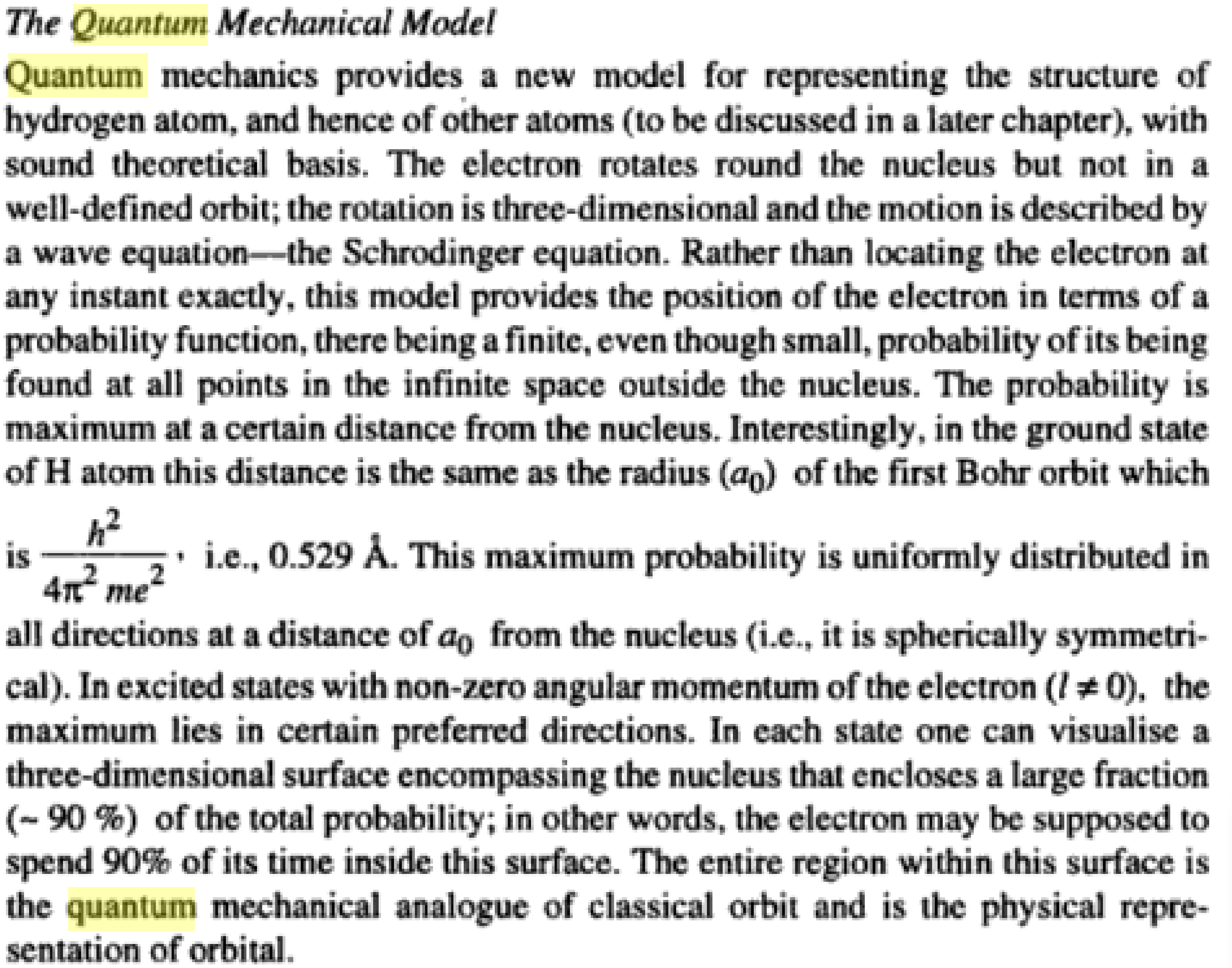
Similar angular probability plots may be drawn for $2p_x$ and $2p_y$ orbitals (Figs. 7.13 (*a*) and (*b*)).



(a) (b)

Fig. 7.13

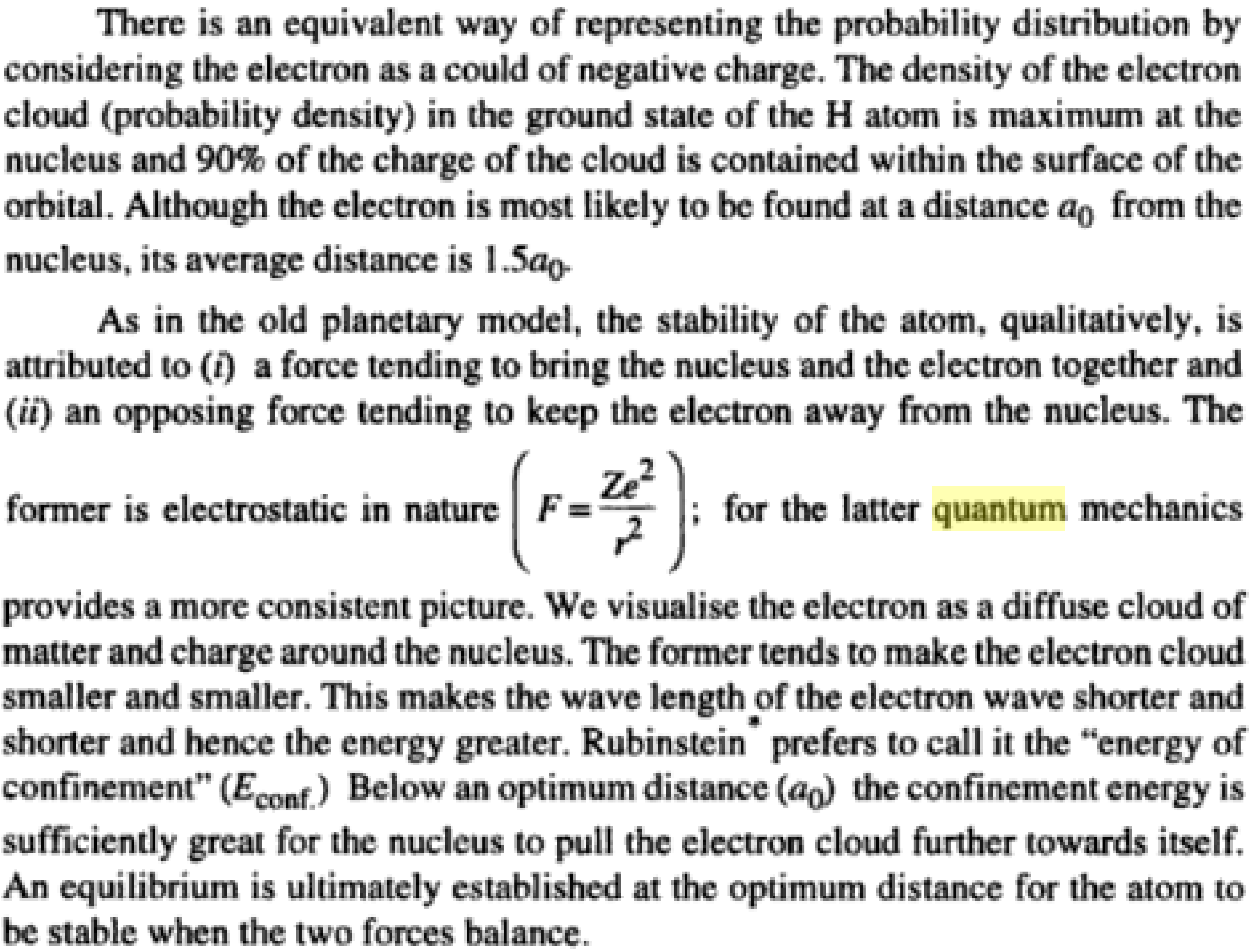
HYDROGEN ATOM



The Quantum Mechanical Model

Quantum mechanics provides a new model for representing the structure of hydrogen atom, and hence of other atoms (to be discussed in a later chapter), with sound theoretical basis. The electron rotates round the nucleus but not in a well-defined orbit; the rotation is three-dimensional and the motion is described by a wave equation—the Schrodinger equation. Rather than locating the electron at any instant exactly, this model provides the position of the electron in terms of a probability function, there being a finite, even though small, probability of its being found at all points in the infinite space outside the nucleus. The probability is maximum at a certain distance from the nucleus. Interestingly, in the ground state of H atom this distance is the same as the radius (a_0) of the first Bohr orbit which is $\frac{h^2}{4\pi^2 me^2}$, i.e., 0.529 Å. This maximum probability is uniformly distributed in all directions at a distance of a_0 from the nucleus (i.e., it is spherically symmetrical). In excited states with non-zero angular momentum of the electron ($l \neq 0$), the maximum lies in certain preferred directions. In each state one can visualise a three-dimensional surface encompassing the nucleus that encloses a large fraction ($\sim 90\%$) of the total probability; in other words, the electron may be supposed to spend 90% of its time inside this surface. The entire region within this surface is the quantum mechanical analogue of classical orbit and is the physical representation of orbital.

HYDROGEN ATOM



There is an equivalent way of representing the probability distribution by considering the electron as a could of negative charge. The density of the electron cloud (probability density) in the ground state of the H atom is maximum at the nucleus and 90% of the charge of the cloud is contained within the surface of the orbital. Although the electron is most likely to be found at a distance a_0 from the nucleus, its average distance is $1.5a_0$.

As in the old planetary model, the stability of the atom, qualitatively, is attributed to (*i*) a force tending to bring the nucleus and the electron together and (*ii*) an opposing force tending to keep the electron away from the nucleus. The former is electrostatic in nature $\left(F = \dfrac{Ze^2}{r^2}\right)$; for the latter quantum mechanics provides a more consistent picture. We visualise the electron as a diffuse cloud of matter and charge around the nucleus. The former tends to make the electron cloud smaller and smaller. This makes the wave length of the electron wave shorter and shorter and hence the energy greater. Rubinstein* prefers to call it the "energy of confinement" ($E_{\text{conf.}}$) Below an optimum distance (a_0) the confinement energy is sufficiently great for the nucleus to pull the electron cloud further towards itself. An equilibrium is ultimately established at the optimum distance for the atom to be stable when the two forces balance.