The Radial solutions

$$\text{Coulombic potential energy,} \qquad V = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\text{Hamiltonian,} \quad \hat{H} = \widehat{KE}_e + \widehat{KE}_N + \hat{V} \;=\; -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

Since potential is spherically symmetric, we can write, $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$

The equation separates and we have to solve,

$$\Lambda^2 Y = -l(l+1)Y \qquad \text{These give rise to the spherical harmonics}$$

$$\text{and} \quad -\frac{\hbar^2}{2m_e r^2}R''(r) \pm \frac{\hbar^2}{m_e}\frac{1}{r}R'(r) + \left[\frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r} - E\right] R(r) = 0\,,$$

$$\text{where } V_{eff} = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

V_{eff} is made up of Coulombic and centrifugal term

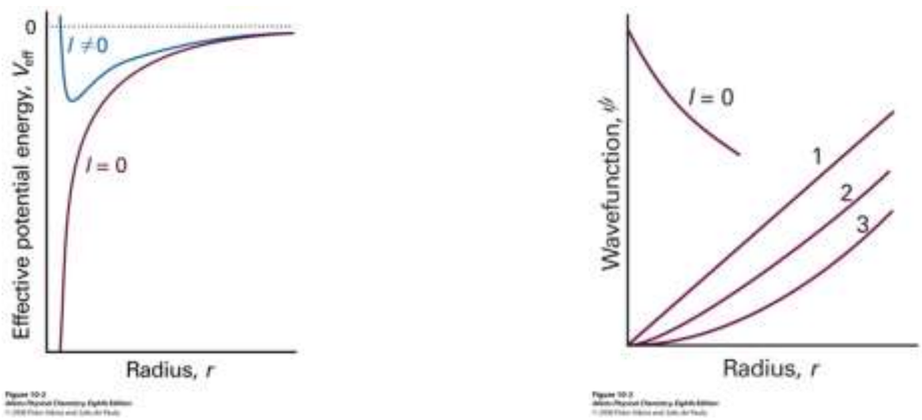

Figure 7.1: Effective potential and the wavefunctions at small radius

$$E = \frac{Z^2\mu e^4}{32\pi^2\epsilon_0^2\hbar^2 n^2}$$

$$\rho = \frac{2Zr}{na_0} \qquad \text{Bohr radius, } a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 52.9 \text{ pm}$$

The radial part of the S.E. (substituted $\beta = l(l+1)$)

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

Or write as,

$$-\frac{\hbar^2}{2m_e r^2}R''(r) + -\frac{\hbar^2}{m_e}\frac{1}{r}R'(r) + \left[\frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r} - E\right] R(r) = 0$$

(Use natural units, $\hbar = 1, m_e = 1, e = 1\ 4\pi\varepsilon_0 = 1$)

$$-\frac{1}{2}R''(r) + -\frac{1}{r}R'(r) + \left[\frac{l(l+1)}{2r^2} - \frac{1}{r} - E\right] R(r) = 0$$

Asymptotically, $R''(r) - 2|E|R(r) \approx 0$, solution is $R(r) \approx const\ e^{-\sqrt{2|E|}r} \approx Ae^{-Br}$

This is exactly the solution for the G.S.!

General solution:

$R(r)$ (is a polynomial in r) × (decaying exponential in r) $\quad R_{n,l}(r) = N_{n,l}\,\rho^l\, L_{n+l}^{2l+1}(\rho)e^{-\rho/2}$

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2} \quad n = 1,2,3 \ldots$$

$$E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \qquad where\ a_0 = \varepsilon_0 h^2/\pi m_e e^2 = 4\pi\varepsilon_0\hbar^2/m_e e^2$$

$$\mathbf{H-spectra}: \bar{v} = R_H\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) \qquad R_H = 109677\ \mathrm{cm}^{-1}$$

Condition: $n \geq l+1 \quad or \quad 0 \leq l \leq n-1 \quad n = 1,2,3,\ldots$

$$R_{nl}(r) = -\left\{\frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2}\left(\frac{2}{na_0}\right)^{l+3/2} r^l\, e_0^{-r/na}\, L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

Normalized: $\int_0^\infty R_{nl}^*(r)R_{nl}(r)r^2dr\ = 1$

$$\int_0^\infty dr\, r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\ \psi_{n'l'm'}^*(r,\theta,\phi)\,\psi_{nlm}(r,\theta,\phi) = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$

Table 10.1 Hydrogenic radial wavefunctions

Orbital	n	l	$R_{n,l}$
1*s*	1	0	$2\left(\frac{Z}{a}\right)^{3/2} e^{-\rho/2}$
2*s*	2	0	$\frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (2-\rho)e^{-\rho/2}$
2*p*	2	1	$\frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho e^{-\rho/2}$
3*s*	3	0	$\frac{1}{243^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (6-6\rho+\rho^2)e^{-\rho/2}$
3*p*	3	1	$\frac{1}{486^{1/2}}\left(\frac{Z}{a}\right)^{3/2} (4-\rho)\rho e^{-\rho/2}$
3*d*	3	2	$\frac{1}{2430^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \rho^2 e^{-\rho/2}$

$\rho = (2Z/na)r$ with $a = 4\pi\varepsilon_0\hbar^2/\mu e^2$. For an infinitely heavy nucleus (or one that may be assumed to be so), $\mu = m_e$ and $a = a_0$, the Bohr radius. The full wavefunction is obtained by multiplying R by the appropriate Y given in Table 9.3.

Table 10-1
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1. exp factor: ψ approaches 0 far away from the nucleus
2. ρ^l ensures ψ is zero at the nucleus for $l \neq 0$
3. Associated Laguerre polynomial: responsible for the nodes

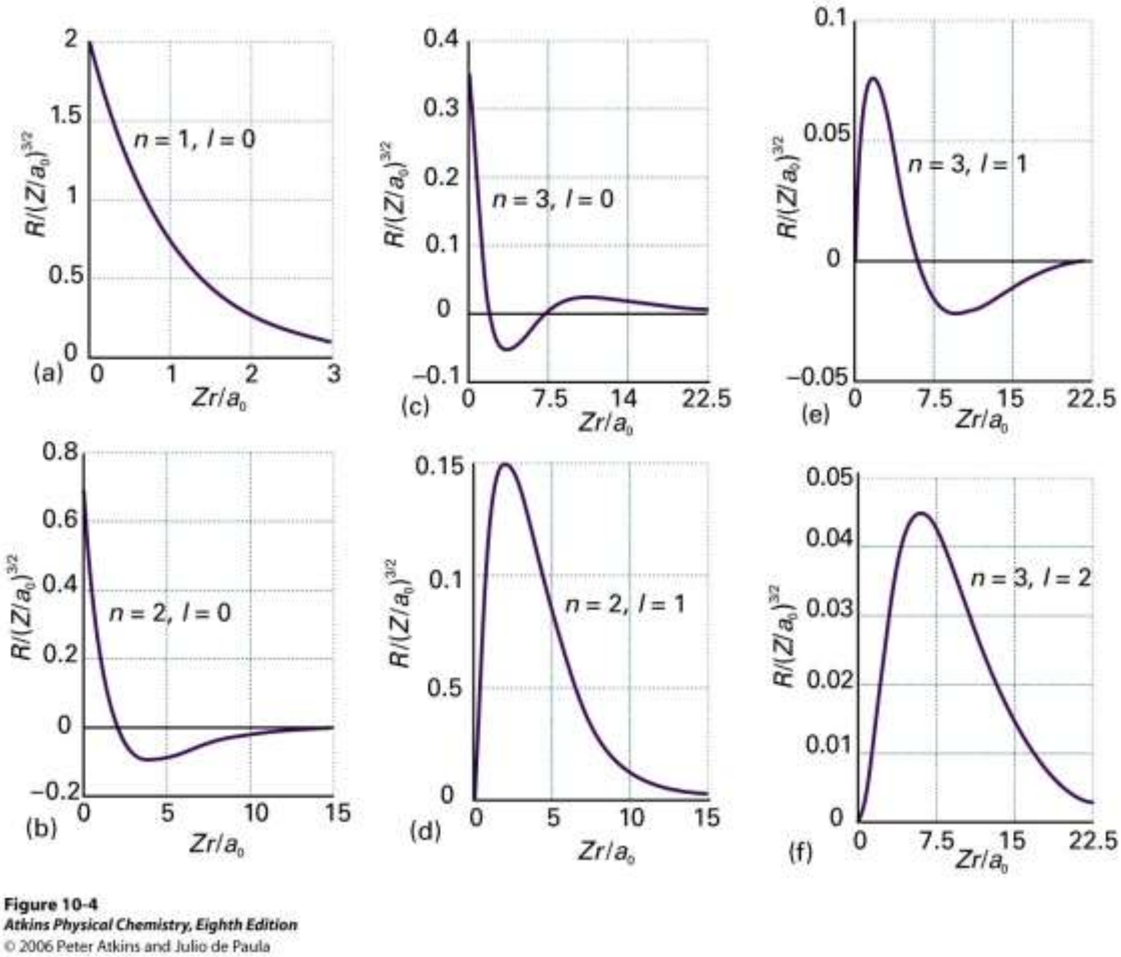
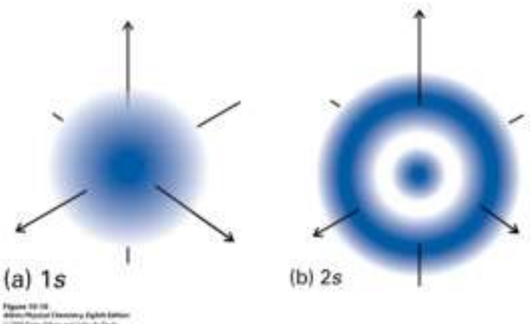


Figure 7.2: The first few wavefunctions



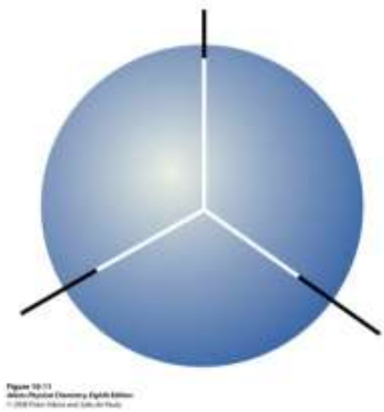


Figure 7.3: 1s and 2s hydrogen atomic orbitals

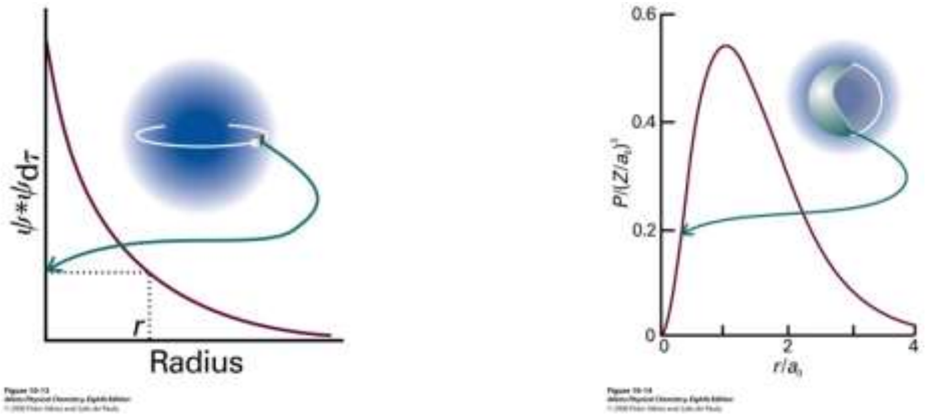


Figure 7.4: s orbital and the radial distribution function

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

$$= r^2 R(r)^2 dr \int_0^{2\pi}\int_0^{\pi} |Y(\theta,\phi)|^2 dr \sin\theta \; d\theta \; d\phi = r^2 R(r)^2 dr$$

$P(r)$ is a probability density. When multiplied by dr it gives the probability of finding the electron in a thin shell.

Most probable radius can be found by differentiation of $P(r)$

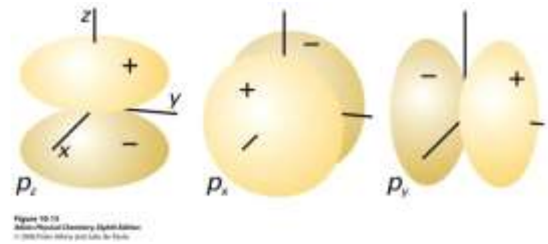


Figure 7.5: The p-orbitals

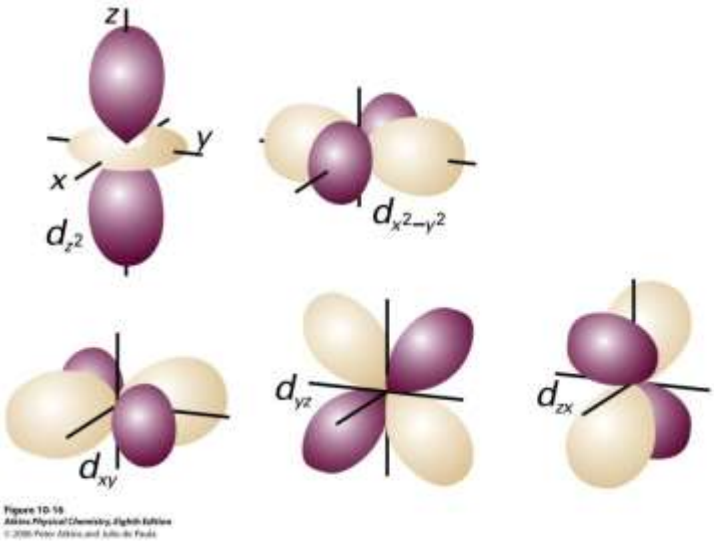


Figure 7.6: The d-orbitals