H-Spectra

$$\bar{\nu} = R_H\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right) \qquad R_H = 109677\ \mathrm{cm}^{-1}$$

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,

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

$$\text{and} \quad -\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + V_{eff}u = Eu\,, \quad \text{where } u = rR \quad and\ V_{eff} = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

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

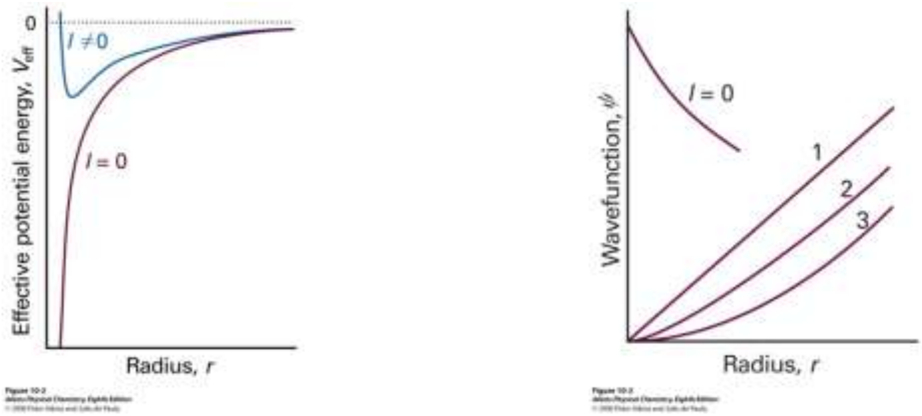

Figure 7.1: Effective potential and the wavefunctions at small radius

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

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

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

Table 10.1 Hydrogenic radial wavefunctions

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

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

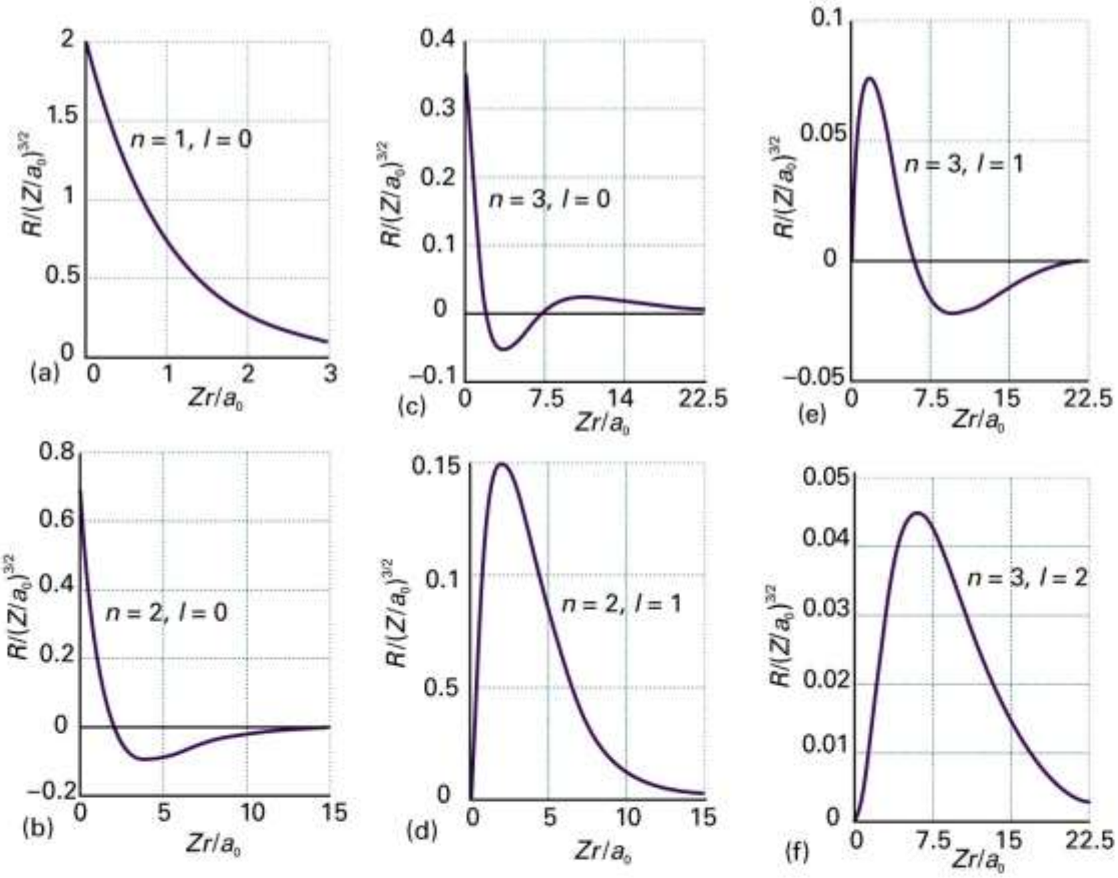

Figure 10-4
Atkins Physical Chemistry, Eighth Edition

Figure 7.2: The first few wavefunctions

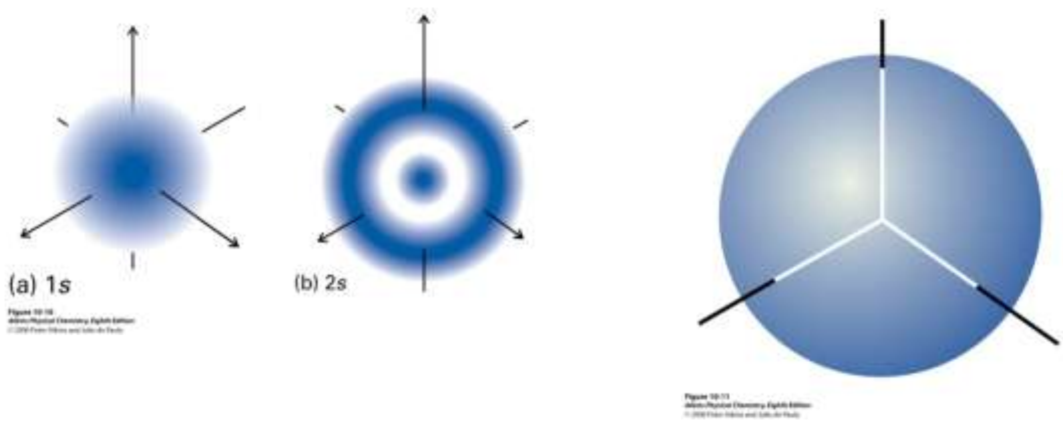

Figure 7.3: 1s and 2s hydrogen atomic orbitals

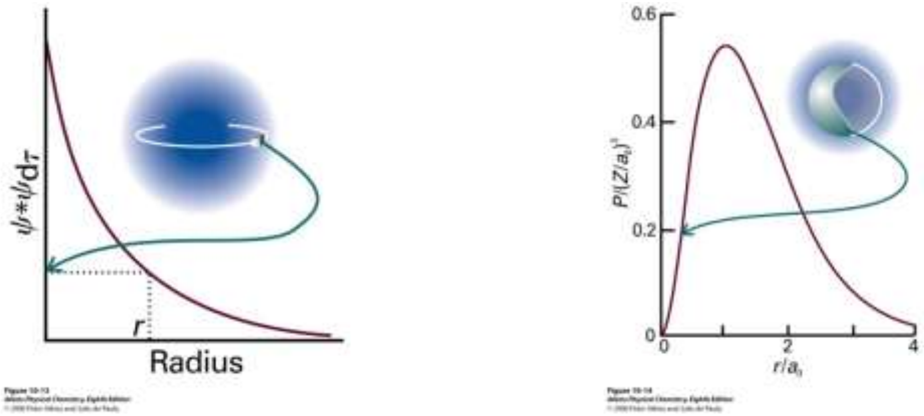

Figure 7.4: s orbital and the radial distribution function

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

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

$P(r)$ 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 $P(r)$

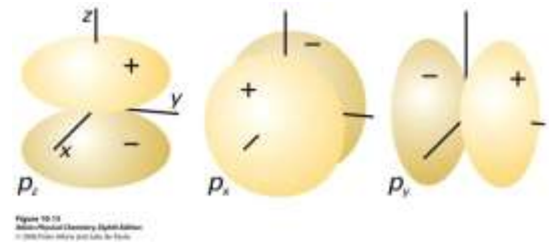

Figure 7.5: The p-orbitals

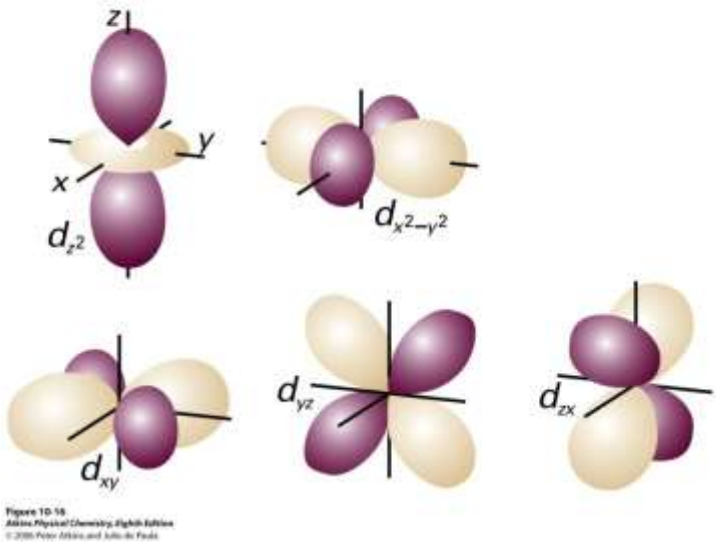

Figure 7.6: The d-orbitals