The Hydrogen Atom.

The Φ equation.

The first equation we want to solve is

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi$$

This equation is of familiar form; recall that for the free particle, we had

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

for which the solution is

$$\psi(x) = a_0 \cos kx + a_1 / k \sin kx$$

Since

$$e^{\pm ix} = \cos x \pm i \sin x$$

a more general solution to equations of this type is

$$\Phi = A\, e^{im\varphi} + B\, e^{-im\varphi}$$

In order that

$$\Phi(\varphi) = \Phi(\varphi + 2\pi)$$

The value of Φ at some value of φ must be the same at $\varphi + 2\pi$, since Φ is periodic.

it is necessary that

$$A\, e^{im\varphi} + B\, e^{-im\varphi} = A\, e^{im(\varphi+2\pi)} + B\, e^{-im(\varphi+2\pi)}$$
$$= A\, e^{im\varphi}\, e^{im2\pi} + B\, e^{-im\varphi}\, e^{-im2\pi}$$

Since $e^{\pm im2\pi} = \cos(m\,2\pi) \pm i \sin(m\,2\pi) = 1$ only when $m = 0, \pm1, \pm2\ldots$, the Φ equation has solutions

$$\Phi = A\, e^{im\varphi}, \quad m = 0, \ \pm 1, \ \pm 2, \ldots$$

We can determine A by requiring that the wavefunctions be normalized,

$$\int_0^{2\pi} \Phi^*\Phi \, d\varphi = |A|^2 \int_0^{2\pi} e^{-im\varphi} \cdot e^{im\varphi} \, d\varphi = |A|^2 \int_0^{2\pi} d\varphi = 1$$

$$|A|^2 (2\pi - 0) = 1 \Rightarrow |A|^2 = \frac{1}{2\pi}, \quad A = \frac{1}{\sqrt{2\pi}}$$

so

$$\Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \qquad m = 0, \pm 1, \pm 2, \ldots$$

are the final solutions to the Φ equation.

A postscript.

These wavefunctions are complex. Sometimes it is more useful to have real wavefunctions. These can be constructed by first defining

$$\Phi_+ = \frac{1}{\sqrt{2\pi}} e^{+i|m|\varphi} = \frac{1}{\sqrt{2\pi}} (\cos m\varphi + i \sin m\varphi)$$

$$\Phi_- = \frac{1}{\sqrt{2\pi}} e^{-i|m|\varphi} = \frac{1}{\sqrt{2\pi}} (\cos m\varphi - i \sin m\varphi)$$

and then adding and subtracting Φ_+ and Φ_- …we say, "forming linear combinations":

$$\Phi_{symm} = \frac{1}{\sqrt{2}} (\Phi_+ + \Phi_-) = \frac{1}{\sqrt{\pi}} \cos |m|\varphi$$

$$\Phi_{antisymm} = \frac{1}{\sqrt{2}} (\Phi_+ - \Phi_-) = \frac{1}{\sqrt{\pi}} \sin |m|\varphi$$

These functions are also solutions to the Φ equation. Try it!

each of which is a real function. We cannot associate with these functions a particular m value, but only with $|m|$. The first three of these functions are

$$\Phi_0 = \frac{1}{\sqrt{2\pi}}$$

$$\Phi_{\pm 1} = \frac{1}{\sqrt{\pi}} \cos \varphi$$

$$\Phi_{\mp 1} = \frac{1}{\sqrt{\pi}} \sin \varphi \qquad \textit{etc.}$$

The Θ equation.

The Θ equation is

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{d\Theta}{d\theta}\right) - \frac{m^2\Theta}{\sin^2\theta} + \beta\Theta = 0.$$

Rearranging,

$$\frac{d^2\Theta}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{d\Theta}{d\theta} + \left(\beta - \frac{m^2}{\sin^2\theta}\right)\Theta = 0.$$

Now, make the substitutions

$$x = \cos\theta \quad , \quad \sin^2\theta = 1 - x^2$$

$$\frac{d}{d\theta} = \frac{d}{dx}\frac{dx}{d\theta} = -\sin\theta\,\frac{d}{dx} \quad , \quad \frac{d^2}{d\theta^2} = \sin^2\theta\,\frac{d^2}{dx^2} - \cos\theta\,\frac{d}{dx}$$

After some algebra, we get

$$(1-x^2)\,\frac{d^2\Theta}{dx^2} - 2x\,\frac{d\Theta}{dx} + \left(\beta - \frac{m^2}{(1-x^2)}\right)\Theta = 0.$$

This equation is identical to the associated equation of Legendre

$$(1-x^2)\,\frac{d^2P}{dx^2} - 2x\,\frac{dP}{dx} + \left(\ell(\ell+1) - \frac{m^2}{(1-x^2)}\right)P = 0$$

if we identify P with Θ and β with $\ell\,(\ell + 1)$.

The solutions P of the associated Legendre equation are called the associated Legendre functions; these may be expressed in closed form as (since $x = \cos\theta$)

$$P_\ell^{|m|}(\cos\theta) = (1-\cos^2\theta)^{\frac{|m|}{2}} \sum_{k=0} \frac{(-1)^k\,(2\ell-2k)!(\cos\theta)^{\ell-|m|-2k}}{2^\ell\,(\ell-k)!\,k!\,(\ell-|m|-2k)!}$$

Here, $P_\ell^{|m|}$ is a polynomial of degree ℓ and order $|m|$, where ℓ and m are integers. k is an (integer) index, and the sum (Σ) runs from k = 0 to an upper limit of

$$k = (\ell - |m|)/2 \quad \text{if} \quad (\ell - |m|) \text{ is even}$$

$$k = (\ell - |m| - 1)/2 \quad \text{if} \quad (\ell - |m|) \text{ is odd}$$

Since m is an integer, and since the solutions to the associated Legendre equation are acceptable only if $(\ell - |m|)$ is an integer, it is necessary that

$$\ell = \text{integer} \quad , \quad \text{with} \quad \ell \geq |m|.$$

The solutions $P(\Theta)$ must of course be normalized; the requirement that

$$1 = \int_0^\pi \Theta_{\ell,m}^* \, \Theta_{\ell,m} \, d\theta = \int_{-1}^{1} |A|^2 \, P_\ell^{*|m|}(\cos\theta) \, P_\ell^{|m|}(\cos\theta) \, d(\cos\theta)$$

leads to

$$A = \left\{ \left(\frac{2\ell + 1}{2} \right) \frac{(\ell - |m|!}{(\ell + |m|!} \right\}^{\frac{1}{2}}$$

which gives

$$\Theta_{\ell,m}(\theta) = \left\{ \left(\frac{2\ell + 1}{2} \right) \frac{(\ell - |m|)!}{(\ell + |m|)!} \right\}^{\frac{1}{2}} P_\ell^{|m|}(\cos\theta).$$

These wavefunctions, though they appear to be complicated, are not, at least for small ℓ. For example,

$$\ell = 0, \quad m = 0. \qquad \Theta_{0,0}(\theta) = \frac{\sqrt{2}}{2} \qquad \text{(s)}$$

$$\ell = 1, \quad m = 0. \qquad \Theta_{1,0}(\theta) = \frac{\sqrt{6}}{2} \cos\theta \qquad \text{(p)}$$

$$\ell = 1, \quad m = \pm 1. \qquad \Theta_{1,\pm 1}(\theta) = \frac{\sqrt{3}}{2} \sin\theta \qquad \text{(p)}$$

$\ell = 2, \quad m = 0. \qquad \Theta_{2,0}(\theta) = \frac{\sqrt{10}}{4}(3\cos^2\theta - 1)$ (d)

$\ell = 2, \quad m = \pm 1. \qquad \Theta_{2,\pm 1}(\theta) = \frac{\sqrt{15}}{4}\sin\theta\cos\theta$ (d)

$\ell = 2, \quad m = \pm 2. \qquad \Theta_{2,\pm 2}(\theta) = \frac{\sqrt{15}}{4}\sin^2\theta$ (d)

You have already met these functions before, though possibly not in this form. These are the angular functions describing the probability amplitudes in s, p, d orbitals!

Some postscripts.

- The associated Legendre functions are derivatives of the Legendre polynomials P_ℓ $(\cos\theta)$

$$P_\ell^m(x) = \left(1 - x^2\right)^{\frac{m}{2}} \frac{d^m}{dx^m} P_\ell(x)$$

The L. polynomials

$$P_\ell(x) = \sum_{k=0} \frac{(-1)^k (2\ell - 2k)!\, x^{\ell - 2k}}{2^\ell (\ell - k)!\, k!\, (\ell - 2k)!}$$

upper limit on Σ: $\ell/2$ if ℓ even. $(\ell-1)/2$ if ℓ odd.

are, in turn, solutions of the Legendre equation

$$(1 - x^2)\frac{d^2z}{dx^2} - 2x\frac{dz}{dx} + \ell(\ell + 1)\, z = 0 \qquad (z = P).$$

- The functions $\sqrt{\ell + \frac{1}{2}}\;\; P_\ell(\cos\theta)$ and $P_\ell^{|m|}(\cos\theta)$ form an orthonormal set in the interval $-1 \le \cos\theta \le 1$.

- The L. functions are symmetric or antisymmetric as ℓ is even or odd

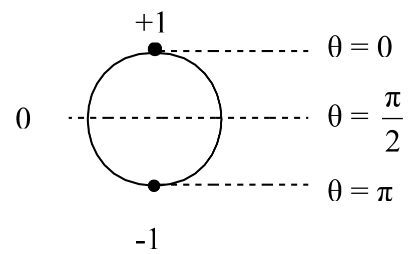
$$P_\ell(-\cos\theta) = (-1)^\ell\, P_\ell(\cos\theta)$$

$$P_\ell^{|m|}(-\cos\theta) = (-1)^{\ell - m}\, P_\ell^{|m|}(\cos\theta)$$

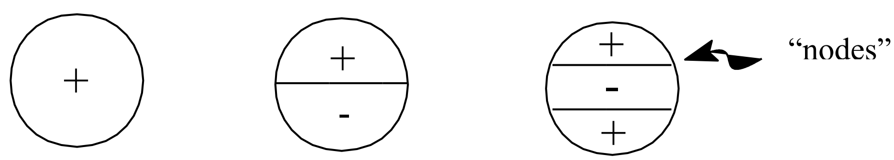
- The functions do not exceed 1 in absolute value

$$\left|P_\ell(\cos\theta)\right| \le 1 \quad ; \quad e.g. \quad P_\ell(1) = 1 \quad , \quad P_\ell(-1) = (-1)^\ell .$$

- Since the $P_\ell(x)$ are polynomials, there exist ℓ roots, or ℓ values of cos θ, for which $P_\ell(x)$ changes sign. The sign of $P_\ell(x)$ is often indicated by a circular diagram,



At the north pole in this diagram, θ = 0 and x = cos θ = +1; at the equator, x = cos $\frac{\pi}{2}$ = 0; at the south pole, x = cos π = -1. We then use lines on the circle to indicate the values of θ at which the polynomial is zero:



$P_0 = 1$ $P_1 = \cos\theta$ $P_2 = ½\,(3\cos^2\theta - 1)$

- Recurrence relations exist for both the $P_\ell^{|m|}$ and P_ℓ, *e.g.*

$$(2\ell+1)\,(\cos\theta)\,P_\ell^m = P_{\ell+1}^{m+1} - P_{\ell-1}^{m+1}$$

- The product functions $Y_\ell^m(\theta,\varphi)$

$$Y_\ell^m(\theta,\varphi) = \Theta_{\ell,m}(\theta)\,\Phi_m(\varphi)$$

are called spherical harmonics. These are given by the formula

$$Y_\ell^m(\theta,\varphi) = \left\{\frac{(2\ell+1)\,(\ell-|m|)!}{4\pi\,(\ell+|m|)!}\right\}^{\frac{1}{2}} P_\ell^{|m|}(\cos\theta)\,e^{im\varphi}.$$

The R equation.

The radial equation for the electron "in orbit" about the nucleus of the hydrogen atom is

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[\frac{2m}{\hbar^2}\left(E + \frac{Ze^2}{r}\right) - \frac{\ell(\ell+1)}{r^2}\right]R = 0$$

If we consider bound states (E < 0) only, and introduce the new variables n and ρ, where

$$E = -\frac{m\,Z^2\,e^4}{2\,n^2\,h^2} = -\frac{Z^2\,e^2}{2\,n^2\,a_0} \qquad \left(a_0 = \frac{\hbar^2}{m\,e^2}\right)$$

$$r = \frac{1}{2}\left(\frac{n^2\,\hbar^2}{m\,Z\,e^2}\right)\rho = \frac{1}{2}\left(\frac{n\,a_0}{Z}\right)\rho$$

the radial equation becomes

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left(-\frac{1}{4} + \frac{n}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right)R = 0. \qquad \text{(A)}$$

We seek solutions of the form

$$R = c\ u(\rho)\ \rho^{\ell}\ e^{-\rho/2} \qquad \text{(B)}$$

If (B) is substituted into (A), we find that u (ρ) must satisfy the differential equation

$$\rho\frac{d^2u}{d\rho^2} + (2\ell + 2 - \rho)\frac{du}{d\rho} + (n - \ell - 1)\,u = 0 \qquad \text{(C)}$$

Eq. (C) is of the same form as the associated equation of Laguerre,

$$x\frac{d^2L}{dx^2} + (\beta + 1 - x)\frac{dL}{dx} + (\alpha - \beta)\,L = 0. \qquad \text{(D)}$$

(D) has solutions, known as the associated Laguerre polynomials, which are of the form

$$L_{\alpha}^{\beta}(x) = -\sum_{k=0}^{\alpha-\beta} (-1)^k \frac{(\alpha!)^2}{(\alpha-\beta-k)!\,(\beta+k)!\,k!}\ x^k$$

where α and β are integers, k is an index running from 0 to (α - β), and (α - β) is an integer greater than zero. Thus, the solutions u(ρ) of Eq. (C) are of the form $L_{\alpha}^{\beta}(x)$, providing one makes the identifications

$$x = \rho \quad , \quad (\beta + 1) = (2\ell + 2) \quad , \quad (\alpha - \beta) = (n - \ell - 1)$$

Combining these relations, one finds

$$\beta = 2\ell + 1 \quad , \quad \alpha = n + \ell.$$

and

$$L_{n+\ell}^{2\ell+1}(p) = \sum_{k=0}^{n-\ell-1} (-1)^{k+1} \frac{[(n+\ell)!]^2}{(n-\ell-1-k)!\,(2\ell+1+k)!\,k!} \rho^k$$

Eigenvalues.

Since the condition for solution is

$$(\alpha - \beta) = (n - \ell - 1) > 0$$

and since $\ell = 0, 1, 2, \ldots$, n may take the values

$$n = 1, 2, 3, \ldots$$

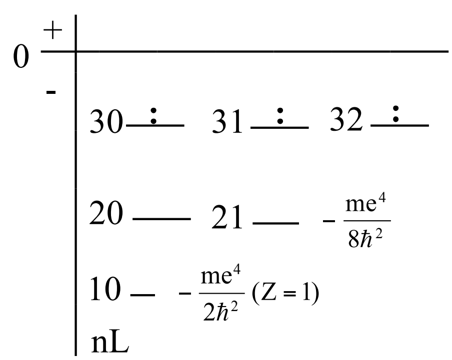
with the restriction that

$$n \geq \ell + 1$$

This gives the allowed (negative) values of the energy

$$E_n = -\frac{m Z^2 e^4}{2 n^2 \hbar^2} \quad , \quad n = 1, 2, 3, \ldots \quad (\text{independent of } \ell, m).$$

This result is identical with the values obtained by means of the Bohr theory. The resulting energy level diagram is shown on the right.



Eigenfunctions.

The radial wavefunctions for the hydrogen atom are of the form

$$R(\rho) \quad = \quad c\,\rho^{\ell}\, e^{-\rho/2}\, L_{n+\ell}^{2\ell+1}(\rho)$$

To determine the normalizing constant c, we require that

$$\int_0^\infty |R(r)|^2 r^2 dr \quad = \quad c^2 \int_0^\infty \rho^{2\ell}\, e^{-\rho} \left|L_{n+\ell}^{2\ell+1}(\rho)\right|^2 r^2 dr \quad = \quad 1$$

Substituting $r = (na_0/2Z)\rho$, this becomes

$$1 \quad = \quad c^2 \left(\frac{na_0}{2Z}\right)^3 \int_0^\infty \rho^{2\ell+2}\, e^{-\rho} \left|L_{n+\ell}^{2\ell+1}(\rho)\right|^2 d\rho$$

$$= \quad c^2 \left(\frac{na_0}{2Z}\right)^3 \frac{2n[(n+\ell)!]^3}{(n-\ell-1)!} \qquad \text{(EWK, p. 66).}$$

so that

$$c \quad = \quad \pm \left\{ \left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right\}^{\frac{1}{2}}$$

We choose $c < 0$ to make the (total) wavefunction positive, so

$$R_{nL}(r) \quad = \quad -\left\{ \left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right\}^{\frac{1}{2}} \left(\frac{2Zr}{na_0}\right)^{\ell} e^{-Zr/na_0}\; L_{n+\ell}^{2\ell+1}\left(\frac{2Zr}{na_0}\right)$$

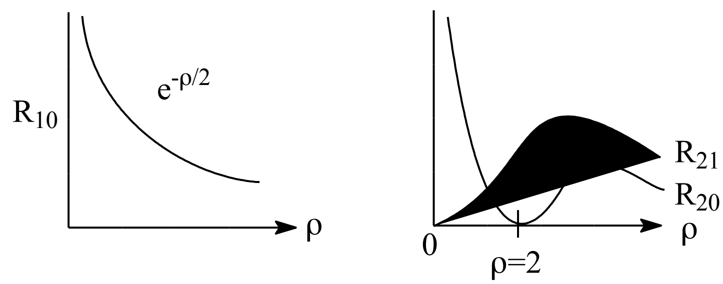
The first few $R_{nL}(r)$ are, expressed in terms of $\rho = 2Zr/na_0$,

$$R_{10} \quad = \quad 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\rho/2} \qquad\qquad R_{30} \quad = \quad \frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (6-6\rho+6\rho^2)\, e^{-\rho/2}$$

$$R_{20} \quad = \quad \frac{2}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (2-\rho)\, e^{-\rho/2} \qquad\qquad R_{31} \quad = \quad \frac{1}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} (4-\rho)\,\rho\, e^{-\rho/2}$$

$$R_{21} \quad = \quad \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho\, e^{-\rho/2} \qquad\qquad R_{32} \quad = \quad \frac{1}{9\sqrt{30}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho^2\, e^{-\rho/2}$$

Note the very important "structure" of these wavefunctions. Each function consists of a constant, times a polynomial in ρ, times an exponential factor in $-\rho/2$. The last factor looks, of course, like



so R_{10} is a simple exponential. But R_{20}, which contains, in addition, the factor $(2-\rho)$, has a **node** at $\rho = 2$, as shown above. And R_{21}, which contains the factor ρ, goes to **zero** at the origin, also as shown above.

Also note that, as n increases, the number of nodes increases as (n - 1)…this structure being dictated by the highest power of ρ appearing in the polynomial!

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Tables of Hydrogenlike Wavefunctions, from Pauling & Wilson, "Introduction to Quantum Mechanics", McGraw-Hill, 1935.

TABLE 21-1.—THE FUNCTIONS $\Phi_m(\varphi)$

$$\Phi_0(\varphi) = \frac{1}{\sqrt{2\pi}} \quad \text{or} \quad \Phi_0(\varphi) = \frac{1}{\sqrt{2\pi}}$$

$$\Phi_1(\varphi) = \frac{1}{\sqrt{2\pi}}e^{i\varphi} \quad \text{or} \quad \Phi_{1\cos}(\varphi) = \frac{1}{\sqrt{\pi}}\cos\varphi$$

$$\Phi_{-1}(\varphi) = \frac{1}{\sqrt{2\pi}}e^{-i\varphi} \quad \text{or} \quad \Phi_{1\sin}(\varphi) = \frac{1}{\sqrt{\pi}}\sin\varphi$$

$$\Phi_2(\varphi) = \frac{1}{\sqrt{2\pi}}e^{i2\varphi} \quad \text{or} \quad \Phi_{2\cos}(\varphi) = \frac{1}{\sqrt{\pi}}\cos 2\varphi$$

$$\Phi_{-2}(\varphi) = \frac{1}{\sqrt{2\pi}}e^{-i2\varphi} \quad \text{or} \quad \Phi_{2\sin}(\varphi) = \frac{1}{\sqrt{\pi}}\sin 2\varphi$$

Etc.

TABLE 21-2.—THE WAVE FUNCTIONS $\Theta_{lm}(\vartheta)$
(The associated Legendre functions normalized to unity)

$l = 0$, s orbitals:

$$\Theta_{00}(\vartheta) = \frac{\sqrt{2}}{2}$$

$l = 1$, p orbitals:

$$\Theta_{10}(\vartheta) = \frac{\sqrt{6}}{2}\cos\vartheta$$

$$\Theta_{1\pm1}(\vartheta) = \frac{\sqrt{3}}{2}\sin\vartheta$$

$l = 2$, d orbitals:

$$\Theta_{20}(\vartheta) = \frac{\sqrt{10}}{4}(3\cos^2\vartheta - 1)$$

$$\Theta_{2\pm1}(\vartheta) = \frac{\sqrt{15}}{2}\sin\vartheta\cos\vartheta$$

$$\Theta_{2\pm2}(\vartheta) = \frac{\sqrt{15}}{4}\sin^2\vartheta$$

$l = 3$, f orbitals:

$$\Theta_{30}(\vartheta) = \frac{3\sqrt{14}}{4}\left(\frac{5}{3}\cos^3\vartheta - \cos\vartheta\right)$$

$$\Theta_{3\pm1}(\vartheta) = \frac{\sqrt{42}}{8}\sin\vartheta(5\cos^2\vartheta - 1)$$

$$\Theta_{3\pm2}(\vartheta) = \frac{\sqrt{105}}{4}\sin^2\vartheta\cos\vartheta$$

$$\Theta_{3\pm3}(\vartheta) = \frac{\sqrt{70}}{8}\sin^3\vartheta$$

TABLE 21-3.—THE HYDROGENLIKE RADIAL WAVE FUNCTIONS

$n = 1$, K shell:

$l = 0$, $1s$ $\quad R_{10}(r) = (Z/a_0)^{3/2}\cdot 2e^{-\frac{\rho}{2}}$

$n = 2$, L shell:

$l = 0$, $2s$ $\quad R_{20}(r) = \dfrac{(Z/a_0)^{3/2}}{2\sqrt{2}}(2 - \rho)e^{-\frac{\rho}{2}}$

$l = 1$, $2p$ $\quad R_{21}(r) = \dfrac{(Z/a_0)^{3/2}}{2\sqrt{6}}\rho e^{-\frac{\rho}{2}}$

$n = 3$, M shell:

$l = 0$, $3s$ $\quad R_{30}(r) = \dfrac{(Z/a_0)^{3/2}}{9\sqrt{3}}(6 - 6\rho + \rho^2)e^{-\frac{\rho}{2}}$

$l = 1$, $3p$ $\quad R_{31}(r) = \dfrac{(Z/a_0)^{3/2}}{9\sqrt{6}}(4 - \rho)\rho e^{-\frac{\rho}{2}}$

$l = 2$, $3d$ $\quad R_{32}(r) = \dfrac{(Z/a_0)^{3/2}}{9\sqrt{30}}\rho^2 e^{-\frac{\rho}{2}}$

$n = 4$, N shell:

$l = 0$, $4s$ $\quad R_{40}(r) = \dfrac{(Z/a_0)^{3/2}}{96}(24 - 36\rho + 12\rho^2 - \rho^3)e^{-\frac{\rho}{2}}$

$l = 1$, $4p$ $\quad R_{41}(r) = \dfrac{(Z/a_0)^{3/2}}{32\sqrt{15}}(20 - 10\rho + \rho^2)\rho e^{-\frac{\rho}{2}}$

$l = 2$, $4d$ $\quad R_{42}(r) = \dfrac{(Z/a_0)^{3/2}}{96\sqrt{5}}(6 - \rho)\rho^2 e^{-\frac{\rho}{2}}$

$l = 3$, $4f$ $\quad R_{43}(r) = \dfrac{(Z/a_0)^{3/2}}{96\sqrt{35}}\rho^3 e^{-\frac{\rho}{2}}$

Table 21-4.—Hydrogenlike Wave Functions

K Shell

$n = 1, l = 0, m = 0$:

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

L Shell

$n = 2, l = 0, m = 0$:

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

$n = 2, l = 1, m = 0$:

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma e^{-\frac{\sigma}{2}}\cos\vartheta$$

$n = 2, l = 1, m = \pm 1$:

$$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma e^{-\frac{\sigma}{2}}\sin\vartheta\cos\varphi$$

$$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma e^{-\frac{\sigma}{2}}\sin\vartheta\sin\varphi$$

M Shell

$n = 3, l = 0, m = 0$:

$$\psi_{3s} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(27 - 18\sigma + 2\sigma^2)e^{-\frac{\sigma}{3}}$$

$n = 3, l = 1, m = 0$:

$$\psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(6 - \sigma)\sigma e^{-\frac{\sigma}{3}}\cos\vartheta$$

$n = 3, l = 1, m = \pm 1$:

$$\psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(6 - \sigma)\sigma e^{-\frac{\sigma}{3}}\sin\vartheta\cos\varphi$$

$$\psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(6 - \sigma)\sigma e^{-\frac{\sigma}{3}}\sin\vartheta\sin\varphi$$

$n = 3, l = 2, m = 0$:

$$\psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\frac{\sigma}{3}}(3\cos^2\vartheta - 1)$$

$n = 3, l = 2, m = \pm 1$:

$$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\frac{\sigma}{3}}\sin\vartheta\cos\vartheta\cos\varphi$$

$$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\frac{\sigma}{3}}\sin\vartheta\cos\vartheta\sin\varphi$$

$n = 3, l = 2, m = \pm 2$:

$$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\frac{\sigma}{3}}\sin^2\vartheta\cos 2\varphi$$

$$\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\frac{\sigma}{3}}\sin^2\vartheta\sin 2\varphi$$

with $\sigma = \frac{Z}{a_0}r$.