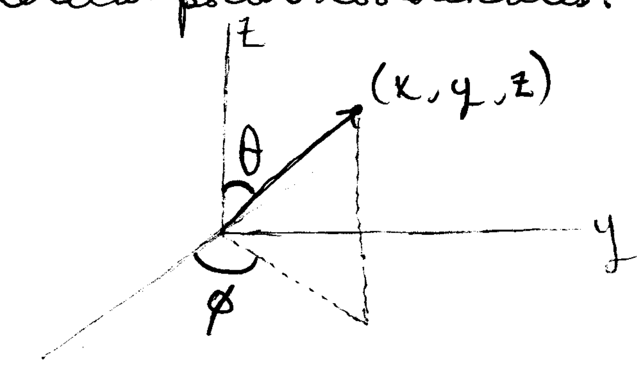
It is most convenient to use spherical polar coordinates.

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$



Volume element for integration is

$$dx\,dy\,dz = \underbrace{r^2\sin\theta}_{\text{Jacobian}}\,dr\,d\theta\,d\phi$$

range of variables is
$$0 \le r \le \infty$$
$$0 \le \theta \le \pi$$
$$0 \le \phi \le 2\pi$$

Integration looks like $\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} F(r,\theta,\phi)\, r^2\sin\theta\, dr\, d\theta\, d\phi$

and ∇^2 becomes

$$\nabla^2\psi = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$

We will use separation of variables for the stationary states

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi$$

central force ⇒ no θ or φ in the potential

Try $\psi(r,\theta,\phi) = R(r)P(\theta)Q(\phi)$. Plug in:

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[PQ\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{RQ}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) + \frac{RP}{\sin^2\theta}\frac{d^2Q}{d\phi^2}\right] + V(r)RPQ = ERPQ$$

Divide through by RPQ

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{P\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) + \frac{1}{Q\sin^2\theta}\frac{d^2Q}{d\phi^2}\right] + V(r) = E.$$

Clearly the expression in [...] is a function of r only (to see this solve for it). Therefore, the sum of the 2nd and 3rd terms in [...] must be a constant because they have angle dependence only. Call this constant $-\lambda$.

$$\frac{1}{P\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{dP}{d\theta}\right)+\frac{1}{Q\sin^2\theta}\frac{d^2Q}{d\phi^2}=-\lambda$$

Finally, note that the term $\frac{1}{Q\sin^2\theta}\frac{d^2Q}{d\phi^2}$ must be a function of θ only (solve for it) which can only hold if

$$\frac{1}{Q}\frac{d^2Q}{d\phi^2}=\text{another constant}=-m^2 \quad \text{(not mass, just a constant)}$$

We have obtained 3 separated 1d equations and we shall consider each of them in turn:

$$\frac{d^2Q}{d\phi^2}=-m^2Q$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{dP}{d\theta}\right)-\frac{m^2}{\sin^2\theta}P=-\lambda P$$

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\lambda R\right]+V(r)R=ER$$

$\boxed{\text{The } \phi \text{ Equation}}$ $\quad \frac{d^2Q}{d\phi^2}=-m^2Q \quad , \; 0\le\phi\le 2\pi$

Just the "particle on a ring" problem again in slightly different form.

Solutions are $\sin m\phi$ or $\cos m\phi$ (or $e^{im\phi}$)

$$\text{B.C.}\quad \left.\begin{array}{l} Q(0) = Q(2\pi) \\ Q'(0) = Q'(2\pi) \end{array}\right\} \text{requires that } m = \text{integer}$$

But we only need $m \geq 0$ ($m=0$ gives non-trivial cos solution)

Hence the unnormalized solutions are

$$Q_m(\phi) = 1 \qquad\qquad m = 0$$

$$\left.\begin{array}{l} Q_m^{\sin}(\phi) = \sin m\phi \\ Q_m^{\cos}(\phi) = \cos m\phi \end{array}\right\} \qquad m > 0$$

$\boxed{\text{The } \theta \text{ Equation}}$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{dP}{d\theta}\right) - \frac{m^2}{\sin^2\theta}P = -\lambda P$$

Associated Legendre Equation

Looks horrible! But seems likely that

$$P = \sin^m\theta\,\cos^\alpha\theta \quad \text{might work!}$$

m is the obvious choice of power for the sin function because the second term $\frac{m^2}{\sin^2\theta}P$ will then cancel out some of the derivative operations in the first term.

Plug this guess in and get (after using some trig. identities)

$$-(m+\alpha)(m+\alpha+1)\sin^m\theta\cos^\alpha\theta + \alpha(\alpha-1)\sin^m\theta\cos^{\alpha-2}\theta = -\lambda\sin^m\theta\cos^\alpha\theta$$

SUCCESS if $\alpha = 0$ or $\alpha = 1$ and $\lambda = (m+\alpha)(m+\alpha+1)$

For any other α, the terms $(\alpha)(\alpha-1)\sin^m\theta\cos^{\alpha-2}\theta$ is uncompensated for. However, we can compensate for this term by adding lower order corrections to P as follows:

$$P = \sin^m\theta\left[\cos^\alpha\theta + ?\cos^{\alpha-2}\theta + ?\cos^{\alpha-4}\theta + \cdots\right]$$

As long as $\alpha \in \mathbb{Z} > 0$, the chain of leftover term thus generated will terminate because of the $\alpha(\alpha-1)$ prefactor.

This is similar to our earlier discussions of the harmonic oscillator ie power series solution.

We therefore conclude that, for a given m,

$$\lambda = (m+\alpha)(m+\alpha+1) \text{ where } \alpha \in \mathbb{Z} \geq 0.$$

This can be rephrased by defining $l = m+\alpha$, in terms of which we can say $\lambda = l(l+1)$, $l \in \mathbb{Z} \geq 0$

and also $m \leq l$ since $m = l-\alpha$, $\alpha \in \mathbb{Z} \geq 0$.

Finally, the solutions look like

$$P_{lm}(\theta) = \sin^m\theta\left[\cos^{l-m}\theta + ?\cos^{l-m-2}\theta + ?\cos^{l-m-4}\theta + \cdots\right]$$

Notice that each solution has two labels (quantum numbers) l and m. A brief table follows (unnormalized):

Unnormalized

$l=0 \qquad P_{00} = 1$

$l=1 \qquad P_{10} = \cos\theta$

$\qquad\qquad P_{11} = \sin\theta$

$l=2 \qquad P_{20} = 3\cos^2\theta - 1$

$\qquad\qquad P_{21} = \sin\theta\cos\theta$

$\qquad\qquad P_{22} = \sin^2\theta$

$l=3 \qquad P_{30} = 5\cos^3\theta - 3\cos\theta$

$\qquad\qquad P_{31} = \sin\theta\,(5\cos^2\theta - 1)$

$\qquad\qquad P_{32} = \sin^2\theta\cos\theta$

$\qquad\qquad P_{33} = \sin^3\theta$

$\vdots$

Spherical Harmonics

So far, nothing has depended on the actual potential energy $V(r)$. The $Q_m(\phi)$ and $P_{lm}(\theta)$ functions thus apply to <u>any</u> central force problem!

The products $P_{lm}(\theta)\,Q_m(\phi)$ are called <u>spherical harmonics</u> and are denoted by $Y_{lm}(\phi, \theta)$.

Normalized with respect to θ, ϕ parts of 3d integration in polar coordinates:

$l=0 \quad Y_{00} = \left(\frac{1}{4\pi}\right)^{1/2}$

$l=1 \quad Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$

$Y_{11} = \left(\frac{3}{4\pi}\right)^{1/2}\sin\theta \begin{cases}\sin\phi \\ \cos\phi\end{cases}$

two possibilities

$l=2 \quad Y_{20} = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$

$Y_{21} = \left(\frac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta \begin{cases}\sin\phi \\ \cos\phi\end{cases}$

$Y_{22} = \left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta \begin{cases}\sin 2\phi \\ \cos 2\phi\end{cases}$

Notice that, for each l, there are $2l+1$ different spherical harmonics. Using

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

and various trig. identities, the spherical harmonics up to $l=2$ can be rewritten as: (normalized)

$l=0$ $\quad Y_{00} = \left(\frac{1}{4\pi}\right)^{1/2} \longrightarrow$ "s" orbital

$l=1$ $\quad Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \frac{z}{r} \longrightarrow$ "p_z" orbital

$\quad Y_{11}^{\sin} = \left(\frac{3}{4\pi}\right)^{1/2} \frac{y}{r} \longrightarrow$ "p_y" orbital

$\quad Y_{11}^{\cos} = \left(\frac{3}{4\pi}\right)^{1/2} x/r \longrightarrow$ "p_x" orbital

$l=2$ $\quad Y_{20} = \left(\frac{5}{16\pi}\right)^{1/2}\left(\frac{3z^2-r^2}{r^2}\right) \longrightarrow$ "d_{z^2}" orbital

$\quad Y_{21}^{\sin} = \left(\frac{15}{4\pi}\right)^{1/2} \frac{yz}{r^2} \longrightarrow$ "d_{yz}" orbital

$\quad Y_{21}^{\cos} = \left(\frac{15}{4\pi}\right)^{1/2} \frac{xz}{r^2} \longrightarrow$ "d_{xz}" orbital

$\quad Y_{22}^{\sin} = \left(\frac{15}{4\pi}\right)^{1/2} \frac{xy}{r^2} \longrightarrow$ "d_{xy}" orbital

$\quad Y_{22}^{\cos} = \left(\frac{15}{16\pi}\right)^{1/2} \frac{x^2-y^2}{r^2} \longrightarrow$ "$d_{x^2-y^2}$" orbital

You can now understand the origin of the traditional designations of $p_x, p_y, p_z, d_{xy}, \ldots$

The Radial Equation

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\lambda R\right]+V(r)R=ER$$

Note: any two-particle problem in which the potential energy depends only on the distance between the particles (ie HCl) can be reduced to an effective one-particle central force problem for the relative motion.

In this case, r is the relative separation between particles and m is the reduced mass $m=\frac{m_1 m_2}{m_1+m_2}=\mu$

Use $\lambda=l(l+1)$ and rearrange:

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]R=ER$$

centrifugal potential

Cannot solve exactly, so...
let us examine the behavior of the solutions in the limits $r\to 0$ and $r\to\infty$.

$\boxed{r\to 0}$

Of the last 3 terms the centrifugal potential dominates because it blows up like $1/r^2$ whereas $V(r)$ goes at most like $1/r$ (Coulomb potential)

Therefore the ODE becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{l(l+1)}{r^2}R \qquad \boxed{r\to 0 \text{ limit}}$$

Easy to show that $R = r^l$ solves this.

$\boxed{r \longrightarrow \infty}$

Of the last 3 terms, the energy E dominates because V(r) and the centrifugal potential go to zero.

Therefore the ODE becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = -\frac{2mE}{\hbar^2}R \qquad \boxed{r\to\infty \text{ limit}}$$

Easy to show that $R = e^{-\alpha r}$ where $\alpha = \sqrt{-\frac{2mE}{\hbar^2}}$ is a solution as $r \longrightarrow \infty$ (Must take limit after plugging in)

Another possibility is $e^{\alpha r}$ but this blows up at large r which makes it unacceptable.

(E is negative for bound states)

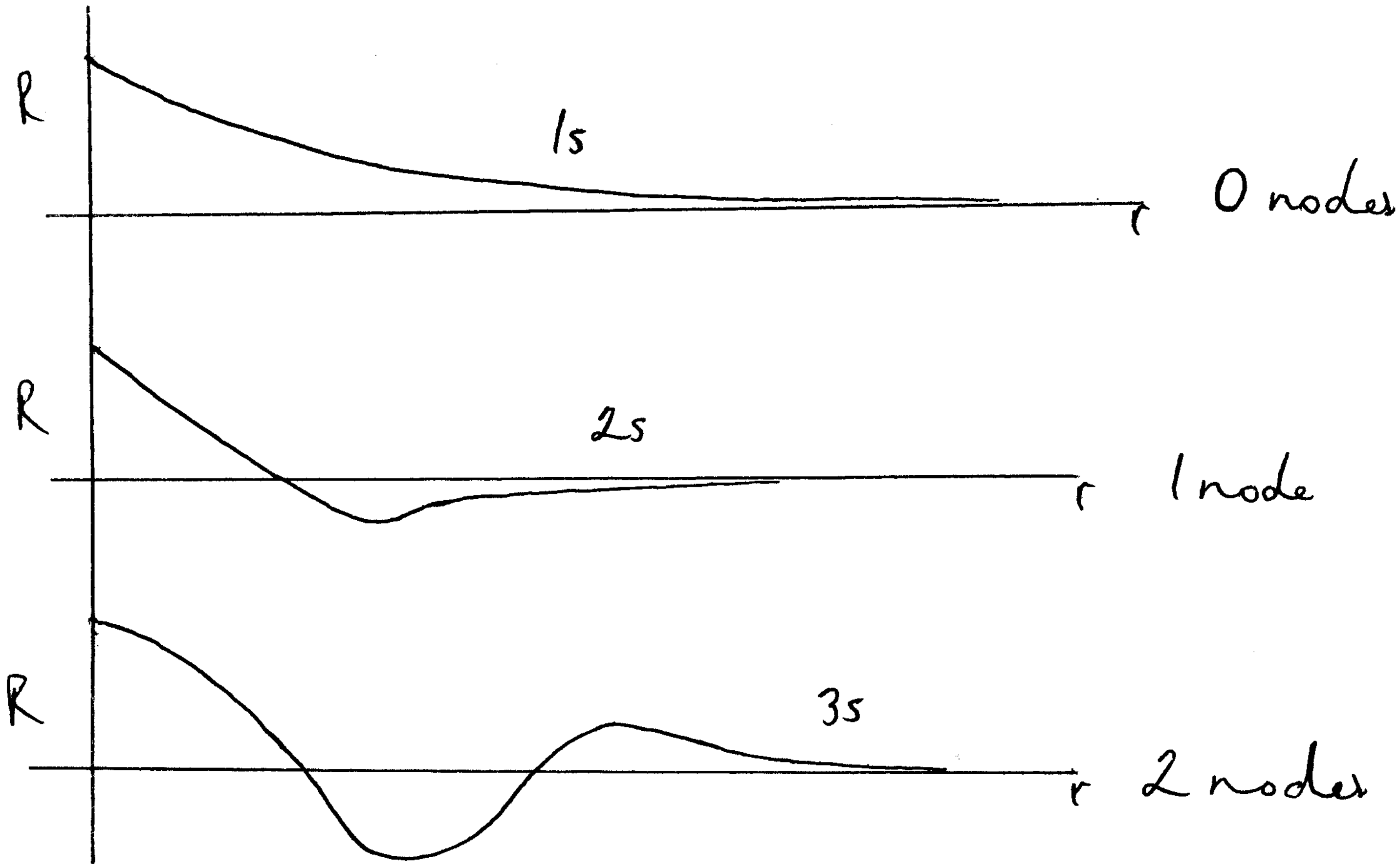
For any V(r) which goes to zero at infinity (always true in chemistry) and diverges more weakly than $1/r^2$ as $r \longrightarrow 0$ (always true in chemistry), we have deduced that

$$\boxed{\begin{array}{ll} R \sim r^l & \text{near } r = 0 \\ R \sim e^{-\alpha r} & \text{as } r \longrightarrow \infty \end{array}}$$

We can use this to sketch the general appearance of any atomic orbital.

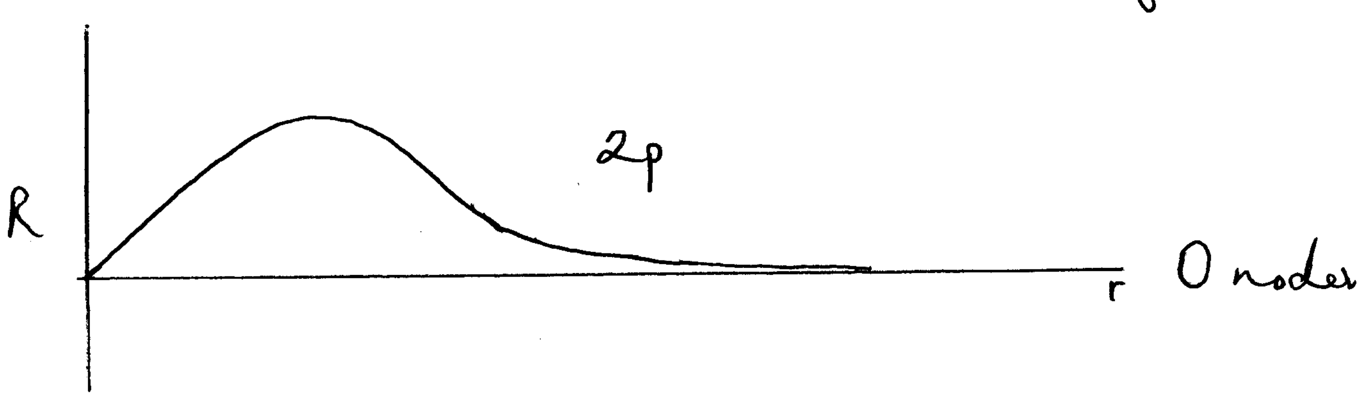
$\boxed{s \text{ orbitals} \quad l = 0}$

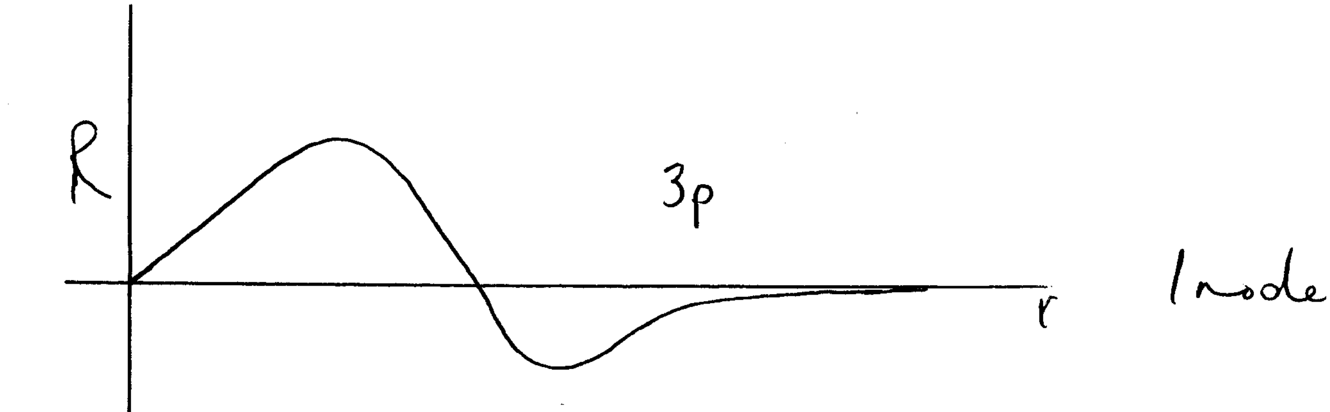
Near the nucleus, $R \sim r^0 \Rightarrow$ finite value at nucleus

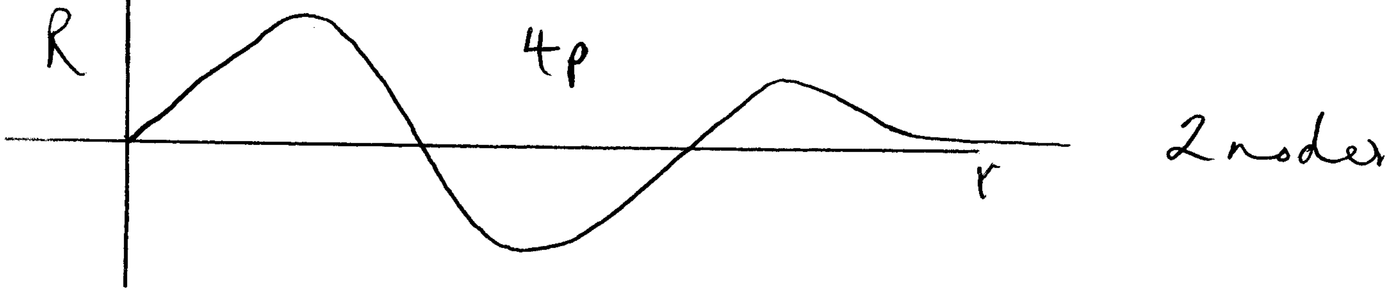


$\boxed{p \text{ orbitals} \quad l = 1}$

Near the nucleus $R \sim r^1 \Rightarrow$ 0 value at the nucleus, but has a finite slope

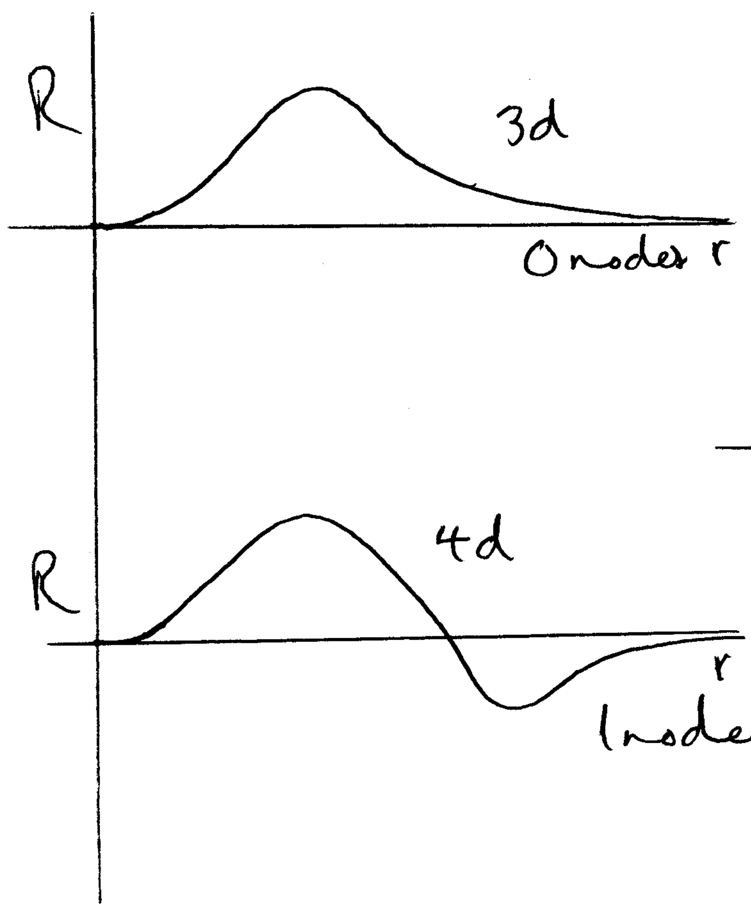


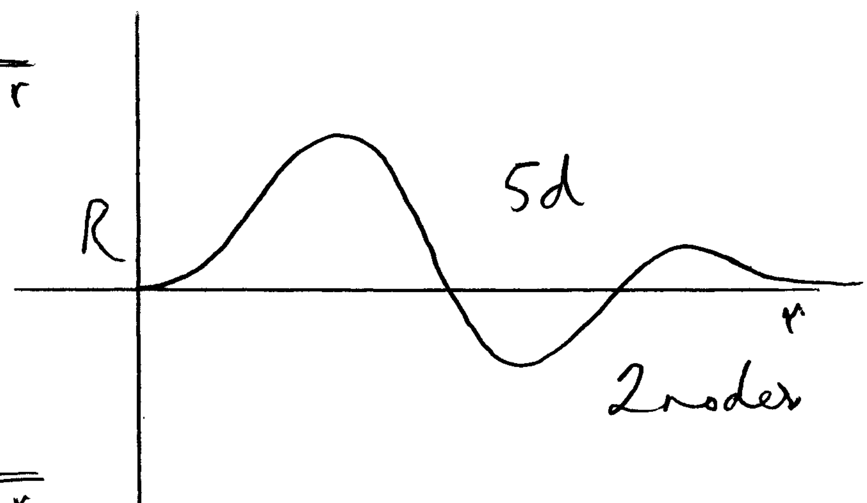




$\boxed{d \text{ orbitals} \quad l=2}$

Near the nucleus $R \sim r^2 \Rightarrow 0$ value, 0 slope at nucleus





General Observations

- tails (ie $r \to \infty$) decay exponentially
- probability of being close to the nucleus has the trend

$$s > p > d > \cdots$$

because of short range $R \sim r^l$ behavior.

ie $r^0 > r^1 > r^2 > \cdots$ near $r = 0$.

- Lowest energy radial function for a given l has 0 nodes
- One node is added for each successive higher energy state. This is required by orthogonality!

- In general, the energy depends on the "principle" quantum number n (labeling which state of a given l we are talking about)

$$n = \underbrace{l+1}_{\text{1st state of given } l}, l+2, l+3, \ldots$$

1st state of given l.

and also on l.

However, energy does not depend on the m quantum number. because the radial equation does not contain it.

Hence the correct labeling for solutions of the radial equation is $R_{nl}(r)$, E_{nl} and each E_{nl} is $(2l+1)$-fold degenerate due to the $2l+1$ different m values corresponding to each l

Total $\Psi(r,\theta,\phi)$ has the form $\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi)$

Hydrogenic Atoms

Single electron attracted to a nucleus of charge Ze.

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \qquad \text{(S.I. units)}$$

Can apply methods similar to those for the harmonic oscillator and the θ-equation to find that

$$E_n = -\frac{Z^2 m_e e^4}{32\pi^2 \hbar^2 \varepsilon_0^2} \frac{1}{n^2} \qquad \text{(S.I. units)}$$

where $n = l+1, l+2, \ldots$

or equivalently $l \leq n-1$, $n \in \mathbb{Z} > 0$.

Only for hydrogenic atoms does the energy E depend only on n and not on l.

This is essentially accidental.