Central Force Problem

$$x = r\sin\theta\cos\phi \tag{1}$$

$$y = r\sin\theta\sin\phi \tag{2}$$

$$z = r\cos\theta \tag{3}$$

Rangle of variables is

$$0 \le r < \infty \tag{4}$$

$$0 \le \theta \le \pi \tag{5}$$

$$0 \le \phi < 2\pi \tag{6}$$

Volume element for integration is

$$dx\,dy\,dz = \underbrace{r^2\sin\theta}_{\text{Jacobian}}\,dr\,d\theta\,d\phi \tag{7}$$

The Laplacian becomes

$$\nabla^2\psi = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] \tag{8}$$

the ϕ equation

$$\frac{d^2Q}{d\phi^2} = -m^2Q\ , \qquad 0 \le \phi < 2\pi \tag{9}$$

This is just the "particle on a ring" problem again in a slightly different form. Thus we know the solutions are $\sin m\phi$ or $\cos m\phi$, or $e^{\pm im\phi}$ with boundary conditions $Q(0) = Q(2\pi)$ and $Q'(0) = Q'(2\pi)$. The unnormalized solutions in real form are $Q_0(\phi) = 1$ for $m = 0$ and $Q_m(\phi) = \sin m\phi$, $Q_m(\phi) = \cos m\phi$ for $m > 0$ (doubly degenerate).

the θ equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) - \frac{m^2}{\sin^2\theta}P = -\lambda P \tag{10}$$

This equation is called the Associated Legendre Equation. A solution of the form $P(\theta) = sin^m\theta\cos^\alpha\theta$ 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 to obtain (after using some trig. identities)

$$-(m+\alpha)(m+\alpha+1)\sin^m\theta\cos^\alpha\theta+\alpha(\alpha-1)\sin^m\theta\cos^{\alpha-2}\theta=-\lambda\sin^m\theta\cos^\alpha\theta \tag{11}$$

This works if $\alpha=0$ or $\alpha=1$ and $\lambda=(m+\alpha)(m+\alpha+1)$. For any other α, the term $\alpha(\alpha-1)\sin^m\theta\cos^{\alpha-2}\theta$ is uncompensated for. However, we can compensate for this term by adding lower order corrections to P as follows

$$P=\sin^m\theta\left[\cos^\alpha\theta+A\cos^{\alpha-2}\theta+B\cos^{\alpha-4}\theta+\cdots\right] \tag{12}$$

As long as $\alpha\in\mathbb{Z}>0$, the chain of leftover terms thus generated will terminate because of the $\alpha(\alpha-1)$ prefactor. We therefore conclude that, for a given m,

$$\lambda=(m+\alpha)(m+\alpha+1)\qquad\text{where}\quad\alpha\in\mathbb{Z}\geq 0 \tag{13}$$

This can be rephrased by defining $\ell=m+\alpha$, in terms of which we can say $\lambda=\ell(\ell+1)$, $\ell\in\mathbb{Z}\geq 0$ and also $m\leq\ell$ since $m=\ell-\alpha$, $\alpha\in\mathbb{Z}\geq 0$. Finally, the solutions look like

$$P_{\ell m}(\theta)=\sin^m\theta\left[\cos^{\ell-m}\theta+A\cos^{\ell-m-2}\theta+B\cos^{\ell-m-4}\theta+\cdots\right] \tag{14}$$

Notice that each solution has two labels (quantum numbers) ℓ and m.

the radial equation

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\left[\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\lambda R\right]+V(r)R=ER \tag{15}$$

Note: any two-particle problem in which the potential energy depends only on the distance between the particles (*i.e.* 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

$$m=\frac{m_1m_2}{m_1+m_2}=\mu \tag{16}$$

Use $\lambda=\ell(\ell+1)$ and rearrange

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[V(r)+\underbrace{\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}}_{\text{centrifugal potential}}\right]R=ER \tag{17}$$

We cannot solve this equation exactly without knowing the exact form of the function $V(r)$, but we can examine the behavior of the solutions in the limits $r \to 0$ and $r \to \infty$.

$\boxed{r \to 0}$

Of the last three 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 differential equation becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{\ell(\ell+1)}{r^2}R\,, \qquad r \to 0 \text{ limit} \tag{18}$$

It is easy to show that $R(r) = r^\ell$ solves this.

$\boxed{r \to \infty}$

Of the last three terms, the energy E dominates because $V(r)$ and the centrifugal potential go to zero. Therefore the differential equation becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = -\frac{2mE}{\hbar^2}R\,, \qquad r \to \infty \text{ limit} \tag{19}$$

It is easy to show that $R(r) = e^{-\alpha r}$ where $\alpha = \sqrt{-2mE/\hbar^2}$ is a solution as $r \to \infty$ (must take the limit after plugging in; E is negative for bound states). Another possibility is $e^{\alpha r}$ but this blows up at large r which makes it unacceptable. For <u>any</u> $V(r)$ which goes to zero at infinity (always true in chemistry) and diverges more weakly than $1/r^2$ at $r \to 0$ (always true in chemistry), we have deduced that

$$R(r) \sim r^\ell \qquad \text{near } r = 0 \tag{20}$$

$$R(r) \sim e^{-\alpha r} \qquad \text{as } r \to \infty \tag{21}$$

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

$\boxed{s \text{ orbitals } \ell = 0}$

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

$\boxed{p \text{ orbitals } \ell = 1}$

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

$\boxed{d \text{ orbitals } \ell = 2}$

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

<u>General Observations</u>

The tails (*i.e.* $r \to \infty$) decay exponentially

The probability of being close to the nucleus has the trend $s > p > d > \cdots$ because of the short ranged $R \sim r^\ell$ behavior, *i.e.* $r^0 > r^1 > r^2 > \cdots$ near $r = 0$.

The lowest energy radial function for a given ℓ value has zero 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), $n = \ell + 1, \ell + 2, \ell + 3, \ldots$, and also on ℓ. However, the 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 $R_{n\ell}(r)$ with the energy labeled as $E_{n\ell}$.Each $E_{n\ell}$ is $(2\ell + 1)$-fold degenerate due to the $2\ell + 1$ different m values corresponding to each ℓ.

The total wavefunction has the form $\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)\mathcal{Y}_{\ell m}(\theta, \phi)$.

Hydrogenic Atoms

For a single electron attracted to a nucleus of charge Ze,

$$V(r) = -\frac{Ze^2}{r\pi\epsilon_0 r} \qquad \text{S.I. units} \tag{22}$$

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

$$E_n = -\frac{Z^2 m_e e^4}{32\pi^2\hbar^2\epsilon_0^2}\frac{1}{n^2} \qquad \text{S.I. units} \tag{23}$$

where $n = \ell + 1, \ell + 2, \ldots$ or equivalently $\ell \leq n - 1$, $n \in \mathbb{Z} > 0$. Only for hydrogenic atoms does the energy E depend only on n and not on ℓ. This is essentially accidental.