The H atom

Chem:2430

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

$$= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{\hat{L}^2}{r^2\hbar^2}$$

For a one particle system with a spherical (centrosymmetric) potential

$$\hat{H} = \frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right] + V(r) + \frac{\hat{L}^2}{2mr^2}$$

$$\left[\hat{H}, \hat{L}^2\right] = 0$$

$$\left[\hat{H}, \hat{L}_z\right] = 0$$

So there are simultaneous eigenfunctions of $\hat{H}, \hat{L}^2$, and $\hat{L}_z$

$$\hat{H}\psi = E\psi$$

$$\hat{L}^2\psi = \ell(\ell+1)\hbar^2, \ell = 0,1,2,\ldots$$

$$\hat{L}_z\psi = m\hbar\psi, m = -\ell, -\ell+1, \ldots\ell$$

$$\hat{H} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\ell(\ell+1)}{r^2}\right)\psi + V\psi = E$$

$$V_{\text{eff}} = V + \frac{\hbar^2\ell(\ell+1)}{2mr^2}$$

ψ is of the form $R(r)Y_\ell^m(\theta,\phi)$

Substitute and find

$$\frac{-\hbar^2}{2m}\left(R'' + \frac{2}{r}R'\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}R + V(r)R = ER$$

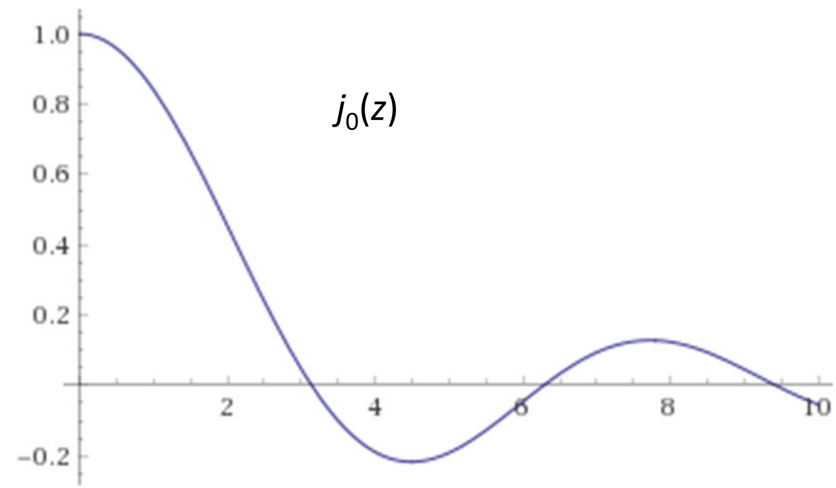
Radial equation gives energy quantization.

Particle in a spherical box: $V = 0$ inside the box, and $V =$ infinity for $r > a$.

The solutions are the Bessel functions

$$j_0(z) = \frac{\sin(z)}{z}$$

$$j_1(z) = \frac{\sin(z)}{z^2} - \frac{\cos(z)}{z}$$



Order of energy levels

1*s* < 1*p* < 1*d* < 2*s* < 2*p* < 1*f*

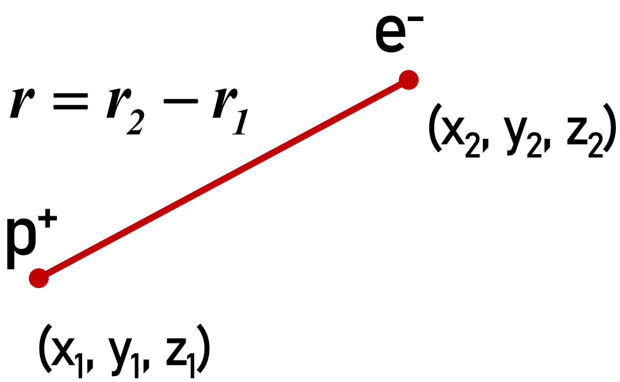
Note how different this is from the H atom

However, just as for the H atom, the $\ell \geq 1$ wave functions → 0 as r → 0

This is due to the repulsive angular momentum term

The H atom is actually a 2-particle problem.

$$\boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1$$



center of mass

$$\boldsymbol{R} = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{m_1 + m_2}$$

$$M = m_1 + m_2$$

Classical problem

$$T = \frac{1}{2}M\,|\dot{\boldsymbol{R}}^2| + \frac{1}{2}\mu\,|\dot{\boldsymbol{r}}|^2$$

Motion of center of mass — Internal motion

or

$$T = \frac{\left|\boldsymbol{p}_M\right|^2}{2M} + \frac{\left|\boldsymbol{p}_\mu\right|^2}{2\mu}$$

The Hamiltonian for a one electron atom is

$$H = \frac{p_M{}^2}{2M} + \left[\frac{p_\mu{}^2}{2\mu} + V(r) \right]$$

The QM Eigenvalue problem for the relative motion is

$$\left[\frac{p_\mu{}^2}{2\mu} + V(r) \right] \psi(x,y,z) = E\psi(x,y,z)$$

The radial equation is

$$\frac{-\hbar^2}{2m}\left(R'' + \frac{2}{r}R' \right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}R - \frac{Ze'^2}{r}R = ER$$

$Z|e'|$ is the nuclear charge, where Z is an integer

$$-\left(R'' + \frac{2}{r}R' \right) + \frac{\ell(\ell+1)}{r^2}R - \frac{2me'^2}{\hbar^2 r}R = \frac{2mE}{\hbar^2}R$$

$$-\left(R'' + \frac{2}{r}R' \right) + \frac{\ell(\ell+1)}{r^2}R - \frac{2Z}{ar}R = \frac{2E}{ae'^2}R$$

$$a = \hbar^2 / me'^2$$

Lets try $\psi = e^{-br}$

$$b^2 e^{-br} - \frac{2b}{r} e^{-br} + \left[\frac{2E}{ae'^2} + \frac{2Z}{ar} - \frac{\ell(\ell+1)}{r^2} \right] e^{-br} = 0$$

The solution is given by

$$\ell = 0$$

$$b = Z / a$$

$$-b^2 = \frac{2E}{ae'^2}$$

This is the solution corresponding to the 1s orbital

What would be a reasonable guess for the wave function for the 2*s* orbital?

$$E = \frac{-ae'^2 b^2}{2} = \frac{-e'^2 Z^2}{2a} = -\frac{1}{2} \frac{Z^2 \mu e'^4}{\hbar^2}$$

In atomic units *a* = 1 and if *Z* also = 1, then *b* = 1 and *E* =-1/2 a.u. → -13.61 eV

Now try $\psi = re^{-br}$

$$\psi' = e^{-br} - bre^{-br}$$

$$\psi'' = -be^{-br} - be^{-br} + b^2re^{-br} = \left(br^2 - 2b\right)e^{-br}$$

$$-\left(R'' + \frac{2}{r}R'\right) + \frac{\ell\left(\ell+1\right)}{r^2}R + -\frac{2Z}{ar}R = \frac{2E}{ae'^2}R$$

$$b^2r - 2b + \frac{2}{r} - 2b + \frac{2E}{ae'^2}r + \frac{2Z}{a} - \frac{\ell\left(\ell+1\right)}{r} = 0$$

$$2 = \ell\left(\ell+1\right) \Rightarrow \ell = 1$$

This corresponds to a 2*p* orbital

$$\Rightarrow -4b = \frac{2Z}{a} \Rightarrow \quad b = Z/2a$$

$$-b^2 = \frac{2E}{ae'^2} \Rightarrow \quad E = \frac{-b^2}{2}ae'^2 = \frac{-Z^2e'^2}{8a}$$

Note why the ℓ ends up NOT contributing to the energy

The general solution is

$$E_n = \frac{-Z\mu e'^4}{2n^2\hbar^2}$$

degeneracies

$n=1 \quad \ell=0, m=0, \quad s$

$n=2 \quad \ell=0, m=0, \quad s$
$\quad\quad\;\; \ell=1, m=-1,0,1, \quad p$

$n=3 \quad \ell=0, m=0, \quad s$
$\quad\quad\;\; \ell=1, m=-1,0,1, \quad p$
$\quad\quad\;\; \ell=2, m=-2,-1,0,1,2 \quad d$

So degeneracy = n^2

Actually $2n^2$ accounting for spin.

$$\mu_H = 0.999456 m_e$$

If we use m_e

$$a = a_0 = \frac{\hbar^2}{m_e e'^2} = 0.52918 \text{ Å}$$ Bohr radius

$$E = -\frac{e'^2}{2a}$$

$1 \text{ eV} = 1.022 \times 10^{-19} \text{ J}$

$1 \text{ a.u.} = 27.211 \text{ eV}$

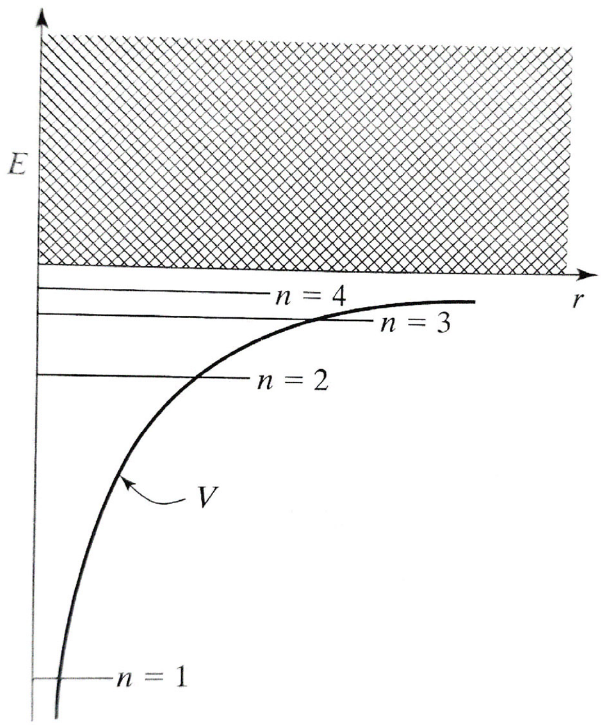
1s level

$$\langle T \rangle = \frac{e'^2}{2a}$$

$$E = -\frac{e'^2}{2a}$$

$$\langle V \rangle = \frac{-e'^2}{a}$$

Note how the relation of the KE and PE contributions differs from the H.O. problem.



Continuum levels:
infinite fold degenerate

Fig. 6.6 from Levine

$1s: \quad e^{-r/a_0}$

$2s: \quad (2 - r/a_0)e^{-r/2a_0}$

$2p_0: \frac{r}{a_0}e^{-r/2a_0}$

Note the wave functions for s orbitals are finite at $r = 0$
wavefunctions for p, d, f…functions are 0 at $r = 0$

This is due to the repulsive angular momentum term in V_{eff}

Consider ψ_{100} for $y = 0$ and $z = 0$

$\psi_{100} \sim e^{-|x|/a}$ has a cusp.

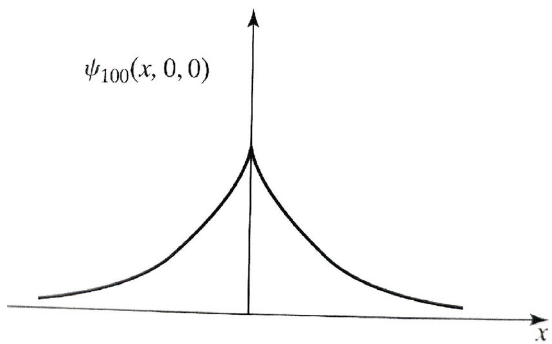


Fig. 6.7 from Levine

This is connected with V → -∞ at r = 0

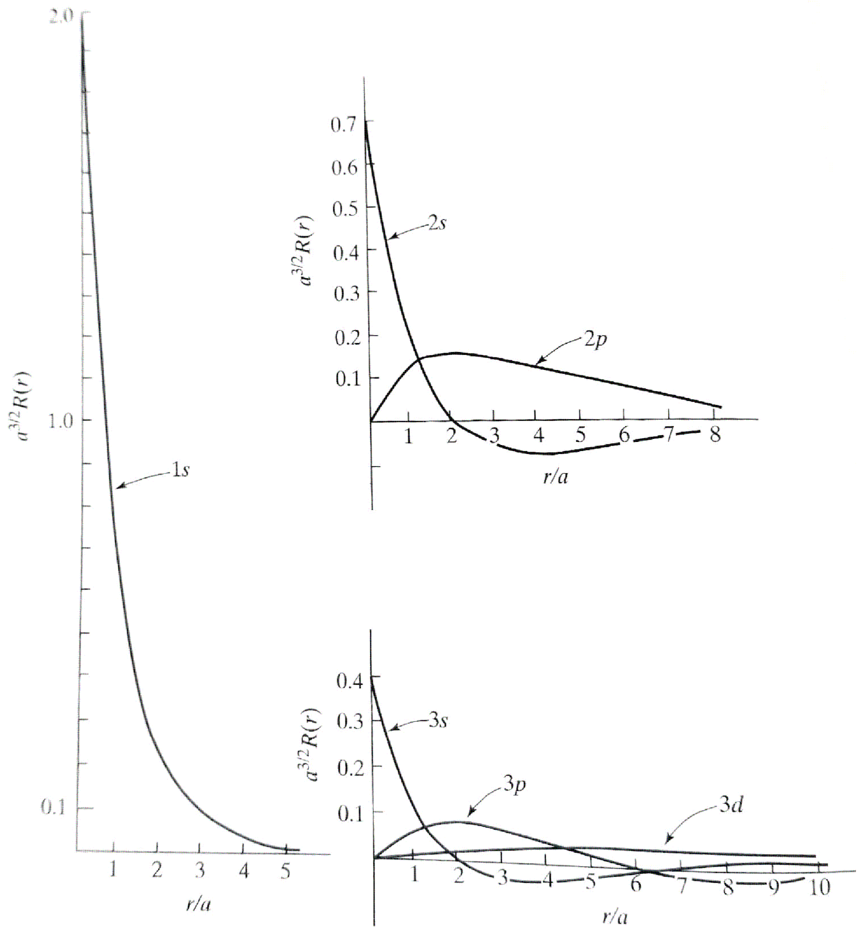


Fig. 6.8 from Levine

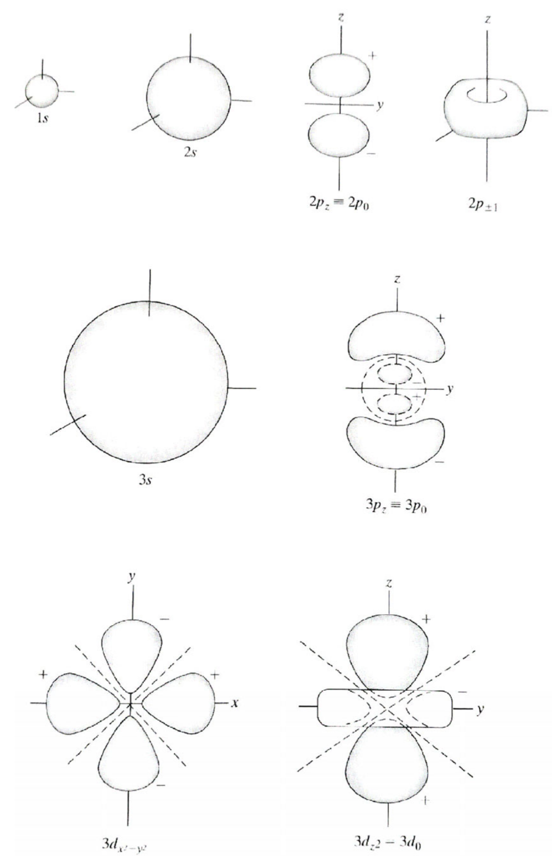


Fig. 6.9 from Levine

Radial distribution functions

What is the probability of finding the electron in a shell around r?

$$R_{n\ell}{}^2 r^2 dr$$

For the 1s orbital what is the maximum of the radial distribution function?

$$R^2 r^2 \sim r^2 e^{-2Zr/a}$$

$$\frac{d}{dr} R^2 r^2 = \left(2r - \frac{2Z}{a} r^2 \right) e^{-2Zr/a}$$

This = 0 when r = 0 and when $r_{\max} = \frac{a}{Z}$

For 1s H $r_{\max} = a_0 =$ Bohr radius