Chapter 3 The H-Atom

- last example we will solve analytically

- foundation of electronic structure theory

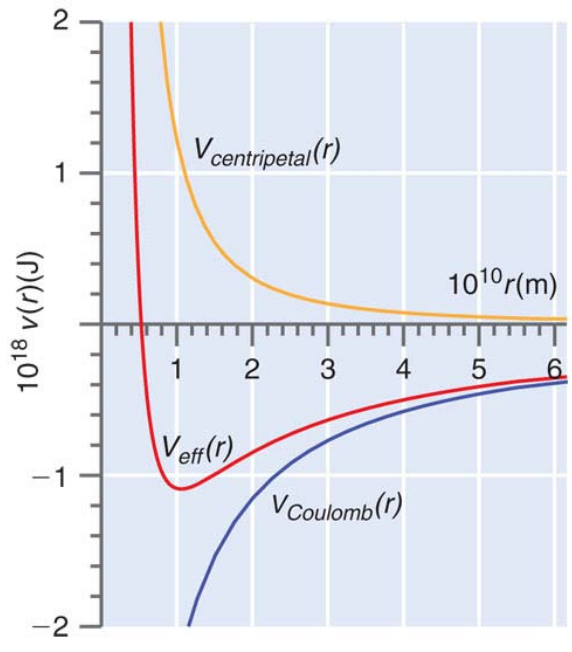
- fixed nucleus of charge +1e
  electron charge –1e

$$\hat{H}(x,y,z) = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{e^2}{4\pi\varepsilon_0 r}, \quad r=\sqrt{x^2+y^2+z^2}$$

↓ Go to spherical coordinates

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r\psi+\frac{1}{r^2}\Lambda^2\psi\right]-\frac{e^2\psi}{4\pi\varepsilon_0 r}=E\psi$$

This equation separates into a radial equation and an equation involving the angular part, which we have already solved



Radial equation for each ℓ :

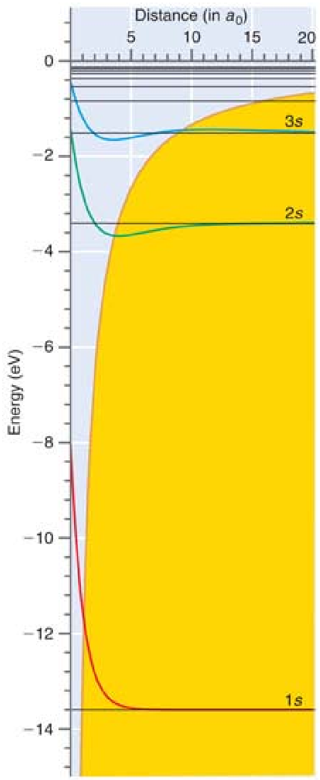
$$\left(-\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\underbrace{\frac{\hbar^2\ell(\ell+1)}{2m_e r^2}-\frac{e^2}{4\pi\varepsilon_0 r}}_{V_{eff}}\right)R(r)=ER(r)$$

This equation gives a new quantum number *n, in addition to* ℓ and *m*.

The solutions are of the form of exponentials times associated Laguerre polynomials

- Energy levels $$E_n=\frac{-m_e e^4}{8\varepsilon_0{}^2h^2}\frac{1}{n^2}=-\frac{13.6eV}{n^2}$$

Note that the ℓ and m quantum numbers do not appear in the energy expression n = 1 and 2 levels of the H atom



$n=1,\ l=0,\ m_l=0 \qquad \psi_{100}(r)=\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

$n=2,\ l=0,\ m_l=0 \qquad \psi_{200}(r)=\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right) e^{-r/2a_0}$

$n=2,\ l=1,\ m_l=0 \qquad \psi_{210}(r,\theta,\phi)=\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0} e^{-r/2a_0}\cos\theta$

$n=2,\ l=1,\ m_l=\pm1 \qquad \psi_{21\pm1}(r,\theta,\phi)=\frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0} e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$

$$\rho=\frac{2z}{ma_0}r$$

a_0 = Bohr radius = $\frac{4\pi e_0\hbar^2}{m_e e^2}=$ 0.5291Å

n = 3 levels of the H atom.

$n=3,\ l=0,\ m_l=0$ $$\psi_{300}(r)=\frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$$

$n=3,\ l=1,\ m_l=0$ $$\psi_{310}(r,\theta,\phi)=\frac{1}{81}\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{1}{a_0}\right)^{3/2}\left(6\frac{r}{a_0}-\frac{r^2}{a_0^2}\right)e^{-r/3a_0}\cos\theta$$

$n=3,\ l=1,\ m_l=\pm1$ $$\psi_{31\pm1}(r,\theta,\phi)=\frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6\frac{r}{a_0}-\frac{r^2}{a_0^2}\right)e^{-r/3a_0}\sin\theta\, e^{\pm i\phi}$$

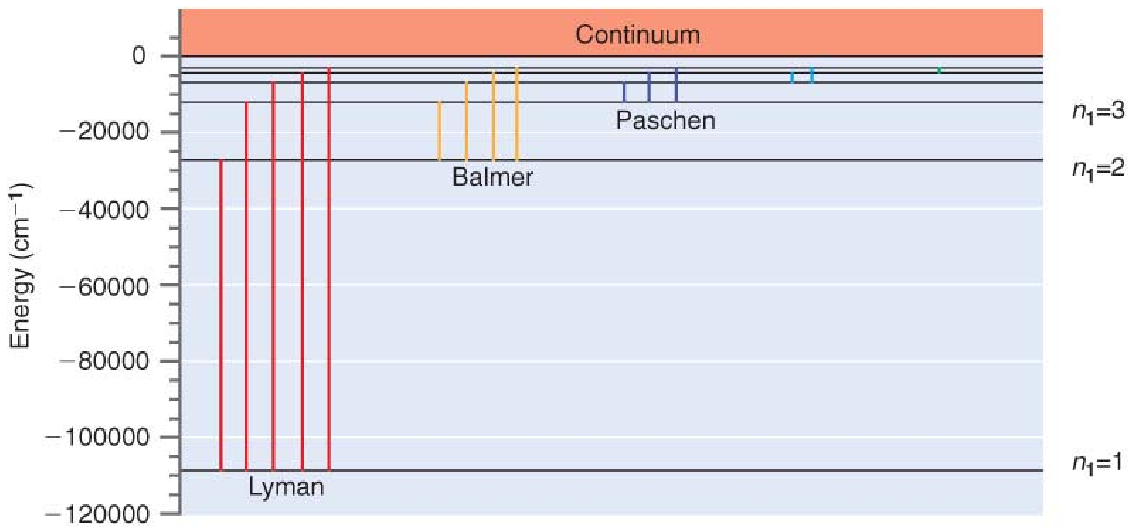
$n=3,\ l=2,\ m_l=0$ $$\psi_{320}(r,\theta,\phi)=\frac{1}{81\sqrt{6\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}\left(3\cos^2\theta-1\right)$$

$n=3,\ l=2,\ m_l=\pm1$ $$\psi_{32\pm1}(r,\theta,\phi)=\frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$$

$n=3,\ l=2,\ m_l=\pm2$ $$\psi_{32\pm2}(r,\theta,\phi)=\frac{1}{162\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$$

•Energy levels $$E_n = \frac{-m_e e^4}{8\varepsilon_0 h^2}\frac{1}{n^2} = -\frac{13.6eV}{n^2}$$

1 Rydberg = 0.5 au = 13.605 eV



Energy is independent of ℓ, m

$$n = 1, 2, 3, \ldots$$
$$\ell = 0, \ldots, n-1$$
$$m = -\ell, \ldots, \ell$$
$$1s, 2s, 2p_x\, 2p_y, 2p_z$$

• Wavefunctions = Atomic orbitals

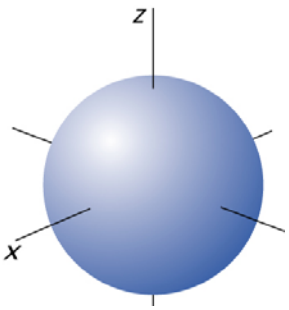
$$\psi(r,\theta,\varphi) \propto Y_\ell^m(\theta,\varphi) \bullet e^{-r/na_0} \bullet (polynomial\ in\ r)$$

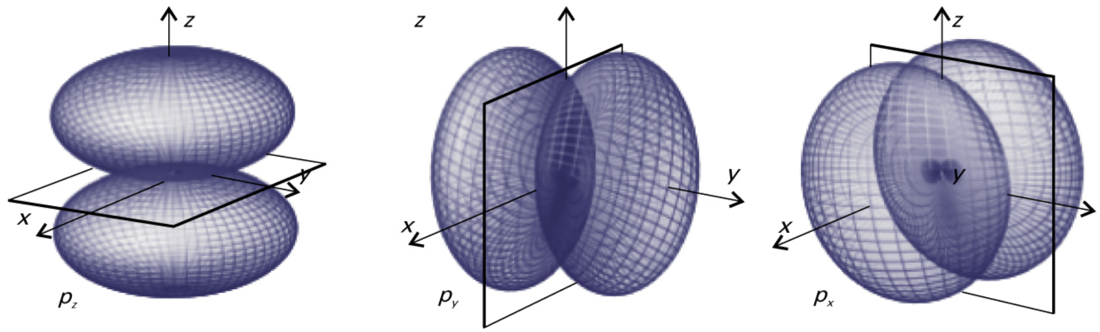
• Spectroscopy

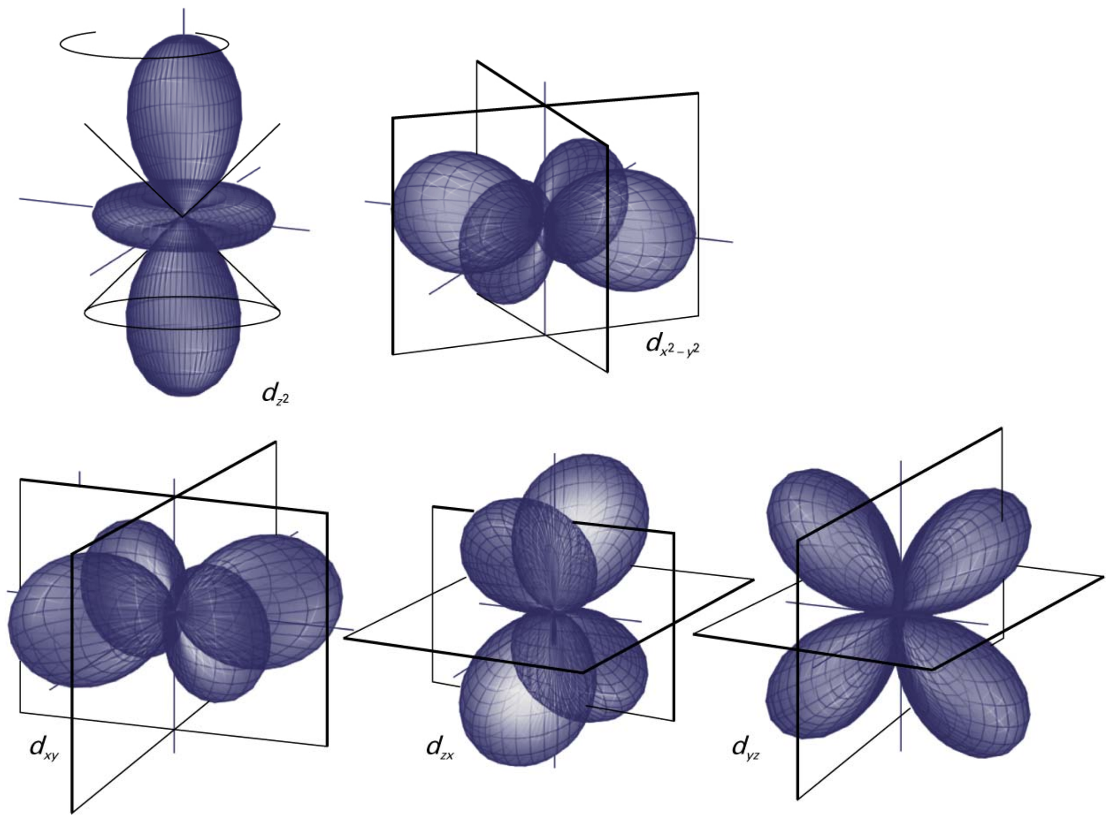
$$\Delta n: \text{ any}$$
$$\Delta\ell = \pm 1$$
$$\Delta m = 0,\ \pm 1$$

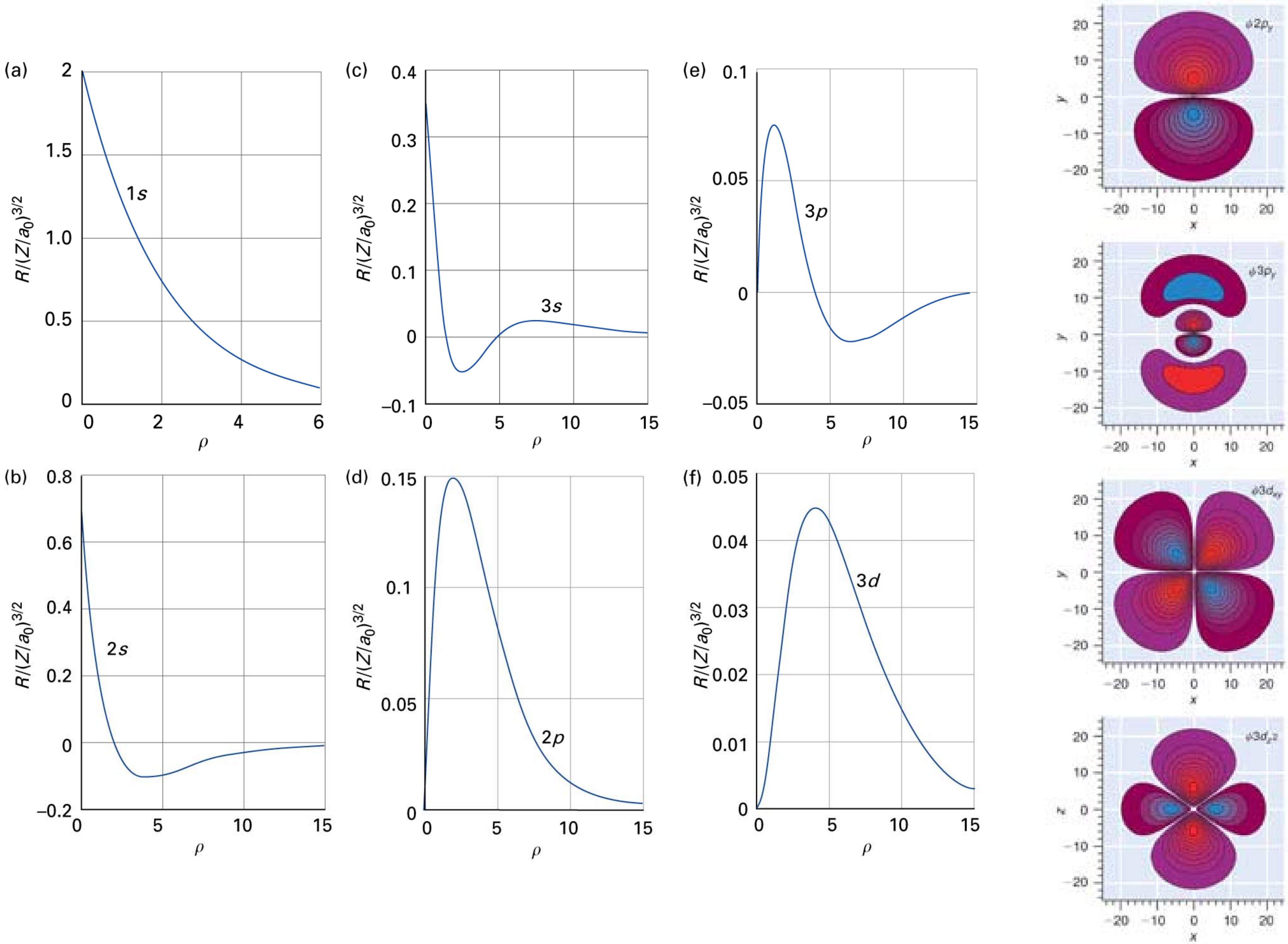
Note x, y, z have same angular dependence as p_x, p_y, and p_z. This is why s → p is allowed.

Angular parts of the s, p, and d H orbitals








(a)
1s
(b)
2s
(c)
3s
(d)
2p
(e)
3p
(f)
3d
R/(Z/a0)^3/2
ρ
ψ2p_y
ψ3p_y
ψ3d_xy
ψ3d_z2
x
y
z

Normalization

$$N^2\int_0^{\pi}\sin\theta d\theta\int_0^{2\pi}d\phi\int_0^{\infty}\left(e^{-r/2a_0}\right)^2 r^2 dr = 1$$

$$N = \frac{1}{2\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}$$

ψ^2 = probability density

$r^2[R(r)]^2$ = radial distribution function

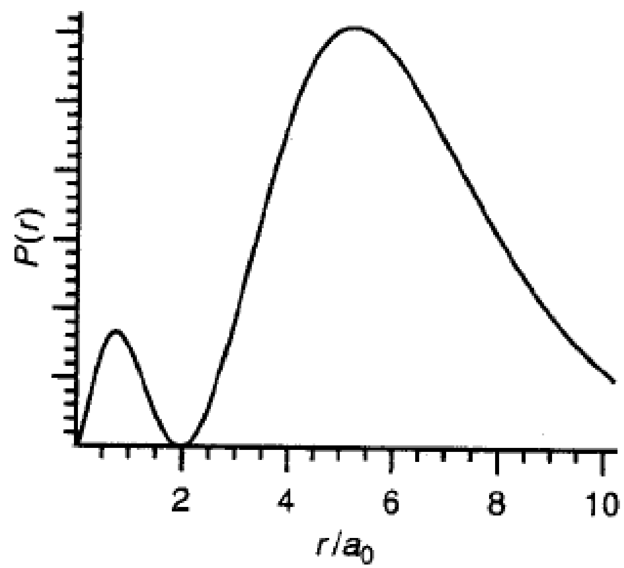
probability of being found in a shell of radius *r* of thickness *dr*

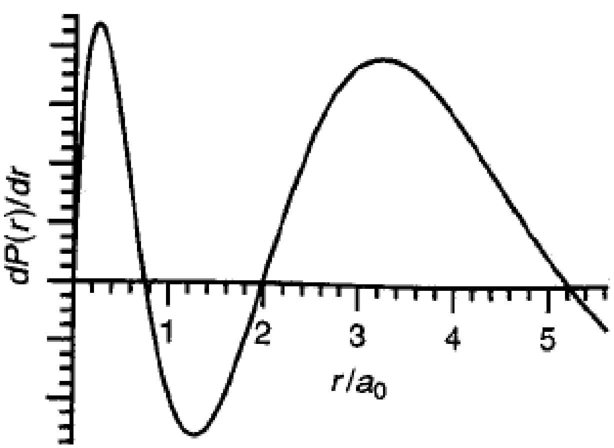
ϕ and θ *have been integrated out*

Maximum in radial distribution function of the *2s* orbital?

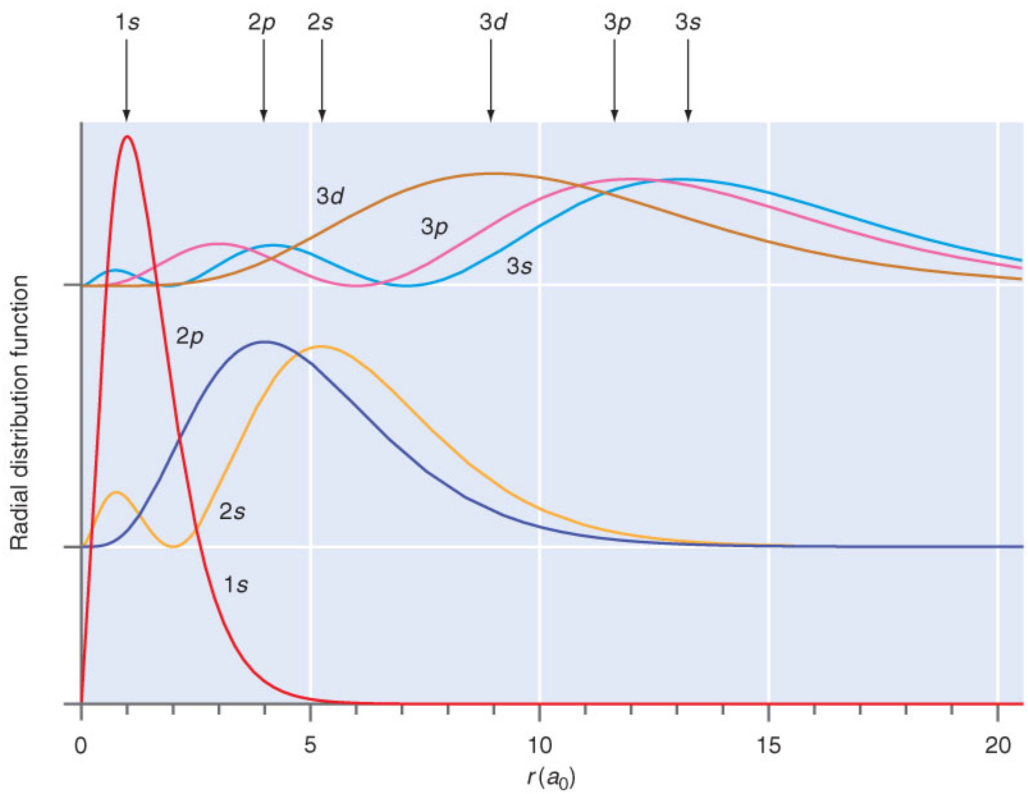
$$P(r) = \frac{1}{32\pi}\left(\frac{1}{a_0}\right)^3 r^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0}$$

$$\frac{dP}{dr} = \frac{r}{32\pi a_0^6}\left(8a_0^3 - 16a_0^2 r + 8a_0 r^2 - r^3\right)e^{-r/a_0}$$

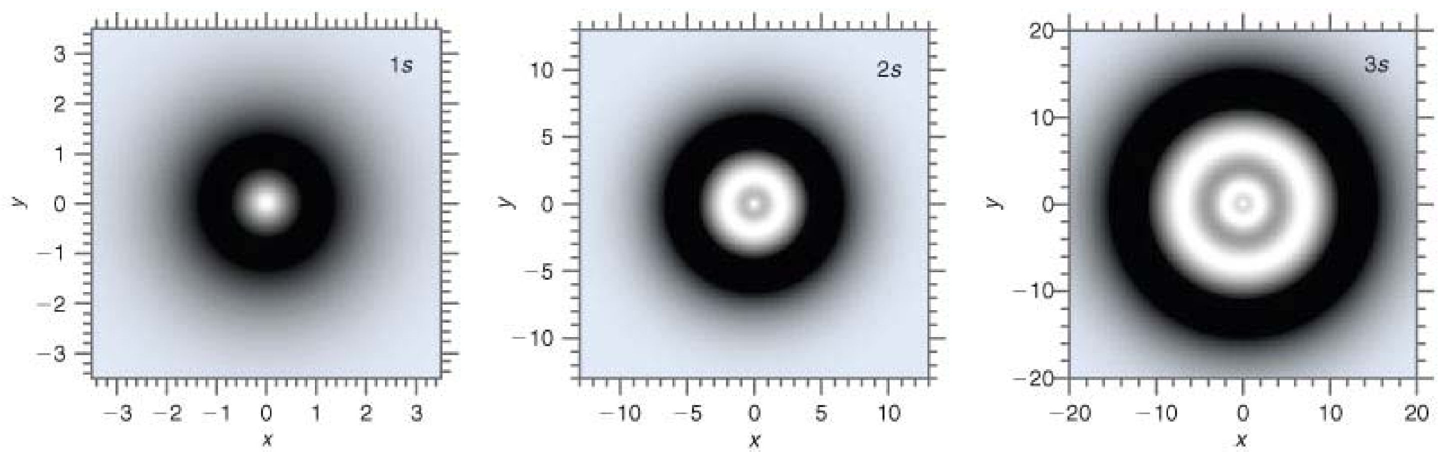




Shell Model



The orbital plots provide some justification to the use of shell models.



$$\langle r \rangle_{n\ell m_e} = \frac{n^2 a_0}{z}\left\{1+\frac{1}{2}\left(1-\frac{\ell(\ell+1)}{h^2}\right)\right\}$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{z}{a_0 n^2}$$

$\uparrow$

all orbitals of a shell have the same PE

$$\langle E_k \rangle = -\frac{1}{2}\langle E_p \rangle$$

$$g_n = \sum_{\ell=0}^{n-1}(2\ell+1) = n^2$$

H atom has a hidden symmetry

H atom

$$E = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{1}{2}\frac{m_e e^4}{(4\pi\varepsilon_0)^2 n^2 \hbar^2} = \frac{-1}{2n^2} \quad \text{in a. u.}$$

$$a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2} = 0.529\text{Å}$$

atomic units

$$\left.\begin{aligned} \hbar &= 1 \\ e &= 1 \\ m_e &= 1 \\ 4\pi\varepsilon_0 &= 1 \end{aligned}\right\}$$

energy: 1 a.u. = 27.211 eV
distance 1 a.u. = 0.529 Å

Note: We really should be using μ instead of m_e.

H, D, T have slightly different μ and thus can be distinguished spectroscopically.

Treatment of H atom applies to He^+, Li^{2+}, … U^{91+}