Chapter 9 The H-Atom

- last example we will solve analytically

- foundation of electronic structure theory

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

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

spherical polar coordinates *r*, θ, φ

$$x = r\sin\theta\cos\varphi$$

$$y = r\sin\theta\sin\varphi$$

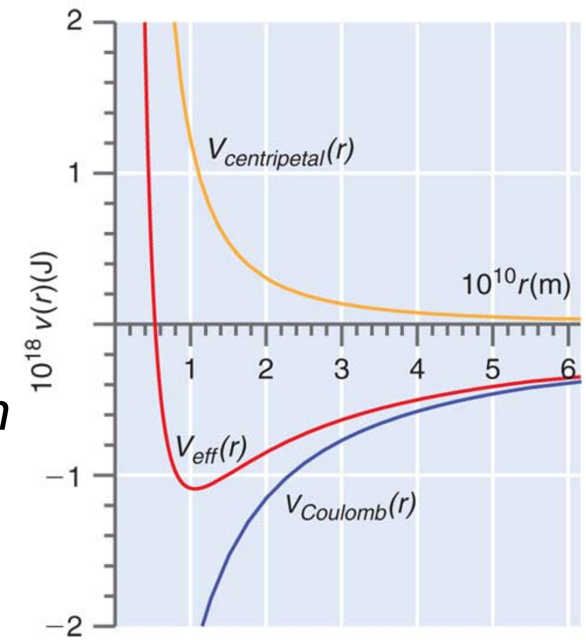
$$z = r\cos\theta$$

$$\hat{H}(r,\theta,\varphi) = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hat{\ell}^2}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r}$$

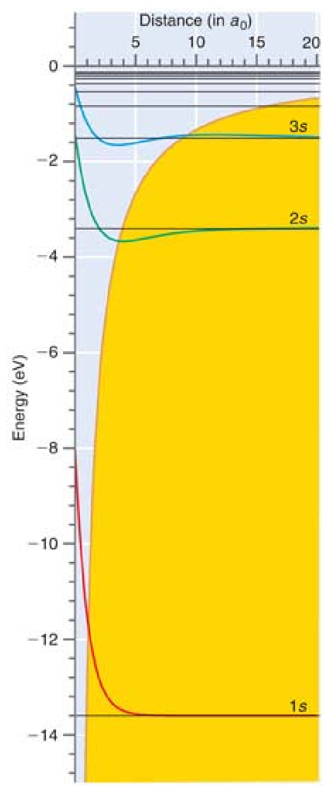
$$\psi(r,\theta,\varphi) = R(r)\bullet Y_\ell^m(\theta,\varphi)$$

Radial equation for each ℓ:

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



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



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

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

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

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

n = 3 levels of the H atom.

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

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

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

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

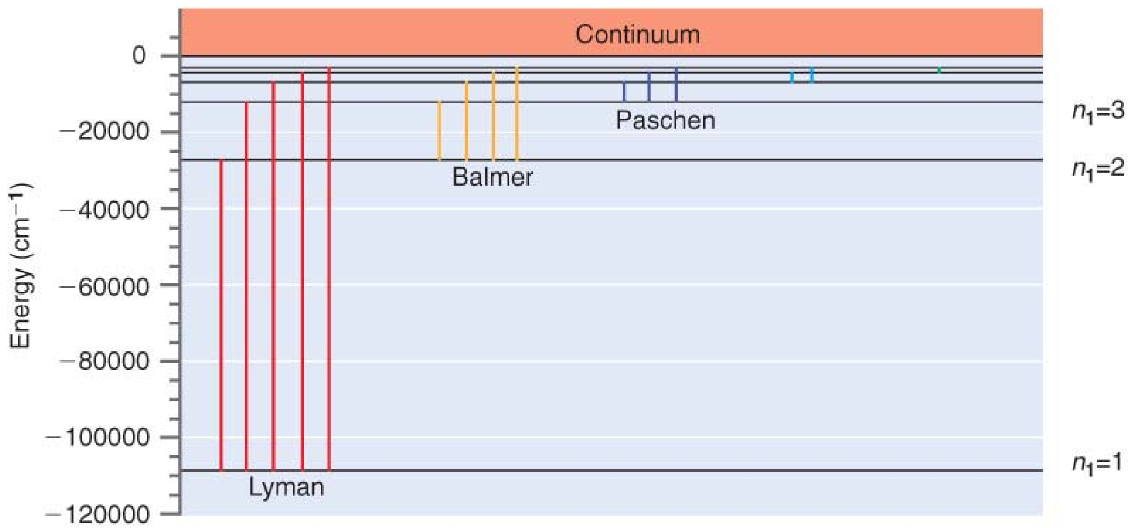
$n = 3,\ l = 2,\ m_l = \pm 1$ $$\psi_{32\pm1}(r,\theta,\phi) = \frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$$

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

•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

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

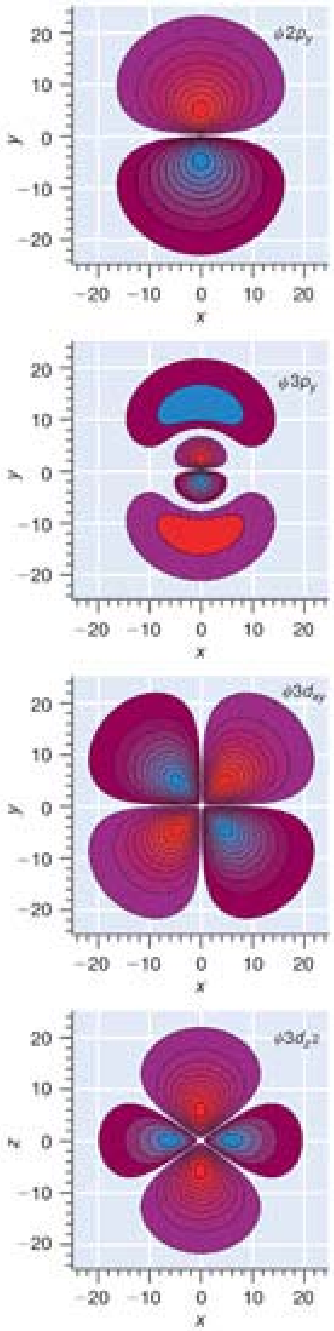
• Wavefunctions = Atomic orbitals

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

• 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.



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

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

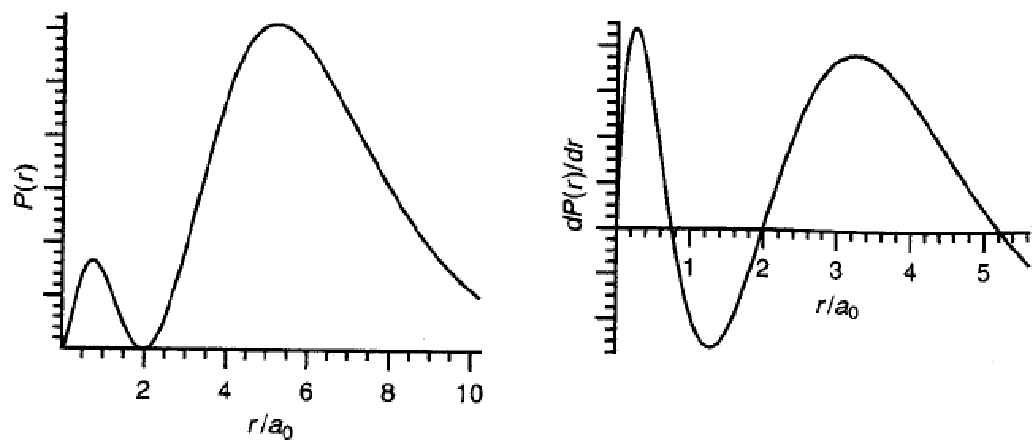
probability of being found in a shell of radius r of thickness dr

(We have integrated out ϕ and θ)

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

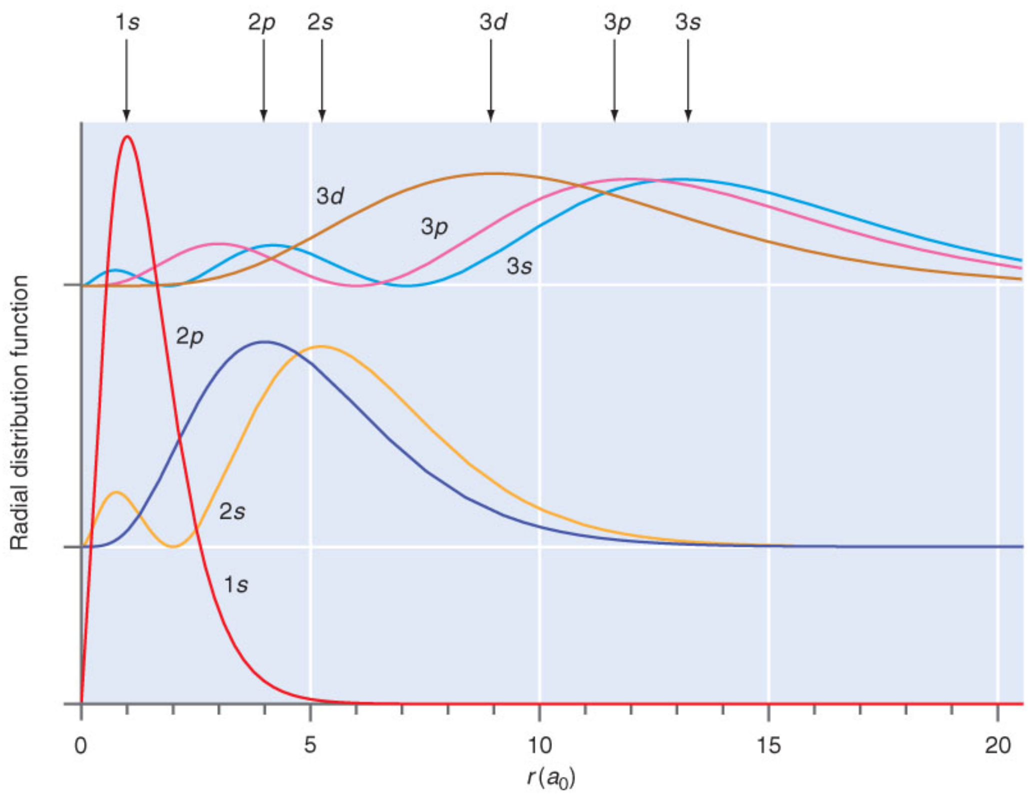
$$P(r) = \frac{1}{32\pi}\left(\frac{1}{a_0}\right)^3 r^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0}$$

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



We see that the principal maximum in $P(r)$ is at 5.24 a_0. This corresponds to the most probable distance of a 2*s* electron from the nucleus. The subsidiary maximum is at 0.76 a_0. The minimum is at 2 a_0.

Shell Model



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