

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

$$\hat{H}(x, y, z) = -\frac{\hbar^2}{2m_e} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{e^2}{4\pi\epsilon_0 r}, \quad r = \sqrt{x^2 + y^2 + z^2}$$

spherical polar coordinates r, θ, φ

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

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

$$z = r \cos \theta$$

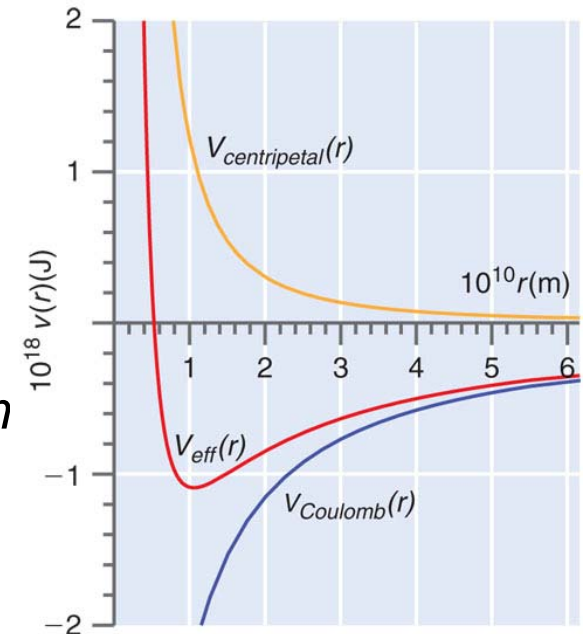
$$\hat{H}(r, \theta, \varphi) = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{\hat{\ell}^2}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r}$$

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

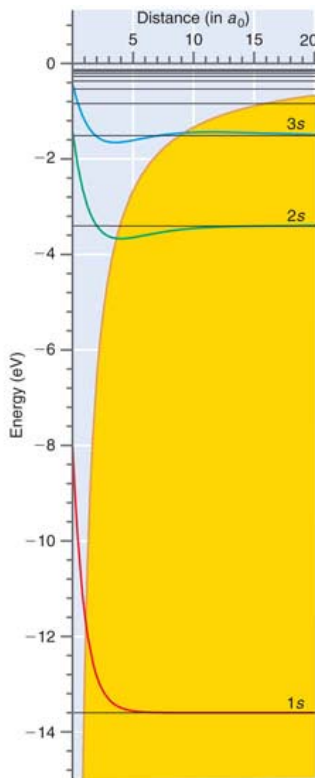
Radial equation for each ℓ :

$$\left(-\frac{\hbar^2}{2m_e r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{\hbar^2 \ell(\ell+1)}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) R(r) = ER(r)$$

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



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$$a_0 = \epsilon_0 \hbar^2 / \pi m_e e^2$$

$n = 1, l = 0, m_l = 0$	$\psi_{100}(r) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$
$n = 2, l = 0, m_l = 0$	$\psi_{200}(r) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0} \right)^{3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$
$n = 2, l = 1, m_l = 0$	$\psi_{210}(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
$n = 2, l = 1, m_l = \pm 1$	$\psi_{21\pm 1}(r, \theta, \phi) = \frac{1}{8\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$

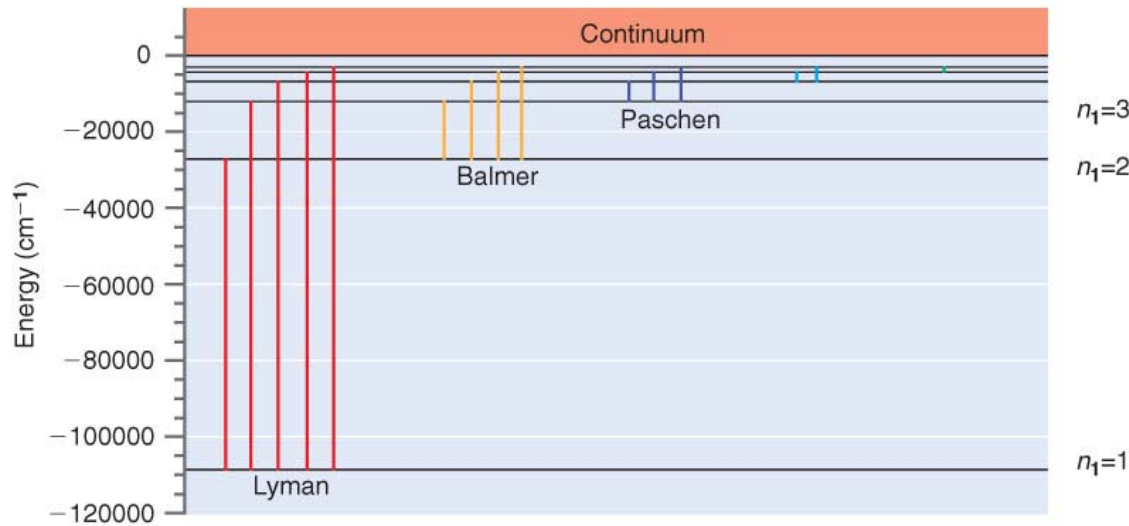
$n = 3$ levels of the H atom.

$$\begin{aligned}n = 3, l = 0, m_l = 0 \quad \psi_{300}(r) &= \frac{1}{81\sqrt{3\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0} \\n = 3, l = 1, m_l = 0 \quad \psi_{310}(r, \theta, \phi) &= \frac{1}{81} \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{1}{a_0}\right)^{3/2} \left(6\frac{r}{a_0} - \frac{r^2}{a_0^2}\right) e^{-r/3a_0} \cos \theta \\n = 3, l = 1, m_l = \pm 1 \quad \psi_{31\pm 1}(r, \theta, \phi) &= \frac{1}{81\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(6\frac{r}{a_0} - \frac{r^2}{a_0^2}\right) e^{-r/3a_0} \sin \theta e^{\pm i\phi} \\n = 3, l = 2, m_l = 0 \quad \psi_{320}(r, \theta, \phi) &= \frac{1}{81\sqrt{6\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1) \\n = 3, l = 2, m_l = \pm 1 \quad \psi_{32\pm 1}(r, \theta, \phi) &= \frac{1}{81\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi} \\n = 3, l = 2, m_l = \pm 2 \quad \psi_{32\pm 2}(r, \theta, \phi) &= \frac{1}{162\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}\end{aligned}$$

• Energy levels

$$E_n = \frac{-m_e e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = -\frac{13.6 \text{ eV}}{n^2}$$

1 Rydberg = 0.5 au = 13.605 eV



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• Wavefunctions = Atomic orbitals

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

• Spectroscopy

$$\Delta n: \text{ any}$$

$$\Delta \ell = \pm 1$$

$$\Delta m = 0, \pm 1$$

Energy is independent of

ℓ, m

$$n = 1, 2, 3, \dots$$

$$\ell = 0, \dots, n-1$$

$$m = -\ell, \dots, \ell$$

$$1s, 2s, 2p_x, 2p_y, 2p_z$$

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

Normalization

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

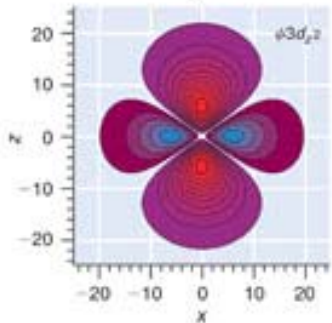
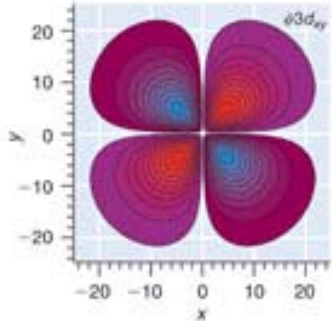
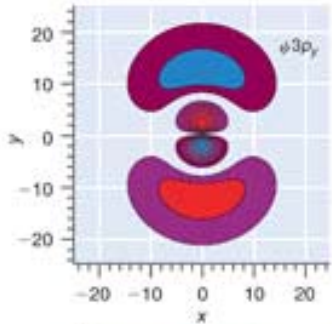
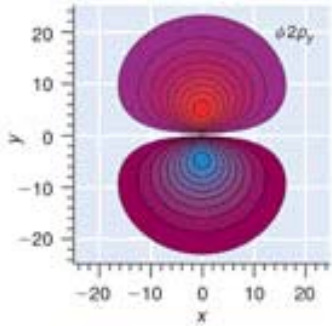
$$N = \frac{1}{2\sqrt{2\pi}} \left(\frac{1}{a_0} \right)^{3/2}$$

ψ^2 = probability density

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

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

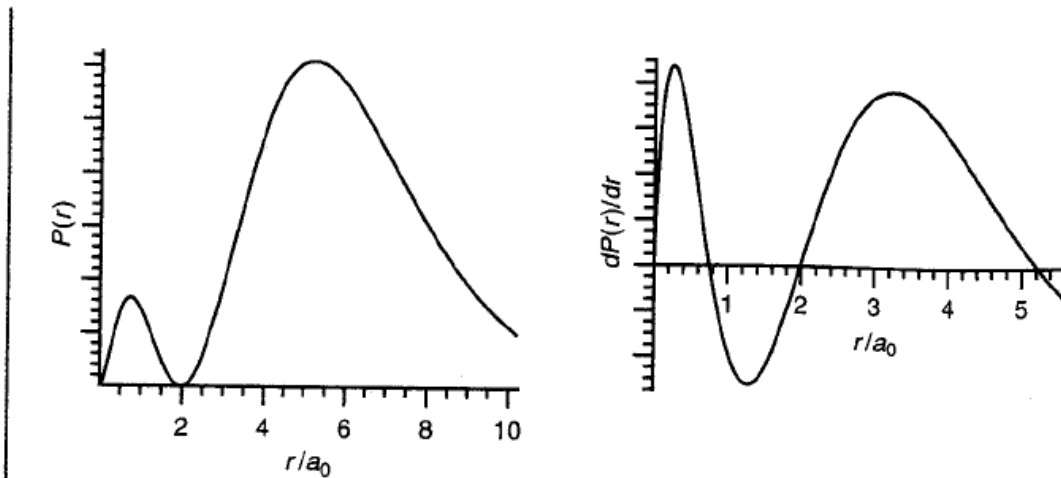
(We have integrated out ϕ and θ)



Maximum in radial distribution function of the 2s orbital?

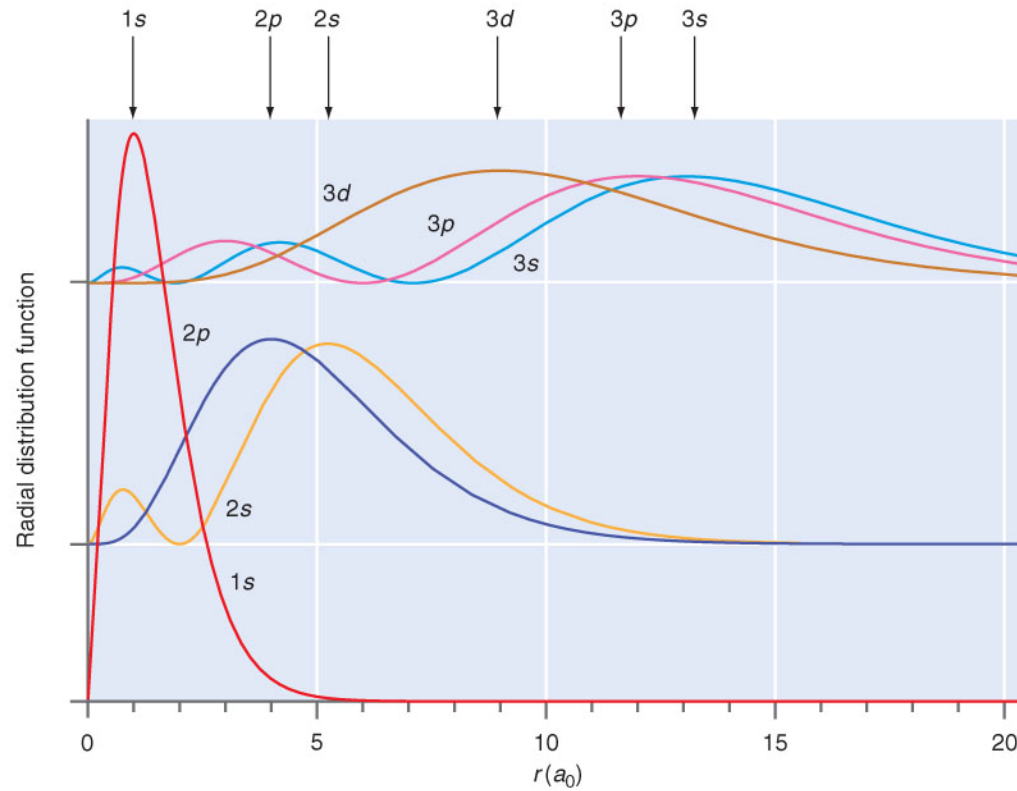
$$P(r) = \frac{1}{32\pi} \left(\frac{1}{a_0} \right)^3 r^2 \left(2 - \frac{r}{a_0} \right)^2 e^{-r/a_0}$$

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



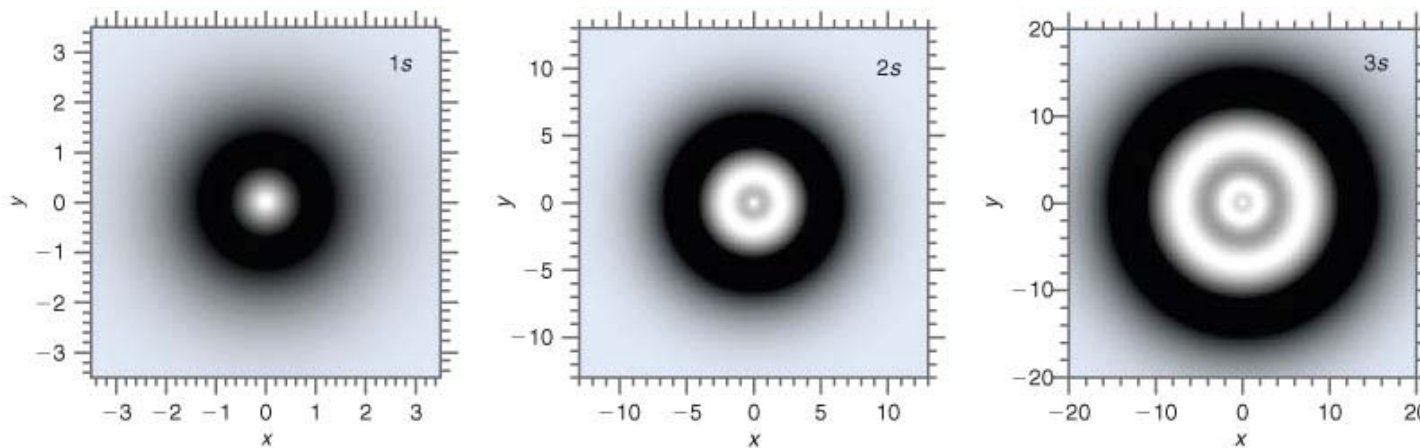
We see that the principal maximum in $P(r)$ is at $5.24 a_0$. This corresponds to the most probable distance of a 2s electron from the nucleus. The subsidiary maximum is at $0.76 a_0$. The minimum is at $2 a_0$.

Shell Model



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

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