Hydrogen atom

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze}{r}$$

Spherical coordinates

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

$$+ \frac{1}{r^2 \sin^2\theta}\partial^2/\partial\varphi^2$$

L^2

$$\psi(r,\theta,\varphi) = R(r)\, Y_{lm}(\theta,\varphi)$$

$$L^2\, Y_{lm} = l(l+1)\hbar^2\, Y_{lm}$$

$$\hat{H} = \left(-\frac{\hbar^2}{2\mu r^2} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r} \right)$$

centrifugal

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

For $l \neq 0$, $V_{eff}(r) = \frac{l(l+1)}{r^2} - \frac{Ze^2}{r}$

$$V_{eff}(r) \to +\infty \quad \text{as} \quad r \to 0$$

$$R(r) \to 0 \quad \text{as} \quad r \to 0$$

For $l = 0$, $V_{eff}(r) = -\frac{Ze^2}{r} \to -\infty$ as $r \to 0$

$$R(r) = \frac{g(r)}{r}$$

$r = \frac{\hbar^2}{\mu Z e^2} \rho$ → a_0 Bohr radius

$E = \frac{Ze^2}{a_0} \epsilon$ → atomic unit of energy

ρ → dimensionless length

ϵ → dimensionless energy

$$-\frac{d^2 g}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2} g - \frac{2}{\rho} g = 2\epsilon g$$

Case A:

For $\ell = 0$

Step 1: Look for solution at large ρ

$$g(\rho) \sim e^{-b\rho} \qquad b^2 = -2\epsilon$$

$$g(\rho) = \rho\, e^{-b\rho}$$ so that $g(\rho) = 0$ at $\rho = 0$

$$R(r) = \frac{g(r)}{r} \qquad R(\rho) = \frac{g(\rho)}{\rho}$$

No nodes $g_1(\rho)$: $\rho\, e^{-b\rho}$

$g_1(\rho)$ is an eigenfunction of the radial Schrödinger equation when $\ell = 0$

$$2\epsilon_1 = -1 \quad \text{or} \quad \boxed{\epsilon_1 = -\frac{1}{2}}$$

$\frac{1}{n^2}$ one node $g_2(\rho) = (c_0 \rho - c_1 \rho^2)\, e^{-b\rho}$

$$\epsilon_2 = -\frac{1}{8} = \frac{1}{4}\epsilon_1$$

two nodes $g_3(\rho) = (a\rho + b\rho^2 + c\rho^3)\, e^{-b\rho}$

$$\epsilon_3 = \frac{1}{9}\epsilon_1$$

Case B: $\ell \neq 0$

For large ρ $g(\rho) \sim e^{-b\rho}$

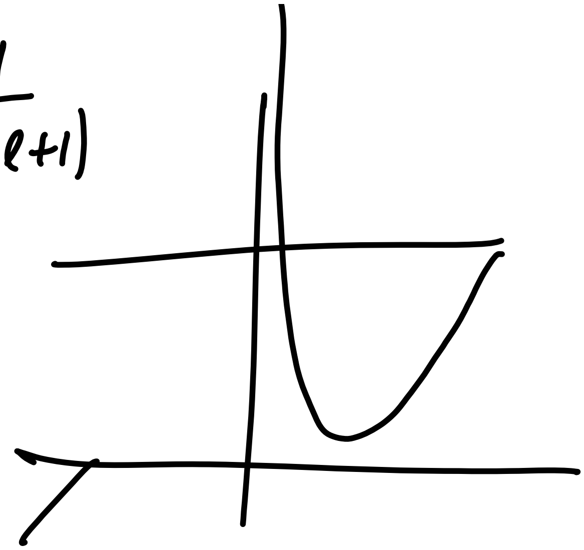
For small ρ, $g(\rho) \sim \rho^{-\ell}$ or $\rho^{\ell+1}$

$$g(\rho) = \rho^{\ell+1} e^{-b\rho} \times \text{polynomial in } \rho$$

$$\epsilon = -\frac{1}{2}\frac{1}{(\ell+1)^2}$$

$$V_{eff} = \frac{\ell(\ell+1)}{r^2} - \frac{Ze^2}{r}$$

$$V_{eff}^{min} = \frac{1}{\ell(\ell+1)}$$



$\ell < 0 \to n-1$

$$\frac{d V_{eff}}{d \rho} = 0$$

solve for ρ

V_{eff}

$$\Psi_{n\ell m} = R_{n\ell}(r) \; Y_{\ell m}(\theta, \varphi)$$

principal quantum number

$$R_{n\ell}(r) = r^{\ell} e^{-\frac{Zr}{n a_0}} \times \text{polynomial in } r$$

orbital angular momentum

# of nodes

$$R(r) = e^{-Zr/a_0} \times 1$$

$$\int R_{nl}^{*}(r)\, R_{nl}(r)\, r^2\, dr = \underline{1}$$

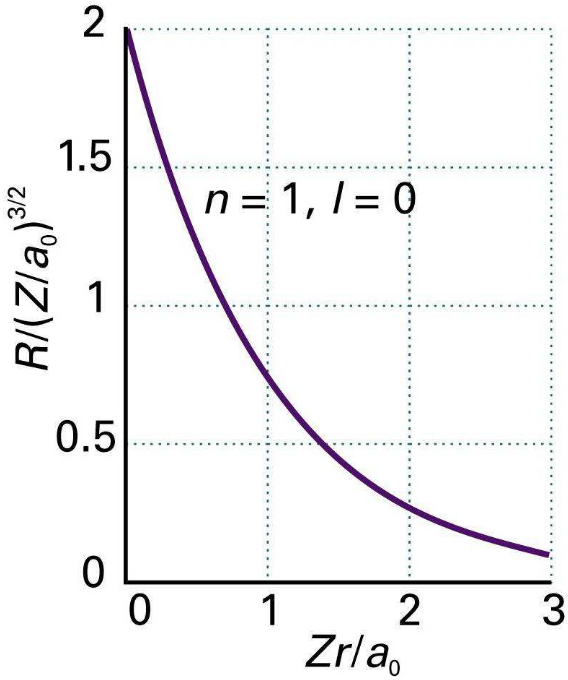


Figure 10-4a
Atkins Physical Chemistry, Eighth Edition

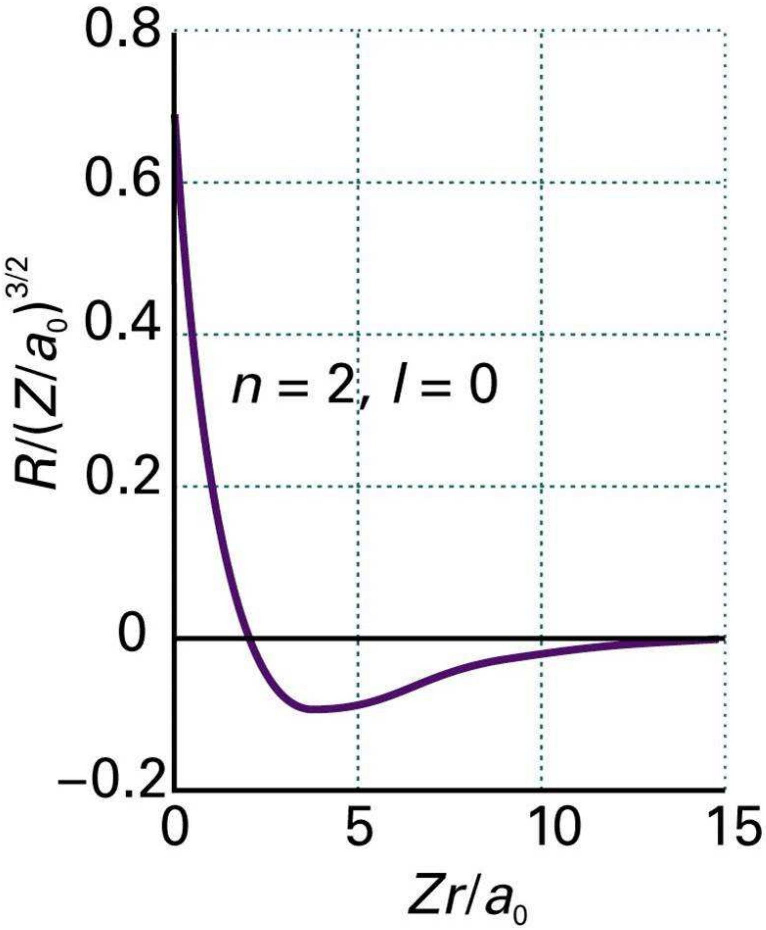


Figure 10-4b
Atkins Physical Chemistry, Eighth Edition

$$R_{21} = e^{-\frac{Zr}{2a_0}} \times \rho$$

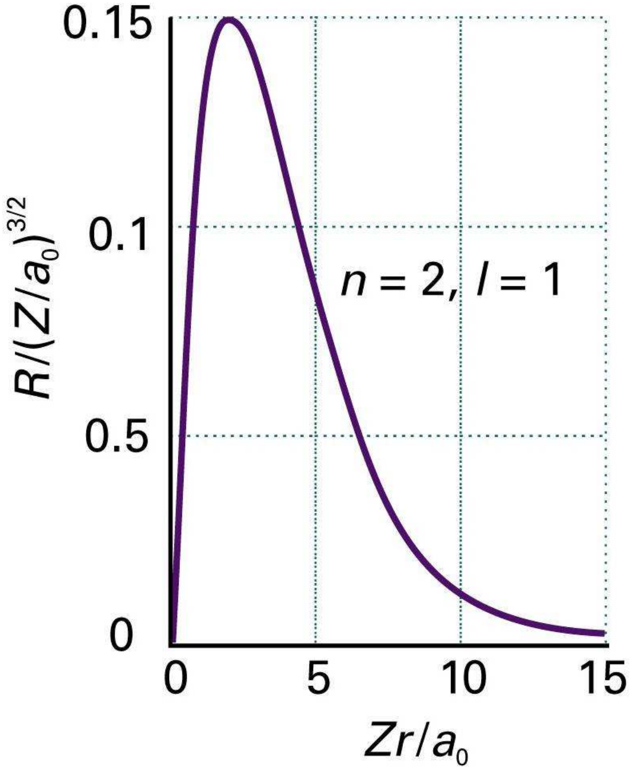


Figure 10-4d
Atkins Physical Chemistry, Eighth Edition

$$\langle r \rangle = \int R_{nl}^*(r)\ r\ R_{nl}(r)\ r^2\, dr \ \underbrace{\int Y_{lm}^*\, Y_{lm} \sin\theta\, d\theta\, d\varphi}_{1}$$

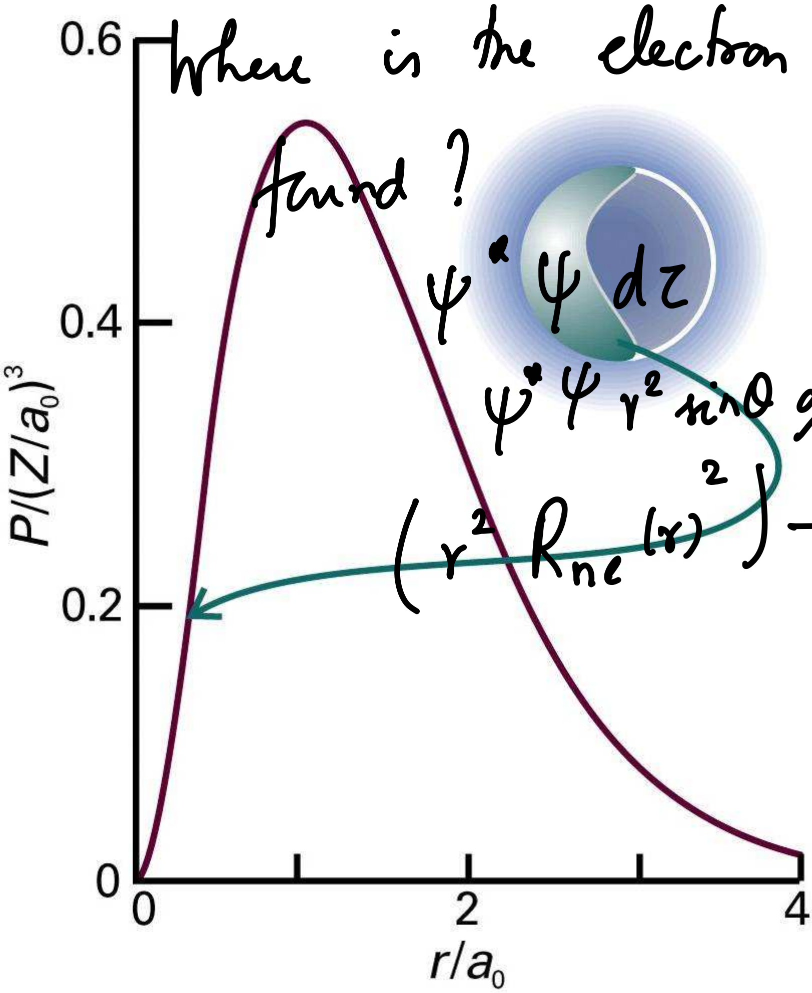
$$\langle O_p \rangle = \int \psi^*\, O_p\, \psi\, d\tau$$

$$\langle r \rangle = \int R_{nl}^*(r)\, Y_{lm}^*(\theta, \varphi)\, r\, R_{nl}(r)\, Y_{lm}(\theta, \varphi)\, r^2 \sin\theta\, dr\, d\theta\, d\varphi$$

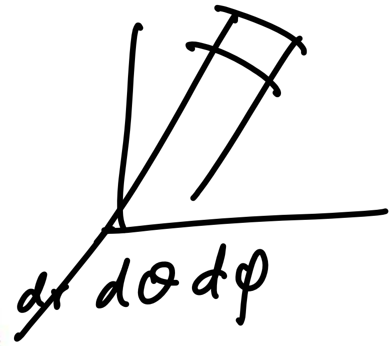
$$= \boxed{\int R_{nl}^*(r)\, R_{nl}(r)\, r^2\, dr} \times \int\int Y_{lm}^*(\theta, \varphi)\, Y_{lm}(\theta, \varphi) \sin\theta\, d\theta\, d\varphi$$

$$1$$

Where is the electron most likely to be found?



$\psi^* \psi \, d\tau$



$\psi^* \psi \, r^2 \sin\theta \, dr \, d\theta \, d\phi$

$\left(r^2 R_{nl}(r)^2 \right) \to$ maximized

$r^2 R_{1s}^2$ is maximum at $r = a_0$ (Bohr radius)

Figure 10-14
Atkins Physical Chemistry, Eighth Edition

$$\psi = R(r)\, Y_{lm}(\theta, \varphi)$$

$$\psi^* \psi\, d\tau = R^2 \left| Y_{lm} \right|^2 r^2\, dr \sin\theta\, d\theta\, d\varphi$$

$$\langle r \rangle \neq r_{mp}$$

$$\sqrt{\langle r^2 \rangle} = \sqrt{\int R_{nl}(r)\; r^2\, R_{nl}(r)\, \cancel{r}^{2}\, dr}$$

Statistics of the minor

Class average = 32

Std dev = 14

Max = 67

Min < 0