Hydrogen atom

CML101

IIT Delhi

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Recap

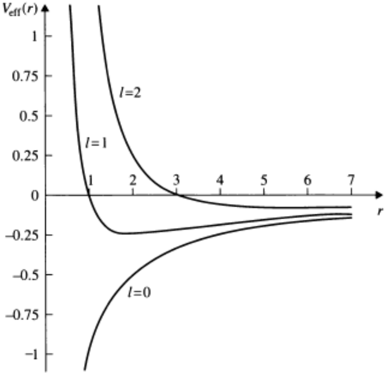
$$\hat{\mathcal{H}} = -\frac{1}{2}\nabla^2 - \frac{1}{r}; \quad \hat{\mathcal{H}}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

$$\left[\frac{1}{2r^2}\frac{d}{dr}r^2\frac{d}{dr} + \left(E + \frac{1}{r} - \frac{l(l+1)}{2r^2}\right)\right]R(r) = 0$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta} + \left[l(l+1) - \frac{m^2}{\sin^2\theta}\right]P(\theta) = 0$$

$$\frac{d^2Q}{d\phi^2} + m^2Q = 0$$

Effective potential energy



- When $l = 0$, $V_{eff}(0) = -\infty$

$$R(0) \neq 0$$

- When $l \neq 0$, $V_{eff}(0) = +\infty$

$$R(0) = 0$$

Ground state: guess $R_{gs}(r) = \mathrm{e}^{-\frac{r}{a_0}}$ - no node

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right) - \frac{e^2}{4\pi\epsilon_0 r}\right]R_{gs}(r) = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}$$

$$E_{gs} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} = -13.6 \text{ eV} = -\frac{1}{2} \text{ hartree}$$

$$N^2\int_0^\infty R_{gs}^* R_{gs}\, r^2 dr = 1$$

$$R_{gs}(r) = R_{10}(r) = \frac{2}{a^{3/2}}\mathrm{e}^{-\frac{r}{a_0}}$$

An excited state: guess $R_{es}(r) = \left(2 - \frac{r}{a_0}\right) \mathrm{e}^{-\frac{r}{2a_0}}$ - one node

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right) - \frac{e^2}{4\pi\epsilon_0 r}\right] R_{es}(r) = -\frac{1}{4}\frac{me^4}{32\pi^2\epsilon_0^2\hbar$$

$$E_{es} = -\frac{1}{4}\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} = -\frac{13.6}{4}\ \mathrm{eV} = \frac{1}{8}\ \mathrm{hartree}$$

Normalized form of $R_{es}(r)$

$$R_{es}(r) = R_{20}(r) = \left(2 - \frac{r}{a_0}\right)\frac{1}{2\sqrt{2}a_0^{3/2}}\mathrm{e}^{-\frac{r}{2a_0}}$$

Another excited state - $R_{aes}(r) = r\left(4 - \frac{2r}{3a_0}\right) \mathrm{e}^{-\frac{r}{3a_0}}$

Orbital angular momentum $l = 1$

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right) + \frac{1(1+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}\right] R_{aes} =$$

$$E_{aes} = -\frac{1}{9}\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} = -\frac{13.6}{9}\ \mathrm{eV} = \frac{1}{18}\ \mathrm{hartree}$$

Normalized form of $R_{aes}(r)$

$$R_{aes}(r) = R_{31}(r) = \frac{1}{27\sqrt{6}a_0^{3/2}} r\left(4 - \frac{2r}{3a_0}\right) \mathrm{e}^{-\frac{r}{3a_0}}$$

Radial wavefunctions

$$R_{nl}(r) = N_{nl} r^{l} \mathrm{e}^{-\frac{r}{na_0}} L_{nl}$$

Note: Atkins defines $\mathrm{e}^{-\frac{\rho}{2}}$ where $\rho = \frac{2r}{na_0}$

- Asymptotic solution when $r \to 0$ is r^l
- Asymptotic solution when $r \to \infty$ is $\mathrm{e}^{-\frac{r}{na_0}}$
- Polynomial L_{nl} of degree $(n - l - 1)$ for intermediate r

Quantum numbers obtained from $R(r)$

$$R_{nl}(r) = N_{nl} r^{l} \mathrm{e}^{-\frac{r}{n a_0}} L_{nl}$$

- Principal quantum number n - exponential term
- Orbital quantum number l - exponent in r^l
- Radial nodes $(n - l - 1)$ determined by degree of L_{nl}

Find n and l for the state with

$$R(r) = \frac{1}{(243 a_0^3)^{1/2}} \left(6 - \frac{4r}{a_0} + \frac{4r^2}{9a_0^2} \right) \mathrm{e}^{-\frac{r}{3a_0}}$$

Plots of radial wavefunctions

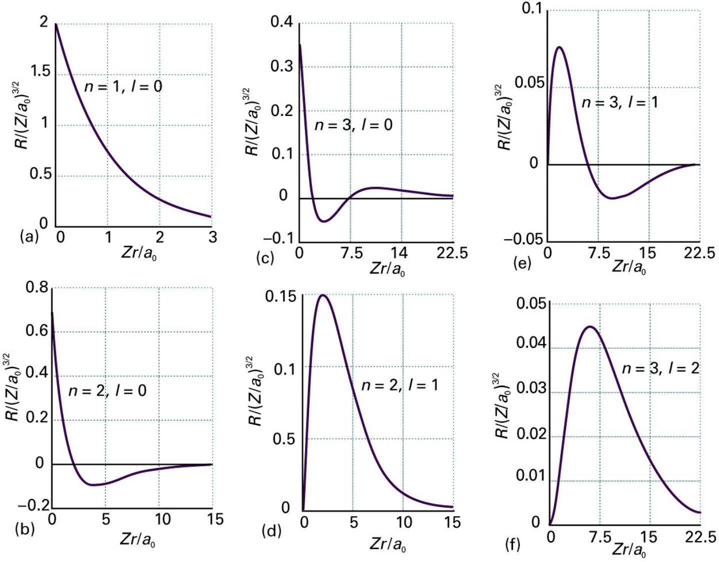


Figure 10-4
Atkins Physical Chemistry, Eighth Edition

Energy of H-atom $= -Z^2/2n^2$

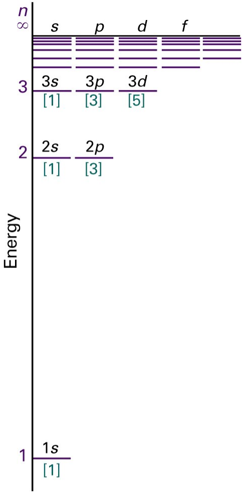


Figure 10-7
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Probability around a location

Electrons without angular momentum have a finite probability of being at the nucleus

Born postulate - Probability of finding the electron in a volume dV at a point is $\psi^*\psi dV$.

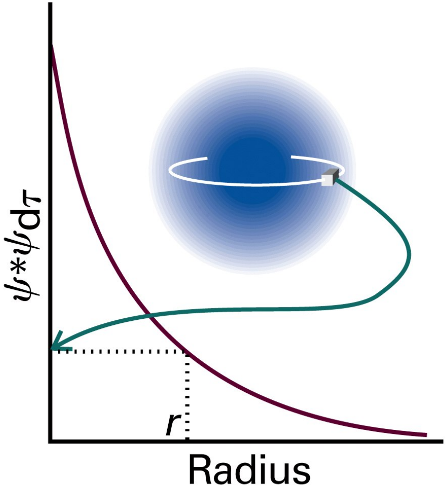

Figure 10-13
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Probability in a spherical shell

Probability of finding the electron in a spherical shell is called the radial probability distribution/density.

$$\int_0^{\pi}\int_0^{2\pi}\psi^*\psi\,\sin\theta\,d\theta\,d\phi$$

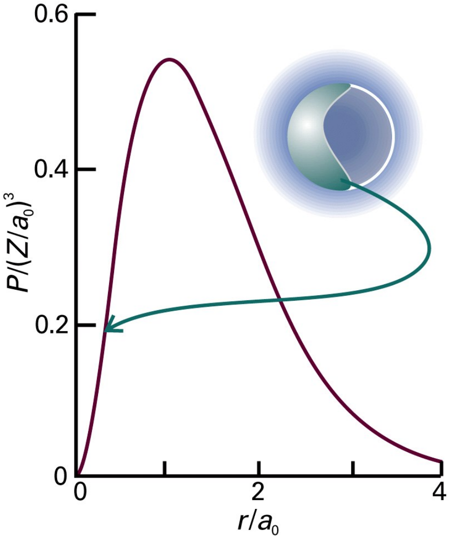

Figure 10-14
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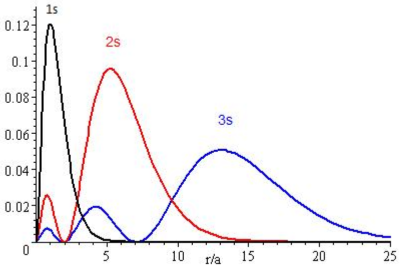
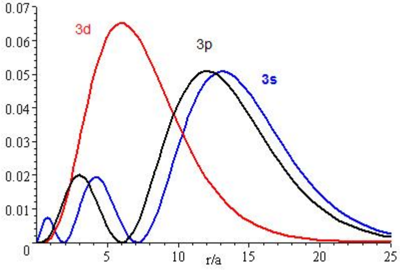
Where is an electron most likely to be found?





Where will a gs electron be found?

Angular solutions determine shapes of orbitals

$$\hat{\mathcal{H}} = -\frac{1}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$\hat{\mathcal{H}} = -\frac{1}{r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2r^2} - \frac{1}{r}$$

$$\hat{\mathcal{H}}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

Angular momentum is quantized

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin\theta}\right)\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{\hbar^2}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)$$

Solutions are denoted $Y_{lm}(\theta, \phi)$ and eigenvalues are $l(l+1)\hbar^2$

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

Possible values for l are 0, 1, 2, $\cdots$.

Angular wavefunctions are products of θ and ϕ solutions

$$Y(\theta, \phi) = P(\theta) Q(\phi)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta} + \left[l(l+1) - \frac{m^2}{\sin^2\theta}\right] P(\theta) = 0$$

$$\frac{d^2 Q}{d\phi^2} + m^2 Q = 0$$

$Q(\phi)$ is $A\mathrm{e}^{im\phi}$

$$\frac{d^2Q(\phi)}{d\phi^2} = -m^2Q(\phi)$$

$$Q(\phi) = A\mathrm{e}^{im\phi}$$

"Single-valuedness" of

$$Q \implies Q(\phi) = Q(\phi + 2\pi)$$

$$m = 0, \pm 1, \pm 2, \cdots$$

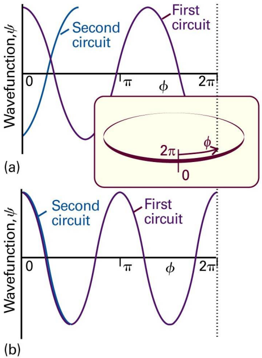


Figure 9-28
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$$A = 1/\sqrt{\int^{2\pi} d\phi} = \frac{1}{\sqrt{2\pi}}$$

$P(\theta)$ are solutions of a well-known DE

$$(1-x^2)\frac{d^2P}{dx^2}-2x\frac{dP}{dx}+\left(l(l+1)-\frac{m^2}{1-x^2}\right)P=0$$

where

$$x=\cos\theta$$

Acceptable solutions when l is a positive integer and $|m|\leq l$. They are denoted $P_{l|m|}$. Normalization of $P_{l|m|}$ is given by

$$\int_0^{\pi}|P_{l|m|}|^2\sin\theta d\theta=1$$

$P(\theta)$ are polynomials in $\cos\theta$

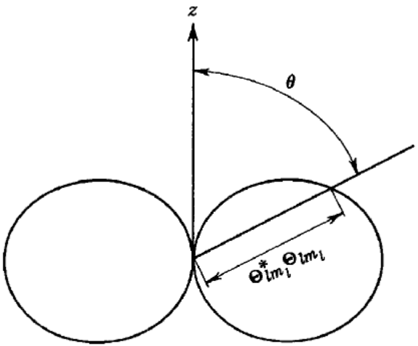
$$P_{00} = \frac{1}{2}\sqrt{2}$$

$$P_{10} = \sqrt{\frac{3}{2}}\cos\theta$$

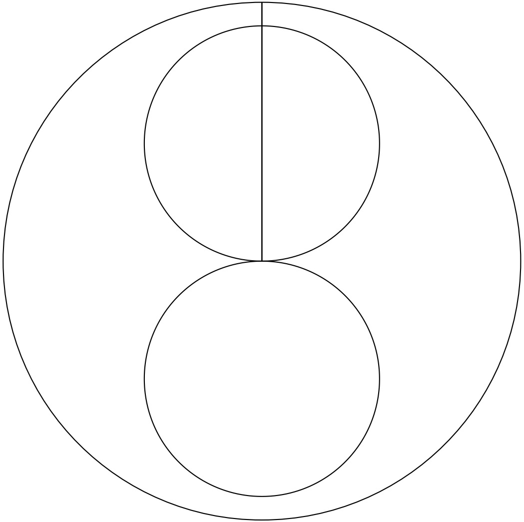
$$P_{1\pm1} = \sqrt{\frac{3}{4}}\sin\theta$$

$$P_{20} = \sqrt{\frac{5}{8}}\left(3\cos^2\theta - 1\right)$$

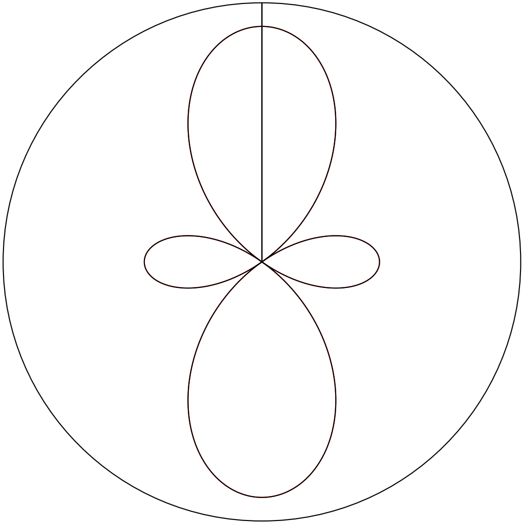
Polar plots show the distance from the origin, equal to the value of $P_l^{m*} P_l^m$, to the curve at θ



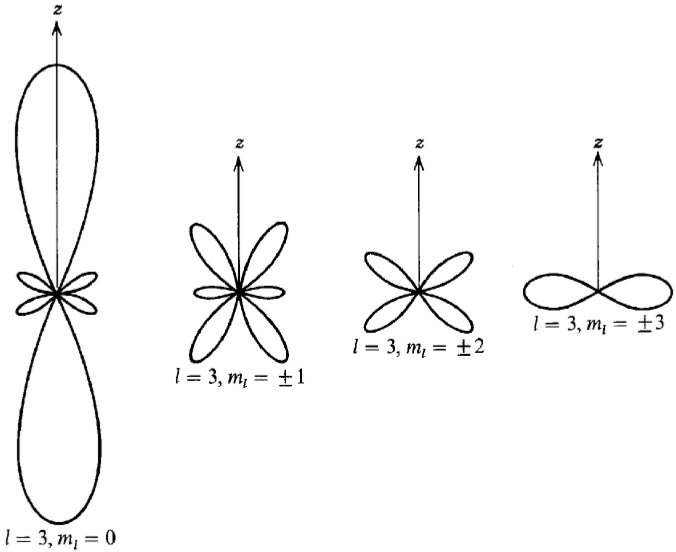
P_{10} is the p_z orbital



P_{20} is the d_{z^2} orbital



Polar plots of f orbitals



Y_{lm} is a product of $P_{l|m|}$ and Q_m

Wavefunctions of the square of the angular momentum are

$$Y_{lm} = P_{l|m|}(\theta) Q_m(\phi)$$

For example,

$$Y_{2-1} = P_{2\pm1}(\theta) Q_{-1}(\phi) = \sqrt{\frac{15}{4}} \sin\theta \cos\theta \frac{1}{\sqrt{2}} \mathrm{e}^{-i\phi}$$

p_x orbital is a linear combination of Y_{11} and Y_{1-1}

$$
\begin{aligned}
\frac{Y_{11} + Y_{1-1}}{\sqrt{2}} &= \sqrt{\frac{3}{4}} \sin\theta \frac{(\exp(i\phi) + \exp(-i\phi))}{\sqrt{2}} \\
&= \sqrt{\frac{3}{4}} \sqrt{2} \sin\theta \cos\phi
\end{aligned}
$$

The angular part looks like $\sin\theta\cos\phi$ which is identical to $x = r\sin\theta\cos\phi$. Orbitals oriented along any Cartesian axes ($p_y, d_{xy}, d_{x^2-y^2}, \cdots$) formed by linearly combining appropriate Y_{lm}.

Y_{lm} are simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$

Y_{lm} are eigenfunctions of $\hat{L}^2$ with eigenvalue $l(l+1)\hbar^2$

$$-\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y_{2-1} = 2(3)\hbar^2 Y_{2-1}$$

$$\hat{L}_z Y_{2-1} = -i\hbar\frac{\partial}{\partial\phi}Y_{2-1} = -1\hbar Y_{2-1}$$

$\psi_{nlm}(r,\theta,\phi)$ are products of r, θ, and ϕ parts

$$R_{nl}(r)Y_{lm}(\theta,\phi) = R_{nl}(r)P_{l|m|}(\theta)Q_m(\phi)$$

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{a_0}}$$

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

$$\psi_{322} = \frac{1}{81\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \sin^2\theta e^{i2\phi}$$

Real hydrogen atom wavefunctions

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \cos\theta$$

$$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \sin\theta \cos\phi$$

$$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \sin^2\theta \cos 2\phi$$