Angular momentum and shapes of orbitals

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Angular solutions determine shapes of orbitals

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) - \frac{e^2}{4\pi\epsilon_0 r}$$

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}$$

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

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

Solutions of radial Schrödinger equation are $R(r)$.

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, $\cdots$.

Separation of θ and ϕ is possible

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

$$\left[-\left(\frac{1}{\sin\theta}\right)\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right] PQ = l(l+1)PQ$$

$$-Q\left(\frac{1}{\sin\theta}\right)\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) P - P\frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) Q = l(l+1)PQ$$

Multiply by $\frac{\sin^2\theta}{PQ}$

$$-\frac{\sin\theta}{P}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) P(\theta) - l(l+1)\sin^2\theta = \frac{1}{Q}\left(\frac{\partial^2}{\partial\phi^2}\right) Q(\phi)$$

Separation constant $-m^2$

$Q(\phi)$ is $Ae^{im\phi}$

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

$$Q(\phi) = Ae^{im\phi}$$

"Single-valuedness" of $Q \implies Q(\phi) = Q(\phi + 2\pi)$

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

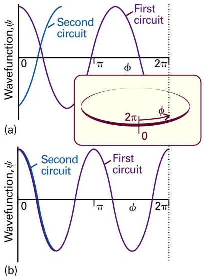


Figure 9-28
Atkins Physical Chemistry, Eighth Edition

Normalization of Q gives A

$$A = \frac{1}{\sqrt{\int_0^{2\pi} d\phi}} = \frac{1}{\sqrt{2\pi}}$$

$P(\theta)$ 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 $\cos\theta$

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

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

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

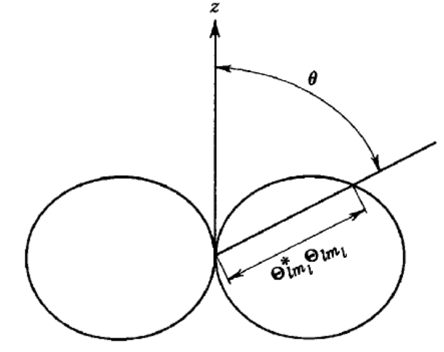
$$P_{20} = \sqrt{\frac{5}{8}}\left(3\cos^2\theta - 1\right)$$

$$P_{2\pm1} = \sqrt{\frac{15}{4}}\sin\theta\cos\theta$$

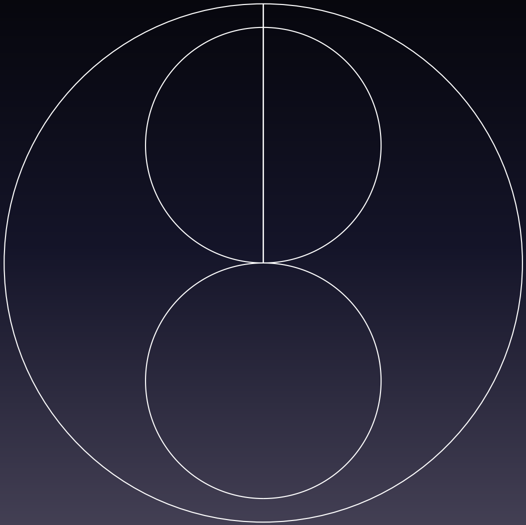
$$P_{2\pm2} = \sqrt{\frac{15}{16}}\sin^2\theta$$

Shapes of the atomic orbitals are determined by $P(\theta)$.

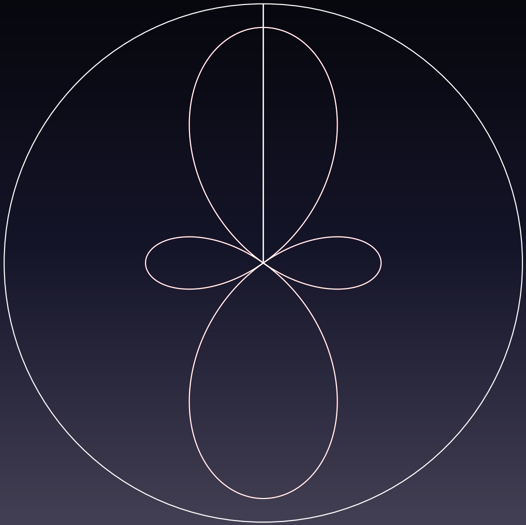
Polar plots of wavefunctions



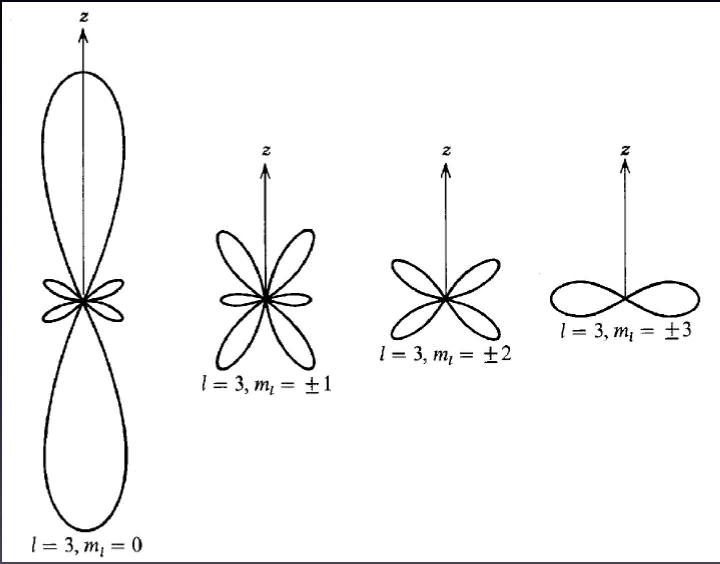
P_{10} is the p_z orbital



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



Polar plots of wavefunctions



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,

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

$$Y_{10} = P_{10}(\theta)Q_0(\phi) = \sqrt{\frac{3}{2}}\cos\theta\frac{1}{\sqrt{2}}$$

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

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

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 $\left(p_y, d_{xy}, d_{x^2-y^2}, \cdots\right)$ 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 $l(l+1)\hbar^2$

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

Y_{lm} are also eigenfunctions of $\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$ with eigenvalue $m\hbar$

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

Hydrogen atom wavefunctions are products of r, θ, and ϕ parts

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

$n = 1, 2, 3, \cdots; l = 0, 1, \cdots, (n-1);$
$m = -l, -(l-1), \cdots, (l-1), l$

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

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

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

Energy of hydrogen atom independent of l and m.

Real hydrogen atom wavefunctions

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

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

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

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

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