5.1 The Born-Oppenheimer approximation

So far we have tacitly assumed that the motion of the electrons can be described separately from the motion of the nuclei. This assumption is also implicit in general chemistry, when we picture a molecule as a nuclear framework bound together by molecular orbitals. Its theoretical justification is the *Born-Oppenheimer approximation,* which is based on the fact that nuclei are much heavier than electrons ($m_p/m_e = 1836$), and therefore much slower. Unless we need very high accuracy, the motion of the nuclei can be ignored completely when we are interested in the electrons. That is, we treat the nuclei as 'clamped' in position while we work out the electronic wavefunction. This gives us the 'clamped-nucleus' electronic Hamiltonian,

$$H_{\text{elec}} = \hat{T}_e + \hat{V}\left(\boldsymbol{Q},\boldsymbol{q}\right)$$

and the *electronic Schrodinger equation,*

$$H_{\text{elec}}\psi_{\text{elec}}\left(\boldsymbol{q};\boldsymbol{Q}\right) = E_{\text{elec}}\left(\boldsymbol{Q}\right)\psi_{\text{elec}}\left(\boldsymbol{q};\boldsymbol{Q}\right)$$

which is the first half of the Born-Oppenheimer approximation.

$$H_{\text{elec}}\psi_{\text{elec}}(\boldsymbol{q};\boldsymbol{Q}) = E_{\text{elec}}(\boldsymbol{Q})\psi_{\text{elec}}(\boldsymbol{q};\boldsymbol{Q}) \qquad (1)$$

This equation includes the electronic kinetic energy $\hat{T}_e$ and the total potential energy $V(\boldsymbol{Q},\boldsymbol{q})$, which depends on the positions of the electrons $\boldsymbol{q}$, with the nuclei clamped at position $\boldsymbol{Q}$.

If we are just interested in the electronic energy levels and orbitals at one particular nuclear geometry (e.g. the equilibrium geometry), then we solve eq. (1) once, with $\boldsymbol{Q}$ set equal to the nuclear positions at this geometry.

However, if we also want to treat the nuclear motion, we must solve this eq at many different nuclear positions $\boldsymbol{Q}$, in order to obtain $E_{\text{elec}}(\boldsymbol{Q})$ as a function of $\boldsymbol{Q}$. $E_{\text{elec}}(\boldsymbol{Q})$ is then used as the potential energy in the *nuclear hamiltonian,*

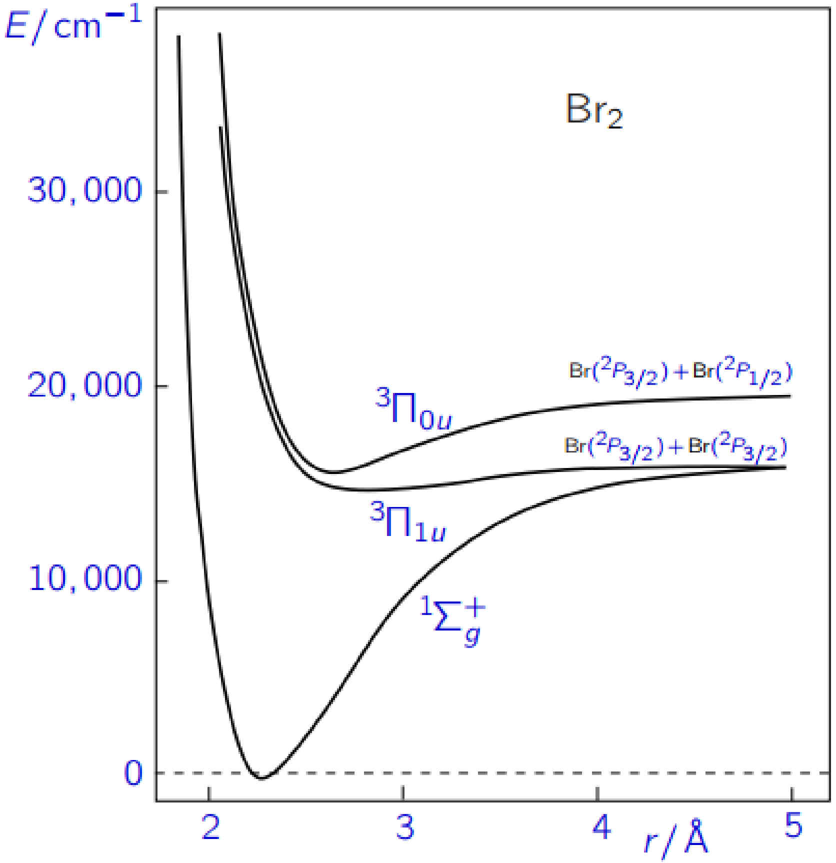
$$H_{\text{nuc}} = \hat{T}_N + V_{\text{elec}}(\boldsymbol{Q})$$

where $\hat{T}_N$ is the nuclear kinetic energy operator. The nuclear wave function $\psi_{\text{nuc}}(\boldsymbol{Q})$ is calculated by solving the *nuclear dynamics Schrodinger equation,*

$$H_{\text{nuc}}\psi_{\text{nuc}}(\boldsymbol{Q}) = E\psi_{\text{nuc}}(\boldsymbol{Q})$$

where E is the total energy.

- Note that each electronic energy level gives rise to its own potential energy function $E_{\mathrm{elec}}(\boldsymbol{Q})$. In general, these functions are completely different, because the bonding described by each electronic energy level is different.
- The diagram shows the potential energy curves $E_{\mathrm{elec}}(r)$ for the three lowest electronic energy levels of the Br_2 molecule. The symbols are standard labels for the electronic energy levels which will be explained.



Each of the curves in the above diagram has a set of vibrational wave functions $\psi_{\text{nuc}}(\boldsymbol{Q})$ and energy levels E associated with it, which we could calculate by solving

$$H_{\text{nuc}}\psi_{\text{nuc}}\left(\boldsymbol{Q}\right) = E\psi_{\text{nuc}}\left(\boldsymbol{Q}\right)$$

separately for each curve. Note that E is the total (electronic + vibrational) energy, and that the energy differences between successive E are the vibrational energy spacings. The zero point energy is the difference between the lowest E and the potential $E_{\text{elec}}(\boldsymbol{Q})$ at equilibrium (i.e. the lowest energy point).

In a practical calculation, one sometimes approximates each of the potential curves using a Morse potential, or, if only low-lying vibrations are of interest, using a harmonic oscillator potential.

The *total wave function* $\psi_{\text{tot}}(\boldsymbol{q},\boldsymbol{Q})$ describing the combined motion of all the electrons and nuclei in the molecule is the product,

The Born-Oppenheimer approximation is usually very accurate, although it can break down when different potential surfaces get close together.

5.2 The hydrogen atom

In the hydrogen atom there is only one nucleus, and we take it to be clamped at the origin of coordinates. We consider the general 'hydrogen-like' one-electron atom, with nuclear charge Ze. The potential energy is

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

and the kinetic energy is

$$\hat{T} = \frac{\boldsymbol{p}^2}{2m_e} = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m_e}\nabla^2$$

It is more convenient to express this in spherical polar coordinates, using the expression for ∇^2 :

$$\hat{T} = -\frac{\hbar^2}{2m_e}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

The hydrogen atom Hamiltonian

For the hydrogen-like atom, then,

$$H = T + V = -\frac{\hbar^2}{2m_e}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

We can recognise in the angular part of the kinetic energy the expression for the square of the angular momentum, but in the case of the hydrogen atom it is conventional to use the symbol $\hat{\boldsymbol{l}}$ for the orbital angular momentum of the electron, reserving $\hat{\boldsymbol{J}}$ (or $\hat{\boldsymbol{j}}$) for the total angular momentum including spin.

The complete Hamiltonian is then

$$H = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hat{\boldsymbol{l}}^2}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

Note that the radial part can be written in several equivalent ways:

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\psi = \frac{1}{r}\frac{\partial^2}{\partial r^2}r\psi = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\psi$$

Atomic units

The H atom Hamiltonian is rather cluttered with fundamental constants. To get rid of the clutter, we use *atomic units*:

Unit	Symbol	Name	Definition	SI value
Length	a_0	bohr	$4\pi\epsilon_o\hbar^2/m_e e^2$	52.917721 pm
Mass	m_e	electron mass		0.910938×10^{-30} kg
Charge	e	proton charge		$1.6021765 \times 10^{-19}$ C
Energy	E_h	Hartree	$e^2/4\pi\epsilon_o a_o$	4.359744×10^{-18} J
Angular momentum	$\hbar$			$1.0545717 \times 10^{-34}$ Js

When we work in atomic units, m_e, e, $\hbar$ and $4\pi\epsilon_o$ all have a numerical value of 1, as do the quantities a_0 and E_h derived from them.

This simplifies the equations, but has the disadvantage that it becomes difficult to check the dimensions of an expression.

We write $r' = r/a_0$, and find that

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Ze^2}{4\pi\epsilon_0 a_0 r'} = -\frac{Z}{r'}E_h$$

Similarly, writing $\hat{\boldsymbol{l}}' = \hat{\boldsymbol{l}}/\hbar$, the angular kinetic energy becomes

$$\frac{\hat{\boldsymbol{l}}^2}{2m_e r^2} = \frac{\hbar^2}{m_e a_0^2}\frac{\hat{\boldsymbol{l}}'^2}{2r'^2} = \frac{\hbar^2}{m_e a_0}\frac{m_e e^2}{4\pi\epsilon_0\hbar^2}\frac{\hat{\boldsymbol{l}}'^2}{2r'^2} = E_h\frac{\hat{\boldsymbol{l}}'^2}{2r'^2}$$

In this way we find

$$H/E_h = -\frac{1}{2r'^2}\frac{\partial}{\partial r'}r'^2\frac{\partial}{\partial r'} + \frac{\hat{\boldsymbol{l}}'^2}{2r'^2} - \frac{Z}{r'}$$

or, dropping the primes, and remembering that energies will be in Hartree,

$$H = -\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hat{\boldsymbol{l}}^2}{2r^2} - \frac{Z}{r}$$

5.3 Wavefunctions for the hydrogen atom

The Hamiltonian contains the angular variables only as the operator $\hat{\boldsymbol{l}}^2$; the potential energy depends only on r. Knowing that the eigenfunctions of $\hat{\boldsymbol{l}}^2$ are the spherical harmonics, we look for solutions of the form $\psi(r,\theta,\varphi) = R(r)Y_{lm}(\theta,\varphi)$. We get

$$H\psi = -\frac{1}{2}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{\hat{\boldsymbol{l}}^2}{r^2}\right)RY_{lm} - \frac{Z}{r}RY_{lm} = ERY_{lm}$$

and since $\hat{\boldsymbol{l}}^2 Y_{lm} = l(l+1)Ylm$ we can cancel out Y_{lm} to get the *radial equation*

$$-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} + \frac{l(l+1)}{2r^2}R - \frac{Z}{r}R = ER$$

For each value of l (i.e., $0, 1, 2,$ ...) there are infinitely many solutions of this equation. They are conventionally labelled by the *principal quantum number* n, which runs from $l+1$ to ∞.

The quantum number m has dropped out of this eq, so the radial wavefunctions don't depend on m. We label them R_{nl}, and the complete wavefunction is $\psi_{nlm} = Rnl(r)Y_{lm}(\theta,\varphi)$.

Solution of R equation

$$-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r}+\frac{l(l+1)}{2r^2}R-\frac{Z}{r}R=ER$$

In this eq, write $\rho = Zr$. Then $\frac{\partial}{\partial r} = Z\frac{\partial}{\partial \rho}$ and we get

$$-\frac{Z^2}{2\rho^2}\frac{\partial}{\partial \rho}\rho^2\frac{\partial R}{\partial \rho}+\frac{Z^2 l(l+1)}{2\rho^2}R-\frac{Z^2}{\rho}R=ER$$

or

$$-\frac{1}{2\rho^2}\frac{\partial}{\partial \rho}\rho^2\frac{\partial R}{\partial \rho}+\frac{l(l+1)}{2\rho^2}R-\frac{1}{\rho}R=\frac{E}{Z^2}R$$

So the radial equation is the same for all Z, except that the energies scale with Z^2.

$$E=-\left(\frac{h^2}{8\pi^2 m a_0^2}\right)\cdot\frac{Z^2}{n^2}=-R\frac{Z^2}{n^2}$$

R is called Rydberg constant with the value of 13.6 eV

necessary condition: n ≥ l+1

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

$l = 0, 1, 2, \ldots\ldots$

n: Principal quantum number

The first few normalized radial wavefunctions are, writing $\rho = Zr$

$$R_{1s} = Z^{3/2} 2\exp(-\rho)$$

$$R_{2s} = Z^{3/2} \sqrt{\frac{1}{8}} \left(2-\rho\right) \exp(-\rho/2)$$

$$R_{2p} = Z^{3/2} \sqrt{\frac{1}{24}} \rho \exp(-\rho/2)$$

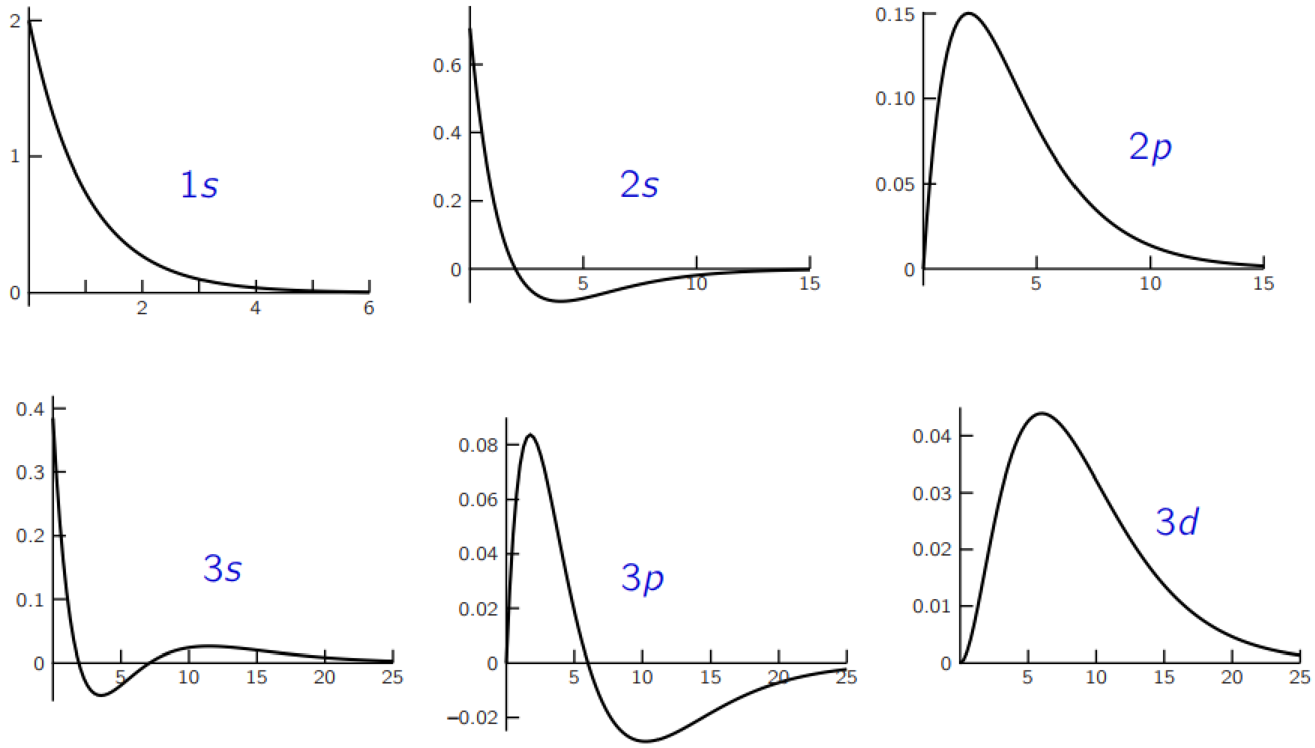
$$R_{3s} = Z^{3/2} \frac{2}{81} \sqrt{\frac{1}{3}} \left(27-18\rho+2\rho^2\right) \exp(-\rho/3)$$

$$R_{3p} = Z^{3/2} \frac{4}{81} \sqrt{\frac{1}{6}} \left(6\rho-\rho^2\right) \exp(-\rho/3)$$

$$R_{3d} = Z^{3/2} \frac{4}{81} \sqrt{\frac{1}{30}} \rho^2 \exp(-\rho/3)$$

As is customary, we write nl using the letters s, p, d, f, ... to represent $l = 0, 1, 2, 3, \ldots$.Each of these has to be multiplied by one of the corresponding Y_{lm} ($l = 0$ for s, 1 for p, etc.). For each value of l, m can have any integer value from $-l$ to l, so there are three $2p$ orbitals, five $3d$ orbitals, and so on.

Radial wavefunctions for hydrogen



These are the functions of the previous slide, with $Z = 1$. Note the differences in horizontal and vertical scales; the functions with higher principal quantum number extend much further from the nucleus.

Radial probability density

The probability of finding the electron in an element of volume $\mathrm{d}v$ is $|\psi|^2\mathrm{d}v = |\psi|^2 r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi$, where ψ is the normalized wavefunction for the electron.

If we integrate over the angles we get the probability of finding the electron in a spherical shell between r and $r + \mathrm{d}r$:

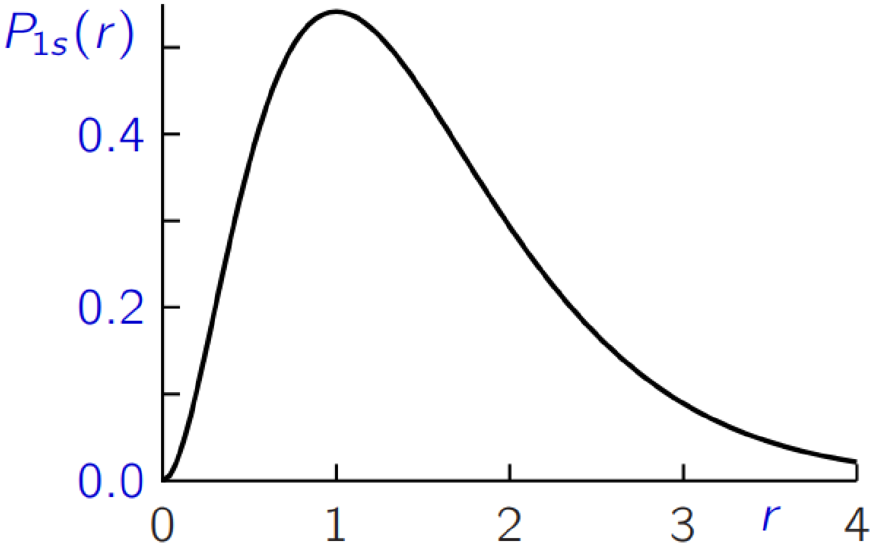
$$
\begin{aligned}
P_{nl}(r)\mathrm{d}r &= \int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}|\psi|^2 r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi \\
&= \int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\left(R_{nl}Y_{lm}\right)^* R_{nl}Y_{lm} r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi \\
&= r^2 R_{nl}^2 \mathrm{d}r \int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi} Y_{lm}{}^* Y_{lm} \sin\theta \mathrm{d}\theta\mathrm{d}\varphi \\
&= r^2 R_{nl}^2 \mathrm{d}r
\end{aligned}
$$

$P_{nl}(r)$ is called the *radial probability density.* Note that it is independent of m

E.g., for hydrogen $1s$,

$$\psi = R_{1s}(r)Y_{00}(\theta,\varphi)$$

$$= 2e^{-r} \times \sqrt{\frac{1}{4\pi}}$$



so

$$P_{1s}(r) = r^2(R_{1s})^2 = 4r^2e^{-2r}$$

To find the maximum in $P_{1s}(r)$:

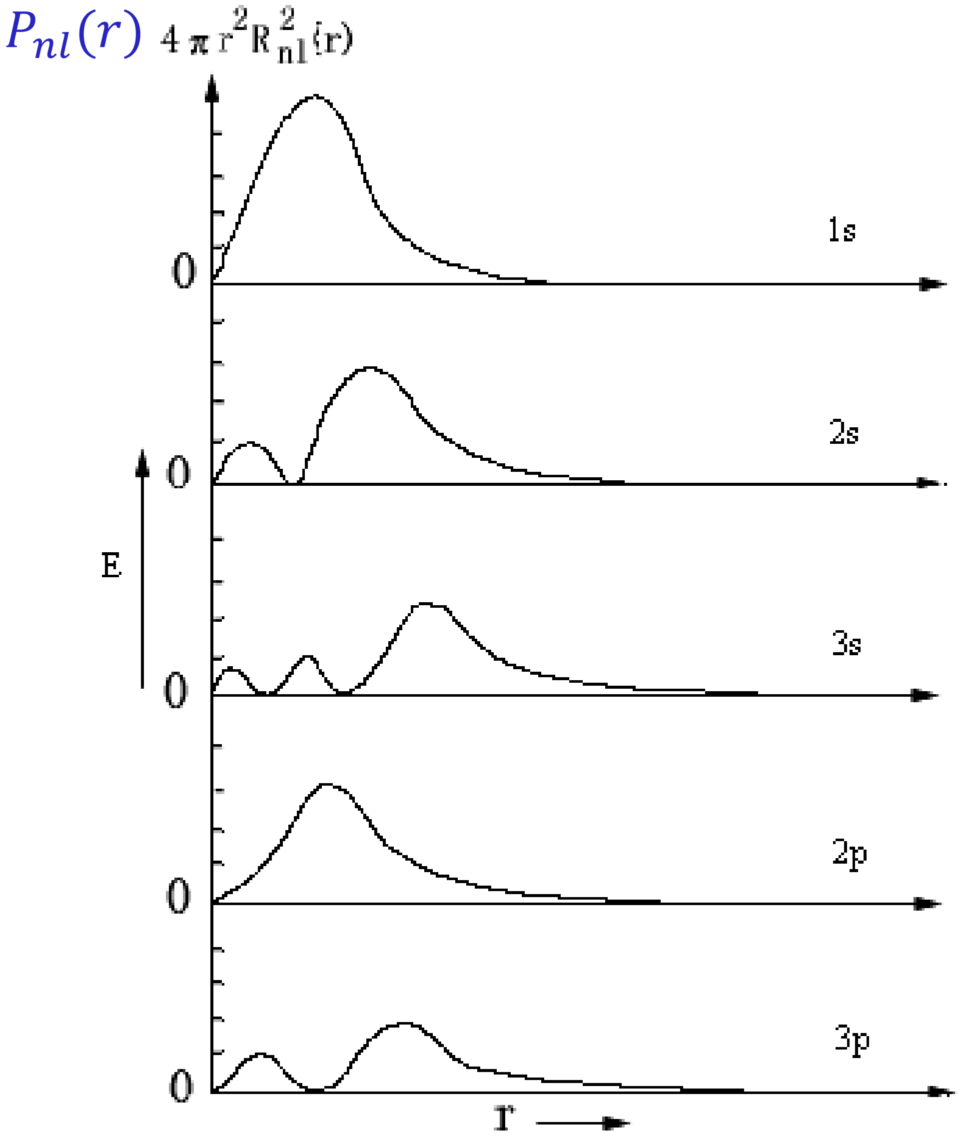
$$0 = \frac{\partial}{\partial r}P_{1s} = \frac{\partial}{\partial r}\left(4r^2e^{-2r}\right) = \left(8r - 8r^2\right)e^{-2r}$$

so the maximum is at $r = 1$.

Note that this is not the same as the expectation value of r:

$$\langle r \rangle = \int_0^\infty rP_{1s}(r)\,dr = \int_0^\infty 4r^3e^{-2r}\,dr = \frac{3}{2}$$

- A spherical surface with the electron density of zero is called a *node*, or *nodal surface*.
- The radial distribution function has (n-*l*) maxima and (n-*l*-1) nodal surfaces



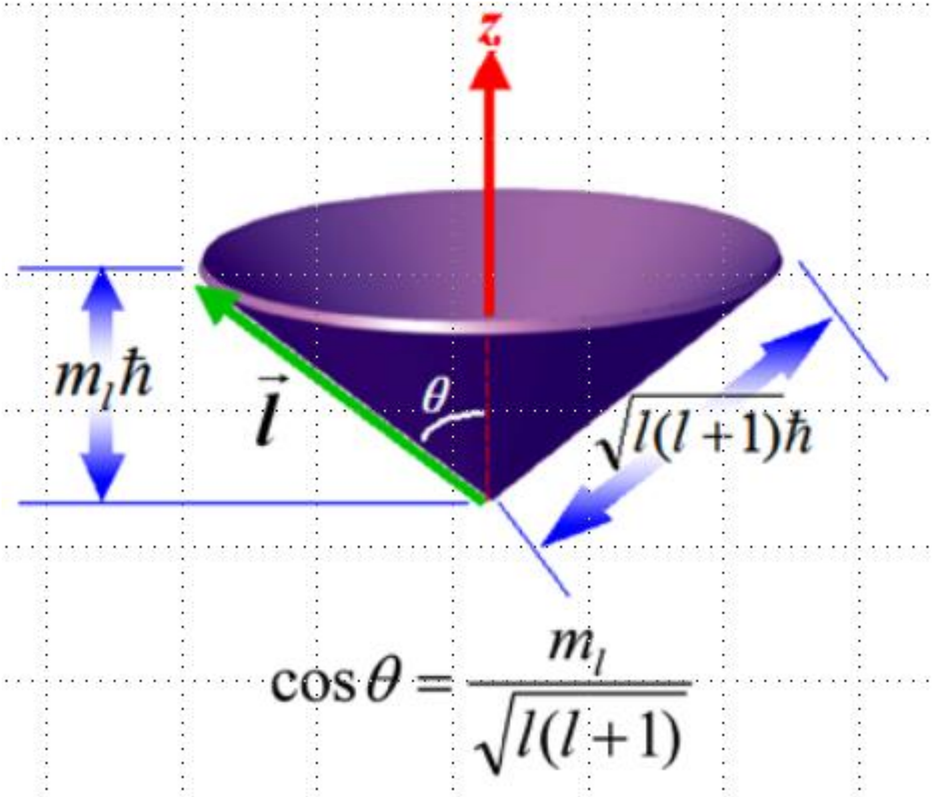
The angular functions $Y_{lm}(\theta,\varphi)$ for hydrogen

Indicates the angular distribution of an atomic orbital.

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

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

$$\hat{L}_z Y_{lm}(\theta,\varphi) = m\hbar Y_{lm}(\theta,\varphi)$$



Nodes

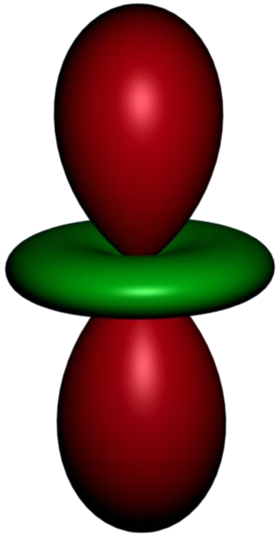
A node is a surface on which an electron is not found. For a given orbital, the total number of nodes equals n-1. The number of angular nodes is *l*.

$$\boldsymbol{Y_{lm}(\theta,\varphi)=0}$$

$$Y_{20}=Y_{dz^2}=\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$$

$$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)=0$$

$$\cos\theta=\pm\frac{1}{\sqrt{3}},\quad \theta=54°44'\ ,\ 125°16'$$

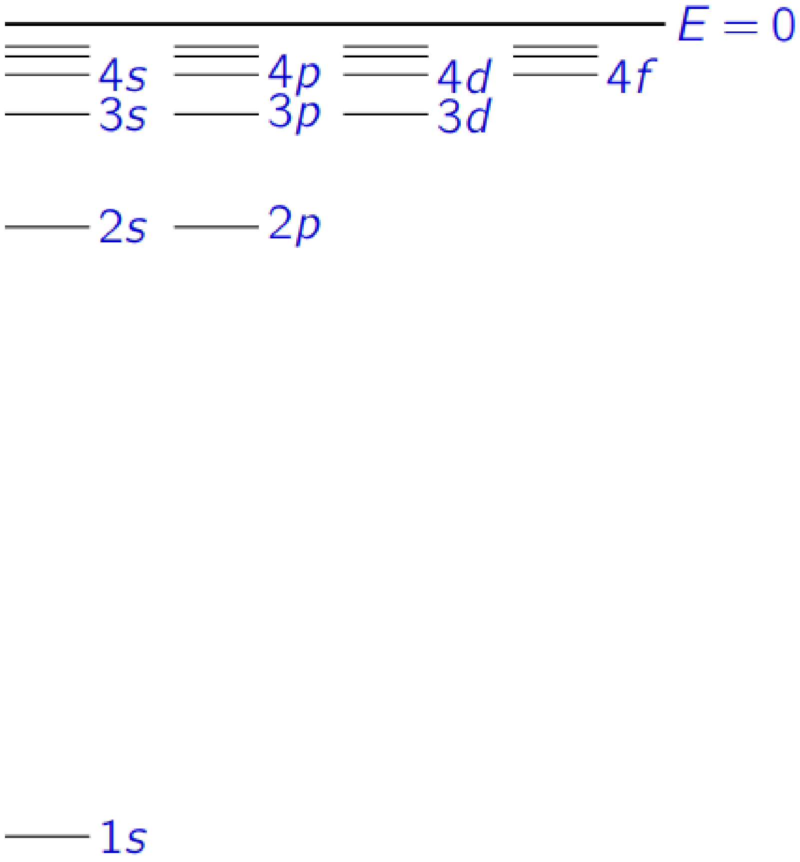


Atomic orbitals

The wavefunctions $R_{nl}(r)Y_{lm}(\theta,\varphi)$ are the *atomic orbitals.* For the hydrogen atom, the energy depends only on n, not on l or m:

$$E_{nlm} = -\frac{Z^2}{2n^2}$$

The energy level pattern is as shown (to scale).



Real or complex orbitals?

If we assemble the complete $2p$ orbitals for the hydrogen atom $(Z = 1)$, we get:

$m = 0$:

$$\psi_{2p0} = \sqrt{\frac{1}{24}} r\exp(-r/2) \times \sqrt{\frac{3}{4\pi}} \cos\theta$$
$$= N_{2p} z\exp(-r/2)$$

$m = 1$:

$$\psi_{2p1} = -\sqrt{\frac{1}{24}} r\exp(-r/2) \times \sqrt{\frac{3}{8\pi}} \sin\theta\exp(i\varphi)$$
$$= -N_{2p}\sqrt{\frac{1}{2}}\left(x+iy\right)\exp(-r/2)$$

$m = -1$:

$$\psi_{2p\bar{1}} = \sqrt{\frac{1}{24}} r\exp(-r/2) \times \sqrt{\frac{3}{8\pi}} \sin\theta\exp(-i\varphi)$$
$$= N_{2p}\sqrt{\frac{1}{2}}\left(x-iy\right)\exp(-r/2)$$

Here $N_{2p} = (32\pi)^{-1/2}$.

Real or complex *p* orbitals

The complex orbitals ψ_{nlm} are eigenfunctions of H, ***c***and $\hat{l}_z$ and are suitable for use when we are interested in angular momentum.

For many purposes, however, it is more convenient to construct the real functions

$$2p_x = \sqrt{\frac{1}{2}}\left(-\psi_{2p1} + \psi_{2p\bar{1}}\right) = N_{2p}x\exp(-r/2)$$

$$2p_y = i\sqrt{\frac{1}{2}}\left(\psi_{2p1} + \psi_{2p\bar{1}}\right) = N_{2p}y\exp(-r/2)$$

together with

$$2p_z = \psi_{2p0} = N_{2p}z\exp(-r/2)$$

These real functions are still eigenfunctions of H and $\hat{\boldsymbol{l}}^2$, but not of l_z when $m \neq 0$.

$$H\left(a\psi_{2p0} + b\psi_{2p1} + c\psi_{2p\bar{1}}\right) = E_{2p}\left(a\psi_{2p0} + b\psi_{2p1} + c\psi_{2p\bar{1}}\right)$$

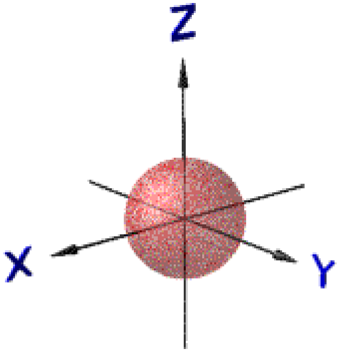
Angular function ($Y_{lm}(\theta,\varphi)$)

s-Orbital (l=0, 2l+1=1)

Y_{00}

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}$$

$$s = \frac{1}{\sqrt{4\pi}}$$

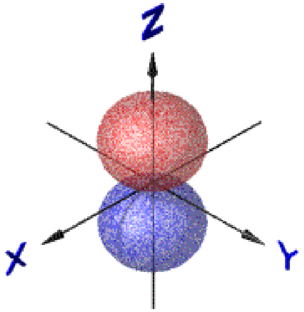


p-Orbital (l=1, 2l+1=3)

Y_{10}

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$p_z = \sqrt{\frac{3}{4\pi}}\cos\theta$$



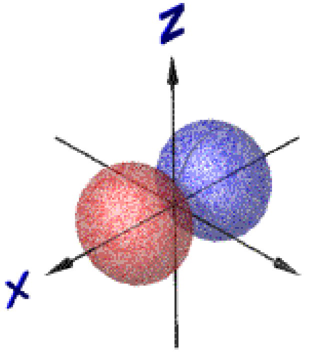
$Y_{1\pm1}$

$$Y_{1,1} = \frac{\sqrt{3}}{2}\sin\theta\cdot\frac{1}{\sqrt{2\pi}}e^{i\varphi}$$

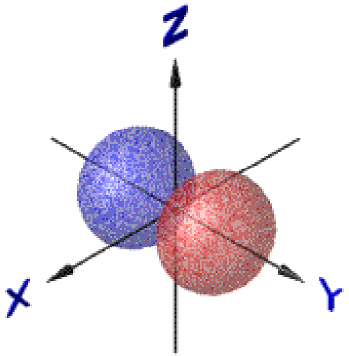
$$Y_{1,-1} = \frac{\sqrt{3}}{2}\sin\theta\cdot\frac{1}{\sqrt{2\pi}}e^{-i\varphi}$$

$$p_x = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\varphi$$

$$p_y = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\varphi$$



p_x



p_y

d orbitals

The $3d$ orbitals are constructed from the R_{3d} radial function and the Y_{2m} spherical harmonics:

$$\psi_{3d0} = R_{3d}Y_{20} = N_{3d}r^2\exp(-r/2)\frac{1}{2}\left(3\cos^2\theta - 1\right)$$

$$\psi_{3d\pm1} = R_{3d}Y_{2\pm1} = \mp N_{3d}r^2\exp(-r/2)\sqrt{\frac{3}{2}}\cos\theta\sin\theta\mathrm{e}^{\pm i\varphi}$$

$$\psi_{3d\pm2} = R_{3d}Y_{2\pm2} = N_{3d}r^2\exp(-r/2)\sqrt{\frac{3}{8}}\sin^2\theta\mathrm{e}^{\pm 2i\varphi}$$

where the normalising factor $N_{3d} = \frac{4}{81}\sqrt{\frac{1}{30}}\cdot\sqrt{\frac{5}{4\pi}} = \frac{2}{81}\sqrt{\frac{1}{6\pi}}$.

Just as for the p orbitals, we can write $r\sin\theta\mathrm{e}^{\pm i\varphi} = x \pm iy$ and $rcos\theta = z$, and take real and imaginary parts to obtain the $3d$ orbitals in the familar real form.

(Note that $r^2\sin^2\theta\mathrm{e}^{\pm 2i\varphi} = (r\sin\theta\mathrm{e}^{\pm i\varphi})^2 = (x \pm iy)^2 = x^2 - y^2 \pm 2ixy$.)

d orbitals in real form

The $3d$ orbitals in real form are:

$$3d_{z^2} = N_{3d}\frac{1}{2}\left(3z^2 - r^2\right)\exp(-r/3) \qquad m = 0$$

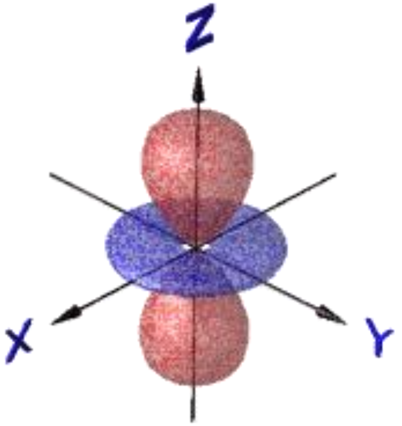
$$\left.\begin{aligned} 3d_{xz} &= N_{3d}\sqrt{3}xz\exp(-r/3) \\ 3d_{yz} &= N_{3d}\sqrt{3}yz\exp(-r/3) \end{aligned}\right\} \quad m = \pm 1$$

$$\left.\begin{aligned} 3d_{x^2-y^2} &= N_{3d}\sqrt{\frac{3}{4}}\left(x^2 - y^2\right)\exp(-r/3) \\ 3d_{xy} &= N_{3d}\sqrt{3}xy\exp(-r/3) \end{aligned}\right\} \quad m = \pm 2$$

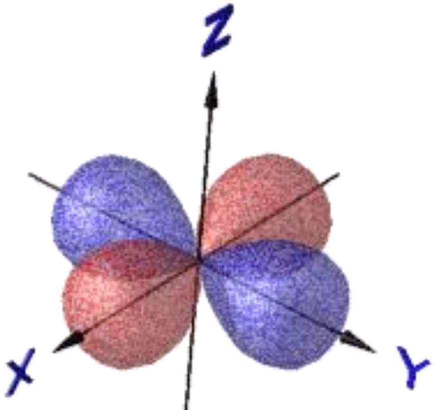
Note that the so-called d_{z^2} orbital is in fact proportional to $(3z^2 - r^2)$.

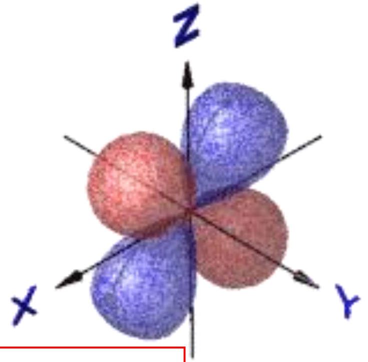
d-Orbital

$$d_{z^2} = \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$$

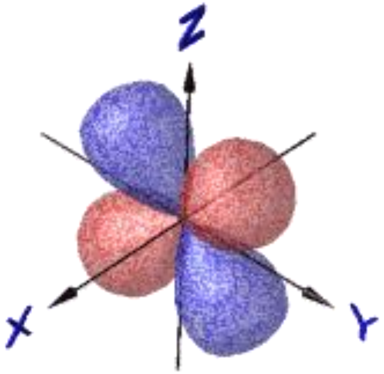


$$d_{x^2-y^2} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\varphi$$



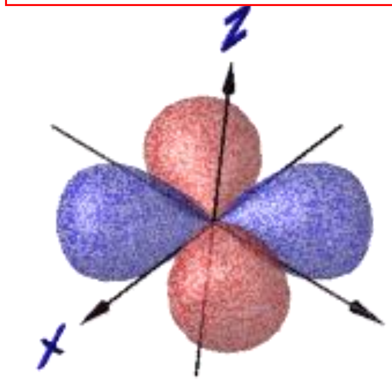


$$d_{xz} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin 2\theta\cos\varphi$$



$$d_{xy} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\varphi$$

$$d_{yz} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin 2\theta\sin\varphi$$



Y_{20}

$$d_{z^2} = \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$$

$Y_{2\pm1}$

$$d_{xz} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin 2\theta\cos\varphi$$

$$d_{yz} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin 2\theta\sin\varphi$$

$Y_{2\pm2}$

$$d_{x^2-y^2} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\varphi$$

$$d_{xy} = \frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\varphi$$

Nodal structure of the atomic orbitals

The radial wavefunctions R_{1s}, R_{2s}, R_{3s}, etc. are solutions of the same eigenvalue equation, so they have to be orthogonal with respect to radial integration. Like the wavefunctions for the particle in the box and the harmonic oscillator, the lowest-energy function has no nodes, the next has one node, and so on, each function having one more node than the previous one.

The radial p functions are solutions of a *different* equation (because l is different), so they don't have to be orthogonal to the radial s functions. However they too are orthogonal to each other, with the number of nodes increasing with increasing energy.

Also the *complete* p orbitals are orthogonal to the s orbitals and to each other, because of the orthogonality of the angular functions Y_{lm}.

The atomic orbitals with principal quantum number n all have $n - 1$ nodal surfaces. Of these, l are *angular* nodes and the rest are *radial*. The radial nodes are spherical surfaces at particular values of r; for instance, the $2s$ orbital for the H atom is zero when $r = 2$, for any θ and φ.

Angular nodes

Of the angular nodes, $|m|$ are planes perpendicular to the equator (the xy plane) and the rest are conical surfaces defined by particular values of θ. For example, the d_{z^2} orbital has nodes where $3\cos^2\theta = 1$, i.e.,$\theta = 54.74°$ or $125.26°$.