4.4 Hydrogenic atoms

Bohr model[a]

Quantisation condition	$\mu r_n^2 \Omega = n\hbar$	(4.71)	r_n Ω n	nth orbit radius orbital angular speed principal quantum number (>0)
Bohr radius	$a_0 = \dfrac{\epsilon_0 h^2}{\pi m_e e^2} = \dfrac{\alpha}{4\pi R_\infty} \simeq 52.9\,\mathrm{pm}$	(4.72)	a_0 μ $-e$	Bohr radius reduced mass ($\simeq m_e$) electronic charge
Orbit radius	$r_n = \dfrac{n^2}{Z} a_0 \dfrac{m_e}{\mu}$	(4.73)	Z h $\hbar$	atomic number Planck constant $h/(2\pi)$
Total energy	$E_n = -\dfrac{\mu e^4 Z^2}{8\epsilon_0^2 h^2 n^2} = -R_\infty hc \dfrac{\mu}{m_e} \dfrac{Z^2}{n^2}$	(4.74)	E_n ϵ_0 m_e	total energy of nth orbit permittivity of free space electron mass
Fine structure constant	$\alpha = \dfrac{\mu_0 c e^2}{2h} = \dfrac{e^2}{4\pi\epsilon_0 \hbar c} \simeq \dfrac{1}{137}$	(4.75)	α μ_0	fine structure constant permeability of free space
Hartree energy	$E_H = \dfrac{\hbar^2}{m_e a_0^2} \simeq 4.36 \times 10^{-18}\,\mathrm{J}$	(4.76)	E_H	Hartree energy
Rydberg constant	$R_\infty = \dfrac{m_e c \alpha^2}{2h} = \dfrac{m_e e^4}{8h^3 \epsilon_0^2 c} = \dfrac{E_H}{2hc}$	(4.77)	R_∞ c	Rydberg constant speed of light
Rydberg's formula[b]	$\dfrac{1}{\lambda_{mn}} = R_\infty \dfrac{\mu}{m_e} Z^2 \left(\dfrac{1}{n^2} - \dfrac{1}{m^2}\right)$	(4.78)	λ_{mn} m	photon wavelength integer $>n$

[a] Because the Bohr model is strictly a two-body problem, the equations use reduced mass, $\mu = m_e m_{nuc}/(m_e + m_{nuc}) \simeq m_e$, where m_{nuc} is the nuclear mass, throughout. The orbit radius is therefore the electron–nucleus distance.
[b] Wavelength of the spectral line corresponding to electron transitions between orbits m and n.

Hydrogenlike atoms – Schrödinger solution[a]

Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\nabla^2\Psi_{nlm}-\frac{Ze^2}{4\pi\epsilon_0 r}\Psi_{nlm}=E_n\Psi_{nlm} \qquad \text{with} \quad \mu=\frac{m_e m_{nuc}}{m_e+m_{nuc}} \tag{4.79}$$

Eigenfunctions

$$\Psi_{nlm}(r,\theta,\phi)=\left[\frac{(n-l-1)!}{2n(n+l)!}\right]^{1/2}\left(\frac{2}{an}\right)^{3/2}x^l e^{-x/2}L_{n-l-1}^{2l+1}(x)Y_l^m(\theta,\phi) \tag{4.80}$$

with $a=\frac{m_e}{\mu}\frac{a_0}{Z}$, $\quad x=\frac{2r}{an}$, $\quad$ and $\quad L_{n-l-1}^{2l+1}(x)=\sum_{k=0}^{n-l-1}\frac{(l+n)!(-x)^k}{(2l+1+k)!(n-l-1-k)!k!}$

Total energy

$$E_n=-\frac{\mu e^4 Z^2}{8\epsilon_0^2 h^2 n^2} \tag{4.81}$$

Radial expectation values

$$\langle r\rangle=\frac{a}{2}[3n^2-l(l+1)] \tag{4.82}$$

$$\langle r^2\rangle=\frac{a^2n^2}{2}[5n^2+1-3l(l+1)] \tag{4.83}$$

$$\langle 1/r\rangle=\frac{1}{an^2} \tag{4.84}$$

$$\langle 1/r^2\rangle=\frac{2}{(2l+1)n^3a^2} \tag{4.85}$$

Allowed quantum numbers and selection rules[b]

$$n=1,2,3,\ldots \tag{4.86}$$

$$l=0,1,2,\ldots,(n-1) \tag{4.87}$$

$$m=0,\pm1,\pm2,\ldots,\pm l \tag{4.88}$$

$$\Delta n\neq 0 \tag{4.89}$$

$$\Delta l=\pm1 \tag{4.90}$$

$$\Delta m=0 \quad \text{or} \quad \pm1 \tag{4.91}$$

E_n	total energy
ϵ_0	permittivity of free space
h	Planck constant
m_e	mass of electron
$\hbar$	$h/2\pi$
μ	reduced mass ($\simeq m_e$)
m_{nuc}	mass of nucleus
Ψ_{nlm}	eigenfunctions
Ze	charge of nucleus
$-e$	electronic charge
L_p^q	associated Laguerre polynomials[c]
a	classical orbit radius, $n=1$
r	electron–nucleus separation
Y_l^m	spherical harmonics
a_0	Bohr radius $=\frac{\epsilon_0 h^2}{\pi m_e e^2}$

$$\Psi_{100}=\frac{a^{-3/2}}{\pi^{1/2}}e^{-r/a} \qquad \Psi_{200}=\frac{a^{-3/2}}{4(2\pi)^{1/2}}\left(2-\frac{r}{a}\right)e^{-r/2a}$$

$$\Psi_{210}=\frac{a^{-3/2}}{4(2\pi)^{1/2}}\frac{r}{a}e^{-r/2a}\cos\theta \qquad \Psi_{21\pm1}=\mp\frac{a^{-3/2}}{8\pi^{1/2}}\frac{r}{a}e^{-r/2a}\sin\theta\, e^{\pm i\phi}$$

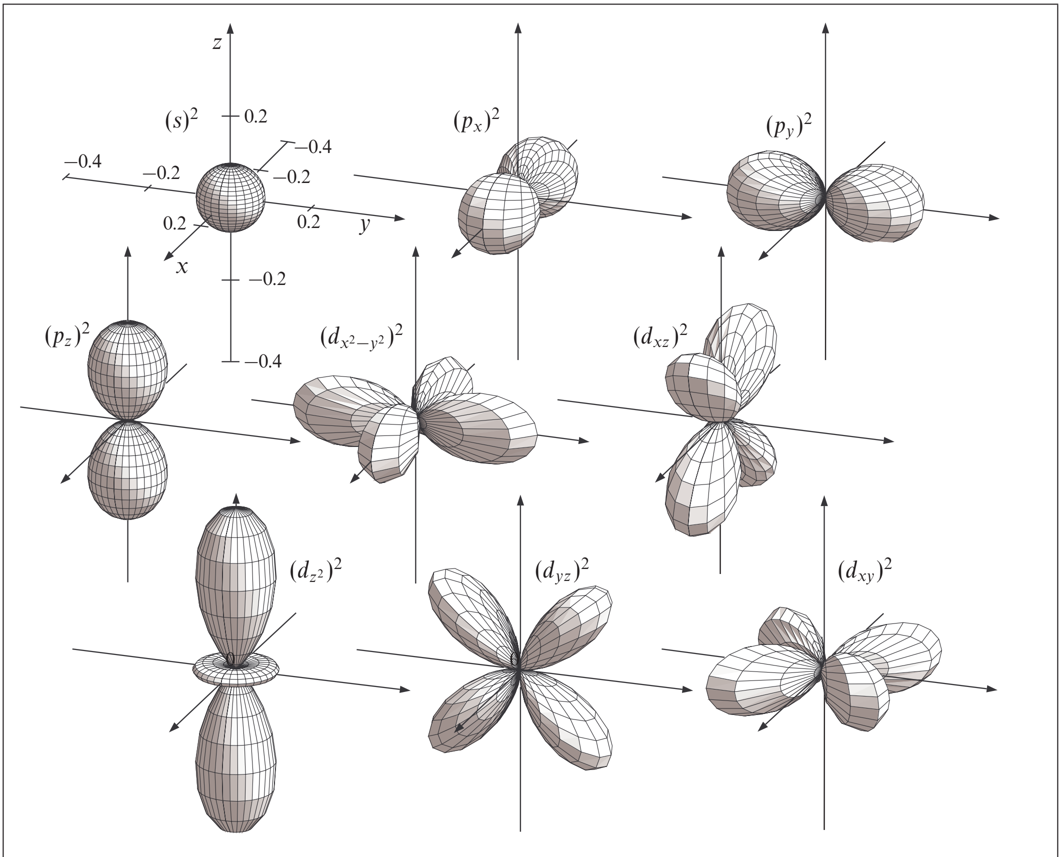
$$\Psi_{300}=\frac{a^{-3/2}}{81(3\pi)^{1/2}}\left(27-18\frac{r}{a}+2\frac{r^2}{a^2}\right)e^{-r/3a} \qquad \Psi_{310}=\frac{2^{1/2}a^{-3/2}}{81\pi^{1/2}}\left(6-\frac{r}{a}\right)\frac{r}{a}e^{-r/3a}\cos\theta$$

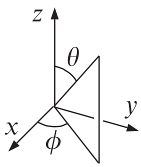
$$\Psi_{31\pm1}=\mp\frac{a^{-3/2}}{81\pi^{1/2}}\left(6-\frac{r}{a}\right)\frac{r}{a}e^{-r/3a}\sin\theta\, e^{\pm i\phi} \qquad \Psi_{320}=\frac{a^{-3/2}}{81(6\pi)^{1/2}}\frac{r^2}{a^2}e^{-r/3a}(3\cos^2\theta-1)$$

$$\Psi_{32\pm1}=\mp\frac{a^{-3/2}}{81\pi^{1/2}}\frac{r^2}{a^2}e^{-r/3a}\sin\theta\cos\theta\, e^{\pm i\phi} \qquad \Psi_{32\pm2}=\frac{a^{-3/2}}{162\pi^{1/2}}\frac{r^2}{a^2}e^{-r/3a}\sin^2\theta\, e^{\pm 2i\phi}$$

[a]For a single bound electron in a perfect nuclear Coulomb potential (nonrelativistic and spin-free).
[b]For dipole transitions between orbitals.
[c]The sign and indexing definitions for this function vary. This form is appropriate to Equation (4.80).

Orbital angular dependence



s orbital ($l=0$)	$s = Y_0^0 = \text{constant}$	(4.92)	Y_l^m spherical harmonics[a]
p orbitals ($l=1$)	$p_x = \frac{-1}{2^{1/2}}(Y_1^1 - Y_1^{-1}) \propto \cos\phi \sin\theta$	(4.93)	
	$p_y = \frac{\mathrm{i}}{2^{1/2}}(Y_1^1 + Y_1^{-1}) \propto \sin\phi \sin\theta$	(4.94)	θ,ϕ spherical polar coordinates
	$p_z = Y_1^0 \propto \cos\theta$	(4.95)	
d orbitals ($l=2$)	$d_{x^2-y^2} = \frac{1}{2^{1/2}}(Y_2^2 + Y_2^{-2}) \propto \sin^2\theta \cos 2\phi$	(4.96)	
	$d_{xz} = \frac{-1}{2^{1/2}}(Y_2^1 - Y_2^{-1}) \propto \sin\theta \cos\theta \cos\phi$	(4.97)	
	$d_{z^2} = Y_2^0 \propto (3\cos^2\theta - 1)$	(4.98)	
	$d_{yz} = \frac{\mathrm{i}}{2^{1/2}}(Y_2^1 + Y_2^{-1}) \propto \sin\theta \cos\theta \sin\phi$	(4.99)	
	$d_{xy} = \frac{-\mathrm{i}}{2^{1/2}}(Y_2^2 - Y_2^{-2}) \propto \sin^2\theta \sin 2\phi$	(4.100)	

[a]See page 49 for the definition of spherical harmonics.