## 4.4 Hydrogenic atoms

### Bohr model[a]

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

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

**Eigenfunctions**

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

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

| | | |
|---|---|---|
| Total energy | $E_n = -\frac{\mu e^4 Z^2}{8\epsilon_0^2 h^2 n^2}$ | (4.81) |
| Radial expectation values | $\langle r\rangle = \frac{a}{2}[3n^2 - l(l+1)]$ | (4.82) |
| | $\langle r^2\rangle = \frac{a^2n^2}{2}[5n^2+1-3l(l+1)]$ | (4.83) |
| | $\langle 1/r\rangle = \frac{1}{an^2}$ | (4.84) |
| | $\langle 1/r^2\rangle = \frac{2}{(2l+1)n^3a^2}$ | (4.85) |
| Allowed quantum numbers and selection rules[b] | $n = 1,2,3,\ldots$ | (4.86) |
| | $l = 0,1,2,\ldots,(n-1)$ | (4.87) |
| | $m = 0,\pm1,\pm2,\ldots,\pm l$ | (4.88) |
| | $\Delta n \neq 0$ | (4.89) |
| | $\Delta l = \pm 1$ | (4.90) |
| | $\Delta m = 0 \quad \text{or} \quad \pm 1$ | (4.91) |

| | |
|---|---|
| $E_n$ | total energy |
| $\epsilon_0$ | permittivity of free space |
| $h$ | Planck constant |
| $m_e$ | mass of electron |
| $\hbar$ | $h/2\pi$ |
| $\mu$ | reduced mass ($\simeq m_e$) |
| $m_{nuc}$ | mass of nucleus |
| $\Psi_{nlm}$ | 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 $= \frac{\epsilon_0 h^2}{\pi m_e e^2}$ |

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

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

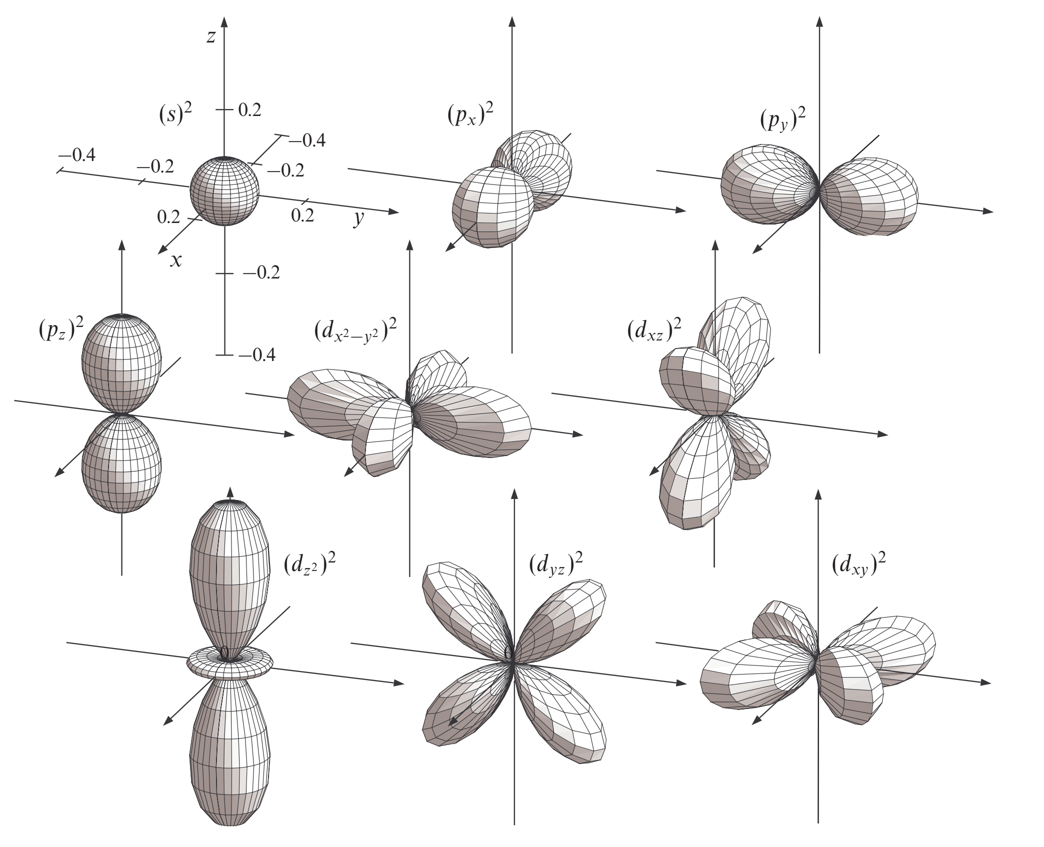
$$\Psi_{300} = \frac{a^{-3/2}}{81(3\pi)^{1/2}}\left(27-18\frac{r}{a}+2\frac{r^2}{a^2}\right)e^{-r/3a} \qquad \Psi_{310} = \frac{2^{1/2}a^{-3/2}}{81\pi^{1/2}}\left(6-\frac{r}{a}\right)\frac{r}{a}e^{-r/3a}\cos\theta$$

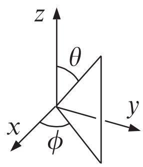
$$\Psi_{31\pm1} = \mp\frac{a^{-3/2}}{81\pi^{1/2}}\left(6-\frac{r}{a}\right)\frac{r}{a}e^{-r/3a}\sin\theta\, e^{\pm i\phi} \qquad \Psi_{320} = \frac{a^{-3/2}}{81(6\pi)^{1/2}}\frac{r^2}{a^2}e^{-r/3a}(3\cos^2\theta - 1)$$

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

[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) | $\theta,\phi$ spherical polar coordinates |
| | $p_y = \frac{\mathbf{i}}{2^{1/2}}(Y_1^1 + Y_1^{-1}) \propto \sin\phi\sin\theta$ | (4.94) | |
| | $p_z = Y_1^0 \propto \cos\theta$ | (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) | |
| | $d_{yz} = \frac{\mathbf{i}}{2^{1/2}}(Y_2^1 + Y_2^{-1}) \propto \sin\theta\cos\theta\sin\phi$ | (4.99) | |
| | $d_{xy} = \frac{-\mathbf{i}}{2^{1/2}}(Y_2^2 - Y_2^{-2}) \propto \sin^2\theta\sin 2\phi$ | (4.100) | |

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