The Hydrogen atom

Nonrelativistic description

The stationary Schrödinger-equation

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$$

The Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + V(\vec{r})$$

In case of spherical symmetry we use spherical coordinates (radial, polar and azymuthal)

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{2m}{\hbar^2}[E - V(r)]\psi = 0$$

Second-order partial differential equation with 3 variables

Separation of variables

$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$$

3 ordinary differential equations

$$\begin{aligned} \frac{d^2\Phi}{d\varphi^2} + m_l^2\Phi &= 0 \\ \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta &= 0 \\ \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\left(E - V(r)\right) - \frac{l(l+1)}{r^2}\right]R &= 0. \end{aligned}$$

m_l^2 and $l(l+1)$ are constants

The solution of the orbital equations

The spherical harmonics $Y_l^{m_l}(\theta, \varphi)$

Valid for any spherically symmetric potential

Orthogonal and normalized basis set

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta Y_l^{m_l *}(\theta,\varphi) Y_{l'}^{m_l'}(\theta,\varphi) = \delta_{ll'}\delta_{m_l m_l'}.$$

A few examples

$$\begin{aligned}
Y_0^0 &= \frac{1}{\sqrt{4\pi}}; & Y_1^0 &= \sqrt{\frac{3}{4\pi}}\cos\theta \\
Y_1^{\pm1} &= \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi}; & Y_2^0 &= \frac{1}{2}\sqrt{\frac{5}{4\pi}}(3\cos^2\theta - 1) \\
Y_2^{\pm1} &= \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\varphi}; & Y_2^{\pm2} &= \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{\pm i2\varphi}
\end{aligned}$$

The eigenfunctions and the eigenvalues of the angular momentum

The operators H, L^2 and L_z commute

They have a common system of eigenfunctions – the spherical harmonics

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

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

$$L = \sqrt{l(l+1)}\hbar$$

L – the eigenvalue

l – the orbital quantum number

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\varphi}$$

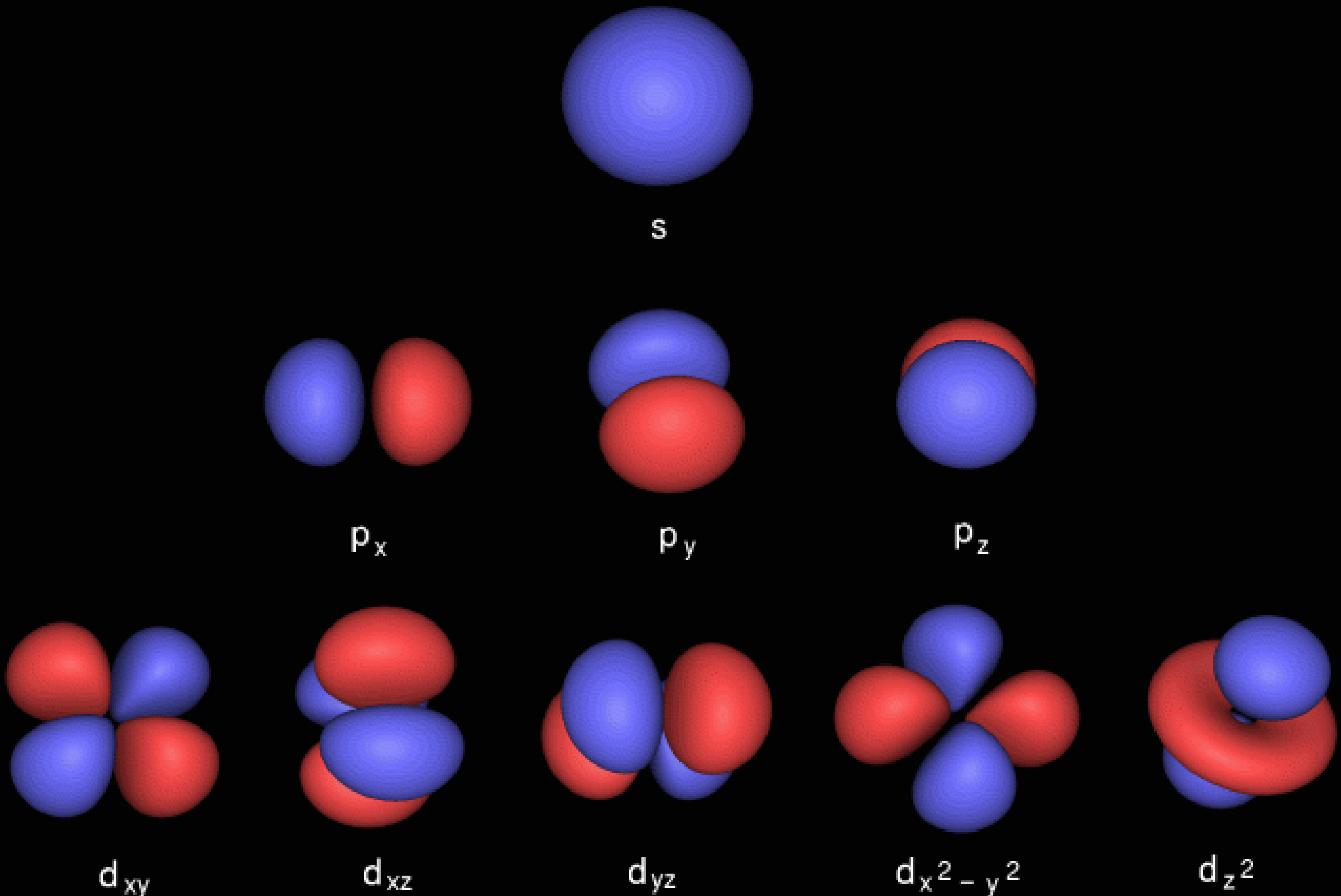
$$\hat{L}_z \psi(r,\theta,\varphi) = L_z \psi(r,\theta,\varphi)$$

$$L_z = m_l \hbar$$

L_z – the eigenvalue

m_l – the magnetic quantum number

The orbitals



The radial Schrödinger-equation

The atomic units

$$e = 1; \qquad m = 1; \qquad \hbar = 1; \qquad 4\pi\varepsilon_0 = 1.$$

$$V(r) = -\frac{Z}{r}.$$

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

The eigenvalues of the energy do not depend on l

$$E_n = -\frac{Z^2}{2n^2}.$$

n – the pricipal quantum number

The radial wavefunctions

$$R_{nl}(r) = N_{nl} r^l e^{-\frac{r}{n}} L_{n+1}^{2l+1}\left(\frac{2r}{n}\right)$$

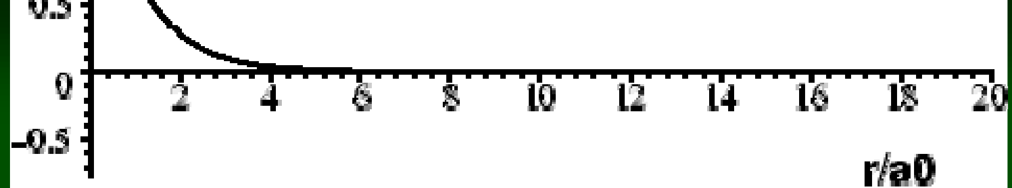
L – Laguerre polinomials

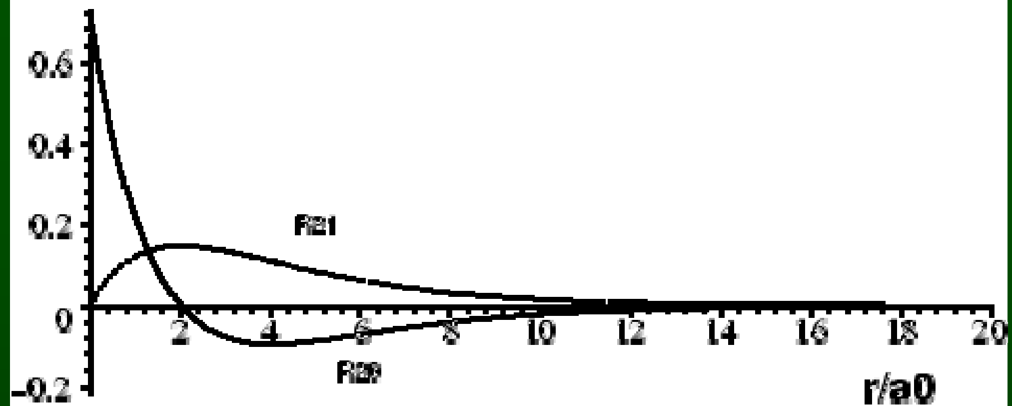
- normalization:

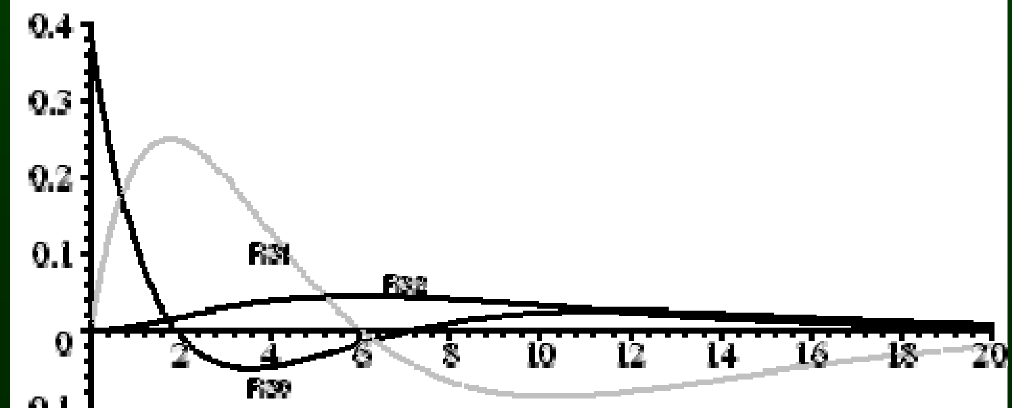
$$\int_0^\infty R_{nl}^2 r^2 dr = 1$$

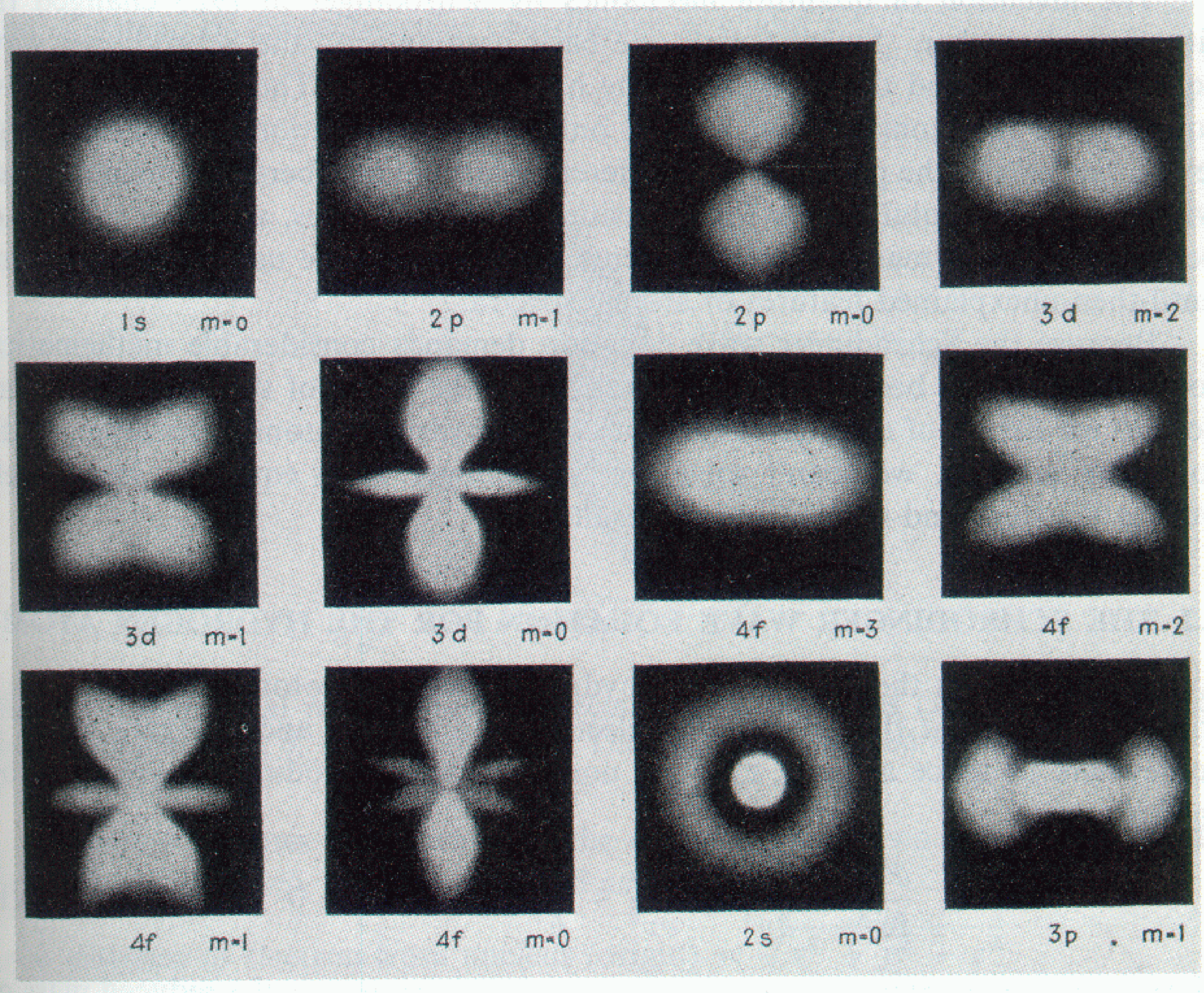
A few examples

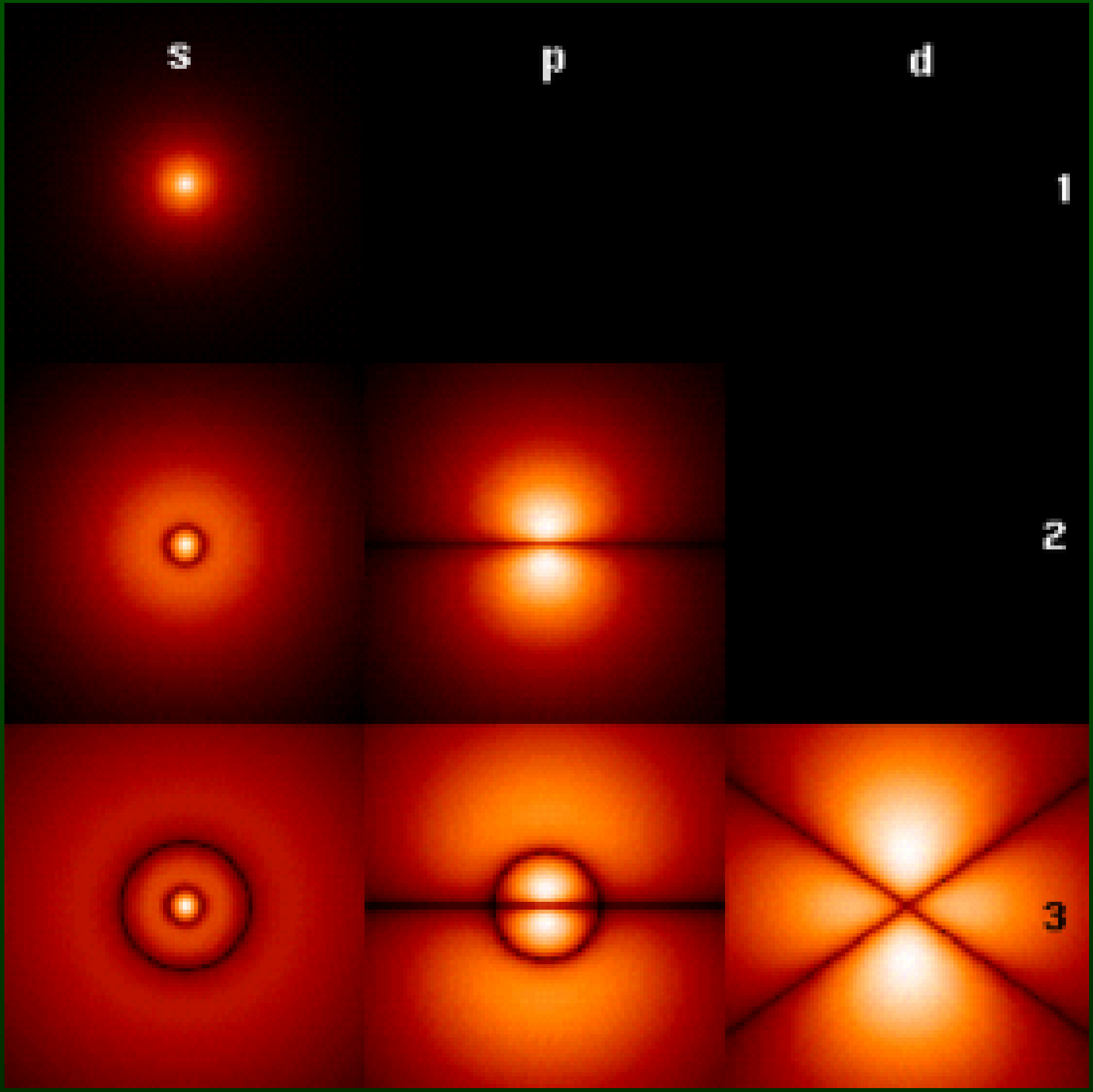
$$\begin{aligned} R_{10} &= 2e^{-r} \\ R_{20} &= \frac{1}{\sqrt{2}}\left(1 - \frac{r}{2}\right) e^{-\frac{r}{2}} \\ R_{21} &= \frac{1}{2\sqrt{6}} r e^{-\frac{r}{2}}. \end{aligned}$$

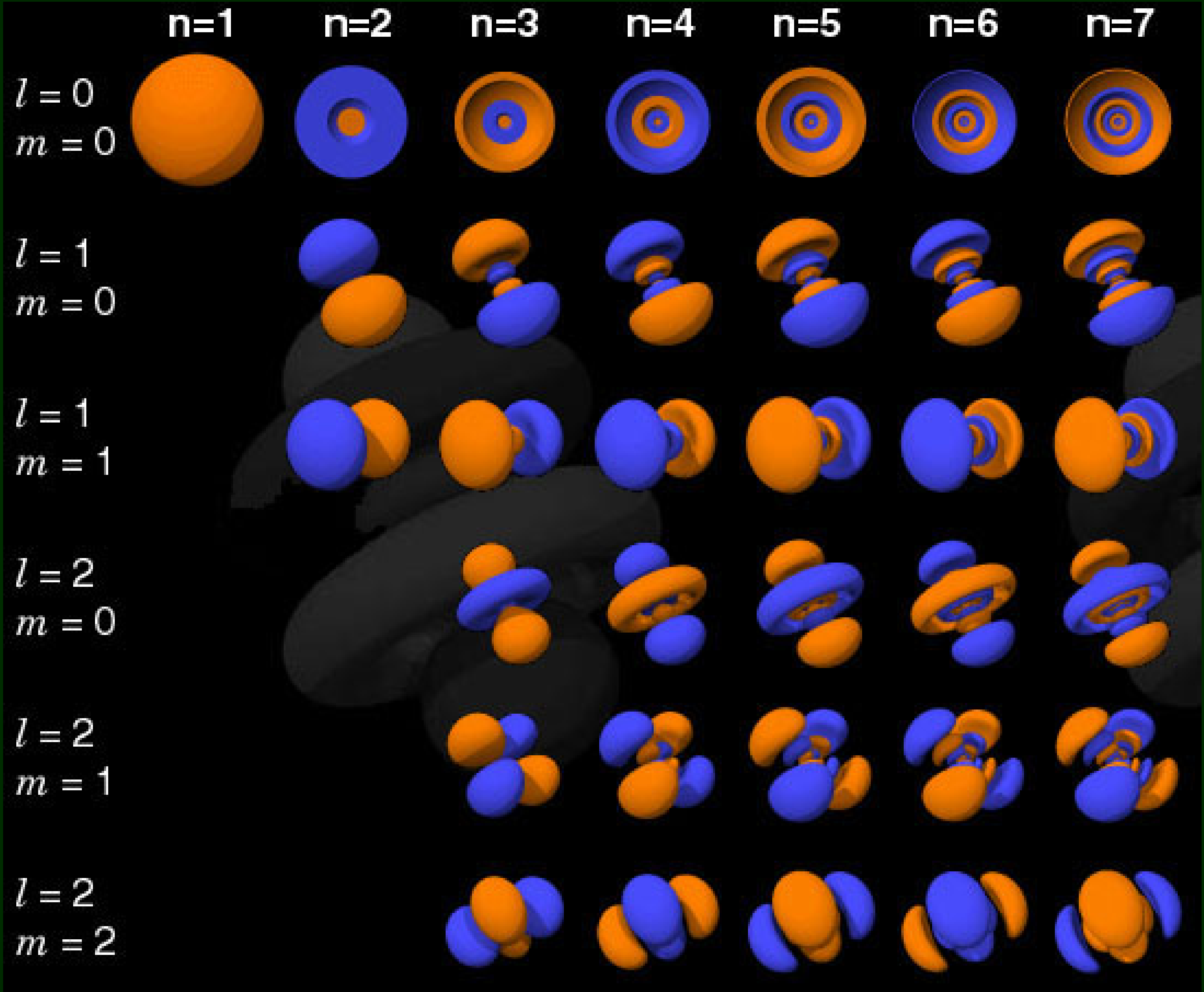

0.5
0
-0.5
2 4 6 8 10 12 14 16 18 20
r/a0


0.6
0.4
0.2
0
-0.2
R21
R20
2 4 6 8 10 12 14 16 18 20
r/a0


0.4
0.3
0.2
0.1
0
R31
R32
R30
2 4 6 8 10 12 14 16 18 20

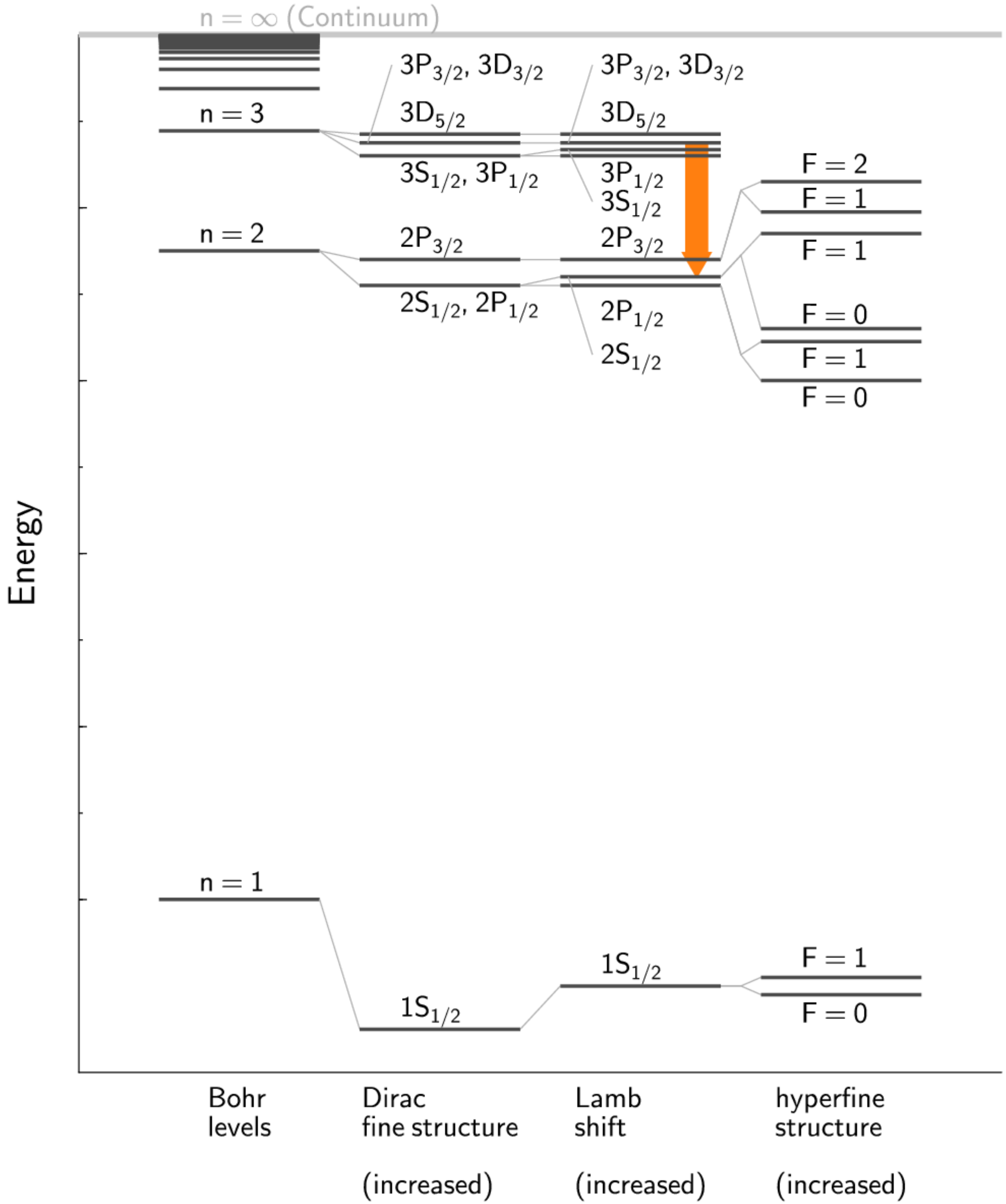

1s m=o
2p m=1
2p m=0
3d m=2
3d m=1
3d m=0
4f m=3
4f m=2
4f m=1
4f m=0
2s m=0
3p m=1


s
p
d
1
2
3


n=1
n=2
n=3
n=4
n=5
n=6
n=7
$l = 0$ $m = 0$
$l = 1$ $m = 0$
$l = 1$ $m = 1$
$l = 2$ $m = 0$
$l = 2$ $m = 1$
$l = 2$ $m = 2$

The energy levels are n^2-fold degenerate
– do not depend on l and m_l

Experimentally: the situation is more complicated


n = ∞ (Continuum)
Energy
n = 3
n = 2
n = 1
3P3/2, 3D3/2
3D5/2
3S1/2, 3P1/2
2P3/2
2S1/2, 2P1/2
1S1/2
3P3/2, 3D3/2
3D5/2
3P1/2
3S1/2
2P3/2
2P1/2
2S1/2
1S1/2
F = 2
F = 1
F = 1
F = 0
F = 1
F = 0
F = 1
F = 0
Bohr levels
Dirac fine structure (increased)
Lamb shift (increased)
hyperfine structure (increased)