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Hydrogen Atom

Spherical harmonics and Radial solution

From: Eva Pavarini, The LDA+DMFT approach, lecture notes 2011
Qian Zhang, Calculation of multiplets across the periodic table

Hamilton Operator

$$H = -\frac{\hbar^2}{2m_e}\Delta - \frac{Ze^2}{4\pi\epsilon_0 r}$$

In atomic units

$$m_e = a_B = e = \frac{1}{4\pi\epsilon_0} = 1$$

$$H = -\frac{1}{2}\Delta - \frac{Z}{r}$$

Hydrogen: $Z = 1$

Schrödinger Equation

$$H = -\frac{1}{2}\Delta - \frac{Z}{r}$$

$$H\Psi_{nlm}(\vec{r}) = \epsilon_n \Psi_{nlm}(\vec{r})$$

Separating the solutions

$$\Psi_{nlm}(\vec{r}) = AR_{nl}(r)Y_{lm}(\theta, \phi)$$

Energy Eigenvalues

$$\epsilon_n = -\frac{Z^2}{2n^2}$$ in Hartree, n^2 degenerated

1 Hartree = 2 Rydberg ≈ 27.2114 eV ≈ 4.3597e−18 J

$$l = 0, 1, 2, \cdots, n-1$$

$$m = -l, -l+1, \cdots, l-1, l$$

n=1	l=0 s-orbital	m=0
n=2	l=0 s	m=0
	l=1 p	m=-1,0,1
n=3	l=0 s	m=0
	l=1 p	m=-1,0,1
	l=2 d	m=-2,-1,0,1,2

Radial solution

$$\rho = Zr$$

$$R_{nl}(\rho) = \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\rho/n} \left(\frac{2\rho}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right)$$

Laguerre polynomials of degree r

$$L_r^s(x) = \frac{x^{-s}e^x}{r!}\frac{d^r}{dx^r}(e^{-x}x^{r+s})$$

Calculate $R_{2p}(\rho)$ and $R_{2s}(\rho)$

Radial solution

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

$$R_{2s}(\rho) = \frac{1}{2\sqrt{2}} Z^{3/2} \qquad (2-\rho)\, e^{-\rho/2}$$

$$R_{2p}(\rho) = \frac{1}{2\sqrt{6}} Z^{3/2} \qquad \rho\, e^{-\rho/2}$$

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

$$R_{3p}(\rho) = \frac{4\sqrt{2}}{9\sqrt{3}} Z^{3/2} \qquad \rho(1-\rho/6)\, e^{-\rho/3}$$

$$R_{3d}(\rho) = \frac{2\sqrt{2}}{81\sqrt{15}} Z^{3/2} \qquad \rho^2\, e^{-\rho/3}$$

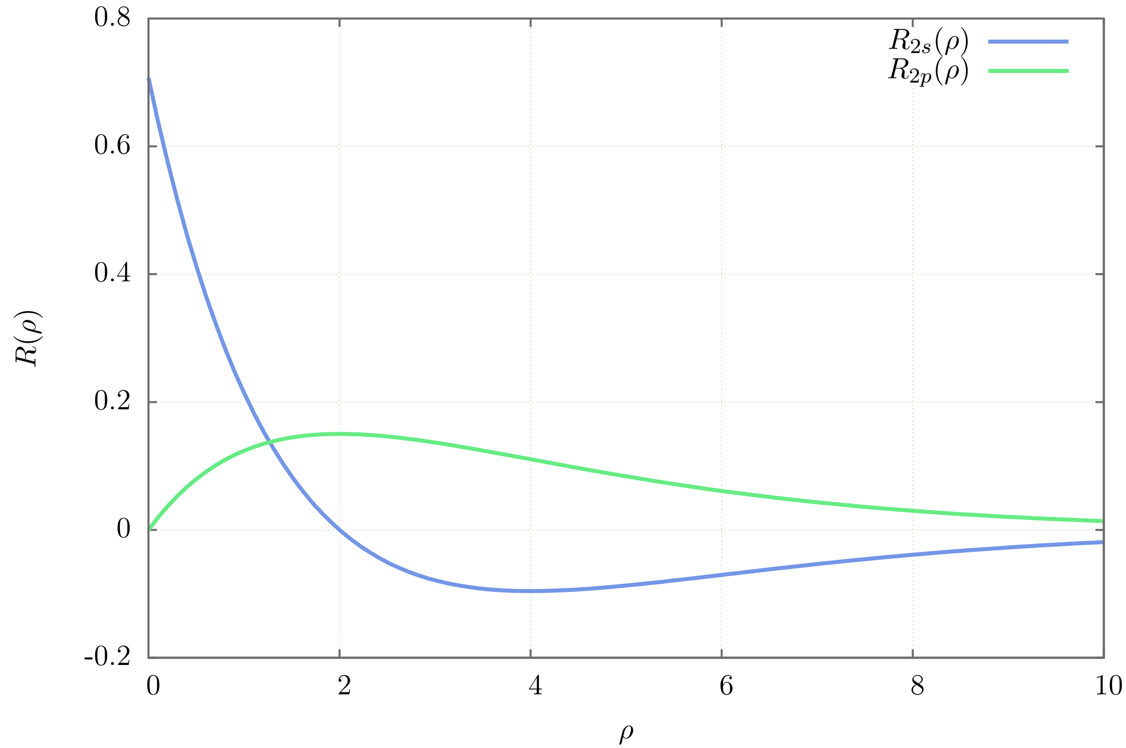
Draw $R_{2p}(\rho)$ and $R_{2s}(\rho)$

Radial solution

nodes: $N = n - l - 1$

$$R_{2s}(\rho) = \frac{1}{2\sqrt{2}} \; Z^{3/2} \; (2-\rho)\, e^{-\rho/2}$$

$$R_{2p}(\rho) = \frac{1}{2\sqrt{6}} \; Z^{3/2} \; \rho\, e^{-\rho/2}$$



Spherical harmonics

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(cos\theta)e^{im\phi}$$

Associated Legendre polynomials

$$P_l^m(x) = \frac{(-1)^m}{2^l l!}(1-x^2)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l$$

$$P_l^{-m}(x) = (-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(x)$$

Calculate Y_{00}, Y_{1-1}, Y_{10} and Y_{11}

Spherical harmonics

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

$$Y_{1,\ 0} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

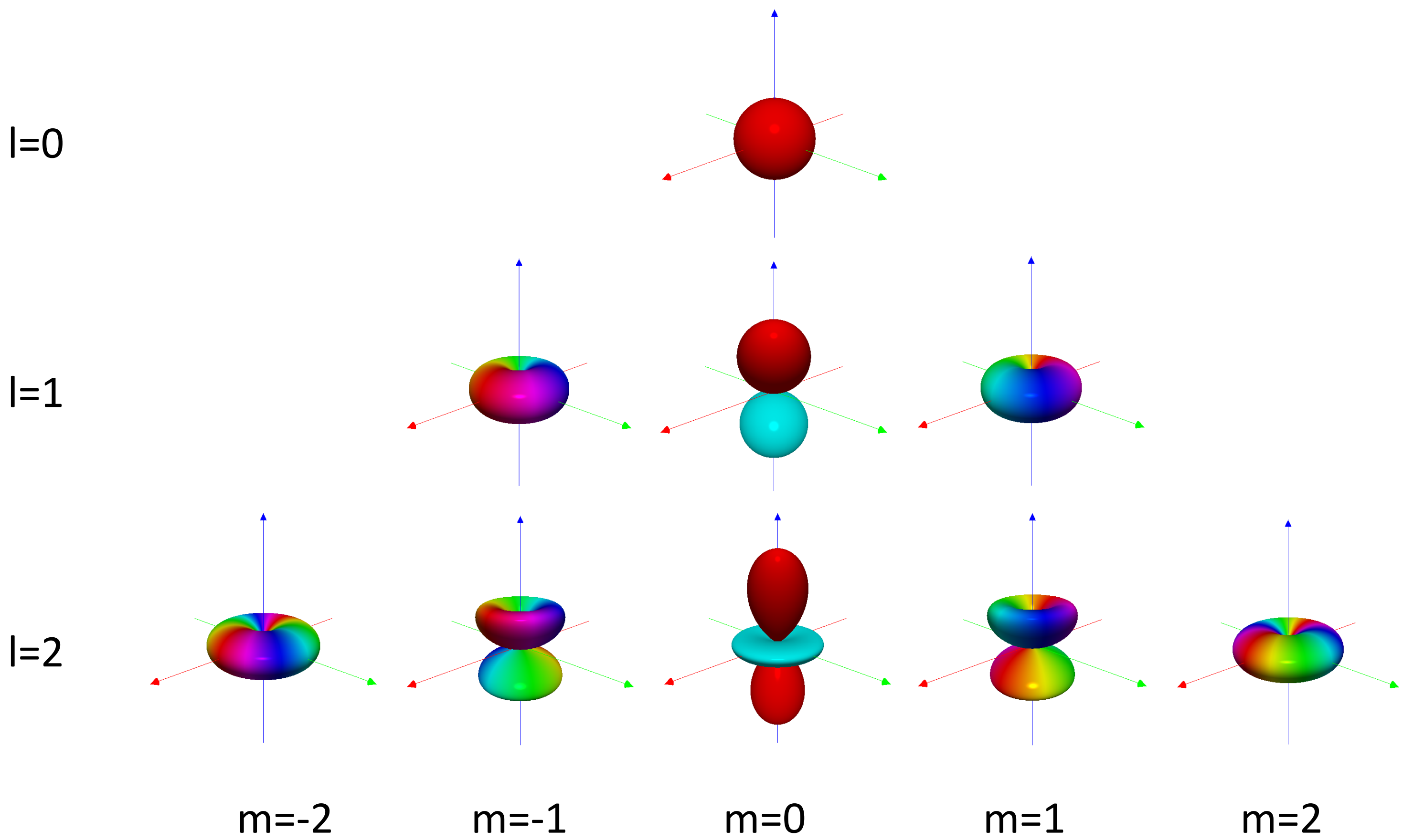
$$Y_{1,\pm 1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\phi}$$

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

$$Y_{2,\pm 1} = \mp\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta \, e^{\pm i\phi}$$

$$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{\pm 2i\phi}$$

Spherical harmonics



Real harmonics

$$y_{l0} = Y_0^l$$

$$y_{lm} = \frac{1}{\sqrt{2}}(Y_{-m}^l + (-1)^m Y_m^l)$$

$$y_{l-m} = \frac{i}{\sqrt{2}}(Y_{-m}^l - (-1)^m Y_m^l)$$

Calculate y_{10}, y_{11} and y_{1-1}

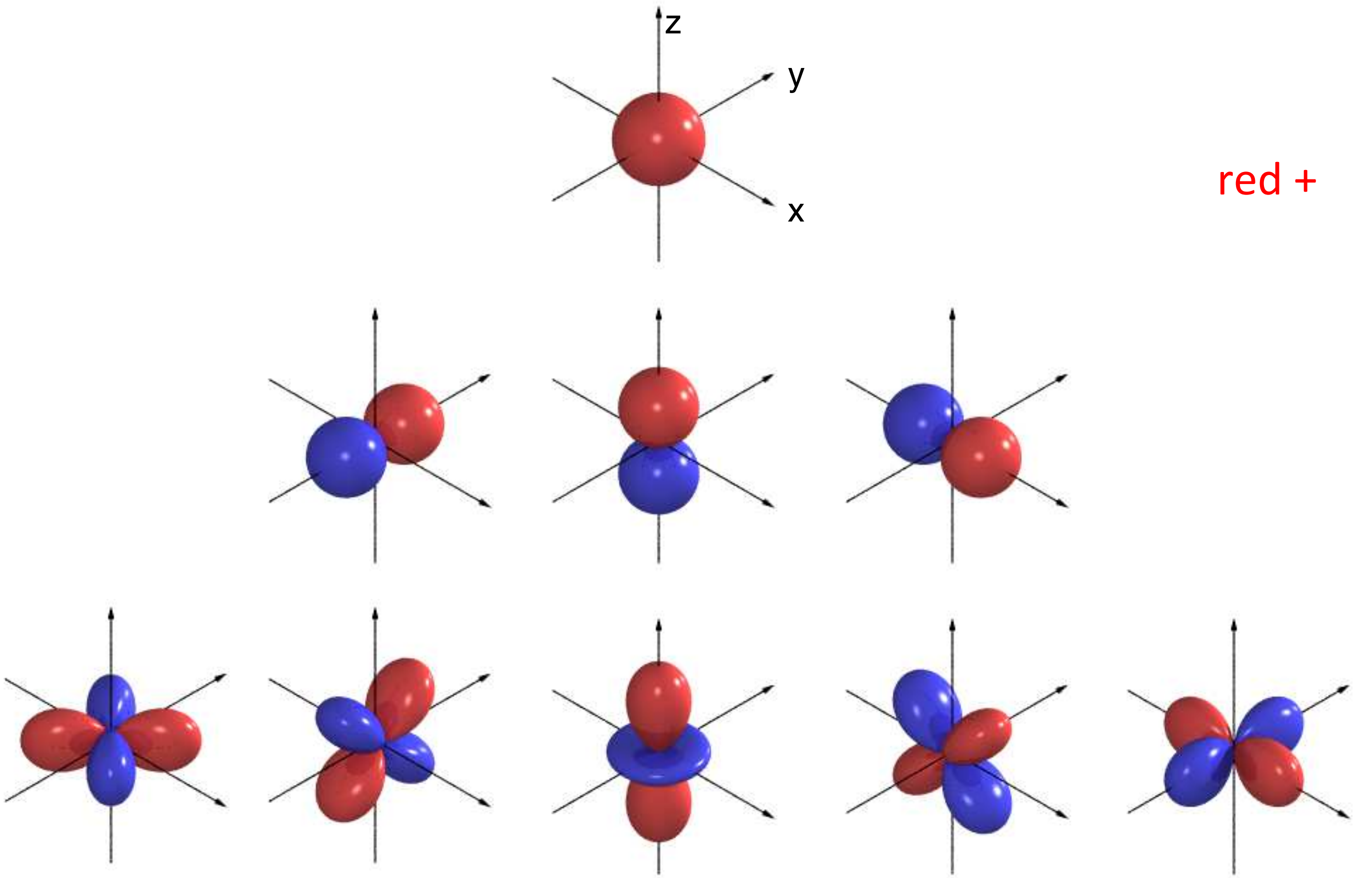
Real harmonics

$$
\begin{aligned}
s &= y_{00} &&= Y_0^0 &&= \sqrt{\tfrac{1}{4\pi}} && \\
p_y &= y_{1-1} &&= \tfrac{i}{\sqrt{2}}(Y_1^1 + Y_{-1}^1) &&= \sqrt{\tfrac{3}{4\pi}} && y/r \\
p_z &= y_{10} &&= Y_0^1 &&= \sqrt{\tfrac{3}{4\pi}} && z/r \\
p_x &= y_{11} &&= \tfrac{1}{\sqrt{2}}(Y_1^1 - Y_{-1}^1) &&= \sqrt{\tfrac{3}{4\pi}} && x/r \\
d_{xy} &= y_{2-2} &&= \tfrac{i}{\sqrt{2}}(Y_2^2 - Y_{-2}^2) &&= \sqrt{\tfrac{15}{4\pi}} && xy/r^2 \\
d_{yz} &= y_{2-1} &&= \tfrac{i}{\sqrt{2}}(Y_1^2 + Y_{-1}^2) &&= \sqrt{\tfrac{15}{4\pi}} && yz/r^2 \\
d_{3z^2-r^2} &= y_{20} &&= Y_0^2 &&= \sqrt{\tfrac{15}{4\pi}}\tfrac{1}{2\sqrt{3}} && (3z^2 - r^2)/r^2 \\
d_{xz} &= y_{21} &&= \tfrac{1}{\sqrt{2}}(Y_1^2 - Y_{-1}^2) &&= \sqrt{\tfrac{15}{4\pi}} && xz/r^2 \\
d_{x^2-y^2} &= y_{22} &&= \tfrac{1}{\sqrt{2}}(Y_2^2 + Y_{-2}^2) &&= \sqrt{\tfrac{15}{4\pi}\tfrac{1}{2}} && (x^2 - y^2)/r^2
\end{aligned}
$$

$$x = r\sin\theta\cos\phi,\ y = r\sin\theta\sin\phi,\ z = r\cos\theta$$

Draw y_{10}, y_{11} and y_{1-1} in the x-y plane

Real harmonics



l=0

l=1

l=2

red + blue -