Exercise 06

Hydrogen wavefunctions

Introduction

The hydrogen atom can be studied as a two-body system governed by the hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

Exploiting the spherical geometry, we can use a spherical coordinate system with the proton at the origin. The time-independent Schrodinger equation becomes:

$$-\frac{\hbar}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi) - \frac{e^2}{4\pi\epsilon_0 r}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

The solution can be found separating the radial and the angular part:

$$\psi(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi) = R_{nl}(r)f_{lm}(\theta)g_m(\phi)$$

The normalized radial wave function is:

$$R_{nl}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}}\, e^{-\frac{r}{na_0}} \left(\frac{2r}{na_0}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na_0}\right)$$

where a_0 is the Bohr radius (use $a_0 = 1$ for the exercise) and L^{2l+1}_{n-l-1} are the Laguerre polynomials. The quantum numbers have to respect the following relation:

$$0 \leq l \leq n-1 \qquad n = 1, 2, ...$$

The angular part of the solution is made by the two functions:

$$f_{lm}(\theta) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{lm}(\cos\theta)$$

$$g_m(\phi) = e^{im\phi}$$

where $P_{lm}(\cos\theta)$ are the associated Legendre polynomials and with quantum numbers:

$$l = 0, 1, 2, ...$$

$$m = 0, \pm 1, \pm 2, ...$$

0.1 Radial part (10 points)

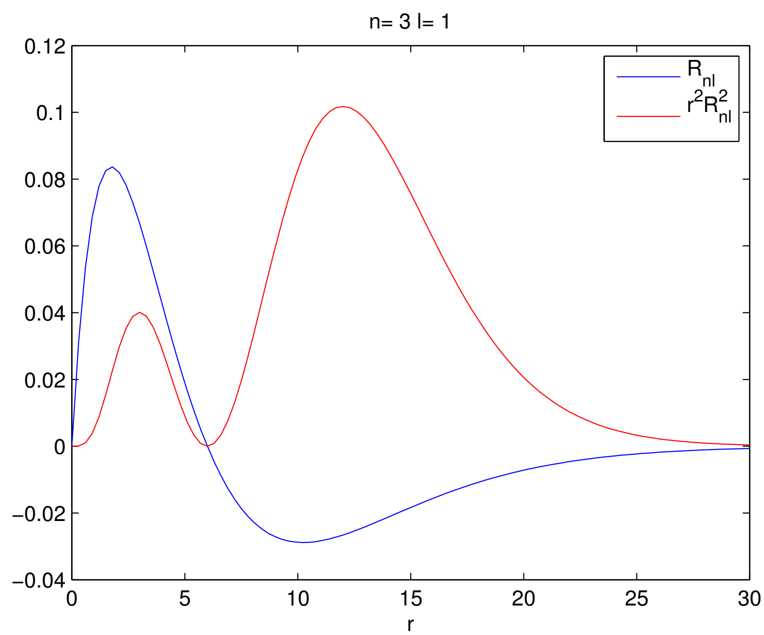
Write a MATLAB script to plot the radial wavefunction $R_{nl}(r)$ and the radial probability distribution $r^2 R_{nl}(r)^2$ (the term r^2 comes from the integral in spherical coordinates). To solve this part of the exercise, it is necessary to implement correctly the Laguerre polynomials, that are defined by the function:

$$L^k_j(x) = (-1)^k \frac{d^k}{dx^k}\left(e^x \frac{d^{j+k}}{dx^{j+k}} e^{-x} x^{j+k}\right)$$

The first six radial wavefunctions are:

$$R_{1,0}(r) = 2a_0^{-3/2}e^{-r/a_0}$$
$$R_{2,0}(r) = \frac{1}{\sqrt{2}}a_0^{-3/2}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0}$$
$$R_{2,1}(r) = \frac{1}{\sqrt{24}}a_0^{-3/2}\frac{r}{a_0}e^{-r/2a_0}$$
$$R_{3,0}(r) = \frac{2}{\sqrt{27}}a_0^{-3/2}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$$
$$R_{3,1}(r) = \frac{8}{27\sqrt{6}}a_0^{-3/2}\left(1 - \frac{r}{6a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$$
$$R_{3,2}(r) = \frac{4}{81\sqrt{30}}a_0^{-3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}$$

Your graph should look similar to the following:

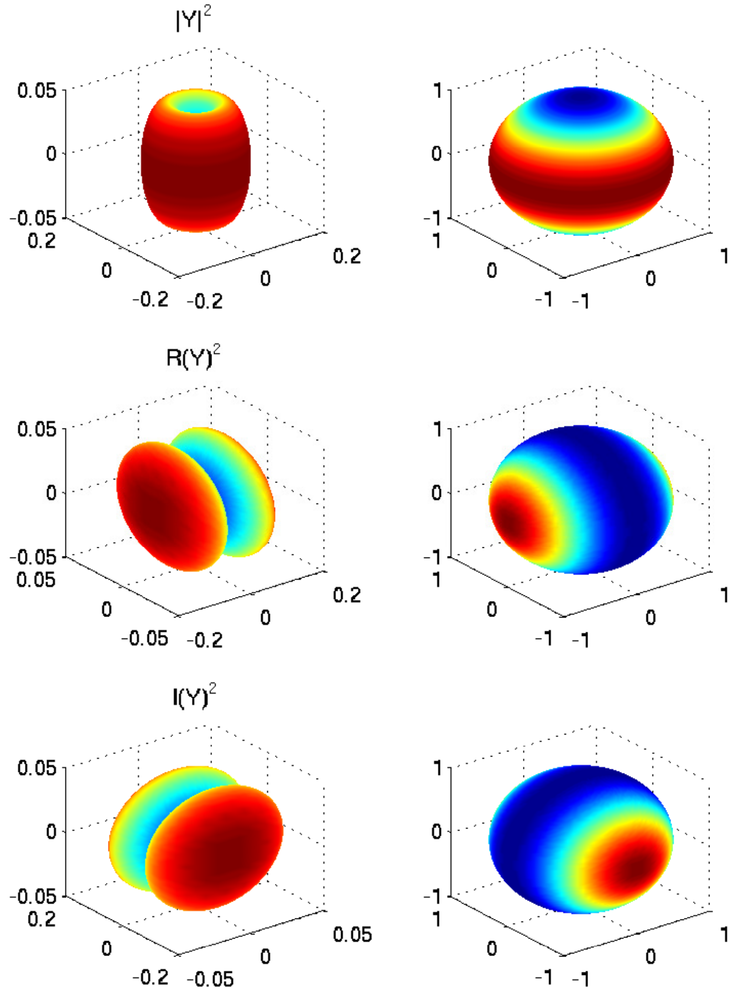


0.2 Angular part (10 points)

For the second part of the exercise you have to plot the angular part of the wavefunction. To solve this part, you need the associated Legendre polynomials:

$$P_0^0(x) = 1$$
$$P_1^0(x) = x = \cos\theta$$
$$P_1^1(x) = -\sqrt{1 - x^2} = -\sin\theta$$
$$P_2^0(x) = 1/2(3x^2 - 1) = 1/2(3\cos^2\theta - 1)$$
$$P_2^1(x) = 3x\sqrt{1 - x^2} = 3\cos\theta\sin\theta$$
$$P_2^2(x) = 3(1 - x^2) = 3\sin^2\theta$$

You should plot the squared spherical armonics in cartesian coordinates and then map them to a unit sphere, like in the example:



For the graphs in cartesian coordinates, we need to take the right angles, $\theta \in [0, \pi]$ is the Altitude, $\phi \in [0, 2\pi]$ is the Azimuthal:

```
N=100;
theta=0:pi/N:pi;
phi=...
```

We have to implement the two functions $f_{lm}(\theta)$ and $g_m(\phi)$. Then we have to compute the function $Y_{lm}(\theta, \phi)$ as product column-row. In this way, we get $Y_{lm}(\theta, \phi)$ as a matrix, where each element is the product $f_{lm}(\theta)g_m(\phi)$.

We are interested in $|Y_{lm}(\theta, \phi)|^2$, $(\mathrm{Re}Y_{lm}(\theta, \phi))^2$ and $(\mathrm{Im}Y_{lm}(\theta, \phi))^2$, so we need to use the functions `abs(), real()` and `imag()`. Finally, we have to convert everything in cartesian coordinates:

```
X=rho.*(sin(theta)'*cos(phi));
Y=rho.*(sin(theta)'*sin(phi));
Z=rho.*(cos(theta)'*ones(size(phi)));
```

where `rho` is $|Y_{lm}(\theta, \phi)|^2$, $(\mathrm{Re}Y_{lm}(\theta, \phi))^2$ and $(\mathrm{Im}Y_{lm}(\theta, \phi))^2$. To plot the spherical harmonics, we use the function:

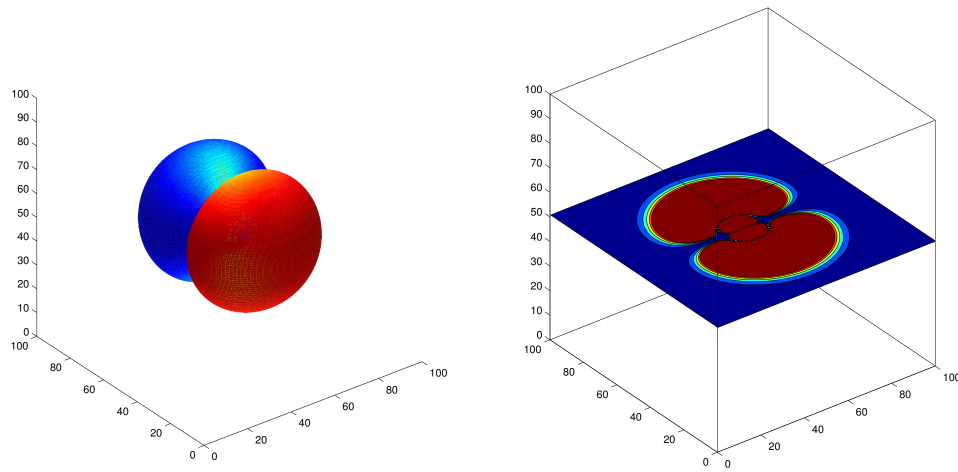
```
surf(X,Y,Z,rho)
```

To get the representation of the spherical harmonics mapped to a unit sphere, we have to gen-

erate the coordinates of the sphere with the command:
`[XS YS ZS]=sphere(N);`
and we realize the graph with:
`surf(XS, YS, ZS,rho)`
After the function `surf()`, you can remove the black lines with `shading interp`.

0.3 Orbitals (10 points)

Finally, we are going to plot the full orbitals, like in the example:



To plot the orbitals, we use the function `meshgrid(xrange,yrange,zrange)`, that replicates the grid vectors to produce the coordinates of a 3D rectangular grid (X, Y, Z):

```
xrange=-32:64/N:32;
yrange=xrange;
zrange=xrange;
[x y z] = meshgrid(xrange,yrange,zrange);
```

Then we convert the grids in spherical coordinates, with the command:

```
[theta,phi,r] = cart2sph(x,y,z);
```

Now we can compute $R_{nl}(r)$, $f_{ml}(\theta)$, $g_m(\phi)$ and then $\psi(r, \theta, \phi)$, that is a 3D array, containing the value of the wavefunction in each point of the 3D space that we generated.
The function: `isosurface(real(PSI).^2,probability)`
plots the surface that represents the points with the same probability.

In the right graph, we have a section of the orbital. The isolines, i.e. the line of plane with the same probability, are obtained with the function:

```
contourf(real(PSI(:,:,50)).2,[0:delta:probability])
```

The second argument of the function `contourf()` tells to MATLAB to find the isolines from 0 to "probability" every "delta" steps.

Send the .m scripts by email to luca.donati@fu-berlin.de before Wednesday the January the 7th 2015 at noon.