Problem Solving Class: Van Quark tot Biomaterie

Test Set: Numerical solutions to the Schrödinger equation of the hydrogen atom

The known wave functions for electrons in a hydrogen atom are (do not take *Z=1*, see below):

$$\psi_{n,l,m}(r,\theta,\varphi) = \frac{u_{n,l}(r)}{r} Y_{l,m}(\theta,\varphi)$$

$$u_{n,l}(r) = \sqrt{\frac{2Z}{n\,a_0}} \sqrt{\frac{(n-l-1)!}{2n(n+l)!}} \exp(-\frac{Z\,r}{n\,a_0}) \left(\frac{2\,Z\,r}{n\,a_0}\right)^{l+1} L_{n-l-1}^{2l+1}(\frac{2\,Z\,r}{n\,a_0})$$

Here *L* is a generalized Laguerre polynomial and *Y* is a spherical harmonic function.
Look up in the Mathematica library and find the functions: **`LaguerreL`** and **`SphericalHarmonicY`**, and use these functions in the following.
We found that Mathematica only finds solutions as long as *Z* remains defined as a variable; this is strange and we do not understand but use this hint to your advantage. (A bug ?).

a) Write the wave function for a *1s* orbital (electronic wave function).
b) Do the same for a *3p* orbital.
c) Show that this *3p* gives a solution to the Schrödinger equation (by simply substituting).
d) Write a general expression for an *np* wave function (with variable *n*, declared as an integer).

We now proceed in trying to calculate *intensities* of spectral lines. In general the intensity of a spectral line is given by the square of a matrix element, like in:

$$|<\psi_f \mid z \mid \psi_i>|^2$$

Here this squared matrix element represents the intensity of a spectra line for a transition from the initial state $|i>$ to a final state $|f>$ where the external field is linearly polarized along the *z*-axis. Note that through a frame transformation this can e written as:

$$|<\psi_f \mid z \mid \psi_i>|^2 = |<\psi_f \mid r\cos(\theta) \mid \psi_i>|^2$$

This is needed because the wave functions are defined in the coordinate system (r, θ, ϕ).

Selection Rules
Now write down an expression for a transition from state $|1s>$ to state $|3p>$. Since we are only interested in a selection rule you may ignore the radial part of the wave functions; focus on the angular part !
Make a calculation for the transition line intensity for three different possibilities. For the *1s* state there is only one option, namely the wave function:

$$\psi_{1,0,0}$$

For the *3p* state there are three possibilities however:

$$\psi_{3,1,1},\ \psi_{3,1,0} \text{ and } \psi_{3,1,-1}$$

Do the calculation for each of these three cases and find a selection rule for *m*-quantum numbers.

Polarization of the light

Now do the same calculation for the polarization vector ($x+iy$) instead of z.

$$|<\psi_{3p} \mid x+iy \mid \psi_{1s}>|^2$$

Now you find a different m-selection rule. Note that $x+iy$ represents circularly polarized light.

Lyman series

Now we try to find a generalized expression for the spectral line intensity of the Lyman series. This is about the transitions: $1s \rightarrow np$. Use the knowledgde from the previous section, while we use linearly polarized light (defined along the z-axis); then the quantum numbers are:

$n_i=n \quad l_i=1 \quad m_i=0$

$n_f=1 \quad l_f=0 \quad m_f=0$

We need to calculate the following integral:

$$<\psi_{1,0,0} \mid z \mid \psi_{n,1,0}>=<\psi_{1,0,0} \mid r\cos(\theta) \mid \psi_{n,1,0}>$$

This can be rewritten as:

$$<\psi_{1,0,0} \mid r\cos(\theta) \mid \psi_{n,1,0}>=\int d^3r(\psi_{1,0,0})^* r\cos(\theta)\psi_{n,1,0}$$

$$=\int_0^{2\pi}\int_0^{\pi} Y_{0,0}(\theta,\varphi)^* \cos(\theta) Y_{1,0}(\theta,\varphi)\sin(\theta)d\theta\, d\varphi \int_0^{\infty}(\frac{u_{1,0}(r)}{r})^* r(\frac{u_{n,1}(r)}{r})r^2 dr$$

e) Use Mathematica and calculate the integral for the angular part.

Note that the intensity of a spectral line is given by the square of the matrix element. Neglect a proportionality factor:

$$I=|<\psi_{1,0,0} \mid z \mid \psi_{n,1,0}>|^2=|<\psi_{1,0,0} \mid r\cos(\theta) \mid \psi_{n,1,0}>|^2$$

f) Calculate the n-dependence of this intensity. It should be possible to calculate this in algebraic form (with some difficulties); but if that does not turn out to be possible then attempt to obtain numerical solutions.

g) Approximate this n-dependence in the limit for large n.