Review of Hydrogenic wave functions

Here are some of the low-order wave functions \( \psi_{n\ell m} = R_{n\ell}(r) Y_{\ell}^m(\theta, \phi) \) for the (simple) hydrogen atom:

\[
\psi_{1,0,0} = \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \\
\psi_{2,0,0} = \left( \frac{1}{32\pi a_0^3} \right)^{1/2} \left( 2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} \\
\psi_{2,1,0} = \left( \frac{1}{32\pi a_0^3} \right)^{1/2} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \cos \theta \\
\psi_{2,1,\pm 1} = \mp \left( \frac{1}{64\pi a_0^3} \right)^{1/2} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \sin \theta e^{\pm i\phi}
\]

Let us recall the expressions for the low-order spherical harmonics:

\[
Y_{0}^0 = \frac{1}{\sqrt{4\pi}}; \quad Y_{1}^\pm = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}; \quad Y_{1}^0 = \sqrt{\frac{3}{4\pi}} \cos \theta.
\]

Therefore, we can write the radial wave functions down:

\[
R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-\frac{r}{2a_0}}; \quad R_{20}(r) = \frac{1}{2\sqrt{2} a_0^{3/2}} \left( 2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} \\
R_{21}(r) = \frac{1}{\sqrt{24} a_0^{3/2}} r e^{-\frac{r}{2a_0}}
\]

One of the features of the wave function in one dimension that is important is the node, a zero of the wave function in the interior of the region in which it is defined. In one dimension we have a theorem that for reasonable potentials the ground state has zero nodes and the \( n \)th energy eigenstate has \( n - 1 \) nodes. Please take a look at the eigenfunctions of the infinite potential well and the simple harmonic oscillator.

The nodes where the wave function goes through zero linearly yields a large contribution to the kinetic energy since

\[
\left\langle \frac{p^2}{2\mu} \right\rangle = \frac{\hbar^2}{2\mu} \int dx \left| \frac{d\psi(x)}{dx} \right|^2
\]

and the slope is non-vanishing.

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1The principal quantum number \( n \) determines the energy \( E_n = -\frac{\hbar^2 q^2}{2m \ell^2} \frac{1}{n^2} \) \( \ell \) the eigenvalue of \( L^2 \) and \( m\hbar \) is the eigenvalue of \( L_z \).

2Sturm-Liouville theory of the generalized eigenvalue problem \( Ly(x) = \lambda w(x)y(x) \) for a so-called weight function \( w(x) \) (you are familiar with the case \( w(x) = 1 \)) of the self-adjoint operator

\[
L \equiv -p(x) \frac{d^2}{dx^2} - p'(x) \frac{d}{dx} + q(x)
\]

shows these general properties. This was done in the mid-nineteenth century well before quantum mechanics was a twinkle in the eye of its founders.
$R_{10}(r)$ is the ground state wave function; it has zero nodes and is a constant at $r = 0$. $R_{20}$ is the radial part of the 2s state; it has one node and this is a consequence of the orthogonality of the 1s and 2s states both of which are spherically symmetric and so the angular parts are the same. We check this with Mathematica; note that we have to include the $r^2 dr$ from the three-dimensional volume integral:

$$\text{In[2]:= Integrate[Exp[-r/a] Exp[-r/(2a)] (2-(r/a)) r^2, \{r,0,Infinity\}, Assumptions -> Re[a]>0]}$$

$$\text{Out[2]= 0}$$

$R_{21}$ gives the radial part of the 2p wave function. It has zero nodes but is nevertheless orthogonal to the 1s state which also has zero nodes because the angular parts are orthogonal. Recall that

$$\int_0^\pi \sin \theta d\theta \int_0^{2\phi} d\phi \left(Y_{\ell'}^m(\theta, \phi)\right)^* Y_{\ell}^m(\theta, \phi) = \delta_{\ell,\ell'} \delta_{m,m'} .$$

The following facts about $R_{n\ell}(r)$ are worth noting:

- It has $n - \ell - 1$ zeros.
- It varies as $r^\ell$ for small $r$; higher the angular momentum the lower the probability
- The mean radius grows roughly as $n^2 a_0$.

More about the ground state: At what value of $r$ is the wave function most likely to be found? The probability density reaches a maximum when $|\psi_{n\ell m}|^2 r^2$ is maximum. Do not forget the $r^2 dr$ factor which comes from the fact that finding the electron between $r$ and $r + dr$ corresponds to finding the electron in a spherical shell whose volume increases as $r^2$. For the 100 state it is easy to check that this occurs at $r = a_0$. One can also compute $\langle r \rangle$ in the ground state:

$$\text{In[7]:= Integrate[(1/(Pi a^3)) Exp[-r/a] r Exp[-r/a] 4 Pi r^2, \{r,0,Infinity\}, Assumptions -> Re[a]>0]}$$

$$\text{Out[7]=3 a /2}$$

We can also determine $\langle 1/r \rangle$:

$$\text{In[9]:= Integrate[(1/(Pi a^3)) Exp[-r/a] r^{-1} Exp[-r/a] 4 Pi r^2, \{r,0,Infinity\}, Assumptions -> Re[a]>0]}$$

$$\text{Out[9]=1/a}$$

Why is this exactly $1/a$? Note that $\langle 1/r \rangle \neq 1/\langle r \rangle$.

The general result for $\langle r \rangle$ in the state $n\ell m$ can be obtained by using the associated Laguerre polynomials and is given by

$$\langle r \rangle_{n\ell m} = \frac{a_0}{2} \left[3n^2 - \ell(\ell + 1)\right]$$

$$2$$
Figure 1: The radial wave function for the 1s (in Red), 2s (in Green), and 2p (in Blue). I have cut off the upper part of the figure for clarity. Note that $R_{2s}(r)$ has a node at $r/a_0 = 2$.

Figure 2: The radial probability density ($\rho(r) = R^2(r) r^2$) for the 1s (in Red), 2s (in Green), and 2p (in Blue) states of the wave function.