

Non-relativistic Hydrogen Wavefunctions

Ref. Zettili §6.3.5, Shankar Ch 13, Sakurai §A.6

As already mentioned, for this initial treatment of hydrogen, we assume that both the proton and the electron are spinless point particles, interacting only *via* the Coulomb potential, and that they are moving very slowly compared to the speed of light, so that non-relativistic mechanics can be used.

The probability of finding the electron at a particular place within the atom is given by the square of the wavefunction $\psi(\vec{r})$. That is, the **position probability density** (probability per unit volume) for finding the electron at a displacement \vec{r} relative to the nucleus is $|\psi(\vec{r})|^2$. If we integrate over some volume V , we get the probability of finding the electron within that volume:

$$P(V) = \int_V |\psi(\vec{r})|^2 d^3r. \quad (1)$$

Note this is a three-dimensional integral; if we use rectangular coordinates, $d^3r = dx dy dz$; in spherical polar coordinates, $d^3r = r^2 \sin\theta dr d\theta d\phi$. We often combine the angular parts of this by writing $d\Omega = \sin\theta d\theta d\phi$; then the full 3-dimensional volume element is $d^3r = r^2 dr d\Omega$. (Here Ω stands for a solid angle and is measured in steradians, with the total solid angle surrounding a point being 4π steradians.) Since the probability of finding the electron somewhere must be 1 (100%), it must be a fact that

$$\int |\psi(\vec{r})|^2 d^3r = 1 \quad (2)$$

if the integral is taken over all space.

For hydrogen we know the wavefunction quite well. It is simplest to use spherical polar coordinates, because it turns out that the angular dependence of $\psi(\vec{r})$ is determined by the electron's orbital angular momentum, which we know is both conserved and quantized. Thus the functional form of the electron wavefunction is closely connected to the quantum numbers used to classify the states and energy levels. For given values of the three quantum numbers (n, l, m) the wavefunction is written

$$\psi_{nlm}(\vec{r}) = R_{nl}(r) Y_{lm}(\theta, \phi). \quad (3)$$

(Here m stands for the quantum number m_l ; we are just using m for simplicity.) The functions Y_{lm} are known as **spherical harmonics**. They are not specific to the hydrogen atom, but occur in many problems in mathematics in which spherical coordinates are used. For the first few values of l, m they are easy to write down.

Spherical harmonics:

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

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos(\theta) \quad (5)$$

$$Y_{1,1} = -\sqrt{\frac{3}{8\pi}} \sin(\theta) e^{i\phi} \quad (6)$$

$$Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin(\theta) e^{-i\phi} \quad (7)$$

Of course $e^{i\phi} = \cos\phi + i\sin\phi$ and $i = \sqrt{-1}$. The spherical harmonics are so well known that we normally do not write them out in formulas like these, but simply use $Y_{lm}(\theta, \phi)$ in our equations

just as we use any familiar function such as $\sin \theta$ for example. One simple feature of the Y_{lm} is their normalization:

$$\int |Y_{lm}(\theta, \phi)|^2 d\Omega = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta |Y_{lm}(\theta, \phi)|^2 = 1. \quad (8)$$

The functions $R_{nl}(r)$ are called the **radial wavefunctions** for hydrogen, and are also well known. In complex atoms, we often assume that each electron has a wavefunction of form $\psi_{nlm}(\vec{r})$, with the same spherical harmonics Y_{lm} , but then the radial functions must be found in some approximate way, and will not be as simple as for hydrogen. Also we often define a different radial function $P_{nl}(r)$ by writing $P_{nl}(r) = rR_{nl}(r)$. Then the full wavefunction is

$$\psi_{nlm}(\vec{r}) = \frac{1}{r} P_{nl}(r) Y_{lm}(\theta, \phi). \quad (9)$$

One advantage of $P_{nl}(r)$ is that its normalization is simple. If we combine the two normalizing equations from above, we get

$$\int |\psi|^2 d^3r = \int_0^\infty r^2 R_{nl}(r)^2 dr = \int_0^\infty P_{nl}(r)^2 dr = 1. \quad (10)$$

Thus $P_{nl}(r)^2$ has the meaning of probability per unit length: in other words $P_{nl}(r)^2 dr$ is the probability for the electron to be at a distance between r and $r + dr$ from the nucleus.

For the first few states of hydrogen, we have the following radial functions, sometimes called **orbitals**. In these equations we are using the atomic unit of length a_0 , the first Bohr radius. So r is measured in units of a_0 and R in units of $a_0^{-3/2}$ so that R^2 is probability density per unit volume.

Hydrogen radial functions:

$$1s : R_{10}(r) = 2e^{-r} \quad (11)$$

$$2s : R_{20}(r) = \frac{1}{\sqrt{2}}(1 - r/2)e^{-r/2} \quad (12)$$

$$2p : R_{21}(r) = \frac{1}{2\sqrt{6}}re^{-r/2} \quad (13)$$

$$3s : R_{30}(r) = \frac{2}{3\sqrt{3}}(1 - 2r/3 + 2r^2/27)e^{-r/3} \quad (14)$$

$$3p : R_{31}(r) = \frac{8}{27\sqrt{6}}(r - r^2/6)e^{-r/3} \quad (15)$$

$$3d : R_{32}(r) = \frac{4}{81\sqrt{30}}r^2e^{-r/3} \quad (16)$$

Some things to notice about these functions:

- (1) The factor $e^{-r/n}$ determines the orbital's size, which increases with the principal quantum number n , since the wavefunction goes to zero quickly for $r \gg na_0$.
- (2) For small r , the functions behave like r^l .
- (3) The number of nodes (zeros) is $n - l - 1$.
- (4) For a given n , the functions with maximum l ($1s, 2p, 3d, \dots$) have no nodes, and correspond to the circular orbits in the Kepler theory; as l decreases, the Kepler ellipses become more eccentric (elongated).

More general results

The general equations for a one-electron atom, with nuclear charge (atomic number) Z , neglecting spin and relativity, are summarized below as given in section A.6 of the appendix to Modern Quantum Mechanics by J.J. Sakurai. In these equations the factor e^2 must be divided by $4\pi\epsilon_0$ if using SI units. The electron mass m must be replaced by the reduced mass μ for best precision. The constants which appear here have the approximate values:

$$e^2 = 1.44 \text{ eV}\cdot\text{nm}, \quad \hbar c = 197 \text{ eV}\cdot\text{nm}, \quad a_0 = \frac{\hbar^2}{me^2} = 0.0529 \text{ nm}, \quad E_0 = \frac{e^2}{2a_0} = 13.6 \text{ eV}.$$

Hydrogenic atoms.

Given $V(r) = -\frac{Ze^2}{r}$ we have the energy eigenvalues

$$E_n = -\frac{Z^2 e^2}{2n^2 a_0} = -\frac{Z^2 E_0}{n^2}$$

for n a positive integer, and eigenfunctions

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

for integers $|m| \leq l < n$. The radial functions are most easily written in terms of the dimensionless variable

$$x = \frac{2Zr}{na_0}$$

The general result is

$$R_{nl}(r) = -\left(\frac{2Z}{na_0}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} x^l e^{-x/2} L_{n+l}^{2l+1}(x)$$

where $L_{n+l}^{2l+1}(x)$ is the associated Laguerre polynomial.

The associated Laguerre polynomial is defined by

$$L_p^q(x) = \frac{d^q}{dx^q} L_p(x) \quad \text{and} \quad L_p(x) = e^x \frac{d^p}{dx^p} (x^p e^{-x})$$

Using the known properties of the Laguerre functions, radial integrals for expectation values of powers of r can be calculated:

$$\begin{aligned} \langle r^k \rangle &= \int_0^\infty r^{2+k} R_{nl}(r)^2 dr \\ \langle r \rangle &= \frac{a_0}{2Z} [3n^2 - l(l+1)] \\ \langle r^2 \rangle &= \frac{a_0^2 n^2}{2Z^2} [5n^2 + 1 - 3l(l+1)] \\ \langle r^{-2} \rangle &= \frac{Z^2}{n^3 a_0^2 (l+1/2)} \end{aligned}$$

Exercises for the reader.

(1) Derive the formula for $\langle r^{-1} \rangle$ without doing an integral.

(2) Do the required integral for $\langle 2p | r^{-2} | 2p \rangle$ without using Laguerre polynomials and check against the general result above.