Kvantfysik Lecture notes No. 11

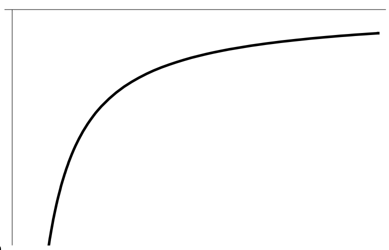
1 The Hydrogenic atom

The hydrogenic atom refers to a single electron bound to a nucleus with atomic number Z. The hydrogen atom has $Z = 1$. The electric charge of the electron is $-e$ while that of the nucleus is $+Ze$. The electron's reduced mass is

$$\mu = \frac{M_n m_e}{M_n + m_e} \approx m_e\,, \quad \text{since } m_e << M_n$$

where m_e and M_n are the masses of the electron and nucleus respectively. The potential due to the electrostatic attraction between the electron and the nucleus is

$$\begin{aligned} V(r) &= \frac{(+Ze)(-e)}{4\pi\epsilon_0\, r} \\ &= -\frac{Ze^2}{4\pi\epsilon_0\, r} \end{aligned}$$



where r is the radial separation between the electron and the nucleus. This potential is shown in the figure.

We are using SI (standard international) units here, where charges are in coulombs, voltages are in volts *etc.* ϵ_0 is the vacuum permittivity which has the value

$$\begin{aligned} \epsilon_0 &\approx 8.854 \times 10^{-12}\ \mathrm{A^2\,s^4\,kg^{-1}\,m^{-3}} \\ &\approx 0.05526\,\mathrm{eV\,V^{-2}\,nm^{-1}}\,. \end{aligned}$$

(It is also convenient to use $(4\pi\epsilon_0)^{-1} = 9 \times 10^9$ ohm-m/sec.) The electric charge e is $e \approx 1.602\times10^{-19}$ coulombs, the electron mass is $m_e \approx 9.109\times10^{-31}$ kg, and the proton mass is $m_p \approx 1.67 \times 10^{-27}$ kg

1.1 Solutions to the Schrödinger equation

Since the potential is radially symmetric, we look for solutions where we have separation of variables in spherical coordinates. This leads us to the radial Schrödinger equation

$$E\, u_\ell(r) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}u_\ell(r) + \left(\frac{\ell(\ell+1)\hbar^2}{2\mu\, r^2} - \frac{Ze^2}{4\pi\epsilon_0\, r}\right)u_\ell(r)\,, \qquad (1)$$

where recall that $u_\ell(r) = rR_\ell(r)$ and the full wave-function is

$$\psi(r, \theta, \phi) = R_\ell(r) Y_{\ell m}(\theta, \phi) .$$

We wish to find the bound state solutions, and since $V(r) < 0$ and approaches 0 as $r \to \infty$, the bound states have $E < 0$. For r very large, $V_{eff}(r)$ falls off to zero, so the Schrödinger equation for large r is approximately

$$E\, u_\ell(r) \approx -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} u_\ell(r)$$

We have already seen this equation many times and the only normalizable solution is

$$u_\ell(r) \approx A e^{-\kappa r} , \qquad r \gg 0 \qquad \kappa = \sqrt{-\frac{2\mu E}{\hbar^2}}$$

This of course is not the exact solution, but we will use it to help us find it. It is convenient to divide eq. (1) by E. This leads to

$$\begin{aligned} u_\ell(r) &= -\frac{\hbar^2}{2\mu E} \frac{d^2}{dr^2} u_\ell(r) + \left(\frac{\ell(\ell+1)\hbar^2}{2\mu E\, r^2} - \frac{Ze^2}{4\pi\epsilon_0 E\, r} \right) u_\ell(r) \\ &= \frac{1}{\kappa^2} \frac{d^2}{dr^2} u_\ell(r) - \left(\frac{\ell(\ell+1)}{\kappa^2 r^2} - \frac{2Ze^2\mu}{4\pi\epsilon_0 \hbar^2 \kappa^2 r} \right) u_\ell(r) \end{aligned}$$

Defining the dimensionless variable $\rho = \kappa r$, we then end up with

$$\frac{d^2}{d\rho^2} u_\ell(r) = \left(1 - \frac{2\lambda}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right) u_\ell(r) \tag{2}$$

where

$$\lambda \equiv \frac{Ze^2\mu}{4\pi\epsilon_0\hbar^2\kappa} = \frac{Ze^2}{4\pi\epsilon_0\hbar} \sqrt{-\frac{\mu}{2E}} .$$

It will be helpful later to define a dimensionless constant α, known as the "fine structure constant",

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137} \tag{3}$$

where c is the speed of light. In terms of α,

$$\lambda = Z\alpha \left(-\frac{\mu c^2}{2E} \right)^{1/2} . \tag{4}$$

The relativistic rest energy of an electron is $m_e c^2 \approx \mu c^2$. We will shortly see that the smallness of α ($\alpha \ll 1$) will lead to $|E| \ll m_e c^2$. Hence, the speed of the electron inside the atom is much less than the speed of light.

Our goal now is to find the values of λ that lead to normalizable solutions. We have already seen that for large ρ, the normalizable solution for (2) has

$$u_\ell(r) \approx Ae^{-\rho} \qquad \rho \gg 1\,.$$

We now let

$$u_\ell(r) = h_\ell(\rho)e^{-\rho}$$

which automatically incorporates the large ρ behavior, assuming that $h_\ell(\rho)$ does not grow too rapidly. Using that

$$\frac{d^2}{d\rho^2}(h_\ell(\rho)e^{-\rho}) = \left(h_\ell(\rho) - 2\frac{d}{d\rho}h_\ell(\rho) + \frac{d^2}{d\rho^2}h_\ell(\rho)\right)e^{-\rho}\,,$$

we can reduce eq. (2) to the differential equation for $h_\ell(\rho)$,

$$\left(\frac{d^2}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}\right)h_\ell(\rho) = 2\left(\frac{d}{d\rho} - \frac{\lambda}{\rho}\right)h_\ell(\rho)\,. \tag{5}$$

Let us now assume that $h_\ell(\rho) = h_{n\ell}(\rho)$ is a polynomial in ρ of order n,

$$h_\ell = \sum_{k=s}^{n} a_k\rho^k\,. \tag{6}$$

We must have $s > 0$ so that $h_{n\ell}(0) = 0$, ensuring that $R_\ell(0)$ is finite. Inserting (6) into (5) we get

$$\sum_{k=s}^{n}\Big(k(k-1) - \ell(\ell+1)\Big)a_k\rho^{k-2} = 2\sum_{k=s}^{n}(k-\lambda)a_k\rho^{k-1}\,. \tag{7}$$

Since the highest power of ρ on the lefthand side (*lhs*) of (7) is ρ^{n-2}, we must have $\lambda = n$ so that there is no ρ^{n-1} term on the righthand side (*rhs*). Likewise, since the lowest power on the *rhs* of (7) side is ρ^{s-1}, we must have $s = \ell + 1$ so that there is no ρ^{s-2} term on the *lhs*. Matching powers of ρ on the *lhs* with those on the *rhs*, we find the recursion relation

$$a_{k+1} = -\frac{2(n-k)}{k(k+1) - \ell(\ell+1)}\,a_k = -\frac{2(n-k)}{(k-\ell)(k+\ell+1)}\,a_k\,. \tag{8}$$

This determines the polynomial up to an overall normalization factor[1].

From now on we will replace λ by the integer n, which is known as the "principle quantum number". It satisfies $n \geq \ell+1$, since ρ^n is the top power

[1] In the appendix A.1 we show what would happen if $h_\ell(\rho)$ were an infinite series instead of a polynomial.

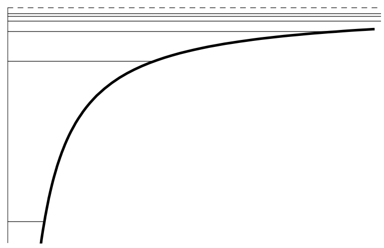
of $h_{n\ell}(\rho)$ and $\rho^{\ell+1}$ is the lowest power. Therefore, for $n = 1$, the only allowed value for ℓ is $\ell = 0$. For $n = 2$ we can have $\ell = 0, 1$. For $n = 3$ we can have $\ell = 0, 1, 2$. *etc.*

Using (4) we can find the energies

$$E_n = -\frac{Z^2\alpha^2\mu c^2}{2\lambda^2} = -\frac{Z^2\alpha^2\mu c^2}{2n^2} .$$

Observe that the energies only depend on the principle quantum number and not directly on ℓ. Of course ℓ comes into play by telling us which values of n are allowed. Notice that there are an infinite number of bound states since n can be made arbitrarily large. As n is increased, the energy gets closer and closer to zero.

Here are the first 6 energy levels.
Notice that their spacings get small as we go to larger n.



Notice that $|E_n| \ll \mu c^2$ (assuming that Z is much smaller than 137), confirming our previous statement that the electron's speed is nonrelativistic. Another way to express the energy levels is to write one factor of α in E_n as in (3). This gives

$$E_n = -\frac{Z^2\alpha}{2n^2} \cdot \frac{e^2}{4\pi\epsilon_0\hbar c} \cdot \mu c^2 = -\frac{Z^2}{2n^2} \cdot \frac{e^2}{4\pi\epsilon_0} \cdot \frac{\alpha\mu c^2}{\hbar c} = -\frac{Z^2}{2n^2} \cdot \frac{e^2}{4\pi\epsilon_0\, a_\mu}$$

where a_μ is the Bohr radius and is given by

$$a_\mu = \frac{\hbar}{\alpha c\mu} \approx 0.529 \text{ Å} = 0.529 \times 10^{-10} \text{ m}$$

In the case of the hydrogen atom where $Z = 1$, the lowest lying state has $E_1 = -\frac{1}{2}\frac{e^2}{4\pi\epsilon_0\, a_\mu}$ and so the energy is half the potential energy if the electron were located at a_μ. Hence the Bohr radius should be roughly equivalent to the size of the hydrogen atom in its ground state. If we plug in the charge of the electron, $e = 1.6 \times 10^{-19}$ Coulombs and $4\pi\epsilon_0 = (9 \times 10^9)^{-1}$ sec/ohm-m, we get $E_1 = -2.18 \times 10^{-18}$ joules $= -13.6$ eV. This is known as the ionization energy since it takes this much energy for an electron in the ground state to escape from the proton.

Expressing ρ in terms of r we have

$$\rho = \kappa r \;\; = \;\; \left(-\frac{2\mu E}{\hbar^2}\right)^{1/2} r = \left(\frac{Z^2\alpha^2\mu^2c^2}{n^2\hbar^2}\right)^{1/2} r = \frac{Z}{n} \cdot \frac{\alpha\mu c}{\hbar} \cdot r$$

$$= \frac{Z}{n} \cdot \frac{r}{a_\mu} . \tag{9}$$

The characteristic size of the hydrogenic atom should be where $\rho \sim 1$, which occurs when $r = na_\mu/Z$. We can see that this is sensible. For larger values of n the energy is higher, so we expect the electron to be farther away from the nucleus. Likewise, if Z is bigger the electrostatic potential is bigger so we expect the electron to be more tightly bound to the nucleus.

1.2 Spectra

The emission lines seen from atoms are due to photon emission when electrons jump between energy levels. The photon energy is given by $\mathcal{E} = h\nu = \frac{hc}{\lambda}$ where ν is the frequency and λ is the wavelength[2]. Hence if an electron jumps from an energy level with principle quantum number n_2 to an energy level with principle quantum number n_1, the energy of the photon is

$$\mathcal{E} = h\nu = \frac{Z^2 e^2}{8\pi\epsilon_0\, a_\mu}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = Z^2 hcR_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where R_H is the Rydberg constant

$$R_H = \frac{e^2}{8\pi\epsilon_0 hca_\mu} = \frac{\alpha}{4\pi a_\mu} = 1.10 \times 10^7 \text{ m}^{-1}$$

Therefore the wavelength is

$$\lambda = \frac{c}{\nu} = \frac{1}{Z^2 R_H} \cdot \frac{n_1^2 n_2^2}{n_2^2 - n_1^2}.$$

For more details on the spectra see the # 4x notes.

1.3 Eigenfunctions and normalization

We label the eigenfunctions by the principle quantum number n and ℓ. It is conventional to define a new polynomial $g_{n\ell}(\rho)$ where

$$h_{n\ell}(\rho) = g_{n\ell}(\rho)\rho^{\ell+1} .$$

Hence we have

$$u_{n\ell}(r) = g_{n\ell}(\rho)\rho^{\ell+1}e^{-\rho}$$

[2]Not to be confused with the previous definition of λ which has been replaced by n.

or in terms of $R_\ell(r)$

$$R_{n\ell}(r) = g_{n\ell}(\rho)\rho^\ell e^{-\rho}$$

where we have absorbed a factor of κ into $g_{n\ell}(\rho)$ for this last expression. If we write

$$g_{n\ell}(\rho) = \sum_{k=0}^{n-\ell-1} c_k \rho^k\,, \tag{10}$$

then the recursion relation in (8) becomes

$$c_{k+1} = -\frac{2(n-k-\ell-1)}{(k+1)(k+2\ell+2)}\, c_k\,. \tag{11}$$

The polynomials $g_{n\ell}(\rho)$ are related to famous polynomials in mathematics known as Laguerre polynomials (you can read about them in Griffiths). But we can find them using the recursion relation in (11). The first few examples are

$$g_{10}(\rho) = c_{10} \qquad g_{20}(\rho) = c_{20}(1-\rho) \qquad g_{21} = c_{21}\,, \qquad g_{30}(\rho) = c_{30}(1-2\rho+\frac{2}{3}\rho^2)$$

The coefficients $c_{n\ell}$ are determined by normalization. To normalize the wave-functions we set

$$1 = \int_0^\infty r^2 R_{n\ell}(r) R_{n\ell}(r)\, dr$$

where we have assumed that $R_{n\ell}(r)$ is real. It is more convenient to convert $r^2 dr$ to ρ variables then to convert the ρ in $R_{n\ell}$ back to r. Using (9) we have

$$1 = \left(\frac{n\, a_\mu}{Z}\right)^3 \int_0^\infty \rho^2 g_{n\ell}^2(\rho) \rho^{2\ell} e^{-2\rho}\, d\rho$$

The integrals are a sum of integrals of the form

$$\int_0^\infty \rho^j e^{-2\rho} d\rho \overset{\substack{\text{change}\\ \text{var.}}}{=} 2^{-(j+1)} \int_0^\infty z^j e^{-z}\, dz = 2^{-(j+1)} j!\,.$$

For example, for R_{10} we have

$$1 = \left(\frac{a_\mu}{Z}\right)^3 \int_0^\infty \rho^2 (c_{10})^2 e^{-2\rho}\, d\rho = \frac{1}{4}\left(\frac{a_\mu}{Z}\right)^3 (c_{10})^2 \qquad \Rightarrow \quad c_{10} = 2\left(\frac{Z}{a_\mu}\right)^{3/2}$$

The full wavefunctions are written in terms of the three "quantum numbers" n, ℓ and m, that is

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r) Y_{m\ell}(\theta,\phi)$$

1.4 Expectation values

Suppose we wish to find $\langle r^2 \rangle_{n\ell}$. As you might expect

$$\langle r^2 \rangle_{n\ell} \;=\; \int_0^\infty r^2 R_{n\ell}(r) r^2 R_{n\ell}(r)\, dr = \left(\frac{n\, a_\mu}{Z}\right)^5 \int_0^\infty \rho^4 g_{n\ell}^2(\rho) \rho^{2\ell} e^{-2\rho}\, d\rho$$

In the R_{10} example we then have

$$\langle r^2 \rangle_{10} = \left(\frac{a_\mu}{Z}\right)^5 \int_0^\infty \rho^4 (c_{10})^2 e^{-2\rho}\, d\rho = \left(\frac{a_\mu}{Z}\right)^5 4 \left(\frac{Z}{a_\mu}\right)^3 \frac{1}{32} \cdot 4! = 3 \left(\frac{a_\mu}{Z}\right)^2$$

We can define the square root of this as the size of the atom, hence for hydrogen we have

$$\sqrt{\langle r^2 \rangle_{10}} = \sqrt{3}\, a_\mu$$

If the expectation values involve angles then you will need to use the $Y_{\ell m}(\theta, \phi)$.

A Appendix

A.1 Generating the unwanted solution

Suppose λ were not an integer, such that the expansion for $h_\ell(\rho)$ is an infinite series,

$$h_\ell(\rho) = \sum_{k=\ell+1}^{\infty} a_k \rho^k \,, \tag{12}$$

with the recursion relation

$$a_{k+1} = -\frac{2(\lambda - k)}{(k-\ell)(k+\ell+1)}\, a_k \,. \tag{13}$$

Since λ is noninteger, the series does not terminate. For large values of k where $k >> \ell$ and $k >> \lambda$, we see that

$$a_{k+1} \approx \frac{2k}{k \cdot k} a_k = \frac{2}{k} a_k \,.$$

This suggests for large ρ that

$$h_\ell(\rho) \approx c \sum_k \frac{(2\rho)^k}{k!} = c\, e^{2\rho} \,.$$

In this case $u_\ell \sim e^{2\rho} e^{-\rho} = e^\rho$. By having λ be noninteger we have generated the unwanted nonnormalizable solution for $u_\ell(\rho)$.