Lecture 15:
The Hydrogen atom

We will now consider a relatively simple bound system composed of an electron and a proton: the Hydrogen atom.

If m_e and m_p are the electron and proton mass, respectively, the reduced mass is $m = m_e m_p/(m_e + m_p) \approx 0.995 m_e \approx m_e$. The large difference between the electron and proton mass thus allows us to neglect the proton dynamics and focus exclusively on the electron dynamics. The Hamiltonian associated to the system is then:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} \quad , \quad H\psi(r) = E\psi(r) \tag{1}$$

In spherical coordinates, the radial part of the Schrödinger equation is:

$$\frac{\mathrm{d}^2}{\mathrm{d}\,r^2}R + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}\,r}R - \frac{\ell(\ell+1)}{r^2}R + \frac{2m}{\hbar^2}(E + \frac{e^2}{r})R = 0 \tag{2}$$

To simplify the equations, we will adopt the following transformations:

$$\tilde{E} = \frac{mE}{\hbar^2} \quad , \quad \frac{me^2}{\hbar^2} = 1 \quad , \quad \rho = \frac{2r}{\lambda} \quad , \quad \lambda = \frac{1}{\sqrt{-2\tilde{E}}} \tag{3}$$

The term $me^2/\hbar^2$ will then be retrieved at the end of the derivation, using simple dimensional arguments. Also, the last transformation is possible because we are looking for bound states ($\tilde{E} < 0$).

The radial equation thus becomes:

$$R'' + \frac{2}{\rho}R' + \left[-\frac{1}{4} + \frac{\lambda}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]R = 0 \tag{4}$$

where we have $R' = (\mathrm{d}/\mathrm{d}\,\rho)R$.

For small ρ, the third term in the square brackets dominates, leading to a solution of the form: $R_\ell \propto \rho^\ell$. On the hand, for large ρ the first term in the square brackets dominates, leading to a solution of the form: $R_\ell \propto e^{\pm\frac{1}{2}\rho}$; for normalisation consideration, only the result with a minus is acceptable (the result with a plus would lead to a divergence to infinity as ρ goes to infinity and it is thus not acceptable). We therefore need to find a general solution of the form:

$$R = \rho^\ell e^{-\frac{1}{2}\rho}\mu_\ell \tag{5}$$

That equation defines μ_ℓ, which must then satisfy the equation:

$$\rho\mu_\ell'' + (2\ell + 2 - \rho)\mu_\ell' + (\lambda - \ell - 1)\mu_\ell = 0 \tag{6}$$

The solution of this equation can be found expanding μ_ℓ in a polynomial series. We will neglect here the details of the derivation and show only the main conclusions.

It can be demonstrated that a necessary condition to find a solution for Eq. **??** is that λ is an integer number: $\lambda = n$, $n = 0, 1, 2, \ldots$.. Recalling the definition of λ and $\tilde{E}$, we have: $E = -\hbar^2/(2mn^2)$. This result does not have the dimension of an energy, simply because we are adopting units so that $me^2/\hbar^2 = 1$. Returning to physical units we obtain:

$$E = -\frac{me^4}{2\hbar^2 n^2} \tag{7}$$

which is the energy formula for Bohr's atom.

For each n, the value ℓ can take any value between 0 and $n-1$. For each value of ℓ there are $2\ell + 1$ possible values of m. Since the energy is not a function of ℓ, it results that each energy level is:

$$\sum_{\ell=0}^{n-1}(2\ell + 1) = n^2 \tag{8}$$

times degenerate. This degeneracy is typical for a Coulomb interaction. Without going into the details of the derivation, the wavefunctions of the hydrogen atom can be written as:

$$R_{n,\ell} = C_{n,\ell}\rho^\ell e^{-\rho/2} L_{n+\ell}^{2\ell+1}(\rho) \tag{9}$$

$C_{n,\ell}$ is the normalisation constant:

$$C_{n,\ell} = -\frac{2}{n^2} r_B^{-3/2} \sqrt{\frac{(n-\ell-1)!}{[(n+\ell)!]^3}} \tag{10}$$

r_B is the Bohr radius of the hydrogen atom: $r_B = \hbar^2/me^2 \approx 5.291 \times 10^{-9}$ cm.

$L_{n+\ell}^{2\ell+1}$ are the associated Laguerre polynomials. They can be directly obtained from a generatrix function, but we will not discuss them here.

We will only provide the first radial functions:

$$\begin{cases} R_{1,0} = 2r_B^{-3/2} e^{-r/r_B} \\ R_{2,0} = \frac{1}{2\sqrt{2}} r_B^{-3/2} \left(2 - \frac{r}{r_B}\right) e^{-r/2r_B} \\ R_{2,1} = \frac{1}{2\sqrt{6}} r_B^{-3/2} \frac{r}{r_B} e^{-r/2r_B} \end{cases} \tag{11}$$

apart from the specific form of these functions, it is interesting to note that the probability distribution of the electron around the nucleus decreases exponentially with the distance, with a typical spatial scale given by the Bohr's radius.

The angular component of the function is instead given by the spherical harmonics. The complete wavefunction of an electron in the hydrogen atom is thus given by:

$$\psi_{(n,\ell,m)} = R_{n,\ell}(r) Y_{\ell,m}(\theta, \phi) \tag{12}$$