

Lecture 11

The Hydrogen atom

11.1 Introduction

The H atom is a bound state of a proton and an electron. The masses of the two particles are respectively:

$$m_p = 1.7 \times 10^{-27} \text{ kg}, \quad (11.1)$$

$$m_e = 0.91 \times 10^{-30} \text{ kg}. \quad (11.2)$$

They have opposite charges, q and $-q$, with:

$$q = 1.6 \times 10^{-19} \text{ C}. \quad (11.3)$$

The ratio of the two masses is:

$$m_p/m_e = 1836.15267247(80); \quad (11.4)$$

it is known to 5 parts per billion!!

The interaction between the two particles is due to electromagnetism; in a nonrelativistic formulation we can therefore model the H atom as a particle of reduced mass m :

$$\frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e} \approx \frac{1}{0.995m_e}, \quad (11.5)$$

in a Coulomb potential:

$$V(r) = -\frac{q^2}{4\pi\epsilon_0 r} \equiv -\frac{e^2}{r}. \quad (11.6)$$

Given that the proton mass is much larger than the electron one, the reduced mass of the ep system is very close to the electron mass. The distance r that appears in the expression for the Coulomb potential is the distance between the electron and the proton. We can identify the origin of our reference frame with the position of the proton; the potential is clearly symmetric under rotations around the origin. The parameters that specify the physical system are the reduced mass μ and the electron charge e .

The H atom is an example of motion in a central force, and we are going to use the formalism developed in Lecture 10 to find the stationary states of this system.

11.2 Stationary states

The Hamiltonian for the system is:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{r}. \quad (11.7)$$

The time-independent Schrödinger equation

$$\hat{H}\psi(\underline{r}) = E\psi(\underline{r}), \quad (11.8)$$

is solved as usual by separation of variables. Using for the solution $\psi(\underline{r})$ the Ansatz:

$$\psi(r, \theta, \phi) = \frac{\chi_{nl}(r)}{r} Y_{\ell}^m(\theta, \phi), \quad (11.9)$$

we obtain the radial one-dimensional equation:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{e^2}{r} \right] \chi_{nl}(r) = E_{nl} \chi_{nl}(r). \quad (11.10)$$

Eq. (11.10) is simply Eq. (10.7) for the specific case of the Coulomb potential. The effective potential in this case is:

$$V_l(r) = -\frac{e^2}{r} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}. \quad (11.11)$$

The effective potential is sketched in Fig. 11.1. The boundary condition for the radial function $\chi_{nl}(r)$ is:

$$\chi_{nl}(0) = 0. \quad (11.12)$$

Remember that, since we are looking for the bound states of the system, we are only interested in solutions with *negative* energy, *i.e.* $E_{nl} < 0$. Eq. (11.10) suggests that the energy levels will depend on the total angular momentum ℓ .

It is useful to describe the solutions of the Schrödinger equation in terms of two physical quantities; a characteristic length:

$$a_0 = \frac{\hbar^2}{\mu e^2} \approx 0.52 \text{ \AA}, \quad (11.13)$$

and energy:

$$E_I = \frac{\mu e^4}{2\hbar^2} \approx 13.6 \text{ eV}. \quad (11.14)$$

Let us denote by E_{nl} the energy levels, and introduce the dimensionless variables:

$$\rho = r/a_0, \quad \lambda_{nl} = \sqrt{-E_{nl}/E_I}. \quad (11.15)$$

Eq. (11.10) can be written as:

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{a_0^2} \frac{d^2}{d\rho^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu a_0^2 \rho^2} - \frac{e^2}{a_0 \rho} - E_{nl} \right] \chi_{nl}(a_0 \rho) = 0. \quad (11.16)$$

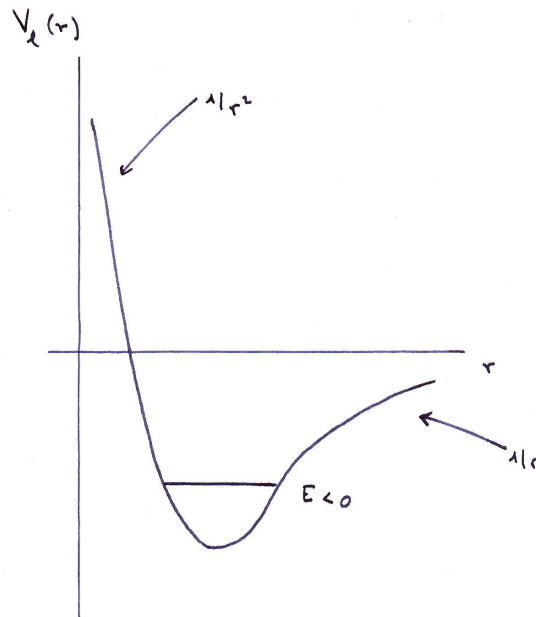


Figure 11.1: Effective potential for the one-dimensional radial Schrödinger equation for a system with total angular momentum l . We look for solutions of the time-independent Schrödinger equation with negative energy E corresponding to bound states of the proton/electron system.

Introducing

$$u_{nl}(\rho) = \chi_{nl}(a_0\rho), \quad (11.17)$$

Eq. (11.16) can be rewritten as:

$$\left[\frac{d^2}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2} + \frac{2\mu e^2 a_0}{\hbar^2} \frac{1}{\rho} + \frac{2\mu a_0^2}{\hbar^2} E_{n,\ell} \right] u_{nl}(\rho) = 0, \quad (11.18)$$

and finally

$$\boxed{\left[\frac{d^2}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2} + \frac{2}{\rho} - \lambda_{nl}^2 \right] u_{nl}(\rho) = 0.} \quad (11.19)$$

We need to solve Eq. (11.19) in order to find the eigenvalues of the Hamiltonian E_{nl} and the corresponding radial wave functions $u_{nl}(r)$. Remember that the angular part of the wave functions is given by the spherical harmonics.

11.3 Solution of the radial equation

In this section we shall discuss some technical details related to the solution of the radial equation (11.19). We wish to keep the mathematical details of the solution separated from the physical interpretation, which will be discussed in the next section.

In order to shine a light on the form of the solution, we can start by considering its limiting behaviours as $\rho \rightarrow 0$ and $\rho \rightarrow \infty$.

Let us first discuss the large-distance regime. As ρ is increased, both the centrifugal and Coulomb potentials tend to zero and become unimportant in Eq. (11.19), which becomes:

$$\left[\frac{d^2}{d\rho^2} - \lambda_{nl}^2 \right] u_{nl}(\rho) = 0. \quad (11.20)$$

The solutions to this latter equation are simply:

$$u_{nl}(\rho) = \exp(\pm \lambda_{nl} \rho), \quad (11.21)$$

and the solution that grows exponentially must be discarded because it yields a non-normalizable wave function.

Of course we cannot completely neglect the potential terms, so we will look for a complete solution of the form:

$$u_{nl}(\rho) = e^{-\lambda_{nl} \rho} \eta_{nl}(\rho). \quad (11.22)$$

Eq. (11.19) becomes:

$$\eta_{nl}'' - 2\lambda_{nl} \eta_{nl}' + \left(-\frac{\ell(\ell+1)}{\rho^2} + \frac{2}{\rho} \right) \eta_{nl} = 0, \quad (11.23)$$

where the prime symbol “ \prime ” denotes the differentiation with respect to ρ . The boundary condition for u_{nl} translates into a boundary condition for η_{nl} , namely $\eta_{nl}(0) = 0$.

As $\rho \rightarrow 0$ we know from the discussion in Lecture 10 that $u_{nl} \sim \rho^{\ell+1}$. Therefore we can look for a solution for η_{nl} expanded as a power series in ρ :

$$\eta_{nl}(\rho) = \rho^{\ell+1} \sum_{q=0}^{\infty} c_q \rho^q. \quad (11.24)$$

Inserting this Ansatz into Eq. (11.23) we obtain:

$$\begin{aligned} \sum_q (q+l+1)(q+l) c_q \rho^{q+\ell-1} - 2\lambda_{nl} (q+l+1) c_q \rho^{q+\ell} + \\ + 2c_q \rho^{q+\ell} - \ell(\ell+1) c_q \rho^{q+\ell-1} = 0, \end{aligned} \quad (11.25)$$

and hence:

$$\sum_q q(q+2\ell+1)c_q\rho^{q+\ell-1} - 2[\lambda_{nl}(q+\ell+1)-1]c_q\rho^{q+\ell} = 0. \quad (11.26)$$

Shifting the summation index, $q \rightarrow q-1$, in the second term of the sum above, we obtain:

$$\sum_q [q(q+2\ell+1)c_q - 2[\lambda_{nl}(q+\ell)-1]c_{q-1}]\rho^{q+\ell-1} = 0. \quad (11.27)$$

Since the last equality must hold for all values of ρ , we deduce:

$$q(q+2\ell+1)c_q - 2[\lambda_{nl}(q+\ell)-1]c_{q-1} = 0. \quad (11.28)$$

Eq. (11.28) is a recursion relation between the coefficients of the Taylor expansion of η_{nl}/ρ^{l+1} . It is crucial to note that for large q :

$$\frac{c_q}{c_{q-1}} \underset{q \rightarrow \infty}{\sim} \frac{2\lambda_{nl}}{q}, \quad \text{i.e. } c_q \sim \frac{(2\lambda_{nl})^q}{q!}. \quad (11.29)$$

The asymptotic behaviour for c_q would yield a solution:

$$\eta_{nl}(\rho) \sim \rho^{\ell+1} e^{2\lambda_{nl}\rho}, \quad (11.30)$$

which in turn yields a wave function u_{nl} that is not normalizable.

Therefore we *must* have $c_q = 0$ for some finite value of q , that we will denote $q = n_r > 0$. According to Eq. (11.28) this can only happen if:

$$\lambda_{nl} = \frac{1}{n_r + \ell} \equiv \frac{1}{n}. \quad (11.31)$$

Then the expansion in Eq. (11.24) only contains a finite number of terms, i.e. it is simply a polynomial in ρ of finite order n_r .

We can see from Eq. (11.31) that this condition implies that the energy eigenvalues are quantized. Remember that λ_{nl} is related to the eigenvalues of the Hamiltonian via Eq. (11.15). Energy quantization is a consequence of having required the wave function to be normalizable.

11.4 Physical interpretation

The computation in the previous section shows that the eigenvalues of the Hamiltonian for the H atom are:

$$E_{nl} = \frac{-E_I}{(n_r + \ell)^2}, \quad (11.32)$$

where ℓ is the angular momentum of the state, and $n_r > 0$ is an integer. We see that for the H atom the value of the energy does not depend on n_r and ℓ , but only on their sum $n = n_r + \ell$. The integer n is called the *principal quantum number*; its value characterizes the so-called *electron shells*.

We can rewrite Eq. (11.14) as:

$$E_I = \frac{1}{2}\alpha^2\mu c^2, \quad (11.33)$$

where α is the *fine-structure constant*:

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137}. \quad (11.34)$$

Note that $\mu \simeq m_e$, and therefore μc^2 is the rest energy of the electron. Eq. (11.33) shows that the typical scale of the energy levels in the H atom is 10^{-4} the rest energy of the electron. This justifies the nonrelativistic treatment of the H atom that we have used here. Clearly there *are* relativistic corrections; however they are small effect, typically of order α , and can be studied in perturbation theory.

Using Eq. (11.13) we can express the energy levels as:

$$E_n = -\frac{e^2}{2n^2 a_0}, \quad n = n_r + l. \quad (11.35)$$

This the formula put forward by Bohr in 1913, before Quantum Mechanics was fully developed.

Eq. (11.35) shows clearly that for a given principal quantum number n , ℓ can take the values $\ell = 0, 1, \dots, n-1$ (corresponding respectively to $n_r = n, n-1, \dots, 1$). Since for each value of ℓ we have a $(2\ell + 1)$ degeneracy, the total degeneracy of the level E_n is:

$$\sum_{\ell=0}^{n-1} (2\ell + 1) = n(n-1) + n = n^2. \quad (11.36)$$

The polynomials w_{nl} are called the *associated Laguerre polynomials*, their explicit expression can be found in standard textbooks on special functions¹. The full solution for the eigenfunctions of the energy is:

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{\ell}^m(\theta, \phi). \quad (11.37)$$

¹see e.g. M. Abramowitz and I.A. Stegun, *Handbook of mathematical functions*.

The first few radial functions are:

$$R_{1,0} = 2a_0^{-3/2} e^{-r/a_0}, \quad (11.38)$$

$$R_{2,0} = \frac{1}{2\sqrt{2}} a_0^{-3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/(2a_0)}, \quad (11.39)$$

$$R_{2,1} = \frac{1}{2\sqrt{6}} a_0^{-3/2} \frac{r}{a_0} e^{-r/(2a_0)}. \quad (11.40)$$

It is worthwhile to conclude this Lecture with a few remarks.

- The formula for the energy levels reproduces the Bohr spectrum, in agreement with the experimental data. The degeneracy of each level can only be obtained by the proper quantum-mechanical description that we have presented.
- The Bohr radius a_0 is the typical spatial extension of the ground state.
- The treatment described here can be applied to any hydrogen-like atom, i.e. an atom with an electron and a nucleus of charge Zq . Simply replace everywhere $e^2 \rightarrow Ze^2$.
- It is interesting to compute the expectation value of the momentum. Since the typical size of the atom is a_0 , we deduce from the Heisenberg uncertainty relation that $\sqrt{\langle p^2 \rangle} \sim \mu e^2 / \hbar$. Thus we obtain:

$$v \sim p/\mu \simeq e^2/\hbar = \alpha c \simeq \frac{1}{137} c \ll c. \quad (11.41)$$

We see *a posteriori* that motion of the electron is nonrelativistic, and hence our nonrelativistic description is accurate. Relativistic corrections are expected to be $\mathcal{O}(v/c) \simeq \mathcal{O}(\alpha)$.

- The ionization energy is the energy needed to extract the electron from the bound state and is E_I . This is known as the *Rydberg energy*.
- The electron in the H atom can go from one shell to a lower one by emitting a photon. The series of transitions from principal number $n \geq 2$ to $n = 1$ is called the *Lyman series*². The transitions are named by Greek letters: the transition from $n = 2$ to $n = 1$ is called Lyman- α , from 3 to 1 Lyman- β , etc. Likewise the transitions from $n \geq 3$ to $n = 2$ form the *Balmer series*. These transitions, which were discovered before Quantum Mechanics was established, have been observed with great precision and provide a strong experimental evidence in favour of Quantum Mechanics.

²A physics department at Harvard University is named after Lyman.

11.5 Summary

As usual, we summarize the main concepts introduced in this lecture.

- Setup of the problem. Hamiltonian for the H atom.
- Separation of variables. One-dimensional equation for the radial wave function.
- Effective potential, boundary condition.
- Solutions for the stationary states, quantization of the energy levels.
- Discussion of the mathematical results. Physical picture.

