

# Lecture 13

## Hydrogen-like Atom I

### Study Goal of This Lecture

- Hamiltonian and Schrödinger equation
- Radial and angular equation
- Electronic energy levels

### 13.1 Review

Now we have discussed the quantization of rotational motions and quantum angular momentum by considering the eigenvalues and eigenfunctions of the rigid rotor Hamiltonian:

$$\hat{H} = \frac{\hat{L}^2}{2I}, \quad (13.1)$$

$$\hat{H}Y_l^m(\theta, \phi) = \frac{l(l+1)}{2I}\hbar^2 Y_l^m(\theta, \phi), \quad (13.2)$$

$$l = 0, 1, 2, 3, \dots ; \quad m = -l, -l+1, \dots, 0, \dots, l.$$

quantum number  $l$  denotes the length of  $\vec{L}$  and  $m$  denotes projection of  $\vec{L}$  on  $\hat{z}$ .

The properties of the rigid rotor lay the foundation for solving the electronic eigenfunctions of a hydrogen-like atom, which will soon be clear. So far, we have been dealing with only "physical" problems, and here we finally start to consider "chemical" system  $\Rightarrow$  Hydrogen-like atom.

## 13.2 A Hydrogen-like atom

A hydrogen-like atom consists of two particles, a nuclei and an electron, bond by a simple Coulomb potential.

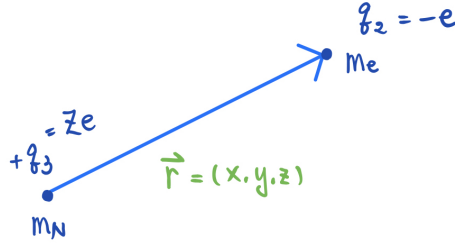


Figure 13.1: Nucleus and electron bond by Coulomb potential.

The many-body Hamiltonian of this system (two body) requires us to treat positions of the nuclei and electron. But, because the nuclei is so much heavier than the electron, it is a good approximation to only consider the electron motion and have  $\frac{m_e}{m_p} \simeq \frac{1}{1836}$  the nuclei fixed at the origin. We have the potential of electron

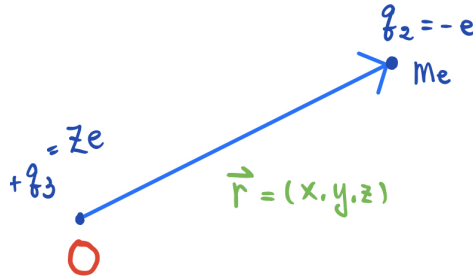


Figure 13.2: Fixed nuclei at the origin.

$$V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}, \quad r = |\vec{r}|. \quad (13.3)$$

$Z$  is atomic number and  $\epsilon_0$  is permittivity of vacuum.

So now the Hamiltonian becomes:

$$\begin{aligned} \hat{H} &= \frac{\hat{p}^2}{2m_e} + \hat{V} \\ &= \frac{-\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}}. \end{aligned} \quad (13.4)$$

Notice that the potential has spherical symmetry, it is thus natural to rewrite the equation in the spherical coordinate using

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r^2} \frac{\hat{L}^2}{\hbar^2}.\end{aligned}\quad (13.5)$$

Note that we have used the spherical condition form of the angular momentum operator

$$\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (13.6)$$

The Schrödinger equation reads:

$$\begin{aligned}\hat{H}\psi &= E\psi \\ \Rightarrow \left\{ \frac{-\hbar^2}{2m_e} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r^2} \frac{\hat{L}^2}{\hbar^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \right\} \psi &= E\psi.\end{aligned}\quad (13.7)$$

The equation can be further rearranged:

$$\frac{1}{2m_e r^2} \left\{ -\hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \hat{L}^2 - 2m_e r^2 \frac{Ze^2}{4\pi\epsilon_0 r} \right\} \psi = E\psi, \quad (13.8)$$

$$\hat{L}^2 \psi = \left\{ 2m_e r^2 E + \hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + 2m_e r^2 \frac{Ze^2}{4\pi\epsilon_0 r} \right\} \psi = \hat{O}(r) \psi. \quad (13.9)$$

The LHS of Equ.13.9 depends only on  $\theta$  and  $\phi$  and the RHS of Equ.13.9 depends only on  $r$ . Thus we can apply the separation of variable on  $\psi$ . The solution must be in the product form:

$$\psi = R(r)A(\theta, \phi). \quad (13.10)$$

$R(r)$  is radial part and the  $A(\theta, \phi)$  is angular part wave function

Let's plug it into

$$\hat{O}(r)\psi = \hat{L}^2\psi, \quad (13.11)$$

then

$$A(\theta, \phi)\hat{O}(r)R(r) = R(r)\hat{L}^2 A(\theta, \phi), \quad (13.12)$$

$$\frac{1}{R(r)}\hat{O}(r)R(r) = \frac{1}{A(\theta, \phi)}\hat{L}^2 A(\theta, \phi) = c. \quad (13.13)$$

We obtain

$$\hat{L}^2 A(\theta, \phi) = cA(\theta, \phi), \quad (13.14)$$

$\Rightarrow A(\theta, \phi)$  is an eigenfunctions of  $\hat{L}^2$ , we solved this before!

$$A(\theta, \phi) = Y_l^m(\theta, \phi), \quad (13.15)$$

the eigenvalues are  $c = l(l + 1)\hbar^2$ . The solution to the angular part is the spherical harmonics, this is actually not surprising.

Now the radial part:

$$\hat{O}(r)R(r) = cR(r) = l(l + 1)\hbar^2 R(r), \quad (13.16)$$

$$\left\{ \hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + 2m_e r^2 \left[ \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{l(l + 1)\hbar^2}{2m_e r^2} + E \right] \right\} R(r) = 0. \quad (13.17)$$

This equation can be further simplified by defining  $R(r) = \frac{S(r)}{r}$ , because

$$\begin{aligned} \frac{d}{dr} \left( r^2 \frac{d}{dr} R(r) \right) &= \frac{d}{dr} \left[ r^2 \left( \frac{1}{r} \frac{dS(r)}{dr} - \frac{1}{r^2} S(r) \right) \right] \\ &= \frac{d}{dr} \left[ r \frac{dS(r)}{dr} - S(r) \right] \\ &= r \frac{d^2 S(r)}{dr^2} + \frac{dS(r)}{dr} - \frac{dS(r)}{dr} \\ &= r \frac{d^2 S(r)}{dr^2}. \end{aligned} \quad (13.18)$$

The equation for  $S(r)$  is

$$\hbar^2 \frac{d^2 S(r)}{dr^2} + 2m_e r^2 \left[ \frac{Ze^2}{4\pi\epsilon_0 r} + E - \frac{l(l + 1)\hbar^2}{2m_e r^2} \right] \frac{S(r)}{r} = 0. \quad (13.19)$$

Divide by  $2m_e$  and rearrange terms, we have

$$\left\{ \underbrace{\frac{-\hbar^2}{2m_e} \frac{d^2}{dr^2}}_{\text{kinetic energy}} + \underbrace{\left[ \frac{l(l + 1)\hbar^2}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right]}_{\text{potential energy}} \right\} S(r) = ES(r). \quad (13.20)$$

Notice that this looks exactly like a Schrödinger equation on one-dimension for the electron in an one-dimension effective potential ( $r \geq 0$ ):

$$V_{eff}(r) = \underbrace{\frac{l(l + 1)\hbar^2}{2m_e r^2}}_{\text{centrifugal force}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r}}_{\text{Coulomb potential}}, \quad (13.21)$$

Stable orbitals on classical mechanics require these two terms to balance out, not in Q.M.

note that the centrifugal term is  $\frac{1}{r^2}$ , while the Coulomb term is  $\frac{1}{r}$ . Therefore, at small  $r$ , the centrifugal term dominant, and at large  $r$ , the Coulomb term dominant. Exception is  $l = 0$ , which does not rotate and has pure Coulomb term. Solving the one-dimensional Schrödinger equation for electron in the effective potential gives energy.

Note that  $V_{eff}(r)$  depends on  $l$ . There is a simple physical picture to this. The effective potential that an electron feels along the radial direction depends on the rotational energy of the electron. If the electron rotates faster (i.e.  $l \uparrow$ ), then there is a tendency for the electron to move "away" from the origin. This feels like that the potential is "repulsive". For more detail description:

This is to sitting on the same rotating frame as the electron, in the classical sense.

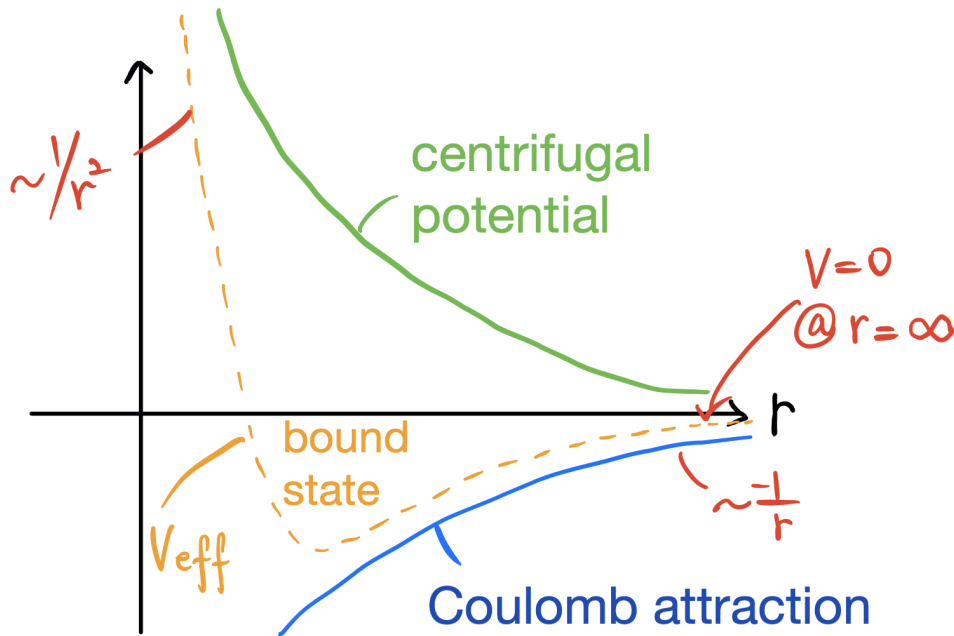


Figure 13.3: Plot of parts of effective potential ( $l \neq 0$ ).

1. The centrifugal term is positive, thus "destabilizing" the H-like atom.
2. The centrifugal term depends on  $l$ , i.e. the magnitude of the angular momentum. This is because the centrifugal force depends on  $\hat{L}^2$ . i.e. the greater the  $l$  (i.e. rotates faster), the less attractive the  $V_{eff}(r)$
3. The net result of point 2 is that the electrons in orbitals with greater  $l$  will locate farther from the nuclei.
4. The radial function  $R(r)$  depends on  $l$ .

### 13.2.1 Physical Picture

This is a 1-D problem, let's consider the eigenfunctions without even solving the equation "qualitatively". Since  $V_{eff}$  depends on  $l$ , then for  $l = 0$ ,  $V_{eff} \simeq -\frac{1}{r}$

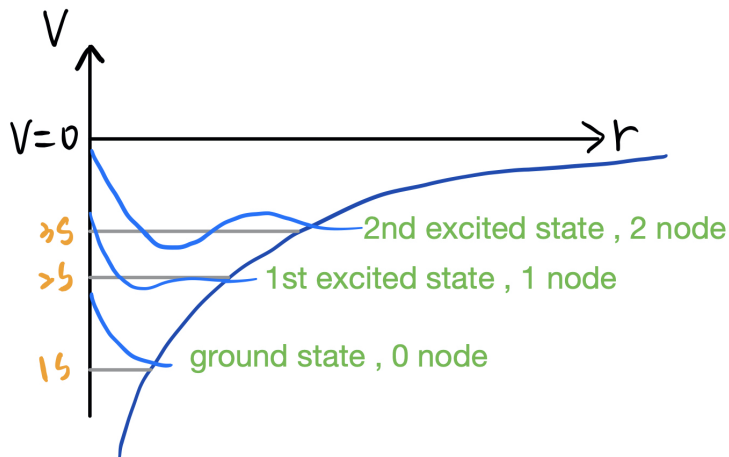


Figure 13.4: The radial function and eigenfunctions for  $l = 0$ .

and for  $l = 0$ ,  $V_{eff} \simeq \frac{C_1}{r^2} - \frac{C_2}{r}$

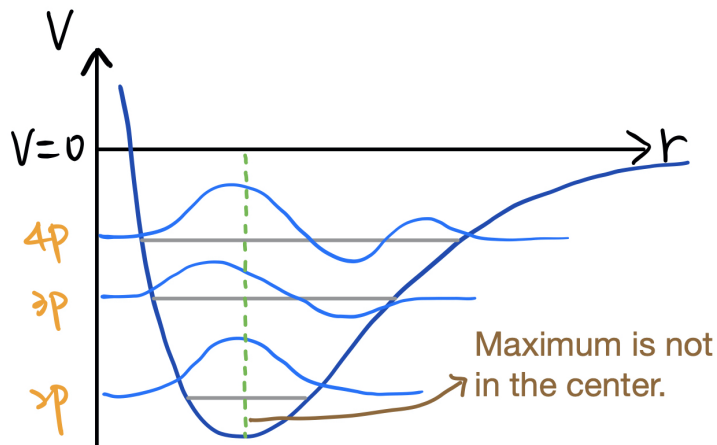


Figure 13.5: The radial function and eigenfunctions for  $l = 1$ .

Actually, the bound states satisfying the equations for  $S(r)$  can be solved using, again, the power-series method. By applying two boundary conditions:

- $R(r=0)$  is finite
- $R(r) \rightarrow 0$  at  $r = \infty$

one can prove that the energy  $E$  is quantized by an additional quantum number  $n$ , called the principle quantum number and the allowed energy levels are

$$E_n = -\frac{\mu e^4 Z^2}{2(4\pi\epsilon_0)^2 \hbar^2 n^2}. \quad (13.22)$$

Now, we go back to the full eigenfunctions of the hydrogen-like atom, they are described by three quantum numbers

$$\psi_{n,l,m_l}(r, \theta, \phi) = R_{nl}(r)Y_l^{m_l}(\theta, \phi), \quad (13.23)$$

where

$$\begin{cases} n &= 1, 2, 3, 4, \dots \\ l &= 0, 1, 2, 3, \dots, n-1 \\ m_l &= 0, \pm 1, \pm 2, \dots, \pm l \end{cases} \quad (13.24)$$

For historical reasons, we also term the orbital of different  $l$  as  $s, p, d, f, \dots$  orbitals.

Since  $E_n$  only depends on  $n$ , there are degenerate levels for  $n > 1$ . The degree of degeneracy is  $n^2$

Why there is no  $1p$  orbital?

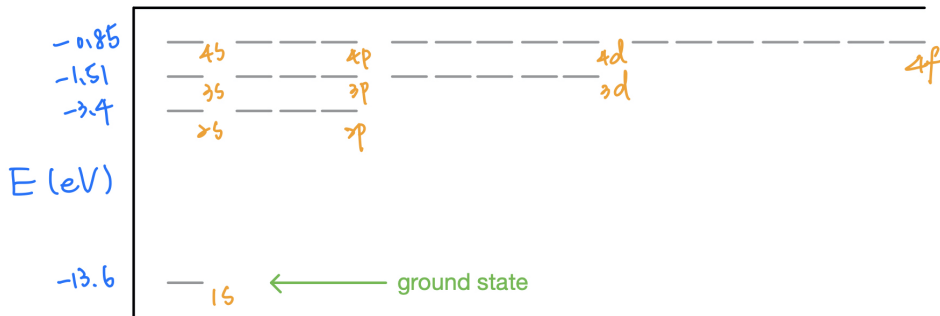


Figure 13.6: Energy level for hydrogen-like atom.

Next time we will discuss the eigenfunctions and the physical implications for hydrogen-like atom.