## Chapter 23

## Hydrogen Atom II

The angular parts of the wavefunctions for the hydrogen atom, governed by the Hamiltonian

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{r},$$
 (23.1)

are given by the spherical harmonics,  $Y_{lm}(\theta, \phi)$ ,

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi), \qquad (23.2)$$

in terms of the principal quantum number n, the orbital angular momentum quantum number l, and the magnetic quantum number m. The energies depend only on n:

$$E_n = -\left(\frac{Ze^2}{\hbar c}\right)^2 \frac{\mu c^2}{2n^2} = -\frac{13.60 \text{ eV}}{n^2},$$
(23.3)

where, although the speed of light does not enter into this nonrelativistic calculation, we have introduced it, because then the energies are given in terms of the rest energy of the electron,  $\mu c^2 = 0.511$  MeV, and the dimensionless *fine structure constant*,

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.036\cdots}.$$
(23.4)

The relevant distance scale is the Bohr radius,

$$a_0 = \frac{\hbar^2}{\mu e^2} = 0.529 \times 10^{-8} \text{ cm.}$$
 (23.5)

The numbers given are for the ideal hydrogen atom, with  $\mu = m_e$  and Z = 1.

The radial wavefunctions are easily given in terms of  $\rho = 2Zr/na_0$ , for n = 1, 2, and 3:

$$n = 1(1s):$$
  $R_{10} = \left(\frac{Z}{a_0}\right)^{3/2} 2e^{-\rho/2},$  (23.6)

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$$n = 2, l = 0(2s):$$
  $R_{20} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{2\sqrt{2}}(2-\rho)e^{-\rho/2},$  (23.7a)

$$n = 2, l = 1(2p):$$
  $R_{21} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{2\sqrt{6}} \rho e^{-\rho/2},$  (23.7b)

$$n = 3, l = 0(3s):$$
  $R_{30} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{9\sqrt{3}} (6 - 6\rho + \rho^2) e^{-\rho/2},$  (23.8a)

$$n = 3, l = 1(3p):$$
  $R_{31} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{9\sqrt{6}} (4-\rho)\rho e^{-\rho/2},$  (23.8b)

$$n = 3, l = 2(3d): \quad R_{32} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{9\sqrt{30}} \rho^2 e^{-\rho/2}.$$
 (23.8c)

In homework, you will verify that these agree with the wavefunctions found previously in Chapter 19, and check that the n = 3 states are correct.

## 23.1 Perturbations due to external fields

Let us now consider the effect of electric and magnetic fields on the hydrogen atom. A constant magnetic field  $\mathbf{B}$  is described by the vector potential

$$\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}, \quad \rightarrow \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}. \tag{23.9}$$

A constant electric field  $\mathcal{E}$  is described by a scalar potential

$$\varphi = -\mathcal{E} \cdot \mathbf{r} \quad \to \quad \mathcal{E} = -\nabla\varphi. \tag{23.10}$$

Thus the Hamiltonian for the perturbed atom is

$$H = \frac{\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2}{2\mu} - \frac{Ze^2}{r} + e\phi.$$
(23.11)

We will assume that the electric and magnetic fields are weak. Expand out the term involving the magnetic field:

$$\frac{\left(\mathbf{p} - \frac{e}{2c}\mathbf{B} \times \mathbf{r}\right)^2}{2\mu} \to \frac{p^2}{2\mu} - \frac{e}{2\mu c}\mathbf{B} \cdot \mathbf{r} \times \mathbf{p} + \frac{\left(\frac{e}{2c}\mathbf{B} \times \mathbf{r}\right)^2}{2\mu},\tag{23.12}$$

and we will neglect the last term in the following, as being small. We recognize that  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ . Then, if only the external magnetic field is present,  $[H_0$  is the unperturbed hydrogen Hamiltonian (23.1)]

$$H = H_0 - \frac{eB}{2\mu c} L_z,$$
 (23.13)

where  $L_z$  takes on the value  $m\hbar$  in a state with magnetic quantum number m,

$$E_{nm} = E_n - \frac{e\hbar}{2\mu c} Bm.$$
(23.14)

This exhibits what is called Zeeman splitting. As a result, the  $n^2$  degeneracy is split. Since l = 0, 1, ..., n - 1, the possible different values of m range from n - 1, n - 2, ..., -(n - 1), so there are now 2n - 1 distinct energy levels, but some degeneracy remains.

The effect of the electric field is called the Stark effect. The corresponding Hamiltonian is

$$H = H_0 - e\mathcal{E} \cdot \mathbf{r}. \tag{23.15}$$

Because the last term is not a constant of the motion, we want to find an effective replacement for  $\mathbf{r}$ . Recall that we solved the unperturbed hydrogen atom problem by introducing the axial vector (19.12) (not to be confused with the vector potential)

$$\mathbf{A} = \frac{\mathbf{r}}{r} - \frac{1}{\mu Z e^2} \mathbf{p} \times \mathbf{L}; \qquad (23.16)$$

we expect the constant of the motion  $\mathbf{A}$  to set the scale for  $\mathbf{r}$ . (We will here ignore noncommutativity, which will not affect the answer.) Rewrite

$$\mathbf{p} \times \mathbf{L} = \mathbf{p} \times (\mathbf{r} \times \mathbf{p}) = -\mathbf{p}(\mathbf{p} \cdot \mathbf{r}) + p^2 \mathbf{r}.$$
 (23.17)

Now, without a vector potential,

$$\mathbf{p} \cdot \mathbf{r} = \mu \mathbf{v} \cdot \mathbf{r} = \mu \frac{d}{dt} \frac{r^2}{2},$$
(23.18)

and

$$p^{2} = 2\mu \left( H_{0} + \frac{Ze^{2}}{r} \right).$$
 (23.19)

 $\operatorname{So}$ 

$$\mathbf{p} \times \mathbf{L} = -\mathbf{p}\mu \frac{d}{dt} \frac{r^2}{2} + 2\mu \left(H_0 + \frac{Ze^2}{r}\right) \mathbf{r}$$

$$= -\frac{d}{dt} \left(\mathbf{p}\mu \frac{r^2}{2}\right) - \frac{Ze^2}{r^3} \mathbf{r}\mu \frac{r^2}{2} + 2\mu H_0 \mathbf{r} + 2\mu Ze^2 \frac{\mathbf{r}}{r}$$

$$= -\frac{d}{dt} \left(\mu \mathbf{p} \frac{r^2}{2}\right) + 2\mu H_0 \mathbf{r} + \frac{3}{2}\mu Ze^2 \left[\mathbf{A} + \frac{1}{\mu Ze^2} \mathbf{p} \times \mathbf{L}\right], \quad (23.20)$$

where, in the second line we used the equation of motion,

$$\frac{d\mathbf{p}}{dt} = -\frac{Ze^2}{r^3}\mathbf{r},\tag{23.21}$$

and in the last line we used Eq. (23.16). So then we have

$$2\mu H_0 \mathbf{r} = -\frac{3}{2}\mu Z e^2 \mathbf{A} + \frac{d}{dt} \left(\mu \mathbf{p} \frac{r^2}{2}\right) - \frac{d}{dt} \left(\frac{1}{2}\mu \mathbf{r} \times \mathbf{L}\right), \qquad (23.22)$$

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where the last uses

$$-\frac{1}{2}\mathbf{p} \times \mathbf{L} = -\frac{1}{2}\mu \frac{d\mathbf{r}}{dt} \times \mathbf{L} = -\frac{d}{dt} \left(\frac{1}{2}\mu\mathbf{r} \times \mathbf{L}\right), \qquad (23.23)$$

because  $\mathbf{L}$  is a constant. Thus, we have

$$\mathbf{r} = -\frac{3}{4} \frac{Ze^2 \mathbf{A}}{H_0} + \frac{d}{dt} \mathbf{F},$$
(23.24)

where  $\mathbf{F}$  is an operator, where the order of factors has to be considered. However, because the last term is a total time derivative, when we do a time average of this, we might expect to get zero. To see that this term has no effect, write the perturbation in Eq. (23.15) is

$$-e\mathcal{E}\cdot\mathbf{r} = \frac{3}{4}\frac{Ze^2}{H_0}e\mathbf{A}\cdot\mathcal{E} + \frac{d}{dt}G.$$
(23.25)

Thus we write the perturbed Hamiltonian as

$$H = H_0 + \frac{3}{4} \frac{Ze^2}{H_0} \mathbf{A} \cdot e\mathcal{E} + \frac{1}{i\hbar} [G, H_0], \qquad (23.26)$$

because G is linear in  $\mathcal{E}$ , so the time dependence can only arise from  $H_0$ .

Now because we are regarding  $\mathcal{E}$  as small, and G depends linearly on  $\mathcal{E}$ , we can write this as

$$H = \left(1 - \frac{i}{\hbar}G\right) \left(H_0 + \frac{3}{4}\frac{Ze^2}{H_0}\mathbf{A} \cdot e\mathcal{E}\right) \left(1 + \frac{i}{\hbar}G\right) + O(\mathcal{E}^2).$$
(23.27)

So to this order, we have an infinitesimal unitary transformation. Because a unitary transformation does not change the energy spectrum, we can replace H by

$$H = H_0 + \frac{3}{4} \frac{Ze^2}{H_0} \mathbf{A} \cdot e\mathcal{E}$$
(23.28)

We have thus solved the problem, since  $\mathbf{A}$  is a constant of the motion.

Now recall the operator  $\mathbf{J}^{(\pm)}$  defined in Eq. (19.42). For a state with definite n,

$$\mathbf{J}^{(\pm)} = \frac{1}{2} (\mathbf{L} \pm n\hbar \mathbf{A}). \tag{23.29}$$

Thus

$$\mathbf{J}^{(+)} - \mathbf{J}^{(-)} = n\hbar\mathbf{A},\tag{23.30}$$

or if we choose the direction of the electric field to be the z direction,

$$nA_z = m^{(+)} - m^{(-)}. (23.31)$$

Now, for each constituent spin,

$$m = j, \dots, -j = \frac{n-1}{2} - k,$$
 (23.32)

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where the integer k runes from 0 to n-1. Thus  $m^{(+)} - m^{(-)} = k^{(-)} - k^{(+)}$ , and thus the first order Stark shift is  $(Ze^2/H_0 \rightarrow -2n^2a_0/Z)$ 

$$E = E_n - \frac{3}{2} \frac{na_0}{Z} e \mathcal{E}(k^{(-)} - k^{(+)}); \qquad (23.33)$$

the level splitting exhibits equal spacing. The atom exhibits an effective electric dipole moment. Since  $k^{(-)} - k^{(+)}$  ranges from n - 1 to -(n - 1), again the  $n^2$  degenerate hydrogenic states are split into 2n - 1 levels, just as in the Zeeman effect.

Suppose both  $\mathbf{E}$  and  $\mathbf{H}$  are present, and are parallel and weak. Then the energy shift is just the sum of the two contributions,

$$E = E_n - \frac{3}{2} \frac{na_0}{Z} e \mathcal{E}(k^{(-)} - k^{(+)}) - \frac{e\hbar}{2\mu c} Bm, \qquad (23.34)$$

where

$$k^{(-)} - k^{(+)} = m^{(+)} - m^{(-)}, \quad m = m^{(+)} + m^{(-)},$$
 (23.35)

 $\mathbf{SO}$ 

$$E = E_n + \left(-\frac{3}{2}\frac{na_0}{Z}e\mathcal{E} - \frac{e\hbar}{2\mu c}B\right)m^{(+)} + \left(\frac{3}{2}\frac{na_0}{Z}e\mathcal{E} - \frac{e\hbar}{2\mu c}B\right)m^{(-)} \quad (23.36)$$

We now have  $(2j+1)(2j+1) = n^2$  distinct levels, the degeneracy is completely broken, except for special values of  $\mathcal{E}/B$ .

There are two characteristic lengths appearing here:

$$a_0 = \frac{\hbar^2}{\mu e^2}, \quad \lambda_c = \frac{\hbar}{\mu c}, \tag{23.37}$$

the second being called the Compton wavelength. What is the ratio of these:

$$\frac{\lambda_c}{a_0} = \frac{e^2}{\hbar c} = \alpha. \tag{23.38}$$

This is of order of v/c for the electron in the atom, since  $p_0 = \mu v_0 = \frac{\hbar}{a_0}$ . Therefore, an enormous magnetic field is necessary to give an effect of the same size as that produced by an electric field.