Chapter 19

Hydrogen Atom I

What is H_{int} ? That depends on the physical system and the accuracy with which it is described. A natural starting point is the form

$$H_{\rm int} = \frac{p^2}{2\mu} + V,$$
 (19.1)

which describes a two-particle system with reduced mass

$$\mu = \frac{mM}{m+M} \approx m, \quad \text{if} \quad m \ll M. \tag{19.2}$$

What is V? It seems reasonable to adopt the known electrostatic potential between electric charges. Does this continue to apply in the atomic realm? Only experiment can answer. In the hydrogen atom, H, there is an electron, of charge -e, and a proton of charge +e. The electrostatic potential is

$$\frac{e(-e)}{r} = -\frac{e^2}{r}.$$
 (19.3a)

For ionized helium, He⁺, the potential is

$$\frac{2e(-e)}{r} = -\frac{2e^2}{r},$$
(19.3b)

and for doubly ionized lithium, Li^{++} , we have

$$\frac{3e(-e)}{r} = -\frac{3e^2}{r}.$$
 (19.3c)

In general, for a single-electron atoms,

$$V = -\frac{Ze^2}{r},\tag{19.3d}$$

where Z is the atomic number. Thus, we take as the Hamiltonian for a hydrogenic atom

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{r}.$$
 (19.4)

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Here, we ignore the spin of the electron and the proton. The equations of motion for the relative position and momentum, which are conjugate variables,

$$[\mathbf{r}, \mathbf{p}] = i\hbar\mathbf{1},\tag{19.5}$$

 are

$$\frac{d\mathbf{r}}{dt} = \frac{1}{i\hbar}[\mathbf{r}, H] = \frac{\partial H}{\partial \mathbf{p}} = \frac{\mathbf{p}}{\mu},$$
(19.6a)

$$\frac{d\mathbf{p}}{dt} = \frac{1}{i\hbar}[\mathbf{p}, H] = -\frac{\partial H}{\partial \mathbf{r}} = -\frac{Ze^2\mathbf{r}}{r^3}.$$
(19.6b)

Is angular momentum conserved? (It must be, since H is a spin-independent scalar.)

$$\frac{d\mathbf{L}}{dt} = \frac{d}{dt}(\mathbf{r} \times \mathbf{p}) = \frac{\mathbf{p}}{\mu} \times \mathbf{p} - \mathbf{r} \times \frac{\mathbf{r}}{r^3} Z e^2 = 0.$$
(19.7)

Is there anything else, besides H itself, of course, that is conserved? An affirmative suggestion comes from the known dynamic situation with the Newtonian potential,

$$-\frac{Ze^2}{r} \to -\frac{GmM}{r},\tag{19.8}$$

describing a planet about the sun, for example. It is familiar that the orbit is an ellipse which holds steady in space. This fact is unique to the 1/r potential, to the inverse square law of force. The clue to finding what is the associated conserved quaity is to consider $\frac{d}{dt}\frac{\mathbf{r}}{r}$. In the following, we will ignore the noncommutativity of operators, and only state the necessary modifications at the end:

$$\frac{d}{dt}\frac{\mathbf{r}}{r} = \frac{\mathbf{v}}{r} - \frac{\mathbf{r}}{r^2}\frac{d}{dt}r,\tag{19.9}$$

where

$$\frac{d}{dt}r = \frac{d\mathbf{r}}{dt} \cdot \frac{\partial r}{\partial \mathbf{r}} = \mathbf{v} \cdot \frac{\mathbf{r}}{r},\tag{19.10}$$

 \mathbf{SO}

$$\frac{d}{dt}\frac{\mathbf{r}}{r} = \frac{\mathbf{v}}{r} - \frac{\mathbf{r}(\mathbf{r} \cdot \mathbf{v})}{r^3} = -\frac{\mathbf{r} \times (\mathbf{r} \times \mathbf{v})}{r^3}$$
$$= -\frac{\mathbf{r}}{r^3} \times \frac{\mathbf{L}}{\mu} = \frac{1}{Ze^2}\frac{d}{dt}\mathbf{p} \times \frac{\mathbf{L}}{\mu}.$$
(19.11)

If we define the axial vector **A** by

$$\mathbf{A} = \frac{\mathbf{r}}{r} - \frac{1}{\mu Z e^2} \mathbf{p} \times \mathbf{L},\tag{19.12}$$

we see that **A** is constant,

$$\frac{d}{dt}\mathbf{A} = 0. \tag{19.13}$$



Figure 19.1: Consider a point a distance d from a fixed line, called the directrix. Let r and θ be polar coordinates from the point as origin, with the angle measured from the normal to the directrix. The ellipse is the locus of points which have a fixed ratio e between the distance r from the point and the distance $r \cos \theta + d$ from the directrix.

Observe that

$$\mathbf{A} \cdot \mathbf{L} = \frac{1}{r} \mathbf{r} \cdot \mathbf{L} - \frac{1}{\mu Z e^2} \mathbf{p} \times \mathbf{L} \cdot \mathbf{L} = 0, \qquad (19.14)$$

because both terms vanish, if we ignore noncommutativity. Leaving the symbols unchanged, but thinking of astronomy, we recognize the elliptical orbit:

$$\mathbf{r} \cdot \mathbf{A} = r - \frac{1}{\mu Z e^2} \mathbf{r} \cdot \mathbf{p} \times \mathbf{L} = r - \frac{L^2}{\mu Z e^2} = re\cos\theta, \quad (19.15)$$

where $e = |\mathbf{A}|$, and θ is the angle between \mathbf{A} and \mathbf{r} , so

$$r = \frac{L^2/\mu Z e^2}{1 - e \cos\theta}.$$
 (19.16)

which is the polar equation of an ellipse, if e < 1, with eccentricity e. [The definition of an ellipse such that the sum of the distances from the two foci is constant,

$$r_1 + r_2 = \text{constant},\tag{19.17}$$

is more familiar, but an alternate definition is the locus of points that make a constant ratio e between the radial distance, and the horizontal distance from a fixed line, the directrix,

$$r = e(r\cos\theta + d), \quad r = \frac{ed}{1 - e\cos\theta}.$$
 (19.18)

See Fig. 19.1.]

Back to quantum mechanics. All that is needed is to make \mathbf{A} Hermitian by symmetric multiplication:

$$\mathbf{p} \times \mathbf{L} \to \frac{1}{2} (\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}).$$
 (19.19)

For example, the z component of this is

$$\frac{1}{2}(p_xL_y - p_yL_x - L_xp_y + L_yp_x) = \frac{1}{2}(p_xL_y + L_yp_x) - \frac{1}{2}(p_yL_x + L_xp_y).$$
 (19.20)

Recall that if A and B are two Hermitian operators, the symmetric product is Hermitian:

$$\frac{1}{2}(AB + BA)^{\dagger} = \frac{1}{2}(BA + AB).$$
(19.21)

The measure of non-commutativity here is

$$(\mathbf{p} \times \mathbf{L} + \mathbf{L} \times \mathbf{p})_z = p_x L_y - p_y L_x + L_x P_y - L_y p_x = [p_x, L_y] - [p_y, L_x] = 2i\hbar p_z,$$
(19.22)

or in general,

$$\mathbf{p} \times \mathbf{L} + \mathbf{L} \times \mathbf{p} = 2i\hbar \mathbf{p}. \tag{19.23}$$

Therefore the Hermitian combination is

$$\frac{1}{2}(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}) = \mathbf{p} \times \mathbf{L} - i\hbar\mathbf{p} = -\mathbf{L} \times \mathbf{p} + i\hbar\mathbf{p}.$$
 (19.24)

It is still true in quantum mechanics that L and A are orthogonal,

$$\mathbf{A} \cdot \mathbf{L} = \frac{1}{r} \mathbf{r} \cdot \mathbf{L} - \frac{1}{\mu Z e^2} (\mathbf{p} \times \mathbf{L} - i\hbar \mathbf{p}) \cdot \mathbf{L} = 0 - \frac{1}{\mu Z e^2} (\mathbf{p} \cdot \mathbf{L} \times \mathbf{L} - i\hbar \mathbf{p} \cdot \mathbf{L}) = 0.$$
(19.25)

So,

$$\mathbf{A} \cdot \mathbf{L} = \mathbf{L} \cdot \mathbf{A} = 0. \tag{19.26}$$

Since there are 6 variables, \mathbf{r} , \mathbf{p} , and 6 constants \mathbf{L} , \mathbf{A} , the constant H cannot be independent of \mathbf{L} and \mathbf{A} . Initially, ignoring the non-commutativity, we observe

$$\mathbf{A}^{2} = 1 - \frac{2}{\mu Z e^{2}} \frac{1}{r} \mathbf{r} \cdot \mathbf{p} \times \mathbf{L} + \frac{1}{(\mu Z e^{2})^{2}} (\mathbf{p} \times \mathbf{L}) \cdot (\mathbf{p} \times \mathbf{L}).$$
(19.27)

The triple scalar product here is actually L^2 , and the square of $\mathbf{p} \times \mathbf{L}$ is just $p^2 L^2 - (\mathbf{p} \cdot \mathbf{L})^2 = p^2 L^2$. Thus,

$$A^{2} = 1 + \frac{2}{\mu Z^{2} e^{4}} \left(\frac{p^{2}}{2\mu} - \frac{Ze^{2}}{r}\right) \mathbf{L}^{2} = 1 + \frac{2}{\mu Z^{2} e^{4}} HL^{2},$$
(19.28)

or solving for H,

$$H = -\frac{\mu Z^2 e^4}{2} \frac{1 - A^2}{L^2}.$$
(19.29)

As an aside, note for Bohr circular orbits, where $\mathbf{A} = 0$ and $L = n\hbar$,

$$H = -\frac{\mu Z^2 e^4}{2} \frac{1}{n^2 \hbar^2}.$$
(19.30)

This looks right, except for the question about why n = 0 is excluded.

The necessary quantum mechanical modification is indicated by the $(\mathbf{p} \times \mathbf{L})^2$ calculation. The latter should be

$$\begin{bmatrix} \frac{1}{2} (\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}) \end{bmatrix}^2 = (-\mathbf{L} \times \mathbf{p} + i\hbar \mathbf{p}) \cdot (\mathbf{p} \times \mathbf{L} - i\hbar \mathbf{p})$$
$$= -(\mathbf{L} \times \mathbf{p}) \cdot (\mathbf{p} \times \mathbf{L}) + i\hbar \mathbf{L} \times \mathbf{p} \cdot \mathbf{p} + i\hbar \mathbf{p} \cdot \mathbf{p} \times \mathbf{L} + \hbar^2 p^2$$
$$= p^2 (L^2 + \hbar^2), \tag{19.31}$$

because

$$-(\mathbf{L} \times \mathbf{p}) \cdot (\mathbf{p} \times \mathbf{L}) = -\mathbf{L} \cdot \mathbf{p} \times (\mathbf{p} \times \mathbf{L}) = -\mathbf{L} \cdot [\mathbf{p}(\mathbf{p} \cdot \mathbf{L}) - p^2 \mathbf{L}] = p^2 L^2,$$
(19.32)

since p^2 is a scalar, and hence commutes with **L**. But the structure of *H* must emerge in Eq. (19.28), so the correct expression must be

$$A^{2} = 1 + \frac{2}{\mu Z^{2} e^{4}} H(L^{2} + \hbar^{2}).$$
(19.33)

Now we turn to the commutation relation of L and A. Of course,

$$\mathbf{L} \times \mathbf{L} = i\hbar \mathbf{L}.\tag{19.34}$$

and A is a vector, so, for example,

$$[A_x, L_y] = i\hbar A_z. \tag{19.35}$$

How about $\mathbf{A} \times \mathbf{A}$? It must be a constant vector, and therefore a multiple of \mathbf{L} and \mathbf{A} . \mathbf{A} is not possible, since it has an odd number of \mathbf{r} s and \mathbf{p} s, when we recognize that $r = \sqrt{\mathbf{r} \cdot \mathbf{r}}$. On the other hand, \mathbf{L} has an even number. The commutator $\frac{1}{i\hbar}[r_k, p_l]$ removes an even number, so $\mathbf{A} \times \mathbf{A}$ must have an even number of \mathbf{r} s and \mathbf{p} s. Therefore we conclude

$$\mathbf{A} \times \mathbf{A} = i\hbar C \mathbf{L}, \quad \text{or} \quad [A_x, A_y] = i\hbar C L_z,$$
(19.36)

where C is a scalar constant. Find C from

$$[\mathbf{A}, A^2] = \frac{2}{\mu Z^2 e^4} H[\mathbf{A}, L^2], \qquad (19.37)$$

since $[\mathbf{A}, H] = 0$ because $d\mathbf{A}/dt = 0$. Then, for example,

$$[A_z, A^2] = [A_z, A_x^2 + A_y^2] = i\hbar C (A_x L_y + L_y A_x - A_y L_x - L_x A_y)$$

= $i\hbar C (\mathbf{A} \times \mathbf{L} - \mathbf{L} \times \mathbf{A})_z,$ (19.38)

on the one hand, and

$$[A_z, L^2] = [A_z, L_x^2 + L_y^2] = i\hbar (L_x A_y + A_y L_x - L_y A_x - A_x L_y)$$

= $-i\hbar (\mathbf{A} \times \mathbf{L} - \mathbf{L} \times \mathbf{A})_z,$ (19.39)

so comparing these two we find

$$C = -\frac{2}{\mu Z^2 e^4} H.$$
 (19.40)

We have therefore,

$$[L_x, L_y] = i\hbar L_z, \quad [A_x, L_y] = i\hbar A_z, \quad [A_x, A_y] = i\hbar \left(\frac{-2H}{\mu Z^2 e^4}\right) L_z, \quad (19.41)$$

etc. Now define

$$\mathbf{J}^{(\pm)} = \frac{1}{2} \left(\mathbf{L} \pm \sqrt{\frac{\mu Z^2 e^4}{-2H}} \mathbf{A} \right), \qquad (19.42)$$

and we find (denote temporarily $s = \sqrt{\mu Z^2 e^4/(-2H)}$)

$$[J_x^{(+)}, J_y^{(+)}] = \frac{1}{4} [L_x + sA_x, L_y + sA_y] = \frac{i\hbar}{4} (L_z + L_z + sA_z + sA_z)$$

= $i\hbar J_z^{(+)}$, (19.43a)

$$[J_x^{(-)}, J_y^{(-)}] = \frac{1}{4} [L_x - sA_x, L_y - sA_y] = \frac{i\hbar}{4} (L_z + L_z - sA_z - sA_z)$$

= $i\hbar J_z^{(-)}$, (19.43b)

$$[J_x^{(+)}, J_y^{(-)}] = \frac{1}{4} [L_x + sA_x, L_y - sA_y] = \frac{i\hbar}{4} (L_z - L_z + sA_z - sA_z)$$

= 0, (19.43c)

etc. We see that $\mathbf{J}^{(\pm)}$ are two independent angular momenta. These momenta have equal magnitude:

$$(\mathbf{J}^{(\pm)})^2 = \frac{1}{4} \left(L^2 \pm s(\mathbf{A} \cdot \mathbf{L} + \mathbf{L} \cdot \mathbf{A}) + s^2 A^2 \right),$$
(19.44)

because the cross term vanishes according to Eq. (19.26). Now substituting in Eq. (19.33), and recalling the definition of s, the L^2 cancels, and we have

$$(\mathbf{J}^{(\pm)})^2 = \frac{1}{4} \left(\frac{\mu Z^2 e^4}{-2H} - \hbar^2 \right), \qquad (19.45)$$

and denoting the common value of $(\mathbf{J}^{(\pm)})^2$ by $j(j+1)\hbar^2$, $j = 0, 1/2, 1, 3/2, 2, \ldots$, we find

$$\hbar^2[4j(j+1)+1] = \hbar^2(2j+1)^2 = \left(\frac{\mu Z^2 e^4}{-2H}\right)' = \frac{\mu Z^2 e^4}{-2E},$$
(19.46)

where E is the energy eigenvalue. Denote 2j + 1 = n, where n = 1, 2, 3, ... We obtain the Bohr energy levels,

$$E_n = -\frac{\mu Z^2 e^4}{2n^2 \hbar^2},$$
(19.47)

without encountering n = 0.

The Bohr energy levels follow from an exact quantum-mechanical treatment. The fact that this agrees with experiment validates our use of the Coulomb potential. It is not merely good agreement with the spectrum of hydrogen that is obtained, but through the nuclear mass M dependence in $\mu = mM/(M+m)$. This is in agreement with the small shift between the H and He⁺ spectra, the latter corrected for the factor of $Z^2 = 4$. Rydberg atoms, where an outer electron is in a highly excited state, can also be described approximately by this energy formula.

The number of states having a given energy, that is, the "degeneracy" of the energy levels, is the number of states for which n = 2j + 1 has a definite value. Since there are 2j + 1 values of m for each of $J_z^{(+)}$ and $J_z^{(-)}$, this number is

$$(2j+1) \times (2j+1) = n^2 = 1, 4, 9, \dots$$
(19.48)

The state of lowest energy, with n = 1, is unique. Since $\mathbf{L} = \mathbf{J}^{(+)} + \mathbf{J}^{(-)}$, and this state is one for which $\mathbf{J}^{(+)} = \mathbf{J}^{(-)} = 0$, this state is also characterized by the angular momentum quantum numbers l = 0, m = 0. In general, we can denote the states of the hydrogen atom by the values of these three quantum numbers,

$$|n,l,m\rangle. \tag{19.49}$$

The lowest energy state obeys

$$\mathbf{L}|1,0,0\rangle = 0, \quad \mathbf{A}|1,0,0\rangle = 0.$$
 (19.50)

The latter equation reads

$$\left(\frac{\mathbf{r}}{r} - \frac{1}{\mu Z e^2} (\mathbf{p} \times \mathbf{L} - i\hbar \mathbf{p})\right) |1, 0, 0\rangle.$$
(19.51)

Because this is a zero angular momentum state, this equation reads

$$\left(\frac{\mathbf{r}}{r} + \frac{i\hbar\mathbf{p}}{\mu Z e^2}\right)|1,0,0\rangle = 0.$$
(19.52)

We construct a differential equation for the wavefunction by multiplying on the left by a position eigenstate,

$$0 = \langle \mathbf{r}' | \left(\frac{\mathbf{r}}{r} + \frac{i\hbar\mathbf{p}}{\mu Z e^2} \right) | 1, 0, 0 \rangle = \left(\frac{\mathbf{r}'}{r'} + \frac{i\hbar}{\mu Z e^2} \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}'} \right) \psi_{100}(\mathbf{r}'), \qquad (19.53)$$

where the ground-state wavefunction is

$$\psi_{100}(\mathbf{r}') = \langle \mathbf{r}' | 100 \rangle. \tag{19.54}$$

Define the "Bohr radius" by

$$a_0 = \frac{\hbar^2}{\mu e^2}.$$
 (19.55)

Then this differential equation reads

$$\left(\frac{\mathbf{r}'}{r'} + \frac{a_0}{Z}\frac{\partial}{\partial\mathbf{r}'}\right)\psi_{100}(\mathbf{r}') = 0.$$
(19.56)

The radial component of this vector equation is

$$\left(1 + \frac{a_0}{Z}\frac{\partial}{\partial r}\right)\psi_{100}(r) \tag{19.57}$$

where we've simplified the notation by dropping the primes, and recognizing that the ground-state wavefunction depends only on the distance from the nucleus, $r = |\mathbf{r}|$, which follows from the other components of the gradient. This is as expected for a state of zero angular momentum. The solution to this equation is immediate:

$$\psi_{100}(r) = Ae^{-Zr/a_0}.$$
(19.58)

To determine A, we apply the normalization condition,

$$\int (d\mathbf{r}) |\psi_{100}(r)|^2 = 1.$$
(19.59)

Here the volume element is

$$(d\mathbf{r}) = 4\pi r^2 dr, \qquad (19.60)$$

and so we have (choosing the phase to be zero)

$$4\pi A^2 \int_0^\infty r^2 dr \, e^{-2Zr/a_0} = 4\pi A^2 \left(\frac{a_0}{2Z}\right)^3 \int_0^\infty dx \, x^2 \, e^{-x}.$$
 (19.61)

Since the last integral is 2, the normalization constant is

$$A = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2},\tag{19.62}$$

and so the normalized ground-state wavefunction of the hydrogenic atom is

$$\psi_{100}(r) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0}.$$
(19.63)

The probability amplitude is concentrated in a region of characteristic size a_0/Z , and it, and the corresponding probability, are sketched in Fig. 19.2.

The next-to-lowest energy levels are n = 2 or j = 1/2. These for states correspond to the combination of two spins of 1/2. This is interesting, because these spin-1/2's certainly have no real existence. The state with $m^{(+)} = m^{(-)} =$ $+\frac{1}{2}$, i.e., n = 2, m = 1, and therefore l = 1, is characterized by

$$(J_x + iJ_y)^{(+)}|211\rangle = 0, \quad (J_x + iJ_y)^{(-)}|211\rangle = 0,$$
 (19.64)



Figure 19.2: Ground-state wavefunction for the hydrogen atom (Z = 1), and the square of the wavefunction (multiplied by $4\pi r^2$), plotted versus r in units of the Bohr radius a_0

because it is both the highest $m^{(+)}$ state and the highest $m^{(-)}$ state. Equivalently, it is the highest m state,

$$(L_x + iL_y)|211\rangle = 0,$$
 (19.65)

and satisfies as well

$$(A_x + iA_y)|211\rangle.$$
 (19.66)

The corresponding wavefunction satisfies

$$\langle \mathbf{r}' | (L_x + iL_y) | 211 \rangle = (L_x + iL_y) \psi_{211}(\mathbf{r}') = L_+ \psi_{211}(\mathbf{r}') = 0.$$
 (19.67)

In the latter equation, L_+ is a differential operator.

Later, we will discuss the general approach to solving this problem in spherical polar coordinates, using spherical harmonics. For the present, however, it will suffice to note that

$$L_{+} = (yp_{z} - zp_{y} + izp_{x} - ixp_{z}) \rightarrow \frac{\hbar}{i} [(y - ix)\partial_{z} - z(\partial_{y} - i\partial_{x})]$$

= $\hbar [-(x + iy)\partial_{z} + z(\partial_{x} + i\partial_{y})].$ (19.68)

Now we note

$$(\partial_x + i\partial_y)(x + iy) = 1 - 1 = 0,$$
 (19.69)

and that if we write the wavefunction as

$$\psi_{211} = (x+iy)f(r), \quad r^2 = x^2 + y^2 + z^2,$$
 (19.70)

we find

$$L_{+}\psi_{211} = \hbar(x+iy)[-(x+iy)\partial_{z} + z(\partial_{x}+i\partial_{y})]f(r)$$

$$= \hbar(x+iy)f'(r)\left[-(x+iy)\frac{\partial r}{\partial z} + z\left(\frac{\partial r}{\partial x} + i\frac{\partial r}{\partial y}\right)\right]$$

$$= \hbar(x+iy)f'(r)\left[-(x+iy)\frac{z}{r} + z\left(\frac{x}{r} + i\frac{y}{r}\right)\right] = 0.$$
(19.71)

Thus the angular momentum condition (19.67) is satisfied.

To determine the radial function f, we use the second equation (19.66). Recall that

$$\mathbf{A} = \frac{\mathbf{r}}{r} - \frac{1}{\mu Z e^2} (\mathbf{p} \times \mathbf{L} - i\hbar \mathbf{p}), \qquad (19.72)$$

and then

$$(\mathbf{p} \times \mathbf{L})_x + i(\mathbf{p} \times \mathbf{L})_y = p_y L_z - p_z L_y + i(p_z L_x - p_x L_z) = ip_z L_+ - i(p_x + ip_y) L_z.$$
(19.73)

Therefore, since

$$L_{+}|211\rangle = 0, \quad (L_{z} - \hbar)|211\rangle = 0,$$
 (19.74)

we have

$$(A_x + iA_y)|211\rangle = \left[\frac{x + iy}{r} - \frac{1}{\mu Z e^2}(-2i\hbar)(p_x + ip_y)\right]|211\rangle = 0.$$
(19.75)

On the wavefunction, this means

$$\left(\frac{x+iy}{r} + \frac{2a_0}{Z}\left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)\right)\psi_{211}(\mathbf{r}) = 0, \qquad (19.76)$$

again dropping the primes on eigenvalues. Now using the construction (19.70) and the identity (19.69), we see that

$$(\partial_x + i\partial_y)f(r) = \frac{x + iy}{r}\frac{d}{dr}f(r).$$
(19.77)

so the differential equation (19.76) reads

$$\frac{2a_0}{Z}\frac{d}{dr}f(r) + f(r) = 0, \qquad (19.78)$$

which has solution

$$f(r) = Ce^{-Zr/(2a_0)}.$$
(19.79)

So the 211 wavefunction is

$$\psi_{211}(\mathbf{r}) = C(x+iy)e^{-Zr/2a_0} = Cr\sin\theta e^{i\phi}e^{-Zr/2a_0},$$
(19.80)

writing this in spherical polar coordinates, and recalling that

$$\cos\phi + i\sin\phi = e^{i\phi}.\tag{19.81}$$

The constant C is determined, up to a phase, by the normalization condition, that the probability of finding the electron somewhere is unity,

$$\int (d\mathbf{r}) |\psi_{211}(\mathbf{r})|^2 = 1, \qquad (19.82)$$

or

$$1 = \int_{0}^{\infty} dr r^{2} \int_{0}^{\pi} d\theta \sin \theta \int_{0}^{2\pi} d\phi |C|^{2} r^{2} \sin^{2} \theta e^{-Zr/a_{0}}$$

= $|C|^{2} \int_{0}^{\infty} dr r^{4} e^{-Zr/a_{0}} 2\pi \int d\cos \theta (1 - \cos^{2} \theta)$
= $\frac{8\pi}{3} |C|^{2} \left(\frac{a_{0}}{Z}\right)^{5} \int_{0}^{\infty} dx x^{4} e^{-x} = 64\pi |C|^{2} \left(\frac{a_{0}}{Z}\right)^{5},$ (19.83)

which gives the magnitude of the normalization constant:

$$|C| = \left(\frac{Z}{a_0}\right)^{5/2} \frac{1}{8\sqrt{\pi}},\tag{19.84}$$

so, writing the wavefunction in a form comparable to that for the ground state,

$$\psi_{211}(\mathbf{r}) = \frac{1}{\sqrt{2\pi}} \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Z}{2a_0} (x+iy) e^{-Zr/2a_0}$$
$$= \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{5/2} r \sin \theta e^{i\phi} e^{-Zr/2a_0}.$$
(19.85)

The probability of finding the electron in a given elements of volume is

$$|\psi_{211}|^2(r,\theta) = \frac{1}{64\pi} \left(\frac{Z}{a_0}\right)^5 r^2 \sin^2 \theta \, e^{-Zr/a_0}.$$
 (19.86)

In the homework, you will work out the three other wavefunctions for n = 2, those corresponding to l = 1, m = -1, 0, and the state with l = m = 0.

It is clear that to proceed further systematically, we need to learn more about combining angular momenta, and describing the angular part of the wavefunctions systematically. So we will now return to that subject.