# PHY 350 — Quantum Mechanics

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#### 1 Problem 1: Exercise 6.2

A particle of mass m moves in the xy plane in the potential

$$V(x,y) = \begin{cases} \frac{1}{2}m\omega^2 x^2, & \text{for all y and } 0 < x < a \\ +\infty, & \text{elsewhere} \end{cases}$$
 (1.1)

(a) Write down the time-independent Schrödinger equation for this particle and reduce it to a set of familiar one-dimensional equations.

**Solution** The particle is in an infinite square well potential bounded in the x-direction from 0 to a, and unbounded in the y-direction. The particle also experiences a harmonic oscillator potential  $\frac{1}{2}m\omega^2x^2$  in this region. To reduce it to a set of familiar one-dimensional equations, we have to first assume a separable solution,  $\psi(x,y) = X(x)Y(y)$ .

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x, y) + V(x, y) \psi(x, y) = E\psi(x, y), \tag{1.2}$$

$$-\frac{\hbar^2}{2m}\left(Y\frac{\partial^2}{\partial x^2}X+X\frac{\partial^2}{\partial y^2}Y\right)+\left(\frac{1}{2}m\omega^2x^2\right)XY=EXY, \tag{1.3}$$

$$-\frac{\hbar^2}{2m} \left( \frac{1}{X} \frac{\partial^2}{\partial x^2} X + \frac{1}{Y} \frac{\partial^2}{\partial y^2} Y \right) + \left( \frac{1}{2} m \omega^2 x^2 \right) = E, \tag{1.4}$$

$$\left[ -\frac{\hbar^2}{2m} \frac{1}{X} \frac{\partial^2}{\partial x^2} X + \frac{1}{2} m \omega^2 x^2 \right] + \left[ -\frac{\hbar^2}{2m} \frac{1}{Y} \frac{\partial^2}{\partial y^2} Y \right] = E. \tag{1.5}$$

We now have a separation constant,  $E = E_x + E_y$ .

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X + \frac{1}{2}m\omega^2 x^2 X = E_x X,$$
(1.6)

$$\mathcal{H}_x X = E_x X,\tag{1.7}$$

where  $\mathcal{H}_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2$ .

$$-\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y = E_y Y \,,$$
(1.8)

$$\mathcal{H}_{y}Y = E_{y}Y,\tag{1.9}$$

where  $\mathcal{H}_y = -\frac{\hbar^2}{2m} \frac{d^2}{du^2}$ .

#### (b) Find the normalized eigenfunctions and eigenenergies.

**Solution** The eigenfunctions X and Y correspond to the one dimensional harmonic oscillator and the free particle wave functions, respectively. Similarly, with the eigenenergies  $E_x$  and  $E_y$ . X is bounded in the x-direction, so we have to find the normalization constant in this case. Rearranging the full equation.

$$\frac{d^2X}{dx^2} + \left[\frac{2mE}{\hbar^2} - \left(\frac{m\omega}{\hbar}\right)^2 x^2\right] X = 0 \tag{1.10}$$

A helpful substitution is  $\alpha = \sqrt{m\omega/\hbar} x$ .

$$\frac{d}{dx} = \frac{d\alpha}{dx}\frac{d}{d\alpha} = \sqrt{\frac{m\omega}{\hbar}}\frac{d}{d\alpha} \tag{1.11}$$

$$\frac{dX}{dx} = \sqrt{\frac{m\omega}{\hbar}} \frac{dX}{d\alpha} \tag{1.12}$$

$$\frac{d}{dx}\left(\frac{dX}{dx}\right) = \sqrt{\frac{m\omega}{\hbar}} \frac{d}{dx}\left(\frac{dX}{d\alpha}\right) = \frac{m\omega}{\hbar} \frac{d^2X}{d\alpha^2}$$
(1.13)

$$\frac{m\omega}{\hbar} \frac{d^2 X}{d\alpha^2} + \left[ \frac{2mE_x}{\hbar^2} - \frac{m\omega}{\hbar} \alpha^2 \right] X = 0 \tag{1.14}$$

$$\frac{d^2X}{d\alpha^2} + \left[\frac{2E_x}{\hbar\omega} - \alpha^2\right]X = 0 \tag{1.15}$$

We attempt a Gaussian type solution of the form:  $X(\alpha) = f(\alpha)e^{-\alpha^2/2}$ .

$$\frac{dX}{d\alpha} = -\alpha e^{-\alpha^2/2} f(\alpha) + e^{-\alpha^2/2} f'(\alpha) \tag{1.16}$$

$$= (f' - \alpha f)e^{-\alpha^2/2} \tag{1.17}$$

$$\frac{d^2X}{d\alpha^2} = (f'' - f - \alpha f')e^{-\alpha^2/2} + (f' - \alpha f)(-\alpha e^{-\alpha^2/2})$$
(1.18)

$$= [f'' - 2\alpha f' + (\alpha^2 - 1)f] e^{-\alpha^2/2}$$
(1.19)

$$[f'' - 2\alpha f' + (\alpha^2 - 1)f]e^{-\alpha^2/2} + \frac{2E_x}{\hbar\omega} fe^{-\alpha^2/2} - \alpha^2 fe^{-\alpha^2/2} = 0$$
(1.20)

$$f'' - 2\alpha f' + \left(\frac{2E_x}{\hbar\omega} - 1\right)f = 0 \tag{1.21}$$

This is Hermite's differential equation,  $y'' - 2xy' + 2\lambda y = 0$ , where  $\lambda$  is typically a non-negative integer. Now we can find the eigenenergies.

$$\frac{2E_x}{\hbar\omega} - 1 = 2n_x \tag{1.22}$$

$$\frac{2E_x}{\hbar\omega} - 1 = 2n_x \tag{1.22}$$

$$E_x = \hbar\omega \left(n_x + \frac{1}{2}\right)$$

For the eigenfunction, since we have found the system to follow Hermite's differential equation,  $f(\alpha)$  takes the form  $H_n(\alpha)$ , with it already being quantized.

$$X_n(\alpha) = e^{-\alpha^2/2} f_n(\alpha) = e^{-\alpha^2/2} H_n(\alpha)$$
(1.24)

Tracing back to  $\alpha = \sqrt{m\omega/\hbar} x$ , let  $x_0 = \sqrt{\hbar/m\omega}$ , so  $\alpha = x/x_0$ .

$$X_n(x) = e^{-x^2/2x_0^2} H_n(x/x_0)$$
(1.25)

We have to normalize the wave function within the bounds, so introduce an overall multiplicative constant N associated with  $X_n(x)$ .

$$1 = \int_0^a |N|^2 \left[ e^{-x^2/2x_0^2} \right]^2 \left[ H_n(x/x_0) \right]^2 dx, \qquad \begin{cases} u = x/x_0 \\ du = dx/x_0 \end{cases}$$
 (1.26)

$$1 = |N|^2 x_0 \int_0^{a/x_0} e^{-u^2} \left[ H_n(u) \right]^2 du \tag{1.27}$$

The orthonormality condition of Hermite polynomials over  $(-\infty, \infty)$  does not directly translate to normalization over finite intervals, so numerical methods must be used. Let's examine the ground state  $X_0(x)$ .

$$X_0(x) = Ne^{-x^2/2x_0^2} H_0(x/x_0) = Ne^{-x^2/2x_0^2}$$
(1.28)

$$|X_0(x)|^2 = \int_0^a |N|^2 e^{-x^2/x_0^2} dx = 1, \qquad \begin{cases} u = x/x_0 \\ du = dx/x_0 \end{cases}$$
 (1.29)

$$1 = |N|^2 x_0 \int_0^{a/x_0} e^{-u^2} du \tag{1.30}$$

This integral is the error function  $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$ .

$$1 = |N|^2 x_0 \frac{\sqrt{\pi}}{2} \operatorname{erf}(a/x_0) \tag{1.31}$$

$$N = \sqrt{\frac{2}{\sqrt{\pi x_0 \,\text{erf}(a/x_0)}}} \tag{1.32}$$

$$X_0(x) = \sqrt{\frac{2}{\sqrt{\pi}x_0 \operatorname{erf}(a/x_0)}} e^{-x^2/2x_0^2}$$
(1.33)

This normalization constant is specific to the ground state wave function. To find the wave function of any excited state we apply the creation operator  $a^{\dagger}$  on the ground state n times.

$$X_n(x) = \langle x|n\rangle = \frac{1}{\sqrt{n!}} \langle x| \left(a^{\dagger}\right)^n |0\rangle = \frac{1}{\sqrt{n!}} \left(\frac{1}{\sqrt{2}x_0}\right)^n \left(x - x_0^2 \frac{d}{dx}\right)^n X_0(x)$$

$$\tag{1.34}$$

$$X_n(x) = \frac{1}{\sqrt{n!}} \left(\frac{1}{\sqrt{2}x_0}\right)^n \left(x - x_0^2 \frac{d}{dx}\right)^n \sqrt{\frac{2}{\sqrt{\pi}x_0 \operatorname{erf}(a/x_0)}} e^{-x^2/2x_0^2}$$
(1.35)

$$= \sqrt{\frac{2}{\sqrt{\pi}2^n n! \operatorname{erf}(a/x_0)}} \frac{1}{x_0^{n+1/2}} \left(x - x_0^2 \frac{d}{dx}\right)^n e^{-x^2/2x_0^2}$$
(1.36)

$$X_n(x) = \sqrt{\frac{2}{\sqrt{\pi} 2^n n! x_0 \operatorname{erf}(a/x_0)}} e^{-x^2/2x_0^2} H_n\left(\frac{x}{x_0}\right)$$
(1.37)

Now for Y and  $E_y$ , a free particle as it is unbounded in the y-direction.

$$\frac{d^2Y}{du^2} + \frac{2mE}{\hbar^2}Y = 0\tag{1.38}$$

$$\frac{d^2Y}{dy^2} + k^2Y = 0 ag{1.39}$$

$$Y(y) = Ae^{iky} + Be^{-iky} (1.40)$$

$$E_y = \frac{\hbar^2 k^2}{2m} \tag{1.41}$$

To normalize the free particle we consider a single plane wave, instead of a superposition, for simplicity. This forces the momentum to travel in one direction. In this case, we use delta function normalization.

$$\int_{-\infty}^{\infty} Y(y)Y^{\star}(y') \ dy = \delta(y - y') \tag{1.42}$$

$$\int_{-\infty}^{\infty} Ae^{iky} A^{\star} e^{-iky'} dy = \delta(y - y')$$
(1.43)

$$|A|^2 \int_{-\infty}^{\infty} e^{ik(y-y')} dy = \delta(y-y')$$
 (1.44)

Using the Fourier transform of  $\delta(x)$  in Appendix A.

$$|A|^2 [2\pi\delta(y - y')] = \delta(y - y')$$
 (1.45)

$$A = \frac{1}{\sqrt{2\pi}} \tag{1.46}$$

$$Y(y) = \frac{1}{\sqrt{2\pi}} e^{iky} \tag{1.47}$$

#### 2 Problem 2: Exercise 6.8

Consider a muonic atom which consists of a nucleus that has Z protons (no neutrons) and a negative muon moving around it; the muon's charge is -e and its mass is 207 times the mass of the electron,  $m_{\mu^-} = 207m_e$ . For a muonic atom with Z = 6, calculate

(a) the radius of the first Bohr orbit,

**Solution** Starting with a Hydrogen atom, we can easily derive the radius of the Bohr orbits with two assumptions: the electron orbits the nucles, the angular momentum of the electron is quantized.

$$m_e \frac{v^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}$$
 (2.1)  $L = m_e v r = n\hbar$ 

$$r = \frac{1}{4\pi\epsilon_0} \frac{e^2}{m_e} \frac{m_e^2 r^2}{n^2 \hbar^2}$$

$$(2.2) \qquad m_e v_n^2 = \frac{n^2 \hbar^2}{m_e r_n^2}$$

$$r_n = \left(\frac{4\pi\epsilon_0 \, \hbar^2}{m_e e^2}\right) n^2 = a_0 n^2 \qquad (2.3) \qquad m_e v_n^2 = \frac{n^2 \hbar^2}{m_e} \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2}\right)^2 \frac{1}{n^4} \qquad (2.7)$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.529 \, 18 \,\text{Å}$$
 (2.4)  $m_e v_n^2 = \frac{m_e}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2}$  (2.8)

$$E = K + U (2.9)$$

$$=\frac{1}{2}m_e v_n^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_n} \tag{2.10}$$

$$= \frac{1}{2} \frac{m_e}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} - \frac{1}{4\pi\epsilon_0} e^2 \left( \frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} \right) \frac{1}{n^2}$$
 (2.11)

$$= \frac{1}{2} \frac{m_e}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2} - \frac{m_e}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2}$$
 (2.12)

$$E_n = -\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2} = -\frac{\mathcal{R}}{n^2} \approx -\frac{13.606 \,\text{eV}}{n^2}$$
 (2.13)

where  $\mathcal{R}$  is the Rydberg constant:

$$\mathcal{R} = \frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \approx 13.606 \,\text{eV} \tag{2.14}$$

For a hydrogen-like atom, we introduce two assumptions: include the mass of the protons M with the reduced mass  $\mu$ , replace  $e^2$  by  $Ze^2$  where Z is the number of protons.

$$\mu = \frac{Mm_e}{M + m_e} = \frac{m_e}{1 + m_e/M} \tag{2.15}$$

$$r_n = \left(\frac{4\pi\epsilon_0 \hbar^2}{\mu Z e^2}\right) n^2 = (1 + m_e/M) \frac{a_0}{Z} n^2$$
(2.16)

$$E_n = -\frac{\mu}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2} = -\frac{Z^2}{1 + m_e/M} \frac{\mathcal{R}}{n^2}$$
 (2.17)

In this case, we have Z=6 and a muon instead of an electron where  $m_{\mu^-}=207m_e$ . Therefore the reduced mass  $\mu$  becomes

$$\mu = 1 + \frac{207m_e}{6m_p} = 1 + \frac{207 \times 9.1094 \times 10^{-31} \text{ kg}}{6 \times 1.6726 \times 10^{-27} \text{ kg}} = 1.0188.$$
 (2.18)

This is not a negligible ratio so we have to keep it in the calculation.

$$r_1 = 1.0188 \times \frac{0.52918 \,\text{Å}}{6} = \boxed{0.089855 \,\text{Å}}$$
 (2.19)

(b) the energy of the ground, first, and second excited states, and

Solution

$$E_1 = -\frac{6^2}{1.0188} \times \frac{13.606 \,\text{eV}}{1^2} = \boxed{-480.78 \,\text{eV}}$$
 (2.20)

$$E_2 = -\frac{6^2}{1.0188} \times \frac{13.606 \,\text{eV}}{2^2} = \boxed{-120.19 \,\text{eV}}$$
 (2.21)

$$E_3 = -\frac{6^2}{1.0188} \times \frac{13.606 \,\text{eV}}{3^2} = \boxed{-53.420 \,\text{eV}}$$
 (2.22)

(2.23)

(c) the frequency associated with the transitions  $n_i = 2 \rightarrow n_f = 1$ ,  $n_i = 3 \rightarrow n_f = 1$ , and  $n_i = 3 \rightarrow n_f = 2$ .

Solution  $hf = \Delta E = E_f - E_i$ .

$$f_{2\to 1} = \frac{E_2 - E_1}{h} = \frac{-120.19 \,\text{eV} - (-480.78 \,\text{eV})}{4.1357 \times 10^{-15} \,\text{eV} \,\text{Hz}^{-1}} = \boxed{87.190 \times 10^{15} \,\text{Hz}}$$
(2.24)

$$f_{2\to 1} = \frac{E_2 - E_1}{h} = \frac{-120.19 \,\text{eV} - (-480.78 \,\text{eV})}{4.1357 \times 10^{-15} \,\text{eV} \,\text{Hz}^{-1}} = \boxed{87.190 \times 10^{15} \,\text{Hz}}$$

$$f_{3\to 1} = \frac{E_3 - E_1}{h} = \frac{-53.420 \,\text{eV} - (-480.78 \,\text{eV})}{4.1357 \times 10^{-15} \,\text{eV} \,\text{Hz}^{-1}} = \boxed{103.33 \times 10^{15} \,\text{Hz}}$$

$$f_{3\to 2} = \frac{E_3 - E_2}{h} = \frac{-53.420 \,\text{eV} - (-120.19 \,\text{eV})}{4.1357 \times 10^{-15} \,\text{eV} \,\text{Hz}^{-1}} = \boxed{16.145 \times 10^{15} \,\text{Hz}}$$

$$(2.26)$$

$$f_{3\to 2} = \frac{E_3 - E_2}{h} = \frac{-53.420 \,\text{eV} - (-120.19 \,\text{eV})}{4.1357 \times 10^{-15} \,\text{eV} \,\text{Hz}^{-1}} = \boxed{16.145 \times 10^{15} \,\text{Hz}}$$
(2.26)

## 3 Problem 3: Exercise 6.13

The wave function of an electron in a hydrogen atom is given by

$$\psi_{2,1,m_l,m_s}(r,\theta,\varphi) = R_{2,1} \left[ \frac{1}{\sqrt{3}} Y_{1,0}(\theta,\varphi) \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} Y_{1,1}(\theta,\varphi) \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right], \tag{3.1}$$

where  $\left|\frac{1}{2},\pm\frac{1}{2}\right\rangle$  are the spin state vectors.

(a) Is this wave function an eigenfunction of  $\hat{J}_z$  the z-component of the electron's total angular momentum? If yes, find the eigenvalue. (*Hint*: For this, you need to calculate  $\hat{J}_z\psi_{2,1,m_l,m_s}$ )

**Solution** The total angular momentum  $\hat{J}$  is the sum of the orbital angular momentum  $\hat{L}$  and the spin angular momentum  $\hat{S}$ , so  $\hat{J} = \hat{L} + \hat{S}$ . Therefore the z-component,  $\hat{J}_z = \hat{L}_z + \hat{S}_z$ . For ease of computation, Let  $\alpha$  and  $\beta$  correspond to the two terms inside the square bracket, where  $|2, 1, m_l, m_s\rangle = R_{2,1} [\alpha + \beta]$ 

$$\hat{J}_z |2, 1, m_l, m_s\rangle = \hat{L}_z |2, 1, m_l, m_s\rangle + \hat{S}_z |2, 1, m_l, m_s\rangle$$
(3.2)

$$= m_l \hbar |2, 1, m_l, m_s\rangle + m_s \hbar |2, 1, m_l, m_s\rangle$$
(3.3)

$$\hat{L}_z |2, 1, m_l, m_s\rangle = R_{2,1} \left[ (0 \times \hbar)\alpha + (1 \times \hbar)\beta \right]$$
(3.4)

$$= \hbar R_{2,1} \beta \tag{3.5}$$

$$\hat{S}_z |2, 1, m_l, m_s\rangle = R_{2,1} \left[ \left( \frac{1}{2} \times \hbar \right) \alpha + \left( -\frac{1}{2} \times \hbar \right) \beta \right]$$
(3.6)

$$=\frac{\hbar}{2}R_{2,1}\left[\alpha-\beta\right] \tag{3.7}$$

$$\hat{J}_z |2, 1, m_l, m_s\rangle = \hbar R_{2,1} \beta + \frac{\hbar}{2} R_{2,1} [\alpha - \beta]$$
(3.8)

$$=\frac{\hbar}{2}R_{2,1}\left[\alpha+\beta\right] \tag{3.9}$$

$$= \boxed{\frac{\hbar}{2} |2, 1, m_l, m_s\rangle} \tag{3.10}$$

(b) If you measure the z-component of the electron's spin angular momentum, what values will you obtain? What are the corresponding probabilities?

**Solution** From the previous part, we know that the values we obtain are  $\hbar/2$  or  $-\hbar/2$ , with probabilities  $P_{\hbar/2}$  and  $P_{-\hbar/2}$ .

$$P_{\hbar/2} = \left| \left\langle \frac{1}{2}, \frac{1}{2} \middle| \psi \right\rangle \right|^2 = \boxed{\frac{1}{3}} \tag{3.11}$$

$$P_{\hbar/2} = \left| \left\langle \frac{1}{2}, -\frac{1}{2} \middle| \psi \right\rangle \right|^2 = \boxed{\frac{2}{3}} \tag{3.12}$$

(c) If you measure  $\hat{J}_z^2$ , what values will you obtain? What are the corresponding probabilities?

**Solution**  $\hat{J}_{z}^{2} = (\hat{L}_{z} + \hat{S}_{z})^{2} = \hat{L}_{z}^{2} + \hat{L}_{z}\hat{S}_{z} + \hat{S}_{z}\hat{L}_{z} + \hat{S}_{z}^{2}$ 

$$\hat{L}_{z}^{2}|2,1,m_{l},m_{s}\rangle = \hat{L}_{z}\left[\hbar R_{2,1}\beta\right] = \hbar^{2}R_{2,1}\beta \tag{3.13}$$

$$\hat{L}_z \hat{S}_z |2, 1, m_l, m_s\rangle = \hat{L}_z \left[ \frac{\hbar}{2} R_{2,1} (\alpha - \beta) \right] = -\frac{\hbar}{2} R_{2,1} \beta \tag{3.14}$$

$$\hat{S}_z \hat{L}_z |2, 1, m_l, m_s\rangle = \hat{S}_z [\hbar R_{2,1} \beta] = -\frac{\hbar}{2} R_{2,1} \beta$$
(3.15)

$$\hat{S}_{z}^{2}|2,1,m_{l},m_{s}\rangle = \hat{S}_{z}\left[\frac{\hbar}{2}R_{2,1}\left[\alpha - \beta\right]\right] = \frac{\hbar^{2}}{4}R_{2,1}\left[\alpha + \beta\right]$$
(3.16)

$$\hat{J}_{z}^{2}|2,1,m_{l},m_{s}\rangle = \hbar^{2}R_{2,1}\beta - \frac{\hbar}{2}R_{2,1}\beta - \frac{\hbar}{2}R_{2,1}\beta + \frac{\hbar^{2}}{4}R_{2,1}\left[\alpha + \beta\right]$$
(3.17)

$$= \frac{\hbar^2}{4} |2, 1, m_l, m_s\rangle \tag{3.18}$$

Only one value,  $\hbar^2/4$  with 100% probability

## 4 Problem 4: Exercise 6.20

The wave function of a hydrogen-like atom at time t = 0 is

$$\Psi(\vec{r},0) = \frac{1}{\sqrt{11}} \left[ \sqrt{3}\psi_{2,1,-1}(\vec{r}) - \psi_{2,1,0}(\vec{r}) + \sqrt{5}\psi_{2,1,1}(\vec{r}) + \sqrt{2}\psi_{3,1,1}(\vec{r}) \right], \tag{4.1}$$

where  $\psi_{nlm}(\vec{r})$  is a normalized eigenfunction (i.e.  $\psi_{nlm}(\vec{r}) = R_{nl}Y_{lm}(\theta,\varphi)$ ).

(a) What is the time-dependent wave function?

**Solution** The wave function at time t is described by  $\Psi(\vec{r},t) = \psi(\vec{r}) \exp\left(-\frac{i}{\hbar}E_nt\right)$ . The energy of the hydrogen atom only depends on the principal quantum number n. Therefore, I expect this atom to have the sum of two energies, as we have n = 2, 3.

$$\Psi(\vec{r},t) = \frac{1}{\sqrt{11}} \left[ e^{-iE_2t/\hbar} \left( \sqrt{3}\psi_{2,1,-1}(\vec{r}) - \psi_{2,1,0}(\vec{r}) + \sqrt{5}\psi_{2,1,1}(\vec{r}) \right) + e^{-iE_3t/\hbar} \left( \sqrt{2}\psi_{3,1,1}(\vec{r}) \right) \right], \tag{4.2}$$

(b) If a measurement of energy is made, what values could be found and with what probabilities?

**Solution** By inspection, two values for energy are found,  $E_2$  and  $E_3$ . With probabilities  $P_{n,l,m}$ .

$$P_{2,1,-1} = |\langle 2, 1, -1 | \Psi \rangle|^2 = \left| \sqrt{\frac{3}{11}} e^{-iE_2 t/\hbar} \langle 2, 1, -1 | 2, 1, -1 \rangle \right|^2 = \frac{3}{11}$$

$$(4.3)$$

Using the same logic with the rest.

$$P_{2,1,0} = |\langle 2, 1, 0 | \Psi \rangle|^2 = \frac{1}{11}$$
(4.4)

$$P_{2,1,1} = |\langle 2, 1, 1 | \Psi \rangle|^2 = \frac{5}{11} \tag{4.5}$$

$$P_{3,1,1} = |\langle 3, 1, 1 | \Psi \rangle|^2 = \frac{2}{11} \tag{4.6}$$

(4.7)

Therefore, the probability  $E_2$  is measured equals 9/11. The probability  $E_3$  is measured equals 2/11

(c) What is the probability for a measurement of  $\hat{L}_z$  which yields  $-\hbar$ ?

Solution

$$\hat{L}_z \Psi(\vec{r}, 0) = \frac{1}{\sqrt{11}} \left[ \sqrt{3} (-1 \times \hbar) \psi_{2,1,-1}(\vec{r}) - (0 \times \hbar) \psi_{2,1,0}(\vec{r}) + \sqrt{5} (1 \times \hbar) \psi_{2,1,1}(\vec{r}) + \sqrt{2} (1 \times \hbar) \psi_{3,1,1}(\vec{r}) \right]$$
(4.8)

$$P_{-\hbar} = |\langle 2, 1, -1 | \Psi \rangle|^2 = \boxed{\frac{3}{11}}$$
 (4.9)