Problem 4.71

In molecular and solid-state applications, one often uses a basis of orbitals aligned with the cartesian axes rather than the basis $\psi_{n\ell m}$ used throughout this chapter. For example, the orbitals

$$\psi_{2p_x}(r,\theta,\phi) = \frac{1}{\sqrt{32\pi a^3}}\frac{x}{a}e^{-r/2a}$$

$$\psi_{2p_y}(r,\theta,\phi) = \frac{1}{\sqrt{32\pi a^3}}\frac{y}{a}e^{-r/2a}$$

$$\psi_{2p_z}(r,\theta,\phi) = \frac{1}{\sqrt{32\pi a^3}}\frac{z}{a}e^{-r/2a}$$

are a basis for the hydrogen states with $n = 2$ and $\ell = 1$.

(a) Show that each of these orbitals can be written as a linear combination of the orbitals $\psi_{n\ell m}$ with $n = 2$, $\ell = 1$, and $m = -1, 0, 1$.

(b) Show that the states ψ_{2p_i} are eigenstates of the corresponding component of angular momentum: $\hat{L}_i$. What is the eigenvalue in each case.

(c) Make contour plots (as in Figure 4.9) for the three orbitals. In Mathematica use **ContourPlot3D**.

Solution

Part (a)

Recall that the spatial wave functions of hydrogen are products of a radial wave function and a spherical harmonic function: $\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^m(\theta,\phi)$. The necessary radial functions and spherical harmonics are listed on page 151 and page 137, respectively. Start by showing that ψ_{2p_x} is a linear combination of $\psi_{n\ell m}$ with $n = 2$, $\ell = 1$, and $m = -1, 0, 1$.

$$\begin{aligned}
\psi_{2p_x} = \frac{1}{\sqrt{32\pi a^3}}\frac{x}{a}e^{-r/(2a)} &= C_1\psi_{21-1} + C_2\psi_{210} + C_3\psi_{211} \\
&= C_1R_{21}Y_1^{-1} + C_2R_{21}Y_1^0 + C_3R_{21}Y_1^1 \\
&= R_{21}(C_1Y_1^{-1} + C_2Y_1^0 + C_3Y_1^1) \\
&= \frac{1}{2\sqrt{6}}a^{-3/2}\left(\frac{r}{a}\right)e^{-r/(2a)}\left[C_1\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi} + C_2\sqrt{\frac{3}{4\pi}}\cos\theta - C_3\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}\right] \\
&= \frac{1}{\sqrt{32\pi a^3}}\frac{r}{a}e^{-r/(2a)}\underbrace{\left(\frac{C_1}{\sqrt{2}}\sin\theta\, e^{-i\phi} + C_2\cos\theta - \frac{C_3}{\sqrt{2}}\sin\theta\, e^{i\phi}\right)}_{\substack{\text{Need this to be } \sin\theta\cos\phi \\ \text{since } x = r\sin\theta\cos\phi}}
\end{aligned}$$

Choosing $C_1 = 1/\sqrt{2}$, $C_2 = 0$, and $C_3 = -1/\sqrt{2}$ gives the correct result.

$$\begin{aligned}
\psi_{2p_x} &= \frac{1}{\sqrt{32\pi a^3}}\frac{r}{a}e^{-r/(2a)}\left(\frac{1}{2}\sin\theta\, e^{-i\phi} + \frac{1}{2}\sin\theta\, e^{i\phi}\right) \\
&= \frac{1}{\sqrt{32\pi a^3}}\frac{r\sin\theta}{a}e^{-r/(2a)}\left(\frac{e^{-i\phi}+e^{i\phi}}{2}\right) \\
&= \frac{1}{\sqrt{32\pi a^3}}\frac{r\sin\theta}{a}e^{-r/(2a)}(\cos\phi) \\
&= \frac{1}{\sqrt{32\pi a^3}}\frac{x}{a}e^{-r/(2a)}
\end{aligned}$$

Therefore,

$$\boxed{\psi_{2p_x} = \left(\frac{1}{\sqrt{2}}\right)\psi_{21-1} + (0)\psi_{210} + \left(-\frac{1}{\sqrt{2}}\right)\psi_{211}.}$$

Show now that ψ_{2p_y} is a linear combination of $\psi_{n\ell m}$ with $n = 2$, $\ell = 1$, and $m = -1, 0, 1$.

$$\begin{aligned}
\psi_{2p_y} = \frac{1}{\sqrt{32\pi a^3}}\frac{y}{a}e^{-r/(2a)} &= C_1\psi_{21-1} + C_2\psi_{210} + C_3\psi_{211} \\
&= C_1 R_{21}Y_1^{-1} + C_2 R_{21}Y_1^0 + C_3 R_{21}Y_1^1 \\
&= R_{21}(C_1Y_1^{-1} + C_2Y_1^0 + C_3Y_1^1) \\
&= \frac{1}{2\sqrt{6}}a^{-3/2}\left(\frac{r}{a}\right)e^{-r/(2a)}\left[C_1\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi} + C_2\sqrt{\frac{3}{4\pi}}\cos\theta - C_3\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}\right] \\
&= \frac{1}{\sqrt{32\pi a^3}}\frac{r}{a}e^{-r/(2a)}\underbrace{\left(\frac{C_1}{\sqrt{2}}\sin\theta\, e^{-i\phi} + C_2\cos\theta - \frac{C_3}{\sqrt{2}}\sin\theta\, e^{i\phi}\right)}_{\substack{\text{Need this to be } \sin\theta\sin\phi \\ \text{since } y = r\sin\theta\sin\phi}}
\end{aligned}$$

Choosing $C_1 = -1/(\sqrt{2}i)$, $C_2 = 0$, and $C_3 = -1/(\sqrt{2}i)$ gives the correct result.

$$\begin{aligned}
\psi_{2p_y} &= \frac{1}{\sqrt{32\pi a^3}}\frac{r}{a}e^{-r/(2a)}\left(-\frac{1}{2i}\sin\theta\, e^{-i\phi} + \frac{1}{2i}\sin\theta\, e^{i\phi}\right) \\
&= \frac{1}{\sqrt{32\pi a^3}}\frac{r\sin\theta}{a}e^{-r/(2a)}\left(\frac{e^{i\phi}-e^{-i\phi}}{2i}\right) \\
&= \frac{1}{\sqrt{32\pi a^3}}\frac{r\sin\theta}{a}e^{-r/(2a)}(\sin\phi) \\
&= \frac{1}{\sqrt{32\pi a^3}}\frac{y}{a}e^{-r/(2a)}
\end{aligned}$$

Therefore,

$$\boxed{\psi_{2p_y} = \left(-\frac{1}{i\sqrt{2}}\right)\psi_{21-1} + (0)\psi_{210} + \left(-\frac{1}{i\sqrt{2}}\right)\psi_{211}.}$$

Show now that ψ_{2p_z} is a linear combination of $\psi_{n\ell m}$ with $n = 2$, $\ell = 1$, and $m = -1, 0, 1$.

$$\begin{aligned}
\psi_{2p_z} = \frac{1}{\sqrt{32\pi a^3}}\frac{z}{a}e^{-r/(2a)} &= C_1\psi_{21-1} + C_2\psi_{210} + C_3\psi_{211} \\
&= C_1 R_{21} Y_1^{-1} + C_2 R_{21} Y_1^0 + C_3 R_{21} Y_1^1 \\
&= R_{21}(C_1 Y_1^{-1} + C_2 Y_1^0 + C_3 Y_1^1) \\
&= \frac{1}{2\sqrt{6}}a^{-3/2}\left(\frac{r}{a}\right)e^{-r/(2a)}\left[C_1\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi} + C_2\sqrt{\frac{3}{4\pi}}\cos\theta - C_3\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}\right] \\
&= \frac{1}{\sqrt{32\pi a^3}}\frac{r}{a}e^{-r/(2a)}\underbrace{\left(\frac{C_1}{\sqrt{2}}\sin\theta\, e^{-i\phi} + C_2\cos\theta - \frac{C_3}{\sqrt{2}}\sin\theta\, e^{i\phi}\right)}_{\substack{\text{Need this to be }\cos\theta \\ \text{since } z = r\cos\theta}}
\end{aligned}$$

Choosing $C_1 = 0$, $C_2 = 1$, and $C_3 = 0$ gives the correct result.

$$\begin{aligned}
\psi_{2p_z} &= \frac{1}{\sqrt{32\pi a^3}}\frac{r}{a}e^{-r/(2a)}(\cos\theta) \\
&= \frac{1}{\sqrt{32\pi a^3}}\frac{z}{a}e^{-r/(2a)}
\end{aligned}$$

Therefore,

$$\boxed{\psi_{2p_z} = (0)\psi_{21-1} + (1)\psi_{210} + (0)\psi_{211}.}$$

Part (b)

Let the angular momentum operators act on the corresponding wave functions aligned with the Cartesian axes. Use Equation 4.127 on page 163 to expand L_x.

$$\begin{aligned}
L_x\psi_{2p_x} &= -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)\psi_{2p_x} \\
&= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)\left(\frac{1}{\sqrt{2}}\psi_{21-1} - \frac{1}{\sqrt{2}}\psi_{211}\right) \\
&= \frac{i\hbar}{\sqrt{2}}\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)[R_{21}(r)Y_1^{-1}(\theta,\phi) - R_{21}(r)Y_1^1(\theta,\phi)] \\
&= \frac{i\hbar}{\sqrt{2}}R_{21}(r)\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)\left(\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi} + \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}\right) \\
&= i\hbar R_{21}(r)\sqrt{\frac{3}{16\pi}}\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)\sin\theta\,(e^{-i\phi} + e^{i\phi}) \\
&= i\hbar R_{21}(r)\sqrt{\frac{3}{16\pi}}\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)\sin\theta\,(2\cos\phi) \\
&= i\hbar R_{21}(r)\sqrt{\frac{3}{4\pi}}\left[\sin\phi\frac{\partial}{\partial\theta}(\sin\theta\cos\phi) + \cos\phi\cot\theta\frac{\partial}{\partial\phi}(\sin\theta\cos\phi)\right] \\
&= i\hbar R_{21}(r)\sqrt{\frac{3}{4\pi}}\,[\sin\phi(\cos\theta\cos\phi) + \cos\phi\cot\theta(-\sin\theta\sin\phi)] \\
&= i\hbar R_{21}(r)\sqrt{\frac{3}{4\pi}}\,(\sin\phi\cos\theta\cos\phi - \sin\phi\cos\theta\cos\phi) \\
&= 0 \\
&= (0)\psi_{2p_x}
\end{aligned}$$

Consequently, ψ_{2p_x} is an eigenfunction of L_x with eigenvalue 0.

Use Equation 4.128 on page 163 to expand L_y.

$$\begin{aligned}
L_y\psi_{2p_y} &= -i\hbar\left(+\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)\psi_{2p_y} \\
&= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)\left(-\frac{1}{i\sqrt{2}}\psi_{21-1} - \frac{1}{i\sqrt{2}}\psi_{211}\right) \\
&= \frac{\hbar}{\sqrt{2}}\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)[R_{21}(r)Y_1^{-1}(\theta,\phi) + R_{21}(r)Y_1^1(\theta,\phi)] \\
&= \frac{\hbar}{\sqrt{2}}R_{21}(r)\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)\left(\sqrt{\frac{3}{8\pi}}\sin\theta\,e^{-i\phi} - \sqrt{\frac{3}{8\pi}}\sin\theta\,e^{i\phi}\right) \\
&= \hbar R_{21}(r)\sqrt{\frac{3}{16\pi}}\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)\sin\theta\,(e^{-i\phi} - e^{i\phi}) \\
&= \hbar R_{21}(r)\sqrt{\frac{3}{16\pi}}\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)\sin\theta\,(-2i\sin\phi) \\
&= -i\hbar R_{21}(r)\sqrt{\frac{3}{4\pi}}\left[\cos\phi\frac{\partial}{\partial\theta}(\sin\theta\sin\phi) - \sin\phi\cot\theta\frac{\partial}{\partial\phi}(\sin\theta\sin\phi)\right] \\
&= -i\hbar R_{21}(r)\sqrt{\frac{3}{4\pi}}\,[\cos\phi(\cos\theta\sin\phi) - \sin\phi\cot\theta(\sin\theta\cos\phi)] \\
&= -i\hbar R_{21}(r)\sqrt{\frac{3}{4\pi}}\,(\cos\phi\cos\theta\sin\phi - \cos\phi\cos\theta\sin\phi) \\
&= 0 \\
&= (0)\psi_{2p_y}
\end{aligned}$$

Consequently, ψ_{2p_y} is an eigenfunction of L_y with eigenvalue 0.

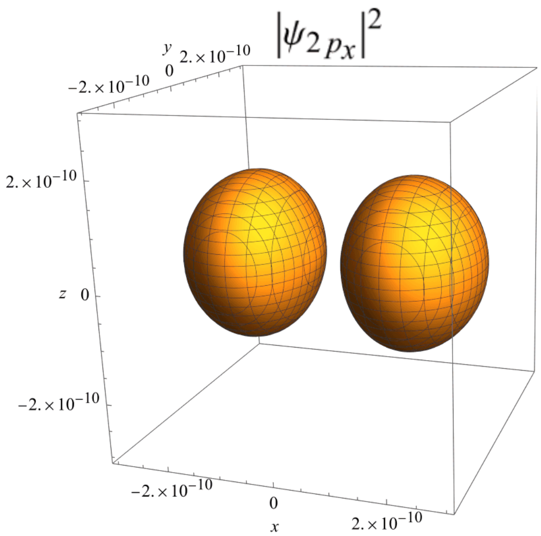
Use Equation 4.129 on page 163 to expand L_z.

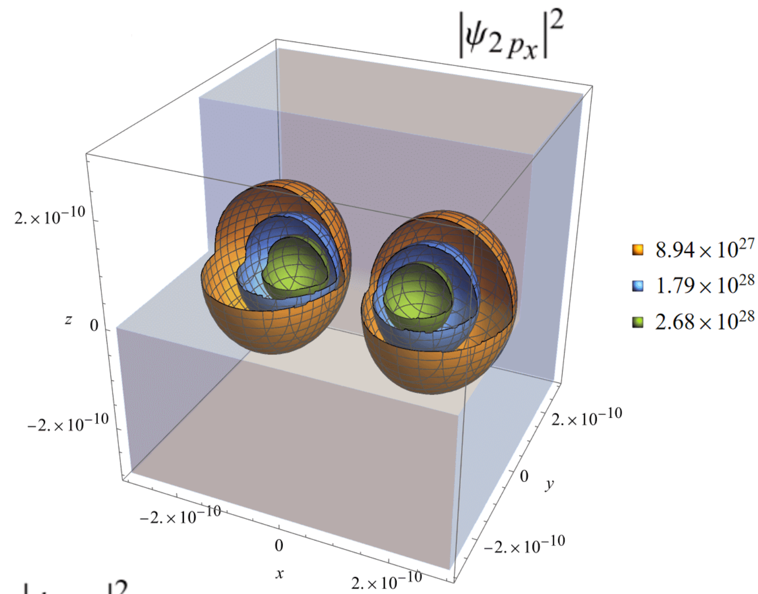
$$
\begin{aligned}
L_z \psi_{2p_z} &= -i\hbar \frac{\partial}{\partial \phi} \psi_{2p_z} \\
&= -i\hbar \frac{\partial}{\partial \phi} \psi_{210} \\
&= -i\hbar \frac{\partial}{\partial \phi} [R_{21}(r) Y_1^0(\theta, \phi)] \\
&= -i\hbar R_{21}(r) \frac{\partial}{\partial \phi} \left(\sqrt{\frac{3}{4\pi}} \cos\theta \right) \\
&= -i\hbar R_{21}(r)(0) \\
&= 0 \\
&= (0)\psi_{2p_z}
\end{aligned}
$$

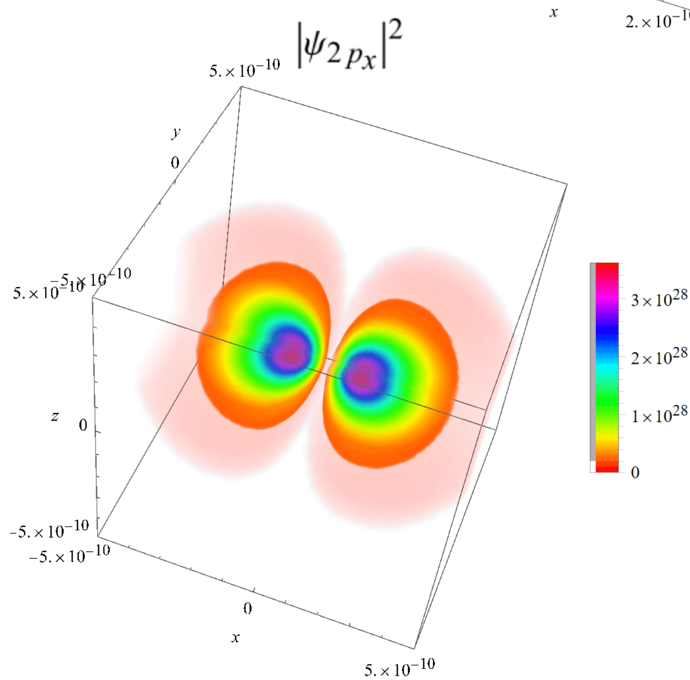
Consequently, ψ_{2p_z} is an eigenfunction of L_z with eigenvalue 0.

Part (c)

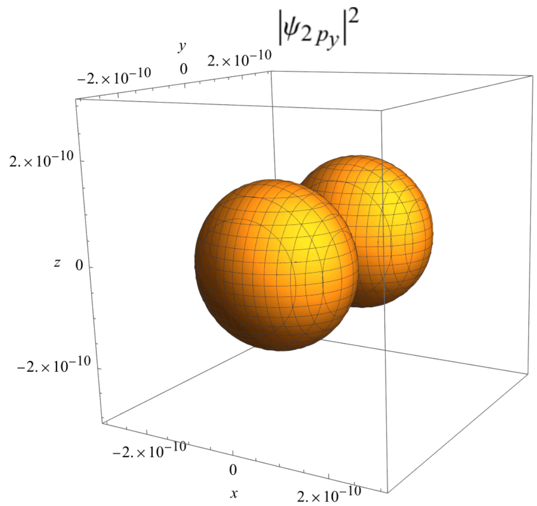
Below are contour and density plots of $|\psi_{2p_x}|^2$. Note that $a = a_0 \approx 5.29 \times 10^{-11}$ m is the Bohr radius.

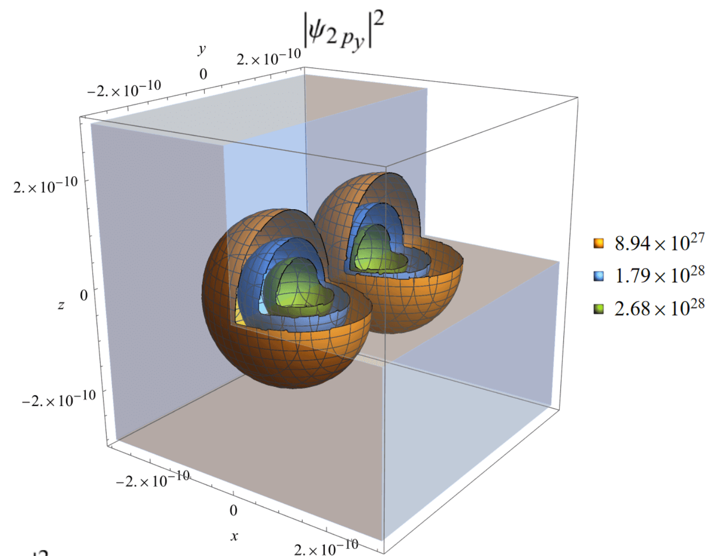


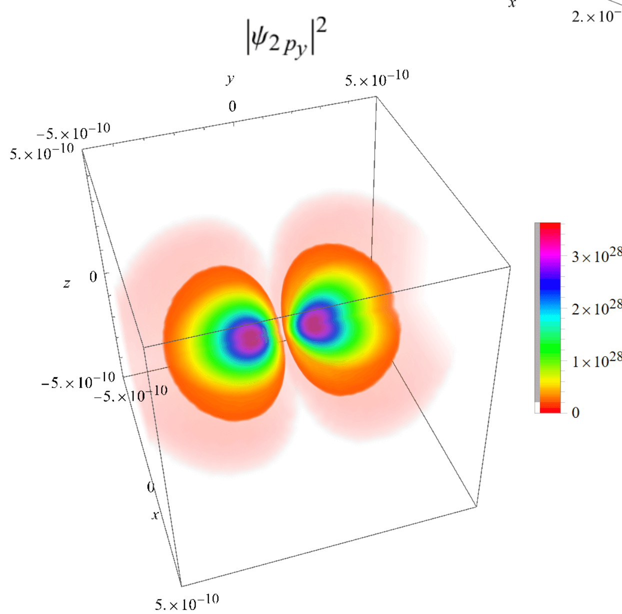




Below are contour and density plots of $|\psi_{2p_y}|^2$. Note that $a = a_0 \approx 5.29 \times 10^{-11}$ m is the Bohr radius.







Below are contour and density plots of $|\psi_{2p_z}|^2$. Note that $a = a_0 \approx 5.29 \times 10^{-11}$ m is the Bohr radius.