Problem 4.49

Warning: Attempt this problem only if you are familiar with vector calculus. Define the (three-dimensional) **probability current** by generalization of Problem 1.14:

$$\mathbf{J} \equiv \frac{i\hbar}{2m}(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi). \tag{4.220}$$

(a) Show that **J** satisfies the **continuity equation**

$$\nabla \cdot \mathbf{J} = -\frac{\partial}{\partial t}|\Psi|^2, \tag{4.221}$$

which expresses local **conservation of probability**. It follows (from the divergence theorem) that

$$\oint_S \mathbf{J} \cdot d\mathbf{a} = -\frac{d}{dt}\int_{\mathcal{V}} |\Psi|^2 \, d^3\mathbf{r}, \tag{4.222}$$

where $\mathcal{V}$ is a (fixed) volume and $\mathcal{S}$ is its boundary surface. In words: The flow of probability out through the surface is equal to the decrease in probability of finding the particle in the volume.

(b) Find **J** for hydrogen in the state $n = 2$, $l = 1$, $m = 1$. *Answer:*

$$\frac{\hbar}{64\pi m a^5} r e^{-r/a} \sin\theta \, \hat{\phi}$$

(c) If we interpret $m\mathbf{J}$ as the flow of *mass*, the angular momentum is

$$\mathbf{L} = m \int (\mathbf{r} \times \mathbf{J}) \, d^3\mathbf{r}.$$

Use this to calculate L_z for the state ψ_{211}, and comment on the result.[71]

[TYPO: Replace $l = 1$ with $\ell = 1$, and either replace $d\mathbf{a}$ with $d^2\mathbf{r}$ or replace $d^3\mathbf{r}$ with dv to be consistent. Also, keep in mind that m sloppily represents the mass and an index.]

Solution

Part (a)

Solve Schrödinger's equation in three dimensions for $\nabla^2\Psi$.

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2M}\nabla^2\Psi + V\Psi \qquad \rightarrow \qquad \nabla^2\Psi = \frac{2M}{\hbar^2}\left(V\Psi - i\hbar\frac{\partial\Psi}{\partial t}\right)$$

Take the complex conjugate of both sides.

$$-i\hbar\frac{\partial\Psi^*}{\partial t} = -\frac{\hbar^2}{2M}\nabla^2\Psi^* + V\Psi^* \qquad \rightarrow \qquad \nabla^2\Psi^* = \frac{2M}{\hbar^2}\left(V\Psi^* + i\hbar\frac{\partial\Psi^*}{\partial t}\right)$$

[71] Schrödinger (*Annalen der Physik* **81**, 109 (1926), Section 7) interpreted $e\mathbf{J}$ as the electric current density (this was *before* Born published his statistical interpretation of the wave function), and noted that it is time-independent (in a stationary state): "we may in a certain sense speak of a *return to electrostatic and magnetostatic atomic models*. In this way the lack of radiation in [a stationary] state would, indeed, find a startingly simple explanation." (I thank Kirk McDonald for calling this reference to my attention.)

Now consider the divergence of the probability current.

$$
\begin{aligned}
\nabla \cdot \mathbf{J} &= \nabla \cdot \left[\frac{i\hbar}{2M}(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi)\right] \\
&= \left(\sum_{j=1}^{3} \boldsymbol{\delta}_j \frac{\partial}{\partial x_j}\right) \cdot \left\{\frac{i\hbar}{2M}\left[\Psi\left(\sum_{k=1}^{3} \boldsymbol{\delta}_k \frac{\partial \Psi^*}{\partial x_k}\right) - \Psi^*\left(\sum_{l=1}^{3} \boldsymbol{\delta}_l \frac{\partial \Psi}{\partial x_l}\right)\right]\right\} \\
&= \left(\sum_{j=1}^{3} \boldsymbol{\delta}_j \frac{\partial}{\partial x_j}\right) \cdot \left[\frac{i\hbar}{2M}\left(\Psi\sum_{k=1}^{3} \boldsymbol{\delta}_k \frac{\partial \Psi^*}{\partial x_k} - \Psi^*\sum_{l=1}^{3} \boldsymbol{\delta}_l \frac{\partial \Psi}{\partial x_l}\right)\right] \\
&= \frac{i\hbar}{2M}\sum_{j=1}^{3} \boldsymbol{\delta}_j \cdot \left[\frac{\partial}{\partial x_j}\left(\Psi\sum_{k=1}^{3} \boldsymbol{\delta}_k \frac{\partial \Psi^*}{\partial x_k} - \Psi^*\sum_{l=1}^{3} \boldsymbol{\delta}_l \frac{\partial \Psi}{\partial x_l}\right)\right] \\
&= \frac{i\hbar}{2M}\sum_{j=1}^{3} \boldsymbol{\delta}_j \cdot \left(\frac{\partial \Psi}{\partial x_j}\sum_{k=1}^{3} \boldsymbol{\delta}_k \frac{\partial \Psi^*}{\partial x_k} + \Psi\sum_{k=1}^{3} \boldsymbol{\delta}_k \frac{\partial^2 \Psi^*}{\partial x_j \partial x_k} - \frac{\partial \Psi^*}{\partial x_j}\sum_{l=1}^{3} \boldsymbol{\delta}_l \frac{\partial \Psi}{\partial x_l} - \Psi^*\sum_{l=1}^{3} \boldsymbol{\delta}_l \frac{\partial^2 \Psi}{\partial x_j \partial x_l}\right) \\
&= \frac{i\hbar}{2M}\sum_{j=1}^{3} \left[\frac{\partial \Psi}{\partial x_j}\sum_{k=1}^{3} (\boldsymbol{\delta}_j \cdot \boldsymbol{\delta}_k)\frac{\partial \Psi^*}{\partial x_k} + \Psi\sum_{k=1}^{3} (\boldsymbol{\delta}_j \cdot \boldsymbol{\delta}_k)\frac{\partial^2 \Psi^*}{\partial x_j \partial x_k} - \frac{\partial \Psi^*}{\partial x_j}\sum_{l=1}^{3} (\boldsymbol{\delta}_j \cdot \boldsymbol{\delta}_l)\frac{\partial \Psi}{\partial x_l} - \Psi^*\sum_{l=1}^{3} (\boldsymbol{\delta}_j \cdot \boldsymbol{\delta}_l)\frac{\partial^2 \Psi}{\partial x_j \partial x_l}\right] \\
&= \frac{i\hbar}{2M}\sum_{j=1}^{3} \left(\frac{\partial \Psi}{\partial x_j}\sum_{k=1}^{3} \delta_{jk}\frac{\partial \Psi^*}{\partial x_k} + \Psi\sum_{k=1}^{3} \delta_{jk}\frac{\partial^2 \Psi^*}{\partial x_j \partial x_k} - \frac{\partial \Psi^*}{\partial x_j}\sum_{l=1}^{3} \delta_{jl}\frac{\partial \Psi}{\partial x_l} - \Psi^*\sum_{l=1}^{3} \delta_{jl}\frac{\partial^2 \Psi}{\partial x_j \partial x_l}\right) \\
&= \frac{i\hbar}{2M}\sum_{j=1}^{3} \left(\frac{\partial \Psi}{\partial x_j}\frac{\partial \Psi^*}{\partial x_j} + \Psi\frac{\partial^2 \Psi^*}{\partial x_j \partial x_j} - \frac{\partial \Psi^*}{\partial x_j}\frac{\partial \Psi}{\partial x_j} - \Psi^*\frac{\partial^2 \Psi}{\partial x_j \partial x_j}\right) \\
&= \frac{i\hbar}{2M}\sum_{j=1}^{3} \left(\Psi\frac{\partial^2 \Psi^*}{\partial x_j^2} - \Psi^*\frac{\partial^2 \Psi}{\partial x_j^2}\right) \\
&= \frac{i\hbar}{2M}\left[\Psi\left(\sum_{j=1}^{3} \frac{\partial^2 \Psi^*}{\partial x_j^2}\right) - \Psi^*\left(\sum_{j=1}^{3} \frac{\partial^2 \Psi}{\partial x_j^2}\right)\right] \\
&= \frac{i\hbar}{2M}(\Psi\nabla^2\Psi^* - \Psi^*\nabla^2\Psi) \\
&= \frac{i\hbar}{2M}\left\{\Psi\left[\frac{2M}{\hbar^2}\left(V\Psi^* + i\hbar\frac{\partial \Psi^*}{\partial t}\right)\right] - \Psi^*\left[\frac{2M}{\hbar^2}\left(V\Psi - i\hbar\frac{\partial \Psi}{\partial t}\right)\right]\right\} \\
&= \frac{i}{\hbar}V\Psi\Psi^* - \Psi\frac{\partial \Psi^*}{\partial t} - \frac{i}{\hbar}V\Psi\Psi^* - \Psi^*\frac{\partial \Psi}{\partial t} \\
&= -\Psi\frac{\partial \Psi^*}{\partial t} - \Psi^*\frac{\partial \Psi}{\partial t} \\
&= -\frac{\partial}{\partial t}(\Psi\Psi^*)
\end{aligned}
$$

Therefore, $\mathbf{J}$ satisfies the continuity equation.

$$\nabla \cdot \mathbf{J} = -\frac{\partial}{\partial t}|\Psi|^2$$

Integrate both sides over a fixed volume $\mathcal{V}$.

$$\iiint_{\mathcal{V}} \nabla \cdot \mathbf{J}\, dv = \iiint_{\mathcal{V}} -\frac{\partial}{\partial t}|\Psi|^2\, dv$$

Apply the divergence theorem on the left to turn this volume integral into a surface integral over the boundary of $\mathcal{V}$. The volume integral wipes out the position variables, so the time derivative is a total derivative in front of the integral.

$$\oiint_{\mathcal{S}} \mathbf{J} \cdot d\mathbf{a} = -\frac{d}{dt}\iiint_{\mathcal{V}} |\Psi|^2\, dv$$

Part (b)

Use the result from part (b) of Exercise 4.13 to get the wave function for hydrogen in the state with $n = 2$, $\ell = 1$, and $m = 1$.

$$\begin{aligned}
\Psi_{211}(r,\theta,\phi,t) &= \psi_{211}(r,\theta,\phi)e^{-iE_2t/\hbar} \\
&= \left(-\sqrt{\frac{1}{64\pi a^5}}\, re^{-r/2a}\sin\theta\, e^{i\phi}\right) e^{-iE_2t/\hbar} \\
&= -\sqrt{\frac{1}{64\pi a^5}}\, re^{-r/2a}\sin\theta\, e^{i\phi}e^{-iE_2t/\hbar}
\end{aligned}$$

Take the complex conjugate.

$$\Psi^*_{211}(r,\theta,\phi,t) = -\sqrt{\frac{1}{64\pi a^5}}\, re^{-r/2a}\sin\theta\, e^{-i\phi}e^{iE_2t/\hbar}$$

The probability current for this state is then

$$\begin{aligned}
\mathbf{J}_{211} &= \frac{i\hbar}{2M}(\Psi_{211}\nabla\Psi^*_{211} - \Psi^*_{211}\nabla\Psi_{211}) \\
&= \frac{i\hbar}{2M}\left[\Psi_{211}\left(\frac{\partial\Psi^*_{211}}{\partial r}\hat{\mathbf{r}} + \frac{1}{r}\frac{\partial\Psi^*_{211}}{\partial\theta}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\frac{\partial\Psi^*_{211}}{\partial\phi}\hat{\boldsymbol{\phi}}\right) - \Psi^*_{211}\left(\frac{\partial\Psi_{211}}{\partial r}\hat{\mathbf{r}} + \frac{1}{r}\frac{\partial\Psi_{211}}{\partial\theta}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\frac{\partial\Psi_{211}}{\partial\phi}\hat{\boldsymbol{\phi}}\right)\right] \\
&= \frac{i\hbar}{2M}\left[\left(\Psi_{211}\frac{\partial\Psi^*_{211}}{\partial r} - \Psi^*_{211}\frac{\partial\Psi_{211}}{\partial r}\right)\hat{\mathbf{r}}\right. \\
&\qquad + \frac{1}{r}\left(\Psi_{211}\frac{\partial\Psi^*_{211}}{\partial\theta} - \Psi^*_{211}\frac{\partial\Psi_{211}}{\partial\theta}\right)\hat{\boldsymbol{\theta}} \\
&\qquad\left. + \frac{1}{r\sin\theta}\left(\Psi_{211}\frac{\partial\Psi^*_{211}}{\partial\phi} - \Psi^*_{211}\frac{\partial\Psi_{211}}{\partial\phi}\right)\hat{\boldsymbol{\phi}}\right].
\end{aligned}$$

Plug in the formulas for Ψ_{211} and its conjugate.

$$\begin{aligned}
\mathbf{J}_{211} &= \frac{i\hbar}{2M}\frac{1}{64\pi a^5}\left\{\left[\left(re^{-r/2a}\sin\theta\, e^{i\phi}e^{-iE_2t/\hbar}\right)\frac{\partial}{\partial r}\left(re^{-r/2a}\sin\theta\, e^{-i\phi}e^{iE_2t/\hbar}\right) - \left(re^{-r/2a}\sin\theta\, e^{-i\phi}e^{iE_2t/\hbar}\right)\frac{\partial}{\partial r}\left(re^{-r/2a}\sin\theta\, e^{i\phi}e^{-iE_2t/\hbar}\right)\right]\hat{\mathbf{r}}\right. \\
&\qquad + \frac{1}{r}\left[\left(re^{-r/2a}\sin\theta\, e^{i\phi}e^{-iE_2t/\hbar}\right)\frac{\partial}{\partial \theta}\left(re^{-r/2a}\sin\theta\, e^{-i\phi}e^{iE_2t/\hbar}\right) - \left(re^{-r/2a}\sin\theta\, e^{-i\phi}e^{iE_2t/\hbar}\right)\frac{\partial}{\partial \theta}\left(re^{-r/2a}\sin\theta\, e^{i\phi}e^{-iE_2t/\hbar}\right)\right]\hat{\boldsymbol{\theta}} \\
&\qquad \left. + \frac{1}{r\sin\theta}\left[\left(re^{-r/2a}\sin\theta\, e^{i\phi}e^{-iE_2t/\hbar}\right)\frac{\partial}{\partial \phi}\left(re^{-r/2a}\sin\theta\, e^{-i\phi}e^{iE_2t/\hbar}\right) - \left(re^{-r/2a}\sin\theta\, e^{-i\phi}e^{iE_2t/\hbar}\right)\frac{\partial}{\partial \phi}\left(re^{-r/2a}\sin\theta\, e^{i\phi}e^{-iE_2t/\hbar}\right)\right]\hat{\boldsymbol{\phi}}\right\} \\
&= \frac{i\hbar}{2M}\frac{1}{64\pi a^5}\left\{\left[\left(re^{-r/2a}\sin^2\theta\right)\frac{d}{dr}\left(re^{-r/2a}\right) - \left(re^{-r/2a}\sin^2\theta\right)\frac{d}{dr}\left(re^{-r/2a}\right)\right]\hat{\mathbf{r}}\right. \\
&\qquad + \frac{1}{r}\left[\left(r^2e^{-r/a}\sin\theta\right)\frac{d}{d\theta}(\sin\theta) - \left(r^2e^{-r/a}\sin\theta\right)\frac{d}{d\theta}(\sin\theta)\right]\hat{\boldsymbol{\theta}} \\
&\qquad \left. + \frac{1}{r\sin\theta}\left[\left(r^2e^{-r/a}\sin^2\theta\, e^{i\phi}\right)\frac{d}{d\phi}(e^{-i\phi}) - \left(r^2e^{-r/a}\sin^2\theta\, e^{-i\phi}\right)\frac{d}{d\phi}(e^{i\phi})\right]\hat{\boldsymbol{\phi}}\right\} \\
&= \frac{i\hbar}{2M}\frac{1}{64\pi a^5}\left\{(0)\hat{\mathbf{r}} + \frac{1}{r}(0)\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\left[\left(r^2e^{-r/a}\sin^2\theta\, e^{i\phi}\right)(-ie^{-i\phi}) - \left(r^2e^{-r/a}\sin^2\theta\, e^{-i\phi}\right)(ie^{i\phi})\right]\hat{\boldsymbol{\phi}}\right\} \\
&= \frac{i\hbar}{2M}\frac{1}{64\pi a^5}\left[\frac{1}{r\sin\theta}\left(-2ir^2e^{-r/a}\sin^2\theta\right)\right]\hat{\boldsymbol{\phi}} \\
&= \frac{\hbar}{64\pi M a^5} re^{-r/a}\sin\theta\,\hat{\boldsymbol{\phi}}
\end{aligned}$$

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Part (c)

Use the result of part (b) to calculate the angular momentum for hydrogen in the state with $n = 2$, $\ell = 1$, and $m = 1$.

$$\begin{aligned}
\mathbf{L}_{211} &= \iiint\limits_{\text{all space}} \mathbf{r} \times (M\mathbf{J}_{211})\, dv \\
&= M \iiint\limits_{\text{all space}} \mathbf{r} \times \mathbf{J}_{211}\, dv \\
&= M \int_0^\pi \int_0^{2\pi} \int_0^\infty (r\hat{\mathbf{r}}) \times \left(\frac{\hbar}{64\pi M a^5} r e^{-r/a} \sin\theta\, \hat{\boldsymbol{\phi}} \right) r^2 \sin\theta\, dr\, d\phi\, d\theta \\
&= \frac{\hbar}{64\pi a^5} \int_0^\pi \int_0^{2\pi} \int_0^\infty r^4 e^{-r/a} \sin^2\theta\, (\hat{\mathbf{r}} \times \hat{\boldsymbol{\phi}})\, dr\, d\phi\, d\theta \\
&= \frac{\hbar}{64\pi a^5} \int_0^\pi \int_0^{2\pi} \int_0^\infty r^4 e^{-r/a} \sin^2\theta\, (-\hat{\boldsymbol{\theta}})\, dr\, d\phi\, d\theta \\
&= -\frac{\hbar}{64\pi a^5} \int_0^\pi \int_0^{2\pi} \int_0^\infty r^4 e^{-r/a} \sin^2\theta\, (\hat{\boldsymbol{\theta}})\, dr\, d\phi\, d\theta \\
&= -\frac{\hbar}{64\pi a^5} \int_0^\pi \int_0^{2\pi} \int_0^\infty r^4 e^{-r/a} \sin^2\theta\, [(\cos\theta\cos\phi)\hat{\mathbf{x}} + (\cos\theta\sin\phi)\hat{\mathbf{y}} + (-\sin\theta)\hat{\mathbf{z}}]\, dr\, d\phi\, d\theta \\
&= -\frac{\hbar}{64\pi a^5} \left(\hat{\mathbf{x}} \int_0^\pi \int_0^{2\pi} \int_0^\infty r^4 e^{-r/a} \sin^2\theta \cos\theta \cos\phi\, dr\, d\phi\, d\theta \right. \\
&\qquad + \hat{\mathbf{y}} \int_0^\pi \int_0^{2\pi} \int_0^\infty r^4 e^{-r/a} \sin^2\theta \cos\theta \sin\phi\, dr\, d\phi\, d\theta \\
&\qquad \left. - \hat{\mathbf{z}} \int_0^\pi \int_0^{2\pi} \int_0^\infty r^4 e^{-r/a} \sin^3\theta\, dr\, d\phi\, d\theta \right) \\
&= -\frac{\hbar}{64\pi a^5} \left[\hat{\mathbf{x}} \left(\int_0^\pi \sin^2\theta \cos\theta\, d\theta \right) \left(\int_0^{2\pi} \cos\phi\, d\phi \right) \left(\int_0^\infty r^4 e^{-r/a}\, dr \right) \right. \\
&\qquad + \hat{\mathbf{y}} \left(\int_0^\pi \sin^2\theta \cos\theta\, d\theta \right) \left(\int_0^{2\pi} \sin\phi\, d\phi \right) \left(\int_0^\infty r^4 e^{-r/a}\, dr \right) \\
&\qquad \left. - \hat{\mathbf{z}} \left(\int_0^\pi \sin^3\theta\, d\theta \right) \left(\int_0^{2\pi} d\phi \right) \left(\int_0^\infty r^4 e^{-r/a}\, dr \right) \right] \\
&= -\frac{\hbar}{64\pi a^5} \left\{ \hat{\mathbf{x}} \left(\int_0^\pi \sin^2\theta \cos\theta\, d\theta \right) (0) \left(\int_0^\infty r^4 e^{-r/a}\, dr \right) \right. \\
&\qquad + \hat{\mathbf{y}} \left(\int_0^\pi \sin^2\theta \cos\theta\, d\theta \right) (0) \left(\int_0^\infty r^4 e^{-r/a}\, dr \right) \\
&\qquad \left. - \hat{\mathbf{z}} \left[\int_0^\pi (1 - \cos^2\theta) \sin\theta\, d\theta \right] (2\pi) \left[\int_0^\infty \frac{\partial^4}{\partial w^4} (e^{-wr}) \bigg|_{w=1/a} dr \right] \right\}
\end{aligned}$$

Continue the simplification by substituting $u = \cos\theta$ and $du = -\sin\theta\, d\theta$.

$$\begin{aligned}
\mathbf{L}_{211} &= -\frac{\hbar}{64\pi a^5}\left\{-\hat{\mathbf{z}}\left[\int_{\cos 0}^{\cos\pi}(1-u^2)(-du)\right](2\pi)\left[\frac{d^4}{dw^4}\left(\int_0^\infty e^{-wr}\,dr\right)\bigg|_{w=1/a}\right]\right\} \\
&= \frac{\hbar}{32a^5}\hat{\mathbf{z}}\left[\int_1^{-1}(1-u^2)(-du)\right]\left[\frac{d^4}{dw^4}\left(\frac{1}{w}\right)\bigg|_{w=1/a}\right] \\
&= \frac{\hbar}{32a^5}\hat{\mathbf{z}}\left[\int_{-1}^{1}(1-u^2)\,du\right]\left[\frac{(-1)^4(4!)}{w^{1+4}}\bigg|_{w=1/a}\right] \\
&= \frac{\hbar}{32a^5}\hat{\mathbf{z}}\left[2\int_0^1(1-u^2)\,du\right]\left(\frac{24}{w^5}\bigg|_{w=1/a}\right) \\
&= \frac{\hbar}{32a^5}\hat{\mathbf{z}}\left(\frac{4}{3}\right)(24a^5) \\
&= \hbar\hat{\mathbf{z}}
\end{aligned}$$

Take the dot product of the angular momentum with $\hat{\mathbf{z}}$ to get the component along the z-axis.

$$\begin{aligned}
L_{211,z} &= \hat{\mathbf{z}}\cdot\mathbf{L}_{211} \\
&= \hbar
\end{aligned}$$

This is consistent with the eigenvalue problem for L_z in Equation 4.133 on page 164 because $m = 1$.

$$L_z\psi = \hbar m\psi \tag{4.133}$$