Appendix S4
Solutions to Chapter 4 exercises

Solution to Exercise 4.1

a) Taking the inner product of the right hand side of Eq. (4.4) with an arbitrary position eigenstate $|\vec{r}^\prime\rangle$, we have

$$\langle \vec{r}^\prime \mid \int \int \int \psi(\vec{r}) |\vec{r}\rangle \, dx\, dy\, dz \rangle = \left( \langle x' \mid \int \int \psi(x, y, z) |x\rangle \otimes |y\rangle \otimes |z\rangle \, dx\, dy\, dz \right)$$

$$= \int \int \int \psi(x, y, z) \langle x' \mid x \rangle \langle y' \mid y \rangle \langle z' \mid z \rangle \, dx\, dy\, dz$$

$$= \int \int \int \psi(x, y, z) \delta(x - x') \delta(y - y') \delta(z - z') \, dx\, dy\, dz$$

$$= \psi(x', y', z'),$$

so Eq. (4.3) holds.

b) Substituting Eq. (4.4) for $|\psi\rangle$ and its analogue for $|\phi\rangle$ into $\langle \psi \mid \phi \rangle$, we find

$$\langle \psi \mid \phi \rangle = \int \int \int \int \int \psi^*(x', y', z') \phi(x, y, z) \langle x' \mid x \rangle \langle y' \mid y \rangle \langle z' \mid z \rangle \, dx\, dy\, dz\, dx'\, dy'\, dz'$$

$$= \int \int \int \int \int \psi^*(x', y', z') \phi(x, y, z) \delta(x - x') \delta(y - y') \delta(z - z') \, dx\, dy\, dz\, dx'\, dy'\, dz'$$

$$= \int \int \int \psi^*(x, y, z) \phi(x, y, z) \, dx\, dy\, dz.$$
Solution to Exercise 4.3. The statement of the Exercise follows from Ex. 2.25 and the definition of the momentum vector eigenstate as \( |\vec{p}\rangle = |\hat{p}_x\rangle \otimes |\hat{p}_y\rangle \otimes |\hat{p}_z\rangle \). However, we can also prove it explicitly by writing, in analogy to Eq. 4.2,

\[
\hat{p}_x^2 |\vec{p}\rangle = p_x^2 |\vec{p}\rangle; \\
\hat{p}_y^2 |\vec{p}\rangle = p_y^2 |\vec{p}\rangle; \\
\hat{p}_z^2 |\vec{p}\rangle = p_z^2 |\vec{p}\rangle. 
\]

Hence \( (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) |\vec{p}\rangle = (p_x^2 + p_y^2 + p_z^2) |\vec{p}\rangle \).

Solution to Exercise 4.4. The potential is separable:

\[
V(\vec{r}) = \frac{M \omega^2 r^2}{2} = \frac{M \omega^2 x^2}{2} + \frac{M \omega^2 y^2}{2} + \frac{M \omega^2 z^2}{2},
\]

so the condition of Ex. 2.25 holds. Hence the energy eigenstate basis for the three-dimensional harmonic oscillator consists of states \( |n_x, n_y, n_z\rangle \), where \( |n_x, n_y, n_z\rangle \) are the number states of the harmonic oscillators associated with the individual axes. The energy of the state \( |n_x, n_y, n_z\rangle \) is, according to Ex. 2.25

\[
E_{n_x, n_y, n_z} = \hbar \omega \left[ \left( n_x + \frac{1}{2} \right) + \left( n_y + \frac{1}{2} \right) + \left( n_z + \frac{1}{2} \right) \right] = \hbar \omega \left[ n_x + n_y + n_z + \frac{3}{2} \right].
\]

Possible energy eigenvalues are therefore \( \hbar \omega [n + \frac{3}{2}] \), where \( n \) is any nonnegative integer. These eigenvalues are degenerate for \( n \geq 1 \). For example, for \( n = 1 \), the degeneracy is triple: states \( |1,0,0\rangle, |0,1,0\rangle, |0,0,1\rangle \) have the same energy \( \frac{3}{2} \hbar \omega \).

The degeneracy of an energy level with a given \( n \) is the total number of combinations \( (n_x, n_y, n_z) \) such that \( n = n_x + n_y + n_z \). Let us find this number. The value of \( n_x \) can be any integer from 0 to \( n \). For a given \( n_x \), the value of \( n_y \) can then be any integer from 0 to \( n - n_x \) (a total of \( n + 1 - n_x \) options). Finally, once both \( n_x \) and \( n_y \) are chosen, there is only one value that \( n_z \) can take, \( n_z = n - n_x - n_y \). Accordingly, the degeneracy is

\[
\sum_{n_x=0}^{n} (n + 1 - n_x) = (n + 1)^2 - \frac{n(n + 1)}{2} = \frac{(n + 1)(n + 2)}{2}.
\]

Solution to Exercise 4.5

a) The statement is quite obvious in view of Eq. (3.44), but if we try to prove it rigorously, the derivation will be quite lengthy. First, let us assume \( |\psi\rangle \) to be a separable state: \( |\psi\rangle = |\psi_x\rangle \otimes |\psi_y\rangle \otimes |\psi_z\rangle \). Then, specializing to the \( x \) component of the momentum, and using Eqs. (2.4) as well as (2.7), we have

\[
\langle \vec{p} | \vec{p} \rangle = \langle x | p_x \rangle \langle y | p_y \rangle \langle z | p_z \rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}(x p_x + y p_y + z p_z)} = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}\vec{p} \cdot \vec{p}}.
\]
\[ \langle \vec{r} | \hat{p}_x | \psi \rangle = \langle x | \hat{p}_x | \psi \rangle \langle y | \psi \rangle \langle z | \psi \rangle = -i\hbar \frac{\partial}{\partial x} \langle x | \psi \rangle \langle y | \psi \rangle \langle z | \psi \rangle \]

If state \(|\psi\rangle\) is not separable, we recall that any element of the tensor product space can be written as a linear combination \(|\psi\rangle = \sum_i |\psi_i\rangle\), where each \(|\psi_i\rangle\) is a separable state. The linearity of the momentum operator and the inner product lets us write
\[
\langle \vec{r} | \hat{p}_x | \psi \rangle = -i\hbar \frac{\partial}{\partial x} \psi(\vec{r}).
\]

**b)** Using the result of part (a), we have
\[
\langle \vec{r} | \hat{\vec{p}} | \psi \rangle = \left( \langle \vec{r} | \hat{p}_x | \psi \rangle , \langle \vec{r} | \hat{p}_y | \psi \rangle , \langle \vec{r} | \hat{p}_z | \psi \rangle \right) = -i\hbar \left( \frac{\partial}{\partial x} \psi(\vec{r}), \frac{\partial}{\partial y} \psi(\vec{r}), \frac{\partial}{\partial z} \psi(\vec{r}) \right),
\]
which can be abbreviated as \(-i\hbar \vec{\nabla} \psi(\vec{r})\).

**c)** The Hamiltonian is the sum of kinetic and potential energies:
\[
\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2M} + V(\hat{r}).
\]

Using the result of Ex. 3.22, we find, by analogy with part (a), that in the position basis
\[
\langle \vec{r} | \hat{p}_x^2 | \psi \rangle = -\hbar^2 \frac{\partial^2}{\partial \vec{r}_i^2} \psi(\vec{r}).
\]

Writing the time-independent Schrödinger equation \(\hat{H} |\psi\rangle = E |\psi\rangle\) in the position basis and substituting the above result, we obtain Eq. (4.9).

**Solution to Exercise 4.6.** Using the relation (3.11a) between the Cartesian and spherical coordinates, we find
\[ J = \begin{vmatrix}
\frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\
\frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\
\frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi}
\end{vmatrix}
\]
\[ = \begin{vmatrix}
\sin \theta \cos \phi & r \cos \theta \cos \phi & -r \sin \theta \sin \phi \\
\sin \theta \sin \phi & r \cos \theta \sin \phi & r \sin \theta \cos \phi \\
\cos \theta & -r \sin \theta & 0
\end{vmatrix}
\]
\[ = r^2 \cos^2 \theta \sin^2 \phi + r^2 \sin^3 \theta \sin^2 \phi + r^2 \cos^2 \theta \sin \theta \sin^2 \phi + r^2 \sin^3 \theta \cos^2 \phi
\]
\[ = r^2 \sin \theta \cos \theta + r^2 \sin^3 \theta
\]
\[ = r^2 \sin \theta.
\]

**Solution to Exercise 4.7**

b) We need to prove that, for any two pairs of states \(|R_{1,2}\rangle\) and \(|Y_{1,2}\rangle\) in \(\mathbb{V}_r\) and \(\mathbb{V}_y\), respectively, the inner product of states \(|R_1\rangle \otimes |Y_1\rangle\) and \(|R_2\rangle \otimes |Y_2\rangle\) equals the algebraic product of inner products \(\langle R_1 | R_2 \rangle\) and \(\langle Y_1 | Y_2 \rangle\) given by Eqs. 4.15. Because the wavefunctions of states \(|R_{1,2}\rangle \otimes |Y_{1,2}\rangle\) are given by products \(R_{1,2}(r)Y_{1,2}(\theta, \phi)\), we use Eq. 4.13 to write
\[\langle R_1 | \otimes | Y_1 \rangle | (R_2 | \otimes | Y_2 \rangle) = \int_0^{2\pi} \int_0^\pi \int_0^\infty R_1^* (r) Y_1^* (\theta, \phi) R_2 (r) Y_2 (\theta, \phi) r^2 \sin \theta dr d\theta d\phi.
\]
This expression is the same as the product of the right-hand sides of the two equations 4.15.

**Solution to Exercise 4.8**

For example, the \(x\) component of the angular momentum is defined as \(\hat{L}_x = \hat{y} \hat{p}_z - \hat{z} \hat{p}_y\). The position and momentum observables are Hermitian; in addition, we have \([\hat{y}, \hat{p}_z] = [\hat{z}, \hat{p}_y] = 0\) because the operators associated with the \(x\) and \(y\) dimensions live in different Hilbert spaces. We can thus write for the Hermitian conjugate of \(\hat{L}_x\)
\[\hat{L}_x^\dagger \overset{\text{Def. 4.8}}{=} \hat{y} \hat{p}_z^\dagger - \hat{z} \hat{p}_y^\dagger = \hat{y} \hat{p}_z - \hat{z} \hat{p}_y = \hat{L}_x.
\]

**Solution to Exercise 4.10**

Both the left- and right-hand sides of Eq. 4.21 depend on four indices \(k, l, m, n\). In addition, the left-hand side contains a dummy (summation) index \(j\). Looking at the left-hand side, we notice that in order for both \(\epsilon_{jkl}\) and \(\epsilon_{jmn}\) to be nonzero at the same time, we must have \(k \neq l\) and \(m \neq n\) and that sets \(\{k, l\}\) and \(\{m, n\}\) must contain the same elements — that is, either \(\{k, l\} = \{m, n\}\) or \(\{k, l\} = \{n, m\}\). For example, if \(m = 2\) and \(n = 3\), nonvanishing \(\epsilon\’s\) must have \(j = 1\) and hence either \(\{k, l\} = \{2, 3\}\) or \(\{k, l\} = \{3, 2\}\). This is what gives rise to the Kronecker symbols in the right-hand side. If \(\{k, l\} = \{m, n\}\) then \(\epsilon_{jkl} = \epsilon_{jmn}\), so \(\delta_{kn}\delta_{lm}\) comes with a positive sign. On the other hand, if \(\{k, l\} = \{n, m\}\) then \(\epsilon_{jkl} = -\epsilon_{jmn}\), so \(\delta_{kn}\delta_{lm}\) has a negative sign.

**Solution to Exercise 4.11**

a) We use \(\hat{L}_j = \epsilon_{jmn} \hat{r}_m \hat{p}_n\) and \([\hat{r}_j, \hat{p}_k] = i\hbar \delta_{jk}\) to write
\[ [\hat{L}_j, \hat{p}_k] = [\varepsilon_{jln}\hat{p}_l\hat{p}_n, \hat{p}_k] \]
\[ = \varepsilon_{jln}\hat{p}_l[\hat{p}_n, \hat{p}_k] \quad (\varepsilon_{jln} \text{ and } \hat{p}_l \text{ commute with } \hat{p}_k, \text{ so we factor them out}) \]
\[ = \varepsilon_{jln}\hat{p}_l(-i\hbar)\delta_{nk} \]
\[ = (-i\hbar)\varepsilon_{jlk}\hat{p}_l \]
\[ = i\hbar\varepsilon_{jkl}\hat{p}_l. \quad (\varepsilon_{jkl} \text{ is an antisymmetric tensor, so } \varepsilon_{jkl} = -\varepsilon_{jlk}) \]

b) Similarly,
\[ [\hat{L}_j, \hat{p}_k] = [\varepsilon_{jml}\hat{r}_m\hat{p}_l, \hat{p}_k] = \varepsilon_{jml}[\hat{r}_m, \hat{p}_l]\hat{p}_k = \varepsilon_{jml}(i\hbar)\delta_{mk}\hat{p}_l = i\hbar\varepsilon_{jkl}\hat{p}_l. \]

c) \[
[\hat{L}_j, \hat{L}_k] = [\varepsilon_{jmn}\hat{r}_m\hat{p}_n, \varepsilon_{klq}\hat{r}_k\hat{p}_q] \\
= \varepsilon_{jmn}\varepsilon_{klq}(\hat{r}_m[\hat{p}_n, \hat{r}_k]\hat{p}_q + \hat{r}_m[\hat{p}_n, \hat{p}_q]\hat{r}_k) \\
= \varepsilon_{jmn}\varepsilon_{klq}\left((-i\hbar)\delta_{nl}\hat{r}_m\hat{p}_q + (i\hbar)\delta_{mq}\hat{r}_l\hat{p}_n\right) \\
= -i\hbar\varepsilon_{jml}\varepsilon_{klq}\hat{r}_m\hat{p}_q + i\hbar\varepsilon_{jmn}\varepsilon_{klq}\hat{r}_l\hat{p}_n \\
= -i\hbar\varepsilon_{jml}\varepsilon_{klq}\hat{r}_m\hat{p}_q + i\hbar\varepsilon_{jmn}\varepsilon_{klq}\hat{r}_l\hat{p}_n \\
= -i\hbar\varepsilon_{jml}\varepsilon_{klq}(\delta_{jq}\delta_{mk} - \delta_{jk}\delta_{mq})\hat{r}_m\hat{p}_q + i\hbar(\delta_{mk}\delta_{jl} - \delta_{ml}\delta_{jk})\hat{r}_l\hat{p}_n \\
= -i\hbar\varepsilon_{jml}\varepsilon_{klq}\hat{r}_m\hat{p}_q + i\hbar\varepsilon_{jmn}\varepsilon_{klq}\hat{r}_l\hat{p}_n \\
= -i\hbar\varepsilon_{jml}\varepsilon_{klq}\hat{r}_m\hat{p}_q + i\hbar\varepsilon_{jmn}\varepsilon_{klq}\hat{r}_l\hat{p}_n \\
= i\hbar\delta_{jk}\hat{p}_j + i\hbar\delta_{jl}\hat{p}_j. \]

On the other hand,
\[ i\hbar\varepsilon_{jkl}\hat{L}_l = i\hbar\varepsilon_{jkl}\varepsilon_{lmn}\hat{r}_m\hat{p}_n \]
\[ = i\hbar\varepsilon_{ijk}\varepsilon_{lmn}\hat{r}_m\hat{p}_n \]
\[ = i\hbar(\delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km})\hat{r}_m\hat{p}_n \]
\[ = i\hbar\varepsilon_{jlm}\hat{p}_k - i\hbar\varepsilon_{jlk}\hat{p}_j. \]

Comparing the two expressions above, we obtain the desired result: \([\hat{L}_j, \hat{L}_k] = i\hbar\varepsilon_{jkl}\hat{L}_l.\]

d) Here we use the fact that the square of a vector is its inner product with itself: \(\vec{v}^2 = \hat{r}_m\hat{r}_m.\) Therefore,
\[ [\hat{L}_j, \hat{p}_k] = \hat{p}_k[\hat{L}_j, \hat{p}_k] + [\hat{L}_j, \hat{p}_k]\hat{p}_k \quad \text{(Ex. 4.11)} \]
\[ = 2i\hbar\varepsilon_{jkl}\hat{p}_k\hat{r}_l \]

This expression vanishes because of the following argument. If we exchange the dummy indices \(k\) and \(l\) in it, we obtain
\[ 2i\hbar\varepsilon_{jkl}\hat{p}_k\hat{r}_l = 2i\hbar\varepsilon_{jlk}\hat{p}_l\hat{r}_k = 2i\hbar\varepsilon_{jkl}\hat{p}_k\hat{r}_l. \]

But \(\varepsilon_{jlk} = -\varepsilon_{jkl}.\) Hence the above expression is equal to its opposite, so it must be zero.

e) The argument is analogous to part (d):
\[ [\hat{L}_j, \hat{p}_k\hat{p}_k] = \hat{p}_k[\hat{L}_j, \hat{p}_k] + [\hat{L}_j, \hat{p}_k]\hat{p}_k = 2i\hbar\varepsilon_{jkl}\hat{p}_k\hat{p}_l = 0 \]

f) Again,
\[ [L_j, L_k L_l] = L_k [L_j, L_l] + [L_j, L_k] L_l = 2i\hbar \epsilon_{jkl} L_k L_l = 0 \]

Solution to Exercise 4.12

The definition (4.19) of the angular momentum can be rewritten as

\[ \hat{L}_j = \epsilon_{jkl} \hat{r}_k \hat{p}_l = -\epsilon_{jkl} \hat{r}_k \hat{p}_l = -\epsilon_{jlk} \hat{r}_l \hat{p}_k. \]

We commuted the position and momentum in the last step above because \( \epsilon_{jlk} \) does not vanish only if \( k \neq l \). The position and momentum related to different Hilbert spaces do commute with each other.

The expression \(-\epsilon_{jlk} \hat{r}_l \hat{p}_k\) is identical to that for the \( j \)th component of vector \(-\hat{p} \times \hat{r}\).

Solution to Exercise 4.13

a) For a centrally symmetric potential, we can write Hamiltonian (4.7) as a sum of functions of observables \( \hat{\rho}^2 \) and \( \hat{\rho}^2 \):

\[ \mathcal{H} = \frac{\hat{\rho}^2}{2M} + V(\sqrt{\hat{\rho}^2}). \]

Each component of the angular momentum, as well as its square, commutes with both \( \hat{\rho}^2 \) and \( \hat{\rho}^2 \) as per Ex. 4.11 and hence it must commute with each of the two terms of the Hamiltonian because these are functions of \( \hat{\rho}^2 \) and \( \hat{\rho}^2 \).

b) The Heisenberg equation (3.128) for an angular momentum vector component is

\[ \frac{d}{dt} \hat{L}_i(t) = \frac{i}{\hbar} [\mathcal{H}, \hat{L}_i(t)]. \]

As per part (a), the commutator in the right-hand side vanishes.

Solution to Exercise 4.14

a) We use Eq. (4.21) to write

\[ \hat{L}^2 = \hat{L}_i \hat{L}_j \]

\[ = (\epsilon_{jkl} \hat{r}_k \hat{p}_l)(\epsilon_{jmn} \hat{r}_m \hat{p}_n) \]

\[ = (\delta_{km} \delta_{ln} - \delta_{kn} \delta_{lm})\hat{r}_k \hat{p}_m \hat{p}_n \]

\[ = \hat{r}_k \hat{p}_m \hat{p}_n - \hat{r}_k \hat{p}_m \hat{p}_n \]

\[ = \hat{r}_k (\hat{r}_k \hat{p}_m - i\hbar \delta_{kl}) \hat{p}_n - \hat{r}_k \hat{p}_m (\hat{r}_k \hat{p}_n + i\hbar \delta_{kl}) \]

\[ = \hat{r}_k (\hat{r}_k \hat{p}_m - i\hbar \delta_{kl}) \hat{p}_n - \hat{r}_k \hat{p}_m (\hat{r}_k \hat{p}_n + i\hbar \delta_{kl}) \]

\[ = \hat{r}_k (\hat{r}_k \hat{p}_m - i\hbar \delta_{kl}) \hat{p}_n - \hat{r}_k \hat{p}_m (\hat{r}_k \hat{p}_n + i\hbar \delta_{kl}) \]

\[ = (\hat{\rho} \cdot \hat{\rho}) (\hat{\rho} \cdot \hat{\rho}) - (\hat{\rho} \cdot \hat{\rho})^2 + i\hbar (\hat{\rho} \cdot \hat{\rho}). \]

Here we wrote \( \hat{\rho}_1 \hat{\rho}_1 = \hat{\rho}_1 \hat{\rho}_1 + 3i\hbar \) because \( \hat{\rho}_1 \hat{\rho}_1 = \hat{\rho}_1 \hat{\rho}_1 + \hat{\rho}_1 \hat{\rho}_1 + \hat{\rho}_1 \hat{\rho}_1. \) Commuting the position and momentum in each of the three terms gives \( 3i\hbar. \)
In the classical version of this calculation, only the first two terms are present; the third one, arising due to the non-commuting observables, vanishes. In the classical case, this relation is obvious from geometry because $|L| = |\vec{r} \times \vec{p}| = |r||p|\sin \alpha$ and $|\vec{r} \cdot \vec{p}| = |r||p|\cos \alpha$, where $\alpha$ is the angle between $\vec{r}$ and $\vec{p}$, and hence $|\vec{r} \times \vec{p}|^2 + |\vec{r} \cdot \vec{p}|^2 = |r|^2 |p|^2$.

b) Multiplying both sides of Eq. (4.8) by $\hat{\vec{r}}^2$, we have

$$\left[ \frac{\hat{\vec{r}}^2 \hat{\vec{p}}^2}{2M} + \hat{\vec{r}}^2 V(\vec{r}) \right] \psi(\vec{r}) = \hat{\vec{r}}^2 E \psi(\vec{r}). \quad (S4.2)$$

Now substituting $\hat{\vec{r}}^2 \hat{\vec{p}}^2 = \hat{\vec{L}}^2 + (\hat{\vec{r}} \cdot \hat{\vec{p}})^2 - i\hbar \hat{\vec{r}} \cdot \hat{\vec{p}}$ from part (a) of this exercise, we obtain Eq. (4.23).

Solution to Exercise 4.15

a) Our goal is to rewrite the Cartesian expressions (4.20) for the components of the angular momentum in the position basis in spherical coordinates. To that end, we use the chain rule from multivariate calculus:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial r} \frac{\partial r}{\partial x} + \frac{\partial \theta}{\partial r} \frac{\partial r}{\partial \theta} + \frac{\partial \phi}{\partial r} \frac{\partial r}{\partial \phi}, \quad (S4.3a)$$

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial r} \frac{\partial r}{\partial y} + \frac{\partial \theta}{\partial r} \frac{\partial r}{\partial \theta} + \frac{\partial \phi}{\partial r} \frac{\partial r}{\partial \phi}, \quad (S4.3b)$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial r} \frac{\partial r}{\partial z} + \frac{\partial \theta}{\partial r} \frac{\partial r}{\partial \theta} + \frac{\partial \phi}{\partial r} \frac{\partial r}{\partial \phi}. \quad (S4.3c)$$

Solving Eqs. (4.11a) we express the spherical coordinates in terms of Cartesian ones:

$$r = \sqrt{x^2 + y^2 + z^2}; \quad (S4.4a)$$

$$\theta = \arccos \left( \frac{z}{r} \right); \quad (S4.4b)$$

$$\phi = \arctan \left( \frac{y}{x} \right). \quad (S4.4c)$$

To derive Eqs. (4.23), we must not only differentiate Eqs. (S4.4), but also express the results in spherical coordinates. We find:

$$\frac{\partial r}{\partial x} = \sin \theta \cos \phi, \quad \frac{\partial \theta}{\partial x} = \frac{1}{r} \cos \theta \cos \phi, \quad \frac{\partial \phi}{\partial x} = -\frac{1}{r} \sin \phi, \quad (S4.5a)$$

$$\frac{\partial r}{\partial y} = \sin \theta \sin \phi, \quad \frac{\partial \theta}{\partial y} = \frac{1}{r} \cos \theta \sin \phi, \quad \frac{\partial \phi}{\partial y} = \frac{1}{r} \cos \phi; \quad (S4.5b)$$

$$\frac{\partial r}{\partial z} = \cos \theta, \quad \frac{\partial \theta}{\partial z} = -\frac{1}{r} \sin \theta, \quad \frac{\partial \phi}{\partial z} = 0. \quad (S4.5c)$$

Now substituting these derivatives into Eqs. (S4.3), we obtain the desired set of derivatives (4.24).

b) Equations (4.25) are obtained by substituting the result from part (a) into (4.20). For example:
\[ L_x \simeq -\hbar \left( \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \]
\[ = -\hbar \left[ r \sin \theta \sin \phi \left( \cos \theta \frac{\partial}{\partial r} - \frac{1}{r} \sin \theta \frac{\partial}{\partial \theta} \right) \right. \]
\[ - \left. r \cos \theta \left( \sin \theta \sin \phi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \sin \phi \frac{\partial}{\partial \theta} + \frac{1}{r} \sin \theta \frac{\partial}{\partial \phi} \right) \right] \]
\[ = -\hbar \left[ -\sin \phi \frac{\partial}{\partial \theta} - \frac{\cos \theta \cos \phi}{\sin \theta} \frac{\partial}{\partial \phi} \right]. \]

\( \hat{L}^2 \simeq -\hbar^2 \left[ \sin^2 \phi \frac{\partial^2}{\partial \theta^2} + \cot^2 \theta \cos^2 \phi \frac{\partial^2}{\partial \phi^2} + \sin \phi \frac{\partial}{\partial \theta} \left( \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \left( \sin \phi \frac{\partial}{\partial \theta} \right) \right] ; \]
\[ \hat{L}_y^2 \simeq -\hbar^2 \left[ \cos^2 \phi \frac{\partial^2}{\partial \theta^2} + \cot^2 \theta \sin^2 \phi \frac{\partial^2}{\partial \phi^2} - \cos \phi \frac{\partial}{\partial \theta} \left( \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \left( \cos \phi \frac{\partial}{\partial \theta} \right) \right] ; \]
\[ \hat{L}_z^2 \simeq -\hbar^2 \frac{\partial^2}{\partial \phi^2}. \]

Adding the three together, we obtain
\[ \hat{L}^2 \simeq -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + (\cot^2 \theta + 1) \frac{\partial^2}{\partial \phi^2} + \cot \theta \frac{\partial}{\partial \phi} \right]. \] (S4.6)

To see that this result is equivalent to Eq. (4.26), we notice that its second term
\[ \cot^2 \theta + 1 = \frac{\cos^2 \theta + \sin^2 \theta}{\sin^2 \theta} = \frac{1}{\sin^2 \theta} \]
is the same as the second term in Eq. (4.26). Also, the first term in Eq. (4.26) can be rewritten as
\[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) = \frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\sin \theta} \frac{\partial}{\partial \phi} \]
which is the same as the sum of the first and third terms in Eq. (S4.6).

d) We observe that, in the position basis,
\[ i\hbar \vec{r} \cdot \vec{p} \simeq \hbar^2 \sum_j \frac{\partial}{\partial r_j} = \hbar^2 \left( \frac{x}{\frac{\partial}{\partial x}} + y \frac{\partial}{\partial y} + z \frac{\partial}{\partial z} \right). \]

To calculate this expression, we rewrite Eq. (4.24) as
\[ \frac{\partial}{\partial x} = \frac{x}{r} \frac{\partial}{\partial r} + \frac{xz}{r^2 \sqrt{x^2 + y^2}} \frac{\partial}{\partial \theta} - \frac{y}{r(x^2 + y^2)} \frac{\partial}{\partial \phi}; \]  
\[ \frac{\partial}{\partial y} = \frac{y}{r} \frac{\partial}{\partial r} + \frac{yz}{r^2 \sqrt{x^2 + y^2}} \frac{\partial}{\partial \theta} + \frac{x}{r(x^2 + y^2)} \frac{\partial}{\partial \phi}; \]  
\[ \frac{\partial}{\partial z} = \frac{z}{r} \frac{\partial}{\partial r} - \frac{\sqrt{x^2 + y^2}}{r^2} \frac{\partial}{\partial \theta} \]  

and hence we find that

\[ x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} + z \frac{\partial}{\partial z} = r \frac{\partial}{\partial r} \]  

and therefore

\[ i\hbar \hat{r} \cdot \vec{p} \simeq \hbar^2 r \frac{\partial}{\partial r}. \]  

Accordingly,

\[ (\hat{r} \cdot \vec{p})^2 \simeq -i\hbar r \frac{\partial}{\partial r} \left( -i\hbar \frac{\partial}{\partial r} \right) = -\hbar^2 \left( r^2 \frac{\partial^2}{\partial r^2} + r \frac{\partial}{\partial r} \right). \]  

**Solution to Exercise 4.16.** Substituting Eqs. (4.27), (4.28) and (4.29) into the Schrödinger equation (4.23), we find in the position basis

\[ \left[ -\frac{\hbar^2}{2M} \left( r^2 \frac{\partial^2}{\partial r^2} + 2r \frac{\partial}{\partial r} \right) + \frac{\lambda}{2M} + r^2 V(r) \right] R(r) Y_\lambda(\theta, \phi) = r^2 ER(r) Y_\lambda(\theta, \phi). \]  

Using

\[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) = r^2 \frac{\partial^2}{\partial r^2} + 2r \frac{\partial}{\partial r} \]  

and canceling \( Y_\lambda(\theta, \phi) \) on both sides, we obtain Eq. (4.44).

**Solution to Exercise 4.17.** Suppose the set of eigenvalues \( \{ \lambda_j \} \) of \( \hat{L}^2 \) is non-degenerate. We know from Ex. 4.11 that \( \hat{L}^2 \) commutes with both \( \hat{L}_x \) and \( \hat{L}_y \) [which, according to Eq. 4.25, are local operators within \( \mathcal{Y} \)]. According to Ex. 1.36, this means that there exists an orthonormal basis, which we denote \( \{ \hat{l}_j^{(x)} \} \), in which both observables \( \hat{L}^2 \) and \( \hat{L}_x \) diagonalize simultaneously, as well as an orthonormal basis \( \{ \hat{l}_j^{(y)} \} \) in which both observables \( \hat{L}^2 \) and \( \hat{L}_y \) diagonalize simultaneously. Therefore we have

\[ \hat{L}^2 = \sum_j \lambda_j \hat{l}_j^{(x)} \hat{l}_j^{(x)*} = \sum_j \lambda_j \hat{l}_j^{(y)} \hat{l}_j^{(y)*} \]  

Non-degeneracy of \( \lambda_j \), by definition, that \( \hat{l}_j^{(x)} = \hat{l}_j^{(y)} \), so the two bases must be the same. However, \( \hat{L}_x \) and \( \hat{L}_y \) do not commute with each other, so they cannot diagonalize in the same basis. We have arrived at a contradiction.
Solution to Exercise 4.18

a) The angular momentum components are Hermitian operators, so \( \hat{L}_z = \hat{L}_x \) and \((i\hat{L}_y)^\dagger = -i\hat{L}_y \). Therefore, 
\[
\hat{L}_x^\dagger = (\hat{L}_x + i\hat{L}_y)^\dagger = \hat{L}_x - i\hat{L}_y = \hat{L}_z .
\]
b) Using the result of Ex. 4.11, we find
\[
[\hat{L}_z, \hat{L}_\pm] = [\hat{L}_z, \hat{L}_x \pm i\hat{L}_y] = \pm \hbar L_z \pm i(-\hbar)\hat{L}_x = \hbar(\pm \hat{L}_x + i\hat{L}_y) = \pm \hbar \hat{L}_\pm ;
\]
\[
[\hat{L}_\pm, \hat{L}_\pm] = [\hat{L}_\pm^2, \hat{L}_\pm] = [\hat{L}_\pm^2, \hat{L}_x \pm i\hat{L}_y] = [\hat{L}_\pm^2, \hat{L}_\pm] = 0;
\]
\[
[\hat{L}_+, \hat{L}_-] = [\hat{L}_x + i\hat{L}_y, \hat{L}_x - i\hat{L}_y] = i[\hat{L}_x, \hat{L}_x] - i[\hat{L}_y, \hat{L}_y] = 2\hbar \hat{L}_z ;
\]
c) From
\[
\hat{L}_+ \hat{L}_- = (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 - i(\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x) = \hat{L}_x^2 - \hat{L}_y^2 - i[\hat{L}_x, \hat{L}_y] = \hat{L}_z^2 - \hat{L}_z^2 + i\hbar \hat{L}_z ;
\]
\[
\hat{L}_- \hat{L}_+ = (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 + i(\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x) = \hat{L}_x^2 - \hat{L}_y^2 + i[\hat{L}_x, \hat{L}_y] = \hat{L}_z^2 - \hat{L}_z^2 - i\hbar \hat{L}_z \quad \text{(S4.12a)}
\]
\[
\hat{L}_+ \hat{L}_- = (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 - i(\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x) = \hat{L}_x^2 - \hat{L}_y^2 - i[\hat{L}_x, \hat{L}_y] = \hat{L}_z^2 - \hat{L}_z^2 + i\hbar \hat{L}_z \quad \text{(S4.12b)}
\]
we find the required relation
\[
\hat{L}_z^2 = \hat{L}_\pm^2 - \hbar \hat{L}_z = \hat{L}_- \hat{L}_+ + \hat{L}_z^2 + \hbar \hat{L}_z .
\]

Solution to Exercise 4.19

a) In order to verify if the state \( \hat{L}_+ |\lambda \mu \rangle \) is an eigenstate of \( \hat{L}_z \) and \( \hat{L}_\pm \), let us subject this state to the action of these operators. Because \( \hat{L}_z^2 \) commutes with \( \hat{L}_\pm \), we have
\[
\hat{L}_z \hat{L}_\pm |\lambda \mu \rangle = \hat{L}_\pm \hat{L}_z |\lambda \mu \rangle = \hat{L}_\pm \hat{L}_z |\lambda \mu \rangle = \lambda \hat{L}_+ |\lambda \mu \rangle = \lambda \hat{L}_\pm |\lambda \mu \rangle .
\]
In other words, \( \hat{L}_+ |\lambda \mu \rangle \) is an eigenstate of \( \hat{L}_z \) with eigenvalue \( \lambda \).
To perform a similar calculation for \( \hat{L}_- \), we rewrite the expression for the commutator of \( \hat{L}_x \) and \( \hat{L}_\mp \) obtained in Ex. 4.18 as follows:
\[
\hat{L}_z \hat{L}_\pm = \hat{L}_\pm \hat{L}_z + \hbar \hat{L}_\pm ,
\]
and thus
\[
\hat{L}_z \hat{L}_\pm |\lambda \mu \rangle = (\hat{L}_\pm \hat{L}_z + \hbar \hat{L}_\pm ) |\lambda \mu \rangle = (\mu \hat{L}_\pm + \hbar \hat{L}_\pm ) |\lambda \mu \rangle = (\mu + \hbar) \hat{L}_\pm |\lambda \mu \rangle .
\]
We see that the action of the operator \( \hat{L}_z \) on the state \( \hat{L}_\pm |\lambda \mu \rangle \) is equivalent to multiplying this state by \( (\mu + \hbar) \), so \( \hat{L}_\pm |\lambda \mu \rangle \) is an eigenstate of \( \hat{L}_z \) with the eigenvalue \( (\mu + \hbar) \).

b) Similarly, because
\[
\hat{L}_z \hat{L}_- = \hat{L}_- \hat{L}_z - \hbar \hat{L}_- ,
\]
we have
\[
\hat{L}_z \hat{L}_- |\lambda \mu \rangle = (\hat{L}_- \hat{L}_z - \hbar \hat{L}_-) |\lambda \mu \rangle = (\mu \hat{L}_- - \hbar \hat{L}_-) |\lambda \mu \rangle = (\mu - \hbar) \hat{L}_- |\lambda \mu \rangle ,
\]
so \( \hat{L}_- |\lambda \mu \rangle \) is an eigenstate of \( \hat{L}_z \) with eigenvalue \( \mu - \hbar \).

Solution to Exercise 4.20 Let \( |\psi \rangle = \hat{L}_+ |\lambda \mu \rangle \). From the previous exercise, we know that \( |\psi \rangle \) is an eigenstate of \( \hat{L}_z \) with the eigenvalue \( \hbar (\mu + \hbar) \), i.e. \( |\psi \rangle = \mu |\lambda \mu + \hbar \rangle \), where \( \mu \) is some constant. We need to find \( \mu \). To this
end, we notice that $\langle \psi | = \langle \lambda \mu | \hat{L}_+^\dagger = \langle \lambda \mu | \hat{L}_- $, and calculate

$$
\langle \psi | \psi \rangle = \langle \lambda \mu | \hat{L}_- \hat{L}_+ | \lambda \mu \rangle = \langle \lambda \mu | \hat{L}_-^2 - \lambda \mu \rangle = \lambda - \mu^2 - \mu \hbar
$$

(in the last equality, we used the fact that $|\lambda \mu \rangle$ is an eigenstate of both $\hat{L}_2$ and $\hat{L}_z$). But on the other hand,

$$
\langle \psi | \psi \rangle = |A|^2 \langle \lambda \mu | \mu \rangle = |A|^2,
$$

(S4.13)
because the eigenstates of the angular momentum operator are normalized. Hence we find $A = e^{i \alpha \sqrt{\lambda - \mu | \mu + \hbar}}$, where $\alpha$ is an arbitrary real number.

Similarly, for the lowering operator, we have $|\phi \rangle = \hat{L}_- |\lambda \mu \rangle = B |\lambda \mu - \hbar \rangle$. Then, on the one hand,

$$
\langle \phi | \phi \rangle = \langle \lambda \mu | \hat{L}_- \hat{L}_+ | \lambda \mu \rangle = \langle \lambda \mu | \hat{L}_-^2 - \lambda \mu \rangle = \lambda - \mu^2 + \mu \hbar
$$

and on the other hand

$$
\langle \phi | \phi \rangle = |B|^2 \langle \lambda \mu - \hbar | \lambda \mu - \hbar \rangle = |B|^2.
$$

(S4.14)

Therefore, $B = e^{i \alpha \sqrt{\lambda - \mu | \mu - \hbar}}$.

**Solution to Exercise 4.21** Consider the operator $\hat{L}_2 - \hat{L}_z^2$. State $|\lambda \mu \rangle$ is an eigenstate of this operator with eigenvalue $\lambda - \mu^2$. But this operator equals $\hat{L}_2^2 + \hat{L}_z^2$ and is therefore non-negative (Ex. A.87) so all its eigenvalues must be non-negative as well (Ex. A.72).

**Solution to Exercise 4.22** We know from Ex. 4.20 that the existence of the state $|\lambda \mu \rangle$ implies, through repeated application of the raising operator, the existence of a chain of states $|\lambda, \mu + j \hbar \rangle$, where $j$ is a nonnegative integer. But this means that at some point $(\mu + j \hbar)^2$ will exceed $\lambda$, which as we found in Ex. 4.21, is impossible. The chain is broken only if there exists a value of $j$, which we denote as $j_0$, such that $\hat{L}_+ |\lambda, \mu + j_0 \hbar \rangle = 0$. According to Eq. (4.32), this happens if $\lambda = |\mu + j_0 \hbar| |\mu + (j_0 + 1) \hbar\rangle$.

Similarly, the chain of states generated by the lowering operator, $|\lambda, \mu - j \hbar \rangle$, is broken only if there exists a non-negative integer $k_0$ such that $\lambda = |\mu - k_0 \hbar| |\mu - (k_0 + 1) \hbar\rangle$. Satisfying both chain breaking conditions at the same time implies that

$$
[\mu + j_0 \hbar][\mu + (j_0 + 1) \hbar] = |\mu - k_0 \hbar| |\mu - (k_0 + 1) \hbar|.
$$

Denoting $\mu + j_0 \hbar = x$ and $\mu - (k_0 + 1) \hbar = y$, we rewrite the above equation as

$$
x(x + \hbar) = y(y + \hbar).
$$

Because we must have $x > y$, this equation has only one solution: $y = -(x + \hbar)$. This means

$$
\mu - (k_0 + 1) \hbar = -\mu - (j_0 + 1) \hbar,
$$

or

$$
\mu = \frac{k_0 - j_0}{2} \hbar.
$$

(S4.15)

This implies, in turn, that

$$
\lambda = [\mu + j_0 \hbar][\mu + (j_0 + 1) \hbar] = \frac{k_0 + j_0}{2} \left( \frac{k_0 + j_0}{2} + 1 \right) \hbar^2.
$$
Solution to Exercise 4.25. Since the state \(|l\rangle\) is an eigenstate of \(\hat{L}^2\) with the eigenvalue \(\hat{L}^2 |l\rangle = \hbar^2 l(l+1) |l\rangle\), we can only take values from \(-l\) to \(l\) in steps of 1. We can now rewrite Eq. (S4.15) as
\[
\langle m| \hat{L}^2 |l\rangle = \hbar^2 l(l+1) \delta_{m,l};
\]
(S4.16)

The action of the raising and lowering operators on states \(|lm\rangle\) is known from Ex. 4.20
\[
\langle lm| \hat{L}_+ |l'm\rangle = \hbar \sqrt{l'(l'+1) - m'(m'+1)} \langle lm| l',m' \rangle = \hbar \sqrt{l'(l'+1) - m'(m'+1)} \delta_{l,l'} \delta_{m,m'} \delta_{m',\pm 1};
\]
(S4.17)

Finally, the \(x\)- and \(y\)-components of the angular momentum can be written as linear combinations of the raising and lowering operators according to the definition (4.31) of the latter:
\[
\hat{L}_x = \frac{\hat{L}_+ + \hat{L}_-}{2};
\]
(S4.19)
\[
\hat{L}_y = \frac{\hat{L}_+ - \hat{L}_-}{2i};
\]
(S4.20)

and hence
\[
\langle lm| \hat{L}_x |l'm\rangle = \frac{\hbar}{2} \left[ \sqrt{l'(l'+1) - m'(m'+1)} \delta_{l,l'} \delta_{m,m'+1} + \sqrt{l'(l'+1) - m'(m'-1)} \delta_{l,l'} \delta_{m,m'-1} \right];
\]
(S4.21)
\[
\langle lm| \hat{L}_y |l'm\rangle = \frac{\hbar}{2i} \left[ \sqrt{l'(l'+1) - m'(m'+1)} \delta_{l,l'} \delta_{m,m'+1} - \sqrt{l'(l'+1) - m'(m'-1)} \delta_{l,l'} \delta_{m,m'-1} \right].
\]

Solution to Exercise 4.27

a) According to the Measurement Postulate, the possible values that a measurement of an observable can yield are the eigenvalues of that observable. Finding the eigenvalues of matrices (4.34) and (4.35) for \(\hat{L}_x\) and \(\hat{L}_y\), we obtain sets (i) \(\{\hbar/2, -\hbar/2\}\) and (ii) \(\{\hbar, 0, -\hbar\}\), respectively.

b) The corresponding normalized eigenstates are
\[i) \]
\[
\begin{align*}
|m_x = \frac{1}{2}\rangle \simeq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}; & \quad |m_x = -\frac{1}{2}\rangle \simeq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \text{ for } L_x, & \text{(S4.22a)} \\
|m_y = \frac{1}{2}\rangle \simeq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}; & \quad |m_y = -\frac{1}{2}\rangle \simeq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \text{ for } L_y & \text{(S4.22b)}
\end{align*}
\]

i)

\[
\begin{align*}
|m_x = 1\rangle \simeq \frac{1}{2} \begin{pmatrix} \sqrt{2} \\ 1 \end{pmatrix}; & \quad |m_x = 0\rangle \simeq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix}; & \quad |m_x = -1\rangle \simeq \frac{1}{2} \begin{pmatrix} 1 \\ -\sqrt{2} \end{pmatrix} \text{ for } L_x, & \text{(S4.23a)} \\
|m_y = 1\rangle \simeq \frac{1}{2} \begin{pmatrix} \sqrt{2}i \\ -1 \end{pmatrix}; & \quad |m_y = 0\rangle \simeq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}; & \quad |m_y = -1\rangle \simeq \frac{1}{2} \begin{pmatrix} 1 \\ -\sqrt{2}i \end{pmatrix} \text{ for } L_y & \text{(S4.23b)}
\end{align*}
\]

Solution to Exercise 4.28

a) The coordinates of the vector \( \vec{R}_{\theta \phi} \) are [see Eq. (4.11a)] \((\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)\). Accordingly, we need to look for the eigenvalues and eigenvectors of the matrix

\[
\hat{L}_{\theta \phi} = \sin \theta \cos \phi \hat{L}_x + \sin \theta \sin \phi \hat{L}_y + \cos \theta \hat{L}_z \equiv \frac{\hbar}{2} \begin{pmatrix} \cos \theta & \sin \theta e^{-i\phi} \\ \sin \theta e^{i\phi} & -\cos \theta \end{pmatrix}. \quad \text{(S4.24)}
\]

Using the standard method, we find the eigenvalues \(\{\hbar/2, -\hbar/2\}\) (cf. Ex. A.93) and corresponding normalized eigenvectors

\[
\{ |\uparrow_{\theta \phi}\rangle, |\downarrow_{\theta \phi}\rangle \} = \left\{ \begin{pmatrix} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} e^{i\phi} \end{pmatrix}; \begin{pmatrix} \sin \frac{\theta}{2} \\ -\cos \frac{\theta}{2} e^{i\phi} \end{pmatrix} \right\} \quad \text{(S4.25)}
\]

b) Using trigonometric identities for the cosine and sine of a double angle, we find
\[ \langle \uparrow \theta \phi | \hat{L}_x | \uparrow \theta \phi \rangle = \frac{\hbar}{2} \left( \cos \frac{\theta}{2} \sin \frac{\phi}{2} e^{-i \phi} \right) \left( \begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \right) \left( \begin{array}{c} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} e^{i \phi} \end{array} \right) \\
= \frac{\hbar}{2} \cos \frac{\theta}{2} \sin \theta (e^{i \phi} + e^{-i \phi}) \]

\[ = \frac{\hbar}{2} \sin \theta \cos \phi; \]

\[ \langle \uparrow \theta \phi | \hat{L}_y | \uparrow \theta \phi \rangle = \frac{\hbar}{2} \left( \cos \frac{\theta}{2} \sin \frac{\phi}{2} e^{-i \phi} \right) \left( \begin{array}{cc} 0 & -i \\ i & 0 \end{array} \right) \left( \begin{array}{c} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} e^{i \phi} \end{array} \right) \\
= \frac{\hbar}{2} \cos \frac{\theta}{2} \sin \theta (-ie^{i \phi} + ie^{-i \phi}) \]

\[ = \frac{\hbar}{2} \sin \theta \sin \phi; \]

\[ \langle \uparrow \theta \phi | \hat{L}_z | \uparrow \theta \phi \rangle = \frac{\hbar}{2} \left( \cos \frac{\theta}{2} \sin \frac{\phi}{2} e^{-i \phi} \right) \left( \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right) \left( \begin{array}{c} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} e^{i \phi} \end{array} \right) \\
= \frac{\hbar}{2} \left( \cos^2 \frac{\theta}{2} - \sin^2 \frac{\theta}{2} \right) \]

\[ = \frac{\hbar}{2} \cos \theta, \]

so \( \langle \hat{L}_x \rangle, \langle \hat{L}_y \rangle, \langle \hat{L}_z \rangle = \frac{\hbar}{2} K_{\theta \phi} \) in the state \( |\uparrow \theta \phi \rangle \). The proof for \( |\downarrow \theta \phi \rangle \) is similar.

**Solution to Exercise 4.29.** According to Eqs. (S4.18) and (S4.19) we find

\[ \langle l m | \hat{L}_x | l m \rangle = \langle l m | \hat{L}_y | l m \rangle = 0 \]

and

\[ \langle \Delta \hat{L}_z^2 \rangle = \langle l m | \hat{L}_z^2 | l m \rangle = \frac{1}{4} \langle l m | \hat{L}_+^2 + \hat{L}_-^2 + \hat{L}_+ + \hat{L}_- | l m \rangle = \frac{\hbar^2}{4} \left[ 2l(l+1) - m(m+1) - m(m-1) \right], \]

\[ = \frac{\hbar^2}{2} [l(l+1) - m^2]. \]

The same uncertainty is obtained for the \( y \) component of the angular momentum:

\[ \langle \Delta \hat{L}_y^2 \rangle = \frac{\hbar^2}{2} [l(l+1) - m^2]. \]

Since, according to Ex. 4.11 \( [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \), the uncertainty principle (1.21) takes the form \[ \langle \Delta \hat{L}_x^2 \rangle \langle \Delta \hat{L}_y^2 \rangle \geq \frac{\hbar^2}{4} |\langle \hat{L}_z \rangle|^2. \]

Substituting the above found uncertainties, as well as \( \langle l m | \hat{L}_z | l m \rangle = m \hbar \), we obtain
\[
\frac{\hbar^4}{4} [l(l+1) - m^2]^2 \geq \frac{\hbar^2}{4} (m\hbar)^2
\]

or simply
\[
[l(l+1) - m^2]^2 \geq m^2.
\]

This relation directly follows from the fact that \( l \geq |m| \). The inequality saturates for \( m = \pm l \) and \( m = -l \), in which case \( \langle \Delta \hat{L}_z^2 \rangle = \langle \Delta \hat{L}_z^2 \rangle = \hbar^2 l/2 \).

**Solution to Exercise 4.30.** If \( Y(\theta, \phi) \) is the wavefunction of an eigenstate of operator \( \hat{L}_z \) with eigenvalue \( m \), we use Eq. (4.25c) to write
\[
-\imath \hbar \frac{\partial}{\partial \phi} Y(\theta, \phi) = m Y(\theta, \phi).
\]

The solution of this equation is \( e^{im\phi} \) multiplied by any function that does not depend on \( \phi \), i.e. it is given by Eq. (4.37).

**Solution to Exercise 4.32.**

a) For \( m = l \), Eq. (4.39) becomes
\[
Y_l^l(\theta, \phi) = \mathcal{N}_l \sqrt{(2l)!} \sin^l \theta e^{i\phi}.
\]

Applying the raising operator (4.38a) to this wavefunction we find
\[
\hat{L}_+ |l\rangle \approx \hbar e^{i\phi} \mathcal{N}_l \sqrt{(2l)!} \left[ \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right] \sin^l \theta e^{i\phi} \\
= \hbar e^{i\phi} \mathcal{N}_l \sqrt{(2l)!} \left[ l \cos \theta \sin^{l-1} \theta e^{i\phi} - l \cot \theta \sin^l \theta e^{i\phi} \right] \\
= 0.
\]

b) To verify the normalization, we evaluate the inner product (4.15b) of the state \( |l\rangle \) with itself. In the calculation below, we replace the integration variable according to \( x = \cos \theta \), hence \( dx = -\sin \theta \, d\theta \):
\[
\langle ll | ll \rangle = \int_0^{2\pi} \int_0^\pi |Y_l^l(\theta, \phi)|^2 \sin \theta \, d\theta \, d\phi \\
= 2\pi \mathcal{N}_l^2 (2l)! \int_0^\pi \sin^{2l} \theta \sin \theta \, d\theta \\
= -2\pi \mathcal{N}_l^2 (2l)! \int_1^0 \sin^{2l+1} \theta \, d\theta \\
= 2\pi \mathcal{N}_l^2 (2l)! \frac{2^{2l+1}(l!)^2}{(2l+1)!} \\
= 4\pi \mathcal{N}_l^2 \frac{2^{2l}(l!)^2}{(2l+1)}.
\]
Setting $\langle l | l \rangle = 1$, we obtain Eq. (4.40).

c) Applying operator (4.26) to Eq. (S4.27) we find

$$
\hat{L}^2 |l\rangle \simeq -\hbar^2 \mathcal{M}_l \sqrt{2l+1} \begin{bmatrix}
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \sin \theta \right) e^{i\phi} + \sin^2 \theta \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} e^{i\phi}
\end{bmatrix}
$$

$$
= -\hbar^2 \mathcal{M}_l \sqrt{2l+1} \begin{bmatrix}
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( l \sin \theta \cos \theta \right) e^{i\phi} - l^2 \sin^2 \theta e^{i\phi}
\end{bmatrix}
$$

$$
= -\hbar^2 \mathcal{M}_l \sqrt{2l+1} \begin{bmatrix}
\frac{1}{\sin \theta} \left( l^2 \sin^2 \theta \cos^2 \theta - l \sin \theta \sin l \theta \right) - l^2 \sin^2 \theta e^{i\phi}
\end{bmatrix}
$$

$$
= -\hbar^2 \mathcal{M}_l \sqrt{2l+1} \left[ l^2 \sin^2 \theta \cos^2 \theta - l \sin \theta \sin l \theta \right] e^{i\phi}
$$

$$
= -\hbar^2 \mathcal{M}_l \sqrt{2l+1} \left[ l(l+1) \sin \theta \right] e^{i\phi}
$$

$$
= \hbar^2 l(l+1) Y_l^m(\theta, \phi).
$$

d) We need to calculate

$$
\hat{L}^2 |l\rangle \simeq -\hbar^2 \mathcal{M}_l \sqrt{2l+1} \begin{bmatrix}
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \sin \theta \right) e^{i\phi} + \sin^2 \theta \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} e^{i\phi}
\end{bmatrix}
$$

$$
= -\hbar^2 \mathcal{M}_l \sqrt{2l+1} \begin{bmatrix}
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( l \sin \theta \cos \theta \right) e^{i\phi} - l^2 \sin^2 \theta e^{i\phi}
\end{bmatrix}
$$

$$
= -\hbar^2 \mathcal{M}_l \sqrt{2l+1} \begin{bmatrix}
\frac{1}{\sin \theta} \left( l^2 \sin^2 \theta \cos^2 \theta - l \sin \theta \sin l \theta \right) - l^2 \sin^2 \theta e^{i\phi}
\end{bmatrix}
$$

$$
= -\hbar^2 \mathcal{M}_l \sqrt{2l+1} \left[ l^2 \sin^2 \theta \cos^2 \theta - l \sin \theta \sin l \theta \right] e^{i\phi}
$$

$$
= -\hbar^2 \mathcal{M}_l \sqrt{2l+1} \left[ l(l+1) \sin \theta \right] e^{i\phi}
$$

$$
= \hbar^2 l(l+1) Y_l^m(\theta, \phi).
$$

Since

$$
\frac{\partial}{\partial \theta} = \frac{\partial}{\partial \cos \theta} \frac{\cos \theta}{\sin \theta} = -\sin \theta \frac{\partial}{\partial \cos \theta},
$$

we have

$$
\frac{\partial}{\partial \theta} Y_l^m(\theta, \phi) = -m \cot \theta Y_l^m(\theta, \phi) + \mathcal{M}_l \sqrt{\frac{(l+m)!}{(l-m)!}} \sin^{-m} \theta (-\sin \theta) \frac{d^{l-m+1}}{d(\cos \theta)^{l-m+1}} \sin^{2l} \theta e^{i\phi}.
$$

On the other hand,

$$
i \cot \theta \frac{\partial}{\partial \theta} Y_l^m(\theta, \phi) = -m \cot \theta Y_l^m(\theta, \phi).
$$

Putting these results together, we obtain

$$
\hat{L} \cdot Y_l^m(\theta, \phi) = \hbar \mathcal{M}_l \sqrt{\frac{(l+m)!}{(l-m)!}} \sin^{-m+1} \theta \frac{d^{l-m+1}}{d(\cos \theta)^{l-m+1}} \sin^{2l} \theta e^{i(l-m-1)\phi}
$$

$$
= \hbar Y_l^{m-1}(\theta, \phi) \sqrt{(l+m)(l-m+1)}.
$$

This is consistent with Eq. (4.33b).
Solution to Exercise 4.35. For the first term in the left-hand side of Eq. (4.44), we have

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial}{\partial r} R_{EI}(r) \right] = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( \frac{U'_{EI}(r)}{r} - \frac{U_{EI}(r)}{r^2} \right) \right] = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r \left( U'_{EI}(r) + rU''_{EI}(r) - U_{EI}(r) \right) \right] = \frac{U''_{EI}(r)}{r},
\]

where primes denote derivatives. Substituting this result into into Eq. (4.44), we obtain Eq. (4.46).

Solution to Exercise 4.36. At \( r \to 0 \), the dominating terms in Eq. (4.46) are those of the lowest power of \( r \), which are the first and second terms in the brackets. The equation becomes

\[
\frac{\partial^2}{\partial r^2} U_{EI}(r) = \frac{l(l+1)}{r^2} U_{EI}(r), \tag{S4.28}
\]

whose solutions are either \( U_{EI}(r) \propto r^{-l} \) or \( U_{EI}(r) \propto r^{l+1} \). The first option results in a discontinuous wavefunction at \( r = 0 \) and must be rejected.

To find the behavior in the limit \( r \to \infty \), we write, according to Eq. (4.47),

\[
\frac{\partial^2}{\partial r^2} U_{EI}(r) = \sum_{j=l+1}^{\infty} A_j \left[ \kappa^2 r^j - 2\kappa j r^{j-1} + j(j-1) r^{j-2} \right] e^{-\kappa r}. \tag{S4.29}
\]

Now the highest power of \( r \) dominates, so Eq. (4.46) becomes

\[-\frac{\hbar^2}{2M} A_n \kappa^2 r^n e^{-\kappa r} = E A_n r^n e^{-\kappa r}.
\]

This is satisfied for \( \kappa = \sqrt{-2ME}/\hbar \).

Solution to Exercise 4.37. Substituting Eq. (S4.29) into Eq. (4.46), multiplying both sides by \( \frac{2M}{\hbar^2} \) and expressing \( E = -\frac{\hbar^2 \kappa^2}{2M} \), we obtain

\[- \left[ \kappa^2 \sum_{j=l+1}^{\infty} A_j r^j - 2\kappa \sum_{j=l+1}^{\infty} j A_j r^{j-1} + \sum_{j=l+1}^{\infty} j(j-1) A_j r^{j-2} \right] + l(l+1) \sum_{j=l+1}^{\infty} A_j r^{j-2} = \frac{2M e^2}{4\pi \varepsilon_0 \hbar^2} \sum_{j=l+1}^{\infty} A_j r^{j-1} = -\kappa^2 \sum_{j=l+1}^{\infty} A_j r^j. \tag{S4.30}
\]

Collecting similar terms, we rewrite this as
\[
\sum_{j=l+1}^{\infty} \left(2\kappa j - \frac{Me^2}{2\pi\varepsilon_0 h^2}\right)A_j r^{j-1} + \sum_{j=l+1}^{\infty} [l(l+1) - j(j-1)]A_j r^{j-2} = 0.
\]

We now change the summation index in the second term according to \(j' = j - 1\) to obtain
\[
\sum_{j=l+1}^{\infty} \left(2\kappa j - \frac{Me^2}{2\pi\varepsilon_0 h^2}\right)A_j r^{j-1} + \sum_{j'=l}^{\infty} [l(l+1) - j'(j'+1)]A_{j'+1} r^{j'-1} = 0. \tag{S4.31}
\]
and notice that because, for \(j' = l\), \(l(l+1) - j'(j'+1) = 0\), the lower summation limit in the second term can be changed to \(j' = l+1\).

The polynomial expression in the left-hand side of Eq. (S4.31) is constant zero for all values of \(r\) only if the coefficient for each power of \(r\) vanishes. This leads us to the desired recursive relation (4.49).

**Solution to Exercise 4.38.** For \(n = 1\) and \(l = 0\), \(\kappa = Me^2/4\pi\varepsilon_0 h^2 = 1/a\) as per Eq. (4.50). Because the index \(j\) of coefficients \(A_j\) must be between \(l+1\) and \(n\), there is only one non-vanishing coefficient, \(A_1\). Accordingly, using Eq. (4.50), and recalling that \(R_{nl}(r) = U_{nl}(r)/r\), we obtain
\[
R_{10}(r) = A_1 e^{-r/a}.
\]
To normalize this radial function, we write integral (4.15a):
\[
\int_0^\infty |R_{10}(r)|^2 r^2 dr = 1.
\]
This integral is calculated using Eq. (4.51):
\[
\int_0^\infty |R_{10}(r)|^2 r^2 dr = A_1^2 \int_0^\infty r^2 e^{-2r/a} dr = 2! \left(\frac{a}{2}\right)^3 A_1^2 = \frac{a^3}{4} A_1^2,
\]
so \(A_1 = 2a^{-3/2}\).

For \(n = 2\), \(\kappa = 1/2a\). Let us start with \(l = 0\). The non-vanishing coefficients are \(A_1\) and \(A_2\) and they are related by Eq. (4.49), which in this case takes the form
\[
\left[2\kappa - \frac{2}{a}\right] A_1 - 2A_2 = 0,
\]
so \(A_2 = -A_1/2a\) and
\[
R_{20}(r) = A_1 \left(1 - \frac{r}{2a}\right) e^{-r/2a}.
\]
Normalizing this radial function yields
\[
\int_0^\infty |R_{20}(r)|^2 r^2 dr = A_1^2 \int_0^\infty \left( r^2 - \frac{r^3}{a} + \frac{r^4}{4a^2} \right) e^{-r/a} dr \\
= A_1^2 a^3 (2! - 3! + 4! / 4) \\
= 2A_1^2 a^3 = 1,
\]

so \( A_1 = (2a^3)^{-1/2} \).

Finally, for \( n = 2 \) and \( l = 1 \), we only have \( A_2 \) and the radial wavefunction is

\[
R_{21}(r) = A_2 r e^{-r/2a}.
\]

The normalization equation is then as follows:

\[
\int_0^\infty |R_{21}(r)|^2 r^2 dr = A_2^2 \int_0^\infty r^4 e^{-r/a} dr = 4!A_2^2 a^5 = 1,
\]

so \( A_2 = (24a^5)^{-1/2} \).

**Solution to Exercise 4.39** For a given \( n \), \( l \) can take on any integer value from 0 to \( n - 1 \). Each of the \( l \) values is, in turn, degenerate with respect to the magnetic quantum number \( m \); the degree of degeneracy is, as we know, \( 2l + 1 \). Additional degeneracy comes from the spin degree of freedom of the electron: the spin quantum number for the electron can take two values, \( \pm \frac{1}{2} \). The total degeneracy associated with a particular value of \( n \) is therefore

\[
2 \sum_{l=0}^{n-1} (2l + 1) = 2n^2.
\]  
(S4.32)

**Solution to Exercise 4.40** From Eq. 4.59 we find for the energy of the photon

\[
\hbar \omega = |E_{n_1} - E_{n_2}| = \frac{1}{1 + M_e/M_p} \text{Ry} \left| \frac{1}{n_1^2} - \frac{1}{n_2^2} \right|.
\]

Using the fact that the optical frequency and wavelength are related via \( \omega = \frac{2\pi c}{\lambda} \), we obtain Eq. (4.61).

According to Eq. 4.59, the Lyman series has photon energies from \((1 - \frac{1}{4})\text{Ry} \) to \( \text{Ry} \), Balmer from \((\frac{1}{2} - \frac{1}{16})\text{Ry} \) to \( \frac{1}{4}\text{Ry} \), Paschen from \((\frac{1}{3} - \frac{1}{16})\text{Ry} \) to \( \frac{1}{8}\text{Ry} \). Given that the energy of the photon is related to its wavelength according to \( \hbar \omega = 2\pi \hbar c / \lambda \), we find that the wavelengths range from 91 to 122 nm for the Lyman series, 365 nm to 656 nm for the Balmer series, and 820 to 1875 nm for the Paschen series (taking into account the reduced mass correction). Only the Balmer series is within the visible range.

**Solution to Exercise 4.41** A classical electron in a circular orbit of radius \( r \) at velocity \( v \) experiences centripetal acceleration \( v^2 / r \) which is known to be caused by the electrostatic attraction by the nucleus, whose force is

\[
F = \frac{e^2}{4\pi \epsilon_0 r^2}.
\]
Writing the second Newton’s law \( F = Mv^2/r \), we find
\[
v^2r = \frac{e^2}{4\pi\varepsilon_0M}.
\]
On the other hand, we can rewrite Eq. (4.58) as
\[
Mvr = n\hbar.
\]
Solving the last two equations for \( r \) and \( v \), we obtain
\[
v = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{n\hbar}
\]
and
\[
r = \frac{4\pi\varepsilon_0}{e^2} \frac{n^2\hbar^2}{M}.
\] (S4.33)
For \( n = 1 \), the result for \( r \) is consistent with the definition (4.55) of the Bohr radius.
The kinetic and potential energies of the electron in the orbit are, respectively,
\[
\frac{Mv^2}{2} = \left( \frac{e^2}{4\pi\varepsilon_0} \right)^2 \frac{M}{2n^2\hbar^2}
\]
and
\[
-\frac{1}{4\pi\varepsilon_0} \frac{e^2}{r} = -\left( \frac{e^2}{4\pi\varepsilon_0} \right)^2 \frac{M}{n^2\hbar^2}
\]
(the former being a negative one-half of the latter in agreement with the virial theorem). The full energy is therefore consistent with Eq. (4.56).

**Solution to Exercise 4.42.** The de Broglie wavelength (3.26) is \( \lambda_{dB} = \frac{2\pi\hbar}{p} \), so Bohr’s condition (4.58) \( pr = n\hbar \) is equivalent to \( 2\pi r = n\lambda_{dB} \), i.e. that the orbit contains an integer number of de Broglie waves. The remainder of the solution is identical to that of the previous exercise.

**Solution to Exercise 4.43.**
a) Following the same logic as in Ex. 4.38 \( \kappa = 1/na \) and \( U_n(r) \) has only one nonvanishing coefficient, \( A_n \).
The radial wavefunction is
\[
R_{n,n-1}(r) = A_n r^{n-1} e^{-r/na}.
\]
The normalization equation is
\[
\int_0^\infty |R_{n,n-1}(r)|^2 r^2 dr = A_n^2 \int_0^\infty r^2 e^{-2r/na} dr = 2^{-2n} a^{2n+1} n^{2n+2} (2n-1)! A_n^2 = 1,
\]
so
\[
A_n = \frac{1}{2} \left( \frac{2}{an} \right)^{n+1} \sqrt{\frac{a}{(2n-1)!}}.
\]
b) For the mean radius, we have

\[ \langle r \rangle = \int_0^\infty |R_{n-1}(r)|^2 r^3 dr = 2^{-2n-2} a^{2n+2} n^{2n+2} (2n+1)! A_n^2 \left( n + \frac{1}{2} \right). \]

\[ \langle z \rangle = \int_0^\infty |\psi_{100}(r)|^2 dr = 0 \]

because \( \psi_{100}(r) \) is an isotropic function and \( z \) is an odd function of \( r \).

The mean square of \( z \) is given by

\[ \langle z^2 \rangle = \int z^2 |\psi_{100}(r)|^2 dr = 2^{2n+1} \pi a^2 \int_0^\infty r^4 e^{-2r/a} dr \]

\[ = 2^{2n+1} \pi a^2 \int_0^\infty r^4 e^{-2r/a} dr \]

\[ = 2^{2n+1} \pi a^2 \int_0^\infty r^4 e^{-2r/a} dr \]

so the root mean square uncertainty is equal to the Bohr radius \( a \).

Because the wavefunction of state \( |100\rangle \) is isotropic, we expect the same result for observables \( x \) and \( y \).

**Solution to Exercise 4.45** Using (4.57), the matrix elements of interest are given by

\[ \langle nlm | r_i | n'l'm' \rangle = \int_0^\infty \int_0^\infty \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} R_{nl}(r) Y_i^m(\theta, \phi) r_j(\theta, \phi) R_{n'l'}(r) Y_j^{m'}(\theta, \phi) r_l^i(\theta, \phi) r_l^j(\theta, \phi) r_l^m(\theta, \phi) \sin \theta dr d\theta d\phi, \]

where \( r_j(\theta, \phi) = r \sin \theta \cos \phi, r \sin \theta \sin \phi, r \cos \theta \) for \( x, y, z \), respectively. We can notice from Ex. 4.33 that all spherical harmonics \( Y_i^m(\theta, \phi) \) are odd functions, i.e. they take on opposite values for the points \((\theta, \phi)\) and \((\pi - \theta, \pi + \phi)\). The same is true for all \( r_j(\theta, \phi) \). Spherical harmonic \( Y_i^m(\theta, \phi) \) is a constant, i.e. an even function. This tells us that the integrand in Eq. (S4.34) is an odd function for \( l = l' \), which means that the integral corresponding to \( |1, 0, 0\rangle | 1, 0, 0 \rangle \) vanishes when the integration is performed over the entire space.

For the matrix elements \( |1, 0, 0\rangle | 2, 1, m \rangle \), we notice that the spherical harmonics \( Y_i^m(\theta, \phi) \) contain the factor \( e^{i\phi} \) while \( Y_i^m(\theta, \phi) \) does not depend on \( \phi \). Additionally, we have \( x = r \sin \theta \cos \phi = r \sin \theta (e^{i\phi} + e^{-i\phi})/2 \) and
The ground state of the hydrogen atom has the principal quantum number \( n = 1 \) and the energy that is approximately equal to the negative Rydberg constant according to Eq. (4.59). It is twice degenerate as per Ex. 4.39. The first excited state has \( n = 2 \), so it is eight times degenerate and has an energy of about \(-\text{Ry}/4\). The ratio of the probabilities for the atom to be in one of the states with \( n = 2 \) and in one of the states with \( n = 1 \) is

\[
\frac{p_2}{p_1} = e^{-\frac{\text{Ry}-\text{Ry}/4}{\hbar}} \approx 7 \times 10^{-180}.
\]

With such a minuscule ratio it is fair to approximate \( p_1 \approx 1 \). Given that the degeneracy of the first excited level is four times that of the ground level, the probability to find the atom in a state with \( n = 2 \) is \( 4p_2/p_1 \approx 3 \times 10^{-179} \).

**Solution to Exercise 4.48**

a) Solving Eqs. (4.62) for \( \theta \) and \( \phi \), we find

\[
\theta = 2\arccos|\psi_1|; \quad \phi = \arg(\psi_1/\psi_2). \tag{S4.35a, S4.35b}
\]

This solution exists for any pair \((\psi_1, \psi_2)\) as long as \(|\psi_1|^2 + |\psi_2|^2 = 1\) and \(\psi_1, \psi_2 \in \mathbb{R}\). This solution is unique within the intervals \(\theta \in [0, \pi], \phi \in [0, 2\pi]\).

b) See the solution to Ex. 4.28(a).

c) In Ex. 4.28(b), we found that \(\langle S_{x,y,z} \rangle = \frac{\hbar}{2} \left( \hat{R}_{\theta\phi} \right)_{x,y,z} \). On the other hand, the Pauli operators and the components of the spin for spin-\(\frac{1}{2}\) particles are related according to \(\hat{S}_{x,y,z} = \frac{\hbar}{2} \hat{\sigma}_{x,y,z}\) (Ex. 4.26). Combining these two results together, we find that \(\langle \hat{R}_{\theta\phi} \rangle_{x,y,z} = \langle \hat{\sigma}_{x,y,z} \rangle\).

**Solution to Exercise 4.49**

A point on the Bloch sphere surface is defined by two real numbers. On the other hand, subspaces with \( l \geq 1 \) have dimension of \(2l+1 \geq 3\). This means that at least three complex numbers are needed to define each element of such a subspace.

**Solution to Exercise 4.51**

If point \( A \) on a sphere has polar coordinates \((\theta, \phi)\), the opposite point is at \((\pi - \theta, \pi + \phi)\). The corresponding quantum states according to Eq. (4.62) are

\[
|\psi_A\rangle \simeq \left( \begin{array}{c}
\cos \frac{\theta}{2} e^{i\phi} \\
\sin \frac{\theta}{2} e^{i\phi}
\end{array} \right);
\]

\[
|\psi_B\rangle \simeq \left( \begin{array}{c}
\cos \frac{\pi - \theta}{2} e^{i(\pi + \phi)} \\
\sin \frac{\pi - \theta}{2} e^{i(\pi + \phi)}
\end{array} \right) = \left( \begin{array}{c}
\sin \frac{\theta}{2} e^{i\phi} \\
-\cos \frac{\theta}{2} e^{i\phi}
\end{array} \right).
\]

\textsuperscript{1} Strictly speaking, the solution for \( \phi \) is indefinite if either \( \psi_1 \) or \( \psi_2 \) vanish. However, these cases still correspond to unique Bloch vectors pointing to the north and south poles of the Bloch sphere, respectively.
Hence $\langle \psi_A | \psi_B \rangle = 0$.

**Solution to Exercise 4.52**

a) According to Eq. (1.5a), a half-wave plate with its optic axis oriented at angle $\alpha$ will transform the horizontally polarized state $|H\rangle \simeq \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ into $|2\alpha\rangle \simeq \begin{pmatrix} -\cos 2\alpha \\ -\sin 2\alpha \end{pmatrix}$. Removing the overall phase factor and reconciling this result with Eqs. (4.62), we find the spherical angles of the corresponding Bloch vector: $\theta = 4\alpha$, $\phi = 0$. So the locus of the resulting polarization states on the Bloch sphere is the meridian crossing the $x$ axis (Fig. S4.1).

![Fig. S4.1](solution_to_exercise_4.52.png)

Solution to Exercise 4.52. The loci on the Bloch sphere corresponding to the states obtained from the horizontal polarization state by half- and quarter-wave plates oriented at different angles.

b) According to Eq. (1.5b), a quarter-wave plate operator transforms state $|H\rangle \simeq \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ into

$$\hat{A}_{\text{QWP}} |H\rangle = \begin{pmatrix} i \cos^2 \alpha + \sin^2 \alpha \\ -(1 - i) \sin \alpha \cos \alpha \end{pmatrix}.$$

Applying Eqs. (S4.35) to this result, we obtain expressions for $\theta$ and $\phi$. The corresponding locus on the Bloch sphere is shown in Fig. S4.1. For the values of $\alpha = \pm \pi/4$, it crosses the $y$ axes, which corresponds to the two circular polarizations.

**Solution to Exercise 4.53** As we found when solving Ex. 4.28, the eigenstates of the projection $\hat{S}_{\theta\phi}$ of the spin onto vector $\hat{R}_{\theta\phi}$ are given by
\[ |↑_{θφ}⟩ = \cos \frac{θ}{2} |↑⟩ + \sin \frac{θ}{2} e^{iθ} |↓⟩; \quad (S4.36a) \]
\[ |↓_{θφ}⟩ = \sin \frac{θ}{2} |↑⟩ - \cos \frac{θ}{2} e^{iθ} |↓⟩. \quad (S4.36b) \]

Projecting Alice’s portion of state \(|Ψ^−⟩\) onto each of these eigenstates, we find for Bob:

\[ \langle ↑_{θφ, Alice} |Ψ^−⟩ = \frac{1}{\sqrt{2}} \left( \cos \frac{θ}{2} |↓⟩ - \sin \frac{θ}{2} e^{-iθ} |↑⟩ \right); \quad (S4.37a) \]
\[ \langle ↓_{θφ, Alice} |Ψ^−⟩ = \frac{1}{\sqrt{2}} \left( \sin \frac{θ}{2} |↓⟩ + \cos \frac{θ}{2} e^{-iθ} |↑⟩ \right). \quad (S4.37b) \]

Multiplying states (S4.37a,b) by the phase factors \(-e^{iθ}\) and \(e^{iθ}\), respectively, we find these states to be physically equivalent to \(\frac{1}{\sqrt{2}} |↓_{θφ}⟩\) and \(\frac{1}{\sqrt{2}} |↑_{θφ}⟩\), respectively. In other words, projecting Alice’s portion of the Bell state \(|Ψ^−⟩\) onto any state will yield the state with the opposite Bloch vector with Bob. This is a consequence of the isotropic nature of \(|Ψ^−⟩\) (Ex. 2.8).

The factor of \(\frac{1}{\sqrt{2}}\) implies that both events occur with probability \(\frac{1}{2}\).

Note also that some particular cases of this problem have been analyzed in Ex. 2.26 and 2.37.

**Solution to Exercise 4.54.** Let \(ω\) be the angular frequency of the particle’s orbital motion. The particle makes a full circle during the period \(T = \frac{2π}{ω}\). Charge \(e\) passing through each point of the orbit during time \(T\) means that the current associated with this motion is \(I = e/T = eω/2π\). The area of the orbit is \(A = πr^2\), where \(r\) is the radius. Substituting these quantities into Eq. (4.64), we find for the magnetic moment

\[ \mu = IA = \frac{eωr^2}{2}. \]

On the other hand, the mechanical angular momentum of the orbiting particle is \(L = m_eωr^2\). The magnetic moment can thus be expressed as

\[ \mu = L \frac{e}{2M_e}. \]

Both the angular momentum and the magnetic moment are actually vectors directed orthogonally out of the plane of the orbit. Therefore, the above expression is also valid in its vector form.

**Solution to Exercise 4.55.**

a) Equation (4.67) holds for all three components of the angular momentum; in particular, the \(z\)-component:

\[ \mu_z = γL_z. \]

The state with a definite magnetic quantum number \(m\) is an eigenstate of \(\hat{L}_z\) with the eigenvalue \(L_z = ℏm\). We can thus write the \(z\) component of the magnetic moment in that state as

\[ \mu_z = γℏm. \]

b) Let us choose the direction of the \(z\) axis along \(\hat{B}\). According to Eq. (4.66), we then have
\[ E = - \mu B = - \gamma \hbar mB. \]

**Solution to Exercise 4.57** The state of the electron corresponds to the point \((\theta, \phi)\) on the Bloch sphere and is decomposed into the canonical basis according to Eq. (4.62). Because the Stern-Gerlach procedure is a measurement of the component of the spin component along the magnetic field — that is, the observable \(\hat{S}_z\) — we have

\[
\begin{align*}
\text{pr}_\uparrow &= |\psi_\uparrow|^2 = \cos^2 \frac{\theta}{2}; \\
\text{pr}_\downarrow &= |\psi_\downarrow|^2 = \sin^2 \frac{\theta}{2}.
\end{align*}
\]

**Solution to Exercise 4.58** Equation (4.75) is derived under the assumption that the magnetic field is pointing along the \(z\) axis. The projection of the spin vector onto that axis (i.e. the direction of the field) plays the role of the observable that defines the measurement basis. The gradient, on the other hand, determines the direction of the force.

**Solution to Exercise 4.59** The subspace associated with \(s = 1\) is 3-dimensional, so the operator \(\hat{S}_y\), measured in this setup has three eigenvalues. Hence the measurement can yield three possible outcomes. To find the splitting proportion, we utilize the Measurement Postulate [Eq. (1.3)] and the result of Ex. 4.27 to write, for the state \(\psi = |m_x = 0\rangle\) being measured:

\[
\begin{align*}
\text{pr}_{m_y = 1} &= |\langle m_y = 1 | m_x = 0 \rangle|^2 = \frac{1}{2}; \\
\text{pr}_{m_y = 0} &= |\langle m_y = 0 | m_x = 0 \rangle|^2 = 0; \\
\text{pr}_{m_y = -1} &= |\langle m_y = -1 | m_x = 0 \rangle|^2 = \frac{1}{2}.
\end{align*}
\]

So although we generally expect to see three spots in a Stern-Gerlach experiment with spin-1 particles, in this case the middle spot will have no events; the probabilities divide equally between the two spots corresponding to \(m_y = \pm 1\).

**Solution to Exercise 4.60** The Stern-Gerlach measurement is that of the spin component \(\hat{S}_y\) with \(\vec{R}\) characterized by the polar angles \((\theta_0, 0)\). The probabilities of possible measurement outcomes are given by the Measurement Postulate of quantum mechanics: \(\text{pr}_i = |\langle v_i | \psi \rangle|^2\), where \(\psi\) is the input state, whose canonical representation is \(\psi \simeq \begin{pmatrix} 0 \\ 1 \end{pmatrix}\), and \(v_i\) are the eigenstates of \(\hat{S}_y\) given by Eq. (S4.37). The associated detection probabilities are therefore

\[
\begin{align*}
\text{pr}_{\uparrow \theta_0} &= |\langle \uparrow \theta_0 | \psi \rangle|^2 = \cos^2 (\theta_0/2); \\
\text{pr}_{\downarrow \theta_0} &= |\langle \downarrow \theta_0 | \psi \rangle|^2 = \sin^2 (\theta_0/2).
\end{align*}
\]

**Solution to Exercise 4.61** The evolution in the Heisenberg picture of the \(j\)th component of the angular momentum under Hamiltonian (4.76) is as follows
\[
\hat{L}_k = \frac{i}{\hbar} [\hat{H}, \hat{L}_k] \\
= \frac{i}{\hbar} \gamma [\hat{L} B_j, \hat{L}_k] \\
= -\frac{i}{\hbar} \gamma B_j [\hat{L}_j, \hat{L}_k] \\
\text{Ex 4.11} \\
= \frac{i}{\hbar} \gamma B_j i\hbar \varepsilon_{ijkl} \hat{L}_l \\
= \varepsilon_{ijkl} \hat{L}_j \gamma B_j.
\]

The last line is equal to the \(k\)th component of \(\gamma \hat{L} \times \vec{B}\), which is identical to the classical result \(4.68\).

**Solution to Exercise 4.62**

a) The Hamiltonian associated with the magnetic field along the \(z\) axis is given by

\[
\hat{H} = -\gamma \hat{S} \cdot \vec{B} - \Omega_L \hat{S}_z - \frac{\hbar \gamma}{2} \Omega_L \hat{\sigma}_z.
\]

The evolution of the electron’s spin is governed by the Schrödinger equation

\[
|\psi(t)\rangle = -\frac{i}{\hbar} \hat{H} |\psi\rangle,
\]

whose solution is

\[
|\psi(t)\rangle = e^{-\frac{i}{\hbar} \hat{H}t} |\psi(0)\rangle = e^{\frac{i}{\hbar} \Omega_L t \hat{\sigma}_z} |\psi(0)\rangle.
\]

This matrix exponent has already been calculated in Ex. A.94

\[
e^{-\frac{i}{\hbar} \hat{H}t} = \begin{pmatrix} e^{\frac{i}{\hbar} \Omega_L t} & 0 \\ 0 & e^{-\frac{i}{\hbar} \Omega_L t} \end{pmatrix}.
\]

Applying this evolution to the eigenstate \(4.62\) of the spin \(\hat{S} \vec{R}\) oriented along vector \(\vec{R}\) characterized by polar angles \((\theta_0, \phi_0)\), we obtain

\[
|\psi(t)\rangle = e^{-\frac{i}{\hbar} \hat{H}t} |\psi(0)\rangle = e^{\frac{i}{\hbar} \Omega_L t \hat{\sigma}_z} |\psi(0)\rangle
\]

\[
= \begin{pmatrix} e^{\frac{i}{\hbar} \Omega_L t} \cos(\theta_0/2) & e^{\frac{i}{\hbar} \Omega_L t} \sin(\theta_0/2) e^{i\phi_0} \\ e^{-\frac{i}{\hbar} \Omega_L t} \sin(\theta_0/2) e^{i\phi_0} & e^{-\frac{i}{\hbar} \Omega_L t} \cos(\theta_0/2) \end{pmatrix}
\]

Comparing this result with Eq. \(4.62\), we find that the state after the evolution is physically equivalent to an eigenstate of the spin \(\hat{S}_{\vec{R}'}\) with \(\vec{R}'\) characterized by spherical angles \((\theta_0, \phi_0 - \Omega_L t)\). In other words, the spin precesses at frequency \(\Omega_L\) around the \(z\) axis.
The trajectory on the Bloch sphere corresponds to the parallel with the polar angle \(\theta_0\) [Fig. S.4.2(a)]. The Stern-Gerlach procedure constitutes a measurement of \(\hat{S}_z\) in the state \(|\psi(t)\rangle\). We find the probability to detect \(|\uparrow\rangle\) as \(p_{\uparrow} = |\langle \uparrow | \psi(t) \rangle|^2 = \cos^2 \frac{\theta_0}{2}\) and the probability to detect \(|\downarrow\rangle\) as \(p_{\downarrow} = |\langle \downarrow | \psi(t) \rangle|^2 = \sin^2 \frac{\theta_0}{2}\). These probabilities are time-independent.

b) Because the magnetic field is in the \(y\) direction, we can write

\[
\hat{H} = -\hat{\mu}_y B = -\frac{\hbar}{2} \Omega_L \hat{\sigma}_y.
\]

The initial state has the matrix

\[
|\psi(0)\rangle \simeq \begin{pmatrix} 1 \\ 0 \end{pmatrix}.
\]

The solution of the Schrödinger equation in this case is

\[
|\psi(t)\rangle = e^{-\frac{i}{\hbar} \hat{H} t} |\psi(0)\rangle = e^{\frac{i}{2} \Omega_L t \hat{\sigma}_y} |\psi(0)\rangle.
\]

Referring, once again, to Ex. A.94

\[
e^{\frac{i}{2} \Omega_L t \hat{\sigma}_y} = \begin{pmatrix} \cos(\Omega_L t/2) & \sin(\Omega_L t/2) \\ -\sin(\Omega_L t/2) & \cos(\Omega_L t/2) \end{pmatrix},
\]

we find the evolution of the spin:

\[
|\psi(t)\rangle \simeq \begin{pmatrix} \cos(\Omega_L t/2) & \sin(\Omega_L t/2) \\ -\sin(\Omega_L t/2) & \cos(\Omega_L t/2) \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \cos(\Omega_L t/2) \\ -\sin(\Omega_L t/2) \end{pmatrix}.
\]

The spherical coordinates on the Bloch sphere are \((\theta = \Omega_L t, \phi = 0)\). Accordingly, the trajectory on the Bloch sphere is the meridian crossing the \(x\) axis [Fig. S.4.2(b)]. The Stern-Gerlach measurement will yield the probabilities \(p_{\uparrow} = \cos^2 (\Omega_L t/2)\) and \(p_{\downarrow} = \sin^2 (\Omega_L t/2)\).

c) We proceed along the lines of the previous problem’s solution, but the Hamiltonian is now

\[
\hat{H} = -\vec{\mu} \cdot \vec{B} = -\gamma \vec{\sigma} \cdot \vec{B} = -\frac{\hbar}{2} \gamma \vec{\sigma} \cdot \vec{B},
\]

where \(\vec{\sigma} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)\) is the “vector” consisting of Pauli operators. The evolution under this Hamiltonian is then given by

\[
e^{-\frac{i}{\hbar} \hat{H} t} = e^{\frac{i}{2} \gamma \vec{\sigma} \cdot \vec{v}} = e^{\frac{i}{2} \gamma \vec{\sigma} \cdot \vec{v}},
\]

where \(\vec{v} = (\sin \theta_0, 0, \cos \theta_0)\) is the unit length vector in the direction of the magnetic field.

Now we are in position to apply the result of Ex. A.93. We find

\[2\] This corresponds to the geographical latitude \(\pi/2 - \theta\).
Fig. S4.2 The trajectories on the Bloch sphere given by the three parts of Ex. 4.62. The trajectory for part (c) is calculated for $\theta_0 = \pi/3$.

\[ e^{-\frac{i}{\hbar}Ht} = \cos(\Omega L t/2) \mathbf{1} + i\sin(\Omega L t/2) \mathbf{\hat{r}} \cdot \mathbf{\hat{G}} \]
\[ \simeq \cos(\Omega L t/2) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + i\sin(\Omega L t/2) \begin{pmatrix} \sin \theta_0 & 0 \\ 0 & \cos \theta_0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]
\[ = \begin{pmatrix} \cos(\Omega L t/2) + i\sin(\Omega L t/2) \cos \theta_0 \\ i\sin(\Omega L t/2) \sin \theta_0 \\ \cos(\Omega L t/2) - i\sin(\Omega L t/2) \cos \theta_0 \end{pmatrix}. \]

Applying this evolution operator to the initial state $|\psi(0)\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, we have

\[ |\psi(t)\rangle = e^{-\frac{i}{\hbar}Ht} |\psi(0)\rangle \simeq \begin{pmatrix} \cos(\Omega L t/2) + i\sin(\Omega L t/2) \cos \theta_0 \\ i\sin(\Omega L t/2) \sin \theta_0 \end{pmatrix}. \]

(S4.41)

The corresponding vector on the Bloch sphere has spherical angles

\[ \theta = 2 \arccos \sqrt{\cos^2(\Omega L t/2) + \sin^2(\Omega L t/2) \cos^2 \theta_0}; \]
\[ \phi = \arg \left( \frac{i\sin(\Omega L t/2) \sin \theta_0}{\cos(\Omega L t/2) + i\sin(\Omega L t/2) \cos \theta_0} \right). \]

When this state is subjected to the Stern-Gerlach measurement, the probability to detect the spin-up and spin-down states are, respectively,

\[ p_{\uparrow} = \langle \uparrow | \psi(t) \rangle^2 = \cos^2(\Omega L t/2) + \sin^2(\Omega L t/2) \cos^2 \theta_0; \]
\[ p_{\downarrow} = \langle \downarrow | \psi(t) \rangle^2 = \sin^2(\Omega L t/2) \sin^2 \theta_0. \]

(S4.42)

The corresponding trajectory is shown in Fig. S4.2 (c). It is a circle around the magnetic field vector that includes the north pole (the original state).
Solution to Exercise 4.63. According to Table 2.3, the operation that Bob needs to perform is, respectively, \( \sigma_y, \sigma_x, \sigma_z \) or \( \hat{I} \) independent on whether Alice’s Bell measurement yields \( |\Phi^+\rangle \), \( |\Phi^-\rangle \), \( |\Psi^+\rangle \) or \( |\Psi^-\rangle \). To implement these operations using spin precession in the magnetic field, we can use the result of Ex. A.94, which, for \( \theta = \pi/2 \), becomes \( e^{i \hat{\theta} \hat{\sigma}_j} = i \hat{\sigma}_j \), where \( j \) can be \( x, y, \) or \( z \). Operator \( e^{i \hat{\theta} \hat{\sigma}_j} \) corresponds to the evolution under the Hamiltonian \( \hat{H} = -\frac{\hbar}{2} \gamma \hat{\sigma}_j \) for time \( \tau \). Using Eq. (S4.40), we find that such a Hamiltonian is obtained when the electron spin is acted upon by the magnetic field \( \vec{B} = \frac{\gamma}{\hbar} \vec{r} \) in the direction \( j \).

Solution to Exercise 4.64. By analogy with Ex. 4.62, we write

\[
\hat{H} = -\vec{\mu} \cdot \vec{B} = -\gamma \vec{\sigma} \cdot \vec{B} = -\frac{\hbar}{2} \gamma (B_0 \hat{\sigma}_z + B_{1f} \hat{\sigma}_x \cos \omega t) \approx \frac{\hbar}{2} \begin{pmatrix} -\Omega_0 & -\gamma B_{1f} \cos \omega t \\ -\gamma B_{1f} \cos \omega t & \Omega_0 \end{pmatrix}.
\]

To find the evolution of the spin vector matrix, we write the Schrödinger equation in the matrix form akin to Eq. (1.32):

\[
\begin{pmatrix} \frac{d}{dt} \psi_i \,(t) \\ \psi_i \,(t) \end{pmatrix} = -\frac{i}{\hbar} \begin{pmatrix} -\Omega_0 & -\gamma B_{1f} \cos \omega t \\ -\gamma B_{1f} \cos \omega t & \Omega_0 \end{pmatrix} \begin{pmatrix} \psi_i \,(t) \\ \psi_i \,(t) \end{pmatrix},
\]

thereby obtaining Eq. (4.80).

Solution to Exercise 4.65. A state \( |\psi(t)\rangle \) with the matrix

\[
\begin{pmatrix} \psi_i \,(t) \\ \psi_i \,(t) \end{pmatrix} = \begin{pmatrix} \cos \theta \\ \sin \theta e^{i\phi} \end{pmatrix}
\]

in the stationary basis corresponds to the Bloch vector with the polar coordinates \( (\theta, \phi) \). In the rotating basis, according to Eqs. (4.82), this state has the matrix

\[
|\psi(t)\rangle \approx \begin{pmatrix} \psi_i \,(t) \\ \psi_i \,(t) \end{pmatrix} = \begin{pmatrix} e^{-i \frac{\omega t}{2}} \psi_i \,(t) \\ e^{i \frac{\omega t}{2}} \psi_i \,(t) \end{pmatrix},
\]

which is physically equivalent to

\[
\begin{pmatrix} \psi_i \,(t) \\ e^{i \omega t} \psi_i \,(t) \end{pmatrix} = \begin{pmatrix} \cos \theta \\ \sin \theta e^{i\phi+i\omega t} \end{pmatrix},
\]

so the corresponding Bloch vector has the polar coordinates \( (\theta, \phi + \omega t) \).

Solution to Exercise 4.66. Substituting Eqs. (4.82) into Eqs. (4.80), we find

\[
\begin{align*}
\dot{\psi}_i e^{i \omega t} + \frac{i}{2} \omega \psi_i e^{i \omega t} &= \frac{i}{2} \Omega_0 \psi_i e^{i \omega t} + \frac{i \gamma}{2} B_{1f} \psi_i e^{-i \omega t} \cos \omega t; \\
\dot{\psi}_i e^{-i \omega t} - \frac{i}{2} \omega \psi_i e^{-i \omega t} &= -\frac{i}{2} \Omega_0 \psi_i e^{-i \omega t} + \frac{i \gamma}{2} B_{1f} \psi_i e^{i \omega t} \cos \omega t.
\end{align*}
\]  

(S4.43a)  

(S4.43b)

Multiplying both sides of Eqs. (S4.43a,b) respectively by \( e^{\pm i \omega t} \) and moving the second term in the left-hand sides of both equations to the right-hand sides, we have
\[ \dot{\psi}_\uparrow = -\frac{i}{2} \Delta \psi_\uparrow + \frac{i\gamma}{2} B_{ef} \psi_\uparrow e^{-i\omega t}; \quad (S4.44a) \]
\[ \dot{\psi}_\downarrow = \frac{i}{2} \Delta \psi_\downarrow + \frac{i\gamma}{2} B_{ef} \psi_\uparrow e^{i\omega t}. \quad (S4.44b) \]

Now expressing \( \cos \omega t = \frac{e^{i\omega t} + e^{-i\omega t}}{2} \), we obtain Eqs. (4.83).

**Solution to Exercise 4.67.** Under the rotating-wave approximation, Eqs. (4.83) become
\[ \dot{\psi}_\uparrow = -\frac{i}{2} \Delta \psi_\uparrow + \frac{i}{2} \Omega \psi_\downarrow; \quad (S4.45a) \]
\[ \dot{\psi}_\downarrow = \frac{i}{2} \Delta \psi_\downarrow + \frac{i}{2} \Omega \psi_\uparrow, \quad (S4.45b) \]
where we substituted \( \Omega = \frac{\gamma B_{ef}}{2} \). On the other hand, writing the Schrödinger equation in the matrix form akin to Eq. (1.32) for the state \( |\psi(t)\rangle = \begin{pmatrix} \psi_\uparrow(t) \\ \psi_\downarrow(t) \end{pmatrix} \) and Hamiltonian (4.84), we obtain
\[ \begin{pmatrix} \dot{\psi}_\uparrow(t) \\ \dot{\psi}_\downarrow(t) \end{pmatrix} = -\frac{i}{\hbar} \begin{pmatrix} \Delta & -\Omega \\ -\Omega & -\Delta \end{pmatrix} \begin{pmatrix} \psi_\uparrow(t) \\ \psi_\downarrow(t) \end{pmatrix} = -\frac{i}{2} \begin{pmatrix} \Delta \psi_\uparrow(t) - \Omega \psi_\downarrow(t) \\ -\Omega \psi_\uparrow(t) - \Delta \psi_\downarrow(t) \end{pmatrix}, \]
which is the same as Eqs. (S4.45).

**Solution to Exercise 4.68.** The Hamiltonian associated with the field (4.86) is calculated via Eq. (S4.40) as
\[ \hat{H} = -\hat{\mu} \cdot \hat{B} = -\frac{\hbar}{2} \gamma \hat{\sigma} \cdot \hat{B} = -\frac{\hbar}{2} \gamma \left( \hat{\sigma}_x \frac{\Omega}{\gamma} - \hat{\sigma}_z \frac{\Delta}{\gamma} \right) \approx \frac{\hbar}{2} \begin{pmatrix} \Delta & -\Omega \\ -\Omega & -\Delta \end{pmatrix}, \quad (S4.46) \]
which is the same as Eq. (4.84).

**Solution to Exercise 4.69.** Referring to Fig. 4.9(a), the Bloch vector at the bottom point of the trajectory has spherical coordinates \( (\theta = 2\theta_0, \phi = 0) \). The corresponding state is
\[ \begin{pmatrix} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} e^{i\phi} \end{pmatrix} = \begin{pmatrix} \cos \theta_0 \\ \sin \theta_0 \end{pmatrix}, \]
so
\[ p_{\uparrow_{\text{max}}} = \sin^2 \theta_0 = \frac{B_x^2}{B_x^2 + B_z^2} \quad (4.86) \]
\[ \frac{\Omega^2}{\Omega^2 + \Delta^2}. \]

**Solution to Exercise 4.70.** This problem is equivalent to Ex. 4.62(c) with \( \Omega_L = \gamma B = \sqrt{\Omega^2 + \Delta^2} \). The state evolution is given by Eq. (S4.41) and the probabilities to observe the spin-up and spin-down states by Eqs. (S4.42). The highest value of \( p_{\uparrow} \) is observed when \( \sin^2(\Omega_L t/2) = 1 \) (i.e., when \( \Omega_L t = \pi, 3\pi, \ldots \)) and equals \( p_{\uparrow_{\text{max}}} = \sin^2 \theta_0 \) in agreement with Ex. 4.69. For example, for \( \Delta = -\Omega / \sqrt{3} \), \( \theta_0 = \frac{\pi}{3} \), so \( p_{\uparrow_{\text{max}}} = \frac{3}{4} \).

**Solution to Exercise 4.71.**
a) Following the solution of Ex. 4.66, but using \( \cos(\omega t + \beta) = (e^{i\omega t + i\beta} + e^{-i\omega t - i\beta})/2 \), we obtain the following differential equations for the evolution in the rotating basis:

\[
\dot{\psi}_\uparrow = -\frac{i}{2} \Delta \psi_\uparrow + \frac{i}{2} \Omega (e^{i\beta} + e^{-2i\omega t - i\beta}) \psi_\downarrow; \\
\dot{\psi}_\downarrow = \frac{i}{2} \Delta \psi_\downarrow + \frac{i}{2} \Omega (e^{-i\beta} + e^{2i\omega t + i\beta}) \psi_\uparrow.
\]

Neglecting the quickly oscillating terms, we determine the rotating-wave Hamiltonian and decompose it into Pauli operators:

\[
\hat{H}_{RWA}(\beta) \simeq \frac{\hbar}{2} \begin{pmatrix} \Delta & -\Omega e^{i\beta} \\ -\Omega e^{-i\beta} & -\Delta \end{pmatrix} \\
= \frac{\hbar}{2} \begin{pmatrix} \Delta & -\Omega \cos \beta - i\Omega \sin \beta \\ -\Omega \cos \beta + i\Omega \sin \beta & -\Delta \end{pmatrix} \\
= \frac{\hbar}{2} (\hat{\sigma}_z - \Omega \hat{\sigma}_x \cos \beta + \Omega \hat{\sigma}_y \sin \beta).
\]

This Hamiltonian can be written as \( \hat{H}_{RWA}(\beta) = -\frac{\hbar}{2} \gamma \vec{\sigma} \cdot \vec{B} \) with the corresponding fictitious magnetic field is

\[
\vec{B} = (\Omega / \gamma \cos \beta, -\Omega / \gamma \sin \beta, -\Delta / \gamma).
\]

On resonance (\( \Delta = 0 \)), it is directed horizontally at angle \(-\beta\) to the \( x \) axis.

b) Hamiltonian (4.79) takes the form

\[
H = -\frac{\hbar}{2} \gamma [B_0 \hat{\sigma}_z + B_{RF} \hat{\sigma}_y \cos(\omega t + \beta)] \simeq \frac{\hbar}{2} \begin{pmatrix} -\Omega_0 & i\gamma B_{RF} \cos(\omega t + \beta) \\ -i\gamma B_{RF} \cos(\omega t + \beta) & \Omega_0 \end{pmatrix},
\]

the evolution in the rotating basis

\[
\dot{\psi}_\uparrow = -\frac{i}{2} \Delta \psi_\uparrow + \frac{1}{2} \Omega (e^{i\beta} + e^{-2i\omega t - i\beta}) \psi_\downarrow; \\
\dot{\psi}_\downarrow = \frac{i}{2} \Delta \psi_\downarrow - \frac{1}{2} \Omega (e^{-i\beta} + e^{2i\omega t + i\beta}) \psi_\uparrow,
\]

and the rotating-wave Hamiltonian

\[
\hat{H}_{RWA}(\beta) \simeq \frac{\hbar}{2} \begin{pmatrix} \Delta & i\Omega e^{i\beta} \\ -i\Omega e^{-i\beta} & -\Delta \end{pmatrix} \\
= \frac{\hbar}{2} \begin{pmatrix} \Delta & i\Omega \cos \beta - \Omega \sin \beta \\ -i\Omega \cos \beta - \Omega \sin \beta & -\Delta \end{pmatrix} \\
= \frac{\hbar}{2} (\hat{\sigma}_z - \Omega \hat{\sigma}_x \sin \beta - \Omega \hat{\sigma}_y \cos \beta).
\]

The corresponding fictitious magnetic field is

\[
\vec{B} = (\Omega / \gamma \sin \beta, \Omega / \gamma \cos \beta, -\Delta / \gamma).
\]
On resonance, it is directed horizontally at angle $-\beta$ to the $y$ axis, or $\pi/2 - \beta$ to the $x$ axis.

In both cases (a) and (b), the magnitude of the field is given by Eq. (4.85).

We see that changing the azimuthal angle and phase of the rf field amplitude has a similar effect in the rotating basis: it changes the azimuthal angle of the fictitious magnetic field.

**Solution to Exercise 4.72** In this case, Hamiltonian (4.79) becomes diagonal:

$$H = -\frac{\hbar}{2} (B_0 + B_{\text{rf}} \cos \omega t) \vec{\sigma}_z \simeq -\frac{\hbar}{2} \begin{pmatrix} \Omega_0 + \gamma B_{\text{rf}} \cos (\omega t + \beta) & 0 \\ 0 & -\Omega_0 - \gamma B_{\text{rf}} \cos (\omega t + \beta) \end{pmatrix}, \quad (S4.54)$$

so the differential equations for the evolution are

$$\dot{\psi}_\uparrow = \frac{i}{2} (\Omega_0 + \gamma B_{\text{rf}} \cos \omega t) \psi_\uparrow; \quad (S4.55a)$$

$$\dot{\psi}_\downarrow = -\frac{i}{2} (\Omega_0 + \gamma B_{\text{rf}} \cos \omega t) \psi_\downarrow. \quad (S4.55b)$$

Such evolution can only change the quantum phases of the spin-up and spin-down components of the state, but not their absolute values.

**Solution to Exercise 4.73** To determine the operator associated with a $\pi/2$ pulse with an arbitrary phase $\beta$, we use the result of Ex. 4.71 with $\Delta = 0$:

$$e^{-i \hat{H}_{\text{RF}}(\beta)t} = -\frac{\hbar}{2} \gamma \vec{v} \cdot \vec{B} = e^{i \vec{v} \cdot \vec{\sigma}},$$

where $\vec{v} = (\cos \beta, -\sin \beta, 0)$ is a unit vector. Now using Ex. A.93 we find

$$e^{-i \hat{H}_{\text{RF}}(\beta)t} \simeq \cos(\Omega t/2) \mathbb{1} + i \sin(\Omega t/2) \vec{v} \cdot \vec{\sigma}$$

$$= \cos(\Omega t/2) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + i \sin(\Omega t/2) \begin{pmatrix} \cos \beta & 0 & -i \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$$

$$= \begin{pmatrix} \cos(\Omega t/2) & i \sin(\Omega t/2) \cos \beta & i \sin(\Omega t/2) \sin \beta \\ i \sin(\Omega t/2) \cos \beta & \cos(\Omega t/2) & \sin(\Omega t/2) \cos \beta \\ i \sin(\Omega t/2) \sin \beta & \sin(\Omega t/2) \cos \beta & \cos(\Omega t/2) \end{pmatrix}.$$

Specializing to the $\pi/2$ pulse ($\Omega t = \pi/2$), this becomes

$$\hat{U}_{\pi/2}(\beta) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & e^{-i\beta} \\ ie^{i\beta} & 1 \end{pmatrix}. \quad (S4.56)$$

We are applying a sequence of two such pulses with phases 0 and $\beta$ in the first and second pulses, respectively, to a spin-up state. Accordingly:
\[ \hat{U}_{\pi/2}(\beta)\hat{U}_{\pi/2}(0)|\uparrow\rangle \simeq \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & ie^{i\beta} \\ ie^{-i\beta} & 1 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \]

\[ = \frac{1}{2} \begin{pmatrix} 1 & i e^{i\beta} \\ ie^{-i\beta} & 1 \end{pmatrix} \frac{1}{i} \]

\[ = \frac{1}{2} \begin{pmatrix} 1 - e^{i\beta} \\ i(1 + e^{-i\beta}) \end{pmatrix} \]

\[ = i \left( -e^{i\beta/2} \sin \frac{\beta}{2} \right) \left( e^{-i\beta/2} \cos \frac{\beta}{2} \right), \]

so the final probability of the spin-down state is \( p_{\downarrow} = \cos^2 \beta/2 \). The case of \( \beta = 0 \) corresponds to two \( \pi/2 \) pulses applied in an immediate sequence without any phase shift, making up a \( \pi \) pulse so the spin flips: \( p_{\downarrow} = \cos^2 0 = 1 \).

In contrast, shifting the phase by \( \beta = \pi \) means that the fictitious magnetic field \( S4.49 \) flips the direction between the two pulses, so the precession during the first and second pulses will be in opposite direction. Hence the particle will return to the spin-up state: \( p_{\downarrow} = \cos^2 \pi/2 = 0 \).

Solution to Exercise 4.74

a) Applying a \( \pi/2 \) pulse to the spin-up state will transform it into the state with the spin pointing along the y axis. After the rf field has been turned off, the fictitious magnetic field \( S4.86 \) is parallel to the z axis. Hence the Bloch vector precesses around that axis at the frequency \( -\Delta \), so its azimuthal angle at time \( t \) is \( \pi/2 + \Delta t \). This vector’s Cartesian coordinates are

\[ \vec{R} = \left( \cos \left( \frac{\pi}{2} + \Delta t \right), \sin \left( \frac{\pi}{2} + \Delta t \right), 0 \right) = (-\sin \Delta t, \cos \Delta t, 0). \]

Since \( \vec{R} = \langle \hat{\sigma} \rangle \) (Ex. 4.48) and the magnetic moment is related to the spin according to \( \hat{\mu} = \gamma \hat{S} = \frac{\hbar}{2} \hat{\sigma} \), we have

\[ \langle \hat{\mu} \rangle = \frac{\hbar}{2} \vec{R} = \frac{\hbar}{2} \left( -\sin \Delta t, \cos \Delta t, 0 \right). \]

b) As we know from Ex. 4.65, the Bloch vectors in the stationary and rotating basis are related by a rotational transformation by angle \( \omega t \) around the z axis. Since we found in part (a) that the Bloch vector in the rotating basis precesses at frequency \(-\Delta \) around that axis, the precession frequency in the stationary basis is \(-\Delta + \omega = \Omega_0 t \), so the azimuthal angle at time \( t \) is \( \pi/2 - \Omega_0 t \). Following the logic of part (a), we find for magnetic moment vector

\[ \langle \hat{\mu} \rangle = \frac{\hbar}{2} \left( \sin \Omega_0 t, \cos \Omega_0 t, 0 \right). \]

Solution to Exercise 4.75

Using the result of Ex. 4.74a, we average over all the detunings to find

\[ 3 \text{ Mind the sign: } \vec{B} \text{ points along the negative z axis for positive } \Delta. \text{ This means that, for positive } \Delta, \text{ the azimuthal angle of the Bloch vector increases with time. This is in contrast with e.g. Ex. 4.62a, where the field is in the positive z direction and the azimuthal angle of the Bloch vector decreases with time.} \]
This vector continues to precess with the frequency $\omega$. Solution to Exercise 4.76 used the result of Ex. D.9(c).

Now integrating the $y$ component of that vector over all detunings, we find, by analogy with the previous exercise,

$$
\langle \mu_y \rangle = \int p(\Delta) \langle \mu_y \rangle \, d\Delta = \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\Delta_0}} e^{-\left(\frac{\Delta}{\Delta_0}\right)^2} \frac{\hbar \gamma}{2} \sin \Delta \, d\Delta = 0;
$$

$$
\langle \mu_z \rangle = \int p(\Delta) \langle \mu_z \rangle \, d\Delta = \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\Delta_0}} e^{-\left(\frac{\Delta}{\Delta_0}\right)^2} \frac{\hbar \gamma}{2} \cos \Delta \, d\Delta = \frac{\hbar \gamma}{2} e^{-\frac{(\Delta_0)^2}{4}};
$$

$$
\langle \mu_x \rangle = \int p(\Delta) \langle \mu_x \rangle \, d\Delta = 0.
$$

In the calculation of the integral for $\langle \mu_z \rangle$ we used the fact that the integrand is an odd function. For $\langle \mu_x \rangle$, we used the result of Ex. D.9(c).

**Solution to Exercise 4.76** Let us first look at the dynamics of an individual spin’s Bloch vector following the line of Ex. 4.74(a). At time $t_0$, before the $\pi$ pulse, this vector has the azimuthal angle $\phi(t_0) = \pi/2 + \Delta t_0$. The $\pi$ pulse rotates the spin by $180^\circ$ around the $x$ axis, resulting in a vector with the azimuthal angle $\phi'(t_0) = -\pi/2 - \Delta t_0$. This vector continues to precess with the frequency $-\Delta$, meaning that its azimuthal angle for $t > t_0$ is $\phi(t) = -\pi/2 - \Delta t_0 + \Delta (t - t_0) = -\pi/2 - 2\Delta t_0 + \Delta t$ and the Cartesian coordinates

$$
\hat{R}(t) = \left( \cos \left[ -\pi + \Delta (t - t_0) \right], \sin \left[ -\pi + \Delta (t - t_0) \right], 0 \right) = (\sin \Delta (t - t_0), -\cos \Delta (t - t_0), 0).
$$

Now integrating the $y$ component of that vector over all detunings, we find, by analogy with the previous exercise,

$$
\langle \mu_y \rangle = 0;
$$

$$
\langle \mu_z \rangle = -\frac{\hbar \gamma}{2} e^{-\frac{(\Delta_0)^2}{4}};
$$

$$
\langle \mu_x \rangle = 0.
$$

**Solution to Exercise 4.77**

a) Applying a pulse of area $\pi/2$ to the spin-up state will transform it into the state with the spin pointing along the $y$ axis, so the spherical coordinates of the Bloch vector are $(\theta = \pi/2, \phi = \pi/2)$. The rf field is then turned off, so the fictitious magnetic field points along the $z$ axis. During time $t$, the Bloch vector will precess around that field by angle $\Delta t$, after which it will have the coordinates $(\theta = \pi/2, \phi = \pi/2 + \Delta t)$. That is, the Bloch vector will be in the $x$-$y$ plane, at the angle $\pi/2 + \Delta t$ to the $x$ axis. The second $\pi/2$ pulse will rotate it by the right angle around the $x$ axis towards the negative $z$ axis, so the resulting Bloch vector will be in the $x$-$z$ plane, at the angle $\pi/2 + \Delta t$ to the $x$ axis, or at the angle $\pi/2 + (\pi/2 + \Delta t) = \pi + \Delta t$ with respect to the positive $z$ axis. Therefore the spherical coordinates of the final Bloch vector are $(\theta = \pi + \Delta t, \phi = 0)$, corresponding to the spin state $\left( \cos \frac{\theta}{2}, \sin \frac{\theta}{2} \right) = \left( -\sin \frac{\Delta t}{2}, \cos \frac{\Delta t}{2} \right)$. The corresponding probability of the spin-down state is $p_{-} = \cos^2 \frac{\Delta t}{2}$.

b) We calculated the evolution operator associated with the $\pi/2$ pulse in Ex. 4.75. Specializing Eq. (S4.56) to $\beta = 0$, this operator is $\hat{U}_{\pi/2}(0) = \frac{1}{\sqrt{2}} \left( \begin{array}{cc} 1 & i \\ i & 1 \end{array} \right)$. To find the evolution operator associated with the interval be-
tween the pulses, we notice that in the absence of the rf field, the rotating-wave Hamiltonian (4.84) becomes
\[
\hat{H}_{\text{RWA,0}} = \frac{\hbar}{2} \begin{pmatrix} \Delta & 0 \\ 0 & -\Delta \end{pmatrix}.
\]
The evolution under this Hamiltonian for time \( t \) is associated with operator
\[
\hat{U}_{\text{free}}(t) = e^{-i \hat{H}_{\text{RWA,0}}t} = \begin{pmatrix} e^{-\frac{i}{2} \Delta t} & 0 \\ 0 & e^{\frac{i}{2} \Delta t} \end{pmatrix}.
\]
Applying a set of operators corresponding to the Ramsey sequence to the spin-up state, we find
\[
\hat{U}_{\pi/2}(0)\hat{U}_{\text{free}}(t)\hat{U}_{\pi/2}(0) |\uparrow\rangle = \frac{1}{2} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix} \begin{pmatrix} e^{-\frac{i}{2} \Delta t} & 0 \\ 0 & e^{\frac{i}{2} \Delta t} \end{pmatrix} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}
\]
\[
= \frac{1}{2} \begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix} \begin{pmatrix} e^{-\frac{i}{2} \Delta t} & 0 \\ 0 & e^{\frac{i}{2} \Delta t} \end{pmatrix} \begin{pmatrix} 1 \\ i \end{pmatrix} \begin{pmatrix} 1 \\ i \end{pmatrix}
\]
\[
= \frac{1}{2} \left( \begin{array}{c} e^{-\frac{i}{2} \Delta t} - e^{\frac{i}{2} \Delta t} \\ i(e^{-\frac{i}{2} \Delta t} + e^{\frac{i}{2} \Delta t}) \end{array} \right)
\]
\[
= \left( \begin{array}{c} -i \sin \frac{\Delta t}{2} \\ i \cos \frac{\Delta t}{2} \end{array} \right).
\]
This is the same state as that found in part (a) up to an overall phase shift.