Problem 4.1

(a) $S_x$ has eigenvalues $\pm \hbar/2$ and corresponding normalized eigenvectors

$$|+, x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad |-, x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

The outcomes of a measurement of $S_x$ are $\pm \hbar/2$ with corresponding probabilities

$$P_+ = |\langle +, x|+\rangle|^2 = \frac{1}{2}, \quad P_- = |\langle -, x|+\rangle|^2 = \frac{1}{2}$$

The probabilities could also be deduced by a symmetry argument: the wavefunction $|+\rangle$ is symmetric under reflection $x \to -x$, therefore the two probabilities must be equal to each other.

(b) The Hamiltonian is

$$H = -\gamma B_0 S_y = \omega_0 S_y, \quad \omega_0 = -\gamma B_0$$

The eigenvalues of $H$ are $\pm \hbar \omega_0/2$ with corresponding eigenvectors

$$|+, y\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}, \quad |-, y\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ +i \end{pmatrix}$$

Expanding $|+\rangle$ in this basis, we obtain

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}} |+, y\rangle + \frac{1}{\sqrt{2}} |-, y\rangle$$

therefore

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} e^{-i\omega_0 t/2} |+, y\rangle + \frac{1}{\sqrt{2}} e^{+i\omega_0 t/2} |-, y\rangle = \begin{pmatrix} \cos(\omega_0 t/2) \\ \sin(\omega_0 t/2) \end{pmatrix}$$

which may also be written as

$$|\psi(t)\rangle = \cos \frac{\omega_0 t}{2} |+\rangle - \sin \frac{\omega_0 t}{2} |-\rangle$$

(c) The values are $\pm \hbar/2$ with probabilities

$$S_x : \quad P_+ = |\langle +, y|\psi(t)\rangle|^2 = \frac{\left[ \cos \frac{\omega_0 t}{2} - \sin \frac{\omega_0 t}{2} \right]^2}{2}, \quad P_- = \frac{\left[ \cos \frac{\omega_0 t}{2} + \sin \frac{\omega_0 t}{2} \right]^2}{2}$$
\[ S_y : P_+ = |\langle +, x |\psi(t)\rangle|^2 = \left| \frac{e^{-i\omega_0 t/2}}{\sqrt{2}} \right|^2 = \frac{1}{2}, \quad P_- = \frac{1}{2} \]

\[ S_z : P_+ = |\langle +|\psi(t)\rangle|^2 = \cos^2 \frac{\omega_0 t}{2}, \quad P_- = \sin^2 \frac{\omega_0 t}{2} \]

The measurement of \( S_x \) is certain when

\[ \tan \frac{\omega_0 t}{2} = \pm 1 \Rightarrow \omega_0 t = n\pi + \frac{\pi}{2}, \quad n \in \mathbb{Z} \]

When this condition is satisfied, \(|\psi(t)\rangle\) is an eigenstate of \( S_x \) and the outcome is certain. The measurement of \( S_y \) is never certain. This is because \(|\psi(t)\rangle\) is never in an eigenstate of \( S_y \).

The measurement of \( S_z \) is certain when either \( \cos \frac{\omega_0 t}{2} = 0 \) or \( \sin \frac{\omega_0 t}{2} = 0 \), i.e., for

\[ \omega_0 t = n\pi , \quad n \in \mathbb{Z} \]

When this condition is satisfied, \(|\psi(t)\rangle\) is an eigenstate of \( S_z \) and the outcome is certain.

**Problem 4.2**

\( a. \) Setting \( \omega_0 = -\gamma B_0 \) as usual, we have

\[ H = \omega_0 \frac{1}{\sqrt{2}} (S_x + S_z) = \frac{\hbar \omega_0}{2\sqrt{2}} \left( \begin{array}{cc} 1 & 1 \\ 1 & -1 \end{array} \right) \]

\( b. \) The eigenvalues of \( H \) are found from \( \det(H - E \mathbb{I}) = 0 \). We obtain

\[ E_1 = + \frac{\hbar \omega_0}{2}, \quad E_2 = - \frac{\hbar \omega_0}{2} \]

Corresponding eigenvectors

\[ |v_1\rangle = \frac{1}{\sqrt{2\sqrt{2}}} \left( \begin{array}{c} \sqrt{\sqrt{2} + 1} \\ \sqrt{\sqrt{2} - 1} \end{array} \right), \quad |v_2\rangle = \frac{1}{\sqrt{2\sqrt{2}}} \left( \begin{array}{c} \sqrt{\sqrt{2} - 1} \\ -\sqrt{\sqrt{2} + 1} \end{array} \right) \]

\( c. \) The outcomes of the measurement are \( E_1 \) and \( E_2 \) with corresponding probabilities

\[ P_1 = |\langle v_1|\rangle|^2 = \frac{\sqrt{2} - 1}{2\sqrt{2}}, \quad P_2 = |\langle v_2|\rangle|^2 = \frac{\sqrt{2} + 1}{2\sqrt{2}} \]
At \( t = 0 \),
\[
|\psi(0)\rangle = |\rangle = \frac{\sqrt{2} - 1}{\sqrt{2} \sqrt{2}} |v_1\rangle - \frac{\sqrt{2} + 1}{\sqrt{2} \sqrt{2}} |v_2\rangle
\]
Subsequently,
\[
|\psi(t)\rangle = \frac{\sqrt{2} - 1}{\sqrt{2} \sqrt{2}} e^{-iE_1t/\hbar} |v_1\rangle - \frac{\sqrt{2} + 1}{\sqrt{2} \sqrt{2}} e^{-iE_2t/\hbar} |v_2\rangle = \frac{1}{\sqrt{2}} \left( \sqrt{2} \cos \frac{\omega_0 t}{2} + i \sin \frac{\omega_0 t}{2} \right)
\]
The mean value of \( S_x \) is
\[
\langle \psi(t)|S_x|\psi(t)\rangle = \hbar \left( i \sin \frac{\omega_0 t}{2} \sqrt{2} \cos \frac{\omega_0 t}{2} - i \sin \frac{\omega_0 t}{2} \right) \left( \sqrt{2} \cos \frac{\omega_0 t}{2} + i \sin \frac{\omega_0 t}{2} \right) = -\hbar \sin^2 \frac{\omega_0 t}{2} = \frac{\hbar}{2} (-1 + \cos \omega_0 t)
\]
This is the \( x \)-component of a classical vector of magnitude \( \hbar/2 \) precessing around an axis in the \( xz \)-plane at 45° with respect to the negative \( x \) and \( z \) axes with angular frequency \( \omega_0 \). It starts on the \( z \)-axis, so its \( x \)-component vanishes at \( t = 0 \). It is always negative.

**Problem 4.3**

**a.** The Hamiltonian is
\[
H = -\gamma \vec{S} \cdot \vec{B} = \omega_x S_x + \omega_y S_y + \omega_z S_z = \hbar M
\]
The evolution operator is
\[
U = e^{-iHt/\hbar} = e^{-iMt}
\]
Explicitly,
\[
M = \frac{1}{2} \begin{pmatrix} \omega_x & \omega_x - i\omega_y \\ \omega_x + i\omega_y & -\omega_z \end{pmatrix}
\]
and
\[
M^2 = \frac{1}{4} \begin{pmatrix} \omega_x^2 + \omega_y^2 + \omega_z^2 & 0 \\ 0 & \omega_x^2 + \omega_y^2 + \omega_z^2 \end{pmatrix} = \frac{1}{4} (\omega_x^2 + \omega_y^2 + \omega_z^2) \mathbb{I} = \frac{\omega_0^2}{4} \mathbb{I}
\]

**b.** Expanding,
\[
U = \sum_{n=0}^{\infty} \frac{(-it)^n}{n!} M^n
\]
Since \( M^2 = \frac{\omega_0^2}{4} \mathbb{I} \), for even \( n \), \( n = 2k \), \( M^{2k} = (\frac{\omega_0}{2})^{2k} \mathbb{I} \) whereas for odd \( n \), \( n = 2k + 1 \), \( M^{2k+1} = (\frac{\omega_0}{2})^{2k} M \).
Separating the sum into even and odd \( n \), we obtain
\[
U = \sum_{k=0}^{\infty} \frac{(-i\omega_0 t/2)^{2k}}{(2k)!} \mathbb{I} + \sum_{k=0}^{\infty} \frac{(-i\omega_0 t/2)^{2k+1}}{(2k + 1)!} M \frac{2}{\omega_0} \mathbb{I} - \frac{2i}{\omega_0} \sin \frac{\omega_0 t}{2} M
\]
c. We have
\[ |\psi(t)\rangle = U|+\rangle \]
so
\[ P_{++}(t) = |\langle+|\psi(t)\rangle|^2 = |\langle+|U|+\rangle|^2 \]

Since
\[ U = \begin{pmatrix} 
\cos \frac{\omega_0 t}{2} - i \frac{\omega_z}{\omega_0} \sin \frac{\omega_0 t}{2} & -i \frac{\omega_x - i \omega_y}{\omega_0} \sin \frac{\omega_0 t}{2} \\
-i \frac{\omega_x + i \omega_y}{\omega_0} \sin \frac{\omega_0 t}{2} & \cos \frac{\omega_0 t}{2} + i \frac{\omega_y}{\omega_0} \sin \frac{\omega_0 t}{2} 
\end{pmatrix} \]
we deduce
\[ P_{++}(t) = \left| \cos \frac{\omega_0 t}{2} - i \frac{\omega_z}{\omega_0} \sin \frac{\omega_0 t}{2} \right|^2 = \cos^2 \frac{\omega_0 t}{2} + \frac{\omega^2}{\omega_0^2} \sin^2 \frac{\omega_0 t}{2} = 1 - \frac{\omega_x^2 + \omega_y^2}{\omega_0^2} \sin^2 \frac{\omega_0 t}{2} \]

This is the square of the projection onto the z-axis of a unit vector precessing about the vector \( \vec{\omega} = (\omega_x, \omega_y, \omega_z) \) starting along the z-axis (so that \( P_{++}(0) = 1 \)).

**Problem 4.4**

a. The Hamiltonian is
\[ H = H_0 + W = \begin{pmatrix} E_0 & -a & 0 \\
-a & E_0 & -a \\
0 & -a & E_0 \end{pmatrix} \]
The eigenvalues are found from \( \det(H - E\mathbb{I}) = 0 \),
\[ E_1 = E_0 + \sqrt{2}a \quad , \quad E_2 = E_0 \quad , \quad E_3 = E_0 - \sqrt{2}a \]
The corresponding normalized eigenvectors are
\[ |v_1\rangle = \frac{1}{2} \begin{pmatrix} 1 \\
-\sqrt{2} \\
1 \end{pmatrix} , \quad |v_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\
1 \\
-1 \end{pmatrix} , \quad |v_3\rangle = \frac{1}{2} \begin{pmatrix} 1 \\
\sqrt{2} \\
1 \end{pmatrix} \]

b. Expanding in stationary states,
\[ |\psi(0)\rangle = \begin{pmatrix} 1 \\
0 \\
0 \end{pmatrix} = \frac{1}{2} |v_1\rangle + \frac{1}{\sqrt{2}} |v_2\rangle + \frac{1}{2} |v_3\rangle \]
we deduce for \( t \geq 0 \),
\[ |\psi(t)\rangle = \frac{1}{2} e^{-iE_1t/h} |v_1\rangle + \frac{1}{\sqrt{2}} e^{-iE_2t/h} |v_2\rangle + \frac{1}{2} e^{-iE_3t/h} |v_3\rangle \]
The probabilities of finding the electron at $A$, $B$, $C$ are, respectively,

\[ P_A = |\langle \phi_A | \psi(t) \rangle|^2 = \left| \frac{1}{4} e^{-iE_1 t/\hbar} + \frac{1}{2} e^{-iE_2 t/\hbar} + \frac{1}{4} e^{-iE_3 t/\hbar} \right|^2 \]

\[ = \frac{1}{16} \left| e^{-i\sqrt{2}a t/\hbar} + 2 + e^{i\sqrt{2}a t/\hbar} \right|^2 = \frac{1}{4} \left( 1 + \cos \frac{\sqrt{2}a t}{\hbar} \right)^2 \]

\[ P_B = |\langle \phi_B | \psi(t) \rangle|^2 = \left| -\frac{\sqrt{2}}{4} e^{-iE_1 t/\hbar} + \frac{\sqrt{2}}{4} e^{-iE_3 t/\hbar} \right|^2 = \frac{1}{2} \sin^2 \frac{\sqrt{2}a t}{\hbar} \]

\[ P_C = |\langle \phi_C | \psi(t) \rangle|^2 = \left| \frac{1}{4} e^{-iE_1 t/\hbar} - \frac{1}{2} e^{-iE_2 t/\hbar} + \frac{1}{4} e^{-iE_3 t/\hbar} \right|^2 = \frac{1}{4} \left( 1 - \cos \frac{\sqrt{2}a t}{\hbar} \right)^2 \]

Since $P_B \leq \frac{1}{2}$, the electron is never perfectly localized about atom $B$.

It is perfectly localized about atom $A$ when $\frac{\sqrt{2}a t}{\hbar} = 2n\pi \ (n \in \mathbb{Z})$.

It is perfectly localized about atom $C$ when $\frac{\sqrt{2}a t}{\hbar} = (2n+1)\pi \ (n \in \mathbb{Z})$.

\(c\). The outcomes are $-d$, 0, $d$ with corresponding probabilities $P_A$, $P_B$, $P_C$ found above.

\(d\). The Bohr frequencies are

\[ \omega_{12} = \frac{E_1 - E_2}{\hbar} = \frac{\sqrt{2}a}{\hbar} = \omega_{23} \quad \omega_{13} = \frac{E_1 - E_3}{\hbar} = 2\frac{\sqrt{2}a}{\hbar} = 2\omega_{12} \]

$D$ may represent the dipole moment of the molecule and the Bohr frequencies are the frequencies of the electromagnetic waves emitted or absorbed by the molecule changing the state of its dipole moment.