Lecture 3

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- Hermitian Operators
  - So far, we have only considered operators acting on kets:

$$|\phi\rangle = A\,|\psi\rangle$$

  - If the operator acts on a bra it must act to the left:

$$\langle\epsilon| = \langle\psi|\,A$$

  - However, the bra, $\langle\epsilon|$, is <u>not</u> the bra that corresponds to the ket, $|\phi\rangle = A\,|\psi\rangle$
  - The bra $\langle\phi|$ is found by defining a new operator A^+ that obeys:

$$\langle\phi| = \langle\psi|\,A^+$$

    * A^+ is called the Hermitian adjoint of A. Consider the inner product:

$$\langle\phi|\beta\rangle = \langle\beta|\phi\rangle^*$$
$$\left\langle\psi|A^+|\beta\right\rangle = (\langle\beta|A|\psi\rangle)^*$$

    * This relates the matrix elements of A and A^+
    * Therefore, A^+ is found by transposing and complex conjugating the matrix representing A
  - An operator, A, is Hermitian if it is equal to its Hermitian adjoint, A^+
  - If an operator is Hermitian, then its bra, $\langle\psi|\,A$ is equal to the bra $\langle\phi|$ that corresponds to the ket $|\phi\rangle = A\,|\psi\rangle$
    * In quantum mechanics, all operators that correspond to physical observables are Hermitian
  - Hermitian matrices have real eigenvalues, which ensures results of measurements are always real-values

- The eigenvectors of Hermitian matrices comprise a complete set of basis states, which ensures the eigenvectors of any observable are a valid basis

- Projection Operators
  - Recall for a spin-1/2 system we had the identity relation:

$$|+\rangle\langle+| + |-\rangle\langle-| = \mathbb{1}$$

  - We can express this in matrix notation as:

$$\begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}1 & 0\end{pmatrix} + \begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}0 & 1\end{pmatrix} = \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$$

  - This gives us the 2x2 identity matrix
  - The individual operators, $|+\rangle\langle+|$ and $|-\rangle\langle-|$, are called projection operators:

$$P_+ = |+\rangle\langle+| = \begin{pmatrix}1 & 0\\0 & 0\end{pmatrix}$$

$$P_- = |-\rangle\langle-| = \begin{pmatrix}0 & 0\\0 & 1\end{pmatrix}$$

  - Thus, for a general state, we may write $P_+ + P_- = \mathbb{1}$
  - From here, we may write:

$$P_+|\psi\rangle = |+\rangle\langle+|\psi\rangle = (\langle+|\psi\rangle)|+\rangle$$
$$P_-|\psi\rangle = |-\rangle\langle-|\psi\rangle = (\langle-|\psi\rangle)|-\rangle$$

  - The effect of the projection operator on a given state is to produce a new, normalized state

$$|\psi'\rangle = P_+|\psi\rangle$$

  - The projection postulate thus becomes:

$$|\psi'\rangle = \frac{P_+|\psi\rangle}{\sqrt{\langle\psi|P_+|\psi\rangle}} = |+\rangle$$

  - This indicates a "collapse" of the quantum state vector

- Measurement
  - In quantum mechanics, one must perform multiple identical measurements on identically prepared systems to infer the probabilities of outcomes

– For example, if one performs N measurements of the projections of $|\psi\rangle$ and obtains $+\hbar/2$ N_+ times, then:

$$\lim_{N\to\infty} \frac{N_+}{N} = |\langle +|\psi\rangle|^2$$

– It is useful to characterize statistical data sets by their mean and standard deviation

$$< S_z >= \frac{\hbar}{2}P_+ + \left(-\frac{\hbar}{2}\right)P_- = \langle\psi|S_z|\psi\rangle = \sum_n a_n P_{a_n}$$

* We may observe that this is the sum of the eigenvalues multiplied by the probability of getting said eigenvalue
* For the spin-1/2 system with $|+\rangle$ we get:

$$< S_z >= \langle +|S_z|+\rangle = \langle +|\hbar/2|+\rangle = \frac{\hbar}{2}\langle +|+\rangle = \frac{\hbar}{2}$$

* Similarly, we may apply $|+\rangle_x$ to observe:

$$< S_z >= {}_x\langle +|S_z|+\rangle_x = {}_x\langle +|\hbar/2|+\rangle_x = \frac{\hbar}{4}(1-1) = 0$$

– It is common to characterize the standard deviation by the root-mean-square:

$$\Delta A = \sqrt{< (A- < A >)^2 >} = \sqrt{< A^2 > - < A >^2}$$

* From the above, it is important to note that in the general case:

$$< A^2 > \neq < A >^2$$

– The square of an operator acts twice on the state:

$$A^2|\psi\rangle = A(A|\psi\rangle)$$

* Similarly, if we consider S_z, we may write:

$$< S_z^2 >= \langle +|S_z^2|+\rangle = \langle +|(\hbar/2)^2|+\rangle = \frac{\hbar^2}{4}$$

* Thus, we may write:

$$\Delta S_z = 0$$

* Now, we check a different orientation:

$${}_x\langle +|S_z^2|+\rangle_x = \frac{\hbar^2}{4}$$

* Thus, we may see:

$$\Delta_x S_z = \frac{h}{2}$$

- Commuting Observables
  - Two incompatible observables may be identified with a commutator:

$$[A, B] = AB - BA$$

  - If $[A, B] = 0$, operators (observables) are said to commute and are compatible
  - Assuming $[A, B] = 0$, then:

$$AB = BA$$

    * Let $|a\rangle$ be an eigenstate of A with eigenvalue a:

$$A|a\rangle = a|a\rangle$$

    * Then we can say:

$$BA|a\rangle = aB|a\rangle$$

    * This can be expanded:

$$AB|a\rangle = A(B|a\rangle) = a|a'\rangle$$

      · Here, we make $B|a\rangle$ an eigenstate of A with eigenvalue a

    * Assuming each eigenvalue has a unique eigenstate, then $B|a\rangle$ must be a scalar multiple of $|a\rangle$

$$B|a\rangle = b|a\rangle$$

    * Thus, we conclude:

$$\text{If } [A, B] = 0, \ A \text{ and } B \text{ have simultaneous sets of eigenstates}$$

    * Conversely, if two operators do not commute, they are incompatible and can not be known simultaneously, like S_z and S_x

- Uncertainty Principle
  - There is an intimate connection between the commutator of two observables and the possible precision of measurements of each:

$$\Delta A \Delta B \geq \frac{1}{2}| < [A, B] > |$$

  - Applying to Stern-Gerlach, we may write:

$$\Delta S_x \Delta S_y \geq \frac{1}{2}| < [S_x, S_y] > |$$

$$\Delta S_x \Delta S_y \geq \frac{\hbar}{2}| < S_z > |$$

* Applying this to $|+\rangle$, we find:

$$\Delta S_x \Delta S_y \geq \left(\frac{\hbar}{2}\right)^2$$

  - This implies that the individual components are both non-zero
  - Therefore, we can not know spin components of either component absolutely
  - As a result, one can not say the spin points in a given direction

- The $\vec{S}$ Operation
  - Let us begin by writing:

$$\vec{S}^2 = S_x^2 + S_y^2 + S_z^2$$

  - It points in no direction in space. We can calculate using matrix notation:

$$\vec{S}^2 = \left(\frac{\hbar}{2}\right)^2 \left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right]$$

$$\vec{S}^2 = \left(\frac{\hbar}{2}\right)^2 [\mathbb{1} + \mathbb{1} + \mathbb{1}]$$

$$\vec{S}^2 = \frac{3\hbar^2}{4}\mathbb{1}$$

  - For any state $|\psi\rangle$ in the Hilbert space $S = 1/2$:

$$\vec{S}^2 |\psi\rangle = \frac{3}{4}\hbar^2 |\psi\rangle$$

  - So, we may conclude:

$$< \vec{S}^2 >= \frac{3}{4}\hbar^2$$

  - This would imply the "length" of the spin vector is:

$$|\vec{S}| = \sqrt{< \vec{S}^2 >} = \sqrt{3}(\hbar/2)$$

  - Thus, this value is greater than the measured component, $\hbar/2$, implying that the spin vector is never fully aligned with any axis

- Spin-1 Systems
  - The Stern-Gerlach experiment produces 3 beams corresponding to z-axis projections $+\hbar$, 0, and $-\hbar$:

$$|1\rangle, |0\rangle, |-1\rangle \Longrightarrow \begin{cases} S_z |1\rangle & = \hbar |1\rangle \\ S_z |0\rangle & = 0\hbar |0\rangle \\ S_z |-1\rangle & = -\hbar |-1\rangle \end{cases}$$

- Recall eigenvectors are unit vectors in their own basis and an operator is always diagonal in its own basis. This gives us:

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad |0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad |-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

  * This then gives us:

$$S_x = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

- We can write the x orientation as:

$$|1\rangle_x = \frac{1}{2}|1\rangle + \frac{1}{\sqrt{2}}|0\rangle + \frac{1}{2}|-1\rangle$$
$$|0\rangle_x = \frac{1}{\sqrt{2}}|1\rangle - \frac{1}{\sqrt{2}}|-1\rangle$$
$$|-1\rangle_x = \frac{1}{2}|1\rangle - \frac{1}{\sqrt{2}}|0\rangle + \frac{1}{2}|-1\rangle$$

- We then do the same for the y orientation:

$$|1\rangle_y = \frac{1}{2}|1\rangle + \frac{i}{\sqrt{2}}|0\rangle - \frac{1}{2}|-1\rangle$$
$$|0\rangle_x = \frac{1}{\sqrt{2}}|1\rangle + \frac{1}{\sqrt{2}}|-1\rangle$$
$$|-1\rangle_x = \frac{1}{2}|1\rangle - \frac{i}{\sqrt{2}}|0\rangle - \frac{1}{2}|-1\rangle$$

- The operators can be written as:

$$S_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$
$$S_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

- New Labels
  - The allowed values of spin are $S = 1/2, 1, 3/2, 2, \cdots$
  - The number of beams exiting the Stern-Gerlach with such spin is $2S + 1$ with a minimum value of $-\hbar S$ and a maximum value $+\hbar S$

– We label the state $|S_m\rangle$

$$\vec{S}\,|S_m\rangle = S(S+1)\hbar^2\,|S_m\rangle$$
$$S_z\,|S_m\rangle = m\hbar\,|S_m\rangle$$
$$[\vec{S}^2, S_z] = 0$$

  * Note, S_m is the magnetic quantum number

– Schrödinger Equation

  * The time evolution of a quantum system, is determined by the Hamiltonian of the total energy operator $H(t)$ through the Schrödinger equation:

$$i\hbar\frac{d}{dt}\,|\psi(t)\rangle = H(t)\,|\psi(t)\rangle$$

– The Energy Eigenvalue Equation

$$H\,|E_n\rangle = E_n\,|E_n\rangle$$

  * Where E_n represents the only allowed energies of the system
  * Since H represents the energy, it is observable, Hermitian, and therefore, its eigenvalues form a complete basis
  * Since H is the only operator appearing in the Schrödinger equation, it is convenient to expand the state vectors in terms of the energy eigenstates:

$$|\psi\rangle = \sum_n \langle n(t)|E_n\rangle$$

  * Substituting the expansion into the Schrödinger equation gets us:

$$i\hbar\frac{d}{dt}\sum_n \langle n(t)|E_n\rangle = \sum_n \langle n(t)E_n|E_n\rangle$$
$$\frac{dC_k(t)}{dt} = -i\frac{E_k}{\hbar}C_k(t)$$

  * We see that a possible solution is:

$$C_k(t) = C_o(t)e^{-iE_k/\hbar}$$

    · Each energy has the same form of the time dependence but a different exponent. At time $t = 0$:

$$|\psi(0)\rangle = \sum_n \langle n|E_n\rangle$$

    · And the time evolution of a time-independent Hamiltonian is:

$$|\psi(t)\rangle = \sum_n C_n e^{-iE_n t/\hbar}\,|E_n\rangle$$

$$H\,|E_n\rangle = E_n\,|E_n\rangle$$

· Note that the factor $e^{-iE_nt/\hbar}$ has the form $e^{-i\omega t}$ found in many areas of physics, such that:

$$\omega_n = \frac{E_n}{\hbar} \Rightarrow E_n = \hbar\omega_n$$

· Energy eigenstates are called stationary states

· If the system is in an energy eigenstate, it remains in that state

∗ The Bohr Frequency

· The Bohr frequency may be found as:

$$\omega_{21} = \frac{E_2 - E_1}{\hbar}$$

- Spin Precession

  – Time-evolution of $S = 1/2$

$$\vec{\mu} = g\frac{q}{2m}\vec{S}$$

  ∗ For an electron:

$$\vec{\mu} = \frac{e}{m_e}\vec{S}$$

  – The Hamiltonian is:

$$H = -\vec{\mu}\cdot\vec{B} = \frac{e}{m_e}\vec{S}\cdot\vec{B} = \frac{eB_o}{m_e}S_z = \frac{\hbar\omega_o}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

  – We can find eigenstates:

$$H\left|+\right\rangle = \frac{\hbar}{2}\omega_o\left|+\right\rangle$$

$$H\left|-\right\rangle = -\frac{\hbar}{2}\omega_o\left|-\right\rangle$$

  – For a quantum state with initial state:

$$\left|\psi(0)\right\rangle = \left|+\right\rangle$$

  – We find time-evolution:

$$\left|\psi(t)\right\rangle = e^{-i\omega_o t/2}\left|+\right\rangle$$

  – Next, let us consider a more general state:

$$\left|\psi(0)\right\rangle = \left|+\right\rangle_n = \cos\left(\frac{\theta}{2}\right)\left|+\right\rangle + \sin\left(\frac{\theta}{2}\right)e^{i\phi}\left|-\right\rangle$$

* Time-dependence may be expressed as:

$$|\psi(0)\rangle = e^{-i\omega_o t/2}\cos\left(\frac{\theta}{2}\right)|+\rangle + e^{t_i\omega_o t/2}\sin\left(\frac{\theta}{2}\right)e^{i\phi}|-\rangle$$

$$|\psi(0)\rangle = e^{-i\omega_o t/2}\left[\cos\left(\frac{\theta}{2}\right)|+\rangle + \sin\left(\frac{\theta}{2}\right)e^{i(\omega_o t+\phi)}|-\rangle\right]$$

- We may use the time-dependence to find the probability of being in the up state:

$$P_+ = |\langle +|\psi(t)\rangle|^2 = \cos^2(\theta/2)$$

  * In this case, the probability is time independent since the z component commutes with the Hamiltonian
  * The angle θ the spin vector $\hat{n}$ makes with the z-axis does not change

- Similarly, we may find:

$$P_{+x} = |{}_x\langle +|\psi(t)\rangle|^2 = \frac{1}{2}\left[1+\sin(\theta)\cos(\phi+\omega_o t)\right]$$

  * We may see that this is time dependent since H and S_x do not commute

- To see spin precession more clearly, we will compute the expectation values for each spin component

$$< S_z >= \langle\psi(t)|S_z|\psi(t)\rangle = \frac{\hbar}{2}\cos(\theta)$$

$$< S_y >= \langle\psi(t)|S_y|\psi(t)\rangle = \frac{\hbar}{2}\sin(\theta)\sin(\phi+\omega_o t)$$

$$< S_x >= \langle\psi(t)|S_x|\psi(t)\rangle = \frac{\hbar}{2}\sin(\theta)\cos(\phi+\omega_o t)$$

  * As such, we see that $< S_x >$ and $< S_y >$ oscillate in time and $< \vec{S} >$ precesses around the magnetic field with the angular frequency ω_o, which is known as the Larmor frequency and precession, respectively
  * The equivalence of the classical Larmor precession and the expectation value of the quantum spin vector is an example of Ehrenfest's theorem, which states that quantum expectation values obey classical laws

- If we start a system in a spin $|+\rangle$ state and find the probability it has later evolved into a spin $|-\rangle$ state, we call this a spin flip

$$P_{+\to-} = |\langle -|\psi(t)\rangle|^2 = \sin^2(\theta)\sin^2\left(\frac{E_+ - E_-}{2\hbar}t\right) = \frac{\omega_1^2}{\omega_o^2+\omega_o^2}\sin^2\left(\frac{\sqrt{\omega_o^2+\omega_1^2}}{2}t\right)$$

  * This is known as Rabi's formula

- Magnetic Field in a General Direction

– Let us take a more general field:

$$\vec{B} = B_o\hat{z} + B_1\hat{x}$$

– We can find the Hamiltonian to be:

$$H = \omega_o S_z + \omega_1 S_x$$

– We can write this as:

$$H = \frac{\hbar}{2}\begin{pmatrix}\omega_o & \omega_1 \\ \omega_1 & -\omega_o\end{pmatrix}$$

– The eigenvalues become:

$$\lambda = \pm\frac{\hbar}{2}\sqrt{\omega_o^2 + \omega_1^2}$$

– This indicates:

$$H = \sqrt{\omega_o^2 + \omega_1^2}S_n$$

  * Such that:

$$|+\rangle_n = \cos\left(\frac{\theta}{2}\right)|+\rangle + \sin\left(\frac{\theta}{2}\right)|-\rangle$$
$$|-\rangle_n = \sin\left(\frac{\theta}{2}\right)|+\rangle - \cos\left(\frac{\theta}{2}\right)|-\rangle$$

– We take the start state as:

$$|\psi(0)\rangle = |+\rangle$$

– Ultimately, we may calculate:

$$|\psi(t)\rangle = e^{-iE_+t/\hbar}\cos\left(\frac{\theta}{2}\right)|+\rangle_n + e^{-iE_-t/\hbar}\sin\left(\frac{\theta}{2}\right)|-\rangle_n$$

  * Where $E_\pm = \pm\frac{\hbar}{2}\sqrt{\omega_o^2 + \omega_1^2}$

– We can find the probability of a spin flip as:

$$P_{+\to-} = |\langle -|\psi(t)\rangle|^2$$
$$P_{+\to-} = |\langle -|[e^{-iE_+t/\hbar}\cos\left(\frac{\theta}{2}\right)|+\rangle_n + e^{-iE_-t/\hbar}\sin\left(\frac{\theta}{2}\right)|-\rangle_n]|^2$$
$$P_{+\to-} = |e^{-iE_+t/\hbar}\cos\left(\frac{\theta}{2}\right)\langle -|+\rangle_n + e^{-iE_-t/\hbar}\sin\left(\frac{\theta}{2}\right)\langle -|-\rangle_n|^2$$
$$P_{+\to-}(t) = \frac{\omega_1^2}{\omega_o^2 + \omega_1^2}\sin^2\left(\frac{\sqrt{\omega_o^2 + \omega_1^2}}{2}t\right)$$

    * This gives us Rabi's Formula
    * We need a large x-component in $\vec{B}$ for significant spin flip probability

- Time-Dependent Hamiltonians
  - Important for magnetic resonance
  - Apply a time-dependent field resonant with the Larmor precession frequency (ω_o)
  - Used in all kinds of applications like medical diagnostics, biology, chemistry, etc.
  - We assume a field:

$$\vec{B} = B_o\hat{z} + B_1[\cos(\omega t)\hat{x} + \sin(\omega t)\hat{y}]$$

    * B_o sets the splitting of up and down, while B_1 produces a flip between up and down

  - In matrix notation, we may write our Hamiltonian as:

$$H = \frac{\hbar}{2}\begin{pmatrix} \omega_o & \omega_1 e^{-i\omega t} \\ \omega_1 e^{i\omega_o t} & -\omega_o \end{pmatrix}$$

  - Since this is time-dependent, we can not use the recipe for Schrödinger time evolution
  - We take the quantum state:

$$|\psi(t)\rangle = c_+(t)\,|+\rangle + c_-(t)\,|-\rangle$$

  - We substitute into the Schrödinger equation to get:

$$i\hbar\frac{d}{dt}\begin{pmatrix} c_+(t) \\ c_-(t) \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} \omega_o & \omega_1 e^{-i\omega t} \\ \omega_1 e^{i\omega t} & \omega_o \end{pmatrix}\begin{pmatrix} c_+(t) \\ c_-(t) \end{pmatrix}$$

  - This gives us:

$$i\hbar\dot{c}_+(t) = \frac{\hbar}{2}\omega_o c_+(t) + \omega_1 e^{-i\omega t}c_-(t)$$
$$i\hbar\dot{c}_+(t) = \frac{\hbar}{2}\omega_1 e^{i\omega t}c_+(t) - \omega_o c_-(t)$$

  - If we go to a frame rotating with the magnetic fireld, the state vector is:

$$\left|\tilde{\psi}(t)\right\rangle = c_+(t)e^{i\omega t/2}\,|+\rangle + c_-(t)e^{-i\omega t/2}\,|-\rangle$$

  - We can further simplify to:

$$\left|\tilde{\psi}(t)\right\rangle = \alpha_+(t)\,|+\rangle + \alpha_-(t)\,|-\rangle$$

– In the non-rotating frame, we have:

$$|\psi(t)\rangle = \alpha_+(t)e^{-i\omega t/2}\,|+\rangle + \alpha_-(t)e^{i\omega t/2}\,|-\rangle$$

– We can then plug this form of the quantum state equation back into the Schrödinger equation. This yields:

$$i\hbar\dot{\alpha}_+(t) = -\frac{\hbar\Delta\omega}{2}\alpha_+(t) + \frac{\hbar\omega_1}{2}\alpha_-(t)$$
$$i\hbar\dot{\alpha}_-(t) = \frac{\hbar\omega_1}{2}\alpha_+(t) + \frac{\hbar\Delta\omega}{2}\alpha_-(t)$$

∗ Where $\Delta\omega = \omega - \omega_o$

∗ We may see that this removes the time dependence element:

$$\tilde{H} = \frac{\hbar}{2}\begin{pmatrix} -\Delta\omega & \omega_1 \\ \omega_1 & \Delta\omega \end{pmatrix} From here, we wish to return to computing the probability of a spin flip$$

∗ We may notice that the rational transformation does not alter the basis states, such that:

$$|\psi(0)\rangle = \left|\tilde{\psi}(0)\right\rangle = |+\rangle$$

∗ We may observe that our solution then becomes Rabi's formula with $\omega_o \to -\Delta\omega$:

$$P_{+\to-}(t) = \frac{\omega_1^2}{(\omega-\omega_o)^2+\omega_1^2}\sin^2\left(\frac{\sqrt{(\omega-\omega_o)^2+\omega_1^2}}{2}t\right)$$

· It is said that, in this case, the spin 'flops'

· When $\omega = 0$, it represents Rabi's formula

∗ If we take $\omega = \omega_o$, then:

$$P_{+\to-} = \sin^2\left(\frac{\omega_1}{2}t\right)$$

· We may observe that there is a 100% probability of spin flop even for small B_1 when $\omega_1 t = \pi$, which is achieved with a "π-pulse

· Moving from a positive to negative spin sign is known as emission (energy is emitted), while moving the other way is known as absorption (energy is absorbed)