Physics 143a – Workshop 4

On Time Evolution

Week Summary

- **Time Evolution:** The properties of a quantum system at a time t are completely defined by specifying the system's state ket at t: $|\varphi(t)\rangle$. The following is a postulate of quantum mechanics:

  –Schrödinger equation: The time evolution of the state ket $|\varphi(t)\rangle$ of a quantum system is governed by the evolution equation

  $$i\hbar \frac{d}{dt}|\varphi(t)\rangle = \hat{H}|\varphi(t)\rangle, \tag{1}$$

  where $\hat{H}$, termed the *Hamiltonian*, is the Hermitian operator associated with the energy of the system.

  Equivalently, we could write this postulate as an integral equation solution to Eq.(1):

  –Evolution Operator: The time evolution of the state of a quantum system from an initial ket $|\varphi(t_0)\rangle$ to a final ket $|\varphi(t)\rangle$ is governed by the evolution equation

  $$|\varphi(t)\rangle = \hat{U}(t, t_0)|\varphi(t_0)\rangle, \tag{2}$$

  where

  $$\hat{U}(t, t_0) = \exp\left(-\frac{i}{\hbar}(t - t_0)\hat{H}\right) \tag{3}$$

  is termed *the time-evolution operator* (here the Hamiltonian $\hat{H}$ is assumed to be time independent).

- **Time Evolution of States and Operators:** The explicit solution to Eq.(1) is:

  $$|\varphi(t)\rangle = \sum_j c_j(t_0) e^{-iE_j(t-t_0)/\hbar}|E_j\rangle \tag{4}$$

  where $c_j(t_0) = \langle E_j|\varphi(t_0)\rangle$, and E_j and $|E_j\rangle$ are the energy-eigenvalue and energy-eigenstate, respectively, of the $\hat{H}$. Technically speaking, we say $|E_j\rangle$ satisfies the *time-independent Schrödinger equation*:

  $$\hat{H}|E_j\rangle = E_j|E_j\rangle. \tag{5}$$

  From Eq.(1), we also find that the time-evolution of the expectation value (for arbitrary states) of an operator $\hat{A}$

  $$\frac{d}{dt}\langle\hat{A}\rangle = \left\langle \frac{\partial}{\partial t}\hat{A}\right\rangle + \frac{i}{\hbar}\langle[\hat{H}, \hat{A}]\rangle. \tag{6}$$

  A corollary of Eq.(6) is that the average values of operators without an explicit time dependence and which commute with the Hamiltonian are independent of time.

1 Problems

1. **Practice with Time-Evolution Operator**
Consider a normalized initial state $|\varphi(0)\rangle$ at $t = 0$, with a spread in energy defined by

$$(\Delta_\varphi E)^2 \equiv \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2. \tag{7}$$

Compute the probability $|\langle \varphi(\Delta t)|\varphi(0)\rangle|^2$ that after a very short time Δt the system is still in state $|\varphi\rangle$. Write the result in terms of $\Delta_\varphi E^2$, $\hbar$ and Δt up to second order in Δt.

2. **Linear Three Atom Molecule (Time-Independent Quantum Mechanics)**
We consider the states of an electron in a linear three-atom molecule (such as N_3 or C_3) with equally spaced atoms L, C, R at a fixed distance from one another.

Figure 1: Linear Three Atom Molecule

Let $|\psi_\mathrm{L}\rangle$, $|\psi_\mathrm{R}\rangle$, and $|\psi_\mathrm{C}\rangle$ be the eigenstates of an observable $\hat{B}$ corresponding to an electron localized in the vicinity of the atoms L, C, and R, respectively:

$$\hat{B}|\psi_\mathrm{L}\rangle = -d|\psi_\mathrm{L}\rangle, \quad \hat{B}|\psi_\mathrm{C}\rangle = 0, \quad \hat{B}|\psi_\mathrm{R}\rangle = +d|\psi_\mathrm{R}\rangle. \tag{8}$$

In the basis $\{|\psi_\mathrm{L}\rangle, |\psi_\mathrm{C}\rangle, |\psi_\mathrm{R}\rangle\}$, the Hamiltonian of the system is represented by the matrix

$$\hat{H} = \begin{pmatrix} E_0 & -a & 0 \\ -a & E_0 & -a \\ 0 & -a & E_0 \end{pmatrix}, \quad a > 0. \tag{9}$$

   (a) Calculate the energy levels and eigenstates of $\hat{H}$.
   (b) Suppose the electron is in the ground state (i.e., the lowest energy state). What are the probabilities of finding the electron in the vicinity of L, C, and R?
   (c) Suppose the electron is in the state $|\psi_\mathrm{L}\rangle$, and we measure its energy. What values can we find, with what probabilities?

3. **Linear Three Atom Molecule (Time-Dependent Quantum Mechanics)**
We consider again the system of the previous problem, but now we consider its time dependence. Suppose, the electron is in the state $|\varphi(0)\rangle = |\psi_\mathrm{L}\rangle$ at time $t = 0$:

   (a) What is $|\varphi(t)\rangle$, the state of the electron at time t?
   (b) Compute the probability of finding the particle at L.
   (c) Using the result from Problem 1, what is $\Delta_\varphi E^2$ (the variance in energy) for this state?
   (d) **(Only if You Have Time)**
      i. Compute two more quantities: the probability of finding the particle at R and the probability of finding the particle at C.
      ii. What is $\langle B \rangle$ as a function of time. (*Hint:* If you write more than three lines, you're taking the scenic route.)
      iii. Using Eq.(6), compute the quantity

$$\big\langle [\hat{H}, \hat{B}] \big\rangle, \tag{10}$$

      as a function of time.

2 Solutions

1. If we begin at $t = 0$ in a state $|\varphi(0)\rangle$, then at a time $t = \Delta t$ we would be in the state

$$|\varphi(\Delta t)\rangle = e^{-i\hat{H}t/\hbar}|\varphi(0)\rangle. \tag{11}$$

Thus computing the square of the inner product between this time-evolved state and the initial state we find

$$\begin{aligned} |\langle\varphi(0)|\varphi(\Delta t)\rangle|^2 &= \left|\langle\varphi(0)|e^{-i\hat{H}t/\hbar}|\varphi(0)\rangle\right|^2 \\ &= \left|\langle\varphi(0)|1 - i\Delta t\hat{H}/\hbar - \Delta t^2\hat{H}^2/2\hbar^2 + \mathcal{O}(\Delta t^3)|\varphi(0)\rangle\right|^2 \\ &= \left|1 - i\Delta t\langle E\rangle/\hbar - \Delta t^2\langle E^2\rangle/2\hbar^2 + \mathcal{O}(\Delta t^3)\right|^2 \\ &= 1 + \Delta t^2\langle E\rangle^2/\hbar^2 - \Delta t^2\langle E^2\rangle/\hbar^2 + \mathcal{O}(\Delta t^3), \end{aligned} \tag{12}$$

where we used the definitions $\langle E\rangle \equiv \langle\varphi(0)|\hat{H}|\varphi(0)\rangle$ and $\langle E^2\rangle \equiv \langle\varphi(0)|\hat{H}^2|\varphi(0)\rangle$. Thus we have

$$|\langle\varphi(0)|\varphi(\Delta t)\rangle|^2 = 1 - \Delta t^2(\Delta_\varphi E)^2/\hbar^2 + \mathcal{O}(\Delta t^3). \tag{13}$$

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2. (a) To compute the energy levels and eigenstates of $\hat{H}$ we employ the standard procedure: Computing the characteristic equation we have

$$0 = \begin{vmatrix} E_0 - E & -a & 0 \\ -a & E_0 - E & -a \\ 0 & -a & E_0 - E \end{vmatrix} = (E_0 - E)\left[(E_0 - E)^2 - a^2\right] - a^2(E_0 - E). \tag{14}$$

Thus we have the eigenvalue constraint $(E_0 - E)\left[(E_0 - E)^2 - 2a^2\right] = 0$, which implies that the energy eigenvalues are $E = E_0$, $E = E_0 + a\sqrt{2}$, and $E = E_0 - a\sqrt{2}$. Given these eigenvalues and the Hamiltonian

$$\hat{H} = \begin{pmatrix} E_0 & -a & 0 \\ -a & E_0 & -a \\ 0 & -a & E_0 \end{pmatrix}, \quad a > 0, \tag{15}$$

we can infer (from inspection or calculation) that the system has the eigenvectors

$$|E_1\rangle = \frac{1}{2}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} \qquad E_1 = E_0 - a\sqrt{2} \tag{16}$$

$$|E_2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \qquad E_2 = E_0 \tag{17}$$

$$|E_3\rangle = \frac{1}{2}\begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix} \qquad E_3 = E_0 + a\sqrt{2}. \tag{18}$$

We can write these eigenvectors in ket notation as

$$|E_1\rangle = \frac{1}{2}\left(|\psi_L\rangle + \sqrt{2}|\psi_C\rangle + |\psi_R\rangle\right) \tag{19}$$

$$|E_2\rangle = \frac{1}{\sqrt{2}}\left(|\psi_L\rangle - |\psi_R\rangle\right) \tag{20}$$

$$|E_3\rangle = \frac{1}{2}\left(|\psi_L\rangle - \sqrt{2}|\psi_C\rangle + |\psi_R\rangle\right). \tag{21}$$

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(b) From the ket representation of the ground state,

$$|E_1\rangle = \frac{1}{2}\left(|\psi_L\rangle + \sqrt{2}|\psi_C\rangle + |\psi_R\rangle\right), \tag{22}$$

we can infer that the probabilities to find the particle in the vicinity of L, C, and R are

$$\text{Prob(L)} = |\langle\psi_L|E_1\rangle|^2 = \frac{1}{4}, \quad \text{Prob(C)} = |\langle\psi_C|E_1\rangle|^2 = \frac{1}{2}, \quad \text{Prob(R)} = |\langle\psi_R|E_1\rangle|^2 = \frac{1}{4}. \tag{23}$$

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(c) From the results of part (a), we know that measurements of energy yield the possible eigenvalues E_0, $E_0 - a\sqrt{2}$, $E_0 + a\sqrt{2}$. With the fact that $|\langle\alpha|\beta\rangle|^2 = |\langle\beta|\alpha\rangle|^2$, we can infer that these eigenvalues occur with the probabilities

$$\text{Prob}(E_0 - a\sqrt{2}) = |\langle E_1|\psi_L\rangle|^2 = \frac{1}{4} \tag{24}$$

$$\text{Prob}(E_0) = |\langle E_2|\psi_L\rangle|^2 = \frac{1}{2} \tag{25}$$

$$\text{Prob}(E_0 + a\sqrt{2}) = |\langle E_2|\psi_L\rangle|^2 = \frac{1}{4}. \tag{26}$$

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3. (a) If our state begins in the state $|\psi_L\rangle$, then by the results of 2 (a), we have

$$|\varphi(0)\rangle = |\psi_L\rangle = \frac{1}{2}|E_1\rangle + \frac{1}{\sqrt{2}}|E_2\rangle + \frac{1}{2}|E_3\rangle. \tag{27}$$

Applying the time evolution operator to Eq.(27), we find

$$\begin{aligned}|\varphi(t)\rangle &= e^{-i\hat{H}t/\hbar}|\varphi(0)\rangle \\ &= \frac{1}{2}e^{-i(E_0 - a\sqrt{2})t/\hbar}|E_1\rangle + \frac{1}{\sqrt{2}}e^{-iE_0 t/\hbar}|E_2\rangle + \frac{1}{2}e^{-i(E_0 + a\sqrt{2})t/\hbar}|E_3\rangle.\end{aligned} \tag{28}$$

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(b) Computing the probability to be in the state $|\psi_L\rangle$ at time t, we find

$$\begin{aligned}\text{Prob(L}, t) &= |\langle\psi_L|\varphi(t)\rangle|^2 \\ &= \left|\frac{1}{2}e^{-i(E_0 - a\sqrt{2})t/\hbar}\langle\psi_L|E_1\rangle + \frac{1}{\sqrt{2}}e^{-iE_0 t/\hbar}\langle\psi_L|E_2\rangle + \frac{1}{2}e^{-i(E_0 + a\sqrt{2})t/\hbar}\langle\psi_L|E_3\rangle\right|^2 \\ &= \left|\frac{1}{4}e^{-i(E_0 - a\sqrt{2})t/\hbar} + \frac{1}{2}e^{-iE_0 t/\hbar} + \frac{1}{4}e^{-i(E_0 + a\sqrt{2})t/\hbar}\right|^2 \\ &= \left|\frac{e^{-iE_0 t/\hbar}}{2}\left(1 + \frac{1}{2}e^{ia\sqrt{2}t/\hbar} + \frac{1}{2}e^{-ia\sqrt{2}t/\hbar}\right)\right|^2\end{aligned}$$

$$= \frac{1}{4}\left(1+\cos(a\sqrt{2}t/\hbar)\right)^2 = \cos^4\left(at/\hbar\sqrt{2}\right) \tag{29}$$

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(c) If we take our time t in Eq.(29) to be small (i.e., $t = \Delta t$, $\Delta t \ll \hbar/a$), then we can expand the result in a Taylor series:

$$\text{Prob(L, } \Delta t) = \langle\psi_L|e^{-i\hat{H}\Delta t/\hbar}|\psi_L\rangle = 1 - \Delta t^2\frac{a^2}{\hbar^2} + \mathcal{O}(\Delta t^4). \tag{30}$$

Comparing this result with that of 1 (b), we find the variance in the energy for the state $|\psi_L\rangle$ to be

$$(\Delta_{\psi_L}E)^2 = a^2. \tag{31}$$

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(d) i. By the procedure exactly analogous to that in 3(a) and 3(b), we find the probabilities to be in the states C and R are

$$\text{Prob(R, } t) = \sin^4\left(at/\hbar\sqrt{2}\right), \quad \text{Prob(C, } t) = 2\sin^2\left(at/\hbar\sqrt{2}\right)\cos^2\left(at/\hbar\sqrt{2}\right). \tag{32}$$

Checking the normalization of this result we have

$$\begin{aligned}
&\text{Prob(L, } t) + \text{Prob(C, } t) + \text{Prob(R, } t) \\
&\qquad = \cos^4\left(at/\hbar\sqrt{2}\right) + \sin^4\left(at/\hbar\sqrt{2}\right) + 2\sin^2\left(at/\hbar\sqrt{2}\right)\cos^2\left(at/\hbar\sqrt{2}\right) \\
&\qquad = \left[\cos^2\left(at/\hbar\sqrt{2}\right) + \sin^2\left(at/\hbar\sqrt{2}\right)\right]^2 = 1,
\end{aligned} \tag{33}$$

as expected.

ii. To compute the time dependent $\langle B\rangle$ we compute the probability weighted sum to be found at $-d$, 0, and d. Doing so we have

$$\begin{aligned}
\langle B\rangle &= -d\cdot\text{Prob(L, } t) + 0\cdot\text{Prob(C, } t) + d\cdot\text{Prob(R, } t) \\
&= -\frac{d}{4}\left(1+\cos(a\sqrt{2}t/\hbar)\right)^2 + \frac{d}{4}\left(1-\cos(a\sqrt{2}t/\hbar)\right)^2 \\
&= -d\cos(a\sqrt{2}t/\hbar)
\end{aligned} \tag{34}$$

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iii. By Eq.(6), we have

$$\langle\varphi(t)|[\hat{H},\hat{B}]|\varphi(t)\rangle = \frac{\hbar}{i}\frac{d}{dt}\langle B\rangle = \frac{da\sqrt{2}}{i}\sin(a\sqrt{2}t/\hbar). \tag{35}$$

We can check this result through explicit computation. Given the Hamiltonian and the position operator, we have

$$\begin{aligned}
[\hat{H},\hat{B}] &= \begin{pmatrix} E_0 & -a & 0 \\ -a & E_0 & -a \\ 0 & -a & E_0 \end{pmatrix}\begin{pmatrix} -d & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & +d \end{pmatrix} - \begin{pmatrix} -d & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & +d \end{pmatrix}\begin{pmatrix} E_0 & -a & 0 \\ -a & E_0 & -a \\ 0 & -a & E_0 \end{pmatrix} \\
&= \begin{pmatrix} -dE_0 & 0 & 0 \\ da & 0 & -da \\ 0 & 0 & dE_0 \end{pmatrix} - \begin{pmatrix} -dE_0 & da & 0 \\ 0 & 0 & 0 \\ 0 & -da & dE_0 \end{pmatrix}
\end{aligned}$$

$$= da \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}. \tag{36}$$

Our time-dependent state ket in the $|\psi_L\rangle$, $|\psi_C\rangle$, $|\psi_R\rangle$ basis is

$$\begin{aligned} |\varphi(t)\rangle &= \frac{e^{-i(E_0 - a\sqrt{2})t/\hbar}}{4} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} + \frac{e^{-iE_o t/\hbar}}{2} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} + \frac{e^{-i(E_0 + a\sqrt{2})/\hbar}}{4} \begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix} \\ &= \frac{e^{-iE_0 t/\hbar}}{2} \begin{pmatrix} 1 + \cos(a\sqrt{2}t/\hbar) \\ i\sqrt{2}\sin(a\sqrt{2}t/\hbar) \\ -1 + \cos(a\sqrt{2}t/\hbar) \end{pmatrix} \end{aligned} \tag{37}$$

Placing $[\hat{H}, \hat{B}]$ between two time-dependent state kets, we have

$$\begin{aligned} &\langle\varphi(t)|[\hat{H}, \hat{B}]|\varphi(t)\rangle \\ &\quad = \frac{e^{iE_0 t/\hbar}}{2}(1 + \cos(a\sqrt{2}t/\hbar), -i\sqrt{2}\sin(a\sqrt{2}t/\hbar), -1 + \cos(a\sqrt{2}t/\hbar)) \\ &\quad\quad \times da \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \frac{e^{-iE_0 t/\hbar}}{2} \begin{pmatrix} 1 + \cos(a\sqrt{2}t/\hbar) \\ i\sqrt{2}\sin(a\sqrt{2}t/\hbar) \\ -1 + \cos(a\sqrt{2}t/\hbar) \end{pmatrix} \\ &= \frac{da}{4}(-i\sqrt{2}\sin(a\sqrt{2}t/\hbar), -2, i\sqrt{2}\sin(a\sqrt{2}t/\hbar) \begin{pmatrix} 1 + \cos(a\sqrt{2}t/\hbar) \\ i\sqrt{2}\sin(a\sqrt{2}t/\hbar) \\ -1 + \cos(a\sqrt{2}t/\hbar) \end{pmatrix} \\ &= \frac{da}{4}\left[-i\sqrt{2}\sin(a\sqrt{2}t/\hbar) - 2i\sqrt{2}\sin(a\sqrt{2}t/\hbar) - i\sqrt{2}\sin(a\sqrt{2}t/\hbar)\right] \\ &= \frac{da\sqrt{2}}{i}\sin(a\sqrt{2}t/\hbar), \end{aligned} \tag{38}$$

as previously calculated.

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