

Lecture #12: Looking Backward Before First Hour Exam: Postulate

Postulates, in the same order as in McQuarrie.

1. $\Psi(r,t)$ is the state function: it tells us everything we are allowed to know
2. For every observable there corresponds a linear, Hermitian Quantum Mechanical operator
3. Any *single* measurement of the property \hat{A} only gives *one* of the eigenvalues of \hat{A}
4. Expectation values. The average over many measurements on a system that is in a states that is completely specified by a specific $\Psi(x,t)$.
5. TDSE

We will discuss these, and their consequences, in detail now.

Postulate 1.

The state of a Quantum Mechanical system is *completely* specified by $\Psi(\mathbf{r},t)$

- * $\Psi \cdot \Psi dx dy dz$ is the probability that the particle lies within the volume element $dx dy dz$ that is centered at

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k} \quad (\hat{i}, \hat{j}, \text{ and } \hat{k} \text{ are unit vectors})$$

- * Ψ is “well behaved”
normalizable (in either of two senses: what are these two senses?)
square integrable [usually requires that $\lim_{x \rightarrow \pm\infty} \Psi(x) \rightarrow 0$]

$$\left. \begin{array}{l} \text{continuous} \\ \text{single-valued} \\ \text{finite everywhere} \end{array} \right\} \Psi \text{ and } \frac{d\Psi}{dx}$$

When do we get to break some of the rules about “well behaved”? (from non-physical but illustrative problems)?

*A finite step in $V(x)$ causes discontinuity in $\frac{\partial^2 \Psi}{\partial x^2}$

*A δ -function (infinite sharp spike) and infinite step in $V(x)$ cause a discontinuity in $\frac{\partial \Psi}{\partial x}$

Nothing can cause a discontinuity in ψ .

When $V(x) = \infty$, $\psi(x) = 0$. Always! [Why?]

Postulate 2

For every observable quantity in Classical Mechanics there corresponds a linear, Hermitian Operator in Quantum Mechanics.

linear means $\hat{A}(c_1\psi_1 + c_2\psi_2) = c_1\hat{A}\psi_1 + c_2\hat{A}\psi_2$. We have already discussed this.

Hermitian is a property that ensures that every observation results in a *real* number (not imaginary, not complex)

A Hermitian operator satisfies

$$\int_{-\infty}^{\infty} f^* (\hat{A}g) dx = \int_{-\infty}^{\infty} g (\hat{A}^* f^*) dx$$

$$A_{fg} = (A_{gf})^* \quad (\text{useful short-hand notation})$$

where f and g are well-behaved functions.

This provides a very useful prescription for how to “operate to the left”.

Suppose we replace g by f to see how Hermiticity ensures that any measurement of an observable quantity must be real.

$$\int_{-\infty}^{\infty} f^* \hat{A}f dx = \int_{-\infty}^{\infty} f \hat{A}^* f^* dx \quad \text{from the definition of Hermitian}$$

$$A_{ff} = (A_{ff})^*$$

The LHS is just $\langle \hat{A} \rangle_f$, the expectation value of \hat{A} in state f .

The RHS is just LHS*, which means

$$\text{LHS} = \text{LHS}^*$$

thus $\langle \hat{A} \rangle_f$ is real.

Non-Lecture

Often, to construct a Hermitian operator from a non-Hermitian operator, $\hat{A}_{\text{non-Hermitian}}$, we take

$$\hat{A}_{\text{QM}} = \frac{1}{2} (\hat{A}_{\text{non-Hermitian}} + \hat{A}_{\text{non-Hermitian}}^*)$$

OR, when an operator $\hat{C} = \hat{A}\hat{B}$ is constructed out of non-commuting factors, e.g.

$$[\hat{A}, \hat{B}] \neq 0.$$

Then we might try $\hat{C}_{\text{Hermitian}} = \frac{1}{2}(\hat{A}\hat{B} + \hat{B}\hat{A})$.

Angular Momentum

Classically

$$\vec{\ell} = \hat{r} \times \hat{p} = \begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix}$$

$\ell_x \hat{i} + \ell_y \hat{j} + \ell_z \hat{k}$

$$\ell_x = yp_z - zp_y$$

Does order matter?

$$\left. \begin{array}{l} [y, p_z] = 0 \\ [z, p_y] = 0 \end{array} \right\} \text{by inspection (of what?)}$$

which is a good thing because the standard way for compensating for non-commutation,

$$\hat{r} \times \hat{p} + \hat{p} \times \hat{r} = 0$$

fails, so we would not be able to guarantee Hermiticity this way

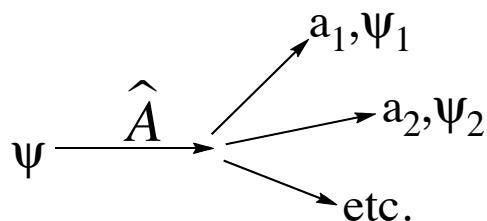
End of Non-Lecture

Postulate 3

Each measurement of the observable quantity associated with \hat{A} gives one of the eigenvalues of \hat{A} .

$$\hat{A}\psi_n = a_n\psi_n \quad \text{the set of all eigenvalues, } \{a_n\}, \text{ is called spectrum of } \hat{A}$$

Measurements:



Measurement causes an arbitrary ψ to “collapse” into one of the eigenstates of the measurement operator.

Postulate 4

For a system in *any* state normalized to 1, ψ , the average value of \hat{A} is $\langle \hat{A} \rangle \equiv \int_{-\infty}^{\infty} \psi^* \hat{A} \psi d\tau$.
($d\tau$ means integrate over all coordinates).

We can combine postulates 3 and 4 to get some very useful results.

1. Completeness (with respect to each operator)

$$\psi = \sum_i c_i \psi_i \quad \text{expand } \psi \text{ in a “complete basis set” of eigenfunctions, } \psi_i$$

(many choices of “basis sets”)

Most convenient to use all eigenstates of \hat{A} $\{\psi_i\}, \{a_i\}$

We often use a complete set of eigenstates of \hat{A} $\{\psi_n^A\}$ as “basis states” for the operator \hat{B} even when the $\{\psi_n^A\}$ are *not eigenstates* of \hat{B} .

2. Orthogonality

If ψ_i, ψ_j belong to $a_i \neq a_j$, then $\int dx \psi_i^* \psi_j = 0$. Even when we have a *degenerate* eigenvalue, where $a_i = a_j$, we can construct orthogonal functions. For example:

$$\hat{A}\psi_1 = a_1\psi_1, \hat{A}\psi_2 = a_1\psi_2, \psi_1, \psi_2 \text{ are normalized but not necessarily orthogonal.}$$

NON-Lecture

Construct a pair of normalized and orthogonal functions starting from ψ_1 and ψ_2 .

Schmidt orthogonalization

$$\begin{aligned}
 S &\equiv \int dx \psi_1^* \psi_2 \neq 0, \text{ the overlap integral} \\
 \psi'_2 &= N(\psi_2 + a\psi_1), \text{ constructed to be orthogonal to } \psi_1 \\
 \int dx \psi_1^* \psi'_2 &= N \int dx \psi_1^* (\psi_2 + a\psi_1) \\
 &= N(S + a).
 \end{aligned}$$

If we set $a = -S$, ψ'_2 is orthogonal to ψ_1 . We must normalize ψ'_2 .

$$\begin{aligned}
 1 &= \int dx \psi_2'^* \psi'_2 = |N|^2 \int dx (\psi_2^* - S^* \psi_1^*) (\psi_2 - S\psi_1) \\
 &= |N|^2 [1 - 2|S|^2 + |S|^2] \\
 N &= [1 - |S|^2]^{-1/2} \\
 \psi'_2 &= [1 - |S|^2]^{-1/2} (\psi_2 - S\psi_1)
 \end{aligned}$$

ψ'_2 is normalized to 1 and orthogonal to ψ_1 . This turns out to be a *very* useful trick.

“Complete orthonormal basis sets”

Next we want to compute the $\{c_i\}$ and the $\{P_i\}$. P_i is the probability that an experiment on ψ yields the i^{th} eigenvalue.

$$\Psi = \sum_i c_i \Psi_i$$

(ψ is any normalized state)

Left multiply and integrate by ψ_j^* (which is the complex conjugate of the eigenstate of \hat{A} that belongs to eigenvalue a_j).

$$\begin{aligned}
 \int dx \psi_j^* \Psi &= \int dx \psi_j^* \sum_i c_i \Psi_i \\
 &= \sum_i c_i \delta_{ji} \\
 c_j &= \int dx \psi_j^* \Psi \text{ (so we can compute all } \{c_i\} \text{)}
 \end{aligned}$$

What about

$$\langle \hat{A} \rangle = \sum_i P_i a_i$$

$$\int dx \psi^* \hat{A} \psi = \int dx \left[\sum_i c_i^* \psi_i^* \right] \hat{A} \left[\sum_j c_j \psi_j \right]$$

$$= \int dx \left[\sum_i c_i^* \psi_i^* \right] \left[\sum_j a_j c_j \psi_j \right]$$

Orthonormality kills all terms
in the sum over j except $j = i$.

$$\int dx \psi^* \hat{A} \psi = \sum_i |c_i|^2 a_i$$

thus $\langle \hat{A} \rangle = \sum_i |c_i|^2 a_i$

$$P_i = |c_i|^2 = \left| \int dx \psi_i^* \psi \right|^2$$

so the “mixing coefficients” in ψ

$$\psi = \sum c_i \psi_i$$

become “fractional probabilities” in the results of repeated measurements of \mathbf{A} .

$$\langle \hat{A} \rangle = \sum P_i a_i$$

$$P_i = \left| \int dx \psi_i^* \psi \right|^2.$$

What does the $[\hat{A}, \hat{B}]$ commutator tell us about

- * the possibility for simultaneous eigenfunctions
- * $\sigma_A \sigma_B$?

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1. If $[\hat{A}, \hat{B}] = 0$, then all non-degenerate eigenfunctions of \hat{A} are eigenfunctions of \hat{B} (see page 10).
 2. If $[\hat{A}, \hat{B}] = \text{const} \neq 0$

$$\sigma_A^2 \sigma_B^2 \geq -\frac{1}{4} \left(\int dx \psi^* [A, B] \psi \right)^2 > 0 \text{ (and real)}$$

note that $[\hat{x}, \hat{p}] = i\hbar$

this gives

$$\sigma_{p_x} \sigma_x \geq \frac{\hbar}{2} \text{ (see page 11)}$$

NON-LECTURE

Suppose 2 operators commute

$$[\hat{A}, \hat{B}] = 0$$

Consider the set of wavefunctions $\{\psi_i\}$ that are eigenfunctions of observable quantity \hat{A} .

$$\hat{A}\psi_i = a_i\psi_i \quad \{a_i\} \text{ are real}$$

commutator is 0

↑

$$\begin{aligned}
 0 &= \int dx \psi_j^* [\hat{A}, \hat{B}] \psi_i = \int dx \psi_j^* (\hat{A}\hat{B} - \hat{B}\hat{A}) \psi_i \\
 &= \int dx \psi_j^* \hat{A}\hat{B}\psi_i - \int dx \psi_j^* \hat{B}\hat{A}\psi_i \\
 &= a_j \int dx \psi_j^* \hat{B}\psi_i - a_i \int dx \psi_j^* \hat{B}\psi_i \\
 &= (a_j - a_i) \int dx \psi_j^* \hat{B}\psi_i \\
 0 &= (a_j - a_i) \underbrace{\int dx \psi_j^* \hat{B}\psi_i}_{B_{ji}}
 \end{aligned}$$

if $a_j \neq a_i \rightarrow B_{ji} = 0$

this implies that ψ_i and ψ_j are eigenfunctions of \hat{B} that belong to different eigenvalues of \hat{B}

if $a_j = a_i \rightarrow B_{ji} \neq 0$

This implies that we can construct mutually orthogonal eigenfunctions of \hat{B} from the set of degenerate eigenfunctions of \hat{A} .

All nondegenerate eigenfunctions of \hat{A} are eigenfunctions of \hat{B} and eigenfunctions of \hat{B} can be constructed out of degenerate eigenfunctions of \hat{A} .

Some important topics:

0. Completeness.

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1. For a Hermitian Operator, all non-degenerate eigenfunctions are orthogonal and the non-degenerate ones can be made to be orthonormal.
 2. Schmidt orthogonalization
 3. Are eigenfunctions of \hat{A} eigenfunctions of \hat{B} if $[\hat{A}, \hat{B}] = 0$?
 4. $[\hat{A}, \hat{B}] \neq 0 \Rightarrow$ uncertainty principle free of any thought experiments.
 5. Why do we define \hat{p} as $-i\hbar \frac{\partial}{\partial x}$?
 6. Express non-eigenstate as linear combination of eigenstates.
-
0. Completeness. Any arbitrary ψ can be expressed as a linear combination of functions that are members of a “complete basis set.”

For a particle in box

$$\Psi_n = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi}{a}x\right)$$

$$E_n = n^2 \frac{\hbar^2}{8ma^2}$$

complete set $n = 1, 2, \dots, \infty$ What do we call these ψ_n in a non-QM context?

$$\Psi = \sum_i c_i \Psi_i, \quad c_i = \int dx \Psi_i^* \Psi$$

To obtain the set of $\{c_i\}$, left-multiply Ψ by Ψ_i^* and integrate. Exploit orthonormality of the basis set $\{\Psi_i\}$.

Fourier series: any arbitrary, well-behaved function, defined on a finite interval $(0, a)$, can be decomposed into orthonormal Fourier components.

$$f(x) = \frac{1}{2}a_0 + \sum_{n=1}^{\infty} \left(a_n \cos \frac{n\pi x}{a} + b_n \sin \frac{n\pi x}{a} \right).$$

For our usual $\psi(0) = \psi(a) = 0$ boundary conditions, all of the $a_n = 0$. We can use particle in box functions $\{\psi_n\}$ to express any ψ where $\psi(0) = \psi(a) = 0$. Another kind of boundary condition is periodic (e.g. particle on a ring) $\psi(x+a) = \psi(x)$ where a is the circumference of the ring. Then, for the $0 \leq x \leq a$ interval, we need both sine and cosine Fourier series.

1. Hermitian Operator

If \hat{A} is Hermitian, all of the non-degenerate eigenstates of \hat{A} are orthogonal and all of the degenerate ones can be made orthogonal.

If \hat{A} is Hermitian

$$\int dx \psi_i^* \underbrace{\hat{A}\psi_j}_{a_j\psi_j} = \int dx \psi_j \underbrace{\hat{A}^*\psi_i^*}_{a_i^*\psi_i^*}$$

$a_i^* = a_i$ because \hat{A}
corresponds to a
classically
observable quantity

rearrange

$$(a_j - a_i) \int dx \underbrace{\psi_i^* \psi_j}_{\substack{\text{order of these} \\ \text{doesn't matter}}} = 0$$

either $a_j = a_i$ (degenerate eigenvalue)

OR

when $a_j \neq a_i$ ψ_i is orthogonal to ψ_j .

Now, when ψ_i and ψ_j belong to a degenerate eigenvalue, they can be made to be orthogonal, yet remain eigenfunctions of \hat{A} .

$$\hat{A} \left(\sum_i c_i \psi_i \right) = a_j \left(\sum_i c_i \psi_i \right)$$

for any linear combination of degenerate eigenfunctions.

Find the correct linear combination. Easy to get a computer to find these orthogonalized functions.

Non-Lecture

2. Schmidt orthogonalization

We can construct a set of mutually orthogonal functions out of a set of non-orthogonal degenerate eigenfunctions.

Consider two-fold degenerate eigenvalue a_1 with non-orthogonal eigenfunctions, ψ_{11} and ψ_{12} .

Construct a new pair of orthogonal eigenfunctions that belong to eigenvalue a_1 of \hat{A} .

$$\begin{aligned}\text{overlap } S_{11,12} &= \int \psi_{11}^* \psi_{12} \\ \psi'_{11} &\equiv \psi_{11} \\ \psi'_{12} &\equiv N[\psi_{12} - S_{11,12}\psi_{11}]\end{aligned}$$

Check for orthogonality:

$$\begin{aligned}\int dx \psi_{11}'^* \psi'_{12} &= N[\int dx \psi_{11}^* \psi_{12} - S_{11,12} \int dx \psi_{11}^* \psi_{11}] \\ &= N[S_{11,12} - S_{11,12}] = 0.\end{aligned}$$

Find normalization constant:

$$\begin{aligned}1 &= \int dx \psi_{12}'^* \psi'_{12} \\ &= |N|^2 \left[\int dx \psi_{12}^* \psi_{12} + |S_{11,12}|^2 \int dx \psi_{11}^* \psi_{11} \right. \\ &\quad \left. - \int dx \psi_{12}^* S_{11,12} \psi_{11} - \int dx S_{11,12}^* \psi_{11}^* \psi_{12} \right] \\ &= |N|^2 [1 + |S_{11,12}|^2 - |S_{11,12}|^2 - |S_{11,12}|^2] \\ &= |N|^2 [1 - |S_{11,12}|^2] \\ N &= [1 - |S_{11,12}|^2]^{-1/2} \\ \psi'_{12} &= [1 - |S_{11,12}|^2]^{-1/2} [\psi_{12} - S_{11,12}\psi_{11}]\end{aligned}$$

Now we have a complete set of orthonormal eigenfunctions of \hat{A} . Extremely convenient and useful.

End of Non-Lecture

3. Are eigenfunctions of \hat{A} also eigenfunctions of \hat{B} if $[\hat{A}, \hat{B}] = 0$?

$$\begin{aligned}\hat{A}\hat{B} &= \hat{B}\hat{A} \\ \hat{A}(\hat{B}\psi_i) &= \hat{B}(\hat{A}\psi_i) = a_i(\hat{B}\psi_i)\end{aligned}$$

thus $\hat{B}\psi_i$ is eigenfunction of \hat{A} belonging to eigenvalue a_i . If a_i is non-degenerate, $\hat{B}\psi_i = c\psi_i$, thus ψ_i is also an eigenfunction of \hat{B} .

We can arrange for one set of functions $\{\psi_i\}$ to be simultaneously eigenfunctions of \hat{A} and \hat{B} when $[\hat{A}, \hat{B}] = 0$.

This is very convenient. For example: n_x, n_y, n_z for 3D box and eigenvalues of \hat{J}^2 and \hat{J}_z for rigid rotor. Another example: 1D box has non-degenerate eigenvalues. Thus every eigenstate of \hat{H} is an eigenstate of a symmetry operator that commutes with \hat{H} .

4. $[\hat{A}, \hat{B}] \neq 0 \Rightarrow$ uncertainty principle free of any thought expt.

Suppose 2 operators do not commute

$$[\hat{A}, \hat{B}] = \hat{C} \neq 0.$$

It is possible (we will not do it) to prove, for any Quantum Mechanical state ψ

$$\sigma_A^2 \sigma_B^2 \geq -\frac{1}{4} (\int dx \psi^* \hat{C} \psi)^2 \geq 0.$$

Consider a specific example:

$$\begin{aligned} \hat{A} &= \hat{x} \\ \hat{B} &= \hat{p}_x \end{aligned}$$

$$\begin{aligned}
[\hat{x}, \hat{p}_x]f(x) &= \hat{x}\hat{p}_x f - \hat{p}_x \hat{x}f \\
&= x(-i\hbar)\frac{\partial}{\partial x}f - (-i\hbar)\frac{\partial}{\partial x}(xf) \\
&= (-i\hbar)[xf' - f - xf'] \\
&= +i\hbar f \\
\therefore [\hat{x}, \hat{p}_x] &= +i\hbar \hat{I} \\
&\quad \Downarrow \\
&\quad \text{unit} \\
&\quad \text{operator}
\end{aligned}$$

so the above (unproved) theorem says

$$\begin{aligned}
\sigma_x^2 \sigma_{p_x}^2 &\geq -\frac{1}{4} \left[\underbrace{i\hbar \int dx \psi^* \psi}_{=1} \right]^2 = -(-1) \frac{\hbar^2}{4} \\
\sigma_x \sigma_p &\geq +\frac{\hbar}{2} \quad \text{Heisenberg uncertainty principle}
\end{aligned}$$

This is better than a thought experiment because it comes from the mathematical properties of operators rather than being based on how good one's imagination is in defining an experiment to measure x and p_x simultaneously.

Non-Lecture

5. Why do we define \hat{p} as $\hat{p} = -i\hbar \frac{\partial}{\partial x}$?

Is the $-i$ needed? Why not $+i$?

$$\langle \hat{p} \rangle = -i\hbar \int_{-\infty}^{\infty} dx \psi^* \frac{d}{dx} \psi$$

which must be real, $\langle \hat{p} \rangle = \langle \hat{p} \rangle^*$. But is it?

integrate by parts,
treat ψ^* and ψ as
linearly independent
functions

$$\langle p \rangle^* = +i\hbar \int_{-\infty}^{\infty} dx \psi \frac{d}{dx} \psi^* = +(i\hbar) \left[\psi \psi^* \Big|_{-\infty}^{\infty} - \int dx \frac{d\psi}{dx} \psi^* \right] = \langle p \rangle$$

\Downarrow
0
 because ψ, ψ^* must
go to zero at $\pm \infty$

took complex conjugate of the equation for $\langle p \rangle$

thus $\langle p \rangle = \langle p \rangle^*$, i is needed in \hat{p} .

i vs. $-i$ is an arbitrary phase choice, supported by a physical argument.

Suppose we have

$$\psi = e^{ikx}$$

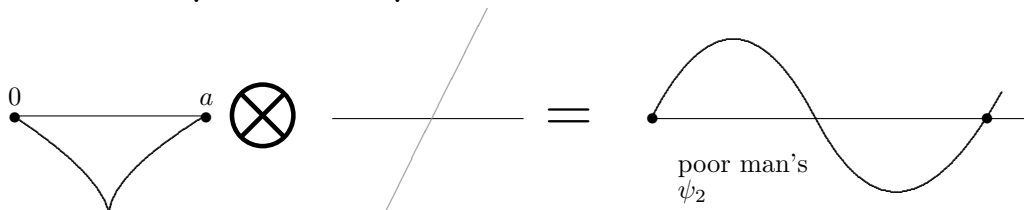
$$\hat{p}\psi = -i\hbar(ik)e^{ikx} = +\hbar ke^{ikx}$$

we like to associate $\langle \hat{p} \rangle$ with $+\hbar k$ rather than $-\hbar k$.

6. Suppose we have a non-eigenstate ψ for the particle in a box

for example,

$$\psi(x) = N \underbrace{x(x-a)}_{\text{triangle}} \underbrace{(x-a/2)}_{\text{circle with X}}$$



Normalize this

$$\int_0^a dx \psi^* \psi = 1 = N^2 \int_0^a dx x^2 (x-a)^2 (x-a/2)^2$$

find that $N = \left(\frac{840}{a^7}\right)^{1/2}$.

Now expand this function in the $\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a}$ basis set.

$$\psi = \sum_{n=1}^{\infty} c_n \psi_n \quad \text{find the } c_n$$

Left multiply by ψ_m^* and integrate

$$\int dx \psi_m^* \psi = \sum_{n=1}^{\infty} c_n \int dx \underbrace{\psi_m^* \psi_n}_{\text{orthogonal}} = c_m$$

$$c_m = (840)^{1/2} a^{-7/2} \left(\frac{2}{a}\right)^{1/2} \int_0^a dx \underbrace{x(x-a)(x-a/2)}_{\substack{\text{odd with respect to} \\ 0,a \text{ interval}}} \sin \frac{m\pi x}{a}$$

needs to be odd on $0,a$ too in order to have an even integrand

thus $c_m = 0$ for all odd- m

$$m = 2n - 1 \quad n = 1, 2, \dots$$

$$c_{2n-1} = 0$$

$$c_{2n} \neq 0 \text{ find them}$$

$$c_{2n} = \frac{(1680)^{1/2}}{a^4} \int_0^a dx \left(x^3 - \frac{3}{2}ax^2 + \frac{a^2}{2}x \right) \sin \frac{2n\pi x}{a}$$

change variables $y = \frac{2n\pi x}{a}$

$$= \frac{1680^{1/2}}{a^4} \int_0^{2n\pi} dy \left[\left(\frac{a}{2n\pi} \right)^3 y^3 - \frac{3}{2}a \left(\frac{a}{2n\pi} \right)^2 y^2 + \frac{a^2}{2} \left(\frac{a}{2n\pi} \right) y \right] \left(\frac{a}{2n\pi} \right) \sin y$$

steps skipped

$$c_{2n} = 1680^{1/2} \frac{6}{(2n\pi)^3} = 0.9914 n^{-3}$$

$c_2 \approx 1$ as expected from general shape of ψ .

Now that we have $\{c_n\}$, we can compute $\langle E \rangle = \int dx \psi^* \hat{H} \psi = \sum_{n=1}^{\infty} \underbrace{P_n}_{\text{prob-ability}} E_n$

$$P_n = c_n^2$$

$$\langle E \rangle = \sum_{n=1}^{\infty} E_{2n} |c_{2n}|^2 = E_1 \sum_{n=1}^{\infty} (2n)^2 [0.9914 n^{-3}]^2$$

$$= 4E_1 (0.983) \sum_{n=1}^{\infty} n^{-4} \approx 4E_1$$

(Is this a surprise for a function constructed to resemble ψ_2 where $E_2 = 4E_1$?)

End of Non-Lecture

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