Topic 2. The Particle in a Box & the Postulates and Tools of Quantum Mechanics
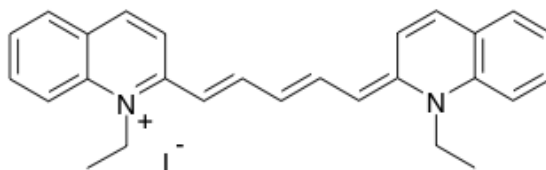
A. The Particle in a Box
1. Motivation: Organic Dyes
The cyanine dye molecules like

or

are often modeled as "electrons in a box." To understand why, start by thinking classically. You learn in organic chemistry that electrons can more "freely" along alternating double bonds. If this is true, then you can imagine that the electrons can more from one Nitrogen to the other, almost without resistance.   On the other hand, there are sp^3-hybridized functional groups attached to the Nitrogen atom, so once the electron gets to Nitrogen atom, it has to turn around and go back whence it came.   A very, very, very simple model would be to imagine that the electron is *totally free* between the Nitrogen atoms, and *totally forbidden* from going much beyond the Nitrogen atoms. This suggests modeling these systems a potential energy like:

$$V(x) = \begin{cases} +\infty & x \le 0 \\ 0 & 0 < x < a \\ +\infty & x \ge a \end{cases} \qquad (1)$$

where *a* is the length of the box.

2. The Wavefunctions for the Particle-in-a-box
The nice thing about this "particle in a box" model is that it is easy to solve the time-independent Schrödinger equation in this case. Because there is no chance that the particle could ever "escape" an infinite box like this (such an electron would have infinite potential energy!), the wavefunction must be zero outside the box. In addition, the wavefunction should be zero at the edges of the box, because otherwise the wavefunction will not be continuous. So we should have a wavefunction like

$$\Psi(x) = \begin{cases} 0 & x \le 0 \\ ?? & 0 < x < a \\ 0 & x \ge a \end{cases} \qquad (2)$$

How do we find the wavefunction inside the box? We solve the Schrödinger equation, which in this case takes the breathtakingly simple form because the potential is zero inside the box:

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Psi_n(x) = E_n\Psi_n(x) \qquad\qquad 0 < x < a \tag{3}$$

What function(s), when differentiated twice, gives back something proportional to itself? Hmmm…a bit of thought reveals that $\sin(cx)$ or $\cos(cx)$ satisfy the equation. So the general solution Eq. (3) has the form:
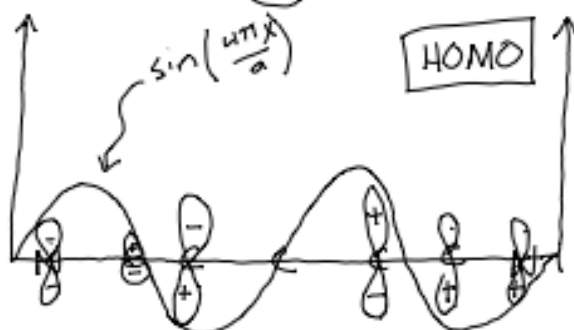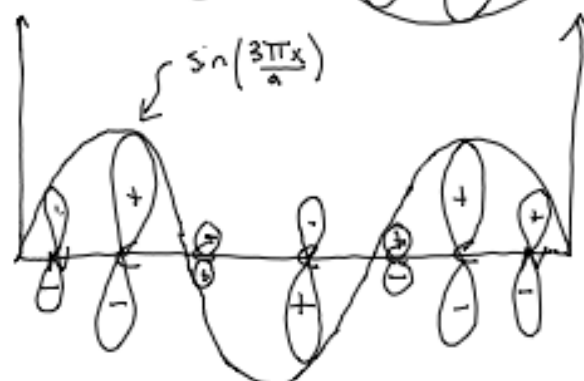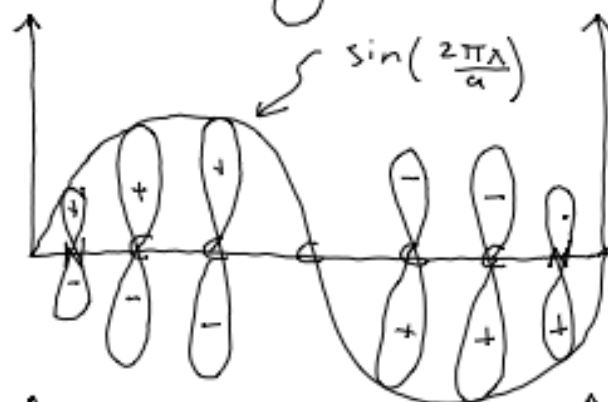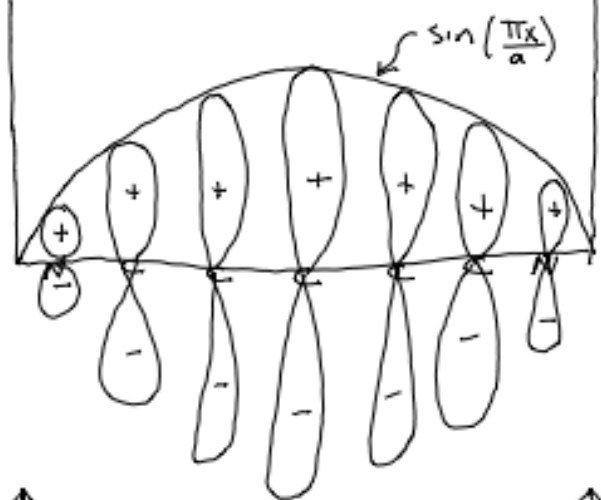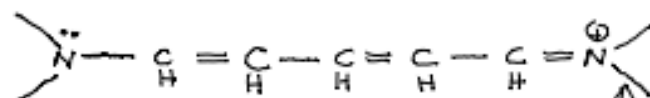
$$\Psi_n(x) = A_n\sin(c_n x) + B_n\cos(d_n x) \tag{4}$$

However, we also know that the wavefunction is zero at the edges of the box. $\cos(dx) = 1$ when $x = 0$, so $B_n = 0$. There is no "cosine part" to the solution. $\sin(cx)$ is automatically zero at $x = 0$, but it is only zero at $x = a$ if c is an integer multiple of π/a. So the only possible solutions have the form

$$\Psi_n(x) = A_n\sin\left(n\left(\frac{\pi}{a}\right)x\right) \qquad\qquad n = 1, 2, 3, \ldots \tag{5}$$

We have now solved our first (of many!) Schrödinger equations.

Let us now return to our organic dye molecules. Notice that the wavefunctions of the particle-in-a-box closely resemble the wavefunctions you drew for π-conjugated systems like these. If you want to compute the frequency of absorption for a dye molecule like these, you first count the number of π-electrons in the system. Then you fill up the "particle-in-a-box orbitals", two-at-a-time, until you run out of electrons. The observed excitation energy is the energy gap between the highest-occupied-orbital (HOMO) and the lowest-unoccupied-orbital (LUMO).

$\ddot{N}$ — C $=$ C — C $=$ C — C $=$ $\overset{\oplus}{N}$
       H   H   H   H   H

$\sin\left(\frac{\pi x}{a}\right)$

$\sin\left(\frac{2\pi x}{a}\right)$

$\sin\left(\frac{3\pi x}{a}\right)$

$\sin\left(\frac{4\pi x}{a}\right)$

HOMO

3. Energies of the Particle-in-a-box

How do we compute the energies of the particle-in-a-box? All we have to do is substitute the wavefunctions (Eq. (5)) back into the Schrödinger equation. We obtain:

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\left(A_n \sin\left(\frac{n\pi x}{a}\right)\right) = E_n\left(A_n \sin\left(\frac{n\pi x}{a}\right)\right)$$

$$A_n \frac{-\hbar^2}{2m}\frac{d}{dx}\left(\frac{n\pi}{a}\cos\left(\frac{n\pi x}{a}\right)\right) = A_n E_n\left(\sin\left(\frac{n\pi x}{a}\right)\right)$$

$$\frac{-\hbar^2}{2m}\left(\frac{n\pi}{a}\left(\frac{-n\pi}{a}\right)\sin\left(\frac{n\pi x}{a}\right)\right) = E_n\left(\sin\left(\frac{n\pi x}{a}\right)\right)$$

$$\frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{a^2}\right)\sin\left(\frac{n\pi x}{a}\right) = E_n\left(\sin\left(\frac{n\pi x}{a}\right)\right)$$

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

$$\frac{\left(\frac{h}{2\pi}\right)^2 n^2 \pi^2}{2ma^2} = E_n$$

$$\frac{h^2 n^2}{8ma^2} = E_n \qquad\qquad n = 1,2,3,\ldots \tag{6}$$

Notice that only certain energies are allowed. This is a fundamental principle of quantum mechanics, and it is related to the "waviness" of particles. Certain "frequencies" are resonant, while other "frequencies" cannot be observed. *The only energies that can be observed for a particle-in-a-box are the ones given by the formula in Eq. (6).*

Naïvely, you might expect that the lowest-energy state of the particle in a box has zero energy. The potential inside the box is zero after all. Since that's true, shouldn't the lowest-energy state be the state with zero kinetic energy? And if the kinetic energy is zero and the potential energy is zero, then the total energy would also be zero.

But this doesn't happen. It turns out that you can never "stop" a quantum particle. Not only that, the more you confine the particle (to try to "stop it"), the bigger its kinetic energy gets. Since the particle in a box has *only* kinetic energy, this is clear from Eq. (6):

$$T_n = E_n = \frac{h^2 n^2}{8ma^2} \qquad\qquad n = 1,2,3,\ldots \tag{7}$$

The kinetic energy (related to the average magnitude of the momentum) increases as $1/a^2$, so the smaller you make the box, the faster (on average) the electron moves.

The residual energy in the electronic ground state is called the **zero-point energy**:

$$E_{\text{zero pt. energy}} = \frac{h^2}{8ma^2} \tag{8}$$

This is a general principle of quantum mechanics.

Zero-Point-Energy-Principle:

Let $V(\mathbf{x})$ be a nonnegative potential. The ground-state energy of the quantum system is greater than zero.

More generally, one has:

Minimum-Energy-Bound:
Given a potential that has a lower bound, $V_<$ —i.e., $V(\mathbf{x}) \geq V_< > \infty$ —the ground-state energy of this system[1] is greater than $V_<$.

4. Normalization of the Wavefunction

We still need to determine A_n. These numbers—which are just the amplitude of the wavefunction—are not specified by quantum mechanics because the Schrödinger equation for any choice of A_n. It is convenient, for reasons that will be clear later, to choose A_n so that the wavefunctions are normalized,[2]

$$\int_0^a \Psi_n^*(x)\Psi_n(x)\,dx = 1 \qquad (9)$$

where $\Psi_n^*(x)$ denotes the complex conjugate of $\Psi(x)$. Determining A_n becomes a straightforward exercise in trigonometric integration:

$$1 = \int_0^a \Psi_n^*(x)\Psi_n(x)\,dx$$

$$1 = \int_0^a \left(A_n \sin\left(\frac{n\pi x}{a}\right)\right)^* \left(A_n \sin\left(\frac{n\pi x}{a}\right)\right)dx$$

$$1 = |A_n|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx$$

$$1 = |A_n|^2 \int_0^a \frac{1}{2}\left(1 - \cos\left(\frac{2n\pi x}{a}\right)\right)dx$$

$$1 = \frac{|A_n|^2}{2}\left(\int_0^a 1\,dx - \int_0^a \cos\left(\frac{2n\pi x}{a}\right)dx\right)$$

$$1 = \frac{|A_n|^2}{2}\left(a - \left[\frac{-a}{2n\pi}\sin\left(\frac{2n\pi x}{a}\right)\right]_0^a\right)$$

$$1 = \frac{|A_n|^2}{2}\left(a - [0-0]\right)$$

$$\frac{2}{a} = |A_n|^2 \qquad (10)$$

Notice that this doesn't *totally* determine A_n. We can choose, for example:

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[1]   Technically this is true only if the potential supports a *bound* state. If the potential is too weak to bind the particle, then the particle can have $E = V_<$.

[2]   While this normalization convention is used 99% of the time, there are some cases where it is more convenient to make a different choice for the amplitude of the wavefunctions. I say this to remind you that normalization the wavefunction is something we do for *convenience*; it is not *required* by physics!

$$A_n = \sqrt{\frac{2}{a}}$$

$$A_n = -\sqrt{\frac{2}{a}}$$

$$A_n = i\sqrt{\frac{2}{a}}$$

$$A_n = -i\sqrt{\frac{2}{a}}$$

(11)

or, more generally, any value of the form

$$A_n = \left(k \pm i\sqrt{1-k^2}\right)\sqrt{\frac{2}{a}}$$

(12)

where *k* is any real number. This arbitrariness of phase is an important aspect of the wavefunction. *Because the wavefunction can be imaginary, it is obvious that the wavefunction is not an observable property of a system. The wavefunction is only a mathematical tool that we use to solve the equations; it isn't a "physical" object.*

The wavefunction contains information about the system. Indeed, it contains *all* the physically meaningful information about the system.

Note that just because the wavefunction contains all of the *physically meaningful* information about the system doesn't mean that it contains "all information." In quantum mechanics, some things are just not observable. Consider that when you squeeze the box, the root-mean-square average momentum, $\bar{p}_{rms} = \sqrt{2m \cdot T} = \sqrt{(2m)\frac{h^2 n^2}{8ma^2}} = \frac{hn}{2a}$ increases. That is, the more you try to constrain the particle in space, the faster it moves. You can't "stop" the particle, no matter how hard you squeeze it. In fact, if you squeeze down the box infinitely far, you'll find that the particle is moving infinitely fast.

B. Postulates of Quantum Mechanics

Quantum mechanics at the level of the Schrödinger equation can be derived from more general principles. *However*, it is more useful for us to simply make some assumptions about the nature of quantum mechanics. For this reason, I will call the following "postulates." These are things that cannot be proved, at least not at the level of this course.

1. The Wavefunction Contains All of the Observable Information About the System

This is the most fundamental principle of quantum mechanics. The wavefunction contains all of the physically relevant information about a system. If the information isn't in the wavefunction, then that information is not observable and, as such, is "philosophy" and not "science." For one particle in one dimension, the wavefunction looks like $\Psi(x,t)$. For *N* particles in *d* dimensions, it is $\Psi\left(x_1^{(1)}, x_1^{(2)}, \ldots, x_1^{(d)}; x_2^{(1)}, x_2^{(2)}, \ldots, x_2^{(d)}; \ldots; x_N^{(1)}, x_N^{(2)}, \ldots, x_N^{(d)}; t\right)$, which is usually written in the more compact form $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_d, t)$ or even just $\Psi(\tau, t)$. We often summarize this as

$$\Psi(\tau, t) \rightarrow \text{everything}$$

(13)

2. The Wavefunction Is Obtained from the Time-Dependent Schrödinger Equation

How does one find the wavefunction? One finds the wavefunction by solving the time-dependent Schrödinger equation. In analogy to the 1-dimensional 1-particle Schrödinger equation,[3]

$$ i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t) \right)\Psi(x,t) \tag{14} $$

the d-dimensional, N-particle Schrödinger equation is

$$ i\hbar \frac{\partial \Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N,t)}{\partial t} = \left(-\sum_{n=1}^{N}\frac{\hbar^2}{2m_n}\sum_{i=1}^{d}\frac{\partial^2}{\partial\left(x_n^{(i)}\right)^2} + V(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N,t) \right)\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N,t) $$

$$ i\hbar \frac{\partial \Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N,t)}{\partial t} = \left(-\sum_{n=1}^{N}\frac{\hbar^2}{2m_n}\nabla_n^2 + V(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N,t) \right)\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N,t) \tag{15} $$

$$ i\hbar \frac{\partial \Psi(\boldsymbol{\tau},t)}{\partial t} = \hat{H}(\boldsymbol{\tau},t)\Psi(\boldsymbol{\tau},t) $$

where we have defined the Laplacian in the usual way,

$$ \nabla^2 = \nabla\cdot\nabla = \sum_{i=1}^{d}\frac{\partial^2}{\partial\left(x^{(i)}\right)^2}\,. \tag{16} $$

Since the Hamiltonian, $\hat{H}$, determines the solutions to the Schrödinger equation, then we may also say that:

$$ \hat{H}(\boldsymbol{\tau},t) \rightarrow \text{everything} \tag{17} $$

3. Observable Properties of the System Correspond to Linear, Hermitian Operators[4]

So the wavefunction determines all the observable properties. How do we determine the values of those properties? For classical particles, if you knew the particles' positions and momenta at a given point in time, then you can compute everything else. Thus, for a property C, there exists some function,

$$ C(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N;\mathbf{p}_1,\mathbf{p}_2,\ldots\mathbf{p}_N;t) \tag{18} $$

that can be used to compute the value of the property. Quantum mechanics is similar, but now there exists a linear, Hermitian, operator that can be used to compute the value of the property.

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[3] Again, this is true only in the nonrelativistic case. Incorporating special relativity can be done without too much trouble. However, including *general* relativity is an open problem in physics, and leads us to the realm of things like string theory. One problem arises in how one deals with the mathematics once the spatial and time coordinates are totally interchangeable. A bigger issue is the fact that mass "curves space" in general relativity.

[4] Depending on the sources you read, you may refer hear this type of "allowed operator" called different things. A mathematician would say that such operators are self-adjoint (which includes linearity already), and consider "Hermitian" to be a small subset of self-adjoint operators. The full set of quantum mechanical operators is even larger than the set of self-adjoint operators. (Essentially any operator that can be "extended" into an "essentially self-adjoint" operator in a nice way is allowed.) Fortunately, for practical calculations—which are always performed in an approximate way—these nuances do not matter very much.

The way that classical functions (which can also be thought of as operators) are transformed into quantum mechanical functions is called the correspondence principle.[5,6]

$$C\left(\mathbf{r}_1,\ldots\mathbf{r}_N;\mathbf{p}_1\ldots\mathbf{p}_N;t\right)\xrightarrow{\text{correspondence principle}}\hat{C}\left(\mathbf{r}_1,\ldots,\mathbf{r}_N,t\right) \tag{19}$$

An operator is linear if

$$\hat{C}\left(\tau,t\right)\left(a\Psi_1\left(\tau,t\right)+b\Psi_2\left(\tau,t\right)\right)=a\left(\hat{C}\left(\tau,t\right)\Psi_1\left(\tau,t\right)\right)+b\left(\hat{C}\left(\tau,t\right)\Psi_2\left(\tau,t\right)\right) \tag{20}$$

for *any* complex numbers a and b ($a,b\in\mathbb{C}$) and *any* wavefunctions $\Psi_1\left(\tau,t\right)$ and $\Psi_2\left(\tau,t\right)$. Why do observables correspond to linear operators? This is a deep result from mathematics. It arises from the mathematical structure of quantum mechanics.[7] I can't expect you to know it, but I'll (try to) explain it in a footnote.[8]

An operator has the "Hermitian property" if it satisfies the relation

$$\int\Psi_1^*\left(\tau,t\right)\hat{C}\left(\tau,t\right)\Psi_2\left(\tau,t\right)d\tau=\int\left(\hat{C}\left(\tau,t\right)\Psi_1\left(\tau,t\right)\right)^*\Psi_2\left(\tau,t\right)d\tau$$

$$\int\Psi_1^*\left(\tau,t\right)\left(\hat{C}\left(\tau,t\right)\Psi_2\left(\tau,t\right)\right)d\tau=\int\Psi_2\left(\tau,t\right)\left(\hat{C}^*\left(\tau,t\right)\Psi_1^*\left(\tau,t\right)\right)d\tau \tag{21}$$

In words, the Hermitian property means that $\hat{C}\left(\tau,t\right)$ can operate "either forwards (on Ψ_2) or backwards (on Ψ_1^*)."[9]

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[5]   A better term would be correspondence principle**s**, because there are many different ways to define quantum mechanical operators that are equivalent to their classical definition. Some of the resulting operators are, however, nonlinear.

[6]   This is rather similar to the situation in classical mechanics. There, if you know Hamilton's principle function, $S\left(\mathbf{r}_1,\ldots,\mathbf{r}_N,t\right)$, you can compute any property as:

$$C\left(\mathbf{r}_1,\ldots\mathbf{r}_N;\nabla_1 S,\ldots,\nabla_N S;t\right)$$

Notice that this says you can compute the value of any observable in classical mechanics using a function (S) that depends on the same number of variables as the time-dependent wavefunction.

[7]   However, one can choose expressions for observables that are *not* linear in the wavefunction. Those expressions, however, are always equivalent to a different, linear, expression. A good example is the kinetic energy, which can be computed from either the "standard" expression

$$\left\langle\hat{T}\left(t\right)\right\rangle=\int\Psi^*\left(\tau,t\right)\left(-\sum_{i=1}^{N}\frac{\hbar^2}{2m_i}\nabla_i^2\right)\Psi\left(\tau,t\right)d\tau$$

or from

$$\left\langle\hat{T}\left(t\right)\right\rangle=\int\sum_{i=1}^{N}\frac{\hbar^2}{2m_i}\nabla_i\left(\Psi^*\left(\tau,t\right)\cdot\nabla_i\Psi\left(\tau,t\right)\right)d\tau.$$

Notice that the second result doesn't have the form that we "expect" for a quantum mechanical observable. However, it is an allowed expression because it is mathematically equivalent to the first form.

[8]   The key is that $\hat{C}\left(\tau,t\right)\Psi_1\left(\tau,t\right)$ must *also* be a physically reasonable wavefunction, $\Psi_C\left(\tau,t\right)=\hat{C}\left(\tau,t\right)\Psi_1\left(\tau,t\right)$. Requiring that $\Psi_C\left(\tau,t\right)$ is a "mathematically legal" wavefunction means that $\hat{C}\left(\tau,t\right)$ must be in the "dual space" to the space of all "mathematically legal" wavefunctions, which means that $\hat{C}\left(\tau,t\right)$ should be a bounded linear operator on the space of "mathematically legal" wavefunctions. I turns out that the "boundedness" constraint can be relaxed.

[9]   This is especially clear if you consider a real-valued operator, where $\hat{C}^*=\hat{C}$.

Why is it essential that the operators be Hermitian? The expectation value of an observable at time t for the system described by the wavefunction $\Psi(\tau,t)$ is computed using

$$\langle C(t)\rangle = \int \Psi^*(\tau,t)\hat{C}(\tau,t)\Psi(\tau,t)d\tau \tag{22}$$

This number should obviously be real. Suppose that $\hat{C}(\tau,t)$ were not Hermitian. Then there would be some wavefunction for which:

$$\int \Psi^*(\tau,t)\hat{C}(\tau,t)\Psi(\tau,t)d\tau \neq \int \Psi(\tau,t)\left(\hat{C}(\tau,t)\Psi(\tau,t)\right)^* d\tau \tag{23}$$

But this implies that

$$\langle C(t)\rangle \neq \langle C(t)\rangle^* \tag{24}$$

If a number is not equal to its complex conjugate, then it must be a complex number. But experimental observables are all (obviously!) real numbers. Therefore, experimental observables must correspond to Hermitian operators.

Not every value for an observable will actually be observed. In fact, the only experimentally observable values for the property C are the eigenvalues of the operator,

$$\hat{C}(\tau,t)\Psi_k(\tau,t) = \quad c_k(t) \quad \Psi_k(\tau,t) \tag{25}$$

<div align="center">these are the
only values that
are observable!!</div>

Let's go back to the particle-in-a-box. We said that the energies of the particle-in-a-box were

$$E_n = \frac{h^2 n^2}{8ma^2} \tag{26}$$

These were the *only* possible energies for the particle in a box. *No other values of the energy can be observed*. This is a consequence of the "waviness" of particles: if you think about waves in a cavity, there are only certain frequencies, certain energies, etc. that can be observed. Similarly, there are only certain "special values" of properties that can be observed for a particle, and these values are the eigenvalues of the linear, Hermitian, operator for that property.

Equation of Motion for an Operator: An example of the use of the Hermitian Property

How does the expectation value of a property change in time? Starting with the definition in Eq. (22)
Consider

$$\frac{d\langle C(t)\rangle}{dt} = \frac{d\int \Psi^*(\tau,t)\hat{C}(\tau,t)\Psi(\tau,t)d\tau}{dt} \tag{27}$$

We can pull the derivative inside the integral, and then we get:

$$\frac{d\langle C(t)\rangle}{dt} = \int \left(\begin{array}{l} \dfrac{\partial \Psi^*(\tau,t)}{\partial t}\hat{C}(\tau,t)\Psi(\tau,t) + \Psi^*(\tau,t)\dfrac{\partial \hat{C}(\tau,t)}{\partial t}\Psi(\tau,t) \\[2mm] + \Psi^*(\tau,t)\hat{C}(\tau,t)\dfrac{\partial \Psi(\tau,t)}{\partial t} \end{array} \right) d\tau \tag{28}$$

The time-dependent Schrödinger equation tells us that

$$\frac{\partial \Psi(\tau,t)}{\partial t} = \frac{-i}{\hbar}\left(\hat{H}(\tau,t)\Psi(\tau,t)\right)$$

$$\frac{\partial \Psi^*(\tau,t)}{\partial t} = \frac{i}{\hbar}\left(\hat{H}^*(\tau,t)\Psi^*(\tau,t)\right)$$

(29)

which allows us to rewrite the equation for the time-dependence of an operator as

$$\frac{d\langle C(t)\rangle}{dt} = \frac{1}{i\hbar}\int\left(\begin{array}{c}-\left(\hat{H}^*(\tau,t)\Psi^*(\tau,t)\right)\left(\hat{C}(\tau,t)\Psi(\tau,t)\right)\\+\Psi^*(\tau,t)\hat{C}(\tau,t)H(\tau,t)\Psi(\tau,t)\end{array}\right)d\tau + \int\Psi^*(\tau,t)\frac{\partial\hat{C}(\tau,t)}{\partial t}\Psi(\tau,t)d\tau$$

$$= \frac{1}{i\hbar}\int\left(\begin{array}{c}-\left(\Psi^*(\tau,t)\right)\left(\hat{H}(\tau,t)\hat{C}(\tau,t)\Psi(\tau,t)\right)\\+\Psi^*(\tau,t)\hat{C}(\tau,t)H(\tau,t)\Psi(\tau,t)\end{array}\right)d\tau + \int\Psi^*(\tau,t)\frac{\partial\hat{C}(\tau,t)}{\partial t}\Psi(\tau,t)d\tau$$

$$i\hbar\frac{d\langle C(t)\rangle}{dt} = \int\Psi^*(\tau,t)\left(\hat{C}(\tau,t)\hat{H}(\tau,t) - \hat{H}(\tau,t)\hat{C}(\tau,t)\right)\Psi(\tau,t)d\tau$$

$$+\int\Psi^*(\tau,t)\frac{\partial\hat{C}(\tau,t)}{\partial t}\Psi(\tau,t)d\tau$$

(30)

Notice that we used the Hermitian property of the operator in next-to-last line,

$$\int\Psi_1^*(\tau,t)\hat{C}(\tau,t)\Psi_2(\tau,t)d\tau = \int\left(\hat{C}^*(\tau,t)\Psi_1^*(\tau,t)\right)\Psi_2(\tau,t)d\tau. \qquad (31)$$

Suggested Exercise: Suppose that the operator for the property of interest does not depend on the time. So one can replace $\hat{C}(\tau,t)$ with just $\hat{C}(\tau)$. Show that the expectation value of the property does not change in time only if one or more of the following three properties holds:

- Ψ is an eigenfunction of the Hamiltonian.
- Ψ is an eigenfunction of the property operator, $\hat{C}(\tau)$.
- The Hamiltonian and the property commute, $\hat{H}\hat{C} = \hat{C}\hat{H}$.

Suggested Exercise: Show that the eigenvalues of a Hermitian operator are always real.

Suggested Exercise: Different textbooks use different definitions of Hermitian operators.

Definition #1. A Hermitian operator, $\hat{C}(\tau)$, satisfies

$$\int\Psi^*(\tau)\hat{C}(\tau)\Psi(\tau)d\tau = \int\left(\hat{C}^*(\tau)\Psi^*(\tau)\right)\Psi(\tau)d\tau \qquad (32)$$

for any wavefunction $\Psi(\tau)$.

Definition #2. A Hermitian operator, $\hat{C}(\tau)$, satisfies

$$\int\Psi_1^*(\tau)\hat{C}(\tau)\Psi_2(\tau)d\tau = \int\left(\hat{C}^*(\tau)\Psi_1^*(\tau)\right)\Psi_2(\tau)d\tau \qquad (33)$$

for any two wavefunctions $\Psi_1(\tau)$ and $\Psi_2(\tau)$.

These two definitions are equivalent! It is easy to see that Definition #2 implies Definition #1; just choose $\Psi(\tau) = \Psi_1(\tau) = \Psi_2(\tau)$. Show that Definition #1 implies Definition #2.

4. The Eigenvectors of an Operator form a Complete, Orthonormal, Set of Functions

The set of all of the eigenvalues and eigenvectors of an operator is called its *spectrum*. It is a general theorem of mathematics, called the spectral theorem, that the set of all eigenvectors of an operator is a complete set. This is a deep result and, unfortunately, it is beyond the scope of this course to prove this.

There are three types of spectra.

a. Discrete Spectrum

The simplest, and most commonly used in chemistry, spectrum is a discrete spectrum. In this case, there are a countable number of eigenvalues and eigenvectors, which can be labeled $k = 0, 1, 2, \ldots,$

$$\hat{C}(\tau,t)\phi_k(\tau,t) = c_k(t)\phi_k(\tau,t) \tag{34}$$

Any wavefunction can be expanded in terms of the eigenvectors,

$$\Psi(\tau,t) = \sum_{k=0}^{\infty} b_k(t)\phi_k(\tau,t) \tag{35}$$

In the most important case where the operator is not time-dependent, this becomes simply

$$\hat{C}(\tau)\phi_k(\tau) = c_k\phi_k(\tau) \tag{36}$$

Any wavefunction can be expanded in terms of the eigenvectors,

$$\Psi(\tau) = \sum_{k=0}^{\infty} b_k\phi_k(\tau) \tag{37}$$

Because *any* wavefunction can be expanded in terms of the eigenvectors of the operator, we say that $\{\phi_k(\tau)\}_{k=0}^{\infty}$ is a *complete set* of functions. In the language of linear algebra, $\{\phi_k(\tau)\}_{k=0}^{\infty}$ is a *basis* for the space of all possible wavefunctions. Notice that Ψ is fully specified by the *coefficients* of the basis functions, $[a_0, a_1, \ldots]$, and so it looks like a vector. For this reason, you will sometimes hear people call Ψ a wave vector (instead of a wavefunction).[10] The space of all wavefunctions is an infinite-dimensional vector space. Infinite-dimensional vector spaces are called *Hilbert spaces*.

The eigenvectors of a linear, Hermitian operator can always be chosen to be orthonormal,

$$\int \phi_l^*(\tau)\phi_k(\tau)d\tau = \delta_{kl} \tag{38}$$

where δ_{kl} is called the Kronecker delta. The Kronecker delta is just the infinite-dimensional identity matrix,

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[10]   I do not like this term because the wave vector in classical electromagnetism is something very different.

$$\ddot{\delta} = \begin{bmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & 1 \end{bmatrix} = \mathbf{I} \tag{39}$$

$$\delta_{kl} = \delta_{lk} = \begin{cases} 0 & k \neq l \\ 1 & k = l \end{cases}$$

If one works in matrix notation, the defining "identity" property of the identity matrix is

$$\mathbf{b} = \mathbf{I}\mathbf{b}$$

$$b_l = \sum_{k=0}^{\infty} [\mathbf{I}]_{lk} \, b_k \tag{40}$$

$$= \sum_{k=0}^{\infty} \delta_{lk} b_k$$

The key defining property of the Kronecker delta is likewise

$$b_l = \sum_{k=0}^{\infty} \delta_{kl} b_k \tag{41}$$

How does one determine the coefficients of the expansion in Eq. (37)? Multiply both sides of the equation by $\phi_l^*(\tau)$ and integrate, obtaining

$$\int \phi_l^*(\tau) \Psi(\tau) d\tau = \int \phi_l^*(\tau) \left(\sum_{k=0}^{\infty} b_k \phi_k(\tau) \right) d\tau$$

$$= \int \left(\sum_{k=0}^{\infty} b_k \phi_l^*(\tau) \phi_k(\tau) \right) d\tau$$

$$= \sum_{k=0}^{\infty} b_k \int \phi_l^*(\tau) \phi_k(\tau) d\tau \tag{42}$$

$$= \sum_{k=0}^{\infty} b_k \delta_{kl}$$

$$\int \phi_l^*(\tau) \Psi(\tau) d\tau = b_l$$

Substituting this equation into Eq. (37) gives

$$\Psi(\tau) = \sum_{k=0}^{\infty} \left[\int \phi_k^*(\tau') \Psi(\tau') d\tau' \right] \phi_k(\tau) \tag{43}$$

An example of a discrete spectrum is the energy spectrum of the particle-in-a box.

The spectrum of the Hamiltonian in the particle-in-a-box is discrete. It is obvious that the set of all eigenvectors is a complete set because

$$\Psi(x) = \sum_{k=0}^{\infty} b_k \sqrt{\frac{2}{a}} \sin\left(\frac{(k+1)\pi x}{a} \right) \tag{44}$$

is just the Fourier series for a function defined on $0 < x < a$ that is zero at the edges of the interval.[11] It is a small, but useful, exercise to show that

$$\delta_{kl} = \int_0^a \left(\sqrt{\frac{2}{a}} \sin\left(\frac{(l+1)\pi x}{a} \right) \right)^* \left(\sqrt{\frac{2}{a}} \sin\left(\frac{(k+1)\pi x}{a} \right) \right) dx . \tag{45}$$

b. Continuous Spectrum

The second most common type of spectrum in chemistry is a continuous spectrum. Operators with a continuous spectrum can have any value in a specified range.

An example of an operator with continuous spectrum is the position operator.

For the particle in a box, an example of an operator with a continuous spectrum is the position operator, x. The position of the particle can be any real number between 0 and a.

The eigenfunctions of the position operator are called the Dirac delta function, $\delta_x(x_0) = \delta(x - x_0)$.[12] The Dirac delta function is the "identity matrix in real space," and is analogous to the Kronecker delta function when summation is replaced by integration,

$$\Psi(\tau_0) = \int \Psi(\tau)\delta_\tau(\tau_0)d\tau = \int \Psi(\tau)\delta(\tau - \tau_0)d\tau \tag{46}$$

Equation (46) is called the *sifting property* of the Dirac delta function.

Because the eigenvectors of an operator are a complete set, any wavefunction can be expanded in terms of a infinite linear combination of Dirac delta functions, and this is what Eq. (46) indicates. Analogous to the Kronecker-delta definition of Eq. (39),

$$\delta(\tau - \tau_0) = \begin{cases} 0 & \tau \neq \tau_0 \\ +\infty & \tau = \tau_0 \end{cases} \tag{47}$$

Choose $\Psi(\tau) = 1$ in Eq. (46). Notice that the Dirac delta function is *not* normalized in the usual way; one has

$$\int \delta(\tau - \tau_0)d\tau = 1 \tag{48}$$

but

$$\int \left(\delta(\tau - \tau_0) \right)^* \delta(\tau - \tau_0)d\tau \rightarrow \infty \neq 1 . \tag{49}$$

This does not cause any problems, because if $f_\tau(\tau_0)$ is an eigenfunction of the position operator at $\tau = \tau_0$, then $kf_\tau(\tau_0)$ also is, where k is any constant. The normalization condition in Eq. (48) is chosen to be most nearly analogous to the Kronecker delta,

$$\sum_{k=0}^{\infty} \delta_{kl} = 1 , \tag{50}$$

which follows from choosing $1 = b_0 = b_1 = b_2 = \cdots$ in Eq. (41).

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[11] Specifically, this is the Fourier half-range series expansion.

[12] In physics the eigenfunctions of position are usually called the *field operators* and are denoted $\hat{\psi}(x)$. The field operators are normalized, but they are difficult to deal with compared to most of the quantities we will use in the course. After you know how to use them, however, they are very beautiful.

The wavefunction can be defined as a "linear combination" of Dirac delta functions, in analogy to Eq. (37). However, because the number of possible values for the position is not countable, the sum in Eq. (37) is replaced by an integral,

$$\Psi(\tau_0) = \int b(\tau)\delta_\tau(\tau_0)d\tau = \int b(\tau)\delta(\tau-\tau_0)d\tau \tag{51}$$

Notice that τ is the analogue of k in this expression. Equation (42) is also replaced by an integral:

$$b(\tau') = \int \Psi(\tau)\delta_\tau(\tau')d\tau = \int \Psi(\tau)\delta(\tau-\tau')d\tau \tag{52}$$

and so Eq. (43) becomes

$$\Psi(\tau_0) = \int \left[\int \Psi(\tau')\delta_{\tau'}(\tau)d\tau' \right]\delta_\tau(\tau_0)d\tau$$
$$= \int \Psi(\tau)\delta_\tau(\tau_0)d\tau = \int \Psi(\tau)\delta(\tau-\tau_0)d\tau \tag{53}$$

There are many other examples of operators with continuous spectra. If $f_\kappa(\tau)$ denote the eigenvectors of these operators with eigenvalues κ, then the formula for the expansion is

$$\Psi(\tau) = \int \left[\int \left(f_\kappa(\tau') \right)^* \Psi(\tau')d\tau' \right] f_\kappa(\tau)d\kappa \tag{54}$$

To understand the Dirac delta function better, let us think about the Dirac delta function in one dimension. The one-dimensional Dirac delta function can be defined as follows,

$$\delta(x-x_0) = \lim_{h\to 0} d_h(x-x_0)$$

$$d_h(x-x_0) = \begin{cases} \dfrac{1}{2h} & |x-x_0| \le h \\ 0 & |x-x_0| > h \end{cases} \tag{55}$$

This corresponds to the limit of an infinitely thin, unit-area box centered at x_0. There are many other ways to write the delta function. One of my favorites uses hyperbolic functions,

$$\delta(x-x_0) = \lim_{\kappa\to\infty} \left(\tfrac{1}{2}\kappa\,\mathrm{sech}^2\left(\kappa(x-x_0)\right)\right) \tag{56}$$

Notice how the curves get higher and higher, but the area under the curves remains the same.
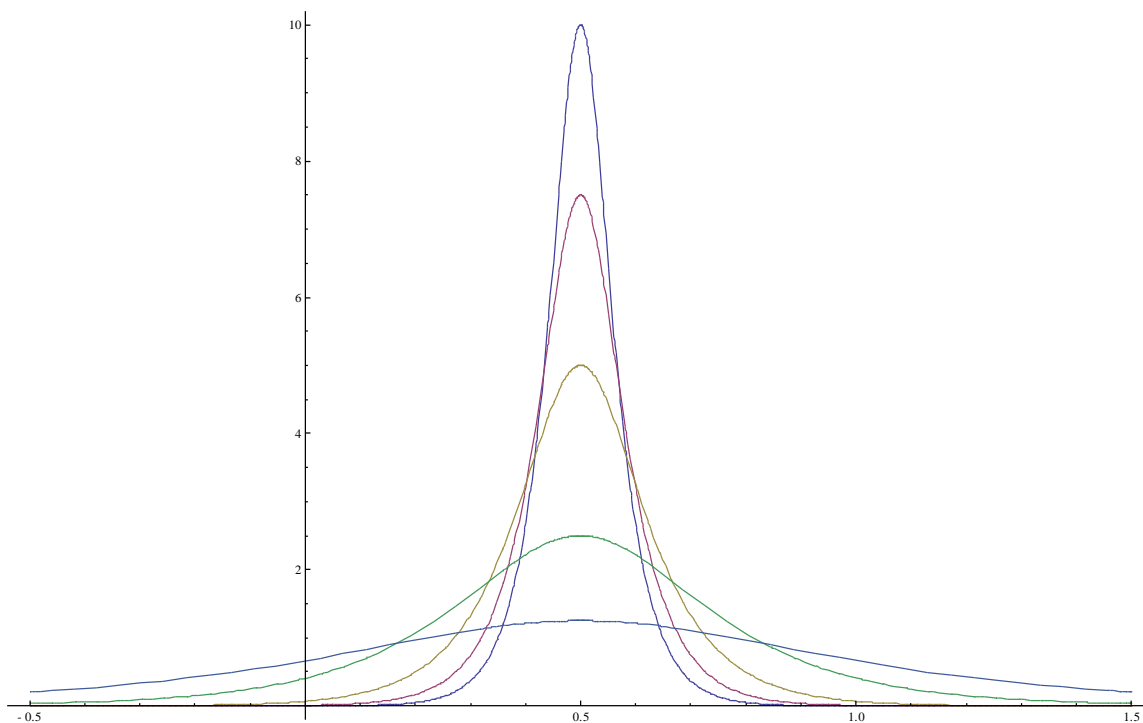
c. Mixed Spectrum

An operator that has partly continuous spectrum but also some discrete eigenvalues is said to have a mixed spectrum.

An example of an operator with a mixed spectrum is the Hamiltonian for the electrons in an atom or a molecule.

The electronic energy spectrum of every atom and molecule is a mixed spectrum. The discrete spectrum corresponds to the bound states of the system. So, at first, when one puts energy into the electrons of an atom/molecule one jumps up in energy (*1s* to *2s* to *3s* to …) in discrete chunks. At some point, one has added enough energy to the system to ionize an electron; at this point the ionized electron is unbound, and can have any energy, depending on how much kinetic energy it is given. So the electronic spectrum of atoms and molecules is discrete up until the ionization threshold, and discontinuous afterwards. If one denotes the eigenvectors of an atom/molecule by $\psi_k(\tau)$, then the expansion in terms of those eigenvectors is

$$\Psi(\;) = \sum_{k=0}^{N_{\text{bound}}} \left[\int \psi_k^*(\tau') \Psi(\tau') d\tau' \right] \psi_k(\tau) + \int_{E_{g.s.}+IP}^{\infty} \left[\int \psi_E^*(\tau') \Psi(\tau') d\tau' \right] \psi_E(\tau) dE$$

$N_{\text{bound}} = \left(\text{number of bound electronic energy states}\right)$

$IP = \text{ionization potential}$

$E_{g.s.} = \text{ground state energy}$

The Dirac Delta Function on a Basis: An Example of Basis-Set Expansion.

The Dirac delta function can be written in a complete, discrete, basis as

$$\delta\left(\tau - \tau_0\right) = \sum_{k=0}^{\infty} \phi_k\left(\tau_0\right)\phi_k^*\left(\tau\right) \tag{57}$$

To prove this, we need to prove that Eq. (46) holds. Substitute Eq. (57) into Eq. (46);

$$\int \Psi\left(\tau\right)\sum_{k=0}^{\infty} \phi_k\left(\tau_0\right)\phi_k^*\left(\tau\right)d\tau = \sum_{k=0}^{\infty} \phi_k\left(\tau_0\right)\int \phi_k^*\left(\tau\right)\Psi\left(\tau\right)d\tau$$

$$= \sum_{k=0}^{\infty} \phi_k\left(\tau_0\right)b_k \tag{58}$$

$$= \Psi\left(\tau_0\right)$$

In the second line we used Eq. (42).

Equation (57) is called the Poisson kernel. When the sum stops at some point (e.g., $k = 10{,}000$, just for computational utility), it is called the Christoffel-Darboux kernel.

<u>Why do we call the functions and numbers in $\hat{C}\left(\tau\right)\psi^{(k)}\left(\tau\right) = c^{(k)}\psi^{(k)}\left(\tau\right)$ eigenfunctions and eigenvalues? An example of the use of the basis-set expansion theorems.</u>

We have been consistently referring to $\left\{\psi^{(k)}\left(\tau\right)\right\}_{k=0}^{\infty}$ and $\left\{c^{(k)}\right\}_{k=0}^{\infty}$ as the *eigenvectors* and *eigenvalues* of the linear, Hermitian, operator $\hat{C}\left(\tau\right)$

$$\hat{C}\left(\tau\right)\psi^{(k)}\left(\tau\right) = c^{(k)}\psi^{(k)}\left(\tau\right) \tag{59}$$

What do these quantities have to do with the eigenvectors and eigenvalues in linear algebra?

Suppose that $\left\{\phi_i\left(\tau\right)\right\}_{i=0}^{\infty}$ is a complete basis. We can expand the wavefunctions in Eq. (59) in this basis set. We have

$$\psi^{(k)}\left(\tau\right) = \sum_{j=0}^{\infty} b_j^{(k)}\phi_j\left(\tau\right) \tag{60}$$

with (cf. Eq. (42))

$$b_j^{(k)} = \int \phi_j^*\left(\tau\right)\psi^{(k)}\left(\tau\right)d\tau . \tag{61}$$

Substitute Eq. (60) into the left-hand-side of Eq. (59),

$$\hat{C}\left(\tau\right)\sum_{j=0}^{\infty} b_j^{(k)}\phi_j\left(\tau\right) = c^{(k)}\psi^{(k)}\left(\tau\right) \tag{62}$$

Because $\hat{C}\left(\tau\right)$ is a *linear* operator, we can (a) pull it inside the summation and (b) pull the expansion coefficients outside the operator. So

$$\sum_{j=0}^{\infty} b_j^{(k)}\hat{C}\left(\tau\right)\phi_j\left(\tau\right) = c^{(k)}\psi^{(k)}\left(\tau\right). \tag{63}$$

Now, just as we did in deriving Eq. (42), multiply both sides of the equation by $\phi_i^*\left(\tau\right)$ and integrate. Then

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$$\int \phi_i^*(\tau) \sum_{j=0}^{\infty} b_j^{(k)} \hat{C}(\tau) \phi_j(\tau) d\tau = c^{(k)} \int \phi_i^*(\tau) \psi^{(k)}(\tau) d\tau$$

$$\sum_{j=0}^{\infty} \left[\int \phi_i^*(\tau) \hat{C}(\tau) \phi_j(\tau) d\tau \right] b_j^{(k)} = c^{(k)} \int \phi_i^*(\tau) \psi^{(k)}(\tau) d\tau$$

(64)

Now the right-hand-side of this equation is just the expansion coefficient (cf. Eq. (61)), so we have

$$\sum_{j=0}^{\infty} \left[\int \phi_i^*(\tau) \hat{C}(\tau) \phi_j(\tau) d\tau \right] b_j^{(k)} = c^{(k)} b_i^{(k)}$$

(65)

Define a matrix $\mathbf{C}$ with elements

$$c_{ij} = \int \phi_i^*(\tau) \hat{C}(\tau) \phi_j(\tau) d\tau = \left[\mathbf{C} \right]_{ij}$$

(66)

Then Eq. (65) is equivalent to

$$\sum_{j=0}^{\infty} c_{ij} b_j^{(k)} = c^{(k)} b_i^{(k)}$$

(67)

or in matrix notation,

$$\mathbf{C} \mathbf{b}^{(k)} = c^{(k)} \mathbf{b}^{(k)}$$

(68)

The eigenvectors of $\mathbf{C}$ are $\left\{ \mathbf{b}^{(k)} \right\}_{k=0}^{\infty}$ and the eigenvalues of $\mathbf{C}$ are $\left\{ c^{(k)} \right\}_{k=0}^{\infty}$. This indicates that solving for the eigenvalues/eigenvectors of a linear-Hermitian operator is equivalent to solving for the eigenvalues/eigenvectors of a infinite-dimensional Hermitian matrix.

Suggested Exercise: Show that Hermitian operators in quantum mechanics correspond to Hermitian matrices (that, is matrices $\mathbf{A}$ whose elements satisfy $a_{ij} = a_{ji}^*$) in linear algebra.

Suggested Exercise: Show that if that you an transform between two complete, orthonormal basis sets, $\left\{ \psi_k(\tau) \right\}_{k=0}^{\infty}$ and $\left\{ \phi_k(\tau) \right\}_{k=0}^{\infty}$, using a unitary transformation. That is, if you have an expansion in one both bases,

$$\Psi(\tau) = \sum_{k=0}^{\infty} b_k^{\psi} \psi_k(\tau) = \sum_{k=0}^{\infty} b_k^{\phi} \phi_k(\tau)$$

(69)

that the relationship between the coefficients of the two expansions is given by

$$b_k^{\psi} = \sum_{l=0}^{\infty} U_{kl} b_l^{\phi}$$

$$\mathbf{b}^{\psi} = \mathbf{U} \mathbf{b}^{\phi}$$

(70)

where $\mathbf{U}$ is a unitary matrix. A unitary matrix is a matrix whose conjugate-transpose is its inverse. So,

$$\mathbf{I} = \left(\mathbf{U}^* \right)^T \mathbf{U} = \mathbf{U}^\dagger \mathbf{U}$$

$$\delta_{km} = \sum_{l=0}^{\infty} \left(u_{lk} \right)^* u_{lm}$$

(71)

If you find this difficult, use the particle-in-a-box eigenfunctions as a special case. Try to show this for two different box widths for example, $a = 1$ and $a = 2$. Then you would have, explicitly,

$$\psi_k(x) = \sqrt{2}\sin\left(\pi(k+1)x\right)$$

$$\phi_k(x) = \sin\left(\frac{\pi(k+1)x}{2}\right)$$

(72)

Suggested Exercise: Show that if two eigenvectors of a linear, Hermitian, operator have different eigenvalues, then these eigenvectors are orthogonal.

4. The Square of the Wavefunction is Probability

What does the wavefunction mean? Well, since the wavefunction can be imaginary, it obviously can't mean anything. How do we turn a complex-valued function into something that is real-valued? We take its complex magnitude. The complex magnitude of the wavefunction, squared,

$$p(\tau,t) = |\Psi(\tau,t)|^2 = \Psi^*(\tau,t)\Psi(\tau,t)$$

(73)

is the probability of observing the system at the spatial location τ at the time t. Since probabilities are measurable but wavefunctions are not, sometimes it is said that "the wavefunction is the square root of reality." The idea that the complex-square-magnitude of the wavefunction equal to the probability originated with Max Born, and is called the Born postulate in his honor.

Eq. (73) cannot really be derived, but it can be justified. To do this, we need to "interpret" the Dirac delta function. It is zero everywhere except at one point, τ_0, and it goes to infinity at τ_0 that point in a way that ensures that $\delta(\tau-\tau_0)$ is normalized. *The Dirac delta function is the probability distribution function for an elementary particle at* τ_0. Related to this, the Dirac delta function is the linear, Hermitian, *operator* for "probability of a particle being at τ_0. So the property "probability of a point being at τ_0" can be computed as

$$
\begin{aligned}
p(\tau_0) &= \langle\delta(\tau-\tau_0)\rangle = \int\Psi^*(\tau)\delta(\tau-\tau_0)\Psi(\tau)d\tau \\
&= \int\delta(\tau-\tau_0)\Psi^*(\tau)\Psi(\tau)d\tau \\
&= \int\delta(\tau-\tau_0)|\Psi(\tau)|^2\,d\tau \\
&= |\Psi(\tau_0)|^2
\end{aligned}
$$

(74)

We used the sifting property of the Dirac delta function in the last line. The "derivation" in (74) helps "justify" the probabilitistic interpretation of $|\Psi|^2$.

C. Allowed Forms for Wavefunctions

We have frequently talked about the "space of all wavefunctions." What is this space? I.e., when is a function a possible wavefunction, and what types of functions can never be a wavefunction for anything?

The key to answering this question is the probabilistic interpretation of $|\Psi|^2$. Since $|\Psi|^2$ is a probability, and the particle must be *somewhere*, the integral of $|\Psi|^2$ over all space must be one:

$$1 = \int \left| \Psi(\tau) \right|^2 d\tau \tag{75}$$

This defines a *set* of wavefunctions but not a space: to be a *space*, it must be that if $\Psi_1(\tau)$ and $\Psi_2(\tau)$ are wavefunctions, then any complex linear combination of them, $c_1\Psi_1(\tau) + c_2\Psi_2(\tau)$, must also be a wavefunction. Mathematically, it is much easier to deal with *spaces* than it is to deal with *sets*. Fortunately, as we discovered with the particle in a box, if Eq. (75) is not satisfied, then we can *normalize* a wavefunction so that it is by simply performing the replacement:

$$\Psi(\tau) \to \frac{\Psi(\tau)}{\sqrt{\int \left| \Psi(\tau) \right|^2 d\tau}} \tag{76}$$

We can now define the *space* of all wavefunctions in two equivalent ways:
- The space of wavefunctions contains is the space of all wavefunctions that are normalizable, plus any function that can be reached as the limit of a convergent sequence of these functions.[13] This means that the space of all wavefunctions is the space of all functions for which

$$\infty > \int \left| \Psi(\tau) \right|^2 d\tau \tag{77}$$

- The space of all wavefunctions that can be written as

$$\Psi(\tau) = c\Psi_0(\tau) \tag{78}$$

where $c \in \mathbb{C}$ is a complex number and $\Psi_0(\tau)$ is a normalized wavefunction. (I.e., $\Psi_0(\tau)$ satisfies Eq. (75).)

In practice, certain other types of wavefunctions—e.g., plane waves ($\Psi(x,t) = e^{i(kx-\omega t)}$) or Dirac delta functions—are also sometimes allowed. However, the extension of the theory to include those wavefunctions is beyond the scope of this course.

The space of all functions, $\Psi(\tau,t)$, for which

$$\int \Psi^*(\tau)\Psi(\tau)d\tau < \infty \tag{79}$$

is called $\mathbb{L}^2\left(\mathbb{R}^d\right)$, where d is the spatial dimension of the space.[14] (That is, $d = \dim(\tau)$.) This is called the space of Lebesgue-2 integrable functions, or simply "el-two" by mathematicians. El-two is the most famous Hilbert space in the world. Though "famous" is probably not the right word.

The space of all wavefunctions is gigantic. It has infinitely many dimensions. There are many wavefunctions that are very strange, but which are totally acceptable mathematically. A few strange cases:

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[13]   The portion of this statement "plus any function….sequence of these functions" is required to form a space, because every space has to have a zero element, but the zero element has $\int \left| \Psi(\tau) \right|^2 d\tau = 0$, and is thus not normalizable in the sense of Eq. (76).

[14]   For technical reasons, it is sometimes useful to allow the positions of particles (which are necessarily real) to be complex. In that case one works in $\mathbb{L}^2\left(\mathbb{C}^d\right)$.

- The wavefunction can be infinitely large at some points. Such wavefunctions are usually considered "not physically reasonable" but there are Hamiltonians that are interesting to physicists that have infinite wavefunctions.
- The wavefunction can be discontinuous. Such wavefunctions are believed to be "nonphysical" (i.e., they are not "real world" wavefunctions) and are rarely, if ever, useful. But they are mathematically allowed.
- A derivative of the wavefunction can be discontinuous. For example, the first derivative of the particle-in-a-box wavefunction is discontinuous at the boundary of the box. The first derivative of the wavefunction for the hydrogen atom is discontinous.[15]

There are also things that no wavefunction will ever do.

- If a wavefunction is infinite at some points in space, $\mathcal{S}$, then the volume of that set of points must be zero. So,

$$0 = \int_{\mathcal{S}} d\tau$$
$$\mathcal{S} = \left\{ \tau \,\middle\|\, \Psi(\tau) \right\| = \infty \right\} \tag{80}$$

- The derivative of an eigenfunction of a Hamiltonian, $\hat{H}(\tau)$, can only be discontinuous if the potential energy is discontinuous at τ.

The set of "physically reasonable" wavefunctions is sometimes defined as the set of wavefunctions that are eigenfunctions for some "reasonable" (i.e., "interesting") Hamiltonian. Most "physically reasonable" wavefunctions are less than infinity everywhere, decay rapidly as one moves away from the system, and "nice" in the sense that they are infinitely differentiable almost everywhere.

Suggested Exercise: Give an example of a wavefunction that is infinite at the origin ($\tau = 0$), but nowhere else. (Hint: use polar/spherical coordinates in two/three dimensions.)

D. Linear Algebra and Quantum Mechanics

1. Dirac Notation: Bra's and Ket's

Eventually we all get tired of writing integrals. Working in the early 1930's, a man named Paul Dirac got tired of writing integrals and decided to replace integrals like

$$\int d\tau \left(\Psi_1^*(\tau) \; \underbrace{\hat{C}(\tau)}_{} \; \Psi_2(\tau) \right) \tag{81}$$

integral over all space — can operate backwards — can operate forwards — just a "dummy" variable

with a compact notation,

$$\left\langle \Psi_1 \middle| \hat{C} \middle| \Psi_2 \right\rangle \tag{82}$$

- There is no mention of the limits of integration because this is always "clear from the problem" and, in any event, can always be taken to be all of real space.

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[15]   This is only true if one assumes that the proton is infinitely small, which is almost (but not quite) true.

- Because of the Hermitian property of the operator, $\hat{C}(\tau)$ it can operate either "forwards" (on $\Psi_2(\tau)$) or "backwards" (on $\Psi_1^*(\tau)$).

- The variable of integration does not need to be specified since it is just a "dummy variable." I.e., you can change τ to another variable with the same dimensionality, $\mathbf{u}$, without changing the interpretation of Eq. (81).

Dirac called the first part of the notation, with the complex-conjugated wavefunction, a "bra", and the second part a ket.

$$\langle \Psi_1 | \hat{C} | \Psi_2 \rangle \qquad (83)$$
$$\underset{\text{bra}}{} \qquad \underset{\text{ket}}{}$$

Together you have a "bra $\hat{C}$ ket". Who says physicists are immune to bad puns?

Everything before the first vertical line in a bracket is automatically complex conjugated. Sometimes the second vertical line is omitted, and then one has notation like

$$\langle \Psi_1 | \hat{C} \Psi_2 \rangle = \langle \hat{C} \Psi_1 | \Psi_2 \rangle \qquad (84)$$

This is a very compact notation. It was basically motivated by the tendency of physicists and mathematicians to write expectation values (that is, mean values) as $\langle C \rangle$. From there it is a short notational step to:

$$\langle C \rangle = \langle \Psi | \hat{C} | \Psi \rangle \qquad (85)$$

When you see an bra all by itself, it indicates the complex conjugate of the wavefunction:

$$\langle \Psi | = \Psi^*(\tau). \qquad (86)$$

An isolated ket means

$$|\Psi\rangle = \Psi(\tau). \qquad (87)$$

Dirac has Asperger's syndrome and was quite immune, it seems, from making sexually suggestive remarks about "bra"s. It seems to have never occurred to him. However, there are strange mathematical objects, which I saw in a physics seminar a long time ago, called "padded bras."

2. Linear Algebra and the Analogy to Quantum Mechanics

Aside from its utility for making jokes (which are in short supply in physics seminars) and the fact it saves one from writer's cramp, physicists like Dirac notation because it makes it easier to see the analogies between linear algebra and the mathematics of quantum mechanics. Almost every result in linear algebra has an analogue in quantum mechanics.

Quantum Mechanics	Linear Algebra
Infinite-dimensional complex-valued vector space. ("Hilbert space.")	Finite-dimensional complex-valued vector space. (Could also be a real-valued vector space.)
Wavefunctions, $\Psi(\tau) = \lvert\Psi\rangle$.	d-dimensional vectors, $\mathbf{v}$
Complex-conjugate wavefunctions, $\Psi^*(\tau) = \langle\Psi\rvert$	Hermitian transpose of vectors, $\mathbf{v}^\dagger = \left(\mathbf{v}^*\right)^T = \left(\mathbf{v}^T\right)^*$.
Space of all wavefunctions is the space of all $\Psi(\tau)$ for which $$\infty > \int \Psi^*(\tau)\Psi(\tau)\,d\tau = \langle\Psi\lvert\Psi\rangle$$	Space of all vectors is the space of all $\mathbf{v}$ for which $$\infty > \mathbf{v}^\dagger\mathbf{v}$$
Norm of wavefunctions is $$\lVert\Psi\rVert = \sqrt{\int \Psi^*(\tau)\Psi(\tau)\,d\tau} = \sqrt{\langle\Psi\lvert\Psi\rangle}$$	Norm of vectors is $$\lVert\mathbf{v}\rVert = \sqrt{\mathbf{v}^\dagger\mathbf{v}}$$
Inner product between wavefunctions is $$\int \Psi_1^*(\tau)\Psi_2(\tau)\,d\tau = \langle\Psi_1\lvert\Psi_2\rangle$$	Inner product ("dot" product) between vectors is $\mathbf{v}_1^\dagger\mathbf{v}_2 = \mathbf{v}_1^* \cdot \mathbf{v}_2$
Linear Hermitian Operators, $$\int \Psi_1^*(\tau)\hat{C}(\tau)\Psi_2(\tau)\,d\tau = \int \left(\hat{C}(\tau)\Psi_1(\tau)\right)^* \Psi_2(\tau)\,d\tau$$ $$= \int \hat{C}^*(\tau)\Psi_1^*(\tau)\Psi_2(\tau)\,d\tau$$ $$\langle\Psi_1\lvert\hat{C}\rvert\Psi_2\rangle = \langle\Psi_1\lvert\hat{C}\Psi_2\rangle = \langle\hat{C}\Psi_1\lvert\Psi_2\rangle$$	Hermitian Matrices, $\mathbf{C} = \left(\mathbf{C}^*\right)^T = \mathbf{C}^\dagger$. $$\mathbf{v}_1^\dagger\mathbf{C}\mathbf{v}_2 = \left(\mathbf{C}\mathbf{v}_1\right)^\dagger \mathbf{v}_2$$

Eigenvalues of Linear, Hermitian, operators are real and the corresponding eigenvectors can be chosen to form a complete, orthonormal, set $$\hat{C}(\tau)\Psi_k(\tau)=c_k\Psi_k(\tau) \qquad c_k \in \mathbb{R}$$ $$\int \Psi_k^*(\tau)\Psi_l(\tau)d\tau = \delta_{kl}$$ $$\hat{C}\lvert\Psi_k\rangle = c_k\lvert\Psi_k\rangle$$ $$\langle\Psi_k\lvert\Psi_l\rangle = \delta_{kl}$$ Any wavefunction can be written as: $$\Phi(\tau)=\sum_{k=0}^{\infty}b_k\Psi_k(\tau) \qquad b_k=\int\Psi_k^*(\tau)\Phi(\tau)d\tau$$ $$\lvert\Phi\rangle=\sum_{k=0}^{\infty}b_k\lvert\Psi_k\rangle \qquad b_k=\langle\Psi_k\lvert\Phi\rangle$$	Eigenvalues of Hermitian matrices are real and the corresponding eigenvectors can be chosen to form a complete, orthonormal, set $$\mathbf{C}\mathbf{v}_k=c_k\mathbf{v}_k \qquad c_k \in \mathbb{R}$$ $$\mathbf{v}_k^\dagger\mathbf{v}_l=\delta_{kl}$$ Any vector can be written as $$\mathbf{u}=\sum_{k=0}^{d-1}b_k\mathbf{v}_k \qquad b_k=\mathbf{v}_k^\dagger\mathbf{u}$$
Inner product expressed with a basis set. $$\Phi(\tau)=\sum_{k=0}^{\infty}b_k\Psi_k(\tau)=\sum_{k=0}^{\infty}b_k\lvert\Psi_k\rangle$$ $$\varphi(\tau)=\sum_{k=0}^{\infty}a_k\Psi_k(\tau)=\sum_{k=0}^{\infty}a_k\lvert\Psi_k\rangle$$ $$\int\Phi^*(\tau)\varphi(\tau)d\tau=\langle\Phi\lvert\varphi\rangle=\sum_{k=0}^{\infty}b_k^*a_k$$ **<u>Suggested Exercise:</u>** Derive this result.	Inner product expressed with a basis set $$\mathbf{u}=\sum_{k=0}^{d-1}b_k\mathbf{v}_k$$ $$\mathbf{w}=\sum_{k=0}^{d-1}a_k\mathbf{v}_k$$ $$\mathbf{u}^\dagger\mathbf{w}=\sum_{k=0}^{d-1}b_k^*a_k$$

Linear, Hermitian, operator expressed with a basis set	Matrix expressed with a basis set
$$\hat{C} \Leftrightarrow \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\Psi_k(\tau)\left(\int \Psi_k^*(\tau'')\hat{C}(\tau'')\Psi_l(\tau'')d\tau''\right)\Psi_l^*(\tau')$$ $$=\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\Psi_k(\tau)c_{kl}\Psi_l^*(\tau')$$ $$\hat{C} \Leftrightarrow \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}|\Psi_k\rangle\langle\Psi_k|\hat{C}|\Psi_l\rangle\langle\Psi_l| = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}|\Psi_k\rangle c_{kl}\langle\Psi_l|$$ $$c_{kl} = c_{lk}^* = \int \Psi_k^*(\tau'')\hat{C}(\tau'')\Psi_l(\tau'')d\tau'' = \langle\Psi_k|\hat{C}|\Psi_l\rangle$$	$$\mathbf{C} = \sum_{k=0}^{d-1}\sum_{l=0}^{d-1}\mathbf{v}_k\left(\mathbf{v}_k^{\dagger}\mathbf{C}\mathbf{v}_l\right)\mathbf{v}_l^{\dagger} = \sum_{k=0}^{d-1}\sum_{l=0}^{d-1}\mathbf{v}_k c_{kl}\mathbf{v}_l^{\dagger}$$ $$c_{kl} = \mathbf{v}_k^{\dagger}\mathbf{C}\mathbf{v}_l$$
Action of a linear, Hermitian, operator on a wavefunction,	Action of a matrix on a vector,
$$\Phi(\tau) = \sum_{k=0}^{\infty}b_k\Psi_k(\tau) = \sum_{k=0}^{\infty}b_k|\Psi_k\rangle$$ $$b_k = \int \Psi_k^*(\tau)\Phi(\tau)d\tau = \langle\Psi_k|\Phi\rangle$$ $$c_{kl} = c_{lk}^* = \int \Psi_k^*(\tau'')\hat{C}(\tau'')\Psi_l(\tau'')d\tau'' = \langle\Psi_k|\hat{C}|\Psi_l\rangle$$ $$\hat{C}(\tau)\Phi(\tau) = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\int \Psi_k(\tau)\left(\int \Psi_k^*(\tau'')\hat{C}(\tau'')\Psi_l(\tau'')d\tau''\right)\Psi_l^*(\tau')\Phi(\tau')d\tau'$$ $$=\sum_{k=0}^{\infty}\Psi_k(\tau)\sum_{l=0}^{\infty}c_{kl}b_l$$ $$\hat{C}|\Phi\rangle = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}|\Psi_k\rangle\langle\Psi_k|\hat{C}|\Psi_l\rangle\langle\Psi_l|\Phi\rangle$$ $$=\sum_{k=0}^{\infty}|\Psi_k\rangle\sum_{l=0}^{\infty}c_{kl}b_l$$ **Suggested Exercise:** Derive this result.	$$\mathbf{u} = \sum_{k=0}^{d-1}b_k\mathbf{v}_k \qquad\qquad b_k = \mathbf{v}_k^{\dagger}\mathbf{u}$$ $$c_{kl} = \mathbf{v}_k^{\dagger}\mathbf{C}\mathbf{v}_l$$ $$\mathbf{C}\mathbf{u} = \sum_{k=0}^{d-1}\sum_{l=0}^{d-1}\mathbf{v}_k c_{kl}\mathbf{v}_l^{\dagger}\mathbf{u}$$ $$=\sum_{k=0}^{d-1}\mathbf{v}_k\sum_{l=0}^{d-1}c_{kl}b_l$$ This is equal to the usual formula if the basis is chosen so that $\mathbf{v}_k$ is the vector that is all zeros, except for a 1 in the k-1st position.

Product of two linear, Hermitian, Operators

$$\hat{C} \Leftrightarrow \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}|\Psi_k\rangle\langle\Psi_k|\hat{C}|\Psi_l\rangle\langle\Psi_l| = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}|\Psi_k\rangle c_{kl}\langle\Psi_l|$$

$$\hat{D} \Leftrightarrow \sum_{m=0}^{\infty}\sum_{n=0}^{\infty}|\Psi_m\rangle\langle\Psi_m|\hat{D}|\Psi_n\rangle\langle\Psi_n| = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty}|\Psi_m\rangle d_{mn}\langle\Psi_n|$$

$$\hat{C}\hat{D} = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}|\Psi_k\rangle\langle\Psi_k|\hat{C}|\Psi_l\rangle\langle\Psi_l|\Psi_m\rangle\langle\Psi_m|\hat{D}|\Psi_n\rangle\langle\Psi_n|$$

$$= \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}|\Psi_k\rangle c_{kl}\delta_{lm}d_{mn}\langle\Psi_n|$$

$$= \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\sum_{n=0}^{\infty}|\Psi_k\rangle c_{kl}d_{ln}\langle\Psi_n|$$

$$= \sum_{k=0}^{\infty}|\Psi_k\rangle\sum_{n=0}^{\infty}\langle\Psi_n|\sum_{l=0}^{\infty}c_{kl}d_{ln}$$

Suggested Exercise: Derive the expression for $\langle\Phi|\hat{C}\hat{D}|\Phi\rangle$ in this basis set.

Product of two matrices:

$$\mathbf{C} = \sum_{k=0}^{d-1}\sum_{l=0}^{d-1}\mathbf{v}_k\left(\mathbf{v}_k^\dagger\mathbf{C}\mathbf{v}_l\right)\mathbf{v}_l^\dagger = \sum_{k=0}^{d-1}\sum_{l=0}^{d-1}\mathbf{v}_k c_{kl}\mathbf{v}_l^\dagger$$

$$\mathbf{D} = \sum_{m=0}^{d-1}\sum_{n=0}^{d-1}\mathbf{v}_m\left(\mathbf{v}_m^\dagger\mathbf{D}\mathbf{v}_n\right)\mathbf{v}_n^\dagger = \sum_{m=0}^{d-1}\sum_{n=0}^{d-1}\mathbf{v}_m d_{mn}\mathbf{v}_n^\dagger$$

$$\mathbf{CD} = \sum_{k=0}^{d-1}\sum_{l=0}^{d-1}\sum_{m=0}^{d-1}\sum_{n=0}^{d-1}\mathbf{v}_k c_{kl}\mathbf{v}_l^\dagger\mathbf{v}_m d_{mn}\mathbf{v}_n^\dagger$$

$$= \sum_{k=0}^{d-1}\sum_{l=0}^{d-1}\sum_{m=0}^{d-1}\sum_{n=0}^{d-1}\mathbf{v}_k c_{kl}\delta_{lm}d_{mn}\mathbf{v}_n^\dagger$$

$$= \sum_{k=0}^{d-1}\sum_{l=0}^{d-1}\sum_{n=0}^{d-1}\mathbf{v}_k c_{kl}d_{ln}\mathbf{v}_n^\dagger$$

$$= \sum_{k=0}^{d-1}\mathbf{v}_k\sum_{n=0}^{d-1}\mathbf{v}_n^\dagger\sum_{l=0}^{d-1}c_{kl}d_{ln}$$

This is equal to the usual formula if the basis is chosen so that $\mathbf{v}_k$ is the vector that is all zeros, except for a 1 in the k-1st position.

D. Momentum and Position

1. The Momentum Operator in Quantum Mechanics

The operator for position in quantum mechanics is just the position itself, τ, or, in one dimension x. The expectation value of the position is thus

$$\langle \tau \rangle = \int \Psi^*(\tau)\,\tau\,\Psi(\tau)\,d\tau = \int \tau \left| \Psi^*(\tau) \right|^2 d\tau \qquad (88)$$

--correspondence principle

2. The Momentum-Space Wavefunction

3. The Heisenberg Uncertainty Principle

Suggested Exercise: Consider a system whose wavefunction has the form $\Psi(\tau) = a\Phi(\tau)$, where $\Phi(\tau) \in \mathbb{R}$ is real and $a \in \mathbb{C}$ is complex. Show that the average momentum of the system is always zero.

Suggested Exercise: Derive the general formula for the average momentum of the particle in a box. Recall that in this case $\Psi_n(x) = \sqrt{\dfrac{2}{a}} \sin\left(\dfrac{n\pi x}{a} \right)$.

Suggested Exercise: Show that the kinetic-energy operator, $\dfrac{-\hbar^2}{2m}\dfrac{d^2}{dx^2}$, for a one-dimensional system is Hermitian.

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References:

On the Particle in a Box:
  A "Modern Treatment" of the Particle in a Box (from Journal of Chemical Education)
  Particle in a Box (from Wikipedia)
Postulates of Quantum Mechanics:
  Postulates of Quantum Mechanics
On the Particle in a Ring:
  Particle in a Ring (from Wikipedia)

This is Chapter 15 in Engel and Reid.

My favorite source for this material is Chapter 3 of:

D. A. MacQuarrie, Quantum Chemistry (University Science Books, Mill Valley California, 1983)