CHM 305 - Midterm Review

Prof. Marissa Weichman

1 Some (non-exhaustive!) ideas on things to review

1. **Solving differential equations and the particle in a box.** You should be able to set up and solve the the time-independent Schrödinger equation for the 1D particle in a box. You should make sure that you understand and can explain all of the following:

   (a) The second order differential equations have two independent solutions, so the most general solution is a linear combination of these two solutions.

   (b) The boundary conditions reduce the number of acceptable solutions and limit the values of E that are "allowed."

   (c) The PIB wavefunction $\psi(x)$ is continuous even at the box boundaries, but $\frac{d\psi}{dx}$ is not. In general $\frac{d\psi}{dx}$ is continuous except at points where the potential $V(x)$ undergoes an infinite jump as it does at the box boundaries.

   (d) The energy levels grow with quantum number n as $E_n \propto n^2$.

   (e) What the wavefunctions $\psi_n(x)$ look like when plotted, e.g. that each wavefunction is symmetric about the center of the box, and that the n^{th} wavefunction has $n-1$ nodes.

2. **Basis set expansion.** You should be able to expand any wavefunction in terms of a nice set of orthonormal basis functions. You should be able to articulate why it's important and useful that basis functions be orthonormal. You should be able to articulate the meaning of the coefficients in your basis set expansion.

3. **Time-dependent wavefunctions.** You should understand how the time evolution of an eigenstate $\Psi(x,0) = \psi_n(x)$ involves a simple $\exp(-iE_nt/\hbar)$ factor, so $|\Psi_n(x,t)|^2$ does not depend on time. However, when $\Psi(x,t)$ is not an energy eigenstate (e.g., when it is a superposition or linear combination of eigenstates), the time-dependent Schrödinger equation produces a $\Psi(x,t)$ whose $|\Psi(x,t)|^2$ probability distribution *does* change with time. There are related arguments to be made for expectation values as well!

4. **Quantum measurement.** You should have some intuition for wavefunction collapse following a quantum measurement. You should be able to articulate how uncertainty in quantum measurement arises when you try to make sequential measurements with non-commuting operators. You should be able to quantify this using the uncertainty principle. You should understand the special relationship between commuting operators, be able to show why commuting operators share a common set of eigenfunctions, and articulate how having shared eigenfunctions allows us to make arbitrarily precise simultaneous measurements.

5. **Quantum tunneling & scattering.** You should understand the derivation of reflection and tunneling probabilities when a particle strikes a finite barrier. You should be able to write out the TISE and its general solutions in different regions of space and the relevant boundary conditions used to stitch these solutions together. You should appreciate how the tunneling probability decays exponentially with the "thickness" and "height" of the barrier. You should be able to argue why tunneling of heavier particles is less likely than for light particles.

6. **The harmonic oscillator and rigid rotor.** You should be familiar with the energy eigenvalue expressions for the quantum harmonic oscillator and the rigid rotor and how they vary with quantum numbers (n in the former case, J, m in the latter). You should be able to describe in plain language how these models connect to molecular behavior, and what the n, J and m quantum numbers represent. You should also know how these energies depend on things like molecular bond length, force constant, and reduced mass.

2 What do we learn from the wavefunction?

- First and foremost, $|\Psi(x,t)|^2$ represents a probability distribution for where we expect to find a quantum particle along the x axis as a function of time, t.

$$\int_a^b |\Psi(x,t)|^2 dx \quad = \quad \left\{ \begin{array}{c} \text{probability of finding the particle} \\ \text{between } a \text{ and } b \text{ at time } t \end{array} \right\}$$

We therefore require a given wavefunction to be normalized, meaning that:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$$

- We can use the wavefunction to calculate any physically measurable quantity by evaluating the expectation value of its corresponding quantum operator:

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \hat{A} \Psi(x,t) dx$$

where $\hat{A}$ might represent something like position, momentum, kinetic energy, etc.

- The time-dependent wavefunction tells us how we expect the system to evolve for all future times (provided we don't make a measurement and mess it up). We typically start with the particle prepared in some initial state at time $t = 0$ given by $\Psi(x, 0)$, then see how it evolves. Valid time-dependent wavefunctions must behave according to the Schrödinger quantum wave equation, the same way that classical waves evolve according to the classical wave equation:

Classical	$\longleftrightarrow$	**Quantum**
$\frac{\partial^2}{\partial x^2}\Psi(x,t) = \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\Psi(x,t)$	$\longleftrightarrow$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x)\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$

3 Time-dependent vs. time-independent Schrödinger equations

All valid wavefunctions $\Psi(x,t)$ – which is to say eigenstates of the Hamiltonian as well as any arbitrary superposition states thereof – obey the **full time-dependent Schrödinger equation** (TDSE):

$$\star \quad \hat{H}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x)\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$$

though the forms and time-dependence of these solutions may be very complicated.

We use a trick to make it much simpler to describe solutions to the Schrödinger equation. We solve it by limiting ourselves to look just for "stationary state" solutions that factor neatly into spatial and temporal components:

$$\Psi(x,t) = \psi(x) \cdot \phi(t)$$

These solutions look like standing waves, because the spatial envelope $\psi(x)$ describes nodes and peaks of the wavefunction whose positions do not vary in time.

Deciding to look only for stationary state solutions allows us to break up the Schrödinger equation into two parts, using a separation constant we call E. The second of these is easy to solve, the first can be much more difficult:

$$\begin{aligned} \textbf{spatial part}: \quad & -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E\psi(x) \\ \textbf{temporal part}: \quad & i\hbar\frac{\partial}{\partial t}\phi(t) = E\phi(t) \end{aligned}$$

The spatial part is what we call the **time-independent Schrödinger equation** (TISE). The temporal part doesn't get its own name because it is so simple to solve and we only need to solve it once.

In fact, these stationary state solutions are convenient because their time dependence is so simple to write down:

$$\phi(t) = e^{-iEt/\hbar}$$

We often find a discrete series of spatial solutions that we label with an integer index $\psi_n(x)$, allowing us to write down a complete expression for our series of standing wave solutions:

$$\Psi_n(x,t) = \psi_n(x) \cdot \phi_n(t) = \psi_n(x) \cdot e^{-iE_nt/\hbar}$$

If we have a non-stationary wavefunction given by some superposition of these standing wave basis states:

$$\Phi(x,t) = \sum_n b_n \Psi_n(x,t)$$

it will still always be a solution to the full Schrödinger equation marked with a $\star$ above. But it **will not** solve the time-independent and time-dependent halves separately! This is the distinction between being a general solution to the Schrödinger equation vs. a stationary state or eigenfunction of $\hat{H}$.

Flow chart for computing the time evolution of a state

Given $\Psi(x,0)$ and the Hamiltonian $\hat{H}$ Find $\Psi(x,t)$

$\hat{H}\psi_m = E_m\psi_m$ Solve time-indep. Schröd. eq.

↓ Time dependence of stationary states

Discrete	Continuous
$\psi_m(x,t) = \exp(-iE_m t/\hbar)\,\psi_m(x)$	$\psi_k(x,t) = \exp(-iE(k)t/\hbar)\,\psi_k(x)$

↓ Expand $\Psi(x,0)$ in terms of stationary states ↓

$\Psi(x,0) = \sum_n c_n\psi_n(x)$	$\Psi(x,0) = \int C(k)\,\psi_k(x)\,dk$

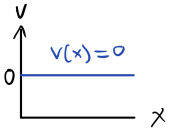
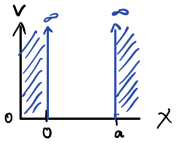
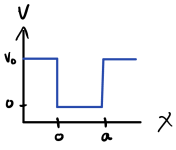
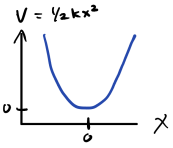
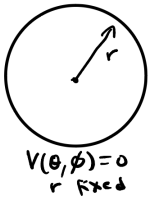
↓ Find c_m or $c(k)$ using orthogonality ↓

$c_m = \int \psi_m^*(x)\,\Psi(x,0)\,dx$	$c(k) = \int \psi_k^*(x)\,\Psi(x,0)\,dx$

↓ General solution using superposition ↓

$\Psi(x,t) = \sum_n c_n\,\psi_n(x,t)$	$\Psi(x,t) = \int c(k)\psi_k(x,t)\,dk$
$= \sum_n c_n\,\exp(-iE_n t/\hbar)\,\psi_n(x)$	$= \int c(k)\,\exp(-iE(k)t/\hbar)\,\psi_k(x)\,dk$

4 Solutions to the TISE for important quantum model systems

	free particle	particle in a box	particle in a finite box	harmonic oscillator	rigid rotor
$V(x)$					
$\psi_n(x)$					
E_n					
discrete or continuous?					
chemical relevance					

5 The Uncertainty Principle

If two operators commute, they share a common set of eigenfunctions, and we can make precise measurements with both simultaneously.

To illustrate this a bit, consider *commuting* operators $\hat{A}$ and $\hat{B}$, which share a set of eigenfunctions $\{\psi_n\}$ with eigenvalues $\{a_n\}$ and $\{b_n\}$, respectively.

- If we make a measurement $\hat{A}\psi_1$, we know with perfect certainty we will measure eigenvalue a_1, because ψ_1 is an eigenfunction of $\hat{A}$.
- Following this measurement, the state of the system is unchanged, as we "collapse" the wavefunction from ψ_1 back to ψ_1 again.
- If we subsequently perform a measurement of the system with $\hat{B}$, we know with perfect certainty we will measure eigenvalue b_1, because ψ_1 is also an eigenfunction of $\hat{B}$.
- We can therefore perform simultaneous measurements with $\hat{A}$ and $\hat{B}$ with perfect certainty, because they commute and therefore share common eigenfunctions.

Now consider instead operators $\hat{A}$ and $\hat{B}$ which *do not commute*. These operators have separate sets of eigenfunctions $\{\psi_n\}$ and $\{\phi_n\}$ with eigenvalues $\{a_n\}$ and $\{b_n\}$, respectively.

- The same as before, if we make a measurement $\hat{A}\psi_1$, we know with perfect certainty we will measure eigenvalue a_1, because ψ_1 is an eigenfunction of $\hat{A}$.
- Following this measurement, the state of the system is unchanged, remaining in ψ_1.
- If we subsequently perform a measurement of the system in state ψ_1 with $\hat{B}$, we now have some uncertainty in what result this measurement will produce, since ψ_1 is not an eigenfunction of $\hat{B}$. In order to figure out what we'd expect to measure, we'd have to express ψ_1 as a linear combination of the eigenfunctions of $\hat{B}$, finding appropriate coefficients c_n such that

$$\psi_1 = \sum_n c_n \phi_n$$

  We'd therefore expect to measure the eigenvalue b_n with probability $|c_n|^2$.
- We therefore cannot have perfect certainty with simultaneous measurements using $\hat{A}$ and $\hat{B}$ if they do not have shared eigenfunctions, which is only the case when they commute.

Finally, let's recall a more explicit metric for uncertainty. The simultaneous measurement certainty of two operators applied to a given wavefunction ψ is given by

$$\sigma_A^2 \sigma_B^2 \geq -\frac{1}{4}\left[\int \psi^* [\hat{A}, \hat{B}] \psi dx\right]^2$$