Chem 442 Review for Exam 1

Energies are quantized

Wave/particle duality

de Broglie wavelength: $\lambda = h/p$

Energy: $E = h\nu$

momentum operator: $\hat{p}_x = -i\hbar \frac{d}{dx}$

position operator: $\hat{x}$

potential energy operator: $\hat{V}(x)$

kinetic energy operator in 1 dimension: $\hat{p}_x^2 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$

Hamiltonian operator in 1 dimension: $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \hat{V}(x)$

first term is kinetic energy, second term is potential energy

Hamiltonian operator in 3 dimensions: $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(x,y,z)$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ in Cartesian coordinates

spherical and cylindrical coordinates: convert to and from Cartesian, $\nabla^2$ expressions

spherical: $(r, \theta, \phi)$; cylindrical: $(r, \phi, z)$

know conversions; don’t need to memorize $\nabla^2$

Eigenvalue equation: $\hat{\Omega} \psi = \omega \psi$

operator $\hat{\Omega}$, eigenfunction $\psi$, eigenvalue $\omega$

Time-independent Schrödinger equation: $\hat{H}\psi = E\psi$

eigenvalue equation with eigenfunction $\psi$ and eigenvalue $E$; quantized energies

Time-dependent Schrödinger equation: $\dot{\hat{H}}\psi = i\hbar \frac{d\psi}{dt}$

Born interpretation: $|\Psi|^2 = \Psi^*\Psi$ is the probability density for $\psi$ normalized

real and non-negative

$|\Psi|^2 \, dx$ is the probability of finding particle between $x$ and $x+dx$
Normalization: total probability of finding the particle somewhere is 1

If a wavefunction $\Psi$ is normalized, $\int |\Psi|^2 \, dx = 1$

If a wavefunction $\Psi$ is not normalized, multiply by constant $N$:

$\Psi' = N \Psi$

$\int |\Psi'|^2 \, dx = 1 \Rightarrow N = \left( \int |\Psi|^2 \, dx \right)^{-1/2}$ in one dimension

straightforward to extend to three dimensions

Conditions on wavefunction: single valued, square-integrable, continuous, and smooth
(although exceptions to smooth if potential has singularity exactly cancelling)

Time-dependent wavefunction: $\Psi(x,t) = \Psi_s(x)e^{-iEt/\hbar}$

phase: $e^{-iEt/\hbar}$

probability density is time-independent: $|\Psi_s(x)|^2$

Hermitian operator: $\int \Psi_b^* \hat{\Omega} \Psi_a \, d\tau = \int \Psi_a^* \hat{\Omega} \Psi_b \, d\tau$

Examples: $\hat{x}, \hat{p}_x, \hat{H}$

Properties of Hermition operator: $\hat{\Omega}\Psi_a = \omega_a \Psi_a$

- its eigenvalues are real
- its eigenfunctions are orthogonal: $\int \Psi_a^* \Psi_b \, d\tau = 0$ (exception for eigenfunctions
  with same eigenvalue, but these can be made orthogonal)
- its eigenfunctions are complete: any function that conforms to the allowed forms of
  wavefunctions can be expressed as a linear combination of the eigenfunctions

Postulates of quantum mechanics:
- The physical state of a particle can be described by a wavefunction $\Psi$.
- $\Psi$ can be normalized. (Note: two wavefunctions differing only by factor of $e^{ik}$ are
  considered the same.)
- $|\Psi|^2$ is the probability density.
- A Hermitian operator exists for each observable physical property.
- Solving the eigenvalue equation, $\hat{\Omega}\Psi = \omega \Psi$, leads to a complete and orthogonal
  set of eigenfunctions and eigenvalues.
- If the wavefunction is equal to one of the eigenfunctions, then a measurement gives a
  definite value that is the corresponding eigenvalue.
- If the wavefunction is NOT equal to one of the eigenfunctions, it can be written as a
  linear combination of eigenfunctions, $\Psi = \sum_{n=1}^{\infty} c_n \Psi_n$, and a measurement will give one
  of the eigenvalues with probability $|c_n|^2$ for eigenvalue $\omega_n$.
- The expectation value or average value of a property is $\langle \omega \rangle = \int \Psi^* \hat{\Omega} \Psi \, d\tau$. 
Commutator: \[ [\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \]

Two operators commute when their commutator is zero: \[ [\hat{A},\hat{B}] = 0 \].

When two operators share the same eigenfunctions, then they commute. If two operators commute, then the two observables associated with these two operators can be determined exactly simultaneously.

Uncertainty principle: When two operators do not commute, the observables associated with them are “complementary observables” and cannot be determined exactly simultaneously. The errors in the two observables cannot be simultaneously zero.

Specific example: Because position and momentum do not commute, it is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle: \[ \Delta p \Delta x \geq \hbar/2 \].

Particle in a one-dimensional box: \( V(x) = 0 \) for \( 0 \leq x \leq L \), \( V(x) = \infty \) elsewhere

\[ \Psi_n(x) = \frac{2}{\sqrt{L}} \sin \left( \frac{n\pi x}{L} \right) \]

\[ E_n = \frac{n^2\hbar^2}{8mL^2} \]

\( n = 1, 2, 3, \ldots \)

Energies: positive zero point energy, quantized energy levels, non-degenerate levels, spacings increase as \( n \) increases, spacings increase as \( m \) and \( L \) decrease

Wavefunctions: symmetric (\( n \) odd) or antisymmetric (\( n \) even) about middle of box, \( n \)-1 nodes, zero outside box

Cannot have \( n = 0 \) because zero everywhere; cannot have \( n < 0 \) because this leads to the same wavefunctions as \( n > 0 \)

Uncertainty principle: as \( L \to 0 \), \( \Delta x \to 0 \), and \( \Delta p \approx 2\hbar \to \infty \). As \( L \to \infty \), \( \Delta x \to \infty \), and \( \Delta p \approx 2\hbar \to 0 \). Need zero point energy or would violate uncertainty principle because would have zero momentum and also completely defined position as \( L \to 0 \).

Classical-quantum correspondence principle: as \( n \) approaches \( \infty \), the probability density becomes more uniform, as in classical case. As \( L \) and \( m \) approach \( \infty \), the energy levels decrease (become nearly continuous, as in classical case).

Wavefunction can also be written as: \[ \Psi_n(x) = \frac{1}{2i\sqrt{L}} \left( e^{ikx} - e^{-ikx} \right), \quad k = n\pi/L . \]

Each of these terms is an eigenfunction of \( \hat{p}_x \), so the measurement of momentum gives either \( \hbar k \) or \( -\hbar k \) with equal probability.
Particle in a two-dimensional well:
Hamiltonian separable: multiply 1D wavefunctions, add 1D energies

\[ \Psi_{n_x,n_y}(x,y) = \sqrt{\frac{2}{L_x}} \sin \left( \frac{n_x \pi x}{L_x} \right) \sqrt{\frac{2}{L_y}} \sin \left( \frac{n_y \pi y}{L_y} \right) \]

\[ E_{n_x,n_y} = \frac{n_x^2 \hbar^2}{8mL_x^2} + \frac{n_y^2 \hbar^2}{8mL_y^2} \]

\[ n_x, n_y = 1, 2, 3, \ldots \]

Square: degenerate energy levels (same energies, different wavefunctions)
Straightforward to extend to three-dimensional box (separation of variables)

One-dimensional harmonic oscillator
potential energy: \( V(x) = \frac{1}{2} kx^2 \)

frequency: \( \omega = \sqrt{\frac{k}{m}} \)

\[ E_v = (v + \frac{1}{2}) \hbar \omega \]

\[ \Psi_v = N_v H_v(y) \exp(-y^2/2) \]

\( H_v(y) \): Hermite polynomial, \( y = x/\alpha \), \( \alpha = \left( \frac{\hbar^2}{mk} \right)^{1/4} \)

\( v = 0, 1, 2, \ldots \)

Energies: positive zero point energy (\( \hbar \omega/2 \)), quantized energy levels, evenly spaced by \( \hbar \omega \), non-degenerate

Wavefunctions: symmetric (\( v \) even) or antisymmetric (\( v \) odd) about \( x=0 \), \( v \) nodes, finite probability for all \( x \), probability beyond classical turning points

Permeation: probability density has non-zero value where it is classically forbidden

Quantum-classical correspondence: as \( v \) gets higher, probability in classically forbidden region gets smaller and probability near the turning point increases (as in classical case, where greatest probability is at turning points).

Particle in a ring:
Hamiltonian: \( \hat{H} = -\frac{\hbar^2}{2mr_0^2} \frac{\partial^2}{\partial \phi^2} \)

Wavefunction: \( \Psi_{m_l} = \frac{1}{\sqrt{2\pi}} \exp(im_l \phi) \)
Energy: $E = \frac{m_l^2 \hbar^2}{2mr_0^2}$

$m_l = 0, \pm 1, \pm 2, \ldots$

Energies: zero point energy is zero ($m_l = 0$), each non-zero energy level is doubly degenerate ($\pm m_l$), spacings increase as $m_l$ increases.

$m_l = 0$ allowed because wavefunction non-zero (particle exists)
$m_l < 0$ allowed because wavefunction is distinct from corresponding positive value

Wavefunctions: integral number of full waves must fit in ring, cyclic boundary conditions
Equal probability density everywhere on ring for all $m_l$
The lack of zero point energy does not violate uncertainty principle because the position on ring is completely unknown.

Angular momentum: $
\hat{l}_z = -i\hbar \frac{\partial}{\partial \phi}
$

$\hat{l}_z \Psi_{m_l} = m_l \hbar \Psi_{m_l}$

These states are eigenfunctions of both angular momentum and the Hamiltonian so both observables can be determined simultaneously and exactly. Therefore, these states have definite angular momentum, and a measurement of momentum for state $\Psi_{m_l}$ will always produce $m_l \hbar$.

$m_l$ positive $\rightarrow$ counter-clockwise around ring, $l_z$ pointing in positive $z$ direction
$m_l$ negative $\rightarrow$ clockwise around ring, $l_z$ pointing in negative $z$ direction

$\hat{l}_z$ and $\phi$ do not commute; uncertainty principle holds because $l_z$ is exactly known ($m_l \hbar$) but angle $\phi$ is unknown (uniform probability around entire ring)

Particle on the surface of a sphere:

Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2$

Use $\nabla^2$ in spherical coordinates, radius fixed so only function of $(\theta, \phi)$

Wavefunction: $\Psi_{l,m_l}(\theta, \phi) = N_{l,m_l} \Theta_{l,m_l}(\theta) \Phi_{m_l}(\phi) = N_{l,m_l} Y_{l,m_l}(\theta, \phi)$

$\Phi_{m_l}(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im_l \phi)$

$\Theta_{l,m_l}(\theta)$: associated Legendre polynomials
$Y_{l,m_l}(\theta, \phi)$: spherical harmonics

Energy: $E_l = \frac{l(l+1)\hbar^2}{2m r_0^2}$ (Note: energy depends only on $l$, not on $m_l$)

$l = 0, 1, 2, \ldots$  \hspace{1cm} $|m_l| \leq l$ so $m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l$
Energies: zero point energy is zero \((l=0)\), degeneracy of each level is \(2l+1\)

Angular momentum:
The total angular momentum is quantized in both its magnitude and orientation – it cannot point in any arbitrary direction (space quantization)

\[
\hat{l}_z \psi_{l,m} (\theta, \varphi) = m_l \hbar \psi_{l,m} (\theta, \varphi) \text{ so observable } \quad l_z = m_l \hbar
\]

\[
\hat{l}_z^2 \psi_{l,m} (\theta, \varphi) = l(l+1)\hbar^2 \psi_{l,m} (\theta, \varphi) \text{ so observable } \quad l_{\text{total}} = \sqrt{l(l+1)} \hbar
\]

\(\Psi_{l,m} (\theta, \varphi)\) are not eigenfunctions \(\hat{l}_x\) and \(\hat{l}_y\)

\[
\left[ \hat{l}_z, \hat{l}_z^2 \right] = 0 \text{ but } \hat{l}_z \text{ does not commute with } \hat{l}_x \text{ and } \hat{l}_y
\]

For a given eigenfunction, we can determine exactly simultaneously the magnitude and \(z\) component of angular momentum and the energy, but NOT the \(x\) and \(y\) components of angular momentum.

Spin: An electron has spin quantum number \(s = 1/2\)

The total spin angular momentum is \(\sqrt{s(s+1)} \hbar = \sqrt{\frac{3}{4}} \hbar\)

The spin magnetic quantum number \(m_s\) has values \(-s, \ldots, s\).
For an electron \(m_s = 1/2, -1/2\).

The \(z\)-component of spin angular momentum is \(m_s \hbar\), or \(\pm \frac{\hbar}{2}\)

Indistinguishable particles: \(|\Psi(r_1, r_2)|^2 = |\Psi(r_2, r_1)|^2\)

Fermions: half-integer spin quantum numbers; electrons, protons, neutrons; antisymmetric (Pauli exclusion principle): \(\Psi(r_1, r_2) = -\Psi(r_2, r_1)\)

Bosons: integer spin quantum numbers; photons; symmetric: \(\Psi(r_1, r_2) = \Psi(r_2, r_1)\)

Tunneling: A particle of energy \(E\) can tunnel through a barrier of potential \(V > E\).
A particle of energy \(E\) can permeate into the potential wall of \(V > E\).
The probability of tunneling increases as the barrier gets thinner, as the barrier gets lower, and as the particle gets lighter.