

Exam 2 Topics

Chapter 4: Structure of the Atom

The exam covers material starting with the Bohr model.

Bohr Model: Planetary model + angular momentum quantization condition; derivation of radii & energy levels; explanation of atomic spectra; correspondence principle; reduced mass and isotope effect; success and limitations of the Bohr model.

Characteristic X-ray spectra: Moseley's measurements, dependence on Z

Atomic excitations by electrons: demonstration of quantized energy levels using electrons to excite the atoms

Chapter 5: Wave Properties and Quantum Mechanics

X-Ray scattering using crystals, crystal planes, Bragg reflection, condition for constructive interference. Be careful about 2θ vs θ .

De Broglie wavelength of particle: $\lambda = h / p$. This relation holds true in all areas of QM and we use it extensively. We also use $p = h / \lambda = \hbar(2\pi / \lambda) = \hbar k$

Waves and particles: Understand that matter has both particle and wave properties. For example, electrons have mass, momentum and energy (matter) but are scattered by crystals and diffracted through slits just like x-rays using their de Broglie wavelength (waves).

Probability and wavefunctions: We covered this in Chapter 6.

Chapter 6: Quantum Mechanics II

The wavefunction ψ and probability: All information about a particle is in the wavefunction ψ but we cannot measure ψ directly. The probability for a particle for being in a small region of size dV at position \mathbf{x} is $|\psi(\mathbf{x}, t)|^2 dV \equiv \psi^*(\mathbf{x}, t)\psi(\mathbf{x}, t)dV$. ψ must be normalizable so that the total probability is 1. We measure the probability by making repeated measurements.

Operators: Momentum, energy, position, angular momentum are operators. Position operator is position itself, but $\hat{p}_x = -i\hbar \partial / \partial x$, $\hat{E} = +i\hbar \partial / \partial t$, $\hat{L}_x = yp_z - zp_y = y(-i\hbar \partial / \partial z) - z(-i\hbar \partial / \partial y)$, etc. are differential operators.

Expectation values: The expectation value for any function or operator is given by

$\langle O \rangle \equiv \int_{-\infty}^{\infty} \psi^*(x) O \psi(x) dx$, where O is a function or operator. We calculated the expectation values of x , x^2 , p , p^2 for various solutions of the SE. Note that the expectation value is often zero. This happens when the operator or function is odd.

Schrödinger equation (SE): The SE is merely the equation for energy conservation for a particle in a potential written in operator form and applied to a wavefunction ψ . It is a second order differential equation. Solving the SE gives ψ and thus all the information about a particle undergoing motion subject to that potential. We solved the SE for several potentials.

Stationary states: For a time independent potential $U(\mathbf{x})$, we can use separation of variables and find that we can always write the wavefunction as $\psi(\mathbf{x}, t) = \psi(\mathbf{x})e^{-iEt/\hbar}$, where E is the energy. $\psi(\mathbf{x})$ satisfies the time-independent SE $-\hbar^2\nabla^2\psi(\mathbf{x})/2m + U(\mathbf{x})\psi(\mathbf{x}) = E\psi(\mathbf{x})$.

Solutions to SE: Each potential gives a different set of solutions for ψ . We worked out the cases of a free particle, particle in an infinite potential box (1D and 3D), particle in a finite potential box, harmonic oscillator (1D and 3D) and coulomb potential (hydrogen atom). The requirement of a normalizable wavefunction and smooth boundary conditions gives quantized energies for bound states.

Free particle (1D): The solution to the SE for $U(x) = 0$ is $\psi(x) = Ae^{ip_x x/\hbar}$ and $\psi(x, t) = Ae^{ip_x x/\hbar} e^{-iEt/\hbar} = e^{ikx} e^{-iEt/\hbar}$, where $k = p_x / \hbar$ and $E = p_x^2 / 2m$. Since $e^{ikx} = \cos kx + i \sin kx$ this solution describes simple wave motion for a particle with momentum p_x , wavenumber $k = p_x / \hbar$ and wavelength $\lambda = 2\pi / k = h / p_x$ (de Broglie wavelength).

Particle in a box (1D) with infinite potential walls: Solutions inside the box are of the form $A \sin(n\pi x / L)$ (wave motion) with energies $E = n^2 \pi^2 \hbar^2 / 2mL^2$. Energy quantization comes from requiring $\psi(x) = 0$ at $x = 0$ and $x = L$.

Particle in a box (1D) with finite potential walls: Bound state solutions are of the form $A \sin(kx) + B \cos(kx)$ inside the box ($k = \sqrt{2mE / \hbar^2}$) and $e^{-\kappa|x|}$ outside the box ($\kappa = \sqrt{2m(V - E) / \hbar^2}$) in the classically *forbidden* region. Energy quantization comes from requiring ψ to be normalizable and that ψ and ψ' be continuous at the two boundaries. Since ψ does not have to go to 0 at the boundaries, the wavelength for each energy level is *larger* than the corresponding wavelength for the rigid box (the wave penetrates into the forbidden region) and thus the energy is *lower*. The *penetration depth* into the forbidden region is defined as $1/\kappa$.

Particle in a box (3D) with infinite potential walls: Use separation of variables to find $\psi(\mathbf{x}) = \psi(x)\psi(y)\psi(z)$ and the energy is the sum of the energies for each dimension, i.e. $E = (n_x^2 + n_y^2 + n_z^2) \pi^2 \hbar^2 / 2mL^2$ (for a box of equal sides L) where $n_x, n_y, n_z \geq 1$. This leads to the concept of *energy degeneracy*, or different wavefunctions having the same total energy. Degeneracy of ground state ($E = 3E_0$) is 1 (111). Degeneracy of 1st excited state ($E = 6E_0$) is 3 (112, 121, 211).

Harmonic oscillator (1D): Potential energy is $\frac{1}{2}m\omega^2x^2$. Solutions are of the form

$H(\sqrt{ax})e^{-ax^2/2}$, where H is a polynomial, with energies $E = \hbar\omega\left(n + \frac{1}{2}\right)$ with $n \geq 0$, i.e. equally spaced energies. Energy quantization comes from requirement that $\psi(x)$ is normalizable. The HO is very important in physics because all potentials with a stable minimum can be expanded as a quadratic in x near the minimum, so the first few energies obtained from the harmonic oscillator are not bad approximations to the true energies.

Harmonic oscillator (3D): Potential energy is $\frac{1}{2}m\omega^2x^2$. Solutions are products of the 1D harmonic oscillator for x, y, z and energies are the sum of 1D energies, e.g.

$E = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right)$ with $n_x, n_y, n_z \geq 0$. The 3D solution again leads to energy degeneracy.

Uncertainty principle: $\Delta x \Delta p_x \geq \hbar/2$, where the terms are the uncertainties in position and its corresponding momentum (a precise definition requires that these be the standard deviations). We worked out the product for the particle in a box and harmonic oscillator and showed that the UC is satisfied. We also showed that one can apply the UC to estimate the ground state energy (and size) of a particle in a box, harmonic oscillator, atoms, etc. You should review this argument and be able to apply it to other potentials.

Chapter 7: Hydrogen atom

Radial potential $U(r)$: The SE for *any* radial potential can be separated into

1. A radial equation depending on $U(r)$, energy E and angular momentum quantum number l
2. An angular part that is *independent* of $U(r)$, depending only on l and m_l , where m_l is the quantum number specifying the z component of angular momentum.

Angular solution: The angular wavefunction for any radial potential is the spherical harmonic $Y_l^{m_l}(\theta, \phi)$, a product $P_l^{m_l}(\cos\theta)e^{im_l\phi}$ of a polynomial in $\cos\theta$ and a phase factor in ϕ . It is normalized as $\int |Y_l^{m_l}(\theta, \phi)|^2 d\Omega = 1$. Increasing l introduces additional nodes in the θ wavefunction.

Solution for coulomb potential: The solution to the SE is $\psi(r, \theta, \phi) = R_{nl}(r)Y_l^{m_l}(\theta, \phi)$, depends on 3 quantum numbers: n, l, m_l , satisfying $n \geq 1, l \leq n-1$ and $|m_l| \leq l$. The integer n is the “principal quantum number” and corresponds to n in the Bohr model. The energies are given by

$E_n = -13.6 \text{ eV} / n^2$ (independent of l), exactly the same as the Bohr model. The radial wavefunctions are normalized as $\int_0^\infty r^2 |R_{nl}(r)|^2 dr = 1$. The radial wavefunction has the form

$K_{nl}(r/a_0)e^{-r/na_0}$ where K is a polynomial and a_0 is the Bohr radius. You should know how the solution changes (energies and radii) if we replace the electron mass by a heavier mass or use Ze instead of e for the central charge.

Quantization: You are not expected to know how to derive the full solution to the hydrogen atom, but you should know the major outlines of separation of variables. You should also know that energy and angular momentum quantization (n, l) come from the requirement that the wavefunctions be normalizable. The quantization of m_l comes from requiring periodicity in ϕ , $\Phi(\phi) = \Phi(\phi + 2\pi)$.

Spatial quantization: The square of the total angular momentum is $l(l+1)\hbar^2$. Spatial quantization expresses the fact that the z component of angular momentum is also quantized with values $m_l\hbar$ ($2l+1$ values).

Magnetic moment and energy splitting: The orbital magnetic moment of an electron in a hydrogen atom is $\vec{\mu} = -\frac{e}{2m_e}\mathbf{L}$ and is similarly quantized along a given direction as

$\mu_{m_l} = -\frac{e\hbar}{2m_e}m_l = -\mu_B m_l$. The energy of a particle in a magnetic field B is $U = -\vec{\mu} \cdot \mathbf{B} = \mu_B B m_l$, thus an orbital with angular momentum specified by l is split into $2l+1$ states each separated by energy $\mu_B B$.

Intrinsic spin: Particles have intrinsic spin. For spin S particles the magnetic moment

$\vec{\mu}_s = \frac{g_e e}{2m_e}\mathbf{S}$, where $S = 1/2$ and $g = 2$ for electrons, protons, neutrons. The factor of 2 means that atomic states are split into two states (spin up, spin down) by the amount $\pm\mu_B B$. Each individual shift is the same amount as the split for $l = 1$ atomic transitions, but there are only two states, not three. These were seen in the Stern – Gerlach experiment.

Selection rules for atomic transitions: We learned that these are

1. $\Delta n = \text{anything}$
2. $\Delta l = \pm 1$
3. $\Delta m_l = 0, \pm 1$
4. $\Delta m_s = 0$

The second and third ones result from the fact that the photon has intrinsic spin 1. You should be able to draw the transitions from an energy level diagram.

Chapter 8: Multi-electron Atoms

Pauli exclusion principle: You should know how this principle explains the filling of atomic shells.

Filling atomic shells: This is normal up through $Z = 18$. You should know how to fill these shells in order. You should also know the changed order for the next shell. Finally, you should know why the order of subshell filled within a given principal quantum number n is s, p, d, f .

Atomic radii vs Z: Why do atomic radii increase dramatically and ionization energies fall drastically for the alkali metals (immediately after noble gases)?