Summary of the Schrodinger picture of quantum mechanics.

The one-dimensional version (meaning the electron can only move along the x-axis) of Schrodinger’s equation for electrons is

\[ \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t} \]

where \( \hbar = h/2\pi \), \( m \) is the electron mass, \( i = \sqrt{-1} \), and \( V(x) \) is the electric potential that the electron feels (for the three dimensional case of an electron trapped in a hydrogen atom \( V(x) \) is the coulomb potential of the nucleus \( V(x) = \frac{-kq}{r} \)).

The ‘recipe’ for solving a quantum problem:

- Write the appropriate Schrodinger equation with the potential that you need.
- Write the generic solutions (these will be the most general solutions and have undetermined constants in them).
- Apply boundary conditions. This may lead to energy quantization. Boundary conditions include matching functions and their derivatives in two or more different regions.
- Substitute the solution into the equation to determine the relationship between various constants and the energy.
- Normalize to get coefficients.

Other points:

- The equation for electrons is different than for electromagnetic waves because electrons have mass and react to electrical potentials (photons do not).
- The equation is not symmetric in space and time (there is a double derivative in \( x \) and a single derivative in \( t \)). This is because Schrodinger’s equation is not relativistic. For many problems this isn’t important. Later we will look at the relativistic electron wave equation (the Dirac equation).
- Generic plane wave solutions for a potential equal to zero are \( \Psi(x,t) = Ae^{i(kx-\omega t)} \).
- For ‘static’ cases where the electron wave is going to basically stay put (analogous to standing waves on a string where there is still oscillation but the waves don’t go anywhere) the space and time parts are independent (just like the standing wave on a string, given by \( A\cos \omega t \sin kx \)). The \( x \) dependent part is called the time independent Schrodinger’s equation \( \frac{-\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \).
- Schrodinger’s equation for the hydrogen problem predicts that energy, angular momentum and the z-component of angular momentum will be quantized. So we get the three quantum numbers \( n, \ l \) and \( m_l \).
- Schrodinger’s equation does not predict the spin of the electron, \( s \) (we have to have Dirac’s equation, the relativistic version of quantum mechanics, to get the fourth quantum number).
What does the electron wave function, $\Psi(x,t)$ tell us?

Everything that can be known about the electron comes from the wave function. But first note that $\Psi(x,t)$ is imaginary so we always have to multiply by the complex conjugate to get something we can measure (we can only measure real quantities). So we will always measure products of $\Psi(x,t)$ and $\Psi^*(x,t)$. For example:

- $\Psi^*(x,t)\Psi(x,t)dx$ is the probability of finding the electron in the region $dx$. (This is kind of like the diffraction pattern for light; for light the pattern tells us where photons will land, for electrons it tells us where the most likely place to find the electron).
- The probability of finding the electron in the region $a \leq x \leq b$ is $\int_a^b \Psi^*(x,t)\Psi(x,t)dx$.
- $\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)dx = 1$, in other words, there is a 100% chance of finding the electron somewhere. This is called normalization.
- The expected (or average) value of any quantity can also be found by integrating. So the expected location (kind of like the average location) is $<x> = \int_{-\infty}^{\infty} \Psi^*(x,t)x\Psi(x,t)dx$. There are expectation values for momentum, energy, etc.
- Note that for some problems we find exact values for some variables (e.g. energy for an electron in an infinite well) but only probabilistic values for other variables (e.g. position for an electron in an infinite well).
- If the wave function solution to a problem is an eigenfunction of a particular operator then the eigenvalues are the exact, quantized values for that variable. For example the energy operator (the Hamiltonian) for the one dimensional infinite well is $\hat{H}_{\text{op}} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$. And we have $\hat{H}_{\text{op}}\psi(x) = E_n\psi(x)$ which shows that the energy values are quantized at exact values. Multiplying the square well solutions by the position operator $\hat{x}_{\text{op}} = x$ does not give back a number times the wave function so the wave functions are not eigenfunctions of the position operator; we only have probabilistic locations for the electron.
- Solutions to Schrodinger’s equation for the hydrogen atom are eigenfunctions of energy, angular momentum and the $z$-component of angular momentum so these physical variables have exact, quantized values. These wave functions are not eigenfunctions for momentum or position operators so we have only probabilistic answers for the values of these other variables.
- The fact that the position probability of the electron in the hydrogen problem is time independent, $\int_{-\infty}^{\infty} \Psi_{n,l,m}^*(r,\phi,\theta,t)\Psi_{n,l,m}(r,\phi,\theta,t)dV = \int_{-\infty}^{\infty} \psi_{n,l,m}^*(r,\phi,\theta)\psi_{n,l,m}(r,\phi,\theta)dV$ (the time factor $e^{iEt/\hbar}$ cancels out), tells us that the hydrogen atom is stable over time.
- A calculation of the probability of the electron to be split between states (note that the quantum number are different for each wave function here), $\int_{-\infty}^{\infty} \Psi_{n,l,m}^*(r,\phi,\theta,t)\Psi_{n',l',m'}(r,\phi,\theta,t)dV$, gives us the frequency of an emitted...
photon if the electron makes the transition: \( E_{n'} - E_n = hf \) and selection rules (the integral is zero unless \( |l-l'| = 1 \) and \( |m-m'| = 0,1 \)): \( \Delta m_l = 0, \pm 1 \) and \( \Delta l = \pm 1 \).

- If we have two electrons each with their own wave functions, \( \psi_n(x_1) \) and \( \psi_m(x_2) \) we can describe the combined state in two different ways: a symmetric state 
  \[
  \psi_s = C[\psi_n(x_1)\psi_m(x_2) + \psi_m(x_1)\psi_n(x_2)]
  \]
  or an anti-symmetric state 
  \[
  \psi_a = C[\psi_n(x_1)\psi_m(x_2) - \psi_m(x_1)\psi_n(x_2)]
  \]
  The anti-symmetric state describes fermions (e.g. electrons, neutrons, protons, subatomic particles with spin \( \frac{1}{2} \)) because trying to put both objects in the same state \( m = n \) results in a probability of zero. This is the exclusion principle; fermions cannot be in the same quantum state. The symmetric state describes bosons (photons and sub-atomic objects with zero spin). Putting these objects into the same state doubles the probability (they prefer to be in the same state). This makes lasers possible (where you have a lot of photons all in exactly the same quantum state).

**Experimental results**

In the laboratory:

- Spectral lines verify that energy levels are quantized; \( E_{n'} - E_n = hf \).
- The fine structure of spectral lines and splitting of spectral lines in an external magnetic field verify that angular momentum and it’s z-component are quantized. This is because any time you have a z-component of angular momentum for a charged object you have a magnetic moment; \( \mu_z = \frac{e\hbar}{2m}m_l \).

In an external magnetic field this magnetic moment will add or subtract a small amount of energy to the electron’s energy: \( U = B\mu_z = B\frac{e\hbar}{2m}m_l \). The photon emitted when the electron changes from one energy level to another has a slightly different energy by this amount. This accounts for the splitting of spectral lines.
- The Zeeman experiment verifies that electrons have two possible values of spin.

Normal quantum mechanical problems involve situations where there is more than one angular momentum involved. This is because if you have two magnet dipoles they tend to interact with each other. Even with just one electron there are two magnetic dipoles; one for the orbital motion, the other for the spin. These two moments interact to form a total magnetic moment, usually denoted as \( \vec{J} = \vec{S} + \vec{L} \). The magnitude of this total angular momentum is \( J = \sqrt{j(j+1)}\hbar \) where \( j = l \pm s \). It is actually the total angular momentum that has a magnetic moment related to its z-component (just like we had for angular momentum and spin) and this causes the splitting when there is an applied magnetic field. Obviously, if there are several electrons there will be many combinations of the z component of \( \vec{J} = \vec{J}_1 + \vec{J}_2 + \ldots \).
Multi-electron atoms

- Schrödinger’s equation cannot be solved analytically for atoms containing more than one electron. Only computer solutions are available (and only after some simplifying assumptions are made).
- We can, however, solve the problem the problem of an atom that has all the electron’s removed except one. The solutions look just like the solutions for the hydrogen atom but with energy levels given in electron volts by
  \[ E_n = \frac{-13.6Z}{n^2} \]
  where \( Z \) is the number of protons in the nucleus.
- If we have more electrons we can make a few assumptions that make solutions possible. The independent particle model assumes each electron can be described by first assuming it interacts with the nucleus independently (Schrödinger’s hydrogen problem again) plus an interaction with other elections via the coulomb potential.
- In many cases we can further simplify the independent particle model by assuming a central field approximation. This treats the other electrons as if they are simply a spherical negative charge distribution centered on the nucleus. So the outermost electron “sees” a coulomb potential of the nucleus plus a cloud of charge around it representing the other electrons.
- The central field approximation means the multiple electron case should be very similar to the hydrogen atom (if the approximation holds). The available energy and angular momentum states can still be designated by quantum numbers \( n, l \) and \( m_l \) (and spin). So we can build up the ground state electron configuration of multi-electron atoms by filling the shells and sub-shells based on the available slots \( n, l, m_l \) and spin values) for electrons (subject to the exclusion principle). This actually works quite well.
- One way to actually carry out a central field approximation is the mathematical method called the Hartree-Fock method. In this method a computer starts with hydrogen wave-like solutions but applies an additional potential energy due to the other electrons in whatever atom that is being investigated. The computer then randomly adjusts and tests the wave functions for stability until it has a set of stable wave functions for the atom.
- The electron ground state configuration arrived at under the central field approximation predicts higher ionization energies for full sub-shells and lower ionization energies for lone electrons in a shell or sub-shell. An electron in an unfilled sub-shell “sees” the charge of the protons in the nucleus as screened by the electrons in the shells and sub-shells in between it and the nucleus. Because of this screening it is less tightly bound and has a lower ionization energy. So the inert gases are more stable than the alkali elements because the outermost electron in an alkali atom is loosely bound. This pretty much explains a whole lot of chemistry.
- The central field approximation also explains the size of atoms. More shielding means less tightly bound electrons which means the electrons can be further from the nucleus and the atom has a bigger diameter.
• The filling of shells and sub-shells as we add electrons isn’t entirely orderly. When two electrons with opposite spins are paired together they have slightly less energy than two electrons with the same spin. So as we add electrons there is a preference to fill a sub-shell in such a way as to have as many paired electrons as possible. This is called Hund’s rule and accounts for some irregularities in the order in which electrons fill the ground state of some atoms.

• The symmetric and anti-symmetric wave functions need to account for the exclusion principle in a multi-electron atom are written in the form of Slater determinants (the above example for two electrons can also be written in the mathematical form know as a determinant).

• Each multi-electron atom has its own spectral lines. Spin and orbital angular momentum coupling, the changes in energy levels due to have more protons in the nucleus with some screening by other electrons plus selection rules give rise to these differences.