

Schrodinger's Model of the Hydrogen Atom – a mathematical summary

Schrödinger's time-dependent wave equation:

In 1 spatial dimension is:

$$i\hbar \frac{\partial \Psi}{\partial \tau}(x, t) = -\frac{\hbar^2}{2M} \frac{\partial^2 \Psi}{\partial x^2}(x, t) + V(x, t)\Psi(x, t)$$

Where $\hbar = h/2\pi$ and h is Planck's constant, M is the mass of the particle (an electron in this case) and Ψ (psi) is a wave function which is a solution to the wave equation. In three spatial dimensions:

$$i\hbar \frac{\partial \Psi}{\partial \tau}(\mathbf{r}, t) = -\frac{\hbar^2}{2M} \nabla^2 \Psi(\mathbf{r}, t) + V(\mathbf{r}, t)\Psi(\mathbf{r}, t)$$

Where ∇^2 is the Laplacian operator, del-squared, $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ in Cartesian coordinates..

To find steady-state solutions we use Schrodinger's time-independent wave equation:

$$-\frac{\hbar^2}{2M} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Introducing the Hamiltonian operator (\hat{H}) which gives us the energy associated with the system (E) this can be written as:

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Where:

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla^2 + V(\mathbf{r})$$

Using the Coulomb potential (which is spherically symmetric and considering an electron of mass M and charge $-e$ bound to the central proton of charge $+e$ the potential energy function $V(r)$ is:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

In spherical polar coordinates, the Hamiltonian operator becomes:

$$\hat{H} = -\frac{\hbar^2}{2Mr} \frac{\partial^2}{\partial r^2} r + \frac{\hat{L}^2}{2Mr^2} - \frac{e^2}{4\pi\epsilon_0 r}$$

Where \hat{L} is the angular momentum operator. (In quantum mechanics, each operator corresponds to an observable property of a system, like angular momentum, or total energy for the Hamiltonian operator). Schrodinger's equation becomes:

$$\left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial r^2} + \frac{\hat{L}^2}{2Mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] (r\psi) = Er\psi$$

Solving by separation of variables (taking out the r-function which we can do since the potential is spherically symmetric):

$$\psi(r,\theta,\phi) = R(r)F(\theta,\phi)$$

Substituting back into Schrodinger's wave equation we obtain an equation for R and an equation for F:

$$\left[-\frac{\hbar^2}{2M} \frac{d^2}{dr^2} + \frac{\hat{L}^2(l+1)\hbar^2}{2Mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] (rR) = ErR$$

$$\hat{L}^2 F(\theta,\phi) = kF(\theta,\phi)$$

Thus $F(\theta,\phi)$ is an eigenfunction of the \hat{L}^2 operator, and so:

$$k = l(l+1)\hbar^2 \text{ and } F(\theta,\phi) = Y_{l,m}(\theta,\phi)$$

Where $Y_{l,m}(\theta,\phi)$ are a set of functions known as the spherical harmonics. The wavefunction now becomes:

$$\psi(r,\theta,\phi) = R(r)Y_{l,m}(\theta,\phi)$$

The set of radial functions, $R(r)$, are not so simple to find, but their form can be deduced intuitively and then checked by substitution and are found to be:

$$R_{n,l} = N_{n,l} (2r/na)^l e^{-r/na} L_p^k(2r/na)$$

$$n = 1, 2, 3, \dots ; \quad l = 0, 1, 2, \dots, n-1$$

Where, L_p^k are the generalized (associated) Laguerre polynomials:

$$L_p^k(x) = \sum_{s=0}^p (-1)^s \binom{p+k}{p-s} \frac{x^s}{s!}$$

Recalling that the brackets refer to the number of combinations given by:

$$\binom{p+k}{p-s} = {}^{p+k}C_{p-s} = \frac{(p+k)!}{(k+s)!(p-s)!}$$

and with $k = 2l + 1$, where $l =$ angular momentum quantum number ($l = 0, 1, 2, 3, \dots$) corresponding to coordinate θ and $p = n - l - 1$, where n is the principal quantum number ($n = 0, 1, 2, 3, \dots$) corresponding to r . The maximum value of l is $n - 1$.

The values of L_{kp} can be found these formulae, for example:

$$n = 1, l = 0 \text{ gives: } L_0^1(x) = 1$$

$$n = 3, l = 2 \text{ gives: } L_0^5 = 1$$

$$L_0^k = 1$$

$$n = 2, l = 0 \text{ gives: } L_1^1(x) = 2 - x$$

$$n = 4, l = 2 \text{ gives: } L_1^5(x) = -x + 6$$

$$L_1^k(x) = -x + k + 1$$

$$n = 4, l = 1 \text{ gives: } L_2^3 = \frac{1}{2}x^2 - 5x + 10$$

$$n = 4, l = 0 \text{ gives: } L_3^1 = -\frac{1}{6}x^3 = 2x^2 - 6x + 4$$

Returning to the spherical harmonics:

$$\psi(r, \theta, \phi) = R(r)Y_{l,m}(\theta, \phi)$$

where: $-l \leq m \leq l$ and m is the magnetic quantum number (corresponding to variable ϕ)

and for $m \geq 0$ (including a normalisation coefficient):

$$Y_{l,m}(\theta, \phi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l-m)!}{(l+m)!}} P_{l,m}^m(\cos\theta) e^{im\phi}$$

for $m < 0$:

$$Y_{l,-m}(\theta, \phi) = (-1)^m Y_{l,m}^*(\theta, \phi)$$

Where $P_{l,m}$ are the associated Legendre polynomials:

$$P_{l,m}^m(u) = (1-u^2)^{m/2} \frac{d^m}{du^m} P_l(u), \quad m = 0, 1, 2, \dots, l$$

Where P_l are the Legendre polynomials:

$$P_l(u) = \frac{1}{2^l l!} \frac{d^l}{du^l} [(u^2 - 1)^l] \\ (l = 0, 1, 2, 3, \dots)$$

These polynomials often appear in the solutions to equations containing the Laplacian operator, ∇^2 . In this case the argument u is $\cos\theta$ and from these formulae the spherical harmonics can be obtained, for example:

$$m = 0, l = 0 \text{ gives: } Y_{0,0} = 1/\sqrt{4\pi}$$

$$m = 0, l = 1 \text{ gives: } Y_{1,0} = \sqrt{3/4\pi} \cos\theta$$

$$m = 1, l = 1 \text{ gives: } Y_{1,1} = -\sqrt{3/4\pi} \sin\theta e^{i\phi}$$

Putting together the equation for $R(r) = R_n(r)$ and $Y(\theta, \phi) = Y_{l,m}(\theta, \phi)$ we obtain the wavefunction ψ , for a given set of values for the quantum numbers n , l and m , which is a solution to Schrodinger's time-independent wave equation. There is a whole family of such wavefunctions, corresponding to different values of the quantum numbers. remember that n can be any positive integer: $n = 1, 2, 3, \dots$; $l = 0, 1, 2, \dots, n - 1$ and m is an integer in the range $-l \leq m \leq l$.

$$\psi(r, \theta, \phi) = R(r)Y_{l,m}(\theta, \phi)$$

Solutions to differential equations that constitute a set of equations each corresponding to a different value are called eigenfunctions and the corresponding values are called eigenvalues and we have an eigenvalue problem. In this case, the wavefunctions, ψ , are the eigenfunctions and each eigenfunction corresponds to a specific value of energy, E , which is the energy of the electron in the system. This energy is found to depend only on the principle quantum number n and is given by:

$$E_n = - \frac{\alpha^2}{2} Mc^2 \frac{1}{n^2} \quad (\text{where: } n = 1, 2, \dots)$$

Where α is the fine structure constant:

$$\alpha = e^2 / (4\pi\epsilon_0)\hbar c$$

where e is the electron charge, ϵ_0 is the permittivity of free space to an electric field and c is the speed of light.

$$\frac{\alpha^2}{2} Mc^2 = 13.61 \text{ eV}$$

is the Rydberg energy, E_R , which is the energy of an electron in a hydrogen atom with $n = 1$. Thus, each eigenfunction, ψ , has a corresponding eigenvalue, E_n .

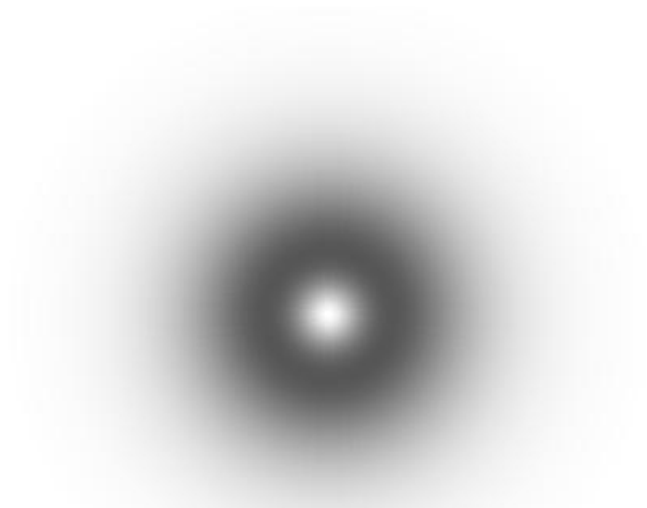
$$\text{Thus, } E_n = E_R/n^2$$

The wavefunctions, ψ , themselves have no direct physical significance, rather it is the $|\psi|^2$ which is physical – this represents the electron probability distribution and is the probability of finding the electron at any point around the nucleus. This function gives rise to the ‘shapes’ of the orbitals for atoms, shapes which are electron charge probability clouds. So far we have only considered the time-independent situation, but it turns out that the time component cancels out when we take $|\psi|_2$. Thus, the wavefunctions or orbitals are stationary states – they do not change with time.

This means that electrons do NOT orbit the nucleus in orbitals! Intuitive arguments to explain such phenomena as Van der Waal’s forces and the liquid state of mercury by the motion of electrons in orbitals are incorrect. However, the electron does have velocity! Some people tend to think of the orbitals as being time-averaged states, with the electron orbiting rapidly, however, this implies hidden motion and current evidence suggests that there are no such ‘hidden variables’ and so the electron is not following some hidden trajectory in the classical sense and the wavefunction contains all there is to know about the electron. The electron will also be found in the same state once it has been measured upon subsequent measurements, unless something happens to change the system. Perhaps, like spin, the electron velocity is not velocity in the classical sense, but rather some quantum observable that we cannot intuitively understand. In any case, Heisenberg’s uncertainty principle forbids particles from following an exact trajectory (unless there are hidden variables).

Motion like that found in classical systems can be recaptured in quantum mechanics by superpositions of eigenfunctions. Since Schrodinger’s wave equation is linear, any linear combination or superposition of two or more eigenfunctions is also a solution. This means that an electron can be, for example, in both the $n = 1$ and the $n = 2$ states simultaneously! However, once measured, the measurement forces the electron to enter either the $n = 1$ or the $n = 2$ state – it can never be found to be in both states simultaneously as the measurement perturbs the system and always puts it into a stationary eigenstate. Superposition states can have motion, for example, in the harmonic oscillator potential (rather than the Coulomb potential) which is used to model chemical bonds, the bond can oscillate when it is described as a superposition of eigenstates and this offers some explanation of bond vibration.

Following are plots of some $|\psi|^2$, in particular the 1s orbital ($n = 1, l = 0, m = 0$), the 2s orbital ($n = 2, l = 0, m = 0$), 3s orbital ($n = 3, l = 0, m = 0$), the 2p orbital ($n = 2, l = 1, m = 0$), the 3p orbital ($n = 3, l = 1, m = 1$), the 3s orbital ($n = 3, l = 2, m = 0$), the 3d orbital ($n = 3, l = 2, m = 0$) and the 3d orbital ($n = 3, l = 2, m = 2$).



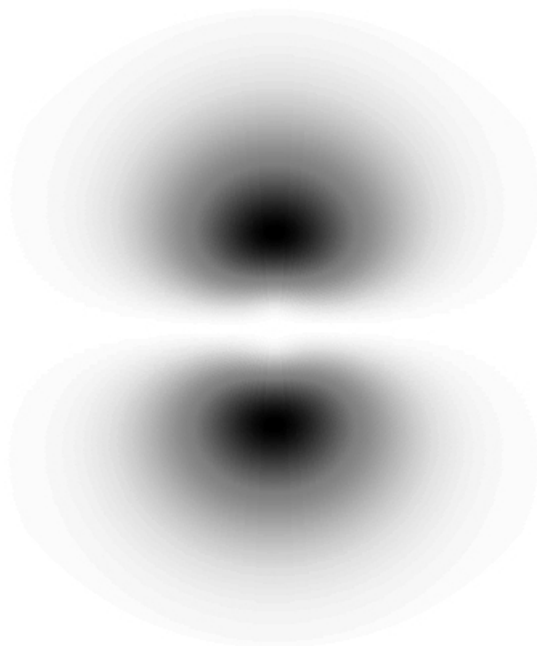
1s orbital



2s orbital



3s orbital



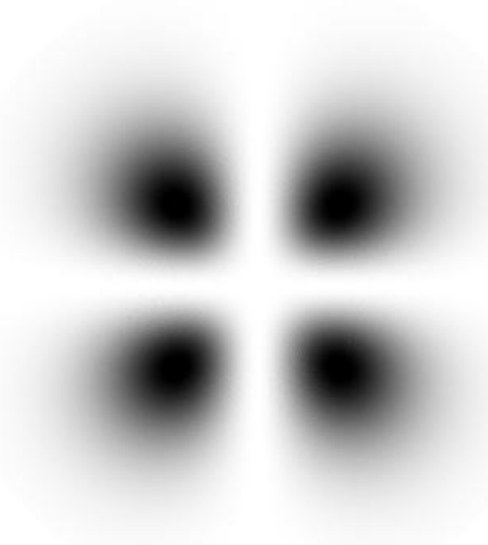
2p orbital



3p orbital



3d ($m = 0$) orbital



3d ($m = 2$) orbital

Note the wave-like nature of these electron probability distributions – there are nodal points and nodal planes where the probability of finding the electron is zero, corresponding to the troughs of the waves. One point that may confuse students is that the wavefunctions for all the p-orbitals (each with a different value of m) look very different from one another and not like the three identical but perpendicular dumb-bell shaped p-orbitals shown in textbooks. The reason being, that in the presence of an external magnetic field, such as that caused by another electron in a multi-electron atom or another atom nearby perturbs these orbitals and they recombine into the three familiar p-orbitals so as to minimise their energy.

These plots show the probability of finding the electron, with the electron occurring more frequently in the darker regions. As we are dealing with probability, the total probability for each plot must = 1, since the electron must occur somewhere! To achieve this a normalisation factor is needed, however, the relative intensity of each plot has been adjusted for clarity. Many standard textbooks get the normalisation wrong, a forgivable error since it is really only when one tries to plot the functions that these errors become obvious.

Schrodinger's model does not actually give a complete description of the electron. Newer models incorporate electron angular momentum or spin. We have already incorporated angular momentum due to the 'orbital motion' of the electron, as this gives us the quantum number l and also m , the magnetic quantum number which becomes important when describing the relative orientation of orbitals to one another and in the presence of magnetic fields. Spin can be thought of as the angular momentum due to rotation of the electron about its own axis. However, again this classical analogy is not quite correct and the quantum property is different – it is quantised! Electrons can only have one of two possible spins, spin-up, \uparrow , or spin-down, \downarrow otherwise indicated by spin $+\frac{1}{2}$ and spin $-\frac{1}{2}$. A helpful analogy is to think of clockwise and anticlockwise rotation. Adding spin to Schrodinger's model is essentially simple, since each orbital can hold a maximum of two electrons, which must have opposite spins, so the 'address' of each electron, given by the four quantum numbers: n , l , m and s for spin, must be unique. The first three numbers, n , l and m , determine the orbital so to have different addresses the electrons must have opposite spins.

However, details become more complex. Electrons are charged particles and moving charges generate magnetic fields and magnetic fields influence moving charges. This leads to a coupling between the magnetic field generated from electron spin and that generated from electron 'orbital motion'. This is spin-orbital coupling and can affect the fine structure of the atom's spectrum – causing shifts and splitting in what appear to be single energy levels when viewed with higher resolution. The fine structure is also affected by relativistic effects – when electron speeds reach a significant fraction of the speed of light, Schrodinger's equation becomes increasingly approximate and Dirac's relativistic equation must be used.

There are also shifts in the energy values of the orbitals, one corrected by the Darwin term and the other called the Lamb shift, which is due to the field nature of electromagnetic forces, as described by QED (quantum electrodynamics). In QED, the emphasis is not so much on individual particles, but rather on energy fields.

Creation and annihilation operators describe mathematical operations that can add and remove quanta of energy (particles) to and from the field. This happens in a vacuum – electron-positron pairs can spontaneously appear in pair-production (as permitted by the energy-time uncertainty principle). Similarly, when the electron produced encounters a positron then the two can annihilate one another. There is nothing to stop a positron produced spontaneously as part of an electron-positron pair from colliding with and annihilating the electron bound to our atom. In this case the spare electron that was produced can become bound to the atom and become its electron – electrons constantly come-and-go and swap places. However, when they swap, one electron disappears and another takes its place but in a different initial position – its as if the electron bound to the atom suddenly hopped (dematerialised and rematerialised somewhere else). This gives rise to the so-called jitter-motion (Zitterbewegung) of the electron and alters the average electron energy.

A correction to the energy levels (Hamiltonian operator) is given by the Darwin term, which is thought to be due to the vacuum field and this jitter-motion of the electron, and affects only the s-orbital electrons when they are near to the atomic nucleus and tends to give the s and p-orbitals the same energy. (Ordinarily the s-orbitals are lowered in energy since only in these orbitals can the electron exist at an arbitrarily close distance to the nucleus (and in principle the electron may occupy the centre of the nucleus in an s-orbital) and so the s-electrons experience a greater average electrostatic attraction to the nucleus, which lowers their average distance from the nucleus and lowers their energy.

The Darwin term and spin-orbit interaction are also relativistic effects and are predicted by Dirac's relativistic equation (essentially the Schrodinger equation with the energy term replaced by the relativistic energy). It is Dirac's model of the hydrogen atom which also predicts electron spin.

The Lamb shift also only affects the s-orbital energy but makes its energy slightly higher than that of a p-orbital with the same value of n. The Lamb shift is also due to the effects of QED and was detected using microwave spectroscopy. It is due to effects not predicted by Dirac's theory and is a correction to this model. It is due to electron self-energy. The electron can spontaneously emit and later absorb photons. These photons are virtual – they cannot be directly detected since this would violate the conservation of energy – these photons can be produced, as if from nothing, causing a momentary creation of energy, so long as they disappear within the time interval permitted by the energy-time uncertainty principle. In this way no observable energy conservation violation occurs.

QED initially predicts that the electron will have resulting infinite energy! However, this difficulty is removed by subtracting one infinite term from another in a process called renormalisation. Other more complicated processes may occur, for example the emitted photon may momentarily be converted into an electron-positron pair which then recombine into a photon which is reabsorbed by the electron. The more complicated the emission / re-absorption process, the more minor a correction it becomes.

Additional correction enter the equation when the nucleus is considered. Since the nucleus contains most of the atom's mass in a very small volume, the approximation of the Coulomb potential which treats the nucleus as a central point charge, is a good approximation. However, the nucleus does have size and the nucleus-electron pair 'orbit' one-another around their common centre of mass. These corrections also contribute to spectral fine structure. Different isotopes, such as deuterium with a neutron in its nucleus, alter the nuclear mass and cause slight differences (shifts in the energy levels) between atoms of the same element that are different isotopes. This is the isotopic shift.

Even finer features exist on the spectrum of hydrogen, so-called hyperfine structure. These features are also due to the nucleus. The proton is electrically charged and undergoing its own motion, so that the magnetic field of the electron and proton weakly interact and couple-together.

With all these refinements in place, the modified Schrodinger model, or the modified Dirac model, give a very accurate description of the spectrum of atomic hydrogen. Indeed, the hydrogen atom has been described as the best modeled of all physical systems. However, this is only true as far as whole atom properties are concerned. There are many more interactions occurring on the sub-atomic scale, concerning nuclear forces and quark interactions. Ultimately, the heart of the atom remains incompletely explained. Difficulties also arise when the model is extended to many-particle systems, such as heavier atoms of other elements. However, good approximations, like the Hartree-Fock method, exist for dealing with multi-electron atoms.