SWEETENED PHYSICS

HOW AN ATOM WORKS
(SHAPES OF ORBITALS)

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Abstract: here is a simple explanation of the shape of an atom. Not so simple, but as simple as one can.

Contents:

GENERAL VIEW

What is following will have a mathematical proof.

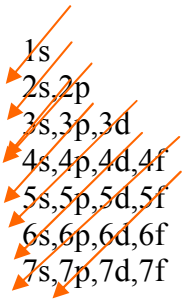
The orbitals n, or shells, are named by the 7 capital letters **K**, **L**, **M**, **N**, **O**, **P** and **Q**.
So, **n** is the principal quantum number (from 1 on).
Then there is the orbital quantum number, or azimuthal quantum number (**l**, "el", from 0 to n-1 and recalls the sublevels and the shape of the orbitals).
Then, there is the magnetic quantum number (**m**, from –l to +l and recalls the orientation of the orbitals).
Finally, there is the spin quantum number (**s**, on the spinning of the electron around itself).
The sublevels are also named by the four letters **s**, **p**, **d** and **f** and every one can contain respectively **2**, **6**, **10** and **14** electrons, as a maximum. Such orbitals have shapes, 8-like, spherical etc. Such shapes are given by graphs from Schrodinger's Equation applied to the atom (nucleus-electrons system).

The filling takes place in the following way:

1s,2s,2p,3s,3p,4s,3d,4p,5s,4d,5p,6s,4f-5d,6p,7s,5f-6d

The first number is that of the orbital.

It seems there is a geometric-mathematical plot behind all that, as such a series of filling can be obtained by writing one after the other all the items barred by the arrows in the triangle below, starting from the higher one, of course:



(Rule of the diagonal)

Examples:

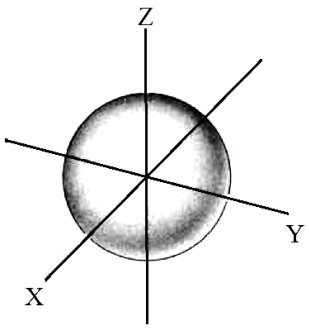
Hydrogen H: $1s^1$ 

Helium He: $1s^2$ 

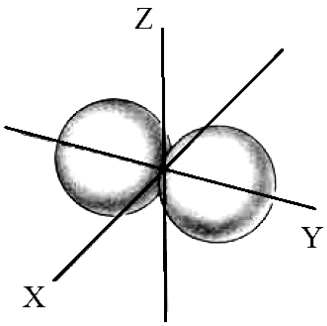
Nitrogen N: $1s^2$, $2s^2$, $2p^3$ 

Then, there is also the Principle of Exclusion of Pauli, according to which in an atom it is not possible to have two electrons which have all four quantum numbers identical.

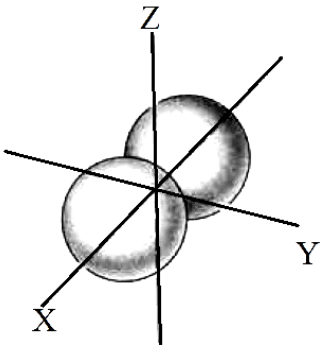
And also the Hund's Rule is in force, according to which, in all groups of orbitals with the same n and l, the electrons will occupy the highest number of orbitals.
Helium has got its two electrons which fill completely its orbital s and so it has reached, as to say, the "duet" and it is complete and will not link to any other atom to seek filling electrons. In fact, it is a noble gas. Regarding all the other noble gases, they have not only the s orbital to be satisfied, as for the helium, but also the p orbital and also their p orbitals are complete (two electrons in s and six in p), so reaching the octect. And because of that, we also have the similarity in the chimical properties among elements in the same columns in the Periodic Table of Elements, as after that the atomic number Z increases, there is an increase of the orbitals to be filled and every time the same filling situation shows up, the same chemical properties show up as well.
We said the sublevels s, p, d and f can contain, as a maximum, 2, 6, 10 and 14 electrons respectively. But why? Well, the magnetic quantum number m, whose values are from –l to +l (from minus el to plus el), which recalls the orientation of the orbitals (z component of the angular momentum), in case of orbital n=1, l=0 and m has a 0 value indeed, and no others, as l=0 and the available values for m are the 0 indeed, that is just one value.
In case of n=2, l=0 or 1 and so m can have values -1, 0 and +1 thet are 3 values. In case of n=3, l=0 or 1, or 2 and so m can have values -2, -1, 0, +1 and +2, that are 5 values. At last, when n=4, l=0 or 1, or 2, or 3 and so m can have values -3, -2, -1, 0, +1, +2 and +3, that are 7 values.
Let's sum up: as a highest number of possible values for m we have 1, 3, 5 and 7. But we know that an electron can tolerate a companion whose spin is opposite, so the above numbers must be multiplied by two, so having 2, 6, 10 and 14, before mentioned. The sum of the first two is 8, that is the octet indeed.
The Schrodinger's Equation for an electron gives such a wave function Ψ which gives us infos on the probability to find the electron in points which have their own coordinates; more exactly, the square modulus of Ψ, which is $|\Psi|^2$, is the probability.



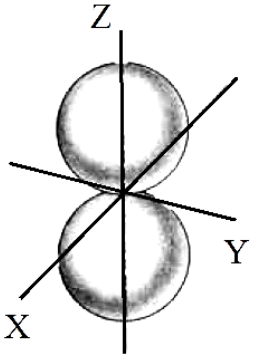
s



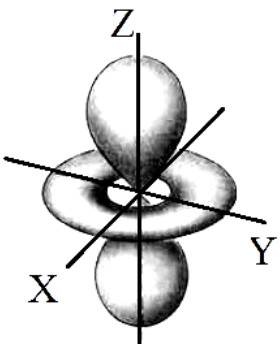
p_y



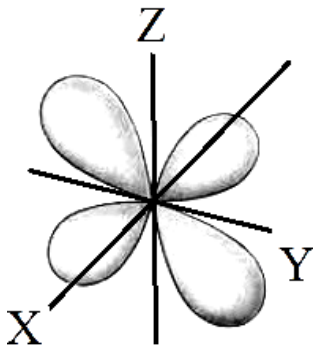
p_x



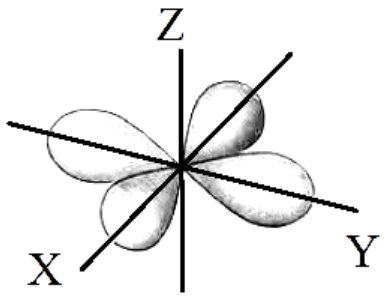
p_z



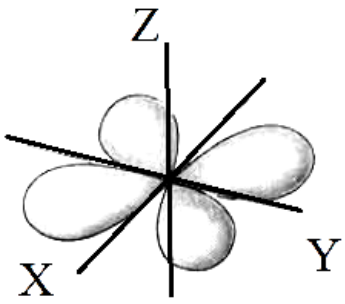
$d\text{-}3z^2\text{-}r^2$



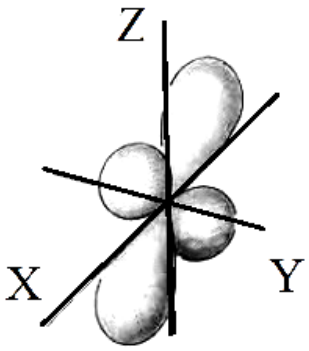
d-yz



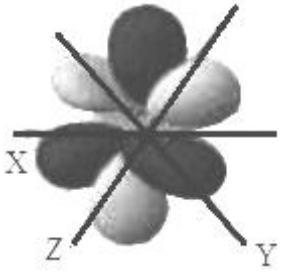
d-x^2-y^2



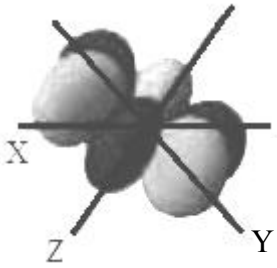
d-xy



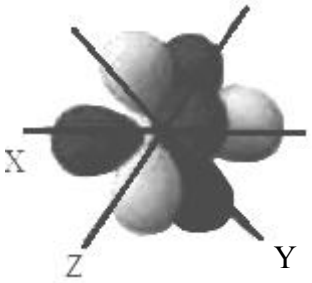
d-xz



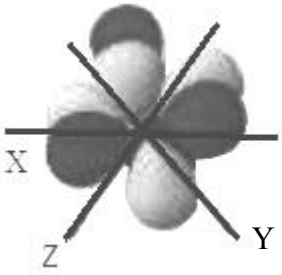
f-5xz^2-xr^2



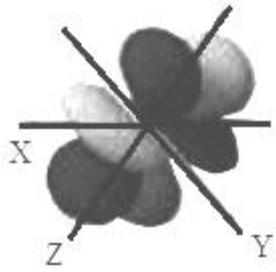
f-x^3-3xy^2



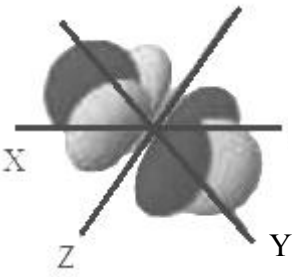
f-xyz



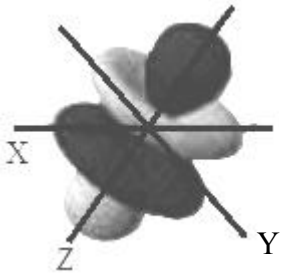
f-zx^2-zy^2



f-5yz^2-yr^2



f-y^3-x^2y



f-z^3-3zr^2

The wave function which describes such orbitals is:

$$\Psi(r,\theta,\varphi) = \phi_{E,l}(r) Y_l^m(\theta,\varphi) \qquad (1)$$

It is in polar coordinates (r,θ,φ) because the calculations are easier than the cartesian(xyz), as we will show later. Such an equation will be proved below. Let's start by reminding that the shape of the orbitals is given by $Y_l^m(\theta,\varphi)$ as by this function we know how the probability to meet the electron changes with moving up and down and left and right (θ,φ). The function $\phi_{E,l}(r)$, on the contrary, just tells us how the probability changes with moving radially (r) (but keeping (θ,φ) unchanged) and so, how it increases or decreases in its intensity, so letting us draw by dots (with thicker or thinner density) the orbital along r.

Let's not forget that the true probability is not $\Psi(r,\theta,\varphi)$, but, more exactly, $|\Psi(r,\theta,\varphi)|^2$. Here are the first values for Y:

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}, \quad Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta, \quad Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\cdot e^{\pm i\varphi}, \quad Y_2^0 = \frac{1}{2}\sqrt{\frac{5}{4\pi}}(3\cos^2\theta - 1),$$

$Y_2^{\pm 1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\cdot e^{\pm i\varphi}$, $Y_2^{\pm 2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\cdot e^{\pm i2\varphi}$, from which, after having reminded through Euler, that $e^{\pm i\varphi} = \cos\varphi \pm i\sin\varphi$, and after having shown for every one of them the m values and finally noticing around which axis the symmetry is developed: (as an example, if φ doesn't appear, then the symmetry is around z, when θ changes)

$s = Y_0^0 = \frac{1}{\sqrt{4\pi}}$, $p_z = Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$, $p_x = Y_1^{+1} \propto \sqrt{\frac{3}{8\pi}}\sin\theta\cdot\cos\varphi$, $p_y = Y_1^{-1} \propto \sqrt{\frac{3}{8\pi}}\sin\theta\cdot\sin\varphi$,

$d_{3z^2-r^2} = Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$, $d_{xz} = Y_2^{-1} \propto \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\cos\varphi$,

$d_{yz} = Y_2^{+1} \propto \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\sin\varphi$, $d_{x^2-y^2} = Y_2^{-2} \propto \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\cos 2\varphi$,

$d_{xy} = Y_2^{+2} \propto \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\sin 2\varphi$.

About the more complex f orbitals, similar reasonings can be carried out and we leave them to the reader, as an exercise. So, by changing θ and φ, the relevant orbits are described, with all the shapes shown in the above figures.

APPENDIX 1
The Bohr's atomic model

We know that: $E = h\nu$, $E = mc^2$. Afterwords, the balance between electric force and centrifugal one, in the nucleus-electron system, yields:

$$\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} = m_e\frac{v^2}{r}; \qquad (1)$$

(Z is the atomic number, that is the number of protons (+) in the nucleus) then, obviously:

$mc^2 = h\nu = mcc$ >>> $h = mc\frac{c}{\nu} = mc\lambda$, from which $\lambda = \frac{h}{mc}$. Now, for a particle whose rest mass is not zero, we have, on the contrary: $\lambda = \frac{h}{mv}$ (De Broglie wavelenght, 1923).

The matter, too, has wave properties, as a shifty particle cannot be reduced to a point with no dimensions, but it is rather a little cloud in which the probability to find it is higher; mathematically speaking: a wave.

If now we suppose that the circumference of the orbital run by the electron is n times λ, then:

$mv\lambda = h = mv\frac{2\pi r}{n}$, from which: $v = \frac{nh}{2\pi mr}$ and here "n" is the principal quantum number.

(by the way, the equation $mv\cdot\lambda = h \rightarrow \Delta p\cdot\Delta x = h$ is here intended as a first sketch of the Heisenberg Uncertainty Principle). Now, starting from (1):

$\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} = \frac{m}{r}(\frac{nh}{2\pi mr})^2$ from which $r = \frac{n^2\varepsilon_0 h^2}{\pi m_e Ze^2}$, or $r = k\frac{n^2}{Z}$.

For the 1st orbital of the hydrogen (n=1), we have the Bohr's radius ($r = 0{,}529\cdot 10^{-10} m = 0{,}529 A$).

Considering now v=0 at an infinite distance from the nucleus, it follows that the work necessary to bring the electron from r to infinite is:

$$V(r) = (-U) = \int_{R=r}^{R=\infty}\vec{F}\cdot d\vec{s} = \frac{1}{4\pi\varepsilon_0}\int_{R=r}^{R=\infty}\frac{Ze^2}{R^2}dR = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

As a total energy: $E = E_k + U = \frac{1}{2} m_e v^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$, but according to (1) we have:

$\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2} = m_e\frac{v^2}{r}$, from which:

$$E = -\frac{Z^2 e^4 m_e}{8n^2\varepsilon_0^2 h^2}. \quad (2)$$

Hence, by jumping from b to a, we have:

$$E_b - E_a = -\frac{Z^2 e^4 m_e}{8n_b^2\varepsilon_0^2 h^2} + \frac{Z^2 e^4 m_e}{8n_a^2\varepsilon_0^2 h^2} = \frac{Z^2 e^4 m_e}{8h^2\varepsilon_0^2}\left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right) = KZ^2\left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right) = h\nu \quad (3)$$

Now, as $\frac{1}{\lambda} = \frac{h\nu}{hc} = \frac{\Delta E}{hc}$, it follows: $\frac{1}{\lambda} = \frac{Z^2 e^4 m_e}{8h^3\varepsilon_0^2 c}\left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right)$.

As a Rydberg constant R, we have:

$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$

APPENDIX 2
Schrodinger's Equation

We know the Planck/Einstein's Equation:

$E = h\nu$ (1)

And we also know the relation between pulsation (angular velocity) ω and frequency ν:

$\omega = 2\pi\nu$ (2)

Then, for the energy of a particle:

$E = m_0 c^2 = \vec{p}\cdot\vec{c}$ (3)

and then the linear momentum:

$\vec{p} = m_0\vec{c}$ (4)

and, moreover, the general relations $c = \lambda\nu$ (velocity is wavelength by frequency)

$\left|\vec{k}\right| = \frac{2\pi}{\lambda}$ (modulus of the wave vector $\vec{k} = \frac{2\pi}{\lambda}\hat{k}$) and $\hbar = \frac{h}{2\pi}$ (Dirac's constant – barred $\hbar$).

Now, from (1) and (3), we have: $p = h\frac{\nu}{c} = \frac{h}{\lambda} = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k$ (5)

Moreover: $E = h\nu = \frac{h}{2\pi}2\pi\nu = \hbar\omega$. (6)

And for a particle, $E = \frac{1}{2}mv^2 = \frac{1}{2m}m^2v^2 = \frac{p^2}{2m}$ (7)

and $E = \hbar\omega = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$. (8)

Now, as in order to locate a particle I have to interfere with it, by illuminating it, or perturbing it somehow, and as, simply speaking, the smaller a particle is, the more that perturbation disturbs it, diverts it, slows sit down, accelerates it etc, one is led not to imagine anymore it as a single point, but rather through a wave.

With De Broglie, we can associate a wavelength to a particle, through (5):

$\lambda = \frac{h}{p} = \frac{h}{mV}$, where, now, V is the velocity of the particle and p is the modulus of $\vec{p} = m_0\vec{V}$.

For what has been just said, we are also led to introduce a wave function $\Psi = \Psi(\vec{r},t) = \Psi(\vec{x},t)$ which describes the particle when moving along $\vec{r}(x,y,z)$ (or $\vec{x}(x,y,z)$).

wave function:

for all what previously said, the particle isn't anymore a dimensionless point, but rather something like a cloud which is the space in which the probability to find the particle is higher; if we put $\rho(\vec{x},t)d^3x$ the probability to find the particle in the volume between $\vec{x}$ and $\vec{x}+d^3x$ (d^3x as we are thinking in three dimensions), it must be proportional, through a proportionality constant, to the square modulus $|\Psi(\vec{x},t)|^2$ of the wave function $\Psi = \Psi(\vec{x},t)$. We are talking here about a square modulus, as, in general, we can express a wave through trigonometric functions, and so also in a complex form, that is, with complex numbers and we have quantifiable quantities in the real field, as long as we take their moduli:

$|\Psi(\vec{x},t)|^2 d^3x = |N|^2 \rho(\vec{x},t)d^3x$ ($|\Psi(\vec{x},t)|^2 = \Psi(\vec{x},t)\Psi^*(\vec{x},t)$), where $\Psi^*(\vec{x},t)$ is the complex conjugated of $\Psi(\vec{x},t)$, (i swapped with –i).

Ψ is typical of every single electron. Now, by the definition of probability, the integration over all the space must yield the maximum probability:

$\int \rho(\vec{x},t)d^3x = 1$, so: $\int |\Psi(\vec{x},t)|^2 d^3x = |N|^2$

Let's normalize the function Ψ so that $\int |\Psi(\vec{x},t)|^2 d^3x = 1$, and we have:

$$\Psi_N(\vec{x},t) = \frac{1}{N}\Psi(\vec{x},t)$$

Let's write down a list of some of the properties Ψ must have:

-it must be continuous, as the probability to find the particle, for instance, in x_0, must be the same, whatever you tend to x_0, whether from left or from right.

-it must be limited everywhere, as well as the probability to find the particle in a certain place is.

-for a particle which is localized in a region Ω, we must have $\Psi = 0$ for $x \notin \Omega$.

-it must be a monodrome function (just one value)

-wave functions which differs just by the normalization describe the same physical system (and $\Psi = 0 \rightarrow$ Vacuum)

-if a system can stay in a state Ψ_1 and also in a state Ψ_2, then it can stay also in a generic state $\Psi = \alpha\Psi_1 + \beta\Psi_2$.

wave function of a free particle:

we know from wave physics that, of course, a wave propagating through time and through x, must have, as an argument, a function like:

$\frac{2\pi}{\lambda}\hat{k}\cdot\vec{x} - \frac{2\pi}{\lambda}vt = \vec{k}\cdot\vec{x} - \omega t$, as if we fix a point in time (as: t=0) we have a variability with x and fixing x we have a variability in time, that is a real wave.

Now, according to (5) and (6) we have: $\vec{k}\cdot\vec{x} - \omega t = \frac{\vec{p}}{\hbar}\vec{x} - \frac{E}{\hbar}t$ and so the wave function must be like:

$$f(\vec{k}\cdot\vec{x}-\omega t)=f(\frac{\vec{p}}{\hbar}\vec{x}-\frac{E}{\hbar}t) \tag{9}$$

We notice that deriving (9) over t means to factor ω, while deriving it over x means to factor k.

Now, as according to (8): $\omega=\frac{\hbar k^2}{2m}$, we understand, for all what has been just said, that we have to take a t-first order wave equation which is also an x-second order:

$$\frac{\partial\Psi}{\partial t}=\gamma\frac{\partial^2\Psi}{\partial x^2}. \tag{10}$$

Now, Fourier should suggest to propose base functions as candidates to be solutions of (10), the following four:

$$A\sin(\vec{k}\cdot\vec{x}-\omega t) \tag{11}$$

$$B\cos(\vec{k}\cdot\vec{x}-\omega t) \tag{12}$$

$$Ce^{i(\vec{k}\cdot\vec{x}-\omega t)} \tag{13}$$

$$De^{-i(\vec{k}\cdot\vec{x}-\omega t)} \tag{14}$$

So, we notice that (11) and (12), in their monodimensional form, (x in place of $\vec{x}$ etc), cannot satisfy (10), while (13) and (14) can, provided that we consider:

$-i\omega=-\gamma k^2$, from which: $\gamma=i\frac{\omega}{k^2}=i\hbar\frac{\hbar\omega}{\hbar^2k^2}=i\hbar\frac{E}{p^2}=\frac{i\hbar}{2m}$ and we notice that γ is here independent from dynamic quantities as p, therefore it works for us.

If, on the contrary, if we chose the d'Alembert wave equation $\frac{\partial^2\Psi}{\partial^2 t}=\gamma\frac{\partial^2\Psi}{\partial x^2}$ (not ok), all four candidates should have satisfied it, but for γ we would have had:

$\gamma=\frac{\omega^2}{k^2}=(\frac{\hbar\omega}{\hbar k})^2=\frac{E^2}{p^2}=\frac{p^2}{4m^2}$, not ok, as such a γ should be a dynamic parameter, as it has p inside, so such an equation would have changed its characteristics with p.

So, we put (13) in our good candidate (10), so getting:

$\frac{\partial\Psi}{\partial t}=\frac{i\hbar}{2m}\frac{\partial^2\Psi}{\partial x^2}$, and, after multiplying both sides by $i\hbar$:

$$i\hbar\frac{\partial\Psi}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} \tag{15}$$

(Schrödinger's Equation for a free particle and on a monodimensional motion)

If now we put the expression for $\Psi(x,t)$ ((13) monodimensional) in (15), we get:

$\hbar\omega\Psi=\frac{\hbar^2k^2}{2m}\Psi$, that is:

$$E\Psi=\frac{p^2}{2m}\Psi \quad ; \tag{16}$$

in fact, we already had: $E=\frac{p^2}{2m}$.

Now, we rewrite, one close to the other, (15) and (16):

$$i\hbar\frac{\partial\Psi}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} \qquad E\Psi=\frac{p^2}{2m}\Psi$$

By a comparison side to side, we see that it is possible to make the following associations of operators:

$E \to i\hbar\frac{\partial}{\partial t}$ and $p^2 \to -\hbar^2\frac{\partial^2}{\partial x^2}$ >>> $p \to -i\hbar\frac{\partial}{\partial x}$

In three dimensions, (15) becomes:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\Delta\Psi \ , \tag{17}$$

which is the three-dimension Schrödinger's equation for a free particle, where $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian, then $\Psi(\vec{x},t) = Ce^{i(\vec{k}\cdot\vec{x}-\omega t)}$, $|\Psi(\vec{x},t)| = C$, $E \to i\hbar\frac{\partial}{\partial t}$, $p^2 \to -\hbar^2\Delta$, $p \to -i\hbar\nabla$, $\vec{p} = \hbar\vec{k}$, $\omega = \frac{\hbar k^2}{2m}$, con $k = |\vec{k}|$.

We notice that the velocity of the wave is $v_f = \frac{\omega}{k} = \frac{E}{p} = \frac{p}{2m}$, that is, a phase velocity, while the particle velocity is $v_g = \frac{p}{m} = \frac{d\omega}{dk} = \frac{d}{dk}\frac{\hbar k^2}{2m} = 2v_f$, and so it is a group velocity.

Now, as in (17) the quantity $-\frac{\hbar^2}{2m}\Delta$ has got the dimension of an energy E, a kinetic one, in this case, and this quantity corresponded to:

$$-\frac{\hbar^2}{2m}\Delta \to \frac{p^2}{2m} = \frac{1}{2m}m^2v^2 = E_k \ , \tag{18}$$

if the particle is also in a potential V, we'll have, in place of the mere kinetic energy, the total energy H=T+V=E_k+V (H is the Hamiltonian) and (17) will become: ($\Psi(\vec{x},t) = Ce^{i(\vec{k}\cdot\vec{x}-\omega t)}$, wave function and $\Psi^*(\vec{x},t) = Ce^{-i(\vec{k}\cdot\vec{x}-\omega t)}$ is its complex conjugated)

$$i\hbar\frac{\partial\Psi}{\partial t} = (-\frac{\hbar^2}{2m}\Delta + V)\Psi$$ **Complete Schrödinger's Equation!** (19)

As an alternative, according to (18) we can write:

$$E_k = \frac{p^2}{2m} = H - V = \frac{p^2}{2m} \tag{20}$$

and also:

$$-\frac{\hbar^2}{2m}\Delta\Psi = (H - V)\Psi \tag{21}$$

that is : $\Delta\Psi + \frac{2m}{\hbar^2}(H - V)\Psi = 0$ **An alternative for the complete Schrödinger's Equation!** (22)

Regarding phase and group velocities, for a photon, which is monocromatic and follows the d'Alembert equation, those two velocities are the same ($v_f = v_g = c$), and all this shows us once again that Schrödinger's Equation is not the same as the d'Alembert wave equation and for it we have: $v_f \neq v_g$.

The Schrödinger's Equation sounds like a tied wave, standing like. As chance would have it. **Wanna see the Schrödinger's Equation, in the formulation of the (22), is a standing wave equation???**

Let's try and see:
first of all, we notice that (22) really looks like the equation of standing waves:

$$\frac{\partial^2\Psi}{\partial x^2}+k^2\Psi=0\,;\ \text{(standing waves equation)} \tag{23}$$

Out of simplicity, we consider (22) in a monodimensional form:

$\frac{\partial^2\Psi}{\partial x^2}+\frac{2m}{\hbar^2}(H-V)\Psi=0$; well, it's exactly the same.

(23) is the standing wave equation, indeed; as a matter of fact, if a generic Ψ_1 propagates in a limited mean, the superposition of it with its reflection Ψ_2 makes a standing wave $\Psi=\Psi_1+\Psi_2$:
$\Psi_1=A\sin(kx-\omega t)$, $\Psi_2=A\sin(kx+\omega t)$.
The difference in sign in the arguments shows that those two waves propagate in opposite directions; moreover, the term $\omega t=2\pi\nu t$ tells us that, if you fix a point x, you have an oscillation in time, while the term kx tells us that if you fix a time t, you'll see an oscillation when you move along x.
Ψ , therefore, oscillates in time and along the direction of propagation.

$$\Psi=\Psi_1+\Psi_2=2A\sin kx\cdot\cos\omega t=2A\sin\frac{2\pi}{\lambda}x\cdot\cos 2\pi\nu t\,; \tag{24}$$

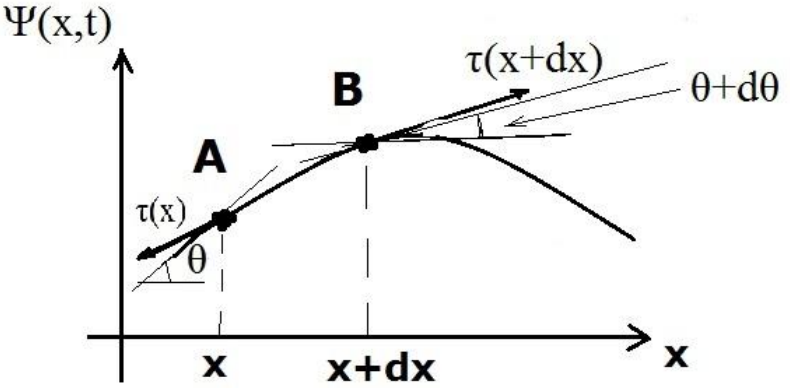
after that we have used the following trigonometric identity:

$$\sin\alpha+\sin\beta=2\cos\frac{(\alpha-\beta)}{2}\cdot\sin\frac{(\alpha+\beta)}{2}\ .$$

Now, if you fix t in (24), you'll have: $\Psi=const\cdot\sin kx$, from which:
$\frac{\partial^2\Psi}{\partial x^2}=-const\cdot k^2\sin kx=-k^2\Psi$, from which, again: $\frac{\partial^2\Psi}{\partial x^2}+k^2\Psi=0$, so the (23), that is, the standing wave equation!
Therefore, as a further intuitive proof of the Schrödinger's Equation, we give the following:
let Ψ be the wave function; it must withstand the following wave equation: $\frac{\partial^2\Psi}{\partial x^2}+k^2\Psi=0$;
then we know from the previous pages that $p=\hbar k$, from which: $k^2=\frac{p^2}{\hbar^2}$ and so:

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{p^2}{\hbar^2}\Psi=0\,. \tag{25}$$

Then, we know through (20) that: $H-V=\frac{p^2}{2m}$, and so: $\frac{2m}{\hbar^2}(H-V)=\frac{p^2}{\hbar^2}$ and (25) yields:
$\frac{\partial^2\Psi}{\partial x^2}+\frac{p^2}{\hbar^2}\Psi=\frac{\partial^2\Psi}{\partial x^2}+\frac{2m}{\hbar^2}(H-V)\Psi=0$ so really the (22) monodimensional!
Naturally, also the case of a vibrating string brings u sto the Wave Equation:



τ is the tension of the string, dm is the infinitesimal element of mass and μ is the linear density of the string.

On the y axis, we have:

$\tau \sin(\theta + d\theta) - \tau \sin\theta = dm \cdot a = \mu dx \frac{\partial^2 \Psi}{\partial t^2}$; now, for small angles, both sine and tangent are approximated by the angle: $\tau(\theta + d\theta) - \tau\theta = \tau d\theta = \mu \frac{\partial^2 \Psi}{\partial t^2} dx$ and also $\theta \approx tg\theta = \frac{\partial \Psi}{\partial x}$ and $d\theta = \frac{\partial \theta}{\partial x} dx = \frac{\partial^2 \Psi}{\partial x^2} dx$, from which: $\frac{\partial^2 \Psi}{\partial x^2} = (\frac{\mu}{\tau}) \frac{\partial^2 \Psi}{\partial t^2}$, where: $v = \sqrt{\frac{\tau}{\mu}}$.

Moreover, if in the Wave Equation $\frac{\partial^2 \Psi}{\partial t^2} = v^2 \frac{\partial^2 \Psi}{\partial x^2}$ we put a wave function in which the space coordinates and the time coordinate are separated, i.e. they are not together in the same argument, so not like that $(\Psi(\vec{k} \cdot \vec{x} - \omega t))$, but like that $\Psi(x,t) = \varphi(x) \sin \omega t$, then we get again the Schrodinger's Equation:

$\frac{d^2 \varphi}{dx^2} + \frac{\omega^2}{v^2} \varphi = 0$

preamble on the mean value of an operator:

we know that by (Ψ, Ψ) we mean the following: $\int \Psi^*(\vec{x},t) \Psi(\vec{x},t) d^3x$, which is 1 for normalized Ψ.

Before, we talked about probability P as a function of the space (x or $\vec{x}$) and proportional ro the square modulus of the wave function:

$P \propto |\Psi(\vec{x},t)|^2 = \Psi(\vec{x},t) \Psi^*(\vec{x},t)$, where $\Psi^*(\vec{x},t)$ is the complex conjugated of $\Psi(\vec{x},t)$ (i swapped with –i). If then you want to calculate the mean value (over the space) for an operator F, we can use the weighed mean value calculation, where the weight evaluated for every point where you want to calculate the mean value, is $\Psi(\vec{x},t)\Psi^*(\vec{x},t)$:

$\langle F \rangle = (\Psi, F\Psi) = \int \Psi^*(\vec{x},t) F \Psi(\vec{x},t) d^3x$ (26)

preamble on fundamental commutators:

we define the commutator of the operator A with the operator B: $[A,B] = AB - BA$. Now, in case A and B are just numbers, their commutator will be zero, but if they are operators, then things can be different.

For fundamental commutators, we have:

$[x_i, x_j] = x_i x_j - x_j x_i = 0$ (x=position)

$[p_i, p_j] = (-i\hbar \frac{\partial}{\partial x_i})(-i\hbar \frac{\partial}{\partial x_j}) - (-i\hbar \frac{\partial}{\partial x_j})(-i\hbar \frac{\partial}{\partial x_i}) = 0$, (we saw that $p \to -i\hbar \frac{\partial}{\partial x}$).

$[x_i, p_j] = i\hbar \delta_{ij}$;

in fact, if you apply the commutator to an auxiliary and generic operator φ:

$[x_i, p_j]\varphi = x_i(-i\hbar \frac{\partial \varphi}{\partial x_j}) - (-i\hbar \frac{\partial}{\partial x_j})(x_i \varphi) = -i\hbar x_i \frac{\partial \varphi}{\partial x_j} + i\hbar \frac{\partial x_i}{\partial x_j} \varphi + i\hbar x_i \frac{\partial \varphi}{\partial x_j} = i\hbar \delta_{ij} \varphi$

where δ_{ij} is the Kronecker's Delta, and is 0 if $i \neq j$ and 1 if $i = j$. In fact, as x_i and x_j are ortogonal and linearly independent (as x, y and z are), we really have $\frac{\partial x_i}{\partial x_j} = \delta_{ij}$.

About the commutator $[t,E]$: (as $E \to i\hbar\frac{\partial}{\partial t}$)

$[t,E]\varphi = it\hbar\frac{\partial\varphi}{\partial t} - i\hbar\frac{\partial}{\partial t}(t\varphi) = it\hbar\frac{\partial\varphi}{\partial t} - i\hbar\frac{\partial t}{\partial t}\varphi - it\hbar\frac{\partial\varphi}{\partial t} = -i\hbar\frac{\partial t}{\partial t}\varphi = -i\hbar\varphi$ and so: $[t,E] = -i\hbar$

preamble on the eigenvalue equation and on deviations:
as x_i is a certain position on a certain axis (for instance, x_1=x, x_2=y, x_3=z), then also Ψ_i is a certain state i, considered as a component i of a wave functio Ψ in a maybe infinite-dimension space i=infinite).
If states "i" exist, where an operator F (which can be simply a real number f) has a well defined value, then we have: $\langle F\rangle_i = f_i$.
F should be an "observable", likely. Then, we know the definition of mean square deviation ΔF for F and we want it becomes zero:
$\Delta F = \sqrt{\langle F^2\rangle_i - \langle F\rangle_i^2} = 0$. We also define the "simple deviation" Δ_F:
$\Delta_F = F - \langle F\rangle_i$. Then, we have:
$\langle\Delta_F^2\rangle_i = \langle(F - \langle F\rangle_i)^2\rangle_i = \langle F^2\rangle_i + \langle F\rangle_i^2 - 2\langle F\rangle_i\langle F\rangle_i = \langle F^2\rangle_i - \langle F\rangle_i^2 = (\Delta F)^2$. Now, the request according to which: $\Delta F = 0$, becomes as follows: $\langle\Delta_F^2\rangle_i = 0 = (\Psi_i, \Delta_F^2\Psi_i) = 0$. And as F is an observable, then hermitian (F*=F), also Δ_F will be hermitian, and so we can write:
$\langle\Delta_F^2\rangle_i = (\Psi_i, \Delta_F^2\Psi_i) = (\Delta_F\Psi_i, \Delta_F\Psi_i) = \int|\Delta_F\Psi_i|^2 d\xi = 0$, from which: $\Delta_F\Psi_i = 0$, that is: $F\Psi_i = f_i\Psi_i$, which is the eigenvalue equation for F.

APPENDIX 3
Links among all the wave functions

This is a proof that the d'Alembert's Wave Equation, that of Schrodinger, of Klein-Gordon and of Dirac are all related one another and show the oscillation of the universe. Moreover, the Klein-Gordon's Equation gives us a three dimensional interpretation of either all relativistic fourth components or the rest energy.

We know from the relativity that the total energy E is:

$$E^2 = p^2c^2 + m_0^2c^4 \quad (1)$$

This is the most general formula we have for the energy and is suitable for a relativistic particle indeed.

Now, for a photon (a particle whose rest mass is equal to zero), we have: $E^2 = p^2c^2$, and:

$$E = pc \quad (2)$$

For a non relativistic particle, we know its kinetic energy is: $E_k = \frac{1}{2}m_0v^2$, but this is hidden in (1), which is more general, indeed. In fact, (1) can be rewritten in this way:

$$E = m_0c^2(1 + \frac{p^2}{m_0^2c^2})^{1/2} \quad (3)$$

and for the developments of Taylor, we have:

$f(x) = \sqrt{1+x} = (1+x)^{1/2} \approx 1 + \frac{1}{2}x$, from this, for the (3):

$E = m_0 c^2 (1 + \frac{p^2}{m_0^2 c^2})^{1/2} \approx m_0 c^2 (1 + \frac{p^2}{2m_0^2 c^2}) = m_0 c^2 + \frac{p^2}{2m_0}$ and, for the kinetic energy, we have:

$E_k = E - m_0 c^2 = \frac{p^2}{2m_0} = \frac{1}{2} m_0 v^2$ qed.

Now, let's take the general expression for a wave:

$$\Psi = A \cdot e^{i(\vec{k}\cdot\vec{x} - \omega t)} = A \cdot e^{i(\frac{2\pi}{\lambda}\hat{k}\cdot\vec{x} - \frac{2\pi}{\lambda}vt)}, \quad (4)$$

as: $\vec{k} = \frac{2\pi}{\lambda}\hat{k}$, $\omega = \frac{2\pi}{T} = 2\pi f = 2\pi\frac{v}{\lambda}$.

Such a wave simultaneously propagates in space (x) and oscillates in time t; in fact, if we fix t=0, we see we have an oscillation along x ($\Psi = A \cdot e^{i(\vec{k}\cdot\vec{x})}$) and if we fix x=0 we have an oscillation in time ($\Psi = A \cdot e^{-i(\omega t)}$).

We also know that:

$$E = hf = \frac{h}{2\pi} 2\pi f = \hbar\omega \quad (5)$$

and being (2) standing, we have:

$pc = \hbar\omega$, from which :

$$p = \hbar\frac{\omega}{c} = \hbar\frac{2\pi}{\lambda} = \hbar k = p \quad (6)$$

and (4) becomes:

$$\Psi = A \cdot e^{i(\frac{\vec{p}}{\hbar}\cdot\vec{x} - \frac{E}{\hbar}t)} \quad (7)$$

By simply putting such a Ψ in the following equations:

$$(i\hbar\frac{\partial}{\partial t})\Psi = E\Psi = (\hbar\omega)\Psi \quad (8)$$

$$(\frac{\hbar}{i}\nabla)\Psi = \vec{p}\Psi = (\hbar\vec{k})\Psi \ ; \quad (9)$$

we have that they give identities, sot they are correct.

In one dimension: $(\frac{\hbar}{i}\frac{\partial}{\partial x})\Psi = p\Psi = (\hbar k)\Psi$; (∇ gradient)

So, we can deduce the following operatorial identities:

$$E \to i\hbar\frac{\partial}{\partial t} \quad (10)$$

$$\vec{p} \to \frac{\hbar}{i}\nabla \quad (11)$$

As (2) stands: $E^2 = p^2 c^2$, we have:

$$(i\hbar\frac{\partial}{\partial t})^2\Psi = c^2(\frac{\hbar}{i}\nabla)^2\Psi\,, \tag{12}$$

that is:

$$\nabla^2\Psi - \frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} = 0 \tag{13}$$

or also ($\nabla^2 = \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, laplacian, divergence of a gradient): $\Delta\Psi - \frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} = 0$,

which is the **d'Alembert's Wave Equation**.

Please notice such an equation, derived in a '' relativistic'' environment (photon, i.e. a particle propagating by speed c and with a zero rest mass) is invariant under a Lorentz's Transformation.

If now we consider non relativistic particles (atoms are like that, ordinarily), we will get a non relativistic ''wave'' equation, which is the Schrodinger's Equation. In fact, if in (7) we no longer consider $E = pc$, but $E_k = \frac{1}{2}m_0v^2$ (a non relativistic equation, indeed), we get:

$$\Psi = A\cdot e^{i(\frac{\vec{p}}{\hbar}\cdot\vec{x} - \frac{E_k}{\hbar}t)} = A\cdot e^{i(\frac{\vec{p}}{\hbar}\cdot\vec{x} - \frac{p^2}{2m_0\hbar}t)} \tag{14}$$

and as well as we got (12), by a direct use of (14) in the following equation:

$$(i\hbar\frac{\partial}{\partial t})\Psi = (-\frac{\hbar^2}{2m_0}\nabla^2)\Psi \tag{15}$$

(which is the **Schrodinger's Equation**)

($(i\hbar\frac{\partial}{\partial t})\Psi = (-\frac{\hbar^2}{2m_0}\frac{\partial^2}{\partial x^2})\Psi$, in one dimension)

we get an identity. Therefore, (15) is true. Please notice that in (14) we have no longer used a total E, but just an Ek, and we are going to take that into account.

The left side of (15) is $(i\hbar\frac{\partial}{\partial t})\Psi = E_k\Psi$, but we know that Ek=H-V, so, still in force of the (15):

$-\frac{\hbar^2}{2m_0}\Delta\Psi = (H-V)\Psi$, that is:

$$\Delta\Psi + \frac{2m_0}{\hbar^2}(H-V)\Psi = 0 \tag{16}$$

which is again the Schrodinger's Equation.

Let' get into a more general situation, where we have a relativistic particle with a rest mass not equal to zero.

As well as we did before, as for (1) we have: $E = \sqrt{p^2c^2 + m_0^2c^4}$, then, by using such an E still in (7) $\Psi = A\cdot e^{i(\frac{\vec{p}}{\hbar}\cdot\vec{x} - \frac{E}{\hbar}t)}$, we will have:

$$\Psi = A\cdot e^{i(\frac{\vec{p}}{\hbar}\cdot\vec{x} - \frac{\sqrt{p^2c^2+m_0^2c^4}}{\hbar}t)} \tag{17}$$

and, as usual, still by introduction of an equation into another, we see that such a Ψ is a solution for the following:

$$(\nabla^2\Psi - \frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2}) - \frac{m_0^2c^2}{\hbar^2}\Psi = 0 \qquad (18)$$

which is nothing but the **Klein-Gordon's Equation** and it is similar to that of d'Alembert, but has an item more. Let's really carry out the introduction of (17) in (18), to see that all this really stands.

We have: $\nabla^2\Psi = (i)^2\frac{p^2}{\hbar^2}\Psi = -\frac{p^2}{\hbar^2}\Psi$ and

$-\frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} = -\frac{1}{c^2}(-i)^2\frac{E^2}{\hbar^2}\Psi = \frac{1}{c^2\hbar^2}(p^2c^2 + m_0^2c^4)\Psi$ and so:

$-\frac{p^2}{\hbar^2}\Psi + \frac{1}{c^2\hbar^2}(p^2c^2 + m_0^2c^4)\Psi - \frac{m_0^2c^2}{\hbar^2}\Psi = 0$, that is 0=0.

Let's set $l = \frac{m_0c}{\hbar}$; such an l is dimensionally like the wave vector k. By such an l, we have that (17) and (18) can be rewritten as follows:

$$\Psi = A\cdot e^{i(\vec{k}\cdot\vec{x} - \sqrt{(k^2+l^2)}ct)} = A\cdot e^{i(\vec{k}\cdot\vec{x} - \omega' t)} \qquad (19)$$

$$\nabla^2\Psi - \frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} - l^2\Psi = 0 \qquad (20)$$

where $\omega' = \sqrt{(k^2+l^2)}c$.

Relativity says that a body with a zero speed, with respect to us, has, on the othe hand, a spatial fourth component ct, a fourth 4-momentum component mc and an intrinsic rest energy m_0c^2. Hence, in jumping from a photon, whose m0 is zero, to a relativistic particle with a rest mass m0, the wave equation jumps from the d'Alembert's (13) to the Klein-Gordon's (20), with a wave function (19), instead of the (4) and the difference is that the rest mass component m0, which causes the existence of a "rest" energy m_0c^2 (whose essence is "four-dimensional" and shows up with Relativity and with the energy-momentum vector) is nothing but an increase of time oscillation, where we go from an angular frequency ω to $\omega' = \sqrt{(k^2+l^2)}c$ higher! This is a three-dimensional interpretation of an entity whose nature is allegedly four-dimensional.

Let's rewrite the Klein-Gordon's Equation (20) in the following way:

$$-\frac{\partial^2\Psi}{\partial t^2} + c^2\nabla^2\Psi - l^2c^2\Psi = 0 \qquad (21)$$

and after taking into account that $i^2 = -1$ and $(a-b)(a+b) = a^2 - b^2$, we have that such an equation can be rewritten like this:

$$[i\frac{\partial}{\partial t} - (i\alpha\cdot\nabla - \beta m_0)][i\frac{\partial}{\partial t} + (i\alpha\cdot\nabla - \beta m_0)] = 0\,, \qquad (22)$$

or also:

$$[i\frac{\partial}{\partial t} - (i\alpha\cdot\nabla - \beta m_0)]\Psi = 0$$
$$[i\frac{\partial}{\partial t} + (i\alpha\cdot\nabla - \beta m_0)]\Psi = 0 \qquad (23)$$

and (22) can be developed as:

$$[-\frac{\partial^2}{\partial t^2}+(\alpha\cdot\nabla)^2+im_0\beta(\alpha\cdot\nabla)+im_0(\alpha\cdot\nabla)\beta-\beta^2m_0^2]\Psi=0 \qquad (24)$$

This equation is equal to the (21) if:

$\beta^2=\frac{c^4}{\hbar^2}$, $\alpha\beta+\beta\alpha=0$, $\alpha_i\alpha_j=c^2$ if i=j and $\alpha_i\alpha_j+\alpha_j\alpha_i=0$ if $i\neq j$

The last two conditions on alphas make us have only ∇^2 and not mixed terms in ∇. (23), here reported:

$$(i\frac{\partial}{\partial t}+i\alpha\cdot\nabla-\beta m_0)\Psi=0 \qquad (25)$$

can be considered as the **Dirac's Equation**, which is usually provided in the following form, in natural units ($\hbar=c=1\rightarrow\beta=1$):

$$(i\gamma^\mu\partial_\mu-m_0)]\Psi=0 \ , \qquad (26)$$

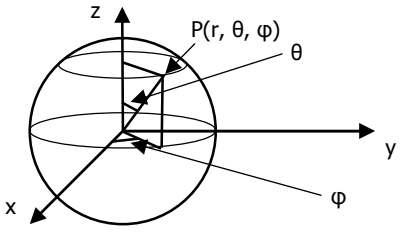
where $i\gamma^\mu\partial_\mu=i\gamma^\mu\,\partial/\partial x^\mu$, which contains a summation under the Einstein convention, gives, under the values of μ, the derivative under the time $\frac{\partial}{\partial t}$ and under x, y and z of $\nabla=(\frac{\partial}{\partial x},\frac{\partial}{\partial y},\frac{\partial}{\partial z})$:

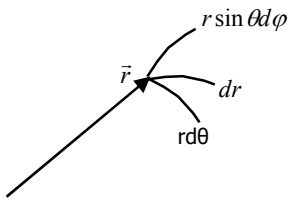
$$i\gamma^\mu\partial_\mu\rightarrow i\frac{\partial}{\partial t}+i\alpha\cdot\nabla$$

APPENDIX 4
Spherical Polar Coordinates

We are going to work with spherical polar coordinates (ρ,θ,φ) as so doing calculations will be much easier, opposite to the Cartesian ones x,y,z.

$$\begin{cases}x=r\sin\theta\cos\varphi\\ y=r\sin\theta\sin\varphi\\ z=r\cos\theta\end{cases}$$





φ spans between 0 and 2π, while θ does between 0 and π. In fact, as an example, on the polar plane the equation of the circle with its center in the origin is $\rho=R$ (no matter how θ and φ are), whilw in Cartesian coordinates we have to start from the implicit equation $x^2+y^2=R^2$, from which, for the first quadrant xy, we have:

$y=\sqrt{R^2-x^2}$ (much more difficult) (1)

and in order to calculate the surface of the circle, in polar coordinates we consider the thin crown as thick as $d\rho$ and at a distance ρ from the center, whose surface is $dA=2\pi\rho\cdot d\rho$ and by integrating between 0 and R, we get:

$A=2\pi\int_0^R\rho\cdot d\rho=\pi R^2$, while with the Cartesian coordinates, we should integrate (1) between 0 and R to have a quarter of A (area below the curve), from which:

$$A=4\int_0^R\sqrt{R^2-x^2}dx=4\left|\frac{x\sqrt{R^2-x^2}}{2}+\frac{R^2}{2}\arcsin\frac{x}{r}\right|_0^R=\pi R^2$$, (which is a bit more difficult job…).

But now let's jump to the shape of the orbitals and to the understanding why they are like they are and why they are exactly how many they are. Change of coordinates from Cartesian to polar. We know that:

$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{cases} \quad (2) \qquad \begin{cases} r^2 = x^2 + y^2 + z^2 & (3) \\ \varphi = arctg\dfrac{y}{x} & (4) \\ \theta = \arccos\dfrac{z}{r} & (5) \end{cases}$$

and so: $\dfrac{\partial}{\partial x} = \dfrac{\partial r}{\partial x}\dfrac{\partial}{\partial r} + \dfrac{\partial \theta}{\partial x}\dfrac{\partial}{\partial \theta} + \dfrac{\partial \varphi}{\partial x}\dfrac{\partial}{\partial \varphi}$ (6)

$\dfrac{\partial}{\partial y} = \dfrac{\partial r}{\partial y}\dfrac{\partial}{\partial r} + \dfrac{\partial \theta}{\partial y}\dfrac{\partial}{\partial \theta} + \dfrac{\partial \varphi}{\partial y}\dfrac{\partial}{\partial \varphi}$ (7) $\qquad$ $\dfrac{\partial}{\partial z} = \dfrac{\partial r}{\partial z}\dfrac{\partial}{\partial r} + \dfrac{\partial \theta}{\partial z}\dfrac{\partial}{\partial \theta} + \dfrac{\partial \varphi}{\partial z}\dfrac{\partial}{\partial \varphi}$ (8)

Now let's differentiate the (3): $rdr = xdx + ydy + zdz$ (9)

On the contrary, by differentiating (4): $d\varphi = -\dfrac{y}{x^2 + y^2}dx + \dfrac{x}{x^2 + y^2}dy$ (10)

(generically: $\partial\varphi = \dfrac{\partial\varphi}{\partial x}dx + \dfrac{\partial\varphi}{\partial y}dy + \dfrac{\partial\varphi}{\partial z}dz$) and by differentiating (5):

$-\sin\theta d\theta = -\dfrac{zx}{r^3}dx - \dfrac{zy}{r^3}dy + (\dfrac{1}{r} - \dfrac{z^2}{r^3})dz$. (11)

(the $-\dfrac{1}{\sin\theta}$, then brought to the left side, is the derivative of the arccos)

Now, by keeping into account (2) and (9), (10), plus (11), we have:

$$\begin{cases} \dfrac{\partial r}{\partial x} = \sin\theta\cos\varphi & (12) \\ \dfrac{\partial r}{\partial y} = \sin\theta\sin\varphi & (13) \\ \dfrac{\partial r}{\partial z} = \cos\theta & (14) \end{cases} \qquad \begin{cases} \dfrac{\partial \varphi}{\partial x} = -\dfrac{\sin\varphi}{r\sin\theta} & (15) \\ \dfrac{\partial \varphi}{\partial y} = \dfrac{\cos\varphi}{r\sin\theta} & (16) \\ \dfrac{\partial \varphi}{\partial z} = 0 & (17) \end{cases}$$

$$\begin{cases} \dfrac{\partial \theta}{\partial x} = \dfrac{\cos\theta\cos\varphi}{r} & (18) \\ \dfrac{\partial \theta}{\partial y} = \dfrac{\cos\theta\sin\varphi}{r} & (19) \\ \dfrac{\partial \theta}{\partial z} = -\dfrac{\sin\theta}{r} & (20) \end{cases}$$

In fact, about the first system of equations, say (12) is (9) where dy=dz=0 and by considering that in order to get x we have to multiply r by $\sin\theta$ first, to project it on the xy plane, so getting the projection r_p and then such a projection has to be multiplied by $\cos\varphi$ to get x indeed. In other words, (9) with dy=dz=0 tells us that $\dfrac{dr}{dx} = \dfrac{x}{r}$, which is really $(\sin\theta\cos\varphi)$, according to the projection reasoning just carried out. About the second system, (15) would be (10) with dy=0 and once again upon the above projection reasoning.

At last, about the third system, (18) would be (11) with dy=dz=0 and ($z = r\cos\theta$) and ($x = r\sin\theta\cos\varphi$).

Finally, let's recall gradient and laplacian in polar coordinates:

By definition, we have: $gradV = \nabla V = \frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j} + \frac{\partial}{\partial z}\hat{k}$; if now we use (6), (7) and (8) to express $\frac{\partial}{\partial x}$, $\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$ and then we gather all terms with $\frac{\partial}{\partial r}$, we get:

$(\nabla)_r = \frac{\partial r}{\partial x}\frac{\partial}{\partial r}\hat{i} + \frac{\partial r}{\partial y}\frac{\partial}{\partial r}\hat{j} + \frac{\partial r}{\partial z}\frac{\partial}{\partial r}\hat{k} = \sin\theta\cos\varphi\frac{\partial}{\partial r}\hat{i} + \sin\theta\sin\varphi\frac{\partial}{\partial r}\hat{j} + \cos\theta\frac{\partial}{\partial r}\hat{k} =$

$= \frac{\partial}{\partial r}(\hat{i}\sin\theta\cos\varphi + \hat{j}\sin\theta\sin\varphi + \hat{k}\cos\theta) = \hat{r}\frac{\partial}{\partial r}$. Similarly, $(\nabla)_\theta = \frac{1}{r}\frac{\partial}{\partial\theta}$ and $(\nabla)_\varphi = \frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}$, from which, to sum up, we have the components of the gradient in spherical polar coordinates:

$(\nabla)_r = \hat{r}\frac{\partial}{\partial r}$, $(\nabla)_\theta = \frac{1}{r}\frac{\partial}{\partial\theta}$ e $(\nabla)_\varphi = \frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}$.

In order to achieve the scalar laplacian, its definition in Cartesian coordinates is:

$\nabla^2 = \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ and in order to calculate every one of those terms, we will first derivate again (6), (7) and (8) and use the results in the above formula for the laplacian, so obtaining:

$\Delta = \frac{1}{r^2}(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2})$.

APPENDIX 5
The angular momentum in the atom

We saw that $\vec{p} = -i\hbar\vec{\nabla}$ and $E = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\Delta$. Now, about the angular momentum L=mvr we know that if a mass point m orbits at r distance from a center point and does it by speed v, we have: (p=mv):

$\vec{L} = \vec{r}\times\vec{p}$, $L = r\times p = -i\hbar r\times\nabla$ (vector product) and as (obviously): $-i\nabla = (-i\frac{\partial}{\partial x}, -i\frac{\partial}{\partial y}, -i\frac{\partial}{\partial z})$,

then: $L_x = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$, $L_y = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})$, $L_z = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$ and

$L^2 = \vec{L}\vec{L} = L_x^2 + L_y^2 + L_z^2$. (1)

By taking into account the above expression for L_z and considering (1) and (12)……(20) in Appendix 4, we get:

$L_z = -i\hbar[r\sin\theta\cos\varphi(\sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}) - r\sin\theta\sin\varphi(\sin\theta\cos\varphi\frac{\partial}{\partial r} +$

$+\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi})]$, which reduces a lot by mutual elimination of terms, so yielding:

$L_z = -i\hbar\frac{\partial}{\partial\varphi}$. Similarly, we get the following:

$L_x = i\hbar(\sin\varphi\frac{\partial}{\partial\theta} + ctg\theta\cos\varphi\frac{\partial}{\partial\varphi})$, $L_y = -i\hbar(\cos\varphi\frac{\partial}{\partial\theta} - ctg\theta\sin\varphi\frac{\partial}{\partial\varphi})$ and finally, by (1) of this Appendix, we calculate:

$$L^2 = -\hbar^2(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}) = -\hbar^2(\frac{\partial^2}{\partial\theta^2} + ctg\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}) \quad (2)$$

The last equality is due to the obvious development: $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} = \frac{\partial^2}{\partial\theta^2} + ctg\theta\frac{\partial}{\partial\theta}$.

To reach (2), we just show, as an example, the calculation for L_x^2 and we will carry out all products one by one, without using ready-to-use formulas on square a+b and so on, as here we are dealing with operators:

$$L_x^2 = i\hbar(\sin\varphi\frac{\partial}{\partial\theta} + ctg\theta\cos\varphi\frac{\partial}{\partial\varphi})\cdot i\hbar(\sin\varphi\frac{\partial}{\partial\theta} + ctg\theta\cos\varphi\frac{\partial}{\partial\varphi}) = -\hbar^2(\sin\varphi\frac{\partial}{\partial\theta}\sin\varphi\frac{\partial}{\partial\theta} +$$

$$+\sin\varphi\frac{\partial}{\partial\theta}ctg\theta\cos\varphi\frac{\partial}{\partial\varphi} + ctg\theta\cos\varphi\frac{\partial}{\partial\varphi}\sin\varphi\frac{\partial}{\partial\theta} + ctg\theta\cos\varphi\frac{\partial}{\partial\varphi}ctg\theta\cos\varphi\frac{\partial}{\partial\varphi}) =$$

$$= -\hbar^2[\sin^2\varphi\frac{\partial^2}{\partial\theta^2} - \sin\varphi\cos\varphi(1+ctg^2\theta)\frac{\partial}{\partial\varphi} + ctg\theta\cos^2\varphi\frac{\partial}{\partial\theta} +$$

$$-\sin\varphi\cos\varphi ctg^2\theta\frac{\partial}{\partial\varphi} + \cos^2\varphi ctg^2\theta\frac{\partial^2}{\partial\varphi^2}]$$

and a similar expression for L_y^2 and a short one for L_z^2. Later, by summing up all the terms, many of them will join or cancel, so leading us to (2) indeed.

Please note that $[\varphi, L_z] = i\hbar$.

About the kinetic energy operator T, we saw that $\vec{p} = -i\hbar\vec{\nabla}$ and $T = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\Delta$, but we also showed that: $\Delta = \frac{1}{r^2}(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2})$ and a comparison between this equation and (2) tells us that:

$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2}$, from which:

$$p^2 = -\hbar^2\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{L^2}{r^2} = p_r^2 + \frac{L^2}{r^2}, \quad (3)$$

after naming $p_r^2 = -\hbar^2\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} = -\hbar^2(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r})$, and after having developed the derivative of a product: $\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})$.

APPENDIX 6
Schrodinger's Equation for the atom

We are obviously in a field of forces with a central symmetry generated by the nucleus, so:

$V(\vec{r}) = V(r)$, $H = T + V = \frac{p^2}{2m} + V(r)$, $p^2 = p_r^2 + \frac{L^2}{r^2}$ and, according to Schrodinger,

$H\Psi(\vec{r}) = E\Psi(\vec{r})$, that is:

$\frac{1}{2m}(p_r^2+\frac{L^2}{r^2})\Psi+V(r)\Psi=E\Psi$, or:

$r^2[p_r^2+2m(V(r)-E)]\Psi(\vec{r})=-L^2\Psi(\vec{r})$, (1)

where (let's remind it):

$L^2=-\hbar^2(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2})=-\hbar^2(\frac{\partial^2}{\partial\theta^2}+ctg\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2})$.

Let's find solutions for (1) with separated variables: $\Psi(\vec{r})=\Phi(r)Y(\theta,\varphi)$; by introducing it into (1) and after naming by $R=r^2[p_r^2+2m(V(r)-E)]$ the f(r) factor of (1) itself, we have:

$R\Phi(r)Y(\theta,\varphi)=-L^2\Phi(r)Y(\theta,\varphi)$, from which:

$R\Phi(r)=-\Phi(r)\frac{L^2Y(\theta,\varphi)}{Y(\theta,\varphi)}$ (2)

and we can name: $\lambda=\frac{L^2Y(\theta,\varphi)}{Y(\theta,\varphi)}$, which is clearly constant with respect to r, as both Y and L^2 don't depend on r. We have:

$L^2Y(\theta,\varphi)=\lambda Y(\theta,\varphi)$, (3)

which is the eigenvalue equation for L^2. As already stated, the $Y(\theta,\varphi)$ will give us infos on the shapes of orbitals, while the other function in r, that is $\Phi(r)$, which will be expressed by us as well, will tell us just how high is the probability to find the electron in the orbital, when we get far away from the center or when we get closer to the center along r, without changing θ and φ.

Well, after making (3) explicit, we get:

$\frac{\partial^2Y(\theta,\varphi)}{\partial\theta^2}+ctg\theta\frac{\partial Y(\theta,\varphi)}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2Y(\theta,\varphi)}{\partial\varphi^2}+\frac{\lambda}{\hbar^2}Y(\theta,\varphi)=0$

Out of convenience, let's define $\lambda=\hbar^2\nu(\nu+1)$, where ν is constant, as well as λ, of course. This will be more clear later on. From all this:

$\frac{\partial^2Y(\theta,\varphi)}{\partial\theta^2}+ctg\theta\frac{\partial Y(\theta,\varphi)}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2Y(\theta,\varphi)}{\partial\varphi^2}+\nu(\nu+1)Y(\theta,\varphi)=0$. (4)

As well as before, here we look for solutions with separated variables: $Y(\theta,\varphi)=A(\theta)B(\varphi)$; after inserting this into (4):

$A''B+ctg\theta A'B+\frac{1}{\sin^2\theta}AB''+\nu(\nu+1)AB=0$. Let's multiply both sides by $\frac{\sin^2\theta}{AB}$:

$\sin^2\theta\frac{A''}{A}+\sin\theta\cos\theta\frac{A'}{A}+\nu(\nu+1)\sin^2\theta+\frac{B''}{B}=0$. (5)

Because of a dimensional matter, we immediately notice that it must be $\frac{B''}{B}=const$, as $\frac{B''}{B}$ is the only item to depend on just φ, while all the other terms depend on just θ. Therefore, after having noticed that Y is periodical with respect to φ, we can write that: $\frac{B''}{B}=-m^2$ (where $B(\varphi)=e^{im\varphi}$ and m=0,±1, ±2,…). By the way, as $L_z=-i\hbar\partial/\partial\varphi$ (see page 18) and applying L_z to $B(\varphi)$, we have: $L_zB(\varphi)=-i\hbar\partial/\partial\varphi e^{im\varphi}=\hbar me^{im\varphi}=\hbar mB(\varphi)$, which is an eigenvalue equation for L_z, from which we have the reference to L_z of the quantum number m. The value found for B''/B, if put into (5), yields: $\sin^2\theta A''+\sin\theta\cos\theta A'+[\nu(\nu+1)\sin^2\theta-m^2]A=0$. If now we put $\cos\theta=x$, (and so: $\frac{d}{d\theta}=\frac{dx}{d\theta}\frac{d}{dx}=-\sin\theta\frac{d}{dx}$, $\frac{d^2}{d\theta^2}=-\cos\theta\frac{d}{dx}+\sin^2\theta\frac{d^2}{dx^2}$), we have:

$\sin^2\theta(\sin^2\theta\frac{d^2A}{dx^2}-\cos\theta\frac{dA}{dx})-\sin^2\theta\cos\theta\frac{dA}{dx}+[\nu(\nu+1)\sin^2\theta-m^2]A=0$; finally, by dividing both sides by $\sin^2\theta=1-x^2$, we get:

$$(1-x^2)\frac{d^2A}{dx^2}-2x\frac{dA}{dx}+[\nu(\nu+1)-\frac{m^2}{(1-x^2)}]A=0 \quad (6)$$

known as Legendre Differential Equation; it has three singularities (fuchsian ones) in $x_0=\pm1$ (and at infinite). Those on $x_0=\pm1$ are due to the "dangerous" tending to zero of the denominator of $\frac{1}{(1-x^2)}$ (about the point at the infinite, we will not care much).

Let's write (6) as follows:

$$\frac{d}{dx}[(1-x^2)\frac{dA}{dx}]+[\nu(\nu+1)-\frac{m^2}{(1-x^2)}]A=0 \quad (7)$$

and let's start by considering the easiest case m=0:

$$\frac{d}{dx}[(1-x^2)\frac{dA}{dx}]+\nu(\nu+1)A=0 \quad (8)$$

We look for solutions as a series of powers, like:

$A(x)=x^s\sum_{n=0}^{+\infty}a_nx^n$ and we use that into (8):

$$\frac{d}{dx}[(1-x^2)\frac{d}{dx}\sum_n a_nx^{n+s}]+\nu(\nu+1)\sum_n a_nx^{n+s}=0$$

$$\frac{d}{dx}[(1-x^2)\sum_n a_n(n+s)x^{n+s-1}]+\nu(\nu+1)\sum_n a_nx^{n+s}=0$$

$$\frac{d}{dx}[\sum_n a_n(n+s)x^{n+s-1}-\sum_n a_n(n+s)x^{n+s+1}]+\nu(\nu+1)\sum_n a_nx^{n+s}=0$$

$$\sum_n a_n(n+s)(n+s-1)x^{n+s-2}-\sum_n a_n(n+s+1)(n+s)x^{n+s}+\nu(\nu+1)\sum_n a_nx^{n+s}=0$$

Now, into the first summation, we rename n by (n-2):

$$\sum_n a_{n+2}(n+s+2)(n+s+1)x^{n+s}-\sum_n a_n(n+s+1)(n+s)x^{n+s}+\nu(\nu+1)\sum_n a_nx^{n+s}=0$$

$$\sum_n[a_{n+2}(n+s+2)(n+s+1)-a_n(n+s+1)(n+s)+\nu(\nu+1)a_n]x^{n+s}=0$$

$$a_{n+2}(n+s+2)(n+s+1)-a_n[(n+s+1)(n+s)-\nu(\nu+1)]=0$$

$$a_{n+2}=a_n\frac{(n+s+1)(n+s)-\nu(\nu+1)}{(n+s+2)(n+s+1)}$$

Function A is limited in x=1 (that is $\theta=0$), so we sooner or later must have: $(n+s+1)(n+s)-\nu(\nu+1)=0$ in order not to have a divergence, with all coefficients a_n not equal to zero, and as n and s are integer, such must be ν, which will be now called l, and so: $\lambda=\hbar^2l(l+1)$. Then, as +m and –m play a role of symmetry, we will have: $-l\le m\le l$, or $|m|\le l$.

Moreover, by a direct use of it, we realize that a solution of (8) is the following:

$$A_l(x)=\frac{1}{2^l l!}\frac{d^l}{dx^l}(x^2-1)^l \quad (9)$$

as well as a solution for (7) is:

$$A_l^m(x)=\frac{(-1)^m}{2^l l!}(1-x^2)^{|m|/2}\frac{d^{l+|m|}}{dx^{l+|m|}}(x^2-1)^l \quad (10)$$

As an example, when l=1 and m=1, (10) becomes: $A_1^1(x)=-\frac{1}{2}(1-x^2)^{1/2}\frac{d^2}{dx^2}(x^2-1)=-\sqrt{(1-x^2)}$, and if we put it into (7), we get 0=0.

After recalling that we had $Y(\theta,\varphi)=A(\theta)B(\varphi)$, we say: $Y_l^m(\theta,\varphi)=A_l^m(\theta)B_m(\varphi)$

Let's evaluate, through (10), the first $A_l^m(x)$ ones: ($x=\cos\theta$)

$A_0^0(x)=1=const$, $A_1^0(x)=x=\cos\theta=const\cdot\cos\theta$, $A_1^{+1}(x)=-(1-x^2)^{1/2}=-\sin\theta=-const\cdot\sin\theta$

and so on, so having all the Y on pages 4 and 5, here reminded: ($B_m(\varphi)=e^{im\varphi}$)

$$Y_0^0=\frac{1}{\sqrt{4\pi}},\quad Y_1^0=\sqrt{\frac{3}{4\pi}}\cos\theta,\quad Y_1^{\pm1}=\mp\sqrt{\frac{3}{8\pi}}\sin\theta\cdot e^{\pm i\varphi},\quad Y_2^0=\frac{1}{2}\sqrt{\frac{5}{4\pi}}(3\cos^2\theta-1),$$

$$Y_2^{\pm1}=\mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\cdot e^{\pm i\varphi},\quad Y_2^{\pm2}=\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\cdot e^{\pm i2\varphi}.$$

But now we ask ourselves why do we have those particular constants? ($\frac{1}{\sqrt{4\pi}}$, $\sqrt{\frac{3}{4\pi}}$, etc) Well, you recall (page 7) that the highest probability all over the space must be 1, from which we get the normalization to 1. So, as an example on case:

$Y_1^0(\theta,\varphi)=A_1^0(\theta)B_0(\varphi)=const\cdot\cos\theta\cdot e^{i0\varphi}=const\cdot\cos\theta=C_1^0\cos\theta$, and after considering that, with reference to the figure on page 16 on polar coordinates, θ is spanned by r, while φ is spanned by the projection of r over the plane x-y, that is $r\sin\theta$, the infinitesimal solid angle $d\Omega$ is given, as we know, by the ratio between the infinitesimal spherical susface dS and r^2, that is:

$d\Omega=\frac{dS}{r^2}=\frac{rd\theta\cdot r\sin\theta d\varphi}{r^2}=d\varphi\sin\theta d\theta$. So, let's integrate over all Ω and let's request that the highest probability is 1: (θ goes from 0 amd π, while φ goes from 0 and 2π)

$$\int_0^{4\pi}(Y_1^0)^*(\theta,\varphi)\cdot Y_1^0(\theta,\varphi)d\Omega=\int_0^{2\pi}\int_0^{\pi}(C_1^0)^2\cos^2\theta d\varphi\sin\theta d\theta=\int_0^{2\pi}d\varphi\int_0^{\pi}(C_1^0)^2\cos^2\theta\sin\theta d\theta=$$

$$=-\int_0^{2\pi}d\varphi\int_0^{\pi}(C_1^0)^2\cos^2\theta d\cos\theta=-2\pi(C_1^0)^2\int_0^{\pi}\cos^2\theta d\cos\theta=-2\pi(C_1^0)^2\left|\frac{1}{3}\cos^3\theta\right|_0^{\pi}=\frac{4}{3}\pi(C_1^0)^2=1,$$

that is: $\frac{4}{3}\pi(C_1^0)^2=1$, or: $C_1^0=\sqrt{\frac{3}{4\pi}}$, which is exactly the coefficient of Y_1^0. Similarly,

$$\int_0^{4\pi}(Y_1^1)^*(\theta,\varphi)\cdot Y_1^1(\theta,\varphi)d\Omega=\int_0^{2\pi}\int_0^{\pi}(C_1^1)^2\sin^2\theta\cdot e^{-i\varphi+i\varphi}d\varphi\sin\theta d\theta=\int_0^{2\pi}d\varphi\int_0^{\pi}(C_1^1)^2\sin^3\theta d\theta=$$

$$=2\pi(C_1^1)^2\left|-\cos\theta+\frac{1}{3}\cos^3\theta\right|_0^{\pi}=\frac{8}{3}\pi(C_1^1)^2=1,$$ so: $\frac{8}{3}\pi(C_1^1)^2=1$, and so: $C_1^1=\sqrt{\frac{3}{8\pi}}$, that is exactly the coefficient of Y_1^1. And so on.

The shapes of the orbitals would be explained just by what has been explained so far. Out of completeness, as the complete solution of Schrodinger's Equation for the atom is (see above): $\Psi(\vec{r})=\Phi(r)Y(\theta,\varphi)$, we just have to give a representation of the pure radial function $\Phi(r)$.

Let's remind here (2):

$R\Phi_{nl}(r)=-\Phi_{nl}(r)\frac{L^2Y(\theta,\varphi)}{Y(\theta,\varphi)}=-\lambda\Phi_{nl}(r)=-\hbar^2l(l+1)\Phi_{nl}(r)=r^2\{p_r^2+2m[V(r)-E]\}\Phi_{nl}(r)$, or:

$-\hbar^2l(l+1)\Phi_{nl}(r)=r^2\{p_r^2+2m[V(r)-E]\}\Phi_{nl}(r)$, from which:

$\frac{p_r^2}{2m}\Phi_{nl}(r)+[V(r)+\frac{\hbar^2l(l+1)}{2mr^2}]\Phi_{nl}(r)=E\Phi_{nl}(r)$ and after reminding also (3) and the subsequent expressions for p_r, that are: $p_r^2=-\hbar^2\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}=-\hbar^2(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r})$, we have:

$-\frac{\hbar^2}{2m}(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr})\Phi_{nl}(r)+[V(r)+\frac{\hbar^2l(l+1)}{2mr^2}]\Phi_{nl}(r)=E\Phi_{nl}(r)$, or:

$$\Phi_{nl}''(r)+\frac{2}{r}\Phi_{nl}'(r)+\{\frac{2m}{\hbar^2}[E-V(r)]-\frac{l(l+1)}{r^2}\}\Phi_{nl}(r)=0\,;$$

Now, considering that $V(r)=-\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$, we have:

$\Phi_{nl}''(r)+\frac{2}{r}\Phi_{nl}'(r)+\{\frac{2m}{\hbar^2}[E+\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}]-\frac{l(l+1)}{r^2}\}\Phi_{nl}(r)=0$, or also (after considering the Bohr's radius $a_0=\frac{4\pi\varepsilon_0\hbar^2}{me^2}$): $\Phi_{nl}''(r)+\frac{2}{r}\Phi_{nl}'(r)+[\frac{2m}{\hbar^2}E+\frac{2Z}{a_0 r}-\frac{l(l+1)}{r^2}]\Phi_{nl}(r)=0$

and after considering the total energy $E=-\frac{Z^2e^4m}{32\pi^2n^2\varepsilon_0^2\hbar^2}$ (see (2) in App. 1 and notice that here we have $\hbar=h/2\pi$ instead of h), we have:

$$\Phi_{nl}''(r)+\frac{2}{r}\Phi_{nl}'(r)+[-\frac{Z^2e^4m^2}{16\pi^2n^2\varepsilon_0^2\hbar^4}+\frac{2Z}{a_0 r}-\frac{l(l+1)}{r^2}]\Phi_{nl}(r)=0 \qquad (11)$$

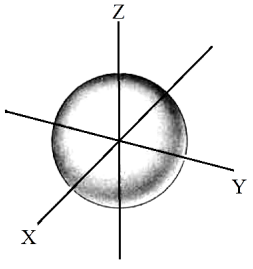
and we also realize that the following functions are solutions for (11):

$$\Phi_{nl}(r)=\frac{1}{n}\sqrt{(\frac{Z}{a_0})\frac{(n-l-1)!}{(n+l)!}}\cdot e^{-Zr/na_0}\frac{1}{r}(\frac{2Zr}{na_0})^{l+1}\cdot L_{n-l-1}^{2l+1}(\frac{2Zr}{na_0})\ , \qquad (12)$$

(where $L_0^\alpha(x)=1$ and $L_1^\alpha(x)=\alpha+1-x$, $L_n^\alpha(x)=\frac{1}{n!}e^x x^{-\alpha}\frac{d^n}{dx^n}[e^{-x}x^{n+\alpha}]$ Generalized Laguerre's Polinomials). Let's give some of them:

$$\Phi_{10}(r)=\sqrt{\frac{Z}{a_0}}\frac{2Z}{a_0}e^{-Zr/a_0}\ ,\ \Phi_{20}(r)=\sqrt{\frac{Z}{8a_0}}\frac{Z}{a_0}(2-\frac{Zr}{a_0})e^{-Zr/2a_0}\ ,\ \Phi_{21}(r)=\sqrt{\frac{Z}{24a_0}}(\frac{Z}{a_0})^2 re^{-Zr/2a_0} \qquad (13)$$

The normalization has been carried out in the following way: $\int_0^\infty r^2|\Phi_{nl}(r)|^2dr$, as functions Y (see above) were normalized over $d\Omega=\frac{dS}{r^2}=\frac{rd\theta\cdot r\sin\theta d\varphi}{r^2}=d\varphi\sin\theta d\theta$, and in order to go from $d\Omega$ to dV we have to multiply $d\Omega$ by r^2dr, as $d\Omega$ x r^2 gives dS and dS x dr gives dV and so the remaining part of the normalization, that is r^2dr is taken by $\Phi_{nl}(r)$ indeed, as it is the radial function. As a simple crosscheck, you can see that (12) is really a solution for (11); in other words, put one by one every (13) in (11) (and by respecting, time by time, values of n and l) and you will see you will always get 0=0. Finally, by considering the example on the s orbital (n=1, l=0, m=0),



it is a sphere, as its function $Y_l^m(\theta,\varphi)=Y_0^0=1/\sqrt{4\pi}$ is constant, so θ and φ don't show up , and so the "angular" probability P_a ($\propto|Y_l^m(\theta,\varphi)|^2$) does not depend on how we orientate, but its radial function is $\Phi_{nl}(r)=\Phi_{10}(r)=\sqrt{\frac{Z}{a_0}}\frac{2Z}{a_0}e^{-Zr/a_0}$, that is a constant by an exponential, so telling us that the radial "probability" P_r ($\propto|\Phi_{nl}(r)|^2$) to find the electron is not in the thin peel of that perfect

spherical surface, but it's cloud-like spread and goes dimming as long as one gets away from the centre.

Schrodinger's Wave Function for the atom:

$\Psi(\vec{r}) = Y_l^m(x=\cos\theta,\varphi)\Phi_{nl}(r) = [A_l^m(x=\cos\theta)B_m(\varphi)]\Phi_{nl}(r)$, or:

$$\Psi(\vec{r}) = \frac{(-1)^m}{2^l nl!}\cdot\sqrt{(\frac{Z}{a_0})\frac{(n-l-1)!}{(n+l)!}}(1-x^2)^{|m|/2}[\frac{d^{l+|m|}}{dx^{l+|m|}}(x^2-1)^l]e^{im\varphi}\cdot e^{-Zr/na_0}\frac{1}{r}(\frac{2Zr}{na_0})^{l+1}\cdot L_{n-l-1}^{2l+1}(\frac{2Zr}{na_0})$$